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Sedimentary controls on arsenic distribution in meander-belt deposits of the Po Valley, Italy

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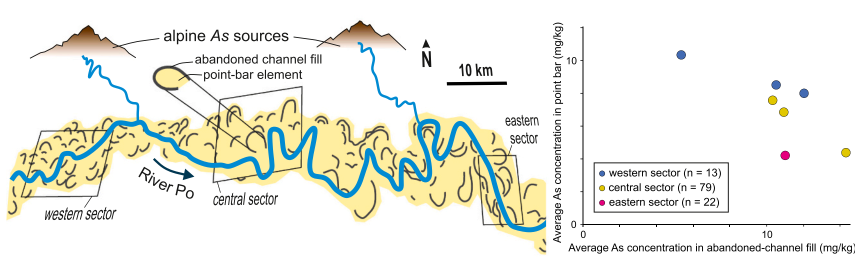
HIGHLIGHTS

- Arsenic distribution in Holocene alluvial sediments of the Po Valley has been characterized.
- A combined analysis of geomorphological, sedimentological and geochemical data is undertaken.
- Mud plugs and organic deposits act as As sources and point-bar facies are variably enriched in As.
- No relationship is seen between As concentrations and different styles of point-bar architectures.
- The integration of variably As-rich catchments is not a major control on As concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Geogenic arsenic in soils and aquifers is a threat to public health, which can be mitigated by improving our understanding of arsenic distribution in natural environments. In alluvial plains traversed by meandering rivers, solid- and aqueous-phase arsenic concentrations tend to vary across sedimentary deposits accumulated by different processes linked to river morphodynamics: mud-prone and commonly organic-rich abandoned-channel fills arising from meander cut-off act as local sources of arsenic, which can be transferred to adjacent point-bar deposits related to meander growth. Meanwhile, spatial variability in arsenic contamination may also arise from variations in sediment provenance across a fluvial landscape, and from inherent downstream changes in a fluvial system. Yet, the relative importance of facies and provenance as controls on arsenic concentrations in fluvial sediments still needs to be assessed. Through integrated analyses of geomorphological, sedimentological and geochemical data, this study examines the spatial variability in arsenic distribution from deposits of the late Holocene channel belt of the Po River, Italy. Three study areas were investigated along a >100 km stretch of channel belt to evaluate the possible roles of downstream changes in river behaviour and sediment supply from variably arsenic-rich catchments. Sedimentological controls on solid-phase arsenic concentrations are recognized at the scales of both elementary lithologies (facies) and depositional sub-environments, highlighting the roles of morphologically recognizable abandoned-channel fills as sources of arsenic that can be mobilized via groundwater flow and become trapped in point-bar elements. Although solid-phase arsenic concentrations are

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dominantly related to the presence of organic matter and clay, local arsenic enrichment may be related to arsenic advection across meander-belt sediments, a process that is itself controlled by petrophysical heterogeneity. No evident relationship is seen between arsenic concentrations and point-bar facies distributions related to styles of meander morphodynamic evolution. Yet, limited variability across the study areas suggests that the facies control remains dominant over a potential provenance control related to catchment integration. The results help elucidate the role of sedimentary heterogeneity in the distribution of arsenic in sediments, soils and aquifers, in the Po Valley and other analogous fluvial environments.

1. Introduction

The current rate of growth in the world's population is placing increasing pressure on the availability of water used for drinking and irrigation purposes (United Nations, 2020; World Health Organization, 2020). The growing demand for potable water cannot always be met by the supply offered by surface water reservoirs. As such, many parts of the world are becoming ever more dependent on groundwater resources (Organisation for Economic Co-operation and Development, 2012). Characterizing and predicting natural sources of groundwater contamination have therefore become increasingly urgent tasks. Arsenic is commonly present as a natural pollutant in siliciclastic aquifers, especially in those where the groundwater is hosted in porous sandbodies of alluvial and deltaic origin associated with catchments draining As-rich rock units (Nordstrom, 2002; Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009; Shaji et al., 2021; Amorosi and Sammartino, 2024). Meanwhile, concentrations of arsenic – of any origin – in surface agricultural soils result in the contamination of crops, both directly, as well as indirectly through irrigation practices (Rosas-Castor et al., 2014; Gillispie et al., 2015). This may have a significant impact on food chains and ultimately on human health (Meharg, 2004; Bundschuh et al., 2012).

Recent research has highlighted how the concentration of arsenic in alluvial sedimentary units and in the water they contain is intimately related to the geomorphological context of deposition. Arsenic accumulation in fluvial sedimentary deposits and in the water hosted in the pore space is a particularly significant problem for groundwater-bearing successions that represent the product of accumulation by large meandering rivers (Acharyya and Shah, 2007; Desbarats et al., 2014). Furthermore, arsenic concentration in fluvial sediments is known to vary as a function of the provenance of terrigenous detritus shed from orogenic belts (Ravenscroft et al., 2005; Tapia et al., 2022). It is therefore important to assess the relative importance of facies and provenance controls on geogenic arsenic accumulation in fluvial sediments, in order to determine the predictive power of geological knowledge on arsenic sources and possible arsenic accumulation hotspots.

Building upon the findings of existing research in this field (e.g., Donselaar et al., 2017), an integrated study of geomorphological, sedimentological and geochemical data has been undertaken on fluvial sediments of the late Holocene channel belt of the Po River, in the central sector of the Po Plain, Italy (Fig. 1). The aim of our study is to

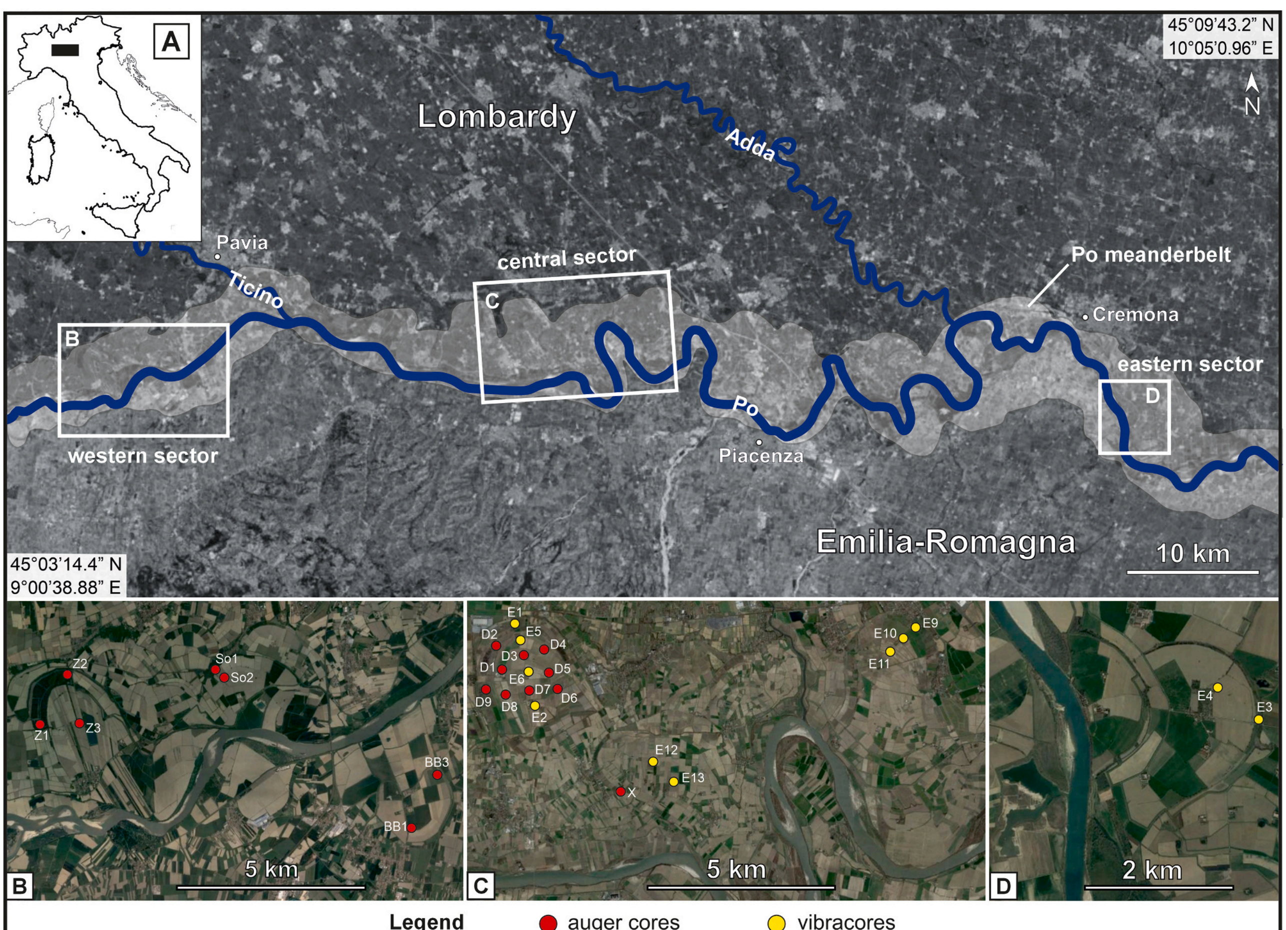

Fig. 1. (A) Map of the study area in the central Po Plain, indicating the three sectors for which data have been collected (satellite image from Google Earth Pro); (B) western sector; (C) central sector; (D) eastern sector. In B–D, spots indicate where samples were taken as augercores (red spots; in B and C) or vibracores (yellow spots; in C and D). See Supplementary Table 1 for further details.

characterize relationships between arsenic accumulation in sediments and its potential sedimentary controls (sediment characteristics and provenance). We focus on the exposed to shallowly (<10 m) buried fluvial succession with a level of detail that allows to examine patterns of arsenic dispersal in relation to sedimentary heterogeneity at the lithofacies scale. The following specific objectives are sought: (i) to assess the degree to which natural arsenic distribution is related to types of fluvial deposits that represent different sub-environments of deposition, namely point bars and abandoned channels; (ii) to investigate the control exerted by the lithofacies that make up the sedimentary record of point-bar and channel-fill elements on the concentration and dispersion of arsenic, with consideration of the vertical and planform spatial distribution of lithological classes based on modal particle size and the content of organic matter; and (iii) to evaluate the relative importance of facies and provenance controls on the concentration of arsenic in alluvial sediments. Identifying the sedimentological factors that can favour the accumulation of arsenic is essential for attempting predictions of natural arsenic enrichment in groundwater and sediments, both in the Po Plain and globally.

2. Background: controls on arsenic distribution in fluvial sediments

The pollution of aquifers by geogenic arsenic (As) is a global problem (Smedley and Kinniburgh, 2002; Shaji et al., 2021). Notably high As concentrations have been identified in the sediment and groundwater of aquifers in Argentina, Chile, Mexico, China, Cambodia and Vietnam, for example (Nicolli et al., 1989; Del Razo et al., 1990; Cáceres et al., 1992; Papacostas et al., 2008; Stuckey et al., 2015; Wang et al., 2019). Recent studies in the Ganges-Brahmaputra delta, an area covering NE India and Bangladesh (Acharyya et al., 2000; McArthur et al., 2001, 2004; Acharyya and Shah, 2007), have highlighted the health hazard posed by As enrichment of groundwater to the general population. Several studies relate the spatial variability in As in contaminated aquifers with their formative depositional setting, and observe that polluted sites commonly correspond to the occurrence of fine-grained (i.e., clay- and silt-prone) delta-plain sediments rich in organic matter (McArthur et al., 2004; Acharyya and Shah, 2007; Papacostas et al., 2008; Winkel et al., 2008; Donselaar et al., 2017; Ghosh and Donselaar, 2023; Amorosi and Sammartino, 2024). Such sediments include those deposited in abandoned channels that are infilled following river avulsion or meander cut-off.

Arsenic is not present in great abundance in the continental crust, having an average concentration of 2.0 mg/kg; yet, it is associated with many common rock-forming minerals, either through its incorporation in mineral lattices or its adsorption onto their surfaces (Mandal and Suzuki, 2002). Notably, arsenic is associated with sulfides, oxides and hydroxides, which tend to be present in aquifer-forming sediments (Smedley, 2008; Masuda, 2018); it can occur in adsorbed form with aluminium, iron and manganese oxides and hydroxides, phyllosilicates and organic matter (Masuda et al., 2012; Gorny et al., 2015; Varner et al., 2023). Sediments that contain 1 to 20 mg/kg of arsenic can give rise to solutions with high amounts (>50 μg/l) of dissolved arsenic; this may occur in response to an increase in pH above 8.5, which can trigger desorption of arsenate, or to the establishment of reducing conditions, which can induce arsenic desorption and the reductive dissolution of oxides (Smedley and Kinniburgh, 2002). Several other factors can affect the solubility of arsenic, such as high concentrations of anions that may act as adsorption competitors, including orthophosphates, or the presence of organic matter in the soil, which provides adsorption sites whilst also affecting redox conditions (Smedley and Kinniburgh, 2002; Gorny et al., 2015).

The study of contaminated sites has revealed some geological contexts that could significantly contribute to the release of arsenic in water: shales rich in organic matter, sites of gold mineralization, recent volcanoclastic accumulations, geothermal sites, and Quaternary alluvial-plain sediments (Nordstrom, 2002; Smedley and Kinniburgh, 2002). In the latter setting, the recent alluvial infill of sedimentary basins acts as the host to arsenic-rich aquifers, particularly where low hydraulic gradients exist (Nordstrom, 2002). In alluvial-plain settings, groundwater contamination by As can be very heterogeneous; this heterogeneity is primarily attributed to the combined effect of organic-matter decomposition and dissolution of iron oxyhydroxides, to which arsenic binds, in a reducing environment (McArthur et al., 2001, 2004; Papacostas et al., 2008). High concentrations of arsenic in water are closely linked to sedimentary deposits enriched in organic matter, where iron reduction and arsenic release can take place; here, methanogenesis associated with available dissolved carbon also plays a role in arsenic mobilization (Stopelli et al., 2020; Kontny et al., 2021). In fluvial depositional systems, depositional niches where these conditions may exist depend critically on river morphodynamic processes, which are commonly reflected in the morphologies of abandoned palaeochannels (cf. Donselaar et al., 2017; Ghosh and Donselaar, 2023). In this context, the main cause of aquifer contamination is identified in the release of arsenic from microbial dissolution of iron oxyhydroxides under reducing conditions, supported by the presence of organic matter in peaty layers inside the aquifer or in surface sediments (McArthur et al., 2004). In shallow groundwater aquifers, the anaerobic reducing conditions that drive arsenic mobilization from fluvial sediments are also in part regulated by the frequency and duration of river floods (Connolly et al., 2021). It is also observed that the age of the sediment has an impact on the sediment concentrations of iron oxyhydroxides and arsenic, and on groundwater arsenic concentration: through time, the reactivity of sedimentary organic carbon decreases due to preferential microbial degradation of the most reactive organic carbon, and the sedimentary pools of both iron and arsenic tend to decline (Postma et al., 2012).

Papacostas et al. (2008), Desbarats et al. (2014) and Donselaar et al. (2017) correlate high arsenic concentrations with the presence of abandoned meander bends, where organic matter is deposited alongside fine-grained sediment as the infill of partly or fully cut-off channels under stagnant water conditions. Based on a study of sand-prone point-bar elements and clay-rich abandoned-channel fills present in Holocene fluvial successions, Donselaar et al. (2017) proposed a general model of arsenic accumulation in aquifers that accounts for relationships between the depositional architecture, its geomorphological expression, and the spatial heterogeneity of arsenic concentration in water. The deepest anoxic zone of an oxbow lake – which is ultimately preserved as a 'mud plug' when infilled – acts as the site of accumulation of organic matter and of bacterial fermentation, which, under conditions of rapid burial below the surface, lead to the development of reducing conditions that trigger the dissolution of iron oxyhydroxides and the consequent release of arsenic in the aquifer. Sand-prone barforms adjacent to the mud plugs act as conduits for the dispersion of arsenic and traps for their accumulation. Arsenic advection in point-bar sediments is promoted by their greater permeability and local connectivity with other porous channel and bar deposits, for example through base-of-channel sands (Donselaar and Overeem, 2008). The physical trapping of dissolved arsenic may be facilitated by the typical clay-prone nature of bar-top and overbank deposits that commonly overlie point-bar elements, which may hinder groundwater oxygenation (Smedley and Kinniburgh, 2002). The sand-prone point-bar bodies deposited by meandering rivers may be amalgamated both laterally and vertically; however, they are commonly compartmentalized by mud plugs, which may cause the trapping of arsenic-bearing water (Donselaar and Overeem, 2008; Colombera et al., 2017). The spatial heterogeneity of the measured dissolved arsenic concentrations is primarily controlled by permeability contrasts in the fluvial depositional architecture, and by compartmentalization of the aquifer where vertical or horizontal connectivity is impeded by barriers or baffles to water flow and solute transport (cf. Larue and Hovadik, 2006). Additionally, the sediment type also affects the partition of arsenic between solid and liquid phases; clay-rich sediments may readily retain arsenic through sorption, exhibiting high solid-phase arsenic concentrations but relatively low arsenic concentrations in the water they host (cf. Polizzotto et al., 2008). Ultimately, part of the dissolved arsenic may be re-sequestered in solids in cases where reducing conditions (i) are high enough to cause precipitation of sulfides, or (ii) become limited through time because of the consumption of organic matter (Quicksall et al., 2008; Papacostas et al., 2008).

3. Geological and environmental setting

The Po Plain of northern Italy is located within the common foreland of the Alps and Apennines (Fig. 1). The foreland basin is largely filled with a >7 km-thick sedimentary succession of deep-marine to continental origin, of Pliocene through Quaternary age, recording a progressive decrease in the degree of tectonic deformation (Pieri and Groppi, 1981). The plain is traversed longitudinally by the Po River, which in the study area has a bankfull depth ranging between ~7 and ~11 m (Domeneghetti, 2016). The Po River is the dominant geomorphic agent of the region (Castiglioni et al., 1997). The area located between the southern boundary of the Alps and the Po River is characterized by a wide low-gradient fluvio-glacial and alluvial geomorphological unit named the Po Low Plain (Marchetti, 2002; Regione Lombardia and Eni Divisione Agip, 2002; Burrato et al., 2003; Bersezio et al., 2004). At present, this surface is dissected by tributary rivers of the Po, which drain the Alps and flow within shallow valleys entrenched into this unit. The composition of fluvial deposits observed in outcrop and in the shallow subsurface differ substantially between the areas north and south of the Po (Marchetti, 2002): the sediments that occur in the northern sector of the basin are sourced from the Alps, where carbonate and clastic sedimentary cover and the crystalline basement are eroded; in contrast, sediments supplied by the Apennines are derived from dominantly marly and arenaceous sources.

The Holocene fluvial deposits of the Po and its tributaries dominate the central part of the plain. These deposits are bounded to the north by an erosional scarp that marks the southernmost boundary of the Po Low Plain unit, due to the northward migration of the river during the Holocene, in response to the tectonic evolution of the basin (Gasperi, 2001; Tellini and Pellegrini, 2001). For most of its course the Po is an alluvial river, dominantly characterized by a sinuous single-thread channel. The river occupies a channel belt that is 3 to 4 km wide (Marchetti, 2002) and is bordered by a mosaic of "loop" morphologies representing past channel courses abandoned following meander-bend cut-off events (Fig. 2).

In the Po Plain, the concentration of arsenic in sampled agricultural soils is heterogeneously distributed, although it is generally below 50 mg/kg (Beone et al., 2015; ARPAV, 2019). Low values of As concentrations, typically in the 4–8 mg/kg range, are observed along the Apennine margin (Marchi and Ungaro, 2019), whereas higher values are recorded in the northern sector (dominantly in the 20–30 mg/kg range in the Lombardy region) and reflect Alpine sources (Cicchella et al., 2015). In the western and central Alps, the principal arsenic sources are identified in metamorphic and igneous units (Zuzolo et al., 2020). Over the drainage area of the transect of the Po studied herein, arsenic concentrations in topsoils are highest in the catchments of the rivers Ticino and Adda (Tarvainen et al., 2013; Cicchella et al., 2015; Zuzolo et al., 2020), in which notable arsenic sources are identified in abandoned gold (*Miniera dei Cani*; Ticino catchment) and arsenic (*Alpe Stabiello*; Adda catchment) mines, respectively.

Although the main source of arsenic in soils and recent alluvial sediments is geological, and therefore dependent on the composition of the source rocks of fluvial catchments, anthropogenic causes of contamination are related to metallurgical industries, to waste from fossil-fuel processing, and to the use of arsenic-bearing pesticides in agriculture until the late 1950s (Marchi and Ungaro, 2019). In Italy, a national statutory limit for concentration of As in soils and subsurface sediments is set at 20 mg/kg (Italian Decree Law 152/2006; Zuzolo et al., 2020), due to the danger it may pose to human health. In 1993 the

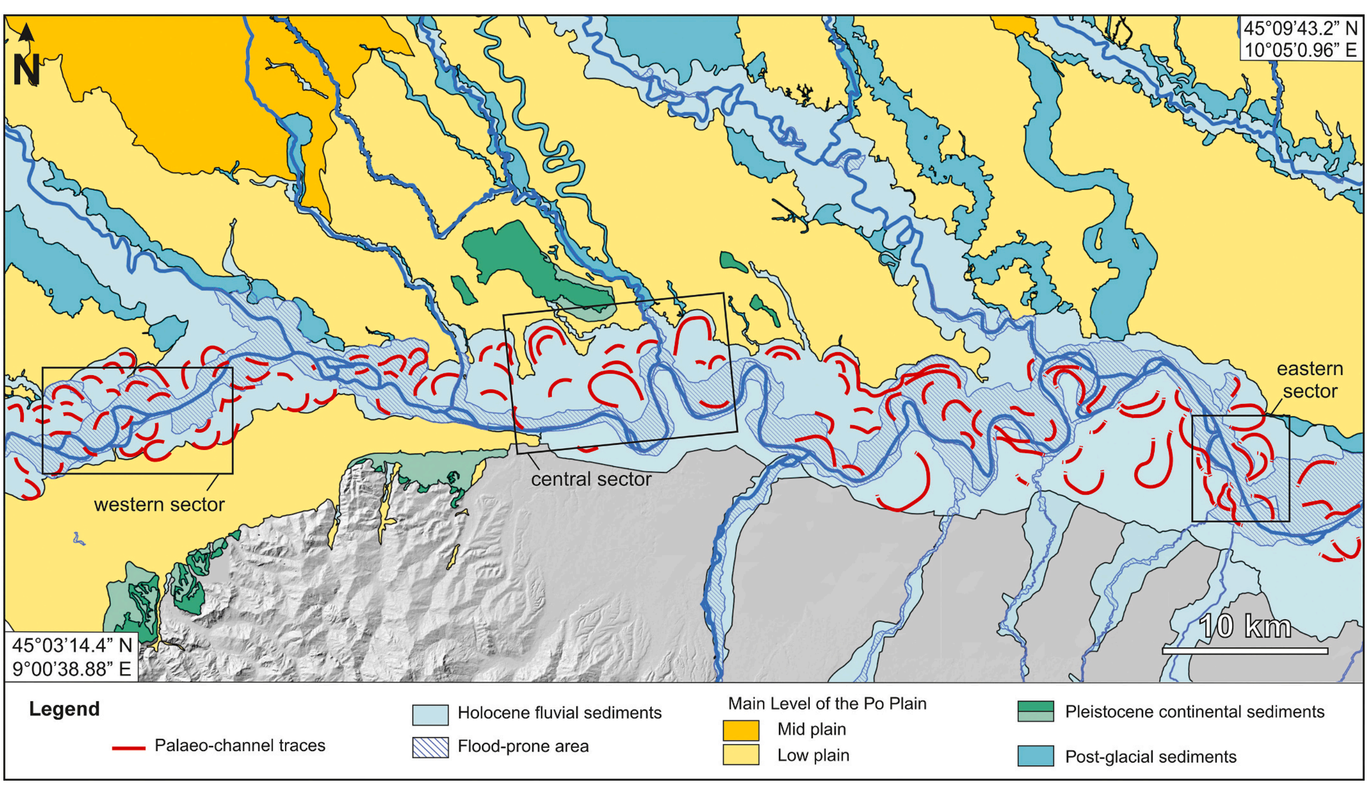

Fig. 2. Geomorphological map of the central Po Plain (Regione Lombardia and Regione Emilia-Romagna digital datasets; Castiglioni et al., 1997). The studied Holocene geomorphological units are shown by frames indicating the sectors reported in Fig. 1. The hillshade digital elevation model in the southern sector shows the relief of the Apennines and Pede-Apennine area.

World Health Organization reduced the guide value of arsenic for drinking water from 50 μg/l to 10 μg/l (World Health Organization, 1993); accordingly, in Italy, the legal limit for arsenic in drinking water is now at 10 μg/l (European Commission, 1998).

4. Data and methods

This research integrates results of geomorphological, sedimentological and geochemical analyses.

To identify sectors of the Holocene Po channel belt that are suited to the scopes of investigation, different areas were screened employing a combination of geological and geomorphological maps (Castiglioni et al., 1997; Castiglioni, 1999), pedological maps (Brenna et al., 2004), and satellite imagery (accessed on Google Earth Pro). On this basis, three study areas located along the Po River (denoted as 'western', 'central' and 'eastern' areas; Fig. 1) were selected in which palaeo-meanders consisting of point-bar and channel-fill elements – considered susceptible to arsenic accumulation – could be recognized. The three study areas have been chosen so that they are respectively located upstream of the confluence between the River Ticino with the Po (western sector; Fig. 1B), between the confluences of the affluents Ticino and Adda with the Po (central sector, ~30 km downstream of the western one; Fig. 1C), and east of the confluence between the River Adda and the Po (eastern study area, ~40 km downstream of the central one; Fig. 1D). Thus, from west to east, the studied channel-belt segments have been produced by reaches of the Po that were supplied solids by tributaries draining increasingly arsenic-rich catchments (Zuzolo et al., 2020, and references therein). The positions of the confluences of the Adda and Ticino rivers with the Po remained relatively fixed over time after abandonment of the studied palaeo-meanders. Therefore, the selection of these study areas allows us to test the impact of sediment supply from catchments hosting notable arsenic sources on arsenic concentration in fluvial sediments.

LiDAR-derived bare-earth digital elevation models (DEMs) with 1 m ground resolution provided by Regione Lombardia have been used for geomorphological analysis of the central sector (Fig. 1C; data from: https://gn.mase.gov.it/portale).

Eight vibracores (cores E2, E4, E5, E6, E10, E11, E12, E13) with a length of 5 to 6 m each were taken on top of three Holocene point-bar units. Three further vibracores (cores E1, E3, E9) with a length of 6 to 7 m each were obtained from meander loops bordering the point-bar units and presumed to be the surface expression of mud plugs, i.e., abandoned-channel fills (Fig. 1C,D). The cores were collected in 1-m-long core tubes with a diameter of ca. 5 cm. The cored sediments were described in terms of grainsize, texture, colour and sedimentary structures; these characteristics were considered to establish classes of depositional facies. Surface sediment samples were collected by means of sixteen 1-m-deep auger cores drilled in three point-bar elements (Z3, SO2, BB1) and in adjacent clay plugs (Z1, Z2, SO1, BB3), at the westernmost location (Fig. 1B), and in the palaeo-meanders located in Fig. 1C (X, D1-D9). Stratigraphic correlations of point-bar deposits in lithological logs from vibracores were attempted to elucidate internal facies architectures. Grainsize analysis was carried out on 111 core samples weighing ca. 80 g each, by means of a sieve stack with a 0.5 phi mesh interval (grainsize range: 0.063–2.800 mm); accordingly, sediments were classified by grainsize classes (Wentworth, 1922) and their statistical parameters were derived based on the 'graphic method' of Folk and Ward (1957). The organic matter was removed via calcination and so it does not affect the results of the grainsize analysis.

Total arsenic concentrations in solids were measured from sediment samples from both vibracores and auger cores. These data were used to analyse relationships between sub-environments of deposition, lithofacies, and arsenic content (Table 1, Figs. 4–5, Supplementary Table 2). Analysis of 111 sediment samples prepared as tablets was performed by XRF (X-ray fluorescence) spectroscopy using a wavelength-dispersive spectrometer PW1480 (Malvern Panalytical Axios), equipped with Rh tube, 5 analyser crystals, and enabling analysis of 4 samples in sequence. The tool has a relative precision of total arsenic in the sediment of 5 %; the accuracy for trace elements is stated as better than 10 % and the detection limit is ~3 mg/kg. The calibration was based on 35 certified reference samples; other certified reference materials not included in the calibration were used for quality control. Complementary XRF data on the concentration of other elements and oxides were also derived (see Supplementary Material 3). The organic matter content was determined via loss-on-ignition (LOI) analysis. Samples consisting of 1 g of dried material and contained in a platinum crucible were placed in a muffle furnace overnight at 950 °C. Organic-matter content estimations based on LOI analyses are affected by the loss of other volatile components, including water released from hydrate minerals and CO_2 from carbonates. Processing and analyses were undertaken at the Department of Biological, Geological and Environmental Science of the University of Bologna (Italy).

Table 1
Facies sedimentological characteristics and associated range of arsenic concentration. The content of organic matter is described quantitatively in terms of loss-on-ignition (LOI) data (see Supplementary Table 2). Mean values are reported with the significant digits of the measurements.

Facies	Grainsize	Structures	Loss-on-ignition readings	Mean As concentration (mg/kg)	N samples
P	Clayey peat	Massive to laminated	Range: 1–36 %; mean: 19 %	20	6
C	Clay	Massive to laminated	Range: 5–18 %; mean: 12 %	11	34
sC	Silty clay	Massive to laminated	Range: 1–15 %; mean: 7 %	9	14
sS	Silty sand	Massive to laminated	Range: 2–16 %; mean: 7 %	10	14
fS	Fine sand	Locally laminated	Range: 2–11 %; mean: 4 %	5	15
mS	Medium sand	Massive	Range: 1–15 %; mean: 4 %	4	24
cS	Coarse sand	Massive	Range: 1–3 %; mean: 2 %	4	7

5. Results

5.1. Geomorphological investigation

A geomorphological study was undertaken of chosen sectors of Holocene channel-belt remnants of the Po. Despite the intense anthropogenic reworking of the Holocene channel-belt surface, primarily by agricultural activities and due to the installation of infrastructures, some relic primary topographic features are evident in the studied sectors, in the form of relief that may represent scroll-bar morphologies or depressions associated with loops bordering the point-bar units. A detailed geomorphological analysis was conducted on the abandoned meander bends located in Fig. 1C, employing LiDAR-derived bare-earth DEMs. Fig. 3 shows DEMs of two meander bends from the central sector, with notable topographic features highlighted. These palaeo-meanders have common general topographic characteristics, observed in the relief maps (Fig. 3A,B) and elevation profiles (Figs. 4 and 5), which demonstrate relative depressions in correspondence of the loops inferred to correspond with clay plugs. The scarp incised by the migrating bend in pre-Holocene glacio-fluvial deposits is between 8 and 10 m high, whereas

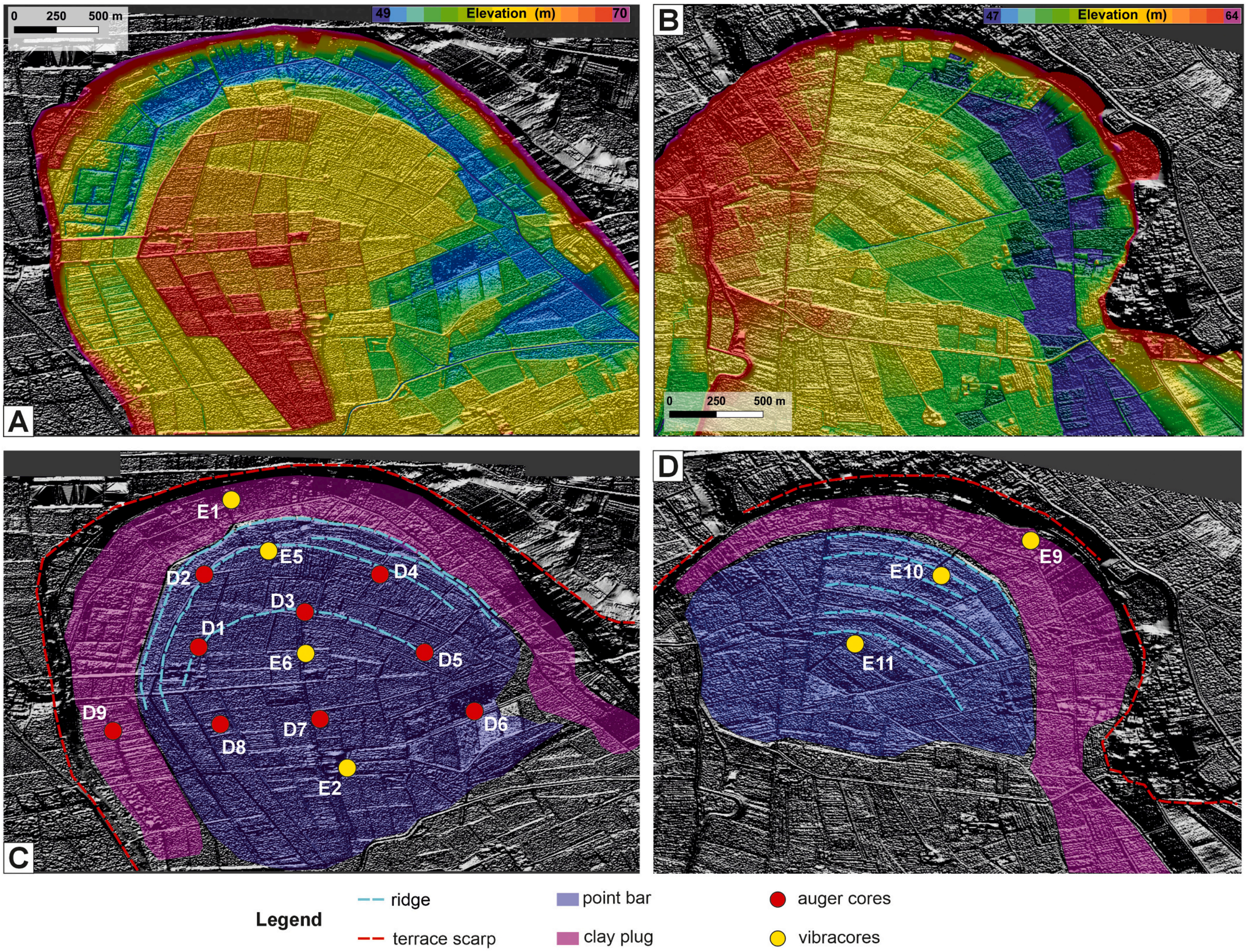

Fig. 3. (A, B) LiDAR digital elevation models of two of the studied palaeo-meanders, located in the northwestern (A) and northeastern (B) parts of the central sector of the study area (see Fig. 1C); elevations above 70 m (A) and 64 m (B) have been cropped to highlight changes in point-bar topography. (C, D) Inferred extent and geometry of point-bar and clay-plug elements, for the examples that are respectively shown in A and B. Shaded relief maps of the LiDAR digital elevation models are shown as a background. In C and D, spots indicate where augercores (red spots) or vibracores (yellow spots) were taken.

the average elevation difference between the point-bar and clay-plug surfaces is between 4 and 5 m. The palaeo-meander-bend in Fig. 3A is associated with an inferred point-bar surface that is 2.7 km long and 2.1 km wide, whereas the inferred clay-plug channel-form appears to be 300 to 400 m wide. The area in Fig. 3B includes an inferred clay plug with a width between 100 and 150 m. On point-bar surfaces, man-made installations are partly aligned with the natural relief, whereby, for example, roads are built on morphological highs whereas canals follow relative lows. In plan-view, numerous crescent-shaped ridges and swales (see Fig. 3C,D) are observed that can be interpreted as preserved scroll bars documenting the style of point-bar accretion (cf. Strick et al., 2018; Yan et al., 2021, and references therein). The radii of curvature of these topographic features preserved on the two point-bar surfaces, measured following the approach of Strick et al. (2018), are 1.3 (example in Fig. 3A) and 1.1. (example in Fig. 3B), respectively.

Based on observations of preserved scroll morphologies and bend geometry, all the studied abandoned meander bends (located in Fig. 1B–D) appear to have migrated predominantly by bend expansion (Daniel, 1971; Jackson, 1976), i.e., in a manner whereby the bend apices are shifted in a direction transverse to the channel-belt axis. Yet, the different examples show considerable variability in the shape and size of point-bar units, and in the radius of curvature of their formative channel, which may relate to differences in the maturity of the river bend at the time of abandonment by cut-off (Willis and Tang, 2010).

Analysis of historical cartography and documents indicates that the deposits studied in the western sector are associated with two meander bends ('Z' and 'So' samples; Fig. 1) that were cut off in the first half of the 19th century as part of a programme of artificial river rectification (Ferrari and Pellegrini, 2007). These are the youngest deposits across all three study areas.

5.2. Sedimentological investigation

5.2.1. Overall lithological organization: point-bar and channel-fill units

Correlation panels (Figs. 4 and 5) of lithological logs of vibracores have been produced for transects E1-E2-E5-E6 and E9-E10-E11, for the two palaeo-meanders of Fig. 3. These correlation panels illustrate the overall lithological motif of the studied meander belt, and of the point-bar and channel-fill deposits of which it is composed. In these, the uppermost ~0.5 m of the stratigraphy may contain material that is not in situ. Both point-bar bodies are sand dominated and are mostly made of apparently massive medium sand, which is mostly well sorted. In both cases, the base of the point-bar units is not intersected by the boreholes, but massive medium sands are seen up to a depth of 6 m below the

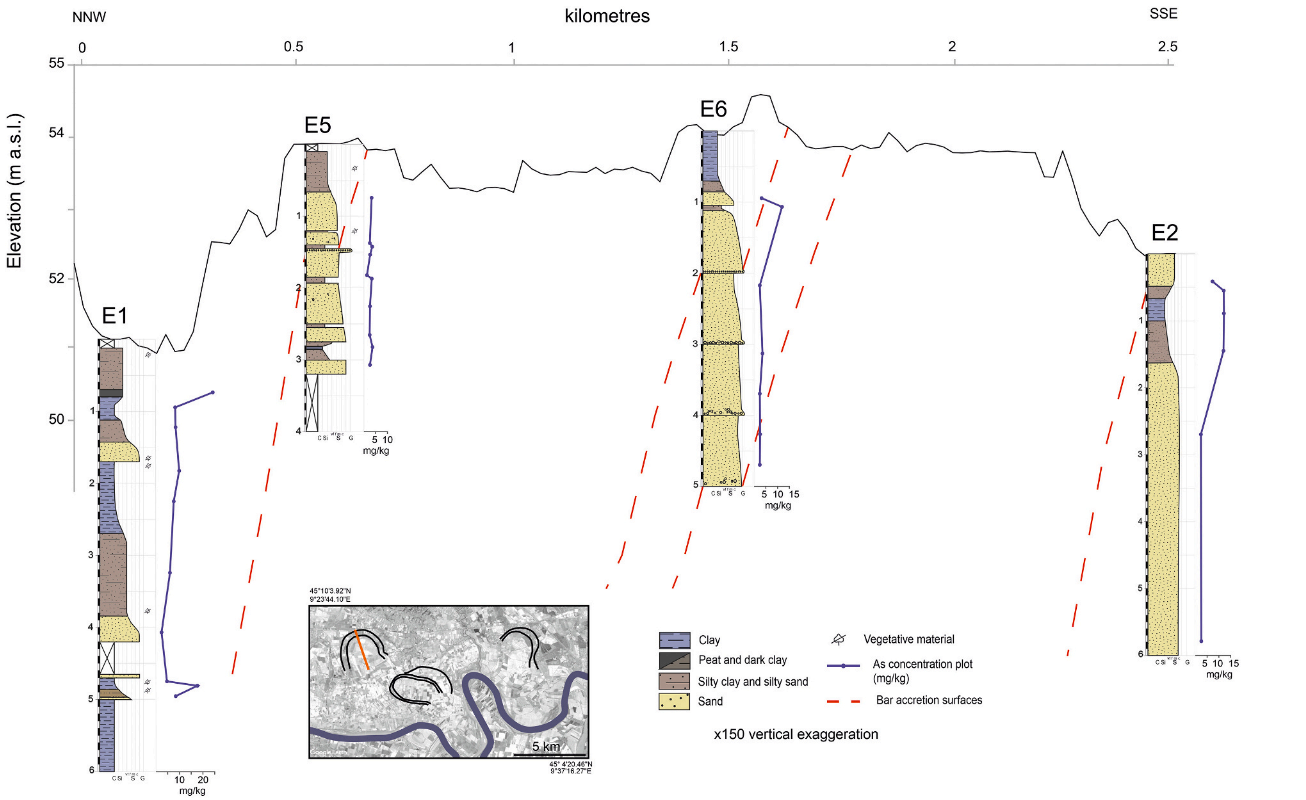

Fig. 4. Lithological profiles of vibracores and sediment As concentrations at sampled depths (blue graphs), for the palaeo-meander shown in Fig. 3A,C. The section is oriented approximately orthogonally to the orientation of the formative palaeochannel, and tracks the migration of the meander apex. The uppermost 0.5 m of the stratigraphy may contain material that is not in situ. Tentative correlations between logs are represented; these reflect the expected gradient of accretion surfaces based on the inferred geometry of the inner channel bank and the likely depth of the formative channel.

surface in E2, and of 5 m in E11. Overall, internally, the point-bar bodies exhibit fining-upward trends; this is evident for example in core E6, in the form of a progressive transition from gravelly coarse sand in the lower point-bar section to clay-prone bar-top deposits. The sand-dominated portions appear to be made of discrete sandy beds of dm-scale thickness, which are in some cases marked by surfaces lined by gravel accumulations (cf. core E6), and which are locally intercalated with thin layers of silts (up to 20 cm thick) and clay (<10 cm thick). Fine-grained sediments are dominant in the cores obtained from the assumed abandoned-channel fills (E1, E9, E10), confirming the interpretations of the geomorphological dataset. The infill documented by E1 demonstrates three separate fining-upward trends, and extends from the surface to a depth of ca. 5 m, where it is in sharp contact with underlying gravels that likely represent a channel-lag deposit. The mud plug seen in E9 sits above massive fine sands that may be of thalweg or lower-point-bar origin; the abandoned-channel fill contains interbedded silty layers (up to 0.5 m thick) as well as a 0.2 m thick horizon of peat, 0.7 m below the surface.

5.2.2. Lithofacies classification and distribution

Point-bar and channel-fill sediments are classified into seven classes of lithofacies on the basis of their organic matter content and grainsize (Table 1 and Fig. 6). Facies classes are only established for deposits for which data on As concentration exist, since they are employed to determine relationships between lithology and As accumulation. These facies are variably distributed across the point-bar and channel-fill sub-environments.

The studied clay-plug deposits are dominantly made of clay (C) and silty clay (sC) facies. Clayey peat units (P) are also seen, where dark organic material is present mixed with a subordinate fraction of clay. A silty sand facies (sS) is recognized in core E1. The colour of the sediment varies from grey to brown, depending on conditions of water saturation associated with oscillations of the water table. The overall fine particle size of these sediments reflects deposition dominantly from suspended load as the passive infill of abandoned meander reaches: following its abandonment, the meander is characterized by the prolonged presence of an isolated body of water with limited inflow, which is infilled progressively by sediment carried in suspension during floods and plant material accumulating in situ (Fisk, 1947; Guccione et al., 1999; Toonen et al., 2012).

The studied point-bar bodies consist mainly of fine (fS), medium (mS), and coarse (cS) sands, with occasional gravel (G) layers (Figs. 4, 5), and silty clay (sC) or silty sand (sS) interbeds. Generally, these sediments do not contain a significant amount of organic matter, and as such inferences of the degree of water saturation are not attempted. The observed lithofacies can be considered typical of point-bar sediments, which accumulate in relation to the migration of sinuous river channels, primarily on the inner bank of meanders (Leopold and Wolman, 1960; Bridge, 2003; Yan et al., 2021). Point-bar deposits can be highly heterogeneous, due to temporal and spatial variability in river hydrodynamics. This variability is related for example to temporal changes in flow velocity during a flood event, and across high and low flow stages and to spatial changes in local flow velocity across the streambed profile and along a meander bend (Bridge, 2003). In the studied sand-prone examples, lithological heterogeneity is relatively limited, and is principally seen in the form of: (i) fining-upward trends, reflecting the spatiotemporal distribution of flow momentum in sinuous channels and energy dissipation on inner banks due to helical secondary flow (cf. Nanson, 1980), and of (ii) fine-grained interbeds, which typically drape the bar accretion surfaces and which may reflect phases of flood recession or of slack water (cf. Willis and Tang, 2010).

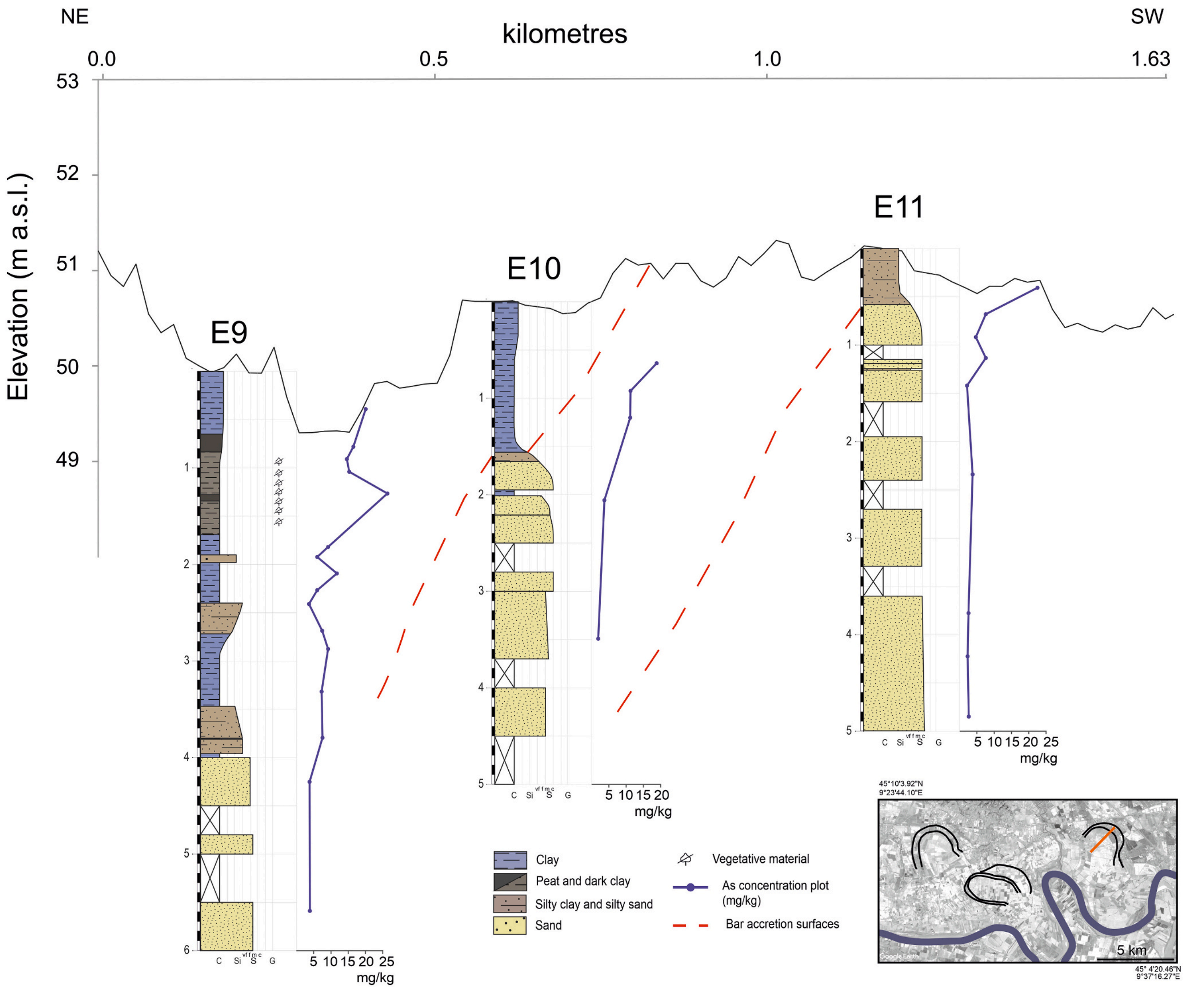

Fig. 5. Lithological profiles of vibracores and sediment As concentrations at sampled depths (blue graphs), for the palaeo-meander shown in Fig. 3B,D. The section is oriented approximately orthogonally to the orientation of the formative palaeochannel, and tracks the position of the meander apex. The uppermost 0.5 m of the stratigraphy may contain material that is not in situ. Tentative correlations between logs are represented; these reflect the expected gradient of accretion surfaces based on the inferred geometry of the inner channel bank and the likely depth of the formative channel.

5.3. Geochemical investigation

The samples selected for geochemical analyses were taken from all three sectors of the study area ('western', 'central' and 'eastern'; Fig. 1), defined on the basis of the confluences of the affluents Ticino and Adda with the Po. Despite differences in sediment provenance associated with the progressive downstream integration of the two Alpine catchments of the Ticino and Adda, no notable variations in average sediment As concentration are seen across the three sites (mean values of 9 mg/kg, 9 mg/kg, and 8 mg/kg, from west to east).

However, values of arsenic concentration in sediment samples vary significantly over the study area, from <3 mg/kg to 26 mg/kg. Geochemical data were considered with respect to the type of deposits, by relating the content in arsenic with the type of depositional sub-environment (Fig. 7A), facies type and grainsize (Fig. 8; see Supplementary Table 2). Point-bar deposits have generally low As concentrations, <10 mg/kg on average, albeit with values increasing slightly (12–22 mg/kg) in correspondence of fine-grained intercalations. The clay-plug deposits are characterized by higher As concentrations (average of 12 mg/kg), in particular in the organic-rich peat layers, where As content reaches up to 26 mg/kg.

Table 1 reports values of As content with respect to the identified facies classes, defined on the basis of lithology, sedimentary structures and content in organic matter. As grainsize increases and the fraction of organic matter decreases, the arsenic concentration in the facies types tends to decrease on average (Fig. 8). Sandy facies (cS, mS, fS) yield the lowest concentration of As, whereas silty facies (sS, sC) have intermediate values of As content, which expectedly peak in the clayey and peaty facies (C, P). For the sandy deposits, no hydraulic conductivity data are available. However, it is observed that a weak negative relationship exists between mean grain size and As concentration (Pearson's $R = -0.33$, p-value $= 0.077$, $N = 29$; Fig. 8), whereas no correlation is seen between sediment sorting (defined based on grainsize percentiles as: $\frac{D_{84}-D_{16}}{4}+\frac{D_{95}-D_{5}}{6.6}$; Folk and Ward, 1957) and As concentration ($R = -0.0001$, p-value $= 0.998$, N $= 29$); it is therefore inferred that more permeable deposits do not tend to exhibit higher As content.

The relationship between lithology and arsenic content is also described by the correlation between the concentrations of arsenic and silica (Fig. 7A); the latter is considered as a lithological indicator, as sands are naturally rich in quartz and feldspar, whereas fine and/or

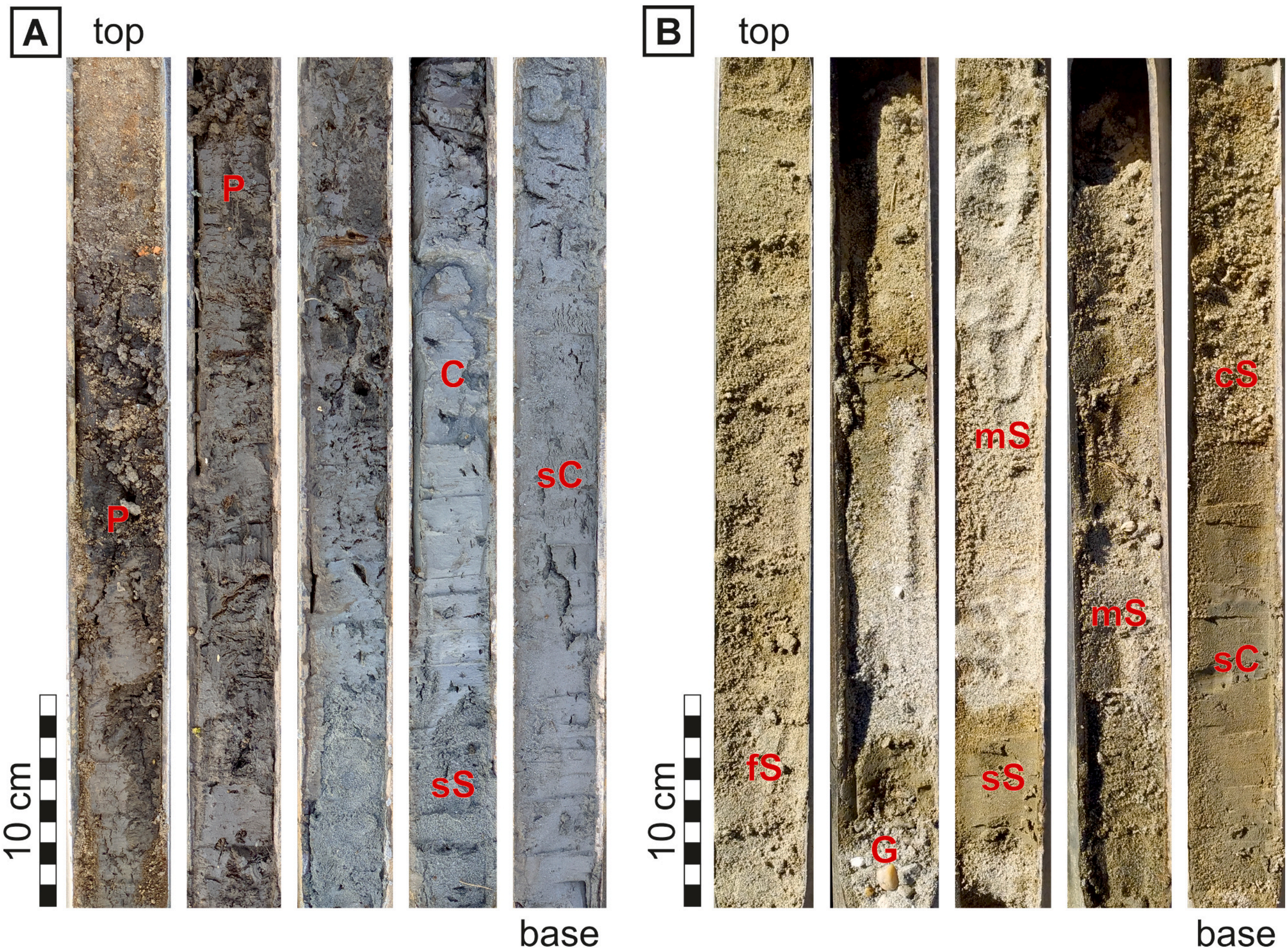

Fig. 6. Core photographs of lithofacies types seen in vibracores 5 and 9, taken immediately after coring. A: example of channel-fill facies sequence; core 9, 0.6–3.0 m. B: point-bar facies sequence; core 5, 0.6–3.0 m.

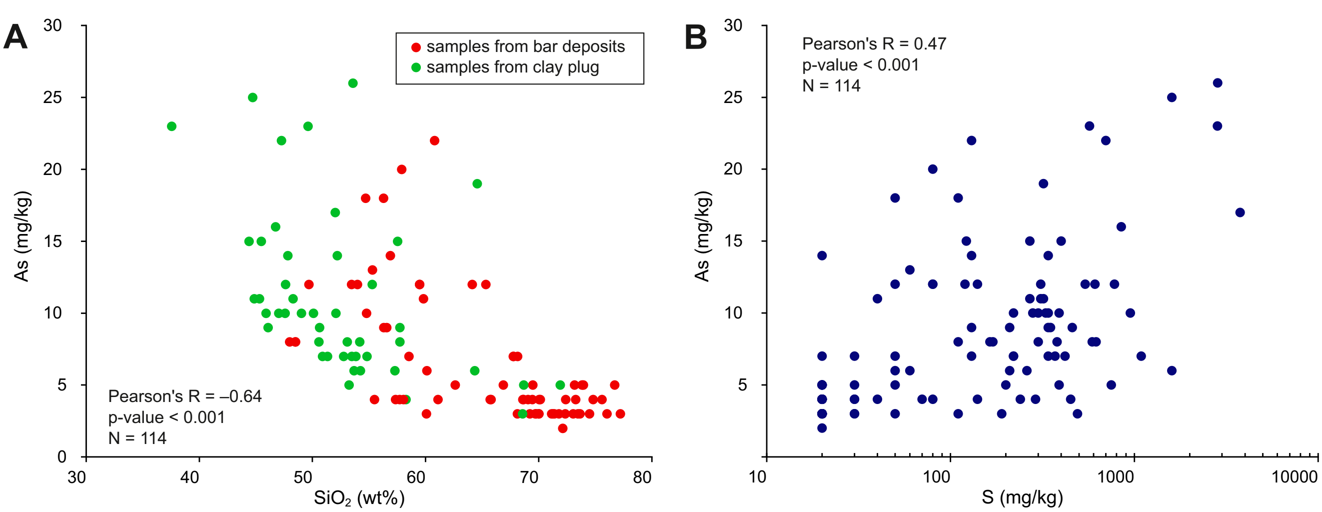

Fig. 7. Scatterplots showing relationships between sediment As concentrations and SiO_2 (A) and between As and S (B).

peaty sediments are enriched in clay minerals and organic matter. A negative correlation is observed between the two variables ($R = -0.64$, p-value <0.001, $N = 111$; Fig. 7A). Positive correlations are instead seen between the concentration of arsenic and those of sulfur ($R = 0.47$, p-value <0.001, N = 111; Fig. 7B) and total iron (Fe_2O_3; $R = 0.73$, p-value <0.001, $N = 90$), and between arsenic content and LOI readings ($R = 0.57$, p-value <0.001, $N = 114$); the former observation can be explained by how the sulfur content correlates with the content in organic matter: peaty sediments, abundant in organic matter and where the highest sulfur values are measured, are those that are richest in arsenic (see Table 1 and Supplementary Table 2).

In the northwesternmost palaeo-meander of the central sector

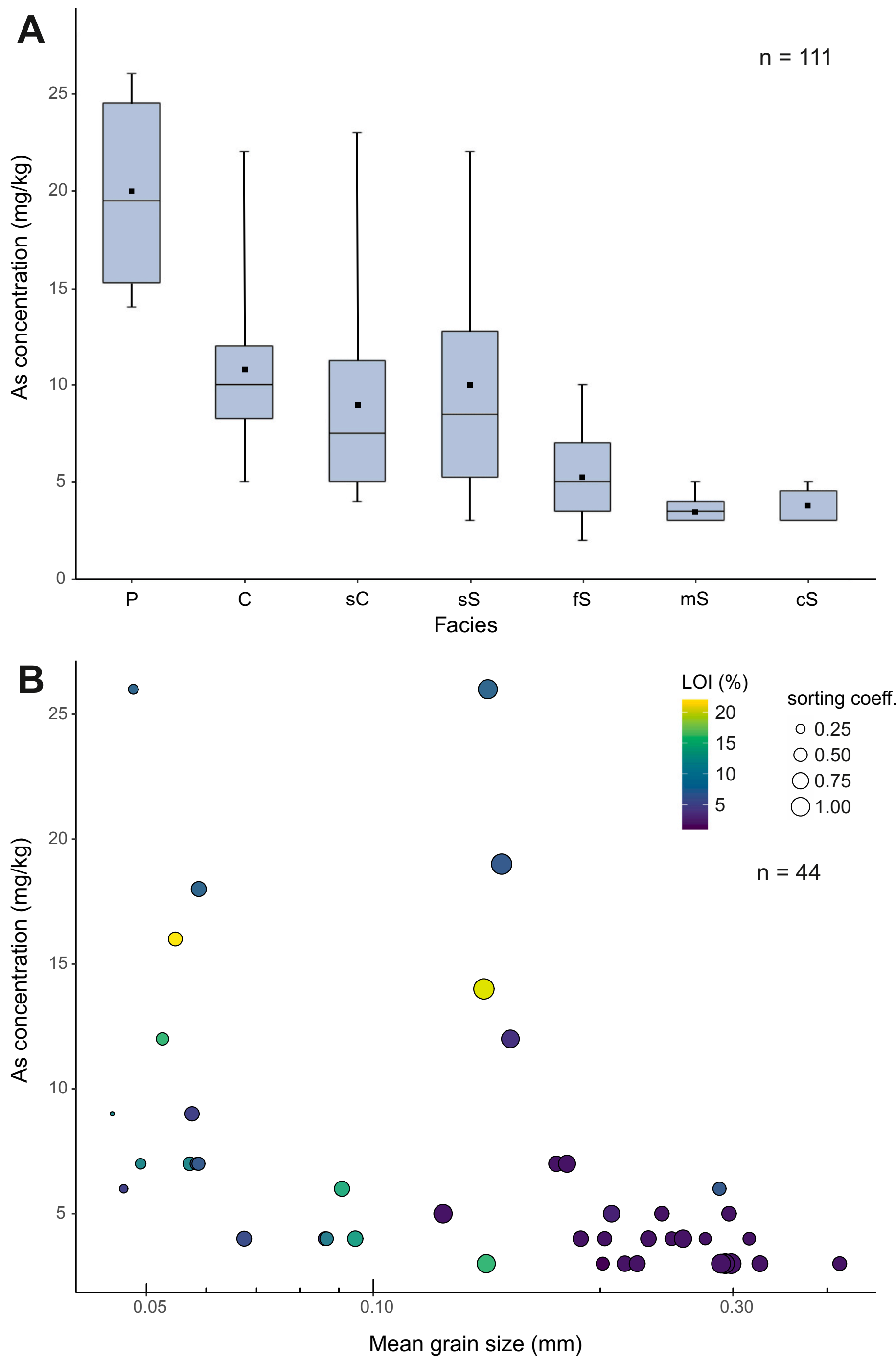

Fig. 8. Relationships between facies characteristics and arsenic concentrations. (A) Box plots of distributions in arsenic (As) concentration for the different lithofacies types (see Table 1 for facies codes). Facies are ordered by decreasing organic-matter content and concurrently increasing modal grainsize. Boxes indicate interquartile ranges; dots and bars indicate mean and median values, respectively. (B) Scatter plot of As concentration plotted against mean grain size. The size of the spots is directly proportional to the sorting coefficient (i.e., inversely proportional to sediment sorting; Folk and Ward, 1957); the colour scale indicates loss-on-ignition readings as a proxy for organic-matter content.

(Fig. 3A, C), As concentrations were measured for sediments sampled from 13 locations based on a combination of vibracore (Fig. 4) and augercore samples (Fig. 1C, Supplementary Table 1). Values of As concentration have been averaged over the vertical sample of each vibracore, whereas individual samples were drawn from the augercores for measurement. These concentration values have been mapped in plan-view and interpolated via an inverse-distance method (Fig. 9), to illustrate the spatial variability in As sediment concentration in a set of co-genetic point-bar and channel-fill elements. Significant spatial variations in average As concentrations are observed; in the sampled point-bar element, these spatial variations do not appear to portray trends that are evidently related to physiographic elements of the bar-form (e.g., from bar head to bar tail), or to the proximity of the samples to the abandoned channel fills.

When related point-bar and channel-fill deposits are considered, an inverse relationship ($R = -0.76, p = 0.046$) is observed between average As concentration in point-bar elements and average As concentration in the genetically related channel fills (Fig. 10). Across the three study areas, a trend of downstream increase in average As concentration is seen in channel-fill sediments, paralleled by a decrease in associated point-bar As concentration (Fig. 10).

6. Discussion

6.1. Sedimentary controls on the distribution of geogenic arsenic

The Holocene meander-belt deposits of the Po River examined in this study demonstrate the typical geomorphological and sedimentological characteristics of point-bar units that accreted dominantly through meander expansion; these are enclosed by dominantly mud-filled channel forms representing meander loops that underwent rapid cut-off and that once hosted oxbow lakes that became progressively infilled. Due to the infill of these oxbow lakes under dominantly waterlogged and oxygen-deficient conditions, the resulting clay-plug units contain abundant sedimentary organic carbon preserved from plant remains. The results of this study corroborate the notion that there exists risk of arsenic accumulation in the sediments and water of aquifers that exhibit sedimentary architectures associated with fluvial meander-belt deposition, and that abandoned channel forms and their sedimentary fills may act as local sources of As, dominantly released by microbially induced reductive dissolution (Nath et al., 2005; Weinman et al., 2008; Desbarats et al., 2014; Sahu and Saha, 2015; Donselaar et al., 2017; Ghosh et al., 2021; Kumar et al., 2021; Ghosh and Donselaar, 2023). Point-bar deposits tend to show relatively low values of As content, mostly between 3 and 4 mg/kg, whereas As concentrations measured in channel-fill sediments are sensibly higher, and highest overall in peaty facies. The dataset also reveals an inverse relationship between the respective values of As concentration in point bars and genetically related channel-fill deposits (Fig. 10). This observation is consistent with the hypothesis that mud plugs act as progressively depleting sources from which As is mobilized, whereas point-bar elements tend to act as enriching As reservoirs into which As migrates via diffusion from the compacting mud plugs and advection along permeability contrasts (cf. Jakobsen et al., 2018; Kumar et al., 2021). However, this idea appears to

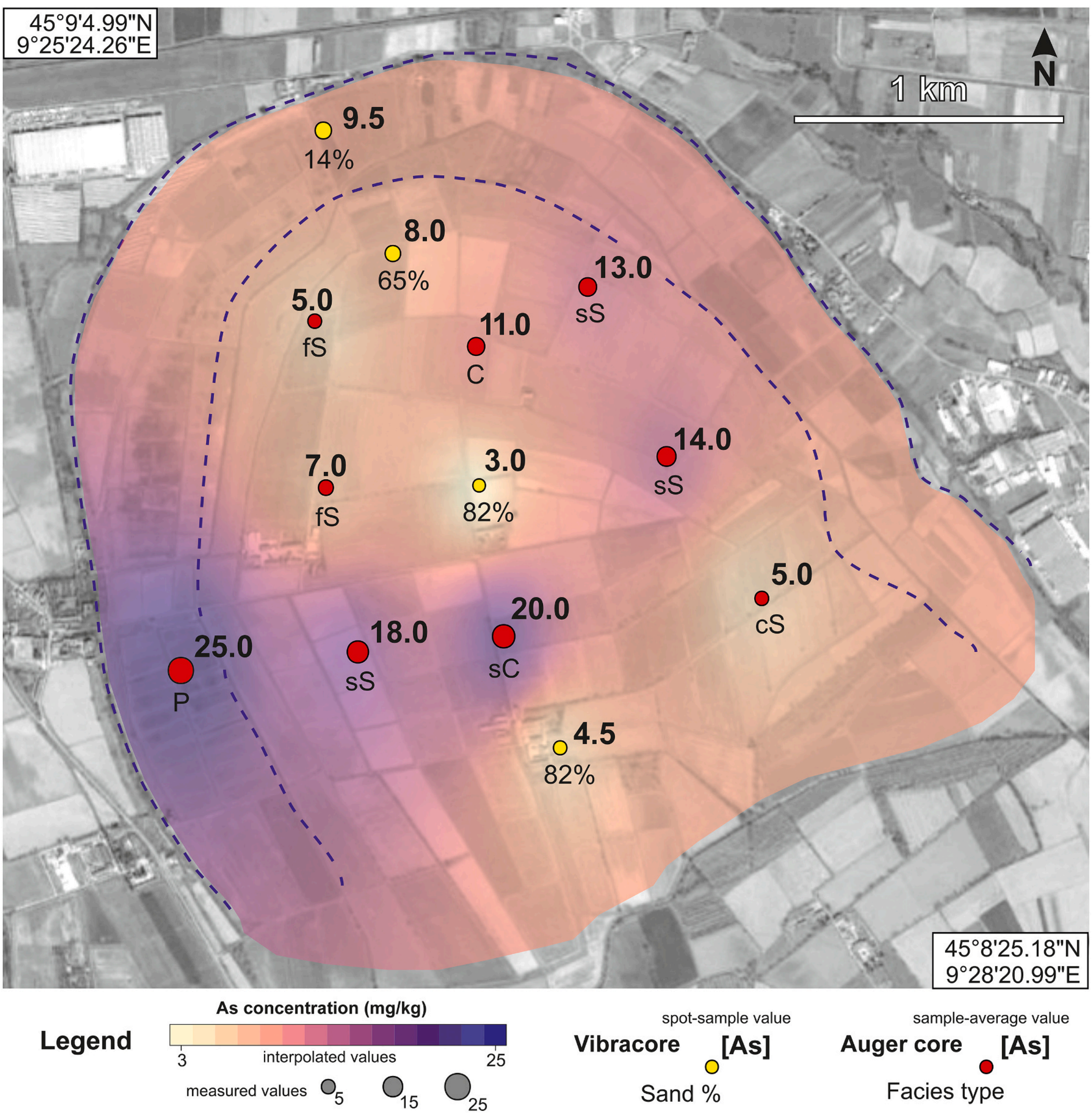

Fig. 9. Map of interpolated values of As concentration (mg/kg), as measured in individual samples taken from augercores at 1 m depth (yellow spots) or as vertically averaged values of vibracore samples (red spots), for the palaeo-meander-bend of Figs. 3A, 4. Percentage of sand in the vertical section and facies types are indicated for vibracores and augercores, respectively. The inferred positions of outer and inner channel banks at the time of channel abandonment are shown as dashed blue lines. Interpolation is performed by an inverse-distance method.

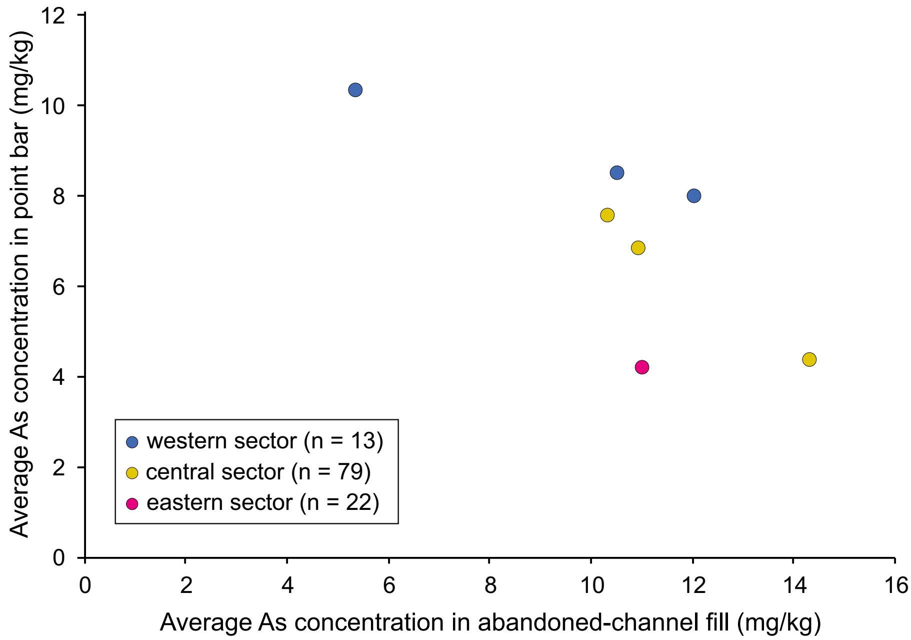

Fig. 10. Scatter plot of relationship between average As concentrations in abandoned-channel fills and spatially and genetically related point-bar deposits, across the three sectors of the study area.

be at odds with the fact that the highest ratio between As concentrations in point-bar and mud-plug deposits are observed in the youngest meander-belt portions ('Z' and 'So' samples; Fig. 1).

Arsenic concentration in alluvial sediments is known to be controlled by the mineralogical composition and presence of organic material. Under oxidizing conditions, arsenic binds to clay minerals and iron oxyhydroxides, whereas, when conditions become reducing due to bacterial activity and presence of organic matter in an anoxic environment, arsenic is desorbed and enters into solution (McArthur et al., 2004). If reducing conditions are particularly intense and As availability is sufficiently high, sulfides precipitation will cause re-sequestration of arsenic in solid form (Quicksall et al., 2008). Peat soils have higher As concentrations principally because of increased prevalence of sulfide mineral phases that developed under reducing conditions (Smedley and Kinniburgh, 2002). Thus, overall, observations on variations in As concentrations across the preserved deposits of point-bar and channel-fill architectural elements conform with expectations based on this knowledge. Notwithstanding, important variations in As content are seen, even in the deposits of the same architectural element.

At facies scale, the distribution of As concentrations is heterogeneous, especially in lithofacies present in both clay-plug and point-bar units, such as C, sC and sS (Fig. 8). In general, the As content in sediments reflects concurrent changes in grainsize and mineralogy, whereby As is naturally enriched in clayey facies and diluted in sandy deposits (mS and cS; cf. Smedley and Kinniburgh, 2002; van Geen et al., 2008). In the C and sC facies that dominate in clay plugs, the As content varies in line with loss-on-ignition (LOI) readings and S concentration; LOI acts as proxy for organic-matter content, which, in line with sulfur, can be taken as an indicator of reducing environmental conditions. Exceptions are seen, however. For example, point-bar facies sS is occasionally associated with high concentrations of As (max: 22 mg/kg), despite low LOI readings and S content (see Fig. 5, core E11; Fig. 9; Supplementary Table 2). Locally, such relatively high As concentrations in point-bar elements might be dominantly related to carbon advection by groundwater flow from the clay plug to the point-bar element. The flow of organic-carbon-rich fluids is commonly controlled by permeability contrasts between the low-permeability clay-plug sediments and the adjacent, more permeable, point-bar sands (Donselaar et al., 2017). The processes of reductive dissolution and desorption driven by influx of carbon-bearing water can cause the release of arsenic from its solid state, leading to its advection or diffusion in the aquifer (Smedley and Kinniburgh, 2002; Sahu and Saha, 2015; Donselaar et al., 2017). The reducing conditions necessary to maintain arsenic in solution may be only transient, however, in relation to consumption of organic carbon, such that As can ultimately become re-sequestered in solid form along groundwater flow pathways (Papacostas et al., 2008). These processes provide a possible partial explanation of the planform variability in As concentration in point-bar deposits. Nevertheless, no evident relationship is seen between inferred sand petrophysical quality (i.e., expected variations in permeability) and As concentration in point-bar deposits. In the studied examples, classes with different values of modal sand grainsize, which are expected to be associated with contrasting hydraulic conductivities, do not differ significantly with respect to As concentrations. Also, no relationship is observed between solid-phase As concentrations and values of sediment sorting, which acts as an additional control on the hydraulic conductivity of the sediment. Thus, the sediment As content does not appear to be dominated by a petrophysical control on advection or flushing of mobilized carbon and/or As. Notwithstanding, the role of sediment permeability in controlling groundwater geochemistry cannot be discounted, due to the lack of data on the As content of pore-filling water.

Although no meaningful trend is observed in the planform variation in As concentration in point-bar deposits, some vertical trends are instead notable in both point-bar and channel-fill sediments. Overall, fining-upward trends seen in point-bar and channel-fill facies sequences tend to be matched by a trend of increase in As sediment concentration, which may reflect changes in original As content as well as vertical redox variations through the profile (cf. Papacostas et al., 2008). Bar-top deposits tend to be mud-prone. Being relatively heterogeneous, less permeable, and comparatively richer in As than point-bar sands, these beds can hinder flushing of the underlying unconfined aquifer by percolation, cause downward transfer of As or carbon (Sahu and Saha, 2015), and facilitate the establishment of reducing conditions in underlying point-bar deposits by inhibiting oxygen convection and diffusion (Smedley and Kinniburgh, 2002). In channel fills, sS facies positioned in the lower portion of the units may act as flow conduits that facilitate the transfer of dissolved As to point-bar deposits; yet, these deposits are characterized by relatively small values of As, S and LOI, which may indicate low concentrations of dissolved As in water (van Geen et al., 2008). Moreover, overlying clayey layers may act as barriers preventing As leaching from overlying peaty facies. The role of base-of-channel sands in transferring dissolved As to point-bar aquifer units may therefore be limited. In channel-fill deposits, peat accumulations tend to occur towards the top, and not at the base, of the fill, similarly to what was observed in other documented cases (cf. Sahu and Saha, 2015; Donselaar et al., 2017; Ghosh et al., 2021); this has implications concerning the risk for aquifer contamination in relation to expulsion of carbon and/or arsenic-rich fluids, which may be expected to be higher if peat layers are seen in the lowermost part of the infills.

The dataset also allows consideration of the potential contribution of the sediment supplied by the Ticino and Adda tributary rivers of the Po (Fig. 1) to As sediment concentrations. A potential increase in concentration of As in sediment and water could be envisaged to arise due to progressive integration of these two Alpine sources. The rivers Ticino and Adda drain catchments in which the topsoils and floodplain sediments display the absolute highest As concentrations of the cumulative catchment of the study areas (Tarvainen et al., 2013; Cicchella et al., 2015; Zuzolo et al., 2020), and the contribution by tributaries draining Apennine sources that could determine As dilution is subordinate. Yet, the average As concentrations measured in Po sediments upstream of, between, and downstream of the confluences with these two rivers do not vary significantly, and portray a trend of weak downstream decrease towards the eastern sector (Fig. 10). On this basis, it appears that the possible provenance control on As sediment concentrations is only secondary relative to the observed facies control, in contrast with other cases associated with different clastic environments (Amorosi and Sammartino, 2007; Sarti et al., 2020; Ruggieri et al., 2021).

6.2. Applied implications

Some general implications can be derived from this study, both of global significance and of particular interest for the Po Valley and its subsurface. Understanding of relationships between As concentration in sediment and sedimentological properties related to sub-environments with distinct geomorphic expressions is useful for assessing risks associated with As uptake from cultivations, thereby informing agricultural practices. In the region, this is especially important given the roles of rice as a natural accumulator of arsenic drawn from paddy soils and as a cause of dietary arsenic exposure (Meharg, 2004; Zavala and Duxbury, 2008; Sommella et al., 2013; Abedi and Mojiri, 2020). In the Po Plain, variability in geogenic As concentrations is also seen to be related to facies heterogeneity in buried confined aquifers used for drawing drinking water (Rotiroti et al., 2015, 2021), although risks associated with water consumption are not as severe as in other regions (Ravenscroft et al., 2009). The results of this study highlight the need for consideration of sedimentary architectures when modelling groundwater flow and As transport (Desbarats et al., 2014; Rotiroti et al., 2015), by considering realistic geometry, size, spacing and hydraulic conductivity of potential As sources and sinks that may occur in the inter-well space. The fact that local variations in sediment As content across sub-environments are more important than regional variations related to As geological sources should be taken into account when mapping As concentrations in soils (Cicchella et al., 2015), sediment (Zuzolo et al., 2020), crops (Cubadda et al., 2010), and water (Schiavo et al., 2024), as variations observed in As concentration in sediments of river floodplains may reflect said facies bias rather than regional trends, especially given that mud plugs, as arsenic sources and hotspots, are below the sampling resolution of regional-scale maps.

Thus, this study demonstrates the value of integrated geomorphological and sedimentological datasets as a tool for screening areas at risk of having high concentration of As in sediment, soil and groundwater. In turn, these predictions can be applied to: (i) guide programmes of phytoremediation of soils with arsenic-rich parent material (Souri et al., 2022) or aquifer cleanup via pump-and-treat or chemical treatment (Wovkulich et al., 2010); (ii) constrain the potential impact of geological heterogeneities on hydrogeological models of arsenic transport (cf. Jakobsen et al., 2018); and to (iii) inform mapping programmes, by helping discriminate between background and anthropogenic variations and highlighting potential facies bias on As concentration readings, on the basis of which a suitable mapping resolution may be chosen (Reimann et al., 2009).

7. Conclusions

An integrated study of geomorphological, sedimentological and geochemical data has been undertaken of Holocene meander-belt deposits of the Po River, to investigate geological controls on arsenic distribution in sediments. The analyses demonstrate that sedimentological controls on As accumulation are expressed at the scale of both lithofacies and larger-scale depositional sub-environments, in accord with other literature studies. The data highlight the role of abandoned-channel fills as sources from which arsenic is transferred to point-bar sediments. Arsenic concentrations are dominantly related to the presence of organic matter and clay, although local As variations may be related to petrophysical heterogeneity controlling fluid flow from As-rich channel fills into point-bar bodies. No evident relationship is seen between As concentrations in sediment and characters of point-bar facies distributions related to the morphodynamic evolution of their formative meanders. However, the documented facies control appears to be dominant over a potential provenance control related to sediment supply from arsenic-rich catchments. The results have implications regarding heterogeneity in arsenic concentration in surface sediment, agricultural soils and aquifers, in the Po Valley and globally.

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CRediT authorship contribution statement

Elisabetta Bosi: Writing – original draft, Investigation, Formal analysis, Data curation. **Luca Colombera:** Writing – review & editing, Writing – original draft, Supervision, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Nigel P. Mountney:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Duccio Bertoni:** Methodology, Investigation. **Giovanni Sarti:** Resources, Methodology. **Alessandro Amorosi:** Supervision, Methodology, Investigation.

Declaration of competing interest

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

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Data availability

Data will be made available on request.

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