Pre-industrial sediment concentrations of metals: insights from the Venice Lagoon (Italy)

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Keywords: Sediments; Pre-industrial Concentrations; Heavy metals; Venice lagoon

Abstract

This study investigated the occurrence of selected metals and metalloids (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in radio-dated sediment cores from a coastal lagoon (Lagoon of Venice, Italy) by critically reviewing and grouping available data. Pre-industrial concentrations (pICs, estimated for the period before the early 1900s) for the Venice lagoon are identified according to the 2σ statistical procedure (2σ-pICs), i.e. the upper bound values of the dataset distribution. Results show the following 2σ-pICs (μg/g, d.w.): As 15,9; Cd 0,6; Cr 38,0; Cu 18,1; Hg 1,1; Ni 32,9; Pb 29,4; Zn 94,5. Most of the estimated 2σ-pICs are comparable to previously assessed background values. In the case of Hg, on the contrary, 2σ-pIC is remarkably higher than background values, reflecting a significant anthropogenic contribution also in the pre-industrial period.

The results of this work may support the evaluation of temporal evolution of metal concentrations in sediment of the Venice Lagoon. Results are compared with background concentrations (BC) observed in previous studies conducted in the lagoon and in other areas of the Adriatic Sea, as well as with benchmarks set in Italy for sediment assessment.

1. Introduction

Sediments in coastal environments origin from a combination of external inputs (i.e. atmospheric, freshwater and seawater inputs) and internal inputs such as direct discharges of municipal and industrial effluents, production and sedimentation of organic matter, and erosion of older deposits (Nichols and Boon 1994; Geiselbrecht et al. 2019). A special case of the depositional environment is represented by coastal lagoons because of the multiple and intense interactions among physical, chemical and biological processes. Sediments transported into a lagoon may undergo repeated cycles of transport, deposition and erosion by tidal currents and wind and wave action, and can be resuspended many times before accumulation (Nichols and Boon 1994; De Lacerda 1994).

Naturally occurring trace elements, i.e. metals (and metalloids), account for the geochemical baseline or “background concentrations” in depositional environments. There are many definitions of geochemical background in the literature (Matschullat et al. 2000; Reimann and Garrett 2005; Reimann et al. 2005, Romano et al. 2022). According to Matschullat et al. (2000) and Dung et al. (2013), the geochemical background is “a relative measure to distinguish between natural concentrations and anthropogenically-influenced concentrations in real samples collectives”. Other authors use the term ‘‘natural background” with reference to the microelements naturally present in the minerals that are weathered and then transported from the catchment basin (Apitz et al. 2009; Gałuszka 2007). These definitions assume no or negligible influence of humans. However, natural or pristine environments are rare, especially in Europe, and the estimate of a natural background concentration will inevitably include a contribution from anthropogenic sources (including non-point sources, e.g. atmospheric deposition) because much of the European landscape has been altered by human activities over millennia and this historical anthropogenic contribution to background concentrations may be obscure and difficult to quantify (EC 2011, Crane et al., 2021). In this sense, the evaluation of pre-industrial concentrations, accounting for historical moderate anthropogenic input even before the industrial revolution (that took place at a large scale in Europe starting from the nineteenth century, but a bit later in certain regions) may be useful to support the analysis of temporal trends to better understand current contamination status of transitional environments.

The chemical analysis of deeper, undisturbed sediments, combined with radio-isotopic techniques using e.g. ^{210}Pb, ^{137}Cs, appears the best approach to evaluate historical trends of sediment contamination and also to estimate the natural background and pre-industrial concentrations (Frignani et al. 2005; EC 2011; Zonta et al. 2018; Romano et al., 2022). Depending on the dataset, different statistical methods can be adopted to establish background concentration (Dung et al. 2013; Apitz et al. 2009). Matschullat et al. (2000) evaluated several statistical methods, applied to different datasets, to explore their potential for the evaluation of a robust background: among tested methods, the authors showed that the statistical iterative 2σ procedure is the most suitable one to derive plausible and realistic background concentrations. This method was applied in different coastal areas of the Mediterranean Sea (Romano et al. 2015; Mali et al. 2015; Hernández-Crespo and Martín Monerris 2015) and proved to be appropriate to determine the upper bound of background range, although additional investigations could be required depending by the features of the site-specific system and available dataset (Romano et al. 2015; Mali et al. 2015; Hernández-Crespo and Martín Monerris 2015; Dung et al. 2013; Gałuszka, 2007).

The recent literature on the Venice lagoon has been focused on distinguishing the anthropogenic contribution to sediment contamination after the development, since early 1900s, of the industrial district of Porto Marghera at the central lagoon border. At that time, the development of the Porto Marghera industrial area (as well as the related infrastructures, such as the commercial port) was considered advantageous due to the favorable geographical position and also due to the availability of a labor force at low cost, since at that time the area was mostly rural and economically depressed (Mannino et al., 2015).

Many investigations used radio dated cores to assess the temporal variability of contaminants in the sediment (Frignani et al., 2005; Bellucci et al., 2005; Gieskes et al., 2015; Zonta et al. 2018). The overall studies provide a good dataset with information on chemical concentration, radio-isotopic analyses and sedimentation rates under present and past conditions. Alongside, the Environmental Protection Agency of the Veneto Region (ARPAV) has recently published a comprehensive dataset of heavy metal background concentrations in soils of the drainage basin of the Venice lagoon (ARPAV 2019) that always played a key role in the delivery of sedimentary material to the lagoon.

The present study aimed to collect and critically evaluate all available information generated by radio-dated sediment cores from the Venice lagoon in order to explore the trends of metal contamination and quantify sediment pre-industrial concentrations (pIC) for selected metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn), as a support to the interpretation of current contaminantion conditions. Derived pIC are then compared with background concentrations (BC) observed in previous studies conducted in the lagoon and in other areas of the Adriatic Sea, as well as with benchmarks set in Italy for sediment assessment (including sediment EQS and Sediment Quality Guidelines defined for sediment management). Specifically, the comparison of site-specific sediment concentrations and trends against background values and sediment benchmarks provides useful information for any site specific assessment, as screening levels to identify metals of potential environmental relevance and to support decisions regarding the need for additional site-specific investigations.

2. Study area

The Venice lagoon (North-eastern Italy, Fig. 1 in SI) is one of the largest coastal environments in the Mediterranean Sea: it extends for about 50 km along the coast and has an average width of 15 km, with a total surface area of 549 km^2. It is connected to the northern Adriatic Sea by three tidal inlets (Lido, Malamocco and Chioggia), which enable the exchange of water and sediments during the tidal cycles on the basis of a microtidal regime (Sarretta et al. 2010). Hydrologically the lagoon can be divided into four sub-areas (Fig. 1 in SI, Solidoro et al. 2004; Tagliapietra and Ghirardini 2006, Molinaroli et al. 2009): northern (N) sub-area (Treporti, total area 88km^2), central-northern (CN) sub-area (Lido, total area 86 km^2), central (C) sub-area (Malamocco, total area 121 km^2) and southern (S) sub-area (Chioggia, total area 111 km^2).

The drainage basin (1850 km^2), with a population of about a million inhabitants, is highly urbanized, with considerable agricultural and industrial activities (Zonta et al. 2005). Twelve main tributaries drain the catchment, providing a mean freshwater discharge of about ~ 1,1x10^9 m^3/y to the lagoon (Zuliani et al. 2005). The associated annual sediment input was calculated at 33-35 × 10^3 tons yr^{-1} (Collavini et al. 2005; Molinaroli et al. 2009).

Sedimentation and resuspension are very intense in the lagoon (settling rate up to 1,0 cm/year) since about 72% of the lagoon is shallow water with a depth range between 0,7-1,5 meters (D'Alpaos et al. 2013; Carniello et al. 2016; Madricardo et al. 2017; Ghinassi et al. 2019). Historically, the main contribution to lagoon sediment flux came from the lagoon drainage basin and, to a minor extent, the northern Adriatic Sea, where a counter-clockwise current from NE to SW transport sediment mainly in the northern lagoon, and from atmospheric deposition (Bettiol et al. 2005). Sediment fluxes play an important role in shaping the morphodiversity of the lagoon as well as in trapping and redistributing chemical contaminants. The lagoon comprises a network of channels of various depths, shallow waters, isles and salt marshes (above mean sea-level). The area of salt marshes, shallow waters and channels in the lagoon is about 40, 308 and 58 km^2 respectively (Molinaroli et al. 2009; Tommasini et al. 2019).

Starting from the 7th century, the Venice lagoon has been subject to morphological transformations and intense anthropogenic pressure with an acceleration during the 20th century which has resulted in the deepening of the lagoon bottom and enhanced the sediment erosion from salt marshes and shallow waters to the channels and the sea (Carniello et al. 2009; Tommasini et al. 2019; Zonta et al. 2018), with a sediment net loss of about 110 Mm^3 since the year 1927 (Sarretta et al. 2010; Rosati et al. 2020). Moreover, the uncontrolled, intensive clam harvesting (1992-2001) contributed to increased sediment loss (Sfriso et al. 2005).

The main sources of chemical contaminants for the lagoon are the effluents from the large industrial area of Porto Marghera (developed after the 1910 and operating since the early 1920s) and the inhabited islands (e.g. historical centre of Venice), as well as atmospheric deposition, emissions from water boats, and pollutants from the drainage basin (Collavini et al. 2005; Zonta et al. 2018). The industrial district severely affected the lagoon with the production of fertilizers and heavy metals (mainly Cd, Hg, Pb and Zn) as by-products (Caliceti et al. 2002). The distribution of contamination is primarily controlled by the proximity to the sources and by tidal circulation (Lucchini et al. 2001). As far Hg, the sediments have shown relatively large inputs as a result of local industrial activity, as well as from sources in the northern Adriatic (Covelli et al. 2012). In the CN sub-basin, since the mid-1930s trace-metal contamination became a significant problem, mainly as a result of the increased industrial activity in the Porto Marghera industrial district (Gieskes et al. 2011). Starting from the 1980s the heavy metal concentrations in the surface sediments decreased due to reduced inputs (Frignani et al. 1997; Degetto et al. 2005) following regulatory actions.

3. Methods

3.1 Dataset development

A literature review was conducted with the aim to i) identify peer reviewed papers and technical reports including spatially distributed metal concentrations from radio dated sediment cores collected in the lagoon of Venice, and ii) create a dataset for the calculation of pre-industrial concentrations based on the most complete studies reporting radio dated sediment core data. Further, also scientific papers and technical reports proposing background concentrations for the lagoon of Venice were evaluated.

Literature was examined to extrapolate information about the sampling year, geographical area and morphological units (shallow water bottom or salt marsh sediment), the analysed sediment thickness, the Sediment Accumulation Rate (S.A.R.), the average age of each analysed sediment layer and the metal concentration associated to a specific time interval. For those studies that reported more than one S.A.R. value (i.e. derived from different methodologies) for the same core, an average value for the whole core profile was reported.

Such information was then used to select the data to be included in the RDC (Radio Dated Cores) dataset; the studies applying data normalization (in case of grain size heterogeneity), including S.A.R., using radionuclides for sediment dating and reporting at least one ancillary parameter among grain size, mineralogy and organic content, were selected. Then, those metal concentrations dated with radio-isotopic techniques before 1910 were included in the RDC pre-1910 dataset, while those dated after 1910 were included in the RDC post-1910 dataset, to evaluate metal concentrations in sediment deposited before and after the beginning of the industrial activities in the area of Porto Marghera. For each dataset, means±standard deviation (SD) were calculated for each metal. Moreover, within the same dataset means±SD were calculated according to geographical area (N, CN, C, S) and morphological unit (shallow water bottom or salt marsh).

3.2 Pre-industrial concentrations (2σ-pICs) for the Venice lagoon

Pre-industrial concentrations were derived from the RDC pre-1910 dataset by adopting the approach proposed by Matschullat et al. (2000). As first step, outlier data above and below the 75° and the 25° percentiles were removed to reduce the overall uncertainty affecting the starting dataset. Then the iterative 2σ technique proposed by Matschullat et al. (2000) was applied: mean and standard deviation (σ) were calculated for each metal distribution and all values beyond the mean±2σ interval were omitted. This procedure was repeated until all remaining values lied within this range. According to this procedure, the pre-industrial concentration is defined as the upper bound of the sub-dataset variability (i.e. the "2σ-pIC"), defined by the mean+2σ.

The 2σ-pICs were then discussed according to temporal trends identified in the RDC dataset and compared with: i) existing data on BCs for the Venice lagoon, ii) sediment EQS set in Italy under the WFD context (Legislative Decree 172/2015) and Sediment Quality Guidelines (SQG) set in national legislation concerning the management of dredged sediment and disposal at sea (Decree 173/2016)[1], iii) background concentrations observed in other coastal areas of the Adriatic Sea, and iv) available information on BCs in soils of the drainage basin of the Venice lagoon (ARPAV 2019), i.e. the solid material transported into the lagoon by freshwater inflows.

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[1] The EQS defined in the Legislative Decree 172/2015 (used to assess the ecological status of marine coastal areas and transitional water bodies) and sediment quality guidelines set in the Decree 173/2016 (defined for sediment management purpose), considered in this study, are considered to represent the sediment concentration at which toxicity and bioaccumulation effects may occur with a low probability (Surricchio et al., 2019, Tornero et al., 2019).

4. Results and discussions

The literature review on the Venice lagoon allowed to generate a dataset including spatially distributed heavy metal concentrations from 17 radio dated cores accounting for a total of 165 samples (Section 4.1), to derive 2σ-pICs, which are discussed by comparison with previously reported BC for the Venice lagoon (Section 4.2) and for the Adriatic Sea as well as with sediment quality criteria set in Italy (Section 4.3).

4.1 The radio dated sediment cores dataset for the Venice Lagoon

The sediment of the Venice lagoon has been extensively studied over the years and 15 scientific publications reporting data on metal concentrations in radio dated cores were found (see Table 1a in SI).

Out of them, four publications (Frignani et al. 1997; MAV-CVN 2000a; MAV-CVN 2000b; Zonta et al. 2018) were selected, according to the criteria reported in paragraph 3.1, to generate the RDC dataset; the selected studies can be considered comparable in terms of methodologies used for sample preparation and analysis (details in Table 1b in SI). As result, the RDC dataset included spatially distributed metal concentrations from 17 radio dated cores accounting for a total of 165 samples, which were further divided into: the RDC pre-1910 dataset (67 samples) and the RDC post-1910 dataset (98 samples), where the year 1910 indicates pre- and post-development of industrial activities in Porto Marghera. Table 2 in SI shows the distribution of the samples in both datasets grouped by geographical area (i.e. sub-areas of the Venice lagoon) and morphological units (i.e. shallow water sediment and salt marsh sediment).

As reported in Table 2 in SI, most samples refer to the sub-areas N and CN (152 samples) and in particular to shallow water sediments in such sub-areas (141 samples), mainly because they were collected over the last decades to support the environmental impact assessment of the Porto Marghera industrial district. Salt marsh sediment cores, which are typically used to assess the atmospheric fallout of heavy metals (Cochran et al. 1998), were less studied in the Venice lagoon and resulted in 24 samples in total, equally distributed between N and S sub-areas.

The RDC pre-1910 dataset offers the most complete collection of sediment core data for deriving pIC for the Venice lagoon. The mean metal concentrations and standard deviations were calculated according to each sub-area and morphological unit (i.e. salt marsh and shallow water sediments), as presented in Table 1.

Table 1. Mean concentration and SD for the RDC pre-1910 dataset selected metals in salt marsh (SM) and shallow water (SW) sediments, in each sub-area (N, CN, C, S). All values are expressed as µg/g d.w.. In brakets, the number of samples available for each morphological unit and sub-area.

RDC pre-1910 dataset		**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
		µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
SM (total)	mean	16	0,2	24	21	0,9	22	26	96
(n=7)	SD	8	0,1	11	4	0,8	7	8	45
SM (sub-area N)	mean	14	0,2	17	17	1,3	17	22	62
(n=4)	SD	8	0,0	3	1	0,9	2	5	4
SM (sub-area S)	mean	20	0,2	34	26	0,3	29	31	140
(n=3)	SD	8	0,1	13	0,2	0,1	3	8	29
SW (total)	mean	13	0,6	35	13	0,7	29	22	93
(n=60)	SD	4	0,5	15	9	0,5	6	10	81
SW (sub-area N)	mean	14	0,4	38	14	1,0	30	23	78
(n=26)	SD	4	0,1	15	5	0,5	4	7	16
SW (sub-area CN+C)	mean	12	0,6	33	12	0,5	29	22	104
(n=35)	SD	3	0,6	14	12	0,4	6	12	106

Considering the total SM sediments and SW sediments samples, metal concentrations in SM are comparable to those in SW with the exception of Cd, higher in SW.

Table 1 shows remarkable differences in the spatial distribution of metals in both SM and SW samples. Metals in the SM sub-area S are higher than in the SM sub-area N, with the exception of Cd i.e. same concentrations, and Hg i.e. concentrations significantly lower in the sub-area S . Metals concentrations in SW are slightly higher in sub-area N except for Cd and Zn. Considering the sub-area N in more details, higher values of Cd, Cr, Ni and Zn were found in SW, while higher concentrations of Cu and Hg were recorded in SM. Hg is particularly affected by spatial distribution, showing higher concentrations in sub-area N.

4.2 Derivation of 2σ-pICs and temporal trends

The pIC obtained by applying the "2sigma" statistical procedure (i.e. 2σ-pICs) to the RDC pre-1910 dataset are presented in Table 2 together with mean±SD calculated for the same dataset.

Table 2. Comparison between 2σ-pICs and mean±SD of the RDC pre-1910 dataset, considering all samples collected in SW and SM. All values are expressed as µg/g d.w.. The 2σ-pICs calculated on the basis of samples collected only in SW do not significantly differ from values estimated considering both SW and SM (reported in the table).

		As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
2σ-pIC *(n sample in the dataset)*		15,9 *(59)*	0,6 *(59)*	38,0 *(66)*	18,1 *(66)*	1,1 *(59)*	32,9 *(66)*	29,4 *(66)*	94,5 *(66)*
RDC pre-1910 dataset	mean	13,6	0,5	34,2	14,3	0,7	29,2	23,0	93,6
	SD	4,9	0,4	15,1	9,7	0,5	6,5	9,9	78,2

As expected, since each 2σ-pIC represents the upper bound of the RDC pre-1910 dataset distribution (Matschullat et al. 2000) for each metal, its value is higher than the mean value of the metal concentration distribution in the dataset.

By comparing 2σ-pICs with previously derived BCs for the Venice lagoon, the 2σ-pICs result to be consistent with values proposed by Apitz et al. (2009) (As 5-35; Cd 0,1-1,2; Cr 4-80; Cu 5-40; Hg 0,2-0,3; Ni 5-45; Pb 5-50; Zn 40-130 µg/g d.w.), who used a statistical method (based on multiple linear regressions) applied to a dataset from sediment cores distributed over the entire lagoon surface to separate background concentrations (expressed as a range of concentrations) from anthropogenic concentrations. The only exception is Hg, whose 2σ-pIC resulted to be higher than the range proposed by Apitz et al. (2009). Moreover, 2σ-pIC for Hg, along with 2σ- pIC for Zn, also resulted higher than the confidence range expressed by the mean±SD of the values proposed by previous studies that investigated background concentrations for the Venice lagoon (As 9,5±3,7; Cd 0,6±0,4; Cr 39,2±18,3; Cu 17,7±8,7; Hg 0,2±0,2; Ni 38,2±16,1; Pb 37,3±23,8; Zn 50,3±27,8 µg/g; Donazzolo et al. 1982; Pavoni et al. 1987; Pavoni et al. 1992; Frignani et al. 1997; Cochran et al. 1998; MAV-CVN 2000a; MAV-CVN 2000b; Lucchini et al. 2001; Degetto et al. 2005).

To better understand the relevance of the derived 2σ-pICs, a comparison with both metal concentrations in the Venice lagoon recorded for the post-1910 period and the EQS and SQG set in Italian legislation was carried out.

More specifically, since the comparison of 2σ-pICs with the mean±SD and maximum concentrations derived for each metal from the RDC post-1910 dataset (Table 3 in SI) could not allow to account for temporal variations in metal concentrations in the post-industrial period, and in particular for the peak of production activities in Porto Marghera over the 1950s-1970s period, a time-space trend analysis was conducted. For each metal, the data of the overall (i.e. pre- and post-1910) RDC dataset (including outliers later removed by the 2σ statistical procedure) were plotted against the derived 2σ-pICs as well as national sediment quality criteria (Figure 1), where the latter values are reported in Table 3 along with metal BC for different areas of the Adriatic Sea and background ranges observed in soils of the drainage basin of the Venice lagoon, and later discussed in paragraph 4.3.

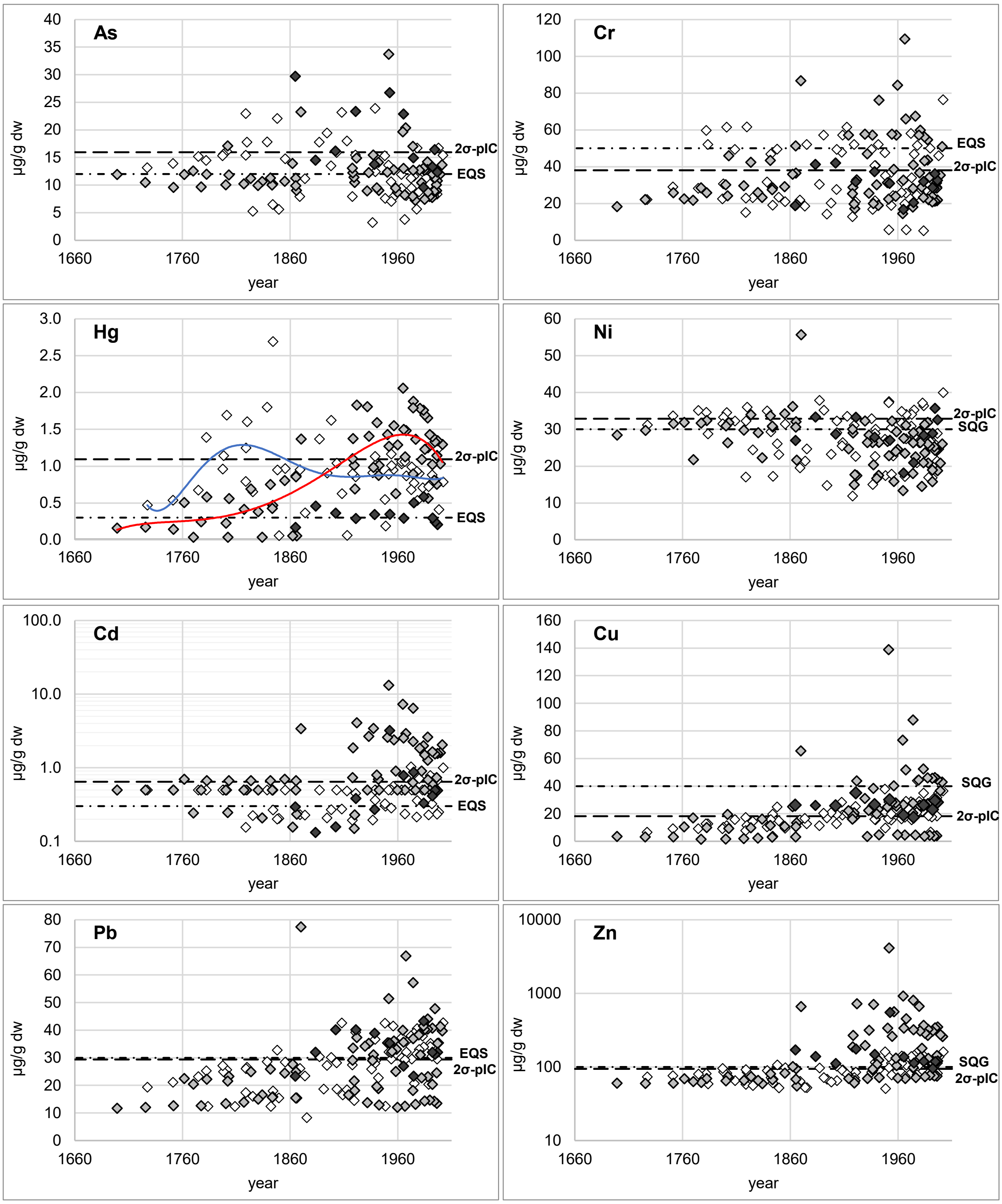

Figure 1: Distribution of concentrations, 2σ-pIC and national sediment quality criteria (EQS and SQG) values for each metal from the overall RDC dataset. Data referred to different sub-areas are marked with different colors (i.e. white for sub-area N, grey for sub-area CN and black for sub-area S) and, only for Hg, the N and CN sub-area trend lines are reported in blue and red colors, respectively.

As shown in Figure 1, the investigated metals can be grouped according to three different temporal trends as recorded in the sub-areas N and CN only; since concentrations in the sub-area S were very few, they were not used for grouping purposes.

As, Cr and Hg belong to the first group in which pre-1910 metals concentrations in sub-area N are generally higher than those reported for sub-area CN and are exceeding in several cases both 2σ-pIC and sediment quality criteria values, while after 1910 the trend is the opposite, showing much higher concentrations in sub-area CN compared to sub-area N. This trend is particularly evident for Hg, as highlighted by the trend lines drawn in Figure 1 the N and CN sub-area trend lines are reported in blue and red colors, respectively showing increasing concentrations of Hg in the sediments of sub-area N after 1760, with a peak around 1810 followed by a clear decrease starting from 1910. Since 1910 on, Hg concentrations in the sediments of sub-area CN increase remarkably, showing a peak around 1950-70s and a decrease in the most recent period (approaching 2010). Such trend is obviously affecting the pre-1910 derivation of the 2σ-pIC for Hg, which resulted to be high compared to previous studies. Indeed, the highlighted pre-1910 Hg concentrations could be due to a sum of factors occurring in the period before the industrial development of Porto Marghera such as historical human activity in the study area (mainly in the sub-area N but partially also in the sub-area CN) and the lagoon drainage basin, which may have contributed to the enrichment of this element in the sedimentary deposits of the lagoon (ARPAV 2019, Ravera, 2000). Factors that could have influenced temporal trend of Hg levels include also changes in atmospheric Hg emissions due to increasing development of craft and industrial activities coupled with changes in organic matter composition and dynamics, as demonstrated in other studies (Hare et al., 2010, Horowitz et al., 2014, Rosati et al., 2020). Additionally, although not experimentally demonstrated and not directly quantifiable, it is also plausible to hypothesize an input of Hg from the Adriatic Sea through the northern inlet of the lagoon as a result of historical mining in the Slovenian mine of Idrija, due to the transport operated by the North Adriatic counterclockwise sea current and atmospheric deposition. Specifically, Covelli et al. (2012) reported that the depositional flux of Hg in sediments of the Grado Marano Lagoon was influenced by anthropogenic inputs after 1800 (thus, in the period evaluated also in our pre-1910 dataset), when mining activity started to be more intense.

As a consequence, available data indicate that in the Venice lagoon (and in particular in the sub-area N) a relevant Hg anthropic pressure dates back to mid-1700, thus much earlier than the beginning of the industrial activities in the area of Porto Marghera. Moreover, similar considerations could be extended, although to a much less extent, to As and Cr (the former showing a 2σ-pIC slightly higher than its sediment quality criteria).

The other two groups which can be identified by the spatial-temporal trends in Figure 1 are the following: first, a group composed of Ni alone, showing a few sediment concentrations exceeding both 2σ-pIC and sediment quality criteria values along the entire investigated period, with a significant number of samples reporting concentrations much lower than 2σ-pIC and sediment quality criteria values after 1910. Second, a group including Cd, Cu, Pb and Zn, which well represents the evolution of anthropic pressure over the last two centuries in the Venice lagoon (and in particular in the sub-area CN), indicating a constant increase in emissions starting from 1900, which reached its peak around the 1960s and then decreased in the last decades.

Figure 1 is also showing that 2σ-pIC and sediment quality criteria values are very similar for Pb, Zn and Ni and slightly different for As (i.e. 2σ-pIC slightly higher than its sediment quality criteria), while there is a significant difference in 2σ-pIC and sediment quality criteria values reported for the other metals, and especially for Hg. Such differences were only partially considered in the previous discussion because they will be thoroughly addressed in the following paragraph.

4.3 Comparison of 2σ-pICs with BCs for the Adriatic Sea and sediment quality criteria

The sediment quality criteria for the examined metals, enforced by Italy in the context of the EU WFD and in national legislation, are reported in Table 3, along with the 2σ-pICs calculated for the Venice lagoon in this study and background levels for selected metals recorded in other areas of the Adriatic

Sea. As far as the latter, the values reported for sediments represent the upper bound of the background concentration range and have been estimated with various approaches, such as the estimate of maximum background levels from deep sediment cores (Frascari et al. 1988) and the evaluation of the 90th percentile of log-transformed data (Guerra et al. 2014). Additionally , the values reported by Lopes-Rocha et al. (2017) and, only for Hg, by Guerra et al. (2014) and Covelli et al. (2006) (that evaluated paleo-sediment), represent the central-tendency background concentration defined as the mean values observed in deep sediments.

The comparison of the national sediment quality criteria with 2σ-pICs (Table 3) shows that: i) the 2σ-pICs for Cr and Cu are lower than the Italian sediment quality criteria; ii) the 2σ-pICs determined for the other metals are similar or even higher than Italian sediment quality criteria. Specifically, the 2σ-pIC for Ni, Pb, Zn are very close to the sediment quality criteria (the 2σ-pIC falls in the confidence interval ±20% of the sediment quality criteria), whilst the 2σ-pIC defined for As is slightly higher than the Italian EQS (the 2σ-pIC falls in the confidence interval of +20% <EQS< +50%), and the 2σ-pICs determined for Cd and Hg are significantly different from EQS (2σ-pIC values > +50% of the EQS).

This result suggests the presence of metals enrichment also in the pre-industrial period, with exceedance of the Italian sediment quality criteria for selected metals, as discussed below.

The pre-industrial (i.e. pre-1910) concentrations determined for Ni, Pb and Zn in the Venice lagoon are indeed similar to background values determined in other areas in the Adriatic sea as well as sediment quality criteria (Table 3). Therefore, these values can be considered useful to identify sediment areas subject to anthropic influence but they give little information about the likelihood and relevance of adverse effects since exceedance of background concentration does not necessarily imply a biological effect or toxicity (Chapman and Wang 2001) and many aquatic organisms are able to adapt to elevated concentrations of naturally occurring metals (EC 2018; Chapman and Wang 2000; Weis et al. 2004; Morgan et al. 2007). The same observation can be applied to As since its 2σ-pIC for the Venice lagoon, which is slightly higher than its EQS, is in the same range of background concentrations determined in other areas of the Adriatic sea.

Tab. 3. Italian sediment quality criteria and metal BC (µg/g d.w.) for different areas of the Adriatic Sea and background ranges observed in soils of the drainage basin of the Venice lagoon.

References	**Area**	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
This study	2σ-pICs - Venice lagoon	16	0,6	38	18	1,1	33	29	95
Sediment quality criteria									
D.Lgs. 172/2015(a) and D. 173/2016(b)	Italy	12[a,b]	0,3[a,b]	50[a,b]	40[b]	0,3[a,b]	30[b]	30[a,b]	100[b]
Sediment BC									
Frascari et al., 1988	Po river delta and South, Italy	-	0,56	25	22	0,12	35	23	70
Lopes-Rocha et al., 2017	Po river delta, Italy	-	-	152	30	-	61	14	84
Lopes-Rocha et al., 2017	Adige river delta, Italy	-	-	57	12	-	23	23	86
Frascari et al., 1988	Middle Adriatic Sea, Italy	-	0,71	45	26	0,3	50	32	89
Covelli et al., 2006	Gulf of Trieste	-	-	-	-	0,13	-	-	-
Guerra et al., 2014	Pialassa Baiona lagoon, NW Adriatic, Italy	-	-	158	46	0,12	97	24	122
Soil background range									
ARPAV, 2019	Drainage basin of the Venice lagoon	14 -46	0,7 -0,93	62 - 63	110 -192	0,26 -0,51	38 - 51	37 -56	120 -143

Notes:

[a] EQS defined implementation of the European WFD (D.Lgs. 172/2015)

[b] SQG from national legislation concerning technical criteria for sediment classification, management of dredged sediment and disposal at sea (Decree 173/2016)

In the case of Cd and Hg, 2σ-pICs appear significatively higher than the corresponding EQS. In the case of Cd, the calculated 2σ-pIC, although higher than its EQS, is similar to the BC observed in the delta of Po river and the Middle Adriatic Sea (Frascari et al. 1988). Considering the data available in the RDC dataset (section 4.2), it is possible to observe the presence of multiple exceedances of the EQS even in the pre-industrial period. Finally, the Cd BC in soils of the drainage basin of the Venice lagoon are in the range 0,7 – 0,93 µg/g (mean value 0,81 µg/g) (ARPAV 2019). On this basis, it is possible that the Cd EQS, defined at national level, represents the central-tendency background concentration (defined as mean value of the natural background range along the Italian coasts), whilst the other values represents the upper bound of background concentrations for the different area.

As far Hg, the 2σ-pIC estimated in the Venice lagoon is always higher than the BC observed in other areas of the Adriatic Sea; the 2σ-pIC appears also higher than the range of BC determined in soils of the drainage basin of the Venice lagoon (range 0,26 – 0,51 µg/g, mean value 0,39 µg/g, therefore very similar to the sediment EQS set in Italy) (ARPAV 2019) (Tab. 3). Although the 2σ-pIC determined for Hg is probably influenced by limitations and uncertainties in the dataset (e.g., extrapolation of sedimentation rate and sediment dating) and adopted method, the analysis of the RDC dataset indicates that Hg EQS was consistently exceeded not only in the last century but also in the pre-industrial period, likely because of the influence of historical human activity in the study area, in the drainage basin as well as the sediment imported from the Adriatic Sea.

5. Conclusions

The estimation of pre-industrial concentrations in areas under the historical influence of humans appears useful for a reliable assessment of historical trends of anthropogenicc contamination. Most of the 2σ-pICs estimated in this study are comparable to the previously assessed background values. In the case of Hg, on the contrary, 2σ-pIC is remarkably higher than background values, indicating significant anthropogenic contribution also in the pre-industrial period. Considering overall available history of sedimentary trace metals in the Venice lagoon, the Italian sediment quality criteria (both sediment EQS and SQG, as previously cited) are likely to fall in the range of pre-industrial sediment concentration, except in the case of Hg. An extension of the dataset considered in this work to include radio dated cores from central and southern lagoon is strongly recommended in order to increase the spatial representativity of the dataset and to better identify sub-areas specificities.

6. Statements & Declarations

Funding

This study was carried out with the contribution of the “Provveditorato Interregionale Opere Pubbliche per Veneto, Trentino Alto Adige e Friuli Venezia Giulia” provided through the Consorzio Venezia Nuova and coordinated by CO.RI.LA -Consorzio per il coordinamento delle ricerche inerenti al Sistema Lagunare di Venezia, within the Venezia2021 project.

Competing Interests

The authors have no competing interests to declare that are relevant to the content of this article.

Authors contribution

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Enrico Marchese and Elisa Bizzotto. The first draft of the manuscript was written by Enrico Marchese and Elisa Bizzotto. Elisa Giubilato, Elena Semenzin and Antonio Marcomini revised and edited the manuscript. Antonio Marcomini supervised and coordinated the research work. Enrico Marchese, Elisa Bizzotto, Elisa Giubilato, Elena Semenzin and Antonio Marcomini read and approved the final manuscript.

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included and/or referenced in this published article (and its Supplementary Information files).

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