

GEMAS: Indium in agricultural and grazing land soil of Europe – its source and geochemical distribution patterns

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Abstract

Indium is a very rare element, which is usually not reported in geochemical data sets. It is classified as a critical metal, with important applications in the electronics industry, especially in the production of solar panels and liquid-crystal displays (LCDs).

Over 4000 samples of agricultural and grazing land soil have been collected for the “Geochemical Mapping of Agricultural and Grazing Land Soil of Europe” (GEMAS) project, carried out by the EuroGeoSurveys Geochemistry Expert Group. Indium concentrations in soil have been analysed using aqua regia extraction followed by ICP-MS. Median values of In for both land use types are nearly identical, 0.0176 mg/kg for agricultural soil and 0.0177 mg/kg for grazing land soil.

The spatial distribution patterns of In in European soil are mainly controlled by geology and the presence of Zn and Sn mineralisation. The preference of In to accumulate in the fine-grained fraction of soil with high clay content dominates the major anomaly patterns on the geochemical maps. In the Mediterranean region, secondary In enrichment is visible in karst areas. A notable feature of the In spatial distribution is the large difference between northern and southern Europe, with median values of 0.012 and 0.021 mg In/kg, respectively, suggesting that, in addition to lithology, weathering and climate are important factors influencing the In soil enrichment over time.

1. Introduction

Indium is a rare metal, which has high strategic importance and broad applications, e.g., in electronics for liquid-crystal displays (LCDs) and solar panels (Alfantazi and Moskalyk, 2003). Since primary In deposits are rare and of small volume, In is produced as a by-product from the processing of sulphide ore deposits, mainly Zn, Pb and Sn (Schwarz-Schampera, 2014; Reimann et al., 2014a). High secondary In concentrations can also be found in fine-grained sedimentary rocks (Jorgenson and George, 2005).

Indium concentrations in European soil have been determined by ICP-MS following an aqua regia extraction during the EuroGeoSurveys continental-scale Geochemical Mapping of Agricultural and Grazing land soil (GEMAS) project (Reimann et al., 2014a, b). The project was carried out by 33 countries and co-sponsored by the European Association of Metals (Eurometaux). GEMAS has been the direct response of the metals industry to the REACH regulation (**R**egistration, **E**valuation and **A**uthorisation of **C**hemicals - EC, 2006), requiring continental-scale information about soil quality and parameters influencing the availability of metals in soil. The main aim of the GEMAS project has been the documentation of the natural background element variation in European soil at the beginning of the 21st century. Therefore, cities, industrial areas, and sites located near railways and major roads were consciously avoided during sampling. To detect the anthropogenic impact from mining, smelting and airborne deposition, the natural background values must be known and taken into account in monitoring and environmental risk evaluations. The main GEMAS sample medium – soil – is the major sink for potentially toxic elements (PTE; e.g., As, Cd, Hg and Pb). High PTE contents in soil may result in uptake by plants, crops, vegetables and subsequently by grazing animals, and finally by humans, causing negative health effects.

Due to the scarcity of publications about indium in general, the discussion of the results is preceded by a broad review of the origin of In and its role in the modern world.

1.1. Chemical and physical properties of indium

Indium is a very soft, malleable and fusible post-transition metal, and it is chemically similar to gallium and thallium. Like gallium, indium is liquid over a wide range of temperatures; it has a very low melting point (156.6°C) and a moderate boiling point (2080°C) (Schroll, 1999). An alloy of In and Ga is liquid at room temperature (Enghag, 2004). Indium occurs in the +1 and +3 oxidation states, the former is a strong reducing agent, while the latter one is more stable (Jones and Stasch, 2011). Indium is not oxidised easily at room temperature. When heated, In reacts rapidly with metalloids (As, Sb, Se, Te), and with halogens, sulphur and phosphorus (Schwarz-Schampera and Herzig, 2002; Schwarz-

Schampera, 2014). Indium does not react with water, silicon and carbon, but can be oxidised by stronger oxidising agents like halogens and oxalic acid. Indium is stable (and volatile) in air, and in water does not react with alkalies and most organic acids, but dissolves in mineral acids and amalgamates with mercury (Schwarz-Schampera and Herzig, 2002; Jorgenson and George, 2005). Indium forms complexes with OH^- , F^- , HS^- and Cl^- and small organic molecules. Its reaction with water results in insoluble In^{3+} hydroxides, but In^{3+} salts of strong acids, such as chloride, sulphate and nitrate are soluble (Wood and Samson, 2006).

1.2. Indium in the Earth's crust

According to Wedepohl (1995), indium with an average value at 0.050 mg/kg is the 61st most abundant element in the Earth's continental crust, and lies between mercury (0.040 mg/kg) and silver (0.070 mg/kg). While various other estimates for the upper continental crust report In values between 0.050 and 0.066 mg/kg (Taylor and McLennan, 1995; Wedepohl, 1995; Rudnick and Gao, 2003; Hu and Gao, 2008), and *ca.* 0.052 mg/kg is given for the composition of the bulk continental crust (Rudnick and Gao, 2003). In the GEMAS atlas (Reimann et al., 2014a), indium is ordered as the 66th most abundant element in the Upper Continental Crust at an average concentration of 0.066 mg/kg (according to the most recent estimate of Hu and Gao, 2008). The oceanic crust tends to be somewhat enriched in indium (0.072 mg/kg) in comparison with the Upper Continental Crust (UCC; Taylor and McLennan, 1985).

The geochemical behaviour of indium in nature is still not well known. The occurrence of In is closely related to the presence of sulphide minerals. However, secondary concentrations can be found in fine-grained sedimentary rocks, volcanic rocks, clay-rich deposits and organic-rich soil. Marine sediments and peat, as well as black coal, lignite (brown coal) and fossil fuel, can show elevated In concentrations (Matthews and Riley, 1970; Smith et al., 1978; Eskenazy, 1980; Filippidis et al., 1996; Sakorafa et al., 1996; Schroll, 1999; Steinnes et al., 2003; Petrotou et al., 2012).

Indium was discovered in 1863 in a polymetallic vein-type zinc ore deposit containing sphalerite, galena, chalcopryrite, arsenopyrite and stannite near Freiberg in Germany (Schwarz-Schampera and Herzig, 2002). It occurs as a trace component in sulphides from different types of ore deposits, more uncommonly as minerals with essential In, and extremely rarely as the native metal (as observed in tin-rich greisens; Nechaev et al., 1987).

Several In minerals are known, such as roquesite (CuInS_2), laforetite (AgInS_2), indite (FeIn_2S_4), cadmoindite (CdIn_2S_4), sakuraiite ($((\text{Cu,Zn,Fe})(\text{In,Sn})_4\text{S}_4)$), petrukite ($((\text{Cu})_2(\text{Fe,Zn})(\text{Sn,In})\text{S}_4)$), yixumite (Pt_3In), and the secondary minerals dzhalindite ($\text{In}(\text{OH})_3$) and yanomamite ($\text{InAsO}_4 \cdot 2(\text{H}_2\text{O})$) (Schroll, 1999; Cook, 2011a, Schwarz-Schampera and Herzig, 2002; Schwarz-Schampera, 2014). In mafic rocks, In may form alloys with Pt (Yu, 1997), and they often occur as submicroscopic inclusions in sulphide minerals (e.g., sphalerite, chalcopryrite, bornite and galena). Overall, sphalerite is the main host mineral for indium in most sulphide deposits due to this mineral's relative abundance, but chalcopryrite usually contains the highest concentrations of indium. Copper and In can substitute for Zn in sphalerite through a coupled substitution that accounts for charge balance ($\text{Cu}^+ + \text{In}^{3+} \rightarrow 2\text{Zn}^{2+}$) (Bente and Doering, 1995; Wood and Samson, 2006). Apart from sulphides (sphalerite, galena, chalcopryrite, bornite, stannite, digenite, etc.), high In concentrations occur in cassiterite, wolframite and magnetite (Briskey, 2005). Trace levels of In can also be found in rock-forming minerals such as pyroxene, amphibole, mica (muscovite, biotite), chlorite and in accessory minerals, such as tourmaline and epidote (Schwarz-Schampera and Herzig, 2002 and references therein).

Even though In is considered to be a quite incompatible element during magmatic processes, and is usually enriched in the late magmatic stage, many ultramafic and mafic rocks show high In concentrations, e.g., peridotite and pyroxenite (up to 0.06 mg/kg), as well as basalt (up to ca. 0.2 mg/kg). Alkaline rocks (e.g., syenite, monzonite with >0.1 mg/kg), granite and felsic volcanic rocks can also have very high In concentrations (>0.5-0.6 mg/kg) (Schwarz-Schampera and Herzig, 2002). Among sedimentary rocks, clay-rich shale and argillite show high In contents (>5 mg/kg), but also karst related deposits and bauxite (containing dzhalindite, In hydroxide) may have elevated In contents (ca. 0.5 mg/kg) (Schwarz-Schampera and Herzig, 2002 and references therein). Indium is often

enriched in hydrothermal systems occurring in active oceanic rift settings. In hydrothermal systems, In chlorides (e.g., InCl^4) and hydroxide chloride complexes can play an important role in the transport of In ([Seward et al., 2000](#)). Chlorine can originate from saline fluids and In chlorides can be formed in an arid climate ([Dill et al., 2013](#)).

1.3. Indium in ore deposits

Indium can be found in many types of ore deposits, e.g., in different types of massive sulphide deposits (Volcanic Massive Sulphide, VMS deposits, and Sediment-Hosted Exhalative Massive Sulphide, SHMS deposits), porphyry copper deposits, polymetallic base metal deposits (vein and stockwork types), tin and tungsten deposits, epithermal gold deposits and skarn deposits (Table 1; [Schwarz-Schampera and Herzig, 2002](#); [Briskey, 2005](#); [Schwarz-Schampera, 2014](#)). Volcanic-hosted and sediment-hosted exhalative deposits are currently the largest and economically most important source of indium in Europe (e.g., Neves-Corvo in Portugal). Indium usually occurs as a minor element in major ore minerals (sphalerite), and more seldom as In-rich minerals, typically forming inclusions in other ore minerals (e.g., roquesite inclusions in sphalerite, chalcopryrite or bornite) (e.g. [Cook et al., 2011a](#), and references therein). The most efficient precipitation of indium appears to occur under high-temperature ore-forming conditions, and In-rich sphalerite may precipitate from hydrothermal fluids in a wide range of temperatures (<200°C to ca. 400°C; [Ohta, 1989](#); [Seifert and Sandmann, 2006](#); [Sinclair et al., 2006](#); [Shimizu and Morishita, 2012](#)).

<Insert near here Table. 1. Overview of indium mineralisation in Europe (compiled from [Schwarz-Schampera and Herzig \(2002\)](#), [Sundblad and Ahl \(2008\)](#), [Cook et al. \(2011b\)](#), [Andersen et al. \(2013\)](#), [Jonsson et al. \(2013\)](#) and [Valkama et al. \(2013\)](#)).>

According to Schwarz-Schampera and Herzig (2002), many of the In-enriched deposits can be related to the following geological features: granitic intrusions of different age, volcanic (mainly felsic) rocks, particularly submarine volcanic sequences, hydrothermal and fumarole activity and resulting alteration, and to tectonic settings, such as collisional belts, recent spreading ridges, back-arc rift basins and fault zones (with related vein mineralisation).

The majority of In-rich deposits are related to geologically young tectonic and orogenic events, e.g., in the Ordovician (Caledonian orogeny), Carboniferous (Variscan orogeny) and Tertiary (Alpine Orogeny). These events were often accompanied by active volcanism, regional metamorphism and hydrothermal activity. In Europe, most of the In mineralisation is located in Variscan units and to a small extend in Proterozoic (Sweden), Caledonian and Alpine formations (Fig. 1). Potential In ore deposits have been found at the ocean floor in active hydrothermal vents, related to basalt and andesite rocks in Italy, e.g. Palinuro Seamount (Aeolian islands) in the Tyrrhenian Sea with In concentrations up to *ca.* 30 mg/kg (Schwarz-Schampera and Herzig, 2002). The growing In industrial demand facilitates the exploration activities in order to evaluate the resources for future mining.

<Insert near here Figure 1. Distribution of Zn, Sn and In-bearing ore deposits in Europe (based on the ProMine database; Cassard et al., 2012; Demetriades and Reimann, 2014). Abbreviations of mineral districts: AE: Ardennes-Eifel; BC: Betic Cordillera; BP: Bergslagen ore province; BF: Black Forest; BRT: Brittany; CAL: Caledonian Zn-Pb deposits; CI: Corsica; CIZ: Central Iberian ore zone; CM: Cantabrian Mts.; EA: Eastern Alps; ERZ: Erzgebirge (Ore Mts.); GTM: Galicia-Trás-os-Montes Zone; HM: Harz Mts.; IPB: Iberian Pyrite Belt; IZP: Irish Zn-Pb ore district; MC: Massif Central; NOD: Norbotten ore district; NPO: North Pennine orefield; PIT: Poitu; PYR: Pyrenees; SCZ: Silesian-Cracowian Zn-Pb district; SI: Sardinia; SM: Serbo-Macedonian ore district; SOD: Skellefte ore district; SPO: South Pennine orefield; SWE: South-west England ore district; VGS: Vosges; VP: Vihanti-Pyhäsalmi ore district; WA: Western Alps; WC: Western Carpathians.>

1.4. Indium in soil and water

Indium is not widely dispersed in the surface environment. In surface soil, total In has been reported in two continental-scale geochemical projects, i.e., the Geochemical Atlas of Europe, where it varies from <0.01 to 0.41 mg/kg, with a median of 0.05 mg/kg (N=840; Salminen et al., 2005), and the Geochemical and Mineralogical Atlas of the Conterminous United States, where it ranges from <0.02 to 4.61 mg/kg, with a median of 0.03 mg/kg (N=4813; Smith et al., 2014). In the Geochemical Atlas of Cyprus, indium in an aqua regia extraction varies at the regional scale from 0.01 to 23.2 mg/kg, with a median of 0.02 mg/kg (N=5340; Cohen et al., 2011); the very high In value of 23.2 mg/kg occurs in alluvial soil with material originating from the mafic-ultramafic rocks of the Troodos ophiolite complex. In contaminated soil, the content of In (occurring together with Zn, Pb, Cd) has been reported from *ca.* 0.1 to 2 mg/kg, and near smelters up to 4.2 mg/kg (Kabata-Pendias, 2010). The In spatial distribution in soil is closely related to the percentage of the clay fraction. In an arid, semi-desert climate, indium may precipitate from decomposing sulphides under oxidising conditions in the vadose zone (Dill et al., 2013). Elevated contents of Li, V and Sr may accompany In precipitation where the saline meteoric water infiltrates downwards sulphide-rich layers and may interact with uprising fluids (e.g., in volcanic regions). Indium hydroxides may occur together with Fe and Mn oxides/hydroxides, which are rather insoluble (Dill et al., 2013). Indium in oxide form can also be transported in the gaseous phase (Möller et al., 2007). Climatic and geomorphological factors are inferred to play a significant role in the spatial distribution of indium in European soil (see below).

In natural water, indium concentrations are very low due to its extreme insolubility, i.e., 2 to 15×10^{-6} mg/l in European stream water (Salminen et al., 2005; De Vos, Tarvainen et al., 2006). Indium hydroxide dominates in water and this form is also common in the particulate fraction in ocean water (Alibo et al., 1999). The sorption of In is presumably controlled by pH; above pH 4, the solubility of In decreases rapidly and it tends to be sorbed onto iron hydroxides (Ogawa et al., 2012). In the ocean and in inland ice, indium (together with Pb and Ba) can be used as an indicator of mineral dust levels, both natural and anthropogenic (Burn-Nunes et al., 2011).

1.5. Indium production and recovery

Nowadays, indium is almost exclusively produced as a by-product of base metal ore processing, with a world production in 2013 of *ca.* 770 t (Tolcin, 2014a). Primary In is produced during nonferrous smelting operations. The highest In recovery comes from zinc, tin and copper metal processing (Schampera, 2014). Indium can also be associated with other industrially valuable elements, such as V, Ti, Ga, Ge and Cd. Indium is usually leached from slag, dust, fumes, residues and further purification is done by electrolysis. Tailings contain rather low In concentrations and seem to be insignificant for its recovery (Tolcin, 2014a, b). Nowadays, as much as 80% of In can be recovered in zinc roasting and refining plants due to improved technology (Alfantazi and Moskalyk, 2003; Jorgenson and George, 2005). A large amount of In present on the market is secondary, and originates from the recycling of electronic components. This recycled In comes from refining of lower grade (99.97%) and standard grade (99.99%) In metals and powders, and from scrap. Indium is produced in the form of In alloys, In-Sn oxide (ITO) coatings and other In products, such as foil, powder, ribbon and wire (Tolcin, 2014a, b). Recycling of In became of economical interest in the mid 1990s, and recently considerable efforts have been made in developing more efficient and environmentally friendly recycling technologies. Secondary In, produced by recycling of In-Sn oxide (ITO), is very inefficient and only 30% In_2O_3 is presently recovered. Globally, *ca.* 70% of In originates from ITO recycling. Another secondary source of In is recycled LCD (liquid-crystal display) panels (Dodbiba et al., 2012).

In Europe, the largest In producers are Belgium, France, Germany and Russia. Canada, China, USA, Peru and Japan are important producers outside Europe (Alfantazi and Moskalyk, 2003; Tolcin, 2014a, b). In Belgium, indium is recovered from dust and residue generated by the lead refining industry. In France, Nyrstar's Aubry zinc smelter recovers a concentrate with 20% indium. In Germany, indium is produced in Langelshiem and in Hamburg (Norddeutsche Affinerie AG) from In containing materials (see Fig. 2 for smelter locations). In Russia, indium is produced as a by-product of Zn smelting and recovered from lead waste, and from large stockpiles of Pb dust at the Ural Mining and Metals Co. and in the Chelyabinsk Zinc Plant (Alfantazi and Moskalyk, 2003).

1.6. Indium demand in industry

The most common industrial form of In is ITO, which is used for electrically conductive purposes in a variety of flat-panel devices such as LCDs. It is a good transparent conducting material used in glass coatings, solar collectors and street lights. Most of ITO production comes from SE Asia, i.e., Japan, China, Korea and Taiwan (Tolcin, 2014a, b). Touch-screen applications (smartphones, tablet computers, car displays) seem to be a novel market for ITO coatings (films). Thin films of ITO are used as de-misting and de-icing agents in aircraft and automobile windshields. Liquid-crystal displays (LCDs) and high-definition television is another new market for In (Wang et al., 2013; Tolcin, 2014a, b). Indium is used in semiconductor materials for light-emitting diodes (LEDs) and laser diodes, in solar batteries and in alkaline batteries. Many thin-film solar cells use the compound CIGS (Cu-In-Ga-selenide) as a semiconductor. Additional applications of In include alloys (with precious and base metals) and solders. Indium-enriched solders have lower crack propagation and improved resistance to thermal fatigue (Tolcin, 2014a, b). Indium alloys with low melting point are used as fuses and plugs for sprinkler systems, in lenses and in polishing tools. Indium alloys are also used in dental alloys, white gold alloys, and as a bonding agent between non-metallic materials, e.g., glass and glazed ceramics (Tolcin, 2014a, b). Indium is a good lubricant and historically it was used during World War II for engine coatings in aircrafts. In nuclear reactors, indium in alloys with cadmium and silver has been used in control rods, which maintain the fission reaction. Radioactive In (In-111) is used in nuclear medicine to follow proteins and white blood cells in the body, e.g., to recognise the inflammation centres and in prostate cancer (Jorgenson and George, 2005).

A long-term demand for In is expected to rise due to development in the flat panel market, and in the solar cell industry.

1.7. Indium toxicity and environmental impact

Indium is not known to be essential for organisms and has no known nutritional role (Hoet et al., 2012); in its metallic form is relatively inactive, and it has not been considered as a hazardous metal for decades. However, indium often occurs in alloys (or compounds) with other toxic metals (e.g., As, Tl or Cd), and in these forms, all In compounds should be regarded as toxic or at least potentially harmful. Major toxic effects of In compounds and alloys have been observed in kidneys, heart, liver and lungs (Miyaki et al., 2003; Nakano et al., 2009; Hoet et al., 2012). The main exposure route, inferred to be carcinogenic, is through inhalation of insoluble In compounds (e.g., ITO, In hydroxide) in dust and aerosol (Cummings et al., 2010; Nagano et al., 2011). In the USA, the maximum occupational air exposure to In has been recommended as a time-weighted average of 0.1 mg/m³ in any 8-hour shift (Jorgenson and George, 2005; White and Hemond, 2012).

Environmental effects of In have not been investigated in sufficient detail, but because of the increasing significance of industrial uses, its environmental impact may be underestimated. Potential environmental consequences of In processing can be related to the recycling technology, e.g., grinding in order to liberate indium in a form of ITO from LCD panels, and acid leaching to extract it from the ITO. In the future, LCD panels may present a serious hazard to the environment, if not disposed of properly due to the wide variety of toxic and potentially toxic compounds, including In, used in their production (Socolof et al., 2005).

The common use of computers, mobile phones and television sets is a growing problem for the future waste management. Indium used in nanotechnology (nanomaterials) may have a potential impact on human health due to its longer transportation route in the atmosphere and resulting longer residence time (White and Hemond, 2012). Additionally, the radioactive isotope, In-111, used in medicine, can be transported to waste water and as such can present a certain environmental risk (Dodbiba et al., 2012). Indium compounds can be released to the atmosphere due to their volatile nature with fumes and exhausts from zinc and tin smelting (if not recovered as a by-product). Additional industrial inputs of In from mining, coal combustion, waste incineration and electronics manufacture into the atmosphere may present a significant environmental problem (White and Hemond, 2012 and

references therein). So far, indium contamination has been detected in historical mining districts, where it occurs together with other potentially toxic metals, like As, Cd, Cu, Pb and Sn (Ketterer et al., 2001; Moreno et al., 2005; Kuwae et al., 2013; Waterlot et al., 2013).

2. Applied methods

2.1. Sampling

Samples of agricultural and grazing land soil have been collected in 2008 and early 2009 according to the Field Manual provided to all participants of the GEMAS project (EuroGeoSurveys Geochemistry Working Group, 2008; Reimann, 2014). In total, 2108 samples of agricultural soil (Ap) and 2024 samples of grazing land soil (Gr) were collected at an average sampling density of 1 site per 2500 km² (grid of 50 x 50 km) across Europe, with 33 countries participating in the survey. Composite samples (ca. 3.5 kg) of agricultural soil have been collected from the uppermost layer (0-20 cm) of the Ap ploughing layer. Grazing land soil samples (land under permanent grass cover) were collected from the uppermost 10 cm. Each sampling site has been carefully documented and field duplicates have been taken at every 20th site.

2.2. Sample preparation and analytical methods

All samples were air dried and sieved using a 2 mm nylon screen in the same laboratory (Mackovych and Lučivjanský, 2014). Subsequently, they were homogenised and split into 10 aliquots for analysis and future reference (Reimann et al., 2009). The samples were then randomised, and analytical replicates and project standards were inserted every 20th sample (Reimann et al., 2009, 2011; Demetriades et al., 2014; Reimann and Kriete, 2014). One such split of samples has been analysed at the ACME Laboratory in Vancouver, Canada, for major and trace elements following aqua regia extraction (Reimann et al., 2009; Birke et al., 2014a). A weight of 15 g of the sieved mineral soil sample (<2 mm) was digested in 90 ml aqua regia (AR) solution and leached for one hour in a hot

(95°C) water bath. The final solution (300 ml with 5% HCL) was analysed for 52 elements using a Spectro Ciros Vision emission spectrometer (ICP-AES) and a Perkin Elmer Elan 6000/9000 inductively coupled plasma emission mass spectrometer (ICP-MS). ACME's 'official' detection limit for In was 0.02 mg/kg, but the practical detection limit turned out to be tenfold lower between 0.001 and 0.005 mg/kg, and the precision was reported to be ca. 20-30 %. A detailed description of analytical procedures and quality control results is available in Reimann et al. (2009).

2.3. Data presentation and map production

Colour raster maps (Figs. 2 & 3) have been prepared at BGR from gridded data. Kriging was used as the interpolation method to convert the values from the irregularly distributed sampling sites to a regular grid. Extracted kriging parameters were based on a detailed variogram analysis. The maximum number of samples per grid point was set to 64, which limits the search radius to ca. 300 km. Class interval limits used for the colour surface maps are based on the 5th, 25th, 50th, 75th, 90th and 95th percentiles of the In data distribution.

Boxplots (Figs. 4 and 6) and the growing dot map (Fig. 5) have been produced in R software. Data analysis follows the methods suggested in Reimann et al. (2008). For the statistical treatment of the data, it is important to note that compositional data do not plot in the Euclidean space, but rather on the Aitchison simplex (Aitchison, 1982, 1986; Buccianti, 2015; Sadeghi et al., 2015). Statistical calculations presented here are thus based on percentiles, and the standard deviation is replaced by the powers, the orders of magnitude variation of the data range (Reimann et al., 2008; Reimann et al., 2012). More details about map production and data presentation can be found in Filzmoser et al. (2014).

<Insert near here Figure 2. Geochemical map of aqua regia extractable indium in agricultural soil (Ap) samples. Explanation to numbered anomalies is provided in Table 3. Locations of zinc smelters according to European Union Risk Assessment Report (Munn et al., 2010).>

<Insert near here Figure 3. Geochemical map of aqua regia extractable indium in grazing land soil (Gr) samples. Explanation to numbered anomalies is provided in Table 4.>

3. Results

The summary of statistical results of aqua regia extractable In is presented in Table 2. The median values for indium in agricultural (Ap) and grazing land (Gr) soil are almost identical 0.0176 and 0.0177 mg/kg, respectively.

Indium extractability in an aqua regia extraction is quite low. Extractability of *ca.* 30% has been calculated for GEMAS soil samples based on certified standards and AR method compared with 4-acid digestion extraction methods (Reimann et al., 2009). The obtained median value represents *ca.* 27% of extracted In relative to the published UCC values of *ca.* 0.05-0.07 mg/kg (e.g., Taylor and McLennan 1985, 1995; Wedepohl, 1995; Rudnick and Gao 2003; Hu and Gao 2008) and median value of 0.05 mg/kg for indium in topsoil (range <0.01-0.41 mg/kg, total concentrations) of the FOREGS Geochemical Atlas of Europe (Salminen et al., 2005; De Vos, Tarvainen et al., 2006), indicating their rather good correspondence.

On the colour maps (both Ap and Gr; Figs. 2 & 3), the areas above the median value (represented by light green to red colour) show, therefore, an enrichment of In relative to the UCC. For comparison, the aqua regia extractability of metals highly correlated with In is: Zn 74%, Pb 77%, Sn 33% and Cu 100% in the GEMAS Ap soil samples (Reimann et al., 2011).

The variation in indium concentrations between Ap and Gr samples is small, with the highest maximum values in agricultural soil (Ap), while generally values above the 75th percentile are higher in grazing land soil (Gr; Table 2).

<Insert near here Table 2. Statistical summary of aqua regia extractable indium concentrations in agricultural (Ap; 0-20 cm) and grazing land (Gr; 0-10 cm) soil samples (Notation: N = number of samples; P = percentile; Median = P50).>

Statistical results comparing all countries participating in the survey indicate significant differences in soil composition, with the Balkan countries (Montenegro, Slovenia, Croatia and Serbia) showing the highest In concentrations, and the Baltic countries (Poland, Latvia, Lithuania, Estonia) together with the Nordic countries (Denmark, Finland and Norway) displaying the lowest In concentrations (Fig. 4). This large difference occurring between northern and southern Europe is well expressed in median values of 0.012 and 0.021 mg/kg, respectively.

<Insert near here Figure 4. Boxplots of aqua regia extractable indium (concentration in mg/kg) from agricultural (Ap; 0-20 cm) and grazing land (Gr; 0-20 cm) soil in the participating countries. The countries are ordered according to a decreasing median indium concentration. AUS: Austria, BEL: Belgium, BOS: Bosnia and Herzegovina, BUL: Bulgaria, CRO: Croatia, CYP: Cyprus, CZR: Czech Republic, DEN: Denmark, EST: Estonia, FIN: Finland, FOM: Former Yugoslavian Republic of Macedonia (FYROM), FRA: France, GER: Germany, HEL: Hellas, HUN: Hungary, IRL: Republic of Ireland, ITA: Italy, LAV: Latvia, LIT: Lithuania, LUX: Luxembourg, MON: Montenegro, NEL: The Netherlands, NOR: Norway, POL: Poland, PTG: Portugal, SIL: Switzerland, SKA: Slovakia, SLO: Slovenia, SPA: Spain, SRB: Serbia, SWE: Sweden, UKR: Ukraine, UNK: United Kingdom.>

4. Discussion

4.1. Spatial distribution pattern of In and its source in European soil

The overall spatial distribution pattern of In concentrations in European agricultural and grazing land soil is very similar (Figs. 2 & 3). The most striking feature of this pattern is the clear difference between northern and southern Europe. The boundary between low concentrations in the north

(median $A_p = 0.012$ mg In/kg) and high in the south (median $A_p = 0.021$ mg In/kg) coincides with the southernmost limit of the maximum extent of the Quaternary ice sheet (Svendsen et al., 2004; Reimann et al., 2014b, c; Scheib, 2014; Scheib et al., 2014). The area located directly north of this limit is particularly depleted in indium (and many other elements, e.g., Scheib et al., 2012; Ottesen et al., 2013; Tarvainen et al., 2013, 2014; Birke et al., 2014b; Cicchella et al., 2014; Reimann et al., 2014b, c), which is explained by the presence of coarse-grained quartz-rich sediments of the last glacial maximum (Scheib, 2014; Scheib et al., 2014).

<Insert near here Table 3. Explanation of aqua regia extractable indium anomalies in agricultural soil (A_p ; 0-20 cm) listed in Figure 2.>

<Insert near here Table 4. Explanation of aqua regia extractable indium anomalies in grazing land soil (Gr; 0-10 cm) listed in Figure 3.>

Among the more than 80 anomalies marked on the A_p and Gr maps (Figs. 2 & 3, and explanation of anomalies in Tables 3 & 4), only twelve are located in Northern Europe. These few anomalies in Finland, Sweden, Norway and Estonia can mainly be explained by the presence of sulphide mineralisation in metavolcanic and intrusive rocks, a high percentage of clay fraction in soil (marine clay deposits in Central Sweden and southern Finland), high organic carbon content in soil, and by the outcrops of oil shale in Estonia. This Estonian anomaly (No. 2 on Gr map, Fig. 3) can be, however, of anthropogenic origin and caused by the burning of oil shale in nearby power plants (Table 4).

In Sweden, elevated In concentrations occur in polymetallic ore deposits (together with Cu, Zn, Pb, Ag, As, Mo, Bi, Sn, W) in westernmost Bergslagen and Dalarna and eastwards, in southern Finland (anomalies 4, 5, 6 in Fig. 2). Indium sulphide mineralisation is known from the Filipstad district, in Långban/Gåsborn area (Burke and Kieft, 1980; Kieft and Damman, 1990; Jonsson et al., 2013), and

recently described in Lindbom's Prospect nearby (Jonsson et al., 2013). Indium mineralisation in this region is hosted mainly by Palaeoproterozoic dolomitic marble and metamorphosed felsic volcanic rocks, and is associated with magnetite, Cu and Zn sulphides, cassiterite, in skarn assemblages. High In concentrations are partly accompanied by high Ag, As, Ba, Be, Pb and Sb concentrations in associated Fe and Mn oxide ores (Cook et al., 2011a; Jonsson et al., 2013 and references therein). In the Mälaren region (central Sweden), high In values relate not only to numerous polymetallic vein mineralisation types (Pb-Zn, Cu, Ag, W), but to secondary In enrichment in marine clay-rich deposits covering the vast areas around Lake Mälaren (Fig. 5; Ladenberger et al., 2013).

In Finland, high In concentrations occur in the southern part of the country and they are a result of the presence of In-bearing, vein-type polymetallic sulphide mineralisation within the rapakivi granite (Cook et al., 2011b; Valkama et al. 2013), and the occurrence of In-enriched clay-rich soil (anomaly 3 in Fig. 2). A smaller anomaly on northern Åland Island can be correlated with the presence of greisen veins in rapakivi granite (Sundblad and Ahl, 2008; Cook et al., 2011b).

In Norway, elevated In concentrations are observed in southern Norway where a large number of Zn deposits with sphalerite have been mined in historical times, e.g., Sauda Zn mines in SW Norway, Konnerudkollen skarn Zn-Pb deposits in addition to epithermal Cu-Au deposits in the Oslo rift (Fig. 5).

<Insert near here Figure 5. Aqua regia extractable indium in Fennoscandian Ap soil samples (0-20 cm). Elevated In concentrations can be explained by the presence of, e.g., ore deposits, black shale, and clay- and organic-rich soil. Abbreviations: CSCB = Central Scandinavian Clay Belt.>

In Great Britain, the largest In anomalies occur in the Welsh basin, a mining region with polymetallic Pb-Zn mineralisation hosted by Ordovician and Precambrian rocks (anomaly 12 in Fig. 2). In south-western England, in Cornwall, anomaly 13 Ap coincides with the historical polymetallic mining district with W, Sn, Cu, Ag, As, Pb, Sb and Zn ore deposits as the main source of high In

concentrations in soil. Although In is a common metal in these magmatic-hydrothermal deposits (Moore and Howie, 1979; Briskey, 2005), it has never been commercially extracted (Andersen et al., 2009, 2013).

South of the maximum extent of the Quaternary glaciation, indium is generally enriched in soil and numerous anomalies have various sources, but are mainly of natural origin; lithology, mineralisation and weathering are the major factors as explained in Tables 3 and 4, and in the discussion below.

In Germany and Czech Republic, most of the elevated In values occur in areas with polymetallic Zn-Pb-Cu-Sn (W) ore deposits of various type, e.g., in central Germany (Harz Mountains), along the German-Czech border (e.g., Krusne Hory-Erzgebirge), and in the central part of the Central Bohemian pluton (anomaly 50 in Gr related to Sn-W mineralisation at Cinovec and Kutna Hora; Fig. 3). In Austria, indium anomalies are related to sulphide mineralisation with sphalerite and pyrite.

In France, the majority of In anomalies can be explained by either sulphide ore deposits (e.g., Pb-Zn ore districts with vein and SEDEX type deposits) or the underlying volcanic rocks. Soil with anomalously high In concentrations in the Massif Central has its parent material originating from the Miocene-Pliocene alkaline volcanic rocks of the Puy and Mont-Dore eruptive belt. Some of the Variscan Sn and U enriched aluminous granite can be another source of indium. Secondary enrichment in indium occurs in areas covered by Tertiary laterite (mined in some cases for Fe cast in the Middle Ages). In the Paris basin, Jurassic organic black marl containing pyrite is inferred to be a local source of In anomalies, which are also followed by elevated Ge and As concentrations in soil (for Ge and As distribution pattern see Reimann et al., 2014a and Tarvainen et al., 2013).

In the Mediterranean region, three major natural factors are responsible for the high In concentrations in soil: climate, karst processes and volcanic activity (past and present). High In values in Balkan soil in the Adriatic region are best explained by the intense weathering in the karst region and the formation of terra rossa.

In central Italy, high In values in soil may be of volcanic origin, e.g., due to the presence of alkaline rocks of the Roman (60 Ap; 59 Gr; Tables 3 & 4) and Neapolitan (63 Ap; 62 Gr) Volcanic Provinces. Some volcanic rocks, especially mafic types, can contain substantial levels of In, around 0.1 mg/kg in some ocean island basalts, e.g., on Iceland (Yi et al., 1995). The residual topsoil developed on the ophiolitic basalt in Cyprus gives In values ranging from 0.01 to 1.38 mg/kg, with a median of 0.04 mg/kg (Cohen et al., 2011). Indium anomalies occur, due to a basaltic parent source, in NE Ireland (10 Ap; 12 Gr) and on the Canary Islands (38 Ap; 40 Gr). In active volcanic regions, indium minerals (sulphides and sulphosalts) have been found in high-temperature sublimates from fumaroles (Yudovskaya et al., 2008; Borisov et al., 2012).

Volcanic emissions and eruptions provide a significant amount of In to the atmosphere. These can be transported over large distances and subsequently deposited (Matsumoto and Hinkley, 2001; Hinkley and Matsumoto, 2001, 2007). The ashes from volcanic eruptions in Italy may have contributed to the extensive In anomaly from southern Croatia to Montenegro in both Ap and Gr samples (Figs 2 & 3); similar patterns are observed for Be, Pd and Pt (Reimann et al., 2014a). In this limestone-dominated region, indium can be readily accumulated in soil under alkaline conditions (e.g., karst region of Slovenia, Croatia, Bosnia and Herzegovina, and Montenegro; Figs. 2 & 3).

In southern Italy (Calabria and northern Sicily), indium anomalies can be explained by local polymetallic mineralisation. Base metal deposits with Pb, Zn, Ag, Cu, Sn, As, Au, W are well known in Calabria and they were locally mined in historical times (e.g., anomalies 64 Gr, 65 Gr, 65 Ap; Saccà et al., 2003). In Sardinia, the main In patterns (67 Ap, 66 Gr) are controlled by the presence of pre- and post-Variscan sulphide mineralisation, located in volcano-sedimentary units and containing, for example, galena, sphalerite, baryte, stibnite, scheelite and arsenopyrite (Boni et al., 2009).

The largest indium anomalies on the Iberian Peninsula overlap with known metallogenic districts, such as the Iberian Pyrite Belt, a ca. 230 km long Variscan structure, which contains over 85 known

sulphide deposits with Cu, Pb, Zn Ag and Au (Matte, 1986). It is one of the biggest resources for massive sulphides globally, and includes deposits such as Neves Corvo in Portugal and Rio Tinto in Spain (Fig. 1). The mineralisation is hosted by volcano-sedimentary complexes of Devonian to Carboniferous age and characterised by high Ag, As, Bi, Cd, Co, Cu, Ge, Sb, Sn and Mn concentrations (Tornos, 2006; Oliveira et al., 2011).

4.2. The main geochemical factors controlling the behaviour of indium in soil

Several factors control the geochemical pattern of the observed indium distribution in European soil. The most important geological factors are: (i) the presence of Zn (and Sn) mineralisation, (ii) limestone-dominated bedrock, (iii) volcanic rocks, (iv) soil type, (v) weathering rate and (vi) karst related weathering processes. Soil properties, such as high content of clay minerals, pH conditions, CEC. and even organic matter. play an additional role with the climate and precipitation rate superimposed.

In general, the indium distribution in soil is closely related to the location of Zn mineralisation in Europe. The most prominent anomalies can be explained with high probability by the nearby locations of known Zn-bearing deposits, historical and active mining centres (compare Fig. 1 and Figs. 2 & 3). Indium also occurs in Sn-bearing minerals, therefore, several anomalies can be linked with well-known tin provinces, i.e., anomalies 28 (northern Portugal) and 13 (Cornwall, UK) in agricultural soil. In relation to ore deposits, indium correlates not only with Zn, Sn and Cu, but also with Fe, Pb, Tl, Bi, Sc, Co, Cr, Ni and V.

In common rocks, indium substitutes in small concentrations for Al in phyllosilicates, so schist belts and granitic regions are often enriched in this element. This explains the In enrichment in Ap anomalies 40 and 42 (Fig. 2), which represent the Ardennes-Rhenish Massif of Variscan age (Belgium and Germany; Fig. 1) containing abundant shale lithologies. In contrast, low In values are present in glaciated areas with quartz-rich sandy sediments, e.g., the glacial drift area stretching from The Netherlands to northern Ukraine and loess deposits, located south of the limit of the maximum

glaciation (e.g., in Hungary). Mafic volcanic rocks of younger age (Mesozoic and younger), particularly basalt, can be enriched in indium. Such elevated In contents can be observed in soil in Italy, central France, Canary Islands (Locutura et al., 2012) and Cyprus (Cohen et al., 2011). Indium levels in ultramafic rocks reach values of *ca.* 0.03-0.04 mg/kg (in clinopyroxene), as known from mantle xenoliths from Cenozoic continental intra-plate volcanic rocks in Germany (Witt-Eickschen et al., 2009). Other types of rocks, which can have high contents of re-mobilised In, are carbonate rocks, limestone and dolomite. Indium in these lithologies is often associated with sulphide mineralisation. For example, most of the mineralisation in karst regions can be classified as vein or palaeokarst types (Boni et al., 2009).

Karst regions (with terra rossa) and lateritic deposits (bauxite) in the Mediterranean region (especially in the Balkan countries; Figs. 2 & 3) have high secondary In concentrations, usually occurring in the oxidation zone with pH values between 4 and 9 under which In becomes immobile and very insoluble. Indium enrichment in karst and calcareous soil may originate from the fact that less soluble In-hydroxycarbonates and carbonates can be formed at higher pH. At pH >4 the sorption and precipitation with Fe-Mn oxides and hydroxides fix indium in the soil layer. On the other hand, at pH <4 soluble In chlorides dominate (Ogawa et al., 2012). At high latitudes (e.g., in Scandinavia, Fig. 5), in peat areas, the mobility of In chlorides increases due to higher acidity at lower temperatures. In contrast, the solubility of the main carrier phases, such as sphalerite and chalcopryite, has an important role in indium transport, and In complexes with sulphur are not very soluble (Wood and Samson, 2006). Therefore, in many areas with polymetallic sulphide ore deposits, indium is not easily released to the surface soil, but immobilised in deeper levels by the formation of sulphides. However, if these deeper horizons can become exposed, the release of metals may have serious environmental consequences, as in regions with acid sulphate soil (ASS) in northern Europe.

A very striking feature of the geochemical behaviour of indium in soil is its tendency to bind to clay minerals (Fig. 6A). Although this affinity is not straightforward at the continental-scale pattern of the GEMAS project, it is obvious on the local scale (e.g., in Northern Europe, covered by clay-rich glacial deposits) where secondary enrichment of In occurs in clayey soil and soil overlying fine-grained

sediments (Fig. 5), e.g., so-called Central Scandinavian Clay Belt (CSCB) recognised in central Sweden and southern Finland (Ladenberger et al., 2013). The strong positive correlation of In with Al and K confirms this phenomenon (Figs. 6B & 6C). Moreover, other trace elements that tend to adsorb to clay minerals also show positive correlation with In, e.g., Be, Cs, Ce, Ga, Li, La, Sc, Rb, Th and Y.

The correlation of In content in soil and soil texture and its maturity can also be seen in the indium spatial distribution in Europe. Young soil developed on sandy glacial and fluvioglacial deposits in northern Europe differs very much from soil developed on the weathering crust of different rocks in central and southern Europe. Generally low In soil concentrations in regions located north of the maximum extent of the glaciations correlate with the general low clay content (see Reimann et al. 2014a, p.123), low pH and low weathering index, expressed, for example, by the chemical index of alteration, CIA (see Reimann et al. 2014a, p.118). On the other hand, old weathered soil of southern Europe, formed often on the carbonate-dominated bedrock (alkaline soil), and with elevated clay percentage, tends to show an enrichment in indium concentrations.

<Insert near here Figure 6. Boxplots of aqua regia extractable indium concentrations (mg/kg) versus quantiles of (a) clay, (b) K (mg/kg) and (c) Al (mg/kg) in agricultural soil samples of Sweden, Norway and Finland.>

4.3. Anthropogenic importance of indium

As demonstrated above, the majority of the observed In anomalies in soil can be explained by natural sources, related either to lithology or mineralisation. Indium anomalies that could be influenced by local anthropogenic sources, for example, metal smelters or power plants, often overlap with natural ones, e.g., known mineralisation and are, thus, difficult to recognise or differentiate at the continental-scale geochemical mapping of the GEMAS project.

Indium correlates closely with metals commonly occurring in fly ash and gaseous emissions from power plants and smelters. Therefore, indium has strong potential to be used as a pathfinder for

industrial contamination. In the vicinity of smelters, the local soil can become contaminated by metals originating from Zn recovery processes, including dust and ash deposition. Apart from Pb, Cd, Zn and In, other chalcophile elements, such as Se, Ag, Sb, Te, Au, Hg, Tl and Bi, can be enriched in local soil, with concentrations reaching several mg/kg (Ketterer et al., 2001). Recent studies of fly ash from power plants using coal revealed an enrichment in Zn, Pb, Sb, Fe and other potentially toxic elements (Moreno et al., 2005; Font et al., 2006). This may imply a possible enrichment in indium as well (Mayfield and Lewis, 2013), which is not normally analysed. Deposition of ash from coal power plants is usually of a local nature and occurs in close vicinity to the power plant. At a very local scale, the contamination by In of urban soil can be explained by domestic combustion of coal for heating. Only few of the In anomalies in Europe can be explained by such contamination sources (Tables 3 & 4).

The locations of major Zn smelters are shown in Figure 2 and some of the isolated In anomalies overlap with their location: 27 Ap, 33 Gr in Spain, 40 Ap in Belgium, 41 Ap, 42 Ap, 43 Ap, 44 Gr, 43 Gr, 45 Gr in Germany, 60 Ap and 59 Gr in Italy (Rome). Other types of smelters (Cu and Pb, not shown on the map) might have a local influence on the elevated In levels in soil, e.g., anomalies 2 Gr in Estonia, 11 Ap and 10 Gr in the United Kingdom, 42 Gr in The Netherlands, 46 Gr and 45 Ap in Germany, 65 Ap, 64 Gr and 65 Gr in Italy (see also Tables 3 and 4). On the other hand, well-known smelters, such as Auby in France and Asarel Medet in Bulgaria (where In is recovered as a by-product) are barely detected in the In spatial distribution pattern.

Indium anomalies related to large cities are uncommon, and only locations close to Amsterdam, Rome and London coincide with elevated In concentrations in soil. Local industrial contamination can be detected in the Lorraine region (NE France; anomalies 19 AP and 17 Gr) with steel industry and iron ore mining, and possibly in Cagliari in Sardinia (anomaly 66 Gr), where Santa Gilla Lagoon has been contaminated by numerous industries. The lagoon has received industrial discharges of Hg, Pb and Zn compounds, as well as, for several decades, municipal untreated sewage from the urban areas and other anthropogenic related activities, i.e., airports, railways, port activities, refineries, incinerators (Cottiglia, 1995; Frontalini et al., 2009).

Due to the usually very low natural In concentrations in soil, this particular element has a high potential for detecting industrial contamination at the local scale.

5. Conclusion

The In spatial distribution patterns in European soil are an excellent example for showing the complexity of the geochemical behaviour of an individual metal in the environment. The majority of In concentrations in the agricultural and grazing land soil samples is of natural origin, directly related to the underlying bedrock, mineralisation and intense weathering, stimulated by climate. Indium has a very strong correlation and common origin with Zn, Cd, Cu, Pb, Sb, Sn and Tl, and, the so-called potentially toxic elements, but is more strongly bound in soil than most of them. Due to its overall low abundance and insolubility, indium has a good potential to be used as pathfinder for mineral exploration, and to trace industrial contamination in cases where other more mobile metals are diluted or removed (e.g., leached away) by surficial processes. Local anthropogenic contamination expected to be related to power plants and metal refineries is very difficult to evaluate at the European scale using the GEMAS data set. Anomalies that might originate from anthropogenic activities do often overlap with the location of natural sources of enhanced In concentrations in soil (e.g., the metals industry is often located where metals occur naturally). The GEMAS agricultural and grazing land soil samples provide, therefore, the background variation at the continental scale.

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Figure captions

Figure 1. Distribution of Zn, Sn and In-bearing ore deposits in Europe (based on the ProMine database; Cassard et al., 2012; Demetriades and Reimann, 2014). Abbreviations of mineral districts: AE: Ardennes-Eifel; BC: Betic Cordillera; BP: Bergslagen ore province; BF: Black Forest; BRT: Brittany; CAL: Caledonian Zn-Pb deposits; CI: Corsica; CIZ: Central Iberian ore zone; CM: Cantabrian Mts.; EA: Eastern Alps; ERZ: Erzgebirge (Ore Mts.); GTM: Galicia-Trás-os-Montes Zone; HM: Harz Mts.; IPB: Iberian Pyrite Belt; IZP: Irish Zn-Pb ore district; MC: Massif Central; NOD: Norbotten ore district; NPO: North Pennine orefield; PIT: Poitu; PYR: Pyrenees; SCZ: Silesian-Cracowian Zn-Pb district; SI: Sardinia; SM: Serbo-Macedonian ore district; SOD: Skellefte ore district; SPO: South Pennine orefield; SWE: South-west England ore district; VGS: Vosges; VP: Vihanti-Pyhäsalmi ore district; WA: Western Alps; WC: Western Carpathians.

Figure 2. Geochemical map of aqua regia extractable indium in agricultural soil (Ap) samples. Explanation to numbered anomalies is provided in Table 3. Locations of zinc smelters according to European Union Risk Assessment Report (Munn et al., 2010).

Figure 3. Geochemical map of aqua regia extractable indium in grazing land soil (Gr) samples. Explanation to numbered anomalies is provided in Table 4.

Figure 4. Boxplots for indium (concentration in mg/kg) from agricultural (Ap; 0-20 cm) and grazing land (Gr; 0-10 cm) soil in the participating countries. The countries are ordered according to a decreasing median In concentration. AUS: Austria, BEL: Belgium, BOS: Bosnia and Herzegovina, BUL: Bulgaria, CRO: Croatia, CYP: Cyprus, CZR: Czech Republic, DEN: Denmark, EST: Estonia, FIN: Finland, FOM: Former Yugoslavian Republic of Macedonia (FYROM), FRA: France, GER: Germany, HEL: Hellas, HUN: Hungary, IRL: Republic of Ireland, ITA: Italy, LAV: Latvia, LIT: Lithuania, LUX: Luxembourg, MON: Montenegro, NEL: The Netherlands, NOR: Norway, POL: Poland, PTG: Portugal, SIL: Switzerland, SKA: Slovakia, SLO: Slovenia, SPA: Spain, SRB: Serbia, SWE: Sweden, UKR: Ukraine, UNK: United Kingdom.

Figure 5. Aqua regia extractable indium in Fennoscandian Ap soil samples (0-20 cm). Elevated indium concentrations can be explained by the presence of, e.g., ore deposits, black shale, and clay- and organic-rich soil. Abbreviations: CSCB = Central Scandinavian Clay Belt.

Figure 6. Boxplots of aqua regia extractable indium concentrations (mg/kg) versus quantiles of (a) clay, (b) K (mg/kg) and (c) Al (mg/kg) in agricultural soil samples of Sweden, Norway and Finland.

Tables

Table 1. Overview of indium mineralisation in Europe (compiled from Schwarz-Schampera and Herzig (2002), Sundblad and Ahl (2008), Cook et al. (2011b), Andersen et al. (2013), Jonsson et al. (2013) and Valkama et al. (2013)).

Table 2. Statistical summary of aqua regia extractable indium concentrations in agricultural (Ap; 0-20 cm) and grazing land (Gr; 0-10 cm) soil samples (Notation: N = number of samples; P = percentile; Median = P50).

Table 3. Explanation of aqua regia extractable indium anomalies in agricultural soil (Ap; 0-20 cm) listed in Figure 2.

Table 4. Explanation of aqua regia extractable indium anomalies grazing land soil (Gr; 0-10 cm) listed in Figure 3.

Table 1. Overview of indium mineralisation in Europe (compiled from Schwarz-Schampera and Herzig (2002), Sundblad and Ahl (2008), Cook et al. (2011b), Andersen et al. (2013), Jonsson et al. (2013), and Valkama et al. (2013)).

Type of mineralisation	Indium minerals and host minerals	Examples
Polymetallic Fe/Mn oxide-associated skarn deposits	Roquesite, sphalerite, chalcopyrite, bornite	Långban and Lindbom (Bergslagen), Sweden
Cu-Sn-Zn-Fe sulphides in granite-related vein-stockwork deposits	Roquesite, sphalerite, chalcopyrite	Charrier (Massif Central), France; W Wiborg batholith, Finland; Cornwall, England
Polymetallic ores in volcanosedimentary rocks	Roquesite, sphalerite, chalcopyrite	La Telhaie, France; Getön (Bergslagen), Sweden
Sn-W deposits, vein-stockwork Sn and/or W deposits	Roquesite, cassiterite, sphalerite, tennantite, dzhalindite	Vaulry (Massif Central), France; Cinovec (Krusne Hory), Czech Republic
Skarn deposits	Roquesite, kesterite-sakuraiite, sphalerite	Gåsborn (Bergslagen) Sweden; Oelsnitz, Germany; Plavno (Krusne Hory), Czech Republic
Volcanic-Hosted Massive Sulphide deposits (VHMS)	Roquesite, sphalerite, chalcopyrite, tennantite, stannite, cassiterite	Neves-Corvo (Iberian Pyrite Belt), Portugal; Bleiberg-Kreuth (Carinthia), Austria
Polymetallic Pb-Zn (Ag, Cu, Sn, W) vein deposits	Laforetite, sphalerite, roquesite	Montgros, France; West Shropshire Orefield, England; Lautaret (Haute Alpes), France; Kutna Hora and Zuloa (Bohemian Massif), Czech Republic; Freiberg, Germany
Stratiform Sediment-Hosted exhalative Massive Sulphide deposits (SHMS)	Chalcopyrite, sphalerite,	Rammelsberg (Harz Mountains), Germany
Epithermal deposits (often with Au and Ag)	Sphalerite, wurtzite	Nagybörzsöny, Hungary; Kirki Mine (Thrace), Hellas; La Union ore district (Cartagena), Spain; Panagyuriste (Sredna Gora Zone), Bulgaria
Porphyry Cu deposits	Chalcopyrite, bornite	Asarel and Elatzite (Central Sredna Gora District), Bulgaria

Table 2. Statistical summary of aqua regia extractable indium concentrations in agricultural (Ap; 0-20 cm) and grazing land (Gr; 0-10 cm) soil samples (Notation: N = number of samples; P = percentile; Median = P50).

Element	Soil type	N	Unit	Min	P25	Median	P75	P90	Max
In	Ap	2108	mg/kg	<0.0030	0.0102	0.0176	0.0260	0.0357	0.3480
In	Gr	2024	mg/kg	<0.0030	0.0103	0.0177	0.0276	0.0379	0.2060

Table 3. Explanation of aqua regia extractable indium anomalies in agricultural soil (Ap; 0-20 cm) listed in Figure 3.

Country	Anomaly no.	Geographical area	Explanation (possible sources)
Finland	1	Lappeenranta	Soil type: Clay-rich soil. Mineralisation: Close to Zn-Pb, Cu (Ag, Au) deposits of Salo-Issakka
Finland	2	Hirvensalmi	Soil type: Organic-rich soil. Mineralisation: Close to Au-Cu, W (Tampere) mineralisation and Ni-Cu mineralisation in mafic rocks
Finland	3	Eastern Uusimaa	Soil type: Clay-rich soil. Mineralisation: Presence of numerous mineralisation with In, e.g., In-rich magnetite and sphalerite (Getmossmalmen), greisen veins (Jungfrubergen), Cu-rich quartz veins (Korsvik, Sarvlaxviken)
Finland	4	Kummalahden Kirkonkylä - Levä	Soil type: Clay-rich soil. Lithology/Mineralisation: Ultramafic and mafic rocks hosting Ni-Cu (Co) mineralisation and felsic volcanic rocks with Cu-Zn-Pb (Au-Ag) mineralisation
Sweden	5	Mälaren region (western part) - western Bergslagen	Soil type: Clay-rich soil. Mineralisation: Close to Pb-Zn, Cu, Fe mineralisation in skarn and marble, in pegmatite and in metavolcanic rocks
Sweden	6	Westernmost peripheries of the Bergslagen District	Mineralisation: Numerous polymetallic sulphide and Fe-Mn oxide mineralisation in the westernmost Bergslagen area, e.g., Långban, Gåsborn, Getön
Norway	7	Kongsberg, Oslo Rift	Mineralisation: Pb-Zn (Ag) skarn mineralisation, e.g., Konnerudkollen
Norway	8	Setesdal	Lithology: Multi-element anomaly (REE enrichment) related to pegmatite. Mineralisation: Sauda Sinkgruver (Birkeland sinkgruver) in Rogaland - Sveconorwegian Massive Sphalerite Ore. Smelter: Slightly enhanced values can be related to Odda, Norway's largest Zn smelter
Great Britain	9	Durham, Newcastle	Mineralisation: Historical (since Roman times) region of zinc mining. Smelter: Possible smelter dust may be a cause of the weaker anomalies in north-east England (Tyneside) and Hull (nearby Ferriby was a major tin-ore smelter). Industry: Old zinc oxide industry in the Newcastle region, coal mining and historical steelworks.
Great Britain	10	Antrim	Lithology: Antrim basalt and rhyolite of Palaeogene age, thick layer of reddish lateritised basalt known as the Interbasaltic Formation. Mineralisation: Iron ore and bauxite related to basalt; lignite and clay deposits overlying basalt. Industry: Zinc plating industry.
Great Britain	11	Leicester	Lithology: Calcareous sedimentary ironstone, enriched in Cr, V and As. Mineralisation: Minor Zn mineralisation. Industry: Zinc plating factories in Leicester, former steel factory in Corby.
Great Britain	12	Wales	Mineralisation: The In anomaly in north Wales is near the Dolgellau gold mineralisation area and may also be associated with local Cu-Zn mineralisation. Smelter: The flue dusts of metal smelters may contribute to the anomaly over southern Wales. Swansea, on the south coast of Wales, was a major smelting centre for base metals, especially of Cu, Zn and Sn ores from the Devon and Cornwall

			orefield
Great Britain	13	Devon, Cornwall	Mineralisation: The complex Sn-Cu-Zn mineralisation (in south-west England, Devon and Cornwall), mainly associated with Hercynian granite. Sedimentary exhalative occurrences of Pb, Zn and Mn occur in the metasedimentary succession north of Bodmin Moor and Dartmoor, while orogenic quartz veins locally carry Au, Ba, Cu, Fe, Sb and Zn
France	14	Brittany	Lithology: Aluminous granite. Mineralisation: Uranium vein mineralisation
France	15	Poitou Charentes	Lithology: Marshy area with Quaternary peat overlying Jurassic chalk
France	16	Poitou ridge	Mineralisation: Pb, Zn occurrences in the Jurassic cover rocks
France	17	SE Paris Basin	Lithology/Soil type: Cretaceous-Jurassic sedimentary rocks and Tertiary iron-rich laterite
France	18	Allier	Lithology: Northern margin of Massif Central (granite and metamorphic rocks). Mineralisation: Vaulry Massif with Sn-W deposits
France	19	Lorraine	Lithology/Weathering: Bituminous marl (Toarcian) and iron-rich oolitic limestone (Aalenian)
France	20	Jura	Lithology: NE end of the Bresse graben with Jurassic limestone and Tertiary, mainly marine deposits
France	21	Alps	Mineralisation: Several Pb-Zn (Cu, Sn) deposits, e.g., in Hautes Alps
France	22	Cote d'Azur	Lithology/Weathering: Possibly related to Cretaceous bauxite (Brignolles)
France	23	Castres, La Châtaigneraie district	Mineralisation: Pb-Zn district (e.g., St Salvy vein), W-As-Sn mineralisation in schist (La Châtaigneraie district, Massif Central); anomaly extending to the east (with polymetallic vein deposits)
France	24	Southern Montagne Noire	Mineralisation: Pb-Zn deposits
France/Spain	25	Central Pyrénées, Huesca and Lérida provinces	Mineralisation: Scheelite skarn occurrences and Pb-Zn deposits in Cambrian rocks. Zn-Pb vein type deposits (Parzán mines, Alfonsina mine, Ana mine) in Cambro-Ordovician to Triassic sedimentary and volcano-sedimentary sequences. Sedimentary exhalative deposits (SEDEX) in Cambro-Ordovician rocks
France/Spain	26	Western Pyrénées, Roncal and Baztán valleys	Mineralisation/Mining: Pierrefite Pb-Zn district (Devonian) and scheelite occurrences. Several old mines within a Cu and polymetallic district in the allochthonous massif of Quinto Real. Vein type and disseminated mineralisation of Cu and other metals (tetrahedrite-tennantite, chalcopryite, bornite, galena, sphalerite) hosted by Palaeozoic formations of different ages (mina de los Alemanes, mina de Txangoa, minas de Arrieta and several other occurrences)

Spain	27	Cantabrian zone of the Iberian Massif, Asturias province	Lithology/Mineralisation: Cu (Co-Ni) district within the Central Carboniferous basin, Cantabrian zone, occurrences of vein type mineralisation and disseminations hosted by Carboniferous limestone (Montaña Limestone unit). Old mining region
Spain/Portugal	28	Western Galicia, Iberian Massif	Mineralisation/Lithology: Sn-W-As mineralisation in Variscan granite and leucogranite
Spain	29	Western Asturian Leonian Zone of the Iberian Massif	Mineralisation/Lithology: The Western Asturian Leonian Zone of the Iberian Massif, comprising lower Palaeozoic siliciclastic rocks intruded by small granitic intrusions, numerous Sb, Zn-Pb and W-Sn-As vein type ores associated with granite and limestone
Spain	30	Iberian Range	Mineralisation/Mining: Small veins and disseminations with Cu-Ag mineralisation in schist, greywacke and rhyolite of the Stephanien unit (e.g., Estrella, Maria Luisa, Urano, Minerva mines in the Pardos area). Related to the deposits with Zn on Figure 1
Spain	31	Cordillera Iberica (Iberian Range)	Mineralisation: Minor deposits with Zn south of Zaragoza; minor veins with Cu, Fe, Pb, Zn, Ba in Palaeozoic rocks, Cu occurrences in Oligocene sediments and conglomerates, small Tertiary deposits with manganese oxides and hydroxides. Lithology: Tertiary sepiolite marl in the Calatayud basin
Spain	32	Maestrazgo area (Castellón province).	Unknown: The source of this anomaly is unclear. It seems to be produced by a very point source and it is located close to the Ebro River mouth. It is not shown on the indium map of the Geochemical Atlas of Spain (Locutura et al., 2012). Possible point contamination is assumed
Spain	33	SE part of the Central Iberian Zone, eastern Sierra Morena, Ciudad Real Province	Mineralisation/Mining: A large number of Pb-Zn-Ag-Cu (mainly galena and sphalerite) deposits hosted by Neoproterozoic and Palaeozoic sedimentary rocks in the Alcadia Valley. Together with Linares and La Carolina fields, known mining since Roman times. Mn-Co mineralisation in the Tertiary sediments (Campos de Calatrava, Bolaños district), Pliocene-Pleistocene basalt in Campos de Calatrava. Power plant: Possible influence from fly ash, rich in Pb, Zn, Ge and Fe sulphides from the Puertollano Power Plant
Spain	34	Iberian Pyritic Belt (Huelva province); the northern part of the anomaly occurs in the Aracena Belt (Ossa Morena zone)	Mineralisation: Massive sulphide deposits of the Spanish part of the Iberian Pyrite Belt (more than 150 polymetallic massive sulphide deposits). The northern part of the anomaly is probably related to a Pb-Zn-Ag district hosted by Cambrian limestone and metavolcanic rocks
Spain	35	Central Iberian zone of Iberian Massif; Cáceres province (extremadura)	Mineralisation/Lithology: Sn-W-As vein type mineralisation (Parrilla mine) within schist, greywacke and volcano sedimentary units intruded by several bodies of Variscan peraluminous granite. Zn-Pb mineralisation occurs in the area, but it is not related to granite
Spain	36	Iberian Pyrite Belt (Huelva province); the northern part of the anomaly occurs in the Aracena Belt (Ossa Morena zone)	Mineralisation: Massive sulphide deposits (many of them polymetallic) of the Spanish part of the Iberian Pyrite Belt (more than 150 massive sulphide deposits). The northern part of the anomaly is probably related to a Pb-Zn-Ag district hosted by Cambrian limestone and metavolcanic rocks (e.g., Rio Tinto)
Spain	37	Cádiz province, Betic Range	Lithology/Mineralisation: An olistostromic complex unit with small Fe-Cu mineralisation hosted by limestone and marl, without an economic value
Spain	38	Tenerife, Canary Islands	Lithology: Mafic, mainly basaltic volcanic rocks

<i>The Netherlands</i>	39	Friesland	Soil type: Clay-rich glacial deposits, heavy clay
<i>Belgium</i>	40	Ardenne	Lithology: Ardennes-Rhenish Massif of Variscan age (Belgium - Germany) containing abundant shale (often metamorphosed) lithologies. Indium in small concentrations substitutes for Al in phyllosilicates. Smelter: Lead smelter in the vicinity
<i>Germany</i>	41	Nordenham	Smelter: Non-ferrous metal smelter emission (Pb-Zn-smelter)
<i>Germany</i>	42	Westerwald, West Rhenish Slate Mountains	Lithology: Ardennes-Rhenish Massif of Variscan age (Belgium - Germany) containing abundant shale (often metamorphosed) lithologies. Indium in small concentrations substitutes for Al in phyllosilicates. Mineralisation/Mining: Fe-ores of the Lahn-Dill type. Smelter: Secondary lead smelter, zinc smelter
<i>Germany</i>	43	Lower Harz Ore Zone, Harz Mountains	Mineralisation: Variscan mineralisation, Harzgeröder zone, sulphide veins, Zn-Pb-Cu deposits in Rammelsberg (Goslar) hosted by Middle Devonian pelitic sediments (SHMS type)
<i>Germany</i>	44	Rhon, Oberweid	Mineralisation: Structurally controlled mineralisation, Kupferschiefer (copper shale); the area is located on the so-called Central European Copper belt that was mined in the Richelsdorfer mountains and in the Mansfeld and Sangerhäuser area
<i>Germany/Czech Republic</i>	45	West Bohemia region, NW Czech Republic, Ore Mountains-Erzgebirge	Mineralisation/Mining: Polymetallic mineralisation in the Erzgebirge (Krusné Hory)
<i>Germany</i>	46	Frankenwald	Lithology/Mineralisation: Skarn mineralisation with Sn related to Variscan granite in Oelsnitz (Saxony), Frankenwald Granite
<i>Germany</i>	47	South of the Danube, SE Nuremberg	Unknown source
<i>Germany</i>	48	Black Forest	Lithology: Variscan granite. Mineralisation/Mining: sulphide vein-type mineralisations (e.g., ore deposit at Schauinsland and Menzenschwand)
<i>Czech Republic/Austria</i>	49	South Bohemian Massif, central Bohemian region	Mineralisation/Mining: In the Austrian part, indium anomaly is closely associated with cassiterite as a primary accessory component of granitic rocks (Eisgarner granite), especially in the area between Gmünd and Litschau; cassiterite is also accumulated in the heavy mineral fraction of stream sediment in this area, caused by intensive weathering and erosion processes. In Czech Republic, the indium anomaly is related to mineralisation with sphalerite (Kutná Hora). The highest indium values (Ap-soil: 0.13 mg/kg (Ap 49); Gr-soil: 0.21 mg/kg (Gr 50) are located in Central Bohemia. Smelter: Possible soil contamination related to the smelters of the nearby Kutná Hora Ag-Pb-Zn district
<i>Czech Republic</i>	50	NE Moravia region, NE edge of Czech Republic, Opava	Mineralisation/Mining: Polymetallic mineralisation in the mining districts of Horní Benetov and Zlatá Hůrka in Jeseníky Mountains
<i>Poland</i>	51	Beskid Żywiecki, Orava basin	Lithology: Carpathian flysch deposits (Palaeocene-Eocene sandstone, shale and marl); deep marine turbidite locally calcareous and with melilitite shale (organic matter rich)
<i>Slovakia</i>	52	Nitra	Soil type: Agricultural land with alluvial soil
<i>Austria</i>	53	Hohe Tauern (Styria)	Mineralisation: Disseminated Sn-mineralisation within the Hohe Tauern crystalline unit

<i>Austria</i>	54	Oetztal Alps (Tyrol)	Mineralisation/Mining: polymetallic Cu-Fe-Zn-Pb mineralisation/small scale mining sites in the Oetztal nappe unit (Upper Austroalpine basement)
<i>Italy</i>	55	Veneto Region	Soil type: Floodplain sediment deposits related to the Piave river
<i>Italy</i>	56	as above	Lithology: Tertiary volcanic rocks (mafic); mid-Triassic sediments dominated by carbonates with some clastic sediments and rare but numerous distal volcanic units. Mineralisation: Gorno region with Mississippi Valley Type deposits (Zn, Pb, Ag, Ba, F)
<i>Italy</i>	57	Liguria Region	Lithology: Sedimentary rocks, mostly arenite with an important ophiolite contribution
<i>Italy</i>	58	Romagna Region	Soil type: Floodplain sediment deposits
<i>Italy</i>	59	Tuscany Region	Lithology: Sedimentary rocks, predominantly flysch
<i>Italy</i>	60	Latium Region	Lithology: Scattered occurrence of alkaline rocks of the Roman Volcanic Province
<i>Italy</i>	61	Apulia Region	Mineralisation/Weathering: Presence of small deposits of bauxite in limestone
<i>Italy</i>	62	Campania Region	Lithology: Scattered occurrence of alkaline rocks of the Neapolitan Volcanic Province
<i>Italy</i>	63	Campania Region	Lithology: Presence of carbonate and siliciclastic sequences
<i>Italy</i>	64	Apulia Region	Lithology: Presence of limestone (but with no bauxite)
<i>Italy</i>	65	Calabria Region	Lithology: Scattered occurrence of igneous and metamorphic rocks of the Alpine Calabria-Peloritani Arc. Mineralisation: Local minor Zn deposits
<i>Italy</i>	66	Sicily Region	Lithology: Scattered presence of limestone
<i>Italy</i>	67	Sardinia Region	Lithology: Presence of Tertiary alkaline volcanic rocks
<i>Slovenia</i>	68	Črnomelj	Lithology/Weathering: residual soil formed on limestone, karst areas with terra rossa. Anthropogenic contamination: The location with the highest indium value is also enriched in elements: Cd, Ba, Be, Co, Cs, Ga, Gr, Hg, Mn, P, Sr, Tl, Y. The In enrichment is probably related to anthropogenic/agricultural contamination
<i>Croatia</i>	69	Vodnjan, Istria	See comments for Gr samples - locations 69, 70 and 71.
<i>Croatia</i>	70	Josipdol	See comments for Gr samples - locations 69, 70 and 71.
<i>Croatia</i>	71	Malička-Perna	Soil type: Soil developed on the young alluvial fine-grained (silt and clay) sediments of River Sava
<i>Croatia/Bosnia Herzegovina/Montenegro</i>	72	Radošić (Croatia) /Strujići-Ravno (Bosnia & Herzegovina) /Grahovo (Montenegro)	See comments for Gr samples - locations 69, 70 and 71.
<i>Montenegro</i>	73	Grahovo-Berane	Soil type: Old residual soil (terra rossa). The FOREGS topsoil samples from this area show also elevated concentration in indium (Salminen et al., 2005)

<i>Serbia</i>	74	Glumač-Metriš	Mineralisation: Cu-Au porphyry/epithermal deposits and Zn skarn mineralisation at Majdanpek - Late Cretaceous Banatitic Magmatic and Metallogenic Belt. Majdanpek is known for its historical mining ca. 5000 BP
<i>Serbia/FYROM</i>	75	Konjino (Serbia) to Hamzali (FYROM)	Mineralisation/Mining: Pb-Zn deposits in Karamanica (Serbia); three mines and flotation plants for Pb and Zn: Zletovo, Sasa and Toranica (FYROM; Stařilov et al., 2010)
<i>Hellas</i>	76	Ioannina (Epirus, NW Hellas)	Unknown: There is no viable explanation for this slightly elevated indium value (0.0574 mg/kg). It occurs in alluvial sediments
<i>Hellas</i>	77	Paloumpa village (Arcadia, Peloponnese)	Unknown: There is no viable explanation for this slightly elevated indium value (0.0372 mg/kg). It occurs in soil developed over limestone and chert. Manganese mineralisation (pyrolusite, psilomelane with chalcedony and quartz) occurs in the area
<i>Bulgaria</i>	78	Stara Planina	Lithology/Mineralisation: Karst region with limestone terrain, Stara Planina metallogenetic district
<i>Cyprus</i>	79	Vrisoules Village (Ammochostos District)	Lithology/Soil type: Soil developed on a capping of marine and/or fluvial gravels and CaCO ₃ accumulation, which has aqua regia extractable In values between 0.030 to 0.070 mg/kg (Cohen et al., 2011). The gravels contain mafic lava clasts, derived possibly from the nearby Troulli ophiolite inlier, and locally a variety of basalt, diabase, gabbro and limestone clasts indicating a derivation mainly from the Troodos ophiolite complex and its local sedimentary cover (Poole and Robertson, 1998); it is presumed that there may be detritus from the massive sulphide deposits
<i>Hungary</i>	80	Sajóecseg	Mineralisation: Sulphide polymetallic mineralisation related to Miocene andesitic volcanism, porphyry copper and Cu-Zn-Pb skarn mineralisation, epithermal gold mineralisation; lignite deposits in Ozd
<i>Hungary</i>	81	Bekescsaba	Soil type: Great Hungarian Plain
<i>Ukraine</i>	82	Eastern Carpathian	Lithology: Carpathian flysch locally with carbonates (Pieniny Klippen Belt) and volcanic rocks

Table 4. Explanation of aqua regia extractable indium anomalies in grazing land soil (Gr; 0-10 cm) listed in Figure 4.

Country	Anomaly no.	Geographical area	Explanation (possible sources)
Finland	1	Joensuu	Soil type: Fine-grained sediment in the eastern part of the Lake Ladoga - Bothnian Bay zone of elevated metal concentrations in soil, e.g., Zn. Close to Zn occurrence of Otravaara
Estonia	2	Narva	Developed soil: Clay-rich soil developed on clay-rich mid-Ordovician limestone and marl and on Cambrian claystone, siltstone and sandstone. Lithology/Mineralisation: Local occurrences of argillite and kukersite oil shale, which contains marcasite-pyrite and limonite (this anomaly correlates well with high Fe contents in Gr). Power plant: Close to location of oil shale-fired Balti and Eesti Power Plants at Narva, which generate about 95% of total power production in Estonia, possible fly ash contamination
Sweden	3	Mälaren region (western part), western Bergslagen	Soil type: Clay-rich soil. Mineralisation: Pb-Zn, Cu, Fe mineralisation in pegmatite, skarn and marble and metavolcanic rocks
Sweden	4	Värmland, western Bergslagen	Mineralisation: Filipstad district (e.g., Långban, Lindbom, Gåsborn) in Bergslagen, Cu-Zn-In-Sn-Bi mineralisation in marble, Fe ore and skarn, in metavolcanic rocks
Sweden	5	Västra Götaland, SW end of the lake Vänern, near Trollhättan	Mineralisation: Regional occurrence of polymetallic (Cu/Pb-Zn etc.) quartz (and carbonate) vein mineralisation, also sediment-hosted Cu deposits
Norway	6	Rogaland	Climate and vegetation: Possible 'long range transport anomaly' at the southern tip of Norway (just like Pb), most likely related to climate and vegetation
Great Britain	7	Northern Lancashire, southern Cumbria, western North Yorkshire	Mineralisation: Occurrences of small Zn deposits
Great Britain	8	East Riding of Yorkshire	Smelter: Tin Smelter run by Rio Tinto Zinc closed in 1991, which produced Sn, and Ag, Cd, Pb, Cu, Sb, Bi, In and Au. Smelter caused also local As and Po (decay product of bismuth) pollution. Pollution in Humber estuary bank sediments. Possible smelter dust may be a cause of the weaker anomalies in NE England (Tyneside) and Hull (nearby Ferriby was a major Tin-ore smelter)
Great Britain	9	Welsh Basin, central Wales	Mineralisation: Welsh basin and central Wales orefield with numerous Zn ore deposits. The In anomaly in north Wales is near the Dolgellau Au mineralisation area and may also be associated with local Cu-Zn mineralisation. Smelter: Possible contamination from flue dusts of metal smelters in southern Wales. The flue dusts of metal smelters are possibly responsible for the anomaly over southern Wales. Swansea, on the south coast of Wales, was a major smelting centre for base metals, especially of Cu, Zn and Sn ores from the Devon and Cornwall orefield

Country	Anomaly no.	Geographical area	Explanation (possible sources)
Great Britain	10	South of London, West Sussex, Crawley region	Soil type: Clayey soil (floodplain region). Smelter: Historical iron smelting area in Roman times.
Great Britain	11	Devon, Cornwall	Mineralisation/Lithology: The complex Sn-Cu-Zn mineralisation of south-west England (Devon and Cornwall) associated with the Hercynian granite. Some mineralisation styles pre-date the intrusion of the granite. Sedimentary exhalative occurrences of Pb, Zn and Mn occur in the metasedimentary succession north of Bodmin Moor and Dartmoor, while orogenic quartz veins locally carry Au, Ba, Cu, Fe, Sb and Zn
Great Britain	12	Antrim	Lithology: Antrim basalt and rhyolite of Palaeogene age; thick layer of reddish lateritised basalt known as the Interbasaltic Formation. Mineralisation: Iron ore and bauxite related to basalt; lignite and clay deposits overlying basalt. Industry: Zinc plating industry
France	13	Finistère	Mineralisation: Hercynian granite and minor uranium occurrences. Minor Pb-Zn-Cu mineralisation in Palaeozoic sedimentary rocks
France	14	Poitou ridge	Mineralisation: Pb-Zn deposits in the basal Jurassic cover
France	15	Northern Massif Central	Mineralisation: U district (vein type); Sn-Li-Ta-Nb mineralisation; quartz-cassiterite veins in mica schist. Lithology: Variscan basement rocks (granite, gneiss)
France/Belgium	16	Lorraine	Industry: Industrial contamination by iron and steel industry
France	17	SE Paris Basin margin	Lithology/Weathering: Secondary iron (Tertiary) compounds within the Jurassic-Cretaceous rocks
France	18	Jura	As No. 17
France	19	Forez	Lithology/Mineralisation: Variscan granite and Pb-Zn veins
France	20	NW Massif central	Mineralisation: U occurrence (Limousin district). Lithology: mafic volcanic rocks
France	21	Southern Alps	Mineralisation: Pb-Zn deposits
France	22	SE Cevennes	Mineralisation: Major Pb-Zn district (3 abandoned mines)
France	23	SE Cevennes	As No. 22
France	24	Castres	Mineralisation/Mining: St. Salvy Pb-Zn abandoned mine, and stratabound mineralisation in Cambrian black shale
France/Spain	25	Central Pyrénées, Huesca and Lérida provinces	Mineralisation: Scheelite skarn occurrences and Pb-Zn deposits in Cambrian rocks; Zn-Pb vein type deposits (Parzán mines, Alfonsina mine, Ana mine) in Cambro-Ordovician to Triassic sedimentary and volcano-sedimentary sequences; sedimentary exhalative deposits (Sedex) in Cambro-Ordovician rocks
France/Spain	26	Western Pyrénées, Roncal and Baztán valleys.	Mineralisation/Mining: Pierrefite Pb-Zn district (Devonian) and scheelite occurrences; several old mines and mineral occurrences in a Cu and polymetallic district within the allochthonous massif of Quinto Real; vein type and disseminated mineralisation of Cu and grey copper (tetrahedrite-tennantite, chalcopryite, bornite, galena, sphalerite) hosted by Palaeozoic formations of different ages (mina de los Alemanes, mina de Txangoa, minas de Arrieta)

Country	Anomaly no.	Geographical area	Explanation (possible sources)
			and several other occurrences)
Spain	27	Cantabrian zone of the Iberian Massif; Asturias province	Mineralisation/Lithology: Cu (Co-Ni) district within the Central Carboniferous basin, Cantabrian zone, vein type and disseminations hosted by Carboniferous limestone (Montaña Limestone unit). The most important mines of this district are close to the Cármenes and Villamanín villages
Spain/Portugal	28	Western Galicia; Iberian Massif	Lithology: Variscan granitic intrusions. Mineralisation: Sn-W-As mineralisation mainly related to leucogranite and evolved granite
Spain	29	Western Asturian Leonian Zone of the Iberian Massif	Mineralisation/Lithology: The Western Asturian Leonian Zone of the Iberian Massif comprising lower Palaeozoic siliciclastic rocks intruded by small granitic intrusions; numerous Sb, Zn-Pb and W-Sn-As vein type ores associated with granite
Spain	30	Central Range, Central Iberian zone, Iberian Massif; close to Madrid city	Mineralisation/Lithology: A small Zn-Pb-Ag district hosted by granitic and metamorphic rocks in its northern part (vein type deposits). The smaller anomaly has a south-west trend towards some vein type Pb-Zn mineralisation related to granite in the Toledo mountains. Contamination: The southern part can be related to the well reported urban contamination of Madrid city
Spain	31	Iberian Range	Mineralisation/Lithology: Small veins and disseminated type Cu-Ag mineralisation hosted by schist, greywacke and rhyolite of the Stephanien unit (Estrella, Maria Luisa, Urano, Minerva mines and others, in the Pardos area)
Spain	32	Maestrazgo area (Castellón province)	Unknown: Point source anomaly of an unclear origin, which is not shown on the In map of the Geochemical Atlas of Spain (Locutura et al., 2012).
Spain	33	Ciudad Real province; eastern end of the Iberian Massif under younger materials cover	Lithology: Ordovician and Silurian schist and minor metavolcanic rocks. Frequent and strong disseminations of pyrite and other sulphides (chalcopryrite) have been reported at the top or upper levels of Ordovician unit (limestone). A probable source related to hydrothermal processes associated with volcanic activity
Spain	34	Pedroches batholith. Ciudad Real (N) and Córdoba (SE) provinces; central Iberian and Ossa Morena zones of the Iberian Massif	Mineralisation/Lithology: The Pedroches batholith and Precambrian-Lower Palaeozoic units of the Central Iberian zone; Carboniferous schist and Ossa Morena zone schist and metavolcanic rocks close to its southern boundary, hosting more than 700 mineral occurrences and old mines related to vein type mineralisation of Pb-Zn-Ag, W-Sn, Bi, and Cu
Spain	35	Central Iberian zone of Iberian massif; Cáceres province	Lithology: Variscan granite; Ordovician schist and greywacke and lower Palaeozoic rocks (schist, quartzite and volcanic rocks), intruded by several Variscan peraluminous granitic plutons. Mineralisation: Sn-W-As vein type mineralisation (Parrilla mine); Zn-Pb mineralisation unrelated to granitic intrusions
Spain	36	Iberian Pyritic Belt (Huelva province); the northern part of the anomaly occurs in the Aracena Belt (Ossa Morena	Mineralisation: Massive sulphide deposits of the Spanish part of the Iberian Pyrite Belt (more than 150 massive sulphide deposits). The northern part of the anomaly is probably related to a Pb-Zn-Ag district hosted by Cambrian limestone and metavolcanic rocks

Country	Anomaly no.	Geographical area	Explanation (possible sources)
		zone)	(e.g., Rio Tinto)
Spain	37	Cádiz province; Betic Range	Lithology/Mineralisation: The olistostromic complex unit with minor Fe-Cu mineralisation hosted by limestone and marl
Portugal	38	Lisabon	Lithology: Bedrock composed of limestone and marl and locally Cretaceous basalt. Soil type: Large delta area with fine-grained sediments and soil with high percentage of clay
Spain	39	Majorka	Unknown: The source of this anomaly is unclear. Possible source - terra rossa soil on limestone
Spain	40	Tenerife, Canary Islands	Lithology: Mafic volcanic rocks
Netherlands, The	41	Friesland	Soil type: Clay-rich glacial deposits, heavy clay
Netherlands, The	42	Amsterdam, Utrecht	Industry: coal-driven power plants, industry contaminated floodplain sediments. Smelter: Pb smelter.
Germany	43	Nordenham and south of Hamburg	Smelter: Non-ferrous metal smelter emission (Pb-Zn-smelter); south of Hamburg Cu-smelter (formerly Norddeutsche Affinerie AG)
Germany	44	Ruhr district, Eastern Rhenish Massif	Mineralisation: Mineralisation and mining in the Eastern Rhenish Massif, e.g., Variscan Pb-Zn-veins, Zn-Pb-Ag deposits at Bensberg and Aachen. Smelter/industry: Emission from coal combustion and smelting industry in the Ruhr area
Germany	45	Lower Harz Ore Zone, Harz Mountains	Mineralisation: Variscan sulphide veins (Cu, Pb, Zn), Harzgeröder zone (Silurian limestone) in the Harz Mountains. Mining: Historical Pb-Ag mining area (e.g., Neudorf, Harzgerode mining district).
Germany	46	Eastern Ore Mountains	Mineralisation: Polymetallic quartz sulphide veins. Mining: Ferrous metal emissions around Freiberg
Germany	47	Frankenwald	Lithology: Frankenwald granite
Germany	48	Black Forest	Lithology: Granite. Mineralisation/mining: Sulphide vein type mineralisation (e.g., Schauinsland, Menzenschwand)
Germany	49	Southern Upper Palatinate Forest	Mineralisation: Pyrite-poor Cu-, Pb- and Zn deposits
Czech Republic	50	Central Bohemia region	Mineralisation: Kutná Hora district with Zn-Pb-Ag deposits. Smelter: Smelters of the nearby Kutná Hora Ag-Pb-Zn district
Czech Republic	51	South Moravia region, south part of Czech Republic	Lithology: High-potassium plutonic rocks 'Třebíč melagranite' (durbachite) of Třebíč Massif in the Moldanubicum with elevated concentrations of the LREEs, K, Th, U, Rb, Cs, Ba, Sr in combination with relatively high contents of MgO, Cr and Ni (Klominský et al., 2010)
Poland	52	Beskid Zywiecki, Beskid Slaski, Moravia region in Czech Republic	Lithology: Carpathian flysch deposits, limestone, marl, sandstone, shale, melilite shale (organic matter rich); local occurrences of mafic volcanic rocks

Country	Anomaly no.	Geographical area	Explanation (possible sources)
Austria/Czech Republic	53	South Bohemian Massif	Mineralisation: Cassiterite as a primary accessory component in granitic rocks (Eisgarner granite), especially in the area between Gmünd and Litschau; mineralisation with sphalerite in Kutná Hora, Czech Republic. Smelter: Smelters of the Kutná Hora Ag-Pb-Zn district
Austria	54	Woelz Alps (Styria)	Mineralisation: Disseminated Sn-mineralisation within the Woelz crystalline unit
Italy	55	Veneto Region	Lithology: Presence of Tertiary alkaline volcanic rocks to the south-east; other anomalies in alluvial deposits
Italy	56	Piemonte Region	Lithology: Scattered occurrences of igneous and metamorphic rocks
Italy	57	Liguria Region	Lithology: Sampling site in an area dominated by carbonates
Italy	58	Tuscany Region	Lithology: Sedimentary rocks, mostly flysch; in the western area scattered occurrences of ophiolite
Italy	59	Lazio Region	Lithology: Scattered occurrences of alkaline rocks of the Roman Volcanic Province
Italy	60	Campania Region	Lithology: Scattered occurrences of alkaline rocks of the Neapolitan Volcanic Province
Italy	61	Apulia Region	Mineralisation: Small deposits of bauxite in limestone
Italy	62	Campania Region	Lithology: Carbonate and siliciclastic sequences
Italy	63	Apulia Region	Lithology: Limestone dominated bedrock
Italy	64	Calabria Region	Lithology: Scattered occurrences of igneous and metamorphic rocks of the Alpine Calabria-Peloritani Arc. Mineralisation: Local minor Zn deposits, Fe and Cu mineralisation in karst cavities; vein mineralisation with sphalerite, galena and chalcopyrite
Italy	65	Sicily Region	Lithology/Mineralisation: Scattered presence of igneous and metamorphic rocks of the Alpine Calabria-Peloritani orogen; minor Zn deposits
Italy	66	Sardinia Region	Lithology: Presence of Hercynian igneous and metamorphic rocks. Mineralisation: Post-Variscan hydrothermal activity and mineralisation in southern Sardinia, e.g., Silius mine. Anthropogenic: Polluted Santa Gilla Lagoon by numerous industries and possibly related to the local power plant. The lagoon has received industrial discharges of Hg, Pb and Zn compounds, as well as, for several decades, municipal untreated sewage from the urban area of Cagliari (ca. 400,000 inhabitants), its industrial area (Macchiareddu–Grogastu), and other anthropogenic related activities (i.e., airports, railways, port activities, refineries, incinerators, etc.; Cottiglia, 1995).
Slovenia	67	Črnomelj	Anthropogenic/Agricultural influence: The location with the highest In value is also enriched with some other elements: Cd, Ba, Be, Co, Cs, Ga, Gr, Hg, Mn, P, Sr, Tl and Y. The In enrichment is probably related to anthropogenic/agricultural influence, most probably because this soil is developed on carbonate rocks and the soil is here residual on karst limestone. This is also the reason that the Slovenian median value is high; most of Slovenian

Country	Anomaly no.	Geographical area	Explanation (possible sources)
			GEMAS samples were taken on carbonate rocks
Croatia	68	Lještani	Lithology: Badenian carbonates with intercalations of mafic volcanic rocks (basalt) and 10 km eastward Palaeozoic granite massif
Bosnia & Herzegovina/Croatia	69	Resanovci (Bosnia & Herzegovina)/Tiškovac Lički (Croatia)	Lithology: Carbonate dominated bedrock (also location 70 and 71 in Montenegro) with the old residual soil (terra rossa). The FOREGS topsoil samples from this area show also elevated In concentration (Salminen et al., 2005).
Bosnia & Herzegovina/Croatia	70	Ilidža - Čvaljina (Bosnia & Herzegovina)/Čilipi - Nova Sela (Croatia)	As No. 69
Montenegro	71	Dragalj	As No. 69
Serbia	72	Dragušica-Dolac	Mineralisation: Cu-Au porphyry/epithermal deposits and -Zn skarn mineralisation at Majdanpek - Late Cretaceous Banatitic Magmatic and Metallogenic Belt. Pb-Zn deposits. Ultramafic rocks with Ni-Cr-Co deposits
Serbia	73	Gornja Lisina (SE Serbia) and Neokazi (NE FYROM)	Mining: 3 mines and flotation plants for Pb and Zn in SE FYROM: Zletovo, Sasa and Toranica
Hellas	74	Kalivia village (Konitsa, Epirus) and Pedhini (Ioannina, Epirus)	Lithology/Soil type: The In anomaly includes two samples in a NNW-SSE trend. The northern sample (Kalivia village; In = 0.0517 mg/kg) is in reddish-brown soil developed on the floodplain of Voidomatis River with many limestone pebbles, whereas the southern one (Pedhini; In = 0.0473 mg/kg) is in alluvial soil
Hellas	75	Delphi (Fokida, Central Hellas)	Soil type/Mineralisation: Reddish brown soil developed on limestone; bauxite mineralisation nearby (about 4 km to the south)
Hellas	76	Stimphalia (Korinthia, N. Peloponnese)	Soil type/Lithology: Brownish clayey soil developed on limestone. The only known nearby mineralised occurrences are lenses of haematite at a distance of about 14 km to the NW of the sampling site
Hellas	77	Aghios Ioannis (Monemvasia, S.E. Peloponnese) Methoni (Messinia, S.W. Peloponnese)	Lithology/Mineralisation/Weathering: Reddish brown soil (terra rossa) developed on limestone. To the NW of the sampling site there is magnetite mineralisation within serpentinised pyroxene peridotite (about 5 km NW), and hydrothermal mineralisation along joints comprising chalcopyrite and haematite (about 5 km WNW); bauxite mineralisation at a distance of approximately 4 km ESE of sampling site at Methoni
Hellas	78	Sitia (Crete Island)	Lithology/Soil type: Reddish brown soil developed on Neogene sediments
Hellas	79	Nikitae village (Sappes, Rhodope, Thrace)	Lithology/Mineralisation/Soil type: Yellow-brown soil developed on molasse sediments; polymetallic sulphide mineralisation (galena, sphalerite, chalcopyrite, pyrite) with Au and Sb in the eastern Rhodope region

<i>Country</i>	<i>Anomaly no.</i>	<i>Geographical area</i>	<i>Explanation (possible sources)</i>
Bulgaria	80	Eastern Srednogorie Zone, Silistar area, SE Bulgaria	Soil type: Deltaic deposits of Rezovo River draining the Strandzha mountains. Mineralisation: Numerous deposits and prospects of porphyry and epithermal types, related to the Late Cretaceous magmatism with high Cu and Zn contents. Industry: In ancient times, the area was subject to large-scale metallurgical activity, with the largest ancient deposit of slag in Bulgaria (Nakov et al., 2002)
Bulgaria	81	Balkan Mountains, Stara Planina	Mineralisation: Polymetallic deposits with Au, Ag, Cu, Mo
Bulgaria	82	Stara Planina	Lithology/Mineralisation: Karst region with limestone terrain; Stara Planina metallogenetic district with Pb-Zn deposits
Hungary	83	Karcag, Northern Great Plain region, eastern Hungary	Soil type/Mineralisation: Agricultural land with good soil, semi-natural grassland, locally marshy areas; ore deposits related to andesitic volcanism
Hungary	84	NE Hungary	Mineralisation: Sulphide polymetallic mineralisation related to Miocene andesitic volcanism, porphyry copper and Cu-Zn-Pb skarn mineralisation, epithermal Au mineralisation; lignite deposits in Ozd
Ukraine	85	Eastern Carpathian Mts.	Lithology: Carpathian flysch, locally with carbonates (Pieniny Klippen Belt) and subordinate volcanic rocks

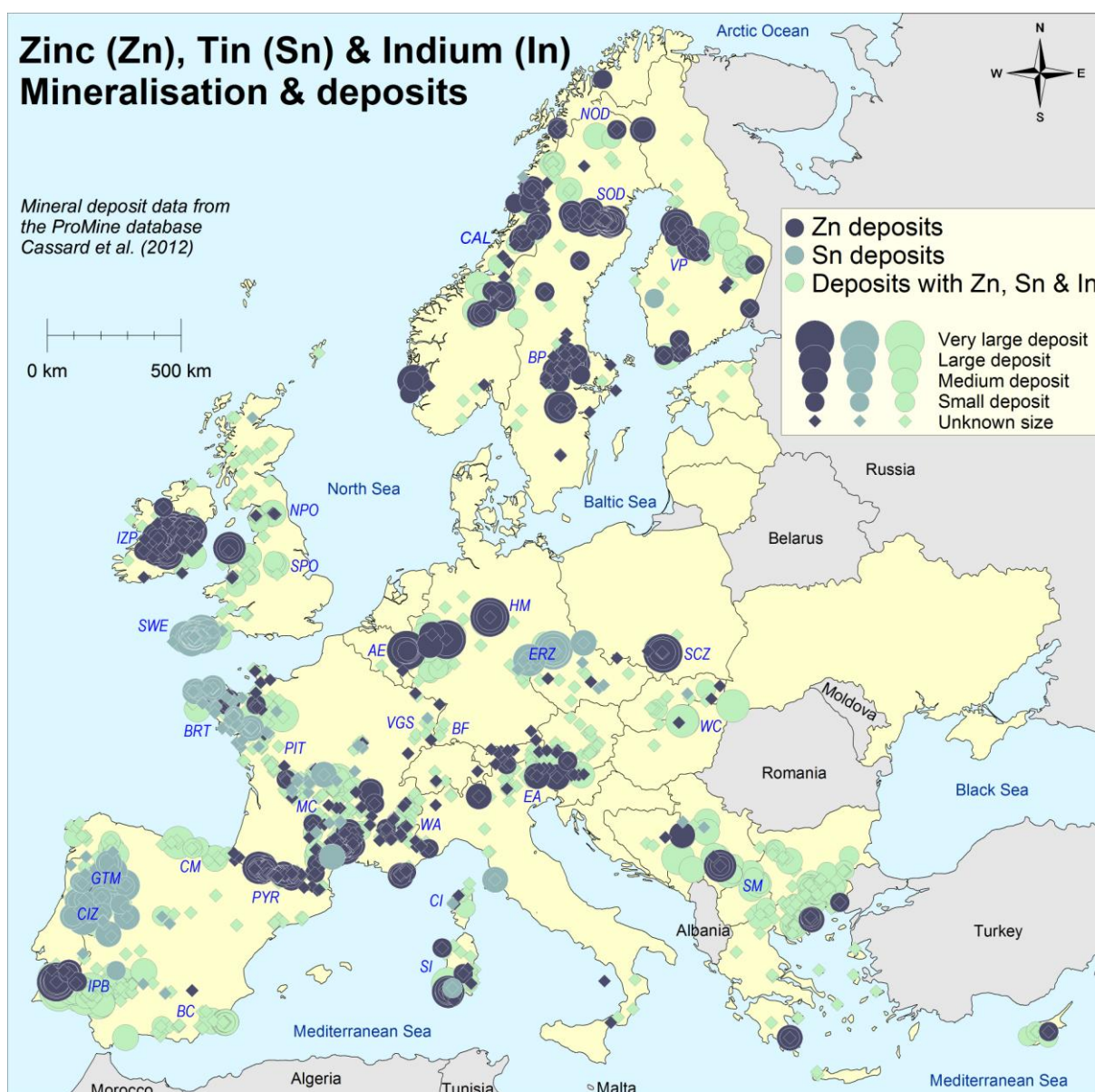


Figure 1

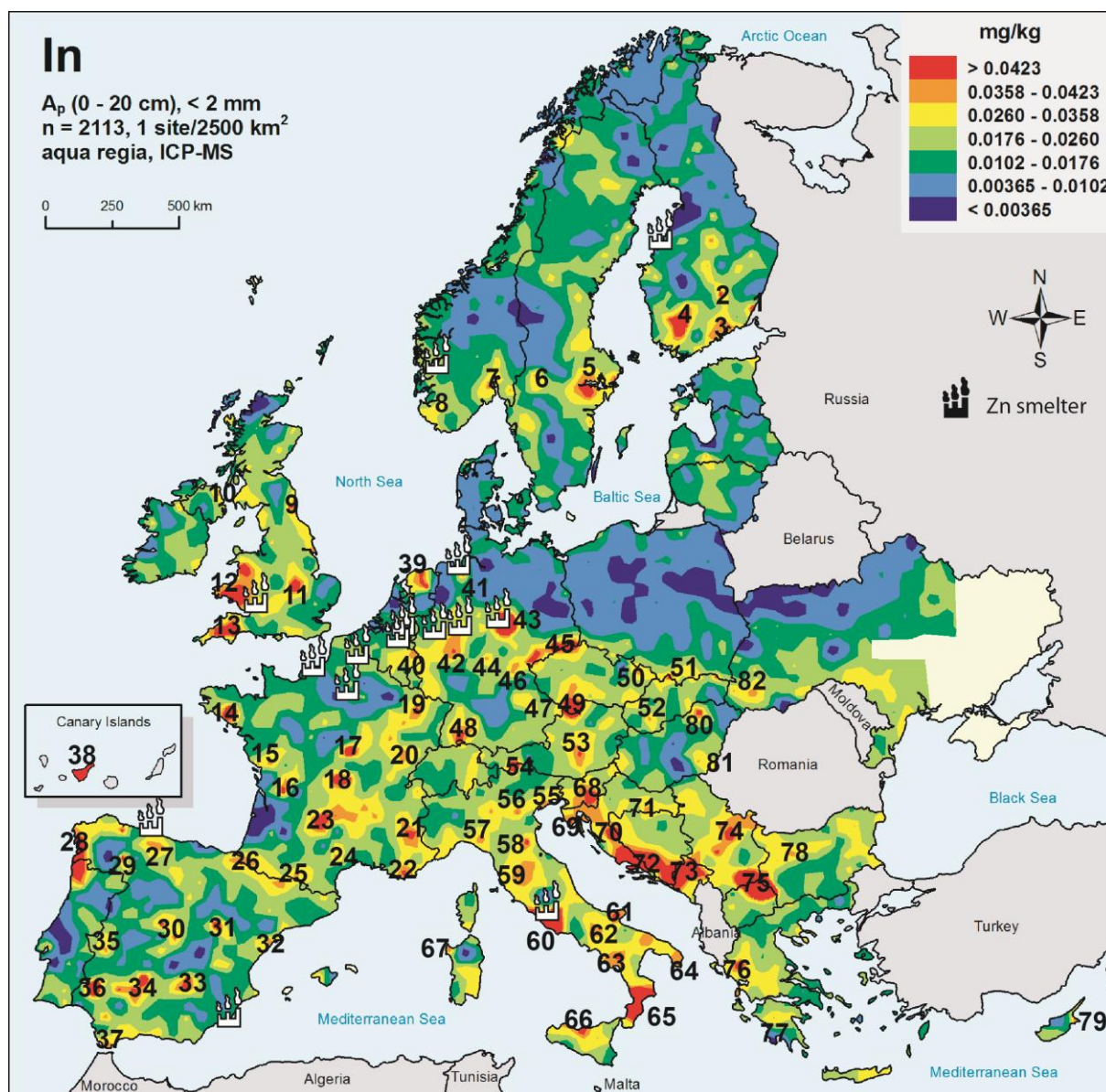


Figure 2

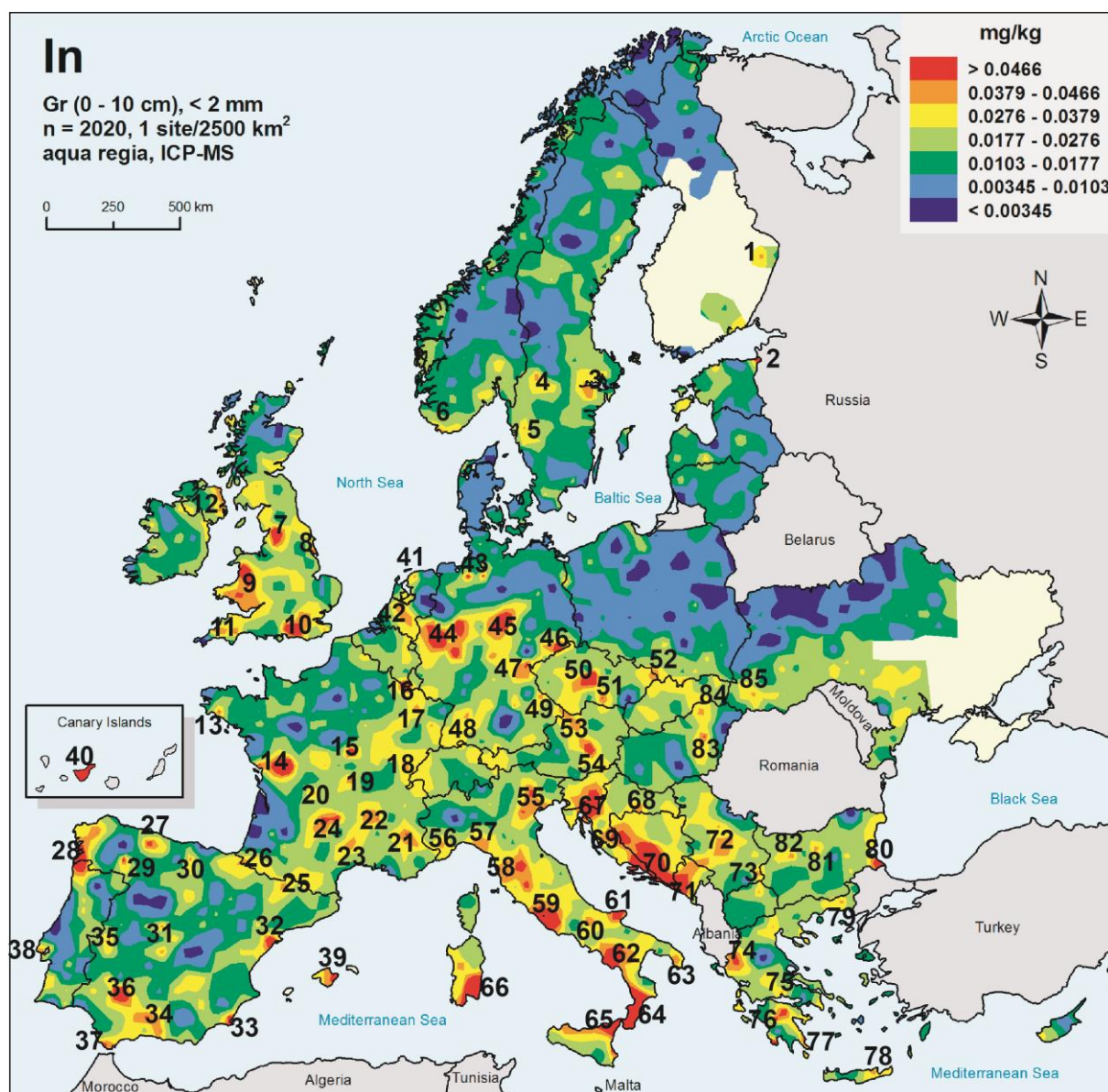


Figure 3

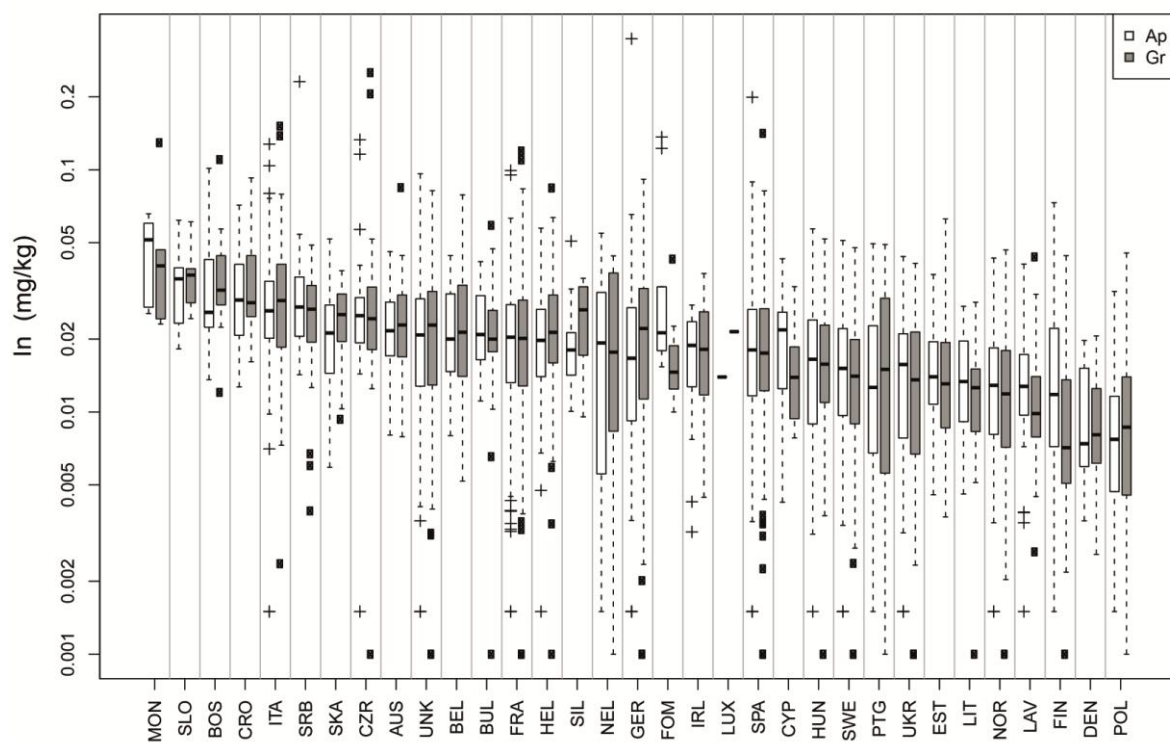
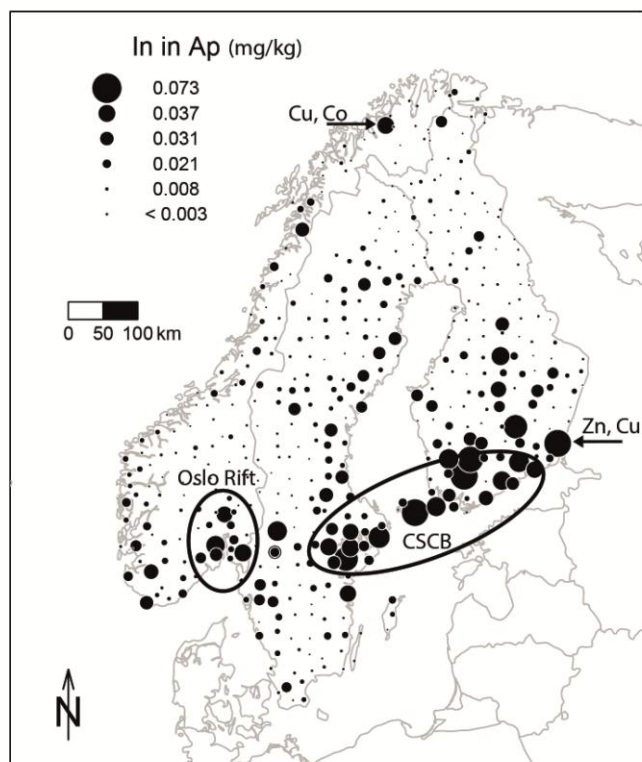


Figure 4

**Figure 5**

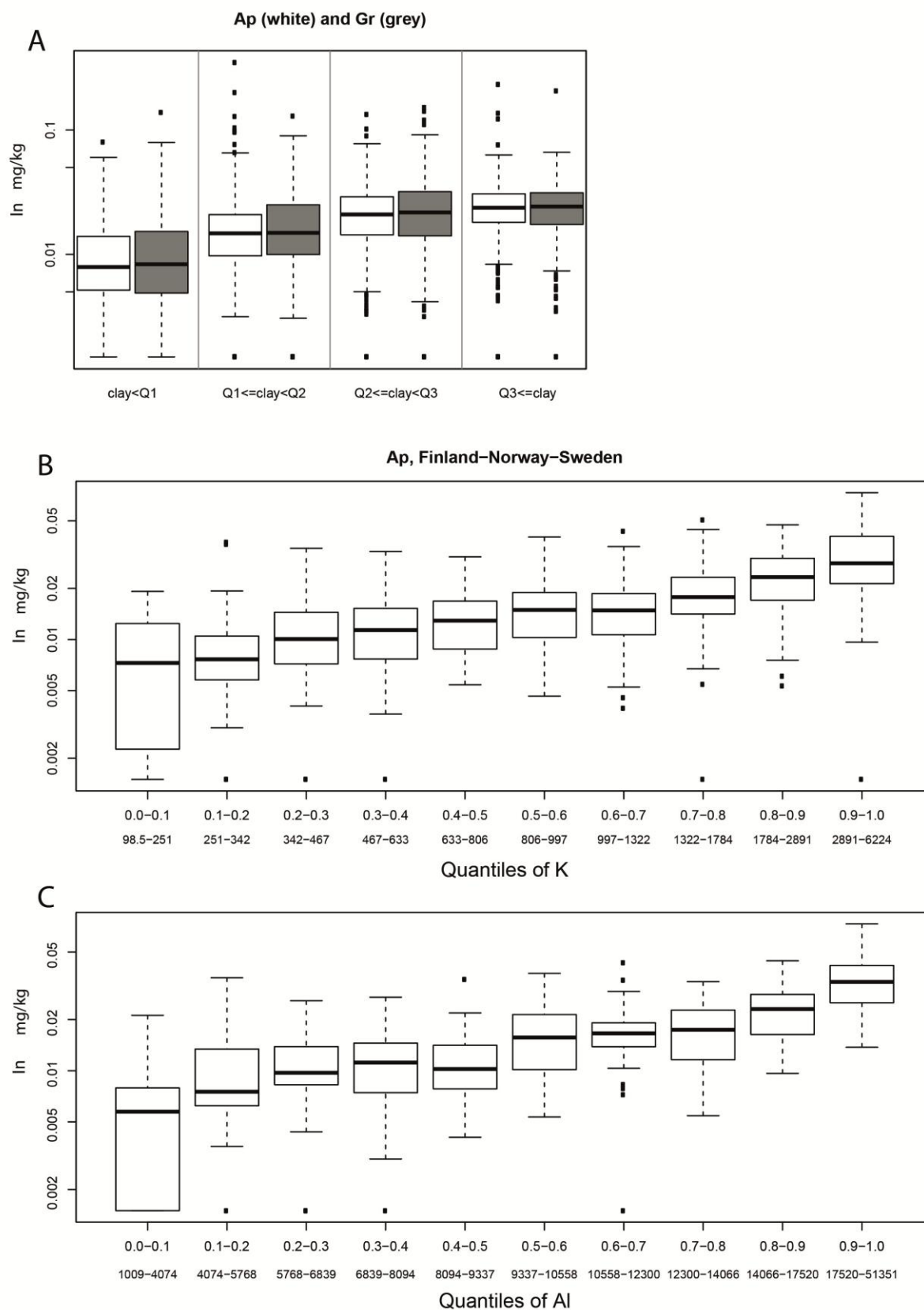


Figure 6

Highlights

- Continental scale geochemical mapping provides indium content in agricultural soil
- The distribution pattern is strongly controlled by natural sources
- Anthropogenic pollution cannot be detected at the continental scale
- Any contamination overlaps spatially with natural sources of metals

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GEMAS: Indium in agricultural and grazing land soil of Europe – its source and geochemical distribution patterns

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