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Research Paper

Risk management for arsenic in agricultural soil–water systems: lessons learned from case studies in Europe

Kirsti Loukola-Ruskeeniemi [a,*], Ingo Müller [b], Susan Reichel [c], Celia Jones [d], Fabienne Battaglia-Brunet [e], Mark Elert [d], Marina Le Guédard [f], Tarja Hatakka [a], Jennifer Hellal [e], Isabel Jordan [c], Juha Kaija [a], Riitta L. Keiski [g], Jana Pinka [c], Timo Tarvainen [a], Auli Turkki [g], Esa Turpeinen [g], Hanna Valkama [g]

[a] Geological Survey of Finland, P.O. Box 96, FI-02151 Espoo, Finland
[b] Saxon State Office for Environment, Agriculture and Geology, Dep. 42 Soil, Contaminated Sites, Halsbrückerstr. 31a, 09599 Freiberg, Germany
[c] G.E.O.S. Ingenieur-gesellschaft mbH, Postfach 1162, 09581 Freiberg, Germany
[d] Kemakta Konsult AB, Box 126 55, 112 93 Stockholm, Sweden
[e] BRGM, 3 avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex 2, France
[f] LEB Aquitaine Transfert-ADERA, 71. Avenue Edouard Bourlaux, CS20032, 33140 Villenave d'Ornon, France
[g] University of Oulu, Environmental and Chemical Engineering Research Unit, University of Oulu, P.O. Box 4300, FI-90014, Finland

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ABSTRACT

Chronic exposure to arsenic may be detrimental to health. We investigated the behaviour, remediation and risk management of arsenic in Freiberg, Germany, characterized by past mining activities, and near Verdun in France, where World War I ammunition was destroyed. The main results included: (1) pot experiments using a biologically synthesized adsorbent (sorpP) with spring barley reduced the mobility of arsenic, (2) the Omega-3 Index ecotoxicological tests verified that sorpP reduced the uptake and toxicity of arsenic in plants, (3) reverse osmosis membrane systems provided 99.5% removal efficiency of arsenic from surface water, (4) the sustainability assessment revealed that adsorption and coagulation–filtration processes were the most feasible options for the treatment of surface waters with significant arsenic concentrations, and (5) a model was developed for assessing health risk due to arsenic exposure. Risk management is the main option for extensive areas, while remediation options that directly treat the soil can only be considered in small areas subject to sensitive use. We recommend the risk management procedure developed in Germany for other parts of the world where both geogenic and anthropogenic arsenic is present in agricultural soil and water. Risk management measures have been successful both in Freiberg and in Verdun.

1. Introduction

There are no globally accepted recommendations, regulation or guidelines for arsenic (As) in agricultural soil and water, even though dietary intake is an important source of exposure (*e.g.*, Nachman et al., 2018; Shibata et al., 2016) and As-contaminated irrigation water leads to transfer into crops and vegetables (*e.g.*, Bhatti et al., 2013).

Chronic exposure to inorganic As may cause various illnesses, from cognitive impairment, mental health and skin disorders to different types of cancer (*e.g.*, Pearce et al., 2012; Cubadda et al., 2017; Chen and Costa, 2021). Current guideline values and risk management recommendations for As mainly focus on drinking water even though rice has been proved to be another major exposure route to humans (*e.g.*, Heikens et al., 2007; Signes-Pastor et al., 2021; Upadhyay et al., 2019; Mondal et al., 2020). Arsenic uptake from water and soil to maize may represent an important exposure route for humans and livestock as well, especially in Latin America, Africa and Asia, where maize consumption is high (Rosas-Castor et al., 2014).

In plants, As is mainly taken up by root adsorption through distinct pathways and transporters, depending on both the plant species and the chemical speciation of As in soil. In general, the higher the total soil As concentration, the greater the uptake of As by crops (Punshon et al., 2017), with the exception that As can be immobilized by iron oxides in aerated soils derived from iron-bearing bedrock or an influx of

* Corresponding author.
E-mail address: kirsti.loukola-ruskeeniemi@gtk.fi (K. Loukola-Ruskeeniemi).

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iron-bearing groundwater (Gerdelidani et al., 2021). Arsenic accumulation generally decreases from roots to seeds (Allevato et al., 2019). The accumulation of As varies between different plants; for example, rice accumulates more than eggplant (Huang et al., 2006). Transfer and accumulation vary between plants species and cultivars and with the characteristics of the soil and growing substrate, including amendments (Mench et al., 2006).

An understanding of primary As sources is essential to prevent exposure *via* water, food and fodder (*e.g.*, Mahimairaja et al., 2005). In one of our study areas in Saxony, Germany, elevated As concentrations basically result from geological events that occurred millions of years ago (Banning, 2021). In another study area, in Verdun, France, As contamination occurs because of the destruction of ammunition.

Exposure to As *via* the oral ingestion due to contact with As-rich soil depends on bioaccessibility (Martínez-Sánchez et al., 2013) which has been shown to depend on soil properties (Petruzzelli et al., 2019; Lake et al., 2021). Frequent access to bare soil by children playing on the ground can lead to the intake of soil hand-to-mouth, generating a higher As-related risk compared to adults (Yin et al., 2021), especially if the intake of As from soil and vegetables is added as a result of gardening activities (Manjón et al., 2020). Moreover, contaminated bare soil can be a local source of dust if both dryness and wind frequently occur, directly affecting human health *via* the inhalation of dust (Tu et al., 2020; Zhang et al., 2020) or *via* deposition onto crops and vegetables (Manjón et al., 2020) or grassland (Steinhöfel and Müller, 2018). Dust can also affect water bodies and rainwater harvesting systems used to provide drinking water (Quaghebeur et al., 2019). Arsenic associated with foodstuff such as vegetables can be mainly present as polluted soil particles adherent to the edible parts, in this case cleaning and dust control may reduce the associated risk (Paltseva et al., 2018).

The main goal of our research was to develop As risk management options starting from risk assessment. Therefore, we evaluated the As content of soil and water at two agricultural sites in central Europe and developed treatment methods. Our research covered water, soil, microorganisms, plants, risk management, and ecological and health risks. Ecological risks are linked to both soil and aquatic ecosystems. Risk assessment considered risks originating both from the study site and from other sources. Risk management refers here to actions aimed at avoiding and minimizing risks to humans (health risks, excluding occupational health) and risks to other organisms in the environment (ecological risks).

Comprehensive data from our study sites formed the backbone for the strategy development. Since the data has mostly not been published in English before, please see a summary of previous studies in the following section. The materials and methods of the present project are described in Section 3 and the results are provided in Section 4. Finally, we present a general procedure for the establishment of a risk management strategy.

2. Previous projects in the study areas

2.1. Arsenic concentrations in agricultural topsoil in Europe

An important data source for European agricultural soil is the GEMAS dataset (Reimann et al., 2014a, 2014b). During 2008–2009, a total of 2108 soil samples from ploughed agricultural land (0–20 cm) and 2023 soil samples from grazing land (0–10 cm) were collected at a density of 1 site/2500 km^2 each from 33 European countries (Fig. 1a). The samples were analysed for 52 chemical elements after aqua regia extraction, for 41 elements by XRF (total) and for soil properties and pH ($CaCl_2$) following external quality control procedures. The GEMAS project provided data on element concentrations, including total and *aqua regia* extractable concentrations of As, as well as soil properties known to influence bioavailability and toxicity.

Another project, the FOREGS Geochemical Baseline Mapping Programme, included 151 sampling sites representing agricultural soil (Salminen et al., 2005). The total As concentration in topsoil (0–25 cm) and in subsoil (*ca.* 50–75 cm) and the concentrations of As in adjacent stream water can be found in this dataset. Sampling sites located in randomly selected small drainage basins (<100 km^2) in Austria, the Czech Republic, Estonia, France, Germany, Hungary, Italy, Latvia, Lithuania, Poland, Portugal, Spain, Switzerland and the United Kingdom. Both GEMAS and FOREGS datasets include determinations of total As concentrations analysed by strong multi-acid extraction from the < 2 mm size fraction and *aqua regia* extractable As concentrations analysed from the < 2 mm size fraction of soil samples.

2.2. Previous studies in Saxony, Germany

The Freiberg region in Saxony has a history of mining and ore processing activities extending over more than eight centuries (Schirmer, 2001; Richter and Schwabenicky, 2007). The silver deposits consist of more than a thousand polymetallic hydrothermal veins. Silver minerals, mainly Ag_2S, are accompanied by arsenopyrite (FeAsS) and proustite ($Ag_3[AsS_3]$), which are mainly responsible for widespread As pollution in the region (Ossenkopf et al., 1993; Baumann et al., 2001). Numerous investigations have been carried out to establish an extensive database for risk assessment (*e.g.*, Büschel et al., 2010; Landesdirektion Chemnitz, 2011a, 2011b; Klose, 2012; Landesamt für Umwelt, Landwirtschaft und Geologie, 2020b). There are several permanent soil monitoring sites providing information on As concentrations in soil, seepage water and plants under changing seasonal conditions. A recently updated survey comprising over 1000 km^2 of agricultural land and 2000 km^2 of soil in Saxony yield geochemical data from some 40 000 soil samples (Landesamt für Umwelt, Landwirtschaft und Geologie, 2020b). Since a large part of the land in the Freiberg area is used for agriculture, extensive research has been carried out to investigate the transfer of As, Cd, and Pb into agricultural crops. Laboratory studies using pot trials as well as field studies have been performed, testing different cultivars and several amendment procedures for the amelioration of soil (Klose, 1998, 2012; Haßler and Klose, 2006; Serfling and Klose, 2008; Müller et al., 2017; Neu et al., 2018a, 2018b, 2020; Röhricht et al., 2011).

2.3. Previous studies in Verdun, France

The contaminated site represents a facility for the destruction of World War I chemical weapons. The land has been used for agricultural purposes (Hube, 2017). This land was exploited for pasture until 2012 and then converted to crop production for human and animal consumption (wheat, barley and corn) from 2012 to 2015. In 2015, investigations were performed on agricultural soils, which revealed high concentrations of toxic organic compounds, heavy metals (Zn, Pb and Cu) and As (Hube, 2017). Consequently, studies were conducted in 2015–2016 to assess the risk to human health through the consumption of plant and animal products originating from this area (ANSES, 2016; Gorecki et al., 2017). These studies suggested that cereals should not be grown on certain plots because of high concentrations of inorganic As. Cultivation was banned and some fields have remained fallow ground since 2015. In 2017, our research project started and focused on these plots, with varying concentrations of As ranging from 15 mg/kg in the reference zone to 775 mg/kg in the highly contaminated site.

2.4. Previous studies in the Tampere-Hämeenlinna region, Finland

The geogenic 'As province' of the Tampere-Hämeenlinna region in southern Finland contains some 5 mg As in the fine fraction of glacial till. The concentration is not high compared with those met close to sulphide deposits and occurrences, but the concentration is higher than the average values in Finnish glacial till. The As-rich veins are in many cases associated with mafic volcanic intrusions. Risk assessment and risk management of As has been studied in two projects co-funded by the European Union, namely the RAMAS project 'Risk assessment and risk

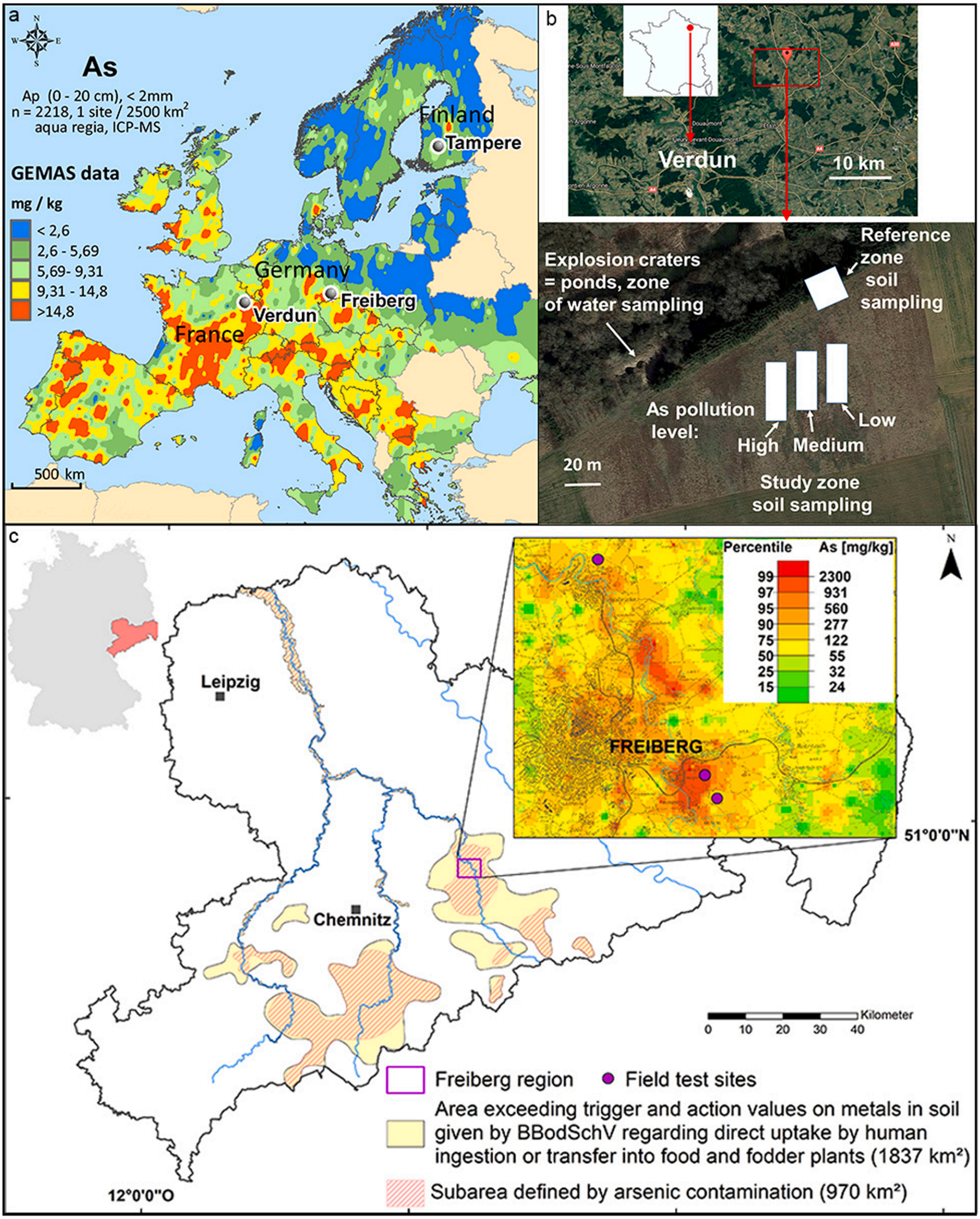

Fig. 1. a. Arsenic concentrations in European agricultural soils (0–20 cm) and the locations of the study areas: Verdun in France and Freiberg in Germany. The results were compared with those from the Tampere region in Finland, representing geogenic arsenic concentrations in bedrock and glacial till. **b**. The study area near Verdun, France, where World War I ammunition was destroyed (Hube, 2017). **c**. Contaminated sites in Saxony, Germany, based on a total of 39 578 geochemical soil samples (Landesamt für Umwelt, Landwirtschaft und Geologie, 2020a). Data on industrial, brownfield and waste disposal sites were excluded. The arsenic content in

soil and at the field test sites is presented on a detailed map of the Freiberg region.
a. Source: GEMAS data (Reimann et al., 2014a, 2014b).

management procedure for arsenic in the Tampere region' and the ASROCKS project 'Guidelines for sustainable exploitation of aggregate resources in areas with elevated arsenic concentrations' (Loukola-Ruskeeniemi et al., 2007; Parviainen et al., 2015). In addition, the Geological Survey of Finland has investigated the geochemical baseline values.

3. Materials and methods

3.1. Inventory of European and country-wide geochemical databases

We summarized European-wide databases and publications on As concentrations in soil and water in order to identify areas with high As concentrations and areas for which data are lacking. This was followed by a literature review and a questionnaire on national-level data sources concerning As concentrations in agricultural soil and water.

In addition to the evaluation of the GEMAS (Reimann et al., 2014a) and FOREGS (Salminen et al., 2005) datasets, we carried out a literature review and a questionnaire study in most European countries.

3.2. Studies in the Freiberg area in Germany

In the Freiberg region in Germany the geochemical baseline values for As are naturally elevated (Banning, 2021). For the present research, the field work and sampling campaign was carried out on 17 August 2017 on a 10 m x 10 m area. The sampled soil was used to perform experiments dedicated to studying the effect of fertilizers (organic amendment and lime ammonium nitrate) and to test soil treatment using mineral amendment (Table 1). Various analytical methods were tested for the determination of contaminants in soil. *Aqua regia* extraction (DIN EN 41617, 2012) was used to determine the pseudo-total As concentration in soil, while a laboratory-scale intestinal model procedure according to DIN 19738 (2017) was used to obtain bioavailability *via* oral human ingestion. To evaluate the As content available to plants, soil samples were extracted with 1 M NH_4NO_3 according to DIN, 1997. The water-soluble As concentration was determined by water extraction (1:10 w/w) using the procedure described in DIN 38414 part 4 (1984). All filtered (<0.45 μm) extracts were finally analysed by ICP-MS for dissolved As.

3.3. Studies at a site near Verdun, France

The site is a sensitive area for both agriculture and groundwater. Two sampling campaigns were carried out by the French team in the commune of Muzeray, 25 km northeast of Verdun. This site is affected by the historical legacy arising from the destruction of World War I chemical ammunition (Bausinger et al., 2007). Soil sampling was performed on 15–16 May 2017 for two types of laboratory experiments whose results are presented in previous reports but exploited here for risk assessment, *i.e.* a microcosm (Battaglia-Brunet et al., 2021) and a pot experiment with barley (Battaglia-Brunet et al., 2019). Soils were sampled in a reference zone, far from the contaminated area, and along a three-zone transect representing a gradient of pollution with As (Battaglia-Brunet et al., 2018), namely low (close to 15 mg/kg As), medium (200 mg/kg As) and high concentrations (800 mg/kg As).

Soils were sampled in the 0–20-cm layer with an auger for small quantities and with a spade for larger amounts. Each sample was taken as a composite of 5 points from 3 m x 3 m squares. The quantities sampled from five points were mixed to form a composite sample. Small samples of soils for analyzes were mixed in a bucket and sieved to 4 mm before sub-sampling into three sterile plastic bags. Larger samples were gathered in plastic bins for all laboratory experiments of the project.

Table 1
Two examples of pot experiment designs used in our studies testing agricultural amendments and iron-based adsorbents.

A pot experiment by BRGM to investigate the impact of agricultural amendments on arsenic mobility in Freiberg soil.	
Applied amendment	Lime-ammonium nitrate
Test conditions	3 different dosages of fertilizer (1 g, 10 g, 100 g)
Number of replicates	1
Tested cultivar	Spring barley
Amount of soil per pot	14 kg
Analyses of soil	Leaching test using Mont Roucous natural mineral water Arsenic speciation using the ion exchange method Separation of As (III) and As (V) using anionic resin (AG 1-X8©, Biorad, Hercules, CA, USA)
Analyses of plants	AsIII and AsV in the grains, HPLC – ICP-MS after extraction with HNO_3 0.28–90 min at 95 °C.
Analyses of plants	Omega-3 Index of leaves (NF EN ISO 21479, 2020) Concentration of arsenic in crops at harvest, extraction with HNO_3
Pot experiments to investigate the immobilization of As in Freiberg soil using a novel iron-based adsorbent produced by G.E.O.S.	
Applied amendments	Basic fertilization for each condition Adsorbent sorpP Adsorbent sorpP modified with pH-stabilizing agents (chalk, ash) Additional (double) phosphorus (P) fertilization
Test conditions	1 control without adsorbent 3 tested adsorbent modifications: sorpP pure, sorpP + chalk, sorpP + ash 3 different adsorbent dosages: 0.125%, 0.25% and 0.50% w/w 1 doubled P fertilization at a moderate adsorbent dosage of 0.25% w/w: sorpP pure +P, sorpP + chalk + P, sorpP + ash + P
Number of replicates	3 per condition
Tested cultivar	Spring barley
Amount of soil per pot	5.5 kg
Analyses of soil	Most probable number and activity of As(III)-oxidizing and As(V)-reducing microorganisms Concentration of As, Cd, Pb (extraction with aqua regia, extraction with ammonium nitrate) Concentration of P (extraction with calcium acetate lactate) Soil pH (0.01 M $CaCl_2$ extract)
Analyses of plants	Omega-3 Index of leaves at the 3–4-leaf stage and at harvest (NF EN ISO 21479, 2020) Concentrations of As, Cd and Pb in crops at harvest (by digestion treatment using a solution of HNO_3 and H_2O_2 and a microwave oven)

During the same sampling campaign, plants were collected, identified and analysed for their As content (Battaglia-Brunet et al., 2018), and the ecotoxicological effect of As was evaluated using the standardized Omega-3 Index test (NF EN ISO 21479, 2020). More precisely, this ecotoxicological test measures the peroxidation of polyunsaturated fatty acids in plant leaves induced by available contaminants present in soils.

Finally, water samples were collected from ponds close to the soil sampling area (please see figures in the Supplementary Materials). Water samples were filtered using 0.2-μm filters and transferred to anaerobic sterile N_2-filled bottles for As speciation, which was performed by the UT2A Laboratory (Pau, France) by HPLC (high performance liquid chromatography) coupled to an inductively coupled plasma mass spectrometry (ICP-MS) method. The total As concentration in pond water was 125 μg/l, and the speciation included 75.6 μg/l AsV, 0.72 μg/l arsenobetaine, 1.97 μg/l dimethylarsine (DMA), 8.99 μg/l monomethylarsine (MMA) and 38 μg/l of unidentified As species.

3.4. Stabilization treatment experiments in soil

Widespread contamination of agricultural land poses a challenge for soil treatment, as conventional technologies such as soil washing are not applicable to large areas for economic reasons. Moreover, some technologies destroy the structure and some of the functions of the treated soil and hinder further agricultural land use (EPA, 2002). However, attenuation of the effects of As in soils is possible, and an alternative treatment option based on the immobilization of As using amendments was therefore tested. For this purpose, a biologically synthesized schwertmannite-based adsorbent (sorpP) was used in pot experiments with spring barley. The schwertmannite used has a defined chemical composition, since it was produced in a microbial pilot plant using iron oxidizing bacteria (https://www.imwa.info/docs/imwa_2010/IMWA2010_Janneck_420.pdf). The pure material and two modifications containing stabilizing agents (chalk and ash) were tested in three different dosages: 0.125% w/w, 0.25% w/w and 0.50% w/w. Because iron-based adsorbents retain not only As but also phosphorus (P), which can influence the nutrient supply of plants as well as the efficiency of As retention through competition for adsorption sites, an additional test series was conducted using a doubled level of P fertilization at a medium adsorbent dosage (0.25% w/w). Experiments were carried out with soil from Freiberg, which is contaminated not only by As but also by Cd and Pb, and this must be taken into account in the assessment of adsorbents in agricultural soils (Table 1). Aside from analysing the concentration of contaminants in soil and crops, further investigations were performed on bioindicators for assessing the effectiveness of adsorbents in reducing the mobility, transfer and toxicity of As present in agricultural soils. The most probable number of As (III)-oxidizing (Thouin et al., 2016) and As (V)-reducing microbes (Thouin et al., 2018) in treated soil was investigated as a potential bioindicator of the bioavailability of As in soils. In addition, the Omega-3 Index of plants was determined during the experiment as an indicator of the oxidative stress in plants caused by soil contaminants (NF EN ISO 21479, 2020).

3.5. Water treatment technologies

The removal of As and other contaminants from surface waters collected in autumn 2018 from our study site in Verdun was examined using membrane technologies, *i.e.*, nanofiltration (NF), low-pressure reverse osmosis (RO), adsorption and a combination of RO and adsorption, at the University of Oulu in Finland. The concentration of As was ≈ 230 μg/l (tot) and ≈ 180 μg/l (dissolved). The other elements analysed at the University of Oulu were Mn, Fe and Ca, with initial concentrations of ≈ 230 μg/l, 4880 μg/l and 332 mg/l, respectively.

As a first step, screening experiments with NF and RO membranes were performed with synthetic water samples to identify suitable membranes and operating conditions, *i.e.*, pressure and temperature. The composition of the synthetic water simulated the surface waters in Verdun and Freiberg. The NF270 membrane from Dow Filmtec (currently DuPont) and Osmonics AK from SUEZ Water Technologies & Solutions were used in the NF and RO experiments, respectively.

After the screening stage, RO and adsorption experiments were carried out with contaminated surface water from Verdun sampled from ponds near the contaminated soil spots. The Osmonics AK RO membrane was selected for these experiments, since it showed higher removal efficiencies in the screening stage (Kursula, 2018; Valkama et al., 2018). Two low-cost, by-product-based adsorbents were selected for the research. The schwertmannite-based adsorbent SorpP and Sachtofer from Sachtleben Pigments Oy (currently Venator P&A Finland Oy) were also used in the soil remediation experiments. Sachtofer is a by-product of TiO_2 pigment production. The As removal experiments were conducted by RO combined with adsorption, first separately and then sequentially, *i.e.*, first RO followed by adsorption. All tests were duplicated.

The sustainability assessment for the potential water treatment technologies was based on a multi-criteria approach including technological, economic, environmental and social issues. Multi-criteria analysis is a versatile and user-definable assessment method and supports the comparison of different alternatives based on one or several criteria. To conduct a wide-ranging assessment, 22 criteria were selected. The technologies chosen for this assessment were adsorption, coagulation–filtration, ion exchange and membrane technology.

The technological criteria used in the sustainability assessment were suitability, flexibility/scalability, robustness and reliability, removal efficiency, the capacity to remove other impurities, the need for pretreatment, the need for chemicals and the water production rate. The economic criteria were investment costs, operating and maintenance costs, waste disposal costs, operation life and commercialization potential. The environmental criteria were operational wastes, the simplicity of waste treatment, water losses and used materials. The social criteria were innovativeness, operator skill requirements, safety issues, usability, ease of use and ease of installation (Turpeinen and Keiski, 2019).

All the studied technologies were rated with these criteria, and a weight was assigned to each criterion to indicate its relative importance. Criterion scores were summed to derive an overall technology ranking, with the highest scoring alternative being the preferred choice.

3.6. Risk assessment

Health risks to humans were estimated using the As exposure model developed within our study. The exposure model assesses exposure to As through all relevant exposure pathways, as shown in Fig. 2. The model is described in detail in Jones et al. (2019a, 2019b) and was implemented as a spreadsheet model.

The model is an equilibrium model that assumes that the concentration of As in various pools (sources of As in soil and water) is constant in time. Based on the literature data on mass fluxes and As concentrations (EU Directive, 2004; Unkovich et al., 2010; Hausmann, 2013; EFSA, 2015; EMEP, 2018), scoping calculations of the inputs and losses of As to a mobile pool and an immobile pool in agricultural soil indicate that the turnover of the mobile pool is around 4% per year and that of the immobile pool is only 0.1% per year (Fig. 3). Thus, the turnover in soil is very slow. A changing source term, *i.e.* increasing or decreasing concentrations of As in soils with time, is not significant for health risk assessment, and equilibrium models of the transport of and exposure to As in agricultural soils are deemed appropriate.

The model considers adults and children who are directly exposed to As in the soil in several ways: through direct contact by getting soil in the mouth and on the skin or by inhalation of soil dust. Persons can also be exposed to As when eating food grown on As-contaminated soil or eating meat, dairy products and eggs from farm animals raised in the contaminated area. Furthermore, groundwater contaminated with As can be an important pathway for exposure if it is used as drinking water. How much As people are exposed to depends on their habits and consumption patterns. The model allows for the use of a site-specific description of human habits using standard equations to estimate the exposure through the various pathways.

Exposure has been calculated separately for children and adults. The general form for calculating the exposure *via* exposure pathway j is:

$$Exp_j = \quad C_j \quad f_{bio-or} \quad R_j \quad DF_j$$

Where:

C_j= the concentration in the exposure media (*e.g.*, soil, water, plants)
R_j= the average intake of the exposure media per unit body weight
$f_{bio\text{-}or}$= the bioavailability of As in the exposure media

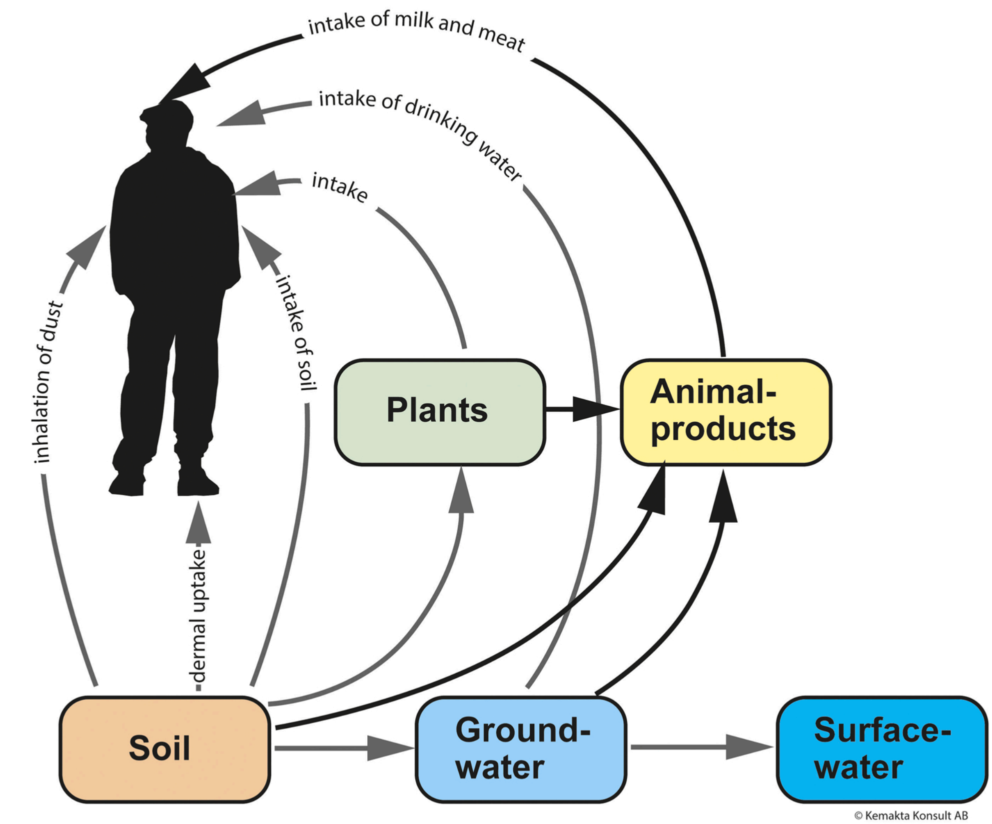

Fig. 2. Exposure pathways included in the health risk assessment.

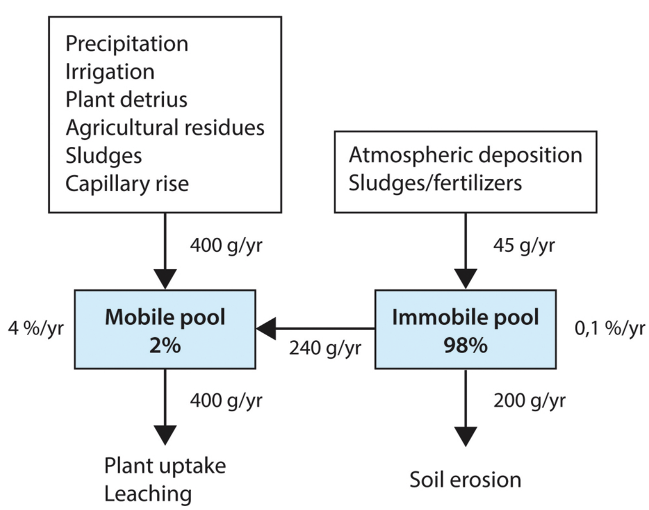

Fig. 3. Summary of the calculation of arsenic fluxes in soil (per hectare). 'Pool' refers to sources of arsenic in soil and water.

DF_j= a factor for possible dilution from the original media to the exposure media

The equations for calculating exposure for the different exposure pathways were based on models developed for the risk assessment of contaminates sites (Swedish EPA, 2009; Brand et al., 2007; US EPA, 1989). For example, the exposure due to soil ingestion was calculated as:

$$Exp_{soil} = C_{is} \quad f_{bio-or} \quad R_{is} \quad 10^{-6}$$

where:

C_{is}= concentration in soil (mg/kg dry matter)
f_{bio-or}= relative bioavailability of As in the soil for oral exposure (-)
R_{is}= the average soil intake per unit body weight (mg/kg bw and day)

The average daily soil intake per unit body weight (child or adult) is calculated as:

$$R_{is} = \frac{SI \quad t_{is}}{m}$$

where:

SI= the average soil intake with separate values for children or adults (mg/day).
t_{is}= the fraction of time spent on the site leading to soil exposure for children or adults (-).
m= body weight of child or adult (kg).

The total exposure *via* all the relevant pathways is the sum of exposure from each pathway.

The integrated life-time exposure was calculated as:

$$Exp_{int,j} = \frac{T_{child} \quad Exp_{j,child} + T_{adult} Exp_{j,adult}}{T_{int}}$$

where:

T_{child} = Years of exposure as a child (years)
T_{adult} = Years of exposure as an adult (years)
T_{int} = Integration time, assumed to equal life expectancy (years)

In addition to As exposure arising from the contaminated site, exposure to As can occur due to its presence in foodstuffs coming from other regions or countries with elevated levels of As. The calculation of this exposure to off-site As was based on country- or region-specific compilations of As concentrations in the contact media, soil, water and foodstuffs. The model estimated the exposure to As on the contaminated site (on-site) and the exposure to As from other sources (off-site). The total exposure is important to evaluate the risk of health effects in general, while a comparison of the on-site and off-site exposure is important for applying successful risk management options.

The model was structured to be used with different levels of data availability by allowing the input of available site-specific data and to complement the data with model estimates and generic data, as appropriate. Estimates can be based on measured concentrations of As in soil with transfer along the exposure pathways calculated with generic parameters, or site-specific parameters. Alternatively, measured concentrations in the exposure media (for example, drinking water, agricultural produce) can be used. Soil is also an exposure medium for direct exposure pathways such as direct oral intake and dust inhalation. In the absence of site-specific concentrations in the exposure media, generic concentrations, for example country-specific concentrations such as those from the European Food Safety Authority (EFSA, 2014), can be used.

To determine the likelihood of harmful health effects, the estimated or measured exposure is usually compared with toxicological reference values, which indicate an exposure level at which the risk of harmful health effects is judged to be at a reasonable level. The model allows the user to choose the toxicological reference value for the risk assessment and it allows the assessment of threshold and non-threshold toxicological effects, such as cancer. The risk per 100 000 people for each exposure pathway was calculated by taking the estimated exposure from that particular pathway and dividing it by a permissible reference value of intake:

$$Risk_{pathway\quad i} = \frac{Exp_{int,\quad i}}{Reference\quad Value\quad for\quad intake\quad of\quad Arsenic}$$

The widely accepted toxicological reference values for As refer to inorganic As, based on studies of exposure to As in drinking water (EFSA, 2010; WHO, 2017).

For non-threshold effects the risk is additive, and the total risk can be calculated by adding the risk from the individual exposure pathways:

$$Total\ Risk = \sum Risk\ from\ pathway\ i$$

A number of threshold effects have been reported as a result of As exposure, such as skin lesions, developmental toxicity, neurotoxicity, cardiovascular diseases, abnormal glucose metabolism and diabetes. For these types of effects, chronic exposure is calculated in mg/kg body weight and day for different age groups. The exposure of children and adults, respectively, is divided by a TDI (tolerable daily intake) for non-cancer effects to estimate a hazard index, HI. The TDI in the model can be changed but is set as a default to 0.45 μg/kg body weight and day, based on Schuhmacher-Wolz et al. (2009).

There are, however, different chemical forms of As in the environment and in foodstuffs. Generally, inorganic As is assumed to be more toxic than organic As, the most common forms of which are di- and monomethyl As (DMA and MMA), arsenosugars and arsenolipids. However, knowledge of the bioaccessibility and toxicity of organic species of As is incomplete (Taylor et al., 2017; Cubadda et al., 2017), and there are no widely accepted toxicological reference values (Gorecki et al., 2017). Thus, in the risk assessment model, health risk assessments of As are based on inorganic As. In the future, health risk assessments could be improved if it were possible to consider the differing toxicities of different forms of As to which people are exposed.

The model developed within our research project was used for assessing the health risks at the study sites in Freiberg, Germany, and Verdun, France, before and after remediation measures were applied. For both sites, the initial risk estimates were carried out using site-specific input data as far as possible.

4. Results

4.1. Arsenic concentrations in agricultural topsoils in Europe

The literature review we carried out revealed that there is a considerable amount of large-scale data on As concentrations in soil, surface waters and/or groundwaters in many European countries (Tarvainen and Hatakka, 2017). However, none of the countries has published regional maps of As concentrations in crops. Data on As concentrations in soil are available at least from Austria, the Czech Republic, Finland, Germany, Lithuania, Poland, Slovakia and parts of Estonia, Italy, Norway and the United Kingdom. Surface water data are available from Finland, Germany and Romania, and groundwater data from Germany, Norway and Slovakia.

Arsenic concentrations in soil, surface water and groundwater have both geogenic and anthropogenic origins. Most of the European geological surveys have carried out geochemical mapping using two sample media: agricultural and pasture soils. The distribution of As reflects the geogenic sources of As in the surface environment (Tarvainen et al., 2013; Reimann et al., 2014a, 2014b). Due to the presence of minerals containing As in bedrock and regolith, groundwater and surface waters can contain As. Natural concentrations of As in agricultural and pasture soils vary in different parts of Europe. The median As concentration in the agricultural soils of southern Europe is more than three times higher than in those of northern Europe (Fig. 1a). Median values are 8.0 mg/kg *vs.* 2.5 mg/kg (*aqua regia*) and 10 mg/kg *vs.* 3 mg/kg (total), respectively (Tarvainen et al., 2014). Although most of the anomalies in Fig. 1a are geogenic, some anomalies have an anthropogenic origin.

There are currently no global estimates for As concentrations in agricultural soil, even though geochemical studies have been carried out in many countries. The median As concentration of agricultural soils in China is 9.7 mg/kg, for example, and the concentrations in South and North-East China are higher than in other parts of the country, with median values of 18.7 and 15.8 mg/kg, respectively (Zhou et al., 2018).

4.2. Studies on agricultural amendment procedures

Pot experiments with barley were conducted to investigate the effects of various agricultural amendment procedures on the availability of soil As. For the Verdun site, three amendments were applied: a PK fertilizer (phosphorus-potassium), ammonium sulphate and organic matter. For the Freiberg site, the amendments chosen were lime-ammonium nitrate and organic matter. The results indicated that the addition of amendments, at the real average dose applied by farmers on the sites, did not significantly influence the speciation or quantity of mobile As. The observed tendencies for the Verdun site were an increase in As mobility with the addition of PK fertilizer, a decrease in mobility with ammonium sulphate amendment and a neutral response for the organic amendment (Battaglia-Brunet et al., 2021). The increase in the mobility of As related to the KP amendment was confirmed by a small increase in As concentrations in plants. Moreover, the standardized Omega-3 Index test (NF EN ISO 21479, 2020) carried out to evaluate the influence of amendments on As toxicity revealed that the contaminated soil amended with ammonium sulphate appeared to be significantly less phytotoxic than the unamended soil. For the Freiberg site, the two amendments tested, lime-ammonium nitrate and organic matter, tended to cause a slight but statistically nonsignificant decrease in the mobility of As and can therefore be recommended for that site.

The toxicity of As mainly results from the inhibition of basic cellular functions linked with energy metabolism. At the Verdun site, As-transforming microbes were more abundant in the contaminated than in the less contaminated zone (Battaglia-Brunet et al., 2021).

4.3. Stabilization treatment experiments in soil

The results of the experimental work revealed a successful reduction in the mobility of the contaminants in soil (Table 2). Immobilization of phosphorus (P) in the soil was also observed, but a doubled level of P fertilizer could compensate for this. However, the higher P fertilization was accompanied by a reduction in the efficiency of As immobilization at agricultural sites due to the competing adsorption on the schwertmannite-based adsorbent. When compared with the concentrations measured in harvested crops, the As content was successfully reduced for each adsorbent type and each concentration tested. In contrast, the use of adsorbents led to a higher concentration of Cd and Pb in crops compared to the control condition. However, the use of the modified adsorbent sorpP + chalk resulted in a decrease in the concentration of Cd and Pb in crops. Statistical investigations revealed neither significant results for sorpP + stabilizers nor high coefficients of determination, and the results for Cd and Pb do not therefore allow clear conclusions to be drawn (Jordan et al., 2018a, 2018b).

Investigations on bioindicators revealed that the most probable number of As-transforming microbes in treated soil was not an effective indicator of As mobility or the efficiency of the soil treatment. However, a high ratio of As(III)-oxidizing/As(V)-reducing microbes was a good indicator of As speciation, and hence indirectly of its geochemical behaviour. The Omega-3 Index values determined from the leaves of cultivated spring barley corresponded with the results obtained from the analysis of contaminants in soil and crops, and this index is thus valuable in assessing the impact of adsorbents on plant health. Based on the Omega-3 Index, the adsorbents with additional chalk and ash were identified as the best options for soil amelioration, with a positive effect on plant health.

4.4. Water treatment technologies

Reverse osmosis was effective in the removal of As and other contaminants from surface water collected in Verdun, resulting in high water quality. Arsenic removal higher than 99.5% was readily achieved at a relatively low pressure (10 bar). The As concentration of the purified water varied from 1 μg to below 0.2 μg/l, which was the limit of the quantification of the analysis method, therefore being significantly below the WHO maximum contaminant level of 10 μg/l (WHO, 2017). Additionally, RO was efficient in the removal of the other contaminants.

Table 2
Pot experiments with soil from Freiberg contaminated with arsenic. Spring barley amended with the iron-based adsorbent sorpP, ash and chalk. Arrows indicate the effect of treatments on arsenic, lead and cadmium in crops. Arrows up: increase of concentration. Arrows down: decrease of concentration.

	Arsenic (As)	Cadmium (Cd)	Lead (Pb)
Condition			
SorpP (soil)	↓	↑	↑
SorpP + ash (soil)	↓	↓	↓
SorpP + chalk (soil)	↓	↓	↓
Change in crops related to control with sorpP alone	-24%	+ 17%	+ 12%
Concentration in crops [μg/kg] (min/max)	444 / 1106	197 / 346	54 / 107
Limit value			
Food [μg/kg] (European Commission, 2001)	–	100–200[a]	200
Fodder [μg/kg] (European Commission, 2002)	2000	1000	10 000

Mobility reduced (↓) or raised (↑) due to amendments using water and ammonia-nitrate extraction procedures.
— No limit value for arsenic provided by the regulation regarding crops grown at the Freiberg study site.
[a] Different limit values provided for food products (*e.g.*, for cereals like wheat, barley or oat)

The removal efficiencies for manganese, iron and calcium were > 99.5%, > 99.0% and > 99.5%, respectively.

The WHO drinking water level (WHO, 2017) was not met with the used adsorbents and their doses. However, the produced water could be applicable for other uses requiring lower water quality. In the future, As removal by the used adsorbents could be further improved by optimizing the process parameters.

The sustainability assessment was based on the multi-criteria approach to ensure the evaluation of technological, economic, environmental and social aspects. The aim of the sustainability assessment was to provide an overview of the sustainability of technologies available for As remediation in aquatic environments. The results provided guidelines for the selection of the most sustainable technology. The main results of the assessment are listed below:

1. Sustainability assessment revealed that the adsorption and coagulation–filtration processes are the most feasible options for the treatment of surface waters having significant As concentrations.
2. If all sustainability dimensions are equally taken into account, adsorption technology is the most sustainable technology, followed by coagulation–filtration technology.
3. If the focus is on economic issues, coagulation–filtration technology is superior to other options.
4. If environmental issues and especially very high water quality are of importance, reverse osmosis is also a feasible option.
5. There is no universal As removal technology suitable for all possible situations. The best removal technology for As must be selected case by case, especially considering the design parameters (*e.g.,* the quantity of water to be treated and target water quality and application) and properties of the source water (chemical characteristics and composition of water contaminated with As).

4.5. Risk assessment of the study sites

For the Freiberg site, the risk assessment was based on the median concentration of As in topsoils derived from the investigations carried out in our study. Arsenic concentrations in grains and fodder and site-specific plant uptake factors (grains and fodder) both before and after mitigation measures were derived from our results (Battaglia-Brunet et al., 2019). Previous results were used to derive input values for plant uptake factors for a number of plant species, including barley, winter wheat, pasture, grass and herb species (Haßler and Klose, 2006; Serfling and Klose, 2008; Röhricht et al., 2011; Klose, 2012), As concentrations in some animal products (Boguhn et al., 2009) and As concentrations in dust in air (Hausmann, 2013). For the Verdun site, the concentrations in soils were derived from the results of field investigations of the present study (Battaglia-Brunet et al., 2019).

Arsenic concentrations in plants and plant uptake factors were derived for lettuce and barley from the experimental studies (Battaglia-Brunet et al., 2019) and for some other plant groups from the results of field studies. The As concentrations in fodder and some further food groups, including some animal products, were taken from a previous study of As at a similar ammunition destruction site (Gorecki et al., 2017). Plant uptake factors were higher for grains than for other plant groups. Only generic data were available for non-leafy vegetables, root vegetables and fruit (Environment Agency of the United Kingdom, 2009). The measured concentrations of As in animal products at both sites were used to validate the generic fodder to animal product transfer factors that are included in the model (Rodrigues et al., 2012). The modelling results for animal products showed that for beef cattle and sheep, ingestion of soil can be as important as fodder consumption for the total intake of As.

A summary of the example cases studied is listed here:

1. Freiberg 1 (261 mg As/kg dry weight soil): Base case.

2. Freiberg 2 (261 mg As/kg dry weight soil): Remediation reduced plant uptake factors by 50%, grains only.
3. Freiberg 3 (261 mg As/kg dry weight soil): Remediation reduced plant uptake factors by 50%, all crops.
4. Verdun 1 (30 mg As/kg dry weight soil): Base case, low As concentrations.
5. Verdun 2 (200 mg As/kg dry weight soil): Base case, high As concentrations.
6. Verdun 3 (200 mg As/kg dry weight soil): Remediation reduced plant uptake factors by 50%, all crops.

For both sites, the preliminary assessment demonstrated that the risks from exposure to As at the contaminated site dominated the total As exposure. For the case Verdun 2, on-site exposure accounted for more than 75% of the total exposure due to the intake of plant and animal products. The corresponding value for the Freiberg site was 90%. The model indicated that the most important exposure pathways were the intake of vegetables and fruit from the contaminated site. The intake of animal products also substantially contributed to the total exposure, followed by the direct oral intake of soil and dermal contact at the contaminated site (Fig. 4). However, risk management measures have already taken place in Freiberg, and the risk situation today is not that presented in Fig. 4. Direct dermal contact and oral intake are minimized in public and private areas (Landesdirektion Chemnitz, 2011a, 2011b) and advice has been give about the most appropriate agricultural practices. At present, the Verdun site is not used for agriculture, and many of the exposure pathways in Fig. 4 do not therefore exist today.

The amelioration of the effects of As in agricultural soils using various soil amendments was examined with the model. If the amendments can at the most reduce plant uptake from soil by 50%, the maximum reduction in risk is about 25% at the Freiberg site and about 23% at the Verdun site, assuming amendments are used on all crops. This reduction in risk is slightly greater than the risk from off-site exposure. The modelling results indicate that the exposure at the two test sites could be about 3–5 times higher than the average exposure in the two respective countries. Using amendments, risk would be reduced but still be 2.5–4 times higher than average.

4.6. Risk management procedure

4.6.1. Evaluation of anthropogenic and geogenic As risks at the study sites

The anthropogenic influence is significant in Verdun and Freiberg. For comparative purposes, we selected the Tampere region in Finland, which has locally elevated but not high geogenic concentrations of As. In the Verdun and Freiberg study areas, the main concern is the contamination of agricultural soils. However, groundwater and surface water recipients from sites with high As concentrations in soils can be contaminated by leaching from soils. Risk management in the Freiberg area differs from that in Verdun where the As is concentrated in hot spots (Table 3). In Verdun, the growing of agricultural products in these plots ceased in 2015. In the Tampere area in Finland, the main uptake route is As in drinking water from private bedrock wells (Loukola-Ruskeeniemi

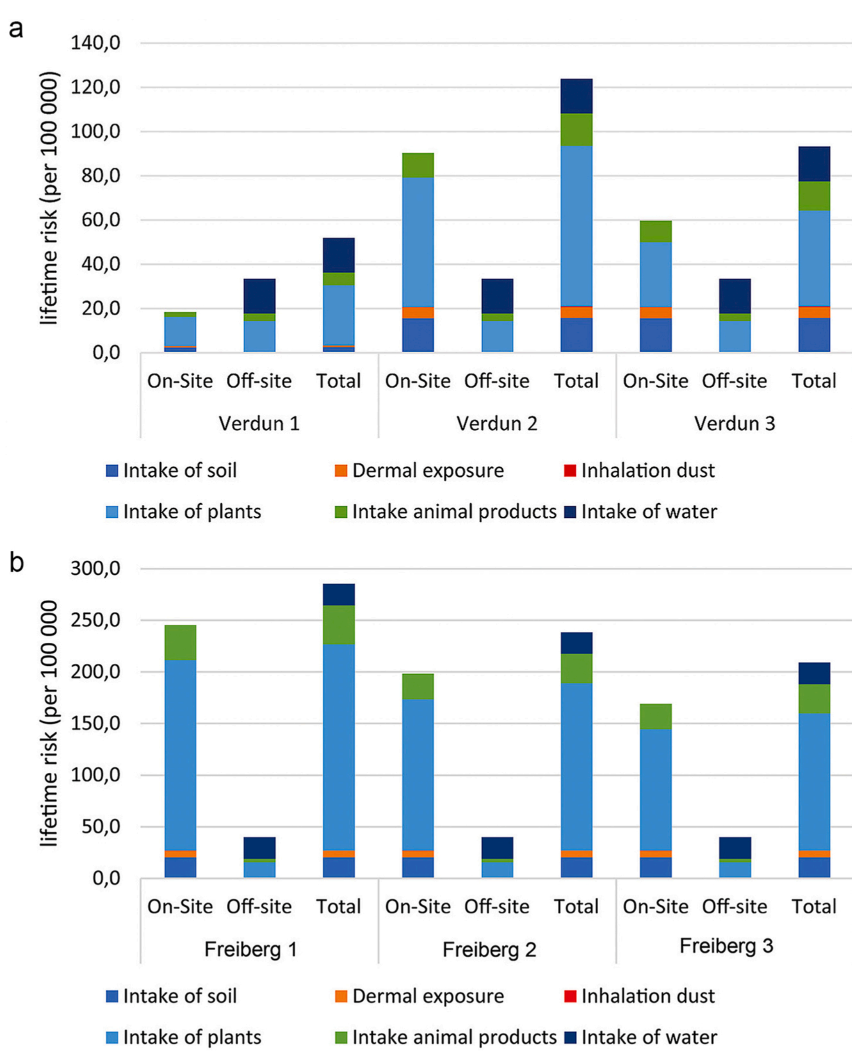

Fig. 4. Risk from on-site and off-site exposure to arsenic for the example cases studied: **a.** The study site near Verdun, France; **b.** The Freiberg area, Germany. Description of the three calculation cases both from Verdun and Freiberg is given in Section 4.5. The risk per 100 000 people for each exposure pathway was calculated by taking the estimated exposure from that pathway and dividing it by a permissible reference value of intake. The model estimated the exposure to arsenic on the contaminated site (on-site) and the exposure from other sources (off-site).

Table 3
Comparison of the concentrations of arsenic in soil, surface water, groundwater, crops and fodder in our study areas in France, Germany and Finland (Fig. 1).

	Verdun, France	Freiberg region, Germany	Tampere region, Finland
Arsenic source	Anthropogenic: Ammunition from World War I	Geogenic: bedrock Anthropogenic: mining and ore processing	Geogenic: bedrock
Extent of arsenic contamination in soil	Hot spots of 100–10 000 m^2 with up to 12 000 mg/kg As	288 km^2 with > 50 mg/kg As at Freiberg, 1837 km^2 in Saxony	7400 km^2 with 5–30 mg/kg in glacial till
Geochemical background value of arsenic	18 mg/kg	20–40 mg/kg	30 mg/kg
Highest arsenic concentration in soil	12 000 mg/kg	5000 mg/kg; ore veins and waste rock > 1% As	Topsoil 1050 mg/kg, subsoil 9280 mg/kg
Arsenic concentration in surface water	Usually 2–3 µg/l As, but higher near the ammunition destruction sites, for example 125 µg/l As in a pond	Usually < 5 µg/l As, but near the tailings and old mining shafts higher	Usually < 1 µg/l As (Parviainen et al., 2015)
Arsenic concentration in groundwater	Usually 2–4 µg/l As	Usually < 10 µg/l As, but higher near the tailings and old mining shafts	Usually < 10 µg/l As, but elevated in some private wells (Ruskeeniemi et al., 2011; Pedretti et al., 2019)
Arsenic concentrations in crops	No crops at present. Max. concentration in wheat grains 0.01 ± 0.04 mg fresh weight/kg dry weight (Gorecki et al., 2017)	Yes: Maximum 0.4 mg/kg dry weight in winter wheat grains in Saxony (Klose, 2012)	Very low: 0.005 mg/kg As in wheat grains (Mäkelä-Kurtto et al., 2006)
Arsenic concentrations in fodder	No fodder crops at present. Maximum concentrations at similar sites 0.06 ± 0.02 mg fresh weight/kg in maize silage and 1.5 ± 0.6 mg/kg fresh weight in barley (Gorecki et al., 2017).	Yes: Maximum 2.97 mg/kg dry weight in pasture in Saxony (Röhricht et al., 2011)	Very low: 0.014 mg/kg As in timothy (Mäkelä-Kurtto et al., 2006)
Health risk assessment: main local source of As	Consumption of plants	Consumption of plants	Drinking water from some private wells (Sorvari et al., 2007)
Agricultural land use	No, stopped in 2015	Yes, but closely monitored	Yes, not affected by arsenic (Mäkelä-Kurtto et al., 2006; Lehtinen et al., 2007)

et al., 2007; Parviainen et al., 2015) and no contamination was found in agricultural soils and crops (Mäkelä-Kurtto et al., 2006).

Below, we describe the German risk management procedure in more detail, since it is more advanced than in other jurisdictions, while also covering a wide area and embracing both financial and health issues.

4.6.2. *Guidelines to manage arsenic, cadmium and lead concentrations in agricultural soil in Freiberg, Germany*

The ore deposits of the Freiberg mining area contained not only silver and lead in galena, but also zinc and cadmium in sphalerite and As in arsenopyrite. All these minerals were mined and smelted together, and the resultant residues and waste materials accumulated in tailings and waste rock dumps. Because industrial ore processing, agriculture and settlement areas are located close together, it is essential to assess the impact of exposure to As and other mining-related pollutants on the environment and human health.

Extensive investigations have been carried out since the 1990 s to assess the transfer of As 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 revealed that crop grains contained 0.5–1.0 mg As/kg, and the limit value of 2 mg/kg for fodder was not exceeded, although concentrations in other parts of the plants exceeded the threshold value (Serfling and Klose, 2008; Klose, 2012).

Based on the data gathered, generic guidelines for farming and gardening were developed to optimize farming procedures, even to the extent of choosing suitable cultivars of plants characterized by a lower potential of As uptake (Haßler and Klose, 2006; Serfling and Klose, 2008; Schürer, 2011; Röhricht et al., 2011; Kaufmann-Boll et al., 2013; Müller et al., 2013; Klose, 2017).

A toolbox was developed to manage As, Cd, and Pb concentrations in agricultural soil in the Freiberg area including the measures on grassland and arable land (crops):

4.6.2.1. *Measures on grassland.*

1. Ideal pH and lime.
2. Reduce pollution from adhering soil.
3. Change grassland species composition.
4. Analysis of yield.

4.6.2.2. *Measures on arable land (crops).*

1. Ideal pH and lime.
2. Selection of species.
3. Selection of cultivars.
4. Pre-harvest analysis.

4.6.3. *Agricultural practices*

Agricultural practices provide efficient risk management tools. Depending on the land use and transfer pathways, different measures are proposed for the adaption of agricultural practices. Since it has been established that As contamination in agricultural crops is mainly caused by the adherence of soil particles – directly or *via* dust – and not by systemic uptake by plant roots, measures can be taken to reduce the presence of soil particles on harvested products. This can be done using cleaning procedures for harvested crops and efficient removal of husks, as they contain a large proportion of the contaminants present in grains. This especially applies where plants are intended to be used as fodder. There is clearly a need for the modification of harvesting practices and technological improvements to reduce the uptake of soil particles and subsequently of contaminants.

Laboratory studies using pot trials and field studies have been performed in the Freiberg area testing different cultivars (Klose, 2012) and several amendment procedures (Neu et al., 2018a, 2020) for the amelioration of soil. Values for As uptake by different agricultural crops are being progressively updated with new data obtained in varietal trials (Schürer, 2011; Kaufmann-Boll et al., 2013; Klose, 2017). In addition, various analytical methods have been tested for the determination of contaminants in soil to find a solution that gives reliable information for the risk assessment of contaminants in agriculture (Kumpiene et al., 2014).

Due to high background concentrations of As, Pb and Cd in subsoil, the disturbance of deep subsoil should be discouraged, as this can bring contamination to the surface. Based on the fact that As is mobile under reducing conditions, aeration of wet soil is recommended. A well-functioning drainage system can prevent waterlogging and allows sufficient aeration of soil.

The choice of fertilizer at an appropriate dosage can be included in routine farming activities. Moderate application of fertilizer with phosphorus at the beginning of the growing season can reduce As uptake in plants, as As and P compete for uptake *via* the roots (Klose, 2017). The interaction of P and N fertilizers and its impact on As uptake by plants was also investigated by Brackhage et al. (2014), who reported that the dosage of P and N fertilizer affects the concentration of As in different parts of the plants. A high dosage of N at a low dosage of P resulted in lowered As concentrations, while for a low dosage of N and a high dosage of P, elevated As concentrations were found, explained by competition for limited binding sites in soil. It may therefore be assumed that a simultaneous high dosage of N and P would compensate for the observed effect; however, this was not evidenced within the study and needs to be verified in further examinations (Brackhage et al., 2014).

Liming aims at the establishment of an optimized pH value whereby As is immobile in soil and agricultural land use is still possible. Therefore, a range of 5.5–7 can be recommended for arable land and 4.5–6.5 for grassland. The ambient pH value, the soil type and the humus content are all important for the dosage of lime, as well as the options for land use, *e.g.*, as grassland, arable land or vegetable gardening. Depending on the soil structure and nutrient availability, a certain amount of lime should not be exceeded, as too much lime can promote As uptake into plants (Klose, 2017). Because of this, the applied dosage needs to be adapted based on the presence and mobility of As and other relevant contaminants, *e.g.*, cadmium. However, in case of an As concentration in soil that exceeds the trigger and action values defined by German regulation (Bundes-Bodenschutz- und Altlastenverordnung, 1999), it can be categorically stated that liming alone will not be sufficient to successfully reduce concentrations in crops (Feldwisch et al., 2014).

As a result of long-term experience in using contaminated sites as arable land for the production of crops and fodder, it could be recommended to use cultures and varieties with a proven low As and Cd uptake rate to ensure that limit values for food and fodder are not exceeded. Controls, *e.g.*, regular harvest examinations, that are routinely carried out can guarantee safe agricultural goods. Pre-harvest examinations allow a decision to be made concerning the marketing of products as food or fodder, or for incineration if the concentration of pollutants exceeds a limiting value. If energetic utilization is the only option, farmers are informed beforehand in order to harvest the whole plant and not only the grains.

If the concentration of contaminants in agricultural crops cannot be reduced by an adapted agricultural practice, a change in land use might be the only available option. This could be achieved by short rotational plantations as well as the cultivation of plants for energy production by anaerobic digestion or the combustion of contaminated biomass (Bert et al., 2017). An overview summarizing recommendations for adapting agriculture to reduce contaminants in crops was compiled by Müller et al. (2013) and is presented in Table 4.

As each site is unique and has different characteristics, the most relevant recommendations must be selected according to existing circumstances, requiring case-by-case assessment for each site to identify an appropriate solution for sustainable agriculture.

Table 4
Recommendations for sustainable agricultural practices at sites contaminated by arsenic in Saxony, Germany.

All agricultural areas		
- Reduction of contamination by soil adhered to plants - Choice of fertilizer - Fertilization and liming adapted to the mobilization potential of As - Enhanced aeration of wet soils - Abandonment of (deep) tilling and disturbance of subsoil/underlying substrate - Change of land use		
Pasture and grassland	Arable land	Garden
- Use of harvesting technologies that avoid soiling - Change of plant species composition - Examination of plants and harvested products	- Choice of varieties - Use of cultivation procedures without (or with less) soiling - Pre-harvesting examinations	- Recommendations for cultivation, changes in attitudes, behaviour and consumption

4.6.4. *Criteria for soil, water, food and fodder in the European Union*

We have summarized the criteria for soil, groundwater, surface water, air, dust, foodstuffs and fodder throughout Europe in Table 5. There are very few guidelines or limit values for As in foodstuffs that are commonly grown in Europe. The European Union has only prescribed limit levels of inorganic As for rice and rice products. Some individual countries have defined concentration limits for As in fruit juices, fish and cereals, as well as for rice. However, the EU does give limit values for As in different types of animal fodder.

Guideline values for soils include recommendations for the protection of human health and guidelines for the protection of the soil ecosystem or recipient aquatic ecosystems. Some of the guideline values derived for agricultural and pastureland are based on toxicity to plants, some are based on compliance with regulations on animal fodder, and some are based on compliance with local regulations on foods. Soil guideline values that are intended to protect soil ecosystems are in most cases based on compilations of literature data, presented in the form of a species sensitivity distribution. Guidelines to protect the aquatic ecosystem are based on how As affects a range of species at different levels of the ecosystem. Because As is naturally present in the environment, all soils contain some As. When assessing the risks of agricultural soils, it is necessary to set these risks in the context of the risks occurring at natural background concentrations. Because there are no generally available methods for taking site-specific conditions into account when deriving environmental protection guidelines for As, we suggest that site-specific investigations of the toxicity of As to animals and plants and the effects of As on the soil or aquatic ecosystems should be carried out where the levels of As are high and an impact on the environment can be expected.

Remediation options have been developed for both soil and water. Criteria for As concentrations in agricultural soil, surface water, drinking water, air quality, foodstuffs and fodder are needed to encourage the effective implementation of these options.

4.6.5. *Regulation in Freiberg, Germany*

The German Federal Soil Protection Ordinance (Bundes-Bodenschutz- und Altlastenverordnung, 1999), which governs the handling of contaminated sites and the sampling, analyses and quality management of soil, contains orientation values for different threats and land uses. If given values are exceeded and a hazardous impact has been confirmed, appropriate measures, *e.g.*, adaption of agricultural practices, changes in land use and soil remediation, have to be taken to ensure safe management of such sites.

In Germany, a regulation using trigger and action values was established in 1999 (Bundes-Bodenschutz- und Altlastenverordnung, 1999) using standard exposure scenarios. The trigger values indicate a need for further assessment, but the action values indicate that measures such as remediation are required. Regarding the threat to health *via* soil ingestion, trigger values have targeted different land uses: 25 mg/kg for playgrounds, 50 mg/kg for residential areas, 125 mg/kg for parks and leisure facilities and 140 mg/kg for industrial or commercial areas. Regarding food and fodder safety an action value of 50 mg/kg for

Table 5
Criteria in Europe for soil, groundwater, surface water, water for agricultural purposes, crops, animal fodder and air.

Medium	European regulations	Other regulations	Comment
Soil	None	Individual countries have derived soil guidelines/limit values.	Wide range of numerical values, as different sets of values are intended for different purposes. Values include: • Land use -specific values • Single values for specific purpose, or paired trigger and action values • Integrated or separate values for the protection of health, groundwater resources, terrestrial and aquatic environments. • Different ways of taking regional or local background concentrations into account. In some cases, background concentrations can replace trigger values
Groundwater	None under the Water Framework Directive (EU Water Policy Directive, 2000)	Individual countries have derived guideline/ limit values. Usually based on drinking water criteria.	Alternative precautionary approach (prohibition of direct discharge and monitoring/action levels).
Surface water	No environmental quality standards under the Water Framework Directive (EU Water Policy Directive, 2000)	Individual countries have complementary values based on ecotoxicological effects (PNEC-values).	
Water for agricultural purposes	None	WHO guidelines	From 1985
Crops	Rice/rice products only (EU Commission regulation, 2015b)	None	
Animal fodder	EU Commission regulation (2015a)	None	
Air	EU Directive (2004)		Based on WHO evaluation

grassland was set up, as well as trigger values for plants on arable land, *i.e.* 200 mg/kg (50 mg/kg, if the soil temporarily suffers reducing conditions) based on the pseudo-total (*aqua regia*) As concentration.

Because the area surrounding Freiberg is characterized by widespread contamination, a simplified solution had to be found to overcome the vast number of complex assessments and legal obligations for each individual agricultural site or settlement estate. Thus, after excessive investigation and assessment, the soil planning area Freiberg was established to assign classes of risk due to contamination to each site and plot (Landesdirektion Chemnitz, 2011a, 2011b). For each of the classes, appropriate measures were defined to be applied to the corresponding area. For the ease of implementation, several maps were generated, including: (1) a soil management strategy for the re-use of excavated soil (obligatory), (2) measures in residential areas (obligatory), and (3) recommendations for farming practices on grassland and arable land. The latter are informative only since there are already mandatory EU regulations regarding the concentration of contaminants in food and fodder.

For example, the re-use or disposal of contaminated soil arising from construction activities can be based on special maps that classify areas with a specific contaminant concentration where material of equal or lower concentrations can be transferred to without site-specific analysis. A deterioration in the contamination status of soil could therefore be avoided.

4.6.6. Regulation applied to the contaminated sites in Verdun, France

Agricultural production in Verdun included soft winter wheat, winter and spring barley for human consumption and maize silage for the feeding of dairy herds at two local farms. The French Agency for Food, Environmental and Occupational Health and Safety (ANSES) was asked to determine whether the consumption of plant and animal products originating from this area was safe for consumers. In this study, a specific methodology was proposed for assessing health risks related to the consumption of foodstuffs produced on areas with a battlefield history. Based on this assessment, only the two most contaminated plots were declared inappropriate for farming, including our study site.

5. Discussion

5.1. Geogenic and anthropogenic concentrations of arsenic

The exchange between water and As-bearing minerals in the bedrock depends on the intensity of fracture networks, as well as discharge and recharge flow rates (Pedretti et al., 2019). Arsenic occurs in thermal springs, as well as in certain types of sedimentary and volcanic rocks and black shales (Nordstrom, 2002; Parviainen and Loukola-Ruskeeniemi, 2019). Several As compounds in rock can contribute to the release of As to water, notably arsenopyrite (FeAsS), löllingite ($FeAs_2$) and pyrite (FeS_2). For this reason, aggregate production is an issue in areas characterized by As-rich bedrock and soil (Parviainen et al., 2015).

The concentration of As in agricultural topsoil in Europe illustrates the effect of the last glaciation over 9 000 years ago. This led to lower average As levels in northern Europe compared to those in central and southern Europe due to ice movement, which consumed the upper parts of soil and bedrock in the north (Fig. 1a; Tarvainen et al., 2020). Many As anomalies in agricultural soil coincide with sulphide occurrences and deposits. Some anomalies may result from earlier use of As-based herbicides (Tarvainen et al., 2014). As-containing pesticides used, for example, in cotton cultivation, as well as As-processing industries, have increased As contamination in places (*e.g.*, Li et al., 2021). Urban and industrial sources include the smelting of non-ferrous metals, iron and steel works, electronics, incinerators and coal-fired power stations (Albanese and Breward, 2011).

5.2. Soil remediation

The sorption and release of As in soil and its transfer into plants strongly depend on various soil properties (Rahman et al., 2019), providing an approach for soil remediation. Amendments could change soil properties, *e.g.*, to reduce the leaching of As (Doherty et al., 2017) or its transfer into crops (Neu et al., 2018a, 2018b), but application is usually limited to the topsoil layer. Using specific genotypes of crops and agricultural management practices could reduce As transfer into food, especially rice (Islam et al., 2016; Biswas et al., 2020). Reducing transfer into plants simultaneously from multi-element-contaminated soils remains a challenge, especially regarding As and Cd co-contamination

(Zhao and Wang, 2020). Technical approaches such as electro-remediation (Singh et al., 2015) or biologically driven approaches such as phytoremediation (Matzen et al., 2020) could become suitable options.

Among the most important aspects to be considered when assessing the application of different soil remediation technologies to agricultural sites are: (1) the stage of development of the technology, (2) the implementation of the technology in a chain of treatments or in a single step, (3) the state of the produced residues (solid, liquid, gas), (4) the availability of the technology, (5) the reliability of the system, and (6) the requirements of the maintenance. Furthermore, the ecological sustainability of the treatment processes is of particular interest regarding their application to agricultural sites, and treatment methods that are not ecologically sustainable can be ruled out in advance. An appropriate treatment technology must be selected on a case-by-case basis, depending on several factors, *e.g.*, the extent of the contaminated area, the concentration of contaminants, the type of soil, the type of agricultural land use (*e.g.*, grassland with livestock or arable land), agricultural practices such as ploughing and fertilizing, weather and climate conditions, and irrigation. The addition of soil improvers can be combined with conventional farming practices (Kumpiene et al., 2008; Vangronsveld et al., 2009; Beesley and Marmiroli, 2011; Lee et al., 2011; Bolan et al., 2014). Due to the specific soil conditions for each site, small-scale testing is recommended to assess the influence of different amendments and their dosage on the soil and plants. In this way, an efficient and environmentally friendly soil treatment programme can be realised, taking into consideration the current conditions and requirements. The application of soil improvers for As retention is rarely used on a larger scale due to the current lack of knowledge concerning long-term behaviour. To establish this technology for agricultural sites, further testing should be conducted on the long-term effectiveness of amendments for plant health and the impact of changing conditions.

The use of a schwertmannite-based adsorbent for the retention of As in soil was tested with pot trials using spring barley (please see Section 4.3. above). The results revealed that the tested adsorbent successfully retained As and resulted in decreased concentrations of mobile As in soils, as well as in harvested crops. However, the effects of the applied amendments on other contaminants present in the investigated soil must be taken into account. In the present case, it was evident that As concentrations could be reduced, but concentrations of Cd and Pb in crops conversely increased under certain conditions, posing a significant problem due to the current threshold values for concentrations of these elements in food and fodder. However, through the combined application of the adsorbent and an additional additive (chalk or ash), the As concentration was significantly reduced in crops, while the concentrations of Cd and Pb were observed to remain unchanged, or slightly fall, compared to the control samples. These studies indicate the importance of being aware of the possible interrelationships and feedback mechanisms and that before the large-scale application of amendments, careful analysis of all factors needs to be carried out.

5.3. Agricultural amendment procedures

We carried out pot experiments with barley to investigate the effects of various agricultural amendment procedures on the availability of soil As. Our results corroborated the generic recommendations for fertilization and liming as an effective adaptation practice regarding the mobilization potential of As (Klose, 2017; Neu et al., 2020). They also highlighted the need for specific agricultural treatments to be assessed on a small scale on a site-by-site basis before attempting the treatment of large areas.

The use of soil amendments is a simple technology, as the addition of soil improvers can be combined with conventional farming practices such as the application of fertilizers (Kumpiene et al., 2008; Vangronsveld et al., 2009; Beesley and Marmiroli, 2011; Lee et al., 2011; Bolan et al., 2014). A technology that is extensively applied in agriculture is liming, which aims at increasing the soil pH to immobilize metals. A further approach is the use of amendments that retain As, based on the adsorption process. To date, this technology has only been tested at laboratory and pilot scales. Since the adsorption process could be reversible, release is possible if certain conditions change. For this reason, further adjustment of actively influencing parameters is necessary. Additional stabilizing agents, *e.g.*, lime for the pH value, and adapted agricultural practices such as ploughing and drainage systems to avoid reductive zones are required to maintain As retention on adsorbents.

Oxidative stress is one of the most common consequences of As accumulation in plants, as it generates reactive oxygen species, which leads to growth inhibition, physiological disorders and finally death (Meharg and Hartley-Whitaker, 2002; Stoeva et al., 2003; Gunes et al., 2009). As shown in our studies with the Omega-3 Index measuring the degradation of polyunsaturated fatty acids in plant leaves, lipid peroxidation is an important consequence of oxidative stress caused by the toxicity of As (Battaglia-Brunet et al., 2019, 2021).

The correlation between the phytotoxicity of As and its concentration in plants may depend on parameters that influence the growth of and oxidative stress in plants (Romero-Freire et al., 2014; Pigna et al., 2015).

5.4. Water treatment technologies

Reverse osmosis was effective in our studies in the removal of As and other contaminants from contaminated agricultural water, resulting in high water quality. Each of the common water treatment techniques has its own advantages and disadvantages in terms of removal efficiency, cost of operation, type of water, scale-up and operating conditions. Arsenic exists in four forms in terms of oxidation state, *i.e.*, arsenates As (V), arsenite As (III), arsenic As(0) and arsine As (-III). The precise form of As in water must be considered when selecting the treatment method.

The sustainability assessment was based on the multi-criteria approach to ensure the evaluation of technological, economic, environmental and social aspects. There is no universal As removal technology suitable for all possible situations. The best removal technology for As must be selected case by case, especially considering the design parameters (*e.g.,* the quantity of water to be treated and target water quality and application) and properties of the source water (chemical characteristics and composition of water contaminated with As).

5.5. Risk assessment and risk communication

The risk assessment model developed during our project proved useful for performing risk assessments for sites with a highly varying degree of available data. The model can thus be used to gradually increase the accuracy of the predictions by identifying the most important exposure pathways to prioritize further studies. The risk assessment performed for the study sites showed that site-specific values for some important parameters where not available and generic data had to be used, for example for the uptake of As in edible plants and in animal products, two potentially important exposure pathways.

Plant uptake of As varies depending on the soil conditions, the chemical form of As and on the species and variety of plant. The soil conditions influence the chemical form of As present in the soil. Translocation within the plant is also affected by the chemical form of As (Azama et al., 2016; Punshon et al., 2017). At present, information about the uptake and translocation in plants of different As species is very limited. In addition, the speciation of As in the soil varies from site to site and with time and is difficult to predict. Therefore, in our risk assessment, no attempts were made to take speciation into account. The uncertainties associated with estimates of speciation and the transport of As in agricultural systems are possibly so large that site-specific measurements of As concentrations and speciation in environmental media are required to enable a detailed site-specific risk assessment. Broader modelling studies should be encouraged as a means of studying the importance of various processes and increasing the understanding of the system.

The risk assessment scenarios we compiled are probably over-conservative, especially for Verdun. On a small site, it will not be possible to grow all the crops or to produce all the animal products considered. Therefore, more detailed site-specific information about occupation times at the site and the consumption of locally produced food needs to be gathered to make realistic risk assessments. Moreover, the assessment of health effects was based on inorganic As, but in the future, health risk assessments could be improved by taking into account the toxicities of different forms of As to which people are exposed.

Risk communication is needed to turn science-based information into awareness, risk perception and finally into action (Lundgren and McMakin, 2018; Singh and Taylor, 2019). In general, the road from raising awareness to action is long and full of obstacles, whether dealing with rice (Mondal et al., 2019), regional regulations (Kardel et al., 2011) or national policies (Fisher et al., 2017). Issues of trust, recognition and confidence often result in delay in decision-making, with prolonged consultations before plans can be turned into action (Jardine et al., 2013). Risk communication could even become a discourse of fear if official information or agencies are mistrusted in general (Altheide, 2010).

The risk assessment model developed within our project could be a tool in risk communication, as it can be used to express the risks from As at the contaminated site in relation to the total risks from As. The model can also be applied to assess risks for both cancer and non-cancer effects of As exposure.

5.6. Risk management

In previous sections, we have presented key steps for improved As risk management in agriculture resulting from intensive research and administrative work in European countries since the 1990s. A set of risk management procedures has been developed for the German State of Saxony. Nowadays, several thousands of square kilometers of contaminated soils are used for agriculture, settlement and gardening and are closely monitored and regulated (Landesdirektion Sachsen, 2012).

The risk management of a contaminated agricultural soil–water ecosystem depends on the extent of the contaminated area and the severity of its environmental impact. It is evident that no single risk management strategy will be applicable to these specific and differing situations, so that case-by-case decisions are required. However, a general procedure for the establishment of a risk management strategy for the remediation of contaminated agricultural sites can be described.

The results of risk assessment form the basis of a risk management strategy. For the establishment of a soil management system aimed at preventing potentially hazardous exposure to As, the development of a comprehensive database is recommended for contaminated sites, including information on geochemical data, soil characteristics, the extent of contamination and concentrations in soil, water and plants, land use and agricultural practices in the past and present (Barth et al., 2001; Rank et al., 2001). Additional long-term monitoring of the behaviour of contaminants as in Saxony can provide information for the identification of a potential risk, the development of risk management options, *e.g.*, the derivation of recommendations for farmers and landowners to optimize agricultural and gardening procedures.

If remediation of agricultural land is to be carried out while preserving agricultural use, a combined approach of treatment and management possibilities will be the most efficient way to ensure the safe use of contaminated agricultural sites. Land-use planning is the main option for extensive regions rich in As, while remediation options can only be considered at much smaller scales. Arsenic is seldom the only potentially harmful element or compound at an agricultural site. Future research could focus on the interactions of As with other contaminants such as microplastics, pesticides and specific pharmaceuticals.

5.7. Social, economic and policy aspects

The ways in which the results of environmental research are communicated differ from one country to another (*e.g.*, Rodrigues et al., 2009). Communication to the public of sensitive subjects with implications for human health, land use and land value can be influenced by economic and political concerns. The European Union, for example, has been actively working on the issue of facilitating access to reporting of environmental matters, including the potential pollution of agricultural soils, through a decision to repeal the standardised reporting directive (EU Council Directive Environment, 1991) and by amending six related legal acts. This decision is intended to ensure legal clarity, enhance transparency and reduce the administrative burden in the field of environmental reporting (press release of 4 October 2017, https://www.consilium.europa.eu/en/press/pressreleases/2017/10/04/environmental-reporting/).

We presented the soil planning area in Freiberg as an example of comprehensive contaminated land management developed by both scientists and stakeholders in consultation with the whole community. All data and maps are available online, together with guidelines for farmers (http://www.smul.sachsen.de/bful/14107.htm).

In order to progress towards intelligent management of the risks associated with As in agricultural soils, an analysis is recommended, from a sociological point of view, of the obstacles that currently preclude the following:

1. The availability to the general public of data, presented in an easily understandable way, about the distribution of As in soils, water and crops.
2. Communication of the results of risk assessment studies.
3. Communication about the risk of As in agricultural soils in relation to other issues, at local, regional, national and international scales in order to promote rational and optimal political decisions.
4. The integration of these studies in the further development of land management strategies involving the participation of both stakeholders and the whole society, informed in a transparent way.

Once the sociological obstacles are identified, strategies to overcome them can be developed. The European Commission presented recommendations for a soil protection strategy in 2006, with the proposed Directive of the European Parliament and of the Council establishing a framework for the protection of soil (European Commission, 2006). Prolonged discussions between the member states and the European parliament between 2006 and 2014 failed to deliver an agreement.

Many European countries are currently discussing how they can address problems with agglomeration or sealing of soils, because of its impact on the reduction of subsequent groundwater recharge. The input of chemical substances also disturbs the soil–groundwater pathway. The European Commission has made some demands on the Common Agricultural Policy, for example the obligatory greening or the Nitrate Directive. However, a European Soil Thematic Strategy needs to address the prevention of further deterioration of soil quality, conservation of soil functions, and protection against erosion, sealing, salting, acidification, loss of organic matter and contamination.

6. Concluding remarks and perspectives

We evaluated the impact of selected agricultural practices on the bioavailability, speciation, mobility and toxicity of arsenic (As) and compiled general conclusions based not only on the experiments of our project but also on the results of previous studies. Contamination of agricultural soils was the main concern at both investigated sites, Freiberg in Germany and Verdun in France. We investigated the effects of agricultural amendment procedures on the availability of As. The experimental results corroborated the generic recommendations for fertilization and liming as an effective adaptation practice regarding the mobilization potential of As. Overall toxic effects on organisms depended more on speciation, solubility and phosphorus availability than on total As concentrations.

The adsorption and coagulation–filtration processes were the most feasible options for the treatment of contaminated surface waters from Verdun.

It was recognized during our experimental work that each site has different characteristics, and the recommendations therefore require a case-by-case assessment to identify the best practices or treatment solutions for sustainable agriculture, especially if attempting to treat large areas.

A model was developed for assessing the health risk due to As exposure, both from the contaminated site and from other sources. The model used available site-specific data and complemented missing data with model estimates or generic data, as appropriate. The wide scope of the used modelling approach, which also included exposure from off-site sources, gave information for remedial and protective activities.

A general procedure for establishing a risk management strategy for contaminated agricultural sites was developed. The first stage is to identify whether there is a risk to humans and the environment. If the results of site investigations indicate the need for action, there are two options: (1) the adaption of agricultural and soil management activities to prevent exposure and (2) the removal of contaminants from soil by remediation measures. Risk management establishing a controlled safe land use is suggested as a main option for extensive agricultural areas, while remediation options that directly treat the soil can only be considered in urban areas subject to sensitive use (*e.g.*, playgrounds and kindergartens). Water treatment is needed if drinking water or water for agricultural use is contaminated. If remediation of agricultural land is to be carried out while preserving agricultural use, a combined approach of treatment and management possibilities ensure the safe use of contaminated agricultural sites.

As yet, there are no globally accepted recommendations for risk management procedures, regulations or guidelines related to As in agricultural soils and waters. We present the soil planning area of Freiberg, Germany, as an example for comprehensive and rational contaminated land management developed by both scientists and stakeholders in consultation with the whole community.

CRediT authorship contribution statement

Kirsti Loukola-Ruskeeniemi: Writing – original draft, Writing – review & editing, Conceptualization, Supervision, Methodology, Project administration. **Ingo Müller**: Writing – original draft, Methodology, Supervision. **Susan Reichel**: Writing – original draft, Investigation. **Celia Jones**: Writing – original draft, Investigation. **Fabienne Battaglia-Brunet**: Writing – original draft, Investigation. **Mark Elert**: Writing – original draft, Investigation. **Marina Le Guédard**: Writing – original draft, Investigation. **Tarja Hatakka**: Writing – original draft, Investigation. **Jennifer Hellal**: Writing – original draft, Investigation. **Isabel Jordan**: Writing – original draft, Investigation. **Juha Kaija**: Writing – original draft, Project administration. **Riitta Keiski**: Writing – original draft, Methodology, Supervision, Investigation. **Jana Pinka**: Writing – original draft. **Timo Tarvainen**: Writing – original draft. **Auli Turkki**: Writing – original draft. **Esa Turpeinen**: Writing – original draft, Investigation. **Hanna Valkama**: Writing – original draft, Investigation.

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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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.127677.

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