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Arsenic in agro-ecosystems under anthropogenic pressure in Germany and France compared to a geogenic As region in Finland

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ABSTRACT

Arsenic concentrations in soil and water were examined at the European level via a literature review and data inventory in the first phase of the AgriAs European Water JPI project. Arsenic in soil can be derived from both natural and anthropogenic sources. At the European scale, the distribution of arsenic in agricultural topsoil can mostly be explained by geology. In the next step, the AgriAs project investigated arsenic concentrations in soil and water in two regions: Saxony in Germany and Verdun in France. The results were compared with arsenic data from a geogenic arsenic region around the city of Tampere in Finland. In Saxony, arsenic is partly natural and partly derived from the widespread mining and ore processing activities in the area that have lasted for centuries. Areas contaminated with As were found to cover 970 km² in Saxony. The soil baseline for As is only 20–40 mg/kg but the highest concentrations in soil are up to 5000 mg/kg. The large number of investigations in Saxony has given a possibility to evaluate As transfer into plants, fodder and food and to develop guidelines for farmers. In Verdun, arsenic is derived from a former chemical ammunition destruction facility that operated in the interwar period. Today, there are hot spots of As in topsoil with concentrations ranging from 100 to 1000 mg/kg, while the baseline concentration in soil is 18 mg/kg. In the Tampere region, baseline concentrations of As in glacial till forest soils are relatively high (30 mg/kg) over an area of 7400 km², with hot spots of 1050 mg/kg in topsoil. However, agricultural soils contain clearly lower As concentrations. In all three regions, As concentrations in surface waters and in groundwater were found to be relatively low, and the As concentration in topsoil could not be linked to irrigation with As-containing water. Fortunately, As transfer from soil into plants via root systems is generally low in aerated soil, but As-containing dust can affect fodder plants. Especially in the Freiberg area of Saxony, As is usually associated with Cd contamination in topsoil, and guidelines for farmers based on Cd concentrations are also a good risk management method for As.

1. Introduction

Arsenic (As) is a potentially harmful metalloid that can enter the environment from both natural and anthropogenic sources. The occurrence of As in the environment, its toxic effects in aquatic ecosystems (Zuzolo et al., 2020) and technologies for the removal of As from water (Ng et al., 2004; Ravenscroft et al., 2009) and soil (Wan et al., 2020) have been investigated over the past decades. However, several gaps remain, for example in the ecotoxicity of As and removal options in agro-ecosystems and related water bodies in Europe. These topics were investigated during 2017–2019 in a European Water JPI project

entitled “AgriAs: Evaluation and management of arsenic contamination in agricultural soil and water.”

The AgriAs project started with an inventory of available European-wide datasets on As concentrations in agricultural soils, water bodies and crops (Tarvainen and Hatakka, 2017). Arsenic in soil can be derived from both natural and anthropogenic sources. At the European scale, the distribution of arsenic in agricultural topsoil can mostly be explained by geology (Tarvainen et al., 2013). The concentrations of As in the soils of northeastern Europe are up to three times lower than in the southwest of Europe. The break in concentrations occurs along the southern limit of the last glaciation (Tarvainen et al., 2013). Fig. 1

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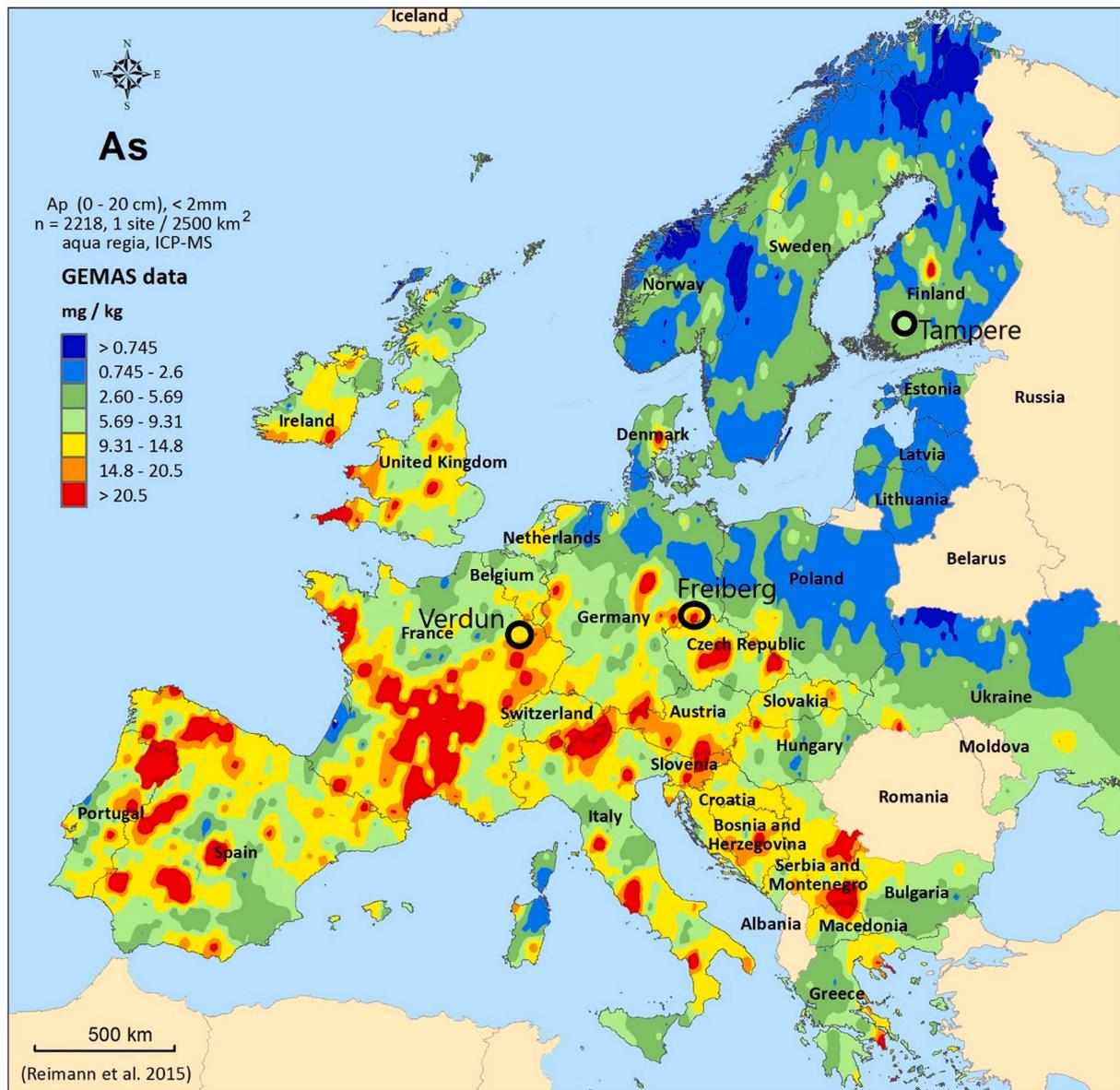


Fig. 1. Arsenic concentrations in European agricultural soils (0–20 cm) and the three target areas: Tampere in Finland, Freiberg in Germany and Verdun in France. Source: GEMAS data (Reimann et al., 2014).

shows continental scale anomalies of As in European agricultural soils based on the GEMAS (Geochemical Mapping of Agricultural Soils of Europe) mapping data (Reimann et al., 2014). However, the sampling density of the GEMAS mapping was relatively low and smaller anomalies cannot be recognized in this scale. According to the literature review, most European countries have a considerable amount of large-scale data on As concentrations in soil, surface waters and/or groundwaters, often collected by the national Geological Survey organisations (Tarvainen and Hatakka, 2017). Arsenic anomalies in old mining areas probably result from a combination of naturally elevated arsenic concentrations in bedrock and soil parent material and additional contamination from local mining and the metal processing industry. In general, atmospheric pollution and the application of phosphate fertilizers can be regarded as the main contributors to anthropogenic arsenic deposition in agricultural soils (EFSA, 2009). The application of sewage sludge is one potential anthropogenic source of arsenic. In earlier times, arsenic and arsenic-containing compounds were used as wood preservatives, pesticides and feed additives.

Understanding of arsenic concentrations and the mobility of arsenic in European agri-ecosystems is important, because As can cause toxicity

to plants following its uptake from soil. Arsenic can also be toxic to livestock through the consumption of As-containing fodder or water. As-rich soil particles can enter the fodder, and grazing on pasture on As-rich soil can also lead to As intake. The most important pathway to humans is through drinking water, but the consumption of As-containing food products and inhalation of As-contaminated dust might also be important (Barret, 2017; Ravencroft et al., 2009; Zuzolo et al., 2020). The ecological risks of As can be linked to soil or aquatic ecosystems.

An elevated As concentration in agricultural soil is not necessarily linked to elevated As concentrations in surface waters. Arsenic concentrations in soil and surface waters were investigated in the European-wide FOREGS (Forum of European Geological Surveys) geochemical baseline mapping programme (Salminen, 2005). Because the soil sampling was focused on residual soils within forest land or unused land, only a small part of the FOREGS soil data set represented agricultural soil in land-use characterization. We calculated Spearman's rank correlation coefficients between As concentrations in agricultural topsoil and in stream water at the agricultural soil sampling sites of the

FOREGS dataset (Salminen et al., 2005) and found no significant correlation (Spearman's $\rho = 0.000$).

Within the AgriAs project, detailed studies were carried out on two target areas: Verdun in France and Freiberg in Saxony, Germany. The French site was formerly the location of a large facility near Verdun for breaking down a huge quantity of chemical ammunitions during the interwar period and was subsequently converted into agricultural land despite the severe contamination. The other target area in Saxony, Germany, was an old centre of the mining industry characterized by 800 years of ore mining, with a focus on silver, lead and zinc. We compared these target areas with a third area around the city of Tampere, Finland, having elevated arsenic concentrations in topsoil (Fig. 1). The Verdun site has been impacted by the anthropogenic input of As, while the Tampere region is an example of a geogenic As-rich region under natural conditions. The area of the Saxony site has been impacted by both natural and anthropogenic As due to its natural As-specific geochemical situation and ore mineralisation on the one hand and the additional burden of widespread mining and ore processing activities lasting centuries on the other.

2. Materials and methods

The countrywide geochemical mapping projects revealed that average arsenic concentrations in glacial till were greater in the Tampere region than in other parts of Finland (Koljonen, 1992). Water in certain drilled bedrock wells exceeded the recommended arsenic levels in the area (Backman et al., 2006). Because Tampere is the second largest city outside the capital area, numerous projects were launched. A LIFE Environment project, RAMAS (Risk Assessment and Risk Management Procedure for Arsenic in the Tampere Region), gathered diverse As information from the Tampere region and identified the risk areas (Loukola-Ruskeeniemi et al., 2007). Subsequently, the LIFE+ project, ASROCKS, continued the work (Parviainen et al., 2015). The geochemical databases maintained by GTK include results from bedrock and soil surveys and ore exploration (Salminen, 1995; Rasilainen et al., 2007; Hatakka et al., 2010). Additionally, the databases include results from a nationwide groundwater survey of well water (Lahermo et al., 2002) and groundwater quality data from municipalities. The sampling methods were based on Finnish standards and general guidelines used in geochemical mapping projects (e.g., Salminen, 1995, and Lahermo et al., 2002; Gustavsson et al., 2012). Arsenic concentrations are available for bedrock, soil, surface water and groundwater samples (Table 1). Bedrock samples have been analysed either by XRF or by ICP-OES from crushed and pulverized samples after aqua regia extraction. In the till geochemical sampling at the reconnaissance scale (Koljonen, 1992), total As concentrations were determined using neutron activation analysis. In other projects, soil samples have been analysed by ICP-OES or ICP-MS after aqua regia extraction from soil samples sieved to <2 mm grain size (baseline

studies) or sieved to <0.06 mm grain size (other projects). Filtered (<0.45 μm) and acidified surface water and groundwater samples were prepared for the analyses of dissolved As by ICP-MS. Arsenic concentrations in crop plant samples were analysed by ICP-MS after concentrated nitric acid leach (Mäkelä-Kurtto et al., 2006). The sampling and analytical methods are described in detail in the above-mentioned references.

In Saxony, investigations of the samples yielded different types of data on arsenic in soil. The pseudo-total As concentration in soil was determined by aqua regia extraction (DIN EN 16174). Availability via oral human ingestion was obtained using a lab-scale intestinal model procedure according to DIN 19738. To evaluate the bioavailable arsenic content or availability via plants, the soil samples were extracted with NH_4NO_3 according to DIN 19730. The water-soluble arsenic concentration was determined by water extraction (1:10) using the method described in DIN38414 part 4. The filtered (<0.45 μm) extracts were analysed by ICP-MS for dissolved arsenic.

Besides pot tests and field tests on As transfer into plants and on cultivar selection and amendments (Klose, 2017; Müller et al., 2017; Serfling and Klose, 2008; Müller et al., 2017; Klose, 2012), ecotoxicological tests with invertebrates (Neu et al., 2017) and investigations on arsenic transfer into sheep (Boguhn et al., 2009) were carried out.

In Verdun, extensive top-soil sampling campaigns have been conducted on the site to identify the unusual and complex mixture of organic and inorganic compounds and to delimit hot spots of severe contamination. The list of analytes is the result of both detailed historical studies focused on the composition of ammunition from the First World War, the processes used to break it down during the interwar period (Hubé, 2017) and on case studies in France (Bausinger et al., 2007) and Belgium (Bausinger and Preuss, 2005). Composite samples of 1 to 2 kg made of 5 to 10 single punctual samples have been taken from 0 to 10 cm depth following the German guidelines for the investigation of ammunition destruction sites (Schwendner, 2009). Samples have been analysed for As, Cd, Cu, Pb, Sn and Zn by ICP-MS (NF EN ISO 17294-2(A)) from crushed and pulverized samples after aqua regia extraction (NF ISO 11466(A)). PCDD and PCDF have been analysed following German standards DIN 38414 S24(A). Nitroaromatic compounds (and their environmental transformation by-products) and diphenylarsinic were determined by HPLC-DAD on an acid preparation of aqueous soil eluates (0.75 kg soil + 0.75 kg water, 24 h elution) after centrifugation and solid-phase extraction. Organoarsenic and organosulfur compounds, chlorobenzene and tetrabromoethane were determined using GC/MS after ultrasonic extraction with dichloromethane.

2.1. Tampere region

The arsenic anomaly of the Tampere region can barely be distinguished on the European-scale map based on low-density GEMAS

Table 1
Samples analysed for As in the Tampere region in Finland by GTK.

Sample type	Number of samples	Year	Project
Bedrock	603	1989–1995	GTK geochemical mapping campaigns
Bedrock	155	2012–2014	LIFE+ project ASROCKS (GTK)
Bedrock	180	2014	EAKR project POSKI (GTK)
Soil (glacial till)	10,869	1980–2006	GTK geochemical mapping campaigns
Soil (arable land, clay)	50	2005–2006	LIFE Environment project RAMAS (GTK)
Soil	116	2012–2014	LIFE+ project ASROCKS (GTK)
Groundwater	1510	1992–2006	GTK, LIFE Environment project RAMAS
Surface water	104	1994–2006	GTK, LIFE Environment project RAMAS
Surface water	51	2012–2014	LIFE+ project ASROCKS (GTK)
Sand or gravel	146	2006–2008	GTK, geochemical baseline studies
Soil (glacial till)	184	2006–2008	GTK, geochemical baseline studies
Clay or silt	111	2006–2008	GTK, geochemical baseline studies
Crop plants	21	2005–2006	LIFE Environment project RAMAS

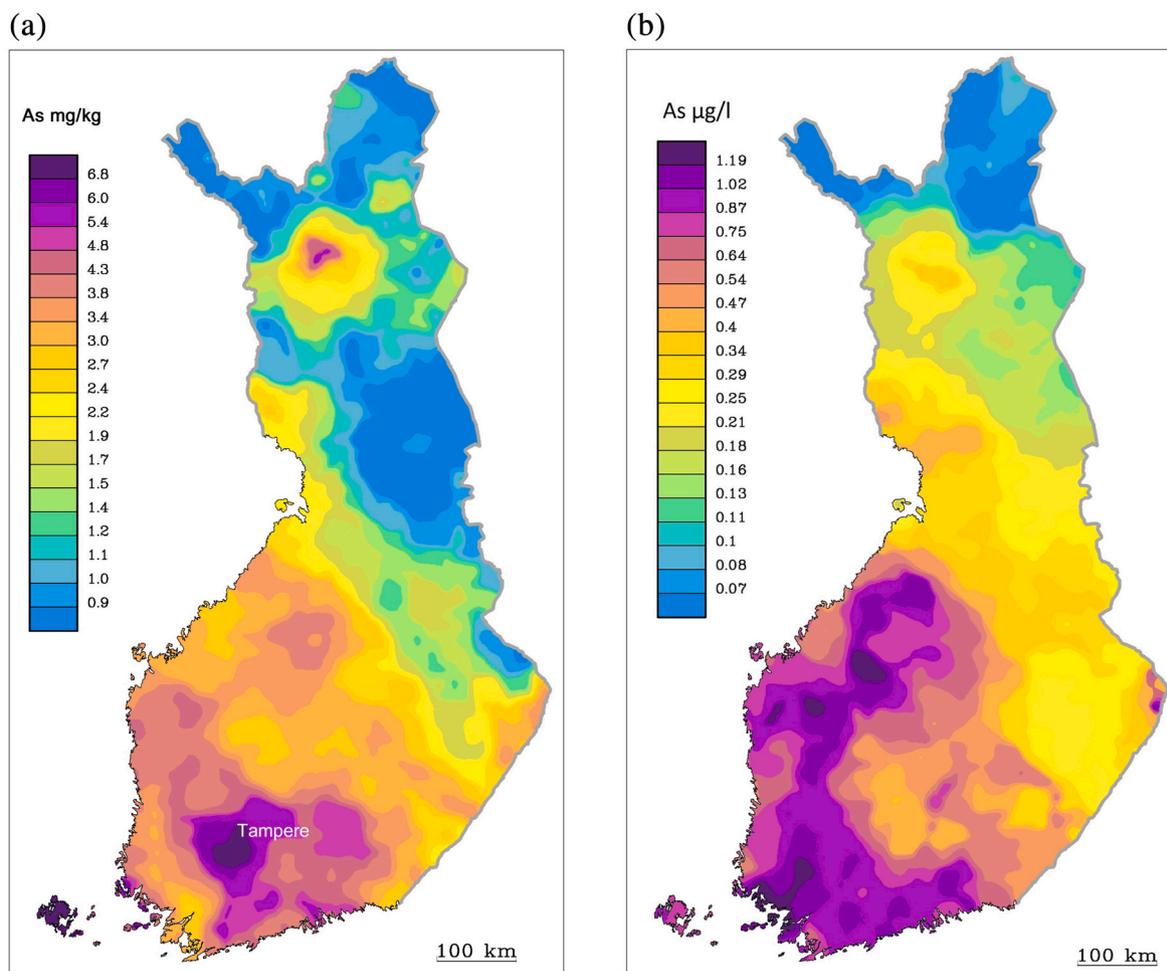


Fig. 2. (a) Concentration of arsenic in glacial till in Finland. Concentrations of As on the scale are low due to the smooth interpolation technique. Concentrations over 20 mg/kg are common in the upper dark red class. Source: Koljonen, 1992. (b) Concentration of arsenic in small headwater stream water in Finland. Source: Lahermo et al., 1996. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sampling illustrated in Fig. 1. Concentrations of As in soil are generally much lower in glaciated areas of northern Europe compared to western and southern Europe. However, the Tampere region can be clearly recognized as an As anomaly on the Nordic soil geochemical map (Reimann et al., 2003) and the Finnish geochemical map at the reconnaissance scale (Fig. 2a; Koljonen, 1992).

Jarva et al. (2010) recognized the Tampere region as one of the Finnish arsenic provinces (violet area in Fig. 2a). According to Jarva et al. (2010), the upper limit of baseline variation for As was 26 mg/kg for glacial till, 15 mg/kg for clayey soil parent material and 7 mg/kg for sandy soils. Naturally high As levels can be explained by the composition of the underlying bedrock. In bedrock, the highest concentrations were found from the narrow volcanic-dominated Tampere Schist Belt. Lehtinen et al. (2014) measured As concentrations as high as 1090 mg/kg from gabbro samples in the Tampere region. There are also several As-containing mineralizations, e.g. Cu-W, Ni-Cu and Au-Cu. Arsenopyrite has been found in gold-bearing quartz veins.

Elevated As concentrations in bedrock (black schists, gabbro, and some metavolcanic and metasedimentary rocks) are reflected in glacial till more than in other soil parent materials. Hatakka et al. (2010) reported up to 233 mg/kg As from glacial till topsoil samples (depth 0–25 cm, <2 mm grain size, aqua regia extraction) from the Southern Pirkanmaa arsenic province around Tampere.

The occurrence of As in the environment in the Tampere region, as well as risk assessment and risk management, were investigated during 2004–2007 in the EU LIFE-funded RAMAS project. The aims of the

project were to locate the sources of natural and anthropogenic arsenic in the study area, assess the health and ecological risks, present recommendations for preventive or remediation actions and develop risk assessment and risk management tools (Loukola-Ruskeeniemi et al., 2007). Agricultural soil and As concentration in plants (wheat, potato, timothy) were determined from 15 sites. Concentrations of As were lower in the agricultural soils compared to the glacial till soil samples; the range of As concentrations was 2.9–6.8 mg/kg in the plough layer (Mäkelä-Kurtto et al., 2006). Arsenic concentrations in the plough layer were slightly higher than in the subsoil of arable land. Thus, fertilizers and atmospheric deposition appear to have influenced As concentrations in topsoil (Mäkelä-Kurtto et al., 2006). Arsenic concentrations were also low in plants: 0.005 mg/kg in wheat grains, 0.008 mg/kg in potatoes and 0.014 mg/kg in timothy. These concentrations were lower than the median values reported in a study by the European Food Safety Authority (EFSA, 2009).

Arsenic concentrations in small headwater streams are higher in the southern and western parts of Finland compared to the rest of the country (Fig. 2b): As concentrations in these areas were 0.4–2.4 µg/l, while the median value for Finland was 0.36 µg/l (Lahermo et al., 1996). Arsenic concentrations in soil are higher in the Tampere region compared to the other parts of southern and western Finland. However, this was not the case for As concentrations in stream water, which were not higher in the Tampere region compared to other parts of southern and western Finland. The Pirkanmaa Regional Environment Centre analysed about 100 stream water samples from the Tampere region in

1994–2004, and the highest concentrations were recorded from the river Juupajoki, where the mean value from 77 samples was 0.9 µg/l (Backman et al., 2006). At the European scale, As concentrations in stream water in southern and western Finland were at the same level as the median values in 26 countries in the FOREGS Geochemical Baseline mapping programme (Salminen et al., 2005). The arsenic concentration was also generally below 1 µg/l in shallow groundwater in the Tampere area (Backman et al., 2006).

Concern has mainly focused on deep drilled bedrock wells in the Tampere area. Aquifers of this kind have been used by private households or other small units. In 2006, water samples from 1272 drilled bedrock wells were analysed and 22.5% of the samples exceeded the drinking water limit value of 10 µg/l for As (Backman et al., 2006). Alternative sources of drinking water, as well as purification methods, have now been implemented in this area.

2.2. Freiberg region

According to BGR (2019), the background concentration of As in topsoil is higher in the German mountain regions compared to the northern parts of Germany. Baseline concentrations are <10 mg/kg in the north, 10–25 mg/kg in the middle and southern parts of Germany and over 25 mg/kg in local hot spots. Our test area around the city of Freiberg in Saxony belongs to the macrochore of the Ore Mountains (Erzgebirge), with a baseline concentration of 20–80 mg/kg As (Fig. 3; Rank et al., 1999). The region around Freiberg matches the core centre of a specific Soil Planning Area where counter-measures have been applied due to its contamination level (LfULG, 2009; LD Sachsen, 2011): interpolated mean values for As in topsoil are 320 mg/kg for topsoil and 80–320 mg/kg for alluvial plains. Local hot spots contain up to 5000 mg/kg of arsenic, with even higher concentrations in ore veins close to the surface and widespread waste rock material.

There is a geological reason for the high background concentrations of metals and metalloids in Saxony: silver and lead are bound to galena,

zinc and cadmium in sphalerite, and arsenic in arsenopyrite (Rank et al., 1999). Mining and ore processing in the ore mountains (Erzgebirge) over >800 years has led to mining heaps, tailings and dust deposition, as well as discharges of mining waters. This has caused the significant release of As (and other elements), affecting agricultural sites and alluvial plains (Rank et al., 2006).

Many sampling campaigns have been carried out by the Saxon State Office for Environment, Agriculture and Geology (LfULG) to evaluate the levels of pollution. In 2019, the Scientific Soil Database (FIS Boden) included 23,000 analysed soil profiles, 67,500 analysed soil samples and a total of 2,093,000 analytical results, including a data set of 21,800 samples analysed for the As pseudo-total concentration (aquaregia) in topsoil. Data and maps are available from Sachsen.de (2019).

There is evidence for large-scale contaminated regions at risk according to German regulations (LEP, 2013). According to BBodSchV (1999), areas where trace element concentrations in soil exceed trigger and action values for threat via soil-to-human (ingestion) and soil-to-plant pathways cover 1837 km² in Saxony (Fig. 4). Among these trace element contaminated areas, 970 km² are polluted with As. The concentration of As in many of these areas is higher than 50 mg/kg, causing a potential risk to humans or plants.

Due to the evidence of large-scale As contamination in the area, a permanent soil monitoring site has been established close to Freiberg on a site with an As concentrations of >800 mg/kg (Barth and Forberg, 2013). In addition to the As measurements and monitoring, various remediation measures (liming, iron-based amendments, phytoremediation) and protection measures (e.g. species and cultivar selection for crops) have been evaluated (Klose, 2017).

The enormous number of investigations in Saxony and especially in the Freiberg region has provided a possibility to evaluate As transfer into plants, food and fodder and to develop guidelines for farmers. Human exposure to arsenic has also been evaluated, and the soil planning area of Freiberg (LD Sachsen, 2011) has been developed to allow the efficient management of polluted sites.

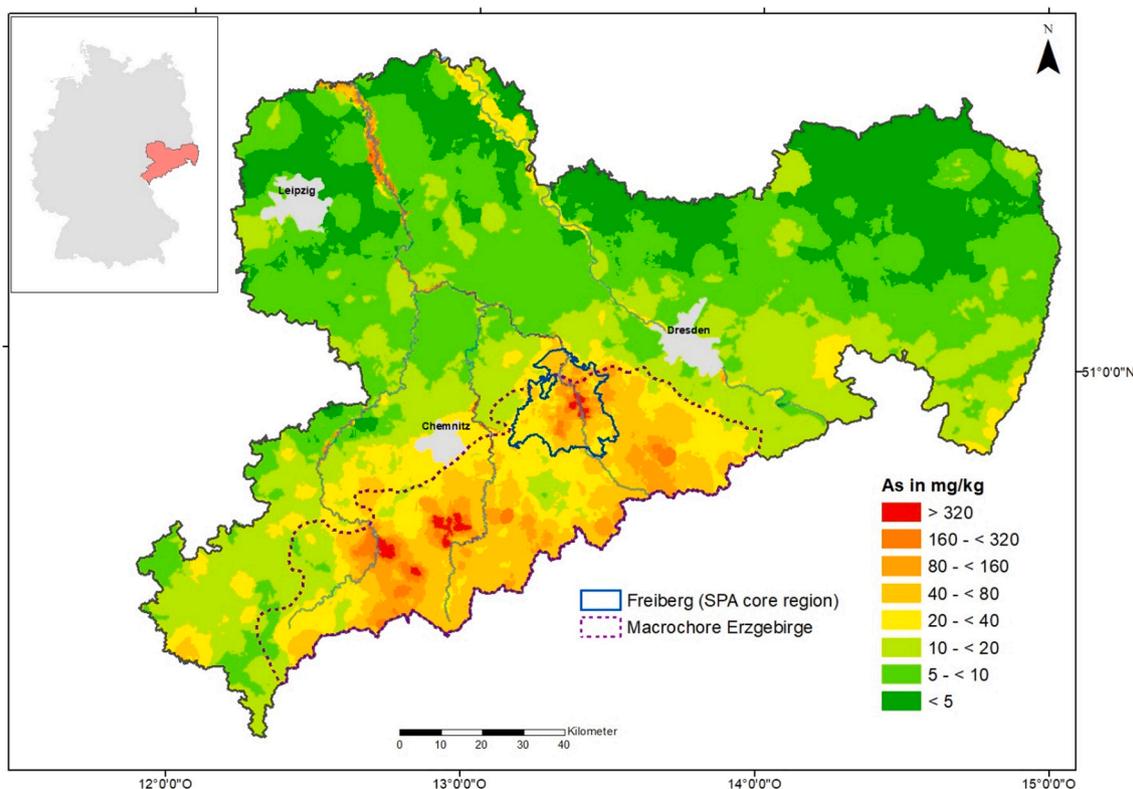


Fig. 3. Arsenic concentration in topsoil in Saxony in the macrochore Erzgebirge (Ore Mountains) and in the Soil Planning Area's core centre of Freiberg (LD Sachsen, 2011), Germany, based on 13,569 soil samples (LfULG, 2009).

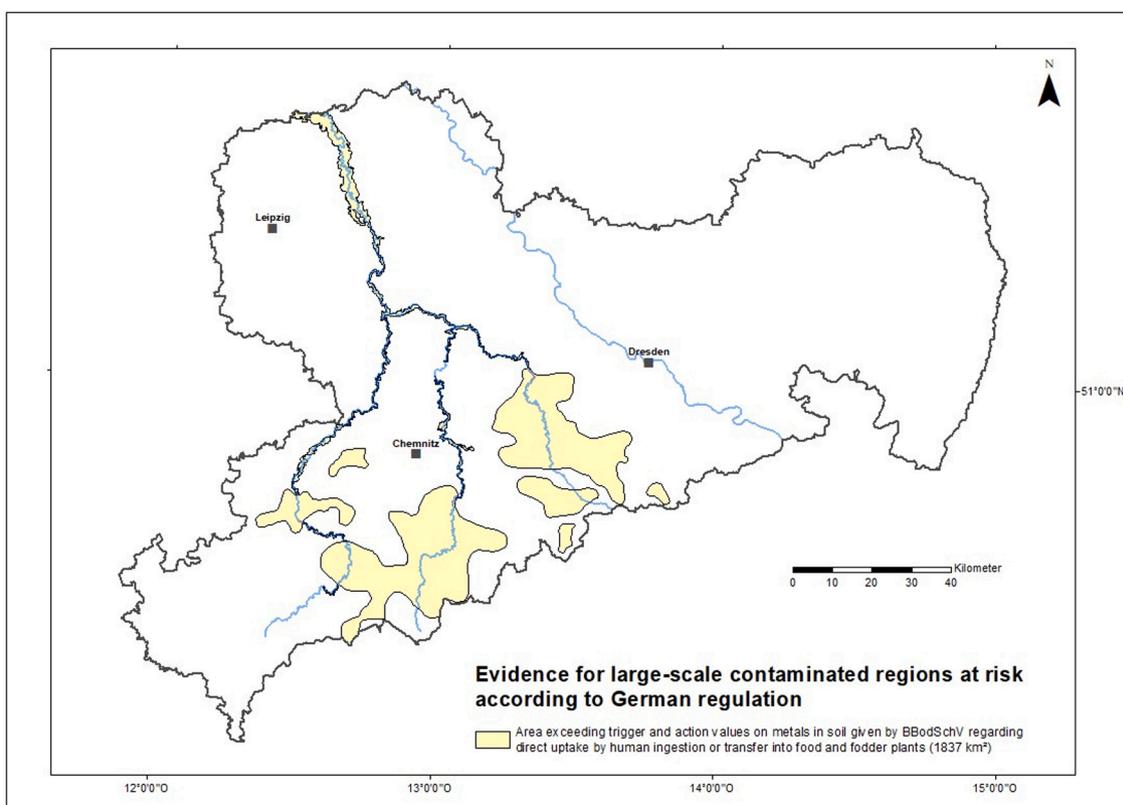


Fig. 4. Large-scale contaminated regions at risk in Saxony, Germany, based on the evaluation of 31,946 soil samples.

2.3. Verdun area

The median concentration of As in topsoil in France is 18 mg/kg (Marchant et al., 2017). Arsenic anomalies are primarily attributed to geology and mineralisation, although mining activities within the Massif Central and the use of pesticides to the southwest of this region are also cited (Tarvainen et al., 2014). The Verdun target area of the AgriAs project has a very special source of As: the destruction of old chemical ammunition from World War I. Ammunition was used on an unprecedented scale during the First World War (1914–1918). Chemical warfare began in April 1915 in Yper (Belgium). Arsenic was used in chemical projectiles as a smoke producing agent (AsCl_3) and in German “Blue Cross” shells as solid emetic, sneezing and lachrymatory agents (diphenylchlorarsine (Clark 1), diphenylklyanoarsine (Clark 2)). The German 77 mm, 105 mm (see Fig. 5), 155 mm and 210 mm “Blue Cross” shells appeared on the Western Front in September 1917.

During the interwar period, authorities were challenged with the disposal of large amounts of old ammunition, estimated to total ca. 2.5 million tons. Severe topsoil contamination with arsenic has been reported for the old open-burning grounds in Western Flanders (Belgium) (Bausinger et al., 2005) and in France near Verdun (Bausinger et al., 2007).

The Verdun target area is located on former German backlines about 20 km northeast of Verdun (Fig. 6). The history of the site has been described in detail by Hubé (2017). The site is a former German ammunition dump and the location of a former large chemical ammunition destruction facility during the interwar period. The industrial-scale destruction of old ammunition occurred in a complex of three sites, including facilities and open-detonation pits, operated by the company “Clere & Schwander” during 1920–1925. In this period, 1,500,000 German, French and British chemical projectiles were demilitarized on this spot. The site was later converted into agricultural land, and the area is currently a sensitive zone for agriculture (barley, corn and wheat), as well as open water and groundwater uses. Almost 100 years

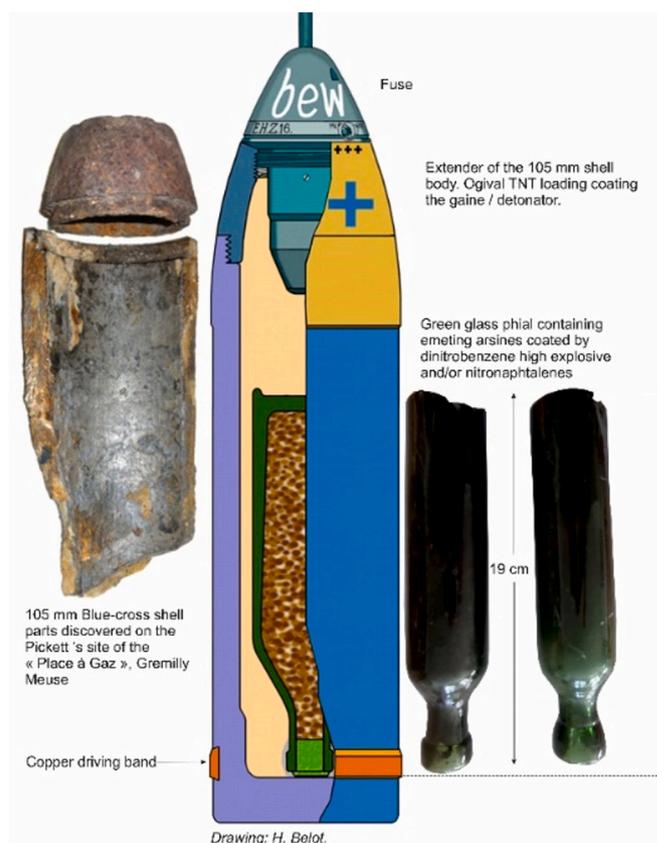


Fig. 5. Cross-section of a 105 mm German “Blue Cross” shell and arsine green glass phials collected from an ammunition destruction site near Verdun. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. The Verdun target area in France.

after the destruction of weapons, severe pollution has been identified, with resultant inhibition of the growth of crops. The remains of old ammunition and explosives also crop out on the ground. Such findings have resulted in crop destruction and temporary impoundment of agricultural land due to possible risks for human health and the environment.

Currently, there are hot spots of As in topsoil (Figs. 7 and 8), with As concentrations ranging from 100 to 1000 mg/kg. Reference zones with similar soil types but low As concentrations in topsoil are also available. Thus, the Verdun target area is an excellent model site to investigate the influence of agricultural practices on arsenic behaviour and transfer. A cross-section through a former ammunition burning trench (Fig. 7) revealed As-rich burning residues (100 to 12,000 mg/kg). Arsenic is mainly inorganic but also associated with low concentrations of organic arsenical compounds such as the highly toxic diphenylarsinic acid (DPAA) (230 µg/kg) and triphenylarsine (0.14 mg/kg). DPAA is a result of the abiotic oxidation of diphenylarsines, and triphenylarsine is generated during the combustion at low temperature of diphenylarsines in “Blue cross” shells. High concentrations of zinc (580 mg Zn/kg), lead

(350 mg Pb/kg) and tin (130 mg Sn/kg) are also present. The concentration of chlorinated dioxins (PCDD) and furans (PCDF) reaches 2000 ng/kg (ΣPCDD + PCDF), and traces of nitroaromatic high explosive compounds have been measured in the residues: 3-dinitrobenzene (0.12 mg/kg), 1,3,5-trinitrobenzene (0.11 mg/kg), 2,4,6-trinitrotoluene (TNT, 3.42 mg/kg), and isomers of dinitronaphthalene and trinitronaphthalene ranging from 0.1 to 4.1 mg/kg associated with their environmental transformation (biotic and abiotic) by-products such as 2-amino-4,6-dinitrobenzoic acid (0.27 mg/kg), and isomers of amino-dinitrotoluene (0.18 to 0.3 mg/kg).

The topsoil contamination by arsenic and other elements and compounds is due to the mixing of agricultural soil and the highly polluted residues of the open-burning trenches through ploughing. Ploughing also results in the homogenization of soil material and a spreading of contamination.

Eight samples of barley grain have been taken on the site, near or on the top soil contamination hot spot to measure total inorganic As (with a limit of quantification of 0.01 mg/kg DM), triphenylarsine, triphenylarsine oxide (with a limit of quantification of 0.1 µg/kg DM for the



Fig. 7. Cross-section of an open-burning (OB) trench at the Verdun site and old aerial photography (1922) of the site. Upper photograph D. Hubé, BRGM, 2019.

sum of both compounds) and diphenylarsinic acid (with a limit of quantification of 5 µg/kg DM). At the Verdun site, inorganic As, triphenylarsine and triphenylarsine oxide have been detected in all samples with concentrations ranging from 0.018 mgAs/kg DM to 2 mgAs/kg DM for inorganic As, and 0.15 to 0.87 µg/kg DM for the sum triphenylarsine + triphenylarsine oxide. Diphenylarsinic acid has been detected in three samples with concentrations ranging from 5 to 23 µg/kg DM. The presence of organoarsenical compounds in the edible part of barley provides evidence of the uptake of these compounds by the crop from the soil (in which these compounds have also been measured). Pollutants seemed to decrease the plant biodiversity in the highly-As polluted zone, and soil from this spot was toxic for plants, according to the omega-3 index bio-indicator (Battaglia-Brunet et al., 2018).

A 13-m-deep monitoring well was installed in March 2018 near the soil contamination spot. The static groundwater table is approximately 5 m under the ground level. Arsenic has been detected in groundwater samples but at concentrations close to the natural hydrochemical background of this region (2 to 4 µg/l). Background data were available from wells drilled on the site and near the site, in the same aquifer, and further water samples have been taken from springs, rivers and ponds in relation to this aquifer. Additional background data have been obtained from the River Othain, which flows through the site. Nitroaromatic compounds and other mobile elements have not been detected. DPAA and triphenylarsine oxide have been measured at respective concentrations of 1.72 µg/l and 0.66 µg/l. Traces of 1,4-dithiane (0.78 µg/l), 1,4-oxathiane (0.51 µg/l) and 1-oxa-4,5-dithiepane (0.46 µg/l) are also present in the aquifer. These compounds (thianes) are sulphur cyclic compounds present as impurities in yperite (“mustard gas”), giving the garlic-like smell.

The first risk assessment of the Verdun site was carried out just before the AgriAs project. Gorecki et al. (2017) analysed maize silage, barley and wheat samples, as well as foodstuffs of animal origin (meat and milk). Edible parts of the plants growing on or near sites with severe topsoil contamination (“hot spots”) show the presence of arsines (triphenylarsine and triphenylarsine oxide) and arsenic due to the transfer of these compounds from the soil to the plants. Exposure to

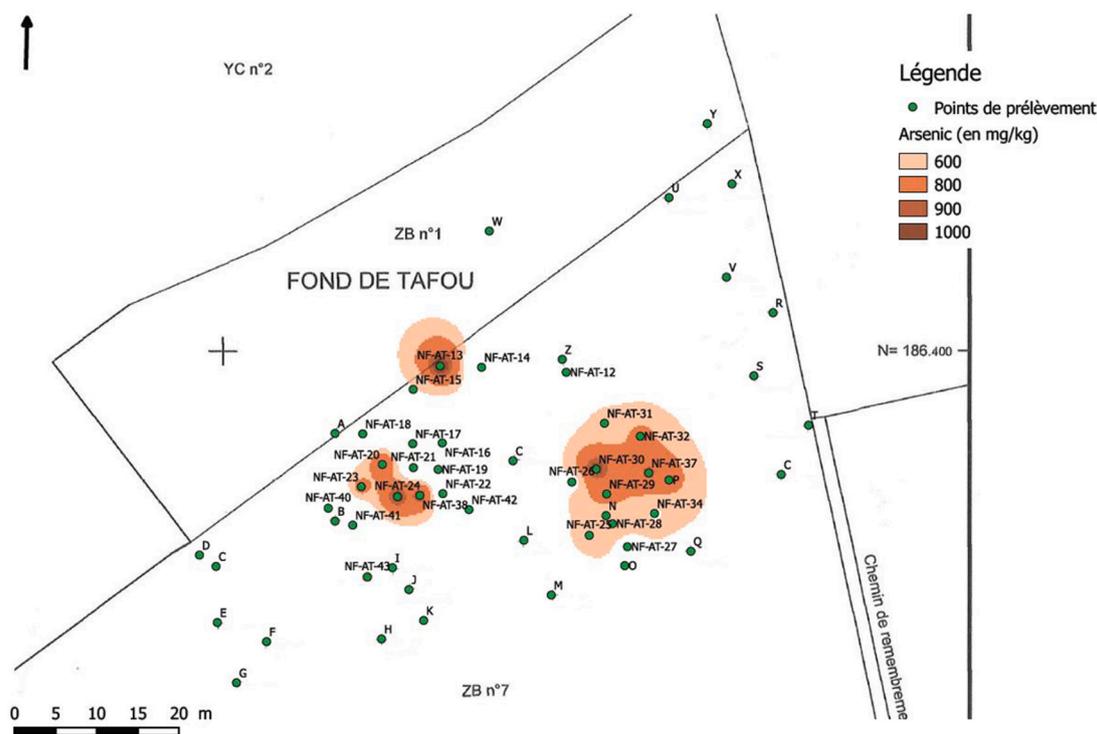


Fig. 8. Arsenic hot spots in topsoil of the Verdun target site, France. Map production D. Hubé, BRGM 2019.

Table 2

Comparison of the Tampere, Freiberg and Verdun regions with higher than average As concentrations in soil. Reference to the As concentration in groundwater and stream water in Freiberg: [LfULG, 2020](#).

	Tampere (FI)	Freiberg (GER)	Verdun (FRA)
As source	Geogenic (bedrock)	Geogenic (bedrock): anthropogenic (mining industry)	Anthropogenic (destruction of chemical ammunition)
Extent of contamination	7400 km ² (5–30 mg/kg in glacial till)	288 km ² (> 50 mg/kg) at Freiberg, 1837 km ² in Saxony	Hot spots (100–10,000 m ²)
As: Soil baseline concentration	30 mg/kg	20–40 mg/kg	18 mg/kg
Highest As concentration in soil	Topsoil 1050 mg/kg, subsoil 9280 mg/kg	5000 mg/kg; ore veins and waste rock material > 1%	12,000 mg/kg
As concentration in stream water	Usually < 1 µg/l, usually geogenic	Usually < 5 µg/l	2–3 µgAs/l, geogenic
As concentration in groundwater	Usually < 10 µg/l, but elevated in some drilled bedrock wells	Usually < 10 µg/l	2–4 µgAs/l, geogenic
Agricultural land use	Yes: not affected by arsenic	Yes: still ongoing	No: stopped in 2015

different contaminants (including As) through the consumption of foodstuffs produced locally on the considered site was considered unlikely to be a health concern. However, as for inorganic arsenic, given the presence of highly contaminated zones, it was suggested that cereals should not be grown on certain plots.

According to the final results of the AgriAs project, the site will not be remediated. However, the agricultural use of the contaminated ground will be abandoned.

3. Discussion

Arsenic concentrations can be higher than average in bedrock and overlying glacial till sediments in the Tampere region of Finland (Table 2). However, As concentrations are lower in soil types that are used for agriculture, and As concentrations measured from wheat and potatoes are insignificant. In the Tampere region, the most important pathway for As to humans is via drinking water from deep wells drilled into the crystalline bedrock, which has naturally elevated As concentrations. When the quality of drinking water is assured, there is no need for special risk management actions on agricultural sites in the Tampere region.

In the Freiberg area of Germany, arsenic was originally geogenic, but the long history of mining and ore processing has increased As mobility, and elevated levels of As can be observed in topsoil. As a result of thorough investigations, including the monitoring and evaluation of As transfer to plants, food and fodder, it has been possible to develop guidelines for local farmers.

There are no EU-wide regulations regarding As concentrations in food (e.g. cereals such as wheat, rye or barley), but there is an EU-based regulation for the As concentration in forage (green fodder, silage, cereals for animals). In addition to As in local food products, the daily intake of As depends on food products from other regions. Thus, the regulatory plan can shift from concentration limits in food to the specific risk assessment associated with their consumption. This has been taken into account in the risk assessment model developed for the AgriAs project (Loukola-Ruskeeniemi et al., 2019a). For example, in 2019 the Italian Ministry of the Environment adopted a statutory instrument that includes criteria for exposure-based risk analysis based on the consumption of agricultural products (Zuzolo et al., 2020). Arsenic transfer from soil into plants via the root system is generally low in aerated soils, and contamination of fodder plants is mainly due to the adherence of As-containing soil material and dust on plant surfaces. Within aerated soils, arsenic predominates in the As(V) oxidation state and typically binds strongly to soil solids. Arsenate and phosphate compete for the same adsorption site of soil particles; nevertheless, phosphate more easily occupies the sorption sites (Anawar et al., 2018). Several studies (Huang and Matzner, 2006; Zhao et al., 2010) have reported that P input to soil (e.g. via fertilizer) could induce the desorption of As from the particle surface, therefore increasing its phytoavailability. In the rhizosphere, As(V) can be considered an analogue of

phosphate and finds its way into the roots and other plant compartments via phosphate transporters (Kopittke et al., 2012). In general, soils around Freiberg are not rich in P (regarding fertilizer status), except for garden soils, which usually exceed even the highest class of P status. Recent recommendations aim at avoiding both excessive P fertilization and a poor P status in soil (Kaufmann-Boll et al., 2012). In the Freiberg area, As is usually associated with Cd, which has a similar origin in agricultural topsoil. Restrictions for farmers are ultimately based on Cd due to its higher availability to plants and its quite strict regulation in food products. Thus, controlling Cd concentrations in agriculture is usually also a good risk management method for As in the Freiberg area. In addition, As concentrations in food and fodder crops are monitored by both farmers and administrative bodies. Gardeners have received recommendations on which crop species they should not to grow, and are advised to wash, strip, peel and clean all fruits and vegetables.

While both the Tampere region and the Freiberg/Saxony region can be seen as As anomalies on European-scale or national geochemical maps, the final target area of this study in Verdun is too small to be distinguished with low-density mapping. A more detailed geochemical survey and information on the historical land use was needed to determine the As risk. High arsenic concentrations are present at hot spots in the area of the Verdun target site. Risk assessment requires further studies on As mobility and bioavailability in the area. The first risk management measure has been to cease crop production on As-contaminated plots. The best long-term future for the site will require a balance between risk-based assessment, geoscientific expert evaluation, socio-political acceptance and remediation costs for the community. The site is not an isolated case. Another ammunition destruction site described by Bausinger et al. (2007) and Hubé (2017) is located 20 km from the Verdun site, in the Forest of Spincourt, where 200,000 “Blue Cross” shells were destroyed, causing extremely high As concentrations in the soil exceeding 100,000 mg /kg As. Nothing grows in this blackened area. Due to the risks to human health and stream water ecosystems, the site will be remediated by gathering the residues in one spot for containment with an appropriate liner and capping material. A chemical ammunition destruction plant operated after WWI in Kelterbach near Frankfurt, Germany. The site and related contamination were discovered in the 1980s and remediated at the beginning of the 1990s. Altogether, 250,000 tons of polluted material showing high As concentrations (over 2000 mg /kg As) have been excavated and remediated. A high concentration of As (over 3000 µg/l As) has been recorded in groundwater, and the plume of As has been remediated by pumping and treating the polluted water using reverse-osmosis units, with operational costs of around 25 million euros.

The median value for the total As concentration in European agricultural soils, 7 mg/kg, is 1.23 times higher than the As abundance in the Earth's upper crust, which is 5.7 mg/kg (Reimann et al., 2014). The USGS has investigated As concentrations throughout the conterminous United States. The median value was 5.2 mg/kg in the soil A horizon

and 5.7 mg/kg in the C horizon (Smith et al., 2014). In China, the baseline soil As concentration mainly depends on the parent material, but urbanization and agricultural practices such as the increased application of fertilizers, insecticides and herbicides has increased topsoil As concentrations. For example, in the Zengcheng District near Guangong, As concentrations in soil vary between 1.06 and 31.2 mg/kg. The mean value of 7.42 mg/kg was close to the European average concentration in agricultural soil (Hu et al., 2016). Bangladesh and the neighbouring East Bengal area in India are areas with elevated As concentrations in shallow groundwater. Although the natural As concentration in agricultural soil is relatively low, e.g. 1.5–3.0 mg/kg in 12 rice fields in Bangladesh that were not affected by As-containing irrigation water, As has accumulated in topsoil in areas irrigated with As-rich water (79–436 µg/l) (Saha and Ali, 2007). Huang et al. (2016) also reported that arsenic contamination in agricultural soil in the Mekong Delta area, Vietnam, was caused by the As-contaminated groundwater used for irrigation. In the National Geochemical Survey of Australia, the median value for the total As concentration in top outlet sediments (0–10 cm) was 3.1 mg/kg in the <2 mm grain-size fraction. Soil geochemical baselines in Tampere, Freiberg and Verdun are higher than typical topsoil As concentrations in other parts of the world. The concentration of As in surface or groundwater was also elevated in some samples from all three study areas, but the elevated As concentrations in agricultural topsoil cannot be linked to irrigation with As-contaminated water, as in many other parts of the world.

Detailed studies in the AgriAs study areas of Verdun and Freiberg and the risk management options selected for the Freiberg area and the whole of Saxony can be used to further develop risk management methods for arsenic-rich agricultural soil and waterbodies in Europe (Loukola-Ruskeeniemi et al., 2019b, 2020). Experience from the European study sites may be applicable in other areas with elevated As concentrations in soil or in water bodies, such as Nepal, Bangladesh and the neighbouring East Bengal area in India, the Mekong Delta area in Vietnam, parts of China and the United States, and several areas in South America.

4. Conclusions

Arsenic in the environment can have either geogenic or anthropogenic sources, and human activities can also spread geogenic arsenic to a greater extent. Geogenic As explained the As concentrations in the Tampere region, while in Verdun the As contamination was anthropogenic. In Saxony (and Freiberg), elevated As concentrations had both a geogenic and an anthropogenic origin. There were similarities between all three studied regions: the baseline concentration of As was up to 30–40 mg/kg in topsoil, which is slightly higher than the average concentration of 7 mg/kg in European agricultural soils. Arsenic concentrations were usually relatively low in surface waters and in groundwater, and elevated As concentrations in topsoil could not be explained by the application of As-containing irrigation water. The highest concentrations of As were over 1000 mg/kg in topsoil.

Extensive studies have been carried out at all three sites. Regional risk assessment indicated that As did not affect agriculture in the Tampere region, as the As concentrations were low in soil types used for agriculture. In Saxony, As is usually associated with Cd contamination in topsoil, and guidelines for farmers based on Cd concentrations are also a good risk management method for As. In the Verdun area, As contamination is concentrated in few hot spots, and the growing of food products already ceased in 2015. The agricultural land use will be definitively abandoned.

CRedit authorship contribution statement

Timo Tarvainen: Writing - original draft, Writing - review & editing, Conceptualization, Methodology. **Susan Reichel:** Writing - original draft, Investigation. **Ingo Müller:** Writing - original draft,

Methodology, Supervision. **Isabel Jordan:** Writing - original draft, Investigation. **Daniel Hube:** Writing - original draft, Methodology, Investigation. **Merja Eurola:** Writing - original draft, Methodology, Investigation. **Kirsti Loukola-Ruskeeniemi:** Writing - original draft, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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