Evaluation and management of arsenic contamination in agricultural soil and water - AgriAs

Arsenic contamination in European agricultural soils, water and crops

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ABSTRACT

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AgriAs Task 1.2 Assessment of As contamination in European agricultural soils has summarized areas with enhanced arsenic concentrations in agricultural soil or surface water that can be recognized from European-wide mapping projects. There are no European-wide data on As concentrations in crops. The anomalous As concentrations in soils and stream water were studied based on the results of the GEMAS project's dataset (Reimann et al. 2015) and on the FOREGS Geochemical Baseline Mapping Programme's dataset (Salminen et al. 2005).

According to the GEMAS results, the anomalous arsenic concentrations in European soils are explained by geology. The concentrations of As in the soils of northeastern Europe are up to three times lower than in the south-west of Europe. The break in concentrations occurs along the southern limit of the last glaciation. Reimann and others (2017) have calculated the threshold values for As concentrations in topsoil separately for northern Europe (17 mg As/kg) and southern Europe (38 mg As /kg) based on the Tukey inner fence (TIF) value. These values are feasible to use in assessing areas with anomalous As concentrations.

Arsenic concentrations in stream water do not follow the geology as clearly as in soils, and concentrations may markedly differ between areas and countries and vary considerably over short distances. Thus, the threshold values for assessing the anomalous As concentrations in stream water need to be based on the results of regional mapping with an adequate density of sampling.

However, elevated arsenic concentrations in soil or surface water above background levels do not directly indicate a risk or even a need for risk assessment. The need for risk assessment should be based on toxicological evidence and guidelines based on ecotoxicological data or data on concentrations that might be harmful for human health.

In addition, the AgriAs project's target areas in Freiberg, Saxony, in Germany and Verdun in France and their arsenic history are presented.

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Appendix 1. Background data for the Freiberg study site in Germany.
Appendix 2. Background data for the Verdun study site in France.

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1. Introduction

AgriAs Task 1.2 Assessment of As contamination in European agricultural soils has summarized areas with elevated As concentrations in agricultural soil and surface water that can be recognized from European-wide mapping projects. The work concerning European agricultural soils is based on the dataset of the GEMAS project (Reiman et al. 2015) and the work concentrating on surface water is based on the dataset of the FOREGS Geochemical Baseline Mapping Programme (Salminen et al. 2005). In addition, the definition of an As anomaly is discussed. Furthermore, descriptions of two anomalous As areas, the AgriAs project's target areas in Freiberg, Saxony, in Germany and Verdun in France, and their As history are presented in appendices.

Anthropogenic arsenic contamination sources include the smelting of non-ferrous ores, iron and steel works, electronics, incinerators, domestic coal burning and coal-fired power stations, the pressure impregnation of wood with chromium, copper and arsenate (CCA), and the application of some phosphate fertilizers or earlier application of As-based herbicides (Albanese and Breward 2011, Mielke et al. 2011, EFSA 2009, Tarvainen et al. 2015). Irrigation with arsenic-bearing groundwater can also lead to elevated arsenic concentrations in agricultural soils and impacts on crops and human health. The repeated input of arsenic in irrigation water can lead to a significant increase in soil As concentrations and enhance As transfer into plants (Gillispie et al. 2015). However, anomalous As concentrations do not always refer to anthropogenic contamination. Relatively high arsenic concentrations in soil and in surface water or groundwater can be geogenic.

There are no European-wide data on arsenic concentrations in crops. Thus, the focus in this report is on the As in surface water and soil.

2. European-wide data availability

The AgriAs project has concentrated on European data for agricultural soil and related surface water or groundwater. The availability of European-wide data sources and large-scale regional geochemical mapping data was discussed in the first report of the AgriAs project, D1.1 Arsenic concentrations in agricultural soils and waters at the European level. The most important European-wide datasets were the following: FOREGS, the Baltic Soil Survey, GEMAS and LUCAS.

The FOREGS Geochemical Baseline Mapping Programme's main aim was to provide high quality, multi-purpose environmental geochemical baseline data for Europe. The mapping programme was carried out by the European geological surveys: first by the Forum of European Geological Surveys (FOREGS) and later by EuroGeoSurveys (http://www.eurogeosurveys.org/). The geochemical data are based on the analysis of samples of stream water, stream sediment, floodplain sediment (or alluvial soil), residual soil and humus collected from 26 European countries (Salminen et al. 2005). According to Salminen and others (2005), the As concentrations in 807 stream water samples around Europe varied from <0.01 µg/l to 27.3 µg/l, with a median value of 0.63 µg/l (Fig. 1).

The Baltic Soil Survey (Reimann et al. 2003) covered agricultural soils from ten northern European countries (Western Belarus, Estonia, Finland, Northern Germany, Latvia, Lithuania, Norway, Poland, Western Russia and Sweden).

The most promising European-wide source of data on arsenic concentrations in agricultural soils is the GEMAS dataset. Reimann et al. (2015) described the GEMAS project as follows: during 2008 and early 2009, a total of 2108 samples of agricultural (ploughed land, 0–20 cm) and 2023 samples of grazing land (0–10 cm) soil were collected at a density of 1 site/2500 km^2 each from 33 European countries, covering an area of 5,600,000 km^2.

The LUCAS Topsoil Survey, with its 1 site/200 km^2 sampling, represents the first effort to build a consistent spatial database of soil properties for environmental assessments ranging from the regional to the continental scale on all major land use types across Europe (http://esdac.jrc.ec.europa.eu/content/lucas-2009-topsoil-data). According to Toth et al. (2015a and b), topsoil geochemistry presents an adequate information base to assess the heavy metal load to the environment and its potential to enter the food chain. Arsenic is one of the potentially harmful elements that has been analysed from topsoil samples in the LUCAS survey.

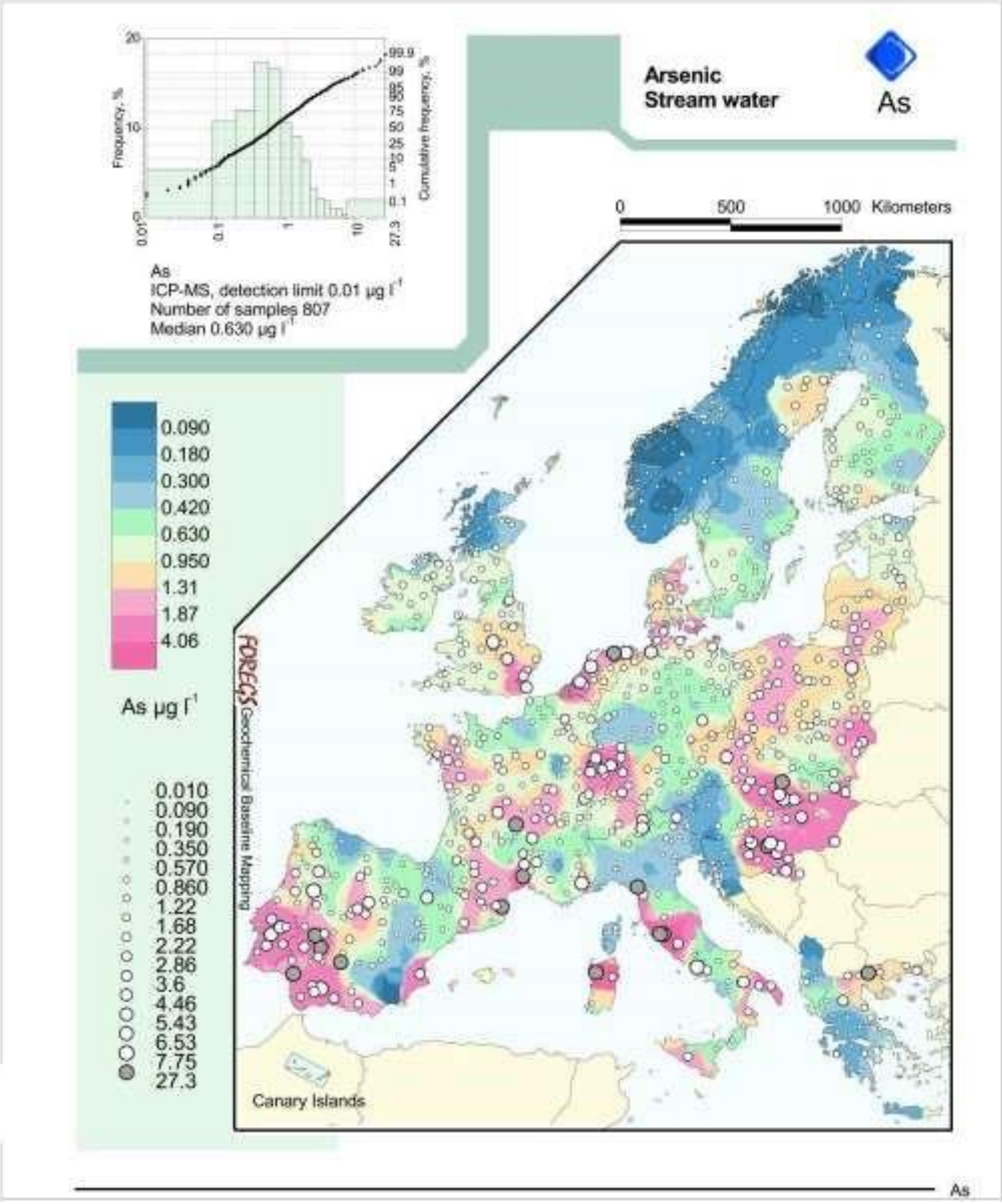

Fig. 1. Arsenic concentrations in European stream water. Source: FOREGS data (Salminen et al. 2005).

Figure 2 illustrates the distribution of arsenic in agricultural topsoil. According to Tarvainen et al. (2013), the median As concentration in the agricultural soils of southern Europe was found to be more than 3-fold higher than in those of northern Europe (median values of *aqua regia* extractable concentrations: 2.5 mg/kg vs. 8.0 mg/kg; median values of total As concentrations: 3 mg/kg vs. 10 mg/kg). Most of the As anomalies on the maps can be directly linked to geology (ore occurrences, As-rich rock types). However, some features have an anthropogenic origin (Tarvainen et al. 2015).

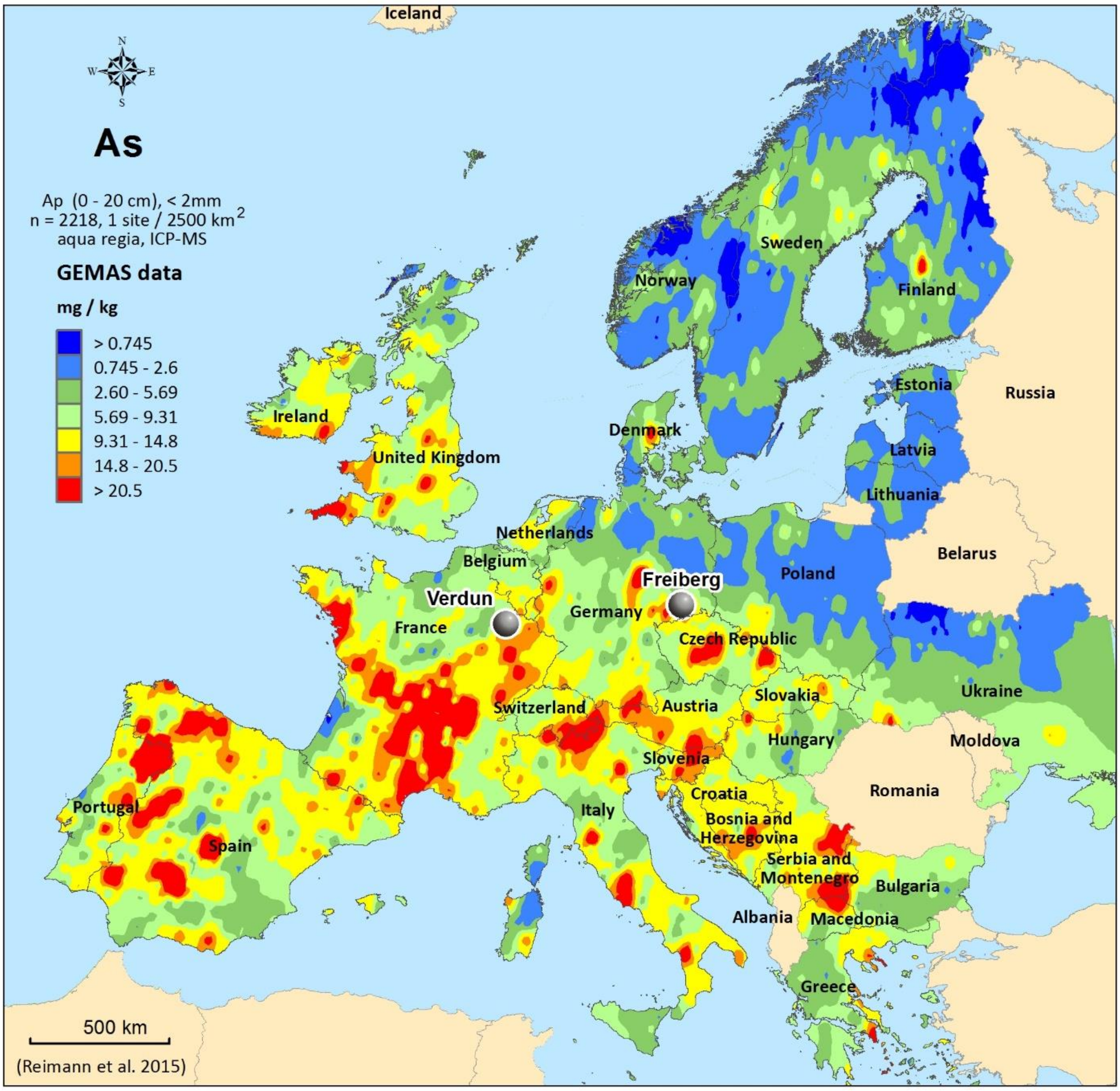

Fig. 2. Arsenic concentrations in European agricultural soils (0–20 cm). Source: GEMAS data (Reimann et al. 2015) and AgriAs target areas: Verdun in France and Freiberg in Germany.

3. Definition of an arsenic anomaly

The arsenic anomalies in European agricultural soil and stream water are described in the following chapter. The As anomalies in agricultural soil are based on GEMAS data and anomalies in stream water on FOREGS data. Arsenic concentrations higher than 20.5 mg/kg (95th percentile of the GEMAS dataset) are considered potentially anomalous in agricultural topsoil in southern and western Europe in this discussion. These anomalous areas do not always refer to any contamination, while the local geological background concentration can be even higher. In the northeast, the geological background concentration is generally lower, and even lower concentrations can be defined as local anomalies. For example, in most parts of Finland, As concentrations higher than 5 mg/kg exceed the national threshold value designated for soil contamination assessment.

Reimann et al. (2017) stated that it may make little sense to define a general geochemical background and threshold value to identify unusually high arsenic concentrations for the whole European continent. They presented separate values for northern Europe (17 mg As/kg) and for southern Europe (38 mg As /kg) based on the Tukey inner fence (TIF). They used log-transformed values in the calculation, as the As distribution was clearly right-skewed. The TIF is calculated as follows:

TIF = Q3 + 1.5 x IQR, where

Q3 = 75th percentile
IQR = the interquartile range (75th – 25th percentile).

Reimann et al. (2017) compared various methods to estimate a threshold value for anomalous metal and arsenic concentrations in European agricultural soil. The CP diagram, the 98th percentile and the TIF emerged as the three methods that can deliver useful geochemical threshold values to identify locations with an unusually high element concentration, whatever the survey scale. Jarva et al. (2010) also applied the TIF approach to identify areas in Finland needing closer attention.

In the next chapter, most of the areas shown with a red colour in Fig. 2 (exceeding the 95th percentile) are discussed as potential arsenic anomalies. In Fennoscandia and the Baltic States, even lower As concentrations could be defined as anomalies. A few more anomalies are included in the discussion than those that would have been identified by Reimann et al. (2017).

Arsenic anomalies in surface waters are based on the results of the FOREGS geochemical baseline mapping, in which all values higher than 1.87 µg/l (85th percentile of the FOREGS dataset) are considered anomalous (Fig. 1). An elevated As concentration in surface water does not always refer to any anthropogenic contamination. Arsenic in surface water can also be a result of the weathering of As-bearing soil or bedrock in the catchment. While the geological background concentration is lower in northwest Europe, some local anomalies with lower As concentrations are discussed in Chapter 5.

In the following chapters, we describe regions where the arsenic concentration in soil or water is relatively high compared to the general concentration in Europe. However, elevated concentrations above the background level (“anomalies”) do not directly indicate a risk or even a need for risk assessment. The need for risk assessment should be based on toxicological evidence and “limit values” based on ecotoxicological data or data on concentrations that might be harmful for human health.

For example, Finland has two types of guideline values for metals in soils: those based on health risks and those based on ecological risks (Reinikainen 2007). Guideline values can be useful in the assessment of soil contamination. Health risk-based limit values are fixed numbers that do not take into account natural concentrations. They are based on a metal concentration that is considered to be potentially harmful to human health. However, most of the guideline values, including the upper and lower guideline values for arsenic, are based on ecological risk and they are calculated by adding the natural background concentration to a value from ecotoxicological data. These guideline values can be modified in areas where the baseline concentration is high. In Finland, there are no guidelines for As concentrations in surface waters.

In France, there is officially no threshold value for arsenic (or other elements) in soils. The anomalies have to be demonstrated at each site, and this demonstration must follow a standardized methodology. This procedure was chosen by the French government because of the important variation in the concentration of As (or other elements) related to the geochemical background (Fabienne Battaglia, pers. comm. 2018).

In the German regulations, it has been pointed out that the As background concentration (e.g. 90th percentile) could sometimes be above the risk level. There is no evidence to follow a rule that “there is no risk because it is natural”. In some cases, one could later determine that, for instance, bioavailability is quite low at “naturally contaminated” sites and could state that there is no risk.

German regulations (BBodSchG, 1998 and BBodSchV, 1999) define a certain risk level from which "risk" is turns towards "hazard" or "danger". This is indicated by specific concentration values: trigger values for quite unlikely scenarios (but still possible in some situations) and action values, where it is quite realistic that the risk exceeds a non-tolerable level. Regarding soils with naturally elevated pollutant contents, BBodSchV (1999) states that harmful soil changes (meaning a hazard exceeding the tolerable risk level) could not be based on naturally elevated concentrations alone: it depends on the amount of pollutants released from soil, entering different pathways and affecting the targets (e.g. human health, groundwater quality, food or fodder quality). Thus, if a (usually pseudo-total) concentration exceeds German trigger or action values in soils with naturally elevated concentrations, one has to assess mobility, plant availability or bioaccessability regarding human ingestion to decide whether there is a non-tolerable risk. For some cases or scenarios (e.g. groundwater quality), there is statistical evidence that regarding naturally elevated concentrations of metals, the mobility (measured via water extraction procedures) is quite low. For other cases, e.g. transfer into plants, this evidence (especially for Cd) is not assured, as it is not for availability via direct oral ingestion by children playing on soil. Thus, in practice, there is no difference in Germany between cases of naturally elevated concentrations and anthropogenic sources if values given by the regulations are exceeded: in both situations, there is a need to consider the amounts of pollutants released to determine whether they really cause an impact on the targets (LfUG, 2006).

4. Arsenic anomalies in European agricultural soil

Based on GEMAS results, the median arsenic concentration in the agricultural soils of southern Europe was more than 3-fold higher than in those of northern Europe. The median values of aqua regia extractable concentrations was 2.5 mg/kg in northern Europe and 8.0

mg/kg in southern Europe (Tarvainen et al. 2015). Arsenic anomalies found in agricultural soil were similar to those detected in grazing land soil samples. According to Tarvainen et al. (2013), most of the As anomalies seen on the map (Fig. 1) can be directly linked to geology.

Fennoscandia and the Baltic States

In northern Sweden, arsenic anomalies coincide with the Skellefteå ore district. In mineralized areas, As anomalies can be partly enhanced by mining. In southern-central Sweden, the As anomalies are located close to the Bergslagen mining district, but some of the high As concentrations may also be due to the presence of marine clays. Arsenopyrite containing black shales can partly explain the As anomalies in southern Norway (Tarvainen et al. 2015).

The Tampere region (Pirkanmaa) is a well-known arsenic area in southwestern Finland. The RAMAS project, partly funded by the EU LIFE Environment programme, carried out a regional risk assessment of the region (Backman et al. 2006; Parviainen et al. 2015). In that study, As concentrations in wheat grains, potato tubers and timothy grass were low and represented typical international levels in uncontaminated areas (Mäkelä-Kurtto et al. 2006). In the Tampere region, the most important exposure route is arsenic-containing drinking water derived from drilled bedrock wells (Loukola-Ruskeeniemi et al. 2007).

A single arsenic anomaly in Denmark was not explained in the assessment work of the GEMAS project. The As anomaly in northern Estonia is most probably caused by industrial emissions (Tarvainen et al. 2015).

Ireland and the United Kingdom

An arsenic anomaly in southeast Ireland is located in a region of Ordovician metavolcanic formations. These formations host some gold deposits and massive sulphide deposits. According to Tarvainen et al. (2015), most of the other As anomalies in the United Kingdom and in Ireland can also be linked to geological sources. One anomaly in southern England can be connected to the processing of As-rich metal ores.

Central Europe

In central Europe, many of the arsenic anomalies coincide with known mineral belts. Erzgebirge (Ore Mountains) in Saxony, Germany, one of the target sites of the AgriAs project, is a typical example. In the region of the Saxony target site, one GEMAS sampling site was located about 20 km southeast of Freiberg. The As concentration was 29.2 mg/kg, which is higher than the average concentration in European agricultural soils, but still low compared to the anomalous concentrations found in some other sites near Freiberg. More detailed sampling in Saxony has demonstrated that most of the anomalies can be traced back to known ore bodies. Elevated As concentrations are found in a much larger area due to anthropogenic activities in this old mining district (Rank et al. 1999; Tarvainen et al. 2015; see also Appendix 1).

Other examples of anomalies connected to known mineral belts are the Rhenish Massive and Harz Mountains in Germany, vein-type As mineralisations in France, mineralisations of the southern Massif Central in France, an area of complex tectonic structures and mineralisations in the Swiss–Austrian–Italian border area, and a metallogenic province in the border area of Serbia, Bulgaria and the former Yugoslavian Republic of Macedonia.

In the Czech Republic, the As anomalies can be linked to more than one source; the anomalies can be derived from mineralisations, such as As–Ag–U vein mineralisation in the Erzgebirge region or Kutná Hora Ag–Pb–Zn mining district, or they can be linked to anthropogenic contamination due to brown coal combustion, as well as chemical or other industries. Some anomalies in Poland may also be linked to anthropogenic emissions, e.g. coal-fired electricity power plants (Tarvainen et al. 2015).

Some arsenic anomalies in France may indicate that As-based herbicides have been used on ploughed fields (Tarvainen et al. 2015). The AgriAs project target area in Verdun is a special case of an anthropogenic As source, as it is a former facility for breaking down chemical ammunition from the interwar period (see Appendix 2). None of the GEMAS sampling sites were located very close to the Verdun target site in France. The nearest sampling point was situated ca. 23 km south of the target site, and the As concentration in agricultural topsoil was 7.7 mg/kg. Thus, the anthropogenic As input from the target site could not be observed in the low density GEMAS sampling.

South Europe

An arsenic anomaly in Lisbon, Portugal, is the best example of As enrichment in urban surroundings. Another anomaly in Portugal can be linked to a gold mineralisation vein (Tarvainen et al. 2015). In Spain, As anomalies are controlled by geology and mineralisation. Granitic bodies containing Au–As–(W) mineralisation are found in Galicia and in Asturias. In other parts of Spain, the As anomalies are most likely associated with Sn–W and precious metal mineralisations or other geological sources (De Vos & Tarvainen 2006).

In Italy, many anomalies are found in the Po River plain. In that area, soil has mostly developed on Quaternary alluvial and glacio-fluvial deposits characterised by a clayey texture. In this environment, As is usually adsorbed on the surface of Fe hydroxides and it is not easy to determine the primary source of As. Both geogenic and anthropogenic sources are possible (Tarvainen et al. 2015). Other anomalies in Italy are mostly linked to geological sources. In Greece, an As anomaly can be linked to the Lavrion Ag deposit and mining in the Attica region.

5. Arsenic anomalies in European surface waters

Arsenic anomalies in surface waters in this report are based on the results of the FOREGS geochemical baseline mapping (Salminen et al. 2005). According to Salminen and others (2005), the distribution of As in European stream water (Fig. 1) is similar to the distribution of As in soil (Fig. 2). The lowest As concentrations in stream water are found in Precambrian shield terrains in western and northern Sweden, northern Finland and Norway, and over Caledonian rocks in most of Norway and in Scotland. In addition, low As concentrations in stream water are found on Variscan terrains in small areas in Spain and France and in Corsica. On the Alpine Orogen, low As occurs in a small area in northern Italy, in a belt from west Croatia and Slovenia across central Austria to southeastern Germany and the Czech Republic, in north Albania, central and southern mainland Greece and Crete, and in the eastern Baetics of southern Spain (Salminen et al. 2005).

The concentrations of arsenic in the soils of northeastern Europe are up to three times lower than in southwest Europe. The break in concentrations occurs along the southern limit of the last glaciation and is thus directly related to geology (see chapter 2). According to FOREGS data, the median concentrations of As in stream water in Fennoscandia are 5–20 times lower than the highest As concentrations on average in stream water in southern Europe (e.g. Norway 0.12 µg/l vs. Hungary 2.3 µg/l), and the difference is even greater if the maximum values are compared (Table 1). The break in the As concentration in soils occurs along the southern limit of the last glaciation and is thus directly related to geology. For As concentrations in stream water, the break does not occur so clearly, and it does not appear to follow the limit of the last glaciation to the extent that it does in soils. However, there is a significant positive correlation (0.247**, Spearman's rho) between As concentrations in topsoil and in stream water (n = 772) in the FOREGS dataset. Thus, elevated As concentrations in surface water do not always refer to any anthropogenic contamination, but they can also be a result of weathering of As-bearing soil or bedrock in the catchment. However, when we considered only those catchments that are dominated by agricultural land use in the FORGES data, no correlation between As concentrations in topsoil and in stream water could be found.

In the FOREGS geochemical maps (Salminen et al. 2005), the arsenic anomalies in surface waters were based on the As concentrations in stream water, with all values higher than 1.87 µg/l (85th percentile of the FOREGS dataset) being considered anomalous (Fig. 1). While the geological background concentration of As is lower in northwest Europe, some local anomalies with lower As concentrations may be hided. Thus, using the FOREGS stream water dataset, we calculated the 85th percentile of the As concentrations in stream water for each country and formed a map presenting those sampling points where the country-based 85th percentiles were exceeded (Fig. 3). In Albania, Belgium, Denmark and Slovenia, the number of stream water samples was too low to determine the 85th percentile, and instead of this, the maximum As values for these countries are presented in the map. The 85th percentile As concentrations in stream water for each country are presented in Table 1.

Reimann et al. (2017) stated that for soils, it may make little sense to define a general geochemical background and threshold value to identify unusually high arsenic concentrations for the whole European continent. They presented separate values for soils in northern and southern Europe based on the Tukey inner fence (TIF) value. They used log-transformed values in the calculation, as the As distribution was clearly right-skewed. The threshold value calculated with the same formula for the FOREGS stream water dataset (n = 807) gives a value of 12.0 µg/l. If this value is used as the limit for anomalous As concentrations in stream water, such anomalous As concentrations in Europe countries only occur in Croatia, Italy, the Netherlands and Spain. In addition, we calculated threshold values separately for each country using the original As concentrations as well as the log-transformed As values. The calculations were only performed for those countries that had enough samples (>30 stream water samples) for statistical analysis. All the threshold values and the number of anomalous As concentrations in stream water are presented in Table 2.

Table 1. The median, 85th percentile (P_{85}) and maximum As concentrations in stream waters of each country studied in the FOREGS Geochemical Mapping Programme (Salminen et al. 2005).

Country	Median µg/l	P_{85} µg/l	Maximum µg/l	Number of samples above P_{85}	Total number of stream water samples
Albania	0.22	-	0.67	-	3
Austria	0.51	1.9	3.3	3	20
Belgium	0.76	-	2.6	-	5
Czech Republic	1.2	3.1	4.7	1	10
Croatia	2.3	10.5	22.1	1	10
Denmark	1.2	-	1.6	-	5
Estonia	0.60	1.5	2.1	1	11
Finland	0.44	0.79	1.3	10	65
France	0.73	2.2	10.0	18	119
Germany	0.62	1.6	6.0	10	74
Greece	0.35	1.5	9.1	4	27
Hungary	2.1	5.3	6.3	1	10
Ireland	0.61	0.85	0.89	1	11
Italy	0.47	2.9	13.0	7	48
Latvia	0.81	1.7	1.8	1	7
Lithuania	1.1	2.0	2.2	2	14
The Netherlands	1.5	11.2	16.1	1	9
Norway	0.12	0.23	0.54	9	58
Poland	1.2	1.8	6.3	8	56
Portugal	1.7	4.9	7.0	3	19
Slovakia	2.2	5.1	8.0	2	15
Slovenia	0.20	-	0.38	-	4
Spain	0.67	2.8	27.3	13	87
Sweden	0.36	0.83	2.1	7	51
Switzerland	1.5	4.7	5.3	1	10
United Kingdom	0.72	1.3	5.6	9	59
All FOREGS countries	0.63	1.9	27.3	98	807

Fig. 3. The highest arsenic concentrations in stream waters of each country based on the FOREGS database (Salminen et al. 2005). The colour of the dots indicates the As concentration level: red = As concentration > 1.87 µg/l (85th percentile in the FOREGS stream water As dataset), orange = As concentration above the median concentration of 0.63 µg/l, but lower than the 85th percentile in the FOREGS stream water As dataset, green = As concentration < 0.63 µg/l (median value in the FOREGS stream water As dataset). In Albania, Belgium, Denmark and Slovenia, the number of the stream water samples was too low to determine the 85th percentile and the maximum As values are presented on the map instead.

Elevated As concentrations above the regional baseline and anomalous As concentrations in stream water as well as in soils do not directly indicate a risk or a need for risk assessment. The need for risk assessment should be based on toxicological evidence and limit values based on ecotoxicological data or data on concentrations that might be harmful for human health. Arsenic does not belong to the 45 priority substances identified by the EU water framework directive 2000/60/EC, in Decision 2455/2001/EC and Directive 2013/39/EU.

Therefore, no environmental quality standards are defined for As (Jones et al. 2017). However, there are some other guidelines for As concentrations in surface water. According to Jones et al. (2017) guideline values for the protection of the freshwater environment vary from 5 µg/l to 890 µg/l. CCME (1999) have set an interim water quality guideline for total As of 100 µg/l in irrigation water. This value is intended to protect agricultural crop species and is based on toxicity data for 25 crop species (Jones et al. 2017).

Elevated arsenic concentrations in stream water in northern Sweden are located in the Skellefteå ore district and could be enhanced by mining activities. In Finland, elevated stream water As concentrations are located in national arsenic provinces (Jarva et al. 2010), the recognition of which is based on geochemical till mapping results (Koljonen 1992). The As concentrations in the delineated provinces are naturally elevated in till. In Norway, As concentrations in stream water are very low (Figs 1 and 3). The arsenic anomaly in stream water of northern Estonia is most probably caused by industrial emissions, as Tarvainen et al. (2015) have supposed concerning the soil As anomaly.

In Spain, France, Italy, the Czech Republic, Poland and Switzerland, elevated arsenic concentrations in stream water follow the same anomalous distributions as have been recognised for soil (see chapter 4).

Table 2. The 85th percentile (P_{85}) and Tukey inner fence (TIF) values calculated using the original As concentrations (TIF1) and log-transformed As concentrations (TIF2), and the number of anomalous As concentrations in stream water for each country that had enough samples (>30 samples) for statistical analysis. The calculation is based on the stream water dataset of the FOREGS Geochemical Mapping Programme (Salminen et al. 2005).

Country	Maximum µg/l	P_{85}	TIF1 (As) µg/l	TIF2 (Log As) µg/l	Number of samples above P85/TIF1/TIF2	Total number of stream water samples
Finland	1.3	0.79	1.3	3.2*	10/1/0	65
France	10.0	2.2	3.4	11.2*	18/7/0	119
Germany	6.0	1.6	2.3	5.3	10/7/1	74
Italy	13.0	2.9	4.0	32.4*	7/6/0	48
Norway	0.54	0.23	0.35	0.79*	9/5/0	58
Poland	6.3	1.8	2.6	3.6	8/1/1	56
Spain	27.3	2.8	3.9	18.6	13/8/3	87
Sweden	2.1	0.83	1.3	4.3*	7/2/0	51
United Kingdom	5.6	1.3	2.0	4.9	9/5/1	59
All FOREGS countries	27.3	1.9	2.8	12.0	98/70/7	807

* The value is higher than the maximum As concentration in the stream water samples

According to Salminen et al. (2005), elevated As levels in stream water are found in Variscan terrains, southwest Germany, Vosges, the Massif Central, southern parts of Brittany and in southwestern France, extending across the Alpidic eastern Pyrenees to northeast Spain and southern Portugal. In France, the high As values are inherited from natural geogenic anomalies, following the late Hercynian distensive system developed in the southern Brittany fault system and in the Argentat faults of the Massif Central (Salminen et al. 2005). In Lorraine, the high As concentrations are correlated with As-contaminated mine water, and the anomalous As value in southwest France, near the border with Spain, is probably related to a previously mined Pb–Zn district. The elevated As concentrations in stream water in southern Spain and in southwest Italy are a result of recent volcanic activity. The highest anomalous content of As in western Slovakia is related to a seepage flow of natural mineral water into stream water (Salminen et al. 2005).

There are 151 agricultural catchments in the FOREGS Geochemical Mapping Programme dataset. The arsenic concentrations have been analysed from 148 stream water samples from 14 countries. The median and maximum values, as well as the 85th percentile of the As concentrations, are presented in Table 3. The sites with the highest As concentrations (As concentration > 85th percentile) in stream water for each country are indicated on the map in Fig. 4. In general, the median concentrations of As in stream water are higher in agricultural catchments than in other sampling areas (Tables 1 and 3), but only in Estonia and Spain were the samples with maximum As concentrations for the country taken from agricultural catchments. The calculated threshold value, the Tukey inner fence (TIF), for the FOREGS agricultural catchment stream water dataset (n = 148) is 10.1 µg/l.

Table 3. The median, 85th percentile (P_{85}) and maximum As concentrations in stream water in agricultural catchments of each country studied in the FOREGS Geochemical Mapping Programme (Salminen et al. 2005).

Country	Median µg/l	P_{85} µg/l	Maximum µg/l	Number of samples above P_{85}	Total number of stream water samples
Austria	0.16	-	0.16	-	1
Czech Republic	1.5	-	1.86	-	2
Estonia	0.60	1.5	2.1	1	11
France	1.1	2.2	7.9	4	29
Germany	0.96	3.1	3.1	1	6
Hungary	2.9	-	3.1	-	2
Italy	0.58	2.4	7.1	2	18
Latvia	1.1	-	1.1	-	1
Lithuania	1.3	2.0	2.0	1	8
Poland	1.2	1.7	2.4	4	35
Portugal	0.47	-	1.7	-	4
Spain	1.4	5.2	27.3	3	24
Switzerland	0.85	-	0.85	-	1
United Kingdom	1.1	3.8	3.9	1	6
All FOREGS countries with agricultural catchments	1.1	2.4	27.3	17	148

Although arsenic in surface water can result from the weathering of As-bearing soil or bedrock in the catchment, high As concentrations in stream water indicate, in addition to geological sources, more distinctly anthropogenic sources for As anomalies. For example, for Denmark and Lithuania, the soil map (Fig. 2) indicates quite low As concentrations, but elevated As concentrations are found in the stream water of these countries. According to Salminen and others (2005), at least in Lithuania, As is possibly a result of agrogenic contamination. In general, there is no significant correlation between the As concentration in topsoil and stream water (Fig. 5). However, in agricultural catchments, in some cases the anomalous As concentrations in stream water may be geogenic, because they occur in the same locations as anomalous As concentrations in soil, such as in Spain and eastern France (Figs 4 and 5).

Water is the most important pathway for arsenic exposure. The anomalous As concentrations in soil and stream water in Estonia and the Czech Republic, for example, show that As is not always in an easily leachable form (Fig. 5, samples 2 and 4). Thus, a high As concentration in soil or bedrock does not necessarily refer to anomalous As concentrations in stream water. There is no significant correlation between the As concentration in stream water and in stream sediment in agricultural catchments. As with the relationship between As concentrations in stream water and topsoil, a high As concentration in stream sediment does not by definition indicate a high As concentration in stream water, and vice versa. For example, in Portugal, the As concentration in stream sediment is elevated, but the As concentration in water is low (Fig. 6, sample 18), and in Spain there is an anomalous As concentration in stream water, despite the moderate As concentration in stream sediment (Fig. 6, sample 21).

None of the FOREGS water sampling sites was located close to the AgriAs target area near Verdun in France. The nearest stream water sampling point was situated ca. 70 km northwest of the target site. The As concentration in the nearest stream water sampling point was 1 µg/l, while the As concentrations in surface water at the Verdun study site vary from 1.36–2.53 µg/l, and 125 µg/l has been recorded in a pond (see Appendix 2).

In Germany, the FOREGS stream water sampling site close to Freiberg, the Sachsen target area, was located 26 km southeast of Freiberg, near the German–Czech border. The As concentration in that stream water was 0.8 µg/l. A slightly higher As concentration was observed at a FOREGS sampling point located near Colditz, about 45 km northwest of Freiberg. At the Freiberg study site, the maximum As concentration in stream water has been 6.0 µg/l (see Appendix 1).

Fig. 4. The highest arsenic concentrations in stream water of agricultural catchments in each country based on the FOREGS database (Salminen et al. 2005). The colour of the dots indicates the As concentration level: red = As concentration > 1.87 µg/l (85th percentile in the FOREGS stream water As dataset), orange = As concentration above the median concentration of 0.63 µg/l but lower than the 85th percentile in the FOREGS stream water As dataset, green = As concentration < 0.63 µg/l (median value in the FOREGS stream water As dataset). The numbers indicate the sample numbers in Fig. 5.

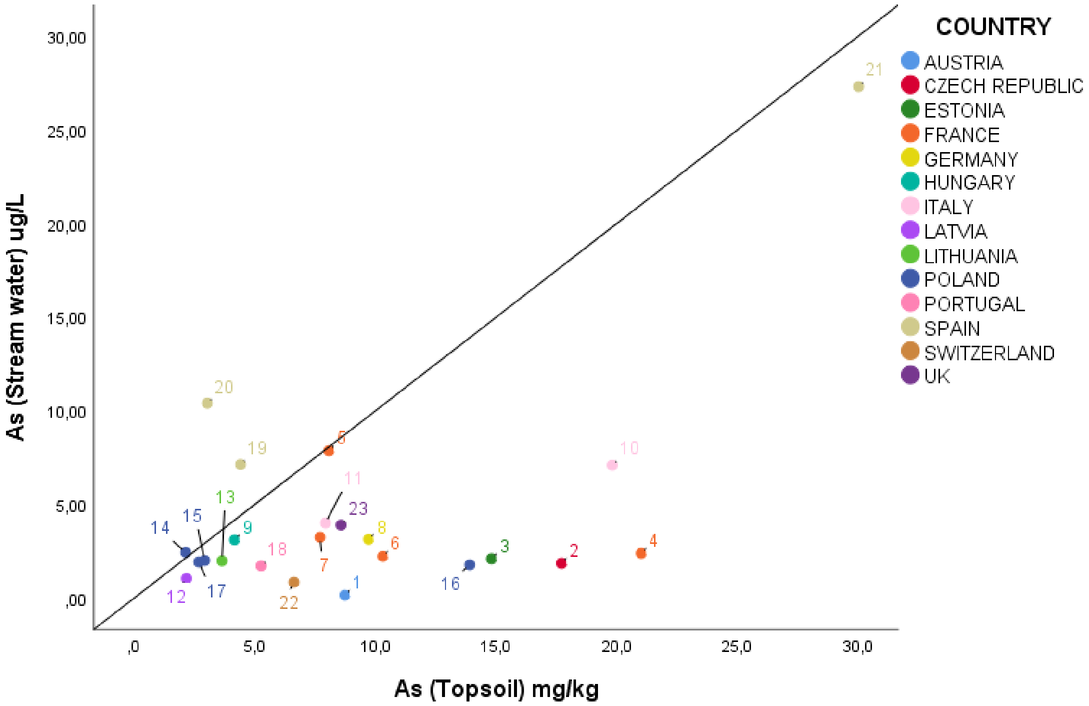

Fig. 5. A scatter diagram of the highest arsenic concentrations (As concentration > P_{85} value of the country's stream water dataset) in stream water and topsoil of agricultural catchments in each country based on the FOREGS database (Salminen et al. 2005). The numbers indicate the sample numbers in the map (Fig. 4).

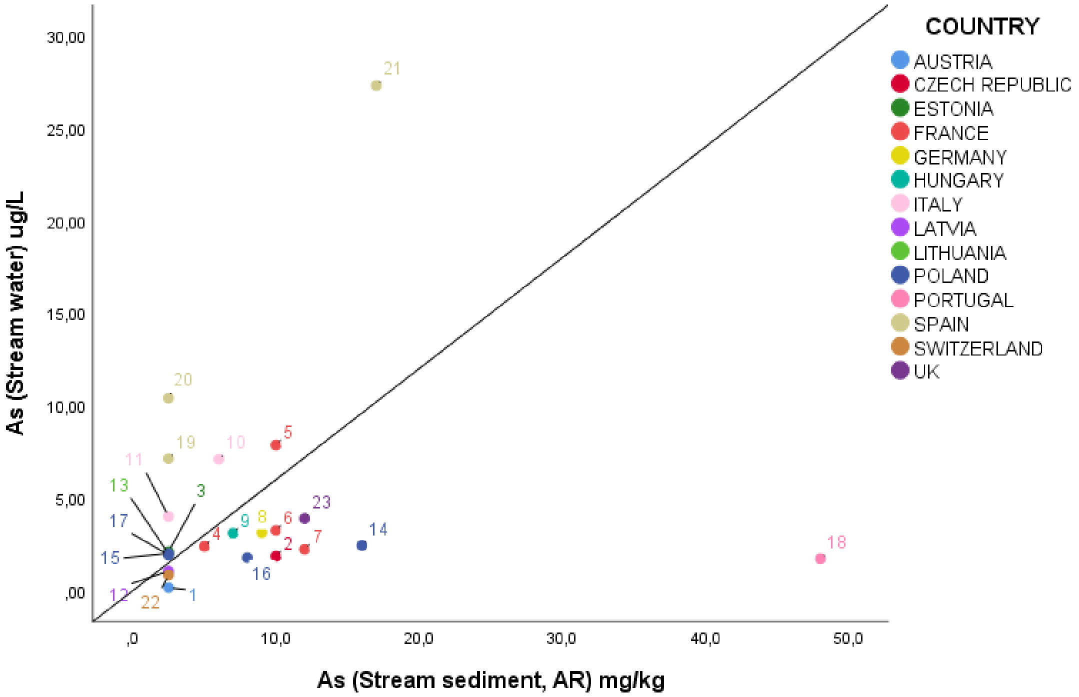

Fig. 6. A scatter diagram of the highest arsenic concentrations (As concentration > P_{85} value of the country's stream water dataset) in stream water and stream sediment of agricultural catchments in each country based on the FOREGS database (Salminen et al. 2005). The numbers indicate the sample numbers in the map (Fig. 4).

6. Conclusions

The AgriAs Task 1.2 Assessment of As contamination in European agricultural soils has summarized areas with enhanced arsenic concentrations in agricultural soil and surface water that can be recognized from European-wide mapping projects. The concentrations of As in the topsoils of northeastern Europe are up to three times lower than in southwest Europe. The break in concentrations occurs along the southern limit of the last glaciation and is thus directly related to geology. Reimann et al. (2017) stated that it may make little sense to define a general geochemical background and threshold value to identify unusually high As concentrations for the whole European continent. They presented separate threshold values for agricultural topsoil for northern Europe and for southern and western Europe. These values are feasible to use in assessing areas with anomalous As concentrations in topsoil.

The stream water dataset of the FOREGS Geochemical Mapping Programme provides an excellent overview about the arsenic distribution in stream waters in European countries. According to the FOREGS dataset, the As concentrations and the concentration levels in stream water do not follow the geology as clearly as the As concentrations in soil. In addition, As concentrations in stream waters markedly differ between areas and countries and may vary considerably over short distances, and there are also countries, such as Albania, Belgium, Slovenia and Denmark, with very few stream water samples to represent the stream water As level of the whole country. Furthermore, for example, the AgriAs project’s target areas with their high As concentrations do not appear in the dataset, which has a low sample density from a national point of view. Thus, finding and assessing the local As anomalies and contamination in stream water, as well evaluating whether these originate from geogenic or anthropogenic sources, needs to be based on regional threshold values. The regional values could be provided by the results of regional geochemical stream water mapping with an adequate sampling density.

The anomalous areas do not always indicate any contamination, and the local geological background concentration can be even higher. In northeast Europe, the geological background concentrations of As in soil and stream water are generally lower, and even lower concentrations can be defined as local anomalies. However, an elevated concentration above the background level does not directly indicate a risk or even a need for risk assessment. The need for risk assessment should be based on toxicological evidence and guidelines based on ecotoxicological data or data on concentrations that might be harmful for human health. There is, in addition, no evidence to support a rule of “there is no risk because it is natural”.

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Background data for the Freiberg study site in Germany

1 History of the site and reason for investigations

The area of Freiberg in Germany is located in the middle of the federal state of Saxony, on the northern slope of the Erzgebirge (Ore Mountains). In 1168, silver was discovered in Freiberg. It is said that wagoners found a piece of silver ore on their way to Prague. They analysed the stone and discovered silver in the galena on an outcrop of a vein. The discovery led to the foundation of a mining settlement. This was the beginning of silver mining in Freiberg, and up to the 16th century the Erzgebirge became the centre of development of the central European mining industry. More than 800 years of mining and ore processing led to economic wealth and a specific regional self-image: the Erzgebirge region is striving for UNESCO World Heritage status as the “Ore Mountain Mining Region”. Over the years, mining in Freiberg went through several phases. In the 18th century, in particular, the mining industry increasingly depended on scientific knowledge, and the Freiberg Mining Academy was subsequently founded in 1765. The days of active mining were over in 1969, when no further economic recovery of resources was feasible.

Due to the specific geochemical situation in the Erzgebirge and the consequences of mining and ore processing, about one thousand square kilometres of agricultural soils show metal contamination, with an area of 288 km² where the arsenic concentration exceeds the German action value of 50 mg/kg. The ore of the Freiberg mining area contains not only silver and lead in galena, but also zinc and cadmium in sphalerite and arsenic in large quantities in arsenopyrite. All of these compounds were mined and smelted together, and the residues were deposited in heaps until the end of mining activities in 1969. Thus, over 800 years of mining and ore processing in Freiberg also means over 800 years of environmental pollution. Beside tailings and former mining and ore processing sites, large areas of agricultural land and alluvial plains were affected by huge quantities of trace elements, especially arsenic, cadmium and lead, extending over a distance of a hundred kilometres. As mining, industrial ore processing, agriculture and settlement areas are located close together, the impact of exposure to As and other mining pollutants on the environment and human health had to be assessed. This is why comprehensive studies were initiated by the local authorities (especially the Saxon State Office for Environment, Agriculture and Geology, LfULG). Contaminants in soil and water have been regularly measured for many years up to today. In areas with high amounts of contaminants, permanent soil monitoring systems were installed that should provide an early warning in case of harmful changes of soil characteristics. One of these permanent monitored sites is located in a village near Freiberg. Recommendations have been given by the local authorities for the treatment of contaminated soils to be used in agriculture and gardening.

2 Background data for surface water

The pollution of Saxon surface waters with As and other pollutants (especially heavy metals) was investigated in bedrock-influenced areas of the Erzgebirge (Ore Mountains) and documented in a report on geogenic background values by LfULG (A. Greif and W. Klemm 2010). This report focusses on the existing geogenic conditions and their influence on the water quality for different catchment areas.

In addition to this report, LfULG regularly provides physical-chemical and biological quality data online. For the catchment area of the River Freiberger Mulde, values for the period from 1999 until 2016 are available as monthly records. It can be maintained that As concentrations are very low, with maximum values of 6 µg/L (LfULG 2016). As the limit value for drinking water is set to 10 µg/L, there is no problem with As in surface water bodies. However, concentrations in sediments of surface water bodies are significantly higher, with up to 160 mg/kg being recorded (A. Greif and W. Klemm 2010).

3 Background data for soil

The following Fig. 1 provides an overview of As concentrations in the topsoil for the whole of Saxony. The map is based on 13569 samples that were interpolated over the area by kriging (LfULG 2009).

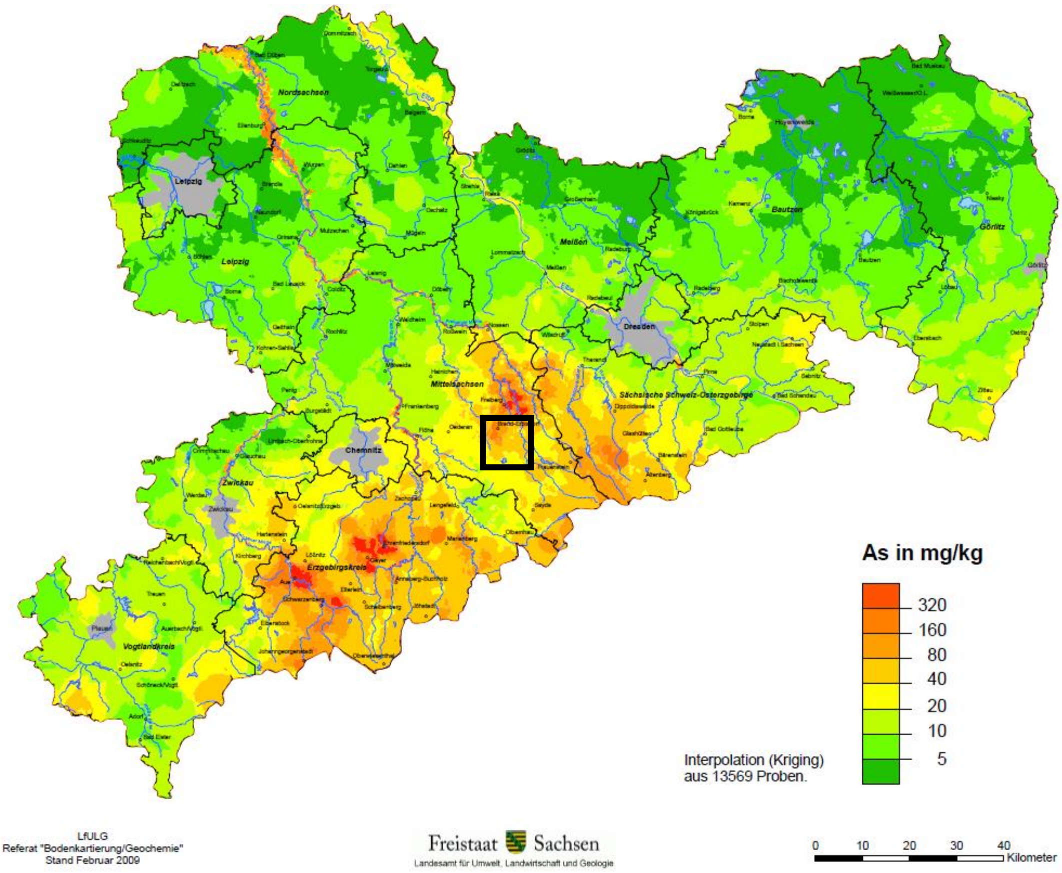

Fig. 1 Arsenic concentrations in the topsoil of Saxony, Germany. The Freiberg area is framed in black. Values interpolated by kriging from 13596 samples.

Source: (LfULG 2009)

The map shows that especially in the Erzgebirge in the southern part of Saxony, As concentrations are elevated and reach interpolated mean values of approximately 320 mg/kg. In addition, alluvial soil in the floodplains along rivers in this region has mean concentrations of 80–320 mg/kg due to drainage water from mining tunnels and discharged process water and sediments from ore processing industries. Altogether, about 288 km² are affected by arsenic concentrations exceeding the German regulation (e.g. 50 mg/kg as an action value for grassland and trigger value for residential areas). Detailed information on the As concentrations in soil for the area of Freiberg (framed in black in Fig. 1) is published online by LfULG (2001). The maps for As in topsoil and subsoil are presented in the following Fig. 2 and Fig. 3.

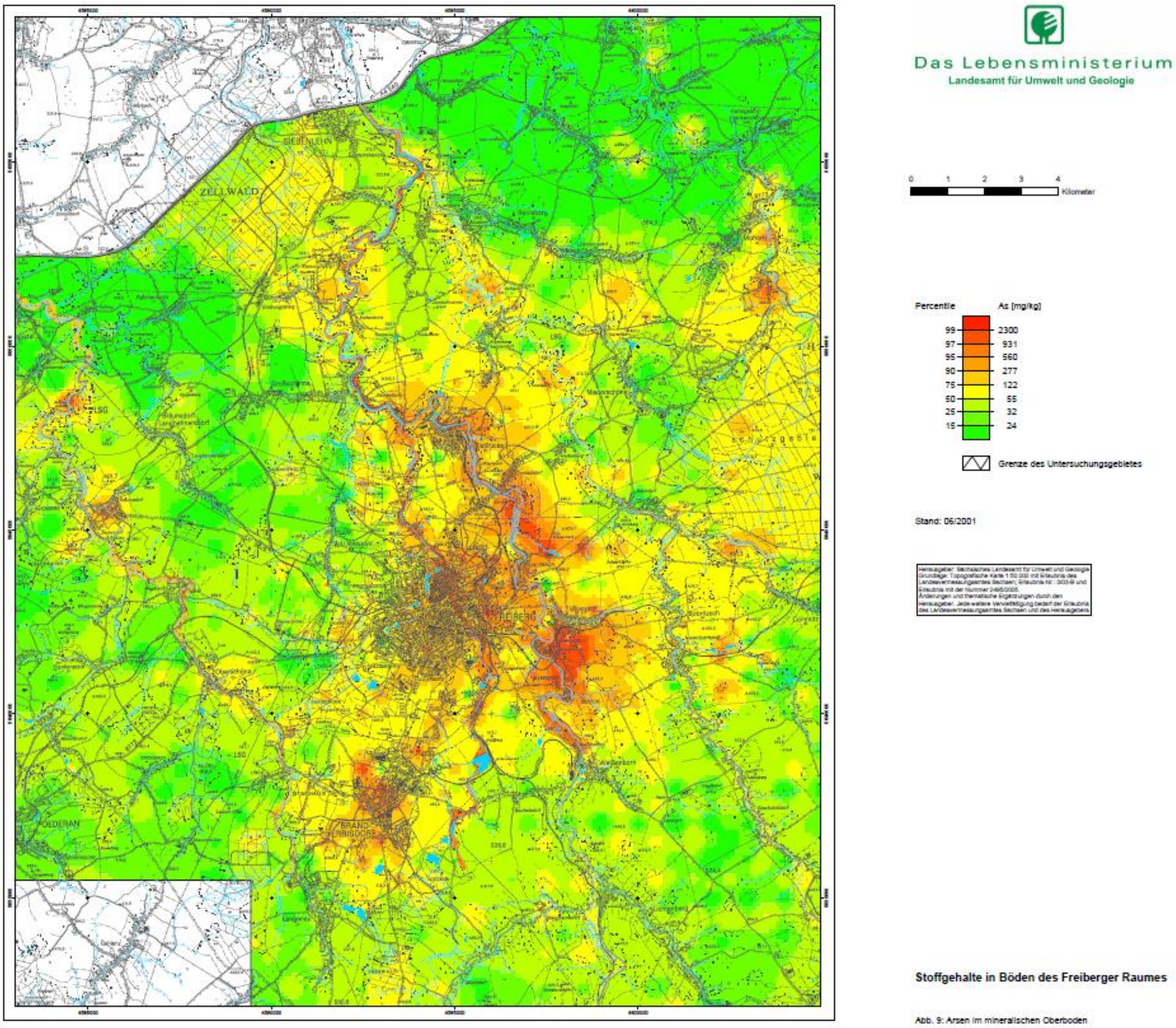

Fig. 2 As in topsoil in the Freiberg area
Source: LfULG (2001)

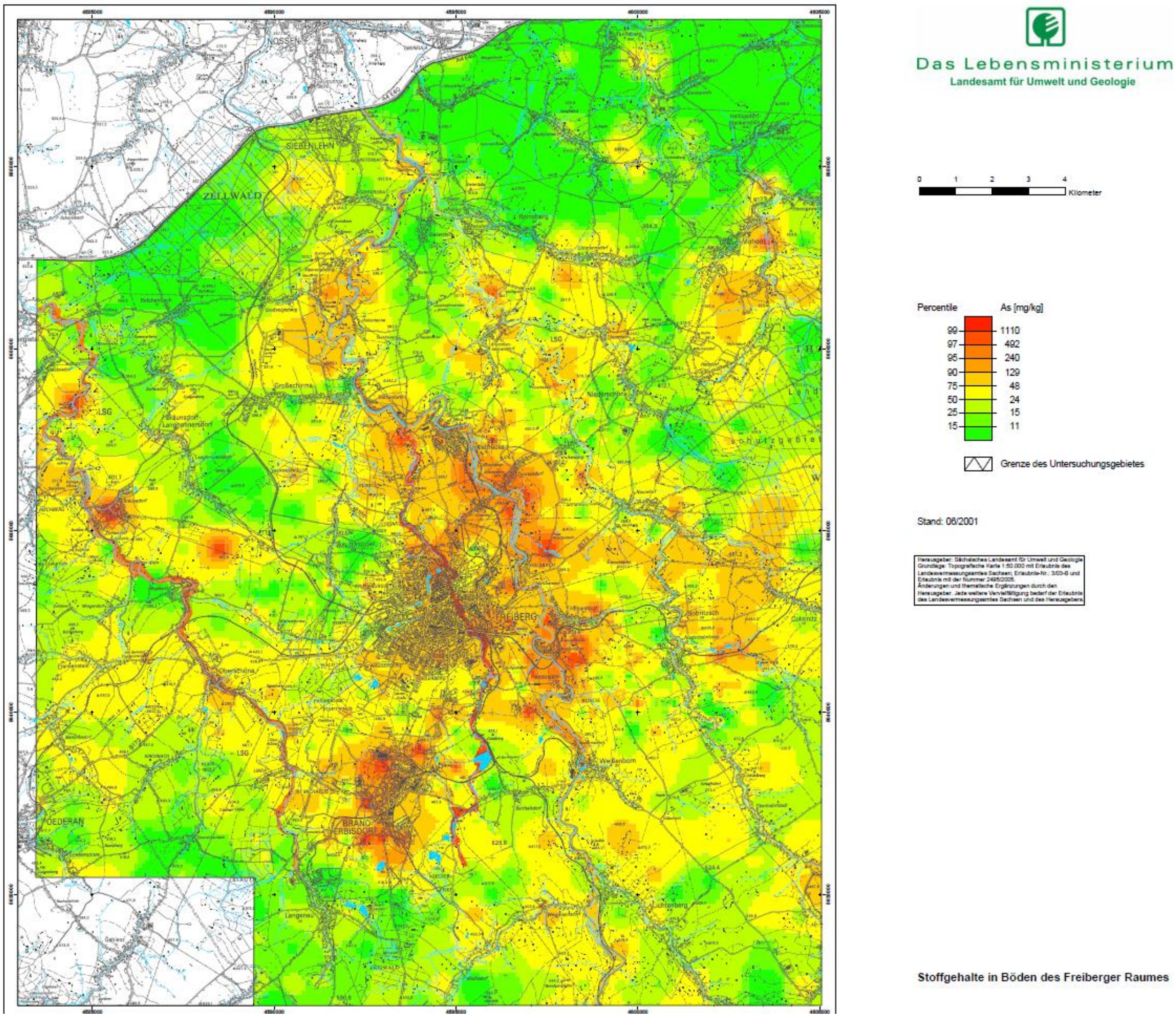

Fig. 3 As in subsoil in the Freiberg area
Source: LfULG (2001)

From the maps, it is clear that As concentrations are high in both topsoil and subsoil, confirming that As concentrations originate from both geogenic and anthropogenic sources. When comparing the As concentrations in the topsoil and subsoil in Fig. 2 and Fig. 3, it should be noted that the map legend is scaled differently, as the interpolated maximum value is 2300 mg/kg for topsoil and 1100 mg/kg for subsoil. At first glance, it appears that the concentrations in subsoil are higher than in topsoil, but taking into account the different scales, the values do not really differ.

The evaluation of pollutants in the soils of Freiberg and the assessment of the soil–human, soil–plant and soil–groundwater pathways have been documented (Rank *et al.* 2001) and partly discussed internationally (Hertwig et al. 2010; Müller et al. 2014; Müller et al. 2017a, 2017b). Further background values considering the relationships of the substrate units and the influence of different land uses such as arable, agricultural and forestry land were published in 2015 (Kardel & Müller 2015). It has to be mentioned that this report does not include municipal areas and areas influenced by mining activities (e.g. Freiberg), because it is intended to present natural background concentrations for the whole federal state of Saxony, allowing a general assessment of sites depending on their geogenic inventory.

Permanent soil monitoring site

One of the 55 sites of the Saxon Soil Monitoring Programme can be found close to Freiberg. The permanent soil monitoring site is equipped with instruments for measuring meteorological, chemical and physical parameters, which are continuously recorded and evaluated. Some of the instruments are installed in a cabin that protects them against adverse weather conditions. The cabin is shown in Fig. 4, and the measured parameters are listed in Table 1.

Fig. 4 Permanent soil monitoring site close to Freiberg (Source: H. Forberg, LfULG)

Table 1 Continuously measured parameters at the permanent soil monitoring site

Above ground	Underground	Additional
Weather/ climate: - Global radiation - Humidity - Air temperature - Wind speed - Wind direction - Precipitation As total deposition: - Main elements - Heavy metals - Nonmetals	Soil: - Temperature - Water suction tension - Water content Seepage water: - pH value - Electrical conductivity - Main elements - Heavy metals, arsenic - Nonmetals in leachate	- Plant constituents (heavy metals, arsenic) - Microbial biomass - Soil respiration

Pollutants can enter the soil via air or precipitation water. Furthermore, a change in the chemical soil conditions can cause the mobilisation of As and heavy metals. With the continuous monitoring of influencing parameters, changes in and the risks associated with pollutants (As, Cd, Pb) in soils can be detected at an early stage. Thus, appropriate preventive measures can be undertaken early. Detailed information on permanent soil monitoring in Saxony can be found in Barth *et al.* (2001).

The measured amount of As deposited in dust is listed in the following Table 2 for the years 2012 to 2016.

Table 2. Measured deposition of As in dust at the permanent soil monitoring site. (Data provided by LfULG).

Year	As Deposition [g/(ha*a)]	As Deposition [µg/(m^2*d)]	Limit value TA Luft [µg/(m^2*d)]
2012	12.66	3.47	4.00
2013	8.28	2.27	4.00
2014	13.74	3.76	4.00
2015	11.72	3.21	4.00
2016	8.07	2.21	4.00

The values show that the deposition of As varies between 8 and 14 g/ha*a (2.2 and 3.8 µg/m^2*d, respectively). The values do not exceed the limit value of 4.0 µg/m^2*d specified by German legislation (TA Luft). It can therefore be assumed that dust deposition in the Freiberg area is not a significant source of pollution. Nevertheless, these values are mean values for a whole year, and the exposure can therefore be higher at certain times. Particularly when dry soil is treated, such as during harvesting, dust and arsenic exposure can be much higher, and a potential risk for farmers cannot therefore be excluded. In addition, in the residential area of Freiberg, every soil-related construction site has to be kept under wet conditions (e.g. by spraying water) to avoid dust dispersion.

4 Background data for As in crops

Since a large part of the land in the Freiberg area is used for agriculture, extensive investigations were carried out into the transfer of As along the pathway from soil to plants in order to quantify the uptake of As in food and fodder. Investigations on soil with As concentrations of 50 and 100 mg/kg showed that grains contained between 0.5 and 1.0 mg As/kg, and the limit value of 2 mg/kg for fodder was not therefore exceeded, even though concentrations in other parts of the plants were higher than the limit value (Serfing and Klose 2008). It has also been shown that As uptake depends on the plant variety as well as on the type of soil, phosphate content and existing mycorrhization. (Serfing and Klose 2008) Based on the studies, recommendations were derived and are annually updated online for the treatment of arsenic and heavy metal contaminated soils to be used for agriculture and gardening (Klose 2015; Müller *et al.* 2017c). Investigations on EU FP7 greenland project sites showed that in most cases, As concentrations in plants were below 2 mg/kg, but maximum values of up to 16 mg/kg were also recorded. Accumulation in herbs was higher than in grass, which is why the careful cultivation of greenland sites is suggested in order to support the growth of grass instead of herbs (Haßler and Klose 2006). In order to assess the impact of polluted fodder from greenland sites, further investigations have been carried out with sheep (Boguhn *et al.* 2009).

5 Evaluation of available background data

The background data provided for Saxony is very extensive and forms the basis for the efficient and sustainable management of polluted sites. With permanent soil monitoring sites and research projects at laboratory and field scales, fundamental information on the fate of As in the environment has been obtained, which enables reliable risk assessment and the derivation of possible approaches to the treatment and management of polluted sites.

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Appendix 2

Background data for the Verdun study site in France

1 History of the site and reason for investigations

Almost 100 years after the end of the First World War, the scars of battle can still be observed along the front line. Hupy and Schaetzl (2008) investigated the effect of shelling on soil structure and landscape recovery after the conflict. Meerschman et al. (2011) assessed the regional spatial occurrence of heavy metals in topsoil of the former battlefield near Yper (Belgium) by performing optimized geostatistical modelling. The First World War was the first incidence of major warfare that made massive use of chemical weapons.

The history of the site selected for the AgriAs project is documented in detail in the publication "*Industrial-scale destruction of old chemical ammunition near Verdun: a forgotten chapter of the Great War*" (Hube 2017). The following information was sampled from this document. In 1918, the canton of Spincourt, near Verdun, already contained major quantities of German ammunition in dumps. On 17 November 1918, the creation of a huge ammunition dump was ordered by the allied armies near Spincourt, close to an existing German ammunition and material dump from the war (near Rampont farm in the village of Muzeray). In September 1919, the stock was evaluated at 1 million asphyxiating shells and 300,000 explosive rounds. Another document, dated 22 April 1922, mentions 1,500,000 chemical shells. They arrived by freight at Spincourt station. After sorting, the explosive ammunitions were destroyed using open-detonation methods. The demolition pits are located 800 m east of the village of Muzeray, in Warphemont forest. Subsequently, all chemical shells recovered after the Great War from the second and sixth military regions originated from a large section of the former Western Front and converged on the Spincourt canton and forest. The French probably began blowing up explosive shells immediately after the Armistice near the dump at the 'Noire Fontaine' destruction pits (commune of Vaudoncourt). Between the end of 1918 and 1919, large-scale ammunition destruction was carried out near and along the former Western Front. The Spincourt dump, previously under military authority, was transferred to Clere & Schwander in September 1919. This private firm retained the scrap, brass and other materials, which were recycled and sold for industrial or agricultural purposes. The recovered metals were sold for smelting, and the ammonium nitrates of the nitrated explosives were recycled as fertilizers. Clere & Schwander ceased working in the Spincourt canton in October 1924. Another private society, Pickett & Fils, recovered a residual stock of shells left behind in 1925 by a first ordnance removal contractor, and became the most important of such contractors in the interwar period in France. Between 1920 and 1925, Pickett & Fils operated 14 specialized plants in France, and ended operations in Spincourt forest in 1928. On the ground at the 'Place à Gaz' clearing, Pickett & Fils demolished at least 200,000 projectiles that a previous company was unable to destroy in a profitable manner, burning and emptying the German chemical shells, in particular those that contained arsenic. The German sneeze-provoking poison could not be eliminated in any other way. However, combustion was not always complete.

In the early 2000s, several sites where First World War chemical ammunition was destroyed were found to be contaminated by inorganic pollutants. Only two of these were extensively investigated: the first is located in Belgium (Bausinger and Preuss, 2005) and the second is northeast of Verdun in France (Bausinger et al., 2007). Chemical shells were disposed of by open burning at both of these sites during the 1920s. The munitions destroyed were mainly German “blue cross shells” containing emetic organoarsenical warfare agents. The Belgian burning ground has since been used for agriculture (Bausinger and Preuss, 2005), but the well characterized French site “Place-à-Gaz”, located in the forest, has been unaffected by human activities and undisturbed since destruction of the shells. Bausinger et al. (2007) showed that the “Place-à-Gaz” site had locally limited but severe soil contamination with arsenic, zinc, copper and lead, with concentrations respectively reaching 150 g/kg, 130 g/kg, 15 g/kg and 25 g/kg. The metals came from various parts of the munitions. The shells mainly contained iron, while the fuses, driving bands and shell casings were made from copper or zinc. Lead was used for shrapnel balls, primary explosives and chemical warfare equipment. “Blue cross shells” were filled with diphenylchloroarsine (Clark I) and diphenylcyanoarsine (Clark II). These organoarsenical compounds were probably oxidized during combustion, releasing huge amounts of inorganic arsenic into the surrounding environment. Bausinger et al. (2007) estimated that, over a century, most of the arsenic oxides have been transformed into arsenates or sorbed onto iron oxides or clays, abundant in the inherited soil.

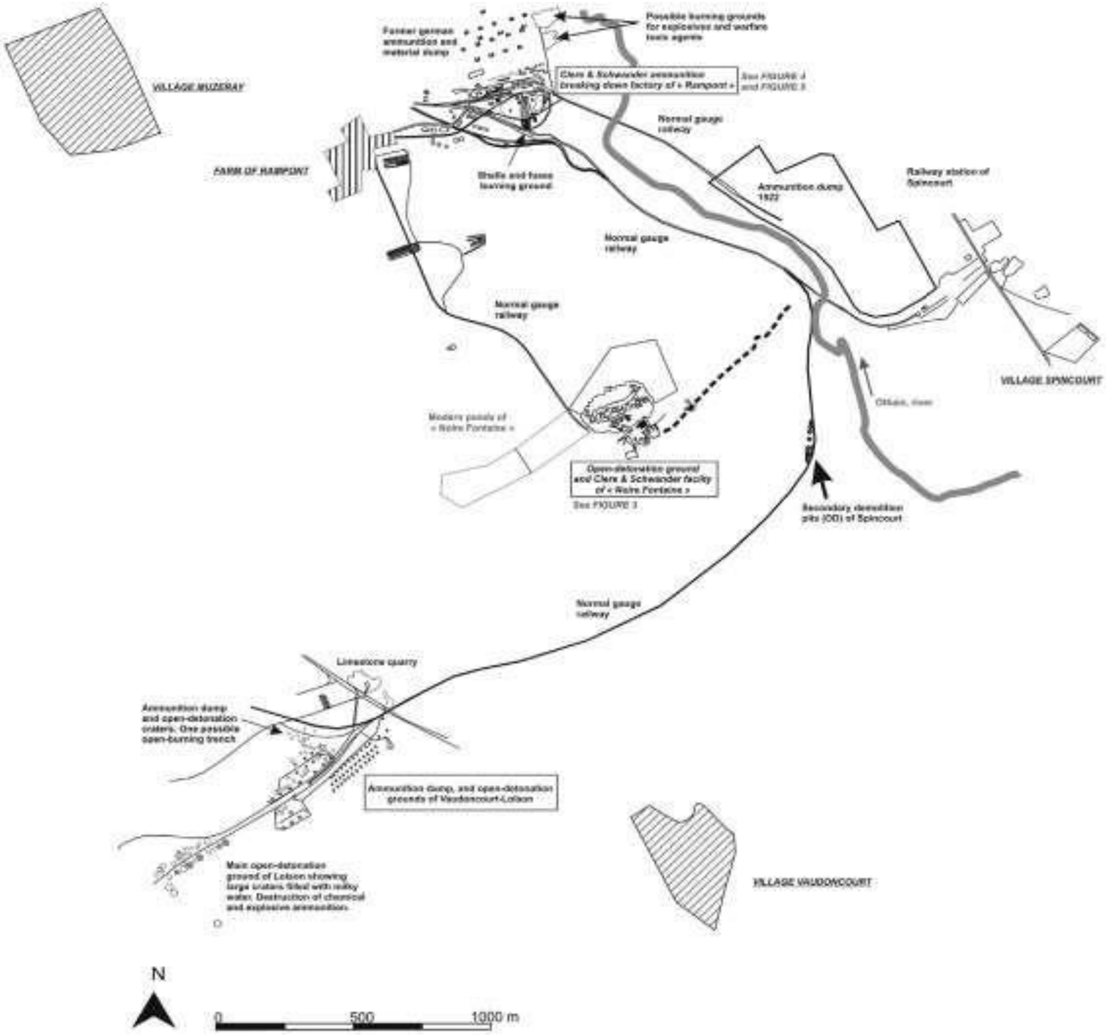


Fig. 1 The Clere & Schwander chemical ammunition complex. Commune of Muzeray, Vaudoncourt. Source: Hube 2017.

The large “Clere & Schwander Meuse” site is now comprises 100 ha of farmland and grassland, and the extended characterization of the polluted zones of this large site is in progress.

2 Background data for surface water

Arsenic concentrations markedly higher than the background level were detected in the River Othain near the studied site. The surface water of the River Othain shows a high natural arsenical background (Table 1) in relation to a high geochemical background in the sediments (25 to 29 mg As/Kg DM).

Table 1. Results of arsenic species quantification in surface water of the AgriAs site near Verdun

Sampling date	25/08/2016	21/12/2017
Unit	µg/L	µg/L
OTHAIN upstream	2.48	1.56
OTHAIN downstream	2.53	1.36

Results of the AgriAs project

Samples of surface water were collected in the framework of the AgriAs project in May 2017. The results are presented in Table 2. The highest concentration was found in a pond on the site, with 125 µg/L total As. Diverse arsenic species were detected in this surface water.

Another sample was collected from the pond in August 2017. It revealed a high concentration of diphenylarsinic acid (23.6 µg/L).

Table 2. Results of arsenic species quantification in surface water of the AgriAs site near Verdun

		Verdun May 2017	
		Pond	**Spring**
	pH	7.7	7.55
	Eh mV (ref H2)	357	366.2
	dissolved O2 mg/L	4.33	8.26
As III	µg/l	<QL	0.94
As V	µg/l	75.6	<QL
Arsenobetaine	µg/l	0.72	<QL
DMA	µg/l	1.97	<QL
MMA	µg/l	8.99	<QL
Other As species	µg/l	38.12	0.41
Total As	**µg/l**	**125.4**	**1.35**

3 Background data for soil

A common characteristic of the different sites polluted with arsenic by the destruction of chemical ammunition in Verdun region is the high heterogeneity in the spatial distribution of arsenic concentrations, with localised very high concentrations (more than 1000 ppm, Thouin et al., 2016) and strong gradients, with concentrations in nearby non-polluted zones being as low as 20 ppm. A diagram of arsenic in topsoil (0–20 cm) at the site selected for the AgriAs project, with sampling performed before the beginning of this project, is presented in Figure 2.

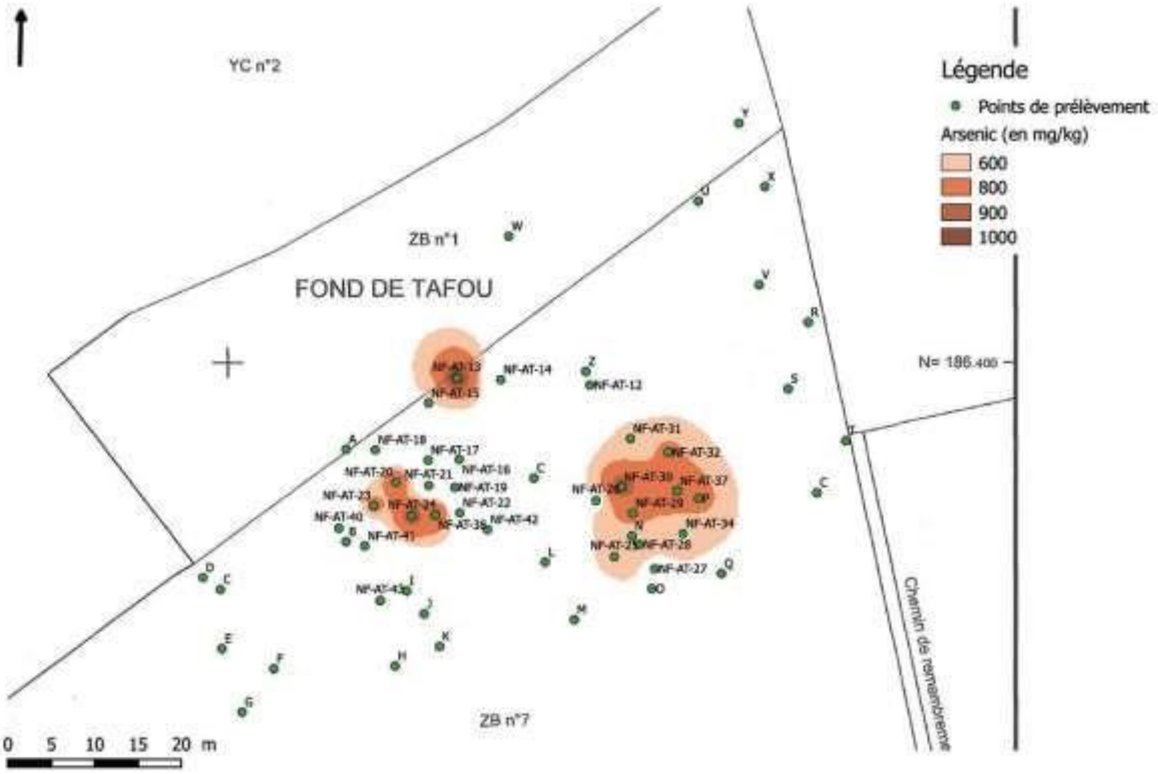


Fig. 2. As in topsoil at the Verdun site selected for the AgriAs project. Source: D. Hube, personal communication.

Arsenic is present in some compounds constituting the large series of organic and inorganic pollutants inherited from the destruction of WWI chemical ammunition present at the sites: PAHs, dioxins, nitro-aromatic compounds, chlorate and perchlorate, and metals (Zn, Pb, Cu, Hg, Cd, Sn). In the specific zone studied in the Agri-As project, arsenic is the main element of the metal/metalloids group previously quantified.

Results of the AgriAs project

The field is located 25 km northeast of Verdun. The field was used as a pasture in 2002 and was cultivated from 2002 to 2015. Since 2015, it has been fallow ground because cultivation was forbidden when the pollution was detected. The sampling was performed in May 2017. Many vegetal species could be observed. The diversity was lower in the most polluted locations, but plants were observed even in these places. Soils were sampled in a reference zone far from the polluted area, and along a three-zone transect representing a gradient of As pollution. Soils were sampled from the 0–20 cm layer. Each sample was taken as a composite of 5 points from 3 m x 3 m squares. The arsenic concentration in the soil surface was determined on site with an X-ray fluorescence (NITON) analyser. The speciation of arsenic was performed by HPLC-ICP-MS after H_3PO_4 extraction. Diphenylarsinic acid was determined by HPLC-DAD and apolar organoarsenicals by GC/MS.

The arsenic concentration ranged from 15 ppm in the unpolluted reference area of the site to 775 ppm in the highly polluted location (Table 3).

Table 3. Concentrations of arsenic species in the soil samples. ND: not detected

Zones	AsV ppm	AsIII ppm	Diphenylarsinic acid ppm	Triphenylarsine ppm
Reference	15	0.3	ND	ND
Transect Low	20	0.2	ND	ND
Transect Medium	192	1.4	ND	ND
Transect High	756	14.4	2.19	0.95

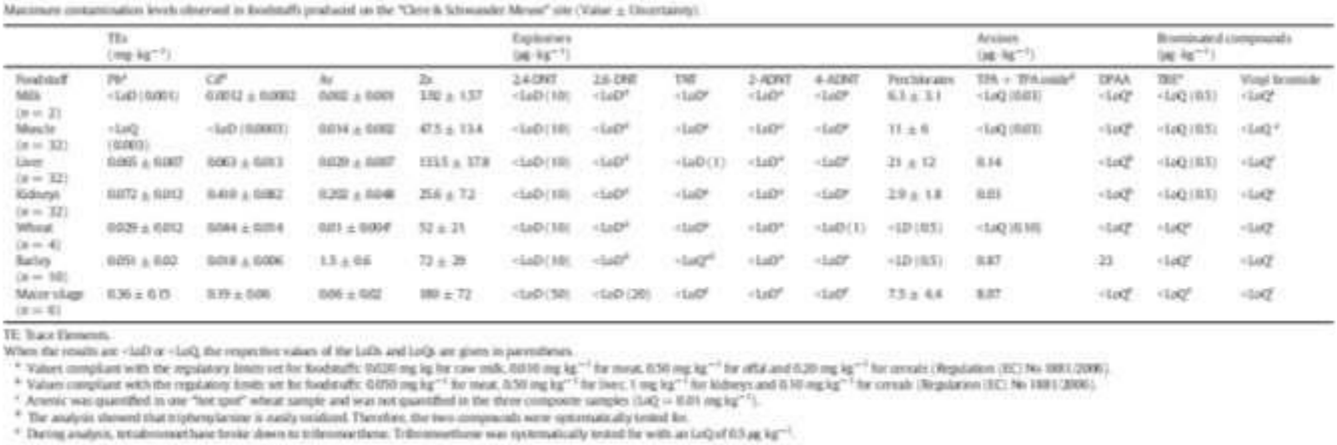
The main arsenic form was AsV, although the proportion of AsIII was higher in the polluted location. Two organic molecules derived from the weapons were only detected in the highly polluted zone: diphenylarsinic acid and thriphenylarsine.

4 Background data for As in crops and foodstuffs

The “Clere & Schwander Meuse” site now comprises 100 ha of farmlands and grasslands. The agricultural production in this zone includes cereals for human consumption (soft winter wheat, winter and spring barley) and maize silage for the feeding of the dairy cow herds of two local farms. The analysis undertaken by the BRGM in the “Clere & Schwander Meuse” area revealed the presence in nearby forest soils of nitrates, zinc, arsenic, organo-arsenical agents, tetrabromoethane (a solvent used for the manufacture of arsenic warfare agents) and locally high levels of nitroaromatic compounds (BRGM, 2015). Consequently, the French Agency for Food, Environmental and Occupational Health & Safety (Anses) was asked to determine whether the consumption of plant and animal products originating from this area was safe for consumers (Gorecki et al., 2017).

Samples of maize silage, barley and wheat were collected for analysis from seven growing plots located on the “Clere & SchwanderMeuse” site. Regarding straw cereals (barley and wheat), in order to ensure representative samples for each plot, ten sampling points were randomly selected in the field. These ten sub-samples were pooled into equal shares to form composite samples before the analysis. Additional samples were taken in highly contaminated areas (referred to as “hot spots”) determined by the BRGM based on the preliminary soil analyses. As for foodstuffs of animal origin, two dairy cattle farms were considered in this study because their animals were fed with maize silage grown on the “Clere & SchwanderMeuse” site. Therefore, 32 animals including 16 dairy cows, one heifer, three young bulls and 12 calves from these two farms were slaughtered. For each of these animals, muscle, liver and kidney tissues were sampled for analyses. Composite samples of raw milk were constituted for analysis. All the samples were shipped in a frozen state to the laboratories in charge of the analyses.

The maximum contamination levels detected in the frame of this study are presented in Table 4.



Maximum contamination levels observed in foodstuffs produced on the "Clere & Schwander Meuse" site (Value ± Uncertainty).

	TEs (mg kg⁻¹)				Explosives (µg kg⁻¹)						Arsines (µg kg⁻¹)		Brominated compounds (µg kg⁻¹)	
Foodstuff	Pb	Cd	As	Zn	2,4-DNT	2,6-DNT	TNT	2-ADNT	4-ADNT	Perchlorates	TPA + TPA oxide	DPAA	TBE	Vinyl bromide
Milk (n = 2)	<LoD (0.001)	0.0012 ± 0.0002	0.002 ± 0.001	3.92 ± 1.57	<LoD (10)	<LoD	<LoD	<LoD	<LoD	6.3 ± 3.1	<LoQ (0.03)	<LoQ	<LoQ (0.5)	<LoQ
Muscle (n = 32)	<LoQ (0.003)	<LoD (0.0003)	0.014 ± 0.002	47.5 ± 13.4	<LoD (10)	<LoD	<LoD	<LoD	<LoD	11 ± 6	<LoQ (0.03)	<LoQ	<LoQ (0.5)	<LoQ
Liver (n = 32)	0.065 ± 0.007	0.063 ± 0.013	0.029 ± 0.007	153.5 ± 37.8	<LoD (10)	<LoD	<LoD (1)	<LoD	<LoD	21 ± 12	0.14	<LoQ	<LoQ (0.5)	<LoQ
Kidneys (n = 32)	0.072 ± 0.013	0.410 ± 0.082	0.202 ± 0.048	25.6 ± 7.2	<LoD (10)	<LoD	<LoD	<LoD	<LoD	2.9 ± 1.8	0.03	<LoQ	<LoQ (0.5)	<LoQ
Wheat (n = 4)	0.029 ± 0.012	0.044 ± 0.014	0.01 ± 0.004	52 ± 21	<LoD (10)	<LoD	<LoD	<LoD	<LoD (1)	<LD (0.5)	<LoQ (0.10)	<LoQ	<LoQ	<LoQ
Barley (n = 10)	0.051 ± 0.02	0.018 ± 0.006	1.5 ± 0.6	72 ± 29	<LoD (10)	<LoD	<LoQ	<LoD	<LoD	<LD (0.5)	0.87	23	<LoQ	<LoQ
Maize silage (n = 6)	0.36 ± 0.15	0.19 ± 0.06	0.06 ± 0.02	180 ± 72	<LoD (50)	<LoD (20)	<LoD	<LoD	<LoD	7.5 ± 4.4	0.07	<LoQ	<LoQ	<LoQ

TE: Trace Elements.

When the results are <LoD or <LoQ, the respective values of the LoDs and LoQs are given in parentheses.

[a] Values compliant with the regulatory limits set for foodstuffs: 0.020 mg kg for raw milk, 0.010 mg kg⁻¹ for meat, 0.50 mg kg⁻¹ for offal and 0.20 mg kg⁻¹ for cereals (Regulation (EC) No 1881/2006).

[b] Values compliant with the regulatory limits set for foodstuffs: 0.050 mg kg⁻¹ for meat, 0.50 mg kg⁻¹ for liver, 1 mg kg⁻¹ for kidneys and 0.10 mg kg⁻¹ for cereals (Regulation (EC) No 1881/2006).

[c] Arsenic was quantified in one "hot spot" wheat sample and was not quantified in the three composite samples (LoQ = 0.01 mg kg⁻¹).

[d] The analysis showed that triphenylarsine is easily oxidized. Therefore, the two compounds were systematically tested for.

[e] During analysis, tetrabromoethane broke down to tribromoethene. Tribromoethene was systematically tested for with an LoQ of 0.5 µg kg⁻¹.

Table 4. Concentrations of arsenic and other contaminants in foodstuffs produced at the site. Source: Gorecki et al., 2017.

The contaminants considered in this study were trace elements (TEs, primarily Zn, As, Pb and Cd), nitroaromatic explosives (trinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2-amino-4,6-dinitroluene and 4-amino-2,6-dinitrotoluene), phenylarsenic compounds including diphenylarsinic acid and triphenylarsine, perchlorate, tetrabromoethane and vinyl bromide. Depending on the compound, different approaches were used to assess the risk to both adults and children. Exposure to these contaminants through the consumption of foodstuffs produced locally on the considered site was 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.

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