



Arsenic movement and fractionation in agricultural soils which received wastewater from an adjacent industrial site for 50 years

Cristiana Morosini ^a, Elisa Terzaghi ^a, Giuseppe Raspa ^b, Marco Grotti ^c, Stefano Armiraglio ^d, Simone Anelli ^e, Antonio Di Guardo ^{a,*}

^a DiSAT, University of Insubria, Via Valleggio 11, Como, Italy

^b DICMA, Sapienza University of Rome, Via Eudossiana 18, Rome, Italy

^c Dept. of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, Genoa, Italy

^d Municipality of Brescia - Museum of Natural Sciences, Via Ozanam 4, Brescia, Italy

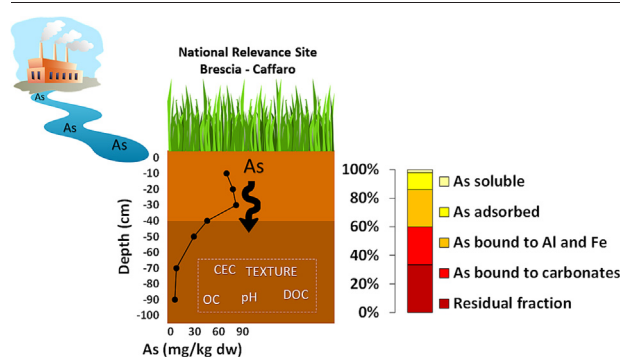
^e ERSAF, Via Pola 12, Milan, Italy



HIGHLIGHTS

- Arsenic was measured in industrially polluted agricultural soils in Italy.
- As pesticide production wastewater was used as irrigation water for 50 years.
- Vertical (up to 1 m) and horizontal (field wide) gradients were obtained for soil.
- Concentrations were between 10 and 200 mg/kg and mostly in the plow layer.
- Fractionation of As species was related to specific plant species potted in soil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Damia Barcelo

Keywords:

Arsenate
Solid phase speciation
Vertical movement
Horizontal diffusion
SIN Brescia-Caffaro

ABSTRACT

Arsenic (As) is an element with important environmental and human health implications due to its toxic properties. It is naturally occurring since it is contained in minerals, but it can also be enriched and distributed in the environment by anthropogenic activities. This paper reports on the historic As contamination of agricultural soils in one of the most important national relevance sites for contamination in Italy, the so-called SIN Brescia-Caffaro, in the city of Brescia, northern Italy. These agricultural areas received As through the use of irrigation waters from wastewater coming from a factory of As-based pesticides (lead and calcium arsenates, sodium arsenite). Pesticide production started in 1920 and ended in the '70. Concentrations in the areas are generally beyond the legal threshold values for different soil uses and are up to >200 mg/kg. Arsenic contamination was studied to assess the long-time trend and the dynamics related to the vertical movement of As down to 1 m depth and its horizontal diffusion with surface irrigation in the entire field. Arsenic fractionation analysis (solid phase speciation by sequential extraction procedure) was also performed on samples collected from these areas and employed in greenhouse experiments with several plant species to evaluate the long-term contamination and the role of plant species in modifying As availability in soil. The results of this work can help in the evaluation of the conditions controlling the vertical transfer of As towards surface aquifers, the bioaccumulation likelihood in the agricultural food chain and the selection of sustainable remediation techniques such as phytoremediation.

* Corresponding author.

E-mail address: antonio.diguardo@uninsubria.it (A. Di Guardo).

1. Introduction

Arsenic (As) is a metalloid with a relevant potential for bioaccumulation and whose environmental occurrence is ubiquitous. Arsenic can be found in four different oxidation states: -3 (arsine), 0 (elemental arsenic), $+3$ (such as, for example, arsenite) and $+5$ (such as, for example, arsenate). Its inorganic compounds (such as trivalent arsenite and pentavalent arsenate) are more toxic than the organic forms in terrestrial environments (Rahman et al., 2014), where they can exert endocrine disrupting and carcinogen activities. Inorganic As compounds are, in fact, classified as “Group 1 human carcinogen” (IARC, 2012), whereas methylated As species exhibit significantly lower toxicity (Kaise et al., 1989). On the other hand, bi-methylation can increase the volatilization and biogeochemical cycling of As, such as by the formation of volatile arsines (Wang et al., 2014). Arsenic derives both from natural and anthropogenic sources (Huang et al., 2018). Among the former, rock weathering and soil erosion are the main actors, since As is the main constituent of >200 minerals (IARC, 2012); among the latter, on the contrary, ore mining and smelting, use of As-containing fertilizers and pesticides, and combustion of fossil fuels can be found (Rahman et al., 2014; Wang et al., 2014). It was estimated that mean background concentration of As in soils varies between 0.42 mg/kg for Florida soils to 2.8 and 8.25 mg/kg for California and Mississippi soils, respectively (Zhang and Selim, 2008), while in a large recent review on Chinese soils the median concentration was 10.4 mg/kg (Gong et al., 2020). In other regions, As values around 5 mg/kg were detected in the uncontaminated soils of Poland (Loska et al., 2004), similar to the topsoil levels in the agricultural region of Yangzhong, China, around 10 mg/kg, below the Chinese natural background level, which is 15 mg/kg (Huang et al., 2007).

The results reported in this study deal with As contamination in agricultural soils in one of the most important national relevance site for contamination in Italy, the so-called SIN (*Sito di Interesse Nazionale*, in Italian) Brescia-Caffaro, located in the city of Brescia, northern Italy. Concentrations here are often beyond the legal threshold values for different soil uses (20 mg/kg d.w., 30 mg/kg d.w. and 50 mg/kg d.w. for residential, agricultural and industrial areas, respectively) (Italian Parliament, 2006; MOE, 2019). The site was contaminated by the activities of the former Caffaro S.p.A. chemical factory, which was the main producer of polychlorinated biphenyls (PCBs) and other chemicals, including As-containing pesticides (Di Guardo et al., 2017). Some of these chemicals, including mercury (Hg) and As, ended up into wastewaters (Morosini et al., 2021). The production of As-containing pesticides (lead and calcium arsenates, sodium arsenite) started in 1920, with an estimated initial production of 5 t/month, and ended in the '70, due to the law restriction on As use in pesticides (Ruzzenenti, 2001). Since wastewaters were discharged in an adjacent stream, these chemicals reached a wide network of irrigation canals, and they were spread for a long period (~ 50 years), through the irrigation system, over an agricultural area of more than a hundred hectares. Arsenic was incorporated into the soil which was continuously cropped for the following 50 years. Previous studies on PCBs and Hg discharged in the same way and in the same areas (Di Guardo et al., 2020; Morosini et al., 2021) demonstrated that the highest levels of contamination occurred in the topsoil (corresponding to the first 40 cm, the plowing layer) and at the entry point of irrigation water into the cultivated areas.

In this work, As was studied in three former agricultural areas of the SIN Brescia-Caffaro with the main objective of assessing the long-time trend and the dynamics related to the vertical movement of As down to 1 m depth, as well as its horizontal diffusion with surface irrigation in the entire field. Such information is peculiar to plan the effective bioremediation of polluted areas, especially when multiple contamination is present (PCBs, dioxins and furans, Hg) and single techniques cannot be operated. In addition, it is important, to accomplish such results, to evaluate the long-term contamination and the role of plant species in modifying the As fractionation in soil, thus exploring the potential modification in the As mobility induced by a specific plant cultivation.

2. Materials and methods

2.1. Experimental locations

Arsenic was measured in three different agricultural areas (A, R, and T, Fig. 1), located southwest of the Caffaro Plant. The area is flat land, bordering the Lombardy Prealps. This lowland sector is occupied by Quaternary deposits, with the presence of a layer of fluvial deposits. This plane is slightly inclined towards the South and altitudes varying from North to South between 190 and 105 m a.s.l. (Provincia di Brescia, 2016). The average annual temperature is comprised between 10 and 14.4 °C. Average annual rainfall is 1002 mm, with most abundant precipitation in Autumn and May (Provincia di Brescia, 2016). Crop cultivation ceased by law in 2002; while the input of As to soils ended with the end of production of As containing insecticides in the late '70. No other arsenic sources are known. The areas were selected for their different soil use and cropping, as well as for their different distribution within the contaminated fields (Di Guardo et al., 2020). For AREA A (5.1 ha), water meadows (with winter irrigation) and corn were the main crops, whereas AREA R (5.5 ha) was characterized by a peculiar crop rotation (e.g., corn, clover, and alfalfa). Finally, AREA T (8.0 ha) was mostly cropped with alfalfa and corn; in this area, important leveling activities were historically performed since field and canal rearrangement was accomplished. All these areas were assessed to evaluate the vertical As distribution, whereas only the results for area A are shown to illustrate As horizontal spatial spreading.

2.2. Sampling activity

A preliminary sampling activity was conducted in spring 2014 to evaluate the range of concentrations in the topsoil of SIN Brescia-Caffaro (Di Guardo et al., 2017) and As range was found to be comprised between 27 and 79 mg/kg. Based on these data, further sampling was scheduled to observe the vertical and the spatial (2D) distribution in soil.

2.2.1. Arsenic vertical distribution

Three sampling points were selected in each area (Fig. 1) from North to South according to the (surface) irrigation direction, for a total of 9 points, named A1, A2, A3; R1, R2, R3; T1, T2, and T3 (Di Guardo et al., 2020; Morosini et al., 2021). Points were selected to gather levels close to the points of entry (north points), central and end of the field (south points). Soil cores were obtained at each point in October 2014, using a direct push mechanical dual tube corer (Geoprobe DT7822), which utilized a 7.35 cm DT45 liner. For each area, the first sampling points (i.e., A1, R1 and T1) were located at about 11 m from the irrigation stream (Fig. 1, top) (Mason, 1992; US EPA, 2023). Samples were collected by coring the soil down to 1 m, after removal of turf. Three cores (within 1 m) were obtained at each of the 9 sampling points, for a total of 27 cores. Seven subsamples were then obtained from each of the three cores for each point, for the following depths (cm): $0-10$; $10-20$; $20-30$; $30-40$; $40-60$; $60-80$; $80-100$. The subsamples gathered at the same depth interval for each point were in situ pooled to get 63 homogenous composite samples in total. The reason for collecting three cores for each sampling point was to realize a suitable local average concentration for each depth, thus preventing potential outliers due to punctual sampling.

2.2.2. Spatial gradient of As in soils

The spatial trend of As concentration in area A was obtained by collecting 17 soil samples (Fig. 1, B) in December 2014, using the corer described above but with a different, ~ 5 cm (2 in.), DT325 liner. Specifically, 5 replicated samples ($0-40$ cm depth) were collected in the center and at the four vertices of a 1 m² square for each point. The samples were in situ pooled to gather a homogenous sample for each point (Mason, 1992; US EPA, 2023). The points were selected in order to produce a regular spaced grid, with a distance of approximately 50 m among the different points (systematic grid sampling) (US EPA, 2015). The concentrations measured at each point were then interpolated using geostatistical

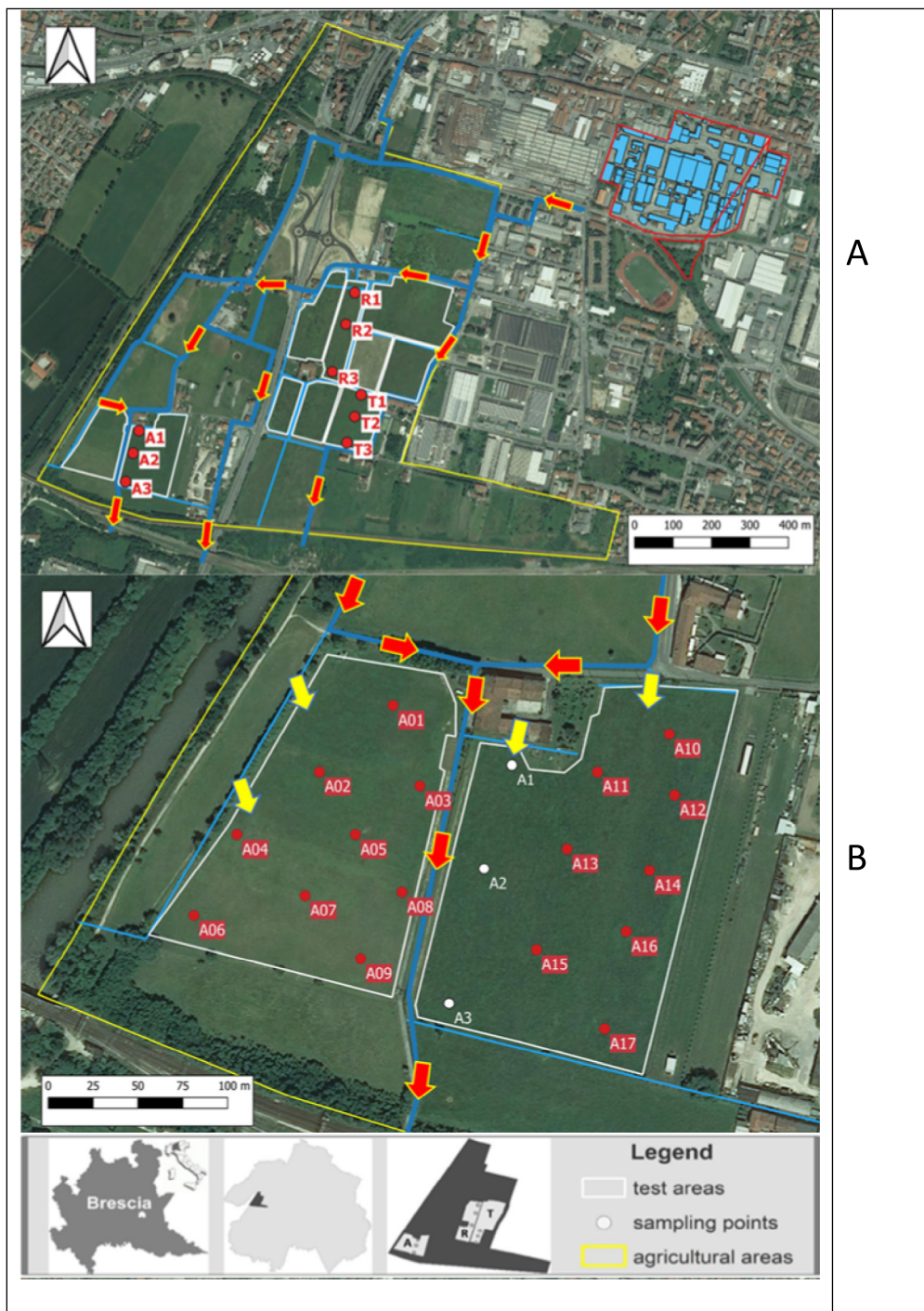


Fig. 1. Map of the agricultural areas. In section A, the agricultural areas (in yellow the perimeter, in blue the irrigation canal network, the red arrows show surface water direction) with the points for vertical profile analysis (A1 to A3, R1 to R3, T1 to T3); in section B, the points used for the spatial analysis. Yellow arrows indicate the point of entry of surface irrigation water.

techniques. Sampling procedures as well as the chemical analyses for this part of the study were realized by a commercial laboratory (Theolab S.p. A., now Mérieux NutriSciences, Volpiano TO, Italy).

2.3. Greenhouse experiment

Arsenic fractionation and mobility were further investigated to evaluate the role of plant species in altering these parameters in soil, by performing a long-term (18 months) greenhouse experiment. Soil samples

(0–40 cm depth) were collected in a specific point of area R, selected because the concentrations of As and other chemicals were high enough to perform the greenhouse experiment in reasonably worst-case conditions. Four plant species, i.e., *Brassica juncea* (L.) Czern (brown mustard), *Festuca arundinacea* Schreb. (tall fescue), *Medicago sativa* L. (alfalfa), *Salix caprea* L. (goat willow) were used (Terzaghi et al., 2019a). Plants were grown in polypropylene pots containing about 6 kg of soil. The experiment lasted from spring 2015 up to autumn 2016. As fractionation in soils was measured at the beginning of the experiment (unplanted control) and

at the end, after 18 months (planted soil). One soil replicate was analyzed for As fractionation. Moisture level was kept at near field capacity conditions (30 % of the soil total volume) using drip irrigation. Further details on the experimental conditions were previously reported (Terzaghi et al., 2019a).

2.4. Chemical analyses

2.4.1. Field soil samples

Soils were prepared following US EPA 3051A Method (US EPA, 2007a). In brief, about 0.5 g of sample (air dried and sieved at 2 mm) were mineralized using a microwave digester (Ethos Touch Control-Milestone) with H₂O₂ (2 mL, 30 %), HNO₃ (2 mL, 65 %) and HCl (6 mL, 37 %). After the digestion, samples were diluted to 500 mL using ultrapure water and finally filtered with 0.45 µm pore size membrane filters (Millipore Millex-HA). Total As was measured following US-EPA 6020A method (US EPA, 2007b) by inductively coupled plasma mass spectrometry (Agilent, model 7500). The internal standard used was Indium. Three washing steps were employed after each sample to minimize memory effects: a 4 % mixture of nitric and hydrochloric acid, a 2 % mixture of ammonia and hydrogen peroxide and lately a 2 % mixture of nitric and hydrochloric acid.

2.4.2. Greenhouse soil samples

Fractionation of As in soil was investigated following the Selective Sequential Extraction (SSE) procedure by (Shiowatana et al., 2001), (Table A1 in the Supporting Information) that is considered more suitable for assessing the bioavailability of As in soil compared to other SSE procedures developed for heavy metals (Wan et al., 2017). According to this procedure, As in soil is divided into five fractions: the water-soluble fraction (F1), the surface-adsorbed fraction (F2), the Fe/Al associated fraction (F3), the carbonate-bound fraction (F4), and the residual fraction (F5). More details in the Supporting Information.

A procedural blank was concomitantly prepared for each step. Finally, the solutions F1-F5 and the blanks were analyzed by inductively coupled plasma optical emission spectrometry (Varian, model Vista Pro), measuring the emission intensity at four specific wavelengths (188.980 nm, 193.696 nm, 197.198 nm, 228.812 nm) and compensating for the matrix effects by internal standardization (Grotti et al., 2013).

2.5. QA/QC

2.5.1. Field soil samples

Calibration curves were obtained in the range 1–1000 µg/L, utilizing multielement aqueous standard solutions (LGC, range 1–20 mg/L in nitric acid) and external standard quantitation. LOQ was set as the lowest point in the calibration curve, 1 µg/L. Laboratory Control Samples (LCS) were used to monitor soil extraction (US EPA, 2007a) and recovery. Several field and transport blanks were analyzed to evaluate the potential contamination at the different times, especially for the volatile species. These blanks, together with method blanks (analyzed at a ratio of 1 out of 20 samples), were at concentrations lower than 0.5 LOQ. NIST 2711A Montana II Soil was employed as certified reference material for quality control. Recovery was 95.11 % on average. Method detection limit (MDL) was obtained according to (US EPA, 2016) and corresponded to 0.225 mg/kg d.w. Measurement uncertainty was obtained according to (Horwitz et al., 1980), and was 3.97 %.

2.5.2. Greenhouse soil samples

The detection limit, computed as 3 times the standard deviation of the intercept of the calibration curve, was 0.3 µg/g. Since no certified reference material was available to control the accuracy of the SSE procedure, the method was verified by summing the fractions of extracted As in each phase and comparing the obtained value with the total As in the sample, determined by microwave-assisted acid digestion of an independent portion (same conditions as step 5) and instrumental analysis. The ratio found was 1.03 ± 0.05 (mean and 95 % confidence interval, *n* = 11). The

accuracy of the residual As and total As determination was validated by analyzing the certified reference sediment MESS-2 from the National Research Council of Canada. The reproducibility of the Shiowatana procedure was assessed to be better than 10 % (Wan et al., 2017).

2.6. Statistical analyses

Statistical analyses were obtained using XLSTAT (Addinsoft SARL, Version 2023.1.2, Boston, USA). Regression analysis was employed to analyze the trend of As concentration with increasing distance from the surface irrigation canals. Correlation analysis was also employed to evaluate the strength of the association between soil properties and As concentrations in soil. Principal component analysis (PCA) was also used to evaluate the correlation between the environmental properties and to highlight the differences among the samples. The spatial concentrations map for area A was realized using the intrinsic kriging method with automatic identification of the generalized covariance (Chilès and Delfiner, 2012; Goovaerts, 1999; Goovaerts et al., 2008; Saito and Goovaerts, 2001). The map was then created interpolating the estimated concentration points in the grid and the isoconcentration curves were displayed.

3. Results and discussion

The agricultural soils of the SIN Brescia Caffaro represent a peculiar case in which the most important As contamination source derived from the industrial production of As based insecticides. No information exists on other sources or uses of As in these areas. The scenario of contamination was as follows: As was produced and released in wastewater for a long time (about 50 years), chemical was discharged via surface irrigation, therefore from single or a few points in each area (see the yellow arrows in Fig. 1, bottom panel.), crop cultivation was carried out for many years after. This situation therefore allows to evaluate the movement of As in vertical and horizontal profiles, as well as to investigate the role of plants in making As more bioavailable and/or immobile in soil, a starting point for any bioremediation activity, among the only options available considering the size of the SIN Brescia Caffaro.

3.1. Soil properties

Several soil properties (organic carbon content, texture, pH and cation exchange capacity) were obtained for the core samples of the three areas, at different depths (Di Guardo et al., 2020) (Tables A3 and A4 in the Supporting Information). Dissolved organic carbon (DOC) was measured, for all samples in the plow layer (0–40 cm) and was comprised. Typically, the most common textural class was sandy loam, but loamy sands could also be found (Maidment, 1993). Organic carbon was highly variable: from 0.34 % to 3.81 % in the plow layer (0–40 cm), and from 0.26 % to 1.86 % in deeper soil layers (40–100 cm). Cation exchange capacity generally reduced from plow to bottom layer, from 21.7 ± 3.1 meq/100 g (0–40 cm) to 16.6 ± 3.3 meq/100 g (40–100 cm). The pH was comprised between 7.02 and 8.76. DOC was comprised between 2.44 and 9.60 mg/L.

3.2. Arsenic levels in soil and comparison with other sites

Arsenic was released in Caffaro outflowing streamwater which was used for >100 years as part of the irrigation water of the agricultural areas (Fig. 1). Surface water irrigation was the prevalent irrigation method and water was generally spread from the north part of the fields until it reached the end of the same field. Topsoil As concentrations (in the plow layer) were generally comprised between 30 and 95 mg/kg, values well above the general background concentrations in non-contaminated areas and generally larger than the Italian As threshold for agricultural soils (30 mg/kg) (MOE, 2019). In fact, the background values of As in soil are generally reported in a range of 1 to 40 mg/kg, with an average of 5 mg/kg (IARC, 2012). For example, As background values of

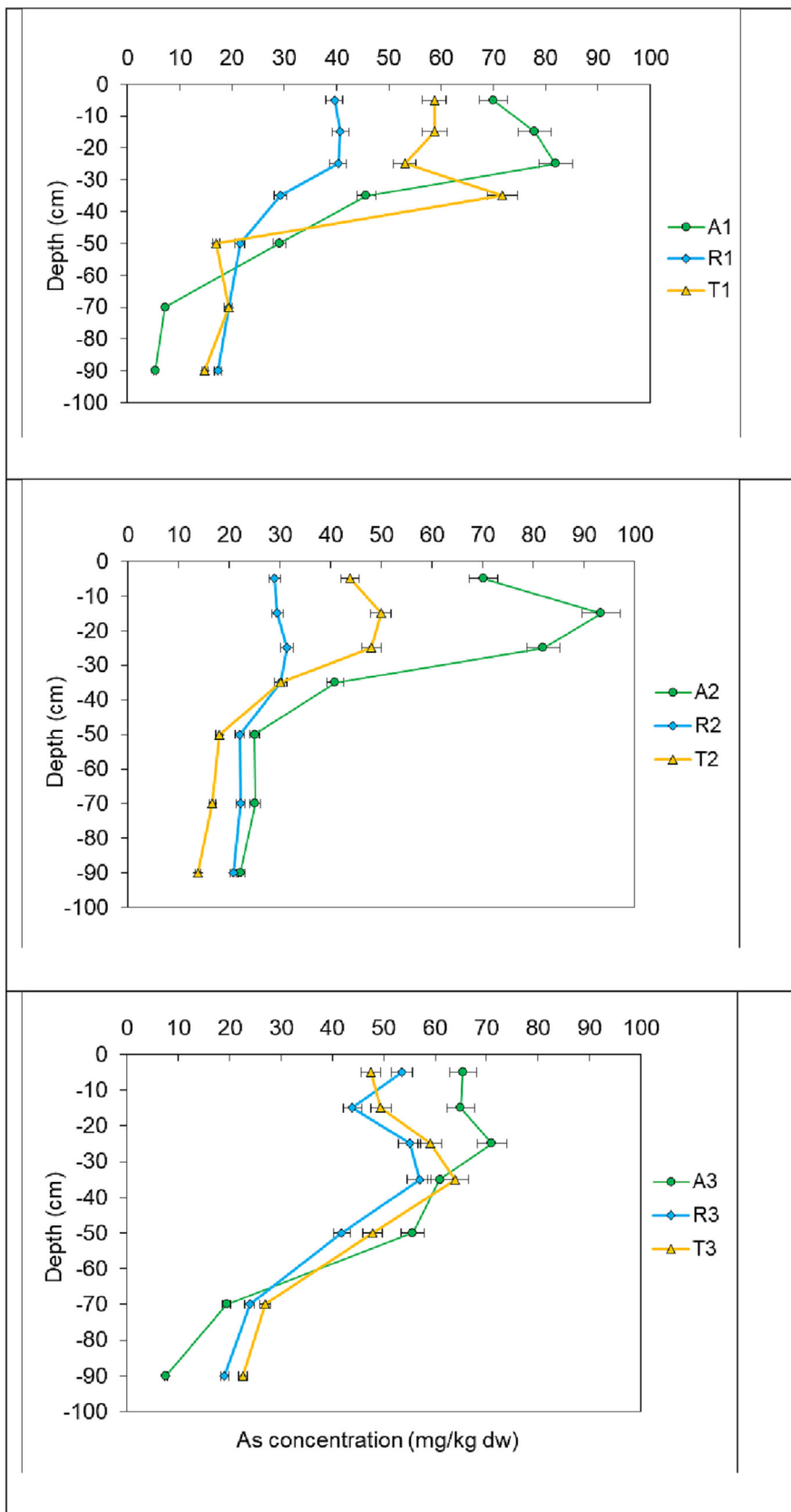


Fig. 2. Variation of As concentration with depth at the three sampling points (areas A, R, T in Fig. 1). Bars represent the analytical measurement uncertainty (3.97 %).

5–10 mg/kg were measured in an uncontaminated reference area (Norra et al., 2005) in the agricultural area of Bengal Delta Plain, India. Average concentrations of As in Brescia soils are instead closer to those present in areas characterized by industrial activities and agricultural use of As (Atafar et al., 2008). Areas characterized by higher levels than those found in this work are mine soils, such as those of the Shimen realgar mine area in China, in which total As concentration in soil was found up to 5240 mg/kg (Wan et al., 2017).

3.3. Arsenic concentrations in soil profiles

Variations of As concentration with depth (Table A3) are plotted in Fig. 2. Given the entry points, which were located north of point 1 in the three areas (A, R, T), we decided to group the plots according to point number to evaluate respective concentration gradients: points 1 of the three areas can be seen in the top chart of Fig. 2, points 2 in the middle chart and points 3 in the bottom chart. Concentrations in the plow layer (0–40 cm) were generally comprised between about 30 to 90 mg/kg d.w. in the first two points, while they were generally lower (40–70 mg/kg d.w.) in the most distant points from the irrigation water entry point.

Concentrations in area A were generally higher (up to about 50 %) than those in areas R and T. This can be explained considering that the irrigation water was used more intensively in area A because of the presence of a water meadow and the continuous use of water, especially in winter, while the other areas were not continuously irrigated over the year. When focusing on the layers comprised between 40 and 100 cm, a different behaviour can be observed, with a consistent drop of concentrations (about 40–60 % lower than the corresponding topsoil levels in each area and point). This reduction with depth is, however, smaller than that reported by (Morosini et al., 2021) for Hg, probably due to the higher mobility of arsenate in low clay soils (Walsh et al., 1977). Mercury was also discharged at comparable times and went through the same pathways, irrigation, plowing, redistribution, etc. For this reason, a comparison with Hg can be useful to evaluate the behaviour of As in the same soils.

A correlation analysis between As and soil properties was performed for the soil profiles (Fig. A1 in the Supporting Information) and reveals that As was mostly correlated with organic carbon and cation exchange capacity and to a lesser extent to silt, while the correlation with clay, sand and pH was weaker. Similarly, the PCA on the samples from the different depths, averaged as 0–40 cm and 40–100 cm for all the three areas and points (Fig. A2 in the supporting information) showed that the points from areas A and R generally behave differently from those in area T. This difference is highlighted by the gradient of silt (areas A and R) versus sand (Area T) by moving from top-right to bottom-left of the PCA plot. Moreover, a partial differentiation of topsoil versus bottom soil samples along the first axis can be observed, which can be explained by pH on one side and by clay, organic carbon, cation exchange capacity and As content on the other side. The results of the PCA in part differentiate areas A and R from Area T, which was characterized by soil displacement and leveling. As is inversely related to pH and directly to organic carbon, clay, and cation exchange capacity.

Similar depth profiles of As concentration can be found in the literature. In six orchard soils contaminated by former use of lead arsenate as insecticide in the State of Washington, most of the As was concentrated in the upper 40 cm of soil, where concentrations were comprised in the range 58–364 mg/kg (Peryea and Creger, 1994). The authors reported an As enrichment between 45 and > 120 cm in the soil profile, thus demonstrating that the high loading rates of lead arsenate, combined to the use of water irrigation, a coarse soil texture and a low organic matter content contributed to the downward movement of As. Similarly, in an intensively cultivated agricultural area of the Bengal Delta Plain, India, As concentration in the topsoil of a rice paddy field irrigated with As-rich groundwater (38 mg/kg) was found to be higher than the As concentrations in soil of a less irrigated wheat field (18 mg/kg) and in the soil of a rice paddy watered

with uncontaminated water (7 mg/kg) (Norra et al., 2005). In this study, a decrease in As concentration with depth (up to 11 mg/kg at 100–110 cm depth) was observed both in the rice paddy soil and in the wheat soil, with a different enrichment along the vertical profile due to the different use of irrigation water.

3.4. Spatial variability of As in area A

The spatial distribution of As in topsoil was studied for all the areas but here illustrated for area A (Table A4 in the Supporting Information), characterized by the highest concentrations and vertical gradient. The objective in this case was to evaluate the spatial spreading along surface water movement at irrigation events, in order to determine the phenomenology occurred, the point of As entry and the spreading of chemical in time and space. This information is important to evaluate the mobility of As in real field conditions, especially in a long-term contamination such as that in Brescia, where precise information exists on soil use and water irrigation (Di Guardo et al., 2020; Morosini et al., 2021).

Fig. 3 shows the 2D distribution of As in area A, where concentrations in topsoil (0–40 cm) vary from about 42 mg/kg in the middle part of area (point A03 in Fig. 1) up to 219 mg/kg in point A10, located in the north-eastern part of the map. In fact, while concentrations in the western part are lower and so is the gradient, much higher concentrations can be observed close to the entry points in the eastern part of the field, showing either a higher flow of contaminated water or higher concentrations in the top canal compared to the western canal (Fig. 3). A similar pattern was observed for Hg in the same area, even if, in this case, a much more evident gradient is present both in the middle and in the eastern part of area A (Morosini et al., 2021). In the eastern part of the area, As concentrations decreased from the top to the bottom part of the map by about 60 % in about 170 m. This depletion can be observed in Fig. 4 as well, where a relationship between As concentrations in topsoil of area A and the distance from the irrigation ditches is plotted both for the western and for the eastern part of the area. Regression analysis shows a good fit as regards the eastern part ($R^2 = 0.73$), but not as regards the western one ($R^2 = 0.13$), where a sort of random pattern seems to take place. In the eastern part of area A, historically cultivated with water meadows and corn, a progressive depletion in As concentrations occurred, within a distance, from the first sampling point close to the inlet (A10) and the one where As concentration is halved (A14), of 77 m. An analysis of the relationship and the influence of soil properties and As presence can be seen in the correlation matrix calculated for the spatial points (Fig. A3 in the Supporting Information). As is positively correlated mostly with the presence of clay and DOC, while inversely correlated, although to a minor extent, to the presence of sand and organic carbon. More details can be sought for the principal component analysis (Fig. A.4 in the supporting information) which first confirms the direct correlation among As and clay and DOC and the inverse correlation with

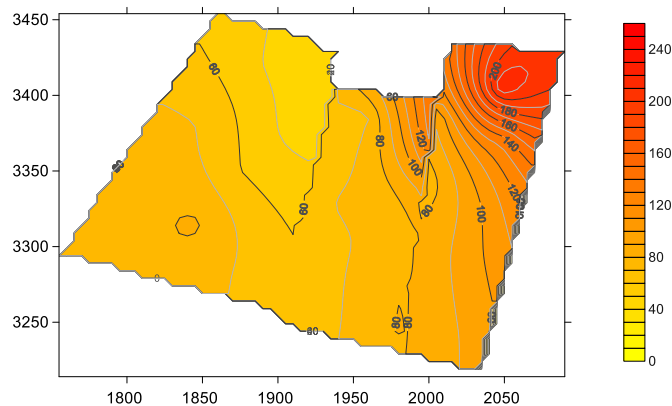


Fig. 3. Spatial map of As concentrations in area A. Values are in mg/kg.

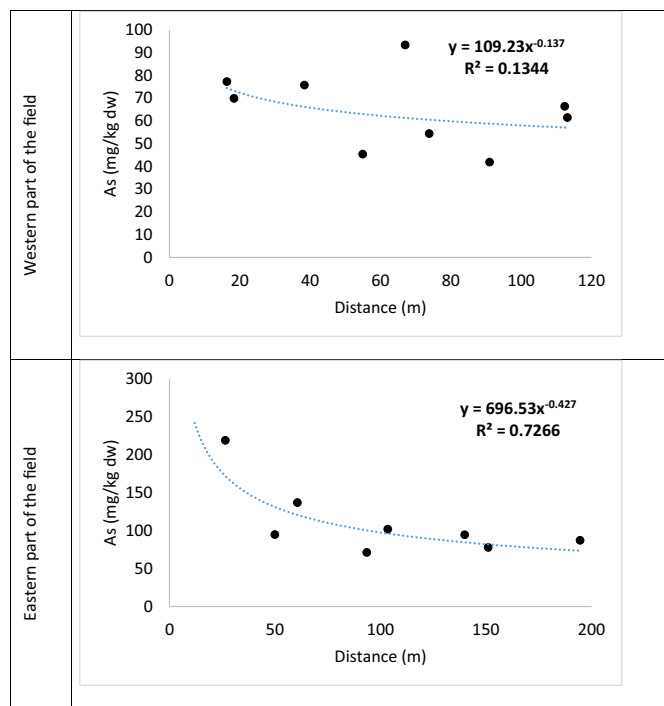


Fig. 4. Variation of As concentration in topsoil with distance from irrigation canals in area A: western field (top chart) and eastern field (bottom chart).

organic carbon. In addition, the PCA allows to separate the two different fields present in Area A, the bottom one (with a blue dashed oval), corresponding to the eastern portion of the area, from the top one (with a green dashed oval) corresponding to the western portion. PCA add therefore the type of cropping, which was different in the two portions: mostly permanent meadows in the western area and mostly corn and water meadows in the eastern area. The different cropping may have therefore contributed to influence As distribution and some soil parameters (such as DOC and OC).

A similar trend was observed by (Dittmar et al., 2007), who reported a decrease in As concentration with increasing distance from the water entry point in paddy fields irrigated with As-rich groundwater. They observed a reduction of about 50 % of As concentration (from about 30 to about 15 mg/kg) in the topsoil (0–10 cm) of one of the investigated field in about 60 m from the inlet irrigation point. They attributed this loss to chemical changes in the irrigation water, which interacts with the soil surface. They furtherly stated that the As distribution pattern is strongly dependent on the type of irrigation system used. In field A the same reduction (50 %) was obtained about 100 m away from the inlet point (Fig. 3), probably depending on the surface irrigation methods, in which a laminar flow of water is produced on the entire field to properly reach the entire area.

3.5. Arsenic fractions in soil

Arsenic is generally associated with sulfide minerals and its mobility in soils is strictly related to the pH, the redox potential, the ionic composition and the mineral type (Bauer and Blodau, 2006). The As compounds can, in fact, undergo oxidation/reduction and methylation/demethylation processes that could affect their mobility, which also depends on their

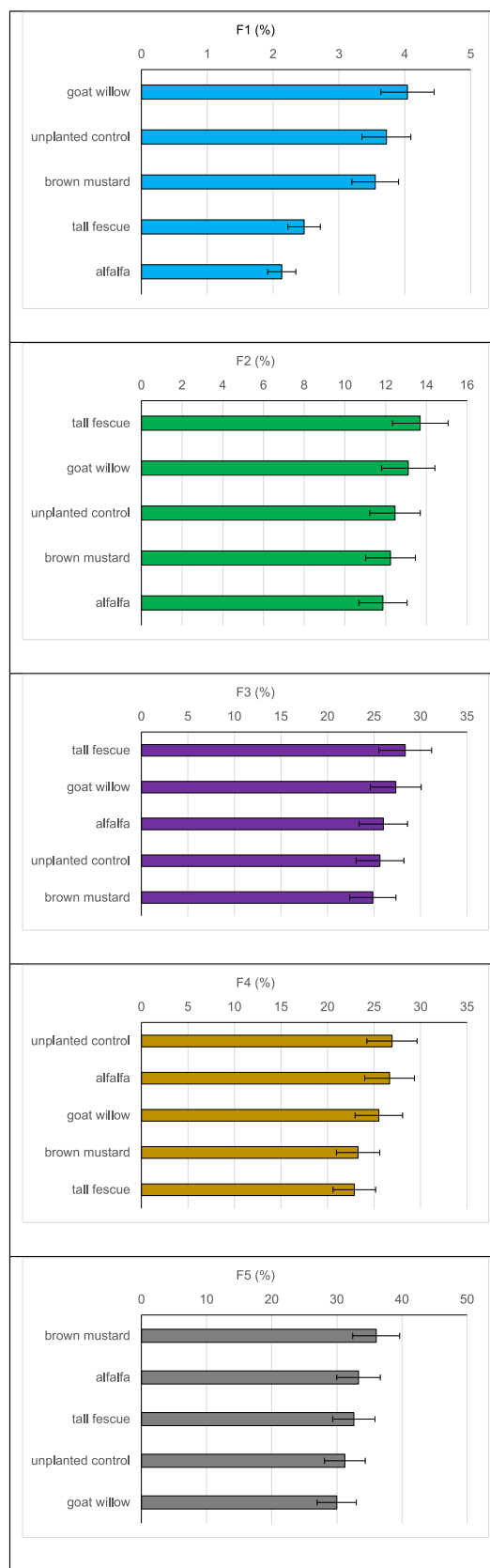


Fig. 5. Percent distribution of As in the soil fractions in which different plant species were grown: the water-soluble fraction (F1), the surface-adsorbed fraction (F2), the Fe/Al associated fraction (F3), the carbonate-bound fraction (F4), and the residual fraction (F5). The soil was planted with *Brassica juncea* (L.) Czern (brown mustard), *Festuca arundinacea* Schreb. (tall fescue), *Medicago sativa* L. (alfalfa), *Salix caprea* L. (goat willow) and bare soil (no plant species present). Error bars represent reproducibility of the measurement (10 %).

chemical form (e.g., arsenite is much more soluble and mobile than arsenate) and on changes in solid phase speciation (Bauer and Blodau, 2006; Peryea and Creger, 1994). When present in soils with neutral pH and oxic

conditions, As is sorbed or co-precipitate with metal oxides, since it is influenced by compounds of iron, manganese, aluminum, calcium and magnesium, natural organic matter, and clay minerals, which could represent important adsorbents for dissolved As, thus affecting its movement. In the case of lower pH values and reduced redox potential, instead, the mobility of As increases due to dissolution of metal oxides. The sorption of As is favoured by dissolved calcium and decreases when anions like phosphate and bicarbonate are present; wetland soils rich in dissolved organic carbon (DOC) content show an increase in As mobility (Bauer and Blodau, 2006; Kalbitz and Wennrich, 1998; Peryea and Greger, 1994).

The SIN Brescia-Caffaro soils are characterized by neutral or sub alkaline pH (average pH = 8) (Table A4 in the Supporting Information), little organic carbon percentage (around 1.8 %) and therefore presumably low DOC concentrations, and general oxic conditions due to the sand-dominated textural properties. In these conditions, a limited mobility of As is expected, as confirmed by the results discussed in the previous sections. Since the investigated area is used for agricultural purposes, it is important to evaluate whether different crops could affect the bioavailability of As, especially in long-contaminated soil, in which higher adsorption could be expected due to the diffusion of arsenate species to reaction sites within the soil matrix, also influenced by the long residence time of As in soil (Zhang and Selim, 2008).

The solid phase speciation analysis performed on greenhouse soil samples showed that the most soluble fractions, F1 and F2, generally represented a small percentage, comprised in the 2.1–13.7 range (Table A5 in the Supporting Information and Fig. 5), similarly to what occurred for Hg, even if the F1 and F2 fractions were even lower in that case (Morosini et al., 2021). F1 represented the smallest percentage among the five fractions and its value did not greatly differ among the treatments and the unplanted control, except for tall fescue and alfalfa, whose F1 was almost half of that in goat willow planted soil or the control soil. The most abundant fraction was F5, the so-called residual fraction, followed by F3, which represents the As bound to iron and aluminum, and by F4 (As bound to carbonates). This means that the actual forms of As present in soil are relatively low mobile and characterized by low bioavailability. In fact, looking at the overall data, most (between 78 and 91 %) of As in soil samples was actually present as relatively refractory compounds and this can explain its relatively low vertical and horizontal dispersion in these soils. By looking at the percentages of the different fractions compared to the control soil, it is evident that little changes among different planted soils occurred during the 18 months of the experiment. However, although it is not possible to observe statistically significant differences, possibly such differences could be obtained in the long run since tall fescue, alfalfa and perhaps brown mustard seem to be the species most influencing the fractions.

In the Shimen realgar mine area in China, the Shiowatana sequential extraction procedure was applied to 9 of the 34 topsoil samples collected to evaluate As pollution of the area. In agreement with our results, F1 represented a small portion of the total extracted As, ranging from 0.9 to 4.5 %, while F2 varied from 0.4 to 7.9 %. F3 fraction was an important portion of total As and together with the residual fraction F5 (Wan et al., 2017). In a pot experiment carried out by (Hartley et al., 2009), As mobility was studied in three different brownfield soils cultivated with *Miscanthus* and differently amended in order to investigate the plant role in enhancing As mobility. However, no effect was found.

4. Conclusions

The behaviour of As (likely arsenate, derived from the pesticide production in the Caffaro plant) was investigated in soil samples from three agricultural areas of the National relevance site for contamination (SIN) Brescia Caffaro. The contamination, due to irrigation with polluted waters deriving from the Caffaro plant, took place for about 50 years while in the following 50 years the soil was normally cultivated. The results obtained confirm that As was mostly confined in the plow layer (0–40 cm), with concentrations up to about 100 mg/kg, although not negligible

amounts were leached to deeper soil layers (concentrations around 10–30 mg/kg). When the surface water input was about double (area A), concentrations at bottom layers were not increased proportionally but were generally comparable in the three areas, confirming the slow vertical movement of As in these soils. Also, the spatial gradient in topsoil showed that concentrations are reduced with distance, with 50 % of As found at about 60 m from the inlet. The 2D plot clarified that the slow spreading in time from a single entry point allowed to react a gradient from >240 mg/kg near the irrigation canal to about one third at about 200 m away in the irrigation water flow direction. The fractionation analyses confirmed that most of As occurs as relatively immobile or slowly exchangeable forms, but also illustrates the role of several plant species in making As more (bio)available in soil, first condition for plant uptake and therefore to conduct an effective phytoextraction of As and therefore deploy a bioremediation strategy. The plant species responsible for these effect were goat willow and brown mustard which were among the species (Terzaghi et al., 2019a, 2019b), effective for the rhizoremediation of PCBs, other compounds heavily polluting these areas. Other plant species (alfalfa and tall fescue) seemed to be capable to additionally reduce the soluble fraction and increase the more immobile ones, therefore reducing As movement with soil water. This result shows that, even in long-contaminated soil, plants could have a role in influencing As mobility in soil.

The results of this work can be helpful in the evaluation of the conditions controlling the vertical transfer of As towards surface aquifers and, in contrast, the bioaccumulation likelihood in the agricultural food chain even in long-time contaminated soils, although further work is needed to corroborate the results obtained and to select the best species and conditions to phytoextract As from soils for an effective bioremediation of contaminated sites. Additionally, more research is needed to measure As runoff from contaminated soil in order to fully evaluate the mass balance and the potential for contamination of further areas along the irrigation canal pathway. Also, the fine details and the temporal trends of As fractionation obtained by selected plant species should be evaluated, possibly with focused lab or greenhouse experiment. These studies would permit to select the best conditions for As removal, in conjunction with other problematic co-pollutants of this and many other areas worldwide, such as PCBs, dioxins and furans and mercury.

CRedit authorship contribution statement

Cristiana Morosini: Investigation, Writing- Original draft preparation, Visualization; Elisa Terzaghi: Resources, Data curation, Writing- Reviewing and Editing; Giuseppe Raspa: Data curation, Writing- Reviewing and Editing; Marco Grotti: Investigation, Data curation, Writing- Reviewing and Editing; Stefano Armiraglio: Writing- Reviewing and Editing; Simone Anelli: Resources, Data curation, Writing- Reviewing and Editing; Antonio Di Guardo: Funding Acquisition, Resources, Writing- Reviewing and Editing, Supervision.

Data availability

Data will be made available on request.

Declaration of competing interest

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

Acknowledgements

The authors acknowledge the funding agency Ente Regionale per i Servizi all'Agricoltura e alle Foreste (ERSAF), Decreto ERSAF n. III/5426 del 09.12.2013 and all the participants of the SIN Brescia-Caffaro remediation group coordinated by ERSAF. ET acknowledges a grant from DiSAT of University of Insubria.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.165422>.

References

- Atafar, Z., Mesdaghinia, A., Nouri, J., Homae, M., Yunesian, M., Ahmadi-moghaddam, M., Mahvi, A.H., 2008. Effect of fertilizer application on soil heavy metal concentration. *Environ. Monit. Assess.* 160, 83. <https://doi.org/10.1007/s10661-008-0659-x>.
- Bauer, M., Blodau, C., 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* 354, 179–190. <https://doi.org/10.1016/j.scitotenv.2005.01.027>.
- Chilès, J.-P., Delfiner, P., 2012. *Geostatistics: Modeling Spatial Uncertainty*. 2nd ed. Wiley Series in Probability and Statistics. Wiley, Hoboken, N.J.
- Di Guardo, A., Terzaghi, E., Raspa, G., Borin, S., Mapelli, F., Chouaia, B., Zanardini, E., Morosini, C., Colombo, A., Fattore, E., Davoli, E., Armiraglio, S., Sale, V.M., Anelli, S., Nastasio, P., 2017. Differentiating current and past PCB and PCDD/F sources: the role of a large contaminated soil site in an industrialized city area. *Environ. Pollut.* 223, 367–375. <https://doi.org/10.1016/j.envpol.2017.01.033>.
- Di Guardo, A., Raspa, G., Terzaghi, E., Vergani, L., Mapelli, F., Borin, S., Zanardini, E., Morosini, C., Anelli, S., Nastasio, P., Sale, V.M., Armiraglio, S., 2020. PCB vertical and horizontal movement in agricultural soils of a highly contaminated site: role of soil properties, cultivation history and PCB physico-chemical parameters. *Sci. Total Environ.* 747, 141477. <https://doi.org/10.1016/j.scitotenv.2020.141477>.
- Dittmar, J., Voegelin, A., Roberts, L.C., Hug, S.J., Saha, G.C., Ali, M.A., Badruzzaman, A.B.M., Kretzschmar, R., 2007. Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 2. Paddy Soil. *Environ. Sci. Technol.* 41, 5967–5972. <https://doi.org/10.1021/es0702972>.
- Gong, Y., Qu, Y., Yang, S., Tao, S., Shi, T., Liu, Q., Chen, Y., Wu, Y., Ma, J., 2020. Status of arsenic accumulation in agricultural soils across China (1985–2016). *Environ. Res.* 186, 109525. <https://doi.org/10.1016/j.envres.2020.109525>.
- Goovaerts, P., 1999. Geostatistics in soil science: state-of-the-art and perspectives. *Geoderma* 89, 1–45. [https://doi.org/10.1016/S0016-7061\(98\)00078-0](https://doi.org/10.1016/S0016-7061(98)00078-0).
- Goovaerts, P., Trinh, H.T., Demond, A., Franzblau, A., Garabrant, D., Gillespie, B., Lepkowski, J., Adriaens, P., 2008. Geostatistical modeling of the spatial distribution of soil dioxins in the vicinity of an incinerator. 1. Theory and application to Midland, Michigan. *Environ. Sci. Technol.* 42, 3648–3654. <https://doi.org/10.1021/es702494z>.
- Grotti, M., Soggia, F., Ianni, C., Magi, E., Udidi, R., 2013. Bioavailability of trace elements in surface sediments from Kongsfjorden, Svalbard. *Mar. Pollut. Bull.* 77, 367–374. <https://doi.org/10.1016/j.marpolbul.2013.10.010>.
- Hartley, W., Dickinson, N.M., Riby, P., Lepp, N.W., 2009. Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. *Environ. Pollut.* 157, 2654–2662. <https://doi.org/10.1016/j.envpol.2009.05.011>.
- Horwitz, W., Kamps, L.V.R., Boyer, K.W., 1980. Quality Assurance in the Analysis of foods for trace constituents. *J. AOAC Int.* 63, 1344–1354. <https://doi.org/10.1093/jaoac/63.6.1344>.
- Huang, S.S., Liao, Q.L., Hua, M., Wu, X.M., Bi, K.S., Yan, C.Y., Chen, B., Zhang, X.Y., 2007. Survey of heavy metal pollution and assessment of agricultural soil in Yangzhong district, Jiangsu Province, China. *Chemosphere* 67, 2148–2155. <https://doi.org/10.1016/j.chemosphere.2006.12.043>.
- Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X., He, Z., 2018. Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in south-east China. *J. Environ. Manag.* 207, 159–168. <https://doi.org/10.1016/j.jenvman.2017.10.072>.
- IARC (Ed.), 2012. *Arsenic, Metals, Fibres, and Dusts*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. International Agency for Research on Cancer, Lyon.
- Italian Parliament, 2006. *National Environmental Law (No. D.Lgs April 3, 2006, n. 152)*. Rome.
- Kaise, T., Yamauchi, H., Horiguchi, Y., Tani, T., Watanabe, S., Hirayama, T., Fukui, S., 1989. A comparative study on acute toxicity of methylarsonic acid, dimethylarsinic acid and trimethylarsine oxide in mice. *Appl. Organomet. Chem.* 3, 273–277. <https://doi.org/10.1002/aoc.590030311>.
- Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* 209, 27–39. [https://doi.org/10.1016/S0048-9697\(97\)00302-1](https://doi.org/10.1016/S0048-9697(97)00302-1).
- Loska, K., Wiechula, D., Korus, I., 2004. Metal contamination of farming soils affected by industry. *Environ. Int.* 30, 159–165. [https://doi.org/10.1016/S0160-4120\(03\)00157-0](https://doi.org/10.1016/S0160-4120(03)00157-0).
- Mason, B.J., 1992. *Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies (No. EPA/600/R-92/128)*. U.S. Environmental Protection Agency, Washington, D.C.
- MOE, 2019. Decree of March 1st 2019, n. 46. Regulation on remediation of contaminated agricultural areas. Official Journal of the Italian Republic. Ministry of the Environment and Protection of the Territory and the Sea.
- Morosini, C., Terzaghi, E., Raspa, G., Zanardini, E., Anelli, S., Armiraglio, S., Petranich, E., Covelli, S., Di Guardo, A., 2021. Mercury vertical and horizontal concentrations in agricultural soils of a historically contaminated site: role of soil properties, chemical loading, and cultivated plant species in driving its mobility. *Environ. Pollut.* 285, 117467. <https://doi.org/10.1016/j.envpol.2021.117467>.
- Norra, S., Berner, Z.A., Agarwala, P., Wagner, F., Chandrasekharan, D., Stüben, D., 2005. Impact of irrigation with as rich groundwater on soil and crops: a geochemical case study in West Bengal Delta Plain, India. *Appl. Geochem.* 20, 1890–1906. <https://doi.org/10.1016/j.apgeochem.2005.04.019>.
- Peryea, F.J., Creger, T.L., 1994. Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. *Water Air Soil Pollut.* 78, 297–306. <https://doi.org/10.1007/BF00483038>.
- Provincia di Brescia, 2016. *Attività Di Affinamento Delle Conoscenze Sulla Contaminazione Delle Acque Sotterranee in Cinque Aree DELLA Provincia Di Brescia Con Definizione Dei Plumes Di Contaminanti Ed Individuazione Delle Potenziali Fonti Di Contaminazione (No. EG/R1/0316/PBS/MM), Fase 1 Relazione Idrogeologica Di Inquadramento*.
- Rahman, S., Kim, K.-H., Saha, S.K., Swaraz, A.M., Paul, D.K., 2014. Review of remediation techniques for arsenic (As) contamination: a novel approach utilizing bio-organisms. *J. Environ. Manag.* 134, 175–185. <https://doi.org/10.1016/j.jenvman.2013.12.027>.
- Ruzzenenti, M., 2001. *Un secolo di cloro e... PCB: storia delle industrie Caffaro di Brescia, Terra-terra*. Jaca book. Alce nero, Milano [Isola del Piano].
- Saito, H., Goovaerts, P., 2001. Accounting for source location and transport direction into geostatistical prediction of contaminants. *Environ. Sci. Technol.* 35, 4823–4829. <https://doi.org/10.1021/es010580f>.
- Shiowatana, J., McLaren, R.G., Chanmekha, N., Samphao, A., 2001. Fractionation of arsenic in soil by a continuous-flow sequential extraction method. *J. Environ. Qual.* 30, 1940–1949.
- Terzaghi, E., Vergani, L., Mapelli, F., Borin, S., Raspa, G., Zanardini, E., Morosini, C., Anelli, S., Nastasio, P., Sale, V.M., Armiraglio, S., Di Guardo, A., 2019a. Rhizoremediation of weathered PCBs in a heavily contaminated agricultural soil: results of a biostimulation trial in semi field conditions. *Sci. Total Environ.* 686, 484–496. <https://doi.org/10.1016/j.scitotenv.2019.05.458>.
- Terzaghi, E., Vitale, C.M., Salina, G., Di Guardo, A., 2019b. Plants radically change the mobility of PCBs in soil: role of different species and soil conditions. *J. Hazard. Mater.* 121786. <https://doi.org/10.1016/j.jhazmat.2019.121786>.
- US EPA, 2016. *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 (No. EPA 821-R-16-006)*. U.S. Environmental Protection Agency, Office of Water.
- US EPA, 2023. *Soil Sampling*. U.S. Environmental Protection Agency Laboratory Services & Applied Science Division Athens, Georgia.
- US EPA, O, 2007a. *U.S. EPA Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils [WWW Document]*. US EPA. <https://www.epa.gov/esam/us-epa-method-3051a-microwave-assisted-acid-digestion-sediments-sludges-and-oils> (accessed 3.18.21).
- US EPA, O, 2007b. *U.S. EPA Method 6020A: Inductively Coupled Plasma - Mass Spectrometry [WWW Document]* [URL /homeland-security-research/epa-method-6020a-sw-846-inductively-coupled-plasma-mass-spectrometry (accessed 3.18.21)].
- US EPA, O, 2015. *Superfund Soil Screening Guidance [WWW Document]*. <https://www.epa.gov/superfund/superfund-soil-screening-guidance> (accessed 6.24.23).
- Walsh, L.M., Sumner, M.E., Keeney, D.R., 1977. Occurrence and distribution of arsenic in soils and plants. *Environ. Health Perspect.* 19, 67–71.
- Wan, X., Dong, H., Feng, L., Lin, Z., Luo, Q., 2017. Comparison of three sequential extraction procedures for arsenic fractionation in highly polluted sites. *Chemosphere* 178, 402–410. <https://doi.org/10.1016/j.chemosphere.2017.03.078>.
- Wang, P., Sun, G., Jia, Y., Meharg, A.A., Zhu, Y., 2014. A review on completing arsenic biogeochemical cycle: microbial volatilization of arsines in environment. *J. Environ. Sci.* 26, 371–381. [https://doi.org/10.1016/S1001-0742\(13\)60432-5](https://doi.org/10.1016/S1001-0742(13)60432-5).
- Zhang, H., Selim, H.M., 2008. Reaction and transport of arsenic in soils: equilibrium and kinetic modeling. *Advances in Agronomy*. Elsevier, pp. 45–115. [https://doi.org/10.1016/S0065-2113\(08\)00202-2](https://doi.org/10.1016/S0065-2113(08)00202-2).