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Fingerprinting isotopic signatures for metal
enrichment in European trees:
Developing vectors for mineral exploration

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Danijela Mavrić

Summary

This study consists of a detailed investigation into the biogeochemical (higher plants) and soil geochemical expression of the Navan Zn-Pb deposit. Additional reconnaissance sampling programs were undertaken, at the Ballinalack Zn-Pb deposit (Ireland) and the Laver Cu deposit in Sweden.

Trace-element geochemistry of plant species including ash, beech, blackberry, hawthorn, oak, poplar and sycamore are reported for study areas above the Navan Zn-Pb deposit and at three independent control sites. Plant biogeochemistry involving analysis of dried plant material using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was applied to seven deciduous plant species providing baseline trace-element data for the characterisation of biogeochemical haloes above the Navan Zn-Pb deposit.

Spatial vectoring around the Navan deposit revealed that all plant species examined under this study exhibited significantly higher As, Cd, Pb and Zn contents above the orebody than at the control sites. Sampling in autumn (September) showed increased ranges in metal uptake, and wider variation in metal values for As, Cu, Cd and Zn than the spring (May) dataset. Hawthorn species (*Crataegus monogyna*) displayed the most distinct enrichment factors for Cd, Pb and Zn in leaves while exhibiting the lowest impact for seasonal variations and an overall strong capacity for metal uptake and accumulation. Soil sampling provided further insight into trace element migration through soil and uptake into plants. Plant-soil correlations between As, Cd, Pb and Zn typify the anomalous geochemistry of surficial materials overlying the deposit. In order to recognise differences in metal distribution through time dendrochronology was applied to tree cores extracted from beech (*Fagus sylvatica*) and oak (*Quercus* spp.) in the Navan area. Tree ring analysis in oak display increased accumulations of Cd, Pb and Zn prior to mining operations (1950–1960) than during a period (2000–2010) of mining activities. These metal accumulations in woody material confirm the natural uptake of metals through the ore-soil-plant pathway model, independent of mining activities.

Stable metal isotopes provide further insight into biogeochemical processes above Zn-Pb mineralisation and for the development of new analytical tools for biogeochemical prospecting. In order to confirm metal sources and resolve the ore-soil-plant pathway of the metal anomalies, Cu and Zn isotopes were measured using Multi Collector

Inductively Coupled Plasma – Mass Spectrometry (MC ICP-MS) applied to two large natural systems (control vs. experimental). A natural system with known Zn-Pb mineralisation displays significantly lighter $\delta^{66}\text{Zn}$ signatures in hawthorn leaves (*Crataegus monogyna*) above the Zn-Pb orebody, whereas the unmineralised natural system (control sites) reveals heavier $\delta^{66}\text{Zn}$ signatures in hawthorn. A lighter $\delta^{66}\text{Zn}$ signature corresponds to the underlying Zn-Pb mineralisation whilst the heavier Zn isotopic composition at the control sites represent basement rock signature. Measurements of $\delta^{65}\text{Cu}$ signatures were unable to differentiate between vegetation samples over mineralisation and the controls site and did not provide any additional information for the overall interpretation of the ore-soil-plant system.

Broadening the study to aid in the development of exploration protocols in diverse botanical/climate settings, an experimental site was chosen in a northern European climate (Sweden) and characterised by a predominance of silviculture Norway Spruce trees (*Picea abies*). Spruce needles were collected in two profiles over the Laver area, intersecting porphyry-skarn Cu-Au-Mo mineralisation of the Laver Mine and Lill-Laverberget deposit, in addition to sampling in the independent control sites. Trace element results revealed significantly high Mn (1600 ppm on average) followed by elevated Zn concentrations (82 ppm, on average). Furthermore, this study illustrates clear and strong interactions between Cu, Mn and Fe in spruce needles. From an exploration point of view, spruce needles would be a preferred medium to sample in any biogeochemical survey in northern European forests (Boreal) for base metal exploration.

The use of biogeochemistry in exploration can be a useful tool in identifying metal anomalies due to buried mineralisation. With a general trend towards deeper exploration targets, new techniques for the discovery of blind targets will be crucial for future resources. Furthermore, stable metal isotopes can be useful in distinguishing metal anomalies due to mineralisation from passive signatures in barren host lithotypes.

Fingerprinting isotopic signatures for metal enrichment in European trees: Developing vectors for mineral exploration

Danijela Mavrić

Abstract: The trace-element geochemistry of native and common plant species in Ireland including ash, beech, blackberry, hawthorn, oak, poplar and sycamore was systematically determined above the Navan Zn-Pb deposit, currently mined by Boliden Tara Mines Limited. The study area represents a sub-outcropping carbonate-hosted base metal orebody characterised by a large shallow soil Zn-Pb anomaly.

The new results show that Zn contents in leaf materials across all species vary from 22 ppm to 735 ppm (dry weight) above the orebody while control sites concentrations ranged from 15 ppm to 263 ppm. The highest concentrations of Zn are observed in poplar trees (735 ppm) growing above the sub-cropping mineralisation. Levels of Pb are anomalously high (3.8 ppm, on average) in all investigated tree species compared to the background values from control sites (0.54 ppm, on average). Soil geochemistry determined above the deposit exhibited 1111 ppm of Zn and 390 ppm of Pb, on average. In order to better understand the source pathway of metal anomalies, stable metal isotopes were measured in plants, soil and tree cores to investigate typical ranges of Zn and Cu isotopes above the Navan deposit. The Zn isotope composition of hawthorn growing over unmineralised bedrock exhibits enrichment in heavy isotopes ($\delta^{66}\text{Zn}_{JMC}$ of 0.15‰ to 0.48‰). In contrast, much lighter Zn isotopes ($\delta^{66}\text{Zn}_{JMC}$ of -0.12‰ to -0.62‰) were detected in the same plant species above the Navan orebody (Nevinstown Zone). In addition, the Nevinstown area exhibits lighter Cu isotopes in hawthorn leaves ($\delta^{65}\text{Cu}_{mean}=+0.23$ ‰) when compared to the control sites ($\delta^{65}\text{Cu}_{mean}=+0.55$ ‰). Differences in isotopic signatures in vegetation can be interpreted as representing two possible Zn sources with signatures imparted on soil from: 1) Zn mineralisation (sphalerite), or 2) Zn contents in carbonate minerals within the host limestone sequence.

This study demonstrates that plant geochemistry at Nevinstown successfully detected Zn anomalies in all investigated species and hawthorn showed the clearest enrichment of Zn peaks and the lowest impact of seasonal variations. Plants are providing the geochemical signature of a large volume of soil horizons which is one of the advantages of using biogeochemical prospecting over traditional exploration methods. Furthermore, this thesis contributes to a better understanding of biogeochemical metal cycling in the surficial environment and for the development of new geochemical tools for Zn-Pb exploration in temperate European climates.

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1 Introduction

New challenges in geochemical exploration led by a steadily increasing demand for metals has led to the development of new exploration techniques. The increasing consumption of mineral resources due a growing population and intensity or raw material consumption indicates that more metals will need to be produced by 2050 than the last 100 years combined (Vidal et al., 2017). Base metal production has continuously increased at an almost exponential rate from the 1990's as a result of global industrialization (Fig. 1).

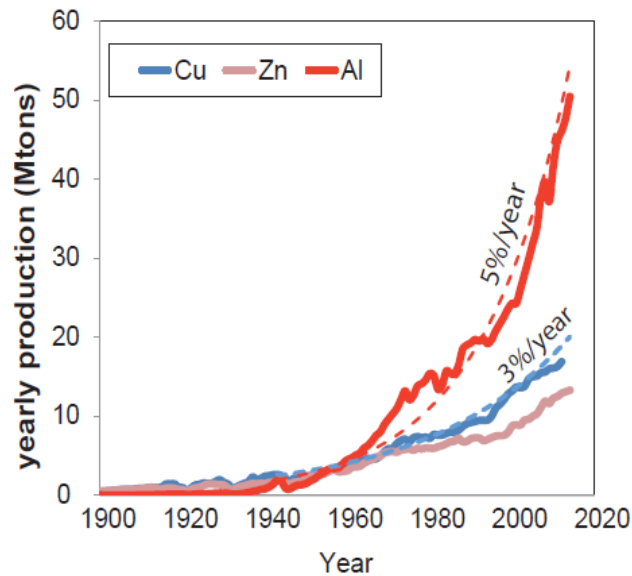


Figure 1. Annual production of Al, Cu and Zn from 1900's to 2020 (adopted from Vidal, 2017).

Among various elements, zinc (Zn) is of particular interest because it can be found in all types of soils, plants and the animal kingdom. Together with boron, chlorine, copper, iron, manganese, molybdenum and nickel, it is one of the eight trace elements essential for the normal healthy growth of living organisms (Alloway, 2008). Zinc is used in many industrial applications, but mainly in the galvanizing of steel for corrosion protection. It is an important component of various alloys and is widely used as catalyst in chemical

production (Kabata-Pendias, 2011). If the future supply of mineral resources is to match demand, the discovery of new metal resources is essential for society's future growth.

Ore deposits represent a significant metal enrichment above background crustal levels produced chiefly by hydrothermal processes but may also include magmatic and weathering processes. Underlying crustal zones with high concentration of base metals such as Cu, Fe, Pb and Zn are an ideal geochemical setting for the formation of a base metal ore deposits (Wilkinson et al., 2005). Over the past decade only 20% of base metal deposits were discovered as sub-cropping mineralisation near surface (Schodde, 2014b). As a result, most recent discoveries of base metal and Au mineralisation were made at depths in excess of 100 m (below surface). With the number of near surface discoveries steadily decreasing, new geochemical techniques for the detection of deep exploration targets and discovery of blind mineralisation are necessary.

Ireland is host to numerous carbonate-hosted, base metal ore deposits which together represents one of the highest concentrations of Zn per km² in the world (Singer, 1995). The Navan orebody (Tara Mines) is the largest of these Irish-type base metal deposits (Ashton et al., 1986, 2003) comprising stratabound sulphide lenses hosted by Lower Carboniferous shallow-water marine carbonates of Tournasian age. The deposit is largely controlled by a system of normal faults, which developed during the rifting of the Dublin Basin (Blakeman et al., 2002). Sphalerite (ZnS) and galena (PbS) are the principal ore minerals accompanied by pyrite (FeS₂), marcasite (FeS₂), arsenopyrite (FeAsS), chalcopyrite (CuFeS₂) and various trace sulphide phases, including sulfosalts (antimonides). The main gangue minerals are barite (BaSO₄), calcite (CaCO₃) and dolomite (CaMgCO₃) (Ashton et al., 2015).

1.1 Challenges in Mineral Exploration

In order for the discovery of new orebodies to be made in increasingly explored (brownfields) terrains, exploration criteria need to be refined to target mineralisation at greater depths. The basic objective of any exploration geochemistry program is to detect anomalies which indicate proximity to a potential resource. Furthermore, once an anomaly has been successfully detected it is necessary to identify the extent of mineralisation and quantify the new economic resource (Arndt et al., 2017). Since the late 1940's the mining industry has overwhelmingly discovered new orebodies through surface prospecting and direct detection methods (geochemistry and geophysics) (Cox and Singer, 1986). Modern exploration focus is placed on exploration models involving tectonic concepts and geological-geochemical data in order to generate discovery targets at surface and greater depths. Hence, the principal search methods involving geochemical techniques had contributed to over 40% of all discoveries made by the mid 1970's. Further advances in trace element analysis (ICP-MS) have led to improvements in exploration geochemistry which can be applied across varied terrains where an orebody might be deeply buried and undetectable through prospecting methods (Ginzburg, 1960, Kelley et al., 2006, Kyser et al., 2015).

Mineral exploration in many regions can be challenging due to the lack of fresh bedrock outcrop or the extremely weathered nature of regoliths. Using geobotanical prospecting as a fit-for-purpose tool in such areas can successfully detect trace element anomalies relevant to buried mineralisation. Recent studies have shown great potential for using plants in mineral exploration, for example grass root geochemistry, which led to the discovery of a new Australian metallogenic province (Collerson et al., 2015). Spinifex grass is native to Australia and has roots reaching depths of 30 m interacting with extensive thicknesses and types of soil. One of the benefits of using plants instead

of only soils is that vegetation can interact with a larger volume of soil material due to the extent of the root systems, in comparison to a single shallow soil sample. In South Australia, research on the biogeochemical expression of buried Cu anomalies *Eucalyptus* (mallee growth habit) has confirmed that plants can be effectively used as a geochemical indicator for exploration (Wolff et al., 2018). Moreover, they concluded that specific plants such as *Eucalyptus* can be used for targeting anomalies associated with Fe-oxide-Cu-Au (IOCG) mineral systems. Hence, it is crucial to identify particular plant species exhibiting metal anomalies related to mineralisation and their occurrence within the exploration areas of interest. Furthermore, different type of deposits and their location demand different approaches when working in a European temperate climate. For example, buried rare earth elements (REE) mineralisation at the Norra Kärr Alkaline Complex in southern Sweden can be observed as REE anomalies in leafy tissue of fern species (Bluemel et al., 2013). In addition, numerous biological media have been investigated and analysed for trace element anomalies including sap, fungi, moss and seaweed (Dunn, 2007). With major advances in analytical chemistry biogeochemical exploration is potentially a very effective, low-cost exploration method with minimal impact on the environment, when compared to soil-till sampling, trenching and drilling.

1.2 The importance of plant anatomy in biogeochemical prospecting

Plants are considered as a surface expression of the underlying soil and host rock because of their complex root system. Plant structure is characterised by the part of the plant above the ground – the shoots while those parts below the ground are called roots (Fig. 2A). The root system keeps the plant firmly in the ground providing it a support. Also, one of the main function of roots is absorbing nutrients, water and minerals from soil matrix into the plant (Howell, 1998).

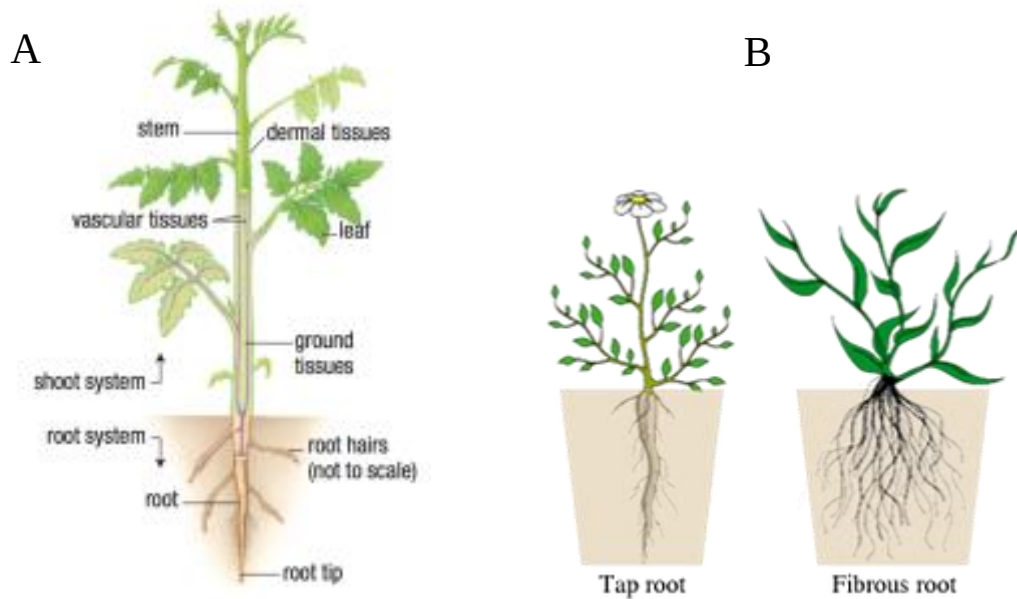


Figure 2. General plant structure consists of shoot and root system (A*). Two main root systems (B**). Retrieved from *www.emaze.com, Plants: Anatomy, and **www.thebrucezone.weebly.com, Structures and adaptations 2019.

There are two kind of root systems (Fig. 2B):

- A Tap Root System has a main root that grows vertically downwards and penetrates deep into the soil.
- A Fibrous Root System is located closer to the surface, building a dense network of roots. The Tap Root System is typically found in dicots such as dandelions while the Fibrous System can be seen in monocots such as grasses (Polverigiani et al., 2011, Faustino et al., 2015).

Deciduous trees such as ash or oak have extensions called root hairs which increase root surface area and increase nutrient and water uptake. Evergreen trees such as pine may not have root hairs but possess mycorrhizae, a fungi which lives in a symbiotic way (Rindels, 1996). Deciduous tree roots usually develop down to depths of 0.7 m with decreasing density. Deeper roots tend to lower fungal colonization and absorptive

capacity for nutrients while finer or shallow roots increase nutrient uptake and assimilation (Wang et al., 2015).

Plant anatomy is characterised by three types of tissues systems each of which comprises different components. Each different component has an accompanying function (Tab. 1).

Table 1. Diagram of tissue systems, components and functions in plant. Retrieved from: www.biologydiscussion.com in May, 2019.

<i>Tissue System</i>	<i>Components</i>	<i>Functions</i>
Dermal Tissue System	Epidermis, Periderm (stems and roots)	Protection Prevention of water loss
Ground Tissue System	Parenchyma tissue Collenchyma tissue Sclerenchyma tissue	Photosynthesis Food storage Regeneration Support Transport of food
Vascular Tissue System	Vascular bundles Xylem tissue Phloem Tissue	Transport of water and minerals Transport of food (sugars)

Root structure and vascular tissue system has a major impact on the metal uptake and metal transport within the plant. Once elements are absorbed by plant roots they are transferred through vascular tissue (xylem and phloem) to a preferable plant organ (stem, leaves, flowers and fruits) in the shoot system (Algreen, et al., 2012). This research will mainly focus on the foliage since it represents the best medium for sampling because metals accumulate in the leaves of many deciduous and evergreen species and the concentrations are commonly greater than metal concentrations in other plant organs such as twigs or needles (Dunn et al., 2007).

1.3 Research objectives

Research into plant biogeochemistry over Zn-Pb vein and porphyry-skarn Cu deposits will provide new insights into geobotanical exploration in varied European terrains and climates. Metals are transported from bedrock, through glacial till and soils to plants providing a bio-geochemical signature of the buried mineralisation. In the terms of an ore-soil-plant model, large natural systems illustrate element migration and uptake in different materials (ore, soil and leaves) on a macro-scale, therefore can be used for a comparison of two natural systems (mineralised and unmineralised). Both of these natural systems are based on their similar geological and botanical settings. The main focus will be placed on the end member ‘plants’ of an ore-soil-plant model even though other members are investigated too.

Using multi-element geochemistry and stable metal isotopes, element pathways in the ore-soil-plant model can be fingerprinted, having direct implications for industry and for promoting a better understanding of biogeochemical metal cycling.

In order to construct an ore-soil-plant model, three main objectives were set:

- Establish the uptake of trace elements in vegetation typical of a temperate European climate (Chapter 6);

Plant biogeochemistry involves analysis of dried plant material (leaves, needles and tree cores) using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) which is applied to seven deciduous plant species and one evergreen species. The aim is to identify background and enrichment trace-element data for the characterisation of biogeochemical haloes above the Navan Zn-Pb deposit in Ireland and above the Laver Cu deposit in Sweden.

- Use trace-element signatures and stable metal isotopes to characterise the sources (spatial, temporal and seasonal) of metal absorption in tree and plant species overlying blind mineralisation (Chapter 7);

Spatial vectoring around the Navan deposit illustrates which plant species examined in this study exhibit significantly higher heavy metals such as As, Cd, Pb and Zn contents above the orebody in comparison to control sites. Seasonal sampling shows increased ranges in metal uptake, and wider variation in metal values for As, Cu, Cd and Zn. In order to recognise differences in metal distribution through time dendrochronology was applied to tree cores extracted from beech (*Fagus sylvatica*) and oak (*Quercus* spp.) in the Navan area. Stable metal isotopes provide further insight into biogeochemical processes above Zn-Pb mineralisation and for the development of new analytical tools for biogeochemical prospecting.

- Develop exploration criteria for future biogeochemical surveys (Chapter 5 & 7);
- Plants are providing the geochemical signature of a large volume of soil horizons which is one of the advantages in using biogeochemical prospecting over traditional exploration methods. For this study, the primary goal was to find a representative native and common, deciduous and evergreen plant species which might serve as an ideal exploration tool to test the geochemical method above the Navan deposit in Ireland and Laver deposit in Sweden. In addition, long lived trees such as oak and beech illustrated that they can be used as monitors of temporal environmental changes.

Using trace-element analysis, anomalies can be detected, but uncertainties remain concerning their sources (host rock versus mineralisation). Furthermore, metal distribution in plants is species dependent meaning some species will not exhibit a strong anomaly peak to background contrast. There are limitations with using this approach which are seasonal variations and also two possible sources of contamination: atmospheric deposition and extensive usage of fertilisers. Mitigating the effects of both soil and air contamination effect on the overall chemical signature of plants is a potential challenge (see discussion in Chapter 7).

Isotope analyses can have the potential to help fingerprint metal pathways from ore, through soil and till to vegetation at surface. During migration, elements can fractionate into heavier and lighter isotopes showing a transport pattern over a specific isotopic range. This orientation study will demonstrate that the Navan Zn-Pb orebody has a unique isotope migration fingerprint when compared to unmineralised control areas representing a similar bedrock geological and surface botanical setting.

In most case studies, data is limited in terms of sample coverage, mass balance and the ability to quantify relative fractionations. To resolve this, future research should focus on testing fractionation pathways of Cu and Zn isotopes phases in a controlled laboratory environment and to expand the existing botanical dataset from natural systems. Using established isotopic values for geological samples and introducing a new range of botanical sample analyses, augmented with soil values, this study is among the first research to investigate Cu and Zn isotopes as an exploration tool. It is shown herein that novel stable metal isotopes can be used as a geochemical tool for the exploration for buried mineralisation and to investigate the origin of base metal anomalies.

Additionally, knowledge on the fractionation of stable isotopes within plants can also be used to understand the transport mechanisms of some metals (e.g. Cu, Zn; Weiss et al., 2005, Guelke and von Blackenburg, 2007, Viers et al., 2007, Black et al., 2008, Cenkci-Tok et al., 2009, von Blackenburg et al., 2009)

2 Literature Review

Non-traditional stable isotopes (e.g. Cu, Fe, Zn) can provide new insights into the genesis of ore systems (Kelley et al., 2009). They can be used as a potential tool for tracing metal pathways from source rocks to plants by constraining ore-soil-plant-models and to monitor transport mechanisms of some metals within the plant body (Black et al., 2008, Cenki-Tok et al., 2009, von Blanckenburg et al., 2009). During element migration, from ore through soil to plants, metals can fractionate into heavier or lighter isotopes showing a migration pattern over a specific isotope range which can be linked to the source signature.

Since the development of Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), in which a multiple array of collectors allows for simultaneous mass determinations, extremely precise isotope ratios measurements of heavier elements have become possible (Halliday et al., 1998). This has led to the discovery of significant isotope fractionation of transition elements resulting from equilibrium and kinetic reactions in both abiotic and biotic processes, notably for Fe (Anbar et al., 2000, Zhu et al., 2002, Beard et al., 2003) as well as Zn and Cu (Maréchal et al., 1999, 2000, Maréchal and Albarède, 2002, Zhu et al., 2002).

Copper has two isotopes, ^{63}Cu and ^{65}Cu with respective abundances of 69.174% and 30.826%; this is reflected in the reference metal SRM-NIST 976 (Shields et al., 1964). Bulk silicate earth has an average $\delta^{65}\text{Cu}$ of $+0.06 \pm 0.20\text{‰}$ and is based on a compiled dataset of peridotites and basalts (Liu et al., 2015). Zinc has five stable isotopes ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn with average natural abundances of 48.63, 27.90, 4.10, 18.75, and 0.62%, respectively (Rosman and Taylor, 1998). Bulk silicate earth has a reported

signature of $\delta^{66}\text{Zn} = +0.31 \pm 0.08\text{‰}$, reflected in values for reference material JMC- $\delta^{66}\text{Zn}$ (White, 2013).

Using a Multi Collector ICP-MS equipped with a magnetic mass analyser, Maréchal et al. (1999) demonstrated that a combination of standard bracketing and normalisation with an external element (typically Zn for Cu and Cu for Zn) are efficient at correcting for mass bias (instrumental mass fractionation;) they produced data on a variety of ores, rocks, and biological materials with a precision of 40–50 ppm. As with other elements for which the stable isotope proportions are sought, extraction of Cu and Zn from rock and biological samples must be quantitative to prevent mass fractionation at this stage.

After the development of high ionisation efficiency and rapid sample throughput most scientists are now pursuing Fe isotope studies by MC-ICP-MS. Instrumental mass bias corrections are made using bracketing standards (e.g., Belshaw et al. 2000, Beard et al. 2003b, Albarède and Beard, 2004), or by comparison to mass bias inferred from an element spike, such as Cu or Ni, that has been added to the solution (e.g., Sharma et al., 2001, Kehm et al., 2003, Malinovsky et al., 2003, Albarède and Beard, 2004).

Measurement techniques

Most recent Zn measurements use the double spike technique as a common method; which was originally introduced by Bermin et al. (2006). According to Moeller et al. (2012) the double spike ^{64}Zn - ^{67}Zn can be added pre-column chemistry after completion of a sample digestion. Some of the advantages of using the double spike method, is that it is faster than the doping methodology and any artificial fractionation (laboratory method induced) of Zn can be corrected afterwards; meaning the double spike method provides absolute elemental abundances with the isotope ratios (Caldelas et al., 2011, Arnold et al., 2015).

Another common methodology is to dope the sample; e.g. for $\delta^{66}\text{Zn}$ determinations, dope with a Cu standard solution and use standard bracketing during the actual Zn measurements (Weiss et al., 2005, Dolgoplova et al., 2006, Viers et al., 2007, Cloquet et al., 2008, Moynier et al., 2009). This methodology takes longer compared to the double spike method, as the recovery has to be determined to ensure, that no artificial fractionation has taken place. Furthermore, for the standard bracketing method it is useful to perform three repetitions of sample measurements which will lead to longer measurement times. This technique can be used for $\delta^{65}\text{Cu}$ determinations as well. Here, doping with Zn (Chen et al., 2009) or Ni (Larner et al., 2011, Moeller et al., 2012) are common. Artificial fractionation of Cu and Zn could occur during ion-exchange chromatography, therefore quantitative yields during the procedure are recommended. The precision of Cu and Zn isotopic measurement will depend on correction of the instrumental bias (Moynier et al., 2017), e.g. ^{62}Ni interference (for Zn) and interference of Na and Mg (Archer and Vance 2004, Larner et al., 2011, Savage et al., 2015b) for Cu measurement, and on the quality of the chemical extraction.

Stable metal isotopes in plants

The uptake of Zn by roots in the soil can lead to the enrichment in heavy isotopes. Once Zn is in the xylem, it will be transported within the plant. During this transport, both diffusion and active uptake of heavy isotopes by cells out of the xylem favour the mobility of light isotopes to the most aerial parts of plant (Caldelas et al., 2011, Arnold et al., 2015). The terrestrial range in $\delta^{66}\text{Zn}$ values is quite small (approx. 1.7‰) in comparison with other transition metal isotopes (e.g. $\delta^{65}\text{Cu}$, 9‰). The principal reason for this is the single oxidation state in which Zn occurs in nature (in contrast to the three oxidation states for Cu) because fractionation during redox reactions is a major control affecting stable isotope variations (Wilkinson et al., 2005). Weiss et al. (2005) reported

that the observed isotopic depletion in heavy Zn from root to shoot (-0.13‰ to -0.26‰ per atomic mass unit) is equivalent to roughly a quarter of the total reported terrestrial variability of Zn compositions (0.84‰ per atomic mass unit). Metal uptake by plants, therefore represents an important source of isotopic variation in the biogeochemical cycling of Zn.

Higher plants induce chemical reactions in the rhizosphere, facilitating metal uptake by roots. Several processes can cause isotope fractionation within most plants: 1) transport of the metal isotope or translocation from roots into stems and leaves; 2) the redox state of the metal (e.g. reduction of Cu (II) to Cu (I) initiates fractionation) and 3) associated ligands which are binding to functional groups. Every plant can exhibit a considerable variation in isotope composition (von Blanckenburg et al., 2009).

Zinc is an essential element and its isotopes potentially offer a powerful tool for studying geosphere – biosphere interactions. To date, Zn isotope studies of higher plants (Tab. 2) suggest that several processes control isotopic signatures, with the uptake favouring isotopically lighter Zn and adsorption favouring heavier isotopes of Zn (Weiss et al., 2005). Both Cu and Zn are extensively used in biological processes (Lippard and Berg, 1994, Frausto da Silva and Williams, 2001). The zinc concentration varies from a few parts per trillion (ppt) to tens of parts per million (ppm) in the cytoplasm of most cells (Outten and O'Halloran, 2001) and in some vesicles. Copper is normally one to two orders of magnitude less concentrated. Furthermore, Cu and Zn play a fundamental role (metabolism) in the functioning of a number of enzymes.

Compared to other heavy metals, Cu is particularly interesting as it combines versatile chemical and molecular structures commonly with two oxidation states (+1 and +2) both in solution and in solid form (Pokrovsky et al., 2008). The magnitude of Cu isotopic fractionation during adsorption processes [$\Delta^{65}\text{Cu}$ (solid-solution) = $+1.3\text{‰}$ to -1.8‰

($\pm 0.1\%$) exceeds that of Zn by a factor of 5-10 and is comparable with the fractionation of Fe (Icopini et al., 2004).

Results of Jouvin et al. (2008) and Zhu et al. (2010) highlight the fractionation of Cu isotopes in plant systems. It was reported that plants fractionate Cu isotopes during internal translocation $\Delta^{65}\text{Cu}$ (root to -shoot) = 0.41‰ (Jouvin et al., 2008) and uptake from soil (Zhu et al., 2010) which may influence the Cu isotope composition of organic surface horizons of soils. Plant cycling might change the Cu isotope composition of mineral horizons by removing light Cu isotopes in the main rooting area and transfer them to the plant biomass and organic horizons (Jouvin et al., 2008, Zhu et al., 2010).

In order to better understand isotopic variability in different environments Cu and Zn isotope data in Figures 3 and 4 illustrate the typical ranges of metal stable isotopes that might be expected in diverse geological, botanical and environmental settings. This knowledge can be used to attribute isotope values to particular processes and to develop a model, which can be applied to a Navan orebody in the terms of isotopic ranges.

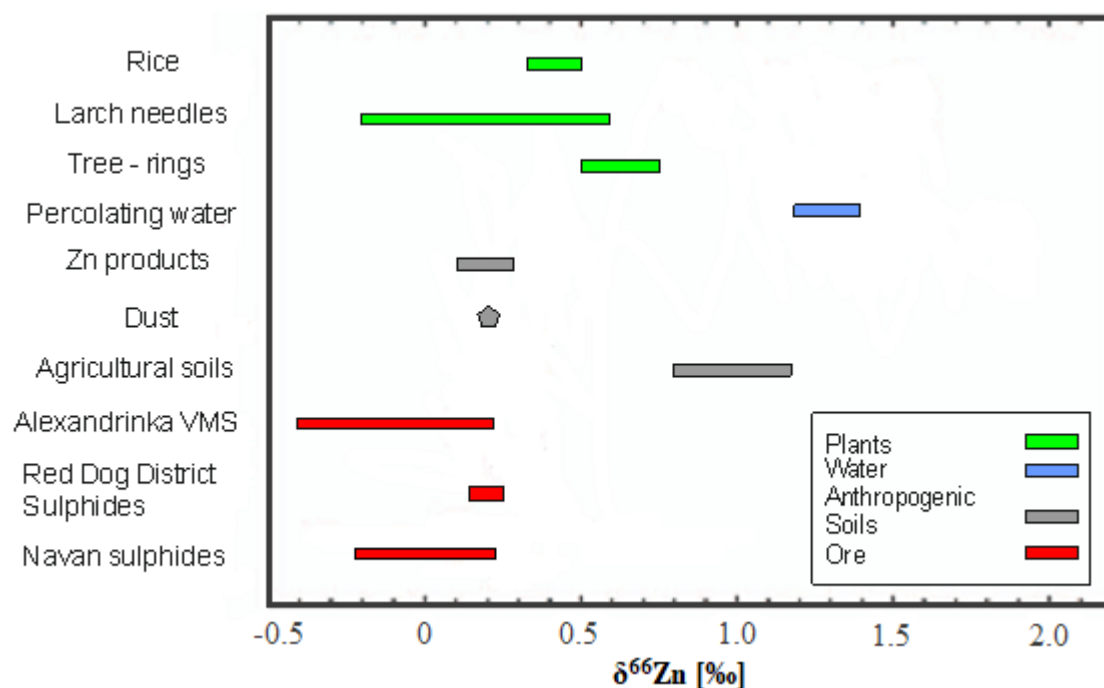


Figure 3. Regional zinc isotope signatures for plants, natural waters, anthropogenic dusts, soil and selected Zn ore sulphides. Sulphide ores reported are from Navan (Gagnevin et al., 2012); the main deposit in the Red Dog District zone – North Alaska (Kelley et al., 2009); Alexandrinka – VMS deposit in Russia (Mason et al., 2005). Cloquet et al. (2008) reported Zn isotopes in agricultural soils and dust in France. Zinc products include metal dust and galvanized steel in USA reported by John et al. (2007). Zinc isotopes in percolating water near a Zn smelter in France were reported by Sivry et al. (2008). Diagram shows isotopic ranges for tree rings of white spruce in Alberta, Canada (Dinis et al., 2015); larch needles from Central Siberia (Viers et al., 2015) and for rice (Arnold et al., 2015). All data was reported using the JMC 3-0749L standard except for Navan sulphides which used the IMC 27040 standard.

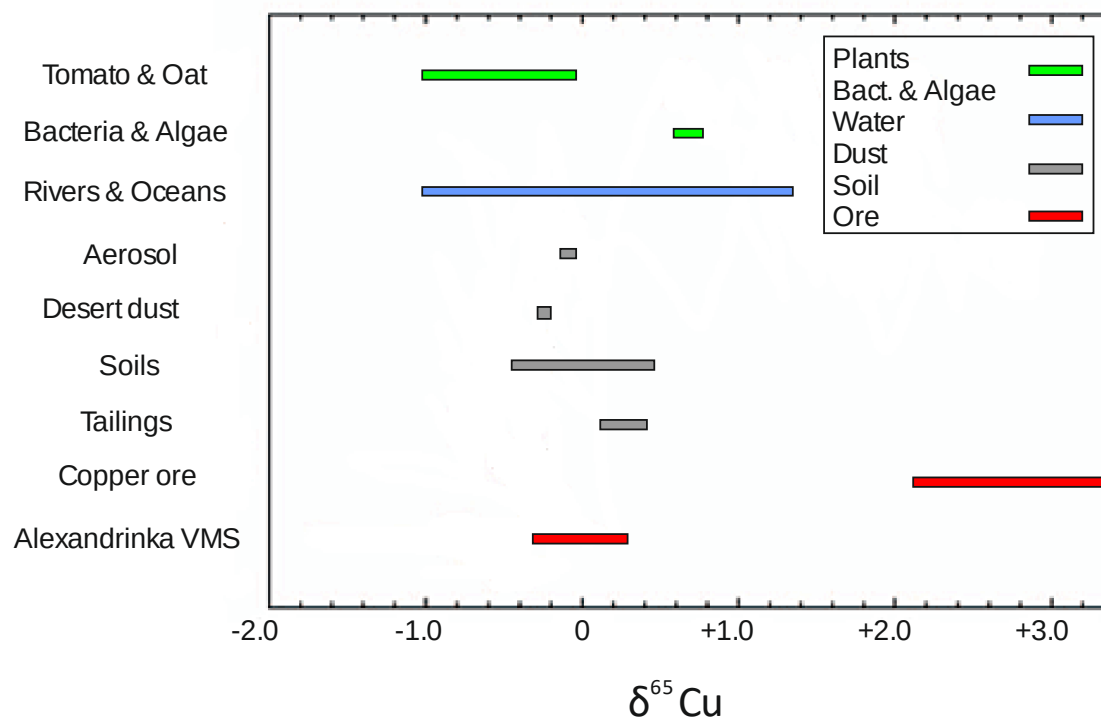


Figure 4. Regional copper isotope signatures for plants, bacteria, algae, natural waters, anthropogenic dusts, soils, selected ore sulphides and mining waste. Isotopic ranges for sulphide ores are from the Alexandrinka VMS deposit in Russia (Mason et al., 2005) and the El Salvador porphyry Cu deposit in Chile (Mathur et al., 2014). Rodriguez et al. (2013) reported isotopic ranges for test tailings from the Kristineberg deposit, Sweden. Podzolic soils from Germany and Slovakia were reported by Bigalke et al. (2011). Aeolian dust data was published by Dong et al. (2013). Diagram shows isotopic ranges for rivers and oceans (Song et al., 2015); bacteria and algae (Pokrovsky et al., 2008) and in tomato and oat (Ryan et al., 2013). All data was reported using the NIST 976 standard except for tailings from Kristineberg which used ERM – AE633 standard.

2.1 Case studies of Zn and Cu isotopes in Higher plants

Zn isotopes

Using MC ICP-MS, Weiss et al. (2005) measured isotopic fractionation of Zn in rice (*Oryza sativa*), lettuce (*Lactuca sativa*) and tomato (*Lycopersicon esculentum*) plants during uptake from nutrient solutions. For all three species the roots showed a similar extent of heavy Zn enrichment relative to the nutrient solution, probably reflecting preferential adsorption on the external root surface. Average $\delta^{66}\text{Zn}$ values are $0.631 \pm 0.046\text{‰}$ (± 2 SD) relative to an in-house standard of $0.044 \pm 0.035\text{‰}$ per atomic mass unit (Johnson-Matthey PurotronicTM Batch NH 27040).

Dolgoplova et al. (2006) reported Pb and Zn isotope data for biological samples (lichens and birch leaves) from the Orlovka-Spokoinoe rare metal mining district in Russia. Zn isotope data of 11 lichen samples showed differing Zn isotopic signatures with the total range of $+0.4\text{‰}$ to $+1.4\text{‰}$ $\delta^{66}\text{Zn}$ relative to Lyon JMC 3-0749L Zn standard. The sources of isotopically heavy Zn relative to the host rocks within the mine site suggest an important contribution from sources other than natural dust derived from the host rocks in the local environment. One of their main objectives was to distinguish between geological and anthropogenic sources within the mining environment using Pb and Zn isotopes.

Viers et al. (2007) were the first to determine Zn isotopic compositions of different soil horizons, parent rock, litter and plants from a single pristine tropical watershed in Nsimi, Cameroon (Africa). Six plants and two litter samples were analysed for their Zn isotopic composition. $\delta^{66}\text{Zn}$ varied from $+0.75\text{‰}$ to -0.91‰ among all samples. Plant roots and shoots are generally enriched in heavy isotopes ($\delta^{66}\text{Zn}$ of $+0.42\text{‰}$ to 0.76‰) relative to the litter layer (0.12‰ to 0.25‰), similar to the controlled plant growth study

of Weiss et al. (2005). Negative $\delta^{66}\text{Zn}$ values were obtained for tree leaves (the most aerial part of the tree). Based on biomass data for the tropical forest, vegetation is on average enriched in light isotopes compared to the litter and soils. All Zn isotope data were measured relative to the standard JMC 3-0749L.

Cloquet et al. (2008) focused on biological processes inducing Zn isotope fractionation in plants, animals and humans and assessed the potential of Zn isotope ratio determination for elucidating sources of atmospheric particles and contamination. They reported a total range of $\delta^{66}\text{Zn}$ values found for palm leaves (-0.9‰) and the highest $\delta^{66}\text{Zn}$ values for rye grass (0.8‰).

Moynier et al. (2009) analysed the Zn isotopic composition of different plant components (seeds, leaves and rhizome, stem and leaves) of lentils (*Lens culinaris*) and bamboo (*Phyllostachys aurea*), respectively. Leaves are enriched in light Zn isotopes compared to other parts of the plants. The range in fractionation is up to 0.52‰ per atomic mass unit and is clearly mass dependent.

Caldelas et al. (2011) investigated the effect of high Zn concentrations on the isotopic fractionation patterns of Common Reed (*Phragmites australis*) grown in nutritive solution. *Phragmites australis* was chosen as a model plant because it is tolerant to toxic Zn concentrations and responds by accumulating excess Zn, mainly in the roots. They showed that during Zn sufficiency, roots, rhizomes and shoots were isotopically heavy ($\delta^{66}\text{Zn}_{\text{JMC Lyon}}=0.2\text{‰}$) while the youngest leaves were isotopically light (-0.15‰). The enrichment in light isotopes of shoots and leaves is consistent with long distance root to shoot transport, in agreement with the observations by Viers et al. (2007) and Moynier et al. (2009).

Deng et al. (2014) observed plant-solution and shoot-root fractionations during uptake of Zn and Ni in the nonaccumulator field penny-cress (*Thlaspi arvense*) and hyperaccumulator yellow-tuft (*Alyssum murale*) plant in both low and high Ni and Zn solutions. They noted that the Ni isotopic compositions in stems were usually heavier than that in leaves, whereas Zn exhibited the opposite effect.

Table 2. Compilation of the isotopic composition of Zn (relative to reference material) for plant matter and lichen.

Standard	Type of material	$\delta^{66}\text{Zn}$ (‰)	References
JM Purotronic™ Batch NH 27040	Rice (<i>Oryza sativa</i>)	+0.631	Weiss et al. (2005)
	Lettuce (<i>Lactuca sativa</i>)		
	Tomato (<i>Lycopersion esc.</i>)		
JMC 3-0749 L	Lischen	+0.4 to +1.4	Dolgoplova et al. (2006)
JMC 3-0749 L	Litter	+0.75 to -0.91	Viers et al. (2007)
	Tree leaves (Tropical forest)		
JMC 3-0749 L	Bamboo	-0.55 to +0.55	Moynier et al. (2009)
JMC 3-0749 L	Common Reed (<i>Phragmites australis</i>)	-0.50 to +0.50	Caldelas et al. (2011)

Cu isotopes

Pokrovsky et al. (2008) quantified the main environmental factors controlling isotope fractionation of Cu during its adsorption from aqueous solutions onto common organic (bacteria, algae) and inorganic oxy(hydro)oxide surfaces. It was found that only a decrease in pH is capable of inducing a significant isotopic shift ($0.6\text{--}1.8 \pm 0.05\text{‰}$) between solution and the bacterial surfaces.

Bigalke et al. (2011) reported that Cu stable isotope ratios are fractionated during various biogeochemical processes and may trace the fate of Cu during long-term pedo-genetic processes (Tab. 3). Results of Jouvin et al. (2008) and Zhu et al. (2010) point to the fractionation of Cu isotopes in plant systems. It was reported that plants fractionate

Cu isotopes during internal translocation ($\Delta^{65}\text{Cu}_{(\text{root-shoot})} = 0.41\text{‰}$, Jouvin et al.) and uptake from soil (Zhu et al.) which may influence the Cu isotope composition of organic surface horizons of soils. The O horizons had, on average significantly lighter Cu isotope compositions (-0.21‰) than the A horizon (0.13‰) which can either be explained by Cu isotope fractionation during cycling throughout the plants or deposition of isotopically light Cu from the atmosphere.

Weinstein et al. (2011) reported the Cu isotopic compositions of different plant components (seeds, germinated seeds, leaves and stems) of the dicot, lentil (*Lens culinaris*), and of two monocots, Virginia wild rye (*Elymus virginicus*) and hairy-leaved sedge (*Carex hirsutella*). The plants are enriched in the lighter isotope of Cu (^{63}Cu) in comparison to the soil in which they grow. Furthermore, different components within the plants are isotopically fractionated. These results are similar to what has been observed for Zn isotopes, which are assumed to be transported through plants by means of diffusion and kinetic fractionation across cell membranes.

Ryan et al. (2013) determined Cu speciation and isotopic compositions in tomato and oat plants. Isotopically light Cu was preferentially incorporated into tomatoes ($\Delta^{65}\text{Cu}_{\text{whole plant-solution}} = -1\text{‰}$); whereas, oats showed minimal isotopic fractionation.

Table 3. Compilation of the isotopic composition of Cu (relative to reference material) for plants, soil, algae and bacteria.

Standard	Type of material	$\delta^{65}\text{Cu}$ (‰)	References
NIST 976	Bacteria	+0.60 to 0.80	Pokrovsky et al. (2008)
	Algae		
NIST 976	Soils	-0.01 to +0.57	Bigalke et al. (2011)
NIST 976	Lentile		Weinstein et al. (2011)
	Virginia Wild Rye	+0.36 to -0.71	
	Hairy leaved-sedge		
NIST 976	Tomatoe		Ryan et al. (2013)
	Oat	-1.05 to -0.11	

2.2 Summary overview

The study of isotopic fractionation of essential elements such as Cu, Fe, and Zn can make a substantial contribution to developing plant metallomics, by helping to unravel the mechanisms of uptake, distribution, and compartmentation of metabolically relevant metals (see Caldelas et al. 2011). However, there is no literature data on the Zn, Fe and Cu isotopic composition in plants that are used as a biogeochemical indicator in mineral exploration. Instead, available data are from experiments performed under abiotic or biotic conditions while basic constraints were set for the plant uptake of Fe isotopes.

The experiments conducted by Weiss et al. (2005) show a systematic depletion in the heavy isotopes of Zn from roots to shoots caused by preferential adsorption on the external root surface. Here, it is important to make a distinction between metals bound to the surface of plant roots and those taken up for metabolic processes. Viers et al. (2007) followed up with Zn isotopic data in a soil–plant system in a tropical watershed in Cameroon. While the emphasis of the study was on the soil horizon, they also measured the Zn isotopic composition of roots, shoots and leaves for three herbaceous species and three tree species. Their main conclusions are somehow different from the ones drawn by Weiss et al. (2005). There was no significant enrichment in light Zn isotopes in shoots, and the Zn isotopic compositions of the leaves, shoots and roots of the three analysed herbaceous species did not differ significantly. Whether or not bulk plant Zn isotopic composition is lighter or heavier than the external bioavailable pool it will depend on the uptake of free Zn or a complex. Free Zn can be either adsorbed to the root or cell surfaces or bound to the functional groups or complexes (Opfergelt et al., 2017). Furthermore, case study from Caldelas et al. (2011) illustrated that the plant will preferentially transfer lighter Zn isotopes into stems and leaves relative to the heavier external pool (Zn sufficient nutrient solution). The root system becomes isotopically heavier and

fractionation is then controlled by the difference in Zn speciation between root system and the most aerial parts of the plant.

Plant growth and decaying plant material is one of the main sources of lighter Cu isotopes in the organic-rich soil (O horizon) in comparison to A horizon as reported by the Zhu et al. (2010). This source would imply that all plants contain lighter bulk Cu isotopic composition relative to soils which requires reduction of soil Cu (II) to Cu (I).

The basic constraints of plant uptake systems for Cu and Zn:

Free Zn can be adsorbed on the plant roots or cells or bound to complexes;

Bulk plant Zn isotopic composition is lighter or heavier in relation to external pool while Cu bulk plant composition is usually lighter;

All plants preferentially transfer lighter Cu and Zn isotopes into stems and leaves;

For Fe and Cu isotope fractionation requires a reduction step while for Zn there is no oxidation state involved.

History of tree ring dating

The field of dendrochronology developed early in the 20th century, with tree ring dating the only recognized scientific technique of precise age determination until the 1950s. During the second half of the 20th century dendrochronology rapidly evolved as a dating method when radiocarbon dating was developed (see Becker, 1992). One of the first pioneers in dendrochronology was A.E. Douglass who established tree ring dating and reconstructed past climate conditions using tree records. Using ancient bristlecone pines (*Pinus aristata* and *P. longaeva*) he developed long dendrochronological records from modern conifer trees dating back to year AD 1260 (Schulman, 1958). It was not until the 1970s that archaeologists saw the benefits of tree ring data in their own field.

There are many disciplines, including environmental, archaeological and climate science, in which tree ring still has important applications.

Tree ring research in Ireland began in 1968 on sub-fossil material such as oak and pine. Precise cross-dating for Irish oak and pine timber was established for periods 8000 years before the present. In constructing tree ring chronology, major climatic events can serve as environmental indicators. Even though, such events did not take place recently, the wet climate helped to preserve timber which grew under bog conditions (Pilcher, 1973). One advantage of using timber is the ability to calibrate the radiocarbon timescale: Baillie et al. (1983), used Belfast dendrochronology as a background for such a high-precision calibration. By establishing a continuous chronology within the British Isles and cross-dating links with German chronology, an absolute Irish standard was confirmed (Brown et al., 1986).

Dendrochronological records of metal absorption could be used in order to distinguish the metal footprint of Zn-Pb and Cu mineralisation from anthropogenic sources. Dinis et al. (2016, 2018) showed that isotope ratios of Pb and Zn in spruce tree rings can discriminate contributions from additional, remote sources such as anthropogenic activities or dust in the Northern Athabasca Oil Sands Region of western Canada. Characterisation of metal sources in European tree and shrub species can be achieved through using trace element and stable metal isotope analysis. This research will be used in the development of new criteria for biogeochemical surveys that detect the uptake of indicator elements in vegetation typical of a temperate European climate.

3 Geological setting

The geology of Europe is tectonically diverse and preserves five main orogenies, Svecofennian (1.8 Ga), Cadomian (550 Ma), Caledonian (400 Ma), Variscan (290 Ma) and Alpine (65 Ma). Base metal (Cu, Pb, Zn) deposits are closely related to specific tectonic events in the Precambrian and Palaeozoic which led to the accretion of cratonic terrains (Large, 2001) and preservation of mineralised settings. The geological setting for deposits relevant to this study, Carboniferous Irish type Zn-Pb and a Proterozoic porphyry Cu in Sweden are described in the following sections.

3.1 Regional geology of Ireland

During the Caledonian orogeny, collision of the northern Laurentian plate with a southern segment of the Gondwanan margin of the East Avalonian plate, resulted in the closing of the Iapetus Ocean. Collision and strong tectonic activity took place in the late Silurian to early Devonian and form the geological basement to much of the Irish Midlands (Phillips et al., 1976, Beamish and Smythe, 1986, McKerrow, 1987, Freeman et al., 1988, Harper and Parkes, 1989, Chadwick and Holliday, 1991, Todd et al., 1991, Vaughan, 1991, Owen et al., 1992, Vaughan and Johnston, 1992). Subsequently, several basement terrains developed within the Iapetus suture zone (Fig. 5) such as Grangegeeth, Bellewstown and the Central Belt (Owen et al., 1992). Caledonian magmatism was accompanied by granite emplacement and major structural activity between 420 – 390 million years ago during which the Kentstown Granite intruded into Lower Palaeozoic sequences in the Navan area (O'Reilly et al., 1997). As a result of the orogeny, Lower Devonian Basins subsided between the Highland and Boundary faults and are characterised by conglomerates and sandstone with inter-bedded volcanic layers (Max and Riddihough, 1975).

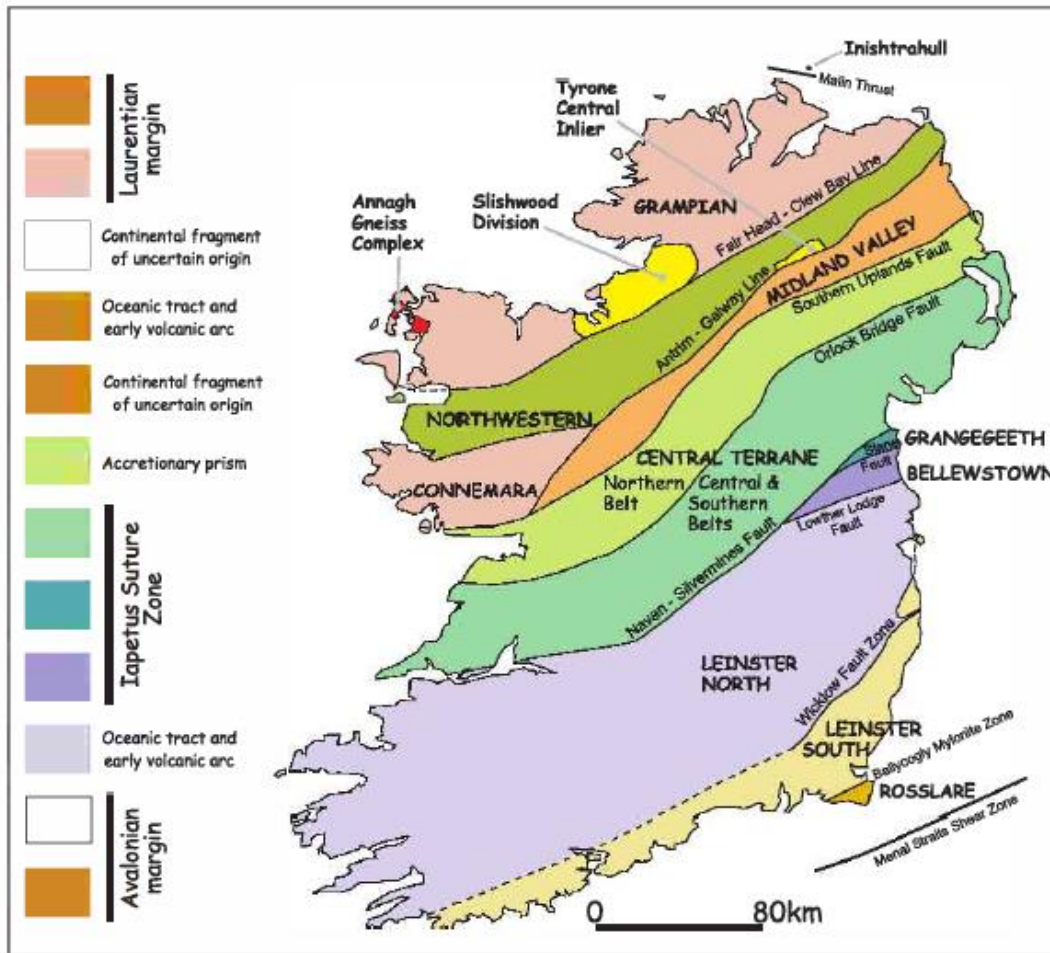


Figure 5. Sketched map of the terranes of Ireland and the main terrane-bounding faults (source: Geological Survey of Ireland, 2004).

The Munster Basin is one of the most important Devonian sequences with sedimentary rocks up to 6.5 km thick (Williams et al., 1989). The basin was dominated with coarse to fine grained fluvial rocks; alluvial fan deposits inter-bedded with aeolian sediments and fluvial coastal sandstones. This type of deposition was mainly a result of erosion by two major river systems (Graham et al., 1983, MacCarthy et al., 1990). During the late Devonian, Ireland was situated near equatorial latitudes when the marine transgression began to encroach across the basin, and confirmed by a presence of brachiopods, dark-grey marine rocks and mudstones. The transgression continued throughout the Lower Carboniferous with sandstone, shale and limestone deposition (MacCarthy et al., 1987).

3.1.1 Irish (Zn-Pb) type of deposit

In order for a world class Zn-Pb deposit such as Navan to form, special lithostratigraphic, tectonic and hydrological conditions are needed to form a trap for metal bearing fluids migrating from the basement source into the carbonate sequences. Hydrothermal ore fluids containing metals such as Pb and Zn triggered sulphide mineralisation which appeared in several different stratigraphic and structural locations (Wilkinson, 2005).

Historically, there has been debate on whether the Irish-type carbonate hosted Zn-Pb deposits belong to the sediment-hosted hydrothermal deposits, SEDEX class or Mississippi Valley Type (MVT) regarding their origin (Large, 1980, Gustafson and Williams, 1981). SEDEX is an early term for hydrothermal deposits which often formed by the exhalation of basinal fluid onto the sea floor while Mississippi Valley type dominantly formed within carbonate host rocks near the edges of the sedimentary basins (Goodfellow and Lyndon, 2007, Arndt et al. 2017). Both deposit types have characteristics reflected in the Irish type deposits for example primarily lead and zinc sulphides, generally stratiform in shape and formed on the carbonate platforms or shelves. For the purpose of exploration in Ireland it was proposed that this type of deposits should be classified as a hybrid of the two members and termed Irish-type carbonate hosted deposits (Hitzman and Large, 1986). The deposits consist of mainly sphalerite, pyrite and galena, and to a lesser extent barite, marcasite, and chalcopyrite, with localised occurrences of silver, nickel and arsenic bearing minerals.

3.1.2 History of mining in Ireland

One of the first major Irish-type carbonate-hosted base metal orebodies discovered was the Tynagh deposit, Co Galway (Clifford et al., 1986). In 1961, the Zn-Pb-Ag deposit at Tynagh (~10Mt) was the first new significant discovery found in Britain and Ireland for over 100 years; several small historical mine workings dating back to 1859 are situated close to the more recent discovery site (Derry et al., 1965). In addition, during exploration drilling at Tynagh, an iron formation unit consisting of ironstone minerals such as hematite, jasper and chert (Schultz et al., 1966) was discovered and subsequently supported syngenetic exhalative models for the Irish Midlands at the time; subsequently, these ironstones have been shown to be a stratiform alteration/replacement facies (Cruise, 1996). In order to understand the genesis of the Tynagh orebody hosted by Waulsortian limestone, systematic studies of the ore and ore forming minerals were undertaken using lithogeochemical tools in mineral exploration (Russell et al., 1974, Boast et al., 1981, Clifford et al., 1988). A number of other significant deposits such as Lisheen, Silvermines, Galmoy, and the world-class Navan orebody (Fig. 6) were subsequently discovered in the Irish Midlands basin (Hitzman et al., 2002).

The Silvermines (~17Mt) Zn-Pb-barite deposit in northern County Tipperary is one of several large stratiform base metal zones which occur in Courcayan siliciclastic and calcareous marine sediments. The deposit is mainly controlled by the Silvermines Fault while the early Carboniferous timing of hydrothermal activity responsible for its formation is broadly contemporaneous with the Navan and Tynagh deposits (Taylor, 1984, Andrew, 1986, Sampson and Russell, 1987, Phillips et al., 1988, Lee and Wilkinson, 2002).

Intensive and sustained exploration for base-metal mineralisation in Carboniferous limestone throughout Ireland led to the discovery of the Navan Zn-Pb orebody in 1970 (described in detail in the following section).

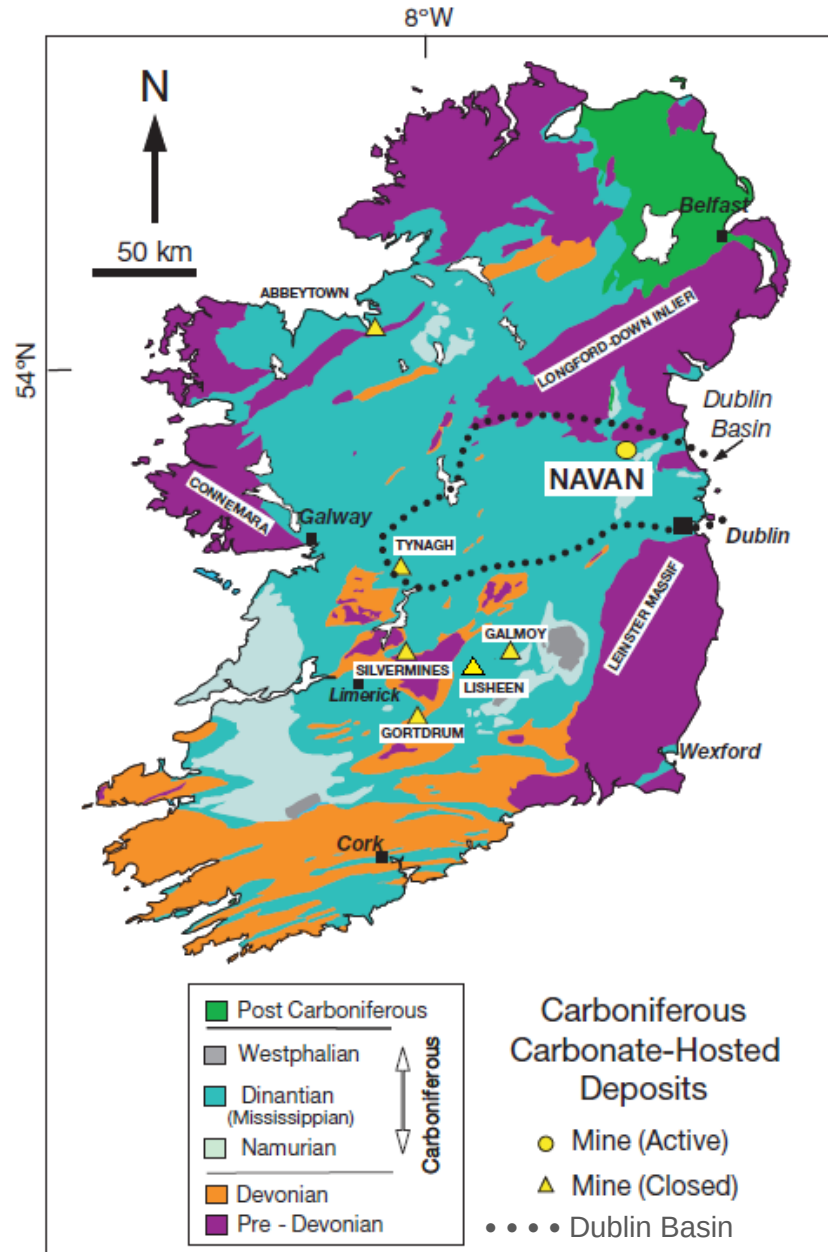


Figure 6. Geologic map of Ireland with the locations of the active and closed Zn-Pb mines (adopted from Gagnevin et al., 2014)

In the southern midlands of Ireland, the Galmoy Zn-Pb deposit (~9.7 Mt) was discovered in 1986 based on a geophysical survey (Induced Polarisation/Resistivity).

The orebodies are mainly hosted by dolomitized Waulsortian limestone sitting on an East-West trending normal fault (Doyle et al., 1992, Lowther et al., 2003). Only 10 km SW from the Galmoy deposit a group of strata-bound pyritic sulphide lenses containing 22 Mt of Zn-Pb ore comprise the Lisheen Zn-Pb-Ag deposit, located in County Tipperary in southeast-central Ireland (Fusciardi et al., 2003). It represents the second most significant base metal discovery in Ireland since the giant Navan deposit was discovered in 1970 (Hitzman et al., 2002, Wilkinson et al., 2005).

The Navan discovery

During the late 1960s, the Tara Exploration and Development Company maintained a prospecting licence near the town of Navan which included the majority of the area now occupied by Tara Mines (Libby et al., 1985). In order to locate the deposit, extensive soil sampling and diamond drilling was undertaken north of the Blackwater River. Soil geochemical results revealed shallow Zn-Pb anomalies ranging from 200 ppm to 5000 ppm at depths of 0.6 m (O'Brien and Romer, 1971). The prospecting licence included several farms which were owned by private landowners. Through private mineral ownership, Bula Ltd. acquired one of these farms at Nevinstown northeast- from the Blackwater River where the orebody sub-crops. Due to this action and subsequent difficulties in obtaining a mining lease, production did not commence at Nevinstown until 2004 after Boliden Tara Mines Ltd. purchased part of the Nevinstown from the receiver Bula Ltd (Libby et al., 1985). At the time of discovery, the Navan deposit was estimated to contain a resource totalling 69.9 Mt grading 10.1% Zn and 2.6 % Pb (Libby et al., 1985). Subsequent diamond drilling, led to the discovery of the South West Extension (SWEX): containing over 30 Mt of Zn-Pb resources (Ashton et al., 2003). Since 2000 continuous surface and underground exploration work has increased Navan resources,

most recently in 2016 with the discovery of the Tara Deep deposit, located 2 km south of the SWEX with over 10 Mt of inferred resources.

Currently, the world class Navan orebody represents the largest Zn-Pb deposit in the Irish Midlands ore field, with a total of 130 Mt at 7.7 % Zn and 1.8 % Pb (production + unmined resources). It shares similar characteristics with the four other economic (past producing) Irish type deposits. One of the most common features is the stratabound nature of the ore, developed in Lower Carboniferous limestone sequences (Johnston et al., 1996).

The Navan stratigraphy

The Lower Carboniferous stratigraphy (Fig. 7) hosting the Navan deposit is mainly dominated by carbonates, originating from generally deepening marine environments, that overlie early Carboniferous fluvial to shallow water marine sediments.

Fluvial sediments comprise Red Beds of Tournasian age. The Red Beds were developed after the erosion of the Old Red Sandstone and redeposited by rivers (Ennis et al., 2015). The sedimentary environment changed upwards into the Laminated Beds and the Muddy Limestone which resulted from occasionally changing, intertidal to shallow marine environments (Strogen et al., 1990, McNestry and Rees, 1992, Rizzi, 1992). The Muddy Limestone comprises crinoidal limestones (biogenic sediment) originating from a marine lagoon environment. Occasionally limestone deposition was disrupted by channelling containing limestone conglomerates which is preserved in the west part of the Navan deposit (Anderson, 1990, Rizzi, 1992). In many areas, due to the marine transgression, this facies progressed from littoral to offshore.

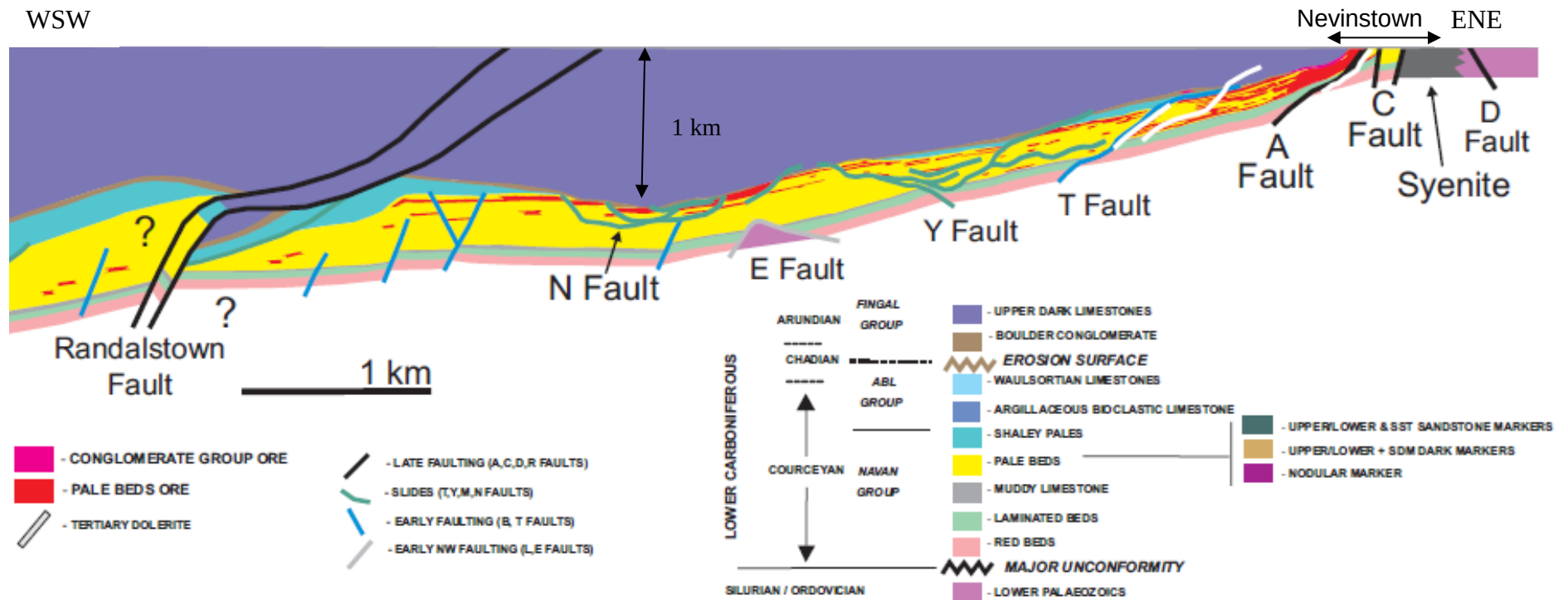


Figure 7. A cross-section of the SWEX and the Main Orebody WSW-ENE with the stratigraphic classification of the main rock types in the Navan area (adopted from Ashton et al. 2015).

The Pale Beds originate from lower and higher energy shallow-water carbonate environments. They represent the main host rocks of the Navan orebody. The Pale Beds consist of distinctive sequences of pale to medium grey micrite, oolitic and bioclastic grainstones and calcareous sandstone (Ashton et al., 2015). The lower part of the sequence contains micrites with bird's eye textures and is broadly referred to as the Micrite Unit which marks different sedimentary features in a tidal environment (Strogen et al., 1990, McNestry and Rees, 1992, Rizzi and Braithwaite, 1996).

In the middle and upper Pale Beds, channel deposits occur and there is also a series of a distinctive marker horizons, including the USM (Upper Sandstone Marker), SST (U Lens Sandstone), ARG (U Lens Argillite) and the UDM (Upper Dark Marker), a particularly well-defined horizon of dark shale (Andrew and Ashton, 1985, Anderson, 1990, Rizzi, 1992). The overlying bryozoan-rich Shaley Pale Limestones were deposited in a deeper water environment. The Shaley Pales are overlain by dark, crinoidal Argillaceous Bioclastic Limestone (ABL) which passes upwards into Waulsortian (WAL) micritic limestone (Philcox, 1984, 1989).

Lower Carboniferous sedimentation was interrupted by an episode of a complex extensional faulting during the late Tournasian with an erosional surface developing over the early Carboniferous and Lower Palaeozoic rocks (Boyce et al., 1983, Philcox, 1989, Ashton et al., 1992). The erosional surface is overlain by the Boulder Conglomerate (BC) which is variable in thickness, texture and composition and formed as a result of a marine debris flow (Boyce et al., 1983, Cook and Mullins, 1983, Ashton et al., 1992, Ford, 1996). During syn-sedimentary rifting, thick, well-bedded limestones termed the Upper Dark Limestones (UDL) were deposited as a major infill of the Dublin Basin and include several stratigraphic units of Late Tournasian to Visean age (Rees, 1987, Strogen et al., 1990, Pickard et al., 1992, Altinok, 2005).

The Main Navan Orebody is composed of stratabound ore lenses hosted by the Pale Beds at 500 m to 1000 m depth below the surface. Five basal ore lenses with complex mineralisation are developed above and mostly on the southeast side of a horst. Major and minor faults have local control on the metal distribution over the entire orebody (Andrew and Ashton, 1985, Blakeman et al., 2002). The size and structure of the orebody is reflected by the size and irregularity of the surrounding lithogeochemical halo in the Pale Beds and Upper Dark Limestones (Marks et al., 2013). In addition, the Main Orebody is developed between its surface suboutcrop at Nevinstown and an elevation of about 700 m below surface, dipping southwest at about 15° over a maximum area of 2.5 by 1.3 km (Ashton et al., 2015).

In general, a lithogeochemical halo can be defined as a metal distribution pattern which surrounds an orebody and may have a distinctive geometry (Hawkes, 1957). The formation of irregular lithogeochemical halos in the Pale Beds at Navan can be associated with fluids being trapped in localised structures resulting in the enrichment of Zn, Pb, Fe, Sb, Cu, Tl, Ba and Mg. Moreover, 100 m above the southwest extension (SWEX) of the orebody, hydrothermal fluids escaped into the Upper Dark Limestones forming a regular halo of Zn, Pb, Fe, Sb, Cd, Cu, Co, Ni, As, Tl, Mn and P (Walker, 2005; Walker, 2010).

In order to recognise the distribution patterns of representative elements within the Navan orebody and its lithogeochemical halo, plants in this study will mainly focus on As, Cd, Pb and Zn as typical elements for Navan mineralisation. An overview of essential elements for plants such as Cu, Fe and Mn and their interactions are given in more detail in Chapter 4).

3.2 Swedish (Cu) porphyry type deposits

Porphyry Cu deposits account for approximately 65% of annual global Cu production (Arndt et al., 2017). In the European context, most production comes from the Fennoscandian Shield (Fig. 8). The Fennoscandian Shield or Baltic Shield is one of the major Precambrian terrains in Northern Europe (Weihed, 2001). Within the shield, many types of mineral deposits formed, including volcanogenic massive sulphide, skarn, Fe-Cu-Au ore and porphyry Cu. The Laver porphyry Cu deposit is situated in the southern Norrbotten region, which is further presented in the following description.

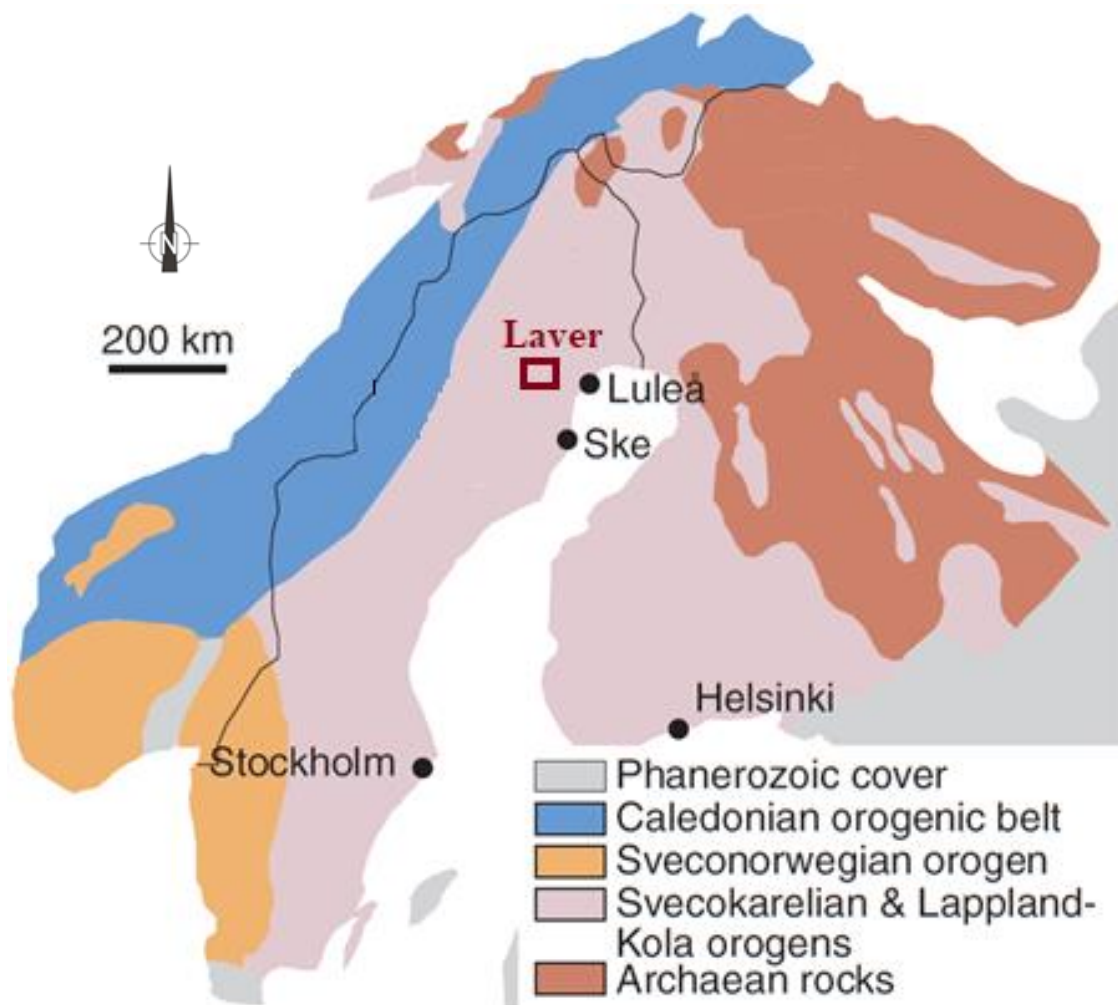


Figure 8. Simplified geological map of the Fennoscandian Shield (source: internal Boliden exploration report, 2014).

3.2.1 Laver – porphyry style Cu-Au-Mo deposit

In 1933, a Cu-rich boulder was found about 10 km south east of Laver by mining company Boliden which led to the discovery of Laver deposit. The Laver Cu mine operated between 1938 and 1946 as an open pit and underground operation. The high-grade Cu ore was situated along narrow zones, and with extracted resources totalling 1.3 Mt @ 1.5% Cu, 0.2 g/t Au and 36 g/t Ag. The main ore minerals consist of chalcopyrite, pyrrhotite and pyrite. During the 1970s, the company continued with outcrop mapping, till sampling and diamond drilling which was followed up with rock chip sampling and IP ground surveying in the 1990s (Wasström, 2009). Boliden extracted approximately 1.5 Mt of ore with Cu, Ag and Au (Rodriguez et al., 2011).

Host rocks to the Laver deposit (Fig. 9) comprise 1.88-1.86 Ga Arvidsjaur volcanic rocks and granitoids (porphyries of felsic to mafic composition). The mineralization comprise mainly of sulphides in dissemination and veins. The main minerals are chalcopyrite, pyrrhotite, pyrite, molybdenite, magnetite and sphalerite. The metamorphic grade is upper greenschist to lower amphibolite facies. Most lithologies are feldspar porphyritic with a fine-grained groundmass and a dacitic-andesitic composition, but rhyolites and basalts occur as well. Volcanic rocks consist of lava flows, pyroclastic rocks, sub-volcanic intrusions and dykes. In addition, rocks exhibit a porphyritic texture in the form of alteration zonation and flow-banding. Associated with these porphyries are breccias, volcanoclastic rocks and debris flows derived from the above-mentioned porphyries, some of these also contain rare pumice clasts (Knipfer et al., 2014).

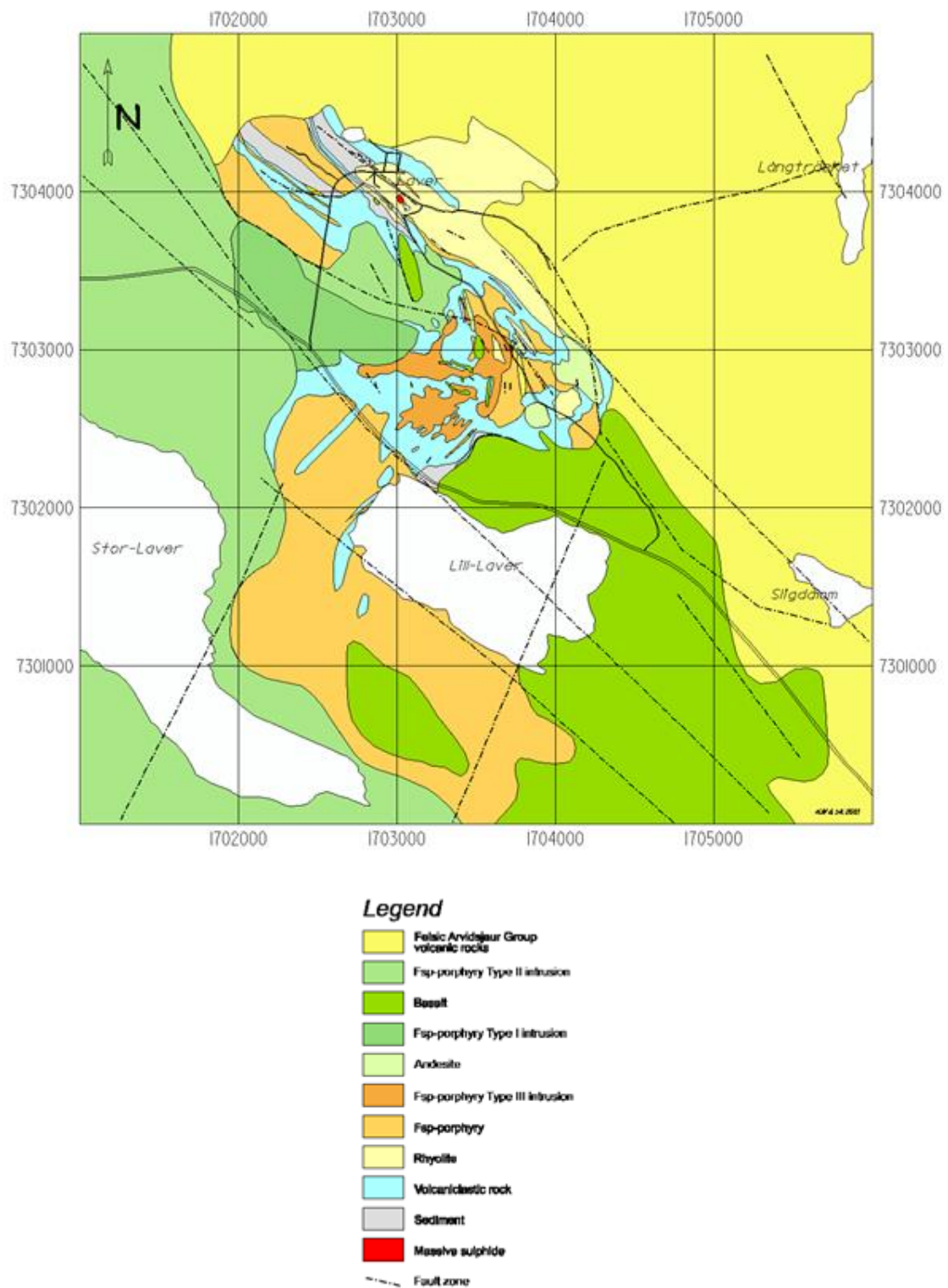


Figure 9. Simplified geological map of Laver regional geology (adopted by Knipfer et al., 2014). Swedish coordinate system SWEREF TM 99.

4 Biogeochemistry

Biogeochemistry is a chemical approach which combines the three disciplines of biology, chemistry and geology. Even though biology mainly consists of studies of flora and fauna, here the focus is placed only on the plant kingdom (greek; *phyto*). The understanding of the interaction between living organisms, rocks, water and air was already accepted as an ancient Greek Theory (Meinwald, 2018). However, the term: biosphere originated from the Austrian geologist Eduard Suess in the early 1900's. It was the Russian geochemist and mineralogist Vladimir Vernadsky who founded and developed biogeochemistry as a discipline (Gorham, 1991, Schlesinger, 2005).

The evolution of land plants has been developing for over 400 million years. Over that period, vascular land plants have managed to adapt to a wide range of both physical and chemical conditions. Since they contain elements drawn from soil, sediment, rock, and groundwater, they can be considered as a surface expression of the underlying soil and host rock. Similarly, plant materials, because of their extensive root system represent a signature which can include multiple soil horizons, till and bedrock (Dunn, 2007).

The following successful case studies show the relevance of biogeochemical surveys in mineral exploration. This exploration method had been widely used in different latitudes and terrains, ranging from arid to humid climates.

In 1969 Rio Tinto, conducted one of the first 'reconnaissance' biogeochemical surveys, carried out over Zn-Pb mineralisation hosted by Carboniferous limestone at the Keel deposit in Ireland. They collected samples of hawthorn (*Crataegus monogyna*), ash (*Fraxinus excelsior*), grasses (*Agrostis* spp.), bracken (*Pteridium aquilinum*) and gorse (*Ulex europaeus*) at Ardagh, Drumming and Keel (Ireland) concluding that vegetation trace element analysis was a more effective method of outlining Zn-Pb mineralisation than

analysis of near-surface (< 40 cm) soil samples (Rio Tinto, 1969, Smyth, 2004). In 1996, an orientation study was conducted successfully to determine the concentration of Au in specimens of vegetation collected in the vicinity of the Curraghinalt gold deposit in Northern Ireland. Gorse (*Ulex europaeus*) proved to be the most practical medium to sample in this area which confirmed the presence of detectable Au originating from the Curraghinalt gold mineralisation (Smyth, 2001).

Some of the world's largest and richest uranium deposits are based in northern Saskatchewan (Canada). A small-scale orientation survey in 1979 identified some unusually high levels of uranium in twigs of black spruce (*Picea mariana*). Even though underlying soils exhibited no significant variations, U concentrations in black spruce were up to 1000-times higher than the background U distribution. Combining different exploration methods (geobotanical prospecting and soil sampling) an extraordinarily large biogeochemical U 'province' was discovered (Dunn, 2007).

A recent regional scale study has shown the biogeochemical expression of buried Fe-oxide-Cu-Au (IOCG) mineralisation in *Eucalyptus* which grow as clusters of multiple stems (mallee growth habit) on the Yorke Peninsula, South Australia (Wolff et al., 2018). Results suggest that biogeochemical sampling of multiple mallee species over large regions could be a useful exploration technique in covered areas of southern Australia where mallee species are widespread and densely populated.

Representative plants for geochemical exploration in Ireland are the most common and native species across the investigated site. When conducting a biogeochemical survey, targeted tree population should be of comparable age. From a practical point of view the trees should to be fully developed, disease-free and accessible for sample collection. Since proposed tree species are deciduous their chemistry changes

substantially during plant growth so it is important to consider seasonal variations (Kovalevsky, 1987). Long lived trees such as oak and beech provide more information regarding historical changes within the atmosphere and can serve as monitors of air contamination. Compared to a soil sample, a tree covers a much larger area and the diameter of the root area extends well beyond the crown of a tree (Polomski and Kuhn, 1998).

Furthermore, the efficiency of root system depends on the distance of their depth of penetration into the soil and the surface roots that comes into contact with the ground. In general, geobotanical prospecting is more suitable in temperate and boreal forests rather than in tropical forests. This is due to biodiversity of tree and shrub species available with the ability to accumulate wide ranges of many elements. The widespread occurrence of ash, beech, blackberry, hawthorn, poplar, oak and sycamore over the studied locality and their ability to grow above the shallow soils with extremely high Pb-Zn anomaly served as a good indicator of which tree species to collect in this study.

In order to establish a suitable biogeochemical exploration protocol for the Irish Orefield, it is necessary to understand metal uptake and interactions across various vascular plant species. Furthermore, this research will demonstrate that representative tree species for Ireland generally differ in chemistry where underlying mineralisation occurs.

Elemental distribution within a plant can originate in soil or from atmospheric deposition. In environmental conditions where soils are being enriched with certain trace elements, plants will prefer adsorption on the root system and following the trend roots > foliage > wood. If more metals are being deposited from an airborne source than currently present in the soil, particulate matter could adhere on the leaf surface which

would imply that more metals are concentrated in leaves rather than in roots (see Chapter 7). Plant chemistry reflects the conditions of the environment within which it is growing, often referred as growth media. Here, the soil solution is a media in which the plant is growing and absorbing metals in the form of ions, chelated metals and complexes (Kovalevsky, 1987). Absorption of dissolved metals on root systems can be influenced by several factors such as: pH and Eh, soil organic matter (SOM), cation-exchange capacity (CEC), ion selectivity, soil solution concentration, type of plant and the stage of plant development (Kabata-Pendias, 2011). Hence, the size and depth of the root system also plays an important role in element uptake and in hydrological cycling. The maximum reported rooting depths for boreal forests is 2.0 ± 0.3 m while temperate deciduous forests exhibit root depths of approximately 2.9 ± 0.2 m (Canadell et al., 1996).

Once elements are absorbed by a root system they are translocated to different parts of the plant. There are several transportation pathways for cations or complexes within plants: migration to phloem and xylem (described below, see Dendrochronology section) and accumulation or storage (Ryan and Asao, 2014). Each of these processes varies for the type of metal and metal species. Plants have control over micronutrient concentrations and certain metals can be concentrated or removed. Therefore, the following section reviews element behaviour (Cd, Cu, Fe, Mn, Pb and Zn) in soils and plants for a better understanding of metal cycling processes in the environment (Tab. 4).

4.1 Element behaviour in soils and plants

Cadmium is a non-essential and toxic metal which can accumulate in the environment. Anthropogenic activities such as Pb and Zn mining, smelting operations and the use of fertilisers can influence the accumulation of Cd in soil and plants (Zawoznik et al. 2007). In most cases, the origin of Cd in uncontaminated soils is reflected by the underlying parental material. It can be highly mobile in acidic environments (pH 4.5 – 5) and during sulphide weathering where free Cd^{2+} is available for plants (Das et al., 1997, Shiel et al., 2012, Wei et al., 2016, Wiggerhauser et al., 2016). Once, taken up by a plant, Cd is translocated through phloem and accumulates in various plants tissues; especially in protein fractions (Gill and Tuteja, 2011). Toxic levels of Cd can induce oxidative stress and metabolic disruptions in plants manifested as stunted growth and chlorosis (Grataño et al. 2009, Gallego et al. 2012). Most recent studies include Cd stable metal isotopes for a better understanding of its behaviour in the environment (Zhu et al., 2018).

Copper is considered an essential and rather immobile element in soil. In addition, it is one of the constituents of fertilisers and agricultural waste. The bioavailability of Cu in soil is strongly affected by a pH, organic matter, redox potential and the water regime (Wang et al., 2017). It may occur in various forms in soils where the Cu^{2+} form predominates (Weber et al., 2009). Furthermore, Cu can play an important role in plant growth processes although this is dependent on the level of Cu supply. Mobile forms of Cu can be strongly controlled by root tissue or transported within the phloem and xylem to plant shoots (Ando et al., 2013).

Iron is an essential element for all living organisms due to its role in a variety of biological processes. Iron typically occurs as either reduced ferrous Fe^{2+} in oxygen-poor environments, or as oxidised ferric Fe^{3+} in oxygen-rich environments (Guelke et al., 2010). The solubility of Fe in alkaline soils is very low and is likely to form oxides and hydroxide whilst at lower pH it becomes mobile and available for plant uptake (Morissey and Guerinot, 2009). Soil horizons rich in organic matter exhibit chelated forms of Fe such as siderophores produced by microorganisms and plants (Ahmed and Holmström, 2014). Plants developed two strategies for Fe uptake: Strategy I in Dicotyledonous (flowering plants) while Strategy II uses iron-chelating agents in Graminaceous (woody plants) (Von Blackenburg et al., 2009). Strategy I plant such as cucumber reduces Fe(III) to Fe(II) under deficiency stress during Fe uptake while a Strategy II plant (e.g. barley) do not necessarily use Fe reduction in the course of the uptake of Fe (Murata et al., 2017). Furthermore, Fe illustrates complex interactions with Mn and Ca which are considered important for plant metabolism.

Manganese is one of the most important micronutrients among essential metals such as Cu, Fe and Zn. The presence of Mn in soils is usually in the form of oxides and hydroxides and can be controlled by redox reactions and hydrolyses (Vodyanitskii, 2009). In acidic environments, the Mn^{2+} form is predominant and highly mobile in soil solution and therefore, bioavailable for plants (Marschner, 1995, Adriano, 2001). In contrast, higher pH values result in Mn (III) and Mn (IV) forms which are less available for plant uptake; thus, adsorbing on soil particles (Rengel, 2000, Fageria et al., 2002). Soluble forms of Mn are translocated within the xylem from roots to the most aerial parts of the plants. One of the most important metabolic processes of Mn is its involvement in oxygen evolution in photosynthesis in green plants responsible for aerobic conditions in the atmosphere (Burnell, 1988).

Lead is a non-essential element for plants and is often used as an environmental indicator of atmospheric pollution coming from lead-utilising industries, including smelters and Pb – Zn mining activities (Lageard et al., 2007). Lead (II) is the most common and reactive form of Pb, forming oxides and hydroxides in soils. Excess Pb tends to accumulate in the top soil horizon reflecting the underlying parental material, but it can also accumulate from atmospheric sources (Markus and McBratney, 2001). The soil acidity induces Pb mobility and availability for plant uptake by roots and translocation to the most aerial parts of the plant. Furthermore, airborne Pb is readily absorbed through foliage making trees as useful medium for the reconstruction of historic Pb contamination (Lageard et al., 2007).

Zinc is an essential micronutrient which can be found in most soils. It is readily soluble as Zn^{2+} and in the form of complexed ions in soil solution. It is controlled by several factors such as pH, clay fractions and soil organic matter (SOM). Soil components in the form of a clay fraction or Fe-Mn oxides and oxy-hydroxides bind Zn in their structure and thus, reduce its mobility within soils (Bowen, 1979, Pedler et al., 2004). Zinc uptake and translocation to plant roots is driven by its concentration in the growth media (Tsonev and Lidon, 2012). In order to be translocated to the plant shoots, Zn occurs as divalent cation or complexed with N-, O- and S-donor ligands (Marschner, 1995, Alloway, 2008). Biochemical functions and plant photosynthesis can be affected by excessive and toxic Zn concentrations in plants (Prasad, 1999, Artetxe et al., 2002, Di Baccio et al., 2005); however, the range in Zn concentrations is plant species dependent.

Table 4. Forms, functions of non-essential and essential elements in plants according to Bowen (1979), Szpunar et al. (2003) and Kabata-Pendias (2011).

ELEMENT	TYPE	FUNCTIONS	FORMS
Cd	non-essential	toxic (stunted growth and chlorosis)	proteins, polysaccharides
Cu	essential micronutrient	photosynthesis, N ₂ fixation	proteins
Fe	essential micronutrient	photosynthesis, N ₂ fixation	proteins, ligands
Mn	essential micronutrient	photoproduction of oxygen in chloroplasts	proteins, enzymes
Pb	non-essential	toxic (stunted foliage, brown short roots)	polysaccharides
Zn	essential micronutrient	lipid metabolism	proteins, peptides

In summary, plant essential elements such as Cu, Mn, Zn and especially Fe are crucial for enzymatic processes within a plant. Based on their quantities, they are considered to be micro elements with an active uptake and intermediate phloem mobility (Bowen et al., 1979). One of the main roles of Fe and Cu in plants are photosynthesis and N₂ fixation whilst Zn is mainly involved in lipid metabolism; and Mn in photoproduction of O₂ in chloroplasts (Clarholm and Skjellberg, 2013). Cadmium and Pb are considered to be non-essential elements for plants even though Cd can be readily absorbed by root and leaf systems. Zinc as an element of interest in this study revealed significant antagonistic interactions among Cd and Fe during uptake processes (Anthea et al., 2011). Moreover, hydrated Zn or Zn²⁺ can be influenced by the presence of Ca in soil solution which contributes to Zn deficiency in plants. Element interactions among other micronutrients, of which Mn effects on Fe absorption in trees also known as Fe-Mn antagonism (Cinelli et al., 2004) could be illustrated in Norway spruce from the case study Laver in Appendix B.

4.2 Biodiversity of the study area

Many geological localities in Ireland are considered as a natural heritage (biodiversity). Surficial geological structures formed during the Quaternary era, when Pleistocene glaciations and the post-glacial Holocene (10 000y–12 000y ago) shaped the present landscape and influenced on its flora and fauna (Lucey and Doris, 2001).

Native forests cover less than one per cent of the land area in Ireland due mainly to the extensive export of timber from the 15th through to the 17th centuries. Some of the native and naturalised tree species in Ireland are: cherries, conifers, birches, alder, oak, ash and hawthorn (Nelson and Walsh, 1993, Cross, 1998).

The principal habitat of the survey area consists of cultivated grassland surrounded by hedgerows, woodland, the Blackwater River and associated marginal vegetation. The hedgerows are well developed and species diversity is fairly typical of the hedgerows in Co. Meath, Ireland (Fossit, 2000).

Botanical overview of tree species

Ash (*Fraxinus excelsior*) is a deciduous (Fig. 11: a, b), ring porous, tall tree (up to 30 m) from the Olive family (Oleaceae). It is common in Ireland and the British Isles, and is well distributed throughout mainland Europe, United States, Canada and New Zealand. It prefers a habitat of hedges, woods and rocky area, especially on moist and alkaline-soils involving calcareous substrates such as limestone (Wardle, 1961). Clusters of small blackish flowers grow from April to May.

Beech (*Fagus sylvatica*) is a large deciduous tree (Fig. 11 c, d) up to approximately 30 m in height with grey and smooth bark. It belongs to the Beech family (Fagaceae) together with Oak and Sweet Chestnut. Sometimes referred to as the European Beech, it is native to the south of England and Wales and is very well distributed across the whole of mainland Europe (Rose, 2006). Originally introduced, Beech is naturalised throughout Ireland. It can be found in woodlands, on well-drained calcified or mildly acidic soils. The root system is shallow, and it spreads laterally in all directions. Furthermore, roots form a symbiotic association with different fungi for nutrient uptake (Blanchette and Biggs, 1992).

Bramble (Blackberry), *Rubus fruticosus*, is a flowering, thorny shrub (Fig. 11 e, f) belonging to a larger genus *Rubus* which is a member of the Rose family (Rosaceae). Similar to Hawthorn, it is very common in Ireland and the British Isles (Blamey and Grey-Wilson, 1989). It can grow from 1 to 3 m in height and its white flowers can be seen from May through September while soft fruit develops in mid-September. Also, blackberry fruit has a significant ability to uptake trace elements such as Fe and Zn (Ensminger et al., 1994).

Hawthorn (*Crataegus monogyna*) is a thorny deciduous shrub or small tree (Fig. 11 g, h) which can grow up to 10 m in height. It belongs to the large Rose family (Rosaceae) and is native to Northern Europe, North America and Asia. It is common in Ireland and the British Isles except in north Scotland where it is quite rare. Usually it can be seen in hedgerows, scrub and open woods (Williamson, 2013). It grows rarely on very acidic and wet soils. During May to June it develops white flowers and berries (haw) form in September.

Oak (*Quercus* spp.) is a long-lived, diffuse porous, deciduous tree (Fig. 11 i, j, k) up to 30 m in height and a member of the Beech family (Fagaceae) and genus (*Quercus*). The name of the tree species was defined as “spp” (species plural) since it is not certain which of the following species it belongs to: Pedunculate Oak (*Quercus robur*) or Sessile Oak (*Quercus petraea*). *Quercus* also includes evergreen species such as Evergreen Oak (*Q. ilex*) which is distributed from tropical areas towards higher latitudes covering the Northern Hemisphere (Kelleher et al., 2005). Pedunculate Oak is generally associated with heavy lowland soils with root system up to 1 m underground while Sessile Oak is found more commonly on poor acid soils (Tree Council of Ireland, 2018).

Poplar (*Populus alba*) is a member of the genus *Populus* from the Willow family (Salicaceae). It is a deciduous, diffuse porous tree (Fig. 11: l, m, n) up to 20 m in height with characteristic diamond shaped marks on the bark and with leaves featuring white undersides. It's extremely aggressive root system prefers moist with neutral to acidic soil. White poplar (*P. alba*) could be hybridised with Aspen (*Populus tremula*) into Grey Poplar (*P. x canescens*). Even though Poplar trees are native to North America it was recorded that the plant species was imported from Netherlands to the British Isles in the 16th century (Tutin et al., 1964).

Sycamore (*Acer pseudoplatanoides*) is a deciduous, diffuse porous, broadleaved tree (Fig. 11 o, p) up to 30 m in height and featuring a wide crown. It is a member of the Maple family (Aceraceae) together with the Field Maple and Norway Maple. In the 16th century it was introduced to the British Isles and is now naturalised throughout Europe, USA, Canada and western Asia (Milner, 2011). During the month of May, it develops catkins and flowers. It is quite common in woodland areas and hedgerows growing on rich soil (root system from 90 – 120 cm) as well as in cultivated areas (Stace, 1992).

Norway Spruce (*Picea abies*) is a large coniferous tree (Fig. 10) from the Pine family (Pinaceae). It is mainly native to Scandinavia, Siberian areas, in mountain ranges such as the Urals, Alps and Dinarides while it has been introduced to Canada and central Europe.



Figure 10. Twigs of Norway spruce (September, 2015) collected from the Laver Cu deposit, Sweden during orientation field work. The spruce tree is growing directly above the Cu-Au-Mo mineralisation. The purpose of this orientation work was to collect spruce and pine needles and analyse them in order to provide an overview of metal distribution in conifers in the former mining area.

In Ireland, habitats range from dry woods to swamp woodland. Here, woodland habitats are divided into three categories. Deciduous woods (oak, beech, etc.) preferring mostly acidic soils; woods on limestone of which ash-sycamore-poplar are principal components and the third category is hedgerow comprising hawthorn and blackberry (Curtis and McGough, 1988).



Ash



Beech



Blackberry



Hawthorn

Figure 11. Examples of deciduous tree species collected at Nevinstown and the control sites, represented on the left-hand side of columns while plant material such as leaves, bark and wood material are on the right-hand side. Photos were taken during the biogeochemical survey in spring and autumn 2015. Continued on the following page.

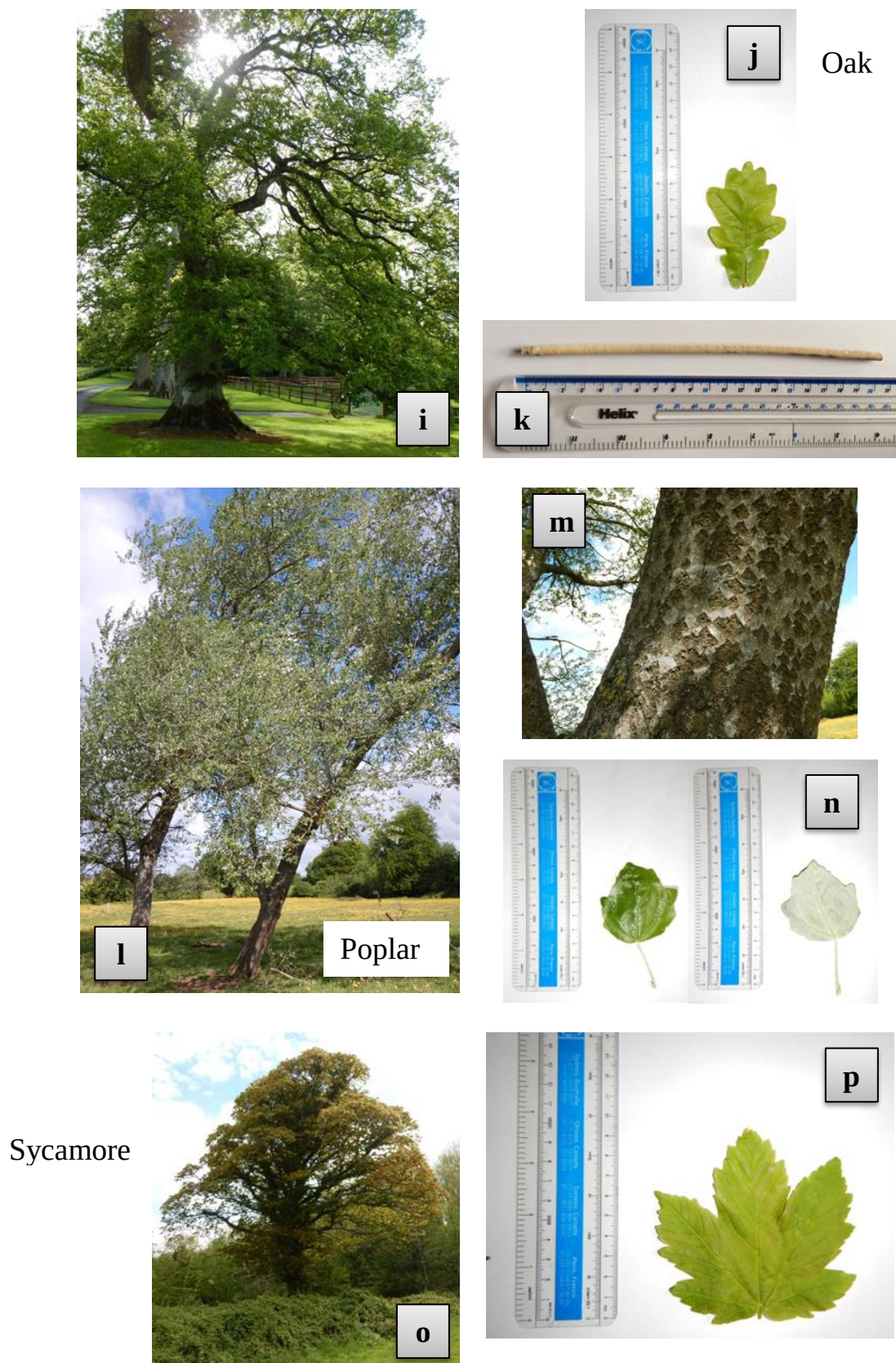


Figure 11. Examples of deciduous tree species collected at Nevinstown and the control sites, represented on the left-hand side of columns while plant material such as leaves, bark and wood material are on the right-hand side. Photos were taken during the biogeochemical survey in spring and autumn 2015.

4.3 Dendrochronology

One of the questions raised in this study was whether the source of metal enrichment observed in trees was due to buried mineralisation or anthropogenic effects (e.g. mining, agriculture). To distinguish between these possibilities, dendrochronological records of metal absorption in oak and beech tree species were examined; as tree records record periods of growth, prior to local Zn-Pb mining and its associated anthropogenic atmospheric emissions.

Most of the trees in temperate climates develop one growth ring per year. The ring width will increase or decrease according to the amount of rainfall in a given year. Wider growth rings will form during the wet season while narrower rings are related to dry years or drought periods. This climatic record is preserved as a series of concentric rings, as exhibited in a horizontal cross-section (Fig. 11) of a tree trunk (Vieira et al., 2009).

The tree cross-section displays vascular cambium as a thin layer of cells between xylem and phloem which is responsible for the burst of large vessels as the leaves expand early in the growth season with the xylem vessels getting smaller throughout the growth seasons. In addition, xylem and phloem are components of vascular tissue of the plant. Xylem transports water and nutrients from roots to leaves while phloem transports sugars and other metabolic product from leaves to roots (Ryan and Asao, 2014). The role of the vessels which are under the bark is to transport fluids with nutrients from the roots to the leaves especially throughout winter until next season growth (Friedrich et al., 2004).

Anatomy of a tree trunk

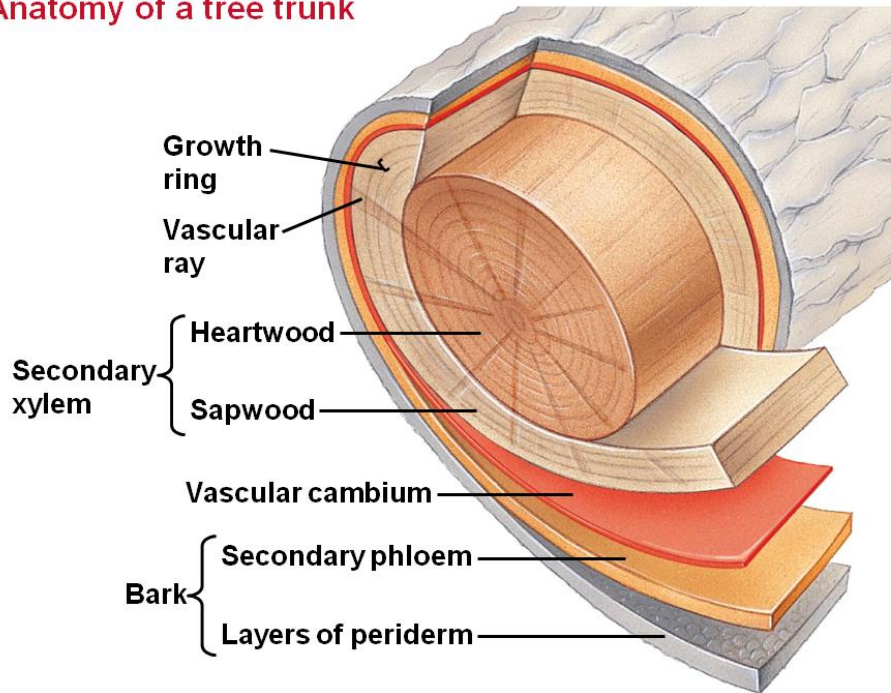


Figure 12. Horizontal cross-section of a tree trunk illustrating different parts of the tree: outer bark to protect the tree trunk, phloem and xylem (sapwood) where nutrients and essential elements are being translocated, a thin layer of cells (phloem) and heartwood (oldest part of the tree). Tree trunk anatomy credit: Pearson Education, 2008 [Online]. Available: <http://www.sliderbase.com/spitem-1455-7.html>. [Accessed, 2018].

Tree ring data is typically collected outside of the tropics (Fig. 12) as trees in temperate latitudes have annual growth rings in the summer and in the winter forming a distinctive pattern of light and dark bands, which is not the case with tropical trees (Brienen, 2005). Tree species investigated in this study belong to a temperate European climate.

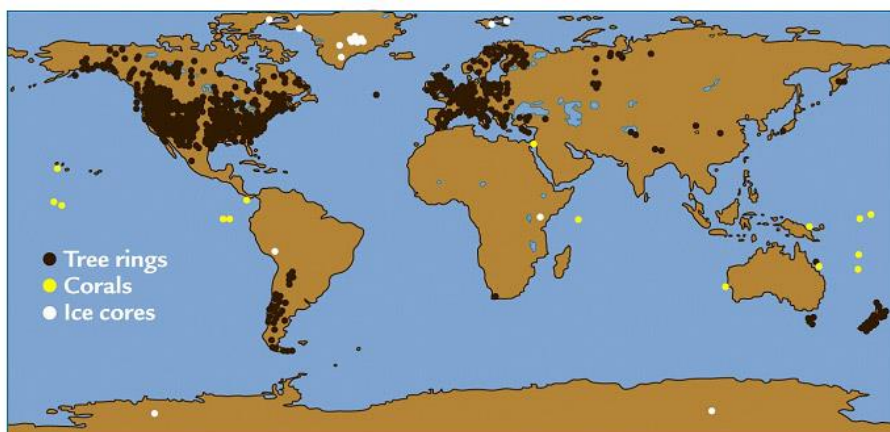


Figure 13. Reported location of the tree ring data from temperate climate zones, coral data in tropical areas and ice cores from highest latitudes (adopted from Russell, 2014) [Online]. Available: https://eo.ucar.edu/staff/russell/climate/paleoclimate/coral_reef_proxy_records.html. [Accessed, 2018]. Photo credit: National Oceanic and Atmospheric Administration Paleoclimatology Program/Department of Commerce.

In order to recognise differences in metal distribution through time (prior and during mining) dendrochronology was applied to tree cores extracted from beech (*Fagus sylvatica*) and oak (*Quercus* spp.) in the Navan area which will be presented in the following chapters.

5 Methodology

Ireland has a typical European temperate climate and is a host to many deciduous plant species. For this study, the primary goal was to find a representative native and common plant species for Ireland that might serve as an ideal biogeochemical exploration tool. Besides the orientation biogeochemical prospecting studies in Northern Ireland by Smyth (2004), this is the first such Irish study in mineral exploration to include extensive field protocols, biogeochemical research, and novel analytical methods in Ireland. The trace element and isotopic content of native plant species such as ash (*Fraxinus excelsior*), beech (*Fagus sylvatica*), blackberry (*Rubus* spp.), hawthorn (*Crataegus monogyna*), oak (*Quercus* spp.), poplar (*Populus* spp.) and sycamore (*Acer pseudoplatanus*) are investigated above the Nevinstown sub-outcrop of the Navan Zn-Pb deposit (Ireland), currently mined by Boliden Tara Mines DAC (Fig. 14). This sub-outcropping carbonate-hosted base metal orebody is characterised by a shallow soil Zn-Pb anomaly. In order to prove that plants can pick up the bio-geochemical signature of the Pb-Zn mineralisation it was necessary to choose the most logical, practical and the closest field site to the orebody itself in the terms of depth. The Main Orebody is developed between its surface sub-outcrop at Nevinstown (the discovery site), and an elevation of about 700 m below surface, dipping southwest at about 15°. Vegetation (trees and shrubs) grow directly above the mineralisation and the soil and reveals the presence of the underlying orebody by elevated Pb and Zn concentration, which makes it an ideal location for comparative biogeochemical surveys. Seasonal sampling, sub-sampling of individual plants and comparison with control locations was investigated with the aim of testing the uptake of trace elements derived from the underlying geology into specific higher plants.



LEGEND:

<i>Lower Carboniferous</i>	
	Upper Dark Limestones
	Boulder Conglomerate
<i>Erosion Surface</i>	
	Waulsortian Limestone
	Argillaceous Bioclastic Limestone
	Shaley Pales
	Pale Beds
	Muddy Limestone
	Laminated Beds
	Red Beds
<i>Regional Unconformity</i>	
<i>Lower Palaeozoics</i>	
	Felsic Intrusive
	Lower Palaeozoics

Map of Ireland

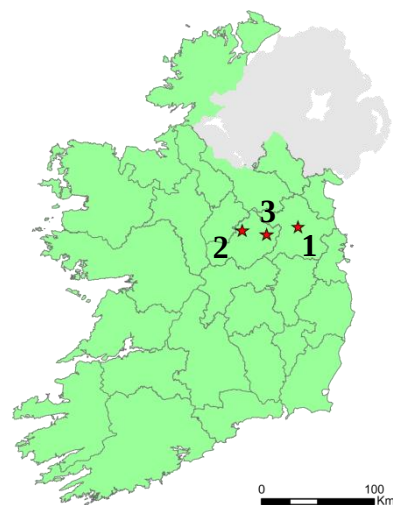


Figure 14. Geological map with accompanying legend showing sampling locations at Nevinstown (1) and three independent control sites (A, B and C). The additional two sampling locations, Ballinalack (2) and Delvin (3) together with Nevinstown (1) are presented on the map of Ireland. The footprint of the sub-outcrop of the Navan orebody is outlined in yellow.

5.1 Sampling strategy and field techniques

First, the biogeochemical survey required a plant survey in the area of interest and a development of a field protocol, including sample locations and quality control which are further explained below.

Vegetation sampling took place in May/June and in September 2015 while soil and tree ring samples were collected in 2016 in the vicinity of the Navan deposit in Ireland (Fig. 14). Four sites were selected of which three were control sites featuring the same plant species. When questioning the occurrence of some background or air contamination it is meaningful to take control of samples. For this, comparable trees and shrub of the same species from non-contaminated areas at the same locality were tested. Since the most common winds blew from west and southwest the control sites were chosen 2 km west, northwest and north from the mine site. The fourth and main field site, Nevinstown covered area of 0.5 km². In 2016, the biogeochemical survey was extended to two additional sites in mineralised and non-mineralised areas, Ballinalack and Delvin, respectively (Fig. 14). The control site at Delvin is situated approximately 40 km west of Navan which mitigates any possible contamination from mining activities. In addition, as a non-mineralised site it represents the regional background of the Irish Midlands. The Ballinalack area (60 km west of Navan) is underlain by a sub-economic Zn-Pb deposit that is hosted by Carboniferous calcareous lithologies. The main reason to additionally include Ballinalack was to investigate whether any impact on metal uptake by hawthorn was affected by varying depth of mineralisation (3 m - 150 m) and thickness of overburden at this location compared to shallow overburden above the Navan deposit (0.5 m).

The sampling site for the Navan orebody is at Nevinstown, north-west of the town of Navan (Fig. 15). Almost the entire site is cultivated land and woodland developed from a former tree nursery north-east of Nevinstown. The River Blackwater, a tributary of the River Boyne is located to the immediate SW of the sampling area. The majority of the site is dominated by improved grassland, either pasture or meadow, with hedgerows marking the main field boundaries. Several patches of scrub occur, and there are stands of planted woodland in the northern sector of the site. Pasture grassland is dominated by common agricultural grass species, mainly rye grass and meadow grasses.

The vegetation types which were identified throughout this study are described herein. Both common English and scientific names are given for plant species; nomenclature follows Rose and O'Reilly (2006). Ash (*Fraxinus excelsior*) is by far the main tall tree species and is accompanied mostly by hawthorn (*Crataegus monogyna*), blackthorn (*Prunus spinosa*) and elder (*Sambucus nigra*), while hedgerows are dominated by blackberry (*Rubus fruticosus*), nettles (*Urtica dioica*) and hogweed (*Heracleum sphondylium*). A block of woodland occurs in the north-east sector of the site; this is planted woodland associated with species including oak (*Quercus* spp.), ash, sycamore (*Acer pseudoplatanoides*), poplar (*Populus alba*) and birch (*Betula* spp.). Further tree species occur such as beech (*Fagus sylvatica*), sycamore and cypress (*Cupressus* spp.) at Nevinstown House.

The Blackwater River is a typical, relatively slow-moving, lowland river. The bankside vegetation along the river is variable. At the eastern end of the site, it is well developed with a typical floodplain appearance. Elsewhere along the river bank the pasture grassland terminates at the water's edge and there is little or no natural riverbank vegetation (Environmental Impact Statement by Boliden Tara Mines, 2010).

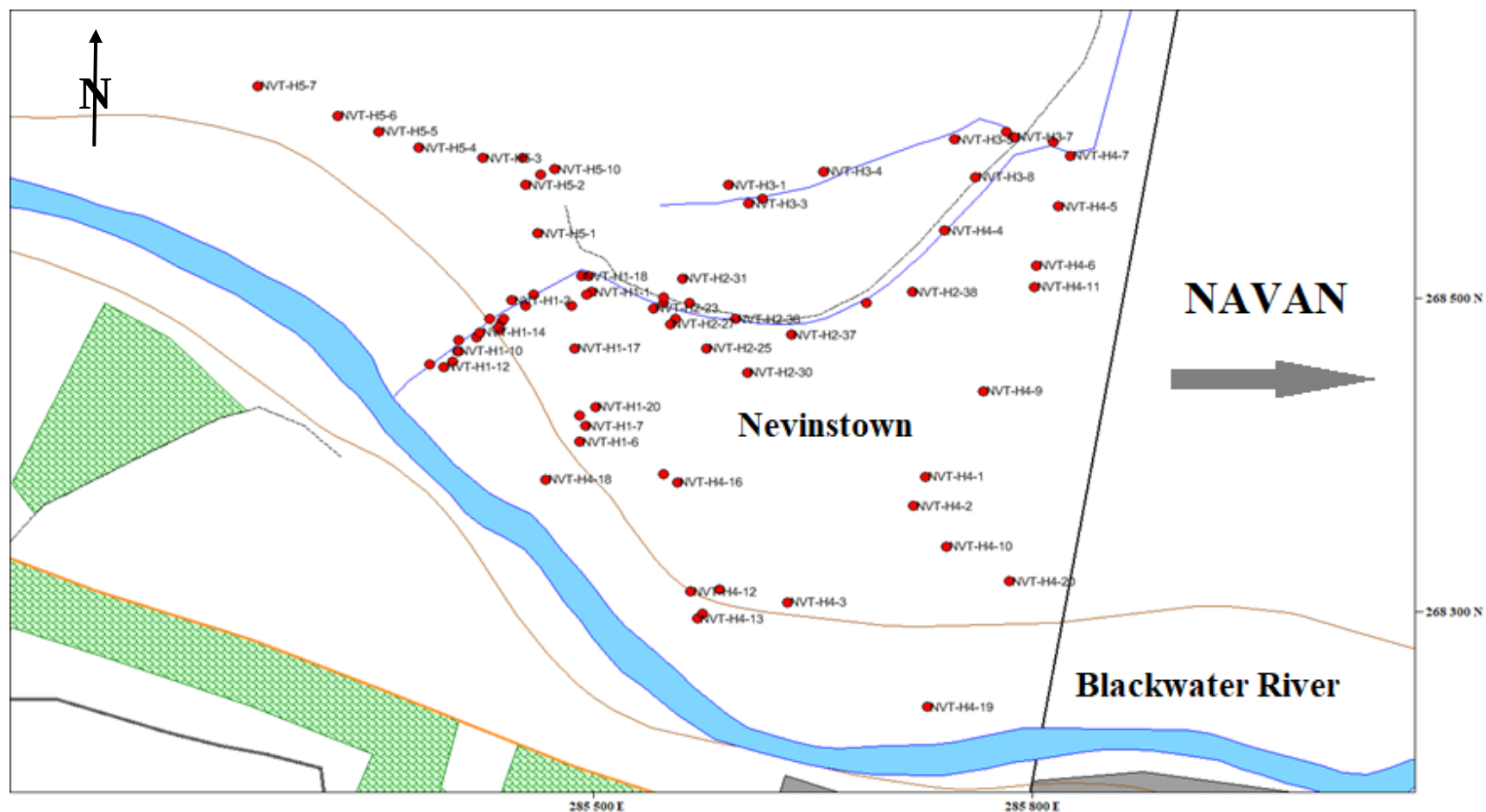


Figure 15. Enlarged main sampling section 1 at Nevinstown (Tara Mines). Plant sample codes are distributed on the topographic map with Irish coordinate system (Irish Grid). Bedrock information of section 1 Nevinstown site can be seen on Figure 14.

The most common native plant species for Ireland were sampled as part of this study. The total number of plant samples collected was 245 including: ash (43), beech (26), blackberry (29), hawthorn (94), oak (13), poplar (9) and sycamore (31). Collected plant material came from fully developed trees; disease-free (visual examination) and accessible for sample collection (Tab. 5).

Table 5. Summary table with the number of samples taken at each site and grid references. Due to a large number of samples taken more information about spatial data and listing codes for each sample are presented in the Appendix A (page numbers are listed in the table).

Sample sites	PLANTS (No. sample)	WOOD (No. sample)	SOIL (No. sample)	GRID REFERENCE	Spatial information and sample codes in Appendix A
Nevinstown	125	6	33	Irish Grid	Tab. A-1, p231
Control	54	5	3	Irish Grid	Tab. A-1, p246
Delvin	24	/	3	Irish Grid	Tab. A-2, p271
Ballinalack	42	/	/	Irish Grid	Tab. A-2, p276
Laver	27	/	/	SWEREF99 TM	Tab. A-3, p286

Furthermore, material consisted of leaves, trunk wood, flowers and soft fruit. During the vegetation period, the elemental composition of living plant tissues can vary considerably during plant growth so it was important to consider seasonal variations in any study. To assess seasonal effects, leaves were collected in the spring and autumn of 2015 during a three-week period; tree cores were collected during summer and winter 2016; hawthorn flowers were sampled in May, and hawthorn and blackberry soft fruit collected in September 2015. Leaves were picked from a height of approximately 2 m using extendable carbide pruning snips which were cleaned with 3% HNO₃ and distilled water prior to collecting each sample. All samples were collected during the morning and stored in plastic bags in order to avoid decomposition of paper bags due to wet vegetation.

Plant sampling

One of the study's goals was to find representative plant material ideal for biogeochemistry. Foliage represents the best medium for sampling because metals accumulate in the leaves of many deciduous and evergreen species and the concentrations are commonly greater than metal concentrations in twigs. According to Dunn et al. (2007) the recommendation for proper twig collection is to obtain several years of growth (at least five years); since this research had a three-year duration, collection of only one or two years twig growth was deemed to be unreliable and was discontinued. Possible cross-contamination from surrounding pastureland might be introduced to the Nevinstown sampling field by cattle. This area includes cattle migration paths which can introduce a cross contamination from nearby pastureland.

During the sampling period, it is important to dry vegetation samples as soon as possible to stop any enzymatic processes; therefore, samples were dried directly the same day of sample collection. Foliage samples in fresh form are preferred for further analysis. Plant samples contain about 50% moisture, thus a sample weight of approximately 100 g has to be collected. Analysis of 1 g samples of dry tissue by ICP-MS is sufficient to provide highly precise and accurate data for most elements; so, the initial sample weight of 50 g of fresh tissue was deemed adequate for this type of survey.

Tree core sampling

Tree core sampling took place mainly in the months of August (six samples) with three samples collected in the months of December to avoid excessive dilution from rainwater; furthermore, plant chemistry is more stable during these seasons. On average, oak and beech trees targeted for the study were in excess of 100 years in age, estimated from a measurement of their circumference (2.7 - 4.1 m), radius (0.44 – 0.65 m) and tree

rings. To obtain optimum concentrations and representative proportions, sampling was carried out at a standard height of 1 m (chest height). In order to extract tree cores from beech and an oak a Haglöf increment borer was used. The Stainless steel increment borer is 5.15 mm in width with a 200 mm bit length with a triple thread tip with a Polytetrafluoroethylene (PTFE) coating. Four beech and three oak tree cores were collected ranging from 0.3 m to 0.4 m in length and were stored in paper straws (see Chapter 4, Fig. 11k).

While extracting tree cores during one of the sampling campaigns a leakage of black coloured discharge with a distinctive acidic scent appeared in oak tree cores. This effect is due to the wet season and increased fluctuation of tree sap in oak trees combined with free iron from the borer reacting with tannins from the tree sap, resulting in the black solution known as Indian ink (Brown 2016, pers. comm.).

Soil sampling

Soils were collected in the summer of 2016 from Nevinstown, control sites (Fig. 17) and in the Delvin area, approximately 40 km west of Navan. Soils were characterised as a Podzolic type using the Soil Geochemical Atlas of Ireland published by Teagasc and the Environmental Protection Agency (2007). In order to investigate trace element behaviour in the soil-plant system (bioaccumulation coefficient), 44 soil samples were collected in an area less than 1 m from the representative plant species. The top soil (A Horizon) was dark coloured and mixed with humus and minerals. Approximately 1 - 2 kg of soil was collected from a depth of 15 – 20 cm and stored in a plastic bag. Initial field measurements of pH and Eh were taken within 12 hours of collection (Fig. 16). A 20 ml portion of soil (by volume) was added to a graduated beaker and made up to 40 ml with the addition of 20 ml of de-ionized water and stirred in order to maintain a consistent

slurry. After pH meter calibration using buffering solutions of pH 4, 7 and 10, pH was measured for the soil samples. Soils for geochemical analysis were dried at $< 60^{\circ}\text{C}$ and sieved through a 180 micron (80 mesh) at ALS Laboratories, Loughrea in Ireland (PREP-41 method).



Figure 16. Soil pH and Eh measurement during soil survey at Nevinstown, control site and in the Delvin area during August 2016.

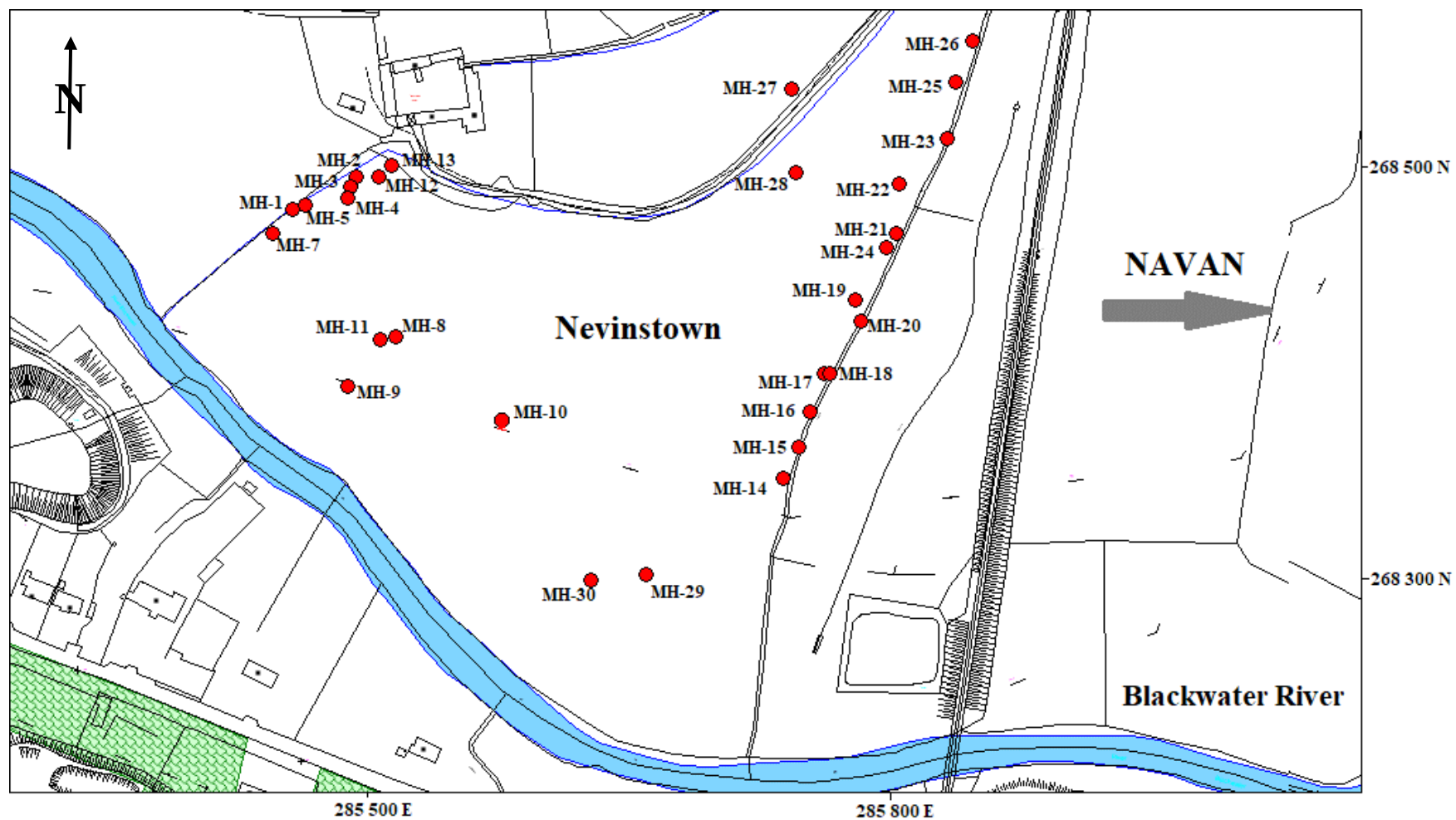


Figure 17. Enlarged main sampling section 1 at Nevinstown (Tara Mines). Soil sample codes are distributed on the topographic map with Irish coordinate system (Irish Grid). Bedrock information of section 1 Nevinstown site can be seen on Figure 14.

Orientation field work at Laver deposit (Sweden)

Laver is a former Cu mine in the north of Sweden. In September of 2015, eleven test samples of spruce and pine needles were collected from an area with high and low-grade Cu mineralisation and also from two potential control sites (Fig. 18).

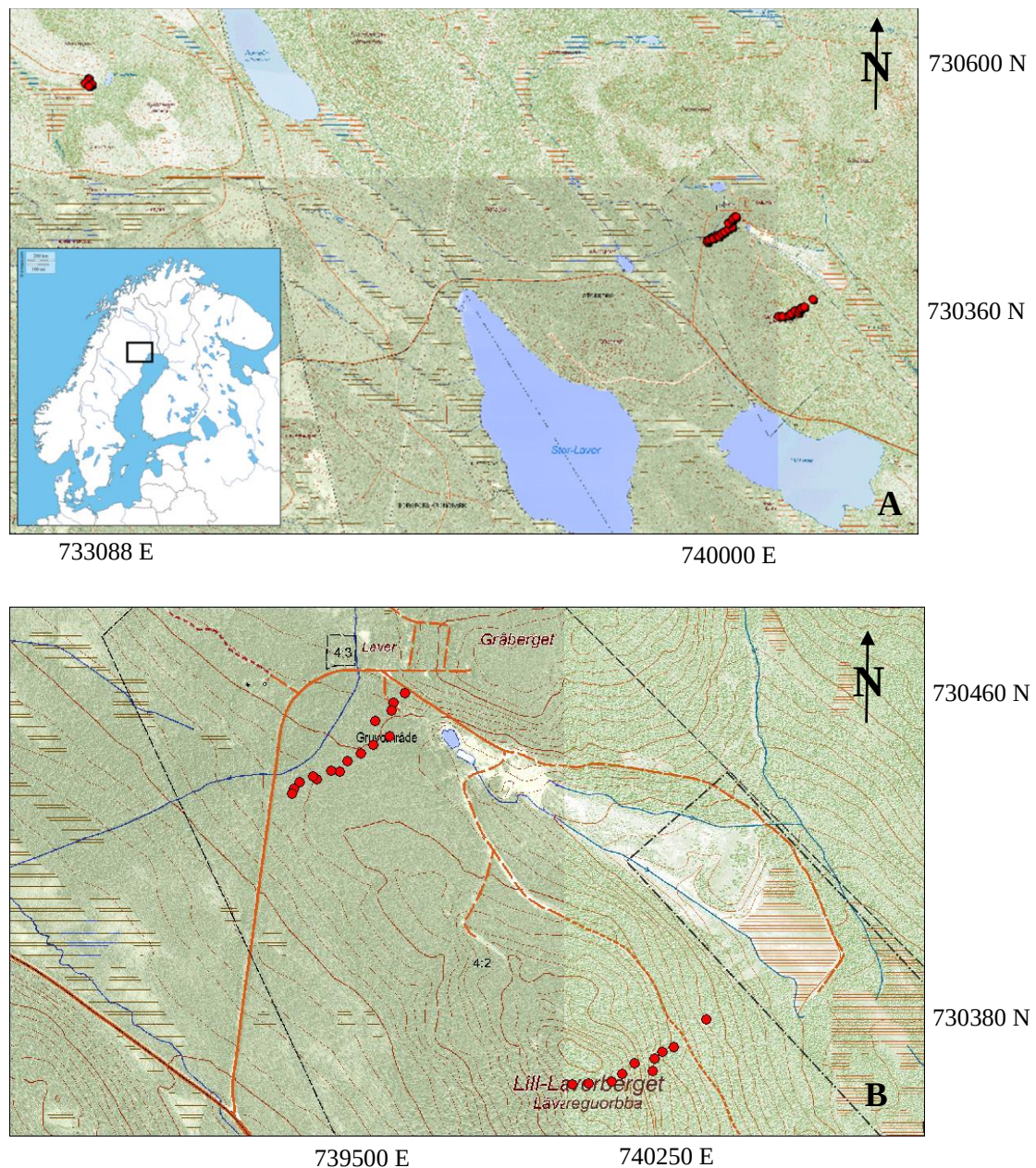


Figure 18: Topographic map of the sampling location (A) at the former Laver mine in Sweden. Two transverse profiles intersect the Laver and Lill-Laverberget area are shown in an enlargement of the map (B). This small biogeochemical survey in Sweden, in which spruce needles were collected, took place in May/June 2016.

Similar techniques were applied for the field sampling programme to that at Navan-Nevinstown site. The purpose of this orientation field work was to test whether pine and spruce trees can be used as an indicator plant species for Cu mineralisation. In 2016, a small biogeochemical survey was conducted on the site in which 38 samples of spruce needles and six tree cores were collected along two profiles situated at Laver (high-grade Cu mineralisation) and Lill-Laverberget (lower-grade Cu mineralisation), with additional sampling at two control sites approximately 20 km NW and SW from the former Laver mine (see Appendix B, Case study Laver).

5.2 Laboratory methods for trace element analysis

5.2.1 Sample preparation

Plant material preparation

The majority of sample preparation was performed at the Environmental Department of Boliden Tara Mines in Navan. During collection, leaf materials were exposed to frequent rainfall and were not washed with water after collection. Samples were transferred from plastic bags into brown paper bags using nitrile gloves and then oven dried at 60° C for 24 hours whilst wood core samples were dried in paper straws. After drying, vegetation samples were milled into a powder using a stainless steel macerator and stored in plastic containers until analysis. Each part of the macerator was thoroughly cleaned with 3% HNO₃ and distilled water between grinding of each sample. Where it was possible, metal tools were substituted with plastic tools (i.e. spoons, spatulas, lids).

Tree core preparation

After drying of tree core samples was complete, the age of the trees was determined through examination of tree rings at Queens University of Belfast in Northern Ireland. Using a microscope and counting each ring from bark towards heartwood (pith), a precise estimate of the age could be determined from the extracted tree core. For further isotopic analyses, representative tree cores were separated into 10-ring segments using a stainless steel craft knife, which was rinsed with 3% HNO₃ and deionised water between cuts. A total of 10-ring segments were weighed (0.079 g – 0.372 g) and divided into two periods. The first period represents 1950 to 1960, prior to any Zn-Pb mining in the Navan region. A second period corresponds to the 10 years between 2000 and 2010, during mining at Tara Mines. Tree ring samples were milled using a stainless-steel macerator. During milling, up to 22% of the initial sample weight was lost due to electrostatic effect between sample and macerator. Entire tree cores, termed as a ‘bulk wood’ here, were milled to 100% passing 1mm using Retsch Mill in ALS Laboratories in Vancouver (VEG-MILL01 method).

Quality control included several measures taken while conducting field work, sample preparation and laboratory work. In order to maintain the validity and quality of the experiment, several control sites were chosen around the study area. For every tenth sample collected an additional field duplicate was collected and analysed. During sample preparation tools made of stainless steel were cleaned in order to avoid any cross-contamination; plastic tools were used where possible. Analytical work involved continuous calibration checks. Certified and internal standard reference materials for vegetation, soils and rocks were analysed at regular intervals with sample unknowns. Laboratory duplicates were analysed for every 20th sample analysed.

5.2.2 Sample digestion and measurements

Analytical work was performed at the Boliden Tara Mines Laboratory in Navan. A digestion method was specially designed for the purpose of this biogeochemical study. Prior to any work, test samples of beech leaves were analysed in order to estimate optimum sample weights and the volume ratio of nitric acid to hydrochloric acid needed to completely digest the sample without producing secondary reactions. During preliminary test analyses, 0.5 g and 1.0 g of dried beech leaves were digested using A) 7 ml of concentrated HNO_3 and 3 ml of concentrated HCl ; B) 8 ml of HNO_3 and 2 ml of HCl and C) 9 ml of HNO_3 and 1 ml HCl ; in addition, different temperatures and digestion times were tested as well. It was concluded that one gram of dried plant material was sufficient to be completely digested using Aqua Regia ($\text{HNO}_3\text{:HCl}=4\text{:}1$) in a MARXpress microwave digestion system. The element concentrations (As, Cd, Co, Cu, Fe, Pb, Sb and Zn) were measured with an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) (see Appendix A, Table A-6). Quality assurance was monitored by analysing two samples of reference material NIST SRM 1515 (Apple leaves, European Community Bureau of Reference); 6 duplicates and 2 blanks were analysed in each batch of 40 samples.

During the initial analyses difficulties were encountered involving lower digestion recoveries ($< 80\%$) of Cu, Fe, Mn and Pb. The Apple leaves standard (NIST 1515) contains low concentrations of Ge. Since the Tara Mines laboratory uses Ge as an internal standard for ICP-MS measurements some values were deemed unreliable. This was overcome by using a combination of Lu, Rh and Sc as internal standards instead of Ge. This combination of internal standards was used because the apple leaves standard does not contain these elements; therefore, they do not interfere with the internal standards for an ICP-MS.

During analysis of plant samples collected in the autumn, the blank sample values exhibited high Cu, Pb and Zn concentrations. With recoveries ranging from 76% - 136% and for the reasons mentioned above, samples were submitted to ALS Laboratories for analysis of 53 elements (Au, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr), as the Tara Mines Laboratory could not measure the proposed full package of elements.

Vegetation samples were analysed in ALS Laboratories in Vancouver, Canada with an 'Ultra-Trace Level method' (ME-VEG41) using ICP-MS and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). Prepared samples (1.0 g) were cold digested for approximately 8 h in HNO₃, before being transferred to a hot block for 15 minutes at 85° C followed by 2 hours at 115° C. The samples were subsequently cooled and brought up to volume with HCl. The resulting solution was mixed thoroughly and analysed by ICP-AES and ICP-MS. The analytical results were corrected for inter-element spectral interferences; the limits of detection are reported in Chapter 6.

Soil samples were submitted to ALS Laboratories in Loughrea, Ireland for analysis of 53 elements (Au, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn and Zr) using the 'Super Trace method' (ME-MS41L). A 0.5 g sample was digested in Aqua Regia and analysed via ICP-MS and ICP-AES. Prior to analyses, the samples were digested in hot boxes at 115° C; this represents the surface temperature off the boxes, such that the solutions would reach a temperature of 90° - 95° C. In addition, a prepared portion (20 g) of each sample was leached with deionized water for 1 hour in the ratio of 1 mL water per 1 g of sample. The mixture was centrifuged and the pH of the supernatant fluid was measured using a pH meter. Loss on

ignition at 550°C was determined by muffle furnace using 1 g of sample. Sample weights before and after were reported as well. For this method (OA-GRA05x) limits of detection are reported in the Chapter 6.

Standard Control Limits (Data Quality)

All data were corrected using values for blank samples. Blank samples consist of reagents only and can be used to observe any contamination in the process of sample preparation or acid digestion. The recovery ratio of trace elements was $100\% \pm 10\%$ using a standard of apple leaves (NIST SRM 1515) for deciduous leaf material; standard of pine needles (NIST SRM 1575a) for spruce needles and oak and beech wood and Internal ALS Standard; and Geochem Base Metal Reference Material (GBM908-10), Mid-range multi-element certified reference material (MRGeo08) and generic metadata standard (GEOMS-03) for soil samples. Element recovery data beyond that range ($< 90\%$ and $> 110\%$) was discarded. The chemical values of Au, Al, Ge, Na, Nb, Sc, Se, Sb, Th, W and Y showed recoveries below 90% and above 110% in plants; therefore, they were discarded. ALS Geochemistry utilizes method precision as the basic principle for setting target performance control limits for analytical reference materials (standards). I.e.:

$$Conc \pm P * Conc \quad \text{Where} \quad (1)$$

$Conc$ = Concentration of the Standard

P = Precision expectation of the method

This differs from the classic approach of using 2 or 3 sigma limits from the manufactures' certificates, for the following reasons:

- I. To establish target performance expectations for the analytical method that are not the factor of the standard itself.
- II. To ensure consistent targets within the method.

By using target precision instead of 2σ limits, the acceptable range for all standards becomes similar. Method Precision Expectations are set according to method type to take into account differences such as test tube vs. volumetric flask digestions, different instrument calibrations etc. In general, geochemical exploration methods have a precision expectation of $\pm 10\%$ (ALS Geochemistry, 2014). Acceptable ranges for standards used in ‘Ultra-Trace Level method’ for plants and ‘Super Trace method’ for soils are shown in Table 6 & 7.

Given the variation in composition between duplicates sampling precision is expressed as scaled mean absolute difference (MAD) as shown below:

$$\text{MAD Precision} = \sqrt{\frac{\pi}{2}} \frac{1}{n} \sum_{i=0}^n |D_1| * 100\% \quad (2)$$

Where

$$D_1 = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{\bar{C}_i}$$

D_1 = relative difference between sampling duplicates

C_{i1}, C_{i2} = concentrations of a sample and its duplicate

$\bar{C}_i$ = mean concentrations of C_{i1} and C_{i2} .

The benefit of using an alternative approach in estimating precision using duplicate measurements such as MAD Precision is less sensitivity to outliers in case of large differences between data pairs according to Hyslop and White (2012). MAD Precision data for all sampling duplicates are reported in Appendix D & E.

Table 6. Reference certified material (standards) for plant analysis. Mean concentrations are expressed as nominal value. Acceptable range is based on targeted precision expectation and on method detection limits. Continued on the next page.

Element	Standard ID Plant Analysis	Nominal value	Acceptable range	Precision expect. & Detection Limit
As (ppm)	NIST SRM 1575a	0.04	0.02-0.06	±10%, DL=0.01
	NIST SRM 1515	0.09	0.02-0.06	
	ALS STD VEG 2	1.37	1.19-1.47	
Ba (ppm)	NIST SRM 1575a	6.98	5-7	±15%, DL=0.1
	NIST SRM 1515	44.58	41.6-56.5	
	ALS STD VEG 2	8.55	6.7-9.3	
Ca (%)	NIST SRM 1575a	0.28	0.22-0.29	±10%, DL=0.01
	NIST SRM 1515	1.43	1.37-1.69	
	ALS STD VEG 2	1.91	1.59-1.96	
Cd (ppm)	NIST SRM 1575a	0.17	0.209-0.257	±10%, DL=0.001
	NIST SRM 1515	0.01	0.01-0.016	
	ALS STD VEG 2	0.04	0.032-0.042	
Co (ppm)	NIST SRM 1575a	0.05	0.053-0.069	±10%, DL=0.002
	NIST SRM 1515	0.08	0.075-0.097	
	ALS STD VEG 2	1.77	1.51-1.85	
Cr (ppm)	NIST SRM 1575a	0.16	0.17-0.23	±10%, DL=0.01
	NIST SRM 1515	0.20	0.1-0.16	
	ALS STD VEG 2	9.30	8.5-10.4	
Cu (ppm)	NIST SRM 1575a	2.49	2.51-3.09	±10%, DL=0.01
	NIST SRM 1515	5.24	5.07-6.21	
	ALS STD VEG 2	7.82	6.97-8.55	
Fe (ppm)	NIST SRM 1575a	35.63	35-45	±10%, DL=1
	NIST SRM 1515	63.59	53-67	
	ALS STD VEG 2	2106	1880-2300	
Hg (ppm)	NIST SRM 1575a	0.03	0.033-0.047	±15%, DL=0.001
	NIST SRM 1515	0.04	0.036-0.052	
	ALS STD VEG 2	0.05	0.036-0.051	
K (%)	NIST SRM 1575a	0.40	0.37-0.47	±10%, DL=0.01
	NIST SRM 1515	1.51	1.44-1.78	
	ALS STD VEG 2	0.17	0.14-0.19	
Mg (%)	NIST SRM 1575a	0.08	0.08-0.1	±10%, DL=0.001
	NIST SRM 1515	0.23	0.233-0.287	
	ALS STD VEG 2	0.11	0.089-0.111	
Mn (ppm)	NIST SRM 1575a	340	439-537	±10%, DL=0.1
	NIST SRM 1515	53.31	48.5	
	ALS STD VEG 2	364	326-399	
Mo (ppm)	NIST SRM 1575a	0.01	0.005-0.04	±10%, DL=0.01
	NIST SRM 1515	0.08	0.07-0.11	
	ALS STD VEG 2	0.18	0.16-0.21	

Table 6. Reference certified material (standards) for plant analysis. Mean concentrations are expressed as nominal value. Acceptable range is based on targeted precision expectation and on method detection limits. Continued on the next page.

Element	Standard ID Plant Analysis	Nominal value	Acceptable range	Precision expect. & Detection Limit
Ni (ppm)	NIST SRM 1575a	1.10	1.28-1.66	±10%, DL=0.04
	NIST SRM 1515	0.86	0.78-1.04	
	ALS STD VEG 2	5.98	5.28-6.55	
P (%)	NIST SRM 1575a	0.09	0.095-0.119	±15%, DL=0.001
	NIST SRM 1515	0.15	0.142-0.176	
	ALS STD VEG 2	0.04	0.033-0.043	
Pb (ppm)	NIST SRM 1575a	0.15	0.14-0.2	±10%, DL=0.01
	NIST SRM 1515	0.75	0.37-0.47	
	ALS STD VEG 2	0.88	0.8-1.01	
Rb (ppm)	NIST SRM 1575a	14.78	14.3-17.5	±10%, DL=0.01
	NIST SRM 1515	9.85	8.54-10.45	
	ALS STD VEG 2	2.31	2.04-2.52	
S (%)	NIST SRM 1575a	0.11	0.08-0.14	±10%, DL=0.01
	NIST SRM 1515	0.17	0.16-0.22	
	ALS STD VEG 2	0.12	0.08-0.13	
Sn (ppm)	NIST SRM 1575a	0.02	0.02-0.06	±10%, DL=0.01
	NIST SRM 1515	0.06	0.04-0.08	
	ALS STD VEG 2	0.06	0.04-0.09	
Sr (ppm)	NIST SRM 1575a	6.43	5.83-7.17	±10%, DL=0.02
	NIST SRM 1515	23.43	22.5-27.5	
	ALS STD VEG 2	111	94.9-116	
Zn (ppm)	NIST SRM 1575a	27.89	34.1-41.9	±10%, DL=0.1
	NIST SRM 1515	11.95	11.2-13.9	
	ALS STD VEG 2	22.31	19.4-24	

Table 7. Reference certified material (standards) for soil analysis. Mean concentrations are expressed as nominal value. Acceptable range is based on targeted precision expectation and on method detection limits. Continued on the next page.

Element	Standard ID Soil Analysis	Nominal value	Acceptable range	Precision expect. & Detection Limit
Al (%)	GBM908-10	1.02	0.85-1.06	±10%, DL=0.01
	MRGeo08	2.76	2.44-3	
	GEOMS-03	1.75	1.63-2.01	
As (ppm)	GBM908-10	57.2	49.5-60.5	±10%, DL=0.01
	MRGeo08	33.70	29.7-36.3	
	GEOMS-03	631	553-677	
Ba (ppm)	GBM908-10	102.5	88.8-121.5	±15%, DL=0.5
	MRGeo08	456	381-517	
	GEOMS-03	1130	969-1310	
Ca (%)	GBM908-10	0.7	0.62-0.79	±10%, DL=0.01
	MRGeo08	1.13	1-1.24	
	GEOMS-03	0.37	0.3-0.38	
Cd (ppm)	GBM908-10	1.69	1.53-1.87	±10%, DL=0.001
	MRGeo08	214	2.02-2.47	
	GEOMS-03	0.328	0.287-0.353	
Co (ppm)	GBM908-10	13.8	12.35-15.15	±10%, DL=0.001
	MRGeo08	19.90	17.1-20.9	
	GEOMS-03	12.65	10.55-12.85	
Cr (ppm)	GBM908-10	23.3	20.2-24.8	±10%, DL=0.01
	MRGeo08	94.50	82.3-100.5	
	GEOMS-03	75.2	67.7-82.8	
Cu (ppm)	GBM908-10	3610	3380-3880	±7%, DL=0.01
	MRGeo08	630	587-675	
	GEOMS-03	131.5	124.5-143.5	
Fe (ppm)	GBM908-10	2.72	2.36-2.88	±10%, DL=0.001
	MRGeo08	3.61	3.23-3.95	
	GEOMS-03	4.14	3.49-4.27	
Hg (ppm)	GBM908-10	0.007	0.007-0.026	±15%, DL=0.004
	MRGeo08	0.007	0.047-0.075	
	GEOMS-03	0.598	0.583-0.798	
K (%)	GBM908-10	0.43	0.37-0.48	±10%, DL=0.01
	MRGeo08	1.32	1.12-1.4	
	GEOMS-03	0.35	0.29-0.37	
Mg (%)	GBM908-10	0.55	0.47-0.59	±10%, DL=0.01
	MRGeo08	1.15	1.03-1.29	
	GEOMS-03	0.44	0.39-0.49	
Mn (ppm)	GBM908-10	292	264-322	±10%, DL=0.1
	MRGeo08	415	382-468	
	GEOMS-03	534	488-596	

Table 7. Reference certified material (standards) for soil analysis. Mean concentrations are expressed as nominal value. Acceptable range is based on targeted precision expectation and on method detection limits.

Element	Standard ID Soil Analysis	Nominal value	Acceptable range	Precision expect. & Detection Limit
Ni (ppm)	GBM908-10	2290	2030-2480	±10%, DL=0.04
	MRGeo08	706	622-760	
	GEOMS-03	56.4	48.3-59.1	
P (%)	GBM908-10	0.087	0.076-0.096	±15%, DL=0.001
	MRGeo08	0.10	0.09-0.113	
	GEOMS-03	0.106	0.092-0.114	
Pb (ppm)	GBM908-10	2060	1860-2270	±10%, DL=0.005
	MRGeo08	1048	959-1175	
	GEOMS-03	5.08	4.43-5.43	
S (%)	GBM908-10	0.38	0.33-0.43	±10%, DL=0.01
	MRGeo08	0.31	0.27-0.35	
	GEOMS-03	0.03	0.005-0.05	
Sn (ppm)	GBM908-10	1.55	1.52-1.88	±10%, DL=0.01
	MRGeo08	3.45	3.05-3.75	
	GEOMS-03	1.64	1.34-1.66	
Sr (ppm)	GBM908-10	32.4	31-37.9	±10%, DL=0.01
	MRGeo08	81.10	72.3-88.3	
	GEOMS-03	100.5	95.4-116.5	
Zn (ppm)	GBM908-10	1075	941-1150	±10%, DL=0.1
	MRGeo08	806	710-868	
	GEOMS-03	45.2	42.2-51.8	
Zr (ppm)	GBM908-10	26.3	24-32.4	±15%, DL=0.01
	MRGeo08	20.85	18.6-25.2	
	GEOMS-03	2.33	2.02-2.76	
LOI (%)	OREAS 90	3.32	1.69-2.09	±10%, DL=0.01
pH	SILICA	7	6.4-8.0	±10%, DL=0.1

5.3 Isotopic analysis

Isotope measurements were carried out at the Department of Mineralogy, Leibniz University in Hannover, Germany. Sample digestion and column chemistry were performed in clean rooms (class 1000) with several laminar flow workstations (cleanroom, class 10).

In order to measure Cu and Zn isotopes, standard sample bracketing was used with certified international standards including Cu NIST 976, NBS C125_1; Ni NIST 986; Zn IRMM 3702 and NIST 683. A Ni standard solution (NIST 986) was used for Zn measurement and a Cu standard solution (NIST C1251) was used for a mass bias correction. Altogether, analysis included 25 samples of which 12 leaf material samples, four wood material samples and nine soil samples with three additional reference materials: USGS BCR-2 (Basalt Columbia River), Analytica METRANAL 33 (soil) and LGC7162 (strawberry leaves) were analysed.

Due to a lack of wood material which was coarse grinded, several possibilities for digestion were considered, these were: 1) ash the wood sample prior to digestion or 2) simple acid digestion without ashing. The challenge of using ashing is that it can significantly reduce the amount of sample available for future analysis but once the sample is ashed it can be completely digested. Thus, there is a possibility of incomplete digestion of larger particles of wood material using only acid digestion. For this purpose, one wood sample was ashed while a small piece of the same wood sample was left soaking in hydrogen-peroxide (H_2O_2) overnight under warm conditions followed by heating at 180° C on a hot plate to test whether it was completely oxidised.

Furthermore, soils ranging from 200 mg to 250 mg were ashed at 460° C for 24 h. Samples, including a soil standard (Metranal 33) and a basalt standard (BCR-2) were each weighed with ceramic crucibles before and after ashing. Loss on ignition was estimated between 25% and 50% (list for all samples is in Appendix A, Table A-4). Ceramic crucibles with lids were pre-cleaned mechanically first using ethanol followed by the addition of 6M HCl and boiling at 110° C for 6 h. Once cooled, the samples were rinsed twice and dried.

Digestion procedure

Soil, plant and wood samples were digested in a microwave digestion system MLS Start (Mikrowellen Laborsystem). Two separate microwave programs were used to avoid any cross-contamination while digesting soil (Tab. 8) and vegetation (Tab. 9) samples. Vegetation samples ranging in weight from 100 to 400 mg were digested using 5 ml of concentrated HNO_3 (~15M) and 2 ml of H_2O_2 (30%). First, $\text{HNO}_3/\text{H}_2\text{O}_2$ was added to a vegetation sample and left approximately 12 hours (overnight) followed by microwave digestion. Nitric acid (~15M) was distilled once from technical grade 65% HNO_3 . Titrated molarity was measured to be 14.4M. A PicoTrace distillery with fused silica distillate was used for the production of low-blank HNO_3 and HCl acids. Even though acids are distilled, through time they can extract Zn from any PolyPropylene (PP) or Nalgene FluoroPolymers (PFA) bottle/pipette since Zn is used as a softener in these products including some types of laboratory gloves. In some instances, up to 1 ppb of Zn has been measured in acids. Due to possible Zn contamination in laboratory acids, these are continually monitored, with its concentration consistently ranging from 0.2 ppb to 0.3 ppb.

Table 8. Microwave conditions for the vegetation digestion.

Time	Electricity	Acids	Temperature	Status
20 min	1000 W	$\text{HNO}_3/\text{H}_2\text{O}_2$	190 ° C	Ramping up
45 min	1000 W	$\text{HNO}_3/\text{H}_2\text{O}_2$	190 ° C	Same temperature
30 min				Cooling

Soil samples ranging from 100 to 150 mg in weight were digested using 3 ml of concentrated HNO_3 (~15M) and 5 ml of ‘Suprapure-Grade’ concentrated HF (40%). All stock acids were produced by Merck (Darmstad, Germany).

Table 9. Microwave conditions for soil digestion.

Time	Electricity	Acids	Temperature	Status
45 min	1000 W	HF/HNO ₃	200 ° C	Ramping up
60 min	1000 W	HF/HNO ₃	200 ° C	Same temperature
60 min				Cooling

After each digestion cycle, tubes were cleaned using only concentrated nitric acid by two rinses with ‘Millipore Milli-Q water’ (18.2 MΩ·cm at 25 °C) and dried. All samples were weighed at a separate workstation using a Sartorius CP225D-OCE scale and a Sartorius ionizer to reduce any electrostatic effects.

Since the microwave used for digestions only had 14 available sample positions, a maximum sample weight of 100 mg was used. For example, a vegetation sample of 300 mg was split into three microwave tubes each containing 100 mg; seven microwave digestion rounds were needed to complete the first step of digestion. Quality control was maintained by including 1-3 blank samples, duplicates, and 1-2 reference materials per batch, and were treated to an identical analytical program as the sample unknowns.

After digestion, acid solutions were transferred into 30 ml, 60 ml and 90 ml Savillex Perfluoroalkoxy alkane (PFA) beakers. All beakers were pre-cleaned using a special cleaning procedure. Note, 9M HCl and 6M HCl were used in all chemical and cleaning procedures. Concentrated HNO₃ was added to vegetation samples in beakers and were heated for 24 h at 180° C. For soils, concentrated HF:HNO₃ (3:1) was added to samples and heated for 24 h at 180° C. All beakers were rinsed several times with Milli Q water between sample digestions. Upon finishing microwave digestion, samples were transferred to pre-cleaned beakers and allowed to evaporate on a hot plate (110° C). Gradually, 1 ml of 9M HCl was added to the beakers. A majority of samples were not completely digested using the microwave digestion protocol. White particles and black

residues, were observed and likely were oxides formed during acid digestion. Several acid dissolution steps using Aqua Regia ($\text{HCl}:\text{c.HNO}_3=3:1$) were applied to dissolve the residues, sometimes requiring one additional step with concentrated HNO_3 and one drop of concentrated H_2O_2 (for vegetation samples) at temperatures ranging from 110° to 180° C. Finally, to ensure all residues were completely digested, samples were mildly heated in an Omnilab ultrasonic bath. After evaporating, samples were re-dissolved in 1 to 4 ml of 9M HCl prior to ion exchange column chemistry.

Column chromatography

For the separation of Cu and Zn, an adopted protocol after Marechal et al. (1999) and Bigalke et al. (2010) was used and slightly modified for the samples investigated. Zinc separation included one purification step while Cu separation required two steps (Tab. 10). One additional step of Cu purification (Tab. 11) is needed to ensure a complete separation of Cu from the matrix since elements such as Al, Mg, Na, Ni and Ti can interfere the Cu signal (Lazarov 2017, pers. comm.).

Column chemistry was carried out according to the procedure outlined in Table 10 without Fe separation which was treated as a matrix elution. Each batch included one procedural blank, one column blank and one sample of reference material (Fig. 19). Columns (stored in 0.35M HCl) were used with Bio Rad lids which were kept in 5% HCl. For the column resin, a 2 M macroporous anion resin 100-200 mesh was used in chloride form (AG-MP-1M) from Bio Rad Laboratories. Prior to loading the sample into the column, samples were centrifuged with a Sigma 3-15 laboratory centrifuge at 4000 rpm for 10 min. Pipette tips for a 20 μl , 200 μl , 1000 μl and 5000 μl for a BioHit pipette used for column chemistry were pre-cleaned with HNO_3 , rinsed twice with Milli Q water and dried.

Table 10. Procedure for Cu and Zn purification by anion-exchange chromatography.

Modified protocol for Cu and Zn		
Step	Volume / mL	Eluent
Column conditioning	12	9M HCl
Sample loading	1-2	9M HCl
Matrix elution	8	9M HCl
Cu elution	18	5M HCl + 0.001% H ₂ O ₂
Matrix elution	12	1M HCl
Zn elution	15	0.5M HNO ₃ : 0.1M HBr

After the column chromatography steps mentioned above, the resin was cleaned by passing 5 ml 9M HCl and 5 ml 1M HCl with a rinse of Milli Q between steps. Cu separation was conducted once again by eluting with 18 ml 5M HCl + 0.001% H₂O₂ (Tab. 11).

Table 11. Procedure for a second step of Cu separation.

Modified protocol for second Cu separation		
Step	Volume / mL	Eluent
Column conditioning	12	9M HCl
Sample loading	1	9M HCl
Matrix elution	8	9M HCl
Cu elution	18	5M HCl + 0.001% H ₂ O ₂
Matrix elution	12	1M HCl
	12	H ₂ O

The resin was cleaned after each batch of samples by passing 10 ml of 9M HCl and 10 ml of 3M HNO₃ through the column two times and rinsing with Milli Q water before and after each step. Eluent used for Zn separation was replaced simply by Milli Q water.

The separated Cu and Zn were collected in 15 and 33 ml Savillex PFA beakers and evaporated. Beakers were pre-cleaned and prepared for sample collection. Beakers for Cu collection were cleaned with 6M HCl while beakers for Zn collection were cleaned with 3M HNO₃. Both were kept on a hot plate at 110° C overnight and rinsed twice with Milli Q water. After evaporation, 200 µl of 2% HNO₃ was added.

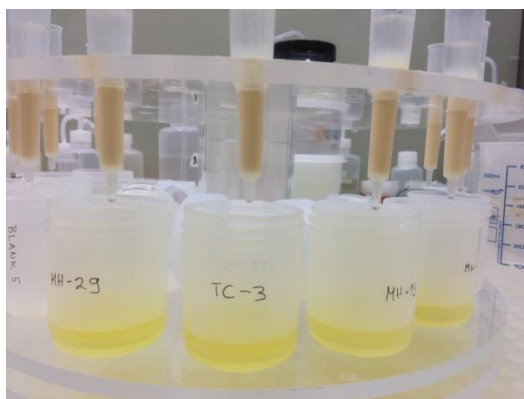


Figure 19. Matrix elution in ion-exchange chromatography. The yellow colour comes from the Fe.

Isotopic measurements were conducted using a ThermoFinnigan Neptune Plus Multi Collector ICP-MS (Thermo Scientific). The Neptune MC-ICP-MS (Fig. 20) is equipped with 9 Faraday cup collectors and two compact discrete dynodes (CDD) for very low signal intensities. Solutions were analysed using the Stable Sample Introduction System (SIS) combined with PFA or glass atomizers. Furthermore, in order to measure a large number of samples, an ESI SC2-DX auto-sampler connected to the Neptune was used.



Figure 20. ThermoFinnigan Neptune Plus MC ICP-MS with ESI SC2-DX auto-sampler.

The samples were dissolved in a mildly acidic solution (e.g. 2% HNO_3) as a final step before introducing them into the MC ICP-MS. The solution was aspirated and ionised in the Ar plasma; an electrostatic analyser (ESA) which creates an electric field that focuses ions with different energies and thus improves abundance sensitivity.

A high strength magnet separates the ions depending on their mass and forces them into different trajectories. The typical Neptune MC-ICP-MS operating conditions are shown in Table 12.

Table 12. Operating conditions for Cu and Zn measurement by Neptune MC ICP-MS.

MC-ICP-MS	Neptune Plus
Extraction	~ 2000 V
Cooling Argon	~ 15.0 l/min
Auxiliary Argon	~ 0.9 l/min
Sample uptake	~ 100 µl/min
Operation power	~ 1300 W
Nebuliser	PFA micro-flow
Spray chamber	Glass type (double pass Scott design)
Cones	Al or Pt
Analysis mode	Static
Low mass resolution mode	

Cu measurement

Copper isotope analyses were completed over two analytical sessions. In each session, masses 60(Ni), 61(Ni), 62(Ni), 63(Cu), 64(Ni) and 65(Cu) were detected using Faraday cups L3, L2, L1, C, H1 and H3 in one block of 60 cycles.

Initially, all purified Cu fractions were diluted to ~ 500 ppb in 2% HNO₃ and doped with 1000 ppb Ni NIST SRM 976. A second dilution step was carried out to obtain concentrations of 200 ppb Cu and 400 ppb Ni in solution. Using the standard-sample bracketing technique, each sample was bracketed by a mixed isotopic reference solution (Cu NIST SRM 976 + Ni NIST SRM 986) achieving a ratio Cu/Ni=1:2 with three samples run between two standards.

Signal intensities of ⁶³Cu were typically between 10V to 15V while ⁶²Ni was higher than 1V in order to obtain statistically valid measurements. In this study, Ni was used for mass bias correction instead of Cu and Zn which is commonly used (e.g. Marechal et al.,

1999). The mass bias of Cu and Ni are more comparable due to similar ionization temperatures and result (Fig. 21) in $\ln(^{65}\text{Cu}/^{63}\text{Cu})$ vs. $\ln(^{62}\text{Ni}/^{60}\text{Ni})$ slopes that are very close to 1 showing a minor mass bias drift (Bigalke et al., 2010).

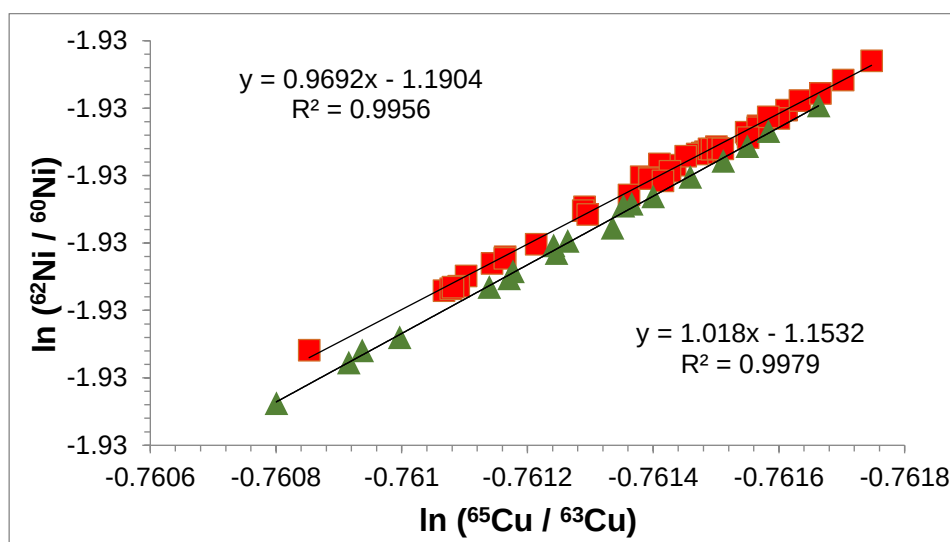


Figure 21. Plot of $\ln(^{62}\text{Ni}/^{60}\text{Ni})$ vs. $\ln(^{65}\text{Cu}/^{63}\text{Cu})$ of NIST 976 spiked with NIST 986 during two analytical sessions (red squares: first Cu measurement, green triangles: second Cu measurement).

Slight differences in comparing these two slopes are related to the elapsed time and instrument settings between the two analytical sessions. A copper ICP standard (NIST SRM C1251) was used as an in-house standard to maintain quality control on the instrument and to check long-term reproducibility and analytical drift (2SD = 0.05 ‰). The average reproducibility of the reference material (N=9) which was separately digested and purified was 0.07‰ (2SD). Copper blanks subjected to column separation and analysed amounted to 1.4 ± 1.19 (2SD) ng compared to at least 1800 ng in the vegetation sample. For all other samples the mean Cu blank was less than 1% of the amount of Cu in the sample unknowns. Therefore, no blank correction was applied.

Recoveries of reference material were as follows: BCR-2 (72-84%), Metranal 33 (80-94%) and LGC7162 (117-130%). Due to certified deviation (1SD) each reference material was presented as a minimum and maximum value. All Cu isotope values were expressed as $\delta^{65}\text{Cu}$ in per mil (‰) relative to the NIST 976 isotope standard following equation:

$$\delta^{65}\text{Cu}_{\text{NIST 976}} = \left(\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST 976}}} - 1 \right) * 1000 \quad (3)$$

Zinc measurement

The Zn isotope analyses consisted of two analytical sessions. In each session masses 63(Cu), 64(Zn), 65(Cu), 66(Zn), 67(Zn) and 68(Zn) were detected using Faraday cups L3, L2, L1, C, H1 and H2 in one block of 60 cycles in average.

Initially, all purified Zn fractions were diluted to ~ 1000 ppb in 2% HNO₃ and doped with a 300 ppb Cu in-house standard (NIST SRM C1251). A second dilution step was carried out to obtain concentrations of 500 ppb Zn and 150 ppb Cu. Using the standard-sample bracketing technique, each sample was bracketed by a mixed isotopic reference solution (Cu NIST SRM C1251 + Zn IRMM 3702) achieving a ratio Cu/Zn=1:3 with three samples run between two standards. A Zn NIST standard (NIST SRM 683) was used as an in-house standard to maintain good quality control on the instrument and to check long-term reproducibility. The average reproducibility of the reference material (N=7) which was separately digested and purified was 0.07‰ (2SD). Zinc blanks for the entire procedure were 112 ± 39.2 (2SD) ng compared to at least 946 ng in the soil sample. For wood samples, a procedural blank represents 18% - 58% (mean: 36.6%) of the Zn concentration. High Zn concentrations can indicate possible contamination during column chemistry which was resolved by applying the blank correction (see Appendix

E, Table E-5). For this purpose, 2σ is introduced using following equation (Lazarov 2017, pers. comm.):

$$2\sigma = \sqrt{\left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{IRMMa}^2 + \left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{sample}^2 + \left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{IRMMb}^2 + \left(\frac{\left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)^2}{\frac{sample}{blank}}\right)_{blank}} * 1000 * 2, (4)$$

Whereby,

$$\left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{IRMMa}^2 \text{ and } \left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{IRMMb}^2$$

represents the absolute standard error of the IRMM 3702 measurement before and after each sample;

$$\left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)_{sample}^2$$

represents the absolute standard error of sample measurement, and

$$\left(\frac{\left(\frac{SE_{abs}}{^{66}Zn/^{64}Zn}\right)^2}{\frac{sample}{blank}}\right)_{blank}$$

shows absolute standard error of blank measurement in relation to each sample which was blank corrected beforehand.

Recoveries of reference material were as follows: BCR-2 (81 - 93%), Metranal 33 (78 - 94%) and LGC7162 (71 - 109%). Due to a certified deviation (1SD), each reference material was presented as a minimum and maximum value. All Zn isotope values were

expressed as $\delta^{66}\text{Zn}$ in per mil (‰) relative to the IRMM 3702 isotope standard using following equation:

$$\delta^{66}\text{Zn}_{\text{IRMM 3702}} = \left(\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{IRMM 3702}}} - 1 \right) * 1000 \quad (5)$$

Zn isotope data reported by different authors (Dolgoplova et al., 2006; Viers et al., 2007; Dinis et al. 2015) was expressed relative to the Johnson Matthey (JMC 3-0749) Lyon Zn standard solution. In addition, Zn isotope values were converted by adding 0.32 ‰ which represents $\delta^{66}\text{Zn}_{\text{JMC}}$ value of the IRMM 3702 standard (Bigalke et al., 2010). $\delta^{66}\text{Zn}_{\text{JMC}}$ values in per mil (‰) were calculated using the following equation:

$$\delta^{66}\text{Zn}_{\text{JMC}} = \sim 0.32 + \left(\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{IRMM 3702}}} - 1 \right) * 1000 \quad (6)$$

Interferences and mass dependency were monitored plotting $\delta^{66}\text{Zn}_{\text{JMC}}$ against $\delta^{68}\text{Zn}_{\text{JMC}}$. Furthermore, this demonstrates that the exponential relation between Zn and Cu was within error thresholds when considering the linear trend line (Fig. 22).

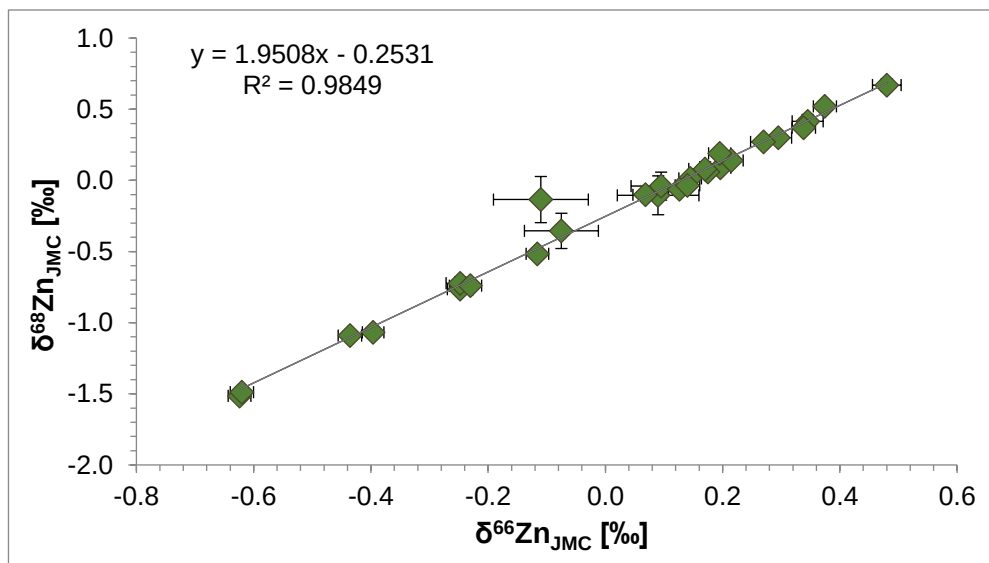


Figure 22. Isotope data of $\delta^{66}\text{Zn}_{\text{JMC}}$ and $\delta^{68}\text{Zn}_{\text{JMC}}$ (2σ) of plant, wood and soil samples.

Accuracy of Zn and Cu isotope measurement

Accuracy of isotope measurements is calculated using isotopic standard (basalt BCR-2) measured in this study and compared to the reported and recommended values in the literature (Tab. 13).

Table 13. Reported isotopic signatures of BCR-2 isotope standard in comparison to measured standard in this study calculated with 2σ error.

Standard	Isotope system	This study	Reported	Literature	Accuracy
BCR-2	$\delta^{66}\text{Zn}_{JMC}$	0.25 ± 0.03	0.23 ± 0.02	Bigalke et al. (2010)	8.7 %
BCR-2	$\delta^{65}\text{Cu}_{NIST976}$	0.17 ± 0.05	0.2 ± 0.05	Bigalke et al. (2010), Bigalke et al. (2011)	15 %

5.4 Data management

Data reduction includes computation of summary statistics (e.g., means, median, standard deviation), Principal Component Analysis (PCA analysis), cluster analysis, calculations of correlation coefficients (Pearson's r) and regression analysis (Multiple R) using statistical software and data analysis in ioGAS Reflex, PAST, Excel and MapInfo. In addition to the above mentioned statistical treatment, summary statistics also included histograms, probability plots and box and whiskers plots. A Shapiro-Wilk test was used to check whether data is normally distributed. For independent groups of data, t – test was used. When it is determined that the data is not normally distributed a Kruskal-Wallis test was used to detect possible significant differences between groups.

Trace elements such as: Au, Ag, B, Be, Bi, Ce, Cs, Ga, Ge, Hf, In, La, Li, Na, Nb, Pd, Pt, Rb, Re, Sb, Sc, Se, Ta, Te, Th, Ti, Tl, U, V, W, Y in soils were not investigated in comparison to plants in this study. In some cases, a concentration of some elements was not available due to detection limits of the ICP-MS or the limits of detection (LOD: 6 standard deviation of the blank); B, Pt, Re and Ta revealed limits of reporting in soils. In addition, Ag, B, Be, Bi, Ce, Cs, Ga, Hf, In, La, Li, Pd, Pt, Rb, Re, Ta, Te, Ti, Tl, U, V and Zr in plants were measured close to limits of detection; thus, not considered. The Relative Percent Difference (RPD) between sample duplicates is calculated according to the following equation:

$$\text{RPD (\%)} = \frac{|DU1-DU2|}{\frac{1}{2}(DU1+DU2)} \times 100 \% \quad (7)$$

DU1 = Sample result; DU2 = Sample duplicate result.

The average RPD between sample duplicates in trace element analysis was within 15%. Error bars on plots in Chapter 6 & 7 (including case study of Laver in Appendix B) are expressed as 2 standard deviations of sampling duplicates. More data about laboratory duplicates and their 2SD can be found in Appendix D & E. PCA and cluster analysis was used to investigate trace element variability trends in different plant species. Data were log-transformed for this statistical analysis. Correlative statistics was performed between different trace elements in the same tree species collected from different sites.

Furthermore, the bioavailability of the elements of interest (As, Cd, Cu, Fe, Mn, Pb and Zn) was calculated as the proportion of the total metals in the soil to that accumulated in plant (see Chapter 7). The bioaccumulation coefficient (BC) is characterised by the ratio following the equation:

$$BC_x = X_{\text{plant}} / X_{\text{soil}} \quad (8)$$

where the BC is a coefficient of metal content (X_{plant}) in plant and total metal content (X_{soil}) in the soil.

In order to recognise depletion or enrichment of particular trace element in plants and in soil, an enrichment factor is calculated (see Chapter 7). Botanical and soil data are normalized to Y values following the equation (adopted from Dolgoplova et al., 2006):

$$EF_x = (X/Y_{\text{sample}}) / (X/Y_{\text{host rocks}})$$

where X is any element of interest; $(X/Y)_{\text{sample}}$ is the ratio of an individual sample (plant or soil material) and $(X/Y)_{\text{host rocks}}$ is the ratio of the host rocks representing the local background value. Here, a denominator (Y) is displayed as Sn which is considered to be an immobile element; has a very low natural concentration in most materials and in the host rock of the Navan area. Sn is rarely present in Zn-Pb mineralisation so it can be used as an indicator of metal enrichment in plants and soils at Nevinstown. In addition, the host rocks of the Navan deposit are represented by Upper Dark Limestones (see Chapter 3).

6 Results

Here, the results are presented in two parts due to the complexity and diversity of the data. The trace element analysis will be reported firstly, followed by the isotopic data. Trace element analysis was used in two diverse case studies in order to test for the biogeochemical response around base metal deposits in a European temperate climate; Navan – Tara Mines (Ireland) and Laver (Sweden) while isotopic analysis was only conducted at Navan – Tara Mines. The Navan case study includes plant and soil geochemistry around the Navan deposit and a comparison on a regional scale, providing more detailed overview on the biogeochemistry of an Irish Type Zn-Pb deposit. A similar exploration protocol was used for plant geochemistry at the Laver Cu deposit in Sweden (see Appendix B).

6.1 Trace element concentration

The mean concentrations of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, P, Pb, S, Sn, Sr and Zn in plant material and soils from Navan and the Irish Midlands are shown in Table 14 to Table 16. The soil dataset contains additional reported concentrations for Al and Zr. Furthermore, biogeochemical data at Laver (Sweden) included the same trace element list as for plant material from Navan with additional Rb concentrations (see Appendix B, Tab. B-1). Note that Al, Rb and Zr had very low concentrations within plants from Navan and Al and Zr within plants from Laver and therefore can be removed from the treatment of trace element data. In addition, any element values at or near the detection limit (LOD) for the rest of the elements were not considered in order to maintain high quality control on the data. A detailed table with all results is shown in Appendix A (from Tab. A-1 to Tab. A-5).

Table 14. Element concentrations and descriptive statistics for all plant species - leaves collected from Nevinstown site in May and September, 2015. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Based on duplicate analysis MAD Precision is < 5%. Values are reported in parts per million (ppm) except for Ca, K, Mg, P, and S (%).

Plants – All Nevinstown	As	Ba	Ca (%)	Cd	Co	Cr	Cu	Fe	Hg	K (%)	Mg (%)	Mn	Mo
Detection limit	0.01	0.1	0.01	0.001	0.002	0.01	0.01	1	0.001	0.01	0.001	0.1	0.01
n	119	119	119	119	119	119	119	119	119	119	119	119	119
Min	0.02	6.30	0.38	0.02	0.01	0.26	1.67	42.00	0.01	0.65	0.09	13.60	0.08
Max	0.54	337.00	3.40	5.13	0.18	4.32	24.30	179.00	0.04	2.49	0.36	266.00	2.05
Mean	0.21	68.64	1.30	0.47	0.05	0.97	8.84	67.92	0.01	1.39	0.20	64.70	0.46
Median	0.19	45.90	1.16	0.18	0.04	0.78	7.47	64.00	0.01	1.35	0.19	47.20	0.36
2 Std Dev	0.01	2.18	0.05	0.01	0.003	0.10	0.38	3.96	0.001	0.03	0.01	2.06	0.02

Plants – All Nevinstown	Ni	P (%)	Pb	S (%)	Sn	Sr	Zn
Detection limit	0.04	0.001	0.01	0.01	0.01	0.02	0.1
n	119	119	119	119	119	119	119
Min	0.36	0.10	0.48	0.12	0.01	3.57	21.90
Max	8.21	0.72	10.30	0.62	0.06	67.80	735.00
Mean	2.00	0.31	3.48	0.24	0.02	21.14	103.17
Median	1.74	0.27	3.02	0.21	0.02	17.35	72.90
2 Std Dev	0.08	0.01	0.11	0.01	0.003	0.82	1.10

Table 15. Element concentrations and descriptive statistics for soil samples collected from Nevinstown site in August, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Based on duplicate analysis MAD Precision is < 10% for Ca, Cd, Hg, Mn, P and < 5% for other elements. Values are reported in parts per million (ppm) except for Al, Ca, K, Mg, P, S and Zr (%).

Soil Nevinstown	Al (%)	As	Ba	Ca (%)	Cd	Co	Cr	Cu	Fe (%)	Hg	K (%)	Mg (%)	Mn
Detection limit	0.01	0.01	0.5	0.01	0.001	0.001	0.01	0.01	0.001	0.004	0.01	0.01	0.1
n	34	34	34	34	34	34	34	34	34	34	34	34	34
Min	1.03	8.04	150.0	0.09	0.94	4.94	18.80	13.25	0.14	0.07	0.05	0.24	316.00
Max	1.55	297.00	1975.0	1.45	21.20	22.00	31.40	58.30	0.40	3.48	0.29	0.49	6430.00
Mean	1.32	47.07	397.4	0.35	4.00	9.70	26.43	22.33	0.21	0.23	0.12	0.39	1241.06
Median	1.31	23.95	329.5	0.31	2.43	8.58	26.65	18.58	0.20	0.12	0.10	0.39	768.00
2 Std Dev	0.17	1.41	29.70	0.03	0.26	0.25	1.70	1.06	0.24	0.02	0.00	0.04	123.04

Soil Nevinstown	Mo	Ni	P (%)	Pb	S (%)	Sn	Sr	Zn	Zr
Detection limit	0.01	0.04	0.001	0.005	0.01	0.01	0.01	0.1	0.01
n	34	34	34	34	34	34	34	34	34
Min	0.71	20.10	0.07	84.10	0.05	0.52	10.10	270.00	0.47
Max	4.71	82.40	0.23	5970.00	0.25	15.40	93.90	4500.00	3.46
Mean	1.73	32.94	0.12	389.30	0.09	1.43	19.44	1110.24	1.24
Median	1.52	29.55	0.12	204.00	0.08	0.80	14.45	759.50	1.01
2 Std Dev	0.18	0.57	0.01	4.24	0.00	0.01	0.99	4.24	0.01

Table 16. Element concentrations and descriptive statistics for all plant species - leaves collected from the Delvin (regional control site) and Ballinalack (sub-economic deposit) in May, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Based on duplicate analysis MAD Precision is < 30% for Sn, < 12% for As and Hg and < 5% for other elements. Values are reported in ppm except for Ca, K, Mg, P, and S (%).

Plants – All Del & Bal	As	Ba	Ca (%)	Cd	Co	Cr	Cu	Fe	Hg	K (%)	Mg (%)	Mn	Mo
Detection limit	0.01	0.1	0.01	0.001	0.002	0.01	0.01	1	0.001	0.01	0.001	0.1	0.01
n	66	66	66	66	66	66	66	66	66	66	66	66	66
Min	0.01	1.90	0.57	0.01	0.02	0.16	4.01	46.00	0.01	0.57	0.09	9.80	0.19
Max	0.06	29.10	2.06	0.63	0.20	3.48	14.70	181.00	0.03	3.50	0.54	166.00	3.79
Mean	0.03	13.52	1.31	0.19	0.09	0.78	8.03	74.08	0.01	1.45	0.24	36.99	1.21
Median	0.03	12.40	1.30	0.15	0.09	0.53	7.74	71.00	0.01	1.45	0.24	23.95	0.91
2 Std Dev	0.01	0.67	0.05	0.01	0.004	0.07	0.35	4.24	0.002	0.05	0.01	2.65	0.03

Plants – All Del & Bal	Ni	P (%)	Pb	S (%)	Sr	Zn
Detection limit	0.04	0.001	0.01	0.01	0.02	0.1
n	66	66	66	66	66	66
Min	0.47	0.13	0.04	0.14	11.55	14.40
Max	6.86	0.50	0.55	0.35	82.70	47.90
Mean	1.47	0.31	0.12	0.22	40.25	27.76
Median	1.19	0.33	0.10	0.21	40.10	26.85
2 Std Dev	0.06	0.01	0.01	0.02	1.66	1.06

6.1.1 Case study Navan, Ireland

The Navan case study combines the Nevinstown discovery area and three local control sites around the Navan deposit. The general trend of specific elements of interest, significant ranges and peak values in leaves for plant species are briefly described below. In the forthcoming text, more detailed observations are made for each plant species including the distribution of elements within a plant followed by any seasonal variations. The distribution of As, Cd, Cu, Fe, Mn, Pb and Zn in each plant species at Nevinstown is shown in Figure 23 while comparisons of the above-mentioned elements are presented as Tukey box and whisker plots (Fig. 24).

In general, the trace element distributions at Nevinstown with the lowest element concentration ranges comprise As (0.02 - 0.45 ppm), Cd (0.02 - 5.13 ppm) and Pb (0.48 - 7.27 ppm) in all plant species. Furthermore, Cu component illustrate mean values ranging between 3.54 ppm to 24.3 ppm. Following Cu levels, element concentrations increase towards ranges of Fe (45 - 179 ppm), Mn (14.30 – 226 ppm) and to Zn ranges of 34.90 ppm to 735 ppm which are the highest. In more detail, poplar showed the highest accumulation of As (0.41 ± 0.02 ppm), Cd (4.34 ± 0.01 ppm), Pb (8.45 ± 0.10 ppm) and Zn (535.50 ± 1.46 ppm). Hawthorn shows an average metal uptake of As (0.20 ± 0.02 ppm) and Pb (3.09 ± 0.10 ppm) which is similar to As (0.22 ± 0.02 ppm) and Pb (3.49 ± 0.10 ppm) concentrations reported in blackberry leaves. However, these plants presented the lowest ability for an uptake of Cu and Mn in hawthorn (7.54 ± 0.26 ppm; 33.29 ± 2.36 ppm) and poplar (4.12 ± 0.26 ppm; 29.95 ± 2.36 ppm). In addition, oak, beech, sycamore and ash showed mean values of Cu and Mn in ash (16.62 ± 0.26 ppm; 34.46 ± 2.36 ppm), beech (13.19 ± 0.26 ppm; 88.03 ± 2.36 ppm), oak (13.48 ± 0.26 ppm; 146.75 ± 2.36 ppm); and Cu and Mn in sycamore of 9.89 ± 0.26 ppm and 86.94 ± 2.36 ppm. The only element with no significant differences across various plant species was iron with mean values of $67.94 \pm$

4.71 ppm. All significant figures implies < 5% MAD precision except for As which implies < 8% MAD precision.

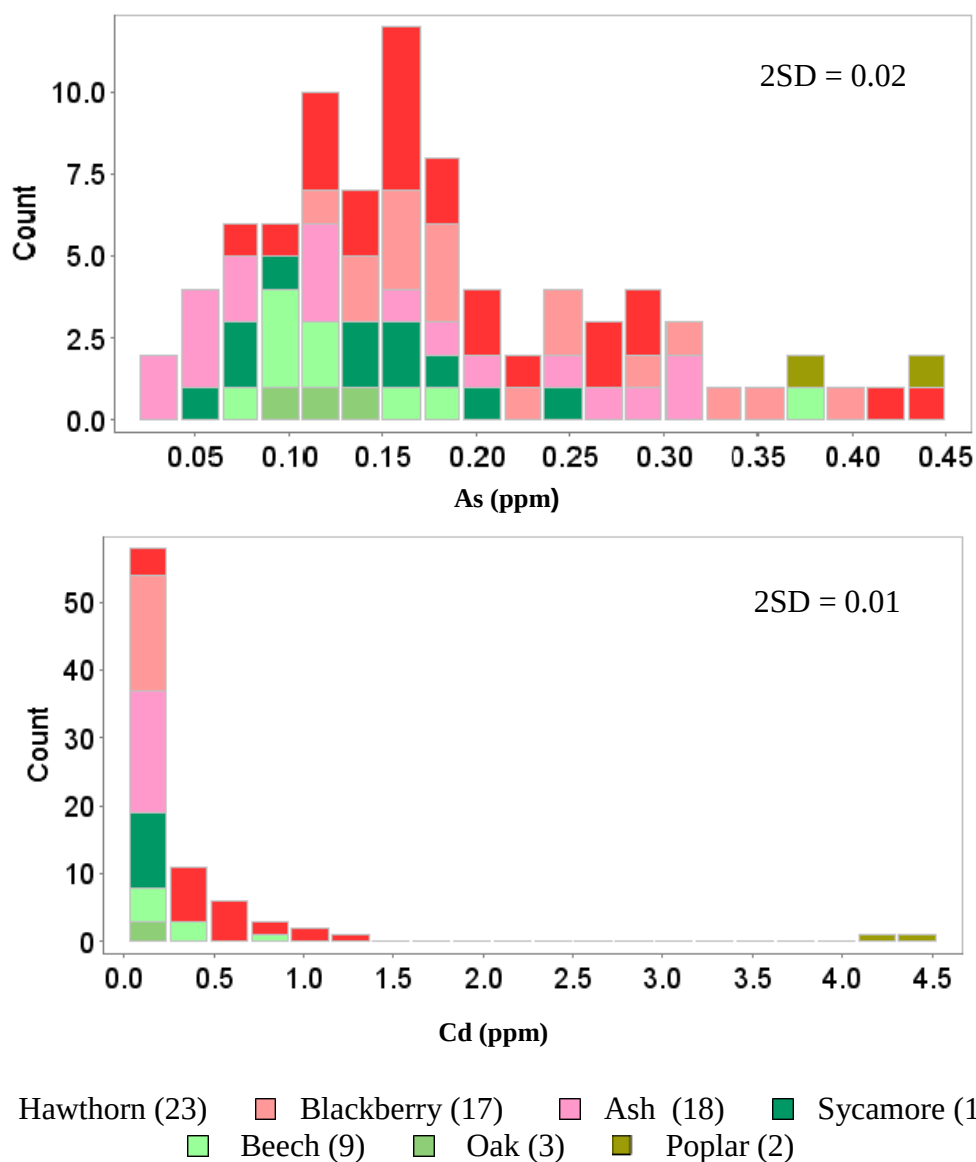
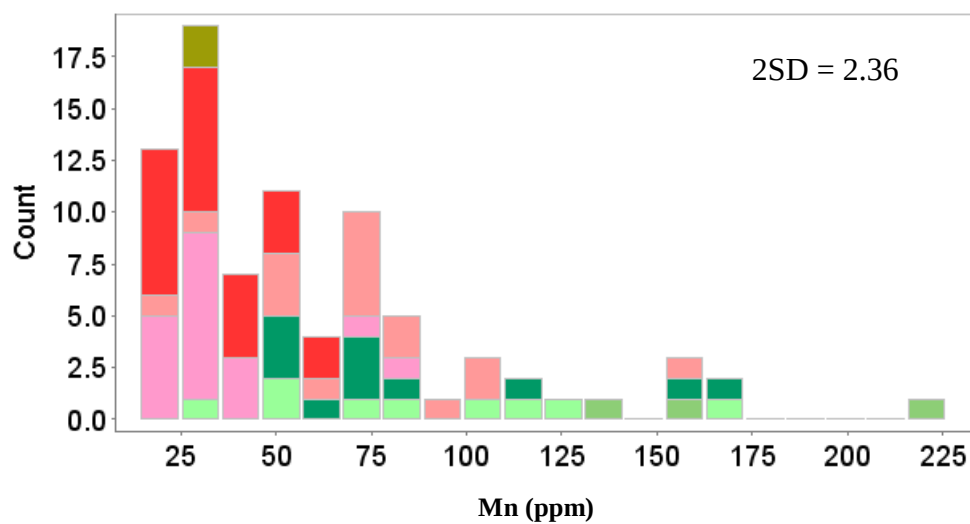
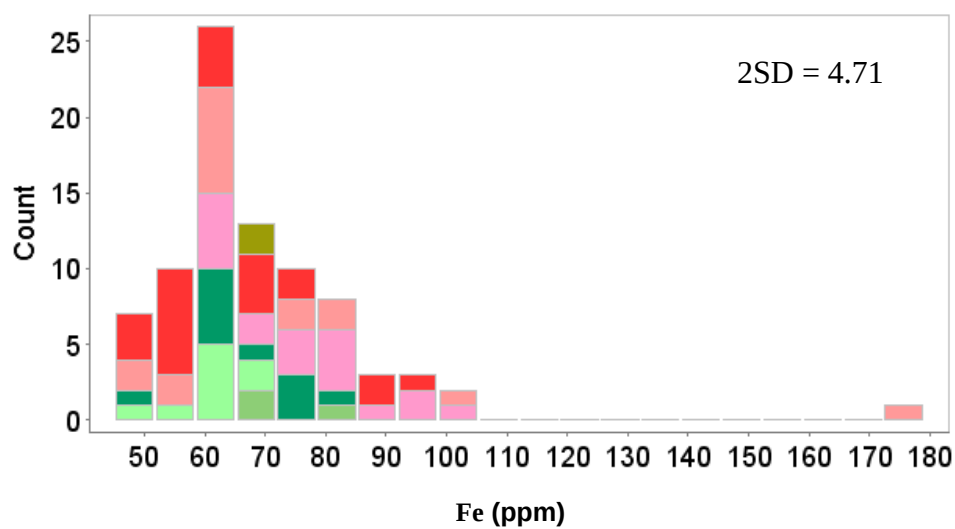
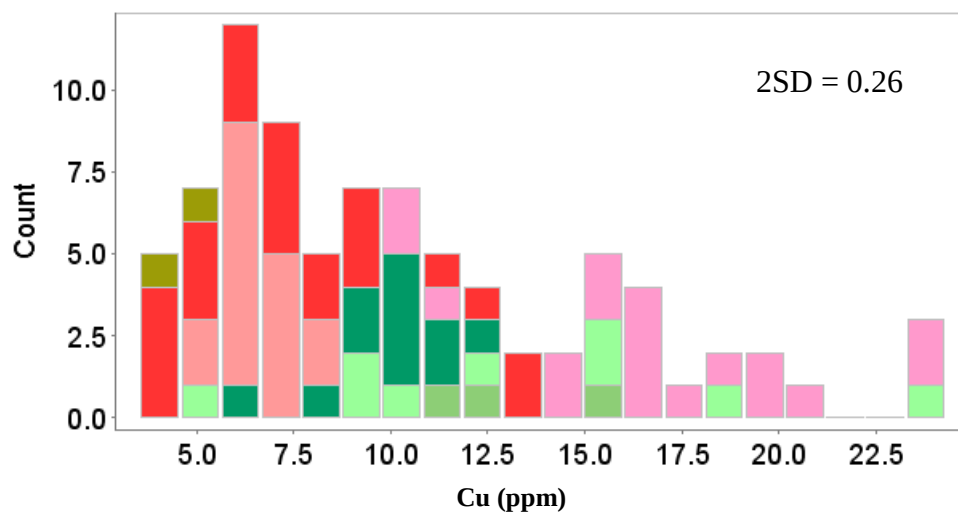
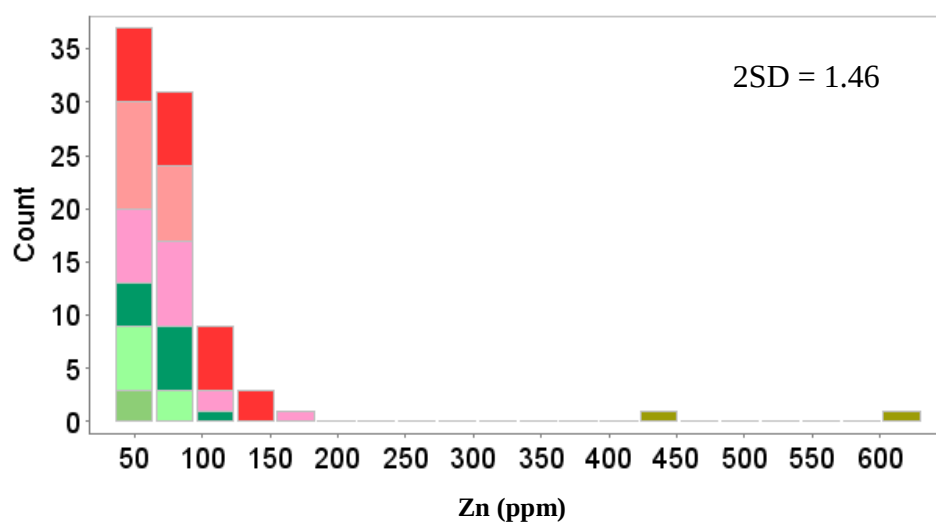
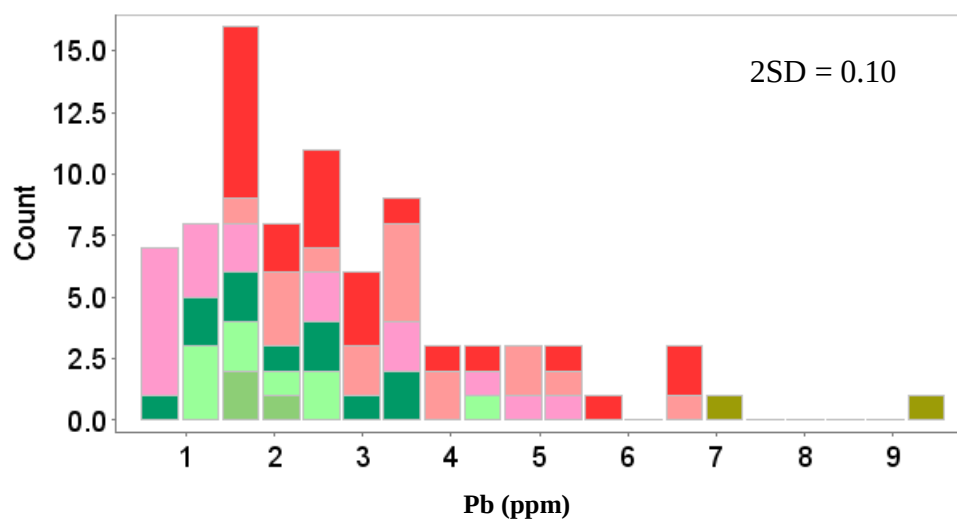


Figure 23. Stacked histogram plots showing distribution of As, Cd, Cu, Fe, Mn, Pb and Zn in different plant species (N=83) collected in spring 2015 at Nevinstown. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Continued on the next pages.



Hawthorn (23) Blackberry (17) Ash (18) Sycamore (11)
 Beech (9) Oak (3) Poplar (2)

Figure 23. Continued on the next page.



■ Hawthorn (23)
 ■ Blackberry (17)
 ■ Ash (18)
 ■ Sycamore (11)
■ Beech (9)
■ Oak (3)
■ Poplar (2)

Figure 23. Last page of stacked histogram plots showing distribution of As, Cd, Cu, Fe, Mn, Pb and Zn in different plant species (N=83) collected in spring 2015 at Nevinstown. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

Stacked histograms illustrate that elemental distribution is positively skewed with the curve tail extended to the right, particularly for Cd and Zn. The distribution of As shows the least extended curve tail.

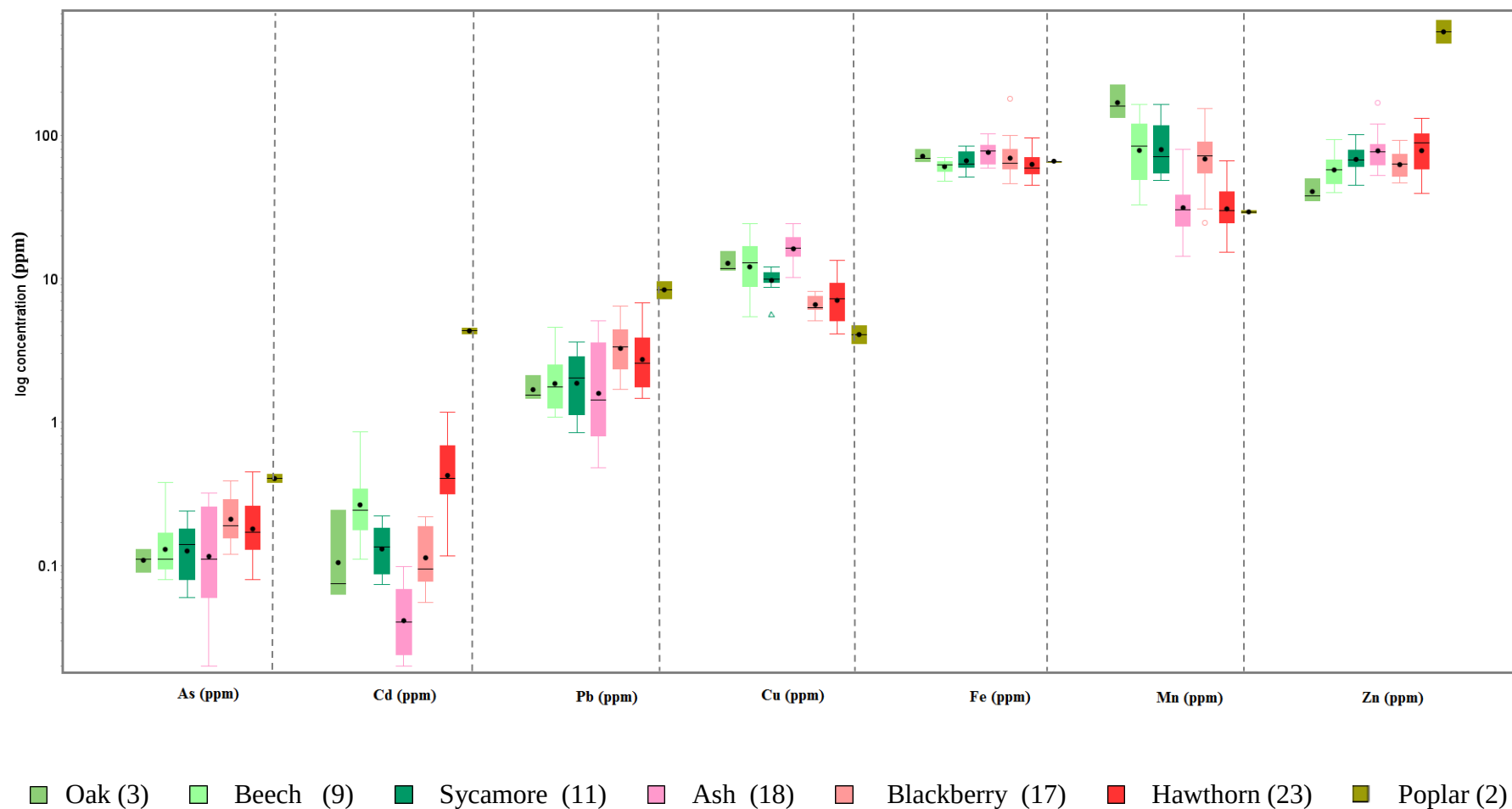


Figure 24. Tukey box plot for As, Cd, Cu, Fe, Mn, Pb and Zn in leaf material (N=83) at Nevinstown on a common Y axis and logged. Solid rectangles represent data within 1 standard deviation of the mean (black dash) and median (black dot). Lines are defined as 2 standard deviation from the mean and outliers represented as empty dots.

6.1.1.1 Distribution of elements within plant species

Metal signatures in plants collected from different localities provide more information on how plants accumulate metals in mineralised and unmineralised areas (Zn in Fig. 25). Furthermore, Tables 17 through 23 show the mean element concentration in the leaves for the seven common species around the Navan deposit collected in spring 2015. In addition, element values are compared with the reported data for each plant species published by numerous authors. Plant species across all sites were compared using a *t*-test at normal data distribution and Kruskal-Wallis test to evaluate not normally distributed data. Both tests are calculated at a 95% confidence level.

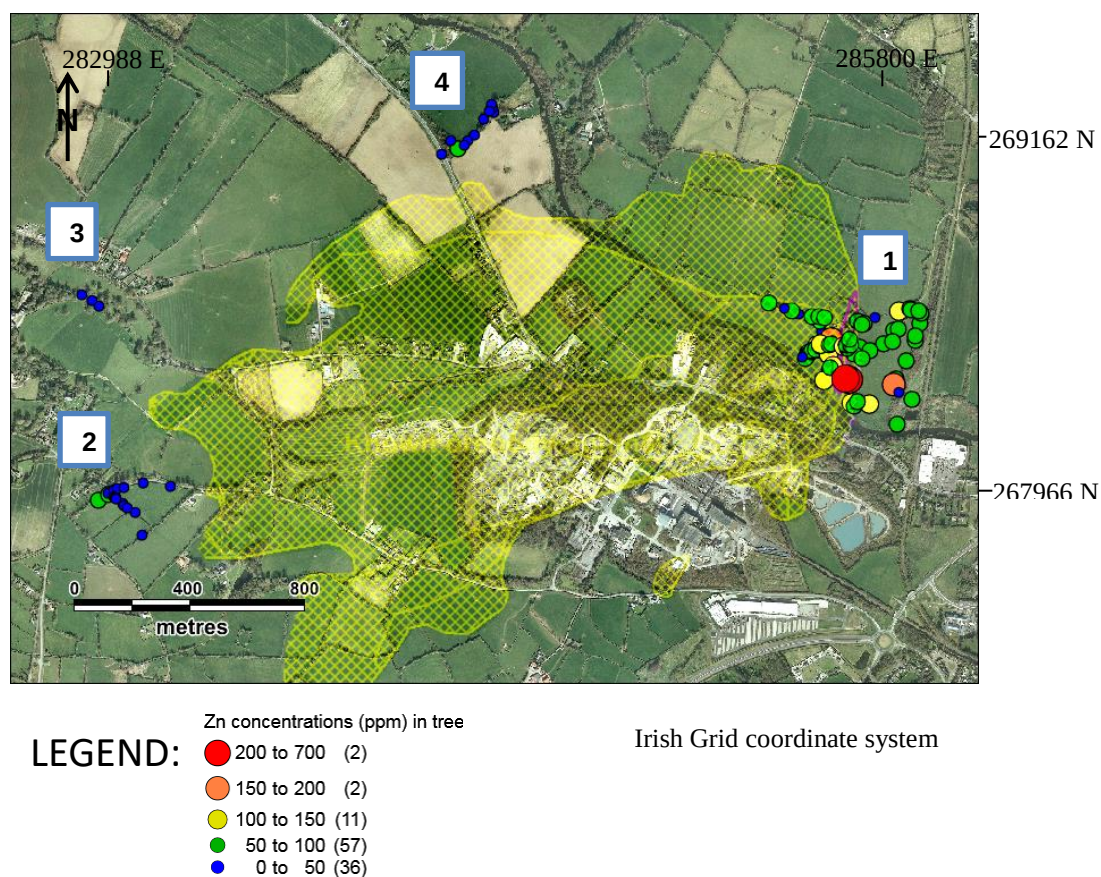


Figure 25. Zinc enrichment in plants (N=83) compared with different sampling sites: Nevinstown (1 on the map) and control sites (2, 3 and 4 on the map). Highest concentrations belong to poplar trees (up to 700 ± 1.46 ppm). Yellow mesh pattern represents the footprint of the Navan orebody.

Hawthorn (*Cratageus monogyna*)

A Shapiro-Wilk test showed that As, Ba, Cu, Ni and Sr data from Nevinstown were not normally distributed in hawthorn (Tab. 17) unlike data for the control sites. Comparing two independent groups such as Nevinstown and the control sites using the Kruskal-Wallis and *t* - test (Tab. 17) revealed significant difference between elements of interest such as As ($p < 0.001$, K.-Wallis test), Ca ($p = 0.017$, *t* - test), Pb ($p < 0.001$, K.-Wallis test) and Zn ($p < 0.001$, *t* - test). Eight significant figures implies $< 5\%$ precision while one figure implies $< 8\%$ MAD precision.

The concentration of hawthorn metal uptake above the orebody was two times higher for As (0.2 ± 0.02 ppm) and increased up to three times for Ba (114 ± 3.02 ppm, $EF_{Ba}=41$), Cd (0.51 ± 0.01 ppm, $EF_{Cd}=30$) and Zn (83 ± 1.46 ppm, $EF_{Zn}=78$) on average when compared to the sites around the ore deposit where As was (0.09 ± 0.03 ppm, $EF_{As}=0.4$), Ba (40.81 ± 0.49 ppm, $EF_{Ba}=14$), Cd (0.18 ± 0.003 ppm, $EF_{Cd}=0.18$) and Zn (31.39 ± 1.91 ppm, $EF_{Zn}=18.2$) on average. The Enrichment Factor was used to illustrate an enrichment or depletion of metals in the investigated plants. For more details about the calculation of the Enrichment Factor (EF) and the statistical tests used see Chapter 5 and Appendix D.

A Pearson Product Moment's test (Fig. 26) was used to track any patterns related to interactions between elements. A strong positive correlation between Cd:Zn ($r=0.86$), As:Pb ($r=0.95$), and Pb:Zn ($r=0.65$) can be observed at Nevinstown ($N=23$).

Generally, the majority of element concentrations show a decrease in metal components during the spring in comparison to autumn seasons at Nevinstown (see Appendix C, Tab. C-1) except for Cd and Cu which exhibited similar (Cd) and increased (Cu) values during spring season. The metal concentrations in spring hawthorn leaves from combined data for Nevinstown and control sites ($N=32$) were depleted in As

(0.17±0.02 ppm), Mn (42.69±1.90 ppm), Pb (2.57±0.07 ppm) and Zn (69.24±1.64 ppm) in comparison to the autumn dataset while only Cu exhibited lowest concentration (4.55±0.39 ppm) in autumn leaves. One significant figure implies < 8% precision while four significant figures implies < 5% MAD precision.

Table 17. Element concentration in hawthorn leaves collected in spring, 2015 from Nevinstown and control sites. Mean values in hawthorn leaves are reported by Zeiner et al. (2013)* and Lozak et al. (2002)**. The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents the number of analysed samples.

Element	Hawthorn leaves		Reported Leaves	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control</i>		<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.20	0.09		0.009	$p < 0.001$	(KW)
Ba Ba	113.37	40.81		0.019	$p < 0.001$	(KW)
Ca (%)	1.52	1.32		normal	$p = 0.017$	(t – test)
Cd	0.51	0.18	0.13*	normal	no sign.	(t – test)
Co	0.06	0.14	0.14**	0.012	$p < 0.001$	(KW)
Cr	0.73	0.80		<0.001	no sign.	(KW)
Cu	7.54	7.57	7*	0.041	no sign.	(KW)
Fe	63.91	72.00		normal	no sign.	(t – test)
Hg	0.01	0.01		normal	no sign.	(t – test)
K (%)	1.42	1.25		normal	no sign.	(t – test)
Mg (%)	0.22	0.18		normal	$p = 0.007$	(KW)
Mn	33.29	25.15	11**	normal	no sign.	(t – test)
Mo	0.43	0.33		<0.001	no sign.	(KW)
Ni	1.19	1.50		<0.001	$p = 0.008$	(KW)
P (%)	0.27	0.34		normal	$p = 0.013$	(t – test)
Pb	3.09	1.26	1.75*	0.002	$p < 0.001$	(KW)
S (%)	0.18	0.19		normal	no sign.	(t – test)
Sn	0.02	0.02		0.004	no sign.	(KW)
Sr	27.16	24.80		0.003	no sign.	(KW)
Zn	83.27	31.39	16.5**	normal	$p < 0.001$	(t – test)
	N=23	N=8				

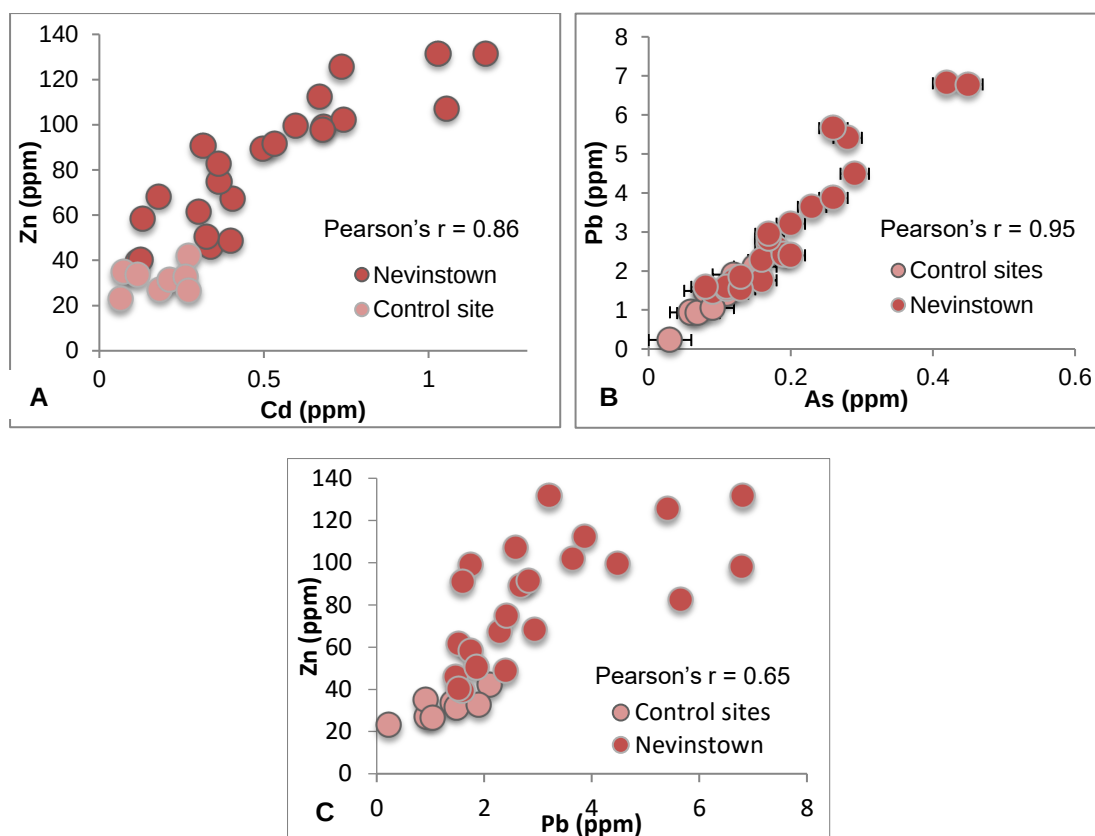


Figure 26. Scattered X/Y plot showing Pearson's correlation for A) Cd:Zn; B) As:Pb and C) Pb:Zn in hawthorn leaves from Nevinstown (N=23). Plot also includes samples from control sites (N=8) collected in spring 2015. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Hawthorn accumulated more Cu in flowers (16.71 ± 0.36 ppm in spring) and fruit ($6.30 \text{ ppm} \pm 0.39$ in autumn) when compared with leaf material in spring (7.54 ± 0.26 ppm) and with leaves in autumn season (4.09 ± 0.55 ppm). In addition, flowers were depleted in Fe (49.67 ± 3.68 ppm; N=3) in comparison to fruit which accumulated more Fe (64.50 ± 2.12 ppm; N=2) at Nevinstown. All significant figures implies $< 5\%$ MAD precision. Note in the Appendix C, Table C-1 that flowers developed during spring (May) while fruit grew in autumn (September).

Blackberry (*Rubus fruticosus*)

A Shapiro – Wilk test showed that Ba ($p = 0.002$) and Cd ($p = 0.012$) values are not normally distributed for the Nevinstown data (Tab. 18). Comparing all sites there was a significant difference between As ($p = 0.003$, t – test), Ca ($p = 0.017$, t - test), Cu ($p = 0.043$, t – test), Mn ($p = 0.002$, t – test), Pb ($p = 0.01$, t – test) and Zn ($p < 0.001$, t – test). At Nevinstown, arsenic was four times higher (0.22 ± 0.02 ppm, $EF_{As}=1$), Pb seven times higher (3.42 ± 0.10 ppm, $EF_{Pb}=17$) and Zn two times higher (64 ± 1.46 ppm, $EF_{Zn}=39$) on average when compared to the control sites around the ore deposit. One significant figure implies $< 12\%$ MAD precision while seven significant figures implies $< 5\%$ MAD precision.

A Pearson's correlation factor ($N=20$) showed strong positive correlations for As:Pb ($r=0.92$) and Cd:Zn ($r=0.78$) for spring blackberry leaves at Nevinstown and control sites (Fig. 27).

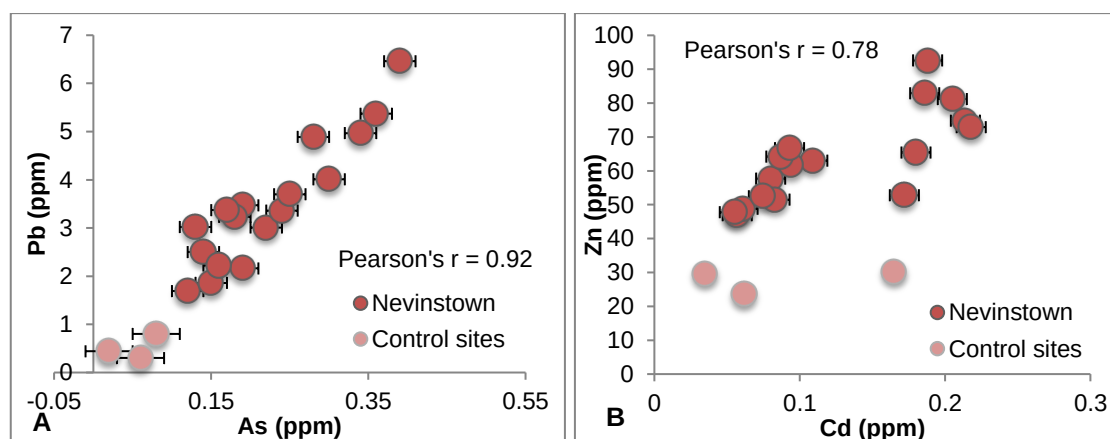


Figure 27. Scattered X/Y plot showing Pearson's correlation between As:Pb (A) and Cd:Zn (B) in blackberry leaves from Nevinstown ($N=17$). Plot also includes samples from control sites ($N=3$) collected in spring 2015. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Table 18. Element concentration in blackberry leaves in spring 2015 from Nevinstown and control sites. Mean values in blackberry leaves are reported by Derya (2009). The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents the number of analysed samples.

Element	Blackberry leaves		Reported Leaves	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control sites</i>		<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.22	0.05		normal	$p = 0.003$	(t – test)
Ba	25.02	6.90		0.002	$p < 0.001$	(KW)
Ca (%)	0.57	0.67		normal	$p = 0.017$	(t – test)
Cd	0.13	0.09		0.012	no sign.	(KW)
Co	0.04	0.04	0.10	normal	no sign.	(t – test)
Cr	1.49	0.81		<0.001	no sign.	(KW)
Cu	6.65	7.95	6.61	normal	$p = 0.043$	(t – test)
Fe	73.18	63.67	165	normal	no sign.	(t – test)
Hg	0.01	0.01		normal	no sign.	(t – test)
K (%)	1.34	1.25		normal	no sign.	(t – test)
Mg (%)	0.19	0.19		normal	no sign.	(t – test)
Mn	74.40	205.47	54.6	normal	$p = 0.002$	(t – test)
Mo	0.61	0.95		normal	$p = 0.016$	(t – test)
Ni	2.39	3.40		normal	no sign.	(t – test)
P (%)	0.26	0.28		normal	no sign.	(t – test)
Pb	3.49	0.51		normal	$p = 0.01$	(t – test)
S (%)	0.20	0.22		normal	no sign.	(t – test)
Sn	0.02	0.03		0.004	no sign.	(KW)
Sr	8.38	9.13		normal	no sign.	(t – test)
Zn	63.73	27.83	12.4	normal	$p < 0.001$	(t – test)
	N=17	N=3				

Overall, elevated concentrations for manganese in blackberry leaves (up to 180.14 ± 0.57 ppm; N=5, < 5% MAD precision) were only observed during the autumn season. However, some variations between Cd, Cu and Zn are reported when comparing leaves collected in spring and during the autumn (see Appendix C, Tab. C-2).

Sycamore (*Acer pseudoplatanoides*)

A *t* - test showed significant differences between As ($p = 0.002$, *t* – test), Pb ($p = 0.001$, *t* – test) and Zn ($p = 0.001$, *t* – test) for sycamore leaves in the Nevinstown area (Tab. 19). Moreover, these observations are similar to data collected for the blackberry plants.

Table 19. Element concentration in sycamore leaves collected in spring 2015 from Nevinstown and control sites. Due to lack of published data for sycamore, concentrations are reported for Norway maple leaves by Tomasevic et al. (2011). The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a *t* - test was performed on normal data distribution. Values above the critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents the number of analysed samples.

Element	Sycamore leaves		Reported Leaves	Shapiro – Wilk W test (<i>p</i> -normal)	Kruskal-Wallis (KW) & <i>t</i> – test (95% conf.)	
	Nevinstown	Control sites		Nevinstown	Nevinstown vs. control	
As	0.14	0.04	0.15	normal	$p = 0.002$	(<i>t</i> – test)
Ba	17.75	8.55		normal	$p < 0.001$	(<i>t</i> – test)
Ca (%)	1.00	1.12		normal	no sign.	(<i>t</i> – test)
Cd	0.14	0.12	0.09	normal	no sign.	(<i>t</i> – test)
Co	0.03	0.04	0.34	normal	no sign.	(<i>t</i> – test)
Cr	0.91	1.32		normal	no sign.	(<i>t</i> – test)
Cu	9.89	9.84	7.94	normal	no sign.	(<i>t</i> – test)
Fe	67.09	77.33	285	normal	no sign.	(<i>t</i> – test)
Hg	0.01	0.01		0.016	no sign.	(KW)
K (%)	1.90	1.70		normal	no sign.	(<i>t</i> – test)
Mg (%)	0.15	0.14		normal	no sign.	(<i>t</i> – test)
Mn	86.94	137.53	116	0.006	no sign.	(KW)
Mo	0.56	0.44		normal	no sign.	(<i>t</i> – test)
Ni	1.54	2.00		normal	$p = 0.038$	(<i>t</i> – test)
P (%)	0.39	0.37		normal	no sign.	(<i>t</i> – test)
Pb	2.08	0.43	2.22	normal	$p = 0.001$	(<i>t</i> – test)
S (%)	0.31	0.27		normal	no sign.	(<i>t</i> – test)
Sn	0.02	0.03		normal	no sign.	(<i>t</i> – test)
Sr	12.46	13.18		normal	no sign.	(<i>t</i> – test)
Zn	69.24	41.38	44	normal	$p = 0.001$	(<i>t</i> – test)
	N=11	N=6				

Above the orebody, As was found to be three times higher (0.14 ± 0.02 ppm, $EF_{As}=0.7$), Pb five times higher (2.08 ± 0.10 ppm, $EF_{Pb}=13$) and Zn two times higher (70 ± 1.46 ppm, $EF_{Zn}=42$) on average when compared to the control values for As (0.04 ± 0.03 ppm, $EF_{As}=0.2$), Pb (2.22 ± 0.01 ppm, $EF_{Pb}=1.3$) and Zn (41.38 ± 1.91 ppm, $EF_{Zn}=13.3$) around the Navan deposit. One significant figure implies < 12% MAD precision while four significant figures implies < 5% MAD precision.

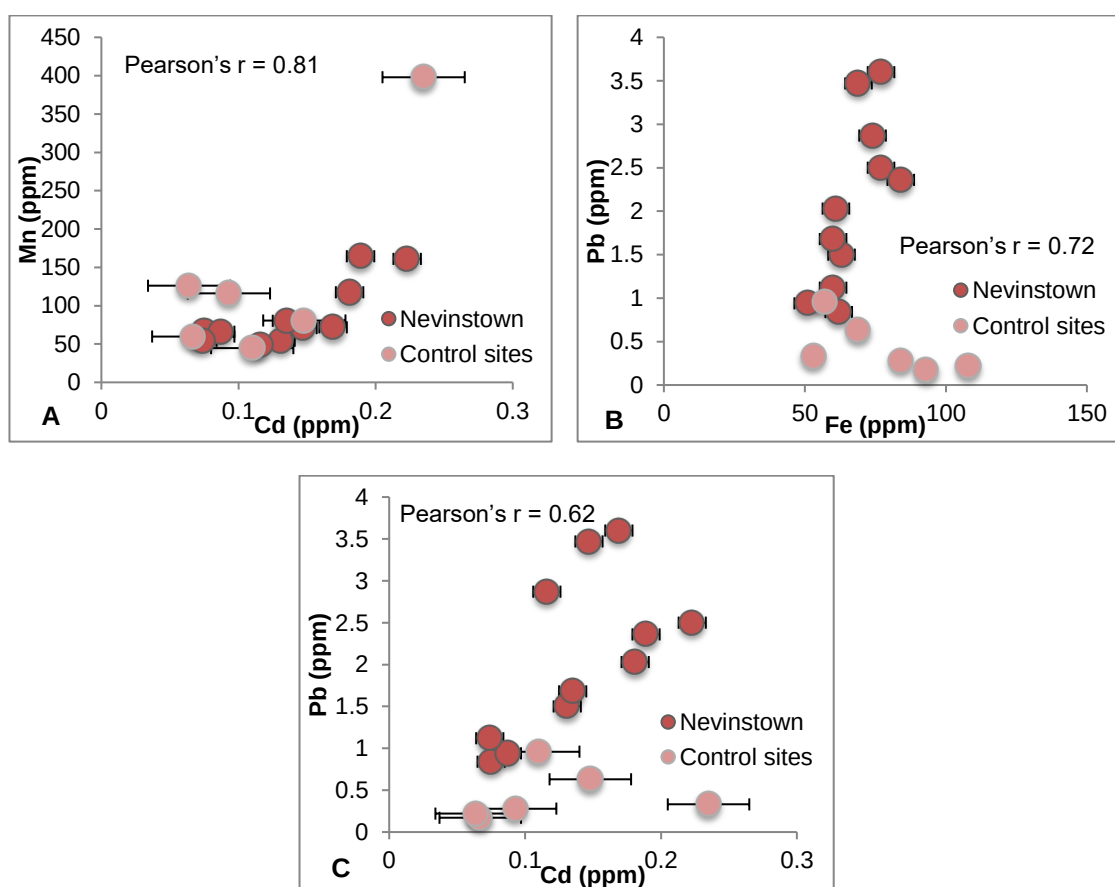


Figure 28. Scattered X/Y plot showing Pearson's correlation for: **A)** Cd:Mn; **B)** Fe:Pb and **C)** Cd:Pb in sycamore leaves from Nevinstown (N=11). Plot also includes samples from control sites (N=6) collected in spring 2015. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

A strong positive Pearson correlation (N=11) is noted for Mn:Cd ($r=0.81$), Fe:Pb ($r=0.72$) and Cd:Pb ($r=0.62$) for spring sycamore leaves at Nevinstown (Fig. 28). Comparing the two different seasons (see Appendix C, Tab. C-3), leaves tend to accumulate more Cd, Mn, Pb and Zn during autumn while Cu was mainly depleted during same season (7.30 ± 0.39 ppm, < 5% MAD precision).

Ash (*Fraxinus excelsior*)

Based on the Shapiro-Wilk test Ba, Mn, Pb and Zn data are not normally distributed in ash. A Kruskal-Wallis and t - test showed significant differences in As, Ba, Cd, Cu, Hg, P, Pb, Sn and Zn when comparing all sites (Tab. 20). Furthermore, arsenic was three times higher (0.15 ± 0.02 ppm, $EF_{As}=0.14$), Pb four times higher (2.08 ± 0.10 ppm, $EF_{Pb}=16$) and Zn two times higher (82 ± 1.46 ppm, $EF_{Zn}=99$) on average compared to an area around the Navan ore deposit. One significant figure implies < 12% MAD precision while seven significant figures implies < 5% MAD precision.

A strong positive Pearson's factor (N=24) is exhibited for Cd:Pb ($r>0.90$) for ash leaves at both sites. A positive correlation (Fig. 29) of Fe:Pb ($r=0.64$) is observed for Nevinstown (N=18) while a negative correlation for Mn:Zn ($r=-0.73$) was noted only for the control sites (N=6). There were no seasonal differences except for Cu, Fe and Zn, which were mainly depleted in leaves collected in autumn (see Appendix C, Tab. C-4).

Table 20. Element concentration in ash leaves collected in spring 2015 from Nevinstown and control sites. Mean concentrations in ash leaves are reported by Aksoy et al. (2005). The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above the critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents the number of analysed samples.

Element	Ash leaves		Reported Leaves	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control sites</i>		<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.15	0.06		normal	$p = 0.036$	(t – test)
Ba	23.79	7.52		0.035	$p < 0.001$	(KW)
Ca (%)	1.10	1.08		normal	no sign.	(t – test)
Cd	0.05	0.01		normal	$p = 0.002$	(t – test)
Co	0.04	0.05		normal	no sign.	(t – test)
Cr	1.01	1.36		normal	no sign.	(t – test)
Cu	16.62	11.32	2.8	normal	$p = 0.006$	(t – test)
Fe	77.11	72.00	46	normal	no sign.	(t – test)
Hg	0.01	0.01		0.01	$p = 0.020$	(KW)
K (%)	1.46	1.37		normal	no sign.	(t – test)
Mg (%)	0.22	0.22		normal	no sign.	(t – test)
Mn	34.46	26.93	488	0.002	no sign.	(KW)
Mo	0.64	0.52		normal	no sign.	(t – test)
Ni	3.60	4.25		normal	no sign.	(t – test)
P (%)	0.54	0.50		normal	no sign.	(t – test)
Pb	2.08	0.53	0.17	0.008	$p = 0.004$	(KW)
S (%)	0.37	0.37		normal	no sign.	(t – test)
Sn	0.01	0.02		0.006	$p = 0.048$	(KW)
Sr	13.56	12.77		normal	no sign.	(t – test)
Zn	81.68	45.50	38	<0.001	$p < 0.001$	(KW)
	N=18	N=6				

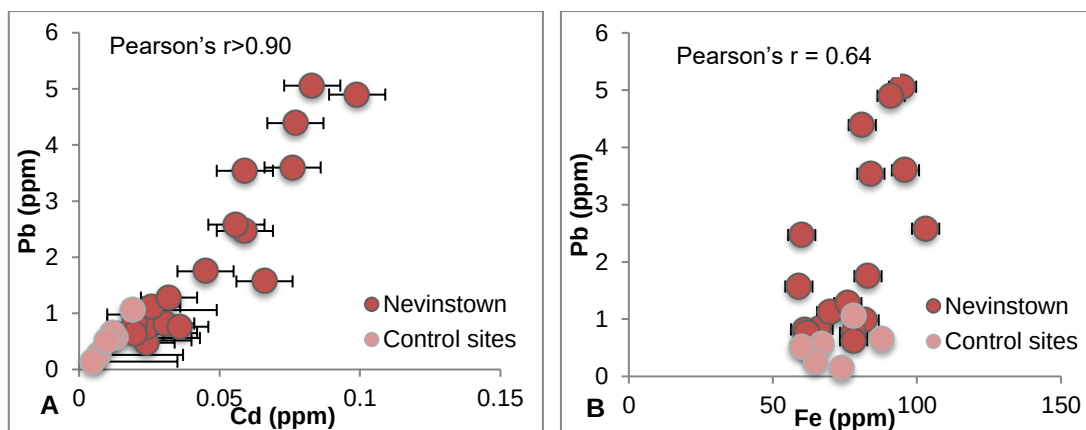


Figure 29. Scattered X/Y plot showing Pearson's correlation for: **A)** Cd:Pb from Nevinstown (N=18) and control sites (N=6) and **B)** Fe:Pb from Nevinstown (N=18) in ash leaves collected in spring 2015. **B** plot also includes samples from control sites (N=6). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Beech (*Fagus sylvatica*)

Arsenic ($p = 0.001$) and Cd ($p = 0.004$) values do not exhibit a normal distribution at Nevinstown based on a Shapiro – Wilk test (Tab. 21). Statistical analysis showed significant differences in As ($p = 0.003$, K.-Wallis test), Pb ($p = 0.003$, K.-Wallis test) and Zn ($p < 0.001$, t – test) when comparing both the Nevinstown and control sites (Tab. 21). In addition, As was found to be seven times higher (0.15 ± 0.02 ppm, $EF_{As}=1.4$); Pb seventeen times higher (2.05 ± 0.10 ppm, $EF_{Pb}=19$) while Zn was two times higher (59 ± 1.46 ppm, $EF_{Zn}=72$) on average compared to the control sites. Also, beech leaves collected in the autumn (see Appendix C, Tab. C-5) were depleted in Cd (0.16 ± 0.07 ppm) and Cu (6.69 ± 0.39 ppm) but enriched in Mn (159.63 ± 0.99 ppm), Pb (2.65 ± 0.08 ppm) and Zn (65.90 ± 0.28 ppm) combining data sets from both sites. One significant figure implies $< 12\%$ MAD precision while four significant figures implies $< 5\%$ MAD precision.

Table 21. Element concentration in beech leaves collected in spring 2015 from Nevinstown and the control sites. Reported mean values of element concentrations in beech leaves (BCR-100) are as published by the European Commission DG Joint Research Center IRMM (2006). A Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above the critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Beech leaves		Reported Leaves	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control sites</i>		<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.15 ± 0.02	0.02		0.001	$p = 0.003$	(KW)
Ba	33.63	34.40		normal	no sign.	(t – test)
Ca (%)	0.66	0.67		normal	no sign.	(t – test)
Cd	0.31	0.20	0.34	0.004	no sign.	(KW)
Co	0.04	0.05		normal	no sign.	(t – test)
Cr	1.38	1.53		0.028	no sign.	(KW)
Cu	13.19	11.60	12	normal	no sign.	(t – test)
Fe	60.78	53.80	550	normal	no sign.	(t – test)
Hg	0.01	0.01		normal	$p = 0.049$	(t – test)
K (%)	1.16	1.07		normal	no sign.	(t – test)
Mg (%)	0.14	0.16		normal	no sign.	(t – test)
Mn	88.03	119.44	133	normal	no sign.	(t – test)
Mo	0.34	0.27		0.005	no sign.	(KW)
Ni	2.47	3.35		normal	$p = 0.043$	(t – test)
P (%)	0.37	0.33		normal	no sign.	(t – test)
Pb	2.05	0.12	16.3	0.03	$p = 0.003$	(KW)
S (%)	0.19	0.18		normal	no sign.	(t – test)
Sn	0.01	0.01		<0.001	no sign.	(KW)
Sr	8.64	8.10		normal	no sign.	(t – test)
Zn	59.16	25.94	69	normal	$p < 0.001$	(t – test)
	N=9	N=5				

In addition, bulk wood (tree cores) accumulated more Fe at Nevinstown while at control sites it accumulated more As; only Pb preserved similar concentrations at both sites when compared to leaves (see Appendix A, Tab. A-5). A positive Pearson's correlation (N=9) is exhibited for Cd:Zn ($r=0.88$), Pb:Zn ($r=0.84$) and Cd:Pb ($r=0.87$) while Mn:Cu showed a negative weak correlation ($r=-0.65$) in the Nevinstown area (Fig. 30). The statistical test was performed on a small sample size and as such will have

extremely small power and a low probability of detection. Therefore, Pearson's correlation was used due to relatively small to medium sampling sizes.

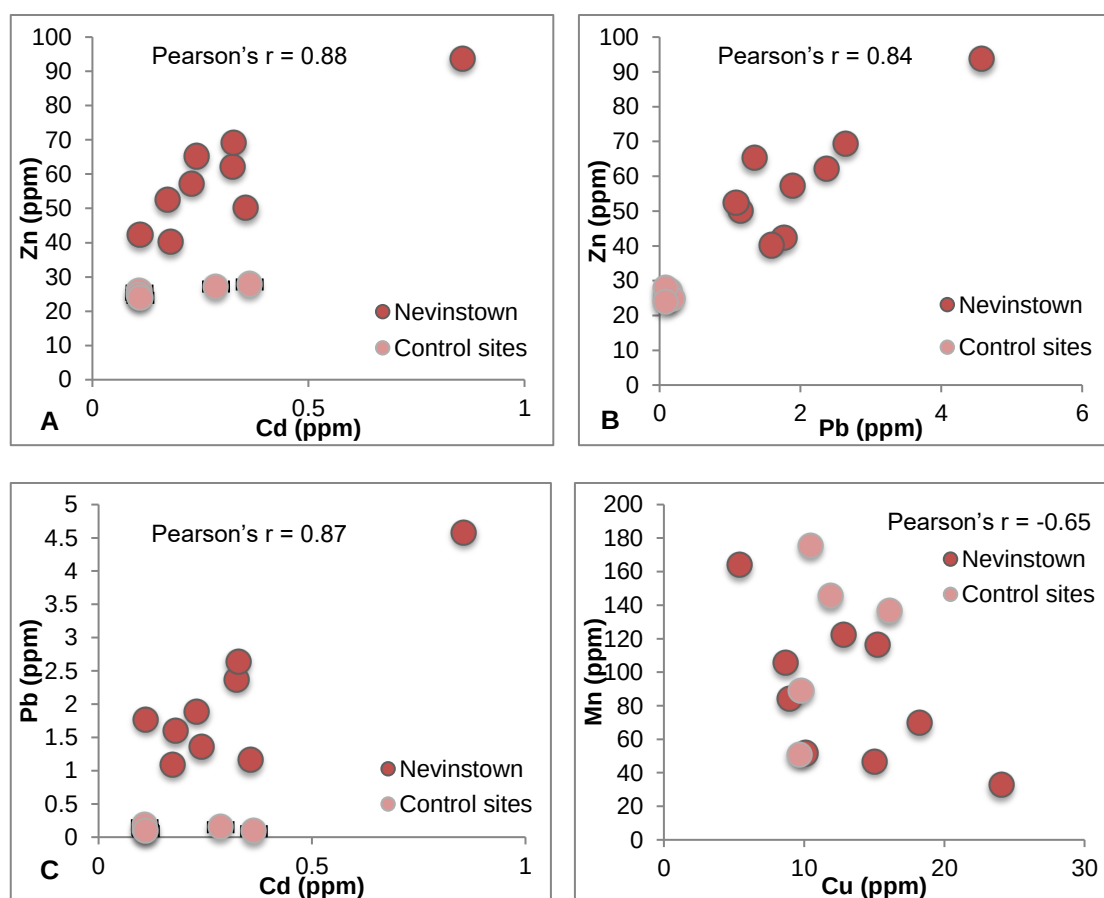


Figure 30. Scattered X/Y plot showing Pearson's correlation for: **A)** Cd:Zn; **B)** Pb:Zn; **C)** Cd:Pb and **D)** Cu:Mn in beech leaves from Nevinstown (N=9) collected in spring 2015. Plots also include samples from control sites (N=5). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Oak (Quercus spp.)

Data for oak leaves in the Nevinstown area is not normally distributed for Ni and S, as well as Cd for the surrounding control sites (Tab. 22). Similarly, to the other plant species at Nevinstown As ($p < 0.001$, t – test), Cu ($p = 0.020$, t – test), Pb ($p < 0.001$, t – test) and Zn ($p < 0.001$, t – test) in oak leaves were significantly different compared to control areas. Note that the power of statistical tests decreases with small sample sizes as is the case Nevinstown (N=3).

Metal enrichment for As was found to be five times higher (0.11 ± 0.02 ppm, $EF_{As}=0.5$); Cu two times higher (13 ± 0.26 ppm, $EF_{Cu}=30$); Pb up to nineteen times higher (1.79 ± 0.10 ppm, $EF_{Pb}=8$) and up to two times for higher Zn (43 ± 1.46 ppm, $EF_{Zn}=26$). Almost all elements of interest were enriched in leaves collected in the autumn from both sites (see Appendix D, Tab. D-5). The only reported depletion is for Cu which averages 10.13 ± 0.36 ppm in spring leaves and less so in autumn foliage (7.02 ± 0.39 ppm). One significant figure implies $< 12\%$ MAD precision while six significant figures implies $< 5\%$ MAD precision. In addition, woody material (obtained from tree cores) tends to accumulate more Fe than leaves at Nevinstown while at the control sites Fe, Cd and As were enriched in wood.

A Pearson's test (N=5) showed a positive correlation (Fig. 31) for Pb:Zn ($r=0.79$) and Cd:Mn ($r=0.81$) at the control sites while a negative correlation was observed for Cd:Zn ($r= -0.82$); however they need to be taken with caution based on the small sample size (N=5). A correlation test at Nevinstown was not considered due to the small sample size (N=3) and low power of the test.

Table 22. Element concentration in oak leaves collected in spring 2015 from Nevinstown and control sites. Element concentrations in oak leaves and wood are reported by Aboal et al. (2004) and Bargagli et al. (2003)*. The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t – test was performed on normal data distribution. Values above the critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Oak leaves		Reported <i>Leaves</i>	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control sites</i>		<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.11	0.02	0.20	normal	$p < 0.001$	(t – test)
Ba	26.75	8.68	16.7*	normal	$p < 0.003$	(t – test)
Ca (%)	0.61	0.45	0.78*	normal	no sign.	(t – test)
Cd	0.07	0.03	0.01	normal	no sign.	(t – test)
Co	0.03	0.03		normal	no sign.	(t – test)
Cr	0.71	0.74	0.12	normal	no sign.	(t – test)
Cu	13.48	8.45	6.40	normal	$p = 0.020$	(t – test)
Fe	67.50	62.40	88.90	normal	no sign.	(t – test)
Hg	0.01	0.01	0.04	normal	no sign.	(t – test)
K (%)	1.53	1.37	0.53*	normal	no sign.	(t – test)
Mg (%)	0.17	0.13	0.19*	normal	$p = 0.004$	(t – test)
Mn	146.75	238.74	304.70	normal	no sign.	(t – test)
Mo	0.17	0.25		normal	no sign.	(t – test)
Ni	2.22	2.05	2.52	0.03	no sign.	(KW)
P (%)	0.38	0.32		normal	no sign.	(t – test)
Pb	1.79	0.09	0.15	normal	$p < 0.001$	(t – test)
S (%)	0.21	0.18	0.20*	0	no sign.	(KW)
Sn	0.02	0.02		0	no sign.	(KW)
Sr	4.79	2.92		normal	$p = 0.045$	(t – test)
Zn	42.50	17.82	12.25	normal	$p < 0.001$	(t – test)
	N=3	N=5				

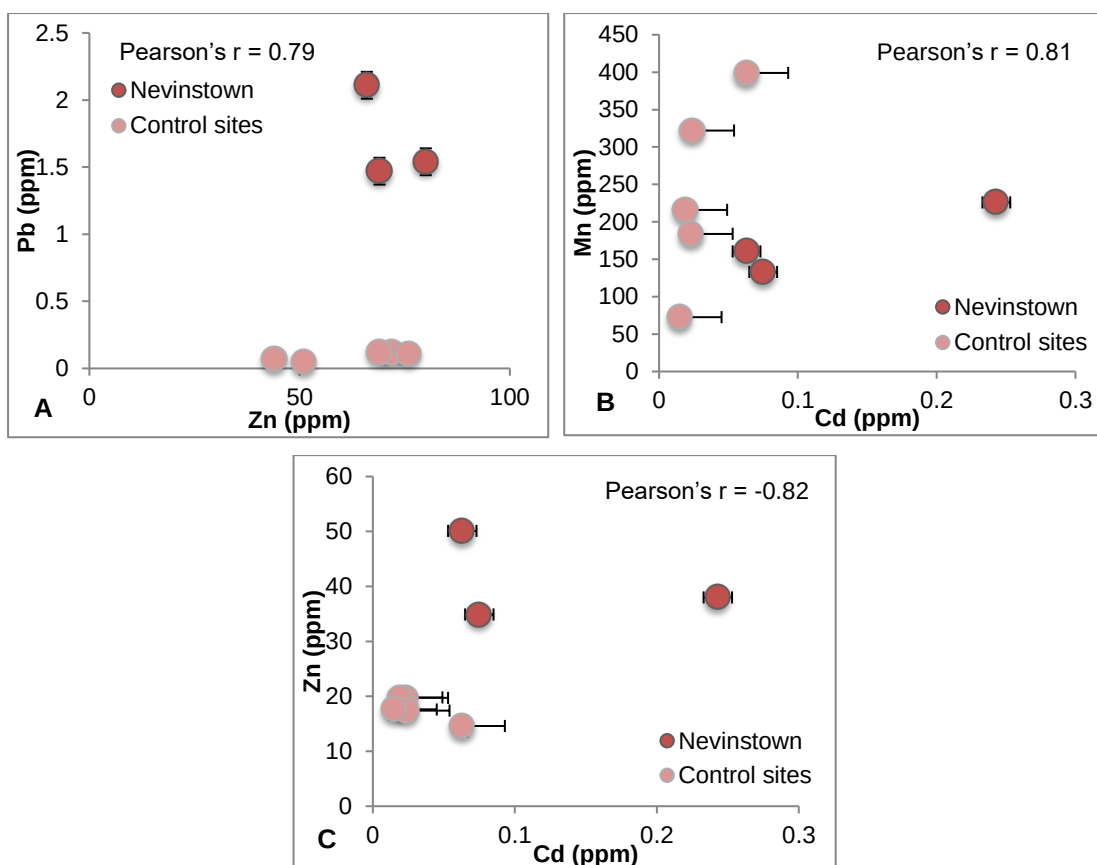


Figure 31. Scattered X/Y plot showing Pearson's correlation for: **A)** Pb:Zn; **B)** Mn:Cd and **C)** Cd:Zn in oak leaves from control sites (N=5) collected in spring 2015. Plots also include samples from Nevinstown site (N=3). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Poplar (*Populus alba*)

A Shapiro-Wilk test showed Fe, Ni and P to be not normally distributed which was not the case with the control sites (Tab. 23). Statistical testing (Kruskal-Wallis and *t*-test, 95% confidence) revealed significant difference between sites for the majority of elements listed except for Cd, Fe, Mo, Ni and Sn (Tab. 23). Note that the power of statistical tests decreases with small sample size such can be seen for Nevinstown (N=4) and control sites (N=3). On average, As was found to be five times higher (0.41 ± 0.01 ppm, $EF_{As}=1.3$); Pb sixteen times higher (8.45 ± 0.13 ppm, $EF_{Pb}=19$) and Zn was three times higher (536 ± 0.57 ppm, $EF_{Zn}=216$) at Nevinstown compared to the control sites. All significant figures implies < 5% MAD precision.

There were no major seasonal variations except for As, Cu and Pb which were depleted in leaves collected for the autumn (see Appendix C, Tab. C-7). Furthermore, a positive correlation (N=4) was observed between Cu:Fe ($r=0.84$) and Cd:Zn ($r=0.69$) in the autumn poplar leaves; however they need to be taken with caution based on the small sample size (N=4) (Fig. 32).

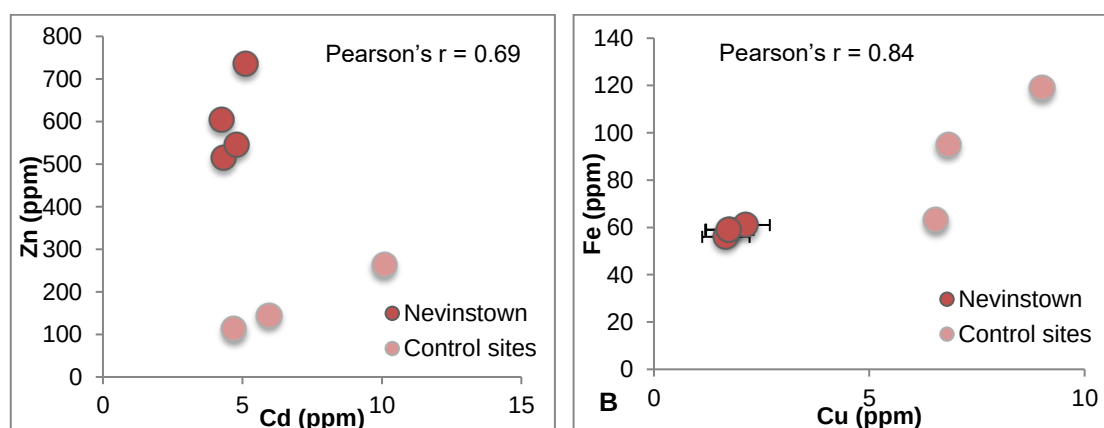


Figure 32. Scattered X/Y plot showing Pearson's correlation for **A)** Cd:Zn and **B)** Cu:Fe in poplar leaves from Nevinstown (N=4) collected in autumn 2015. Plots also include samples from control site (N=3). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Note, a correlation test for spring poplar leaves at Nevinstown was not considered due to the small sample size (N=3) and low power of the test.

Table 23. Element concentrations in poplar leaves collected in the autumn in Nevinstown and the control sites 2015. Mean concentrations in poplar leaves are reported by Dominguez et al. (2008) and Madejon et al. (2004)*. The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distributions. Values above the critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents the number of analysed samples.

Element	Poplar leaves		Reported	Shapiro – Wilk W test p (normal)	Kruskal-Wallis (KW) & t - test (95% conf.)	
	<i>Nevinstown</i>	<i>Control</i>	<i>Leaves</i>	<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	0.41	0.08	0.99	normal	$p = 0.017$	(t - test)
Ba	89.35	18.53		normal	$p < 0.001$	(t - test)
Ca (%)	0.95	2.84		normal	$p < 0.001$	(t - test)
Cd	4.34	6.92	0.21	normal	no sign.	(t - test)
Co	0.10	0.50		normal	$p < 0.001$	(t - test)
Cr	1.69	1.86		normal	no sign.	(t - test)
Cu	4.12	7.47	7.44	normal	$p < 0.001$	(t - test)
Fe	66.00	73.14	92.33	normal	no sign.	(t - test)
Hg	0.01	0.02		normal	$p = 0.017$	(t - test)
K (%)	1.43	2.56		normal	$p = 0.017$	(t - test)
Mg (%)	0.19	0.08		normal	no sign.	(t - test)
Mn	29.25	88.97	51	normal	$p = 0.038$	(t - test)
Mo	0.25	1.31		0.045	no sign.	(KW)
Ni	2.58	7.92	1.05*	0.033	$p = 0.034$	(KW)
P (%)	0.29	0.23		normal	$p = 0.017$	(t - test)
Pb	8.45	0.53	3.93	normal	$p < 0.001$	(t - test)
S (%)	0.27	0.47		normal	$p = 0.006$	(t - test)
Sn	0.03	0.03		0.024	no sign.	(KW)
Sr	21.40	38.87		normal	$p = 0.008$	(t - test)
Zn	535.50	173.50	81.6	normal	$p = 0.002$	(t - test)
	N=4	N=3				

6.1.1.2 Soil geochemistry

Soils samples were collected at a depth of up to 20 cm (A Horizon in Podzolic soils) from Nevinstown (N=33), control sites (N=3) and Delvin area (N=3). Generally, soil data does not exhibit a normal distribution above the deposit at Nevinstown (Tab. 24). A Kruskal-Wallis test reveals a significant difference in As ($p = 0.005$), Cd ($p = 0.005$), Mn ($p = 0.010$), Pb ($p = 0.005$) and Zn ($p = 0.005$) concentrations when comparing both sites. Note that the power of statistical tests decreases with small sample sizes such as can be seen for the control sites (N=3). Furthermore, As was found to be eight times higher (47 ± 1.41 ppm, $EF_{As}=5.5$); Cd eight times higher (4 ± 0.26 ppm, $EF_{Cd}=3.5$); Pb eight times higher (389 ± 4.24 ppm, $EF_{Pb}=31$) and Zn eleven times higher (1110 ± 4.24 ppm, $EF_{Zn}=15$) in soils at Nevinstown (Fig. 33) than background values in soils from the control sites (Tab. 24). All significant figures implies $< 5\%$ MAD precision.

Loss on ignition (LOI) estimates displayed mean values of 17% in soils collected above the orebody which increased up to 19% in soils collected at distances of 2 km and 40 km from the mine area. In order to express the acidity and alkalinity of the soil solution, pH was measured within the range of 4.6 to 7.7 at Nevinstown and in the range of 4.6 to 5.8 at the control sites, indicating minor differences between sites. The electrical conductivity of soils (EC) shows mean values of 48 μ S in soil solution at Nevinstown with an increase of up to 127 μ S at the control sites. In general, EC at Nevinstown ranged from 0 – 1189 μ S and from 96 μ S to 167 μ S at the control sites.

Table 24. Element concentration in soils collected in summer 2016 from Nevinstown and control sites. Element concentrations in soils are reported by Fay et al. (2007) and Kabata-Pendias et al. (2011)*. The Shapiro-Wilk W test is calculated at 95% confidence. Data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above the critical value ($p = 0.05$) displayed no significant differences (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Soil		Reported	Shapiro – Wilk W test (p-normal)	Kruskal-Wallis (KW) & t – test (95% conf.)	
	<i>Nevinstown</i>	<i>Control sites</i>	<i>Soil</i>	<i>Nevinstown</i>	<i>Nevinstown vs. control</i>	
As	43.74	6.09		<0.001	$p = 0.005$	(KW)
Ba	373.01	96.57		0.029	$p = 0.005$	(KW)
Ca (%)	0.35	0.40		<0.001	no sign.	(KW)
Cd	3.72	0.51		<0.001	$p = 0.005$	(KW)
Co	9.60	8.40		<0.001	no sign.	(KW)
Cr	26.34	25.30	65-80	<0.001	no sign.	(KW)
Cu	21.76	15.30		<0.001	$p = 0.075$	(KW)
Fe (%)	0.21	1.97		<0.001	no sign.	(KW)
Hg	0.22	0.12		<0.001	no sign.	(KW)
K (%)	0.12	0.14		<0.001	no sign.	(KW)
Mg (%)	0.39	0.37		normal	no sign.	(t - test)
Mn	1171.03	377.33	500-800	<0.001	$p = 0.010$	(KW)
Mo	1.71	1.54		<0.001	no sign.	(KW)
Ni	32.71	30.00		<0.001	no sign.	(KW)
P (%)	0.12	0.11		<0.001	no sign.	(KW)
Pb	361.65	0.43	20-30	0.004	$p = 0.005$	(KW)
S (%)	0.08	48.23		<0.001	no sign.	(KW)
Sn	1.39	0.07		<0.001	no sign.	(KW)
Sr	19.13	15.68		<0.001	no sign.	(KW)
Zn	1028.58	103.20	47-63*	<0.001	$p = 0.005$	(KW)
	N=33	N=3				

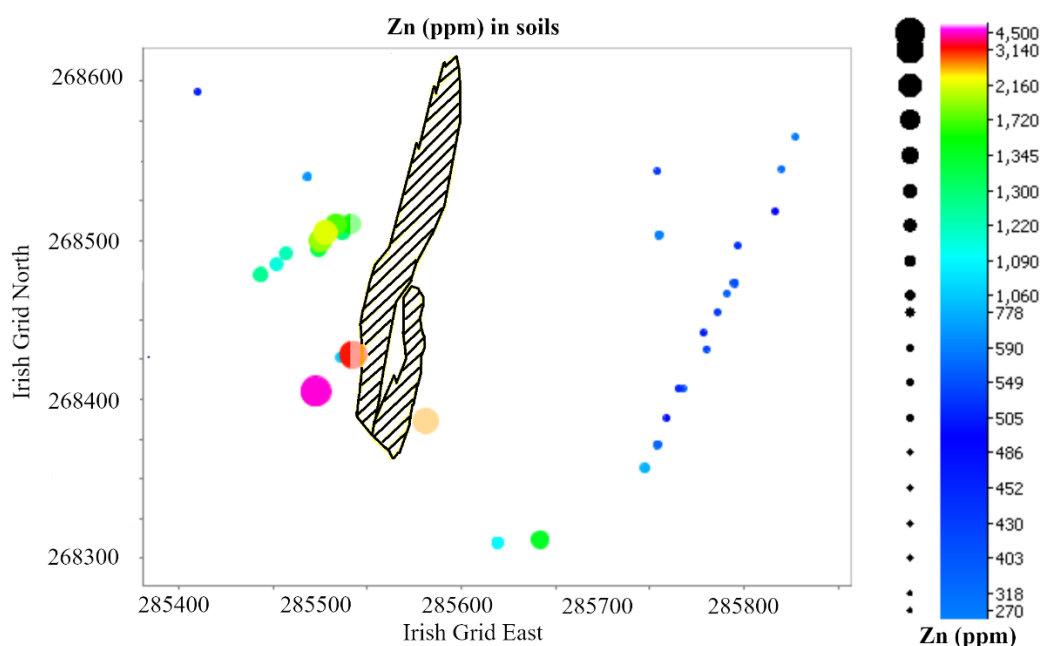


Figure 33. The distribution of zinc concentration in soils at Nevinstown (N=33). The ore sub-outcrop is marked black. Highest element concentrations are marked with pink, red and orange colour ranging up to 4500 ppm with the lowest concentrations at 270 ppm (blue).

The correlation factors using a Pearson Product Moment's test (N=33) revealed several patterns for the elements of interest (Fig. 34). A very strong positive correlation for Cd:Zn ($r=0.97$), As:Mn ($r=0.98$) and Fe:Mn ($r=0.89$) was noted at Nevinstown. In addition, a positive correlation was observed for Cu:pH ($r=0.74$) and Cu:LOI ($r=0.66$).

Further investigation in greater detail, comparing hawthorn leaves with soil samples collected from Nevinstown (Fig. 35A, B and C) yielded positive multiple correlation coefficient (Regression analysis, 95% confidence) for As:Cd ($R=0.79$), As:Zn ($R=0.81$) and Cd:Zn ($R=0.97$) only for Nevinstown.

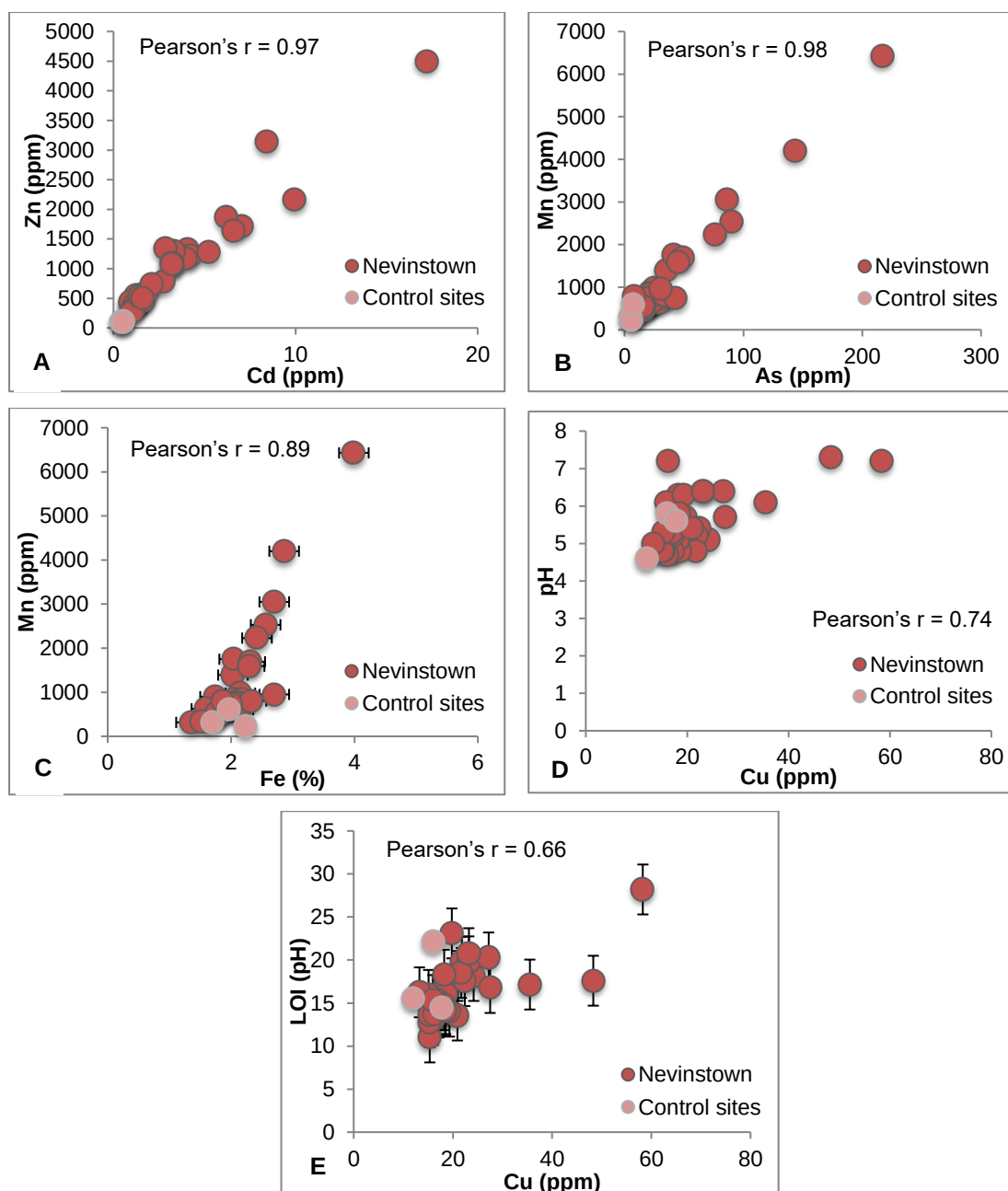


Figure 34. Scattered X/Y plot showing Pearson's correlation for: **A)** Cd:Zn; **B)** As:Mn; **C)** Fe:Mn; **D)** Cu:pH and **E)** Cu:LOI in soils from Nevinstown (N=33) collected in summer 2016. Plots also include samples from control sites (N=3). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Furthermore, a multiple correlation coefficient ($R=0.58$, 95% Confidence) between Ca and Sr is observed in soils and in every plant species (Fig. 35D). Field pH which was measured immediately after soil collection was 10% higher than pH measurements in the laboratory, suggesting pH slowly decreased and soils became more acidified over time. More information about field and laboratory pH and EC is given in Appendix A, Tab. A-7.

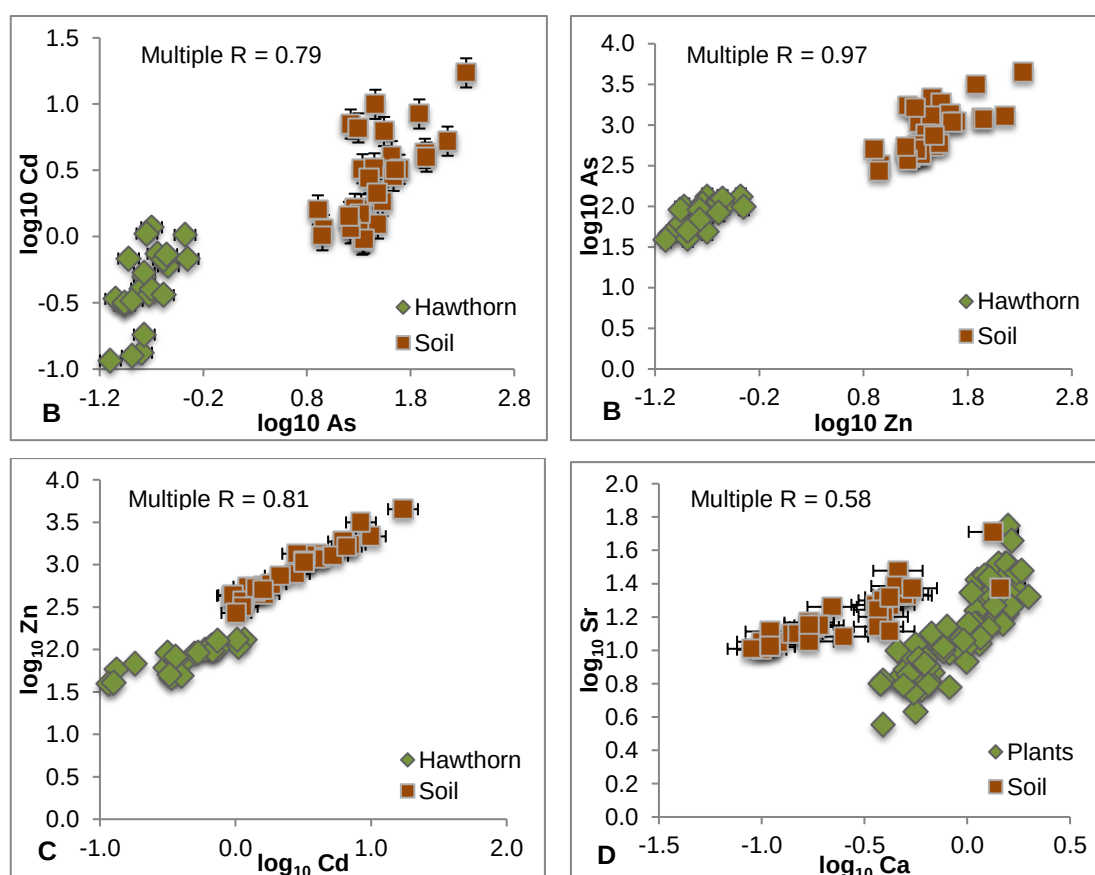


Figure 35. Scattered X/Y plot showing multiple correlation for: **A)** log As:Cd; **B)** log As:Zn and **C)** log Cd:Zn in hawthorn leaves (N=23) and soil (N=33) from Nevinstown. Calcium and Sr multiple correlation coefficient is observed in all plant species (N=83) and soil (N=33) from Nevinstown (**D**). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

6.1.1.3 Dendrochemistry around the Navan Zn-Pb deposit

Oak and beech dendrochronology was broadly constructed using tree-ring width from cores obtained on beech (N=4) and oak (N=3) trees. Wider tree ring width indicates faster growth of the tree followed by a rainier annual season while narrower tree rings display a year with less rainfall resulting in slower tree growth (Fig. 36). Constructed beech and oak chronology corresponds to Northern Ireland chronology, County Antrim in particular (Brown 2016, pers. comm.).

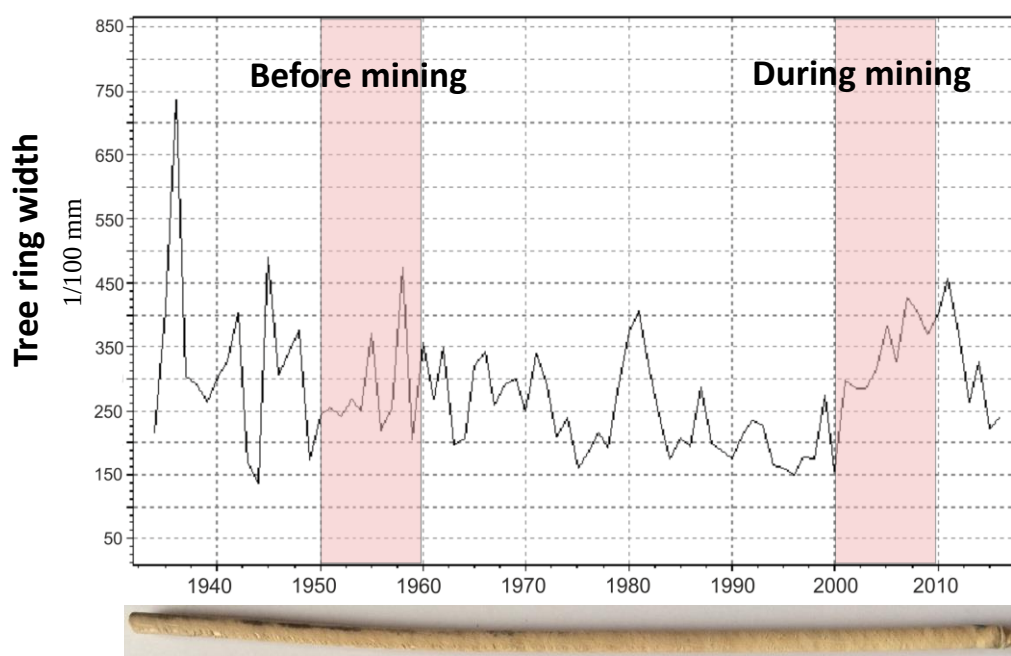


Figure 36. Tree ring width (Y-axis) compared to years (annual ring). Oak tree core dates back to 1934 and the last annual ring belongs to 2016. Highlighted zones represent a 10-year period before the mine started to operate (1950-1960) and a 10-year period during mining (2000-2010).

Trace element analysis of bulk wood (tree cores) revealed depleted concentrations of As, Cd, Cu and Pb for beech and oak, but specifically for oak tree rings in comparison to reported values for Cu, Mn and Pb tree rings (Tab 25). Iron displayed elevated concentration in oak (91 ± 2.99 ppm on average) and in beech (79 ± 2.99 ppm on average). Furthermore, the highest Fe concentrations in the Navan area are reported in oak tree

rings (155 ± 2.99 ppm, on average). Thus, these concentrations are higher during pre-mining time (1950-1960) compared to the periods during mining from 2000 to 2010 (Tab. 25). One significant figure implies $< 9\%$ MAD precision while all other figures implies $< 5\%$ MAD precision.

Table 25. Trace element concentration in oak tree rings for two 10-year periods. Arsenic, Ca, Sn and Sr were not measured. Beech and oak bulk wood samples displayed all measured elements. Element concentrations in oak tree rings are reported by Szczepkowski and Nicewicz (2008)*. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Oak			Beech	Reported
	<i>Bulk wood</i>	<i>Tree rings (1950 – 1960)</i>	<i>Tree rings (2000 – 2010)</i>	<i>Bulk wood</i>	<i>Oak tree rings</i>
As	0.05	n/a	n/a	0.06	
Ca (%)	0.06	n/a	n/a	0.30	
Cd	0.05	0.05	0.03	0.07	
Cu	1.52	1.62	1.65	1.49	2.22*
Fe	90.67	185.15	124.65	67.25	11.70*
Mn	5.90	6.61	5.54	15.15	25.67*
Pb	0.17	0.09	0.02	0.19	0.37*
Sn	0.02	n/a	n/a	0.02	
Sr	2.06	n/a	n/a	7.47	
Zn	1.70	3.30	3.11	10.83	
	N=3	N=2	N=2	N=4	

In contrast, Fe values in leaves are much lower than in bulk wood and tree rings. Moreover, there is no relevant difference between the 10-year periods and bulk wood across the studied area except during 2000-2010 when tree-rings accumulated more Fe (161 ± 1.77 ppm, on average) at control sites (Fig. 37).

In general, Cd and Pb concentration revealed no clear trend between Nevinstown and the control sites except in oak tree-rings (ranging from 1950-1960) which exhibited higher Pb concentrations (0.15 ± 0.11 ppm) on average above the Zn-Pb orebody. Copper and Zn showed differences when comparing Nevinstown and the control sites during

periods from 1950 to 1960 and from 2000 to 2010. Moreover, the tree-rings collected at Nevinstown accumulated more Cu and Zn. In contrast, during the 2000-2010 period, Zn accumulation in tree-rings increases with the distance from the orebody.

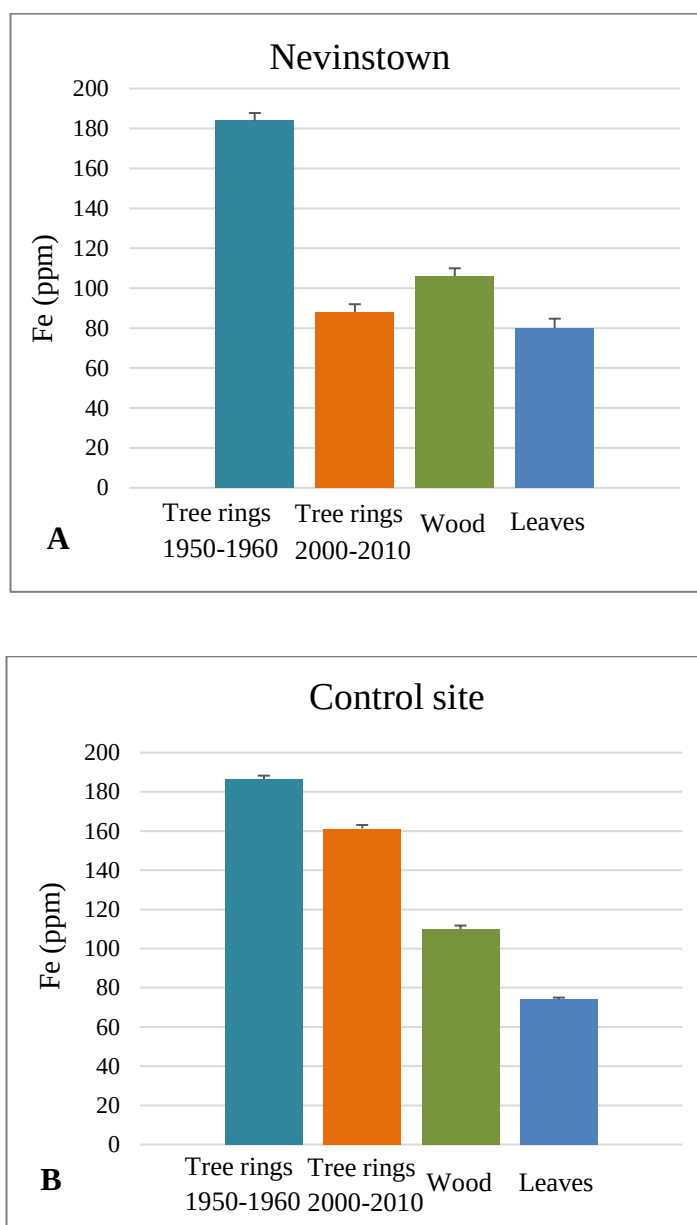


Figure 37. Iron concentration in oak tree rings, wood and leaves from **A)** Nevinstown (above the orebody) and **B)** control sites around the orebody. The tree rings represent ten-year sections for period from 1950 to 1960 and from 2000 to 2010. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

6.1.2 Comparison on a regional scale

In order to get a better overview of the metal distribution in different plant species across a wider area, the survey was expanded to the Irish Midlands (Tab. 16). One of these areas is located close to town of Delvin which is 40 km west from the Boliden Tara Mines. Considering the distance from an active mine and with no on-going agricultural usage of the pasture land, that particular location forms a representative control site which can be used for comparison on a regional scale.

One of the main questions in this thesis is whether plants uptake metals that migrate from bedrock hosted ore covered with a thicker overburden. For this purpose, the Ballinalack site (Fig. 38) was chosen. It is a sub-economic Zn-Pb deposit situated 60 km from the town of Navan. The current ownership consists of a Joint Venture partnership between Group Eleven Exploration Ltd. and Nonfemet (China).

Ballinalack is classified as an Irish Type carbonate-hosted Zn-Pb deposit having an overburden and cover rock thickness of approximately 150 m in the area designated as the profile A-B in Figure 38. Analysis showed Zn concentrations (on average) in hawthorn leaves were similar when comparing all three profiles (A-B, C-D and E-F, see Fig. 38). Thus, the profile C-D accumulated more Zn (30.21 ± 0.57 ppm, $EF_{Zn}=18$) and Cd ($0.17 \text{ ppm} \pm 0.02$, $EF_{Cd}=3$) in leaves than other locations. One of the observations was that the Zn values are the lowest above the Ballinalack sulphide orebody (Co. West Meath, Fig. 39). A Shapiro-Wilk test shows the data to be not normally distributed ($p < 0.05$, 95% confidence) for Cu, Fe and Pb. In addition, they are depleted when compared to the background (E-F) profile. One significant figure implies $< 9\%$ MAD precision while all other figures implies $< 5\%$ MAD precision.

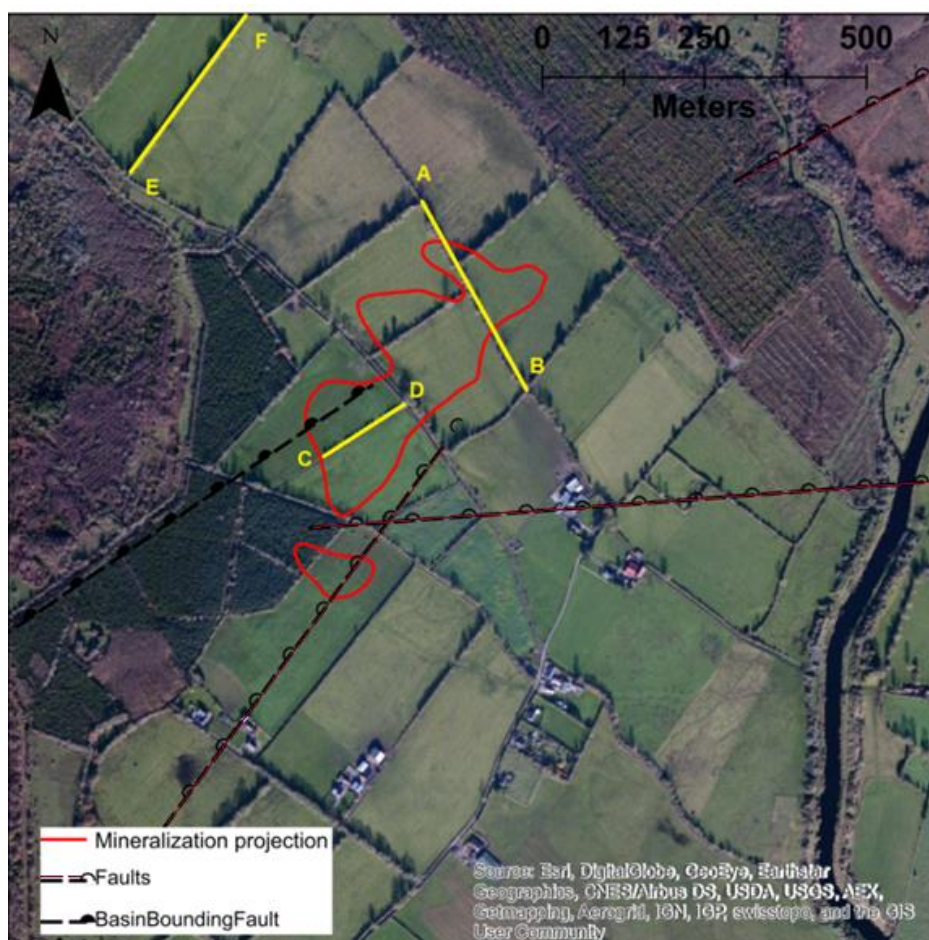


Figure 38. Ballinalack mineralisation projected to the surface is marked with red lines. Faults are marked according to the legend on the map (adopted from Kalveram, 2018). Yellow lines represent profiles A-B, C-D and E-F. Hawthorn leaves were systematically collected on these profiles during spring 2016. Here, the E-F profile serves as a control area for the sub-economic deposit.

A positive Pearson correlation was noted for Ni: Cd ($r=0.78$); Fe: As ($r=0.82$) and between Mn and elevation above sea level ($r=0.71$) above the sulphide orebody. Background values indicated correlations amongst Ba, Cd and Mn ($r>0.8$); and Co: Fe ($r=0.77$). Moreover, one of the strongest correlations was noted for Ca: Sr ($r=0.94$) above the thickest overburden and cover rock.

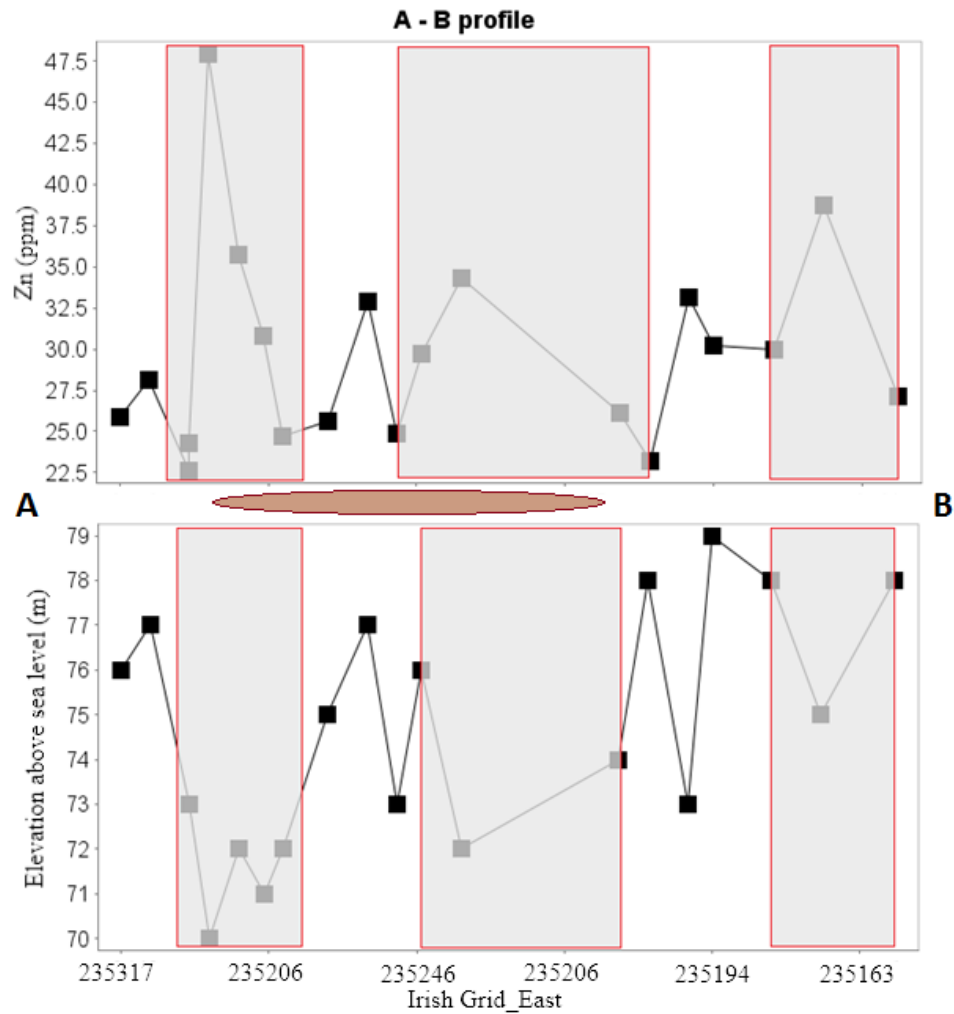


Figure 39. Profile A-B of the Ballinalack deposit where the brown ellipsoid represents the location of the sulphide orebody. Grey rectangles point out highest Zn concentrations on the first plot while the second plot shows the connection with the elevation of the sample locations.

It has been investigated before the influence of changing elevation to trace elements in plants (Wang et al., 2018). Different range of elevation changes soil texture, moisture content and bulk density of the soil. Even though, here the differences in elevation are only few meters but still there might be changes within soil texture and therefore in the plant-soil system.

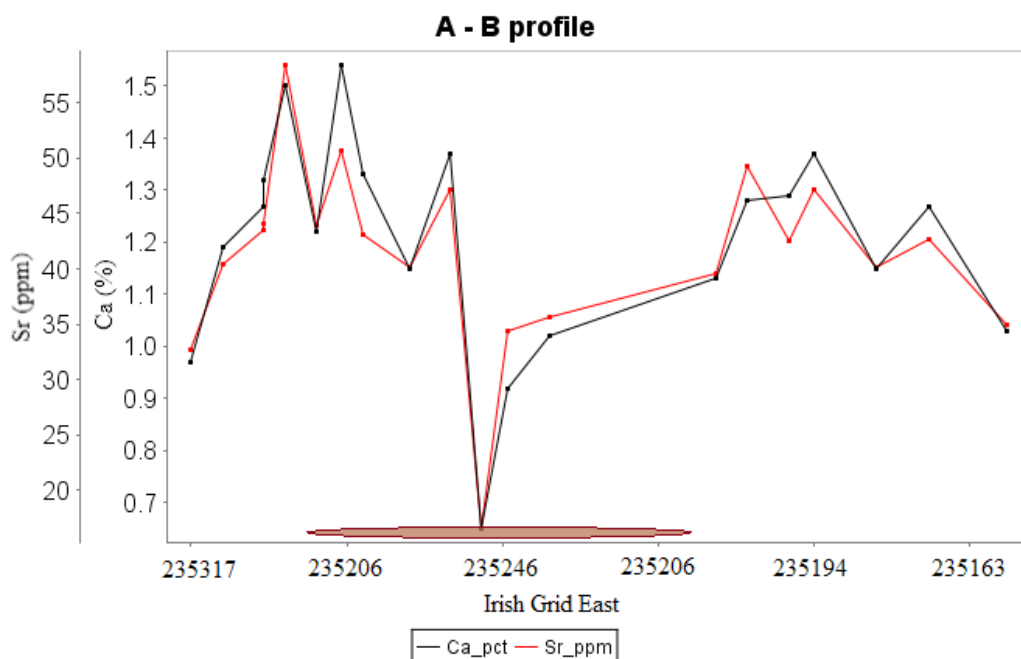


Figure 40. A-B profile of the Ballinalack deposit where the brown ellipsoid represents the location of the sulphide orebody. Calcium (%) and Sr (ppm) at the Y-axis are plotted against latitude on the X-axis.

The lowest concentrations of Ca and Sr occur above the orebody while the flanks of the orebody exhibit the highest element concentrations (Fig. 40). Thus, a similar correlation pattern is visible in every plant species and soil analysis discussed in the next chapter. A Kruskal-Wallis test shows a significant difference in Cd ($p < 0.001$, 95% Confidence) and Zn ($p < 0.001$, 95% Confidence) in hawthorn leaves between Nevinstown, Ballinalack, Delvin and the control sites (Fig. 41). However, with distance from the mine, Pb contents decrease while Cu and Fe gradually increase, with the highest values at Ballinalack (Cu=8.59±0.29 ppm; Fe=70.93±3.54 ppm). Manganese values are similar above both orebodies (at Nevinstown and Ballinalack) and lowest at the control sites around the Navan deposit.

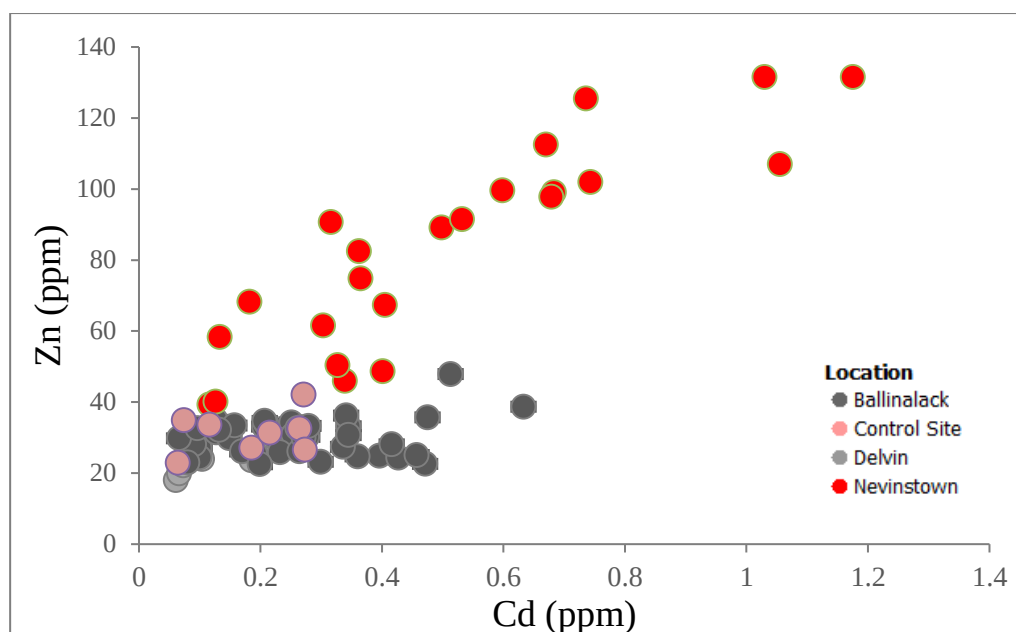


Figure 41. Concentrations of Cd and Zn in hawthorn leaves from all sites (N=80). Regression analysis indicates positive strong multiple correlation coefficient ($R=0.79$) at Nevinstown. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

In general, all plant species at Nevinstown are enriched in Cd, Pb and Zn when compared to sites further away (see Appendix A, Tab. A-1). Copper and Fe accumulated more in ash ($\text{Cu}=7.13\pm0.41$ ppm; $\text{Fe}=76\pm4.95$ ppm) and blackberry ($\text{Cu}=5.96\pm0.41$ ppm; $\text{Fe}=70.5\pm4.95$ ppm) regionally across the Irish Midlands than above the Navan deposit. However, sycamore, beech, oak and poplar show similar or higher concentration of Cu, Fe and Mn above mining area while ash behaves differently being more enriched in those elements at the Delvin area (see Appendix A, Tab. A-2). One significant figure implies < 10% MAD precision while all other figures implies < 5% MAD precision.

On the other hand, soil geochemistry on a regional scale provides an insight into trace element signatures which can be related to possible sources (Fig. 42). Signatures coming from the carbonates are mostly associated with the regional geology around the Navan orebody and Delvin area. Zinc and Pb concentrations in soils are normalised to Ca to

illustrate an impact of carbonates on the Zn and Pb signature above the orebody sub-crop (Nevinstown), control sites and in the Delvin area.

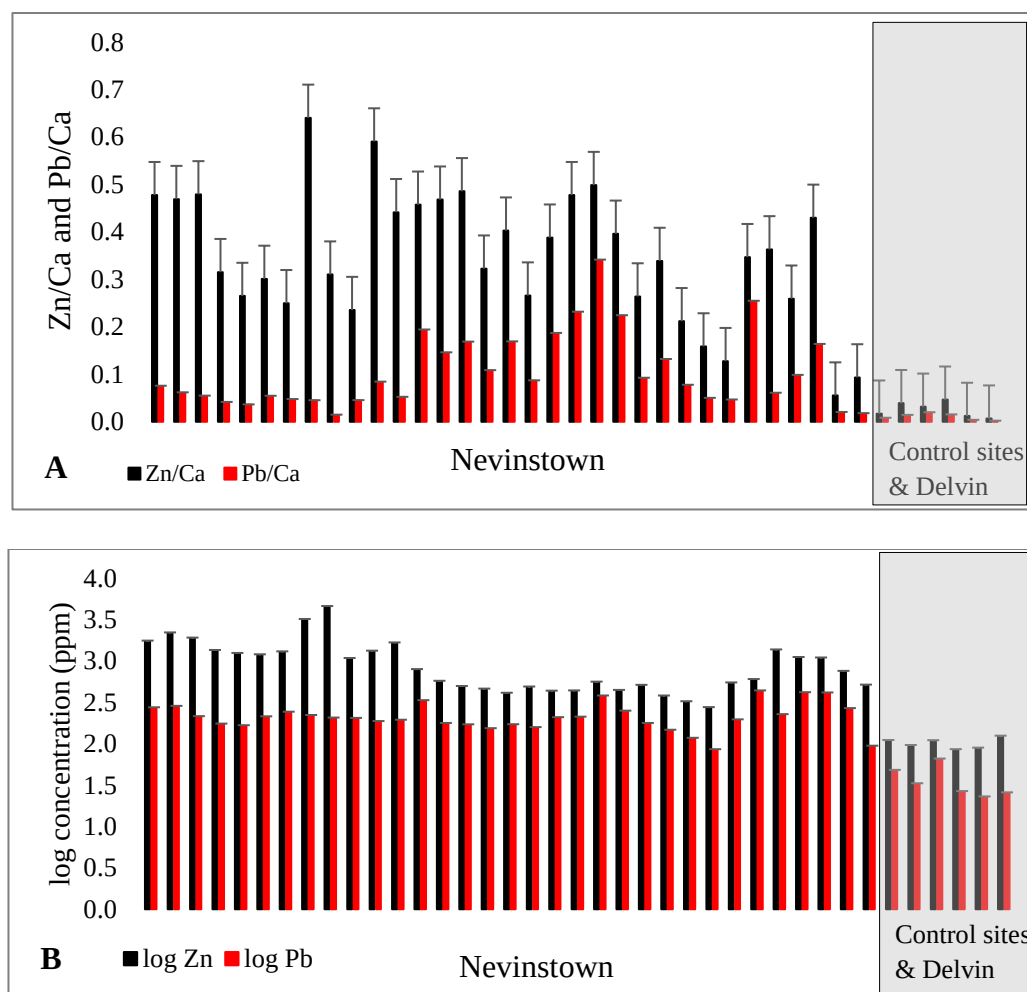


Figure 42. Metal ratios of Zn/Ca and Pb/Ca (A) in comparison to log Zn and log Pb values (B) used as an indicator of possible carbonate sources in surficial soils from Nevinstown (N=33), control sites (N=3) and Delvin (N=3). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

6.2 Non-traditional (Cu and Zn) isotopes - Navan

Based on trace element results, hawthorn leaves were selected to represent the Navan orebody and the control area providing more information on isotope biogeochemistry for Irish Type (Zn-Pb) deposits.

The results of isotopic analysis (Tab. 26) showed that $\delta^{66}\text{Zn}$ in hawthorn leaves range from $-0.62\pm0.07\text{‰}$ to $+0.48\pm0.07\text{‰}$ and $\delta^{65}\text{Cu}$ from $+0.05\pm0.10\text{‰}$ to $+0.66\pm0.10\text{‰}$ based on all sites. Furthermore, oak tree rings display a signature of $\delta^{66}\text{Zn}$ from $-0.11\pm0.07\text{‰}$ to $+0.09\pm0.07\text{‰}$ and $\delta^{65}\text{Cu}$ $-0.04\pm0.10\text{‰}$ to $+0.20\pm0.10\text{‰}$. Generally, soil samples revealed a signature of $\delta^{66}\text{Zn}$ from $+0.13\pm0.08\text{‰}$ to $+0.37\pm0.08\text{‰}$ and $\delta^{65}\text{Cu}$ from $0.04\pm0.07\text{‰}$ to $+0.19\pm0.07\text{‰}$. Isotopic data for plants, soil and ore are split between Nevinstown and the control areas. More information about isotopic signatures at each site is given in the further text.

Zn isotopes

In hawthorn leaves, zinc isotopes clearly show distinctive signatures when comparing all sites (Fig. 43). The lightest and most negative $\delta^{66}\text{Zn}$ ratios show mean values of $-0.35\pm0.07\text{‰}$ above the Zn-Pb orebody at Nevinstown. The two isotopically lightest samples are NVT-H1-6 (Zn=99±1.46 ppm, EF_{Zn}=60) and NVT-H1-18 (Zn=100±1.46 ppm, EF_{Zn}=60) showing ratio at $-0.62\pm0.07\text{‰}$ of $\delta^{66}\text{Zn}$. Control sites around the Navan deposit display the heaviest and most positive fractionation of zinc isotopes (mean=+0.33±0.07‰). Sample CS1-H1-5 (Zn=31±1.91 ppm, EF_{Zn}=19) exhibits the heaviest ratio of $\delta^{66}\text{Zn}=+0.48\pm0.07\text{‰}$. In summary, the diversity of the isotopic signatures of both localities represents 1‰ difference of $\delta^{66}\text{Zn}$ in total. All significant figures imply 7% MAD precision

Table 26. Isotopic composition of Zn and Cu in hawthorn leaves, oak tree-rings and soils from Nevinstown and control sites. Analytical precisions of $\delta^{66}\text{Zn}_{\text{JMC}}$ and $\delta^{65}\text{Cu}_{\text{NIST976}}$ are displayed to 2σ and 2SD. Zinc and Cu isotopes are expressed in per mil and in relation to reference material. Reference materials are soil (METRANAL 33), strawberry leaves (LGC7162) and basaltic rock (BCR-2).

Sample ID	Location	Material	$\delta^{66}\text{Zn}$	2σ	$\delta^{65}\text{Cu}$	2SD
NVT-H1-2	Nevinstown	Leaves	-0.25	0.02	0.24	0.01
NVT-H1-6	Nevinstown	Leaves	-0.62	0.02	0.29	0.09
NVT-H1-16	Nevinstown	Leaves	-0.39	0.02	0.13	0.01
NVT-H1-18	Nevinstown	Leaves	-0.62	0.02	0.19	0.10
NVT-H2-27	Nevinstown	Leaves	-0.25	0.02	0.05	0.05
NVT-H3-4	Nevinstown	Leaves	-0.25	0.02	0.37	0.09
NVT-H4-2	Nevinstown	Leaves	-0.23	0.02	0.22	0.03
NVT-H4-3	Nevinstown	Leaves	-0.44	0.02	0.40	0.02
NVT-H4-9	Nevinstown	Leaves	-0.12	0.02	0.20	0.09
CS1-H1-2	Control site	Leaves	0.15	0.02	0.66	0.01
CS1-H1-5	Control site	Leaves	0.48	0.02	0.49	0.05
CS2-W1-6	Control site	Leaves	0.35	0.03	0.49	0.03
PMT-5	Nevinstown	Tree rings	0.09	0.07	0.20	0.18
DMT-5	Nevinstown	Tree rings	-0.11	0.08	0.17	0.04
PMTC-3	Control site	Tree rings	-0.08	0.06	0.05	0.04
DMTC-3	Control site	Tree rings	0.09	0.05	-0.04	0.05
MH-7	Nevinstown	Soil	0.19	0.02	0.17	0.12
MH-8	Nevinstown	Soil	0.34	0.02	0.19	0.07
MH-13	Nevinstown	Soil	0.13	0.02	0.04	0.14
MH-15	Nevinstown	Soil	0.22	0.02	0.11	0.03
MH-19	Nevinstown	Soil	0.18	0.02	0.10	0.01
MH-29	Nevinstown	Soil	0.14	0.02	0.08	0.16
T-5	Nevinstown	Soil	0.19	0.02	0.10	0.05
TC-1	Control site	Soil	0.29	0.02	0.06	0.01
TC-3	Control site	Soil	0.37	0.02	0.09	0.05

Reference

Material:

METRANAL	Analytica	Soil	0.07	0.02	0.26	0.07
BCR-2	NIST SRM	Basalt	0.27	0.02	0.25	0.06
LGC7162	LGC Lab	Strawberry	0.17	0.03	-0.03	0.07

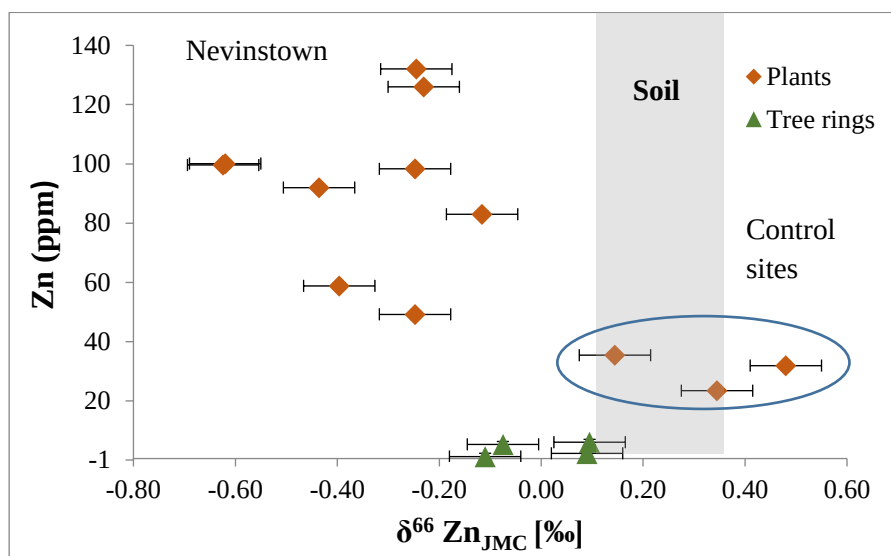


Figure 43. Isotopic Zn composition in hawthorn leaves (N=12) and oak tree rings (N=4) in relation to Zn concentration. The soil isotopic range is highlighted (N=9). Zinc isotopic ratios and Zn concentrations are reported with sampling precision. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol. Note samples with higher Zn concentration illustrated lighter $\delta^{66}\text{Zn}$. Samples marked within the blue circle represent control sites.

Furthermore, hawthorn samples with the highest enrichment factor reveal slightly lighter isotope $\delta^{66}\text{Zn}$ ratios ranging from $-0.23 \pm 0.07\text{‰}$ to $0.44 \pm 0.07\text{‰}$. A positive Pearson correlation (N=9, Fig. 44) is exhibited between $\delta^{66}\text{Zn}$ and Mg ($r=0.74$), Mn ($r=0.62$); a moderate correlation with Fe ($r=0.56$), Ni ($r=0.53$) and negative moderate correlation with S ($r=-0.51$) at Nevinstown. Isotopic composition of $\delta^{68}\text{Zn}$ confirmed same correlation patterns as $\delta^{66}\text{Zn}$ for Mg, Mn, Fe and Ni.

Tree ring samples show similar ranges for both sites (Fig. 43) with minor differences considering Zn isotopic composition. Background values of $\delta^{66}\text{Zn}$ ratios are between $-0.08 \pm 0.07\text{‰}$ and $+0.09 \pm 0.07\text{‰}$ compared to the Nevinstown area where $\delta^{66}\text{Zn}$ in tree rings is $+0.09 \pm 0.07\text{‰}$ to $-0.11 \pm 0.07\text{‰}$. All significant figures imply 7% MAD precision.

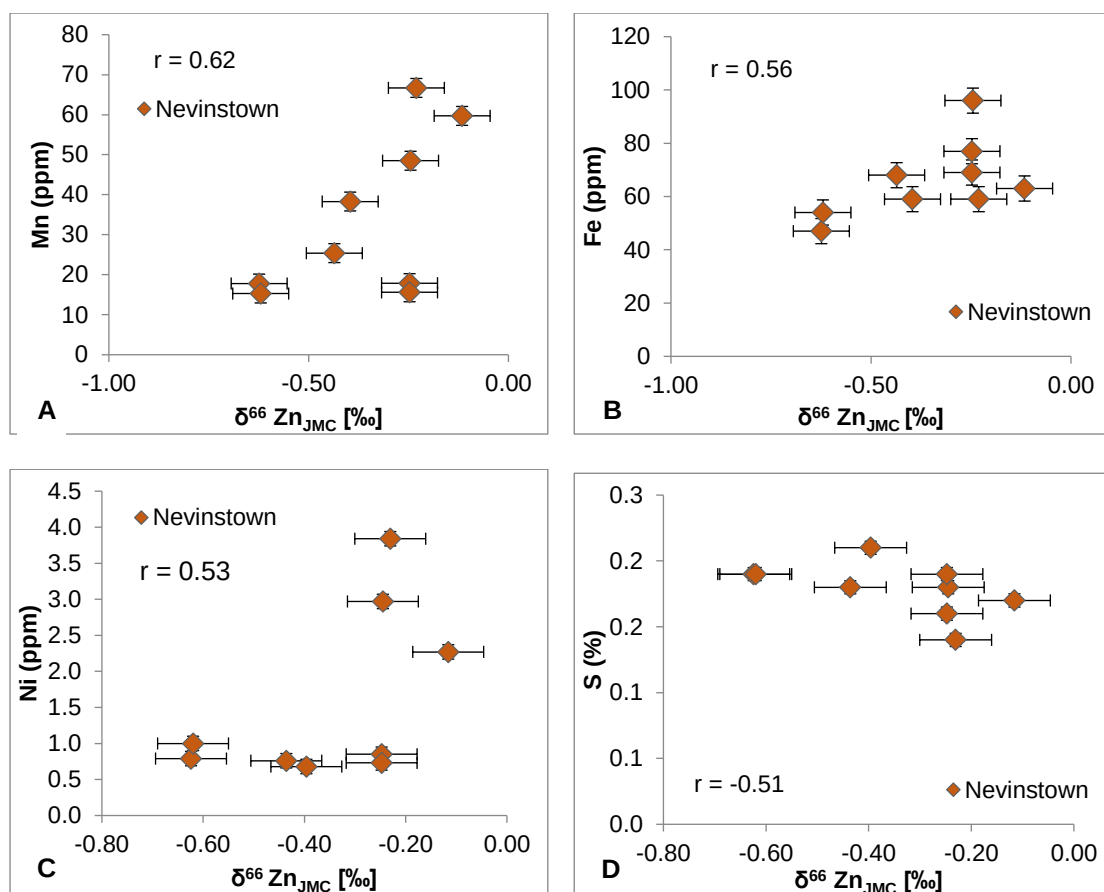


Figure 44. Scattered X/Y plot showing Pearson's correlation for $\delta^{66}\text{Zn}_{\text{JMC}}$ and: **A)** Mn; **B)** Fe; **C)** Ni and **D)** S in hawthorn leaves from Nevinstown (N=9). Errors are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Generally, soil samples display heavy zinc isotopic composition on both sites (Fig. 43). However, the Nevinstown area exhibits slightly lighter $\delta^{66}\text{Zn}$ isotopes (mean= $+0.18 \pm 0.08$ ‰) with the exception of a sample MH-8 with $\delta^{66}\text{Zn} = +0.34 \pm 0.08$ ‰ (Zn= 3140 ± 4.24 ppm, $\text{EF}_{\text{Zn}}=24$). Control samples showed heavier isotope $\delta^{66}\text{Zn}$ ratios for two samples ranging from $+0.29 \pm 0.08$ ‰ to $+0.37 \pm 0.08$ ‰. A strong positive correlation (N=7, Fig. 45) is observed between $\delta^{66}\text{Zn}$ and Hg ($r=0.79$), Mo ($r=0.74$); positive correlation with Zn ($r=0.61$), LOI ($r=0.60$) and moderate correlation with Fe ($r=0.51$), S ($r=0.54$). The isotopic composition of $\delta^{68}\text{Zn}$ confirmed similar correlation patterns except for Zn and Fe concentration. All significant figures imply 8% MAD precision.

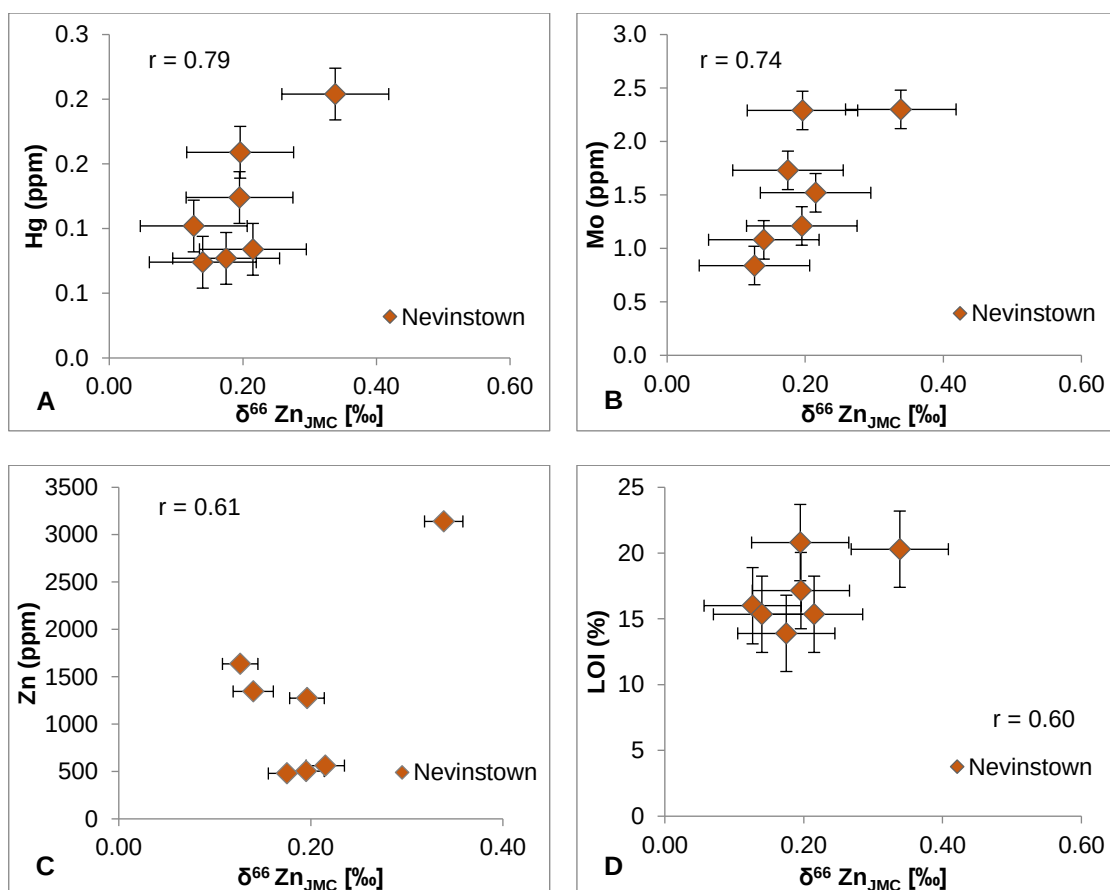


Figure 45. Scattered X/Y plot showing Pearson's correlation for $\delta^{66}\text{Zn}_{\text{JMC}}$ and: **A)** Hg; **B)** Mo; **C)** Zn and **D)** LOI in soils from Nevinstown (N=7). Errors are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Gagnevin et al. (2012) reported Zn isotopic composition in Navan sphalerites which are formed within stratigraphically lower lenses and the largest ore lenses situated in the north-east of the Navan deposit (Tab. 27). Mean values of Zn signatures in sphalerites were $-0.09 \pm 0.03\text{‰}$; ranging between $-0.32 \pm 0.09\text{‰}$ and $+0.23 \pm 0.07\text{‰}$. Also, Zn isotopes were measured in the basement rocks which are drilled beneath the Navan orebody on the foot-wall of the B-fault. Mean Zn isotopic composition in the Navan basement rocks exhibited $+0.11 \pm 0.07\text{‰}$ while ranging from $-0.02 \pm 0.07\text{‰}$ to $0.23 \pm 0.07\text{‰}$.

Table 27. Zn isotopic composition of sphalerites and basement rocks adopted from Gagnevin et al. (2012).
This data was used to construct an ore-soil-plant model discussed in Chapter 7.

Sample name	Mineral phase	$\delta^{66}\text{Zn}$	SD
D1 (21463B)	sphalerite	-0.01	0.04
	sphalerite	0.06	0.07
	sphalerite	0.01	0.00
	sphalerite	-0.12	0.08
	sphalerite	-0.07	0.05
	sphalerite	-0.27	0.1
D2 (21642E)	sphalerite	0.14	0.07
	sphalerite	0.23	0.07
	sphalerite	0.2	0.00
D3 (21642C)	sphalerite	-0.26	0.02
	sphalerite	-0.27	0.00
	sphalerite	-0.32	0.09
	sphalerite	-0.26	0.01
D4 (21644A)	sphalerite	-0.17	0.04
	sphalerite	-0.26	0.01
	sphalerite	-0.25	0.01
	sphalerite	-0.26	0.00
	sphalerite	-0.22	0.02
	sphalerite	-0.23	0.00
D5 (NO1663-NV3)	sphalerite	0.15	0.01
	sphalerite	0.20	0.00
U9555-1	basement rock	0.21	0.07
U9555-2	basement rock	0.12	0.07
U9555-3	basement rock	-0.02	0.07
U9555-4	basement rock	0.12	0.07
U9555-5	basement rock	0.23	0.07
U9555-6	basement rock	0.00	0.07

Cu isotopes

The composition of Cu isotopes in hawthorn leaves reveals a positive trend in all samples with a positive weak correlation (Fig. 46) between $\delta^{65}\text{Cu}$ and Cu ($r=0.63$), and a negative weak correlation with As ($r=-0.66$) and Pb ($r=-0.57$) (Fig. 44). In addition, the Nevinstown area exhibits lighter Cu isotopes ($\delta^{65}\text{Cu}_{\text{mean}}=+0.23\pm0.10\text{‰}$) when compared to the control sites ($\delta^{65}\text{Cu}_{\text{mean}}=+0.55\pm0.10\text{‰}$) which confirms the Zn isotopic signature pattern. The heaviest measured Cu ratio above the orebody is $+0.40\pm0.10\text{‰}$ which belongs to the sample NVT-H4-3 (Cu=13 $\pm$ 0.26 ppm, EF_{Cu}=59). Moreover, this sample has the highest Cu concentration which is confirmed with the enrichment factor (Fig. 46). All significant figures imply 13% MAD precision.

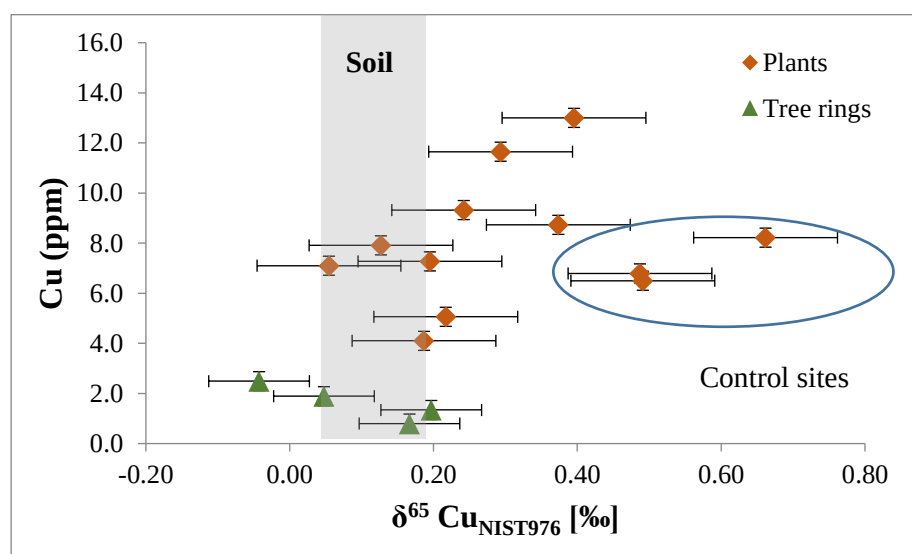


Figure 46. Isotopic Cu composition in hawthorn leaves (N=12) and oak tree rings (N=4) in relation to Cu concentration. Soil isotopic range is highlighted (N=9). Copper isotopic ratios and Cu concentrations are reported with sampling precision. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol. Note samples with higher Cu concentration illustrated heavier $\delta^{65}\text{Cu}$. Samples marked within blue circle represent control sites.

In contrast, tree ring isotopic composition displayed lighter $\delta^{65}\text{Cu}$ in the background area ranging from $-0.04\pm 0.10\text{‰}$ to $+0.05\pm 0.10\text{‰}$ while the deposit area represents slightly heavier $\delta^{65}\text{Cu}$ from $+0.17\pm 0.10\text{‰}$ to $0.20\pm 0.10\text{‰}$ (Fig. 46). All significant figures imply 13% MAD precision.

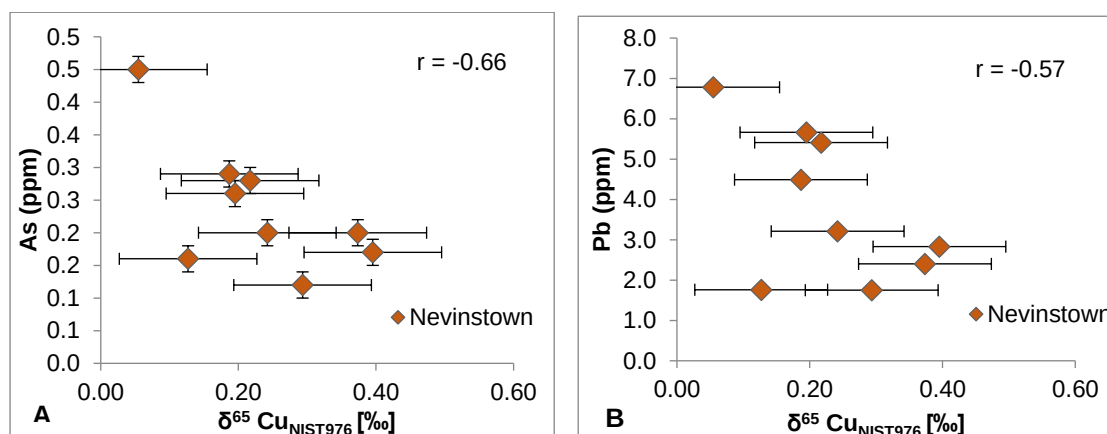


Figure 47. Scattered X/Y plot showing Pearson's correlation for $\delta^{65}\text{Cu}_{\text{NIST976}}$ and: **A)** As and **B)** Pb in hawthorn leaves from Nevinstown (N=9). Errors are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Soils at Nevinstown show a positive trend of heavier Cu isotopes ($\delta^{65}\text{Cu}$ mean= $+0.11\text{‰}$, see Fig. 46) which is a different pattern compared to the Zn isotopic composition. Also, the same observation is made for the control sites exhibiting lighter $\delta^{65}\text{Cu}$ from $+0.06\pm 0.07\text{‰}$ to $+0.09\pm 0.07\text{‰}$. A Pearson's factor (N=7, Fig. 48) displayed very strong correlation in $\delta^{65}\text{Cu}$ with Fe ($r=0.90$), Hg ($r=0.80$), Mn ($r=0.79$), Mo ($r=0.96$). All significant figures imply 9% MAD precision.

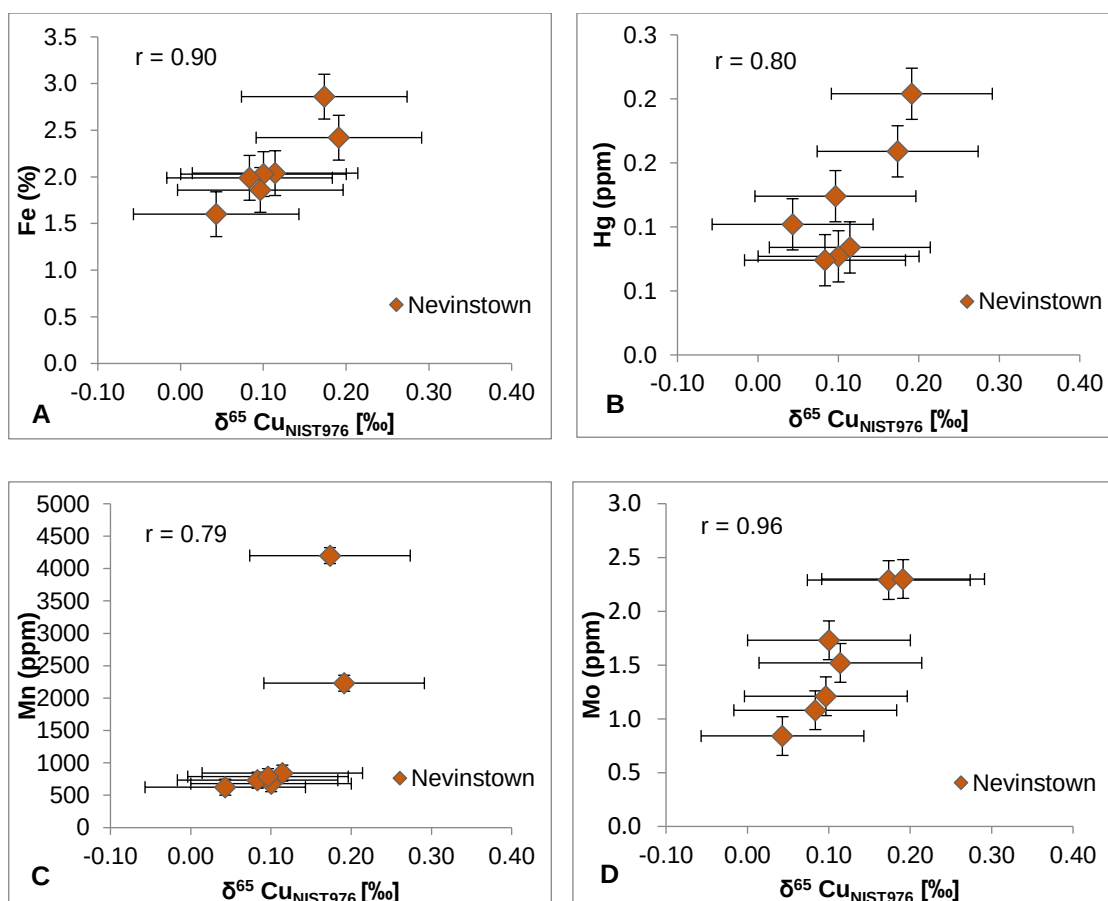


Figure 48. Scattered X/Y plot showing Pearson's correlation between $\delta^{65}\text{Cu}_{\text{NIST976}}$ and: **A)** Fe; **B)** Hg; **C)** Mn and **D)** Pb in soils from Nevinstown (N=9). Errors are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

7 Discussion

The results presented in this orientation study provide a general overview on the biogeochemistry of the Irish Type (Zn-Pb) deposits in temperate and humid European climates. Background levels of metal concentration in deciduous plants and soils illustrate normal ranges one might expect in Ireland. Thus, plant and soil geochemistry is compared to published studies in Mediterranean, boreal and dry temperate European climate, highlighting similarities and/or differences concerning metal distribution in the same plant species. A case study Laver offers another insight into biogeochemistry around a Cu-porphyry deposit in Sweden and is discussed in a greater detail in Appendix B.

Data interpretation is divided into two main sections. The first main section deals with spatial and temporal vectoring using results for different sites (spatial) and for interpretation of element migration through time (temporal) in Ireland. Firstly, the vectoring section relates to potential sources of contamination which displays the possibility of atmospheric and fertiliser impact on plants and soil. In addition, principal component and cluster analysis show trace element similarities between plant species and sources of potential groups of elements in plants. Secondly, enrichment factors are used to show a degree of enrichment while bioaccumulation coefficients demonstrate the degree of metal uptake between soil and plant. A second main section discusses biogeochemical cycling of Cu and Zn isotopes. An ore-soil-plant model for large natural systems illustrates element migration and uptake in different materials (ore, soil and leaves) on a macro-scale and for a comparison of two natural systems (mineralised and unmineralised). In addition, Cu and Zn isotopes are used as a tool to confirm and fingerprint patterns in each system. A revised biogeochemical model for Irish Type (Zn-

Pb) deposits is introduced at the end of this chapter as a summarized exploration protocol for future biogeochemical prospecting.

Based on the trace element analysis Zn concentrations are elevated in every plant species collected at Nevinstown when compared to the control areas (see Chapter 6, Fig. 25). In general, Pb concentrations are nine times higher on average, especially in oak (up to 15 times higher) when compared to background values. Cadmium and As are all moderately enriched, whereas Mn and Cu are mainly lower at Nevinstown. Iron displays no significant variations among plant species at all investigated localities. Even though the majority of plant species exhibit Cu and Fe depletion while in comparison to the reported values it is still evident that elements mentioned above are reduced or similar in plants growing at Nevinstown against same species in the control areas. This can be a result of Zn enrichment in plants growing at Nevinstown. An excess of Zn can lead to a marked reduction in Fe (Ghasemi-Fasaei and Ronaghi, 2008). Furthermore, Fe reduces Cu absorption from soil solutions.

Zinc is very mobile during weathering processes and its dissolved components precipitate during reactions with carbonates; thus, in the presence of sulphur anions Zn is absorbed by minerals and organic matter (Kabata-Pendias, 2011). Nevinstown represents a sub-crop of sulphide body mainly surrounded by calcareous bedrock (Upper Dark Limestones). Ireland's humid and cold climate with abundant rainfall can increase chemical weathering. In these geological settings and environmental conditions large quantities of Zn can be transported from the orebody into soils which can explain high concentration in plants. Some of the plant species such as poplar showed toxic values of Zn in leaves which demonstrates that tolerant species may reduce the effect of excessive Zn concentrations by some form of metabolic adaptation (Dominguez et al. 2008).

Background levels of metal concentration in deciduous plants and soils

The biogeochemistry of plants has a strong impact on nutrient and pollutant cycling in nature. Plants reveal various tendencies in the ability to uptake both major and trace elements. Certain major elements such as Ca, K, Mg, P and S with accompanying Cu, Fe, Mn and Zn as trace elements are considered essential for the uptake processes (metabolic, adsorption, translocation) while elements such as As, Cd and Pb can be passively taken up in trace amounts (Dunn, 2007). Both, normal and toxic levels of metal concentrations have been reported by numerous authors (see Markert, 1992, Marschner, 1995, Andriano, 2001, Dunn, 2007, Kabata-Pendias, 2011, McLaughlin et al., 2011) providing a range for different plant materials such as wood, shoots and foliage. Metal uptake can differ among different plant species dependent on varying degrees of resistance (a barrier mechanism) to element (metal) uptake by roots and the form in which elements occur, as sulphides, chlorites and phosphates in the substrate (Kovalevsky, 1987, Kabata-Pendias, 2011). This research is mainly focused on plant foliage as a representative material and further interpretation will closely examine each of seven deciduous species separately due to different uptake mechanisms.

Main observation points indicate that plant species accumulated significantly more As, Cd, Pb and Zn at Nevinstown than in the control sites except poplar, which accumulated more Cd at the control sites. In addition to these metal distributions, Cu concentration did not show significant variations within blackberry and hawthorn leaves compared to the control sites. Iron and Mn are also invariant in ash leaves while oak leaves exhibited variations only for Fe concentration. In fact, the majority of analysed elements (see Appendix A, Tab. A-1) were significantly variable compared to control sites except for Mn and Fe. For the rest of the elements of interest and species, there were no major accumulations at Nevinstown.

Considering the fact that there are few studies within moderate/humid climates similar to Ireland, studies from Turkey, Finland, Poland, Croatia, Serbia, Italy and Spain are presented in the following in comparison to Ireland (Tab. 28). This is intended to give an estimate of what is expected within the different plant species and plant organs. A study of trace metal concentration in herbs from Turkey, including blackberry, reported slightly depleted and similar values in leaves only for Co (0.10 ppm) and Cu (6.61 ppm) (Derya, 2009). The results of Mn and Zn in blackberry leaves presented in this study show values of 205 ppm and 27.83 ppm, respectively (see Chapter 6, Tab. 18). These results are higher by an order of magnitude than those of the blackberry studies in Turkey. Research on increased heavy metal accumulation in forest berries in Finland reported significant concentrations for Cd (0.44 ppm), Mn (62 ppm) and Zn (37 ppm) in blackberry fruit higher than those observed in fruit at the control sites in Navan (Moilanen et al., 2006). A similar trend can be seen in hawthorn leaves collected at the Nevinstown with 25.15 ppm (Mn) and 31.39 ppm (Zn) while a study of white hawthorn in Croatia and Poland (Lozak et al., 2002; Zeiner et al., 2013) displayed much lower concentrations of Mn (11 ppm) and Zn (16.5 ppm) in leaves while values obtained for Cd, Co and Pb exhibited similar concentrations to those reported here.

In general, uptake of elements in sycamore and beech revealed either similar or significantly lower concentrations of trace metals in leaves at the control sites in Ireland. Due to the lack of data for sycamore leaves in the literature the results reported in leaves from other trees such as Norway maple were used for comparison. Norway maple and sycamore belong to the Maple family which makes them more botanically compatible than any other tree species.

Table 28. A summarizing table comparing studies from different locations with the control site (Ireland) in the terms of background levels of metals.

Plant species	Region	As (ppm)	Cd (ppm)	Co (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Reference
Ash	^a Ireland	n.d.	n.d.	n.d.	11.32	72	26.93	0.53	45.50	This study
	^a Turkey	n.d.	n.d.	n.d.	0.2	31	133.5	0.003	1.62	Aksoy et al. (2005)
Beech	^a Ireland	n.d.	0.20	n.d.	11.60	53.80	119.44	0.12	25.94	This study
	^a EU	n.d.	0.34	n.d.	12	550	133	16.3	69	EU-JRC-IRMM 2006
Blackberry	^a Ireland	n.d.	n.d.	0.04	7.95	63.67	205.47	n.d.	27.83	This study
	^a Turkey	n.d.	n.d.	0.10	6.61	165	54.6	n.d.	54.6	Derya (2009)
	^b Finland	n.d.	0.44	n.d.	4.42	n.d.	4.42	n.d.	37	Moilanen et al. (2006)
Hawthorn	^a Ireland	n.d.	0.18	0.14	n.d.	n.d.	25.15	1.26	31.39	This study
	^a Croatia	n.d.	0.13*	0.14**	n.d.	n.d.	11**	1.75*	16.5**	*Zeiner et al. (2013)
	^a Poland									**Lozak et al. (2002)
Oak	^a Ireland	0.02	0.03	n.d.	8.45	62.40	238.74	0.09	n.d.	This study
	^a Spain	0.20	0.01	n.d.	6.40	88.90	304.70	0.15	n.d.	Aboal et al. (2004)
Poplar	^a Ireland	0.08	6.92	n.d.	n.d.	73.14	88.97	n.d.	173.5	This study
	^a Spain	0.99	0.21	n.d.	n.d.	92.33	51	n.d.	81.6	Dominguez et al. (2008)
Sycamore	^a Ireland	0.04	0.12	0.04	9.84	77.33	137.53	0.43	41.38	This study
N. Maple	^a Serbia	0.15	0.09	0.34	7.94	285	116	2.22	44	Tomasevic et al. (2011)
Soil	^c Ireland	n.d.	n.d.	n.d.	n.d.	n.d.	377.33	0.43	103.2	This study
	^c Ireland	n.d.	n.d.	n.d.	n.d.	n.d.	500-800*	20-30*	47-63**	*Fay et al. (2007)
	^c EU									**Kabata-Pendias et al. (2011)

Note: data is reported for different material (a – leaves, b – fruit, c - soil); n.d. stands for not discussed in the metal background paragraph.

A methodological study (Tomasevic, et al., 2011) on Maple trees from Serbia in different parts of the city of Belgrade revealed similar concentrations of Cd, Cu, Mn and Zn while As (0.15 ppm), Co (0.34 ppm), Fe (285 ppm) and Pb (2.22 ppm) were enriched in comparison to a metal distribution of As (0.04 ppm), Co (0.04 ppm), Fe (77.33 ppm) and Pb (0.43 ppm) in sycamore leaves from this study. Reported metal distribution for beech trees published by the EU Research Centre IRMM in 2006 illustrated higher concentrations than reported in this study. Significant variations were noted for Fe (550 ppm), Pb (16.3 ppm) and Zn (69 ppm) with enrichment in leaf material for the same plant species collected in the control area.

Some of the trees such as oak and pine are often used as geochemical indicators of airborne pollution due to their ability to accumulate certain trace elements (Watmough et al., 2002, Klaminder et al., 2004). Two biomonitoring investigations in rural areas of NW Spain-Galicia (Aboal et al., 2004) and in a former mining area in Tuscany-Italy (Bargagli et al., 2003) reported similar Cd, Cu and Fe, or slightly increased concentrations of As, Mn and Pb in oak leaves except for Zn (17.82 ppm) in relation to background values for oak trees from this project suggesting that control areas around mining sites have similar metal distribution in oak trees (see Chapter 6, Tab. 22). Furthermore, ash could be used as a biomonitor of heavy metal pollution in temperate climates because of its wide geographical range and with ability to differentiate airborne and soil-borne trace elements. Aksoy et al. (2006) recorded trace element concentrations in several urban and rural sites across the Kayseri region in Turkey. The commonly known ash tree (*Fraxinus excelsior*) incorporated less Cu, Fe and Mn compared to ash from this study where ash leaves collected from the Navan control sites obtained values of 11.32 ppm, 72 ppm and 0.53 ppm, respectively. In addition, their study reports significant Mn enrichment reaching up to 488 ppm in ash leaves (Aksoy, et al., 2006). These observations are more

likely to indicate differences related to climatic (Mediterranean vs temperate cold climate) and geographic settings.

Poplars are considered to be an accumulator plant, which can absorb toxic levels of heavy metals such as Cd and Zn from soils and is widely used in phyto-management studies (Madejon et al., 2004, Van Nevel et al., 2011). Moreover, the background control area of the Navan deposit revealed significant concentrations of Cd (6.92 ppm), Mn (88.97 ppm), Ni (7.92 ppm) and Zn (173.50 ppm) in poplar leaves which were quite different to other plant species in this study (see Chapter 6, Tab. 23). A large-scale phytomanagement case study of trace element accumulations in woody plants of the Guadiamar Valley, SW Spain (Dominguez et al., 2008) obtained similar Cu concentrations with significant exceptions for As (0.99 ppm), Fe (251 ppm) and Pb (3.93 ppm) enrichments in poplar leaves compared to the Navan control sites. One significant figure implies 8% MAD precision while all other figures imply <5% MAD precision. This is an indication that the control sites seem to be devoid of any sulphide mineralisation influence.

Even though reported trace element concentrations for all deciduous plants examined in this study can be classified as sufficient or normal compared to the published values in mature leaf tissues generalised for various species by Kabata-Pendias (2011) it is still evident that metal content in plants can be species dependent (Remon et al., 2013).

In general, the element content may originate either from soil via uptake by roots and/or by atmospheric deposition of particles. Grey brown podzolic soils (a classification made by the National Soil Survey of Ireland, 1982) are an important factor in plant-soil interactions for geochemical interpretation. Trace element analysis of background soils from the Navan control sites revealed that the majority of elements levels analysed in this

study are in agreement with the soil geochemical data of Ireland published by Teagasac and the EPA (Fay et al., 2007) and with the reported abundance of various major and trace elements in podzols (Kabata-Pendias, 2011). Differences did occur for Cr and Mn (see Chapter 6, Tab. 24), which exhibit somewhat depleted values of 25.30 ppm and 377 ppm, respectively, compared to the geochemical data of Irish soils with ranges of 65-80 ppm (Cr) and 500-800 ppm (Mn). Furthermore, Pb was slightly enriched (48 ppm) in relation to the Irish soil database (20-30 ppm), also Zn concentrations of 103 ppm in the control area compared to a published zinc range of 47-63 ppm appears high (Kabata-Pendias, 2011) indicating naturally elevated Pb and Zn components in the Navan control soils. All significant figures imply <5% MAD precision.

Potential sources of contamination

As previously discussed, many plant species can be used as an indicator for airborne pollution (Watmough et al., 2002, Klaminder et al., 2004). Atmospheric deposition is considered to be an important source of trace element accumulation in plant leaves (Legind and Trapp 2010, McLaughlin et al., 2011, Gratani et al, 2018). It is also assumed that elements such as Al, Cu, Co, Cr, Cd, Fe and Zn can be a constituent of water-soluble particles adhered on leaves, but easily removed by washing procedure prior to chemical analysis (Baker and Jickells, 2006, Birmili et al., 2006).

The Zn-Pb sub-outcrop at Nevinstown is less than 1 km to northeast of mine infrastructure and the town of Navan is situated 5 km to the east. Potential contamination from atmospheric deposition could be caused by the nearby mining activity in the Navan area (the mining is all underground but concentrating plant and machinery brought to surface could conceivably cause wind-borne contamination, perhaps accentuated by the prevalent westerly winds. However, the high annual rainfall (≥ 1000 mm) in the region

would effectively reduce the potential for deposition of airborne particulate (Smyth, 2004). Air quality in Ireland is continuously monitored by the Environmental Protection Agency. Measured annual metal deposition in the Zone A (Rosemount, UCD) and in the Zone D (Shannon Estuary, Limerick and Valentia, Co. Kerry) is published in an air quality report (EPA, 2015). Even though the closest zone to Navan is classified as zone A it does not illustrate local dust composition. Actually, together with other zones, they represent the annual deposition by air in Ireland. For this purpose, the concentration of two elements of interest namely As and Pb related to the Navan deposit, was investigated to assess the effect of dust interference on the total concentration in leaf material (Fig. 49).

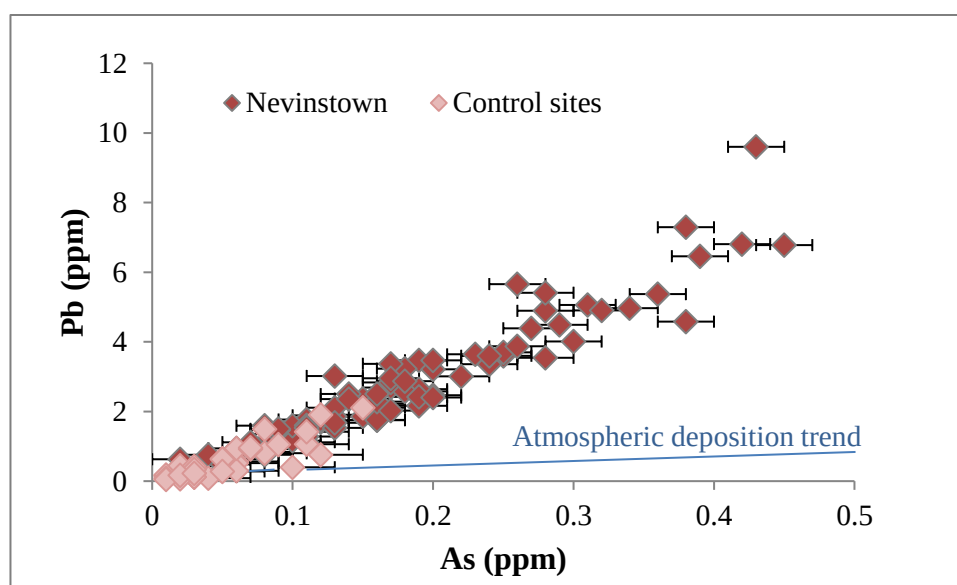


Figure 49. XY plot of As and Pb concentration in all plant species (N=83) collected from Nevinstown and control sites areas in relation to atmospheric deposition of As and Pb in particulate matter (PM₁₀) from several stations across Ireland. The blue line shows the expected trend of airborne contaminant deposition and the slope equation is based on two measurements from Zone A and Zone D. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol and for atmospheric deposition.

There is no clear relationship which suggests that dust deposition contributed to the overall As and Pb accumulation in the leaf material based on the atmospheric deposition

trend reported in Zone A and D. In addition, the annual mean concentrations measured at all stations were all below the respective target or limit values (see Appendix D, Tab. D-3). Still, it is important to consider the possibility that the local atmospheric deposition at Navan would be much higher in the terms of metal concentration than the national EPA average. Therefore, this represents a challenge in mitigating dust contamination from the plant geochemistry analysis.

A strong positive correlation between As:Pb ($r=0.91$, $N=83$) in leaf material (Fig. 49) suggests that trace elements are being sourced from the surficial soils above the Navan orebody since the linear relationship between soils and plants (Multiple $R=0.60$) displays a similar correlation pattern. All significant figures imply 7% MAD precision. Moreover, the concentration of many trace elements in atmospheric particulate is generally very low which makes it difficult to compare with soil values reported in this study. Therefore, main focus was on Zn relation to typical dust constituents such as Al and Zr (Fitzpatrick and Chittleborough, 2002) in Irish soils. Figure 50 shows weak Pearson's correlation coefficient ($N=39$) between Zn and Zr ($r=0.48$) and no correlation between Al and Zr ($r=0.16$). Furthermore, soils at Nevinstown are enriched in As, Cd, Pb and Zn (up to 3000 ppm); and any atmospheric deposition trend would have negligible effect on the overall chemical signature of plant material.

The second potential source of contamination could arise from seasonal fertiliser application. The major constituents of mineral fertiliser used for agricultural soils are N, K, P and S. Phosphate-based fertiliser has a strong interaction with several trace elements in particular Cu, Ni, Pb, Zn and Cd (Jones et al., 1987a, McGrath and Fleming, 2007).

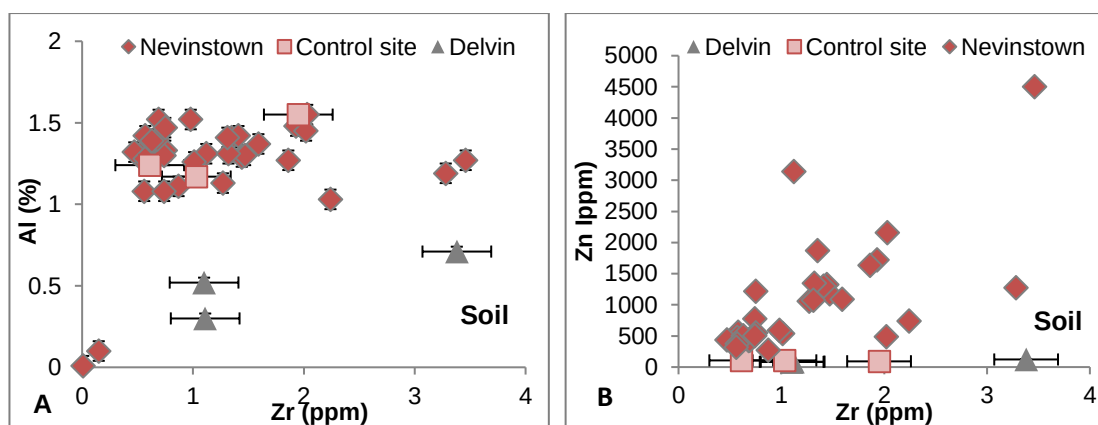


Figure 50. The interactions of Al, Zn and Zr represent precursors of dust contamination in Irish soils (N=39) collected above the orebody, control sites and in the Irish Midlands (around Delvin). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Usage of Phosphate-fertilisers can increase leaching making heavy metals more bioavailable in agricultural soils-dependant on a suitable surface soil pH (Wolf et al., 2018). Agricultural sites will contain more fertiliser input which will make metal uptake easier resulting in more bioavailable metal in farming regions. A study from Belgium investigated inputs of trace elements in agricultural soils via phosphate fertilizers in European countries (Nziguheba et al., 2007). Values of Cd and Pb in fertilizers obtained through their research were higher 7.4 ppm and 2.9 ppm than the majority of plant species from the Nevinstown, except for three samples of poplar leaves collected at the control sites (Fig. 51); no recent agricultural work has occurred at these research localities implying minimal fertiliser impact on investigated soils and plant metal concentrations.

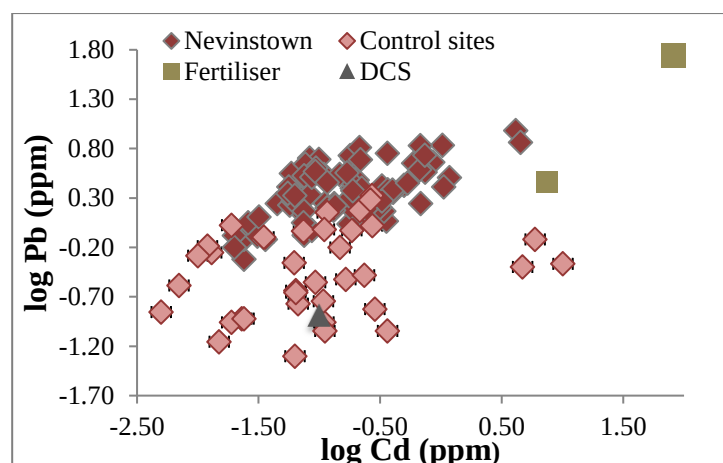


Figure 51. XY plot of log Cd and log Pb concentration in all plant species (N=83, leaf material) collected from both areas in relation to mineral fertiliser from 12 European countries (including Ireland) and dairy cattle slurry (DCS) collected in county Wexford, Ireland. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol and for DCS and fertilisers.

In a recent study (Peyton et al., 2016), organic fertiliser such as dairy cattle slurry (DCS) were treated and applied to an Irish grassland soil in order to estimate nutrient and metal loss caused by surface runoff. Trace element analysis of Cd and Pb in DCS displayed similar or quite depleted values of 0.1 ppm and 0.13 ppm, respectively. Considering that the studied field areas are classified as pastureland one might expect an effect of dairy cattle slurry on surface soils to be significant. However, the impact of Phosphorous-based fertilisers can be considered minimal in this study as the comparison of P with Pb and Zn does not show any pattern with the same elements in soils (Fig. 52).

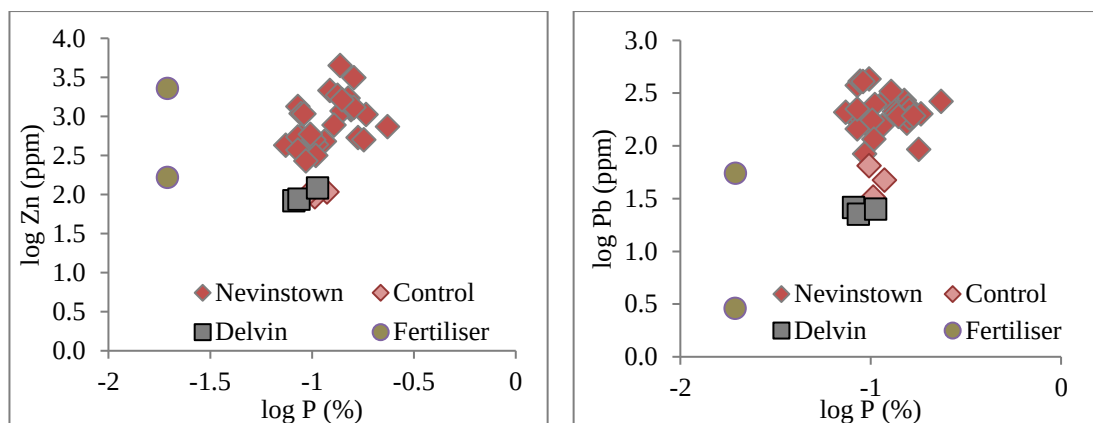


Figure 52. XY plot of log P, log Pb and log Zn concentration in soils collected from all investigated sites (N=39) and mean concentrations of mineral fertilisers from 12 European countries (including Ireland). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol and for fertilisers.

7.1 Biogeochemical spatial and temporal vectoring around Irish Zn-Pb deposit

Leaves of each plant species from the same trees were collected identically in the spring and autumn seasons of 2015. For the purpose of this study, the major difference between these two types of leaves can be considered the date when they were collected (i.e. their age). Otherwise, first leaves started to develop from buds approximately in the same time in spring.

The main purpose of this experiment was to observe how seasonal variation growth status have an effect on metal uptake. In addition, in the autumn, soon before the leaves fall, some elements within the leaves are recovered and stored in woody material (twigs and branches) over the winter months before they remobilise for the next year of growth meaning they would be metal depleted in the leaf material because metals are being more transported to storage than to the most aerial part of the trees (Dunn, 2007). For an additional information on element behaviour in plants see Chapter 4.

In summary, when comparing trace-element concentrations of Zn from autumn and spring sampling campaigns at Nevinstown, it was found that hawthorn, blackberry and sycamore had higher concentrations of metals during the autumn season at Nevinstown while oak showed the opposite trend. Beech and ash did not exhibit seasonal differences between the sites. It is possible that during those seasons Zn is more soluble and mobile within soils. Therefore, the influence of seasonal variation initiates stronger metal uptake for hawthorn, blackberry and sycamore growing in surficial soils with a Zn anomaly.

7.1.1 Plant – soil correlation

Observing the plant – soil system gives more insight in what degree a soil is influencing the plant and which element in plants reflect the signature from surficial soils. In the Nevinstown area, soils overlie Upper Dark Limestones therefore metal concentrations in plants and soils are normalised to Ca minimising the influence of the carbonate signature on the overall metal component. The comparison between the concentration of trace elements in plant leaves and surface soils revealed positive correlations for the several elements of interest (16 out of the 42 comparisons, Tab. 29). Ash and blackberry exhibited weak plant-soil correlation.

Table 29 shows strong (Multiple R > 0.80) plant-soil correlation in trace elements for hawthorn trees rather than for taller trees such as ash, beech and sycamore. Smaller plant species such as hawthorn (Fig. 53A) tend to develop smaller root systems which will reflect a more localised metal distribution soil. Considering the fact that the majority of shrubby species are growing above or in close proximity to an orebody with soil Pb and Zn anomaly (220 ± 0.85 ppm; 1053 ± 5.66 ppm, on average) they likely formed a mechanism which regulates and even restricts uptake of certain trace elements (Dunn, 2007, Dominguez et al., 2008).

Table 29. Regression correlation coefficients (Multiple R) between trace elements in surficial soils and plants from Nevinstown collected in spring. Only, the closest soil samples to an investigated tree species were taken into account; therefore, the number of each plant species correspond to the same number of soils. Correlation coefficients in oak trees are not considered due to small sample size (N=3). For the rest of correlations, significant levels are controlled at 5% ($p < 0.05$). Three significant figures imply <9% MAD precision and five significant figures implies <5% MAD precision.

Species	Samples	As/Ca	Cd/Ca	Cu/Ca	Fe/Ca	Mn/Ca	Pb/Ca	Zn/Ca
Ash	N = 18	0.05	0.24	0.10	0.07	0.19	0.23	0.07
Beech	N = 9	0.03	0.49*	0.79	0.00	0.23	0.10	0.16
Blackberry	N = 17	0.21	0.13	0.43	0.06	0.23	0.29	0.11
Hawthorn	N = 23	0.29	0.89	0.84	0.86	0.86	0.82	0.92
Oak	N = 3	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Poplar	N = 4	0.42	0.59	0.56*	0.76	0.99	0.50*	0.02
Sycamore	N = 11	0.49*	0.00	0.31	0.48	0.06	0.41	0.72

(*) weak to moderate plant-soil correlation

Plant-soil relationship (Fig. 53B, C and D) between Cd:Zn (Multiple R=0.96), As:Pb (Multiple R=0.60) and As:Cd (Multiple R=0.78) could be a reflection of element signatures typical for Zn-Pb mineralisation. Those elements are known to be major and trace elements in sphalerite (Cook et al. 2009), galena (George et al. 2015) and pyrite (Large et al. 2017,), and would confirm the association with sulphide minerals.

Values of As and Pb show a positive correlation in sycamore and ash even though the Pb concentrations were depleted, indicating similar processes (restriction on uptake mechanism) took place in those plant species. Metal distribution in hawthorn revealed significant uptake of all elements of interest in comparison to other investigated plant species. Furthermore, blackberry and sycamore exhibit positive correlation between As, Cd, Pb and Zn implying similar correlation patterns as those seen in soils suggesting that

the element uptake process is related to Zn-Pb mineralisation at Nevinstown (see Chapter 6, Fig. 27 and 28).

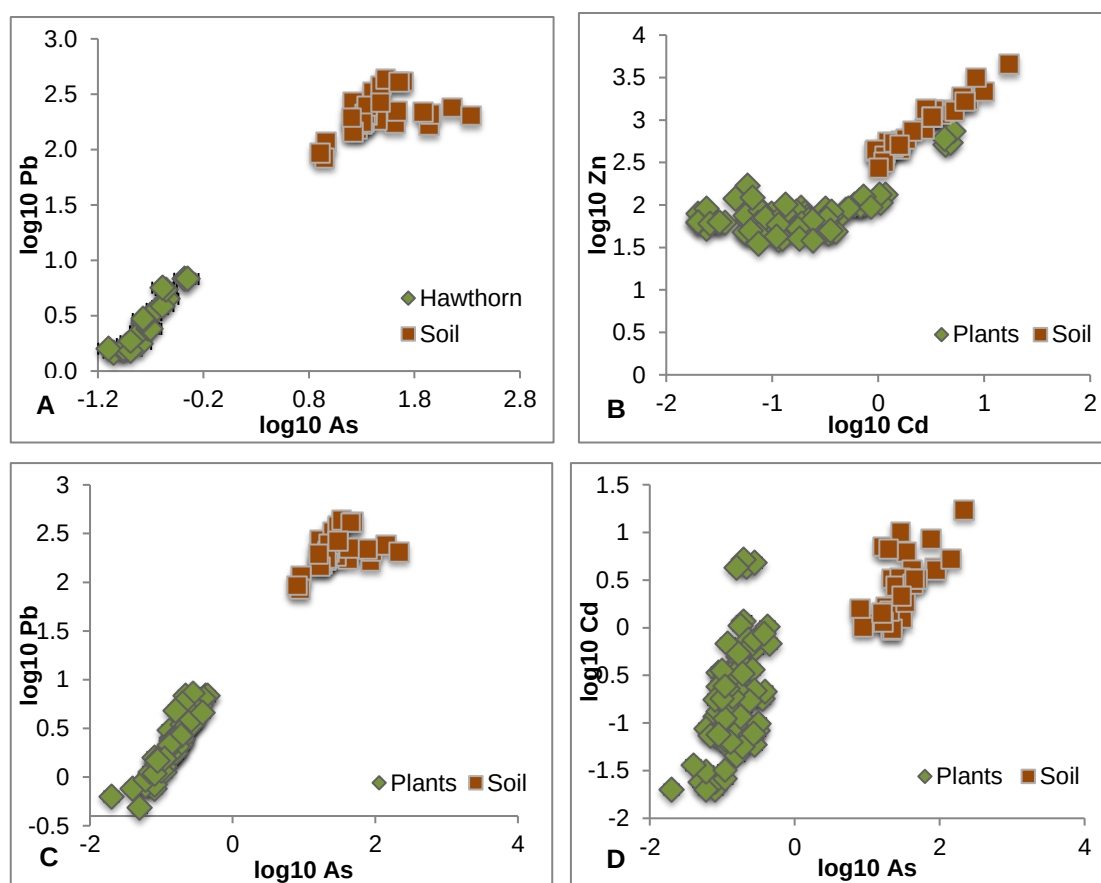


Figure 53. Hawthorn-soil correlation coefficient (A) for As:Pb (N=56) and plant-soil correlation coefficient (B, C and D) for Cd:Zn, As:Pb and As:Cd (N=119) which includes all plant species collected at Nevinstown. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

7.1.2 Temporal vectoring around the Navan deposit

Trace element analysis was performed on the bulk wood (tree cores) of oak and beech trees. Furthermore, oak tree rings were extracted as 10-year sections. The first oak tree-ring section is equivalent to a period before mining (from 1950 to 1960) and a second 10-year tree-ring section corresponds to a period during mining (from 2000 to 2010).

In general, dendrochemistry showed relatively low concentrations of As, Cd, Cu and Pb in beech and oak bulk wood. One significant figure imply 8% MAD precision while five significant figures imply <5% MAD precision. Iron revealed significantly higher accumulation in oak tree rings (155 ± 2.99 ppm, on average) and in bulk wood (79 ± 2.99 ppm, on average) compared to their leafy material. In contrast, oak and beech leaves exhibited higher Fe contents (see Chapter 6, Tab. 21 and 22). One of the possible explanations for high Fe in wood could be that a chemical reaction occurred between tannins in the sapwood (vascular tissue) and free Fe from the increment borer (tool for extracting tree core; see Chapter 2 Methodology). This is possibly due to a strong sap circulation in the sapwood caused by a very humid season in August, 2016. The reaction resulted in development of a black fluid or “Indian Ink” which is a suspended black pigment in sap with a specific vinegar scent (Brown 2016, pers. comm.). Some of the ink could be absorbed by the investigated bulk wood and tree rings; however, it is noted that trees at the control sites experienced less black fluid forming than at Nevinstown. Sampled trees around Navan were mostly formed in woodland while in the area where the orebody sub-crops mainly within hedgerows and closer to a river bank which might affected on stronger sap circulation (see Chapter 5, Fig. 15). Such metal accumulation is related to several processes such as root uptake, selective mechanisms and metal fixation (Beramendi-Orosco et al., 2013). Oak and beech trees have significant differences in their root systems which may explain a lower ability for oaks to accumulate Mn and Zn.

Deciduous tree roots usually develop down to depths of 0.7 m with decreasing density while occupying more than 100 m³ of root zone by tree (Polomski and Kuhn, 1998, Algreen, et al., 2012). In some cases, the root depth for a deciduous forest can be up to 3.9 m (Canadell, 1996). Beech has a slightly more laterally developed root system with finer roots which increase its overall biomass (Leuschner et al., 2001, Crow, 2005). For example, if they are formed in mixed woodland, Leuschner et al. (2001) suggest that the root systems would compete across various tree species. Thus, oaks shallower less spread out root system compared to beech laterally finer rooting system.

Furthermore, the amount of metal accumulation in vegetation follows a bioaccumulation sequence from root to→ bark to→ tree core to→ leaves (see Holm et al., 2011), which explains why elements of interest such as Cd, Cu, Mn, Pb and Zn were enriched in leaves rather than in the bulk wood collected at Nevinstown. Manganese concentrations correspond to those published for English oak in a study from NW England which reported values of 5.3 ppm Mn for the period from 1950 to – 1960 (Watmough et al., 2002). Moreover, both studies confirm a significant Mn increase during more recent decades. In contrast, some authors have reported higher levels of Mn in older annual rings which radially decrease (Butkus et al. 2002, Baltrenaite and Butkus 2004).

Lead values in oak tree rings above the Navan orebody were lower (0.15 ppm Pb) than values reported by Watmough et al., 2002 (2.4 ppm Pb, on average). However, for the period of 1950-1960 oak tree rings display higher Pb concentrations compared to growth periods coinciding with mining from 2000-2010 at both sites (Fig. 54). In fact, Pb was reduced by almost one half in period between 2000-2010; this can be explained by the phasing out of tetraethyl lead (TEL), an engine fuel additive used in road vehicle fuels before the 2000s and has had the effect of lower Pb emissions into the atmosphere.

A number of studies (Watmough et al., 1999 and 2002) reported similar Pb trend in tree rings caused by non-lead fuel; still less than 20% of the total Pb in wood actually derived from the gasoline emission in the UK (Watmough et al., 2002). Meaning that 80% of total Pb in wood could not be connected to the Pb in fuel in the UK. In fact, ring diffuse porous trees such as beech, oak and sycamore accumulate less Pb in the outer rings which would also explain lower concentrations in the recent years (Hagemeyer, 1995). This can indicate that the wood structure controls Pb uptake.

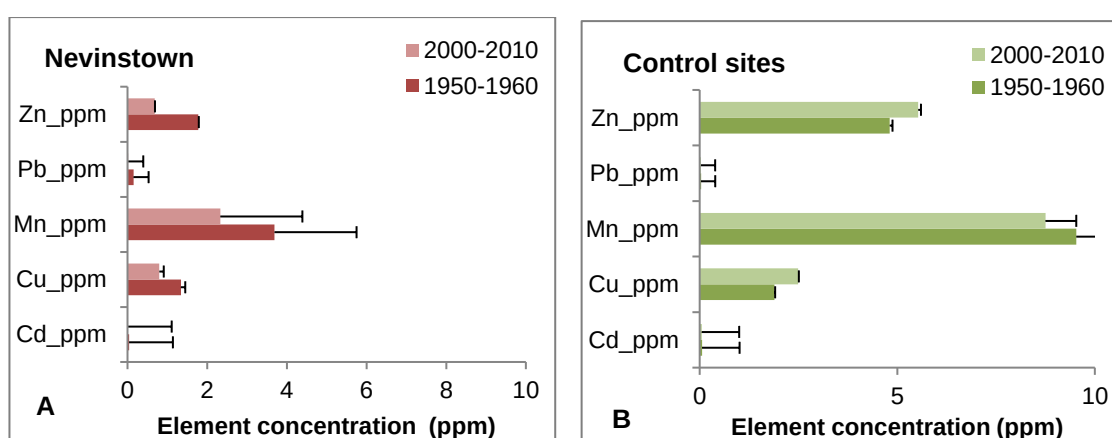


Figure 54. Trace element concentration in oak tree rings extracted at **A** Nevinstown (N=2 tree cores) and **B** control sites (N=2 tree cores). Periods analysed were prior mining (1950-1960) and during mining (2000-2010). Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Tree-rings analysed for Nevinstown display increased accumulations of Zn between 1950 and -1960. However, during the period of 2000-2010, Zn in tree-rings increasing in the control area. A similar observation was reported in a forestry study where Zn concentrations were found to radially increase towards younger tree rings (Larsson and Helmisaari, 1998). One of the major immobilizing factors for Zn is Fe/Mn. In general, Fe concentrations are much higher at the control sites in both periods when compared to Nevinstown; also, Fe accumulation is much higher during recent years. In fact, Fe/Mn ratios are at least ten times higher than the reported range of Fe/Mn=1.5-2.5 which is

considered adequate for plant growth (Wislocka et al., 2006, Kabata-Pendias, 2011). In addition, soils collected at control sites were mildly acidic (pH=5.6) which could induce higher Zn mobility rather than in comparison to soils directly above the orebody. The lower pH around the sub-crop could be a result of sulphide weathering. The H^+ ions are being released and migrated to the surrounding environment reducing the pH. Therefore, Zn alone is not necessarily associated with the sulphide mineralisation and has to be taken with caution. Hence, it cannot be used as mineral exploration indicator alone. A similar pattern can be seen for Cu which is also influenced by Fe and Mn interactions ($Cu/Fe:Mn/Fe=-0.65$, Pearson's r); meaning these elements are mobile within soil under acidic conditions and free to be taken up by plants.

7.1.3 Principal Component and Cluster Analysis

Principal Component Analysis (PCA) was used to provide a non-biased statistical overview of the biogeochemical dataset generated through this study and to further investigate trace-element variability in plant species data (Fig. 55). PCA was carried out using PAST Statistical software and using protocol detailed in Dominguez et al. (2008). Variation patterns in plants collected from Nevinstown ($PCA_{NEVINSTOWN}$ Component 1) were compared with variation patterns in the chemical composition of plants growing at the control sites ($PCA_{CONTROL}$ Component 1) shown in Table 22. $PCA_{NEVINSTOWN}$ Component 1 explained 41% of the variance, and was determined by the differential loading of three elements: As, Cd and Pb, while Component 2 showed a lesser degree of loading from Fe with a negative contribution of Cu. The second $PCA_{CONTROL}$ had a slightly stronger significance (49% of variance) in Component 1, which was associated

with variation in Mn (0.19) and Zn (0.88) while Component 2 was determined by the contributions of Cd (0.78), Pb (0.14) and Zn (0.24).

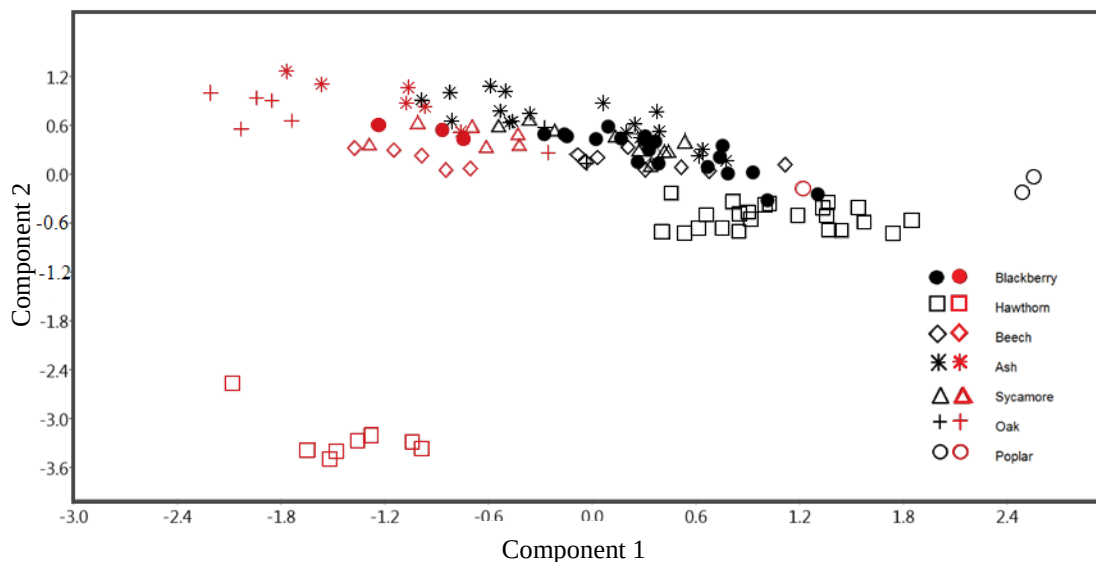


Figure 55. Principal Component Analysis (PCA) of trace element concentrations in the leaves of the studied tree species. Component loadings for each trace element are shown in **Table 30**. Red symbols represent samples from control areas and Nevinstown samples are indicated with black symbols.

Despite the higher accumulation of some trace elements (e.g. As, Cd, Pb and Zn) in the leaves of some tree species, in comparison to the control sites, the concentrations were within the normal ranges for higher plants (as reported by Kabata-Pendias, 2011). A notable exception was poplar sampled exclusively above the sub-cropping orebody, which had foliar Cd up to 7 ± 0.004 ppm and Zn up to 608 ± 0.57 ppm, well above the normal mean ranges of 1.3 ppm Cd and 45 ppm Zn. A difference in poplar data is marked by its graphical distance from other plant data shown in Figure 55. In background control areas hawthorn exhibited significantly different chemical signatures compared to all other species. This can be observed in Figure 55, where hawthorn trees from the control area are located in the lower left corner of the PCA plot. Interestingly, those hawthorn trees grow in a hedgerow which is devoid of any other tree species; therefore, there is no competition between other root types.

The loadings of As, Cd, Pb and Zn in soils from all sites displayed similar trend to plants, confirming that the major principal components of soil contributed to the overall trace element variation within plants.

Table 30. Results of the Principal Component Analysis (factor loadings) of trace elements in leaves of seven plants species from Nevinstown (N=83) and three control sites (N=36).

Plants	PCA Nevinstown		PCA Control sites	
	Comp. 1 (41%)	Comp. 2 (15%)	Comp. 1 (49%)	Comp. 2 (27%)
As	0.22	0.34	-0.14	0.12
Cd	0.67	0.20	-0.12	0.78
Cu	-0.16	-0.02	0.03	-0.03
Fe	-0.02	0.09	-0.006	0.04
Mn	-0.07	0.31	0.19	0.04
Ni	-0.16	0.35	0.12	0.14
Pb	0.26	0.37	-0.23	0.14
Sr	0.23	-0.31	-0.14	0.24
Zn	0.15	0.11	0.88	0.24

Cluster analysis

Cluster analysis was performed using PAST Statistical software. Plant species are grouped in terms of their nearness or similarity to element concentrations. The measurement is based on the squared Euclidean distance (Derya, 2009) which is a straight-line distance between two points; in this case the distance between two concentration values of the same element. In this study, Ward's method was used as a clustering method (see Brereton, 1990). Based on major and trace element interpretations, it is clear that the different plants may be grouped according to their element concentration similarities (Fig. 56).

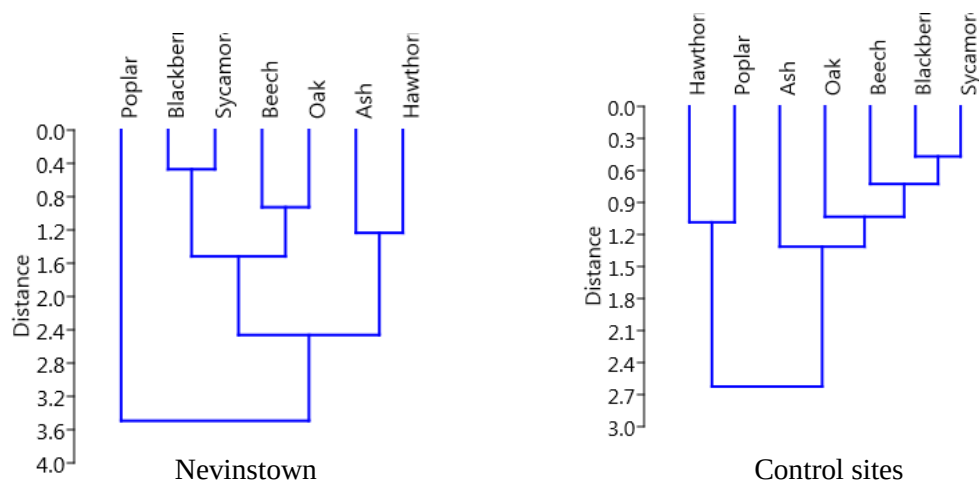


Figure 56. Dendrogram analysis for all plant species (N=119) collected from Nevinstown and control sites.

The following groups contain similar trees above the orebody at Nevinstown:

Group 1: poplar

Group 2: blackberry and sycamore

Group 3: beech and oak

Group 4: ash and hawthorn.

Each concentration of As, Cd, Co, Cu, Fe, Mn, Pb, Sb and Zn was log-transformed. An Euclidian distance is calculated and compared to the same element in every plant species studied. Using Ward's method, plant species were clustered into the classes with a similar Euclidian distance of each element. The locality where the orebody outcrops was compared with the natural setting of the control area in order to distinguish whether there were any similarities between plant species with respect to their chemical composition. For example, a group consisting of blackberry and sycamore represents two plant species with a similar trace element patterns or with a similar ability for metal uptake.

Group 3 which consist of beech and oak behaves in a similar way irrespective of the sample location. These chemical similarities may be related to botanical similarities (height, broad-leaves, depth of rooting system) since they belong to the same Beech Family (Rose, 2004). In contrast, group 1 and group 4 display significant differences when comparing all studied sites. Ash and hawthorn shared similar variability in chemical composition above the deposit, while poplar forms an individual group. At the control sites, minor differences can be seen between ash, beech and oak, but they still share similarities with group 2. However, an elemental concentration in poplar exhibits statistical nearness (small Euclidian distance) towards hawthorn at the control sites which was not the case at Nevinstown (Fig. 56). It is well documented that ash and poplar can be classified as accumulator plants capable of the uptake of toxic concentration of trace elements such as As, Cd, Pb and Zn (Aksoy et al., 2006, Van Nevel et al., 2011). Such mobile metal fractions could be absorbed from a substrate in the presence of a bioavailable pool of these elements in acidic conditions ($\text{pH} < 7$), enhanced by plant rooting systems (Mayer et al., 1998). Hawthorn shows a similar behaviour to ash and poplar based on the systematic interpretation as a result of this research. One of the reasons why hawthorn clusters only with ash and poplar out of all seven species is that they can uptake similar amounts of trace elements under same soil pH.

In greater detail, cluster analysis is also used to compare similarities (Euclidian distances) in concentration between each element and groups of elements within individual plant species. Here, focus was placed on hawthorn as the most common native plant species in Ireland that has a strong capability for metal uptake and accumulation. Hawthorn showed the ability to uptake a wide range of elements, some of which are of interest for this study.

Cluster analysis illustrates three relatively distinct groups of elements in hawthorn leaves (Fig. 57). Group (I) represents the major elements S, Mg, K and Ca which are often found in carbonates such as limestone and dolomites typically occurring in the underlying rocks at Navan (Braithwaite and Rizzi, 1997); S is associated with Barite and sulphides (McArdle, 1990). Group (II) and (III) represent common major and trace elements within the occurring sulphide minerals in Navan sphalerites (e.g. Cook et al., 2009), galena (e.g. George et al., 2015), and pyrite (e.g. Large et al., 2017) and could be associated with the host lithologies, chiefly - the Pale Beds and Upper Dark Limestones (see Chapter 3, Geology). The only significant difference between Group II and Group III from both sites is a stronger relationship between Cu and Sr with Ba, Fe and Zn in hawthorn leaves at the control sites when compared to Nevinstown. In this case, a stronger relationship would indicate similar concentration among these metals considering that Ba and Zn are depleted in hawthorn leaves at control sites. In addition, a similar trend can be seen in all plant species.

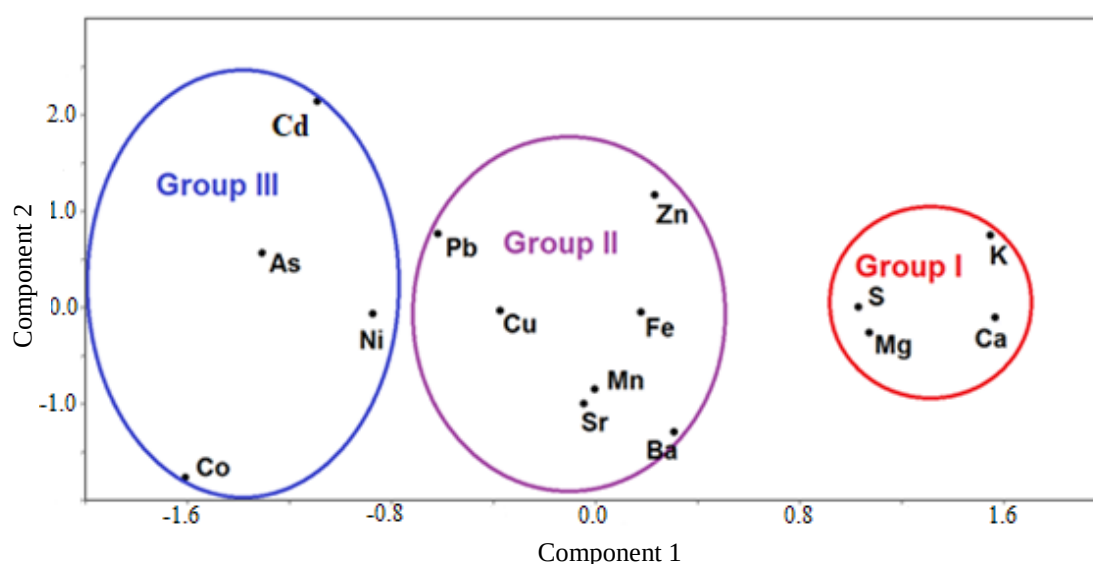


Figure 57. Cluster Analysis of elemental concentration in hawthorn leaves from Nevinstown (N=23).

In general, the use of the cluster analysis in this study and with respect to geobotanical prospecting is to easily see the differences or similarities in a chemical composition between plant species within the background or above the mineralisation site.

Cluster analysis of soils (Fig. 58) form three similar groupings as those for plants but with some key difference at both sites. Copper and Sr are more inclined towards Group III together with As, Cd, Co and Ni. Arsenic, Cd, Co and Ni could be associated with sulphide minerals, most likely pyrite and sphalerite. Also, Fe and Mn are major constituents of Group I together with Ca, Mg, K and S based on their higher concentration when compared to the two other groups. Elements such as Ca, Mg, K, S occur within typical soil minerals in Ireland (e.g. calcite, dolomite, feldspars, muscovite, clay mineral) and organic matter (S), Fe and Mn are typically associated with redox processes taking place within the soil in humid areas such as in Ireland (Fay et al., 2007).

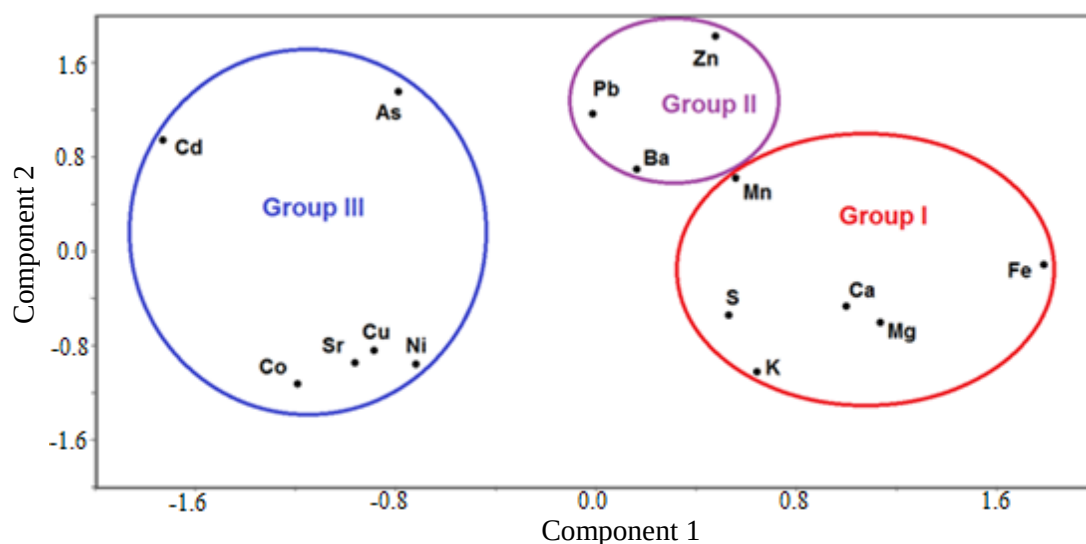


Figure 58. Cluster Analysis of elemental concentration in soils (N=33) from Nevinstown.

Based on Principal Component Analysis and Cluster Analysis Hawthorn showed the clearest trace element contrast between Nevinstown and control sites among seven plant species; therefore, a possible bioprospecting species. In addition, hawthorn metal

composition reflects similar trace element groups as can be seen in soils indicating same source.

7.1.4 Enrichment Factor and Bioaccumulation Coefficient

A bioaccumulation coefficient (BC) was used to investigate trace element behaviour in the soil-plant system. In other words, the ability of a plant to uptake bioavailable heavy metals from soils, expressed as a ratio of the metal content in a plant to that in soil (Remon et al., 2013, Dubale et al., 2015).

Arsenic, Fe and Pb display a low bioaccumulation coefficient ($BC < 0.03$) without major variation between plant species at Nevinstown (Fig. 59). In contrast, Cu exhibited the highest BC on average ($BC = 0.49$) and displays variations among species.

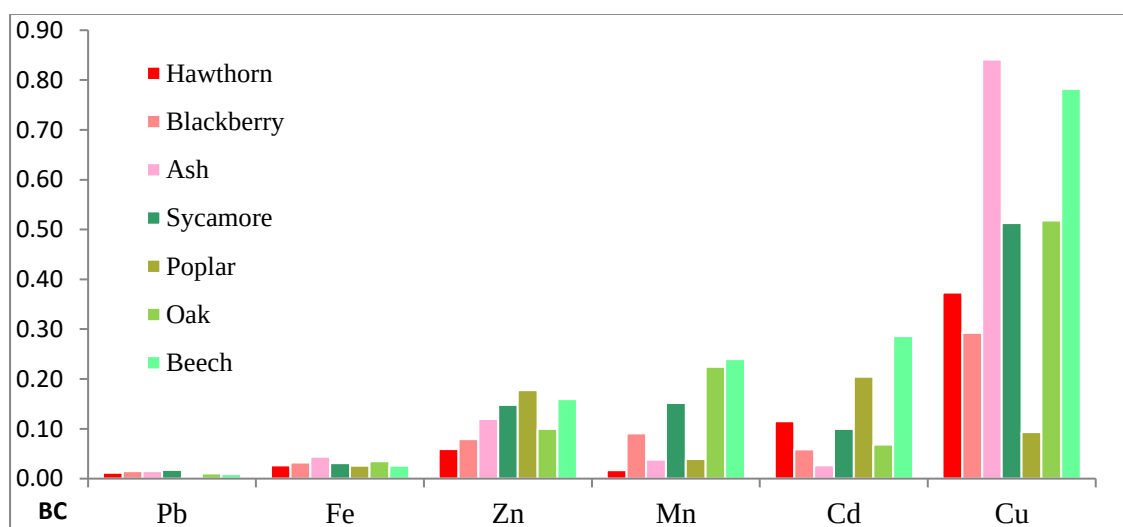


Figure 59. Bioaccumulation coefficients (BC) of all plant species above the ore body. Even though As belongs to a group of elements of interest, its BC was extremely low and was omitted from the figure.

Ash and beech show the highest ability for Cu uptake $BC = 0.84$ (ash); $BC = 0.78$ (beech) in plants above the Navan orebody. Moderate levels of metal accumulation (BC) between all plants were reported for Cd (0.12), Mn (0.11) and Zn (0.12), on average.

Poplar and beech trees have the highest BC values for Zn at 0.18 and 0.16, respectively. In addition, the highest plant uptake for Cd is reported for a beech tree with a BC value of 0.29. The bioavailability of almost all trace elements exhibited a moderate to strong correlation with pH conditions and soil organic matter expressed as LOI. Only the Mn uptake is unaffected by the presence of organic matter while Cu and Zn were not influenced by pH considering low correlation between Mn and LOI and pH to Cu and Zn. Based on these observations, it can be interpreted that pH and LOI were not dominating factors for uptake of these elements (Cu, Mn and Zn) in the studied plants, and were more likely regulated by plant enzymatic processes (Barber 1995, Chen et al., 2008, Nouri et al., 2009).

Overall, Cu was the strongest bioavailable element in the study area which can be related to being more strongly associated with the mobile fraction. Thus, its ability to be mainly situated in roots may explain lower Cu concentrations in leaves at Nevinstown. Accompanied with Zn, both metals exhibit high mobility, being more soluble and exchangeable in soil (Huiying et al., 2014). Also, their dissolution in the soil can be affected by pH-Eh conditions, cation-exchange capacity (CEC), soil organic matter (SOM) and speciation (Barber, 1995, Hough et al., 2004, Swartjes et al., 2007, Legind and Trapp, 2010).

Once elements are absorbed by plant roots they are transferred through xylem and phloem to a preferable plant organ such as the stem, leaves, flowers and fruits (Algreen et al., 2012). In general, hawthorn showed a specific increasing bioaccumulation trend: leaves>flowers>fruit for the majority of elements; exceptions to this trend are for Cu and Fe (BC) which exhibit flowers>fruit>leaves bioaccumulation trend, in agreement with studies of hawthorn organ usage (Goji et al., 2011). Elevated Fe in flowers can be a result of different Fe uptake strategy where flowering plants use Strategy I (transport ferrous

iron). Similar trends are exhibited for blackberry, where leaves>fruit; and oak and beech, where leaves>wood (except for Fe); where woody plants use Strategy II iron-chelating agents (Von Blackenburg et al., 2009).

Overall, different plant material collected from individual plant species confirmed high bioaccumulation of Cu as a plant essential element even though Cu concentrations showed depletion at Nevinstown. The low Cu bioaccumulation factor in poplar coincide with the highest reported Zn concentrations, suggesting strong Zn influence on the Cu uptake. Copper is the most bioavailable metal for plants but elevated Zn interferes with its uptake, leading to lower Cu concentration at Nevinstown.

An enrichment factor (EF) is generally used to express heavy metal accumulation in soils but here it will serve also as a factor of trace element uptake in plants (Barbieri, 2016). Furthermore, it is important to get an overview of such enrichment factors in relation to the geological background of the area studied (Reimann et al., 2005, Galuszka et al., 2011). Usually, an enrichment factor is reported using the chemical composition of the upper continental crust (Taylor and Mclennan, 1985) as normalising factor. Here, Upper Dark Limestones (UDL) will be presented as a background normalising factor, specific to the region. The Upper Dark Limestones (see Chapter 3) are mainly un-mineralised and are collected and analysed by the Exploration Department (Boliden Tara Mines) in County Meath and Westmeath as a part of a lithogeochemical appraisal of rock and drill core samples.

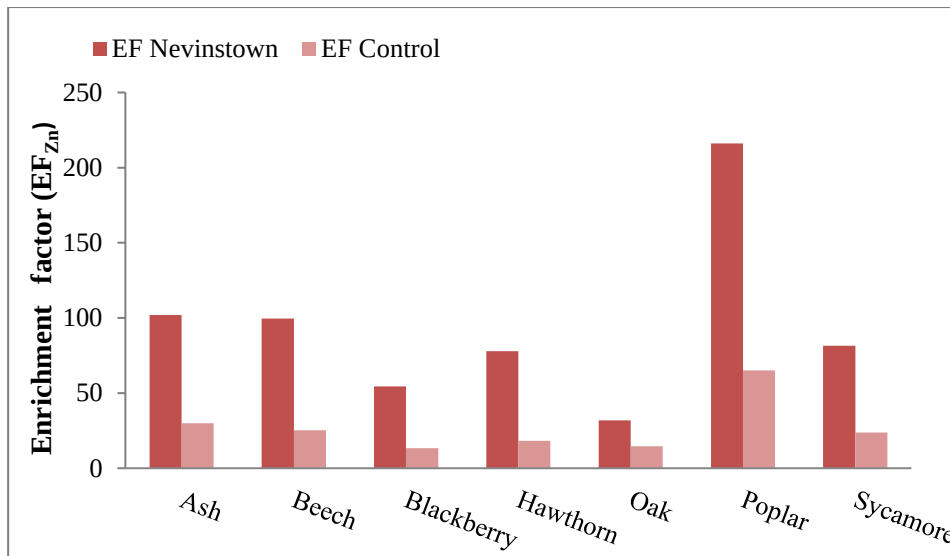


Figure 60. Zn enrichment factor (EF_{Zn}) relative to Cd/Sn and Pb/Sn background values of the host rock (Upper Dark Limestones). EF_{Zn} is reported for ash (24), Beech (14), blackberry (20), hawthorn (31), Oak (8), Poplar (7) and sycamore (17) at Nevinstown and the control sites.

Figure 60 illustrates an EF_{Zn} that is different in plant species at Nevinstown where the orebody sub-outcrops compared to the control areas; $t(6)=4.29$, $p = 0.005$ (paired t – test). Moreover, poplar shows the highest Zn enrichment ($EF_{Zn}=216$) while oak exhibited the lowest enrichment factor ($EF_{Zn}=32$). A similar enrichment trend can be seen for Cd and Pb at both sites (Fig. 61). The lowest factors correspond to control areas. The highest Cd enrichment was observed in poplar (avg. $EF_{Cd}=61$) and hawthorn (avg. $EF_{Cd}=145$) while the highest Pb factor corresponds to ash, blackberry and hawthorn ($EF_{Pb}=20$; $EF_{Pb}=23$, $EF_{Pb}=27$, on average). In contrast, poplar revealed a lower enrichment factor ($EF_{Cd}=114$) above the orebody when compared to the background control area. A high P and Zn anomalies can reduce Cd uptake indicating that uptake will decrease with higher concentrations such as those observed above the Navan deposit (Gratani et al., 2008, Legind and Trapp 2010, McLaughlin et al., 2011).

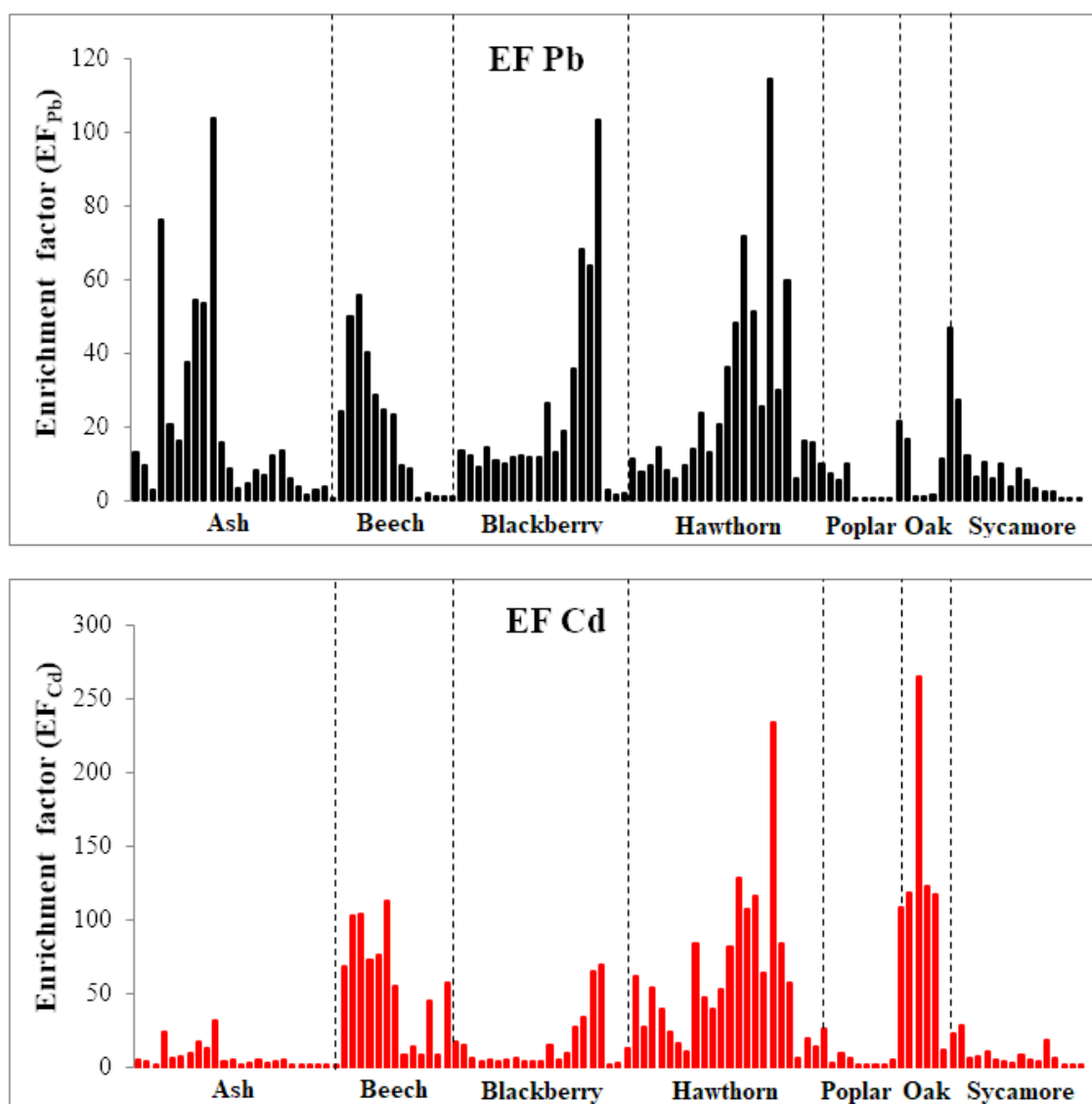


Figure 61. Cadmium and Pb enrichment factor (EF_{Cd}, EF_{Pb}) of the different plant species at both sites relative to Cd/Sn and Pb/Sn background values of the host rock (Upper Dark Limestones).

Furthermore, based on the enrichment factor calculations beech and oak trees accumulated more Cd, Cu and Zn above the orebody (Fig. 62). Interestingly, both tree species have similar bioaccumulation coefficients (BC) between bulk wood and accompanying soil; nevertheless, beech trees accumulated more Cd and Zn at Nevinstown.

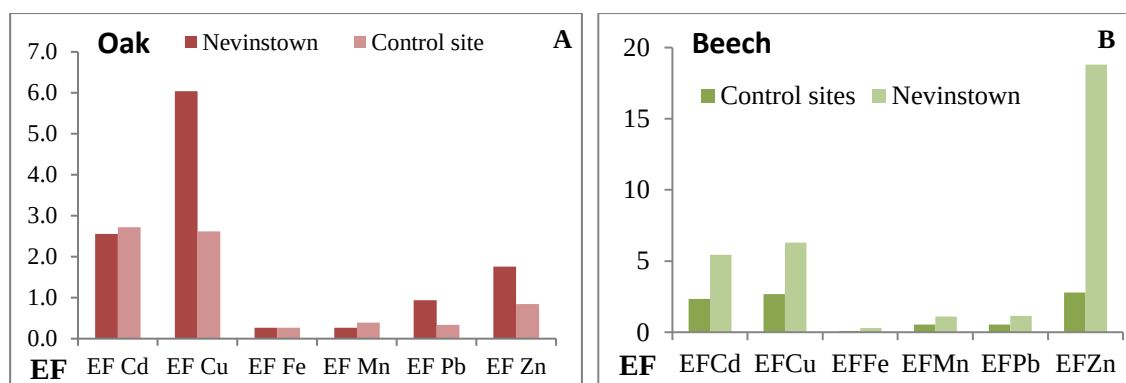


Figure 62. Enrichment factors (EF) of Cd, Cu, Fe, Mn, Pb and Zn in bulk wood of **A)** oak and **B)** beech. Both plots represent an area where the orebody sub-outcrops (Nevinstown) and control areas as a natural background.

Dolgopolova et al. (2006) published Zn and Pb enrichment factors for lichens and birch leaves from the Orlovka–Spokoinoe mining site (Russia) where enrichment factors for Pb (EF=70-100) and Zn (EF=80-300) were reported. Even though birch species were not investigated in this study there are botanical similarities to the investigated species, especially with beech trees. Zinc enrichment in birch leaves from the fore-mentioned Russian mine are comparable with plants above the Navan Zn-Pb ore-body, except for blackberry and oak. Other plant species revealed EF_{Cd} and EF_{Pb} of less than 25 at Navan. However, these differences are probably related to different elemental compositions of the host rock at the Orlovka-Spokoinoe mine. In addition, a different immobile element (Zr) was used to normalise the Orlovka-Spokoinoe data while this study reports enrichment factor normalised to Sn. This could bias the result of the EF comparison; however, an EF of 25 is still significantly high.

7.2. Metal distribution on a regional scale

The distribution of Zn in all deciduous plants from Nevinstown, control sites, Ballinalack and the Irish Midlands revealed a relationship between anomalous metal values and the proximity to known mineralisation on a regional scale (Fig. 63). Similar correlation patterns were found between plants and soil at Nevinstown while exhibiting no major relationship at control sites and Delvin.

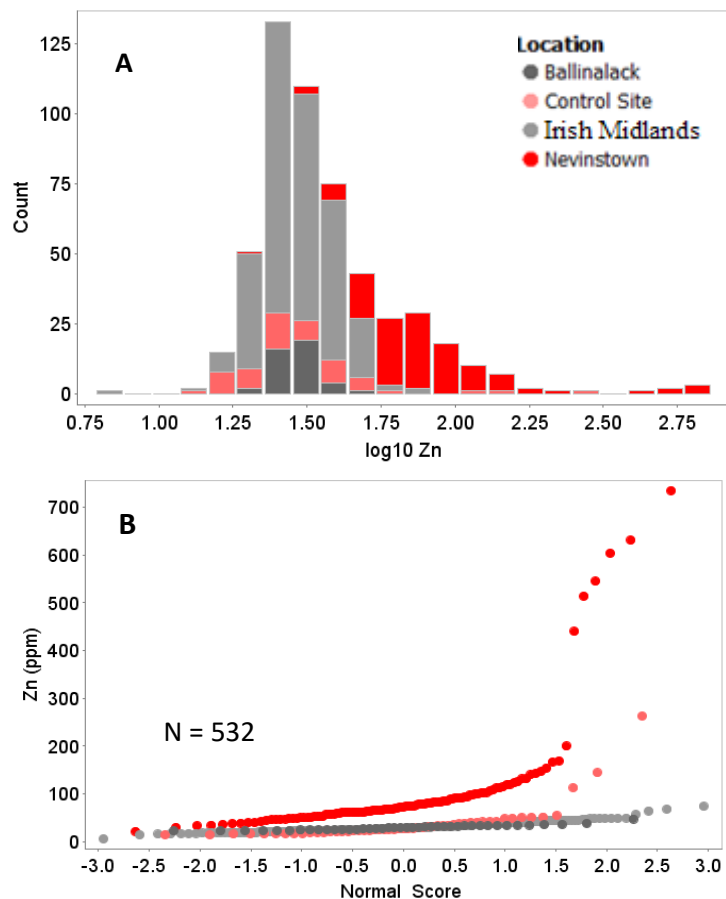


Figure 63. Histogram (A) and probability plot (B) showing Zn distribution with distance in deciduous trees from the Nevinstown (Zn/Pb mineralisation), control sites (<2 km), Irish Midlands (40 km) and Ballinalack (60 km). The biogeochemical survey consisted of 532 samples and 7 plant species.

Regional data for the Irish Midlands represents a compilation of plant data reported in this study together with data collected in a large-scale biogeochemical survey (Project

TME: 756) conducted by the Exploration Department at Boliden Tara Mines in Co West Meath during spring 2017. Plant data from Nevinstown, above the orebody displays mean Pb and Zn values of 3.5 ± 0.10 ppm and 100 ± 1.46 ppm (<6% MAD precision), respectively. Approximately 2 km to the west at the control sites, plants exhibit nearly three-times lower Pb (0.5 ± 0.01 ppm) and Zn (38 ± 0.95 ppm) values (<5% MAD precision). In the Irish Midlands (greater than 40 km distance away), Pb and Zn distribution in plants is lower still with mean values of 0.27 ± 0.01 ppm Pb and 30 ± 1.56 ppm Zn (<6% MAD precision). The biogeochemical orientation studies around the Curraghinalt gold deposit in Northern Ireland reported Pb and Zn concentrations in hawthorn leaves at, <2 ppm and 28 ppm, respectively (Smyth, 2004).

For the Ballinalack Zn-Pb deposit, hawthorn leaves displayed similar Pb and Zn concentrations (0.13 ± 0.01 ppm; 30 ± 0.57 ppm; <5% MAD precision) to the Irish Midlands (0.12 ± 0.051 ppm; 22.4 ± 1.06 ppm). Based on these observations it can be concluded that trees occurring near Zn-Pb orebodies absorb more Pb and Zn. Furthermore, trees which are growing above a Ballinalack deposit with significant overburden did not exhibit major Pb and Zn uptake (see Appendix A, Tab. A-2). In fact, Pb and Zn values were similar to those presented for natural background of the Irish Midlands suggesting that plants did not reveal a Pb and Zn anomaly. Other trace elements in plants did not show significant variations to those reported above the orebody at Nevinstown.

The enrichment factor in soils showed the highest values for Cd, Pb and Zn (see Appendix D, Tab. D-5) at Nevinstown when compared to the control areas and Delvin. Moreover, the control area which is approximately 2 km from Nevinstown exhibited lower Cd and Zn ($EF_{Cd}=0$; $EF_{Zn}=1.5$) enrichment compared to the 40 km distant Delvin

area ($EF_{Cd}=2$; $EF_{Zn}=2$). In contrast, the Pb factor was higher at the control sites ($EF_{Pb}=3.7$) than in the Delvin area ($EF_{Pb}=3$).

The differences in Cd, Pb and Zn enrichment factors between Delvin and control sites are minimal implying those sites represent similar signatures. In addition, Pb and Zn are integral mineral components within carbonates. To distinguish carbonate influence from soil, data was normalised to Ca (see Chapter 6, Fig. 42). Zinc and Pb signatures were reduced at control sites and Delvin suggesting carbonate signature masked Zn signature which initially appeared much higher. At Nevinstown, Zn distribution did not exhibit major changes meaning that the carbonate influence appeared minimal. The base metal signature (Cd, Pb and Zn) observed in surficial soils above the orebody is associated with the sulphides and therefore linked to Navan mineralisation.

7.3 Biogeochemical cycling of Cu and Zn isotopes

The isotopic composition of hawthorn leaves shows variations at both sites for Zn ($\Delta^{66}Zn=1\pm0.07\text{‰}$) and Cu ($\Delta^{65}Cu=0.7\pm0.10\text{‰}$), whereas soils and oak tree rings revealed a smaller range of isotopic signature more so with Cu isotopes. Very few authors have reported on Zn and Cu isotopes in deciduous plants and tree leaves (Fig. 64 and 65) in particular. Viers et al. (2007) have shown Zn fractionation in a plant-soil system at a natural watershed in Cameroon; where they recorded $\delta^{66}Zn$ signatures in tree leaves (tropical forest) range from -0.03‰ to -0.91‰ and in herbaceous species, 0.26‰ to 0.52‰ . The zinc isotope composition of hawthorn leaves in the Navan control sites without known mineralisation would seem to correspond to data obtained for mentioned herbaceous species. The data is also in line with Zn isotopes measured in rice with values of $\delta^{66}Zn$ ranging from 0.32‰ to 0.51‰ (Arnold et al., 2015). However, the rice was

grown in oxic and anoxic soils under laboratory conditions. In fact, the majority of Cu and Zn isotopic studies for grasses, lentils, tomatoes, oat and rye were conducted under controlled laboratory conditions (Weiss et al., 2005, Moynier et al., 2009, Caldelas et al., 2011, Weinstein et al., 2011, Ryan et al., 2013). This study investigates natural system such as Nevinstown which includes many uncontrolled environmental conditions (e.g. pH, temperature, element species) (Fig. 64).

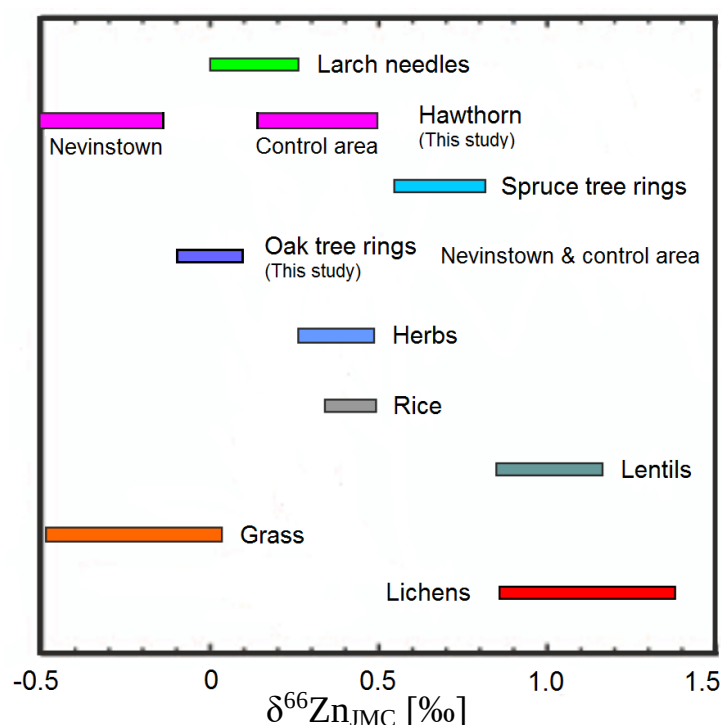


Figure 64. Compilation of data ranges for Zn isotopes in different plants and plant material. Isotopic composition is reported for larch needles (Viers et al., 2015); hawthorn leaves and oak tree rings at Nevinstown and control sites from this study; spruce tree rings (Dinis et al., 2018); herbs (Viers et al., 2007); rice (Arnold et al., 2015); lentils (Moynier et al., 2009); grass (Caldelas et al., 2011) and lichens (Dolgopolova et al., 2006). Ranges of $\delta^{66}\text{Zn}$ are expressed in per mil.

The correlation between Cu and Zn isotopic composition in plants, tree rings and soil confirm the advantages in using both systems which might indicate that similar fractionation processes occurred. A strong positive correlation between $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$ within soils at Nevinstown ($r=0.83$) and moderate correlation between different plant material ($r=0.62$) at the control sites suggests similar mechanisms controlling Cu and Zn

fractionation (Weinstein et al., 2011, Jouvin et al., 2012). While investigating Cu isotopic compositions in lentils, wild rye and hairy-leaved sedge, Weinstein et al. (2011) introduced a similar approach where Cu and Zn isotopes fractionate using similar mechanisms and determined that $\delta^{65}\text{Cu}$ signatures ranged from -0.71‰ to +0.36 ‰. A study on the uptake and translocation mechanisms in oat illustrated $\Delta^{65}\text{Cu}$ in total plant from -0.20‰ to -0.11 ‰, respectively (Ryan et al., 2013). Cu isotopic ratios presented here exhibit slightly heavier $\delta^{65}\text{Cu}$ composition ranging from -0.04 ± 0.10 ‰ to $+0.20 \pm 0.10$ ‰ (Fig. 65).

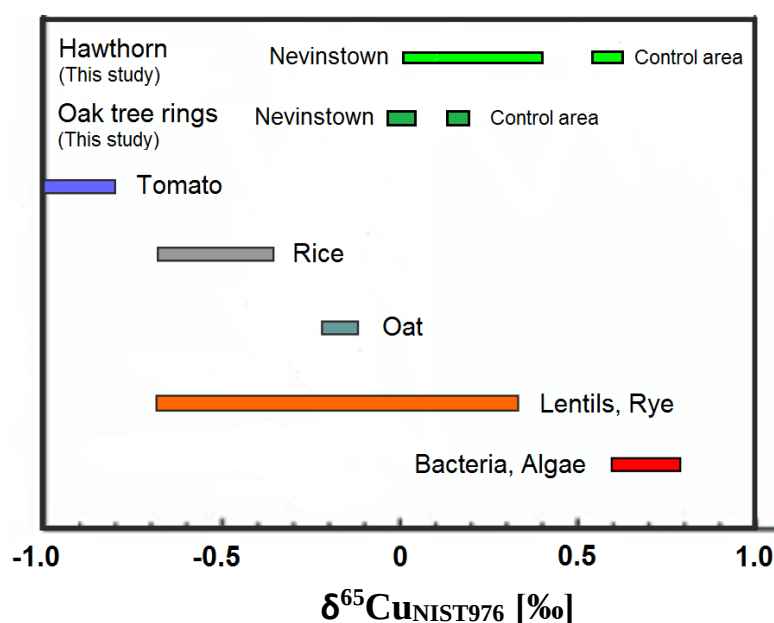


Figure 65. Compilation of data ranges for Cu isotopes in different plants and plant compartments. Isotopic composition is reported for tomato and rice (Jouvien et al., 2012); hawthorn leaves and oak tree rings at Nevinstown and control site from this study; rice (Dinis et al., 2018); oat (Ryan et al., 2013); lentils and rye (Weinstein et al., 2011) and bacteria and algae (Pokrovsky et al., 2008). Ranges of $\delta^{65}\text{Cu}$ are expressed in per mil.

For the Navan area, oak tree rings range from -0.1 ± 0.07 ‰ to $+0.1 \pm 0.07$ ‰ in $\delta^{66}\text{Zn}$ and -0.05 ± 0.10 ‰ to $+0.20 \pm 0.10$ ‰ in $\delta^{65}\text{Cu}$. A moderate variation can be seen with slightly heavier Cu isotope signatures occurring above the mineralisation, but this is within the analytical uncertainty associated with the low Cu concentration in tree rings.

In addition, oak tree rings representing periods prior to mining (1950-1960) revealed slightly heavier $\delta^{66}\text{Zn}$ at Nevinstown, whereas the control sites exhibited lighter $\delta^{66}\text{Zn}$.

In the absence of published Cu and Zn isotopic data for oak tree rings a comparison was made with the spruce tree rings to provide an estimate of those isotopic systems in the woody material. An environmental study on spruce tree rings from the Northern Athabasca Oil Sands Region (NAOSR) of Alberta, Canada recorded a range of +0.54‰ to +0.83 ‰ for $\delta^{66}\text{Zn}$ (Dinis et al., 2018). These Zn isotopic compositions tend to be much heavier than values obtained for oak tree rings from the Navan area. Variations in isotopic fractionation could arise not only between different plant species but also within plant compartments (Viers et al., 2007).

Potential mechanisms that can cause fractionation in plants are organic adsorption, diffusion, translocation and photosynthesis. Organic adsorption usually takes place at the root systems increasing the pool towards heavier isotopic composition. Processes such as diffusion and translocation occur between the root and shoot system and are more inclined to lighter isotopic composition (Cloquet, 2008). In addition, kinetic fractionation is typically associated with biological processes such as photosynthesis in plant leaves (Moynier et al., 2017).

The Zn composition of surficial soils (A Horizon) above Navan deposit showed similar trends to the PhD study of Kalveram (2018) where $\delta^{66}\text{Zn}$ in soils (BC Horizon) above the Ballinalack deposit (Ireland) ranged from +0.16‰ to +0.41 ‰. In addition, Cu isotope ratios in soils investigated in the Nevinstown (ranging from +0.04±0.07 to +0.19±0.07 ‰) obtained similar ranges in comparison to values reported for $\delta^{65}\text{Cu}$ in

soils above the Ballinalack deposit which range from +0.07‰ to +0.25 ‰. The results reported from the fore mentioned research illustrate the influence of sulphide weathering and soil organic matter on Zn and Cu isotope signatures in soils and till such as fractionation towards heavier $\delta^{65}\text{Cu}$ (Mathur et al., 2005, Vance et al., 2008, Borrok et al., 2009, Kimball et al., 2009).

7.3.1 Fingerprinting Cu and Zn isotopic signatures around the Navan deposit

Figure 43 and 46 (see Chapter 6) illustrate the Cu and Zn isotopic distribution in hawthorn leaves, oak tree rings and soils at Nevinstown and the control sites. It can be clearly seen that leaves are significantly enriched in the lighter $\delta^{66}\text{Zn}$ isotope, compared to surficial soils above the orebody; whereas at the control sites $\delta^{66}\text{Zn}$ isotopes in hawthorn leaves are similar to those in the underlying soils.

During Zn uptake by roots, several processes govern zinc mobility within the plant including diffusion and active uptake by cells to the most aerial part of the plant. In both processes Zn is being transported from the root through the shoot and via xylem into leaves resulting in a lighter isotopic composition (Weiss et al., 2005, Viers et al., 2007, Moynier et al., 2009, Caldelas et al., 2011, Jouvin et al., 2012). Moreover, the lightest Zn isotopes corresponded to higher Zn concentration (three-times higher) in leaves in comparison to leaves with depleted Zn concentrations exhibiting much heavier isotopic ratios at the control sites (see Chapter 6, Fig. 43). Deng et al. (2014) investigated fractionation mechanisms in accumulator and non-accumulator plants growing in high and low Zn solutions. During Zn sufficiency, leaves incorporate lighter isotopes (Caldelas

et al., 2011), whereas plants growing in low Zn solution exhibited the opposite effect. Lighter Zn isotopes in hawthorn leaves at Nevinstown in comparison to leaves at the control sites in the Navan study area could be the result of depleted Zn contents in plants and in surficial soils at the control sites. In addition, selective uptake of light isotopes (Weiss et al., 2005) may cause heavier Zn isotopic signature in hawthorn leaves in the control area. Processes such as uptake by ZIP (zinc importer proteins) with a strong affinity to Zn^{2+} or complexation of phytosiderophores in the growth medium solution (strategy II plant only) can induce enrichment in heavier isotopes (Grotz et al., 1998, Jouvin et al., 2012). However, these processes are associated to prefer heavier isotopes during uptake into the plant system. This does not imply enrichment of heavier isotopes in the plant it just increases the isotopic pool towards heavier isotopes in bulk samples or in root samples. Considering that differences in the Zn isotope composition from both sites range up to 1‰ with an average signature of $\delta^{66}\text{Zn}$ of $-0.35 \pm 0.07\text{‰}$ (7% MAD precision), this would imply a strong fractionation mechanism (Viers et al., 2007) in hawthorn leaves.

Tree rings did not exhibit as strong Zn fractionation as shown by hawthorn leaves indicating different enzymatic processes; tree rings are involved in nutrient transport from roots to leaves while processes such as gas exchange and photosynthesis only occur in leaves. However, they displayed lighter $\delta^{66}\text{Zn}$ signatures in comparison to their underlying surficial soils. Moreover, no correlation between Zn concentration and Zn isotopic composition in the woody material can be observed. This study reported up to three-times higher Zn concentrations in tree rings at the control sites and yet the fractionation range is similar to those reported at Nevinstown, between $-0.1 \pm 0.07\text{‰}$ and $+0.1 \pm 0.07\text{‰}$ (7% MAD precision), respectively. Strong Zn fractionation during metal refining results in an extremely wide range of isotopic signatures within dust and

residues. Several studies report an impact of Pb-Zn smelting and refining on Zn fractionation in which particles emitted into the atmosphere resulted in isotopically lighter particles (-0.73‰ to $+0.63\text{‰}$) than in residues where $\delta^{66}\text{Zn}$ reached up to $+1.49\text{‰}$ (Sivry et al., 2008, Sonke et al., 2008, Mattielli et al., 2009, Ochoa Gonzales and Weiss, 2015). Ireland does not host a base metal smelter, with smelting activity last taking place in Dublin during the 19th century. The nearest smelter to the study area is 500 km away in Darley Dale (United Kingdom). Prevailing winds are from the West and effects on the Irish Zn-Pb signatures are probably negligible. Tree rings at both investigated sites (Nevinstown and control sites) did not show strong fractionation ($\delta^{66}\text{Zn}=0.0\pm0.07\text{‰}$, on average) which was not the case with hawthorn leaves. Based on the weak Zn temporal fractionation trend seen in tree rings and low atmospheric deposition of Zn previously discussed, industrial dust impact had low influence at Nevinstown.

Surficial soils revealed a similar positive fractionation range at Nevinstown and control sites even though signatures are slightly heavier above the orebody ($\delta^{66}\text{Zn}=+0.20\pm0.08\text{‰}$ on average, 8% MAD precision). A variety of processes in soil can influence isotopic fractionation such as adsorption on minerals, complexation with organic matter and reactions with oxy (hydroxides) (Pokrovsky et al., 2005, Viers et al., 2007, Bigalke et al., 2010, Opfergelt et al., 2017). Biogeochemical cycling includes vegetation which returns in soils as litter compound. Litter is mainly associated with leaves which present a source of lighter Zn isotopes (Opfergelt et al., 2017). Accumulation of litter in soils increases the organic composition resulting in acidic conditions under which heavy zinc isotopes may become mobile (Fujii et al., 2014, Markovic et al., 2017, Moynier et al., 2017). Both sites display similar pH conditions and contributions of organic matter in soils (pH=5.8; LOI=18%, on average). A moderate correlation between organic matter and $\delta^{66}\text{Zn}$ ($r=0.60$) and between $\delta^{66}\text{Zn}$:Fe ($r=0.51$)

would explain the slightly heavier Zn isotopes in surficial soils at Nevinstown under acidic conditions as reported in this study (see Chapter 6, Fig. 45D).

Overall, hawthorn exhibited heavier Cu isotopes ($\delta^{65}\text{Cu}=+0.31\pm0.10\text{‰}$, on average, 13% MAD precision) in relation to surficial soils composition ($\delta^{65}\text{Cu}=+0.11\pm0.07\text{‰}$, on average, see Chapter 6, Fig. 46). Moreover, leaves collected at Nevinstown displayed similar or heavier Cu isotope ratios which is the opposite of behaviour observed for Zn isotopes. For the control sites, Cu and Zn isotopes presented a similar isotopic range which may indicate that fractionation occurred through similar mechanisms driven by kinetic fractionation and diffusion (Weinstein et al., 2011). Based on Cu concentrations in leaves, there is no clear connection in relation to Cu isotopes except for a negative moderate correlation between $\delta^{65}\text{Cu}:\text{As}$ ($r=-0.66$) and $\delta^{65}\text{Cu}:\text{Pb}$ ($r=-0.57$) in leaves at Nevinstown (Chapter 6, Fig. 47) which could be associated to the underlying sulphides. In fact, the heaviest Cu isotopes were reported in leaves from the control sites. Some authors have indicated enrichment of lighter isotopes ($\delta^{65}\text{Cu}$) in plants as a result of soil-plant transfer when compared to growth medium (Jouvin et al., 2008, Bigalke et al., 2010, Chu et al., 2010). Based on redox reactions, Cu can fractionate over a wide range of isotopic variations. Thus, these variations are usually induced by a pH decrease in soil solution (Pokrovsky et al., 2008). In the case study Navan, such a shift in the isotopic variation cannot be seen considering that a relatively constant pH in surface soil is measured at both sites. The only environmental conditions which contributes to the overall Cu isotopic composition in leaves is much higher and positive electrical conductivity (EC) measured in soils at the control sites. High EC could be a result of more concentrated dissolved salts in soils suggesting perhaps different soil texture and CEC.

The Cu isotopic compositions in tree rings showed a similar distribution as surficial soils and in the isotopic range measured in hawthorn leaves at Nevinstown (see Chapter 6, Fig. 46). For the control sites, $\delta^{65}\text{Cu}$ illustrates heavier isotopes in tree rings than reported in leaves in agreement with the soil isotopic composition. Zn isotopes confirmed a similar trend to Cu isotopes between tree rings and leaves around the deposit at control sites. In general, Cu and Zn composition was consistent between two 10-year sections for periods representing pre-mining (Zn-Pb) operations in Navan (1950-1960) and during mining operations (2000-2010). The consistency in temporal isotopic composition is caused by; similar fractionation process and low Cu and Zn concentrations in tree rings which are influenced by extremely high Fe concentration in wood.

7.3.2 Ore-Soil-Plant model for large natural systems

This study will demonstrate two examples of natural systems which could be applied for an Irish Zn-Pb deposit. Using established isotopic values for geological samples and a range of environmental samples reported in this study it is possible to develop a conceptual model for each natural system based on their similar geological and botanical settings.

A natural system with known Zn-Pb mineralisation (Fig. 66A, B, C) illustrates a Zn isotopic trend from Navan sulphides from moving towards surface and the biosphere with values recorded in surficial soils, oak tree rings and hawthorn leaves. Navan sulphides presented as sphalerites collected from the largest lens of the Navan deposit displayed $\delta^{66}\text{Zn}$ variations ranging from $-0.32 \pm 0.09\text{‰}$ (SD) to $+0.23 \pm 0.07\text{‰}$ (SD) (Gagnevin et al., 2012) which is similar to the isotopic range for hawthorn leaves (-0.62 ± 0.07 to $-0.12 \pm 0.07\text{‰}$) and tree rings ($-0.11 \pm 0.07\text{‰}$ to $0.09 \pm 0.07\text{‰}$). During element migration,

from ore through soil to plants metals can fractionate into heavier or lighter isotopes showing a migration pattern over a specific isotope range. The processes causing fractionation could be caused by diffusion, organic adsorption or translocation within the plant (Cloquet et al., 2008). For a more certain explanation, the phases of Cu and Zn should be determined and further investigated. However, this was beyond the scope of this study and could be an idea for a further research.

The source of isotopically lighter Zn recorded for leaves is likely derived from the Navan sulphides in the underlying sub-cropping bedrock. This is indicated by the correlations of Fe ($r=0.56$), Ni ($r=0.53$) and S ($r=0.51$) concentrations to $\delta^{66}\text{Zn}$ ratios which are major and trace elements occurring in sulphide minerals (sphalerite, galena and pyrite) in the Navan mineralisation. Hence, the studied hawthorn trees, which grow directly above the Zn-Pb mineralisation appear to have a root system that has intersected the underlying orebody, implying direct contact with the Zn-Pb deposit. Even though surficial soils displayed heavier Zn isotopic signatures from those observed in trees and sulphides, they can be linked to the Navan orebody.

In general, normal soil processes would indicate redox reactions in soils. Moreover, the studied soils are close to the Blackwater River and it is known that water table in that area has decreased in the recent past. Therefore, surficial soils above the orebody could indicate the presence of secondary processes such as oxidation or dissolution-precipitation above the Navan deposit, caused by lowering the water table and leading to a stronger fractionation of Cu isotopes (Asael et al., 2007). Copper isotopes at Nevinstown did not provide any additional information for the isotopic interpretation which would contribute to the overall interpretation of this natural system; except that similar Cu isotopic patterns are observed between surficial soil and plant material.

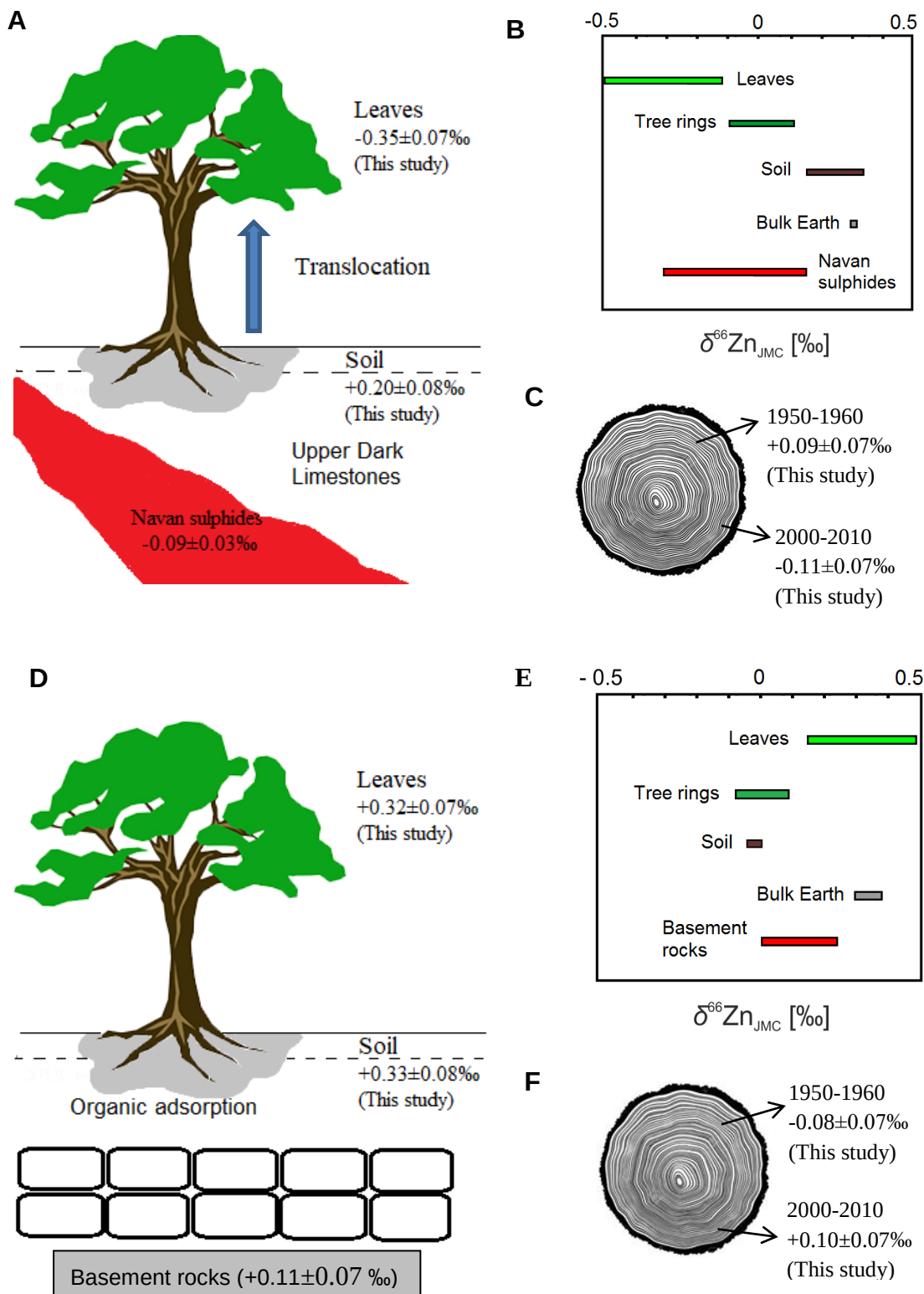


Figure 66. Conceptual model for Zn isotopes in the natural system with known Zn-Pb mineralisation (**A**, **B**, **C**) and without mineralisation (**D**, **E**, **F**). $\delta^{66}\text{Zn}_{\text{JMC}}$ is represented in hawthorn leaves and soil from this study. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Navan sulphides and basement rock mean data (SD) are adopted by Gagnevin et al. (2012). Zinc isotopic ranges (**B**, **E**) for bulk silicate earth are reported by White (2013). Oak tree rings (**C**, **F**) Zn composition is displayed for two 10-year periods. Model of tree (*) and tree ring illustration (**) retrieved from: (*) www.pngtree.com and (**) www.123rf.com.

The conceptual model for the natural system (control sites) situated 2 km away from the Navan deposit is underlain by unmineralised rock (Fig. 66D, E, F). The isotopic Zn composition of the basement rock (drilled beneath the Navan orebody) ranges from $-0.02 \pm 0.07\text{‰(SD)}$ to $0.23 \pm 0.07\text{‰(SD)}$ in $\delta^{66}\text{Zn}$, respectively (Gagnevin et al., 2012). In this context, unmineralised basement rock represents natural geological background for the study control area.

Tree ring $\delta^{66}\text{Zn}$ values are in agreement with underlying lithologies (UDL) while soils and leaf isotope compositions are slightly heavier. Hawthorn leaves display similar Zn isotopic signatures to surficial soils which indicates that a strong fractionation did not occur during plant uptake and/or that the signature represents the underlying bedrock. However, small positive fractionation of Cu in plants can be induced by organic adsorption on roots (Weiss et al., 2005, Cloquet et al., 2008) indicating that the isotopic composition of Zn is dependent on the underlying conditions.

Copper isotope signatures show that strong redox reactions occurred in soils which have induced positive fractionation in leaves (Fig. 67A, B). As mentioned above, a strong correlation between Cu and Zn isotopes suggests similar mechanisms took place; both, in soils and plants. Since different mechanisms can control the fractionation it is important to calculate the mass balance and to identify ion species in order to determine which processes are controlling fractionation. In the absence of fore mentioned calculations focus has been placed on providing new empirical Cu and Zn isotopic data in environmental material and developing models for biogeochemical metal cycling under similar geological settings which may involve Zn-Pb ore deposits. Zinc isotopes might be a useful tool; however, Cu isotopes did not show significant variations and thus are not useful to be used as indicator for mineral exploration on of Zn-Pb signatures in plant systems.

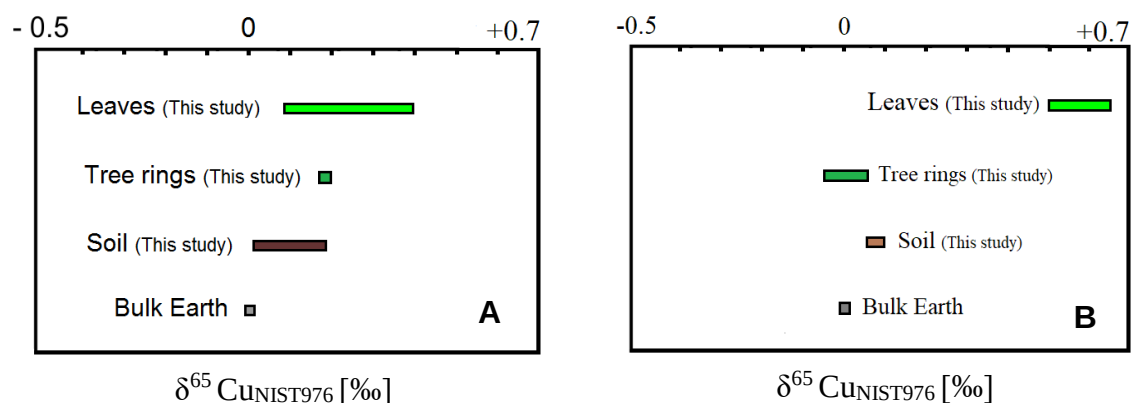


Figure 67. Summary of Cu isotopic ranges in hawthorn leaves, oak tree rings and soils reported in this study. Copper isotopic variations are displayed in the conceptual models from bulk silicate earth data (Liu et al., 2015). **A** plot illustrates natural system with known mineralisation at Nevinstown and **B** plot unmineralised control area.

7.4. Revised geobotanical prospecting in Ireland

These orientation exploration surveys above the Navan deposit have revealed anomalous concentrations of trace elements in plant and soil material. In the spring survey, all seven plant species collected above the Navan orebody exhibited As, Cd, Pb and Zn enrichment in leaves when compared to the control sites. However, the enrichment factors of these elements confirmed metal anomalies only for Cd, Pb and Zn, whereas As factors displayed very low enrichment in all investigated trees. Moreover, variations between Cu, Fe and Mn proved to be minimal when compared to the background values. The uptake patterns for each species significantly differ for Cu and Zn distribution relevant to sampling sites suggesting that Zn anomaly reduces the uptake of Cu in plants.

Trace element analysis for leaf material collected in the autumn at Nevinstown shows Cd, Pb and Zn enrichment only for hawthorn and sycamore while the other species exhibit Pb and Zn anomalies based on absolute concentrations.

In contrast, poplar trees exhibit Cd depletion where the orebody sub-outcrops. Manganese displayed significant variations when compared to the background concentration. Sampling in autumn revealed more variations in plant uptake trend for As, Cu, Cd and Zn relative to the plant uptake at control sites than in the leaf material collected in spring. During spring, plants tend to translocate more essential metals to growing leaves while in autumn these metals are stored in twigs soon before leaves start to fall in a form of preparation for the winter season. The behaviour of the elements within the plant depends on whether or not they are essential for the plant and also their relationship with other elements.

The majority of plant species demonstrated correlations between the same metals such as Cd, Pb and Zn. Based on their typical concentration similarities of metal content they form four groups of plant species as discussed in Cluster analysis. Furthermore, enrichment factors of different plant types between Nevinstown (Fig. 68A) and control sites (Fig. 68B) and between spring and autumn season (Fig. 68C) reveal a similar pattern for metal ratios. In general, zinc shows consistent enrichment between different sites and sampling seasons.

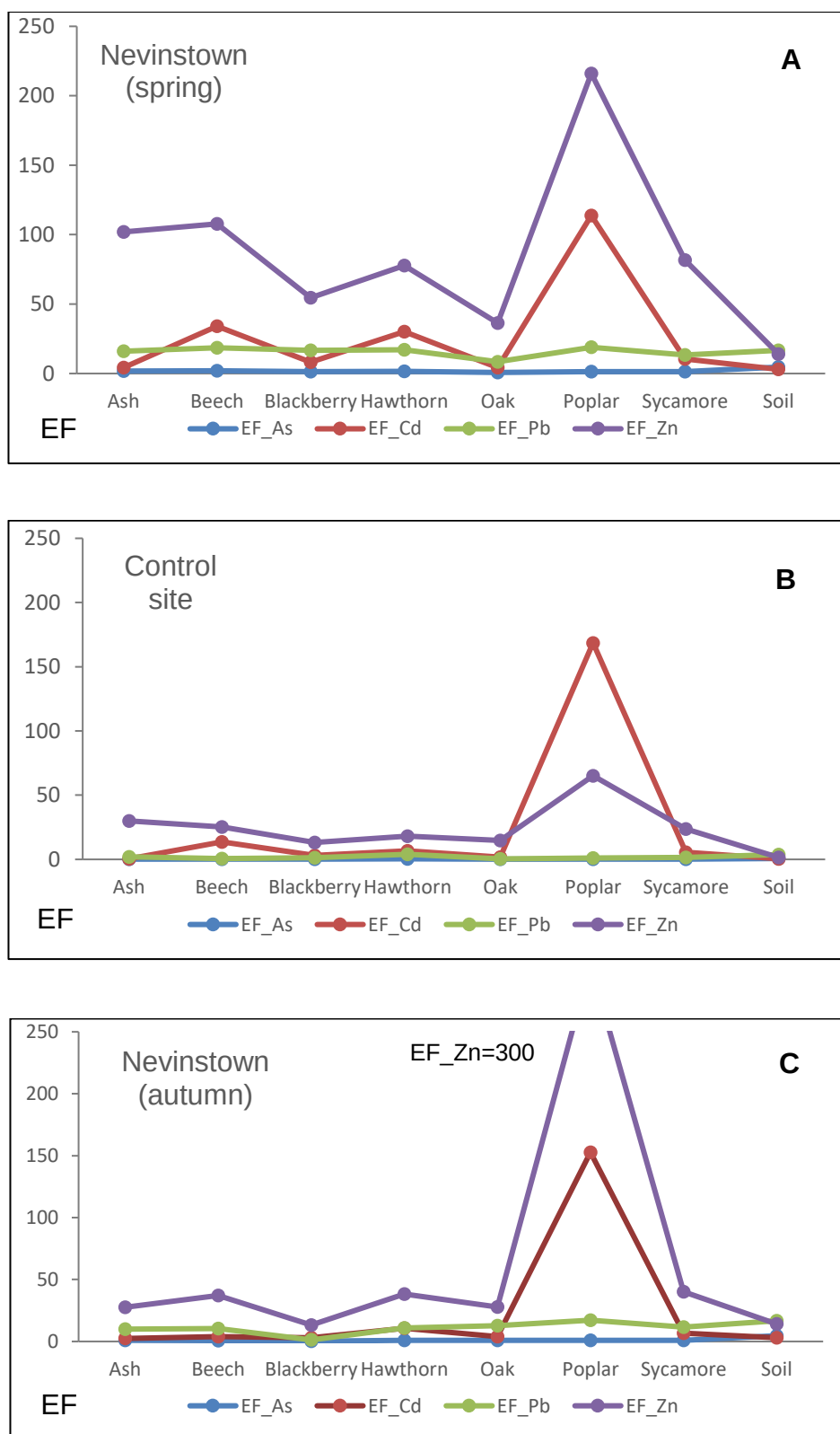


Figure 68. Enrichment factors for all plant species and soil for Nevinstown-spring (A); control site-spring (B) and Nevinstown-autumn (C). Note the Y-scale was set to EF=250 even though Poplar values exceed this factor to EF=300 in C plot for a better overview of the A and B plot.

Taking into account the clearest enrichment factors (forming peaks in relation to background ratios) for Cd, Pb and Zn, seasonal variations and the ability of metal uptake, hawthorn might serve best as a representative species for a biogeochemical exploration programme in Ireland. Even though, poplar exhibited the highest enrichment factor among metals typical for the Navan mineralisation the impact of seasonal variations is far greater than for hawthorn. Hawthorn displayed lower enrichment factors in autumn in relation to spring but still the presence of anomalous Cd, Pb and Zn in leaf material is detectable. However, based on the results presented in this study in order to obtain the highest and the clearest contrast between anomalous concentrations and the background levels it is recommended to conduct a sampling collection during spring time.

The soil geochemistry at Nevinstown confirmed the already identified As, Cd, Pb and Zn anomaly which was reported during the Navan discovery (OBrien and Romer, 1971). Here, the focus was placed on the element interaction in plant-soil systems and to recognize the impact factor of soils during plant uptake. In general, soils exhibited significant variation among all elements of interest (As, Cd, Cu, Fe, Mn, Pb and Zn) when compared to the background values which was not the case with plants. One of the reasons of the fore mentioned anomalous concentrations is that soils directly overlie the sub-outcrop of the Zn-Pb orebody at Nevinstown. Some plant species such as hawthorn and poplar can adapt to the surrounding environmental conditions and regulate uptake of Pb and Zn which can be considered as toxic (Kabata-Pendias, 2011). In the case of Nevinstown, both soil and plant material of each species illustrated clear Pb and Zn anomalies even though plants displayed weaker contrast between Nevinstown and control sites in comparison to soils.

Recommendations for the future exploration work

From an exploration point of view, the widespread occurrence of hawthorn in Ireland and its ability to uptake anomalous concentrations of Pb and Zn could be used as a geochemical indicator for Zn-Pb Irish deposits in a temperate European climate. However, before developing any plan for biogeochemical surveys certain points need to be addressed:

- Identify most common and native plant species at the proposed sampling location;
- Choose botanically and geologically similar control sites in proximity to the investigated locality which will serve as a local background. If possible, avoid urban areas, country roads and agricultural land. Moreover, it is recommended to have one additional control site further far from the studied site (~ 50 km) which would display regional background;
- Take into account several plant species which are known to co-exist in similar environments; that way the anomaly or any change in the environmental condition could be confirmed in other species beside the investigated one;
- Consistently collect plant material (e.g. same part of the day, height, amount) to get a good approximation of the signature variability and it is advised to take soil samples in 1 m distance from the plant sampling location below the tree crown;
- Identify possible sources of contamination such as agriculture or atmospheric deposition.

One of the most important limitations in geobotanical prospecting is to identify and to eliminate possible contamination from soil or air. Once the Pb and Zn anomaly is detected the question arises whether the signature belongs to a human activity or it reflects

the natural metal occurrence. Zinc isotopes can identify possible sources of metal anomalies and/or recognise signature patterns in different natural systems. The necessary steps which need to be taken while using the Zn isotopic system as a tool in biogeochemical survey in Ireland are:

- Identify several plants with anomalous trace element concentration from the investigated site;
- Develop an ore-soil-plant model for the studied locality and a host rock-soil-plant model for the control site. Note similar botanical and geological settings need to exist on both sites;
- Collect plant, soil and ore samples from a vertical profile or use already reported data. For Zn anomaly investigation use the Zn and Cu isotopic system.

The Nevinstown case, classified as a natural system with known mineralisation, illustrates significant different Zn isotopic signatures in hawthorn compared to the control system. The Zn isotopic composition in the ore-soil-plant model possibly originates from the underlying Navan Zn-Pb deposit. However, the suggested interpretation is based on direct observations of the Zn isotope data. An Empirical approach was used because environmental conditions in large natural system model such as Nevinstown could not be reproduced in the laboratory conditions. Therefore, in order to set a simplified model of Nevinstown it is necessary to have a botanical dataset for Cu and Zn isotopes from natural systems, especially near mineralisation zones. The major findings demonstrated in this research can serve as a base model (isotopic dataset) in constructing a hawthorn-soil-ore vertical profile under more controlled conditions with a focus on metal remobilisation within soil and plant.

8 Conclusion

Mineral exploration in many regions today represents a challenge due to diverse geological terrains, extreme weathered soil profiles or the impact of extensive agriculture and industry (anthropogenic effects). The use of biogeochemical prospecting as a low-cost exploration method has minimal impact on the environment and has been successful at detecting anomalies associated with buried mineral deposits. Biogeochemistry is not a standard exploration methodology, since there are a number of factors to be considered in sampling and analysis, (e.g. phytochemistry, seasonal variations and dust contamination). Consequently, detailed sampling strategies, including control locations, need to be investigated with the aim of demonstrating that the uptake of trace elements and stable metal isotopes in higher plants can be used as an exploration tool. Research into plant biogeochemistry above the Navan Zn-Pb deposit provides new insights into biochemical prospecting in temperate European climates.

The major findings of this orientation study are as follows:

- 1) Background levels of metal concentrations in deciduous plants and soils illustrate normal ranges expected in Ireland. Even though reported trace element concentrations for all deciduous plants such as ash, beech, blackberry, hawthorn, oak, poplar and sycamore are classified as normal compared to other published values in Europe, metal content in plants is species dependent. Hence, this study reports that smaller plant species such as hawthorn and blackberry tend to develop smaller root systems which interact with more localised sampling of soil above the Navan deposit. Moreover, tree species such as beech and oak exhibit similar behaviour irrespective of the sampling site. Statistical analysis has shown that chemical similarities are related to common botanical factors (height, broad-

leaves, depth of rooting system) since they belong to the same Beech Family. The following groups of trees above the orebody display similar trace element variations: a) poplar; b) blackberry and sycamore; c) beech and oak and d) ash and hawthorn.

- 2) Spatial vectoring around the Navan Zn-Pb deposit revealed that all plant species accumulated significantly more As, Cd, Pb and Zn above the orebody than in the control sites, except poplar, which accumulated more Cd at one of the three control sites. Also, it is important to note that due to small sample size, some of the mentioned correlations need to be considered, however this does not affect the overall findings of this thesis. Sampling in autumn showed more variations in plant uptake trends for As, Cu, Cd and Zn relative to plant uptake during spring. The dominating factors for uptake of Cu, Mn and Zn in the studied plants are regulated by plant enzymatic processes; copper displayed highest bioaccumulation coefficient in the Nevinstown study area.

Plant-soil correlations between As, Cd, Pb and Zn are a reflection of element signatures typical for Zn-Pb mineralisation. These elements are known to be major constituents and trace element substitutions in sphalerite, galena and pyrite; confirming an association with sulphide minerals. Above the orebody, both soil and plant material displayed Cd, Pb and Zn anomalies even though plants accumulated much lower trace element concentrations overall. Calculated enrichment factors confirm metal anomalies in plants for Cd, Pb and Zn whereas As factors displayed very low enrichment in all investigated plants.

- 3) Clear enrichment factors were exhibited for Cd, Pb and Zn in leaves and Cd and Zn in flowers and fruit. Hawthorn displayed a strong capability for metal uptake and accumulation and the lowest impact from seasonal variations. Based on these

observations hawthorn could serve as a useful representative species for biogeochemical exploration in Ireland. The relationship between metal elements in hawthorn and soil confirmed an association with the underlying Zn-Pb mineralisation at Nevinstown.

The following groups display typical metal distributions between hawthorn and soil: Group (I) represents the major elements Ca, K, Mg and S which are often found in limestone and dolomite of the underlying bedrock geology in the Navan area. Elements from Group (I) combined with Fe and Mn are major constituents within typical soil minerals in Ireland. Group (II) illustrate common major and trace elements such as Ba, Cu, Fe, Mn, Pb, Sr and Zn while Group (III) displays As, Cd, Co and Ni which relate to the occurrence of sulphide minerals in particular sphalerite, galena and pyrite which could be associated with lithotypes hosting mineralisation (Pale Beds and Upper Dark Limestones).

- 4) Dendrochronology around the Navan deposit has revealed relatively low concentrations of As, Cd, Cu and Pb in the tree rings of beech (1918 - 2016) and oak (1858 – 2016). However, beech and oak trees accumulated more Cd, Cu and Zn above the orebody compared to background values in the control sites. Temporal analysis revealed increased accumulations of Cd, Pb and Zn prior to mining operations (1950 – 1960) than during the period of 2000 - 2010 corresponding to mining activities at Tara Mines. This is likely due to a depressed water table from water management practices in the mine.
- 5) A conceptual biogeochemical model for an Irish Type Zn-Pb deposit consists of two large natural systems: a system with Zn-Pb mineralisation displays significantly lighter Zn isotopic signatures in hawthorn leaves above the orebody whereas in an unmineralised natural system situated 2 km away from any known

mineralisation, Zn isotopes signatures in hawthorn are heavier. The lighter Zn isotopic compositions likely originate from the underlying Zn-Pb mineralisation while the basement rock signature in the control sites results in heavier Zn isotopic composition in hawthorn leaves. Copper isotopes displayed similar variations between surficial soil and plant material in both natural systems.

8.1 Implications for exploration

The widespread occurrence of hawthorn in Ireland and its ability to uptake anomalous concentrations of Pb and Zn can be used as a geochemical indicator for Irish Type Zn-Pb mineralisation. Plant geochemistry at Nevinstown successfully highlighted Zn enrichment in all investigated plant species. However, Zn alone cannot be used as a mineral exploration indicator since it is an essential element in plant metabolic processes. Thus, biogeochemistry should be conducted together with other methods such as soil geochemistry in order to recognise anomalous concentrations. Plants may penetrate through large volumes (many cubic metres of soil), and therefore provide the geochemical signature of a large volume of soil and across multiple horizons. Uncertainties may arise concerning the source of anomalies; non-traditional metal isotopes can fingerprint each metal pathway from ore, through soil and to the plant. Zinc isotopes are a useful tool in fingerprinting signatures in hawthorn at Nevinstown. Copper isotopes did not show significant variations and thus are not useful as an indicator for base metal signatures in plant systems in these environments. Nevertheless, Cu isotopes could provide more insight into fractionation processes of both, Cu and Zn isotope systems.

Based on the work presented in this study, the advantages of using biogeochemistry over traditional exploration methods are:

- low-cost exploration method;
- minimal impact on the environment;
- clear detection of Zn anomalies in hawthorn in comparison to background values.

In general, the disadvantages or limitations in biogeochemical prospecting in temperate climates are seasonal variations which can influence the overall trace element signature in plants. Furthermore, metal distribution in plants is species dependent meaning some species did not exhibit a strong peak to background contrast. Mitigating the effects of soil and air contamination remains a challenge.

8.2 Recommendations for further research

Biogeochemical cycling of Cu and Zn isotopes presents a complex natural system with a variety of processes leading to fractionation; future research should focus on testing fractionation pathways of Cu and Zn isotopes phases in a controlled laboratory environment. In addition, further research into the fractionation of stable isotopes within the plant body such as hawthorn or deciduous plants could provide a better understanding of transport mechanisms of trace elements within plants.

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APPENDIX

The content in the appendices is presented below:

APPENDIX A (p. 230):

Raw and corrected trace element data for plants and soils collected in Ireland and Sweden.

APPENDIX B (p. 321):

Case study Laver (Sweden).

APPENDIX C (p. 335):

Metal distribution maps of Nevinstown and the control sites. Trace element concentrations during spring and autumn season in seven plant species.

APPENDIX D (p. 346):

Trace element calculations of soils and plants such as: Principal Component Analysis (PCA); Enrichment Factors; Bioaccumulation Coefficient; MAD Precision and duplicate samples. Published reports for the air deposition in Ireland and the metal content of the European fertilisers.

APPENDIX E (p. 362):

Complete isotope data with calculations of the blank corrections, recoveries, analytical quality control, MAD Precision and duplicate samples.

APPENDIX A

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Table A-1. Raw data of trace element analysis (ALS) from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H1-1	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	31	285525	268511
NVT-H1-2	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	19	285473	268504
NVT-H1-3	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	43	285468	268491
NVT-H1-4	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	36	285459	268491
NVT-H1-5	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	37	285466	268484
NVT-H1-6	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	40	285519	268407
NVT-H1-6F	Nevinstown	Hawthorn	flowers	Spring	-6.71	53.66	40	285519	268407
NVT-H1-7	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	45	285522	268418
NVT-H1-8	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	43	285440	268476
NVT-H1-9	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	40	285440	268468
NVT-H1-10A	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	35	285439	268468
NVT-H1-10B*	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	35	285439	268468
NVT-H1-11	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	41	285436	268461
NVT-H1-12	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	41	285430	268457
NVT-H1-13	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	38	285451	268478
NVT-H1-13F	Nevinstown	Hawthorn	flowers	Spring	-6.71	53.66	38	285451	268478
NVT-H1-14	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	37	285453	268482
NVT-H1-15	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	43	285467	268489
NVT-H1-16	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	34	285465	268486
NVT-H1-17	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	-8	285515	268471
NVT-H1-18	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	45	285518	268522
NVT-H1-19	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	53	285523	268522
NVT-H1-20A	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	35	285529	268431
NVT-H1-20B*	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	35	285529	268431

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H1-1	<0.0002	0.006	<0.01	0.14	23	12.6	<0.01	0.002	0.46	0.186	0.02	0.023	0.74	0.007	6.15
NVT-H1-2	<0.0002	0.004	<0.01	0.2	31	133.5	0.01	0.003	1.62	1.175	0.108	0.068	2.1	0.013	9.32
NVT-H1-3	<0.0002	0.005	<0.01	0.19	28	24	<0.01	0.004	0.62	0.109	0.032	0.063	1.46	0.011	7.47
NVT-H1-4	<0.0002	0.004	<0.01	0.09	37	87.8	<0.01	0.003	1.58	0.339	0.02	0.049	2.08	0.044	13.45
NVT-H1-5	<0.0002	0.005	<0.01	0.12	25	11.9	<0.01	0.003	0.68	0.057	0.021	0.021	0.65	0.007	6.05
NVT-H1-6	<0.0002	0.007	<0.01	0.12	19	80.6	<0.01	0.003	1.55	0.683	0.02	0.026	0.34	0.009	11.65
NVT-H1-6F	<0.0002	0.007	<0.01	0.13	20	48.4	<0.01	0.002	1.09	0.722	0.025	0.033	0.35	0.009	15.85
NVT-H1-7	<0.0002	0.006	<0.01	0.17	20	66.8	<0.01	0.002	1.4	0.498	0.025	0.032	0.49	0.006	6.22
NVT-H1-8	<0.0002	0.011	<0.01	0.3	31	23.7	<0.01	0.004	0.53	0.094	0.041	0.039	2.02	0.011	8.05
NVT-H1-9	<0.0002	0.006	<0.01	0.22	26	17.9	<0.01	0.004	0.5	0.08	0.033	0.065	3.28	0.011	8.14
NVT-H1-10A	<0.0002	0.006	<0.01	0.15	24	16.2	<0.01	0.002	0.63	0.061	0.017	0.027	0.92	0.006	7.23
NVT-H1-10B*	<0.0002	0.005	<0.01	0.19	27	17.7	<0.01	0.003	0.57	0.083	0.028	0.028	1.13	0.009	7.68
NVT-H1-11	<0.0002	0.003	<0.01	0.11	27	95.2	<0.01	0.003	1.53	0.303	0.032	0.041	0.65	0.009	7.78
NVT-H1-12	0.0012	0.004	<0.01	0.24	31	18.3	<0.01	0.003	0.69	0.075	0.032	0.04	1.4	0.007	5.46
NVT-H1-13	<0.0002	0.004	<0.01	0.11	44	123	<0.01	0.002	1.54	0.316	0.026	0.054	0.48	0.008	12.35
NVT-H1-13F	<0.0002	0.004	<0.01	0.08	64	40.8	<0.01	0.002	0.68	0.374	0.02	0.095	0.24	0.011	15.1
NVT-H1-14	<0.0002	0.006	<0.01	0.16	24	12.8	<0.01	0.003	0.52	0.055	0.02	0.043	1.56	<0.005	6.94
NVT-H1-15	<0.0002	0.005	<0.01	0.18	25	13.4	<0.01	0.004	0.56	0.087	0.031	0.039	1.36	0.005	7.68
NVT-H1-16	<0.0002	0.003	<0.01	0.16	23	69.4	<0.01	0.003	1.55	0.133	0.023	0.038	0.59	0.006	7.91
NVT-H1-17	<0.0002	0.005	<0.01	0.18	28	127	<0.01	0.002	1.49	1.055	0.083	0.05	0.52	0.011	9.46
NVT-H1-18	<0.0002	0.006	<0.01	0.29	22	84.8	<0.01	0.002	1.4	0.598	0.063	0.094	0.68	0.013	4.1
NVT-H1-19	<0.0002	0.009	<0.01	0.34	28	26.1	<0.01	0.002	0.39	0.188	0.04	0.044	1.49	0.005	6.11
NVT-H1-20A	<0.0002	0.005	<0.01	0.23	26	72.9	<0.01	0.003	1.71	0.743	0.032	0.051	1.59	0.011	7.29
NVT-H1-20B*	<0.0002	0.006	<0.01	0.26	26	82	<0.01	0.003	1.63	0.67	0.032	0.036	0.88	0.007	5.58

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H1-1	46	<0.004	0.006	<0.002	0.005	<0.005	0.9	0.01	0.1	0.187	30.5	0.42	0.025	0.003	1.42
NVT-H1-2	96	0.004	0.006	<0.002	0.008	<0.005	1.53	0.5	0.1	0.277	48.5	0.33	0.096	0.002	2.97
NVT-H1-3	59	0.005	0.006	<0.002	0.006	<0.005	1.85	0.022	0.1	0.195	71.8	0.74	0.04	0.002	2.94
NVT-H1-4	73	0.004	0.009	<0.002	0.01	<0.005	1.39	0.025	0.1	0.181	31.9	0.15	0.034	<0.002	0.73
NVT-H1-5	50	0.004	0.007	<0.002	0.005	<0.005	1.29	0.014	<0.1	0.209	55.9	0.78	0.02	0.002	1.24
NVT-H1-6	47	0.004	0.008	<0.002	0.005	<0.005	1.48	0.026	0.1	0.161	17.8	0.32	0.069	<0.002	0.79
NVT-H1-6F	47	<0.004	0.007	<0.002	0.005	<0.005	1.9	0.018	0.1	0.158	18.1	0.33	0.06	<0.002	0.93
NVT-H1-7	45	0.004	0.01	0.002	0.007	<0.005	1.54	0.029	0.1	0.176	29.8	0.4	0.07	<0.002	0.68
NVT-H1-8	81	0.007	0.008	<0.002	0.007	<0.005	1.44	0.026	0.1	0.186	97.1	0.52	0.036	0.002	4.08
NVT-H1-9	179	0.008	0.006	<0.002	0.007	<0.005	1.41	0.02	0.1	0.184	83	0.64	0.037	0.003	3.34
NVT-H1-10A	57	0.004	<0.005	<0.002	0.004	<0.005	1.07	0.012	<0.1	0.203	73.2	0.68	0.036	0.002	2.24
NVT-H1-10B*	64	0.005	0.008	<0.002	0.005	<0.005	1.09	0.018	0.1	0.201	71.5	0.61	0.035	0.002	2.58
NVT-H1-11	70	0.004	0.007	<0.002	0.006	<0.005	1.17	0.048	<0.1	0.233	37	0.09	0.026	<0.002	1.24
NVT-H1-12	63	0.006	0.005	<0.002	0.007	<0.005	1.32	0.018	<0.1	0.214	24.4	0.82	0.036	0.003	1.45
NVT-H1-13	56	0.004	0.01	<0.002	0.004	<0.005	1.61	0.035	<0.1	0.19	37.2	0.31	0.032	<0.002	0.95
NVT-H1-13F	43	<0.004	0.005	<0.002	0.004	<0.005	1.5	0.014	<0.1	0.161	22.4	0.2	0.037	<0.002	1.16
NVT-H1-14	56	<0.004	0.007	<0.002	0.003	<0.005	1.42	0.01	<0.1	0.198	53.4	0.68	0.026	0.002	1.93
NVT-H1-15	64	0.005	0.007	<0.002	0.005	<0.005	1.8	0.019	<0.1	0.189	81.5	0.5	0.042	0.002	2.65
NVT-H1-16	59	0.004	0.008	<0.002	0.006	<0.005	1.52	0.018	0.1	0.247	38.3	0.36	0.035	<0.002	0.68
NVT-H1-17	58	<0.004	0.008	<0.002	0.007	<0.005	1.5	0.378	0.1	0.252	47.2	0.21	0.086	<0.002	2.4
NVT-H1-18	54	0.006	0.014	<0.002	0.009	<0.005	1.06	0.048	0.1	0.185	15.3	0.23	0.068	0.002	1
NVT-H1-19	72	0.006	0.007	<0.002	0.006	<0.005	1.25	0.026	0.1	0.184	60.8	0.92	0.063	0.003	1.92
NVT-H1-20A	88	0.006	0.009	<0.002	0.008	<0.005	1.8	0.03	0.1	0.214	28.5	0.48	0.081	0.002	1.13
NVT-H1-20B*	67	0.004	0.009	<0.002	0.009	<0.005	1.69	0.027	0.1	0.204	40.5	0.39	0.063	0.002	0.88

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H1-1	0.241	2.5	<0.001	<0.001	2.4	0.001	0.18	0.06	0.05	0.495	0.02	6.7	0.002	0.03	0.003	<0.001
NVT-H1-2	0.33	3.21	<0.001	<0.001	4.16	<0.001	0.18	0.09	0.16	0.094	0.03	31.7	0.001	<0.02	0.003	<0.001
NVT-H1-3	0.264	3.47	<0.001	<0.001	2.78	<0.001	0.16	0.08	0.12	0.175	0.03	7.03	0.002	<0.02	0.004	<0.001
NVT-H1-4	0.358	1.47	0.001	<0.001	7.91	<0.001	0.24	0.05	0.19	0.624	0.02	56.1	0.001	<0.02	0.002	<0.001
NVT-H1-5	0.264	1.69	<0.001	<0.001	2.29	<0.001	0.22	0.05	0.17	0.411	0.02	7.32	0.001	0.02	0.002	<0.001
NVT-H1-6	0.252	1.75	<0.001	<0.001	4.08	<0.001	0.19	0.06	0.23	0.353	0.02	21.1	0.001	<0.02	0.003	<0.001
NVT-H1-6F	0.24	2.15	<0.001	<0.001	6.51	<0.001	0.14	0.06	0.23	0.098	0.02	14.35	0.001	0.02	0.004	<0.001
NVT-H1-7	0.241	2.69	<0.001	<0.001	2.67	<0.001	0.18	0.06	0.23	0.124	0.02	19.05	0.001	0.02	0.002	<0.001
NVT-H1-8	0.285	4.01	<0.001	<0.001	3.69	<0.001	0.19	0.11	0.2	0.151	0.03	8.31	0.001	0.02	0.004	<0.001
NVT-H1-9	0.287	3.01	<0.001	<0.001	3.96	<0.001	0.19	0.08	0.18	0.158	0.03	7.66	0.001	0.02	0.003	<0.001
NVT-H1-10A	0.255	1.86	<0.001	<0.001	3.28	<0.001	0.23	0.05	0.17	0.177	0.02	8.88	0.001	0.03	0.002	<0.001
NVT-H1-10B*	0.291	2.16	<0.001	<0.001	4.26	<0.001	0.24	0.07	0.21	0.173	0.02	8.01	0.001	0.02	0.003	<0.001
NVT-H1-11	0.35	1.53	<0.001	<0.001	4.09	<0.001	0.21	0.05	0.21	0.092	0.02	33.2	0.001	0.02	0.002	<0.001
NVT-H1-12	0.239	3.36	<0.001	<0.001	2.46	<0.001	0.19	0.09	0.18	0.15	0.03	11.4	0.001	0.02	0.004	<0.001
NVT-H1-13	0.444	1.6	<0.001	<0.001	2.92	<0.001	0.2	0.04	0.2	0.277	0.03	29.2	<0.001	<0.02	0.002	<0.001
NVT-H1-13F	0.309	1.06	<0.001	<0.001	5.26	<0.001	0.15	0.04	0.05	0.243	0.02	10.85	0.002	<0.02	0.002	<0.001
NVT-H1-14	0.32	2.22	<0.001	<0.001	2.45	<0.001	0.22	0.06	0.16	0.33	0.02	6.25	0.001	<0.02	0.003	<0.001
NVT-H1-15	0.31	3.23	<0.001	<0.001	4.53	<0.001	0.2	0.09	0.19	0.249	0.03	4.3	0.001	<0.02	0.003	<0.001
NVT-H1-16	0.344	1.76	<0.001	<0.001	2.47	<0.001	0.21	0.05	0.2	0.134	0.02	18.1	<0.001	0.02	0.002	<0.001
NVT-H1-17	0.322	2.58	<0.001	<0.001	4.37	<0.001	0.16	0.08	0.14	0.07	0.02	30	0.001	<0.02	0.002	<0.001
NVT-H1-18	0.213	4.49	<0.001	<0.001	2.47	<0.001	0.19	0.12	0.19	0.486	0.02	28	<0.001	<0.02	0.004	<0.001
NVT-H1-19	0.278	4.97	<0.001	<0.001	1.97	<0.001	0.17	0.12	0.14	0.061	0.02	6.63	0.001	<0.02	0.004	<0.001
NVT-H1-20A	0.26	3.64	<0.001	<0.001	3.39	<0.001	0.19	0.09	0.16	0.1	0.03	23.7	<0.001	<0.02	0.003	<0.001
NVT-H1-20B*	0.251	3.87	<0.001	<0.001	2.24	<0.001	0.21	0.12	0.17	0.08	0.02	21.4	<0.001	<0.02	0.003	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H1-1	0.012	<0.005	0.06	0.01	0.006	82.9	0.02
NVT-H1-2	0.04	<0.005	0.11	0.01	0.376	131.5	0.02
NVT-H1-3	0.014	<0.005	0.1	0.01	0.013	63	0.02
NVT-H1-4	0.016	<0.005	0.08	0.01	0.013	46	0.02
NVT-H1-5	0.009	<0.005	0.09	0.01	0.013	46.9	0.02
NVT-H1-6	0.033	<0.005	0.1	0.01	0.013	99.1	0.02
NVT-H1-6F	0.025	<0.005	0.09	0.01	0.012	67.4	0.02
NVT-H1-7	0.031	<0.005	0.09	0.01	0.017	89.2	0.02
NVT-H1-8	0.014	<0.005	0.14	0.01	0.014	61.7	0.03
NVT-H1-9	0.014	<0.005	0.12	0.01	0.015	57.7	0.02
NVT-H1-10A	0.008	<0.005	0.1	0.01	0.009	48.8	0.02
NVT-H1-10B*	0.009	<0.005	0.11	0.01	0.011	51.5	0.03
NVT-H1-11	0.008	<0.005	0.08	0.01	0.031	61.6	0.02
NVT-H1-12	0.013	<0.005	0.13	0.01	0.015	52.5	0.03
NVT-H1-13	0.007	<0.005	0.08	0.01	0.017	90.7	<0.02
NVT-H1-13F	0.004	<0.005	0.07	0.01	0.011	49.6	<0.02
NVT-H1-14	0.009	<0.005	0.11	0.01	0.008	47.8	<0.02
NVT-H1-15	0.013	<0.005	0.11	0.01	0.013	64.2	0.02
NVT-H1-16	0.018	<0.005	0.08	0.01	0.009	58.3	0.02
NVT-H1-17	0.033	<0.005	0.08	0.01	0.283	107	0.02
NVT-H1-18	0.018	<0.005	0.09	0.01	0.031	99.6	0.02
NVT-H1-19	0.022	<0.005	0.11	0.01	0.018	92.6	0.02
NVT-H1-20A	0.038	<0.005	0.1	0.01	0.018	102	0.03
NVT-H1-20B*	0.047	<0.005	0.09	0.01	0.016	112.5	0.03

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H1-21	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	40	285519	268425
NVT-H1-32	Nevinstown	Oak	leaves	Spring	-6.71	53.66	42	285482	268501
NVT-H1-33	Nevinstown	Ash	leaves	Spring	-6.71	53.66	44	285523	268522
NVT-H1-34	Nevinstown	Ash	leaves	Spring	-6.71	53.66	46	285488	268508
NVT-H1-39	Nevinstown	Ash	leaves	Spring	-6.71	53.66	45	285421	268459
NVT-H2-22	Nevinstown	Beech	leaves	Spring	-6.71	53.66	49	285512	268501
NVT-H2-23	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	32	285565	268500
NVT-H2-24	Nevinstown	Beech	leaves	Spring	-6.71	53.66	50	285522	268509
NVT-H2-25	Nevinstown	Beech	leaves	Spring	-6.71	53.66	47	285600	268473
NVT-H2-26	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	46	285580	268493
NVT-H2-27	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	49	285576	268489
NVT-H2-28	Nevinstown	Beech	leaves	Spring	-6.71	53.66	44	285572	268504
NVT-H2-29	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	46	285588	268504
NVT-H2-30A	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	51	285626	268457
NVT-H2-30B*	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	51	285626	268457
NVT-H2-35	Nevinstown	Beech	leaves	Spring	-6.71	53.66	56	285571	268508
NVT-H2-36	Nevinstown	Ash	leaves	Spring	-6.71	53.66	49	285618	268494
NVT-H2-37	Nevinstown	Blackberry	leaves	Spring	-6.71	53.66	52	285655	268483
NVT-H2-38	Nevinstown	Blackberry	leaves	Spring	-6.70	53.66	52	285732	268514
NVT-H3-1	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	2	285612	268586
NVT-H3-2	Nevinstown	Ash	leaves	Spring	-6.71	53.66	44	285634	268578
NVT-H3-3	Nevinstown	Ash	leaves	Spring	-6.71	53.66	67	285625	268574
NVT-H3-4	Nevinstown	Hawthorn	leaves	Spring	-6.70	53.66	51	285673	268597
NVT-H3-6	Nevinstown	Sycamore	leaves	Spring	-6.70	53.66	45	285791	268627

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H1-21	<0.0002	0.005	<0.01	0.25	25	14.9	<0.01	0.002	0.6	0.093	0.036	0.08	4.32	0.022	5.68
NVT-H1-32	<0.0002	0.101	<0.01	0.13	22	16.1	<0.01	0.001	0.39	0.063	0.031	0.038	0.45	0.065	15.45
NVT-H1-33	<0.0002	0.004	<0.01	0.2	24	16.6	<0.01	0.002	0.84	0.059	0.029	0.042	0.59	<0.005	10.4
NVT-H1-34	<0.0002	0.004	<0.01	0.16	22	18.8	<0.01	0.002	0.9	0.045	0.026	0.045	1.03	<0.005	19.25
NVT-H1-39	<0.0002	0.002	<0.01	0.05	12	14.4	<0.01	0.003	1.47	0.024	0.017	0.02	0.63	<0.005	10.15
NVT-H2-22	<0.0002	0.04	<0.01	0.38	19	33	<0.01	0.002	0.38	0.857	0.04	0.046	1.57	0.009	18.25
NVT-H2-23	<0.0002	0.006	<0.01	0.42	20	144	<0.01	0.003	1.42	1.03	0.103	0.06	1.11	0.012	7.47
NVT-H2-24	<0.0002	0.027	<0.01	0.15	19	29.1	<0.01	0.002	0.65	0.325	0.021	0.04	1.43	0.014	10.1
NVT-H2-25	<0.0002	0.045	<0.01	0.19	18	48.4	<0.01	0.002	0.77	0.328	0.034	0.051	1.12	0.006	12.85
NVT-H2-26	<0.0002	0.002	<0.01	0.16	19	71.1	<0.01	0.002	1.27	0.405	0.06	0.059	0.46	<0.005	4.24
NVT-H2-27	<0.0002	0.004	<0.01	0.45	22	72.9	<0.01	0.002	1.21	0.679	0.077	0.058	0.78	0.01	7.1
NVT-H2-28	<0.0002	0.026	<0.01	0.12	28	39.2	<0.01	0.003	0.62	0.231	0.018	0.038	1.14	0.011	15.05
NVT-H2-29	<0.0002	0.003	<0.01	0.19	17	57.4	<0.01	0.002	1.27	0.365	0.044	0.099	0.39	0.008	6.3
NVT-H2-30A	<0.0002	0.008	<0.01	0.36	21	49.9	<0.01	0.003	0.46	0.18	0.069	0.046	1.14	0.009	6.3
NVT-H2-30B*	<0.0002	0.009	<0.01	0.17	21	27.4	<0.01	0.003	0.55	0.172	0.044	0.03	0.84	0.005	5.11
NVT-H2-35	0.0003	0.03	<0.01	0.09	25	29.1	<0.01	0.001	0.52	0.242	0.017	0.037	2.75	0.008	24.1
NVT-H2-36	<0.0002	0.01	<0.01	0.25	28	22	<0.01	0.001	0.82	0.076	0.041	0.055	0.94	0.007	19.75
NVT-H2-37	<0.0002	0.005	<0.01	0.39	28	36.1	<0.01	0.002	0.7	0.214	0.047	0.044	0.98	0.011	6.61
NVT-H2-38	<0.0002	0.008	<0.01	0.13	24	68.2	<0.01	0.001	0.67	0.205	0.028	0.027	1.01	0.005	6.14
NVT-H3-1	<0.0002	0.003	<0.01	0.08	21	14.9	<0.01	0.001	0.6	0.075	0.017	0.014	0.49	0.005	9.82
NVT-H3-2	<0.0002	0.004	<0.01	0.08	16	12.1	<0.01	0.001	0.92	0.02	0.028	0.028	0.56	<0.005	23.6
NVT-H3-3	<0.0002	0.002	<0.01	0.08	19	18.6	<0.01	0.002	0.77	0.024	0.024	0.02	0.26	0.008	24.3
NVT-H3-4	<0.0002	0.002	<0.01	0.2	29	64.6	<0.01	0.002	1.25	0.401	0.069	0.051	0.45	0.008	8.73
NVT-H3-6	<0.0002	0.003	<0.01	0.2	25	20.5	<0.01	0.003	0.94	0.147	0.031	0.032	0.54	0.012	9.44

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (%)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H1-21	100	0.006	0.011	<0.002	0.007	<0.005	1.39	0.02	0.1	0.158	52.1	0.95	0.036	0.004	3.43
NVT-H1-32	66	0.004	0.006	<0.002	0.01	<0.005	1.72	0.036	0.1	0.156	160.5	0.08	0.033	<0.002	2.71
NVT-H1-33	60	0.005	0.016	<0.002	0.01	<0.005	1.26	0.02	<0.1	0.21	14.3	0.44	0.039	<0.002	1.8
NVT-H1-34	83	<0.004	0.011	<0.002	0.009	<0.005	1.91	0.027	<0.1	0.211	22.6	0.37	0.023	<0.002	5.79
NVT-H1-39	63	<0.004	0.008	<0.002	0.004	<0.005	0.87	0.031	<0.1	0.252	33.8	0.28	0.024	<0.002	1.95
NVT-H2-22	62	0.004	0.007	<0.002	0.007	<0.005	1.35	0.037	<0.1	0.133	69.5	0.35	0.048	0.002	3.33
NVT-H2-23	86	0.009	0.012	<0.002	0.013	<0.005	1.38	0.111	0.1	0.229	33.8	0.54	0.108	0.002	1.68
NVT-H2-24	60	<0.004	<0.005	<0.002	0.005	<0.005	1.23	0.016	<0.1	0.126	51.5	0.41	0.06	0.002	1.38
NVT-H2-25	70	0.004	0.005	<0.002	0.009	<0.005	1.09	0.064	<0.1	0.156	122	0.22	0.073	0.002	2.39
NVT-H2-26	56	<0.004	0.006	<0.002	0.011	<0.005	1.91	0.185	0.1	0.221	27.8	0.18	0.067	<0.002	0.85
NVT-H2-27	77	0.009	0.006	<0.002	0.016	<0.005	1.7	0.097	0.1	0.219	17.9	0.21	0.104	0.003	0.85
NVT-H2-28	60	<0.004	0.005	<0.002	0.01	<0.005	1.19	0.02	<0.1	0.117	46.6	0.35	0.045	0.002	2.11
NVT-H2-29	58	0.005	0.008	<0.002	0.011	<0.005	1.48	0.041	0.1	0.192	50.4	0.15	0.059	0.002	0.83
NVT-H2-30A	85	0.009	0.008	<0.002	0.01	<0.005	1.34	0.076	0.1	0.149	107	0.39	0.095	0.003	2.27
NVT-H2-30B*	63	0.007	0.008	<0.002	0.01	<0.005	1.05	0.04	<0.1	0.187	103	0.43	0.041	0.003	1.9
NVT-H2-35	64	<0.004	<0.005	<0.002	0.008	<0.005	1.43	0.022	<0.1	0.122	32.7	0.29	0.022	<0.002	2.14
NVT-H2-36	96	0.004	<0.005	0.002	0.009	<0.005	1.79	0.061	<0.1	0.204	23.4	0.69	0.037	0.003	4.21
NVT-H2-37	78	0.006	0.005	<0.002	0.007	<0.005	1.23	0.033	0.1	0.205	73.3	0.7	0.076	0.002	1.64
NVT-H2-38	63	<0.004	0.005	<0.002	0.006	<0.005	1.49	0.027	<0.1	0.181	71.8	0.31	0.051	0.002	1.42
NVT-H3-1	62	<0.004	0.005	<0.002	0.005	<0.005	1.67	0.016	<0.1	0.138	67.5	0.25	0.012	<0.002	1.22
NVT-H3-2	82	<0.004	<0.005	<0.002	0.005	<0.005	1.91	0.026	<0.1	0.164	19.6	0.54	0.01	<0.002	6.45
NVT-H3-3	78	<0.004	0.006	<0.002	0.007	<0.005	1.61	0.023	<0.1	0.164	17.8	0.72	0.017	0.002	3.27
NVT-H3-4	69	0.005	0.008	<0.002	0.02	<0.005	1.69	0.051	0.1	0.225	15.6	0.24	0.083	0.002	0.73
NVT-H3-6	69	0.004	0.006	<0.002	0.01	<0.005	1.77	0.015	<0.1	0.166	70.9	1.08	0.035	0.002	1.38

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H1-21	0.251	3.7	<0.001	<0.001	4.04	<0.001	0.24	0.1	0.15	0.244	0.03	5.82	<0.001	<0.02	0.004	<0.001
NVT-H1-32	0.411	2.11	<0.001	<0.001	12.35	<0.001	0.21	0.06	0.18	0.293	0.02	3.57	<0.001	<0.02	0.003	<0.001
NVT-H1-33	0.458	2.47	<0.001	<0.001	3.01	<0.001	0.28	0.08	0.19	0.987	0.02	10.5	<0.001	<0.02	0.003	<0.001
NVT-H1-34	0.616	1.75	<0.001	<0.001	3.57	<0.001	0.43	0.06	0.16	0.542	0.02	10.65	<0.001	<0.02	0.002	<0.001
NVT-H1-39	0.512	0.48	<0.001	<0.001	2.35	<0.001	0.31	0.02	0.17	0.152	0.02	19.65	<0.001	0.02	<0.002	<0.001
NVT-H2-22	0.502	4.58	<0.001	<0.001	4.38	<0.001	0.22	0.12	0.13	0.164	0.02	6.31	<0.001	0.02	0.004	<0.001
NVT-H2-23	0.291	6.81	<0.001	<0.001	5.56	<0.001	0.16	0.17	0.13	0.07	0.02	33.3	<0.001	<0.02	0.006	<0.001
NVT-H2-24	0.4	2.37	<0.001	<0.001	4.17	<0.001	0.21	0.06	0.1	0.098	<0.01	7.97	0.001	<0.02	0.002	<0.001
NVT-H2-25	0.383	2.64	0.001	<0.001	2.58	<0.001	0.21	0.08	0.11	0.042	<0.01	10.45	<0.001	<0.02	0.003	<0.001
NVT-H2-26	0.216	2.28	<0.001	<0.001	2.49	<0.001	0.17	0.06	0.13	0.018	<0.01	22.2	0.001	<0.02	0.003	<0.001
NVT-H2-27	0.263	6.78	<0.001	<0.001	2.72	<0.001	0.19	0.17	0.11	0.044	0.01	20.2	0.002	<0.02	0.007	<0.001
NVT-H2-28	0.402	1.89	<0.001	<0.001	5.46	<0.001	0.22	0.05	0.15	0.09	<0.01	8.29	0.001	<0.02	0.002	<0.001
NVT-H2-29	0.267	2.42	<0.001	<0.001	3.48	<0.001	0.19	0.07	0.11	0.226	<0.01	22.5	0.001	<0.02	0.003	<0.001
NVT-H2-30A	0.241	5.37	<0.001	<0.001	1.97	<0.001	0.18	0.13	0.1	0.013	0.03	10	0.002	<0.02	0.005	<0.001
NVT-H2-30B*	0.249	3.37	<0.001	<0.001	3.81	<0.001	0.18	0.08	0.09	0.029	0.01	8.94	0.001	0.02	0.003	<0.001
NVT-H2-35	0.45	1.35	<0.001	<0.001	3.6	<0.001	0.23	0.04	0.08	0.068	<0.01	7.17	<0.001	<0.02	0.002	<0.001
NVT-H2-36	0.694	3.6	<0.001	<0.001	5.96	<0.001	0.38	0.1	0.12	0.099	<0.01	9.61	<0.001	<0.02	0.003	<0.001
NVT-H2-37	0.251	6.46	<0.001	<0.001	3.81	<0.001	0.18	0.13	0.1	0.067	0.01	11.65	<0.001	<0.02	0.004	<0.001
NVT-H2-38	0.243	3.02	<0.001	<0.001	1.11	<0.001	0.18	0.07	0.1	0.033	<0.01	12.65	<0.001	<0.02	0.002	<0.001
NVT-H3-1	0.433	0.84	<0.001	<0.001	4.43	<0.001	0.28	0.03	0.14	0.159	<0.01	8.51	<0.001	<0.02	<0.002	<0.001
NVT-H3-2	0.72	0.98	<0.001	<0.001	5.55	<0.001	0.39	0.03	0.14	0.217	<0.01	10.25	<0.001	<0.02	<0.002	<0.001
NVT-H3-3	0.659	0.76	<0.001	<0.001	6.19	<0.001	0.28	0.03	0.15	0.146	<0.01	9.93	0.001	<0.02	<0.002	<0.001
NVT-H3-4	0.275	2.4	<0.001	<0.001	2.77	<0.001	0.16	0.08	0.12	0.182	0.01	21	<0.001	<0.02	0.008	<0.001
NVT-H3-6	0.432	3.47	<0.001	<0.001	7.49	0.002	0.31	0.08	0.16	0.049	<0.01	11.85	<0.001	<0.02	0.003	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H1-21	0.016	<0.005	0.12	0.01	0.013	66.7	0.03
NVT-H1-32	0.277	<0.005	0.07	0.01	0.019	50.1	<0.02
NVT-H1-33	0.009	<0.005	0.07	0.01	0.011	169.5	0.02
NVT-H1-34	0.016	<0.005	0.08	0.01	0.011	119	<0.02
NVT-H1-39	0.003	<0.005	0.06	0.01	0.011	52.5	<0.02
NVT-H2-22	0.018	<0.005	0.08	0.01	0.019	93.7	0.02
NVT-H2-23	0.032	<0.005	0.12	0.01	0.069	131.5	0.06
NVT-H2-24	0.011	<0.005	0.06	0.01	0.01	62.2	0.02
NVT-H2-25	0.01	<0.005	0.07	0.01	0.026	69.2	0.02
NVT-H2-26	0.033	<0.005	0.09	0.01	0.119	67.3	0.06
NVT-H2-27	0.044	<0.005	0.12	0.01	0.051	97.8	0.03
NVT-H2-28	0.006	<0.005	0.08	0.04	0.011	57.2	<0.02
NVT-H2-29	0.011	<0.005	0.08	0.01	0.03	74.8	0.03
NVT-H2-30A	0.016	<0.005	0.13	0.01	0.041	65.4	0.04
NVT-H2-30B*	0.01	<0.005	0.1	0.01	0.017	52.8	0.02
NVT-H2-35	0.007	<0.005	0.07	0.01	0.011	65.2	0.03
NVT-H2-36	0.024	<0.005	0.09	0.02	0.034	81.9	0.02
NVT-H2-37	0.019	<0.005	0.11	0.01	0.014	74.8	0.03
NVT-H2-38	0.009	<0.005	0.09	0.01	0.009	81.2	0.02
NVT-H3-1	0.003	<0.005	0.06	0.01	0.008	62.1	<0.02
NVT-H3-2	0.004	<0.005	0.06	0.01	0.012	78.5	0.02
NVT-H3-3	0.003	<0.005	0.05	<0.01	0.009	91	<0.02
NVT-H3-4	0.013	<0.005	0.12	0.01	0.03	48.7	0.03
NVT-H3-6	0.011	<0.005	0.07	0.02	0.014	65.8	0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H3-7	Nevinstown	Beech	leaves	Spring	-6.70	53.66	52	285796	268623
NVT-H3-8	Nevinstown	Ash	leaves	Spring	-6.70	53.66	45	285770	268595
NVT-H3-9	Nevinstown	Ash	leaves	Spring	-6.70	53.66	50	285745	268554
NVT-H3-10A	Nevinstown	Ash	leaves	Spring	-6.70	53.66	53	285703	268507
NVT-H3-10B*	Nevinstown	Ash	leaves	Spring	-6.70	53.66	53	285703	268507
NVT-H4-1	Nevinstown	Blackberry	leaves	Spring	-6.70	53.66	34	285743	268387
NVT-H4-2	Nevinstown	Hawthorn	leaves	Spring	-6.70	53.66	51	285736	268366
NVT-H4-3	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	48	285656	268298
NVT-H4-3F	Nevinstown	Hawthorn	flowers	Spring	-6.71	53.66	48	285656	268298
NVT-H4-4	Nevinstown	Beech	leaves	Spring	-6.70	53.66	53	285752	268558
NVT-H4-5	Nevinstown	Sycamore	leaves	Spring	-6.70	53.66	53	285826	268576
NVT-H4-6	Nevinstown	Sycamore	leaves	Spring	-6.70	53.66	53	285812	268534
NVT-H4-7	Nevinstown	Sycamore	leaves	Spring	-6.70	53.66	63	285833	268611
NVT-H4-8	Nevinstown	Sycamore	leaves	Spring	-6.70	53.66	53	285822	268620
NVT-H4-9	Nevinstown	Hawthorn	leaves	Spring	-6.70	53.66	51	285780	268447
NVT-H4-10A	Nevinstown	Hawthorn	leaves	Spring	-6.70	53.66	50	285758	268339
NVT-H4-10B*	Nevinstown	Hawthorn	leaves	Spring	-6.70	53.66	50	285758	268339
NVT-H4-11	Nevinstown	Ash	leaves	Spring	-6.70	53.66	43	285812	268520
NVT-H4-12	Nevinstown	Ash	leaves	Spring	-6.71	53.66	45	285593	268304
NVT-H4-14	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	41	285601	268289
NVT-H4-15	Nevinstown	Hawthorn	leaves	Spring	-6.71	53.66	46	285612	268306
NVT-H4-16	Nevinstown	Poplar	leaves	Spring	-6.71	53.66	48	285583	268380
NVT-H4-17	Nevinstown	Poplar	leaves	Spring	-6.71	53.66	48	285574	268385
NVT-H4-18	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	52	285498	268380

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H3-7	<0.0002	0.018	<0.01	0.1	22	46	<0.01	<0.001	1.02	0.356	0.013	0.028	0.89	0.012	15.25
NVT-H3-8	<0.0002	0.002	<0.01	0.28	17	23	0.01	0.001	0.94	0.059	0.081	0.046	1.09	0.016	14.35
NVT-H3-9	<0.0002	0.002	<0.01	0.19	19	23.5	<0.01	0.001	0.86	0.056	0.036	0.068	1.42	0.009	16.4
NVT-H3-10A	<0.0002	0.008	<0.01	0.31	24	32.1	<0.01	0.002	1.11	0.083	0.058	0.06	1.19	0.011	18.1
NVT-H3-10B*	<0.0002	0.011	<0.01	0.32	23	48.7	<0.01	0.003	1.45	0.099	0.064	0.054	1.21	0.009	16.4
NVT-H4-1	<0.0002	0.006	<0.01	0.28	18	34.3	0.01	0.003	0.56	0.218	0.078	0.036	0.95	0.005	6.28
NVT-H4-2	<0.0002	0.004	<0.01	0.28	17	246	0.02	0.001	1.65	0.736	0.168	0.129	0.28	0.005	5.06
NVT-H4-3	<0.0002	0.004	<0.01	0.17	21	149.5	<0.01	0.002	1.32	0.532	0.043	0.044	0.36	0.033	13
NVT-H4-3F	<0.0002	0.005	<0.01	0.22	30	79.9	<0.01	0.002	0.77	0.851	0.028	0.047	0.58	0.056	19.15
NVT-H4-4	<0.0002	0.034	<0.01	0.08	20	35.6	<0.01	0.001	0.96	0.175	0.035	0.021	0.8	<0.005	8.73
NVT-H4-5	<0.0002	0.002	<0.01	0.17	22	25.7	<0.01	0.002	0.8	0.181	0.089	0.048	0.75	0.007	10.55
NVT-H4-6	<0.0002	0.003	<0.01	0.24	20	22.2	<0.01	0.002	0.58	0.169	0.035	0.04	1.08	0.007	11.65
NVT-H4-7	<0.0002	0.002	<0.01	0.06	19	16.9	<0.01	0.001	1.12	0.087	0.026	0.022	0.58	0.011	8.69
NVT-H4-8	<0.0002	0.003	<0.01	0.09	22	20.2	<0.01	0.001	1.09	0.131	0.024	0.03	0.76	0.008	10.4
NVT-H4-9	<0.0002	0.004	<0.01	0.26	21	184	0.01	0.001	1.55	0.362	0.241	0.111	0.45	0.005	7.27
NVT-H4-10A	<0.0002	0.001	<0.01	0.08	15	163.5	<0.01	0.001	1.75	0.116	0.026	0.066	0.37	0.006	4.14
NVT-H4-10B*	<0.0002	0.001	<0.01	0.13	14	178	<0.01	0.002	1.84	0.126	0.031	0.074	0.4	0.01	4.48
NVT-H4-11	<0.0002	0.003	<0.01	0.27	26	43.2	<0.01	0.002	1.46	0.077	0.086	0.077	1.22	0.008	17.8
NVT-H4-12	<0.0002	0.014	<0.01	0.11	15	55.5	0.01	0.001	1.14	0.066	0.052	0.031	0.65	0.008	14.25
NVT-H4-14	<0.0002	0.002	<0.01	0.17	21	123.5	<0.01	0.003	1.99	0.182	0.031	0.033	0.62	0.008	5.75
NVT-H4-15	<0.0002	0.002	<0.01	0.13	15	130	<0.01	0.001	1.35	0.327	0.025	0.041	0.78	0.009	4.86
NVT-H4-16	<0.0002	0.003	<0.01	0.43	25	77.7	<0.01	0.002	0.83	4.14	0.038	0.119	1.73	0.013	3.54
NVT-H4-17	0.0002	0.004	<0.01	0.38	29	101	<0.01	0.002	1.07	4.53	0.051	0.09	1.64	0.013	4.7
NVT-H4-18	<0.0002	0.007	<0.01	0.13	27	12.9	<0.01	0.001	1.5	0.135	0.013	0.027	1.06	0.053	9.93

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H3-7	62	<0.004	<0.005	<0.002	0.007	<0.005	1.14	0.009	<0.1	0.148	116.5	0.79	0.031	0.002	2.97
NVT-H3-8	84	0.005	0.008	<0.002	0.008	<0.005	1.81	0.085	0.1	0.259	31.8	0.34	0.113	0.002	8.21
NVT-H3-9	103	0.005	0.008	<0.002	0.014	<0.005	1.82	0.024	<0.1	0.2	30.5	0.57	0.014	0.003	2.89
NVT-H3-10A	95	0.006	0.007	<0.002	0.013	<0.005	1.86	0.098	0.1	0.241	29.5	0.91	0.099	0.002	3.36
NVT-H3-10B*	91	0.007	0.009	<0.002	0.015	<0.005	1.48	0.135	0.1	0.272	37.1	0.94	0.102	0.002	3.34
NVT-H4-1	64	0.005	0.007	<0.002	0.007	<0.005	1.49	0.167	<0.1	0.177	154.5	0.28	0.077	0.002	4.26
NVT-H4-2	59	0.005	0.009	<0.002	0.009	<0.005	1.23	0.355	0.1	0.255	66.7	0.15	0.122	0.002	3.84
NVT-H4-3	68	0.005	0.009	<0.002	0.012	<0.005	1.19	0.042	<0.1	0.19	25.4	0.45	0.067	<0.002	0.76
NVT-H4-3F	59	<0.004	0.008	<0.002	0.006	<0.005	1.72	0.019	<0.1	0.162	14.7	0.5	0.046	<0.002	1.17
NVT-H4-4	48	<0.004	0.006	<0.002	0.006	<0.005	0.94	0.05	<0.1	0.137	105.5	0.2	0.065	<0.002	2.3
NVT-H4-5	61	<0.004	<0.005	<0.002	0.006	<0.005	2.03	0.118	<0.1	0.145	117.5	0.3	0.059	<0.002	2.06
NVT-H4-6	77	0.004	<0.005	<0.002	0.006	<0.005	2.24	0.039	<0.1	0.149	71.8	0.57	0.065	<0.002	1.81
NVT-H4-7	51	<0.004	<0.005	<0.002	0.004	<0.005	1.38	0.03	<0.1	0.163	66	0.45	0.013	<0.002	1.26
NVT-H4-8	63	<0.004	<0.005	<0.002	0.005	<0.005	1.55	0.022	<0.1	0.209	54.3	0.88	0.02	<0.002	2.06
NVT-H4-9	63	0.005	0.008	0.002	0.012	<0.005	1.35	0.554	0.1	0.227	59.7	0.16	0.125	<0.002	2.27
NVT-H4-10A	51	<0.004	0.006	<0.002	0.006	<0.005	1.1	0.048	<0.1	0.255	24.4	2.05	0.024	<0.002	0.5
NVT-H4-10B*	62	0.004	0.009	<0.002	0.007	<0.005	1.06	0.044	<0.1	0.261	24.6	1.78	0.03	<0.002	0.56
NVT-H4-11	81	0.004	0.007	0.002	0.017	<0.005	1.66	0.162	<0.1	0.247	42.9	0.57	0.101	<0.002	3.9
NVT-H4-12	59	<0.004	<0.005	<0.002	0.004	<0.005	1.3	0.079	<0.1	0.224	43.1	0.41	0.041	<0.002	4.23
NVT-H4-14	54	<0.004	0.006	<0.002	0.011	<0.005	1.16	0.03	0.1	0.223	27.2	0.35	0.044	<0.002	0.46
NVT-H4-15	54	0.004	0.006	<0.002	0.009	<0.005	1.14	0.022	<0.1	0.172	20.2	0.35	0.035	<0.002	0.69
NVT-H4-16	66	0.006	0.008	<0.002	0.009	<0.005	1.29	0.025	0.1	0.184	28.6	0.24	0.099	<0.002	2.25
NVT-H4-17	66	0.006	0.006	<0.002	0.007	<0.005	1.56	0.062	0.1	0.186	29.9	0.25	0.138	0.003	2.91
NVT-H4-18	60	<0.004	0.007	<0.002	0.007	<0.005	2.22	0.01	<0.1	0.128	80.3	0.51	0.041	<0.002	1.09

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H3-7	0.402	1.16	<0.001	<0.001	8.64	<0.001	0.18	0.03	0.14	0.071	<0.01	14.45	<0.001	<0.02	<0.002	<0.001
NVT-H3-8	0.578	3.54	<0.001	<0.001	11.95	<0.001	0.39	0.09	0.14	0.218	0.01	12.35	<0.001	0.03	0.003	<0.001
NVT-H3-9	0.683	2.58	<0.001	<0.001	2.85	<0.001	0.4	0.07	0.13	0.04	<0.01	11.95	<0.001	<0.02	0.003	<0.001
NVT-H3-10A	0.568	5.06	<0.001	<0.001	4.48	<0.001	0.5	0.11	0.13	0.086	0.01	17.35	<0.001	<0.02	0.005	<0.001
NVT-H3-10B*	0.557	4.9	<0.001	<0.001	5.14	<0.001	0.48	0.12	0.15	0.083	<0.01	25.9	<0.001	<0.02	0.005	<0.001
NVT-H4-1	0.221	4.89	<0.001	<0.001	3.79	<0.001	0.17	0.12	0.1	0.02	<0.01	10.85	<0.001	<0.02	0.003	<0.001
NVT-H4-2	0.191	5.41	0.001	<0.001	2.76	<0.001	0.14	0.12	0.12	0.028	<0.01	45.4	<0.001	<0.02	0.003	<0.001
NVT-H4-3	0.25	2.83	<0.001	<0.001	7.98	<0.001	0.18	0.08	0.13	0.315	0.01	20.8	<0.001	0.02	0.003	<0.001
NVT-H4-3F	0.253	2.54	<0.001	<0.001	16.55	<0.001	0.15	0.08	0.11	0.281	0.01	12.55	<0.001	<0.02	0.003	<0.001
NVT-H4-4	0.343	1.09	<0.001	<0.001	3.01	<0.001	0.15	0.03	0.18	0.101	<0.01	11.35	<0.001	<0.02	<0.002	<0.001
NVT-H4-5	0.461	2.03	<0.001	<0.001	6.76	<0.001	0.31	0.05	0.17	0.143	<0.01	13.8	<0.001	<0.02	0.002	<0.001
NVT-H4-6	0.517	3.6	<0.001	<0.001	4.03	<0.001	0.32	0.06	0.11	0.029	0.02	8.96	0.001	<0.02	0.003	<0.001
NVT-H4-7	0.321	0.94	<0.001	<0.001	7.94	<0.001	0.34	0.02	0.18	0.196	0.01	14.4	<0.001	<0.02	<0.002	<0.001
NVT-H4-8	0.42	1.5	<0.001	<0.001	6.12	<0.001	0.32	0.03	0.17	0.157	0.01	14.55	<0.001	0.02	0.002	<0.001
NVT-H4-9	0.201	5.66	0.001	<0.001	2.79	<0.001	0.17	0.11	0.13	0.018	0.01	33	<0.001	<0.02	0.004	<0.001
NVT-H4-10A	0.271	1.59	<0.001	<0.001	4.07	<0.001	0.17	0.03	0.12	0.065	0.03	29	<0.001	<0.02	<0.002	<0.001
NVT-H4-10B*	0.283	1.53	<0.001	<0.001	5.15	<0.001	0.18	0.04	0.12	0.071	0.01	29.9	<0.001	<0.02	<0.002	<0.001
NVT-H4-11	0.516	4.39	<0.001	<0.001	3.47	<0.001	0.41	0.12	0.14	0.046	0.03	20.3	0.002	<0.02	0.004	<0.001
NVT-H4-12	0.426	1.57	<0.001	<0.001	5.35	<0.001	0.32	0.03	0.14	0.057	0.02	13.85	<0.001	<0.02	<0.002	<0.001
NVT-H4-14	0.206	2.95	<0.001	<0.001	1.35	<0.001	0.17	0.07	0.13	0.05	0.02	20.9	<0.001	<0.02	0.002	<0.001
NVT-H4-15	0.19	1.86	<0.001	<0.001	3	<0.001	0.15	0.04	0.14	0.115	0.02	15	<0.001	<0.02	0.002	<0.001
NVT-H4-16	0.285	9.6	<0.001	<0.001	2.92	<0.001	0.25	0.11	0.13	0.043	0.03	20.7	<0.001	<0.02	0.003	<0.001
NVT-H4-17	0.299	7.29	<0.001	<0.001	3.03	<0.001	0.29	0.12	0.14	0.05	0.03	22.1	0.001	<0.02	0.004	<0.001
NVT-H4-18	0.366	1.68	0.001	<0.001	8.26	<0.001	0.25	0.04	0.17	0.293	0.02	14.5	<0.001	<0.02	0.002	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H3-7	0.003	<0.005	0.06	0.01	0.008	50.1	<0.02
NVT-H3-8	0.012	<0.005	0.09	0.01	0.04	64.9	0.03
NVT-H3-9	0.033	<0.005	0.09	0.01	0.02	75.3	0.02
NVT-H3-10A	0.019	<0.005	0.1	0.01	0.044	81.1	0.03
NVT-H3-10B*	0.02	<0.005	0.09	0.01	0.06	80	0.05
NVT-H4-1	0.013	<0.005	0.09	0.01	0.058	72.9	0.02
NVT-H4-2	0.013	<0.005	0.08	0.01	0.2	125.5	0.05
NVT-H4-3	0.077	<0.005	0.09	0.01	0.02	91.5	0.03
NVT-H4-3F	0.095	<0.005	0.08	0.01	0.01	64.5	0.02
NVT-H4-4	0.005	<0.005	0.07	0.01	0.026	52.5	<0.02
NVT-H4-5	0.009	<0.005	0.07	0.02	0.071	69.5	<0.02
NVT-H4-6	0.034	<0.005	0.07	0.01	0.026	82.6	0.02
NVT-H4-7	0.005	<0.005	0.05	<0.01	0.017	70.5	<0.02
NVT-H4-8	0.007	<0.005	0.07	0.01	0.014	78.8	<0.02
NVT-H4-9	0.015	<0.005	0.1	<0.01	0.291	82.5	0.02
NVT-H4-10A	0.007	<0.005	0.06	0.02	0.018	39.3	<0.02
NVT-H4-10B*	0.006	<0.005	0.07	0.02	0.019	40.1	<0.02
NVT-H4-11	0.014	<0.005	0.08	0.01	0.098	85.4	0.02
NVT-H4-12	0.062	<0.005	0.05	<0.01	0.031	120.5	<0.02
NVT-H4-14	0.013	<0.005	0.08	0.01	0.018	68.2	0.02
NVT-H4-15	0.007	<0.005	0.07	<0.01	0.013	50.4	<0.02
NVT-H4-16	0.028	<0.005	0.09	0.01	0.017	440	0.02
NVT-H4-17	0.033	<0.005	0.08	0.01	0.03	631	0.03
NVT-H4-18	0.088	<0.005	0.06	0.01	0.009	101	<0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H4-19	Nevinstown	Ash	leaves	Spring	-6.70	53.66	39	285747	268227
NVT-H4-20A	Nevinstown	Ash	leaves	Spring	-6.70	53.66	55	285799	268315
NVT-H4-20B*	Nevinstown	Ash	leaves	Spring	-6.70	53.66	55	285799	268315
NVT-H5-1	Nevinstown	Beech	leaves	Spring	-6.71	53.66	48	285489	268551
NVT-H5-2	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	44	285481	268584
NVT-H5-3	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	50	285453	268602
NVT-H5-4	Nevinstown	Oak	leaves	Spring	-6.71	53.66	43	285411	268609
NVT-H5-5	Nevinstown	Ash	leaves	Spring	-6.71	53.66	43	285385	268619
NVT-H5-6	Nevinstown	Beech	leaves	Spring	-6.71	53.66	39	285359	268630
NVT-H5-7	Nevinstown	Ash	leaves	Spring	-6.71	53.66	40	285307	268650
NVT-H5-8	Nevinstown	Oak	leaves	Spring	-6.71	53.66	46	285491	268592
NVT-H5-9	Nevinstown	Ash	leaves	Spring	-6.71	53.66	54	285478	268603
NVT-H5-10A	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	51	285499	268596
NVT-H5-10B*	Nevinstown	Sycamore	leaves	Spring	-6.71	53.66	51	285499	268596
CS1-H1-1	Control Site	Hawthorn	leaves	Spring	-6.74	53.66	71	283040	267978
CS1-H1-2	Control Site	Hawthorn	leaves	Spring	-6.74	53.66	73	283046	267975
CS1-H1-3	Control Site	Hawthorn	leaves	Spring	-6.74	53.66	72	283048	267973
CS1-H1-4	Control Site	Hawthorn	leaves	Spring	-6.74	53.66	71	283048	267969
CS1-H1-5	Control Site	Hawthorn	leaves	Spring	-6.74	53.65	72	283072	267955
CS1-H1-6	Control Site	Hawthorn	leaves	Spring	-6.74	53.65	74	283078	267947
CS1-H1-7	Control Site	Hawthorn	leaves	Spring	-6.74	53.65	71	283089	267938
CS1-H2-1	Control Site	Ash	leaves	Spring	-6.75	53.66	59	282988	267966
CS1-H2-2	Control Site	Ash	leaves	Spring	-6.75	53.66	68	283022	267985
CS1-H2-3	Control Site	Sycamore	leaves	Spring	-6.75	53.66	76	283024	267987

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H4-19	<0.0002	0.001	<0.01	0.06	13	8.6	<0.01	0.001	0.66	0.02	0.007	0.048	1.47	0.017	20.2
NVT-H4-20A	<0.0002	0.003	<0.01	0.06	17	27.2	<0.01	0.001	1.55	0.031	0.006	0.039	1.45	0.009	16.2
NVT-H4-20B*	<0.0002	0.002	<0.01	0.04	17	30.3	<0.01	0.001	1.65	0.036	0.006	0.032	1.15	0.01	15.5
NVT-H5-1	<0.0002	0.007	<0.01	0.11	22	23	<0.01	0.002	0.55	0.111	0.023	0.041	1.12	0.007	8.99
NVT-H5-2	<0.0002	0.014	<0.01	0.18	27	20.4	<0.01	0.001	1.36	0.116	0.033	0.034	1.09	0.005	12.05
NVT-H5-3	<0.0002	0.003	<0.01	0.07	17	6.3	<0.01	0.001	0.56	0.074	0.035	0.022	0.87	0.007	5.62
NVT-H5-4	<0.0002	0.02	<0.01	0.11	22	17.4	<0.01	0.001	0.65	0.243	0.026	0.031	0.63	0.179	11.85
NVT-H5-5	<0.0002	0.004	<0.01	0.02	21	11.2	<0.01	0.001	1.15	0.02	0.033	0.032	0.74	<0.005	11.1
NVT-H5-6	<0.0002	0.005	<0.01	0.1	19	19.3	<0.01	0.001	0.49	0.181	0.044	0.048	1.56	0.009	5.41
NVT-H5-7	<0.0002	0.002	<0.01	0.11	22	9.3	<0.01	0.001	0.99	0.026	0.02	0.038	0.6	0.006	15.25
NVT-H5-8	<0.0002	0.043	<0.01	0.09	23	37.4	<0.01	0.001	0.82	0.075	0.018	0.022	0.96	<0.005	11.5
NVT-H5-9	<0.0002	0.002	<0.01	0.11	17	13.1	<0.01	0.001	1.04	0.032	0.042	0.06	2.05	<0.005	16.1
NVT-H5-10A	<0.0002	0.004	<0.01	0.16	29	18.8	<0.01	0.001	1.28	0.223	0.071	0.043	1.47	<0.005	11
NVT-H5-10B*	<0.0002	0.005	<0.01	0.14	30	16.4	<0.01	0.001	1.16	0.189	0.062	0.042	1.37	<0.005	9.63
CS1-H1-1	<0.0002	0.001	<0.01	0.06	24	41.7	<0.01	0.001	1.39	0.185	0.044	0.16	0.49	<0.005	6.34
CS1-H1-2	<0.0002	0.003	<0.01	0.07	20	54.1	<0.01	0.001	1.56	0.074	0.026	0.16	0.35	<0.005	8.22
CS1-H1-3	<0.0002	0.002	<0.01	0.11	28	34.8	<0.01	0.001	1.31	0.116	0.041	0.158	0.31	0.008	7.47
CS1-H1-4	<0.0002	0.002	<0.01	0.15	38	41.7	<0.01	0.002	1.25	0.271	0.068	0.155	0.46	0.026	9.7
CS1-H1-5	<0.0002	0.002	<0.01	0.08	23	38.1	<0.01	0.002	1.22	0.215	0.06	0.134	1.64	0.014	6.5
CS1-H1-6	<0.0002	0.002	<0.01	0.12	28	50.5	<0.01	0.002	1.3	0.264	0.053	0.071	1.35	0.013	6.69
CS1-H1-7	<0.0002	0.001	<0.01	0.09	20	35.6	<0.01	0.001	1.04	0.273	0.063	0.112	0.58	0.02	8.85
CS1-H2-1	<0.0002	0.002	<0.01	0.06	16	8.8	<0.01	0.001	1.1	0.013	0.017	0.055	0.52	0.006	8.53
CS1-H2-2	<0.0002	0.002	<0.01	0.05	17	6.5	<0.01	0.001	1.14	0.012	0.026	0.048	3.04	0.005	8.31
CS1-H2-3	<0.0002	0.005	<0.01	0.07	26	7.9	<0.01	0.002	0.88	0.11	0.024	0.032	0.9	0.007	8.89

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H4-19	66	<0.004	<0.005	<0.002	0.004	<0.005	1.27	0.006	<0.1	0.178	29.3	0.72	0.107	<0.002	1.93
NVT-H4-20A	61	<0.004	0.005	<0.002	0.004	<0.005	0.97	0.007	<0.1	0.253	73.7	1.43	0.015	<0.002	1.81
NVT-H4-20B*	62	<0.004	<0.005	<0.002	0.003	<0.005	0.95	0.008	<0.1	0.271	79.8	1.3	0.011	<0.002	1.48
NVT-H5-1	68	<0.004	<0.005	<0.002	0.005	<0.005	1.28	0.021	<0.1	0.17	84	0.27	0.129	<0.002	2.33
NVT-H5-2	74	0.004	0.005	<0.002	0.007	<0.005	1.66	0.037	0.1	0.174	48.3	0.34	0.102	<0.002	1.2
NVT-H5-3	60	<0.004	<0.005	<0.002	0.004	<0.005	1.49	0.067	<0.1	0.105	54.2	0.22	0.037	<0.002	1.72
NVT-H5-4	80	<0.004	<0.005	<0.002	0.004	<0.005	1.56	0.021	0.1	0.2	226	0.14	0.058	<0.002	1.74
NVT-H5-5	78	<0.004	<0.005	<0.002	0.004	<0.005	1.19	0.058	<0.1	0.156	30.4	0.19	0.031	<0.002	3.31
NVT-H5-6	53	0.004	0.006	<0.002	0.008	<0.005	0.76	0.102	0.1	0.146	164	0.22	0.089	<0.002	3.26
NVT-H5-7	70	<0.004	<0.005	<0.002	0.004	<0.005	1.43	0.022	<0.1	0.171	25.3	0.39	0.042	<0.002	2.46
NVT-H5-8	69	0.004	<0.005	<0.002	0.005	<0.005	1.33	0.015	<0.1	0.186	133	0.26	0.08	<0.002	1.72
NVT-H5-9	76	<0.004	0.005	<0.002	0.005	<0.005	1.25	0.104	<0.1	0.231	35.4	0.62	0.071	<0.002	4.49
NVT-H5-10A	77	0.004	0.007	<0.002	0.016	<0.005	2.41	0.071	<0.1	0.187	161	0.7	0.024	<0.002	1.68
NVT-H5-10B*	84	<0.004	0.006	<0.002	0.014	<0.005	2.49	0.06	<0.1	0.136	164.5	0.84	0.029	0.002	1.42
CS1-H1-1	72	<0.004	0.006	<0.002	0.008	<0.005	0.94	0.045	<0.1	0.188	24.4	0.25	0.091	<0.002	1.02
CS1-H1-2	61	<0.004	0.008	<0.002	0.009	<0.005	1.34	0.042	<0.1	0.146	22.6	0.11	0.088	<0.002	0.77
CS1-H1-3	76	0.005	<0.005	<0.002	0.008	<0.005	1.39	0.032	0.1	0.204	21.1	0.35	0.121	<0.002	0.94
CS1-H1-4	91	0.004	0.009	<0.002	0.011	<0.005	1.56	0.08	0.1	0.179	24.2	0.45	0.146	0.002	1.48
CS1-H1-5	61	0.005	<0.005	<0.002	0.007	<0.005	1.02	0.117	0.1	0.179	25.7	0.35	0.115	<0.002	2.6
CS1-H1-6	62	0.005	0.005	<0.002	0.007	<0.005	1.14	0.171	0.1	0.175	25.9	0.32	0.141	<0.002	1.88
CS1-H1-7	58	<0.004	<0.005	<0.002	0.005	<0.005	1.12	0.163	<0.1	0.177	31.5	0.25	0.097	<0.002	2.12
CS1-H2-1	67	<0.004	0.007	<0.002	0.002	<0.005	1.09	0.027	<0.1	0.235	22.4	0.71	0.026	<0.002	4.31
CS1-H2-2	88	<0.004	0.005	<0.002	0.003	<0.005	1.43	0.033	<0.1	0.24	28.4	0.55	0.03	<0.002	6.34
CS1-H2-3	57	<0.004	0.005	<0.002	0.005	<0.005	1.7	0.025	<0.1	0.091	44.7	0.51	0.025	<0.002	2.08

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H4-19	0.527	0.83	<0.001	<0.001	8.16	<0.001	0.45	0.02	0.14	0.072	0.03	6.44	<0.001	<0.02	<0.002	<0.001
NVT-H4-20A	0.388	0.82	<0.001	<0.001	5.23	<0.001	0.35	0.02	0.14	0.061	0.02	16.65	<0.001	<0.02	<0.002	<0.001
NVT-H4-20B*	0.38	0.76	<0.001	<0.001	5.06	<0.001	0.35	0.02	0.13	0.074	0.01	18.2	<0.001	0.02	<0.002	<0.001
NVT-H5-1	0.257	1.77	<0.001	<0.001	4.5	<0.001	0.17	0.05	0.09	0.067	0.02	5.57	<0.001	<0.02	0.002	<0.001
NVT-H5-2	0.33	2.87	<0.001	<0.001	1.92	<0.001	0.28	0.07	0.19	0.055	0.02	18.6	<0.001	<0.02	0.003	<0.001
NVT-H5-3	0.381	1.12	<0.001	<0.001	7.45	<0.001	0.23	0.03	0.16	0.099	0.02	6.53	<0.001	<0.02	<0.002	<0.001
NVT-H5-4	0.339	1.54	<0.001	<0.001	29.1	<0.001	0.19	0.04	0.13	0.034	0.02	6.25	<0.001	<0.02	0.002	<0.001
NVT-H5-5	0.552	0.63	0.001	<0.001	1.98	<0.001	0.25	0.02	0.15	0.047	0.01	10.9	<0.001	<0.02	<0.002	<0.001
NVT-H5-6	0.15	1.59	<0.001	<0.001	3.91	<0.001	0.12	0.05	0.15	0.038	0.02	6.18	<0.001	<0.02	0.002	<0.001
NVT-H5-7	0.489	1.12	<0.001	<0.001	4.22	<0.001	0.34	0.03	0.11	0.069	0.01	8.51	<0.001	<0.02	<0.002	<0.001
NVT-H5-8	0.351	1.47	<0.001	<0.001	3.38	<0.001	0.21	0.04	0.12	0.041	0.01	6.01	<0.001	<0.02	<0.002	<0.001
NVT-H5-9	0.462	1.28	<0.001	<0.001	4.55	<0.001	0.31	0.04	0.11	0.039	0.01	11.05	<0.001	<0.02	<0.002	<0.001
NVT-H5-10A	0.325	2.5	0.001	<0.001	5.8	0.001	0.41	0.06	0.19	0.113	0.02	13.55	<0.001	<0.02	0.003	<0.001
NVT-H5-10B*	0.341	2.36	<0.001	<0.001	5.79	<0.001	0.39	0.05	0.17	0.098	0.03	11.85	<0.001	<0.02	0.002	<0.001
CS1-H1-1	0.299	0.94	<0.001	<0.001	2.57	<0.001	0.18	0.02	0.12	0.142	0.02	26.6	<0.001	<0.02	0.003	<0.001
CS1-H1-2	0.365	0.92	<0.001	<0.001	1.83	<0.001	0.19	0.02	0.13	0.223	0.02	30.2	<0.001	<0.02	0.002	<0.001
CS1-H1-3	0.436	1.42	<0.001	<0.001	3.61	<0.001	0.21	0.04	0.14	0.1	0.02	22.5	<0.001	<0.02	0.003	<0.001
CS1-H1-4	0.414	2.11	<0.001	<0.001	9.13	<0.001	0.23	0.06	0.13	0.217	0.02	25.5	<0.001	<0.02	0.004	<0.001
CS1-H1-5	0.297	1.49	<0.001	<0.001	5.81	<0.001	0.19	0.04	0.08	0.128	0.02	24	<0.001	<0.02	0.003	<0.001
CS1-H1-6	0.319	1.91	<0.001	<0.001	7.16	<0.001	0.17	0.05	0.1	0.143	0.03	27.9	<0.001	<0.02	0.003	<0.001
CS1-H1-7	0.291	1.05	<0.001	<0.001	8.12	<0.001	0.18	0.03	0.12	0.109	0.02	21.2	<0.001	<0.02	0.002	<0.001
CS1-H2-1	0.46	0.56	<0.001	<0.001	4.67	<0.001	0.35	0.02	0.11	0.376	0.01	13.75	<0.001	<0.02	<0.002	<0.001
CS1-H2-2	0.694	0.65	<0.001	<0.001	4.45	<0.001	0.4	0.02	0.12	0.134	0.02	11.8	<0.001	<0.02	<0.002	<0.001
CS1-H2-3	0.447	0.96	<0.001	<0.001	4.38	<0.001	0.26	0.04	0.16	0.088	0.02	10.75	<0.001	<0.02	0.002	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H4-19	0.038	<0.005	0.05	0.01	0.003	62.2	<0.02
NVT-H4-20A	0.032	<0.005	0.06	0.01	0.003	61.3	<0.02
NVT-H4-20B*	0.026	<0.005	0.05	0.01	0.004	62.2	<0.02
NVT-H5-1	0.006	<0.005	0.07	0.01	0.011	42.2	0.02
NVT-H5-2	0.01	<0.005	0.08	0.01	0.028	58.5	<0.02
NVT-H5-3	0.003	<0.005	0.07	<0.01	0.055	45	<0.02
NVT-H5-4	0.011	<0.005	0.08	<0.01	0.011	38	<0.02
NVT-H5-5	0.004	<0.005	<0.05	0.01	0.03	62.8	<0.02
NVT-H5-6	0.005	<0.005	0.08	0.01	0.051	40.1	<0.02
NVT-H5-7	0.004	<0.005	0.07	<0.01	0.006	59.7	<0.02
NVT-H5-8	0.007	<0.005	0.06	<0.01	0.007	34.9	<0.02
NVT-H5-9	0.006	<0.005	0.07	0.01	0.049	62.5	<0.02
NVT-H5-10A	0.009	<0.005	0.08	0.01	0.036	67.5	0.02
NVT-H5-10B*	0.007	<0.005	0.07	0.01	0.029	60.3	0.02
CS1-H1-1	0.003	<0.005	0.08	<0.01	0.02	27.1	0.02
CS1-H1-2	0.004	<0.005	0.09	<0.01	0.016	34.9	0.02
CS1-H1-3	0.005	<0.005	0.08	0.01	0.016	33.6	0.02
CS1-H1-4	0.007	<0.005	0.12	0.01	0.036	42.1	0.02
CS1-H1-5	0.005	<0.005	0.11	<0.01	0.047	31.4	0.02
CS1-H1-6	0.009	<0.005	0.12	<0.01	0.077	32.5	0.03
CS1-H1-7	0.005	<0.005	0.1	<0.01	0.074	26.6	<0.02
CS1-H2-1	0.002	<0.005	0.07	<0.01	0.01	50.6	<0.02
CS1-H2-2	0.002	<0.005	0.1	0.01	0.016	51	0.02
CS1-H2-3	0.003	<0.005	0.08	0.03	0.018	39.2	<0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
CS1-H2-4	Control Site	Ash	leaves	Spring	-6.74	53.65	65	283115	267922
CS1-H2-5	Control Site	Sycamore	leaves	Spring	-6.74	53.65	72	283140	267843
CS1-H2-6	Control Site	Ash	leaves	Spring	-6.74	53.66	72	283040	268000
CS1-H2-7	Control Site	Blackberry	leaves	Spring	-6.74	53.66	72	283054	268004
CS1-H2-8	Control Site	Ash	leaves	Spring	-6.74	53.66	65	283076	268009
CS1-H2-9	Control Site	Sycamore	leaves	Spring	-6.74	53.66	65	283145	268025
CS1-H2-10A	Control Site	Blackberry	leaves	Spring	-6.74	53.66	72	283238	268011
CS1-H2-10B*	Control Site	Blackberry	leaves	Spring	-6.74	53.66	72	283238	268011
CS2-W1-1	Control Site	Beech	leaves	Spring	-6.72	53.67	4	284357	269308
CS2-W1-2	Control Site	Beech	leaves	Spring	-6.72	53.67	40	284351	269323
CS2-W1-3	Control Site	Beech	leaves	Spring	-6.72	53.67	42	284350	269334
CS2-W1-4	Control Site	Beech	leaves	Spring	-6.72	53.67	40	284341	269311
CS2-W1-5	Control Site	Beech	leaves	Spring	-6.73	53.67	51	284322	269285
CS2-W1-6	Control Site	Hawthorn	leaves	Spring	-6.73	53.67	46	284290	269227
CS2-W1-6F	Control Site	Hawthorn	flowers	Spring	-6.73	53.67	46	284290	269227
CS2-W1-7	Control Site	Sycamore	leaves	Spring	-6.73	53.67	27	284231	269181
CS2-W1-8	Control Site	Sycamore	leaves	Spring	-6.73	53.67	47	284207	269209
CS2-W1-9	Control Site	Sycamore	leaves	Spring	-6.73	53.67	45	284266	269208
CS2-W1-10A	Control Site	Oak	leaves	Spring	-6.73	53.67	-6	284176	269162
CS2-W1-10B*	Control Site	Oak	leaves	Spring	-6.73	53.67	-6	284176	269162
CS2-W1-11	Control Site	Ash	leaves	Spring	-6.73	53.67	51	284254	269195
CS3-W-1	Control Site	Oak	leaves	Spring	-6.75	53.66	80	282967	268656
CS3-W-2	Control Site	Oak	leaves	Spring	-6.75	53.66	68	282932	268676
CS3-W-3	Control Site	Oak	leaves	Spring	-6.75	53.66	83	282989	268636

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
CS1-H2-4	<0.0002	0.005	<0.01	0.03	21	6.7	<0.01	0.001	1.05	0.007	0.027	0.034	0.9	0.007	14.15
CS1-H2-5	<0.0002	0.004	<0.01	0.03	17	10.3	<0.01	0.001	1.09	0.235	0.068	0.044	2.14	<0.005	6.22
CS1-H2-6	<0.0002	0.002	<0.01	0.06	15	7.7	<0.01	0.001	1.13	0.01	0.017	0.055	1.49	<0.005	12.85
CS1-H2-7	<0.0002	0.004	<0.01	0.08	22	6.3	<0.01	0.002	0.67	0.035	0.029	0.032	0.51	0.006	6.61
CS1-H2-8	<0.0002	0.006	<0.01	0.11	18	9.4	<0.01	0.002	1	0.019	0.047	0.042	0.87	0.012	10.95
CS1-H2-9	<0.0002	0.009	<0.01	0.05	19	8.3	<0.01	0.001	0.94	0.148	0.04	0.032	0.8	0.007	11.05
CS1-H2-10A	<0.0002	0.003	<0.01	0.02	31	5.4	<0.01	0.002	0.65	0.062	0.028	0.036	1.13	0.01	8.4
CS1-H2-10B*	<0.0002	0.005	<0.01	0.06	30	9	<0.01	0.001	0.7	0.165	0.048	0.052	0.78	0.01	8.83
CS2-W1-1	<0.0002	0.008	<0.01	0.03	19	45.2	<0.01	0.002	0.76	0.109	0.013	0.049	1.77	<0.005	10.5
CS2-W1-2	<0.0002	0.018	<0.01	0.01	24	48.1	<0.01	0.001	0.74	0.286	0.02	0.031	0.91	<0.005	16.1
CS2-W1-3	<0.0002	0.006	<0.01	0.01	22	31.2	<0.01	0.001	0.52	0.108	0.015	0.041	2.32	<0.005	9.8
CS2-W1-4	<0.0002	0.017	<0.01	0.04	17	31.5	<0.01	0.001	0.62	0.364	0.036	0.085	1.96	<0.005	11.9
CS2-W1-5	<0.0002	0.01	<0.01	0.01	14	16	<0.01	0.001	0.73	0.111	0.008	0.019	0.67	<0.005	9.7
CS2-W1-6	<0.0002	0.001	<0.01	0.03	18	30	<0.01	0.003	1.48	0.064	0.078	0.151	1.21	0.021	6.79
CS2-W1-6F	<0.0002	0.003	0.01	0.05	25	19.2	<0.01	0.002	0.87	0.085	0.138	0.314	1.03	0.031	10.75
CS2-W1-7	0.0002	0.005	<0.01	0.05	19	8.8	<0.01	0.002	1.35	0.093	0.046	0.042	0.9	0.015	13.15
CS2-W1-8	<0.0002	0.002	<0.01	0.02	18	6.8	<0.01	0.002	1.38	0.067	0.038	0.036	1.49	0.005	8.94
CS2-W1-9	<0.0002	0.003	<0.01	0.03	22	9.2	<0.01	0.002	1.09	0.064	0.08	0.063	1.66	0.01	10.8
CS2-W1-10A	<0.0002	0.024	<0.01	0.03	17	8.5	<0.01	0.001	0.3	0.023	0.019	0.022	0.74	0.122	6.66
CS2-W1-10B*	<0.0002	0.022	<0.01	0.02	18	10.8	<0.01	0.001	0.36	0.019	0.017	0.021	0.94	0.101	6.81
CS2-W1-11	<0.0002	0.002	<0.01	0.03	18	6	<0.01	0.002	1.03	0.005	0.022	0.056	1.32	0.009	13.15
CS3-W-1	<0.0002	0.032	<0.01	0.03	15	11.8	<0.01	0.001	0.57	0.024	0.02	0.038	1.08	<0.005	10.05
CS3-W-2	<0.0002	0.032	<0.01	0.02	21	4.4	<0.01	0.001	0.49	0.015	0.009	0.014	0.44	0.019	10.65
CS3-W-3	<0.0002	0.016	<0.01	0.01	16	7.9	<0.01	0.001	0.51	0.063	0.026	0.058	0.5	0.05	8.08

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
CS1-H2-4	65	<0.004	<0.005	<0.002	0.002	<0.005	1.6	0.05	<0.1	0.213	24.9	0.49	0.084	<0.002	4.59
CS1-H2-5	53	<0.004	<0.005	<0.002	0.009	<0.005	1.38	0.091	<0.1	0.112	398	0.43	0.016	<0.002	2.59
CS1-H2-6	60	<0.004	0.005	<0.002	0.007	<0.005	1.49	0.023	<0.1	0.153	18.4	0.54	0.04	<0.002	2.01
CS1-H2-7	73	0.004	0.007	<0.002	0.007	<0.005	1.47	0.025	0.1	0.168	86.9	1.19	0.074	<0.002	1.6
CS1-H2-8	78	0.005	<0.005	<0.002	0.006	<0.005	1.41	0.052	0.1	0.287	39.2	0.26	0.065	<0.002	4.72
CS1-H2-9	69	<0.004	0.006	<0.002	0.007	<0.005	1.71	0.064	<0.1	0.152	80.7	0.44	0.037	<0.002	1.87
CS1-H2-10A	54	0.004	0.005	<0.002	0.006	<0.005	1.16	0.022	<0.1	0.203	156.5	0.87	0.089	<0.002	3.27
CS1-H2-10B*	64	<0.004	<0.005	<0.002	0.007	<0.005	1.11	0.049	0.1	0.202	373	0.79	0.109	<0.002	5.33
CS2-W1-1	64	<0.004	0.005	<0.002	0.006	<0.005	1.08	0.014	0.1	0.158	175.5	0.36	0.056	<0.002	3.33
CS2-W1-2	54	<0.004	<0.005	<0.002	0.005	<0.005	1.3	0.021	<0.1	0.148	136.5	0.12	0.034	<0.002	3.45
CS2-W1-3	57	<0.004	<0.005	<0.002	0.006	<0.005	0.98	0.013	<0.1	0.128	88.9	0.25	0.039	<0.002	3.87
CS2-W1-4	53	<0.004	<0.005	<0.002	0.006	<0.005	1.08	0.041	<0.1	0.123	145.5	0.38	0.037	<0.002	4.13
CS2-W1-5	41	<0.004	<0.005	<0.002	0.004	<0.005	0.89	0.008	<0.1	0.141	50.8	0.26	0.026	<0.002	1.97
CS2-W1-6	95	0.01	0.007	<0.002	0.011	<0.005	1.52	0.053	0.1	0.203	25.8	0.57	0.059	0.002	1.17
CS2-W1-6F	129	0.016	0.006	<0.002	0.003	<0.005	2.14	0.068	0.1	0.181	19.9	0.61	0.048	0.002	1.66
CS2-W1-7	84	0.006	0.006	<0.002	0.01	<0.005	1.73	0.042	<0.1	0.163	116	0.44	0.008	<0.002	1.85
CS2-W1-8	93	0.005	0.007	<0.002	0.013	<0.005	1.76	0.059	<0.1	0.186	59.8	0.35	0.003	<0.002	1.2
CS2-W1-9	108	0.011	0.007	<0.002	0.011	<0.005	1.9	0.054	0.1	0.158	126	0.47	0.02	0.002	2.38
CS2-W1-10A	72	<0.004	<0.005	<0.002	0.002	<0.005	1.5	0.018	<0.1	0.131	184	0.2	0.027	<0.002	1.78
CS2-W1-10B*	76	<0.004	<0.005	<0.002	0.002	<0.005	1.56	0.02	<0.1	0.134	216	0.22	0.026	<0.002	1.97
CS2-W1-11	74	0.004	0.007	<0.002	0.003	<0.005	1.2	0.014	<0.1	0.205	28.3	0.57	0.015	<0.002	3.52
CS3-W-1	69	<0.004	0.005	<0.002	0.004	<0.005	1.4	0.03	0.1	0.129	322	0.28	0.073	<0.002	2.65
CS3-W-2	44	<0.004	0.005	<0.002	0.004	<0.005	1.25	0.01	0.1	0.128	72.7	0.37	0.074	<0.002	1.61
CS3-W-3	51	<0.004	<0.005	<0.002	0.004	<0.005	1.12	0.037	0.1	0.145	399	0.19	0.088	<0.002	2.24

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
CS1-H2-4	0.46	0.26	<0.001	<0.001	5.75	<0.001	0.46	0.02	0.13	0.162	0.02	13.25	<0.001	<0.02	<0.002	<0.001
CS1-H2-5	0.249	0.33	<0.001	<0.001	2.78	<0.001	0.16	0.02	0.15	0.014	0.01	16.55	<0.001	<0.02	<0.002	<0.001
CS1-H2-6	0.571	0.52	<0.001	<0.001	1.56	<0.001	0.33	0.02	0.13	0.079	0.02	13.3	<0.001	<0.02	<0.002	<0.001
CS1-H2-7	0.286	0.8	<0.001	<0.001	2.45	<0.001	0.21	0.04	0.12	0.199	0.03	8.88	<0.001	<0.02	0.002	<0.001
CS1-H2-8	0.333	1.06	<0.001	<0.001	5.85	<0.001	0.33	0.03	0.09	0.084	0.03	13.5	<0.001	<0.02	0.003	<0.001
CS1-H2-9	0.45	0.63	<0.001	<0.001	6.7	<0.001	0.3	0.02	0.19	0.117	0.02	12.65	<0.001	<0.02	0.002	<0.001
CS1-H2-10A	0.259	0.44	<0.001	<0.001	6.98	<0.001	0.22	0.02	0.1	0.08	0.03	7.96	<0.001	<0.02	0.002	<0.001
CS1-H2-10B*	0.284	0.3	<0.001	<0.001	7.99	<0.001	0.22	0.02	0.1	0.123	0.02	10.55	<0.001	<0.02	0.002	<0.001
CS2-W1-1	0.323	0.11	<0.001	<0.001	1.42	<0.001	0.19	0.01	0.18	0.139	0.02	7.75	<0.001	<0.02	<0.002	<0.001
CS2-W1-2	0.394	0.15	<0.001	<0.001	1.64	<0.001	0.21	0.01	0.13	0.122	0.01	10.3	<0.001	<0.02	<0.002	<0.001
CS2-W1-3	0.343	0.18	<0.001	<0.001	1.17	<0.001	0.19	0.02	0.14	0.398	0.02	6.93	<0.001	<0.02	<0.002	<0.001
CS2-W1-4	0.332	0.09	<0.001	<0.001	1.6	<0.001	0.17	0.01	0.14	0.134	0.01	6.91	<0.001	<0.02	<0.002	<0.001
CS2-W1-5	0.263	0.09	<0.001	<0.001	1.72	<0.001	0.15	0.01	0.15	0.135	0.01	8.61	<0.001	<0.02	<0.002	<0.001
CS2-W1-6	0.294	0.23	<0.001	<0.001	3.96	<0.001	0.19	0.03	0.14	0.249	0.02	20.5	<0.001	<0.02	0.007	<0.001
CS2-W1-6F	0.332	0.22	<0.001	<0.001	8.09	<0.001	0.18	0.03	0.14	0.255	0.04	10.3	<0.001	<0.02	0.014	<0.001
CS2-W1-7	0.369	0.28	<0.001	<0.001	3.38	<0.001	0.26	0.02	0.21	0.114	0.04	15.8	<0.001	0.02	0.003	<0.001
CS2-W1-8	0.322	0.17	<0.001	<0.001	2.24	<0.001	0.33	0.02	0.21	0.273	0.03	11.1	<0.001	<0.02	0.003	<0.001
CS2-W1-9	0.388	0.22	<0.001	<0.001	2.43	0.001	0.31	0.03	0.2	0.343	0.03	12.25	<0.001	<0.02	0.007	<0.001
CS2-W1-10A	0.36	0.12	<0.001	<0.001	12.2	<0.001	0.2	0.02	0.14	0.027	0.02	1.74	<0.001	<0.02	<0.002	<0.001
CS2-W1-10B*	0.374	0.11	<0.001	<0.001	12.4	<0.001	0.2	0.02	0.14	0.02	0.02	2.15	<0.001	<0.02	<0.002	<0.001
CS2-W1-11	0.482	0.14	<0.001	<0.001	2.96	<0.001	0.35	0.02	0.13	0.403	0.03	11	<0.001	<0.02	0.002	<0.001
CS3-W-1	0.295	0.12	<0.001	<0.001	3.23	<0.001	0.14	0.01	0.15	0.029	0.02	4.75	<0.001	<0.02	<0.002	<0.001
CS3-W-2	0.335	0.07	<0.001	<0.001	7.96	<0.001	0.17	0.01	0.15	0.077	0.01	3.28	<0.001	<0.02	<0.002	<0.001
CS3-W-3	0.25	0.05	<0.001	<0.001	8.07	<0.001	0.18	0.01	0.15	0.027	0.01	2.67	<0.001	<0.02	<0.002	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
CS1-H2-4	0.003	<0.005	0.09	<0.01	0.013	40.6	<0.02
CS1-H2-5	<0.002	<0.005	0.08	<0.01	0.036	36	0.02
CS1-H2-6	0.004	<0.005	0.09	0.01	0.011	49.3	<0.02
CS1-H2-7	0.002	<0.005	0.1	<0.01	0.015	29.6	0.02
CS1-H2-8	0.006	<0.005	0.1	0.01	0.026	33.1	0.02
CS1-H2-9	0.003	<0.005	0.1	<0.01	0.037	52.2	0.02
CS1-H2-10A	0.002	<0.005	0.11	<0.01	0.014	23.7	0.02
CS1-H2-10B*	<0.002	<0.005	0.08	<0.01	0.026	30.2	0.04
CS2-W1-1	<0.002	<0.005	0.08	0.01	0.006	26	<0.02
CS2-W1-2	<0.002	<0.005	0.08	<0.01	0.014	27.2	<0.02
CS2-W1-3	<0.002	<0.005	0.09	<0.01	0.007	24.8	<0.02
CS2-W1-4	<0.002	<0.005	0.07	0.01	0.017	27.8	<0.02
CS2-W1-5	<0.002	<0.005	0.07	<0.01	0.003	23.9	<0.02
CS2-W1-6	0.002	<0.005	0.18	0.01	0.032	22.9	0.04
CS2-W1-6F	<0.002	<0.005	0.21	<0.01	0.035	30.6	0.06
CS2-W1-7	0.002	<0.005	0.11	<0.01	0.028	54.9	0.02
CS2-W1-8	<0.002	<0.005	0.1	<0.01	0.034	24.1	0.02
CS2-W1-9	0.003	<0.005	0.17	<0.01	0.027	41.9	0.04
CS2-W1-10A	0.003	<0.005	0.09	<0.01	0.013	19.7	<0.02
CS2-W1-10B*	0.002	<0.005	0.07	<0.01	0.013	19.8	<0.02
CS2-W1-11	0.006	<0.005	0.1	<0.01	0.007	48.4	<0.02
CS3-W-1	<0.002	<0.005	0.07	<0.01	0.021	17.4	<0.02
CS3-W-2	<0.002	<0.005	0.08	<0.01	0.008	17.6	<0.02
CS3-W-3	<0.002	<0.005	0.07	<0.01	0.023	14.6	<0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H1-1A	Nevinstown	Blackberry	leaves	Autumn	-6.71	53.66	31	285525	268511
NVT-H1-1FR	Nevinstown	Blackberry	fruit	Autumn	-6.71	53.66	31	285525	268511
NVT-H1-6A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	40	285519	268407
NVT-H1-7A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	45	285522	268418
NVT-H1-13A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	38	285451	268478
NVT-H1-17AI	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	-8	285515	268471
NVT-H1-17AII*	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	-8	285515	268471
NVT-H1-20S	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	35	285529	268431
NVT-H1-32A	Nevinstown	Oak	leaves	Autumn	-6.71	53.66	42	285482	268501
NVT-H1-34A	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	46	285488	268508
NVT-H2-22A	Nevinstown	Beech	leaves	Autumn	-6.71	53.66	49	285512	268501
NVT-H2-23A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	32	285565	268500
NVT-H2-27A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	49	285576	268489
NVT-H2-36A	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	49	285618	268494
NVT-H2-38A	Nevinstown	Blackberry	leaves	Autumn	-6.70	53.66	52	285732	268514
NVT-H2-38FR	Nevinstown	Blackberry	fruit	Autumn	-6.70	53.66	52	285732	268514
NVT-H3-2AI	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	44	285634	268578
NVT-H3-2AII*	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	44	285634	268578
NVT-H3-3A	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	67	285625	268574
NVT-H3-10S	Nevinstown	Ash	leaves	Autumn	-6.70	53.66	53	285703	268507
NVT-H4-1A	Nevinstown	Blackberry	leaves	Autumn	-6.70	53.66	34	285743	268387
NVT-H4-2A	Nevinstown	Hawthorn	leaves	Autumn	-6.70	53.66	51	285736	268366
NVT-H4-3A	Nevinstown	Hawthorn	leaves	Autumn	-6.71	53.66	48	285656	268298
NVT-H4-3FRI	Nevinstown	Hawthorn	fruit	Autumn	-6.71	53.66	48	285656	268298

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H1-1A	<0.0002	0.006	<0.01	0.17	23	47.9	<0.01	0.002	0.94	0.421	0.049	0.027	0.52	<0.005	3.46
NVT-H1-1FR	<0.0002	0.002	<0.01	0.06	11	8.1	<0.01	<0.001	0.22	0.081	0.006	0.018	0.85	<0.005	4.65
NVT-H1-6A	<0.0002	0.002	<0.01	0.32	19	76.6	<0.01	0.002	1.54	0.303	0.058	0.041	0.47	0.006	1.96
NVT-H1-7A	<0.0002	0.004	<0.01	0.41	24	158.5	<0.01	0.003	2.83	0.555	0.061	0.046	0.7	0.011	4.39
NVT-H1-13A	<0.0002	0.003	<0.01	0.25	21	179.5	<0.01	0.002	2.27	0.267	0.049	0.047	0.3	0.009	4.71
NVT-H1-17AI	<0.0002	0.007	<0.01	0.34	26	264	<0.01	0.002	2.83	0.907	0.147	0.05	0.49	0.021	4.12
NVT-H1-17AII*	<0.0002	0.003	<0.01	0.29	28	280	0.01	0.002	2.97	1.03	0.159	0.047	0.39	0.018	4.02
NVT-H1-20S	0.0783	0.012	<0.01	0.4	24	118.5	<0.01	0.002	3.02	0.486	0.061	0.057	0.57	0.012	3.62
NVT-H1-32A	<0.0002	0.031	<0.01	0.27	28	39	0.01	0.002	0.97	0.139	0.077	0.043	0.59	0.04	6.49
NVT-H1-34A	0.0004	0.005	<0.01	0.25	26	73.2	<0.01	0.001	2.94	0.084	0.032	0.018	0.33	0.006	11.75
NVT-H2-22A	<0.0002	0.014	<0.01	0.29	18	45.9	<0.01	0.001	0.72	0.206	0.054	0.039	0.65	0.008	6.03
NVT-H2-23A	<0.0002	0.004	<0.01	0.54	30	185	<0.01	0.002	2.43	0.507	0.099	0.058	0.54	0.009	4.67
NVT-H2-27A	<0.0002	0.004	<0.01	0.37	28	84.5	<0.01	0.002	1.56	0.345	0.086	0.06	0.41	0.008	3.98
NVT-H2-36A	<0.0002	0.003	<0.01	0.32	19	69.3	<0.01	0.001	2.82	0.089	0.046	0.033	0.67	0.011	6.37
NVT-H2-38A	<0.0002	0.014	<0.01	0.09	37	190	<0.01	0.001	1.36	0.319	0.029	0.02	0.79	<0.005	5.05
NVT-H2-38FR	<0.0002	0.004	<0.01	0.02	11	30.4	<0.01	<0.001	0.21	0.07	0.003	0.019	0.86	<0.005	5.68
NVT-H3-2AI	<0.0002	0.002	<0.01	0.1	17	21.4	<0.01	<0.001	1.91	0.039	0.049	0.013	0.28	0.005	5.77
NVT-H3-2AII*	<0.0002	0.001	<0.01	0.12	17	19.4	<0.01	<0.001	1.72	0.042	0.044	0.019	0.55	0.005	5.45
NVT-H3-3A	<0.0002	0.001	<0.01	0.12	24	85.3	<0.01	<0.001	3.4	0.035	0.032	0.01	1.22	0.012	7.12
NVT-H3-10S	<0.0002	0.003	<0.01	0.11	23	70.8	<0.01	0.002	3.35	0.037	0.032	0.017	0.46	0.011	3.74
NVT-H4-1A	<0.0002	0.005	<0.01	0.17	16	91.3	0.01	0.001	1.16	0.379	0.111	0.027	0.49	0.006	4.43
NVT-H4-2A	<0.0002	0.004	<0.01	0.51	25	335	0.03	0.003	2.49	0.615	0.34	0.181	0.42	0.012	3.35
NVT-H4-3A	<0.0002	0.004	<0.01	0.37	23	337	<0.01	0.002	2.77	0.488	0.078	0.046	0.51	0.056	5.51
NVT-H4-3FRI	<0.0002	0.001	<0.01	0.06	16	81.3	<0.01	<0.001	0.71	0.179	0.006	0.105	4.9	0.03	6.07

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H1-1A	51	0.004	<0.005	0.003	0.01	<0.005	1.06	0.036	0.1	0.271	49.2	0.6	0.025	0.003	1.32
NVT-H1-1FR	26	<0.004	<0.005	<0.002	0.001	<0.005	0.96	0.002	<0.1	0.144	12.6	0.44	0.012	<0.002	1.2
NVT-H1-6A	62	0.008	0.005	<0.002	0.018	<0.005	1.8	0.052	0.1	0.148	31.8	0.27	0.013	0.002	0.53
NVT-H1-7A	73	0.01	0.008	<0.002	0.029	<0.005	1.46	0.065	0.1	0.174	23.2	0.19	0.061	0.003	0.92
NVT-H1-13A	49	0.005	0.011	<0.002	0.023	<0.005	1.43	0.05	0.1	0.205	40.1	0.17	0.018	<0.002	0.73
NVT-H1-17AI	63	0.008	0.009	<0.002	0.033	<0.005	1.33	0.728	0.2	0.352	72.3	0.18	0.063	0.002	1.84
NVT-H1-17AII*	65	0.007	0.01	<0.002	0.034	<0.005	1.35	0.782	0.2	0.356	70.8	0.19	0.065	0.002	1.66
NVT-H1-20S	64	0.009	0.01	<0.002	0.024	<0.005	2.32	0.049	0.1	0.234	30.9	0.2	0.043	<0.002	0.63
NVT-H1-32A	84	0.009	0.006	<0.002	0.022	<0.005	0.98	0.105	0.1	0.088	258	0.11	0.074	0.002	2.56
NVT-H1-34A	55	0.004	0.009	<0.002	0.022	<0.005	1.69	0.039	<0.1	0.289	33.2	0.3	0.008	<0.002	1.86
NVT-H2-22A	60	0.005	0.007	<0.002	0.028	<0.005	1.11	0.059	0.1	0.127	136.5	0.21	0.127	<0.002	1.24
NVT-H2-23A	74	0.01	0.012	<0.002	0.037	<0.005	1.41	0.106	0.2	0.293	35	0.35	0.081	0.002	1.04
NVT-H2-27A	71	0.007	0.012	<0.002	0.038	<0.005	2.35	0.172	0.2	0.237	31.5	0.23	0.163	<0.002	0.62
NVT-H2-36A	79	0.005	0.012	<0.002	0.036	<0.005	1.12	0.037	<0.1	0.313	49.7	0.32	0.016	<0.002	0.98
NVT-H2-38A	52	<0.004	0.009	<0.002	0.012	<0.005	1.14	0.034	<0.1	0.354	129	0.49	0.014	<0.002	1.64
NVT-H2-38FR	26	<0.004	0.005	<0.002	0.002	<0.005	0.98	0.003	<0.1	0.131	18.1	0.36	0.009	<0.002	1.22
NVT-H3-2AI	42	<0.004	0.009	<0.002	0.023	<0.005	1.3	0.048	<0.1	0.122	19.9	0.34	0.017	<0.002	1.7
NVT-H3-2AII*	46	0.004	0.008	<0.002	0.023	<0.005	1.24	0.044	<0.1	0.099	13.6	0.36	0.016	<0.002	1.83
NVT-H3-3A	48	<0.004	0.007	<0.002	0.031	<0.005	1.22	0.039	0.1	0.259	26.6	0.77	0.022	<0.002	0.79
NVT-H3-10S	47	0.005	0.009	<0.002	0.026	<0.005	1.23	0.062	0.1	0.328	22.9	1.16	0.012	0.002	0.36
NVT-H4-1A	75	0.005	0.01	<0.002	0.011	<0.005	1.37	0.403	<0.1	0.279	193.5	0.3	0.02	0.002	3.08
NVT-H4-2A	64	0.011	0.014	<0.002	0.026	<0.005	1.07	0.542	0.2	0.348	109.5	0.17	0.055	0.002	4.37
NVT-H4-3A	75	0.009	0.016	<0.002	0.03	<0.005	0.71	0.072	0.1	0.295	25.7	0.39	0.063	0.003	1.16
NVT-H4-3FRI	57	<0.004	0.007	<0.002	0.003	<0.005	0.71	0.006	<0.1	0.091	7	1.17	0.054	0.003	4.78

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H1-1A	0.16	3.58	<0.001	<0.001	0.66	<0.001	0.13	0.07	0.09	0.045	0.03	15.85	0.004	<0.02	0.004	<0.001
NVT-H1-1FR	0.174	0.51	<0.001	<0.001	2.43	<0.001	0.08	0.01	0.06	0.032	<0.01	4.02	0.001	<0.02	<0.002	<0.001
NVT-H1-6A	0.101	5.69	<0.001	0.001	1.46	<0.001	0.12	0.12	0.12	0.057	0.05	22.2	0.001	<0.02	0.005	<0.001
NVT-H1-7A	0.11	5.72	<0.001	<0.001	2.25	0.001	0.16	0.15	0.13	0.255	0.05	42	<0.001	<0.02	0.006	<0.001
NVT-H1-13A	0.21	3.36	<0.001	<0.001	1.77	<0.001	0.17	0.06	0.12	0.428	0.03	40.8	0.001	<0.02	0.003	<0.001
NVT-H1-17AI	0.189	4.83	0.001	<0.001	2.75	<0.001	0.17	0.12	0.13	0.068	0.04	62.7	<0.001	<0.02	0.004	<0.001
NVT-H1-17AII*	0.186	5.25	0.001	<0.001	2.92	<0.001	0.16	0.13	0.12	0.062	0.03	66.3	0.001	<0.02	0.005	<0.001
NVT-H1-20S	0.144	6.39	0.001	<0.001	2.31	<0.001	0.15	0.13	0.14	0.073	0.04	43.4	<0.001	<0.02	0.006	<0.001
NVT-H1-32A	0.191	6.24	<0.001	<0.001	4.34	<0.001	0.19	0.13	0.1	0.246	0.03	9.52	<0.001	<0.02	0.006	<0.001
NVT-H1-34A	0.146	3.17	0.001	<0.001	1.78	0.004	0.46	0.08	0.13	0.332	0.02	46.9	<0.001	<0.02	0.002	<0.001
NVT-H2-22A	0.164	5.75	<0.001	<0.001	2.34	<0.001	0.17	0.14	0.15	0.104	0.03	11.3	<0.001	<0.02	0.004	<0.001
NVT-H2-23A	0.2	9.72	<0.001	<0.001	2.28	<0.001	0.18	0.21	0.1	0.119	0.04	49	<0.001	<0.02	0.006	<0.001
NVT-H2-27A	0.213	5.97	<0.001	<0.001	2.91	<0.001	0.18	0.14	0.1	0.042	0.04	29.9	0.001	<0.02	0.006	<0.001
NVT-H2-36A	0.222	4.32	<0.001	<0.001	1.27	0.001	0.39	0.09	0.13	0.08	0.03	43.5	<0.001	<0.02	0.003	<0.001
NVT-H2-38A	0.226	2.55	<0.001	<0.001	0.68	<0.001	0.18	0.05	0.08	0.015	0.03	30.6	0.001	0.02	0.002	<0.001
NVT-H2-38FR	0.182	0.13	<0.001	<0.001	1.19	<0.001	0.09	0.01	0.05	0.012	<0.01	4.85	<0.001	<0.02	<0.002	<0.001
NVT-H3-2AI	0.246	2.04	0.001	<0.001	2.53	0.005	0.29	0.05	0.12	0.155	0.02	24.8	<0.001	<0.02	0.002	<0.001
NVT-H3-2AII*	0.229	2.08	0.001	<0.001	2.3	0.005	0.25	0.05	0.15	0.153	0.02	23.1	<0.001	<0.02	0.002	<0.001
NVT-H3-3A	0.267	1.54	0.001	<0.001	3.06	0.005	0.35	0.05	0.15	0.277	0.01	62	<0.001	<0.02	<0.002	<0.001
NVT-H3-10S	0.252	2	0.001	<0.001	2.26	0.002	0.62	0.05	0.13	0.249	0.03	51.9	0.002	<0.02	0.003	<0.001
NVT-H4-1A	0.111	3.58	<0.001	<0.001	2.17	<0.001	0.14	0.09	0.08	0.014	0.01	24.2	<0.001	0.02	0.002	<0.001
NVT-H4-2A	0.123	10.3	0.001	<0.001	2.2	<0.001	0.14	0.18	0.11	0.062	0.06	67.8	<0.001	<0.02	0.006	<0.001
NVT-H4-3A	0.136	6.96	0.001	<0.001	3.53	<0.001	0.19	0.15	0.1	0.35	0.04	43.5	<0.001	<0.02	0.006	<0.001
NVT-H4-3FRI	0.112	0.68	<0.001	<0.001	6.01	<0.001	0.06	0.02	0.08	0.067	0.02	11.1	<0.001	0.02	<0.002	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H1-1A	0.013	<0.005	0.08	<0.01	0.019	123.5	0.02
NVT-H1-1FR	<0.002	<0.005	0.05	<0.01	<0.003	19.4	<0.02
NVT-H1-6A	0.059	<0.005	0.12	<0.01	0.033	92.4	0.04
NVT-H1-7A	0.074	<0.005	0.14	0.01	0.042	147	0.05
NVT-H1-13A	0.013	<0.005	0.08	<0.01	0.025	86.2	0.02
NVT-H1-17AI	0.081	<0.005	0.11	<0.01	0.675	143	0.03
NVT-H1-17AII*	0.101	<0.005	0.12	<0.01	0.714	167	0.03
NVT-H1-20S	0.069	<0.005	0.12	<0.01	0.031	103	0.03
NVT-H1-32A	0.373	<0.005	0.11	<0.01	0.071	75.6	0.06
NVT-H1-34A	0.025	<0.005	0.07	<0.01	0.018	72.3	0.02
NVT-H2-22A	0.016	<0.005	0.1	<0.01	0.035	112.5	0.03
NVT-H2-23A	0.049	<0.005	0.14	<0.01	0.047	154.5	0.04
NVT-H2-27A	0.067	<0.005	0.12	<0.01	0.117	84.9	0.03
NVT-H2-36A	0.038	<0.005	0.08	<0.01	0.024	49.4	0.03
NVT-H2-38A	0.004	<0.005	0.06	<0.01	0.017	65.9	0.02
NVT-H2-38FR	<0.002	<0.005	0.05	0.01	<0.003	13.7	<0.02
NVT-H3-2AI	0.006	<0.005	0.06	<0.01	0.021	36.4	<0.02
NVT-H3-2AII*	0.006	<0.005	0.06	<0.01	0.021	33.2	<0.02
NVT-H3-3A	0.007	<0.005	0.05	<0.01	0.016	30.3	<0.02
NVT-H3-10S	0.011	<0.005	0.08	<0.01	0.036	21.9	0.02
NVT-H4-1A	0.011	<0.005	0.07	<0.01	0.17	73.7	0.02
NVT-H4-2A	0.031	<0.005	0.11	<0.01	0.34	200	0.04
NVT-H4-3A	0.215	<0.005	0.11	<0.01	0.031	140.5	0.05
NVT-H4-3FRI	0.027	<0.005	0.05	0.01	<0.003	21.9	<0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
NVT-H4-3FRII*	Nevinstown	Hawthorn	fruit	Autumn	-6.71	53.66	48	285656	268298
NVT-H4-4A	Nevinstown	Beech	leaves	Autumn	-6.70	53.66	53	285752	268558
NVT-H4-5A	Nevinstown	Sycamore	leaves	Autumn	-6.70	53.66	53	285826	268576
NVT-H4-6A	Nevinstown	Sycamore	leaves	Autumn	-6.70	53.66	53	285812	268534
NVT-H4-8A	Nevinstown	Sycamore	leaves	Autumn	-6.70	53.66	53	285822	268620
NVT-H4-9A	Nevinstown	Hawthorn	leaves	Autumn	-6.70	53.66	51	285780	268447
NVT-H4-11A	Nevinstown	Ash	leaves	Autumn	-6.70	53.66	43	285812	268520
NVT-H4-12A	Nevinstown	Ash	leaves	Autumn	-6.71	53.66	45	285593	268304
NVT-H4-16AI	Nevinstown	Poplar	leaves	Autumn	-6.71	53.66	48	285583	268380
NVT-H4-16AII*	Nevinstown	Poplar	leaves	Autumn	-6.71	53.66	48	285583	268380
NVT-H4-17AI	Nevinstown	Poplar	leaves	Autumn	-6.71	53.66	48	285574	268385
NVT-H4-17AII*	Nevinstown	Poplar	leaves	Autumn	-6.71	53.66	48	285574	268385
NVT-H4-18A	Nevinstown	Sycamore	leaves	Autumn	-6.71	53.66	52	285498	268380
NVT-H5-8A	Nevinstown	Oak	leaves	Autumn	-6.71	53.66	46	285491	268592
NVT-H5-10S	Nevinstown	Sycamore	leaves	Autumn	-6.71	53.66	51	285499	268596
CS1-H1-2A	Control Site	Hawthorn	leaves	Autumn	-6.74	53.66	73	283046	267975
CS1-H1-5A	Control Site	Hawthorn	leaves	Autumn	-6.74	53.65	72	283072	267955
CS1-H1-6A	Control Site	Hawthorn	leaves	Autumn	-6.74	53.65	74	283078	267947
CS1-H2-3A	Control Site	Sycamore	leaves	Autumn	-6.75	53.66	76	283024	267987
CS1-H2-5A	Control Site	Sycamore	leaves	Autumn	-6.74	53.65	72	283140	267843
CS1-H2-6A	Control Site	Ash	leaves	Autumn	-6.74	53.66	72	283040	268000
CS1-H2-8A	Control Site	Ash	leaves	Autumn	-6.74	53.66	65	283076	268009
CS1-H2-10AI	Control Site	Blackberry	leaves	Autumn	-6.74	53.66	72	283238	268011
CS1-H2-10AII*	Control Site	Blackberry	leaves	Autumn	-6.74	53.66	72	283238	268011

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
NVT-H4-3FRII*	<0.0002	0.001	<0.01	0.07	18	94.5	<0.01	<0.001	0.79	0.206	0.009	0.141	6.51	0.03	6.53
NVT-H4-4A	<0.0002	0.007	<0.01	0.16	23	34.8	<0.01	0.001	0.88	0.096	0.041	0.021	0.3	0.006	4.88
NVT-H4-5A	<0.0002	0.007	<0.01	0.32	38	64.9	0.01	0.002	1.82	0.347	0.261	0.034	0.85	0.008	7.45
NVT-H4-6A	<0.0002	0.007	<0.01	0.29	36	68.1	<0.01	0.001	1.99	0.344	0.079	0.028	0.46	0.008	7.7
NVT-H4-8A	<0.0002	0.006	<0.01	0.19	49	49.8	<0.01	0.002	2.37	0.204	0.045	0.028	0.53	0.006	6.26
NVT-H4-9A	<0.0002	0.003	<0.01	0.4	23	174.5	0.01	0.001	1.81	0.248	0.296	0.125	0.31	0.007	4.7
NVT-H4-11A	<0.0002	0.003	<0.01	0.21	21	105	0.01	0.001	2.62	0.09	0.103	0.022	0.37	0.006	8.37
NVT-H4-12A	<0.0002	0.012	<0.01	0.25	18	119	<0.01	0.032	2.31	0.082	0.082	0.019	0.37	0.022	9.13
NVT-H4-16AI	<0.0002	0.002	<0.01	0.22	18	88.3	<0.01	0.002	1.13	4.34	0.024	0.113	0.77	0.01	1.67
NVT-H4-16AII*	<0.0002	0.002	<0.01	0.28	20	94.1	<0.01	0.002	1.21	4.8	0.024	0.122	0.85	0.01	1.76
NVT-H4-17AI	<0.0002	0.002	<0.01	0.2	19	111	<0.01	0.002	1.29	5.13	0.033	0.1	2.39	0.008	2.14
NVT-H4-17AII*	<0.0002	0.002	<0.01	0.16	16	90.6	<0.01	0.001	1.05	4.27	0.033	0.094	2.61	0.009	1.74
NVT-H4-18A	<0.0002	0.013	<0.01	0.28	45	20.5	<0.01	0.002	1.58	0.156	0.051	0.034	0.5	0.059	8.34
NVT-H5-8A	<0.0002	0.021	<0.01	0.44	29	112.5	<0.01	0.003	2.16	0.202	0.083	0.069	2.03	0.007	7.59
NVT-H5-10S	<0.0002	0.008	<0.01	0.36	41	27.3	<0.01	0.003	1.46	0.207	0.065	0.049	1.76	0.007	7.45
CS1-H1-2A	<0.0002	0.002	<0.01	0.03	25	62.8	<0.01	0.002	2.14	0.03	0.035	0.168	0.3	<0.005	5.98
CS1-H1-5A	<0.0002	0.001	<0.01	0.06	24	65.7	<0.01	0.002	1.97	0.069	0.121	0.133	0.48	0.013	5.26
CS1-H1-6A	<0.0002	0.001	<0.01	0.07	29	78.5	<0.01	0.002	2.78	0.221	0.073	0.239	0.72	0.006	5.82
CS1-H2-3A	<0.0002	0.005	<0.01	0.03	39	15.3	<0.01	0.002	2.05	0.161	0.052	0.023	0.39	0.009	8.82
CS1-H2-5A	<0.0002	0.005	<0.01	0.05	16	11.3	<0.01	0.003	1.4	0.19	0.095	0.019	0.28	0.006	4.71
CS1-H2-6A	<0.0002	0.002	<0.01	0.07	19	19.6	<0.01	0.002	3.03	0.009	0.02	0.018	0.28	<0.005	8.43
CS1-H2-8A	<0.0002	0.002	<0.01	0.07	21	20.5	0.01	0.002	2.02	0.017	0.088	0.02	0.27	0.014	4.22
CS1-H2-10AI	<0.0002	0.004	<0.01	0.02	28	8.6	<0.01	0.002	1.09	0.043	0.049	0.034	0.37	<0.005	6.23
CS1-H2-10AII*	<0.0002	0.004	<0.01	0.03	30	11.7	<0.01	0.001	1.14	0.157	0.051	0.043	0.41	0.005	5.6

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
NVT-H4-3FRII*	72	0.004	0.007	<0.002	0.003	<0.005	0.79	0.007	<0.1	0.104	8.1	1.57	0.06	0.004	6.8
NVT-H4-4A	56	0.004	0.007	<0.002	0.025	<0.005	0.7	0.04	0.1	0.092	141.5	0.1	0.121	<0.002	0.71
NVT-H4-5A	67	0.005	0.009	<0.002	0.038	<0.005	1.21	0.318	0.1	0.154	220	0.11	0.016	<0.002	1.04
NVT-H4-6A	65	0.006	0.007	<0.002	0.032	<0.005	1.35	0.131	0.1	0.157	148	0.25	0.02	0.002	1.13
NVT-H4-8A	59	0.005	0.008	<0.002	0.026	<0.005	0.65	0.035	<0.1	0.278	63.4	1.12	0.021	<0.002	0.79
NVT-H4-9A	63	0.008	0.012	<0.002	0.038	<0.005	1.39	0.635	0.1	0.263	66.7	0.13	0.076	<0.002	1.72
NVT-H4-11A	53	0.004	0.008	<0.002	0.037	<0.005	0.81	0.197	0.1	0.321	43.8	0.45	0.084	<0.002	1.81
NVT-H4-12A	54	0.005	0.009	<0.002	0.022	<0.005	0.87	0.098	0.1	0.211	25.7	0.35	0.025	0.002	2.7
NVT-H4-16AI	56	<0.004	0.007	<0.002	0.017	<0.005	1.06	0.019	<0.1	0.154	36.2	0.1	0.025	<0.002	0.81
NVT-H4-16AII*	59	<0.004	0.007	<0.002	0.018	<0.005	1.13	0.021	<0.1	0.164	37.8	0.1	0.033	<0.002	0.83
NVT-H4-17AI	61	0.004	0.009	<0.002	0.016	<0.005	1	0.054	<0.1	0.136	27.5	0.38	0.029	<0.002	2.39
NVT-H4-17AII*	59	0.004	0.005	<0.002	0.012	<0.005	0.8	0.047	<0.1	0.11	22.9	0.4	0.013	<0.002	2.42
NVT-H4-18A	70	0.007	0.009	<0.002	0.033	<0.005	0.98	0.026	0.1	0.122	69.7	0.18	0.02	0.002	0.61
NVT-H5-8A	162	0.01	0.01	<0.002	0.023	<0.005	0.94	0.079	0.1	0.233	266	0.41	0.076	0.002	3.05
NVT-H5-10S	87	0.007	0.012	<0.002	0.029	<0.005	1.82	0.062	0.1	0.131	120.5	0.53	0.032	0.002	1.57
CS1-H1-2A	50	0.004	0.008	<0.002	0.022	<0.005	1.63	0.047	0.1	0.179	15.7	0.2	0.027	<0.002	0.6
CS1-H1-5A	67	0.005	0.006	<0.002	0.03	<0.005	1.3	0.283	0.1	0.262	35.9	0.52	0.07	<0.002	2.03
CS1-H1-6A	62	0.007	0.012	<0.002	0.031	<0.005	0.76	0.132	0.1	0.268	20.1	0.33	0.123	<0.002	1.59
CS1-H2-3A	63	0.005	0.007	<0.002	0.025	<0.005	1.53	0.075	<0.1	0.088	68.7	0.6	0.026	<0.002	0.9
CS1-H2-5A	60	0.005	0.008	<0.002	0.03	<0.005	1.1	0.112	<0.1	0.073	375	0.27	0.032	<0.002	0.84
CS1-H2-6A	60	<0.004	0.008	<0.002	0.03	<0.005	0.97	0.019	0.1	0.326	32.1	1.18	0.052	<0.002	0.88
CS1-H2-8A	67	0.006	0.01	<0.002	0.035	<0.005	0.71	0.122	0.1	0.361	50.8	0.15	0.036	<0.002	3.39
CS1-H2-10AI	65	0.004	0.009	<0.002	0.013	<0.005	1.14	0.044	<0.1	0.25	184	1.33	0.032	<0.002	2.05
CS1-H2-10AII*	65	<0.004	0.007	<0.002	0.012	<0.005	0.86	0.053	<0.1	0.296	345	0.92	0.031	<0.002	2.53

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
NVT-H4-3FRII*	0.131	0.79	<0.001	<0.001	6.97	<0.001	0.07	0.02	0.09	0.045	0.02	12.7	<0.001	<0.02	<0.002	<0.001
NVT-H4-4A	0.119	3.64	<0.001	<0.001	1.29	<0.001	0.15	0.09	0.2	0.106	0.03	9.87	<0.001	<0.02	0.003	<0.001
NVT-H4-5A	0.19	6.12	<0.001	<0.001	2.77	0.001	0.29	0.12	0.13	0.168	0.03	33.4	<0.001	<0.02	0.004	<0.001
NVT-H4-6A	0.191	5.58	<0.001	<0.001	1.82	0.001	0.27	0.13	0.15	0.067	0.03	35.2	<0.001	<0.02	0.004	<0.001
NVT-H4-8A	0.145	3.25	<0.001	<0.001	1.79	0.002	0.32	0.08	0.15	0.159	0.03	38.6	<0.001	<0.02	0.003	<0.001
NVT-H4-9A	0.14	7.79	<0.001	<0.001	2.32	<0.001	0.17	0.14	0.1	0.044	0.03	38.1	<0.001	0.02	0.004	<0.001
NVT-H4-11A	0.153	4.85	0.001	<0.001	1.3	0.001	0.37	0.09	0.11	0.075	0.02	54.1	<0.001	<0.02	0.003	<0.001
NVT-H4-12A	0.114	4.21	<0.001	<0.001	3.38	<0.001	0.19	0.09	0.11	0.161	0.02	33.6	<0.001	<0.02	0.003	<0.001
NVT-H4-16AI	0.18	6.83	<0.001	<0.001	1.3	<0.001	0.26	0.1	0.13	0.051	0.02	26.4	<0.001	<0.02	0.002	<0.001
NVT-H4-16AII*	0.191	7.27	<0.001	<0.001	1.4	<0.001	0.29	0.11	0.16	0.06	0.03	28.2	<0.001	<0.02	0.002	<0.001
NVT-H4-17AI	0.183	5.62	<0.001	<0.001	1.22	<0.001	0.27	0.08	0.14	0.082	0.02	27.2	<0.001	<0.02	0.002	<0.001
NVT-H4-17AII*	0.149	4.81	<0.001	<0.001	1	<0.001	0.21	0.06	0.12	0.056	0.03	22.2	<0.001	<0.02	0.002	<0.001
NVT-H4-18A	0.155	5.08	0.001	<0.001	2.38	0.002	0.22	0.13	0.17	0.327	0.03	30.2	0.001	<0.02	0.005	<0.001
NVT-H5-8A	0.288	6.9	<0.001	<0.001	1.75	<0.001	0.18	0.14	0.14	0.068	0.04	17.1	<0.001	<0.02	0.006	<0.001
NVT-H5-10S	0.233	5.81	<0.001	<0.001	4.41	<0.001	0.28	0.13	0.18	0.143	0.03	18.65	<0.001	<0.02	0.004	<0.001
CS1-H1-2A	0.245	0.26	0.001	<0.001	1.87	<0.001	0.23	0.03	0.14	0.277	0.02	43.4	<0.001	<0.02	0.002	<0.001
CS1-H1-5A	0.223	0.63	0.001	0.001	4.21	<0.001	0.26	0.03	0.16	0.124	0.03	39.8	<0.001	<0.02	0.003	<0.001
CS1-H1-6A	0.228	0.76	0.001	0.001	2.91	<0.001	0.23	0.05	0.15	0.207	0.04	59.2	<0.001	<0.02	0.004	<0.001
CS1-H2-3A	0.225	0.66	<0.001	<0.001	2.73	0.001	0.22	0.03	0.17	0.079	0.04	29	<0.001	<0.02	0.003	<0.001
CS1-H2-5A	0.168	0.48	0.001	<0.001	1.58	0.001	0.18	0.03	0.16	0.045	0.02	20.4	<0.001	<0.02	0.003	<0.001
CS1-H2-6A	0.369	0.3	<0.001	<0.001	0.82	0.002	0.46	0.02	0.14	0.148	0.04	44.1	<0.001	<0.02	0.002	<0.001
CS1-H2-8A	0.135	0.67	0.001	<0.001	3.08	0.001	0.33	0.04	0.16	0.1	0.04	34.7	<0.001	<0.02	0.002	<0.001
CS1-H2-10AI	0.163	0.23	<0.001	<0.001	2.88	<0.001	0.19	0.03	0.13	0.271	0.02	15.3	<0.001	<0.02	0.002	<0.001
CS1-H2-10AII*	0.132	0.21	<0.001	0.001	3.16	<0.001	0.15	0.02	0.14	0.098	0.02	17.8	<0.001	<0.02	<0.002	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
NVT-H4-3FRII*	0.031	<0.005	0.06	0.02	0.003	26.4	<0.02
NVT-H4-4A	0.01	<0.005	0.06	<0.01	0.029	71.9	0.02
NVT-H4-5A	0.019	<0.005	0.08	<0.01	0.231	103.5	0.02
NVT-H4-6A	0.068	<0.005	0.07	<0.01	0.078	114.5	0.03
NVT-H4-8A	0.009	<0.005	0.08	<0.01	0.024	94.5	0.02
NVT-H4-9A	0.023	<0.005	0.08	<0.01	0.467	79.8	0.03
NVT-H4-11A	0.015	<0.005	0.06	<0.01	0.126	47.4	0.02
NVT-H4-12A	0.108	<0.005	0.08	0.01	0.034	67.5	0.02
NVT-H4-16AI	0.057	<0.005	0.06	<0.01	0.012	514	0.02
NVT-H4-16AII*	0.06	<0.005	0.07	<0.01	0.011	545	0.02
NVT-H4-17AI	0.053	<0.005	0.08	0.01	0.027	735	<0.02
NVT-H4-17AII*	0.044	<0.005	0.07	0.01	0.021	604	0.02
NVT-H4-18A	0.082	<0.005	0.09	<0.01	0.022	108.5	0.03
NVT-H5-8A	0.022	<0.005	0.12	0.01	0.049	82.8	0.05
NVT-H5-10S	0.017	<0.005	0.11	0.01	0.05	77.3	0.03
CS1-H1-2A	<0.002	<0.005	0.07	<0.01	0.018	21.1	0.02
CS1-H1-5A	0.003	<0.005	0.1	<0.01	0.15	21.5	0.05
CS1-H1-6A	0.016	<0.005	0.12	<0.01	0.055	20.7	0.03
CS1-H2-3A	0.003	<0.005	0.09	<0.01	0.04	40.8	0.03
CS1-H2-5A	0.003	<0.005	0.08	<0.01	0.065	25.2	0.02
CS1-H2-6A	0.004	<0.005	0.08	<0.01	0.011	14.7	0.02
CS1-H2-8A	0.009	<0.005	0.09	<0.01	0.057	16.8	0.03
CS1-H2-10AI	<0.002	<0.005	0.08	0.01	0.018	20.5	0.02
CS1-H2-10AII*	<0.002	<0.005	0.06	<0.01	0.021	26.3	<0.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
CS2-W1-4A	Control Site	Beech	leaves	Autumn	-6.72	53.67	40	284341	269311
CS2-W1-5A	Control Site	Beech	leaves	Autumn	-6.73	53.67	51	284322	269285
CS2-W1-6A	Control Site	Hawthorn	leaves	Autumn	-6.73	53.67	46	284290	269227
CS2-W1-8A	Control Site	Sycamore	leaves	Autumn	-6.73	53.67	47	284207	269209
CS2-W1-9A	Control Site	Sycamore	leaves	Autumn	-6.73	53.67	45	284266	269208
CS2-W1-11A	Control Site	Ash	leaves	Autumn	-6.73	53.67	51	284254	269195
CS3-W-1A	Control Site	Oak	leaves	Autumn	-6.75	53.66	80	282967	268656
CS3-W-3A	Control Site	Oak	leaves	Autumn	-6.75	53.66	83	282989	268636
CS3-W-4A	Control Site	Poplar	leaves	Autumn	-6.74	53.66	67	283010	267950
CS3-W-5AI	Control Site	Poplar	leaves	Autumn	-6.57	53.66	75	283012	267952
CS3-W-5AII*	Control Site	Poplar	leaves	Autumn	-6.57	53.66	75	283007	267948

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
CS2-W1-4A	<0.0002	0.009	<0.01	0.05	24	77.7	0.01	0.001	1.28	0.253	0.098	0.111	1.14	0.006	7.66
CS2-W1-5A	<0.0002	0.006	<0.01	0.06	22	43.1	<0.01	0.003	1.66	0.075	0.063	0.042	1.01	0.008	8.2
CS2-W1-6A	<0.0002	0.001	0.01	0.06	25	45.6	<0.01	0.003	2.04	0.052	0.147	0.221	1.07	0.028	6.18
CS2-W1-8A	<0.0002	0.003	<0.01	0.04	16	7.5	<0.01	0.002	1.44	0.046	0.04	0.018	0.4	<0.005	8.72
CS2-W1-9A	<0.0002	0.005	<0.01	0.09	41	17.4	<0.01	0.002	1.91	0.079	0.105	0.043	0.64	0.013	6.22
CS2-W1-11A	<0.0002	<0.001	<0.01	0.07	20	34.7	<0.01	0.002	4.36	0.012	0.073	0.043	0.42	0.018	7.74
CS3-W-1A	<0.0002	0.015	<0.01	0.05	23	31.4	<0.01	0.002	1.2	0.047	0.115	0.091	1.94	0.01	7.4
CS3-W-3A	<0.0002	0.012	<0.01	0.05	23	24	<0.01	0.002	1.27	0.029	0.067	0.054	2.19	0.019	6.59
CS3-W-4A	<0.0002	0.001	<0.01	0.03	70	18	<0.01	0.001	2.51	10.1	0.225	0.567	1.06	0.058	6.55
CS3-W-5AI	<0.0002	0.001	<0.01	0.1	69	19.7	<0.01	0.002	3.14	4.7	0.075	0.476	1.86	<0.005	6.84
CS3-W-5AII*	<0.0002	0.003	0.01	0.12	84	17.9	<0.01	0.002	2.87	5.96	0.077	0.455	2.66	0.005	9.02

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
CS2-W1-4A	84	0.008	0.008	<0.002	0.025	<0.005	1.15	0.076	0.1	0.181	252	0.28	0.166	<0.002	3.4
CS2-W1-5A	82	0.007	0.007	<0.002	0.028	<0.005	1.03	0.036	0.1	0.242	108.5	0.27	0.127	<0.002	1.63
CS2-W1-6A	143	0.018	0.012	0.002	0.043	<0.005	2.22	0.095	0.1	0.241	31.1	0.69	0.063	0.003	1.06
CS2-W1-8A	90	0.006	0.007	<0.002	0.038	<0.005	1.43	0.051	<0.1	0.092	64	0.15	0.014	<0.002	0.53
CS2-W1-9A	102	0.013	0.007	<0.002	0.029	<0.005	1.85	0.097	0.1	0.188	173	0.17	0.034	0.003	0.97
CS2-W1-11A	96	0.01	0.009	<0.002	0.031	<0.005	1.5	0.045	0.1	0.488	50	0.51	0.028	0.002	1.56
CS3-W-1A	114	0.015	<0.005	<0.002	0.021	<0.005	1.15	0.105	0.2	0.129	613	0.48	0.095	0.003	4.8
CS3-W-3A	99	0.007	<0.005	<0.002	0.034	<0.005	1.13	0.062	0.1	0.151	198.5	0.49	0.103	0.002	4.36
CS3-W-4A	63	<0.004	0.011	<0.002	0.015	<0.005	1.56	0.3	0.1	0.175	134	0.3	0.075	<0.002	5.05
CS3-W-5AI	95	0.009	0.026	<0.002	0.025	<0.005	2.81	0.07	0.1	0.034	81.9	1.61	0.074	0.002	7.32
CS3-W-5AII*	119	0.013	0.037	0.002	0.027	<0.005	3.32	0.06	0.2	0.027	51	2.02	0.076	0.004	11.4

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
CS2-W1-4A	0.185	0.55	<0.001	<0.001	1.43	<0.001	0.17	0.05	0.22	0.181	0.03	17.65	<0.001	<0.02	0.005	<0.001
CS2-W1-5A	0.159	0.64	<0.001	<0.001	1.56	<0.001	0.18	0.04	0.23	0.177	0.03	23.8	<0.001	<0.02	0.006	<0.001
CS2-W1-6A	0.188	0.45	<0.001	<0.001	4.52	0.001	0.19	0.03	0.15	0.397	0.02	23.4	<0.001	<0.02	0.012	<0.001
CS2-W1-8A	0.185	0.31	<0.001	<0.001	0.98	0.001	0.25	0.04	0.2	0.183	0.03	10.15	<0.001	<0.02	0.003	<0.001
CS2-W1-9A	0.21	0.71	<0.001	<0.001	1.36	0.002	0.29	0.06	0.19	0.311	0.03	21.9	<0.001	<0.02	0.008	<0.001
CS2-W1-11A	0.142	0.58	0.001	0.001	2.59	0.002	0.38	0.04	0.16	0.359	0.02	60.8	<0.001	<0.02	0.008	<0.001
CS3-W-1A	0.229	0.6	<0.001	<0.001	2.04	<0.001	0.18	0.04	0.17	0.1	0.04	11.15	<0.001	<0.02	0.007	<0.001
CS3-W-3A	0.282	0.45	<0.001	<0.001	2.56	<0.001	0.16	0.03	0.11	0.133	0.03	12.3	<0.001	<0.02	0.005	<0.001
CS3-W-4A	0.204	0.43	0.001	<0.001	16.35	<0.001	0.37	0.02	0.2	0.226	0.03	45.1	<0.001	<0.02	<0.002	<0.001
CS3-W-5AI	0.24	0.4	0.001	<0.001	1.6	<0.001	0.53	0.03	0.2	1.835	0.03	36.2	<0.001	0.02	0.006	<0.001
CS3-W-5AII*	0.236	0.76	<0.001	0.001	1.56	0.001	0.51	0.04	0.21	2.01	0.04	35.3	<0.001	<0.02	0.007	<0.001

Table A-1. Raw data of trace element analysis from plants collected from Navan area in 2015 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
CS2-W1-4A	0.003	<0.005	0.1	<0.01	0.04	37.5	0.03
CS2-W1-5A	0.003	<0.005	0.11	<0.01	0.021	41.7	0.04
CS2-W1-6A	0.004	0.005	0.2	0.01	0.042	16.2	0.07
CS2-W1-8A	<0.002	<0.005	0.08	<0.01	0.037	16.5	0.02
CS2-W1-9A	0.005	<0.005	0.15	0.01	0.055	24.5	0.05
CS2-W1-11A	0.011	<0.005	0.15	<0.01	0.023	19.5	0.04
CS3-W-1A	0.004	<0.005	0.16	0.01	0.083	17.5	0.04
CS3-W-3A	0.002	<0.005	0.11	0.01	0.044	17.2	0.02
CS3-W-4A	0.002	<0.005	0.06	<0.01	0.1	263	0.02
CS3-W-5AI	0.003	<0.005	0.15	0.01	0.041	113	0.04
CS3-W-5AII*	0.005	0.007	0.16	0.05	0.039	144.5	0.04

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	ING_E UTM	ING_N UTM
DEL-2	Delvin	Sycamore	leaves	Spring	-7.14	53.60	77	256710	261055
DEL-3	Delvin	Ash	leaves	Spring	-7.14	53.60	91	256732	261085
DEL-4	Delvin	Sycamore	leaves	Spring	-7.14	53.60	90	256695	261083
DEL-5	Delvin	Beech	leaves	Spring	-7.14	53.60	83	256681	261075
DEL-6	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	83	256688	261066
DEL-7	Delvin	Beech	leaves	Spring	-7.14	53.60	77	256678	261086
DEL-8	Delvin	Sycamore	leaves	Spring	-7.14	53.60	99	256682	261103
DEL-9	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	99	256689	261112
DEL-10A	Delvin	Beech	leaves	Spring	-7.14	53.60	88	256686	261082
DEL-10B*	Delvin	Beech	leaves	Spring	-7.14	53.60	88	256686	261082
DEL-11	Delvin	Beech	leaves	Spring	-7.14	53.60	85	256672	261101
DEL-12	Delvin	Ash	leaves	Spring	-7.14	53.60	89	256665	261119
DEL-13	Delvin	Beech	leaves	Spring	-7.14	53.60	80	256724	261033
DEL-14	Delvin	Ash	leaves	Spring	-7.14	53.60	79	256731	261061
DEL-15	Delvin	Ash	leaves	Spring	-7.14	53.60	81	256753	261085
DEL-16	Delvin	Ash	leaves	Spring	-7.14	53.60	81	256754	261104
DEL-17	Delvin	Ash	leaves	Spring	-7.14	53.60	77	256780	261124
DEL-18	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	84	256767	261137
DEL-19	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	82	256745	261150
DEL-20A	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	67	256794	261117
DEL-20B*	Delvin	Hawthorn	leaves	Spring	-7.14	53.60	67	256794	261117
DEL-21	Delvin	Blackberry	leaves	Spring	-7.15	53.59	81	256497	260746
DEL-22	Delvin	Blackberry	leaves	Spring	-7.15	53.59	87	256437	260783

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
DEL-1	<0.0002	0.016	<0.01	0.02	19	3.4	<0.01	0.001	0.57	0.014	0.016	0.015	0.48	<0.005	5.87
DEL-2	<0.0002	0.003	<0.01	0.05	26	4.5	<0.01	0.001	1.6	0.101	0.036	0.061	2.9	<0.005	8.83
DEL-3	<0.0002	0.001	<0.01	0.03	21	2.3	<0.01	0.001	1.69	0.005	0.02	0.046	0.74	<0.005	6.24
DEL-4	<0.0002	0.004	<0.01	0.03	26	4.6	<0.01	0.002	1.5	0.056	0.041	0.03	1.24	0.006	7.14
DEL-5	<0.0002	0.005	<0.01	0.02	16	6.9	<0.01	0.001	0.64	0.078	0.013	0.026	1.01	<0.005	6.34
DEL-6	<0.0002	0.001	<0.01	0.03	28	9.2	<0.01	0.002	1.71	0.061	0.043	0.114	1.37	<0.005	4.01
DEL-7	<0.0002	0.005	<0.01	0.02	27	12	<0.01	0.001	0.78	0.042	0.014	0.031	1.27	<0.005	7.03
DEL-8	<0.0002	0.003	<0.01	0.03	23	6.2	<0.01	0.003	1.74	0.104	0.033	0.032	1.08	<0.005	4.83
DEL-9	<0.0002	0.001	<0.01	0.04	24	12.2	<0.01	0.002	1.21	0.066	0.036	0.192	0.41	<0.005	4.57
DEL-10A	<0.0002	0.005	<0.01	0.04	20	22.3	<0.01	0.001	1.27	0.029	0.022	0.019	0.76	<0.005	7.17
DEL-10B*	<0.0002	0.005	<0.01	0.04	13	11.7	<0.01	0.002	1.03	0.091	0.014	0.042	3.48	<0.005	6.75
DEL-11	<0.0002	0.006	<0.01	0.02	14	10.1	<0.01	0.002	1.06	0.076	0.014	0.026	0.87	<0.005	6.43
DEL-12	<0.0002	0.009	<0.01	0.03	18	9.8	<0.01	0.002	0.81	0.088	0.025	0.024	0.81	<0.005	6
DEL-13	<0.0002	0.002	<0.01	0.03	21	3.7	<0.01	0.001	1.91	0.048	0.012	0.027	2.28	<0.005	12.6
DEL-14	<0.0002	0.001	<0.01	0.02	14	3.8	<0.01	<0.001	0.95	0.003	0.008	0.031	1.13	<0.005	8.94
DEL-15	<0.0002	<0.001	<0.01	0.02	14	4.6	<0.01	<0.001	1.47	0.005	0.01	0.025	1.65	0.005	7.88
DEL-16	<0.0002	0.001	<0.01	0.03	23	8	<0.01	<0.001	1.61	0.007	0.009	0.041	1.38	0.007	7.18
DEL-17	<0.0002	0.001	<0.01	0.01	11	1.9	<0.01	0.001	0.64	0.006	0.01	0.028	2.69	<0.005	6.55
DEL-18	<0.0002	0.001	<0.01	0.01	16	20.3	<0.01	<0.001	1.81	0.104	0.016	0.076	1.07	<0.005	5.84
DEL-19	<0.0002	0.002	<0.01	0.06	14	17.7	<0.01	0.002	1.76	0.073	0.029	0.123	1.26	<0.005	5.04
DEL-20A	<0.0002	0.001	<0.01	0.03	20	29.1	<0.01	0.001	2.06	0.229	0.021	0.067	1.28	0.005	7.52
DEL-20B*	<0.0002	0.001	<0.01	0.02	17	25.9	<0.01	0.001	1.8	0.185	0.015	0.073	0.5	0.006	7.85
DEL-21	<0.0002	0.001	<0.01	0.02	61	5.3	<0.01	0.002	1.58	0.01	0.014	0.015	2.15	0.006	4.96
DEL-22	<0.0002	0.002	<0.01	0.04	40	2.9	<0.01	0.001	1.51	0.02	0.016	0.03	0.8	0.012	6.96

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
DEL-1	48	0.004	0.009	<0.002	0.008	<0.005	0.83	0.015	<0.1	0.134	136	0.37	0.031	<0.002	1.18
DEL-2	101	0.007	0.011	<0.002	0.026	<0.005	1.58	0.034	<0.1	0.261	64.7	1.83	0.023	0.004	2.89
DEL-3	89	0.004	0.014	<0.002	0.017	<0.005	3.5	0.019	<0.1	0.272	38.4	0.87	0.086	<0.002	3.28
DEL-4	79	0.008	0.013	<0.002	0.02	<0.005	1.99	0.046	<0.1	0.224	79.3	2.52	0.052	0.003	1.2
DEL-5	79	0.004	0.011	<0.002	0.017	<0.005	0.98	0.01	<0.1	0.141	76.3	0.37	0.042	<0.002	1.32
DEL-6	78	0.007	0.015	<0.002	0.021	<0.005	2.45	0.032	0.1	0.34	29.9	3.05	0.16	0.003	1.17
DEL-7	85	<0.004	0.01	<0.002	0.017	<0.005	0.81	0.011	<0.1	0.159	123	0.47	0.052	<0.002	1.66
DEL-8	79	0.006	0.01	<0.002	0.019	<0.005	1.96	0.025	<0.1	0.237	166	2.49	0.06	0.004	1.31
DEL-9	71	0.005	0.013	<0.002	0.02	<0.005	1.75	0.037	<0.1	0.278	37.2	1.31	0.084	<0.002	0.88
DEL-10A	63	0.004	0.009	<0.002	0.014	<0.005	0.75	0.013	<0.1	0.091	101	0.33	0.088	0.002	1.16
DEL-10B*	181	0.005	0.01	<0.002	0.01	<0.005	0.85	0.008	<0.1	0.126	73.8	0.49	0.043	0.002	1.65
DEL-11	58	<0.004	0.009	<0.002	0.01	<0.005	0.9	0.009	<0.1	0.147	67.5	0.46	0.066	0.002	1.63
DEL-12	68	<0.004	0.011	<0.002	0.01	<0.005	1.01	0.037	<0.1	0.113	98.8	0.42	0.054	0.002	1.61
DEL-13	61	<0.004	0.017	<0.002	0.011	<0.005	1.06	0.015	<0.1	0.259	12.3	0.86	0.029	<0.002	2.42
DEL-14	63	<0.004	0.018	<0.002	0.007	<0.005	1.47	0.004	<0.1	0.18	16.7	0.51	0.017	<0.002	2.63
DEL-15	83	<0.004	0.012	<0.002	0.009	<0.005	1.15	0.007	<0.1	0.224	17.2	0.58	0.02	<0.002	2.98
DEL-16	78	<0.004	0.012	<0.002	0.009	<0.005	1.46	0.005	<0.1	0.268	44.6	0.19	0.014	<0.002	2.34
DEL-17	75	<0.004	0.012	<0.002	0.006	<0.005	1.69	0.006	<0.1	0.127	9.8	0.31	0.018	<0.002	1.46
DEL-18	51	0.004	0.015	<0.002	0.018	<0.005	1.75	0.014	<0.1	0.194	15	0.4	0.031	<0.002	1.22
DEL-19	71	0.005	0.013	<0.002	0.018	<0.005	1.59	0.024	<0.1	0.235	12.2	0.92	0.05	<0.002	1
DEL-20A	78	0.005	0.014	<0.002	0.014	<0.005	1.24	0.014	<0.1	0.252	17.6	1.76	0.046	<0.002	0.69
DEL-20B*	46	<0.004	0.013	<0.002	0.014	<0.005	1.28	0.01	<0.1	0.25	18.6	1.64	0.034	<0.002	0.74
DEL-21	81	<0.004	0.011	<0.002	0.011	<0.005	0.57	0.009	<0.1	0.535	101.5	1.17	0.013	<0.002	0.47
DEL-22	60	0.004	0.015	<0.002	0.006	<0.005	0.7	0.01	<0.1	0.543	29.8	2	0.007	<0.002	1.13

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
DEL-1	0.183	0.07	<0.001	0.001	1.4	<0.001	0.15	0.01	0.19	0.045	0.02	11.65	<0.001	<0.02	<0.002	<0.001
DEL-2	0.324	0.14	<0.001	0.001	1.99	0.001	0.27	0.01	0.21	0.206	0.02	49.3	<0.001	<0.02	0.003	<0.001
DEL-3	0.312	0.07	<0.001	<0.001	5.94	<0.001	0.35	0.01	0.16	0.096	0.01	44	<0.001	<0.02	0.002	<0.001
DEL-4	0.276	0.15	<0.001	<0.001	2.48	0.001	0.27	0.02	0.2	0.099	0.02	47.1	<0.001	<0.02	0.004	<0.001
DEL-5	0.151	0.09	<0.001	0.001	1.8	<0.001	0.15	0.01	0.19	0.055	0.01	17.85	<0.001	<0.02	0.002	<0.001
DEL-6	0.257	0.16	<0.001	<0.001	2.5	<0.001	0.18	0.02	0.15	0.061	0.02	57.3	<0.001	<0.02	0.005	<0.001
DEL-7	0.178	0.1	<0.001	<0.001	1.8	<0.001	0.16	0.01	0.2	0.049	0.01	22.2	<0.001	<0.02	<0.002	<0.001
DEL-8	0.424	0.13	<0.001	<0.001	3.68	0.001	0.3	0.02	0.2	0.069	0.02	56.8	<0.001	<0.02	0.004	<0.001
DEL-9	0.207	0.11	<0.001	<0.001	1.15	<0.001	0.17	0.01	0.15	0.037	0.02	38.1	<0.001	<0.02	0.002	<0.001
DEL-10A	0.133	0.1	<0.001	0.001	2.09	<0.001	0.16	0.02	0.24	0.06	0.02	39.6	<0.001	<0.02	0.003	<0.001
DEL-10B*	0.174	0.11	<0.001	0.001	1.53	<0.001	0.14	0.02	0.24	0.049	0.03	29	<0.001	<0.02	<0.002	<0.001
DEL-11	0.178	0.07	<0.001	0.001	1.42	<0.001	0.14	0.01	0.23	0.055	<0.01	28.9	<0.001	<0.02	<0.002	<0.001
DEL-12	0.18	0.09	<0.001	<0.001	1.32	<0.001	0.16	0.01	0.21	0.035	0.01	21.2	<0.001	<0.02	0.002	<0.001
DEL-13	0.211	0.05	<0.001	0.001	1.62	<0.001	0.25	0.01	0.2	0.889	<0.01	48.8	<0.001	<0.02	<0.002	<0.001
DEL-14	0.17	0.04	<0.001	<0.001	1.52	0.002	0.32	0.01	0.19	0.682	<0.01	19.1	<0.001	<0.02	<0.002	<0.001
DEL-15	0.166	0.05	<0.001	<0.001	1.42	0.003	0.35	0.01	0.17	0.477	0.01	39.3	<0.001	<0.02	<0.002	<0.001
DEL-16	0.184	0.04	<0.001	0.001	2.01	0.001	0.29	<0.01	0.16	0.095	<0.01	37.1	<0.001	<0.02	<0.002	<0.001
DEL-17	0.175	0.05	<0.001	<0.001	1.1	0.001	0.25	0.01	0.18	0.426	<0.01	11.55	<0.001	<0.02	<0.002	<0.001
DEL-18	0.19	0.12	<0.001	0.001	0.69	<0.001	0.18	0.01	0.15	0.506	0.01	54	<0.001	<0.02	0.002	<0.001
DEL-19	0.183	0.13	<0.001	<0.001	1.35	<0.001	0.18	0.01	0.16	0.142	0.01	67.9	<0.001	<0.02	0.003	<0.001
DEL-20A	0.16	0.11	<0.001	0.002	2.77	<0.001	0.19	0.02	0.16	0.268	0.01	82.7	<0.001	<0.02	0.002	<0.001
DEL-20B*	0.185	0.09	<0.001	<0.001	3.16	<0.001	0.17	0.01	0.16	0.224	0.01	69.5	<0.001	<0.02	<0.002	<0.001
DEL-21	0.232	0.08	<0.001	<0.001	1.34	0.003	0.31	0.01	0.13	0.145	0.01	42.2	<0.001	<0.02	<0.002	<0.001
DEL-22	0.289	0.08	<0.001	0.001	2.14	0.002	0.31	0.01	0.12	1.295	0.01	47.2	<0.001	<0.02	0.002	<0.001

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
DEL-1	0.037	<0.005	0.11	<0.01	0.01	14.4	<0.02
DEL-2	0.002	<0.005	0.17	0.01	0.025	44.5	0.02
DEL-3	0.002	<0.005	0.15	<0.01	0.013	22.7	<0.02
DEL-4	0.002	<0.005	0.17	0.02	0.029	25.7	0.02
DEL-5	<0.002	<0.005	0.13	0.01	0.01	20	<0.02
DEL-6	0.003	<0.005	0.16	0.01	0.022	18	0.04
DEL-7	0.003	<0.005	0.12	0.01	0.007	18.2	<0.02
DEL-8	<0.002	<0.005	0.15	0.01	0.018	38.9	0.02
DEL-9	0.003	<0.005	0.14	<0.01	0.023	19.9	0.02
DEL-10A	<0.002	<0.005	0.13	<0.01	0.008	19	0.02
DEL-10B*	<0.002	<0.005	0.13	0.01	0.007	27	<0.02
DEL-11	0.002	<0.005	0.13	0.01	0.006	25.3	<0.02
DEL-12	<0.002	<0.005	0.15	<0.01	0.024	25.1	<0.02
DEL-13	<0.002	<0.005	0.12	<0.01	0.011	28.9	<0.02
DEL-14	0.003	<0.005	0.12	<0.01	0.004	20.7	<0.02
DEL-15	<0.002	<0.005	0.11	<0.01	0.005	24.7	<0.02
DEL-16	0.006	<0.005	0.12	<0.01	0.009	20	<0.02
DEL-17	0.002	<0.005	0.13	0.01	0.006	19	<0.02
DEL-18	<0.002	0.009	0.12	0.01	0.011	24	<0.02
DEL-19	0.009	0.005	0.14	<0.01	0.015	22.2	0.02
DEL-20A	0.003	<0.005	0.14	<0.01	0.013	26.7	0.02
DEL-20B*	0.002	<0.005	0.13	<0.01	0.007	23.6	<0.02
DEL-21	0.003	<0.005	0.14	<0.01	0.003	21	<0.02
DEL-22	0.005	<0.005	0.15	0.01	0.008	27.6	<0.02

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Lines	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
BALDM-1	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	72		
BALDM-2	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	76	235246	266250
BALDM-3	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	73	235250	266240
BALDM-4	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	77	235265	266229
BALDM-5	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	75	235271	266215
BALDM-6	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	72	235278	266198
BALDM-7	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	71	235282	266191
BALDM-8	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	72	235286	266181
BALDM-9	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	70	235291	266170
BALDM-10A	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	73	235298	266163
BALDM-10B*	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	73	235298	266163
BALDM-11	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	77	235309	266148
BALDM-12	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.64	76	235317	266137
BALDM-13	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	74	235206	266324
BALDM-14	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	78	235199	266335
BALDM-15	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	73	235195	266350
BALDM-16	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	79	235194	266359
BALDM-17	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	78	235179	266381
BALDM-18	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	75	235166	266399
BALDM-19	Ballinalack	A - B profile	Hawthorn	leaves	Spring	-7.47	53.65	78	235154	266427
BALDM-20A	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	69	235136	266104
BALDM-20B*	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	69	235136	266104
BALDM-21	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	68	235126	266102
BALDM-22	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	69	235117	266095

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
BALDM-1	<0.0002	0.001	<0.01	0.04	39	20.3	<0.01	0.002	1.02	0.251	0.025	0.169	0.16	<0.005	6.32
BALDM-2	<0.0002	0.002	<0.01	0.02	37	7.8	<0.01	0.001	0.92	0.226	0.044	0.137	0.21	<0.005	6.44
BALDM-3	<0.0002	0.002	<0.01	0.03	18	6.4	0.01	0.001	0.65	0.396	0.08	0.163	0.19	<0.005	6.75
BALDM-4	<0.0002	0.001	<0.01	0.02	32	12.8	<0.01	0.001	1.37	0.267	0.101	0.198	0.21	<0.005	12.35
BALDM-5	<0.0002	0.001	<0.01	0.04	34	8.9	<0.01	0.004	1.15	0.191	0.052	0.113	1.02	<0.005	5.23
BALDM-6	<0.0002	0.003	<0.01	0.03	26	11.6	<0.01	0.001	1.33	0.36	0.058	0.197	0.38	<0.005	9.67
BALDM-7	<0.0002	0.002	<0.01	0.03	30	13.7	<0.01	0.001	1.54	0.254	0.064	0.101	0.7	<0.005	7.84
BALDM-8	<0.0002	0.001	<0.01	0.02	30	13.4	<0.01	0.001	1.22	0.475	0.083	0.125	0.41	<0.005	12.85
BALDM-9	<0.0002	0.001	<0.01	0.03	62	14.9	<0.01	0.002	1.5	0.513	0.078	0.202	0.72	<0.005	14.7
BALDM-10A	<0.0002	0.001	<0.01	0.02	30	12.3	<0.01	0.001	1.27	0.471	0.065	0.094	0.23	0.005	7.74
BALDM-10B*	<0.0002	0.002	<0.01	0.02	31	12	<0.01	0.001	1.32	0.427	0.072	0.104	0.25	<0.005	8.23
BALDM-11	<0.0002	0.001	<0.01	0.04	38	15	<0.01	0.001	1.19	0.416	0.054	0.113	0.36	<0.005	9.11
BALDM-12	<0.0002	0.001	<0.01	0.02	43	7.5	<0.01	<0.001	0.97	0.232	0.022	0.139	0.51	<0.005	7.78
BALDM-13	<0.0002	0.001	<0.01	0.03	29	11.4	<0.01	0.001	1.13	0.264	0.043	0.108	0.7	<0.005	7.42
BALDM-14	<0.0002	<0.001	<0.01	0.03	23	11.8	<0.01	<0.001	1.28	0.299	0.061	0.124	0.22	<0.005	7.75
BALDM-15	<0.0002	0.001	<0.01	0.03	27	11	<0.01	0.002	1.29	0.206	0.064	0.133	0.51	0.005	8.5
BALDM-16	<0.0002	0.001	<0.01	0.03	31	11.3	<0.01	0.001	1.37	0.277	0.079	0.088	0.43	<0.005	9.64
BALDM-17	<0.0002	0.001	<0.01	0.02	24	13.5	<0.01	0.001	1.15	0.271	0.071	0.079	0.42	<0.005	6.67
BALDM-18	<0.0002	0.001	<0.01	0.04	27	19.2	<0.01	<0.001	1.27	0.633	0.127	0.128	0.28	<0.005	9.73
BALDM-19	<0.0002	<0.001	<0.01	0.02	24	12.5	<0.01	0.001	1.03	0.1	0.028	0.049	0.34	<0.005	7.03
BALDM-20A	<0.0002	0.001	<0.01	0.02	21	20.7	<0.01	0.002	1.28	0.073	0.034	0.124	0.8	0.009	6.83
BALDM-20B*	<0.0002	0.001	<0.01	0.03	23	22.9	<0.01	0.001	1.3	0.1	0.037	0.103	0.39	0.006	7.69
BALDM-21	<0.0002	0.001	<0.01	0.03	18	19.1	<0.01	0.002	1.47	0.127	0.026	0.151	0.57	<0.005	9.22
BALDM-22	<0.0002	0.001	<0.01	0.01	30	23.4	<0.01	0.001	1.8	0.21	0.024	0.096	0.27	<0.005	9.07

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
BALDM-1	56	0.004	0.006	<0.002	0.009	<0.005	1.23	0.02	<0.1	0.218	15.5	0.29	0.084	<0.002	0.96
BALDM-2	54	0.005	0.005	<0.002	0.009	<0.005	1.41	0.044	<0.1	0.209	27	0.33	0.101	<0.002	1.02
BALDM-3	58	<0.004	0.005	<0.002	0.006	<0.005	1.89	0.083	<0.1	0.258	65.5	0.55	0.094	<0.002	2.18
BALDM-4	64	0.004	0.005	<0.002	0.008	<0.005	1.35	0.111	<0.1	0.223	23.9	0.59	0.121	0.002	2.9
BALDM-5	103	0.005	0.009	<0.002	0.007	<0.005	1.38	0.053	<0.1	0.22	17.6	0.54	0.144	0.002	1.04
BALDM-6	54	0.005	0.008	<0.002	0.009	<0.005	1.29	0.091	<0.1	0.229	50	0.56	0.122	<0.002	1.41
BALDM-7	72	0.006	0.01	<0.002	0.01	<0.005	1.48	0.085	<0.1	0.232	28.6	0.57	0.11	<0.002	1.36
BALDM-8	89	0.005	0.01	<0.002	0.008	<0.005	1.61	0.121	<0.1	0.212	20.6	0.37	0.102	0.002	1.65
BALDM-9	122	0.006	0.009	<0.002	0.013	<0.005	1.7	0.098	<0.1	0.256	22.7	0.54	0.125	<0.002	2.27
BALDM-10A	70	0.005	0.007	<0.002	0.009	<0.005	1.44	0.07	<0.1	0.247	24.4	0.56	0.212	<0.002	1.73
BALDM-10B*	73	0.004	0.01	<0.002	0.008	<0.005	1.53	0.074	<0.1	0.248	25.2	0.6	0.2	<0.002	1.83
BALDM-11	73	0.005	0.008	<0.002	0.011	<0.005	1.41	0.057	<0.1	0.337	24.9	0.71	0.12	<0.002	1.73
BALDM-12	76	0.004	0.01	<0.002	0.011	<0.005	1.45	0.022	<0.1	0.254	18.8	0.77	0.112	0.002	1.1
BALDM-13	83	0.004	0.007	<0.002	0.012	<0.005	1.62	0.042	<0.1	0.238	34.4	0.84	0.191	<0.002	1.06
BALDM-14	55	0.004	0.012	<0.002	0.01	<0.005	1.31	0.072	<0.1	0.224	16.5	0.24	0.101	<0.002	1.4
BALDM-15	75	0.006	0.01	<0.002	0.015	<0.005	1.52	0.071	<0.1	0.262	22.4	0.78	0.156	0.002	1
BALDM-16	77	0.005	0.01	<0.002	0.016	<0.005	1.53	0.088	<0.1	0.227	23.5	0.43	0.12	0.002	6.86
BALDM-17	71	0.007	0.012	<0.002	0.014	<0.005	1.59	0.109	<0.1	0.235	34.1	1.23	0.133	0.003	1.04
BALDM-18	109	0.004	0.01	<0.002	0.011	<0.005	1.51	0.145	<0.1	0.28	53.9	0.89	0.079	0.002	3.29
BALDM-19	48	0.004	0.006	<0.002	0.009	<0.005	1.43	0.024	<0.1	0.196	21.1	1.15	0.189	0.002	0.83
BALDM-20A	61	0.006	0.033	<0.002	0.008	<0.005	1.38	0.026	<0.1	0.243	12.4	1.5	0.138	0.002	0.92
BALDM-20B*	58	0.005	0.033	<0.002	0.013	<0.005	1.41	0.027	<0.1	0.224	14.7	1.58	0.104	0.003	0.59
BALDM-21	67	0.006	0.016	<0.002	0.009	<0.005	1.68	0.018	<0.1	0.251	17.8	3.79	0.08	0.002	0.64
BALDM-22	57	0.004	0.011	<0.002	0.013	<0.005	1.55	0.018	<0.1	0.275	14.8	2.25	0.1	<0.002	0.66

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
BALDM-1	0.378	0.15	<0.001	<0.001	1.77	<0.001	0.24	0.01	0.14	0.113	0.01	35.6	<0.001	<0.02	0.002	<0.001
BALDM-2	0.307	0.09	<0.001	<0.001	1.9	<0.001	0.21	0.01	0.12	0.046	0.01	34.4	<0.001	<0.02	0.002	<0.001
BALDM-3	0.29	0.07	<0.001	<0.001	4.48	<0.001	0.18	0.01	0.11	0.021	0.01	16.5	<0.001	<0.02	0.002	<0.001
BALDM-4	0.374	0.08	<0.001	<0.001	2.06	<0.001	0.22	0.01	0.15	0.124	0.01	47.1	<0.001	<0.02	0.002	<0.001
BALDM-5	0.335	0.16	<0.001	<0.001	1.6	<0.001	0.21	0.02	0.12	0.074	0.01	40.1	<0.001	<0.02	0.003	<0.001
BALDM-6	0.381	0.09	<0.001	<0.001	2.73	<0.001	0.22	0.01	0.13	0.049	0.01	43.1	<0.001	<0.02	0.002	<0.001
BALDM-7	0.38	0.09	<0.001	<0.001	2.34	<0.001	0.22	0.02	0.14	0.09	0.01	50.7	<0.001	<0.02	0.003	<0.001
BALDM-8	0.378	0.16	<0.001	<0.001	3.5	<0.001	0.24	0.01	0.13	0.105	0.01	44	<0.001	<0.02	0.002	<0.001
BALDM-9	0.421	0.12	<0.001	<0.001	3.69	<0.001	0.28	0.02	0.15	0.206	0.02	58.4	<0.001	<0.02	0.003	<0.001
BALDM-10A	0.317	0.08	<0.001	<0.001	3.27	<0.001	0.25	0.01	0.15	0.073	<0.01	43.5	<0.001	<0.02	0.002	<0.001
BALDM-10B*	0.335	0.07	<0.001	<0.001	3.58	<0.001	0.24	0.02	0.13	0.071	0.01	44.1	<0.001	<0.02	<0.002	<0.001
BALDM-11	0.385	0.07	<0.001	<0.001	1.27	<0.001	0.22	0.02	0.14	0.118	<0.01	40.4	<0.001	<0.02	0.002	<0.001
BALDM-12	0.387	0.05	<0.001	<0.001	2.5	<0.001	0.22	0.01	0.12	0.209	0.01	32.7	<0.001	<0.02	<0.002	<0.001
BALDM-13	0.371	0.09	<0.001	<0.001	1.66	<0.001	0.26	0.02	0.13	0.144	<0.01	39.6	<0.001	<0.02	0.002	<0.001
BALDM-14	0.289	0.12	<0.001	0.001	1.92	<0.001	0.19	0.02	0.13	0.098	0.01	49.3	<0.001	<0.02	0.002	<0.001
BALDM-15	0.357	0.14	<0.001	<0.001	2.49	<0.001	0.21	0.02	0.12	0.096	0.02	42.5	<0.001	<0.02	0.003	<0.001
BALDM-16	0.314	0.09	<0.001	<0.001	2.37	<0.001	0.22	0.02	0.15	0.082	0.01	47.2	<0.001	<0.02	0.003	<0.001
BALDM-17	0.362	0.13	<0.001	<0.001	2.76	<0.001	0.17	0.02	0.14	0.1	0.02	40.1	<0.001	<0.02	0.003	<0.001
BALDM-18	0.403	0.09	<0.001	<0.001	2.88	<0.001	0.19	0.01	0.13	0.105	0.01	42.7	<0.001	<0.02	0.002	<0.001
BALDM-19	0.367	0.1	<0.001	<0.001	1.96	<0.001	0.27	0.01	0.13	0.058	0.01	35	<0.001	<0.02	0.002	<0.001
BALDM-20A	0.328	0.14	<0.001	<0.001	3.96	<0.001	0.16	0.02	0.14	4.83	0.02	36.9	<0.001	<0.02	0.003	<0.001
BALDM-20B*	0.35	0.14	<0.001	<0.001	4.32	<0.001	0.16	0.02	0.14	4.17	0.02	37.5	<0.001	<0.02	0.003	<0.001
BALDM-21	0.408	0.19	<0.001	<0.001	2.46	<0.001	0.2	0.01	0.15	1.035	0.01	39.8	<0.001	<0.02	0.002	<0.001
BALDM-22	0.389	0.11	<0.001	<0.001	3.48	<0.001	0.22	0.01	0.14	0.58	0.01	56.2	<0.001	<0.02	0.002	<0.001

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
BALDM-1	0.008	<0.005	0.11	0.01	0.012	34.3	<0.02
BALDM-2	<0.002	<0.005	0.13	<0.01	0.023	29.7	<0.02
BALDM-3	<0.002	<0.005	0.12	<0.01	0.059	24.9	<0.02
BALDM-4	<0.002	<0.005	0.13	0.02	0.064	32.9	<0.02
BALDM-5	0.002	<0.005	0.14	<0.01	0.021	25.6	<0.02
BALDM-6	<0.002	<0.005	0.12	<0.01	0.047	24.7	<0.02
BALDM-7	<0.002	<0.005	0.13	<0.01	0.042	30.8	<0.02
BALDM-8	<0.002	<0.005	0.12	<0.01	0.047	35.7	<0.02
BALDM-9	<0.002	<0.005	0.13	<0.01	0.04	47.9	0.02
BALDM-10A	<0.002	<0.005	0.1	<0.01	0.023	22.6	<0.02
BALDM-10B*	<0.002	<0.005	0.12	<0.01	0.026	24.3	<0.02
BALDM-11	<0.002	<0.005	0.12	<0.01	0.028	28.1	<0.02
BALDM-12	<0.002	<0.005	0.13	0.01	0.013	25.9	<0.02
BALDM-13	<0.002	<0.005	0.13	<0.01	0.021	26.1	<0.02
BALDM-14	<0.002	<0.005	0.12	<0.01	0.037	23.2	<0.02
BALDM-15	0.002	<0.005	0.13	<0.01	0.03	33.1	<0.02
BALDM-16	<0.002	<0.005	0.13	<0.01	0.039	30.2	<0.02
BALDM-17	<0.002	<0.005	0.14	<0.01	0.045	30	0.02
BALDM-18	<0.002	<0.005	0.12	<0.01	0.078	38.7	<0.02
BALDM-19	<0.002	<0.005	0.13	0.01	0.012	27.1	<0.02
BALDM-20A	0.002	<0.005	0.13	0.01	0.012	23.8	0.02
BALDM-20B*	0.002	<0.005	0.13	0.01	0.015	24.4	0.02
BALDM-21	<0.002	<0.005	0.14	0.02	0.011	31.5	<0.02
BALDM-22	<0.002	<0.005	0.12	0.01	0.009	33.8	<0.02

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Lines	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
BALDM-23	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	80	235086	266083
BALDM-24	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	67	235086	266078
BALDM-25	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	63	235075	266065
BALDM-26	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	68	235061	266057
BALDM-27	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	65	235055	266054
BALDM-28	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	63	235031	266037
BALDM-29	Ballinalack	C - D profile	Hawthorn	leaves	Spring	-7.47	53.64	59	235020	266027
BALDM-30A	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.48	53.65	64	234719	266459
BALDM-30B*	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.48	53.65	64	234719	266459
BALDM-31	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.48	53.65	63	234731	266481
BALDM-32	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.48	53.65	53	234759	266509
BALDM-33	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	66	234771	266541
BALDM-34	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	70	234793	266562
BALDM-35	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	71	234813	266588
BALDM-36	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	67	234828	266612
BALDM-37	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	61	234846	266638
BALDM-38	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	65	234873	266670
BALDM-39	Ballinalack	E – F profile	Hawthorn	leaves	Spring	-7.47	53.65	65	234895	266702

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
BALDM-23	<0.0002	0.014	<0.01	0.03	28	16.4	<0.01	0.001	1.42	0.336	0.025	0.116	0.42	0.007	10.5
BALDM-24	<0.0002	0.001	<0.01	0.04	21	16.9	<0.01	0.001	1.14	0.149	0.039	0.095	0.41	0.008	8.57
BALDM-25	<0.0002	0.006	<0.01	0.02	24	28.5	<0.01	0.001	1.44	0.126	0.024	0.142	0.38	0.005	8.43
BALDM-26	<0.0002	0.001	<0.01	0.03	29	29	<0.01	0.002	1.69	0.091	0.024	0.136	0.22	<0.005	7.58
BALDM-27	<0.0002	0.002	<0.01	0.03	26	17.7	<0.01	<0.001	1.24	0.17	0.064	0.105	0.72	0.005	7.73
BALDM-28	<0.0002	0.001	<0.01	0.04	20	26.2	<0.01	0.001	1.49	0.261	0.032	0.147	0.41	<0.005	7.81
BALDM-29	<0.0002	0.001	<0.01	0.02	23	23.4	<0.01	0.001	1.22	0.157	0.024	0.053	0.18	0.006	8.88
BALDM-30A	<0.0002	0.001	<0.01	0.04	27	19.7	<0.01	0.004	1.3	0.345	0.104	0.123	1.13	0.007	8.68
BALDM-30B*	<0.0002	0.001	<0.01	0.02	27	21.4	<0.01	0.001	1.37	0.341	0.098	0.104	0.61	<0.005	8.98
BALDM-31	<0.0002	0.001	<0.01	0.05	33	18.8	<0.01	0.006	1.26	0.457	0.083	0.091	0.32	0.011	9.53
BALDM-32	<0.0002	0.001	<0.01	0.03	29	20.7	<0.01	0.002	1.37	0.279	0.062	0.14	0.33	0.01	12.8
BALDM-33	<0.0002	0.001	<0.01	0.05	24	8.1	<0.01	0.002	0.8	0.08	0.119	0.116	0.37	<0.005	5.31
BALDM-34	<0.0002	0.001	<0.01	0.05	31	7.7	<0.01	0.003	1.27	0.199	0.05	0.058	0.49	<0.005	6.32
BALDM-35	<0.0002	0.002	<0.01	0.05	37	13.8	<0.01	0.003	1.32	0.207	0.096	0.072	0.67	0.005	12.3
BALDM-36	<0.0002	0.001	<0.01	0.03	37	15.8	<0.01	0.002	1.52	0.066	0.057	0.047	0.49	<0.005	7.74
BALDM-37	<0.0002	0.001	<0.01	0.02	16	11.3	<0.01	0.002	1.26	0.132	0.03	0.078	0.51	0.006	9.76
BALDM-38	<0.0002	0.001	<0.01	0.02	26	12.5	<0.01	0.001	1.15	0.345	0.109	0.081	0.55	<0.005	12
BALDM-39	<0.0002	0.001	<0.01	0.02	26	12.9	<0.01	0.001	1.66	0.096	0.022	0.061	0.57	0.005	9.97

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
BALDM-23	65	0.005	0.012	<0.002	0.01	<0.005	1.53	0.023	<0.1	0.219	14.8	1.75	0.076	0.002	0.75
BALDM-24	77	0.006	0.012	<0.002	0.011	<0.005	1.39	0.026	<0.1	0.211	15.2	2.45	0.096	0.003	0.64
BALDM-25	58	0.004	0.015	<0.002	0.012	<0.005	1.44	0.023	<0.1	0.206	20.3	1.5	0.085	<0.002	0.76
BALDM-26	58	0.005	0.02	<0.002	0.006	<0.005	1.55	0.028	<0.1	0.179	21.2	1.79	0.086	0.002	0.55
BALDM-27	68	0.007	0.017	<0.002	0.011	<0.005	1.51	0.041	<0.1	0.24	15.5	1.15	0.116	<0.002	0.68
BALDM-28	77	<0.004	0.015	<0.002	0.01	<0.005	1.4	0.03	<0.1	0.201	24.2	1.31	0.096	<0.002	0.81
BALDM-29	56	0.004	0.007	<0.002	0.01	<0.005	1.57	0.024	<0.1	0.191	17.3	2.21	0.068	<0.002	0.51
BALDM-30A	131	0.006	0.01	<0.002	0.007	<0.005	1.19	0.112	<0.1	0.255	42.4	1.04	0.03	0.004	1.86
BALDM-30B*	109	0.005	0.01	<0.002	0.011	<0.005	1.28	0.107	<0.1	0.264	42.7	1.22	0.03	0.002	1.61
BALDM-31	72	0.007	0.009	<0.002	0.013	<0.005	1.43	0.081	<0.1	0.289	35.9	1.48	0.056	0.002	1.52
BALDM-32	75	0.006	0.008	<0.002	0.012	<0.005	1.57	0.061	<0.1	0.244	26.6	2.76	0.056	0.002	1.43
BALDM-33	89	0.007	0.008	<0.002	0.009	<0.005	1.36	0.161	<0.1	0.246	18.7	0.61	0.044	0.003	1.12
BALDM-34	59	0.005	0.01	<0.002	0.012	<0.005	1.93	0.047	<0.1	0.295	18.8	3.1	0.083	0.002	0.81
BALDM-35	88	0.008	0.013	<0.002	0.012	<0.005	1.98	0.119	<0.1	0.235	22.3	3.01	0.068	0.003	2.17
BALDM-36	59	0.006	0.012	<0.002	0.009	<0.005	1.39	0.056	<0.1	0.259	19.4	1.91	0.034	0.002	0.64
BALDM-37	59	0.007	0.012	<0.002	0.011	0.008	1.35	0.024	<0.1	0.25	24	1.88	0.046	0.002	0.88
BALDM-38	70	0.004	0.012	<0.002	0.011	<0.005	1.48	0.14	<0.1	0.226	25.7	1.82	0.04	<0.002	1.94
BALDM-39	68	0.005	0.013	<0.002	0.01	<0.005	1.49	0.021	<0.1	0.203	18.9	1.67	0.03	<0.002	0.86

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
BALDM-23	0.337	0.1	<0.001	<0.001	4.29	<0.001	0.18	0.01	0.15	0.389	0.02	38.5	<0.001	<0.02	0.002	<0.001
BALDM-24	0.405	0.13	<0.001	<0.001	2.89	<0.001	0.22	0.02	0.14	0.561	0.03	35.2	<0.001	<0.02	0.004	<0.001
BALDM-25	0.328	0.12	<0.001	<0.001	4.37	<0.001	0.17	0.01	0.14	1.33	0.01	46.5	<0.001	<0.02	0.003	<0.001
BALDM-26	0.27	0.1	<0.001	<0.001	1.07	<0.001	0.19	0.01	0.14	1.57	0.01	47.8	<0.001	<0.02	0.002	<0.001
BALDM-27	0.288	0.55	<0.001	<0.001	1.89	<0.001	0.19	0.02	0.14	1	0.01	36.7	<0.001	<0.02	0.003	<0.001
BALDM-28	0.271	0.07	<0.001	<0.001	1.7	<0.001	0.18	0.01	0.15	0.943	<0.01	40.4	<0.001	<0.02	<0.002	<0.001
BALDM-29	0.366	0.08	<0.001	<0.001	2.58	<0.001	0.18	0.01	0.15	0.268	<0.01	35.6	<0.001	<0.02	<0.002	<0.001
BALDM-30A	0.374	0.22	<0.001	<0.001	3.99	<0.001	0.2	0.03	0.13	0.173	0.05	31.9	<0.001	<0.02	0.004	<0.001
BALDM-30B*	0.419	0.17	<0.001	<0.001	4.29	<0.001	0.22	0.03	0.14	0.153	0.02	34.7	<0.001	<0.02	0.003	<0.001
BALDM-31	0.388	0.17	<0.001	<0.001	13.1	<0.001	0.18	0.02	0.14	0.157	0.03	38.3	<0.001	<0.02	0.004	<0.001
BALDM-32	0.442	0.13	<0.001	<0.001	8.57	<0.001	0.21	0.02	0.15	0.201	0.02	45.7	<0.001	<0.02	0.003	<0.001
BALDM-33	0.27	0.19	<0.001	0.001	1.27	<0.001	0.16	0.02	0.12	0.12	0.02	16.95	0.001	<0.02	0.004	<0.001
BALDM-34	0.424	0.12	<0.001	<0.001	6.64	<0.001	0.21	0.02	0.14	0.105	0.01	28.5	0.001	<0.02	0.004	<0.001
BALDM-35	0.478	0.2	<0.001	0.001	8.26	<0.001	0.22	0.03	0.14	0.052	0.03	34	<0.001	<0.02	0.005	<0.001
BALDM-36	0.466	0.14	<0.001	<0.001	2.58	<0.001	0.23	0.02	0.14	0.08	0.01	43.3	<0.001	<0.02	0.003	<0.001
BALDM-37	0.418	0.12	<0.001	0.001	4.75	<0.001	0.21	0.02	0.15	0.11	0.01	41.5	<0.001	<0.02	0.003	<0.001
BALDM-38	0.5	0.1	<0.001	<0.001	7.78	<0.001	0.23	0.01	0.15	0.037	0.01	32	<0.001	<0.02	0.002	<0.001
BALDM-39	0.387	0.09	<0.001	<0.001	6.39	<0.001	0.23	0.01	0.14	0.259	<0.01	49.5	<0.001	<0.02	0.002	<0.001

Table A-2. Raw data of trace element analysis from plants collected from Irish Midlands in 2016 (this study). Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
BALDM-23	<0.002	<0.005	0.11	0.02	0.008	27.4	<0.02
BALDM-24	0.006	<0.005	0.15	0.01	0.012	29.8	0.02
BALDM-25	0.002	<0.005	0.11	0.01	0.007	35	<0.02
BALDM-26	0.003	<0.005	0.13	0.01	0.013	28.1	<0.02
BALDM-27	0.002	<0.005	0.15	0.01	0.017	26.1	0.02
BALDM-28	<0.002	<0.005	0.13	<0.01	0.015	32.6	<0.02
BALDM-29	0.002	<0.005	0.12	0.03	0.01	33.4	0.02
BALDM-30A	<0.002	<0.005	0.14	0.01	0.042	33.2	0.02
BALDM-30B*	<0.002	<0.005	0.13	0.01	0.038	36.2	0.02
BALDM-31	<0.002	<0.005	0.14	0.01	0.038	25.1	0.02
BALDM-32	<0.002	<0.005	0.14	0.01	0.025	33.3	0.02
BALDM-33	0.002	<0.005	0.17	0.01	0.082	23	0.03
BALDM-34	<0.002	<0.005	0.16	0.01	0.023	22.5	0.02
BALDM-35	0.002	<0.005	0.18	0.01	0.081	34.7	0.03
BALDM-36	<0.002	<0.005	0.14	0.01	0.026	29.8	0.02
BALDM-37	<0.002	<0.005	0.14	0.01	0.013	32.2	0.02
BALDM-38	0.004	<0.005	0.13	0.01	0.086	30.7	<0.02
BALDM-39	<0.002	<0.005	0.14	<0.01	0.01	32.6	<0.02

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	SWEREF99 TM North	SWEREF99 TM East
LV-1	Lil-Laver	Spruce	needles	Spring	7303610	740018
LV-2	Lil-Laver	Spruce	needles	Spring	7303613	740060
LV-3	Lil-Laver	Spruce	needles	Spring	7303617	740119
LV-4	Lil-Laver	Spruce	needles	Spring	7303639	740146
LV-5	Lil-Laver	Spruce	needles	Spring	7303664	740178
LV-6	Lil-Laver	Spruce	needles	Spring	7303646	740223
LV-7	Lil-Laver	Spruce	needles	Spring	7303676	740229
LV-8	Lil-Laver	Spruce	needles	Spring	7303695	740248
LV-9	Lil-Laver	Spruce	needles	Spring	7303707	740279
LV-10A	Lil-Laver	Spruce	needles	Spring	7303777	740361
LV-10B*	Lil-Laver	Spruce	needles	Spring	7303777	740361
LV-11	Laver	Spruce	needles	Spring	7304611	739589
LV-12	Laver	Spruce	needles	Spring	7304588	739561
LV-13	Laver	Spruce	needles	Spring	7304567	739556
LV-14	Laver	Spruce	needles	Spring	7304541	739515
LV-15	Laver	Spruce	needles	Spring	7304501	739550
LV-16	Laver	Spruce	needles	Spring	7304481	739510
LV-17	Laver	Spruce	needles	Spring	7304458	739477
LV-18	Laver	Spruce	needles	Spring	7304439	739443
LV-19	Laver	Spruce	needles	Spring	7304411	739423
LV-20A	Laver	Spruce	needles	Spring	7304415	739401
LV-20B*	Laver	Spruce	needles	Spring	7304415	739401
LV-21	Laver	Spruce	needles	Spring	7304393	739365
LV-22	Laver	Spruce	needles	Spring	7304400	739354

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
LV-1	<0.0002	0.008	0.01	0.04	13	29.5	0.03	<0.001	0.61	0.006	0.057	0.038	0.22	0.072	0.98
LV-2	<0.0002	0.005	0.01	0.02	17	69.6	0.01	<0.001	1.02	0.012	0.02	0.021	0.11	0.095	1.09
LV-3	<0.0002	0.002	0.01	0.02	5	56.5	0.01	<0.001	0.84	0.024	0.021	0.024	0.19	0.057	1.2
LV-4	<0.0002	0.008	0.01	0.03	10	94.1	0.03	<0.001	1.06	0.021	0.04	0.042	0.21	0.133	1.54
LV-5	<0.0002	0.002	0.01	0.02	12	130	0.01	<0.001	1.31	0.013	0.023	0.034	0.2	0.075	1.43
LV-6	<0.0002	0.008	0.01	0.03	6	87.9	0.03	<0.001	1.06	0.009	0.064	0.06	0.15	0.131	1.11
LV-7	<0.0002	0.003	0.01	0.04	8	59.7	0.01	<0.001	0.93	0.024	0.022	0.062	0.18	0.078	1.37
LV-8	<0.0002	0.001	0.01	0.04	11	49.9	0.01	<0.001	0.97	0.039	0.04	0.047	0.21	0.079	1.36
LV-9	<0.0002	0.001	0.01	0.02	6	63.1	0.01	<0.001	1.38	0.031	0.04	0.05	0.31	0.14	1.11
LV-10A	<0.0002	0.019	0.01	0.04	7	76.2	0.01	<0.001	1.07	0.019	0.037	0.034	0.19	0.095	1
LV-10B*	<0.0002	0.026	0.01	0.03	4	76.7	0.01	<0.001	1.08	0.019	0.035	0.033	0.17	0.088	1.13
LV-11	<0.0002	0.016	0.02	0.03	9	82.6	0.03	<0.001	1.19	0.012	0.112	0.076	0.29	0.089	1.46
LV-12	<0.0002	0.006	0.01	0.02	12	92.4	0.01	<0.001	1.25	0.051	0.018	0.073	0.26	0.03	1.41
LV-13	<0.0002	0.009	0.01	0.02	8	83	0.01	<0.001	1.05	0.121	0.023	0.039	0.12	0.069	1.33
LV-14	<0.0002	0.005	<0.01	0.02	6	57.6	0.01	<0.001	0.76	0.021	0.075	0.021	0.16	0.099	1.4
LV-15	<0.0002	0.002	0.01	0.03	7	21	0.01	<0.001	0.71	0.009	0.02	0.018	0.21	0.06	1.33
LV-16	<0.0002	0.003	<0.01	0.01	4	70.2	0.01	<0.001	0.81	0.022	0.016	0.045	0.14	0.121	1.33
LV-17	<0.0002	0.003	0.02	0.03	9	52.7	0.03	<0.001	1.01	0.035	0.049	0.04	0.14	0.197	1.24
LV-18	<0.0002	0.006	<0.01	0.02	7	47.2	0.01	<0.001	1.33	0.005	0.019	0.018	0.13	0.053	1.3
LV-19	<0.0002	0.004	0.01	0.02	8	12.3	0.03	<0.001	0.54	0.003	0.042	0.016	0.14	0.054	1.06
LV-20A	<0.0002	0.011	<0.01	0.01	6	18.1	0.01	<0.001	0.92	0.015	0.012	0.051	0.09	0.051	1.17
LV-20B*	<0.0002	0.012	<0.01	0.02	7	14.3	0.01	<0.001	1	0.025	0.009	0.041	0.11	0.054	1.33
LV-21	<0.0002	0.002	<0.01	0.02	9	67.5	<0.01	<0.001	1.13	0.009	0.017	0.058	0.09	0.03	1.23
LV-22	<0.0002	0.002	<0.01	0.01	9	20.7	<0.01	<0.001	0.94	0.029	0.015	0.053	0.12	0.052	1.46

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
LV-1	18	0.004	0.005	<0.002	0.031	<0.005	0.4	0.081	0.1	0.049	946	0.04	0.004	<0.002	0.85
LV-2	17	0.006	<0.005	<0.002	0.03	<0.005	0.35	0.053	<0.1	0.053	2890	0.05	0.001	<0.002	0.26
LV-3	26	0.007	<0.005	<0.002	0.036	<0.005	0.32	0.042	<0.1	0.04	2520	0.03	0.006	<0.002	0.5
LV-4	18	0.007	<0.005	<0.002	0.029	<0.005	0.33	0.046	0.1	0.056	2960	0.09	0.002	<0.002	0.56
LV-5	23	0.007	<0.005	<0.002	0.038	<0.005	0.41	0.045	0.1	0.059	2570	0.03	0.001	<0.002	0.41
LV-6	17	0.005	<0.005	<0.002	0.029	<0.005	0.44	0.128	0.1	0.07	1205	0.03	0.002	<0.002	0.81
LV-7	21	0.005	<0.005	<0.002	0.03	<0.005	0.43	0.03	<0.1	0.06	1950	0.04	0.005	<0.002	0.56
LV-8	26	0.006	<0.005	<0.002	0.039	<0.005	0.37	0.056	<0.1	0.066	1365	0.08	0.006	<0.002	0.47
LV-9	26	0.006	<0.005	<0.002	0.025	<0.005	0.34	0.03	0.1	0.046	912	0.05	<0.001	0.003	0.56
LV-10A	40	0.005	<0.005	<0.002	0.034	<0.005	0.41	0.1	<0.1	0.059	2120	0.02	0.006	<0.002	0.62
LV-10B*	65	0.005	<0.005	<0.002	0.025	<0.005	0.41	0.097	<0.1	0.055	2010	0.03	<0.001	<0.002	0.66
LV-11	23	<0.004	<0.005	<0.002	0.037	<0.005	0.49	0.164	0.2	0.076	725	0.05	0.006	<0.002	0.88
LV-12	26	<0.004	<0.005	<0.002	0.033	<0.005	0.45	0.081	<0.1	0.067	1050	0.03	0.001	<0.002	0.42
LV-13	17	<0.004	<0.005	<0.002	0.034	<0.005	0.63	0.019	0.1	0.055	956	0.03	0.003	<0.002	0.66
LV-14	18	<0.004	<0.005	<0.002	0.04	<0.005	0.54	0.072	0.1	0.042	380	0.03	0.019	<0.002	0.23
LV-15	21	0.004	<0.005	<0.002	0.034	<0.005	0.48	0.017	<0.1	0.052	1315	0.02	<0.001	<0.002	0.33
LV-16	71	0.004	<0.005	<0.002	0.037	<0.005	0.23	0.013	0.1	0.065	1475	0.03	0.001	<0.002	0.3
LV-17	17	0.006	<0.005	<0.002	0.04	<0.005	0.35	0.065	0.1	0.051	2140	0.02	0.001	<0.002	0.71
LV-18	27	<0.004	<0.005	<0.002	0.036	<0.005	0.23	0.013	<0.1	0.072	1170	0.01	0.002	<0.002	0.2
LV-19	19	<0.004	<0.005	<0.002	0.025	<0.005	0.36	0.067	0.1	0.041	1075	0.02	0.002	<0.002	0.51
LV-20A	25	<0.004	<0.005	<0.002	0.041	<0.005	0.41	0.01	<0.1	0.05	1075	0.02	0.018	<0.002	0.32
LV-20B*	31	0.004	<0.005	<0.002	0.036	<0.005	0.49	0.005	<0.1	0.058	1755	0.02	0.01	<0.002	0.4
LV-21	24	0.005	<0.005	<0.002	0.038	<0.005	0.43	0.01	0.1	0.091	1920	0.02	0.003	<0.002	0.26
LV-22	23	0.006	<0.005	<0.002	0.036	<0.005	0.34	0.009	<0.1	0.075	2360	0.02	0.015	<0.002	0.19

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
LV-1	0.097	0.06	<0.001	0.001	13.95	<0.001	0.06	<0.01	0.29	0.007	0.01	22.9	<0.001	<0.02	<0.002	<0.001
LV-2	0.125	0.06	<0.001	0.001	12.85	<0.001	0.06	<0.01	0.24	<0.005	<0.01	19.85	<0.001	<0.02	<0.002	<0.001
LV-3	0.098	0.1	<0.001	0.001	11.05	<0.001	0.07	<0.01	0.34	0.008	<0.01	29.6	<0.001	<0.02	<0.002	<0.001
LV-4	0.141	0.19	<0.001	0.001	14.35	<0.001	0.06	0.01	0.27	0.011	<0.01	28.1	<0.001	<0.02	<0.002	<0.001
LV-5	0.154	0.08	<0.001	<0.001	14.85	<0.001	0.08	<0.01	0.25	<0.005	0.01	47.9	<0.001	<0.02	<0.002	<0.001
LV-6	0.11	0.07	<0.001	0.001	18	<0.001	0.06	<0.01	0.31	0.007	0.01	55.3	<0.001	<0.02	<0.002	<0.001
LV-7	0.141	0.05	<0.001	0.001	16.2	<0.001	0.07	<0.01	0.31	<0.005	0.01	27.9	<0.001	<0.02	0.005	<0.001
LV-8	0.108	0.07	<0.001	0.001	14.55	<0.001	0.07	<0.01	0.25	0.007	0.01	34.6	<0.001	<0.02	0.004	<0.001
LV-9	0.115	0.07	<0.001	0.001	12.2	<0.001	0.05	<0.01	0.3	0.019	0.01	32.1	<0.001	<0.02	0.004	<0.001
LV-10A	0.086	0.1	<0.001	0.001	14.45	<0.001	0.07	<0.01	0.31	0.008	0.01	31.1	<0.001	<0.02	0.003	<0.001
LV-10B*	0.088	0.08	<0.001	<0.001	14.1	<0.001	0.06	<0.01	0.34	0.008	0.01	33	<0.001	<0.02	0.002	<0.001
LV-11	0.191	0.08	<0.001	0.001	14.2	<0.001	0.06	<0.01	0.33	<0.005	0.01	30.7	<0.001	<0.02	0.002	<0.001
LV-12	0.123	0.05	<0.001	<0.001	10.3	<0.001	0.06	<0.01	0.29	0.005	0.01	38.6	<0.001	<0.02	<0.002	<0.001
LV-13	0.086	0.05	<0.001	0.001	14.5	<0.001	0.06	<0.01	0.29	0.005	0.01	34.4	<0.001	<0.02	<0.002	<0.001
LV-14	0.09	0.07	<0.001	<0.001	13.65	<0.001	0.08	<0.01	0.31	<0.005	<0.01	24.4	<0.001	<0.02	<0.002	<0.001
LV-15	0.091	0.07	<0.001	0.001	11.85	<0.001	0.06	<0.01	0.24	0.011	0.01	16.35	<0.001	<0.02	<0.002	<0.001
LV-16	0.082	0.06	<0.001	0.001	8.75	<0.001	0.08	<0.01	0.28	0.009	0.01	32.5	<0.001	<0.02	<0.002	<0.001
LV-17	0.086	0.07	<0.001	<0.001	14.55	<0.001	0.06	<0.01	0.24	0.031	0.01	22.1	<0.001	<0.02	<0.002	<0.001
LV-18	0.076	0.05	<0.001	0.001	8.69	<0.001	0.06	<0.01	0.28	<0.005	0.01	30.7	<0.001	<0.02	<0.002	<0.001
LV-19	0.086	0.06	<0.001	0.001	10.4	<0.001	0.05	<0.01	0.31	0.012	0.01	11	<0.001	<0.02	<0.002	<0.001
LV-20A	0.119	0.08	<0.001	<0.001	7.24	<0.001	0.08	<0.01	0.28	<0.005	0.01	23.8	<0.001	<0.02	<0.002	<0.001
LV-20B*	0.144	0.09	<0.001	0.001	8.58	<0.001	0.07	<0.01	0.24	0.006	0.01	16	<0.001	<0.02	<0.002	<0.001
LV-21	0.103	0.06	<0.001	<0.001	7.85	<0.001	0.07	<0.01	0.34	0.006	0.01	21.1	<0.001	<0.02	<0.002	<0.001
LV-22	0.137	0.07	<0.001	<0.001	7.87	<0.001	0.07	<0.01	0.2	<0.005	0.01	15.15	<0.001	<0.02	<0.002	<0.001

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
LV-1	0.13	<0.005	0.08	<0.01	0.105	52.6	<0.02
LV-2	0.161	<0.005	0.07	<0.01	0.04	97.7	<0.02
LV-3	0.083	<0.005	0.07	<0.01	0.044	35.2	<0.02
LV-4	0.228	<0.005	0.07	<0.01	0.03	100.5	<0.02
LV-5	0.11	<0.005	0.08	<0.01	0.029	107	<0.02
LV-6	0.157	<0.005	0.08	<0.01	0.13	56.8	<0.02
LV-7	0.176	<0.005	0.07	<0.01	0.033	61.9	<0.02
LV-8	0.096	<0.005	0.08	<0.01	0.038	99.5	<0.02
LV-9	0.002	<0.005	0.09	<0.01	0.013	83.8	<0.02
LV-10A	0.216	<0.005	0.09	<0.01	0.064	86.8	<0.02
LV-10B*	0.171	<0.005	0.07	<0.01	0.063	89.6	<0.02
LV-11	0.002	<0.005	0.08	<0.01	0.12	194	<0.02
LV-12	0.195	<0.005	0.07	<0.01	0.049	155.5	<0.02
LV-13	0.038	<0.005	0.07	<0.01	0.012	183.5	<0.02
LV-14	0.003	<0.005	0.08	<0.01	0.055	72.2	<0.02
LV-15	<0.002	<0.005	0.07	<0.01	0.011	48.6	<0.02
LV-16	0.002	<0.005	0.07	0.02	0.012	32.2	<0.02
LV-17	0.268	<0.005	0.07	<0.01	0.065	66.5	<0.02
LV-18	0.162	<0.005	0.06	<0.01	0.009	68.3	<0.02
LV-19	0.154	<0.005	0.07	<0.01	0.221	35.4	<0.02
LV-20A	0.002	<0.005	0.08	<0.01	0.008	53.9	<0.02
LV-20B*	0.002	<0.005	0.07	<0.01	0.003	75.9	<0.02
LV-21	0.114	<0.005	0.07	<0.01	0.005	67.6	<0.02
LV-22	<0.002	<0.005	0.08	<0.01	0.006	42.8	<0.02

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	SWEREF99 TM North	SWEREF99 TM East
LV-23	Laver	Spruce	needles	Spring	7304384	739321
LV-24	Laver	Spruce	needles	Spring	7304367	739306
LV-25	Laver	Spruce	needles	Spring	7304355	739302
LVC-26	Control	Spruce	needles	Spring	7297900	736191
LVC-27	Control	Spruce	needles	Spring	7297878	736193
LVC-28	Control	Spruce	needles	Spring	7297904	736228
LVC-29	Control	Spruce	needles	Spring	7297812	736326
LVC-30A	Control	Spruce	needles	Spring	7297986	735990
LVC-30B*	Control	Spruce	needles	Spring	7297986	735990
LVC-31	Control	Spruce	needles	Spring	7305992	733101
LVC-32	Control	Spruce	needles	Spring	7305970	733088
LVC-33	Control	Spruce	needles	Spring	7305944	733061
LVC-34	Control	Spruce	needles	Spring	7305933	733131
LVC-35	Control	Spruce	needles	Spring	7305913	733098

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
LV-23	<0.0002	0.002	<0.01	0.03	8	36.5	0.01	<0.001	1.32	0.035	0.049	0.205	0.16	0.098	1.35
LV-24	<0.0002	0.007	<0.01	0.04	14	21.8	0.01	<0.001	0.84	0.008	0.015	0.034	0.14	0.038	1.27
LV-25	<0.0002	0.005	0.01	0.02	10	23.6	0.01	<0.001	1.1	0.006	0.017	0.017	0.15	0.052	1.05
LVC-26	<0.0002	0.004	0.01	0.03	3	53.8	0.01	<0.001	1.18	0.104	0.02	0.117	0.27	0.066	1.49
LVC-27	<0.0002	0.008	0.01	0.02	5	145.5	0.02	<0.001	2.19	0.161	0.025	0.166	0.16	0.065	0.83
LVC-28	<0.0002	0.013	0.01	0.01	9	107	0.02	<0.001	1.48	0.128	0.022	0.062	0.19	0.046	1.05
LVC-29	<0.0002	0.003	0.01	0.02	4	75.6	0.02	0.002	1.04	0.058	0.035	0.037	0.11	0.042	1.63
LVC-30A	<0.0002	0.012	0.01	0.01	9	135	<0.01	<0.001	0.98	0.032	0.017	0.026	0.29	0.031	1.03
LVC-30B*	<0.0002	0.011	<0.01	0.01	9	110	<0.01	<0.001	0.88	0.03	0.015	0.019	0.17	0.032	1.14
LVC-31	<0.0002	0.009	0.02	0.02	12	41.7	0.01	<0.001	0.62	0.007	0.023	0.037	0.19	0.083	1.16
LVC-32	<0.0002	0.02	0.01	0.01	12	18.1	0.01	<0.001	0.65	0.007	0.021	0.041	0.14	0.016	1.27
LVC-33	<0.0002	0.002	<0.01	0.02	12	20.3	<0.01	<0.001	0.79	0.002	0.012	0.014	0.17	0.019	1.35
LVC-34	<0.0002	0.003	<0.01	0.02	18	63.9	<0.01	<0.001	1.31	0.01	0.011	0.021	0.2	0.019	1.13
LVC-35	<0.0002	0.002	<0.01	0.02	14	13	<0.01	<0.001	1.02	0.023	0.014	0.043	0.24	0.006	1.23

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
LV-23	73	0.005	<0.005	<0.002	0.048	<0.005	0.46	0.028	0.1	0.079	1535	0.03	0.006	<0.002	0.27
LV-24	27	0.004	<0.005	<0.002	0.036	<0.005	0.45	0.011	0.1	0.085	1245	0.07	0.026	<0.002	0.27
LV-25	30	0.004	<0.005	<0.002	0.03	<0.005	0.5	0.009	<0.1	0.061	1360	0.02	0.021	<0.002	0.34
LVC-26	23	<0.004	<0.005	<0.002	0.017	<0.005	0.51	0.017	0.1	0.073	1015	0.04	0.02	<0.002	0.31
LVC-27	16	0.006	<0.005	<0.002	0.047	<0.005	0.26	0.024	<0.1	0.055	3040	0.02	0.003	<0.002	0.27
LVC-28	15	0.006	<0.005	<0.002	0.053	<0.005	0.27	0.021	0.1	0.044	2630	0.02	0.009	<0.002	0.28
LVC-29	17	<0.004	<0.005	<0.002	0.026	<0.005	0.36	0.024	0.1	0.032	1210	0.02	0.019	<0.002	0.28
LVC-30A	27	0.005	<0.005	<0.002	0.026	<0.005	0.43	0.037	<0.1	0.044	1885	0.05	0.014	<0.002	0.43
LVC-30B*	27	0.005	<0.005	<0.002	0.017	<0.005	0.49	0.023	<0.1	0.048	2100	0.03	0.001	<0.002	0.27
LVC-31	21	<0.004	<0.005	<0.002	0.017	<0.005	0.4	0.028	0.2	0.054	576	0.03	0.007	<0.002	0.56
LVC-32	39	0.004	<0.005	<0.002	0.027	<0.005	0.57	0.036	<0.1	0.069	994	0.02	0.002	<0.002	0.41
LVC-33	34	<0.004	<0.005	<0.002	0.024	<0.005	0.53	0.012	<0.1	0.047	744	0.02	0.006	<0.002	0.23
LVC-34	23	0.006	<0.005	<0.002	0.024	<0.005	0.53	0.01	<0.1	0.056	2490	0.03	0.008	<0.002	0.2
LVC-35	47	0.007	<0.005	<0.002	0.032	<0.005	0.42	0.013	<0.1	0.039	2510	0.04	0.021	<0.002	0.27

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
LV-23	0.078	0.12	<0.001	0.001	10.8	<0.001	0.07	<0.01	0.25	<0.005	0.01	37	<0.001	<0.02	<0.002	<0.001
LV-24	0.141	0.08	<0.001	<0.001	8.8	<0.001	0.1	<0.01	0.32	<0.005	0.01	20.7	<0.001	<0.02	0.002	<0.001
LV-25	0.095	0.13	<0.001	<0.001	10.8	<0.001	0.08	<0.01	0.31	<0.005	0.01	26.9	<0.001	<0.02	0.002	<0.001
LVC-26	0.107	0.06	<0.001	<0.001	14.05	<0.001	0.08	<0.01	0.31	<0.005	0.01	45.4	<0.001	<0.02	<0.002	<0.001
LVC-27	0.09	0.09	<0.001	0.001	6.05	<0.001	0.06	<0.01	0.43	<0.005	0.01	85.9	<0.001	<0.02	<0.002	<0.001
LVC-28	0.079	0.1	<0.001	<0.001	5.74	<0.001	0.07	<0.01	0.37	<0.005	0.01	38.1	<0.001	<0.02	<0.002	<0.001
LVC-29	0.104	0.08	<0.001	0.001	8.01	<0.001	0.08	<0.01	0.36	0.006	0.01	34.7	<0.001	<0.02	<0.002	<0.001
LVC-30A	0.091	0.07	<0.001	0.001	8.97	<0.001	0.07	<0.01	0.23	<0.005	0.01	32.1	<0.001	<0.02	<0.002	<0.001
LVC-30B*	0.099	0.06	<0.001	<0.001	10.35	<0.001	0.06	<0.01	0.22	<0.005	0.01	25.1	<0.001	<0.02	<0.002	<0.001
LVC-31	0.097	0.07	<0.001	<0.001	12.3	<0.001	0.06	<0.01	0.29	0.016	0.01	24.2	<0.001	<0.02	<0.002	<0.001
LVC-32	0.102	0.08	<0.001	0.001	11.8	<0.001	0.06	<0.01	0.28	0.009	0.01	16.25	<0.001	<0.02	<0.002	<0.001
LVC-33	0.078	0.08	<0.001	0.001	9.5	<0.001	0.06	<0.01	0.26	<0.005	0.01	17.1	<0.001	<0.02	<0.002	<0.001
LVC-34	0.103	0.06	<0.001	<0.001	10.05	<0.001	0.07	<0.01	0.27	<0.005	0.01	29.2	<0.001	<0.02	<0.002	<0.001
LVC-35	0.084	0.08	<0.001	0.001	7.22	<0.001	0.07	<0.01	0.25	0.005	0.01	19.4	<0.001	<0.02	<0.002	<0.001

Table A-3. Raw data of trace element analysis from spruce needles collected from Laver (Sweden) in 2016 (this study). Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
LV-23	0.097	<0.005	0.08	<0.01	0.018	55.1	<0.02
LV-24	0.003	<0.005	0.07	<0.01	0.008	119	<0.02
LV-25	0.154	<0.005	0.09	<0.01	0.005	67.7	<0.02
LVC-26	0.002	<0.005	0.08	<0.01	0.01	99.2	<0.02
LVC-27	0.244	<0.005	0.06	<0.01	0.016	59	<0.02
LVC-28	0.193	<0.005	0.07	<0.01	0.014	113	<0.02
LVC-29	0.065	<0.005	0.07	<0.01	0.02	49.9	<0.02
LVC-30A	0.07	<0.005	0.07	0.08	0.014	118	<0.02
LVC-30B*	0.06	<0.005	0.07	<0.01	0.011	110	<0.02
LVC-31	0.083	<0.005	0.08	<0.01	0.037	49.7	<0.02
LVC-32	0.074	<0.005	0.08	<0.01	0.041	56.1	<0.02
LVC-33	0.169	<0.005	0.07	<0.01	0.01	55.5	<0.02
LVC-34	0.098	<0.005	0.08	<0.01	<0.003	74.6	<0.02
LVC-35	0.067	<0.005	0.08	<0.01	0.007	100.5	<0.02

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Type	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
MH-1	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	36	285468	268495
MH-2	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	47	285502	268512
MH-3	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	50	285499	268506
MH-4	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	43	285498	268501
MH-5	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	48	285475	268497
MH-6	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	45	285463	268488
MH-7	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	40	285457	268482
MH-8	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	44	285523	268427
MH-9	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	43	285497	268401
MH-10B*	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	47	285575	268382
MH-11	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	47	285515	268425
MH-12	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	49	285514	268512
MH-13	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	46	285521	268518
MH-14	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	61	285730	268351
MH-15	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	49	285738	268368
MH-16	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	49	285745	268387
MH-17	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	53	285752	268407
MH-18	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	45	285755	268407
MH-19	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	56	285769	268446
MH-20A	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	47	285771	268435
MH-20B*	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	52	285771	268435
MH-21	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	53	285790	268482
MH-22	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	56	285792	268508
MH-23	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	47	285818	268533

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
MH-1	0.001	0.182	1.48	16.7	<10	366	0.73	0.151	0.36	7.07	30	8.52	30.1	0.748	24.2
MH-2	0.0014	0.227	1.55	28.9	10	743	0.92	0.149	0.46	9.96	31.1	9.1	30.5	0.956	21
MH-3	0.0025	0.217	1.41	35	10	419	0.83	0.134	0.39	6.21	32.7	11.3	29.7	0.883	22.4
MH-4	0.0015	0.228	1.29	41.5	10	325	0.95	0.131	0.42	4.08	31.6	11.5	26.1	0.939	21.8
MH-5	0.005	0.258	1.33	86.5	10	333	1.14	0.125	0.46	4.25	35.6	13.8	27.1	0.842	23.2
MH-6	0.0013	0.333	1.3	89.9	10	326	1.14	0.148	0.39	3.98	33	14.9	28.4	1.025	27.5
MH-7	0.0034	0.4	1.19	143.5	10	485	1.46	0.148	0.51	5.25	34.8	22	27.9	1.78	35.5
MH-8	0.0065	0.397	1.31	76.6	10	377	0.98	0.153	0.49	8.42	35.4	10.6	29.2	1.155	27.2
MH-9	0.0215	0.475	1.27	217	10	487	2.45	0.152	1.45	17.2	36.7	21.3	28.5	5.63	48.3
MH-10A	0.0029	64.3	0.64	2330	10	210	0.59	0.084	0.59	175.5	15.6	8.65	14.1	1.095	281
MH-10B*	0.0023	9.91	1.12	297	10	1975	0.66	0.118	0.45	21.2	25.4	7.72	24.1	0.826	44.2
MH-11	0.0007	0.214	1.13	21.7	10	309	0.6	0.123	0.45	3.25	25.4	7.85	22.8	0.726	19.8
MH-12	0.002	0.167	1.42	28.2	<10	409	0.62	0.117	0.22	3.3	30.8	8.65	27.8	1.1	17.65
MH-13	0.0011	0.175	1.27	19.8	<10	317	0.57	0.124	0.37	6.61	28	7.71	25	0.811	18.6
MH-14	0.0022	0.244	1.3	25.3	<10	348	0.78	0.17	0.17	2.74	32.3	9.47	26.9	0.753	21.7
MH-15	<0.0002	0.192	1.25	21.1	<10	284	0.55	0.117	0.12	1.62	29.7	8.64	24.5	0.842	16.95
MH-16	0.0005	0.206	1.45	20.3	<10	256	0.61	0.137	0.1	1.385	32.4	8.44	28.5	1.09	18.55
MH-17	0.0011	0.184	1.3	18.3	<10	254	0.57	0.134	0.14	1.635	28.9	7.96	25.4	0.978	18.25
MH-18	0.002	0.17	1.36	17.8	<10	268	0.48	0.129	0.1	1.16	30.1	7.81	26.4	0.874	17.1
MH-19	0.0012	0.162	1.42	16.65	<10	259	0.57	0.141	0.18	1.395	31.3	8.22	27.9	0.918	17.15
MH-20A	0.001	0.208	1.4	22.6	<10	339	0.58	0.133	0.11	1.125	31.3	8.24	27.8	1.18	16.1
MH-20B*	0.0006	0.236	1.52	21.6	<10	360	0.57	0.118	0.09	0.941	32.4	8.42	29	1.125	15.35
MH-21	0.0008	0.31	1.47	30.6	<10	562	0.62	0.129	0.11	1.245	31.6	8.31	29	1.045	15.3
MH-22	0.0006	0.206	1.32	22.5	<10	284	0.48	0.138	0.11	0.961	28.2	7.58	26.3	0.915	15.1

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (%)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
MH-1	1.79	4.7	0.051	0.077	0.109	0.02	0.1	13.95	17	0.43	472	0.71	0.007	0.474	32.9
MH-2	1.75	4.84	0.057	0.075	0.178	0.03	0.09	14.4	17	0.46	645	0.93	0.007	0.483	33.3
MH-3	2.03	4.59	0.05	0.05	0.133	0.016	0.09	15.35	16.1	0.47	1390	1.48	0.008	0.495	38.3
MH-4	2.05	4.32	0.06	0.055	0.148	0.019	0.13	15.5	14.8	0.43	1750	1.93	0.006	0.485	38.4
MH-5	2.7	4.68	0.073	0.029	0.106	0.027	0.2	18.5	14.4	0.45	3050	2.54	0.012	0.454	45.4
MH-6	2.56	4.48	0.064	0.058	0.135	0.027	0.14	16.95	14.4	0.41	2530	2.49	0.006	0.45	45.7
MH-7	2.86	4.38	0.08	0.117	0.159	0.016	0.1	17.7	13.5	0.36	4200	2.29	0.004	0.375	64.5
MH-8	2.42	4.2	0.074	0.051	0.204	0.027	0.2	20	14.2	0.44	2230	2.3	0.011	0.48	47.6
MH-9	3.99	4.44	0.095	0.118	0.084	0.02	0.11	22.9	11.8	0.25	6430	4.71	0.008	0.241	82.4
MH-10A	6.03	3.3	0.096	0.025	48	0.011	0.13	7.59	5.5	0.27	750	8.81	0.021	0.269	26.2
MH-10B*	2.57	3.53	0.06	0.033	3.48	0.019	0.18	11.65	11.8	0.36	748	2.67	0.001	0.501	30.7
MH-11	1.74	3.6	0.048	0.057	0.124	0.017	0.19	11.7	13.4	0.39	898	1.9	0.025	0.489	26.7
MH-12	2.03	4.51	0.058	0.067	0.144	0.022	0.11	14.4	16	0.46	791	1.34	0.009	0.466	29.5
MH-13	1.6	3.87	0.055	0.082	0.102	0.022	0.09	12.9	13.7	0.41	625	0.84	0.006	0.403	28.6
MH-14	2.15	4.27	0.065	0.018	0.15	0.027	0.12	14.2	13.5	0.39	978	2.04	0.007	0.447	30.5
MH-15	2.04	3.86	0.053	0.015	0.084	0.02	0.09	13.2	12	0.36	843	1.52	0.006	0.417	25.5
MH-16	2.18	4.56	0.054	0.026	0.11	0.021	0.07	14.35	13.9	0.37	833	1.56	0.007	0.456	26.7
MH-17	1.99	4.08	0.042	0.017	0.088	0.019	0.07	12.85	13	0.35	715	1.43	0.008	0.44	25.2
MH-18	2.12	4.19	0.039	0.013	0.082	0.023	0.1	13.15	13.7	0.37	607	1.51	0.008	0.505	25.9
MH-19	2.03	4	0.04	0.025	0.077	0.031	0.09	13.85	13.4	0.4	679	1.73	0.014	0.503	27.3
MH-20A	2	4.42	0.046	0.025	0.075	0.021	0.06	13.9	13.7	0.35	650	1.54	0.005	0.461	25.7
MH-20B*	2.17	4.52	0.052	0.03	0.089	0.019	0.06	14.45	13.9	0.38	737	1.41	0.007	0.461	26.1
MH-21	2.12	4.39	0.054	0.037	0.149	0.021	0.07	13.45	14	0.39	746	1.49	0.007	0.519	25.4
MH-22	1.9	4.08	0.035	0.01	0.099	0.016	0.08	12.25	13	0.34	642	1.57	0.011	0.507	23.9

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
MH-1	0.15	270	<0.001	<0.002	12.35	<0.001	0.09	6.15	3.18	2.4	5.05	18.75	<0.005	0.02	1.32	0.009
MH-2	0.122	281	0.005	<0.002	13.4	0.001	0.12	6.7	2.73	2.2	2.29	30	<0.005	0.07	1.175	0.01
MH-3	0.133	211	0.001	<0.002	15.1	0.001	0.09	7.2	2.36	2.1	0.99	19.95	<0.005	0.07	0.782	0.011
MH-4	0.154	171.5	0.003	<0.002	15.9	<0.001	0.1	5.49	2.5	1.6	1.11	18.75	<0.005	0.06	0.696	0.014
MH-5	0.155	164	0.004	<0.002	16.7	<0.001	0.09	7.93	2.89	1.7	1.02	21.5	<0.005	0.06	0.484	0.021
MH-6	0.14	210	0.003	<0.002	17.7	0.001	0.08	9.19	2.46	1.9	0.95	15.9	<0.005	0.08	0.721	0.014
MH-7	0.157	239	0.006	<0.002	16.2	0.003	0.07	11.5	3.34	2.2	0.87	21.3	<0.005	0.06	1.35	0.012
MH-8	0.16	218	0.006	<0.002	18.65	0.001	0.11	9.24	2.4	1.4	1.59	21.6	<0.005	0.1	0.58	0.011
MH-9	0.137	203	0.006	<0.002	15.8	0.002	0.09	21.7	4.22	3.3	0.52	23.6	<0.005	0.19	1.755	0.006
MH-10A	0.296	>10000	0.001	<0.002	10.45	<0.001	0.81	655	1.585	2.6	0.58	59.8	<0.005	0.02	0.755	0.008
MH-10B*	0.17	5970	0.006	<0.002	14.65	0.001	0.25	107.5	1.275	1.8	0.8	93.9	<0.005	0.07	0.334	0.01
MH-11	0.184	201	0.001	<0.002	17.9	0.001	0.11	4.38	1.715	1.2	0.85	24.3	<0.005	0.05	0.646	0.011
MH-12	0.16	184	0.004	<0.002	17.3	0.001	0.07	4.33	2.47	0.8	0.96	18.2	<0.005	0.02	0.932	0.011
MH-13	0.14	191	0.007	<0.002	12.85	0.001	0.07	4.56	2.5	1.7	1.4	17.5	<0.005	0.06	0.973	0.01
MH-14	0.128	329	0.003	<0.002	18.1	<0.001	0.1	5.5	1.83	1.1	0.7	14.65	<0.005	0.01	0.45	0.012
MH-15	0.088	174.5	0.001	<0.002	16.9	<0.001	0.06	3.04	1.805	0.8	0.63	11.2	<0.005	0.06	0.486	0.013
MH-16	0.087	168	0.002	<0.002	16.9	<0.001	0.06	3.22	1.8	0.5	0.74	11.25	<0.005	0.03	0.585	0.011
MH-17	0.098	151	0.004	<0.002	18.3	0.001	0.07	2.39	1.37	0.6	0.73	12.55	<0.005	0.02	0.438	0.011
MH-18	0.096	168.5	0.001	<0.002	18.05	0.001	0.07	2.54	1.365	0.7	0.81	10.1	<0.005	0.06	0.429	0.012
MH-19	0.115	155.5	0.001	<0.002	19.25	<0.001	0.06	2.61	1.685	0.7	0.73	13.8	<0.005	0.04	0.467	0.012
MH-20A	0.083	205	<0.001	<0.002	16.7	<0.001	0.05	3.48	1.92	0.4	0.62	10.9	<0.005	0.04	0.702	0.011
MH-20B*	0.074	208	0.001	<0.002	16.8	<0.001	0.05	3.49	2.07	0.8	0.61	10.2	<0.005	0.04	0.794	0.012
MH-21	0.085	375	0.004	<0.002	15.75	<0.001	0.06	5.78	2.14	0.4	0.69	12.95	<0.005	0.04	0.67	0.012
MH-22	0.105	246	0.002	<0.002	17.35	<0.001	0.08	3.94	1.225	0.9	0.78	10.5	<0.005	0.02	0.393	0.012

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH	LOI (%)
MH-1	2.21	1.59	34.7	0.133	11.5	1720	1.93	5.1	18.15
MH-2	3.47	1.415	37	0.521	11.65	2160	2.03	5.3	18.15
MH-3	5.2	1.16	37.4	0.297	12.95	1870	1.35	5.4	17.55
MH-4	3.59	0.857	37	0.2	14	1325	1.44	5.2	19.8
MH-5	4.68	0.821	48.5	0.155	19.3	1220	0.75	6.4	19.85
MH-6	5.11	0.919	43.8	0.194	17	1175	1.47	5.7	16.75
MH-7	6.84	0.968	40.7	0.18	20	1275	3.28	6.1	17.15
MH-8	12.35	1.005	39.9	0.282	20.9	3140	1.12	6.4	20.3
MH-9	26.9	1.44	72.4	0.121	29.9	4500	3.46	7.3	17.6
MH-10A	105	2.34	19	0.164	6.5	>10000	0.85	6.4	25.6
MH-10B*	15.35	1.065	35.2	0.291	9.56	3020	0.65	5.6	24.5
MH-11	2.97	0.659	28	0.135	8.3	1060	1.27	5.7	23.1
MH-12	4.14	0.901	34	0.187	10.25	1300	1.41	5.3	16.15
MH-13	2.83	1.34	31.9	0.127	9.98	1635	1.86	5.3	16
MH-14	1.515	0.85	38	0.334	10.45	778	0.74	4.8	18.5
MH-15	1.305	0.797	36.8	0.147	8.54	562	0.58	4.9	15.35
MH-16	1.325	0.844	40.6	1.11	9.85	486	2.02	4.8	14.3
MH-17	1.23	0.701	34.8	0.123	7.46	452	0.56	5.1	14.75
MH-18	1.05	0.781	37	0.167	7.18	403	0.6	4.8	14.25
MH-19	0.973	0.775	37.8	0.163	7.64	479	0.57	5.2	13.9
MH-20A	1.145	0.807	38.3	0.151	7.89	427	0.68	4.7	13.05
MH-20B*	1.155	0.811	38.6	0.145	8.02	430	0.69	4.8	11
MH-21	1.265	0.837	42.5	0.286	7.63	549	0.75	5	12.75
MH-22	1.1	0.794	37.4	0.243	6.36	436	0.47	4.8	15.95

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Location	Species	Material	Season	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
MH-23	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	47	285818	268533
MH-24	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	46	285785	268475
MH-25	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	46	285822	268562
MH-26	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	53	285831	268585
MH-27	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	47	285735	268559
MH-28	Nevinstown	Podzolic	Soil	Summer	-6.70	53.66	37	285737	268514
MH-29	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	49	285657	268300
MH-30A	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	47	285627	268297
MH-30B*	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	47	285627	268297
TC-1	Control site	Podzolic	Soil	Summer	-6.73	53.67	51	284322	269285
TC-2	Control site	Podzolic	Soil	Summer	-6.72	53.67	40	284351	269323
TC-3	Control site	Podzolic	Soil	Summer	-6.73	53.67	-6	284176	269162
T-4	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	48	285489	268551
T-5	Nevinstown	Podzolic	Soil	Summer	-6.71	53.66	43	285411	268609
TC-8	Delvin	Podzolic	Soil	Summer	-7.14	53.60	81	256706	261029
TC-9	Delvin	Podzolic	Soil	Summer	-7.14	53.60	87	256688	261081
TC-10	Delvin	Podzolic	Soil	Summer	-7.14	53.60	86	256670	261093

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
MH-23	0.001	0.177	1.39	20.5	<10	322	0.56	0.132	0.19	1.49	31.9	8.99	25.7	0.958	17
MH-24	0.0019	0.167	1.28	16.7	<10	242	0.47	0.114	0.11	1.145	28.4	7.47	23.5	0.948	15.4
MH-25	0.0006	0.152	1.08	9.18	<10	150	0.35	0.103	0.15	1.13	20.8	4.94	18.8	0.845	13.25
MH-26	0.0027	0.127	1.11	8.9	<10	153.5	0.45	0.12	0.17	1.015	24.4	5.92	20.9	0.742	16.3
MH-27	0.0009	0.145	1.26	16.05	<10	298	0.57	0.136	0.42	1.42	29.4	7.49	26.1	0.754	18.25
MH-28	0.0014	0.48	1.52	33.9	<10	528	0.76	0.142	0.17	1.84	36.7	9.56	31.4	0.984	20.9
MH-29	0.0017	0.305	1.31	43.2	<10	296	0.71	0.108	0.37	2.85	31.5	7.72	25	1.015	15.95
MH-30A	0.0009	0.419	1.37	49.3	<10	386	0.77	0.133	0.42	3.22	35.6	9.58	26.1	1.32	19.3
MH-30B*	0.0011	0.406	1.41	45.2	<10	372	0.88	0.135	0.25	3.21	35.8	9.48	27.5	1.175	18.4
TC-1	0.0012	0.105	1.17	5.13	<10	95	0.67	0.292	0.63	0.519	29.7	7.97	22	0.431	16.05
TC-2	0.0011	0.095	1.55	5.98	<10	128.5	0.82	0.187	0.24	0.463	39	8.05	30.4	0.453	12.05
TC-3	0.0012	0.124	1.24	7.17	<10	66.2	0.6	0.158	0.34	0.558	34.4	9.19	23.5	0.71	17.8
T-4	0.0059	0.265	1.03	30.2	10	511	1.17	0.199	1.34	2.12	30.1	11.55	22.9	0.508	58.3
T-5	0.0004	0.113	1.08	8.04	<10	168	0.74	0.135	0.54	1.59	33.6	9.09	21.9	0.466	23.2
TC-8	0.0024	0.119	0.52	6.27	<10	33.8	0.46	0.178	0.18	0.967	13.9	4.7	13.05	0.202	12.8
TC-9	0.0017	0.115	0.3	7.1	<10	42.8	0.42	0.134	0.71	1.175	9.91	4.49	9.34	0.165	17.3
TC-10	0.0011	0.17	0.71	11.15	<10	33.5	1.28	0.225	1.83	1.665	29.6	12.9	19.5	0.225	20.6

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	Fe (%)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
MH-23	2.04	4.13	0.041	0.02	0.107	0.019	0.1	13.95	13.7	0.39	747	1.55	0.011	0.472	27.8
MH-24	1.8	3.98	0.036	0.021	0.123	0.017	0.08	12.35	12.6	0.32	501	1.29	0.007	0.495	24.6
MH-25	1.35	3.3	0.037	0.018	0.131	0.017	0.06	10.05	10.3	0.24	316	1.04	0.013	0.421	20.1
MH-26	1.53	3.48	0.01	0.028	0.104	<0.005	0.05	11.45	10.3	0.27	339	1.03	0.009	0.477	22.7
MH-27	1.78	3.71	0.042	0.045	0.098	0.018	0.19	12.65	13.4	0.4	551	1.97	0.023	0.516	27
MH-28	2.33	4.49	0.059	0.028	0.17	0.028	0.09	16.6	15.2	0.43	802	1.49	0.007	0.575	31.7
MH-29	1.99	3.99	0.056	0.062	0.074	0.018	0.1	14.2	13.5	0.4	733	1.08	0.009	0.512	29.9
MH-30A	2.31	4.27	0.067	0.068	0.132	0.019	0.07	16.25	12.4	0.37	1690	1.4	0.006	0.466	29.6
MH-30B*	2.3	4.43	0.049	0.049	0.136	0.022	0.08	16.55	13.1	0.38	1590	1.43	0.008	0.503	29.7
TC-1	1.7	3.89	0.073	0.031	0.113	0.022	0.16	13	13.2	0.37	312	1.3	0.026	0.542	28.6
TC-2	2.24	5.53	0.071	0.068	0.129	0.018	0.13	18.75	15.9	0.39	220	1.59	0.017	0.59	32.4
TC-3	1.97	4.26	0.069	0.027	0.115	0.017	0.12	14.6	12.4	0.36	600	1.73	0.028	0.391	29
T-4	2.7	3.77	0.072	0.078	0.498	0.021	0.29	13.5	13.2	0.49	950	3.29	0.03	0.59	37.8
T-5	1.86	3.77	0.067	0.026	0.124	0.021	0.27	14.25	12.1	0.46	788	1.21	0.031	0.578	33
TC-8	1.08	1.985	0.03	0.034	0.134	0.014	0.2	6.89	4.8	0.07	485	5.45	0.017	0.135	25
TC-9	1.05	1.495	0.031	0.027	0.112	0.01	0.11	5.99	2.4	0.07	881	4.34	0.015	0.117	26.9
TC-10	1.91	1.92	0.073	0.083	0.144	0.026	0.13	17.45	5.3	0.15	739	3.48	0.016	0.139	58.4

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study), continued. Note, field duplicates (*).

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (ppm)
MH-23	0.102	174.5	0.003	<0.002	15.65	0.001	0.08	3.03	1.51	1.1	0.64	14.1	<0.005	0.05	0.515	0.011
MH-24	0.085	144.5	0.004	<0.002	12.95	<0.001	0.06	2.4	1.54	0.6	0.64	10.55	<0.005	0.03	0.536	0.01
MH-25	0.104	115.5	0.002	<0.002	12.7	<0.001	0.08	1.575	1.295	0.9	0.66	12.55	<0.005	0.04	0.497	0.008
MH-26	0.093	84.1	<0.001	<0.002	10.45	<0.001	0.07	1.165	1.545	0.7	0.57	11.3	<0.005	<0.01	0.701	0.01
MH-27	0.168	193	0.003	<0.002	16.3	<0.001	0.09	3.57	1.95	1	0.8	20.8	<0.005	0.01	0.765	0.012
MH-28	0.098	432	<0.001	<0.002	14.25	0.001	0.06	6.1	2.08	0.9	1.08	14.25	<0.005	0.04	0.732	0.011
MH-29	0.085	223	0.005	<0.002	15.85	<0.001	0.07	4.81	2.5	0.3	0.71	13.85	<0.005	0.04	1.17	0.012
MH-30A	0.088	411	0.003	<0.002	16.5	0.001	0.07	7.22	2.77	0.6	0.79	13	<0.005	0.04	1.155	0.012
MH-30B*	0.091	408	<0.001	<0.002	17.2	0.001	0.07	7.02	2.36	1.5	1.07	12.1	<0.005	0.05	0.94	0.012
TC-1	0.118	47.3	0.006	<0.002	8.7	<0.001	0.08	0.658	1.615	0.9	0.79	20.1	<0.005	<0.01	0.711	0.013
TC-2	0.103	32.6	0.004	<0.002	10.7	<0.001	0.06	0.708	2.78	1	0.78	13.8	<0.005	<0.01	1.44	0.009
TC-3	0.098	64.8	0.002	<0.002	13	<0.001	0.06	0.834	1.09	1.2	1.04	13.15	<0.005	0.01	0.374	0.01
T-4	0.234	264	0.003	<0.002	13.3	0.002	0.17	3.76	2.39	1.2	15.4	51.4	<0.005	0.03	0.891	0.014
T-5	0.179	92.7	0.002	<0.002	17	<0.001	0.12	1.73	1.47	0.8	0.89	23.6	<0.005	0.02	0.538	0.015
TC-8	0.081	26.2	<0.001	<0.002	5.52	<0.001	0.09	0.575	0.908	1.5	0.61	14.25	<0.005	0.03	0.338	0.003
TC-9	0.086	22.6	0.004	<0.002	5.13	<0.001	0.11	0.663	0.706	2	0.8	35.8	<0.005	0.02	0.195	0.003
TC-10	0.106	25.3	0.005	<0.002	6.55	<0.001	0.08	1.075	3.13	1.2	0.54	74.3	<0.005	0.04	0.986	0.002

Table A-4. Raw data of trace element analysis from soils collected from Navan and Delvin area in 2016 (this study). Note, field duplicates (*).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)	pH	LOI (%)
MH-23	0.874	0.679	33.1	1.4	8.13	502	0.63	5.3	14.8
MH-24	0.784	0.634	31.5	0.139	6.82	373	0.57	5.3	13.6
MH-25	0.587	0.484	26	0.954	5.74	318	0.56	5	16.25
MH-26	0.53	0.586	30	0.197	7.07	270	0.87	5.1	13.7
MH-27	0.895	0.804	32.7	0.206	7.73	537	1.01	6.3	18.3
MH-28	1.385	0.878	46	0.475	11.85	590	0.98	5.4	13.55
MH-29	3.59	0.698	33.3	0.115	10.6	1345	1.32	6.1	15.35
MH-30A	3.29	0.778	37	0.198	13.2	1090	1.59	6.3	14
MH-30B*	3.27	0.89	37.2	0.373	13.65	1075	1.31	5.8	14.1
TC-1	0.155	0.525	26.5	0.081	7.42	108	1.03	5.8	22.1
TC-2	0.178	0.601	35.8	0.089	12.35	94.1	1.95	4.6	15.5
TC-3	0.326	0.602	30.8	0.069	8.06	107.5	0.61	5.6	14.45
T-4	0.843	0.808	34	0.375	11.85	741	2.24	7.2	28.2
T-5	0.361	0.633	25.2	0.187	9.1	505	0.74	6.4	20.8
TC-8	0.126	1.025	21.4	0.052	8.19	83.8	1.1	4.7	16.4
TC-9	0.143	0.933	20.1	0.057	8.48	87.4	1.11	7.2	20.1
TC-10	0.257	0.747	30.3	0.064	27.6	122	3.38	7.7	15.75

Table A-5. Raw data of trace element analysis from tree cores collected in summer and winter 2016 from Navan area (this study), continued.

Sample name	Location	Species	Material	Age	Circumference (m)	Longitude WGS84	Latitude WGS84	Elevation (m)	Irish Grid East	Irish Grid North
TB-4	Nevinstown	Beech	Tree core	1929 - 2016	3.27	-6.71	53.66	48	285489	268551
TB-7	Nevinstown	Beech	Tree core	1918 - 2016	4.11	-6.71	53.66	49	285512	268501
TCB-1	Control site	Beech	Tree core	1950 - 2016	3.36	-6.73	53.67	51	284322	269285
TCB-2	Control site	Beech	Tree core	1965 - 2016	2.84	-6.72	53.67	40	284351	269323
TB-5	Nevinstown	Oak	Tree core	1934 - 2016	2.78	-6.71	53.66	43	285411	268609
TB-6	Nevinstown	Oak	Tree core	1930 - 2016	4.09	-6.71	53.66	42	285482	268501
TCB-3	Control site	Oak	Tree core	1858 - 2016	2.74	-6.73	53.67	-6	284176	269162
PMT-5	Nevinstown	Oak	Tree rings	1950 - 1960	from TB-5	-6.71	53.66	43	285411	268609
DMT-5	Nevinstown	Oak	Tree rings	2000 - 2016	from TB-5	-6.71	53.66	43	285411	268609
PMTC-3	Control site	Oak	Tree rings	1950 - 1960	from TCB-3	-6.73	53.67	-6	284176	269162
DMTC-3	Control site	Oak	Tree rings	2000 - 2010	from TCB-3	-6.73	53.67	-6	284176	269162

Note: Tree core (TB-4) and leaf material (NVT-H5-1) are collected from the same beech tree;

Tree core (TB-7) and leaf material (NVT-H2-22) are collected from the same beech tree;

Tree core (TCB-1) and leaf material (CS2-W1-5) are collected from the same beech tree;

Tree core (TCB-2) and leaf material (CS2-W1-2) are collected from the same beech tree;

Tree core (TB-5), tree rings (PMT-5 & DMT-5) and leaf material (NVT-H5-4) are collected from the same oak tree;

Tree core (TB-6) and leaf material (NVT-H1-32) are collected from the same oak tree and

Tree core (TCB-3), tree rings (PMTC-3 & DMTC-3) and leaf material (CS2-W1-10) are collected from the same oak tree.

Table A-5. Raw data of trace element analysis from tree cores collected in summer and winter 2016 from Navan area (this study), continued.

Sample name	Au (ppm)	Ag (ppm)	Al (%)	As (ppm)	B (ppm)	Ba (ppm)	Be (ppm)	Bi (ppm)	Ca (%)	Cd (ppm)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Cu (ppm)
TCB-1	0.0016	0.017	<0.01	0.03	<1	21.8	<0.01	0.006	0.19	0.064	0.011	0.051	0.52	<0.005	1.21
TCB-2	0.0006	0.007	<0.01	0.03	<1	18	<0.01	0.005	0.13	0.055	0.006	0.027	0.72	<0.005	1.17
TCB-3	0.0007	0.008	<0.01	0.03	<1	6.3	<0.01	0.004	0.1	0.069	0.003	0.026	0.7	0.016	1.16
TCB-5	0.0004	0.016	<0.01	0.08	<1	5.6	<0.01	0.002	0.04	0.052	<0.003	0.047	0.64	<0.005	1.44
TB-4	0.0007	0.041	<0.01	0.1	4	60	<0.01	0.008	0.45	0.044	0.005	0.058	1	<0.005	1.58
TB-6	0.0021	0.017	<0.01	0.05	2	5	<0.01	0.015	0.05	0.039	0.006	0.045	0.45	<0.005	1.96
TB-7	0.0007	0.022	<0.01	0.07	1	40.7	<0.01	0.006	0.43	0.116	0.005	0.036	0.32	<0.005	2
PMT-5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.04	n/a	n/a	n/a	n/a	1.34
DMT-5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	0.8
PMTC-3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.06	n/a	n/a	n/a	n/a	1.89
DMTC-3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.05	n/a	n/a	n/a	n/a	2.49

Table A-5. Raw data of trace element analysis from tree cores collected in summer and winter 2016 from Navan area (this study), continued.

Sample name	Fe (ppm)	Ga (ppm)	Ge (ppm)	Hf (ppm)	Hg (ppm)	In (ppm)	K (%)	La (ppm)	Li (ppm)	Mg (%)	Mn (ppm)	Mo (ppm)	Na (%)	Nb (ppm)	Ni (ppm)
TCB-1	17	<0.004	<0.005	<0.002	0.013	<0.005	0.1	0.006	<0.1	0.018	14.1	0.43	0.073	0.009	1.31
TCB-2	51	<0.004	<0.005	<0.002	0.012	<0.005	0.33	0.002	0.1	0.019	11.6	0.16	0.037	0.017	0.99
TCB-3	110	<0.004	<0.005	<0.002	0.014	<0.005	0.04	0.003	<0.1	0.003	9.4	0.36	0.036	0.007	0.53
TB-5	106	<0.004	<0.005	<0.002	0.01	<0.005	0.06	0.003	<0.1	0.002	3.7	0.39	0.04	0.004	0.59
TB-4	168	<0.004	0.025	<0.002	0.012	<0.005	0.16	0.006	0.1	0.017	17	0.55	0.04	0.012	0.68
TB-6	56	<0.004	<0.005	<0.002	0.009	<0.005	0.05	0.004	<0.1	0.002	4.6	0.09	0.029	0.009	0.58
TB-7	33	<0.004	<0.005	<0.002	0.012	<0.005	0.17	0.005	0.1	0.027	17.9	0.1	0.043	0.009	0.75
PMT-5	183.8	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	3.69	n/a	n/a	n/a	n/a
DMT-5	88	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	2.33	n/a	n/a	n/a	n/a
PMTC-3	186.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	9.53	n/a	n/a	n/a	n/a
DMTC-3	161.3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.75	n/a	n/a	n/a	n/a

Table A-5. Raw data of trace element analysis from tree cores collected in summer and winter 2016 from Navan area (this study), continued.

Sample name	P (%)	Pb (ppm)	Pd (ppm)	Pt (ppm)	Rb (ppm)	Re (ppm)	S (%)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Te (ppm)	Th (ppm)	Ti (%)
TCB-1	0.01	0.18	0.001	0.001	0.2	<0.001	0.03	0.04	0.09	0.044	0.02	4.37	0.005	<0.02	<0.002	<0.001
TCB-2	0.014	0.14	0.001	0.002	0.6	<0.001	0.02	0.03	0.08	0.047	0.02	3.84	0.015	<0.02	<0.002	<0.001
TCB-3	0.005	0.1	<0.001	0.001	0.7	0.001	0.02	0.02	0.09	0.021	0.02	2.47	0.002	<0.02	<0.002	<0.001
TB-5	0.004	0.26	0.001	<0.001	0.34	0.001	0.02	0.01	0.09	0.032	0.02	1.74	0.005	0.02	<0.002	<0.001
TB-4	0.012	0.17	<0.001	<0.001	0.82	<0.001	0.02	0.03	0.1	0.033	0.02	12.25	0.008	<0.02	<0.002	<0.001
TB-6	0.003	0.15	<0.001	<0.001	0.36	<0.001	0.02	0.02	0.08	0.018	0.01	1.98	0.006	<0.02	<0.002	<0.001
TB-7	0.011	0.26	0.001	0.002	0.66	<0.001	0.03	0.03	0.08	0.026	0.01	9.43	0.009	<0.02	<0.002	<0.001
PMT-5	n/a	0.15	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DMT-5	n/a	0.016	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
PMTC-3	n/a	0.034	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
DMTC-3	n/a	0.032	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table A-5. Raw data of trace element analysis from tree cores collected in summer and winter 2016 from Navan area (this study).

Sample name	Tl (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
TCB-1	0.004	<0.005	0.11	0.36	0.003	5.6	0.03
TCB-2	0.004	<0.005	0.07	0.84	<0.003	3.6	<0.02
TCB-3	0.008	<0.005	0.08	0.21	<0.003	1.4	<0.02
TB-5	0.453	<0.005	0.08	0.25	<0.003	1.6	<0.02
TB-4	0.019	<0.005	0.07	0.58	<0.003	6.1	0.03
TB-6	0.591	<0.005	0.06	0.36	<0.003	2.1	0.02
TB-7	0.038	<0.005	0.06	0.46	<0.003	28	<0.02
PMT-5	n/a	n/a	n/a	n/a	n/a	1.78	n/a
DMT-5	n/a	n/a	n/a	n/a	n/a	0.68	n/a
PMTC-3	n/a	n/a	n/a	n/a	n/a	4.81	n/a
DMTC-3	n/a	n/a	n/a	n/a	n/a	5.53	n/a

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
NVT- H1- 1	93.69	3.37	0.22	28.82	60.07	6.60	0.25	0.44	<0.05
NVT- H1- 2	134.76	3.42	1.19	45.74	112.72	9.81	0.27	0.16	0.06
NVT- H1- 3	74.67	4.03	0.13	68.59	80.01	8.36	0.30	0.17	0.08
NVT- H1- 4	48.45	2.93	0.33	29.24	83.24	14.03	0.14	0.08	0.05
NVT- H1- 5	50.85	2.30	0.06	51.00	59.20	6.17	0.19	0.08	<0.05
NVT- H1- 6	105.45	2.46	0.69	16.88	55.72	12.29	0.16	0.15	<0.05
NVT- H1- 7	101.23	3.57	0.55	28.72	56.34	6.93	0.26	0.12	<0.05
NVT- H1- 8	67.18	5.02	0.11	91.04	92.24	7.87	0.33	0.19	0.06
NVT- H1- 9	56.24	2.96	0.07	73.92	201.18	7.65	0.24	0.12	0.09
NVT- H1- 10 (A)	51.45	3.06	0.07	65.75	65.64	7.32	0.18	0.09	<0.05
NVT- H1- 10 (B)	53.18	2.63	0.09	62.92	70.72	7.75	0.19	0.11	<0.05
NVT- H1- 11	57.86	1.77	0.28	30.74	72.25	7.33	0.14	0.07	<0.05
NVT- H1- 12	54.01	6.85	0.07	20.90	73.24	5.72	0.24	0.10	0.05
NVT- H1- 13	86.46	1.93	0.30	32.18	61.94	12.13	0.14	<0.05	0.06
Duplicate 1	78.68	1.61	0.27	29.64	57.08	11.13	0.12	<0.05	0.05
NVT- H1- 14	51.15	2.79	0.06	52.01	72.52	7.33	0.19	0.08	0.07
NVT- H1- 15	65.68	5.34	0.09	76.87	73.44	7.52	0.28	0.08	0.05
NVT- H1- 16	55.63	9.02	0.13	32.76	61.64	7.31	0.16	0.08	<0.05
NVT- H1- 17	105.45	5.76	1.04	41.66	66.23	9.24	0.21	0.12	0.06
NVT- H1- 18	96.34	6.01	0.59	13.80	67.69	3.79	0.32	0.11	0.12
NVT- H1- 19	89.85	5.71	0.19	54.08	81.43	5.94	0.35	0.11	0.06
NVT-H1-20A	106.68	9.53	0.77	25.61	106.71	7.93	0.27	0.16	0.06
NVT-H1-20B	114.34	5.42	0.67	35.24	79.93	5.93	0.27	0.12	0.05
CS1-H2-1	61.92	9.25	<0.05	24.19	91.89	10.86	0.08	0.08	0.08

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
CS1-H2-2	55.64	13.26	<0.05	26.97	95.09	9.22	0.09	0.15	<0.05
CS1-H2-3	41.60	1.31	0.13	43.21	68.20	10.06	0.07	<0.05	<0.05
CS1-H2-4	43.61	0.44	<0.05	22.83	75.77	15.84	<0.05	<0.05	<0.05
Duplicate 2	37.16	0.26	<0.05	20.43	65.88	13.76	<0.05	<0.05	<0.05
CS1-H2-5	34.82	0.40	0.25	374.95	49.20	6.37	<0.05	<0.05	<0.05
CS1-H2-6	47.69	0.53	<0.05	15.91	65.71	13.44	0.05	<0.05	0.07
CS1-H2-7	28.39	0.83	<0.05	75.99	76.50	6.50	0.06	<0.05	<0.05
CS1-H2-8	33.23	1.27	<0.05	34.36	86.85	11.66	0.07	<0.05	0.06
CS1-H2-9	49.39	0.63	0.15	65.51	69.08	10.85	<0.05	<0.05	<0.05
Duplicate 3	47.71	0.62	0.16	63.50	67.67	10.71	0.05	<0.05	<0.05
CS1-H2-10A	23.84	0.37	0.06	154.94	60.84	8.67	<0.05	<0.05	0.05
CS1-H2-10B	27.55	0.51	0.16	329.10	65.10	8.68	<0.05	<0.05	0.08
Standard 1	9.99	0.38	<0.05	42.23	60.51	4.88	n/a	n/a	0.08
Standard 2	10.10	0.36	<0.05	41.41	60.82	4.82	n/a	n/a	0.08
Apple Leaves CRM	12.50	0.47	0.01	54.00	83.00	5.64	n/a	n/a	0.09
% Recovery	0.80	0.78	n/a	0.77	0.73	0.86	n/a	n/a	0.91

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
HVT-H3-1	64.86	0.90	0.09	60.02	64.53	8.20	0.08	0.26	<0.05
HVT-H3-2	83.49	0.93	<0.05	17.72	86.74	23.43	0.08	0.17	<0.05
HVT-H3-3	98.03	0.84	<0.05	15.26	80.36	24.34	0.06	0.12	<0.05
HVT-H3-4	49.29	2.53	0.38	13.47	74.99	6.84	0.15	0.13	0.06
HVT-H3-5	143.03	9.10	0.20	436.44	132.88	10.33	0.50	0.25	0.11
HVT-H3-6	68.29	3.36	0.14	65.99	78.78	7.91	0.20	0.12	<0.05
HVT-H3-7	51.92	1.23	0.33	118.05	66.77	14.46	0.06	0.06	<0.05
HVT-H3-8	68.06	3.51	0.06	27.10	88.95	12.90	0.20	0.10	0.05
HVT-H3-9	82.23	2.69	0.06	26.18	109.90	15.29	0.21	0.09	0.08
Duplicate 3	81.09	2.41	0.06	25.39	107.65	15.47	0.19	0.07	0.08
HVT-H3-10 A	84.57	4.76	0.08	24.64	97.53	16.86	0.28	0.13	0.06
HVT-H3-10 B	88.03	5.18	0.10	33.23	102.00	15.77	0.29	0.14	0.06
CS1-H1-1	26.34	1.06	0.19	21.23	72.41	4.47	0.06	0.04	0.15
CS1-H1-2	35.39	0.96	0.07	19.41	58.10	6.81	0.05	0.05	0.15
CS1-H1-3	33.35	1.50	0.12	18.53	77.41	6.07	0.08	<0.05	0.15
CS1-H1-4	39.53	2.06	0.25	20.21	89.45	7.41	0.13	0.08	0.14
Duplicate 2	39.89	2.16	0.26	19.87	89.77	7.61	0.11	0.12	0.14
CS1-H1-5	33.49	1.83	0.24	25.64	75.83	5.75	0.09	0.06	0.14
CS1-H1-6	34.88	2.37	0.29	24.38	75.90	5.96	0.13	0.08	0.07
CS1-H1-7	27.55	1.23	0.29	29.35	67.50	8.45	0.07	0.05	0.12
CS3-W-1	17.93	0.13	<0.05	339.26	77.56	10.33	<0.05	<0.05	<0.05
CS3-W-2	19.20	0.06	<0.05	70.44	49.74	11.37	<0.05	<0.05	<0.05
Duplicate 1	19.13	0.17	<0.05	70.88	51.67	11.12	<0.05	<0.05	<0.05
CS3-W-3	14.99	0.04	0.09	386.48	55.18	7.25	0.02	0.13	0.07

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
NVT-H5-1	43.71	1.89	0.13	77.60	77.49	8.03	0.13	0.13	0.05
NVT-H5-2	62.96	3.02	0.13	44.24	83.81	11.31	0.17	0.10	0.05
NVT-H5-3	50.13	1.25	0.08	53.24	66.63	4.85	0.07	0.08	<0.05
NVT-H5-4	40.45	1.68	0.25	242.01	89.28	10.89	0.10	0.07	<0.05
NVT-H5-5	66.13	0.65	<0.05	26.75	79.94	9.98	0.03	0.05	<0.05
NVT-H5-6	44.22	1.73	0.21	188.18	65.38	4.65	0.10	0.07	0.07
Duplicate 4	45.14	1.70	0.20	174.75	61.85	4.75	0.10	0.06	0.06
NVT-H5-7	64.11	1.33	<0.05	24.55	78.40	16.46	0.08	0.05	0.05
NVT-H5-8	38.79	1.81	0.08	150.01	84.20	11.47	0.10	0.05	<0.05
NVT-H5-9	75.80	1.64	<0.05	37.72	96.90	19.19	0.11	0.08	0.09
NVT-H5-10 A	70.65	2.71	0.22	164.51	86.41	10.25	0.16	0.09	0.05
NVT-H5-10 B	59.77	2.39	0.18	153.34	85.60	8.19	0.15	0.08	0.05
Standard 1	11.96	0.41	<0.05	45.37	68.16	4.50	n/a	n/a	0.08
Standard 2	11.01	0.47	<0.05	48.06	71.86	4.35	n/a	n/a	0.09
Apple Leaves CRM	12.50	0.47	0.01	54.00	83.00	5.64	n/a	n/a	0.09
% Recovery	0.92	0.94	n/a	0.87	0.84	0.78	n/a	n/a	0.94

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
NVT- H4- 1	94.09	4.94	0.26	148.41	66.88	7.00	0.34	0.58	0.05
NVT- H4- 2	157.72	5.15	0.80	64.44	61.51	5.88	0.33	0.29	0.13
NVT- H4- 3	107.72	2.25	0.54	22.00	70.59	14.06	0.18	0.15	<0.05
NVT- H4- 3F	79.55	2.24	0.90	13.11	61.77	21.18	0.18	0.14	0.05
NVT- H4- 4	62.37	1.04	0.18	100.72	45.88	9.84	0.08	0.07	<0.05
NVT- H4- 5	80.78	1.98	0.18	108.55	58.72	11.06	0.14	0.13	0.05
Duplicate 3	69.80	2.06	0.17	108.78	60.14	10.50	0.11	0.07	0.05
NVT- H4- 6	97.81	3.19	0.18	64.76	72.97	12.42	0.24	0.15	<0.05
NVT- H4- 7	82.75	1.02	0.10	61.24	44.47	9.64	0.08	0.15	<0.05
NVT- H4- 8	89.57	1.40	0.14	48.45	55.61	11.16	0.12	0.17	<0.05
NVT- H4- 9	96.64	5.93	0.40	58.14	68.94	7.71	0.34	0.23	0.10
NVT- H4- 10 A	44.18	1.68	0.13	22.99	47.02	4.40	0.09	0.18	0.07
NVT- H4- 10 B	43.50	1.56	0.13	22.61	57.14	4.49	0.08	0.13	0.07
NVT- H4- 11	97.09	5.48	0.09	38.60	84.28	18.24	0.31	0.17	0.08
NVT- H4- 12	133.33	1.75	0.08	41.45	57.26	15.03	0.10	0.05	<0.05
NVT- H4- 14	76.02	3.48	0.21	23.71	50.89	6.20	0.18	0.10	<0.05
NVT- H4- 15	55.28	2.38	0.34	19.63	56.87	5.25	0.11	0.10	0.05
NVT- H4- 16	530.94	9.25	4.60	30.26	58.30	3.78	0.25	0.11	0.12
Duplicate 1	506.74	9.83	4.65	28.36	58.65	3.91	0.23	0.32	0.13
NVT- H4- 17	697.78	7.71	4.87	30.05	77.15	4.92	0.33	0.15	0.10

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
NVT- H4- 18	103.97	2.08	0.14	77.36	56.50	10.52	0.11	0.05	<0.05
NVT- H4- 19	76.35	1.12	<0.05	30.19	67.30	21.67	0.06	<0.05	0.06
NVT- H4- 20 A	68.22	0.82	0.08	73.54	66.22	18.50	0.06	0.07	0.06
NVT- H4- 20 B	70.05	0.98	0.05	84.87	69.59	18.04	0.05	0.05	0.05
NVT- H1- 6F	64.22	2.73	0.70	14.80	48.18	15.19	0.14	0.08	<0.05
NVT- H1- 21	64.83	4.08	0.11	48.18	142.91	5.76	0.27	0.32	0.11
NVT- H1- 32	50.64	2.12	0.07	142.05	69.49	15.19	0.14	0.12	<0.05
NVT- H1- 33	172.05	2.34	0.06	11.86	64.10	10.46	0.18	0.09	<0.05
NVT- H1- 34	117.88	1.33	<0.05	17.29	81.40	18.36	0.13	0.05	<0.05
NVT- H1- 39	47.60	0.42	<0.05	29.24	64.26	9.64	<0.05	<0.05	<0.05
CS2- W1- 6F	31.28	0.25	0.09	17.06	144.69	11.67	<0.05	0.08	0.32
Duplicate 2	31.14	0.54	0.10	17.83	150.50	11.38	<0.05	0.15	0.35
NVT- H2- 35	64.34	1.33	0.24	31.36	60.74	23.88	0.08	0.07	<0.05
Duplicate 4	64.93	1.32	0.23	28.90	58.61	23.91	0.08	0.07	<0.05
NVT- H2- 36	83.29	3.89	0.08	20.29	104.73	18.95	0.23	0.17	0.06
NVT- H2- 37	60.25	5.25	0.17	57.65	75.02	5.75	0.24	0.33	<0.05
Standard 1	11.16	0.40	<0.05	47.34	65.48	5.28	n/a	n/a	0.08
Standard 2	11.10	0.38	<0.05	48.99	67.49	5.24	n/a	n/a	0.07
Apple Leaves CRM	12.50	0.47	0.01	54.00	83.00	5.64	n/a	n/a	0.09
% Recovery	0.89	0.83	n/a	0.89	0.80	0.93	n/a	n/a	0.81

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study), continued.

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
CS2- W1- 1	28.97	0.50	0.14	177.22	74.23	14.58	0.06	0.07	0.06
CS2- W1- 2	38.62	0.20	0.41	167.16	68.89	27.78	0.07	0.09	<0.05
CS2- W1- 3	29.22	0.27	0.14	88.78	66.22	16.68	<0.05	<0.05	0.05
Duplicate 3	27.13	0.20	0.08	61.33	115.08	10.47	<0.05	<0.05	<0.05
CS2- W1- 4	32.83	0.11	0.45	155.98	62.02	16.95	<0.05	<0.05	0.10
Duplicate 1	28.33	0.07	0.41	154.46	63.02	13.16	<0.05	<0.05	0.10
CS2- W1- 5	29.22	0.10	0.14	52.29	45.94	16.43	<0.05	<0.05	<0.05
CS2- W1- 6	23.58	0.26	0.07	21.29	100.50	9.52	<0.05	<0.05	0.16
CS2- W1- 7	60.85	0.28	0.11	104.54	85.12	18.73	<0.05	<0.05	<0.05
CS2- W1- 8	25.64	0.27	0.07	51.58	91.38	12.19	<0.05	<0.05	<0.05
CS2- W1- 9	46.14	0.36	0.08	122.82	116.29	15.81	<0.05	<0.05	0.06
CS2- W1- 10 A	20.67	0.16	<0.05	180.48	74.37	9.08	<0.05	<0.05	<0.05
CS2- W1- 10 B	21.70	0.14	<0.05	203.83	77.27	11.33	<0.05	<0.05	<0.05
CS2- W1- 11	47.31	0.36	0.08	113.97	107.94	15.82	<0.05	<0.05	0.06
NVT- H2- 22	99.97	4.09	0.87	63.42	66.28	22.34	0.33	0.13	0.05
NVT- H2- 23	142.58	6.87	1.00	29.53	96.98	7.51	0.48	0.23	0.07
NVT- H2- 24	66.16	2.36	0.33	48.66	61.73	11.35	0.15	0.05	<0.05
NVT- H2- 25	71.84	3.24	0.33	120.01	75.60	13.83	0.16	0.05	0.05
NVT- H2- 26	68.88	3.34	0.39	25.45	54.86	4.56	0.18	0.06	0.07
NVT- H2- 27	101.82	6.82	0.68	14.36	74.06	7.52	0.43	0.18	0.06
Duplicate 2	97.35	7.23	0.65	16.52	90.83	7.25	0.43	0.20	0.05
NVT- H2- 28	53.10	1.83	0.21	41.87	59.97	14.47	0.11	0.05	<0.05
NVT- H2- 29	76.98	2.53	0.36	46.33	62.76	7.16	0.21	0.16	0.08

Table A-6. Corrected trace element data (Tara Mines Laboratory) from plants collected from Navan area in 2015 (this study).

Internal Standard	Rh	Lu	Rh	Sc	Sc	Rh	Rh	In	Sc
Description	Zn (ppm)	Pb (ppm)	Cd (ppm)	Mn (ppm)	Fe (ppm)	Cu (ppm)	As (ppm)	Sb (ppm)	Co (ppm)
NVT- H2- 30 A	64.98	4.99	0.17	105.79	101.17	6.70	0.31	0.27	0.05
NVT- H2- 30 B	51.79	3.33	0.16	108.32	76.71	5.47	0.22	0.17	<0.05
NVT- H2- 38	78.14	2.97	0.18	70.22	65.15	6.43	0.16	0.08	<0.05
NVT- H1- 1	90.26	3.38	0.20	30.74	62.96	6.65	0.20	0.07	<0.05
NVT- H1- 13F	47.15	1.09	0.36	19.75	43.57	15.83	0.07	0.13	0.08
NVT- H4- 18	101.05	1.70	0.14	78.38	59.66	10.92	0.11	0.06	<0.05
Duplicate 4	100.26	1.71	0.13	76.95	59.15	10.48	0.11	0.05	<0.05
NVT- H1- 21	68.98	4.16	0.11	48.64	147.94	5.82	0.28	0.11	0.10
CS2- W1- 6F	32.17	0.18	0.09	19.49	156.68	11.92	<0.05	<0.05	0.29
NVT- H2- 32	63.37	5.31	0.11	27.70	102.25	6.74	0.24	0.16	0.06
Duplicate 5	57.74	4.25	0.11	29.01	104.54	6.30	0.24	0.31	0.07
Standard 1	11.14	0.38	<0.05	51.11	70.68	5.46	n/a	n/a	0.08
Standard 2	10.88	0.36	<0.05	50.11	69.29	5.25	n/a	n/a	0.07
Apple Leaves CRM	12.50	0.47	0.01	54.00	83.00	5.64	n/a	n/a	0.09
% Recovery	0.88	0.79	n/a	0.94	0.84	0.95	n/a	n/a	0.85

Table A-7. Soil pH and Eh measured in the field and laboratory pH (ALS Loughrea), continued (this study).

SOIL SAMPLE	LABORATORY	FIELD	FIELD	FIELD	FIELD
DESCRIPTION	pH	pH	Eh	pH + HCl*	Eh + HCl*
DETECTION	0.1		µS		µS
TIME	60 mins.	60 sec.	60 sec.	60 sec.	20 sec.
MH-1	5.1	5.86	43	4.87	65
MH-2	5.3	5.74	72	4.81	112
MH-3	5.4	6.05	53	5.33	82
MH-4	5.2	5.65	108	4.73	151
MH-5	6.4	6.45	172	6.14	149
MH-6	5.7	6.11	20	5.58	35
MH-7	6.1	6.42	27	6	26
MH-8	6.4	6.55	82	5.86	108
MH-9	7.3	7.98	29	7.6	52
MH-10A	6.4	6.58	130	6.23	158
MH-10B	5.6	6.02	243	5.05	292
MH-11	5.7	6.41	66	5.75	66
MH-12	5.3	6.09	12	5.34	21
MH-13	5.3	6.01	16	5.21	32
MH-14	4.8	5.49	43	4.99	58
MH-15	4.9	5.62	8	4.86	39
MH-16	4.8	5.4	19	4.81	44
MH-17	5.1	5.62	12	4.98	42
MH-18	4.8	4.98	28	4.75	46
MH-19	5.2	5.82	36	5.02	53
MH-20A	4.7	5.47	12	4.71	38
MH-20B	4.8	5.36	21	4.91	39

* one drop of 10% HCl
mean temp. = 22° C

Table A-7. Soil pH and Eh measured in the field and laboratory pH (ALS Loughrea), this study.

SOIL SAMPLE	LABORATORY	FIELD	FIELD	FIELD	FIELD
DESCRIPTION	pH	pH	Eh	pH + HCl*	Eh + HCl*
DETECTION	0.1		μ S		μ S
TIME	60 mins.	60 sec.	60 sec.	60 sec.	20 sec.
MH-21	5	5.52	0	4.93	28
MH-22	4.8	5.2	39	4.41	57
MH-23	5.3	5.9	27	5.23	55
MH-24	5.3	5.63	0	5.18	29
MH-25	5	5.64	43	5.06	54
MH-26	5.1	5.84	39	5.54	45
MH-27	6.3	6.45	112	5.98	131
MH-28	5.4	5.96	18	5.2	46
MH-29	6.1	6.43	46	6.02	52
MH-30A	6.3	6.52	0	6.2	25
MH-30B	5.8	6.11	0	5.75	0
TC-1	5.8	6.46	119	6.11	134
TC-2	4.6	5.33	96	5.2	103
TC-3	5.6	5.89	167	5.66	175
T-4	7.2	7.37	314	7.28	324
T-5	6.4	6.37	1189	6.07	1272
TC-8	4.7	4.79	630	4.51	616
TC-9	7.2	6.85	160	6.5	168
TC-10	7.7	7.55	303	7.1	329

* one drop of 10% HCl
mean temp. = 22° C

APPENDIX B

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Case study Laver, Sweden

Trace element analysis of plants was carried out at the Laver Cu deposit, (Norrbotten region, Sweden, Fig. B-1) to assess whether biogeochemical techniques could help identify porphyry deposits in a northern European temperate climate (see Chapter 5, Fig. 18). A similar exploration protocol as used in the Navan case study (see Chapter 6) was used in plant geochemistry at Laver deposit. Sampling was restricted to spruce needles and wood, due to the prevalence of Norway Spruce. The distribution of vegetation in the region has been affected by silviculture, dominated by one species of spruce of a uniform age and forming dense coverage over areas of Cu-Mo-Au mineralisation. The terrain has been heavily affected by past glaciation events with bedrock covered by a variable thickness of till ranging from 10's of meters to exposed bedrock exhibiting scours from ice movement.

Spruce trees are one of the favoured species widely used for biogeochemical prospecting in boreal forests of North America. Trace element analysis were conducted largely for spruce needles based on reported differences that might occur between other plant tissues coming from the same species (Klaminder et al., 2004, Dunn, 2007).

In general, element concentration data (Table B-3) show that As, Cd, Fe, Ni, Pb and Zn are not normally distributed ($p < 0.05$) in Laver spruce needles based on a Shapiro-Wilk test. Moreover, As, Fe and Pb were not normally distributed at the Lill-Laverberget mineralisation (Table B-3) while As, Ni, Pb, S, Sr and Zn showed similar results for the Swedish control sites. Based on the Kruskal-Wallis test, Cu-Au-Mo mineralisation zones exhibit significant differences regarding As ($p = 0.06$) and Mg ($p = 0.03$), when compared to background. Two significant figures imply <15% MAD precision while four figures imply <6% MAD precision (Table B-2).

The high-grade mineralisation zone at Laver displayed variations in As, Ba, Ni, Rb and Sr in relation to the low-grade mineralisation zone at Lill-Laverberget. Manganese and Rb are two times higher (1648 ± 28.28 ppm; 12.39 ± 0.35 ppm) on average compared to areas further away from the mineralisation. Even though, As and Ni concentrations are low, when the data is normalised against Sn this confirms their differences in enrichment at Laver and Lill-Laverberget in comparison to control sites.

In general, Zn and Mn displayed higher concentrations in spruce needles (Fig. B-2) than previously reported (Brun et al., 2010; Rodriguez et al., 2013). Gold and Ag concentrations were close to or below the detection limit while Cu exhibited extremely low concentrations (1.2 ± 0.04 ppm, on average) at all investigated sites. Iron exerts a strong influence on Cu and Mn; exhibited by a very strong correlation between Mn/Fe and Cu/Fe ($r=0.95$) revealed significant Fe influence. In addition, Pearson's factor revealed a strong positive correlation for Ba:Sr ($r=0.72$) and Ca:Sr ($r=0.56$) in both mineralisation zones and between K and Rb ($r=0.82$) at Lill-Laverberget (Fig. B-3).

Table B-1. Element concentrations and descriptive statistics for spruce needles collected from Laver in Sweden during June, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Values are reported in parts per million (ppm) except for Ca, K, and P (%).

Spruce Laver-Sweden	As	B	Ba	Ca (%)	Cd	Co	Cr	Cu	Fe	Hg	K (%)	Mg	Mn
Detection limit	0.01	1	0.1	0.01	0.001	0.002	0.01	0.01	1	0.001	0.01	0.001	0.1
n	27	27	27	27	27	27	27	27	27	27	27	27	27
Min	0.01	4.00	12.30	0.54	0.01	0.02	0.09	0.98	17.00	0.03	0.23	400.00	380.00
Max	0.04	17.00	130.00	1.38	0.12	0.21	0.31	1.54	73.00	0.05	0.63	910.00	2960.00
Mean	0.03	8.59	56.10	1.01	0.02	0.05	0.17	1.26	28.84	0.03	0.41	604.81	1592.26
Median	0.02	8.00	57.60	1.02	0.02	0.04	0.16	1.30	24.00	0.04	0.41	590.00	1365.00
2 Std Dev	0.01	3.08	1.06	0.02	0.001	0.001	0.03	0.04	0.71	0.004	0.01	0.001	25.46

Spruce Laver-Sweden	Mo	Ni	P (%)	Pb	Rb	S	Sn	Sr	Zn
Detection limit	0.01	0.04	0.001	0.01	0.01	0.01	0.01	0.02	0.1
n	27	27	27	27	27	27	27	27	27
Min	0.01	0.19	0.08	0.05	7.24	500.00	0.01	11.00	32.20
Max	0.09	0.88	0.19	0.19	18.00	1000.00	0.01	55.30	194.00
Mean	0.03	0.46	0.11	0.08	12.05	674.07	0.01	28.29	81.84
Median	0.03	0.42	0.10	0.07	12.20	700.00	0.01	28.10	68.3
2 Std Dev	0.01	0.05	0.004	0.01	0.46	0.000	0.001	1.20	2.33

Table B-2. MAD Precision and duplicate samples of spruce needles collected at the Laver site (Sweden) in June, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

Spruce needles	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
MAD Precision (%)	8.86	0.71	0.78	0.36	1.17	5.72	1.12	1.03	4.64	0.55	0.81	1.08
LV-13	0.02	83	1.05	0.121	0.039	0.12	1.33	17	0.034	0.63	0.055	956
Duplicate	0.03	83.3	1.03	0.123	0.039	0.11	1.33	17	0.037	0.63	0.055	936
2SD	0.01	0.42	0.03	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	28.28
LVC-31	0.02	41.7	0.62	0.007	0.037	0.19	1.16	21	0.017	0.4	0.054	576
Duplicate	0.02	42.9	0.63	0.007	0.039	0.16	1.22	22	0.015	0.41	0.056	592
2SD	0.00	1.70	0.01	0.00	0.00	0.04	0.08	1.41	0.00	0.01	0.00	22.63

Spruce needles	Mo	Ni	P	Pb	Rb	S	Sn	Sr	Zn
MAD Precision (%)	8.86	2.57	1.15	8.33	1.09	0.00	0.00	1.39	1.12
LV-13	0.03	0.66	0.086	0.05	14.5	0.06	0.01	34.4	183.5
Duplicate	0.03	0.64	0.085	0.04	14.25	0.06	0.01	34.9	184.5
2SD	0.00	0.03	0.00	0.01	0.35	0.00	0.00	0.71	1.41
LVC-31	0.03	0.56	0.097	0.07	12.3	0.06	0.01	24.2	49.7
Duplicate	0.02	0.61	0.101	0.06	12.7	0.06	0.01	25.4	52
2SD	0.01	0.07	0.01	0.01	0.57	0.00	0.00	1.70	3.25

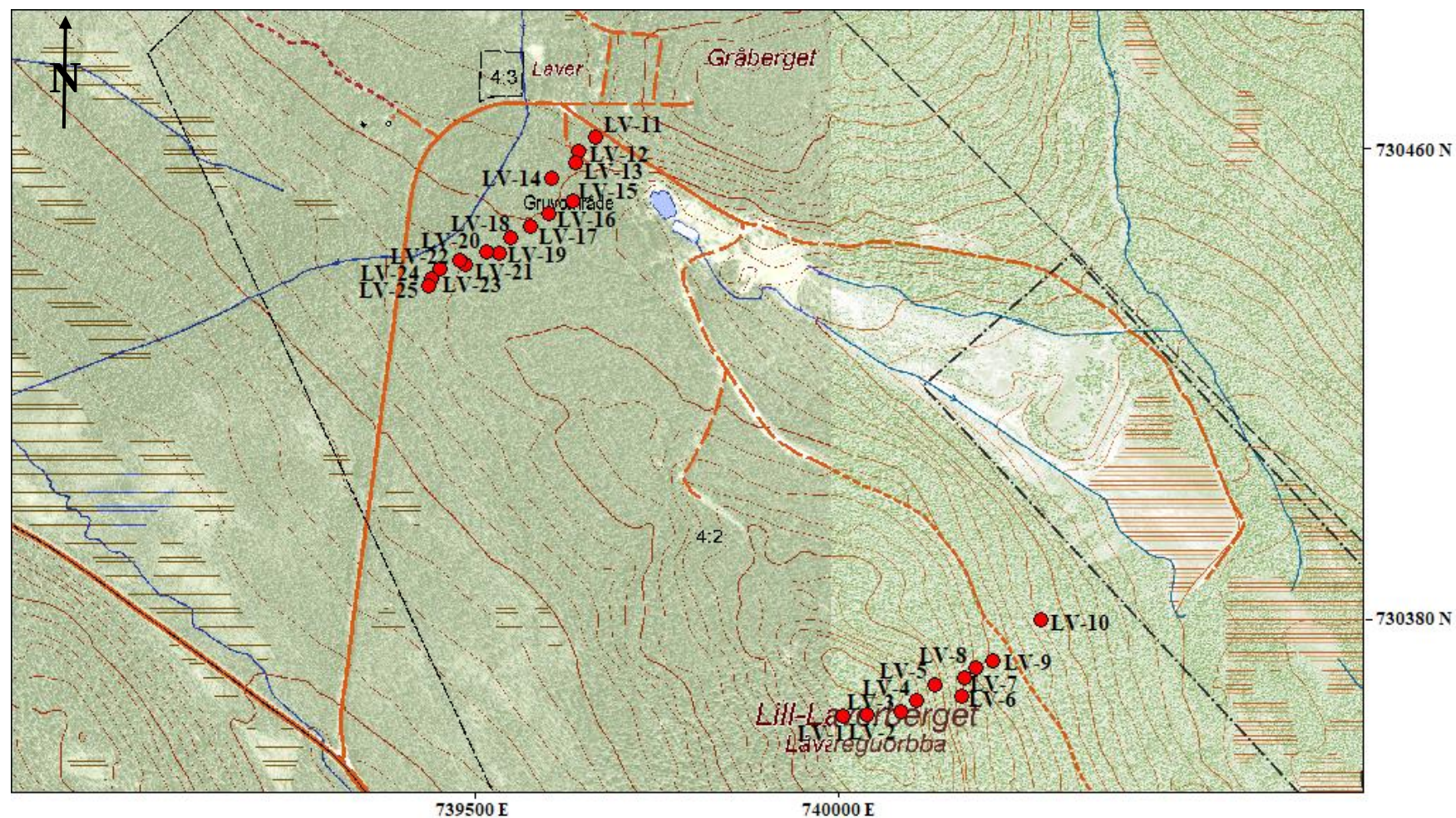


Figure B-1. Sample locations for spruce samples at Laver (Sweden). Swedish coordinate system SWEREF TM 99.

Table B-3. Element concentration in Spruce needles collected from the Laver and Lill-Laverberget mineralisation zone (Sweden) in June 2016. Mean values of trace elements in Pine needles (SRM 1575) are reported by NIST; with spruce green shoots (*) by Brun et al. (2010). The Shapiro-Wilk W test is calculated at 95% confidence. The data distribution is normal if $p > 0.05$. A Kruskal – Wallis test (KW) was calculated for not normally distributed data while a t - test was performed on normal data distribution. Values above critical value ($p = 0.05$) displayed no significant difference (no sign.) between two independent groups. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Spruce needles			Reported	Shapiro – Wilk W test p (normal)	Kruskal-Wallis and t - test
	<i>Laver</i>	<i>Lill- Laverberget</i>	<i>Control</i>	<i>Needles</i>	<i>Laver</i>	Laver vs. Control 95% Confidence
As	0.02	0.03	0.02		0.03	$p = 0.06$ (KW)
Ba	45.09	72.11	71.26		normal	no sign. (t -test)
Ca (%)	0.03	0.02	0.05	0.3*	normal	no sign. (t -test)
Cd	0.03	0.02	0.05		<0.001	no sign. (KW)
Co	0.05	0.04	0.05		<0.001	no sign. (KW)
Cr	0.15	0.19	0.19		0.008	no sign. (KW)
Cu	1.30	1.21	1.21	2.8	normal	no sign. (t -test)
Fe	29.50	27.00	26.27	46	<0.001	no sign. (KW)
Hg	0.04	0.03	0.03		normal	no sign. (t -test)
K (%)	0.43	0.38	0.43	1.25*	normal	no sign. (t -test)
Mg (%)	0.06	0.06	0.05		normal	$p = 0.03$ (t -test)
Mn	1346	1950	1745	125*	normal	no sign. (t -test)
Mo	0.03	0.04	0.03		<0.001	no sign. (KW)
Ni	0.39	0.57	0.32		0.01	no sign. (KW)
P (%)	0.11	0.11	0.09		0.01	no sign. (KW)
Pb	0.07	0.08	0.08	0.17	0.01	no sign. (KW)
Rb	10.55	14.23	9.46	68*	normal	no sign. (t -test)
S (%)	0.07	0.06	0.07		normal	no sign. (t -test)
Sr	25.09	32.94	33.40		normal	no sign. (t -test)
Zn	83.64	79.22	80.50	40*	0.003	no sign. (KW)
	N=16	N=11	N=11			

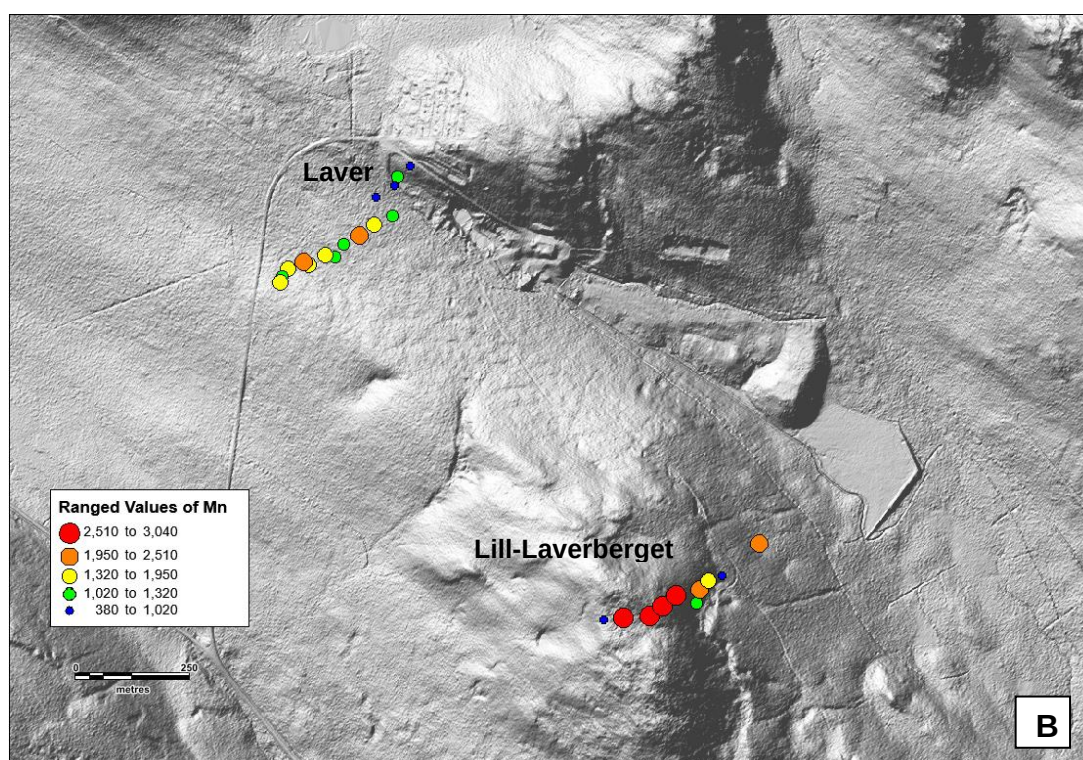
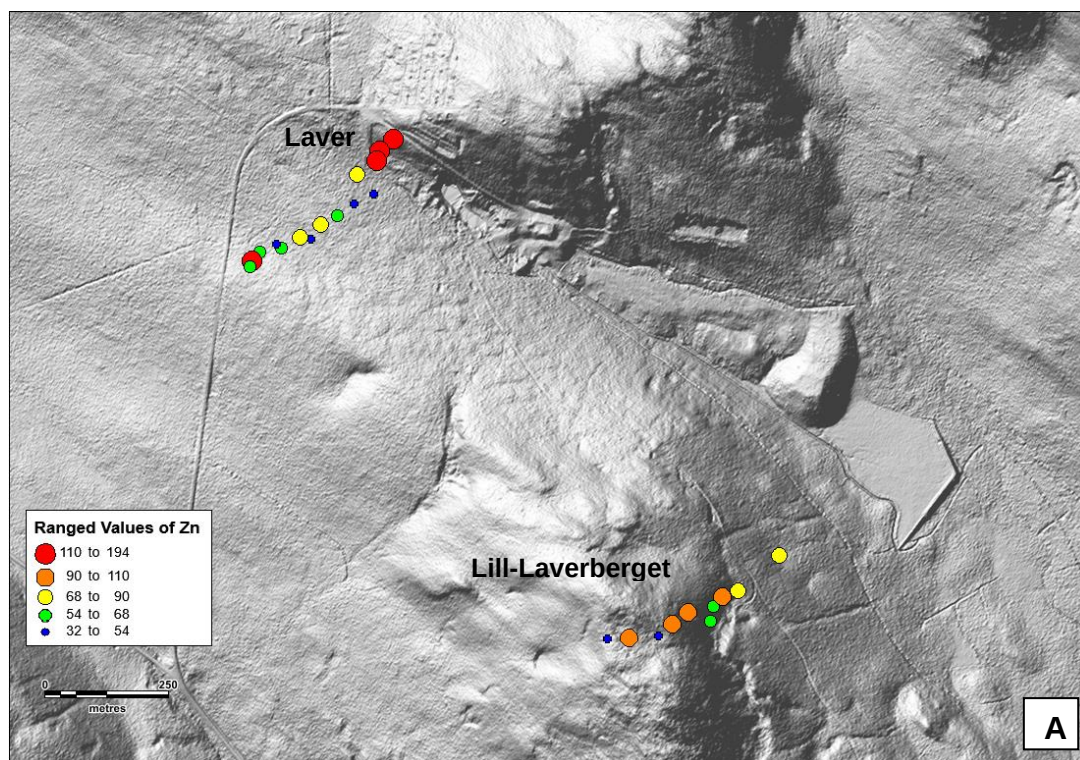


Figure B-2. High resolution topographic map with ranged values of Zn (A) and Mn (B) at Laver and Lill-Laverberget in Sweden. Trace element concentrations (ppm) in spruce needles (N=27) from small biogeochemical survey in spring, 2016.

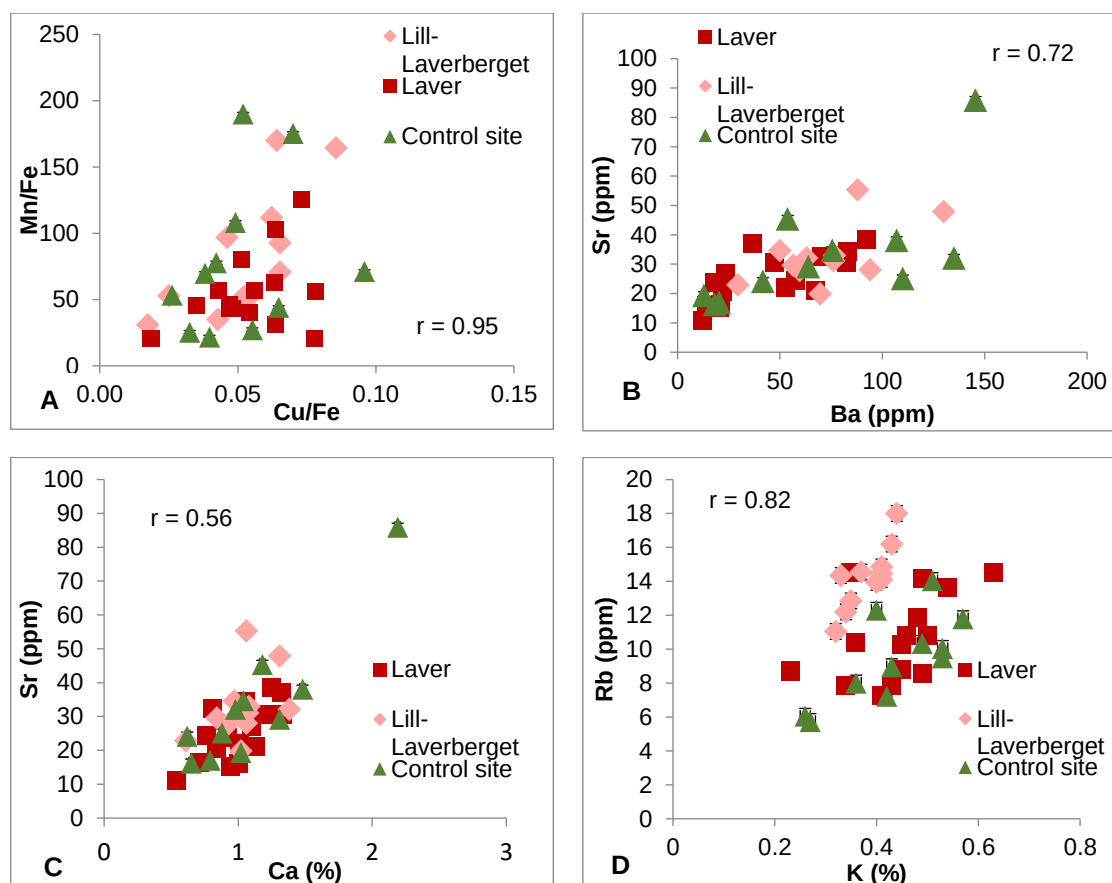


Figure B-3. XY plot of two Cu-Au-Mo mineralisation zones (Laver and Lill-Laverberget) and surrounding control site. Mn/Fe and Cu/Fe ratios (A) were used to reduce Fe impact on the Cu and Mn due to their strong interactions in the plant material. Plot B, C and D shows correlation between Ba:Sr, Ca:Sr and K:Rb. Error bars are 2 standard deviation calculated using replicate analysis of sampling duplicates. Error bars are not shown where error is smaller than symbol.

Trace element vectoring around the Laver deposit in Sweden

A majority of the investigated elements analysed in this study are considered to represent normal ranges and corresponding to values previously published for major, trace and ultra-trace elements in the green shoots of Norway spruce trees collected at Forsmark, Sweden (Brun et al., 2010). The only differences observed were in relation to Mn (1745 ± 22.63 ppm) and Zn (81 ± 3.25 ppm) in spruce needles, compared to the study from the Forsmark site which reported values of 107 ppm Mn and 50 ppm Zn. Moreover, slightly depleted values of Ca, K and Rb in spruce needles from this study in comparison

to the green shoots of Brun et al. (2010) can be explained through an abscission process in which plants release or drop various parts of organs such as leaves, needles or fruit to the ground (Wytenbach et al., 1995). This is especially notable for Ca where abscission can limit its phloem mobility (Dauer et al., 2007). Rodriguez et al. (2013), investigated trace elements in Swedish mining areas; in particular Cu and Fe in soil horizons and grasses over mine tailings at Laver. For this purpose, they analysed common grass and white cotton grass near the soil collection area. Overall, the plants exhibited significantly higher metal concentrations except for Zn which exhibited lower values (18 ppm) on average (Rodriguez et al., 2013) compared to 81 ± 1.41 ppm measured in this study. This could be related to uptake in different plant species types and botanical classification as previously discussed.

Cluster analysis (Fig. B-4) showed that Ba, Fe, Sr, Rb and Zn exhibited similarities with Ca, Mg, Mn, K and S based on the element concentration at Laver. Therefore, they formed one group or cluster of elements. However, at the control sites Ba, Fe, Sr, Rb and Zn shared similar metal distribution with the second group of trace elements including As, Cd, Cr, Co, Mo, Ni, Pb and Sn.

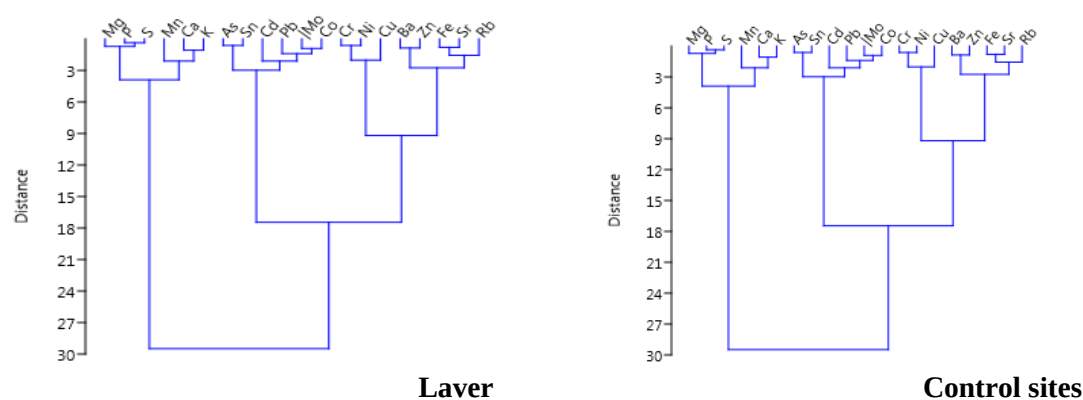


Figure B-4. Cluster Analysis of elemental concentration in spruce needles from Laver region and control sites.

An uptake trend of Mn>Fe>Cu revealed that Norway spruce accumulates more Mn than Fe and Cu in needles. In fact, Mn enrichment and Cu depletion in spruce needles is observed at all sites. Manganese oxide (MnO_2) is often found in soil and strongly associated with Ba, Co, Cu, Fe, Mo, Ni, Pb and Zn. Under acidic and reducing conditions Mn can be easily absorbed at high levels (toxic) in vegetation (Kabata-Pendias and Pendias, 1992).

It has been argued that boggy areas, such as those found around Laver site could accentuate Mn mobility in a low pH environment, but Mn has a high affinity for organic matter and may minimise the effects of pH (Adriano, 2001). As a result, vegetation growing near bogs may not exhibit Mn enrichment. In contrast, depletions in Cu and Fe can be caused by Fe-Mn antagonism where Mn strongly interacts with Fe upon plant uptake; as a result, Fe contents can be significantly lowered in vegetation (Cinelli et al., 2004; Brun et al., 2010). Thus, increases in Fe can lead to reduced Cu concentrations, and this likely explains the low Cu concentrations (1.2 ± 0.02 ppm, on average) reported in this research. A positive correlation between Cu/Fe and Mn/Fe, especially over the Lill-Laverberget zone ($r=0.74$, see Fig. B-3), confirms a strong Mn influence on Cu depletion after normalising data with Fe. Metals will co-precipitate with or adsorb onto Fe hydroxides or organic matter (Heberlein 2016, pers. comm.); normalising data with Fe reveals a clearer Cu and Mn signature. The control sites did not illustrate a clear correlation between Cu and Mn. In fact, the control locality displayed very strong correlation between Ca/Sr and K/Rb ($R=0.9$) which may indicate a strong influence of local bedrock with felsic rocks represented by K/Rb and carbonates (Ca/Sr).

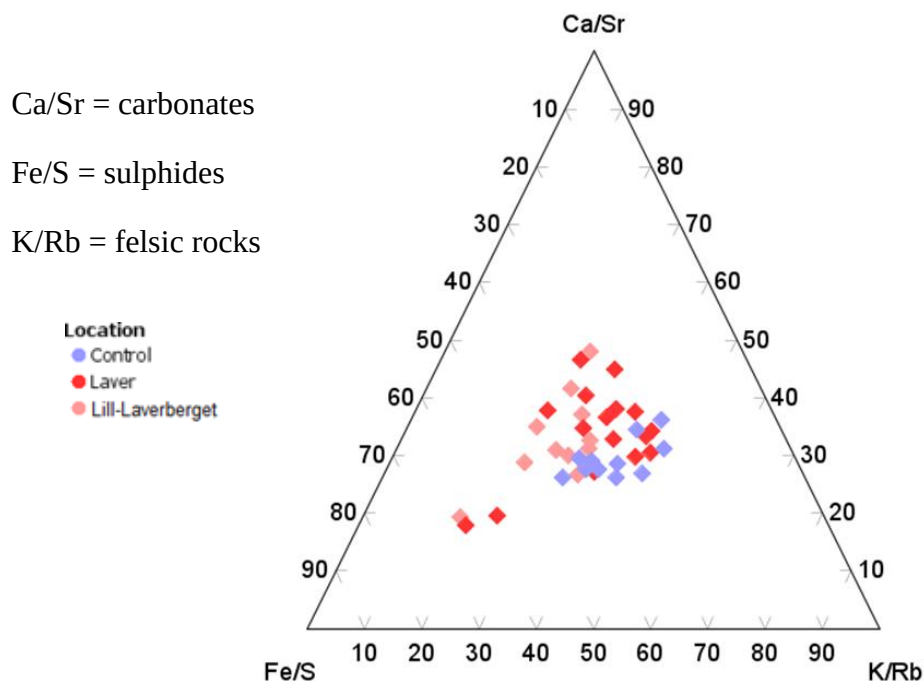


Figure B-5. Ternary plot indicating possible sources (carbonates, sulphides and felsic rocks). Comparison of possible Ca/Sr, Fe/S and K/Rb signatures can be seen in spruce needles (N=38) from Laver, Lill-Laverberget and two control sites in Sweden.

Two transverse profiles over till-covered Cu-Au-Mo mineralisation revealed several possible sources which can be detected in spruce needles. One sample from Lill-Laverberget and two samples from Laver displayed a stronger signature possibly coming from sulphide minerals (Fe/S). Other than this, signatures for carbonates here presented as Ca/Sr and felsic rocks as K/Rb were equally displayed at all sites (Fig. B-5).

In summary, the variation patterns for the concentration of trace elements in spruce needles, as shown by correlation factors and the ternary diagram (Fig. B-5) indicate potential sources. It is evident, that Cu concentrations are unusually low when compared to published values (Brun et al., 2010, Rodriguez et al., 2013) from a same region. Nonetheless, this study illustrates clear and strong interaction between Cu, Mn and Fe in spruce needles caused by Fe-Mn antagonism. Antagonism is a conflict between Fe and

Mn in plant metabolic functions caused by excessive or deficient Fe and Mn concentrations (Kabata-Pendias, 2011).

Furthermore, anomalous values reported in this study could be confirmed by calculating enrichment factors of Mn or Zn in spruce needles, tree cores and soil using the following equation:

$$EF_x = (X/Y_{\text{sample}}) / (X/Y_{\text{host rocks}})$$

where X would be the Mn or Zn; $(X/Y)_{\text{sample}}$ ratio in spruce needles, tree core or soil and $(X/Y)_{\text{host rocks}}$ ratio of the unmineralised volcanic rocks and granitoids representing the local background value of Laver region. Here, an immobile element such as Zr is recommended for normalisation as shown in the denominator (Y).

From an exploration point of view, spruce needles would be a preferred medium for sampling as a part of any biogeochemical survey in a northern European region; although, further investigation into trace element analysis of tree cores and soils would give additional insight into the sources of Mn and Zn anomalies recorded in this study. When investigating biogeochemical haloes around Cu deposits such as Laver, it is strongly recommended to calculate ratios between Fe and elements of interest such as As, Co, Cd, Mo, Sb, Pb, Zn and compare Cu:Fe and Mn:Fe ratios in plant material. This minimises, the influence of Fe:Mn antagonism, as presented in the Laver case. Overall, plant geochemistry can successfully predict metal anomalies and can be effectively used as an exploration tool for porphyry Cu deposits in northern European climates.

Table B-4. Trace element concentration in Pine needles collected from Laver area (Sweden) in September 2015 during orientation survey. Mean values of trace elements in Pine needles (SRM 1575) are reported by NIST. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Pine needles		Spruce needles		Reported
	<i>Laver</i>	<i>Control</i>	<i>Laver</i>	<i>Control</i>	<i>Needles</i>
As	0.04	0.02	0.03	0.04	
Ba	24.45	2.7	62.4	63.1	
Ca (%)	0.53	0.42	0.68	0.82	
Cd	0.18	0.10	0.07	0.02	0.13*
Co	0.09	0.03	0.05	0.10	0.14**
Cr	0.59	0.43	0.80	3.20	
Cu	2.15	1.45	1.21	1.70	7*
Fe	50	64.5	69	231	
Hg	0.01	0.02	0.02	0.02	
K (%)	0.5	0.48	0.35	0.53	
Mg (%)	0.04	0.07	0.04	0.07	
Mn	584	1112	1477	898	11**
Mo	0.04	0.05	0.07	0.21	
Ni	0.58	0.31	0.44	1.61	
P (%)	0.11	0.12	0.09	0.11	
Pb	0.09	0.09	0.08	0.10	1.75*
S (%)	0.06	0.07	0.05	0.08	
Sn	0.02	0.02	0.02	0.03	
Sr	14.16	5.18	20.16	27.15	
Zn	67.65	44.75	80.1	61.1	16.5**
	N=2	N=2	N=2	N=2	

APPENDIX C

Figure C-1. Arsenic and Cd distribution map for plants at Nevinstown and the control sites.....	336
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Figure C-1. Arsenic and Cd enrichment in plants (N=83) compared with different sampling sites: Nevinstown (1 on the map) and control sites from this study (2,3 and 4 on the map).



Figure C-2. Copper and Fe enrichment in plants (N=83) compared with different sampling sites: Nevinstown (1 on the map) and control sites from this study (2,3 and 4 on the map).



Figure C-3. Manganese and Pb enrichment in plants (N=83) compared with different sampling sites: Nevinstown (1 on the map) and control sites from this study (2,3 and 4 on the map).

Table C-1. Element concentration in hawthorn leaves, flowers and fruit collected in spring and autumn 2015 from Nevinstown and control sites. Mean values in hawthorn leaves are reported by Zeiner et al. (2013)* and Lozak et al. (2002)**. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Hawthorn leaves		Flowers	Fruit		Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>	
As	0.17	0.29	0.12	0.07		
Ba	92.96	163.05	47.08	87.90		
Ca (%)	1.44	2.36	0.85	0.75		
Cd	0.43	0.41	0.51	0.19	0.13*	
Co	0.08	0.10	0.12	0.12	0.14**	
Cr	0.73	0.51	0.55	5.71		
Cu	7.79	4.55	15.21	6.30	7*	
Fe	65.28	69.67	69.50	64.50		
Hg	0.01	0.03	0.01	0.01		
K (%)	1.38	1.50	1.82	0.75		
Mg (%)	0.21	0.26	0.17	0.10		
Mn	30.92	42.69	18.78	7.55	11**	
Mo	0.40	0.28	0.41	1.37		
Ni	1.27	1.37	1.23	5.79		
P (%)	0.29	0.18	0.28	0.12		
Pb	2.57	4.94	1.49	0.74	1.75*	
S (%)	0.18	0.18	0.16	0.07		
Sn	0.02	0.04	0.02	0.02		
Sr	26.06	44.77	12.01	11.90		
Zn	69.24	98.52	53.03	24.15	16.5**	
	N=32	N=15	N=4	N=2		

Table C-2. Element concentration in blackberry leaves and fruit collected in spring and autumn 2015 from Nevinstown and control sites. Mean values in blackberry leaves are reported by Derya (2009) while some elements in forest berries are reported by Moilanen et al. (2006). Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Blackberry leaves		Reported	Fruit	Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>	<i>Autumn</i>	<i>Fruit</i>
As	0.20	0.10		0.04	
Ba	22.31	69.90		19.25	
Ca (%)	0.59	1.14		0.22	
Cd	0.12	0.26		0.08	0.44
Co	0.04	0.03	0.10	0.02	
Cr	1.38	0.52		0.86	
Cu	6.85	4.95	6.6	5.17	4.42
Fe	71.75	61.60	165	26.00	23
Hg	0.01	0.01		0.01	
K (%)	1.33	1.11		0.97	
Mg (%)	0.19	0.29		0.14	
Mn	94.06	180.14	54.6	15.35	62
Mo	0.66	0.73		0.40	
Ni	2.55	2.12		1.21	
P (%)	0.27	0.16		0.18	
Pb	3.04	2.03		0.32	
S (%)	0.20	0.16		0.09	
Sn	0.02	0.02		0.01	
Sr	8.49	20.75		4.44	
Zn	58.35	61.98	12.4	16.55	37
	N=20	N=5		N=2	

Table C-3. Element concentration in sycamore leaves collected in spring and autumn 2015 from Nevinstown and control sites. Due to lack of data for sycamore, concentrations are reported for Norway maple leaves instead by Tomasevic et al. (2011). Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Sycamore leaves		Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>
As	0.10	0.18	0.15
Ba	14.50	31.34	
Ca (%)	1.04	1.78	
Cd	0.13	0.19	0.09
Co	0.04	0.03	0.34
Cr	1.06	0.65	
Cu	9.87	7.30	7.94
Fe	70.71	73.67	285
Hg	0.01	0.03	
K (%)	1.83	1.32	
Mg (%)	0.15	0.14	
Mn	104.79	144.70	116
Mo	0.52	0.38	
Ni	1.70	0.93	
P (%)	0.39	0.19	
Pb	1.50	3.11	2.22
S (%)	0.30	0.26	
Sn	0.02	0.03	
Sr	12.72	26.39	
Zn	59.41	67.26	44
	N=17	N=9	

Table C-4. Element concentration in ash leaves collected in spring and autumn 2015 from Nevinstown and control sites. Mean concentrations in ash leaves are reported by Aksoy et al. (2005). Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Ash leaves		Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>
As	0.13	0.15	
Ba	19.72	58.02	
Ca (%)	1.09	2.77	
Cd	0.04	0.05	
Co	0.05	0.02	
Cr	1.10	0.47	
Cu	15.29	7.10	2.8
Fe	75.83	58.82	46
Hg	0.01	0.03	
K (%)	1.44	1.15	
Mg (%)	0.22	0.28	
Mn	32.58	33.48	488
Mo	0.61	0.54	
Ni	3.77	1.62	
P (%)	0.53	0.21	
Pb	1.50	3.11	0.17
S (%)	0.37	0.37	
Sn	0.02	0.02	
Sr	13.36	43.59	
Zn	72.64	37.22	38
	N=24	N=11	

Table C-5. Element concentration in beech leaves collected in spring and autumn 2015 from Nevinstown and control sites. Reported mean values of element concentrations in beech leaves (BCR-100) published by European Commission DG Joint Research Center IRMM (2006). Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Beech leaves		Reported	Wood
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>	<i>Summer</i>
As	0.10	0.14		0.06
Ba	33.91	50.38		35.13
Ca (%)	0.67	1.14		0.30
Cd	0.27	0.16	0.34	0.07
Co	0.04	0.05		0.04
Cr	1.43	0.78		0.64
Cu	12.62	6.69	12	1.49
Fe	58.29	70.50	550	67.25
Hg	0.01	0.03		0.01
K (%)	1.12	1.00		0.19
Mg (%)	0.14	0.16		0.02
Mn	99.25	159.63	133	15.15
Mo	0.32	0.22		0.31
Ni	2.78	1.75		0.93
P (%)	0.35	0.16		0.01
Pb	1.36	2.65	16.3	0.19
S (%)	0.19	0.17		0.03
Sn	0.01	0.03		0.02
Sr	8.45	15.66		7.47
Zn	47.29	65.90	69	10.83
	N=14	N=4		N=4

Table C-6. Element concentration in oak leaves collected in spring 2015 from Nevinstown and control sites. Element concentrations in oak leaves and wood are reported by Aboal et al. (2004), Bargagli et al. (2003)* and Szczepkowski and Nicewicz (2008)**. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Oak leaves		Reported	Wood	Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>	<i>Summer</i>	<i>Wood</i>
As	0.06	0.20	0.20	0.06	
Ba	14.29	51.73	16.7*	5.63	
Ca (%)	0.51	1.40	0.78*	0.06	
Cd	0.07	0.10	0.01	0.05	
Co	0.03	0.06		0.04	
Cr	0.72	1.69	0.12	0.60	0.27**
Cu	10.13	7.02	6.40	1.52	2.22**
Fe	65.88	114.75	88.90	90.67	11.70**
Hg	0.01	0.03	0.04	0.01	
K (%)	1.43	1.05	0.53*	0.05	
Mg (%)	0.15	0.15	0.19*	0.01	
Mn	214.15	333.88	304.70	5.90	25.67**
Mo	0.22	0.37		0.28	
Ni	2.05	3.69	2.52	0.57	
P (%)	0.34	0.25		0.01	
Pb	0.70	3.55	0.15	0.17	0.37**
S (%)	0.19	0.18	0.20*	0.02	
Sn	0.02	0.04		0.02	
Sr	3.80	12.52		2.06	
Zn	26.51	48.28	12.25	1.70	
	N=8	N=4		N=3	

Table C-7. Element concentration in poplar leaves collected in spring and autumn 2015 from Nevinstown and control sites. Mean concentrations in poplar leaves are reported by Dominguez et al. (2008) and Madejon et al. (2004)*. Values are expressed in ppm of dry matter. N represents number of analysed samples.

Element	Poplar leaves		Reported
	<i>Spring</i>	<i>Autumn</i>	<i>Leaves</i>
As	0.41	0.16	0.99
Ba	89.35	62.80	
Ca (%)	0.95	1.89	
Cd	4.34	5.61	0.21
Co	0.10	0.28	
Cr	1.69	1.74	
Cu	4.12	4.25	7.44
Fe	66.00	73.14	251
Hg	0.01	0.02	
K (%)	1.43	1.67	
Mg (%)	0.19	0.11	
Mn	29.25	55.90	51
Mo	0.25	0.70	
Ni	2.58	4.32	1.05*
P (%)	0.29	0.20	
Pb	8.45	3.73	3.93
S (%)	0.27	0.35	
Sn	0.03	0.03	
Sr	21.40	31.51	
Zn	535.50	416.93	81.6
	N=2	N=7	

APPENDIX D

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Table D-1. Principal Component analysis scores for plants from Nevinstown and control site; and hawthorn and soil from Nevinstown (this study).

Plants	<i>Nevinstown</i>		<i>Control site</i>	
	PC1	PC2	PC1	PC2
Eigenvalue	23.29	0.19	24.59	0.23
Variance (%)	98.75	0.83	98.17	0.93
As	-5.23	0.01	-6.58	-0.38
Ba	0.88	0.47	0.02	0.09
Ca	7.16	0.18	7.55	0.44
Cd	-4.95	1.19	-5.31	1.58
Co	-6.83	-0.01	-6.08	0.34
Cr	-3.17	-0.17	-2.84	-0.25
Cu	-0.67	-0.47	-0.45	-0.45
Fe	1.59	-0.19	1.88	-0.16
K	7.75	0.02	8.01	0.19
Mg	5.36	-0.00	5.41	-0.41
Mn	1.47	-0.60	2.19	-0.21
Mo	-4.32	-0.50	-3.84	-0.15
Ni	-2.36	-0.37	-1.72	-0.11
P	6.13	-0.16	6.32	-0.28
Pb	-2.07	0.23	-4.17	-0.31
S	5.69	-0.06	5.99	0.08
Sn	-7.91	-0.23	-7.39	-0.57
Sr	-0.41	0.23	-0.17	0.26
Zn	1.87	0.64	1.19	0.29

Nevinstown	<i>Hawthorn</i>		<i>Soil</i>	
	PC1	PC2	PC1	PC2
Eigenvalue	67.68	0.14	41.58	0.32
Variance (%)	99.43	0.21	98.18	0.76
As	-10.75	0.21	-4.97	0.73
Ba	2.52	-0.48	1.15	-0.30
Ca	12.87	-0.04	6.28	0.67
Cd	-8.97	0.80	-11.04	0.69
Co	-13.23	-0.66	-7.75	-0.36
Cu	-3.08	-0.01	-5.79	-0.42
Fe	1.46	-0.02	11.49	-0.12
K	12.72	0.28	3.99	-0.38
Mg	8.81	-0.09	7.28	-0.52
Mn	-0.03	-0.32	3.77	0.79
Ni	-7.19	-0.02	-4.71	-0.22
Pb	-5.09	0.29	-0.03	-0.49
S	8.46	0.00	3.33	-0.48
Sr	-0.39	-0.37	-6.39	-0.52
Zn	1.89	0.42	3.39	0.90

Table D-2. Trace element data for Upper Dark Limestones (UDL) from Co Meath. Data was used for Enrichment Factor (EF) calculations.

ICP-MA_(UT)	UDL	ICP-MA_(UT)	UDL
Ag_ppm	0.06	Ni_ppm	21.14
Al_pct	1.12	P_pct	0.03
As_ppm	4.30	Pb_ppm	6.12
Ba_ppm	57.14	Rb_ppm	15.15
Be_ppm	0.49	Re_ppm	0.01
Bi_ppm	0.27	S_pct	0.23
Ca_pct	24.07	Sb_ppm	0.54
Cd_ppm	0.52	Sc_ppm	2.59
Ce_ppm	12.12	Se_ppm	1.28
Co_ppm	4.28	Sn_ppm	0.41
Cr_ppm	56.08	Sr_ppm	860.83
Cu_ppm	9.09	Ta_ppm	0.12
Fe_pct	0.84	Te_ppm	0.24
Ga_ppm	2.64	Th_ppm	0.99
Ge_ppm	0.40	Ti_ppm	545.81
K_pct	0.32	Tl_ppm	0.26
La_ppm	8.61	U_ppm	1.43
Li_ppm	6.05	V_ppm	16.79
Mg_pct	0.98	W_ppm	0.26
Mn_ppm	491.81	Y_ppm	8.77
Mo_ppm	1.14	Zn_ppm	33.87
Na_pct	0.17	Zr_ppm	15.76
Nb_ppm	1.70		

Table D-3. Annual mean metal deposition concentrations in 2015 (EPA Report 2015).

Metal deposition from air (Air Quality Report)	Ni µg/m ² /day	Pb µg/m ² /day	Zn µg/m ² /day	Cd µg/m ² /day	Cr µg/m ² /day	As µg/m ² /day
UCD	0.1	1.1	12.6	0	0.5	0.1
Limerick, Shannon Estuary	0.3	1.2	11.4	0	0.8	0.2
Valentia, Co Kerry	0.1	0.4	30.3	0	0.2	0
Converted to ppm	Ni (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	As (ppm)
UCD	0.0004	0.00013	0.00471	0	0.00024	0.00003
Limerick, Shannon Estuary	0.00012	0.00014	0.00426	0	0.00038	0.00007
Valentia, Co Kerry	0.0004	0.00005	0.01133	0	0.00009	0

Table D-4. Trace element concentration in fertilisers (Nziguheba et al., 2007)* and dairy cattle slurry (Peyton et al., 2016)**.

Nutrients	Ni (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	As (ppm)
EU Fertiliser*	14.8	2.9	166	7.4	89.5	7.6
EU P-Fertiliser*	190	55.3	2290	82.7	1100	123
Dairy cattle slurry**	0.44	0.13	14	0.1	1	n/a

Table D-5. Enrichment factor in plants and soil from Navan area relative to X/Sn background values of the host rock (Upper Dark Limestones), continued.

Type	Location	Season	Material	Number of samples	EF As	EF Ba	EF Ca	EF Cd	EF Co	EF Cr	EF Cu	EF Fe	EF K
Hawthorn	Nevinstown	spring	leaves	22	1.6	68	2.0	30.1	0.5	0.3	24.5	0.2	145.6
Hawthorn	Nevinstown	autumn	leaves	11	0.9	37	1.1	11	0.2	0.1	5	0.1	49.5
Hawthorn	Control site	spring	leaves	8	0.4	14	1.1	0.18	0.6	0.3	7.57	0.1	77.3
Hawthorn	Control site	autumn	leaves	4	0.2	17	1.5	2	0.7	0.2	10	0.2	81.7
Blackberry	Nevinstown	spring	leaves	17	1.4	16	8.3	0.13	0.2	0.6	19	0.2	115.1
Blackberry	Nevinstown	autumn	leaves	3	0.8	41	1.1	16	0.1	0.2	11	0.2	89.9
Blackberry	Control site	spring	leaves	3	0.2	2	0.4	3.0	0.2	0.2	14.2	0.2	61.2
Blackberry	Control site	autumn	leaves	2	0.1	4	0.9	4	0.2	0.1	13	0.2	64.1
Ash	Nevinstown	spring	leaves	17	1.4	19	1.9	8.3	0.5	0.8	19.3	0.4	214.3
Ash	Nevinstown	autumn	leaves	7	0.9	30	2.5	3	0.1	0.3	18	0.1	78.9
Ash	Control site	spring	leaves	6	0.2	3	1.0	14.2	0.2	0.5	14.2	0.2	90.2
Ash	Control site	autumn	leaves	3	0.2	7	2.0	0	0.1	0.1	11	0.1	50.0
Beech	Nevinstown	spring	leaves	9	1.9	39	1.9	28.4	0.5	1.5	94.5	0.4	221.1
Beech	Nevinstown	autumn	leaves	2	0.7	10	0.5	4	0.1	0.1	8	0.1	38.7
Beech	Control site	spring	leaves	5	0.2	19	0.9	13.7	0.3	0.8	43.2	0.2	110.3
Beech	Control site	autumn	leaves	2	0.2	14	0.8	4	0.2	0.3	12	0.1	46.6
Sycamore	Nevinstown	spring	leaves	11	1.9	13	1.5	28.4	0.3	0.5	94.5	0.4	230
Sycamore	Nevinstown	autumn	leaves	5	0.92	11	1.0	7	0.1	0.2	11	0.1	51.4
Sycamore	Control site	spring	leaves	6	0.2	3	0.9	13.7	0.2	0.5	43.2	0.2	101.2
Sycamore	Control site	autumn	leaves	4	0.18	3	1.0	3	0.1	0.1	11	0.1	64.9

Table D-5. Enrichment factor in plants and soil from Navan area relative to X/Sn background values of the host rock (Upper Dark Limestones), continued.

Type	Location	Season	Material	Number of samples	EF As	EF Ba	EF Ca	EF Cd	EF Co	EF Cr	EF Cu	EF Fe	EF K
Oak	Nevinstown	spring	leaves	3	0.7	13	0.8	6.0	0.2	0.4	43.4	0.2	127
Oak	Nevinstown	autumn	leaves	2	0.4	15	0.7	4	0.2	0.3	9	0.2	36.0
Oak	Control site	spring	leaves	4	0.1	4	0.6	1.7	0.2	0.3	27.5	0.2	125
Oak	Control site	autumn	leaves	2	0.1	6	0.6	1	0.2	0.4	9	0.2	43
Poplar	Nevinstown	spring	leaves	2	1.3	21	0.5	114	0.3	0.4	6.2	0.1	61
Poplar	Nevinstown	autumn	leaves	4	0.85	29	0.8	153	0.4	0.5	3	0.1	53.6
Poplar	Control site	autumn	leaves	3	0.2	4	1.5	169	1.5	0.4	10.1	0.1	98
Podzolic	Nevinstown	summer	soil	34	5.51	3	0	4	1.1	0.2	1	0.1	0.2
Podzolic	Control site	summer	soil	3	0.67	1	0	0	0.9	0.2	1	0.1	0.2

Table D-5. Enrichment factor in plants and soil from Navan area relative to X/Sn background values of the host rock (Upper Dark Limestones), continued.

Type	Location	Season	Material	Number of samples	EF Mg	EF Mn	EF Mo	EF Ni	EF P	EF Pb	EF S	EF Sr	EF Zn
Hawthorn	Nevinstown	spring	leaves	22	7.3	2.4	10.4	2.1	289	17.1	24.9	0.8	77.8
Hawthorn	Nevinstown	autumn	leaves	11	2.9	1.0	2.0	0.7	60	11	7.5	0.4	38.4
Hawthorn	Control site	spring	leaves	8	3.6	1.0	5.7	1.4	233	4	16.6	0.4	18.2
Hawthorn	Control site	autumn	leaves	4	3.8	0.8	0.8	0.9	124	1.3	15.8	0.5	9.4
Blackberry	Nevinstown	spring	leaves	17	4.9	4.8	12.4	3.1	242	16.6	22.5	0.2	54.5
Blackberry	Nevinstown	autumn	leaves	3	6.8	7.0	8	2.6	114	12.6	14.5	0.4	55.2
Blackberry	Control site	spring	leaves	3	3.1	7.4	13	2.8	154	1.3	15.1	0.1	13.3
Blackberry	Control site	autumn	leaves	2	5.7	11.0	20	2.2	105	0.7	15.2	0.3	14.2
Ash	Nevinstown	spring	leaves	17	9.6	2.8	25.8	8.1	900	16.1	71.3	0.5	102
Ash	Nevinstown	autumn	leaves	7	5.6	1.3	10.2	1.5	152	10.3	33.7	0.8	28.4
Ash	Control site	spring	leaves	6	4.9	1.1	10.7	4.4	380	1.9	34.9	0.2	29.9
Ash	Control site	autumn	leaves	3	5.8	1.3	7	1.2	94	1.2	23.1	0.6	7.1
Beech	Nevinstown	spring	leaves	9	8.5	10.3	19.7	6.7	828	17.1	52.7	0.5	99.6
Beech	Nevinstown	autumn	leaves	2	1.5	3.9	1.9	0.6	68	10.5	9.5	0.1	37.2
Beech	Control site	spring	leaves	5	4.6	7.8	7.7	5.1	378	0.6	25.7	0.2	25.3
Beech	Control site	autumn	leaves	2	3.0	5.0	3.3	1.6	82	1.3	10.4	0.2	16
Sycamore	Nevinstown	spring	leaves	11	6.4	6.8	19.8	3.0	580	13.3	54.1	0.4	81.6
Sycamore	Nevinstown	autumn	leaves	5	2.4	3.5	5.3	0.7	87.1	11.5	16.4	0.4	40.2
Sycamore	Control site	spring	leaves	6	2.7	7.7	7.7	2.0	245	1.5	21.4	0.22	23.7
Sycamore	Control site	autumn	leaves	4	1.6	5.9	3.5	0.6	97.1	1.2	14.5	0.2	11.0

Table D-5. Enrichment factor in plants and soil from Navan area relative to X/Sn background values of the host rock (Upper Dark Limestones).

Type	Location	Season	Material	Number of samples	EF Mg	EF Mn	EF Mo	EF Ni	EF P	EF Pb	EF S	EF Sr	EF Zn
Oak	Nevinstown	spring	leaves	3	5.1	8.9	4.4	2.6	346	5.5	24.4	0.12	102
Oak	Nevinstown	autumn	leaves	2	1.8	6.4	2.5	1.6	96.9	12.7	9.7	0.1	27.8
Oak	Control site	spring	leaves	4	4.2	13.9	6.9	2.8	340	0.4	24.5	0.07	14.7
Oak	Control site	autumn	leaves	2	1.7	9.1	5.1	2.6	108	1.0	8.8	0.11	6.1
Poplar	Nevinstown	spring	leaves	2	2.6	0.8	2.9	1.7	139.1	18.9	16.1	0.24	216
Poplar	Nevinstown	autumn	leaves	4	2.5	1.1	3.7	1.3	105.3	17.2	16.3	0.4	305
Poplar	Control site	autumn	leaves	3	1.1	2.4	13.7	4.5	98.6	1.0	25.5	0.4	65.2
Podzolic	Nevinstown	summer	soil	34	0.18	1.3	0.74	0.7	1.98	30.9	0.17	0.01	15
Podzolic	Control site	summer	soil	3	0.18	0.3	0.64	0.7	1.8	3.7	0.14	0.01	1.5

Table D-6. Bioaccumulation coefficient (BC) for plants above the orebody at Nevinstown.

Species	No. samples	BC As	BC Ba	BC Ca	BC Cd	BC Co	BC Cr	BC Cu	BC Fe	BC Hg	BC K	BC Mg
Hawthorn	6	0.00	0.34	4.19	0.12	0.00	0.03	0.37	0.03	0.07	11.14	0.57
Blackberry	6	0.01	0.07	2.48	0.06	0.00	0.06	0.29	0.03	0.05	14.64	0.46
Ash	4	0.01	0.08	3.58	0.03	0.01	0.04	0.84	0.04	0.12	15.35	0.52
Sycamore	3	0.01	0.09	2.93	0.10	0.00	0.04	0.51	0.03	0.07	27.73	0.48
Poplar	1	0.00	0.05	2.11	0.20	0.01	0.07	0.09	0.03	0.00	7.92	0.51
Oak	2	0.01	0.10	1.01	0.07	0.00	0.03	0.52	0.04	0.05	9.04	0.38
Beech	2	0.01	0.17	1.59	0.29	0.00	0.04	0.78	0.03	0.03	8.06	0.35

Species	No. samples	BC Mn	BC Mo	BC Ni	BC P	BC Pb	BC S	BC Sr	BC Zn
Hawthorn	6	0.02	0.31	0.03	2.25	0.01	2.18	1.38	0.06
Blackberry	6	0.09	0.45	0.08	1.98	0.01	2.58	0.52	0.08
Ash	4	0.04	0.36	0.12	4.26	0.01	4.59	0.79	0.12
Sycamore	3	0.15	0.26	0.06	4.23	0.02	3.74	0.82	0.15
Poplar	1	0.04	0.09	0.08	1.72	0	1.08	0.23	0.18
Oak	2	0.22	0.09	0.06	2.76	0.01	2.42	0.19	0.10
Beech	2	0.24	0.15	0.09	2.57	0.01	2.38	0.41	0.16

Table D-7. MAD Precision for all plant species - leaves collected from Nevinstown site in May and September, 2015.

MAD Precision (%)	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
Navan (all year)	8.09	0.78	0.93	2.24	3.07	4.01	1.41	1.63	2.92	0.92	0.98	1.48
Nevinstown (all year)	4.76	0.74	1.04	1.00	4.79	4.32	1.55	2.24	2.05	0.97	0.88	1.86
Control (all year)	12.25	0.83	0.79	3.79	0.92	3.62	1.23	0.86	4.00	0.85	1.11	1.00
Nevinstown (spring)	7.36	0.95	1.42	1.14	4.57	5.21	1.43	2.66	1.55	1.53	1.41	2.18
Nevinstown (autumn)	0.87	0.42	0.47	0.80	5.11	3.00	1.72	1.62	2.80	0.13	0.08	1.37
Control (spring)	18.17	1.24	1.58	6.08	0.95	5.60	1.56	1.09	2.61	1.44	1.30	1.69
Control (autumn)	6.33	0.71	0.00	1.51	0.89	1.65	0.90	0.63	5.40	0.27	0.93	0.32
Navan (spring)	11.69	1.07	1.48	3.11	3.12	5.37	1.48	2.03	1.97	1.50	1.36	1.99
Navan (autumn)	3.60	0.42	0.23	1.15	3.00	2.32	1.31	1.13	4.10	0.20	0.50	0.85

MAD Precision (%)	Mo	Ni	P	Pb	S	Sn	Sr	Zn
Navan (all year)	2.35	1.69	0.85	1.77	1.02	1.97	1.41	0.66
Nevinstown (all year)	2.08	1.90	0.92	1.97	0.76	3.54	1.23	0.61
Control (all year)	2.70	1.43	0.76	1.51	1.34	0.00	1.64	0.20
Nevinstown (spring)	2.32	2.65	1.34	2.45	0.95	0.00	1.60	0.89
Nevinstown (autumn)	1.72	0.76	0.30	1.26	0.48	8.86	0.67	0.20
Control (spring)	4.84	2.00	0.96	0.24	2.13	0.00	2.85	1.46
Control (autumn)	0.56	0.85	0.55	2.78	1.37	0.00	0.42	0.00
Navan (spring)	3.32	2.39	1.19	1.57	1.09	0.00	2.10	1.12
Navan (autumn)	1.14	0.80	0.43	2.02	0.92	4.43	0.55	0.10

Table D-8. MAD Precision for soil samples collected from Nevinstown site in August, 2016.

MAD Precision (%)	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg
Nevinstown	3.64	2.00	2.66	8.86	7.89	0.96	1.87	2.11	3.61	7.56	0.00	3.64
Control	1.23	1.75	1.30	0.72	0.79	1.19	2.22	0.85	0.23	0.93	0.00	0.00
Navan	2.44	1.88	1.98	4.79	4.34	1.07	2.04	1.48	1.92	4.25	0.00	1.82

MAD Precision (%)	Mn	Mo	Ni	P	Pb	S	Sn	Sr	Zn	Zr	pH	LOI
Nevinstown	5.56	3.90	0.68	5.08	0.64	0.00	0.72	2.94	0.31	0.65	0.93	7.55
Control	1.12	0.51	1.78	0.42	1.04	0.00	0.00	1.29	1.43	2.98	0.00	0.00
Navan	3.34	2.21	1.23	2.75	0.84	0.00	0.36	2.12	0.87	1.81	0.47	3.78

Table D-9. MAD Precision for all plant species - leaves collected from the Delvin (regional control site) and Ballinalack (sub-economic deposit) in May, 2016. The table also includes MAD Precision data for the Irish Midlands region (Boliden Tara Mines survey, 2017).

MAD Precision (%)	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
Ballinalack	8.86	1.89	1.62	1.65	2.16	2.55	1.19	1.55	4.94	1.88	1.32	0.48
Delvin	14.77	0.42	0.55	4.03	1.53	2.68	2.35	1.83	6.40	0.46	0.83	1.94
Irish Midlands	7.42	2.89	1.81	2.58	2.16	2.83	1.77	1.54	22.79	n/a	1.80	2.26

MAD Precision (%)	Mo	Ni	P	Pb	S	Sn	Sr	Zn
Ballinalack	1.39	2.28	1.47	2.95	4.92	29.53	1.01	0.70
Delvin	0.90	0.14	0.96	5.91	1.35	29.53	1.47	2.28
Irish Midlands	2.03	1.26	n/a	4.43	1.99	5.22	1.72	1.87

Table D-10. Duplicate samples for all plant species - leaves collected from Nevinstown and control sites in May and September, 2015. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Continued on the next page.

SAMPLE	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
NVT-H1-39	0.05	14.4	1.47	0.024	0.02	0.63	10.15	63	0.004	0.87	0.252	33.8
Duplicate	0.04	14.6	1.48	0.024	0.019	0.67	10.05	61	0.004	0.89	0.254	33.1
2SD	0.01	0.28	0.01	0.00	0.00	0.06	0.14	2.83	0.00	0.03	0.00	0.99
NVT-H4-4	0.04	35.6	0.96	0.175	0.021	0.80	8.73	48	0.006	0.94	0.137	105.5
Duplicate	0.07	35.8	0.93	0.164	0.017	0.72	8.68	46	0.006	0.92	0.135	103.5
2SD	0.01	0.28	0.04	0.02	0.01	0.11	0.07	2.83	0.00	0.03	0.00	2.83
NVT-H4-15	0.13	130	1.35	0.327	0.041	0.78	4.86	54	0.009	1.14	0.172	20.2
Duplicate	0.15	136	1.43	0.331	0.043	0.94	5.27	60	0.01	1.21	0.185	22.5
2SD	0.03	8.49	0.11	0.01	0.00	0.23	0.58	8.49	0.00	0.10	0.02	3.25
CS1-H1-2	0.07	54.1	1.56	0.074	0.16	0.35	8.22	61	0.009	1.34	0.146	22.6
Duplicate	0.06	54.4	1.53	0.073	0.164	0.34	8.62	63	0.008	1.34	0.144	24
2SD	0.01	0.42	0.04	0.00	0.01	0.01	0.57	2.83	0.00	0.00	0.00	1.98

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn
NVT-H1-39	0.28	1.95	0.512	0.48	0.31	0.02	19.65	52.5
Duplicate	0.28	1.85	0.516	0.45	0.31	0.02	19.65	52.6
2SD	0.00	0.14	0.01	0.04	0.00	0.00	0.00	0.14
NVT-H4-4	0.20	2.30	0.343	1.09	0.15	0.005	11.35	52.5
Duplicate	0.21	2.26	0.339	1.1	2.93	0.005	11.1	51.7
2SD	0.01	0.06	0.01	0.01	0.00	0.00	0.35	1.13
NVT-H4-15	0.35	0.69	0.19	1.86	0.15	0.02	15	50.4
Duplicate	0.39	0.77	0.204	2.04	0.16	0.02	16.35	52.6
2SD	0.06	0.11	0.02	0.25	0.01	0.00	1.91	3.11
CS1-H1-2	0.11	0.77	0.365	0.92	0.19	0.02	30.2	34.9
Duplicate	0.09	0.78	0.363	0.91	0.19	0.02	32.4	36.4
2SD	0.03	0.01	0.00	0.01	0.00	0.00	3.11	2.12

Table D-10. Duplicate samples for all plant species - leaves collected from Nevinstown and control sites in May and September, 2015. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates. Continued on the next page.

SAMPLE	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
CS1-H2-6	0.06	7.7	1.13	0.01	0.055	1.49	12.85	60	0.007	1.49	0.153	18.4
Duplicate	0.03	8.1	1.19	0.013	0.054	1.19	13.15	59	0.007	1.59	0.16	18.7
2SD	0.04	0.57	0.08	0.00	0.00	0.42	0.42	1.41	0.00	0.14	0.01	0.42
NVT-H1-34A	0.25	73.2	2.94	0.084	0.018	0.33	11.75	55	0.022	1.69	0.289	33.2
Duplicate	0.26	74.3	2.99	0.083	0.016	0.31	11.1	52	0.021	1.7	0.29	31.5
2SD	0.01	1.56	0.07	0.00	0.00	0.03	0.92	4.24	0.00	0.01	0.00	2.40
NVT-H4-8A	0.19	49.8	2.37	0.204	0.028	0.53	6.26	59	0.026	0.65	0.278	63.4
Duplicate	0.19	50	2.38	0.209	0.025	0.57	6.13	58	0.024	0.65	0.278	62.8
2SD	0.00	0.28	0.01	0.01	0.00	0.06	0.18	1.41	0.00	0.00	0.00	0.85
CS1-H1-2A	0.03	62.8	2.14	0.03	0.168	0.3	5.98	50	0.022	1.63	0.179	15.7
Duplicate	0.03	62.3	2.14	0.029	0.165	0.29	5.92	49	0.026	1.65	0.18	15.6
2SD	0.00	0.71	0.00	0.00	0.00	0.01	0.08	1.41	0.01	0.03	0.00	0.14

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn
CS1-H2-6	0.54	2.01	0.571	0.52	0.33	0.02	13.3	49.3
Duplicate	0.55	1.86	0.593	0.52	0.35	0.02	14.1	50.5
2SD	0.01	0.21	0.03	0.00	0.03	0.00	1.13	1.70
NVT-H1-34A	0.3	1.86	0.146	3.17	0.46	0.02	46.9	72.3
Duplicate	0.28	1.82	0.147	3.2	0.47	0.02	46.2	72.2
2SD	0.03	0.06	0.00	0.04	0.01	0.00	0.99	0.14
NVT-H4-8A	1.12	0.79	0.145	3.25	0.32	0.03	38.6	94.5
Duplicate	1.13	0.8	0.146	3.1	0.32	0.02	39.2	93.8
2SD	0.01	0.01	0.00	0.21	0.00	0.01	0.85	0.99
CS1-H1-2A	0.2	0.6	0.245	0.26	0.23	0.02	43.4	21.1
Duplicate	0.2	0.58	0.247	0.28	0.24	0.02	42.7	21.1
2SD	0.00	0.03	0.00	0.03	0.01	0.00	0.99	0.00

Table D-10. Duplicate samples for all plant species - leaves collected from Nevinstown and control sites in May and September, 2015. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

SAMPLE	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
CS3-W-5AII	0.12	17.9	2.87	5.96	0.455	2.66	9.02	119	0.027	3.32	0.027	51
Duplicate	0.16	18.1	2.87	5.76	0.445	2.77	8.75	118	0.025	3.32	0.028	50.6
2SD	0.06	0.28	0.00	0.28	0.01	0.16	0.38	1.41	0.00	0.00	0.00	0.57

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn
CS3-W-5AII	2.02	11.4	0.236	0.76	0.51	0.04	35.3	144.5
Duplicate	1.97	11.35	0.24	0.8	0.52	0.04	35.2	144.5
2SD	0.07	0.07	0.01	0.06	0.01	0.00	0.14	0.00

Table D-11. Duplicate samples for all plant species - leaves collected from Delvin site in May, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

SAMPLE	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
DEL-3	0.03	2.3	1.69	0.005	0.046	0.74	6.24	89	0.017	3.5	0.272	38.4
Duplicate	0.03	2.3	1.67	0.005	0.046	0.68	5.91	84	0.014	3.51	0.268	36.7
2SD	0.00	0.00	0.03	0.00	0.00	0.08	0.47	7.07	0.00	0.01	0.01	2.40
DEL-21	0.02	5.3	1.58	0.01	0.015	2.15	4.96	81	0.011	0.57	0.535	101.5
Duplicate	0.04	5.2	1.56	0.012	0.014	2.23	4.71	79	0.01	0.56	0.523	97.3
2SD	0.03	0.14	0.03	0.00	0.00	0.11	0.35	2.83	0.00	0.01	0.02	5.94

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn
DEL-3	0.87	3.28	0.312	0.07	0.35	0.01	44	22.7
Duplicate	0.85	3.26	0.308	0.08	0.36	0.005	42.9	21.5
2SD	0.03	0.03	0.01	0.01	0.01	0.01	1.56	1.70
DEL-21	1.17	0.47	0.232	0.08	0.31	0.01	42.2	21
Duplicate	1.15	0.47	0.225	0.07	0.3	0.005	40.5	20
2SD	0.03	0.00	0.01	0.01	0.01	0.01	2.40	1.41

Table D-12. Duplicate samples for hawthorn - leaves collected from Ballinalack in May, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

SAMPLE	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
BALDM-10A	0.02	12.3	1.27	0.471	0.094	0.23	7.74	70	0.009	1.44	0.247	24.4
Duplicate	0.03	11.9	1.22	0.454	0.087	0.23	7.39	67	0.008	1.37	0.235	23.3
2SD	0.01	0.57	0.07	0.02	0.01	0.00	0.49	4.24	0.00	0.10	0.02	1.56
BALDM-28	0.04	26.2	1.49	0.261	0.147	0.41	7.81	77	0.01	1.4	0.201	24.2
Duplicate	0.04	27.6	1.54	0.271	0.15	0.46	7.87	75	0.009	1.45	0.203	23.7
2SD	0.00	1.98	0.07	0.01	0.00	0.07	0.08	2.83	0.00	0.07	0.00	0.71

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn
BALDM-10A	0.56	1.73	0.317	0.08	0.25	0.005	43.5	22.6
Duplicate	0.53	1.6	0.301	0.07	0.2	0.01	43.2	22.1
2SD	0.04	0.18	0.02	0.01	0.07	0.01	0.42	0.71
BALDM-28	1.31	0.81	0.271	0.07	0.18	0.005	40.4	32.6
Duplicate	1.3	0.79	0.275	0.07	0.18	0.01	42	32.9
2SD	0.01	0.03	0.01	0.00	0.00	0.01	2.26	0.42

Table D-13. Duplicate samples for soils collected from Nevinstown and control sites in August, 2016. Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

SAMPLE	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn
MH-20A	1.4	22.6	339	0.11	1.125	8.24	27.8	16.1	2	0.075	0.06	0.35	650
Duplicate	1.52	21.6	360	0.09	0.941	8.42	29	15.35	2.17	0.089	0.06	0.38	737
2SD	0.17	1.41	29.70	0.03	0.26	0.25	1.70	1.06	0.24	0.02	0.00	0.04	123.04
TC-10	0.71	11.15	33.5	1.83	1.665	12.9	19.5	20.6	1.91	0.144	0.13	0.15	739
Duplicate	0.73	11.6	34.5	1.86	1.695	13.25	20.5	21	1.92	0.141	0.13	0.15	758
2SD	0.03	0.64	1.41	0.04	0.04	0.49	1.41	0.57	0.01	0.00	0.00	0.00	26.87

SAMPLE	Mo	Ni	P	Pb	S	Sn	Sr	Zn	Zr
MH-20A	1.54	25.7	0.083	205	0.05	0.62	10.9	427	0.68
Duplicate	1.41	26.1	0.074	208	0.05	0.61	10.2	430	0.69
2SD	0.18	0.57	0.01	4.24	0.00	0.01	0.99	4.24	0.01
TC-10	3.48	58.4	0.106	25.3	0.08	0.54	74.3	122	3.38
Duplicate	3.44	60.8	0.107	25.9	0.08	0.54	76.5	126	3.16
2SD	0.06	3.39	0.00	0.85	0.00	0.00	3.11	5.66	0.31

APPENDIX E

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Table E-1. Isotopic composition of Zn in hawthorn leaves, oak tree-rings and soils from Nevinstown and control sites (this study), continued. $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ are displayed to 2σ and 2SD. Zinc isotopes are expressed in per mill and in relation to reference material. Reference materials are soil (METRANAL 33), strawberry leaves (LGC7162) and basaltic rock (BCR-2).

Sample name	Location	Material	Elevation (m)	Irish Grid E	Irish Grid N
NVT-H1-2	Nevinstown	leaves	19	285473	268504
NVT-H1-6	Nevinstown	leaves	40	285519	268407
NVT-H1-16	Nevinstown	leaves	34	285465	268486
NVT-H1-18	Nevinstown	leaves	45	285518	268522
NVT-H2-27	Nevinstown	leaves	49	285576	268489
NVT-H3-4	Nevinstown	leaves	51	285673	268597
NVT-H4-2	Nevinstown	flowers	51	285736	268366
NVT-H4-3	Nevinstown	leaves	48	285656	268298
NVT-H4-9	Nevinstown	leaves	51	285780	268447
CS1-H1-2	Control site	leaves	73	283046	267975
CS1-H1-5	Control site	leaves	72	283072	267955
CS2-W1-6	Control site	leaves	46	284290	269227
PMT-5	Nevinstown	tree rings	43	285411	268609
DMT-5	Nevinstown	tree rings	43	285411	268609
PMTC-3	Control site	tree rings	-6	284176	269162
DMTC-3	Control site	tree rings	-6	284176	269162
MH-7	Nevinstown	soil	40	285457	268482
MH-8	Nevinstown	soil	44	285523	268427
MH-13	Nevinstown	soil	46	285521	268518
MH-15	Nevinstown	soil	49	285738	268368
MH-19	Nevinstown	soil	56	285769	268446
MH-29	Nevinstown	soil	49	285657	268300
T-5	Nevinstown	soil	43	285411	268609
TC-1	Control site	soil	51	284322	269285
TC-3	Control site	soil	-6	284176	269162
<i>Reference material:</i>					
METRANAL	Analytica	soil			
BCR-2	NIST SRM	rock			
LGC7162	LGC-Lab	leaves			

Table E-1. Isotopic composition of Zn in hawthorn leaves, oak tree-rings and soils from Nevinstown and control sites (this study). $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ are displayed to 2 σ and 2SD. Zinc isotopes are expressed in per mill and in relation to reference material. Reference materials are soil (METRANAL 33), strawberry leaves (LGC7162) and basaltic rock (BCR-2).

Sample name	No. Replicates	$\delta^{66}\text{Zn}$ on IRMM	$\delta^{66}\text{Zn}$ on JMC	2SD	2 σ	$\delta^{68}\text{Zn}$ on IRMM	$\delta^{68}\text{Zn}$ on IRMM	2SD	2 σ
NVT-H1-2	2	-0.535	-0.245	0.009	0.021	-1.030	-0.740	0.024	0.037
NVT-H1-6	2	-0.914	-0.624	0.006	0.019	-1.805	-1.515	0.014	0.032
NVT-H1-16	2	-0.686	-0.396	0.024	0.018	-1.358	-1.068	0.089	0.034
NVT-H1-18	2	-0.910	-0.620	0.003	0.020	-1.778	-1.488	0.011	0.032
NVT-H2-27	5	-0.538	-0.248	0.020	0.022	-1.055	-0.765	0.031	0.038
NVT-H3-4	4	-0.538	-0.248	0.033	0.024	-1.013	-0.723	0.062	0.044
NVT-H4-2	2	-0.520	-0.230	0.012	0.019	-1.030	-0.740	0.050	0.033
NVT-H4-3	2	-0.726	-0.436	0.026	0.020	-1.381	-1.091	0.020	0.034
NVT-H4-9	2	-0.406	-0.116	0.009	0.019	-0.806	-0.516	0.036	0.033
CS1-H1-2	2	-0.145	0.145	0.007	0.019	-0.276	0.014	0.024	0.034
CS1-H1-5	2	0.190	0.480	0.002	0.024	0.380	0.670	0.024	0.045
CS2-W1-6	2	0.055	0.345	0.044	0.026	0.125	0.415	0.008	0.049
PMT-5	2	-0.200	0.090	0.039	0.070	-0.395	-0.105	0.039	0.136
DMT-5	2	-0.400	-0.110	0.030	0.081	-0.425	-0.135	0.048	0.162
PMTC-3	2	-0.365	-0.075	0.017	0.063	-0.645	-0.355	0.012	0.124
DMTC-3	2	-0.195	0.095	0.014	0.051	-0.330	-0.040	0.041	0.098
MH-7	2	-0.094	0.196	0.008	0.018	-0.202	0.088	0.023	0.032
MH-8	4	0.048	0.338	0.079	0.020	0.080	0.370	0.186	0.033
MH-13	2	-0.164	0.126	0.025	0.018	-0.353	-0.063	0.067	0.031
MH-15	2	-0.075	0.215	0.008	0.020	-0.150	0.140	0.028	0.033
MH-19	2	-0.115	0.175	0.020	0.019	-0.230	0.060	0.008	0.035
MH-29	2	-0.150	0.140	0.043	0.021	-0.324	-0.034	0.085	0.035
T-5	2	-0.095	0.195	0.070	0.019	-0.100	0.190	0.143	0.034
TC-1	2	0.005	0.295	0.018	0.023	0.010	0.300	0.022	0.040
TC-3	2	0.084	0.374	0.036	0.020	0.230	0.520	0.086	0.032
MET-33	7	-0.222	0.068	0.065	0.021	-0.391	-0.101	0.108	0.037
BCR-2	2	-0.020	0.270	0.005	0.022	-0.020	0.270	0.039	0.037
LGC7162	4	-0.120	0.170	0.027	0.028	-0.210	0.080	0.046	0.051

Table E-2. Isotopic composition of Cu in hawthorn leaves, oak tree-rings and soils from Nevinstown and control sites (this study). $\delta^{65}\text{Cu}$ is displayed to 2SD. Copper isotopes are expressed in per mill and in relation to reference material. Reference materials are soil (METRANAL 33), strawberry leaves (LGC7162) and basaltic rock (BCR-2).

Sample name	No. Replicates	$\delta^{65}\text{Cu}$ on NIST	2SD
NVT-H1-2	2	0.24	0.01
NVT-H1-6	3	0.29	0.09
NVT-H1-16	2	0.13	0.01
NVT-H1-18	3	0.19	0.10
NVT-H2-27	3	0.05	0.05
NVT-H3-4	4	0.37	0.09
NVT-H4-2	2	0.22	0.03
NVT-H4-3	2	0.40	0.02
NVT-H4-9	4	0.20	0.09
CS1-H1-2	2	0.66	0.01
CS1-H1-5	2	0.49	0.05
CS2-W1-6	2	0.49	0.03
PMT-5	2	0.20	0.18
DMT-5	2	0.17	0.04
PMTC-3	2	0.05	0.04
DMTC-3	2	-0.04	0.05
MH-7	2	0.17	0.12
MH-8	4	0.19	0.07
MH-13	4	0.04	0.14
MH-15	2	0.11	0.03
MH-19	2	0.10	0.01
MH-29	4	0.08	0.16
T-5	2	0.10	0.05
TC-1	2	0.06	0.00
TC-3	3	0.09	0.05
MET-33	9	0.26	0.07
BCR-2	2	0.25	0.06
LGC7162	3	-0.03	0.07

Table E-3. Recovery calculations of three certified standards during trace element analysis of Cu and Zn.

Standards Vegetation	NIST 1575a Pine needles	ALS internal standard	NIST 1515 Apple leaves
Cu (Batch 1)	111%	99%	101%
Cu (Batch 2)	104%	105%	98%
Cu (Batch 3)	107%	93%	95%
Cu (Batch 4)	105%	93%	87%
Cu (Batch 5)	109%	102%	99%
Cu (Batch 6)	108%	100%	103%
Cu (Batch 7)	103%	102%	n/a
mean (Cu)	107%	99%	97%
Zn (Batch 1)	103%	102%	98%
Zn (Batch 2)	97%	110%	105%
Zn (Batch 3)	98%	93%	94%
Zn (Batch 4)	98%	96%	89%
Zn (Batch 5)	105%	109%	105%
Zn (Batch 6)	98%	99%	102%
Zn (Batch 7)	97%	104%	n/a
mean (Zn)	99%	102%	99%

Table E-4. Recovery (Rec.) calculations of three certified standards used for isotope measurements of Zn for the blank corrections. Zinc isotopic measurements and Cu and Zn ratios in samples are used to check linear relationship during two analytical sessions. MET stands for METRANAL.

Reference material	Min Rec.	Max Rec.	Mean Rec.	$\delta^{66}\text{Zn}_{\text{IRMM}}$ [‰]	$\delta^{68}\text{Zn}_{\text{IRMM}}$ [‰]	$^{64}\text{Zn}/^{63}\text{Cu}$	$\frac{^{64}\text{Zn}_{\text{sample}}}{^{64}\text{Zn}_{\text{IRMM}}}$	Zn (µg)
MET-33A	84	101	91.95	-0.19	-0.36	1.11	0.885	11.972
MET-33B	73	88	80.04	-0.23	-0.46	1.43	1.17	12.28
MET-33C	78	94	85.45	-0.24	-0.46	1.54	1.115	11.972
MET-33D	72	86	78.24	-0.25	-0.35	1.385	1.06	8.829
BCR-2	85	98	91.52	-0.2	-0.41	1.88	1.54	19.368
BCR-2D	81	93	83.3	-0.02	-0.02	1.255	1.11	12.891
LGC7162	64	97	76.8	-0.12	-0.21	1.17	0.92	7.202
LGC7162D	78	120	94.65	-0.12	-0.21	1.155	0.92	2.424

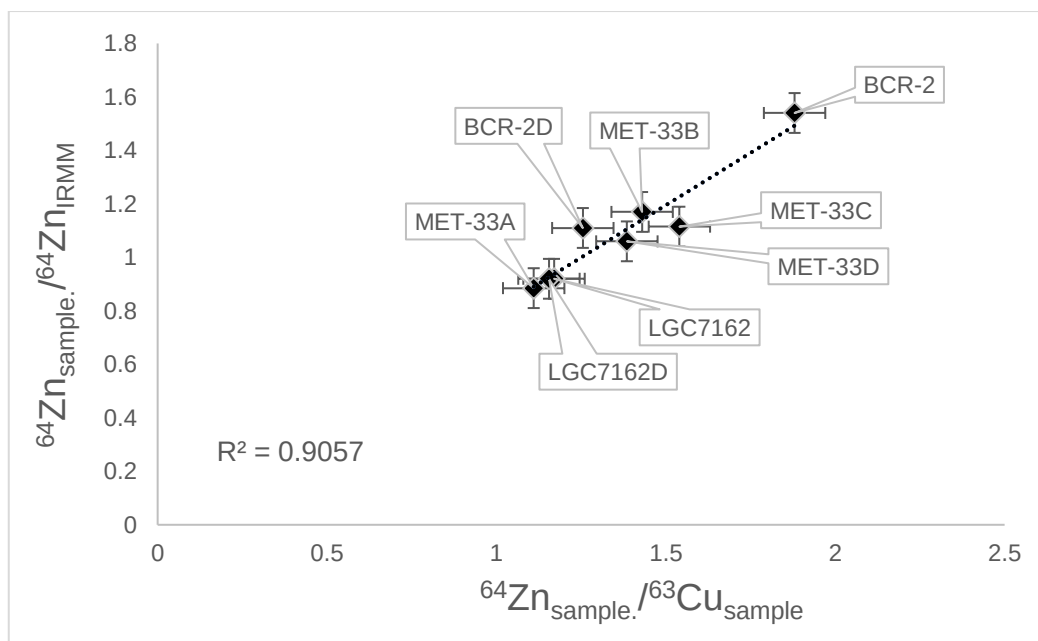


Figure E-1. Linear relationship between ratio of ^{64}Zn in samples and ^{64}Zn in IRMM (standard used for bracketing) and $^{64}\text{Zn}/^{63}\text{Cu}$ ratios within samples from two analytical sessions ran on different days. Very strong correlation indicated no changes between Cu and Zn ratios between measurements. MET stands for METRANAL.

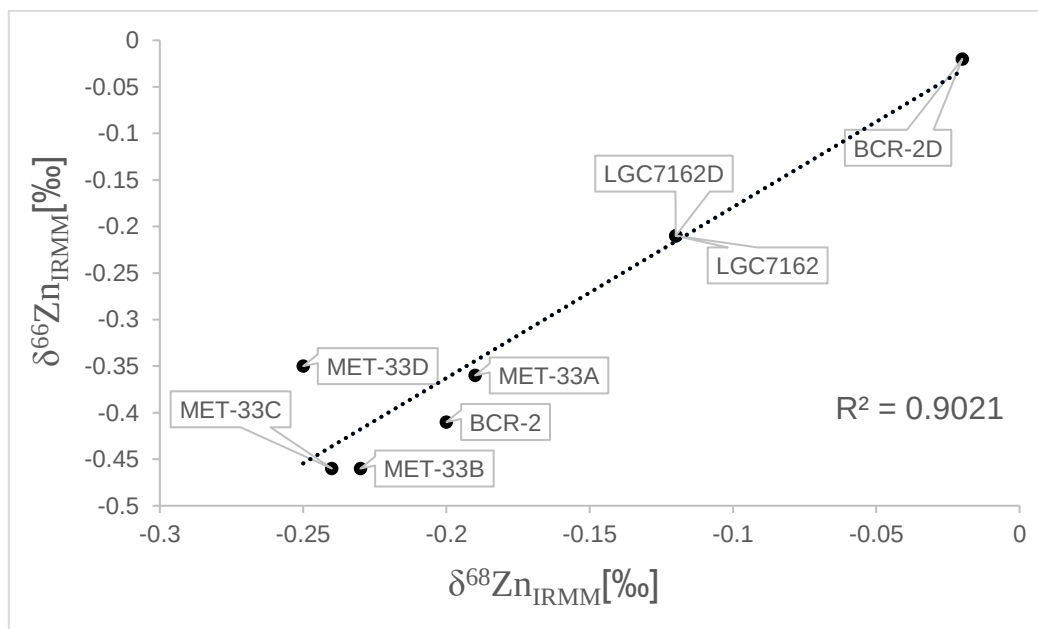


Figure E-2. Linear relationship between $\delta^{66}\text{Zn}_{\text{IRMM}}$ and $\delta^{68}\text{Zn}_{\text{IRMM}}$ in reference material from two analytical sessions ran on different days. Very strong correlation indicated changes between $\delta^{66}\text{Zn}_{\text{IRMM}}$ and $\delta^{68}\text{Zn}_{\text{IRMM}}$ between measurements. MET stands for METRANAL.

Table E-5. Measurements necessary for the blank (blk) correction for $\delta^{66}\text{Zn}$ isotopes (this study), continued.

SAMPLE ID	$^{66}\text{Zn}/^{64}\text{Zn}$ sample	StdErr (abs.) sample	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMa	StdErr (abs.) IRMMa	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMb	StdErr (abs.) IRMMb	sample/blk	2Ω ($^{66}/^{64}\text{Zn}$)
<i>Batch 1</i>								
Total Blk 1	5.64E-01	5.23E-06	5.65E-01	2.78E-06	5.65E-01	2.95E-06		
Column Blk 2	5.64E-01	6.88E-06	5.65E-01	2.78E-06	5.65E-01	2.95E-06		
NVT-H4-9	5.64E-01	2.82E-06	5.65E-01	2.92E-06	5.65E-01	3.59E-06	121.12	0.019
MH-8	5.65E-01	3.36E-06	5.65E-01	4.09E-06	5.65E-01	3.14E-06	3006.23	0.022
MH-29	5.65E-01	3.30E-06	5.65E-01	3.67E-06	5.65E-01	3.25E-06	1291.97	0.021
TC-3	5.64E-01	3.03E-06	5.65E-01	3.16E-06	5.65E-01	3.11E-06	103.06	0.019
TC-3*	5.65E-01	3.00E-06	5.65E-01	3.52E-06	5.65E-01	3.04E-06	103.06	0.020
MH-7	5.65E-01	2.86E-06	5.65E-01	2.93E-06	5.65E-01	3.02E-06	1222.29	0.018
MH-13	5.65E-01	3.08E-06	5.65E-01	2.91E-06	5.65E-01	3.03E-06	1581.02	0.018
MET-33A	5.65E-01	3.19E-06	5.65E-01	3.50E-06	5.65E-01	3.17E-06	56.89	0.020
<i>Batch 2</i>								
Total Blk 2	5.64E-01	4.29E-06	5.65E-01	2.95E-06	5.65E-01	3.13E-06		
Column Blk 1	5.64E-01	6.09E-06	5.65E-01	3.55E-06	5.65E-01	2.78E-06		
NVT-H1-6	5.64E-01	3.03E-06	5.65E-01	3.06E-06	5.65E-01	3.36E-06	109.77	0.019
NVT-H1-16	5.64E-01	2.90E-06	5.64E-01	2.95E-06	5.65E-01	3.10E-06	75.80	0.018
NVT-H4-3	5.64E-01	2.67E-06	5.65E-01	3.10E-06	5.65E-01	3.53E-06	118.53	0.019
NVT-H4-3*	5.64E-01	3.92E-06	5.65E-01	3.04E-06	5.65E-01	2.68E-06	118.53	0.020
CS1-H1-2	5.65E-01	3.37E-06	5.65E-01	2.93E-06	5.65E-01	3.02E-06	39.45	0.019
NVT-H1-18	5.64E-01	3.30E-06	5.65E-01	2.88E-06	5.65E-01	3.49E-06	142.78	0.020
NVT-H4-2	5.64E-01	3.18E-06	5.65E-01	3.13E-06	5.65E-01	3.13E-06	179.87	0.019
MET-33B	5.64E-01	3.20E-06	5.65E-01	3.56E-06	5.65E-01	3.16E-06	68.11	0.020
BCR-2	5.65E-01	2.82E-06	5.65E-01	3.14E-06	5.65E-01	3.47E-06	214.84	0.019

StdErr – Standard Error; abs – absolute; IRMM – bracketing standard; blk – blank; *duplicate

Table E-5. Measurements necessary for the blank (blk) correction for $\delta^{66}\text{Zn}$ isotopes (this study), continued.

SAMPLE ID	$^{66}\text{Zn}/^{64}\text{Zn}$ sample	StdErr (abs.) sample	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMa	StdErr (abs.) IRMMa	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMb	StdErr (abs.) IRMMb	sample/blk	2Ω ($^{66}/^{64}\text{Zn}$)
<i>Batch 3</i>								
Total Blk 6	5.63E-01	2.82E-05	5.65E-01	5.10E-06	5.65E-01	6.32E-06		
Column Blk 3	5.64E-01	3.10E-05	5.65E-01	5.10E-06	5.65E-01	6.32E-06		
NVT-H2-27	5.64E-01	2.96E-06	5.65E-01	3.31E-06	5.65E-01	3.15E-06	142.42	0.021
CS1-H1-5	5.65E-01	3.32E-06	5.65E-01	2.97E-06	5.65E-01	3.15E-06	45.11	0.024
CS2-W1-6	5.65E-01	3.50E-06	5.65E-01	3.15E-06	5.65E-01	3.15E-06	33.56	0.026
NVT-H3-4	5.64E-01	3.47E-06	5.65E-01	3.42E-06	5.65E-01	3.07E-06	71.43	0.024
MH-19	5.64E-01	2.54E-06	5.65E-01	3.19E-06	5.65E-01	3.31E-06	422.10	0.019
TC-1	5.65E-01	3.35E-06	5.65E-01	3.19E-06	5.65E-01	3.31E-06	93.86	0.023
MH-15	5.64E-01	2.96E-06	5.65E-01	3.31E-06	5.65E-01	3.24E-06	488.57	0.020
PMT-5	5.65E-01	5.37E-06	5.65E-01	4.62E-06	5.65E-01	5.07E-06	2.56	0.070
DMT-5	5.64E-01	4.75E-06	5.65E-01	4.21E-06	5.65E-01	4.62E-06	1.73	0.081
PMTC-3	5.64E-01	4.09E-06	5.65E-01	5.07E-06	5.65E-01	4.65E-06	3.15	0.063
PMTC-3*	5.64E-01	7.84E-06	5.65E-01	5.93E-06	5.65E-01	1.13E-05	3.15	0.077
DMTC-3	5.65E-01	4.42E-06	5.65E-01	4.62E-06	5.65E-01	5.07E-06	5.58	0.051
DMTC-3*	5.64E-01	7.62E-06	5.65E-01	7.74E-06	5.65E-01	7.53E-06	5.58	0.063
MET-33C	5.64E-01	3.15E-06	5.65E-01	3.37E-06	5.65E-01	3.19E-06	68.91	0.023
STD-125	5.64E-01	3.75E-06	5.65E-01	3.15E-06	5.65E-01	3.15E-06	34.30	0.027

StdErr – Standard Error; abs – absolute; IRMM – bracketing standard; blk – blank; *duplicate

Table E-5. Measurements necessary for the blank (blk) correction for $\delta^{66}\text{Zn}$ isotopes (this study).

SAMPLE ID	$^{66}\text{Zn}/^{64}\text{Zn}$ sample	StdErr (abs.) sample	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMa	StdErr (abs.) for IRMMa	$^{66}\text{Zn}/^{64}\text{Zn}$ IRMMb	StdErr (abs.) for IRMMb	sample/blk	2Ω ($^{66}/^{64}\text{Zn}$)
<i>Batch 4</i>								
Total Blk 7	5.63E-01	2.51E-05	5.65E-01	5.10E-06	5.65E-01	6.32E-06		
Column Blk 4	5.63E-01	2.16E-05	5.65E-01	5.10E-06	5.65E-01	6.32E-06		
NVT-H1-16D	5.64E-01	3.36E-06	5.65E-01	3.37E-06	5.65E-01	3.14E-06	42.87	0.024
NVT-H2-27D	5.64E-01	3.31E-06	5.65E-01	3.15E-06	5.65E-01	3.56E-06	73.77	0.023
NVT-H1-2	5.64E-01	2.96E-06	5.65E-01	3.42E-06	5.65E-01	3.42E-06	191.30	0.021
NVT-H3-4D	5.64E-01	3.74E-06	5.65E-01	2.85E-06	5.65E-01	3.16E-06	36.49	0.025
MH-8D	5.65E-01	2.75E-06	5.65E-01	3.15E-06	5.65E-01	2.94E-06	2281.68	0.018
T-5	5.64E-01	2.87E-06	5.65E-01	3.04E-06	5.65E-01	3.06E-06	356.31	0.019
MET-33D	5.64E-01	3.39E-06	5.65E-01	3.25E-06	5.65E-01	3.49E-06	64.22	0.024
BCR-2D	5.65E-01	3.18E-06	5.65E-01	3.50E-06	5.65E-01	3.24E-06	93.76	0.022
STD - 125D	5.64E-01	3.12E-06	5.65E-01	3.14E-06	5.65E-01	3.09E-06	17.63	0.029

StdErr – Standard Error; abs – absolute; IRMM – bracketing standard; blk – blank

Table E-6. MAD Precision and duplicate samples of hawthorn leaves and soil collected at Nevinstown (Ireland). Errors are expressed as 2 standard deviation calculated using replicate analysis of sampling duplicates.

Isotopic duplicates	Material	$\delta^{65}\text{Cu}$ [‰]	$\delta^{66}\text{Zn}$ [‰]
NVT-H1-16	plant	0.125	-0.40
Duplicate	plant	0.125	-0.30
2SD	plant	0.17	0.14
NVT-H2-27	plant	0.03	-0.26
Duplicate	plant	0.065	-0.24
2SD	plant	0.05	0.03
NVT-H3-4	plant	0.345	-0.24
Duplicate	plant	0.4	-0.26
2SD	plant	0.009	0.03
MAD Precision (%)	plant	13	7
MH-8	soil	0.21	0.31
Duplicate	soil	0.17	0.37
2SD	soil	0.07	0.08
MAD Precision (%)	soil	9	8