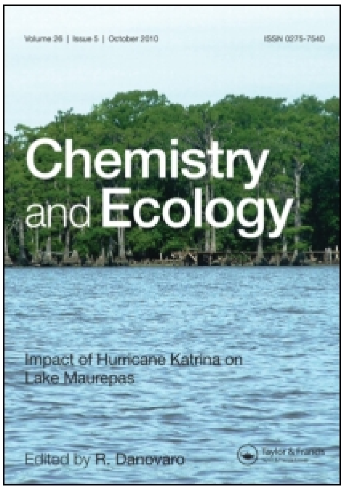

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Accumulation and metal fluxes in the central Venice Lagoon during the last century

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Samples from 18 short sediment cores were analyzed for major and trace metals (Al, Fe, Ca, K, Mg, Mn, Si, Ti, Pb, Zn, Cu, Ni, and Cr), ^{210}Pb, ^{137}Cs, total organic carbon, grain size, and mineralogical composition to find the record of major environmental changes, either natural or anthropogenic, and to establish their chronologies. Some sediments are characterized by nearly constant composition over time, but others clearly show signs of an increasing marine influence, as an increase of the carbonate contents, after the opening of the Malamocco–Marghera Canal in 1969. These changes sometimes obscure the real pattern of pollutants and tracers, which is revealed by normalization against Al. Zn is the most important contaminant, with concentration factors up to 9.3 times the background level, and the most contaminated sediments are those within a few kilometers from the industrial district of Porto Marghera. ^{210}Pb activity-depth profiles were used to calculate apparent accumulation rates that provide a basis for the assessment of metal fluxes. The sediments of several sites show a significant increase in anthropogenic metal contamination starting from the second decade of last century, with maximum inputs from 1930 to 1970. The decrease of heavy metal concentrations observed in surficial sediments of some sampling sites could be related to a recent reduction of pollutant inputs.

Keywords: Sediments; Chronologies; Accumulation rates; Metal fluxes; Venice Lagoon

1. Introduction

During the last century, the Venice Lagoon environment has been heavily affected by anthropogenic activities, such as land reclamation, excavation of canals, construction of industrial areas, dredging, and the uncontrolled discharge of contaminants, both heavy metals and organic chemicals. Many authors studied the distribution of anthropogenic metals in lagoon sediment as a way to understand sources, distribution, and accumulation of contaminants [1–7]. Frignani *et al.* [8] discussed the results of the study of 18 sediment cores taken from the northern part of the lagoon. Their results showed that metal concentration–depth profiles are influenced by anthropogenic sources and sometimes by changes in sediment composition.

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Furthermore, metal concentrations and fluxes showed a significant increase in the anthropogenic metal supply starting from the second decade of last century, with maximum inputs in the period between the 1930s and the 1970s. At some sites, a decrease in heavy metal contamination of surficial sediments was found that could be ascribed to a reduced input of pollutants in recent years. Furthermore, Cochran *et al.* [6] studied a salt marsh sediment and suggested that the atmospheric contribution of heavy metals can be significant or predominant at sites far from the major local inputs. However, most studies have considered only the surficial sediment layers and, in spite of the latest efforts [9], the knowledge of the geochemical and biogeochemical processes that characterize the system is still at an early stage, and the quantitative assessment of the fluxes is still limited.

This work was aimed at understanding the most recent history of environmental changes and anthropogenic metal fluxes within the central part of the Venice Lagoon, thus providing insight into the system evolution.

2. Materials and methods

The study area (figure 1) corresponds to the part of the central Venice Lagoon located SE of the translagunal bridge and the city of Venice; it borders the industrial area (Porto Marghera) and receives inputs from a number of tributaries (Lusore, Naviglio Brenta, Taglio Nuovissimo) and other minor sources. The average depth is ca. 1 m.

Eighteen sediment cores (65 cm long and 4 cm i.d.) were collected in February–March 1992 at the locations shown in figure 1. The area was subdivided into two parts, separated by the first tract of the Malamocco–Marghera Canal, in which stations named G (Giudecca) and SP (San Pietro) were located. Sampling sites were chosen in order to study the mud flat deposits that are the least dynamic environments [10] and may have preserved the record of events

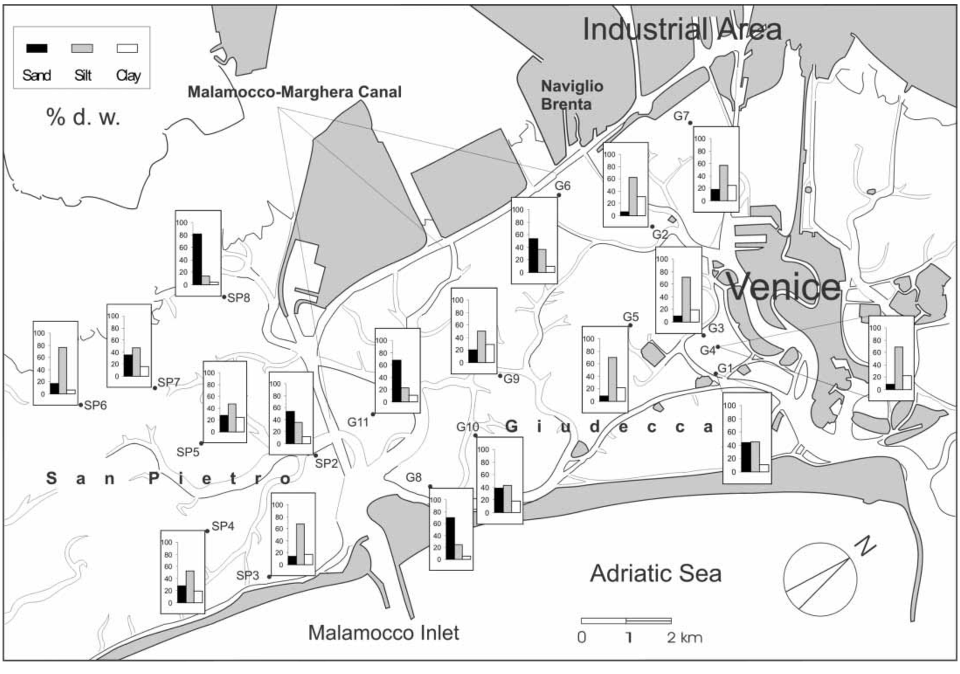

Figure 1. Study area, sampling locations, and grain size composition of surficial sediments (0–2 cm depth).

over the last century. In most cases, the water depth is ca. 0.5 m. Most of the SP stations are characterized by the presence of sea-grasses. In fact, this area was partially vegetated by *Zoostera noltii* Hornem, *Zoostera marina* L., and *Cymodocea nodosa* (Ucria) Asch., whose distribution was mapped by Caniglia *et al.* [11] and, more recently, by Rismondo *et al.* [12]. The SP6 station was located in a relatively deep area (ca. 3 m depth) called Fondi dei Sette Morti.

The cores were extruded immediately after collection and sectioned at intervals of 2–4 cm, with higher resolution near the top of the sediment column. Sediment slices were dried at 60 °C, slightly disaggregated, and then dry sieved through a 2 mm mesh nylon net to discard coarse materials, mostly shell fragments.

Metals were analyzed by wavelength dispersive X-ray fluorescence (XRF) spectrometry, using a SIEMENS sequential SRS 300. Sediment pellets of 3 cm diameter were prepared applying a pressure of $20\,\mathrm{t\,cm^{-2}}$. Package net intensities were computed from raw data correcting for dead time, background, standard, and instrument drift. Calibration curves were established on the basis of available certified reference materials (CRMs) from the National Institute of Standards and Technology (NIST) and Community Bureau of Reference (BCR) with SPECTRA-AT software. Both major constituents (SiO_2, Al_2O_3, CaO, K_2O, Fe_2O_3, MgO, TiO_2, S, and P_2O_5) and the trace elements (Pb, Zn, Cu, Ni, Mn, and Cr) were determined. The overall quality of the data was monitored by analyzing CRMs, as the BCR CRM 277, 280, and 320 [13]. Pellets of the three CRMs were analyzed together with the samples. Although systematic errors were not observed, the precision ($n = 14$) varied for the elements according to the concentration levels in BCR 277, 280, and 320 between 2% and 7%.

The organic matter contents were measured as total organic carbon (TOC) and total nitrogen, which can be assumed to be almost entirely organic, by a Carlo Erba 1106 CHN Element Analyzer. The carbonate fraction was eliminated with HCl treatment in a silver capsule.

Alpha counting of ^{210}Po was used for total ^{210}Pb determinations, assuming secular equilibrium between the two isotopes. ^{210}Po was extracted from the sediment using hot 8 N HNO_3 and plated on silver discs. Excess ^{210}Pb ($^{210}Pb_{ex}$) was calculated by subtracting the constant values measured at the bottom of the cores, assumed to represent supported ^{210}Pb. ^{137}Cs was measured by gamma spectrometry.

Mineralogical composition and grain size were determined in a number of selected samples. The former was analyzed using X-ray diffractometry (XRD) and the latter by wet sieving, to separate the sand fraction from the mud, after a pre-treatment with H_2O_2. Mud was then analyzed by means of an X-ray sedigraph. The silicate/carbonate and calcite/dolomite ratios were calculated from XRD analyses.

3. Results and discussion

3.1 *Sediment features*

Figure 1 shows the grain size composition of surficial sediments, whereas the ratios between mineral constituents (silicate/carbonate and calcite/dolomite) and C/N ratios are presented in figure 2. Grain size and mineralogical composition of surficial sediments follow the same pattern described previously by several authors [14 and references therein]. Grain size is related to hydrodynamics and increases, with some exceptions, from the inner lagoon toward the sea. Although the fine fractions, mostly silts, clearly prevail at sites G2, G3, G4, G5, G7, SP3, and SP6, sand is the major component at G6, G8, G11, SP2, and SP8. In general, owing to higher hydrodynamics, sediments are coarser than in the northern lagoon [8].

The main mineral constituents are, in the order of quantitative ranking, dolomite, quartz, calcite, feldspar, mica, and chlorite. The abundance of silicates is due to terrigenous inputs from the mainland, and silicate/carbonate ratios are at a maximum at sites G7 and SP8 (1.9 and 2.4, respectively), the closest to the inner margin of the lagoon. The silicate component is also high at G6 due to the terrigenous delivery of the Naviglio Brenta (figure 1) and/or to the effects of canal excavations. The carbonate fraction prevails at eight stations. Figure 2 also shows that dolomite, which was delivered directly into the lagoon by the Piave River, is more abundant than calcite. The latter mainly has a biogenic origin [15–17]. At present, the dolomite input is due to the alluvial materials delivered by the Piave River to the Adriatic Sea and then transported into the lagoon by tidal currents. According to Hieke Merlin *et al.* [17], a low calcite/dolomite ratio indicates a highly reworked material. This could explain the lower ratios obtained for the central lagoon with respect to those reported for the northern part [8, 17], where water dynamics are weaker.

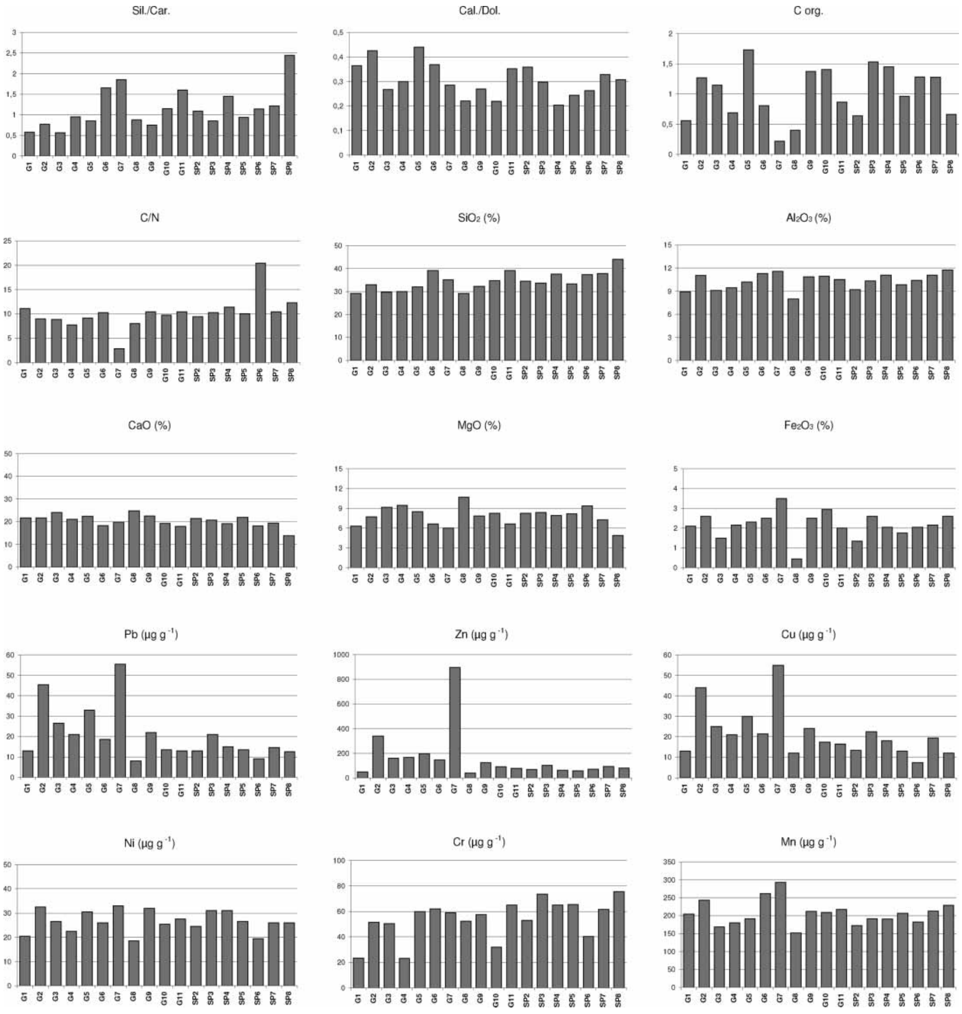

Figure 2. Concentrations of major and trace metals, TOC contents, and C/N and mineralogical ratios (silicate/carbonate and calcite/dolomite) in surficial sediments.

Other differences among surficial samples can be observed in terms of organic material contents (figure 2). The highest values are those of station G5 and confirm the results obtained by Sfriso and Marcomini [18]. TOC concentrations of 0.2–1.8% and 0.7–1.5% were found in G and SP sediments, respectively. Similarly, total nitrogen concentrations span from 0.05% to 0.19% and from 0.06% to 0.15%. The C/N ratios (figure 2) suggest a mixed origin of the organic matter. Only the sediment at SP6 is characterized by a very high value that accounts for a continental influence. G7 has a very low C/N ratio that could be due to either an allochthonous source or the influence of the industrial area. The relatively low TOC concentrations confirm that most of the algal production was efficiently mineralized and did not accumulate in sediments. The lowest TOC values were found in sandy sediments, with the exception of G7.

The concentrations of major components (SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, CaO, and MgO) in surficial samples are also shown in figure 2. The composition of these sediments is rather homogeneous, despite the grain size differences, probably due to a homogeneity of the sources and the contribution of hydrodynamic processes to the dispersal of particles. Fe_2O_3 appears very low at G8, where the content of carbonates, and therefore of Ca and Mg, is particularly high.

The highest trace metal concentrations were found in surficial sediments collected near polluting sources. Zn is by far the most concentrated anthropogenic metal and can be considered as a tracer of the dispersion of waste effluents from Porto Marghera [7]. G7, with a concentration as high as 897 $\mu g\, g^{-1}$, is the most polluted sediment. The distribution of this metal suggests a transport toward SE and the city of Venice. Zn concentrations in the Giudecca mud flat (G1, G3, and G4) are influenced by sediment grain size composition. As a result, the relatively coarse sediment at G1 shows the lowest concentration. Furthermore, Pb and Cu are particularly high at G7 and secondarily at G2. This suggests that Porto Marghera is also a source for these contaminants. The role of the industrial area in supplying heavy metals to the lagoon has been recently discussed by Bellucci *et al.* [7]. As the highly polluted sediments of the industrial canals are not very mobile, their influence on the lagoon environment is modest. Values of Ni show a maximum at G7, but they are relatively low with respect to other polluted areas. Cr distribution is influenced by terrestrial natural sources, because it is supplied by the rivers Adige and Brenta, south of the lagoon, through the Chioggia Inlet [19–21]. The high value of Cr at SP8 suggests that it is mainly bound to the coarse mineral phase.

3.2 *Depth profiles*

Figure 3 shows the depth distributions of some major components in seven selected cores (G1, G3, G7, G8, G11, SP4, and SP6). In general, SiO_2 variations are related to those of metals contained in silicate minerals (Al, Fe, K, and Ti), whereas CaO and MgO concentrations show an opposite trend because they represent the carbonate fraction. As shown by Frignani *et al.* [8] for the northern lagoon, there are three different types of depth distributions: (1) profiles with uniform values or minor variations (*e.g.* G1, G2, G5, G9, G10, SP2, SP3, SP5, and SP7), (2) profiles showing a decrease toward the top, *e.g.* those of the silicatic component in recent times at G3, G4, G6, G7, G8, G11, SP4, SP6, and SP8; and (3) profiles that indicate an increase over time, such as those of Ca and Mg in many cores. The patterns of major constituents confirm trends outlined by grain size and mineralogical analyses, in that the major variations are those shown by cores G7, G11, SP4, SP6, and SP8 that are characterized by dramatic changes of mineral composition, with an abrupt passage from prevailing silicates at the bottom to values of the silicates/carbonates ratio close to or lower than one at the sediment surface. These locations have been subject to a higher input of carbonates in recent times, clearly due to both

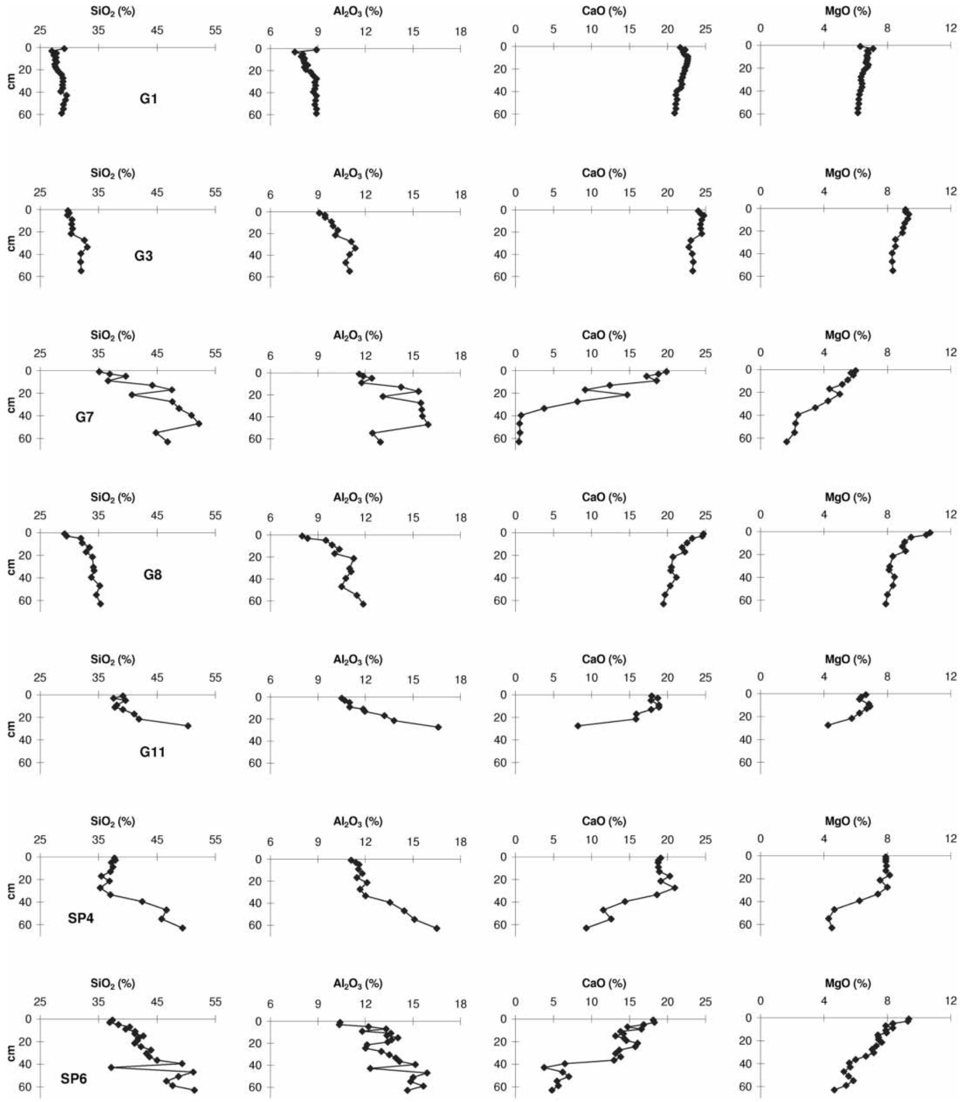

Figure 3. Concentration–depth profiles of major constituent (SiO_2, Al_2O_3, CaO, and MgO) in cores G1, G3, G7, G8, G11, SP4, and SP6.

a higher hydrodynamics and an increased influence of materials coming from the Adriatic Sea. Obviously, this feature can be seen most clearly in the samples taken close to the mainland, as the others have always been subject to a prevailing marine influence.

Figure 4 shows the depth distributions of Cr, Cu, Ni, Pb, and Zn in six selected cores (G2, G7, G8, G11, SP4, and SP6). The profiles of Pb and Cu are very similar, and at many sites, their concentrations are close to the background values suggested by Orio and Donazzolo [20]. These are overcome only at three sites: G2, G5, and G7.

Ni never exhibits peak values close to the water sediment interface. In several cases, the highest concentrations are at depth in cores and decrease through time, such as in G7, G8, G11, SP4, and SP6. At the latter two stations, the high values at depth may result from sediment composition and source, rather than from contamination, due to the particular enrichment in OC and silicate contents.

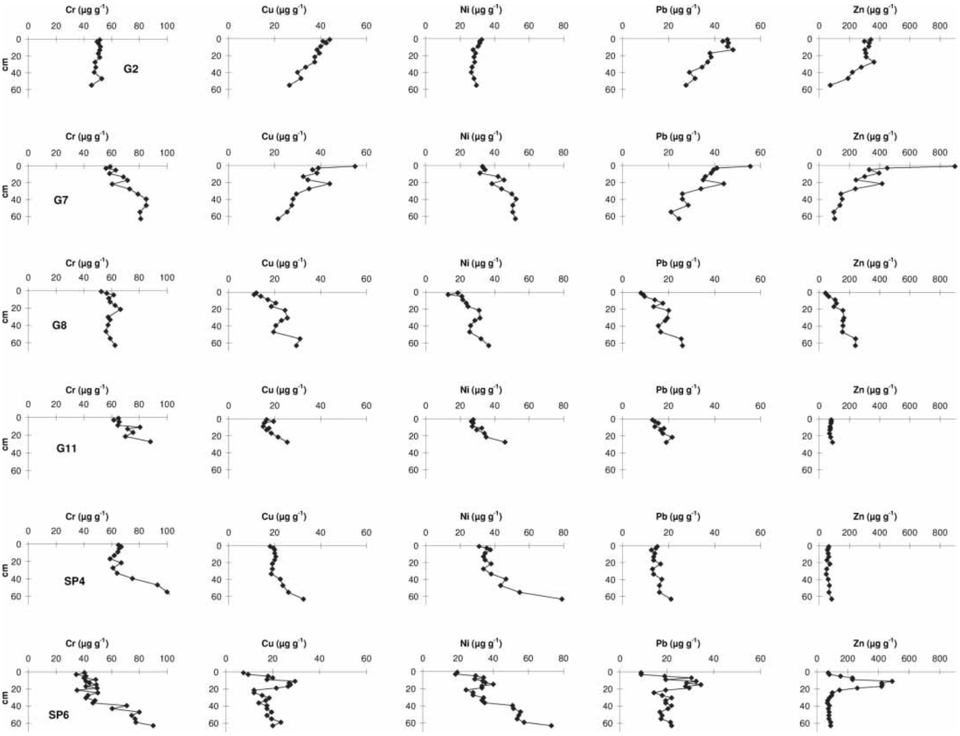

Figure 4. Concentration–depth profiles of trace metal (Cr, Cu, Ni, Pb, and Zn) in cores G2, G7, G8, G11, SP4, and SP6.

Cr concentrations are generally high, with the exception of stations G1, G4, and G10, and are clearly related to the distribution of the silicatic component. Zn, which is the most abundant metal contaminant [5–7, 20], reaches very high concentrations in proximity of the industrial district. In 10 cases, it shows a surficial or subsurficial peak concentration (G1, G2, G3, G4, G5, G6, G7, G9, SP6, and SP7), which indicates a recent contamination.

The history of contamination appears less detailed in cores of the central-southern lagoon than in the northern area [7]. The sites less influenced by contaminant accumulation exhibit profiles of trace metals that parallel those of silicate constituents. Obviously, changes of sediment composition can obscure the pattern of concentrations and fluxes of anthropogenic metals recorded by the sediment. In particular, the effect can be sensible when silicates are substituted by carbonates, which are coarser and less reactive with pollutants and radiotracers. A normalization against Al concentrations [22] is useful to overcome the effects of changes in sediment composition over the depth distributions of trace metals. Figure 5 shows the normalized profiles of Cr, Pb, and Zn obtained for cores G7, G11, SP4, and SP6. While the peak value of anthropogenic metals, such as Pb and Zn, in G7 and SP8 is clearly preserved, a surficial peak value of Zn/Al, not visible without normalization, is shown by G11. On the contrary, Cr does not show significant changes due to its natural origin.

Core SP6, retrieved from the relatively deep sediment of the Fondi dei Sette Morti, shows some peculiarities: (i) TOC reaches concentrations of 2.5% and 6% at 45 and 15 cm depth, respectively; (ii) while Cr and Ni follow changes in major constituents, the patterns of Cu, Pb, and Zn are not related to compositional changes; and (iii) peak concentrations characterize profiles of anthropogenic metals even if the station is far from direct sources. In this latter case,

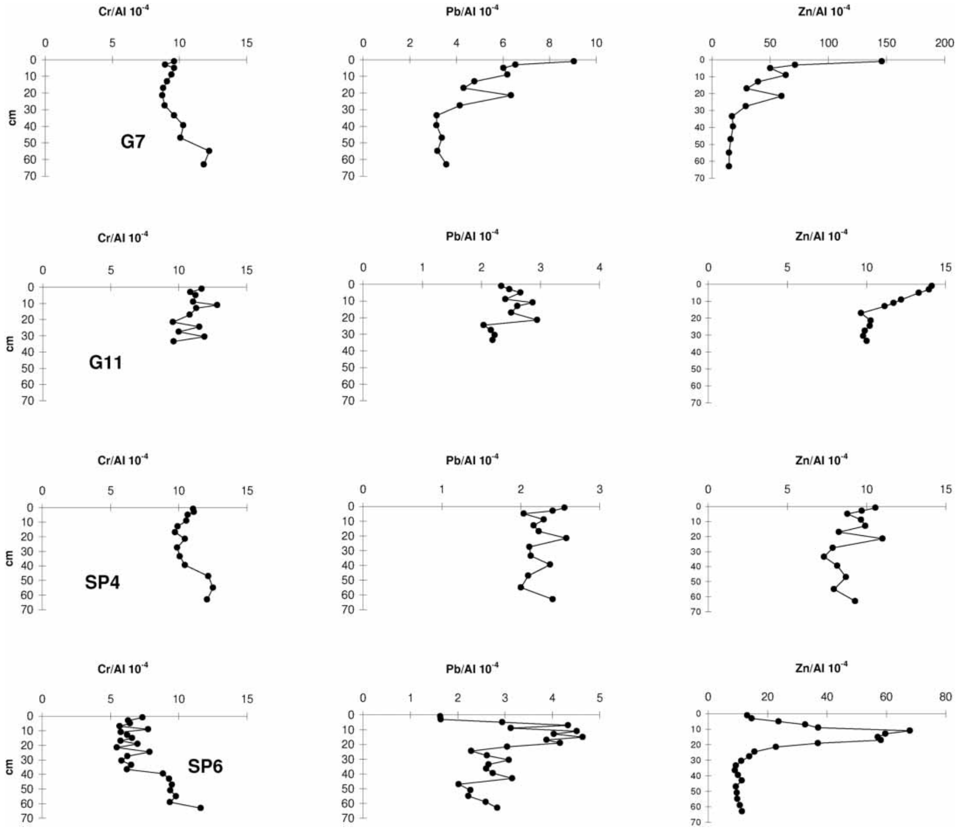

Figure 5. Normalized profiles of Cr, Pb, and Zn in cores G7, G11, SP4, and SP6.

an episodic local discharge, an enrichment process, or a pulse transport of polluted sediment can be hypothesized.

3.3 *Backgrounds and inventories*

The background values are essential for calculating metal concentration factors and inventories. In most cores, constant values measured at the bottom of the profiles can be taken as background. However, if concentrations remain high even at the base of the core, the background value can be calculated through the minimum Al concentration in the profile using the formula: $\mathrm{Me} = \mathrm{Al}(\mathrm{Me}'/\mathrm{Al}')$, where Me′ and Al′ are the background concentration levels in a nearby core. Backgrounds are reported in table 1. Concentration factors (table 1) were calculated by dividing the peak metal concentrations by the background level.

Although Zn has concentration factors ranging between 1.3 and 9.3, the other metals are 1.1 to 3.6 times higher than background levels. With the exception of Zn, these values are a little lower than those reported by Frignani *et al.* [7] for the northern lagoon. SP6 shows high concentration factors for most metals, owing to the peak values at 15 cm depth coupled with relatively low backgrounds. The highest concentration factors of Zn were found close to the industrial district, whereas they are decreased in areas near the inlets.

Inventories of both metals and radiotracers were calculated using excess concentrations, obtained by subtracting the background from the total values, and dry bulk densities. As

Table 1. Maximum concentration factors and background values of trace metals.

Station	Pb	Zn	Cu	Ni	Cr
G1	1.5 (10.0)	2.6 (40.5)	1.5 (9.5)	1.5 (20.5)	1.5 (21.0)
G2	1.7 (27.5)	5.0 (72.5)	1.7 (26.5)	1.2 (26.5)	1.2 (45.5)
G3	1.5 (20.0)	4.0 (60.0)	1.3 (23.5)	1.5 (25.0)	1.1 (47.5)
G4	1.5 (15.0)	3.7 (52.0)	1.3 (16.5)	1.6 (19.0)	1.6 (22.0)
G5	1.4 (25.0)	3.0 (184.0)	1.3 (26.0)	1.3 (28.0)	1.2 (49.0)
G6	2.6 (11.5)	4.1 (50.5)	2.1 (13.0)	1.4 (24.5)	1.3 (56.0)
G7	2.4 (21.0)†	9.3 (70.0)†	2.7 (21.5)†	1.6 (31.5)†	1.4 (58.5)†
G8	2.8 (12.0)†	5.4 (75.0)†	2.5 (15.0)†	2.4 (18.0)†	1.2 (55.0)†
G9	1.6 (15.5)	2.1 (61.0)	1.5 (16.5)	1.2 (32.0)	1.1 (51.5)
G10	1.7 (13.5)	1.5 (60.0)	1.3 (14.0)	1.4 (25.5)	1.4 (28.5)
G11	1.7 (13.0)	1.3 (67.5)	1.7 (15.0)	1.7 (26.5)	1.4 (61.5)
SP2	1.6 (12.0)	1.9 (70.5)	1.8 (13.5)	1.3 (24.5)	1.3 (55.0)
SP3	1.6 (14.5)	1.9 (72.5)	1.4 (18.0)	1.2 (29.0)	1.3 (57.0)
SP4	1.2 (12.5)†	1.5 (48.5)†	1.4 (18.0)†	2.1 (33.0)†	1.4 (64.0)†
SP5	1.5 (11.0)	1.3 (50.0)	1.5 (13.0)	1.4 (23.5)	1.3 (54.5)
SP6	3.5 (9.0)†	7.2 (68.0)†	3.6 (7.5)†	3.5 (25.0)†	2.4 (40.0)†
SP7	1.7 (14.5)	2.4 (69.0)	1.4 (18.0)	1.5 (26.0)	1.2 (55.5)
SP8	1.5 (12.5)	1.4 (70.5)	1.8 (12.0)	1.7 (26.0)	1.2 (73.0)

Note: The background values, in parentheses, are expressed in $\mu g\,g^{-1}$. † Background values estimated by the formula $Me = Al(Me'/Al')$. See text for more details.

inventories are dependent on both concentrations and accumulation rates, they are the most reliable indicators of contaminant accumulation. Trace metal and radionuclide inventories are summarized in table 2. They substantially confirm the pattern observed in the surficial distribution of pollutants.

It should be noted that the inventories of metals at G7 are relatively low even though the concentrations are the highest. This is due to the high-water content of the sediment at that location that makes the sediment dry bulk density rather low. Furthermore, there are lagoon sediments that couple high $^{210}Pb_{ex}$ inventories with low concentrations and inventories

Table 2. Inventories of ^{210}Pb, ^{137}Cs, and trace metals.

Station	^{210}Pb ($Bq\,cm^{-2}$)	^{137}Cs ($Bq\,cm^{-2}$)	Pb ($\mu g\,cm^{-2}$)	Zn ($\mu g\,cm^{-2}$)	Cu ($\mu g\,cm^{-2}$)	Ni ($\mu g\,cm^{-2}$)	Cr ($\mu g\,cm^{-2}$)
G1	0.15	n.d.	220	2040	232	321	281
G2	0.28	0.12	501	10876	487	117	243
G3	0.24	n.d.	226	4479	167	372	122
G4	0.28	n.d.	280	3715	155	456	303
G5	0.38	0.07	253	7639	275	105	268
G6	0.08	n.d.	389	3339	286	307	280
G7	0.12	0.07	359	6548	393	320	358
G8	0.14	0.14	315	4242	383	494	326
G9	0.07	n.d.	325	916	172	127	160
G10	n.d.	n.d.	245	411	168	392	317
G11	n.d.	n.d.	127	247	122	193	324
SP2	n.d.	n.d.	288	2653	372	270	641
SP3	0.85	n.d.	318	2237	179	160	366
SP4	0.06	0.16	129	667	190	516	610
SP5	0.17	n.d.	220	515	283	513	512
SP6	0.41	n.d.	476	3596	441	610	633
SP7	0.02	n.d.	368	1870	278	627	291
SP8	0.05	0.11	94	334	198	313	197

Note: n.d., not detected.

of excess trace metals, especially Zn, and ^{137}Cs. This apparent incongruity derives by the behavior of ^{210}Pb$_{ex}$, in that depth profiles and correspondingly high inventories can be found also in areas of scarce or no accumulation (M. Frignani, unpublished data regarding Adriatic relict sands). The feature is probably caused by physical mixing and downward transport of a small fraction of fine particles rich in ^{210}Pb$_{ex}$.

3.4 *Sediment accumulation rates and chronologies*

Examples of ^{210}Pb$_{ex}$ distributions are shown in figure 6. In some cases, the activities decrease almost monotonically with depth (G3, G4, G5, and SP4), whereas in others, they are very irregular or nearly vertical or show subsurficial peaks. More significant profiles can be obtained from G8 and SP6 by normalizing against Al$_2$O$_3$ and OC, respectively (figure 6).

To obtain chronological information, it is important to establish whether sampling sites are accumulating sediments and if they are sufficiently undisturbed. Radiotracer inventories can be used for this purpose: ^{210}Pb$_{ex}$ inventories of salt marsh cores, derived from atmospheric

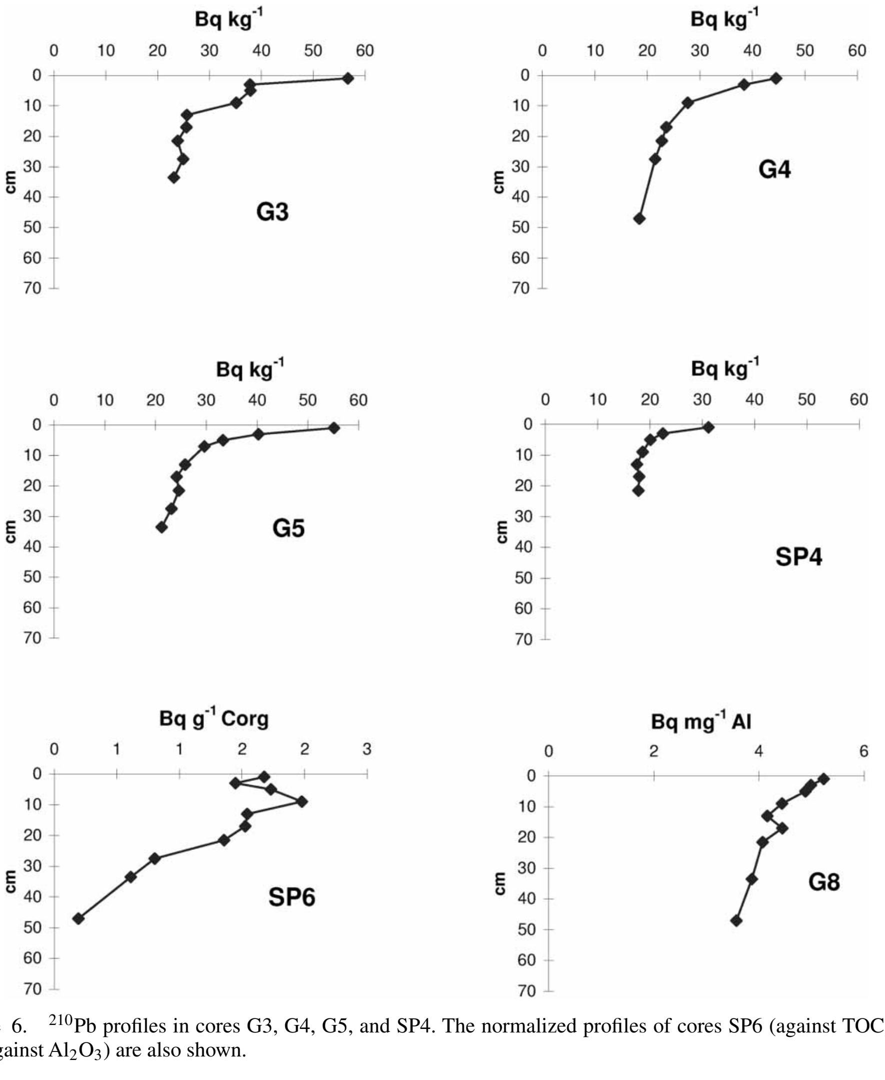

Figure 6. ^{210}Pb profiles in cores G3, G4, G5, and SP4. The normalized profiles of cores SP6 (against TOC) and G8 (against Al$_2$O$_3$) are also shown.

Table 3. Apparent sediment accumulation rates and mass accumulation rates.

Station	Sediment accumulation rate (cm y^{-1})	Mass accumulation rate (g cm^{-2} y^{-1})
G1	0.38	0.59
G2	0.40	0.39
G3	0.41	0.44
G4	0.40	0.43
G5	0.28	0.30
G8	0.74	0.79
SP4	0.20	0.20

fluxes, were reported by Battiston *et al.* [23] and Cochran *et al.* [6] and vary from 0.30 to 0.45 Bq cm^{-2}. Comparable values can be found at G2, G3, G4, G5, and SP6. The inventories in the other cores are very low, with the exception of SP3, thus accounting either for very low accumulation rates or for sediment erosion. Battiston *et al.* [23] found that the ratios of inventories of $^{210}Pb_{ex}$ and ^{137}Cs in the Venice Lagoon were about 3 when both radioisotopes had an atmospheric source. Measured ^{137}Cs inventories (table 2) are very low (0.06–0.16 Bq cm^{-2}), and the activity-depth profiles were not very useful for chronological purposes. Furthermore, although apparent accumulation rates can be obtained for most cores from $^{210}Pb_{ex}$ activity-depth profiles, we chose to use only the data relative to sites G1, G2, G3, G4, G5, G8, and SP4 that seem to have been accumulating sediment on a more or less regular basis over a period of ca. 100 years. Since no simple model [24, 25] is likely representing the actual mechanisms of particle and $^{210}Pb_{ex}$ delivery to the sediment, as suggested by Frignani *et al.* [7], we calculated sediment accumulation rates using several models: constant flux-constant sedimentation (CF-CS), constant initial concentration (CIC), and constant rate of supply (CRS). Results were checked against other independent information. For instance, Cochran *et al.* [6] provided salt marsh metal profiles with a reliable chronology that can be used as an independent reference through correlations. The most reliable sediment and mass accumulation rates are listed in table 3 and range between 0.20 and 0.41 cm y^{-1}, that is from 0.20 to 0.59 g cm^{-2} y^{-1}. As we cannot estimate the effect of biomixing or physical reworking, these rates are probably slightly overestimated [7].

Core chronologies were established using the average accumulation rates. Figure 7 shows the historical changes of MgO concentration along the sediment column at G8. The pattern of CaO is nearly identical. Both metals trace the increase over time of the contribution of the marine with respect to the terrestrial sources, which is accompanied by a coarsening in grain size composition. The effects of the major change in hydrodynamics and marine influence are clearly correspondent to 1969, the date of the opening of the Malamocco–Marghera Canal. This evidence suggests a good reliability of core chronologies.

Figure 7 shows that Zn fluxes at stations G1 and G3 peaked ~15–20 years before core collection and then decreased. This could represent the consequences of industrial discharge limitations provided for in the water pollution law adopted in 1976. In this context, the high surficial concentrations of Zn, Pb, and Cu at G7 could be due to either a recent input from the industrial area or the loss of some centimeters of surficial sediment. In this latter case, the erosion would have exposed the lower part of a subsurficial peak.

3.5 *Fluxes*

Comparing depth profiles of fluxes, instead of concentrations, is more reliable because they are normalized for sediment compaction. Fluxes can be calculated on the basis of excess metal

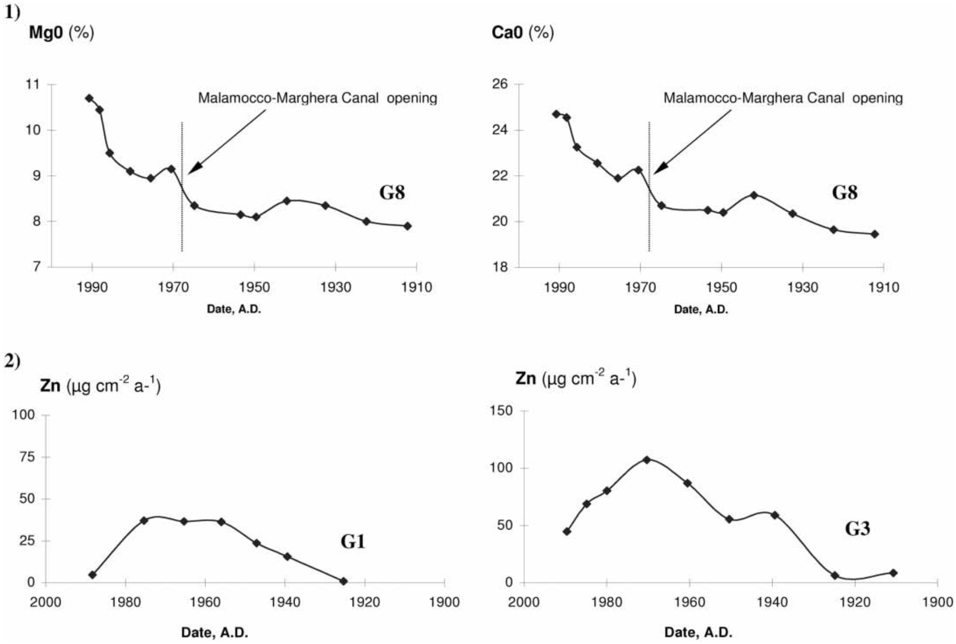

Figure 7. Chronology of (1) major compositional changes in core G8 and (2) Zn fluxes in cores G1 and G3.

concentrations in sediment sections and relative accumulation rates. Figure 7 shows that the oldest clear increases of Zn fluxes at G1 and G3 correspond to the mid-1920s, followed by a peak value in 1970–75 and then a decrease, possibly due to the regulations of industrial discharges with the purpose of environmental protection. The patterns of these fluxes are similar to those found by Cochran *et al.* [6].

It is difficult to evaluate the importance of the process of metal release from the sediment [5, 26, 27] (Capodaglio *et al.* 2003) that may be regulated by the cycles of organic matter, as suggested by Rigollet *et al.* [28]. However, the information derived from metal profiles and from Cochran *et al.* [6] suggests that the surficial decrease of Zn can be due to a discharge reduction.

3.6 *Settings*

Results permit us to make some inferences about sediment accumulation and preservation of the record of metal contamination in the various areas of the central lagoon. The sedimentological characteristics of this area are very heterogeneous. Metal and radionuclide profiles suggest sediment accumulation and formation of sedimentary records at several locations. The sites where these processes clearly take place are G1, G2, G3, G4, and G5, whereas sediments of the area of San Pietro appear coarser and less contaminated due to higher hydrodynamics, which prevents sediment deposition and contaminant accumulation and can cause periodic erosion.

First-order estimates of the total amount of anthropogenic metals in sediments can be obtained using the inventories. For this purpose, the surface areas of the G and SP zones were first calculated (61.4 and 34.6 km^2, respectively). The inventories calculated for cores taken from each zone were then averaged and multiplied by the relating surface area, thus obtaining the total amounts in the sediment. The results are reported in table 4. Contrasting the totals with the values of the northern lagoon [8], the amounts of Cu, Ni, and Cr are roughly

Table 4. Amounts of metal accumulated in sediments of the central part of the Venice Lagoon.

Area	Surface (km^2)	Pb ($kg\times10^3$)	Zn ($kg\times10^3$)	Cu ($kg\times10^3$)	Ni ($kg\times10^3$)	Cr ($kg\times10^3$)
Area G	61	181	2481	159	179	166
Area SP	35	94	587	96	149	161
Total	96	274	3068	255	328	327
Northern lagoon[†]	42	229	1072	120	126	155

[†] From ref. [8].

proportional to the surface areas, whereas Zn and Pb behave differently. This confirms the presence of a source of Zn within the industrial district. On the contrary, in the study area, Pb is less abundant. The values, if calculated as mass of metal per unit surface, are comparable to those obtained by Frignani *et al.* [8] for the northern lagoon.

4. Conclusions

Our results show that the sediments from the central part of the Venice Lagoon are heterogeneous in composition and contaminant accumulation. The area of San Pietro and the sites close to the inlet of the Malamocco channel are characterized by sandy silts and high carbonate content due to the influence of hydrodynamics and materials coming from the Adriatic Sea. Here, the presence of contaminants is scarce. Some cores exhibit an increase in the carbonate fraction over the last 60 years, suggesting an increasing influence of marine inputs as a consequence of the opening of the Malamocco–Marghera Canal in 1969.

The most polluted sediments are those located near the industrial district of Porto Marghera. Zn, among the metals considered in this study, is the major pollutant in the entire area, with concentration factors as much as 9.3 times the background levels. Its distribution seems to trace the influence of the industrial area. Other maximum concentration factors are 3.5, 3.6, 3.5, and 2.4 for Pb, Cu, Ni, and Cr, respectively.

Zn and Pb inventories range from 247 to 10876 $\mu g\,cm^{-2}$ and from 127 to 501 $\mu g\,cm^{-2}$, respectively, depending on the location. Maximum values of Zn were found close to the industrial district and to the town of Venice (G2, G5, and G7), whereas Pb shows more regular accumulation with maximum values at G2 and SP6. Apparent accumulation rates calculated from ^{210}Pb depth distributions span between 0.30 and 0.59 $g\,cm^{-2}\,y^{-1}$. The pattern of Zn fluxes through time shows an increase in sediment contamination starting from the mid-1920s, with decreases after 1970, probably due to environmental regulations. These results, together with those reported by Frignani *et al.* [8], provide the basic knowledge for a quantitative description of the very recent evolution of the lagoon, in terms of sediment composition, contamination, fluxes, sources, and current trends. Since after 1992, sediment resuspension has been greatly enhanced in the central lagoon, especially by illegal clam fishing, these results constitute a fundamental benchmark for any future assessment of environmental changes.

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