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Historical pattern and mass balance of trace metals in sediments of the northwestern Adriatic Sea Shelf

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ABSTRACT

In view of the recent action in Marine Strategy Framework Directive, reconstructing the history of anthropogenic metal inputs and calculating the budgets for the northwestern part of the Italian Adriatic basin can provide a benchmark for comparison with new evidences and enlighten recent environmental changes. Among the metals, the attention was focused on Pb and Zn, as they provide the most significant anthropogenic signals. In 1988, areal distributions clearly identified the Po, Adige and Brenta rivers as the main sources of contaminants. The study area was divided in three compartments. The area in front of the Po delta represented a sink for metals but the accumulation of Zn and Pb integrated over the entire study area suggests an effective export throughout southern boundary. Most concentration-depth/year profiles in cores showed an upward increase from the Italian Unification (1861), with a still significant anthropogenic supply at the time of sampling.

1. Introduction

In 2008, the EU commission established a framework for community action in the field of marine environmental policy. The Marine Strategy Framework Directive (MSFD) aims at achieving "good environmental status" (GES) in the EU marine waters by 2020 at the latest. The MSFD also recognizes the precautionary principle and requests the application of an ecosystem-based approach to the management of human activities in order to minimize their impacts.

In 2010, to ensure consistency so that Member States could fulfill their obligations under the directive, methodological standards, criteria and indicators were adopted through 11 qualitative descriptors. Among these, the 8th indicates that contaminants will have to be at levels that do not give rise to pollution effects.

Contaminant impacts on temporal and spatial scales vary considerably depending on the type of pressure and sensibility of the ecosystem components. Because of their characteristics, some criteria and proxies may require an analysis over various timescales to capture a range of different processes. Moreover, mapping pressures and assessing changes over time are useful bases to evaluate the scale of past trends and the present or potential future impact on marine ecosystems.

The Adriatic Sea is an important marine area in South Europe. As in most other cases, coastal ecosystems face numerous environmental challenges due to increasing economic development. Agriculture, industry and urbanization, through rivers and other discharges, deliver into the sea nutrients and contaminants that may be accumulated in sediments. Moreover, climate change and its impacts constitute increasing threats to coastal areas.

It is known that the study of sediment cores can shed light on concentrations, trends, history and budget of contamination (Bellucci et al., 2005; Giuliani et al., 2008). Few authors have shown concentration-depth profiles of trace metals in Adriatic sediments cores (Guerzoni et al., 1984; Price et al., 1994; Calanchi et al., 1996; Tankèré et al., 2000; Alvisi et al., 2006), whereas other reported only areal distributions (Donazzolo et al., 1984; Frascari et al., 1987; Boldrin et al., 1988; George et al., 2007; Spagnoli et al., 2010). All of them, however, evidenced the presence of anthropogenic signals. Because of this, we would have expected to find excess metals (i.e. over the natural background) in sediment, by analyzing their distributions in sediment cores, to trace input histories and calculate budgets. In particular, Price et al. (1996) discussed the biogeochemistry of anthropogenic elements based on five cores extending from the River Po delta to south of Ancona. They found that Pb and Zn, more than other metals, clearly showed increases over background values. In turn, Calanchi et al. (1996) studied a core from the Mid Adriatic Pit and divided the metals into 4 groups asserting that the major variations were driven by changes in silicate/carbonate ratios. Furthermore, Tankèré et al. (2000) calculated an accumulation of anthropogenic Pb and

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Zn of 730 and 2330 t y^{-1} over the Adriatic shelf from the Gulf of Trieste to the South Adriatic Pit. Recently Spagnoli et al. (2010) presented a review of the current status of major and trace elements in sediments of the central-southern Adriatic Sea. However, they found that availability of biogeochemical parameters and contaminant data are partial or limited to specific areas.

In particular, our goals are the evaluation of time trends of anthropogenic impacts of selected metals in sediments of the northwestern Adriatic Sea and the calculation of budgets. As tracers, Pb and Zn were used, according to Price et al. (1996). Surficial concentrations, together with the annual mass accumulation rates (MARs: g cm^{-2} y^{-1}) provided by Frignani et al. (2005); Palinkas and Nittrouer (2006, 2007); Alvisi (2009), were used to calculate the annual budget of excess metals that accumulated over the shelf in 1986–88. For this purpose the study area was divided into three compartments (Fig. 1a). Furthermore, using an estimate of the input from the continent, the transfer of material between the three areas was calculated.

Even though the data presented here refer to sediment cores taken in the late 1980s, they are still rather important, due to poor available information on both the accumulation of metals in Adriatic sediments and the inputs from the continent. Furthermore, in the view of EU Marine Strategy framework, this work can be used together with newer research to reveal and quantitatively assess recent environmental changes.

2. Study area

The Adriatic Sea is a shallow basin that receives fresh water input from a series of sources, the most important being the Po River, which drains large, intensely cultivated and highly industrialized inland areas and delivers to the sea huge amounts of dissolved and particulate materials, including anthropogenic contaminants. In the Northwestern Adriatic Sea, sediments accumulate along the coast in belts that are hydraulically sorted in grain size in accordance with the classic models of modern sedimentation over continental shelves: coastal sands, mud, and shelf relict sands further offshore (Brambati et al., 1983; Nittrouer et al., 1988). South of the Po delta the belt of fine sediments is wider and better defined than north of it (Correggiari et al., 2001).

3. Materials and methods

Between 1986 and 1988, gravity and box cores were collected (Fig. 1a, where cores are identified by "C") in the marine coastal area from the Gulf of Trieste to Ancona, which covers the Italian sector of the Northwestern Adriatic Sea. Samples were identified by names composed by the acronym of the cruise and the year of sampling (AMA88, NAR88, AAS86, and AAL87, see legend in Fig. 1), and the site number.

Box cores were sub-sampled for surficial levels (0–2 cm), whereas cores were extruded and entirely sliced at intervals 1 cm thick.

Two sediment cores were also collected in 2008: V08-17 in front of the Po delta, at a distance of 2.102 miles from the Po di Pila mouth, at c.a. 20 m depth; and V08-66 off the coastline in front of Comacchio (Fig. 1a). Cores were extruded and sub-sampled at intervals of 0.5–4 cm, with higher resolution at the top.

Subsamples were stored at 4 °C then dried at 60 °C to constant weight before analysis.

58 Surficial sediments (0.5–2 cm thick slices), which 43 box corers and 15 cores (Fig. 1a), were analyzed for metals. Furthermore, all downcore levels from cores collected in late 1980s were taken in consideration, plus selected samples from V08-17 and -66. These latter were chosen based on downcore porosity distributions.

Samples were disaggregated and analyzed for principal (Al, Fe) and trace metals (Cu, Ni, Cr, Pb, Zn, V) composition.

Metal analyses on samples collected between 1986 and 88 were performed by X-ray fluorescence at the University of Edinburgh. Both major (Al, Fe,) and trace elements (Cu, Ni, Cr, Pb, Zn, V) were analyzed by thin film X-ray fluorescence spectrometry. The method was calibrated by graphite furnace atomic absorption spectrometry (Price et al., 1999) and proved to be accurate with respect to reference materials (CRM 277; CRM 320; IAEA-SL-1): results were comprised within the uncertainties of certified values. The analytical precision was estimated by repeated analyses and resulted ±5% for all elements.

Metal analyses on samples collected in 2008 were performed by X-ray fluorescence at University of Bologna. As in the previous case, the method proved to be accurate with respect to lab reference materials, results being comprised in the uncertainties of certified values. Metal concentrations were expressed with respect to dry weight.

Grain size analyses were carried out only on selected samples (AAL86-13, -18, -27; AAS87-3, -10, -15, -16-, -27, -30, -34, -37; NAR88-3, -4, -5, -6, -7, -13, -14, -15, -16; V08-17 and V08-66, Fig. 1b). Wet sieving was used to separate sands, after a pretreatment with H_2O_2. Silt and clay fractions were determined with a Micromeritics X-ray SediGraph.

Sediment cores sampled in 2008 were also measured for ^{210}Pb and ^{137}Cs activities to obtain information on sediment accumulation rates and strata chronologies. Alpha counting of ^{210}Po, considered in secular equilibrium with its grandfather, was used for ^{210}Pb analyses. ^{137}Cs activities were obtained from nondestructive gamma spectrometry. Precision and accuracies of these analyses were reported in detail by Bellucci et al. (2007). Apparent MARs (g cm^{-2} y^{-1}) were calculated using mass depths (g cm^{-2}) obtained from sediment bulk dry densities. ^{137}Cs activity-depth profiles were used, when possible, to check the reliability of $^{210}Pb_{ex}$ derived chronologies.

In order to calculate MARs, Pb and Zn concentrations, fluxes and budgets for the study area and to estimate the magnitude of along-shore mass transfer between compartments, driven by cyclonic circulation, it was necessary to construct a simple model. Therefore, the study area was divided in three compartments (Fig. 1a), defined by different inputs from the continent: (1) alpine rivers and Venice Lagoon, (Northern Adriatic from Trieste to the Adige River), (2) Po River (in front of the delta), and (3) Apennine rivers (south the delta down to Ancona). For each box, mass accumulation rates of sediment, Pb and Zn were calculated.

Following Tesi et al. (2013), to obtain a better MAR spatial distribution different datasets were combined, such as those provided by Frignani et al. (2005); Palinkas and Nittrouer (2006, 2007); Alvisi (2009), Fig. 1C.

A map of gridded metal concentrations (μg g^{-1}) and MARs (g cm^{-2} y^{-1}) was necessary to determine the intervals and median values in the three compartments. Zn and Pb fluxes were calculated by the method of gridding interpolation currently used by geoscientists (i.e., The Generic Mapping Tools-free software, Smith and Wessel, 1990; Wessel and Smith 1991, 1998). To compute grids, an adjustable tension, continuous curvature algorithm was used for values $z(x,y)$ by solving:

$$(1 - T) * L(L(z)) + T * L(z) = 0$$

A null tension factor T was used to minimize spurious oscillations and because it tends to flatten the solution approaching the edges. L indicates the Laplacian Operator (Smith and Wessel, 1990). A mask-grid with no data was matched on the interpolated

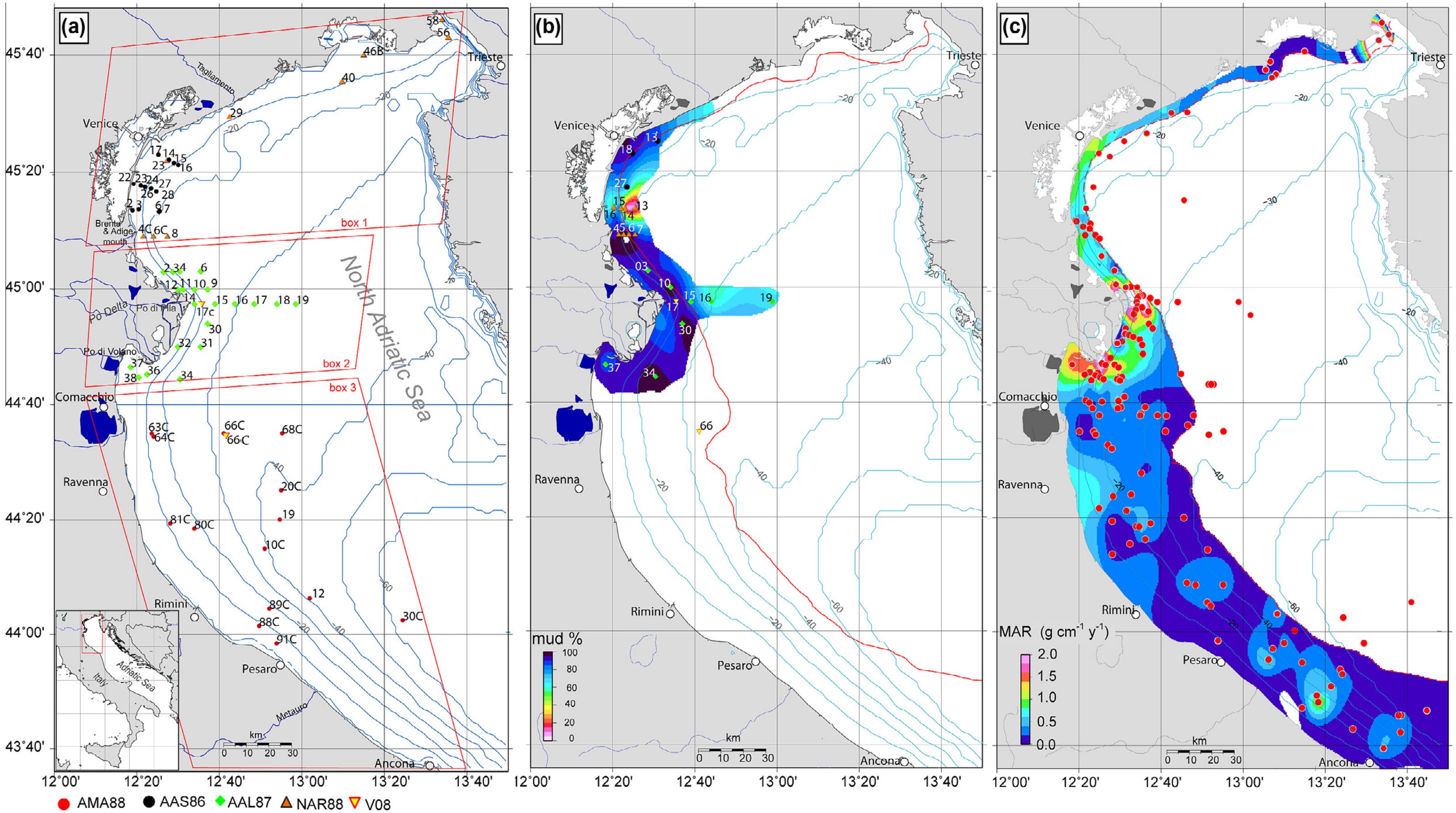

Fig. 1. (a) Study area, sampling locations and box boundaries; (b) fine sediment areal distributions (Brambati et al., 1983; Correggiari et al., 2001), and (c) MARs (g cm^{-2} y^{-1}) according to Frignani et al., 2005; Palinkas and Nittrouer (2006, 2007); Alvisi (2009). Red dots on the map refer to the sample locations of the used data-set. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
MARs (g cm^{-2} y^{-1}), metal concentration intervals (μg g^{-1}) and mud contents (%). Median, scale factor (scale), mean and standard deviation (stdev) in each compartment calculated by gridding interpolation.

Compartments		Surface (km^2)	Elementary area	Grid nodes per compartment	Parameters	MAR	Al	Cr	Cu	Ni	Pb	Zn	V	Mud
1	45.8°N–45.2°N	613	0.1513	4052	Min	0.06	2.11	18.5	4.8	0.92	7.0	26	14.3	9.39[a]
					Max	6.62	7.70	125	38.4	77.8	62.3	219	119	100[a]
					Median	0.52	3.98	61.3	22.1	27.6	26.2	75.3	64.7	–
					(scale)	(0.52)	(1.41)	(37.6)	(11.1)	(21.7)	(19.0)	(46.5)	(41.5)	
					Mean	0.88	4.27	81.5	23.7	35.7	33.4	79.1	68.3	–
					Stdev	1.40	1.29	38.6	11.3	21.1	30.0	37.0	30.4	–
2	45.2°N–44.6°N	898	0.1517	5922	Min	0.07	4.10	63.0	11.8	24.0	18.2	52.8	50.9	59.5[b]
					Max	3.27	7.22	246	94.7	125	234	269	122	98.5[b]
					Median	0.85	6.01	154	42.1	73.6	48.8	151	102	–
					(scale)	(0.46)	(0.48)	(53.3)	(11.6)	(27.6)	(14.3)	(30.2)	(8.00)	
					Mean	1.02	6.08	163	46.9	77.2	48.7	158	102	–
					Stdev	1.17	0.59	42.3	21.1	25.6	14.3	54.0	11.9	–
3	44.6°N–43.6°N	5044	0.1533	32900	Min	0.04	4.49	72.9	10.7	28.4	14.5	38.3	46.7	–[c]
					Max	0.58	7.32	162	45.7	91.4	184	149	132	–[c]
					Median	0.27	6.55	132	33.4	69.2	31.3	101	113	–
					(scale)	(0.08)	(0.77)	(29.7)	(12.9)	(23.8)	(20.4)	(47.6)	(21.8)	
					Mean	0.28	6.33	124	31.3	64.4	37.8	93.2	104	–
					Stdev	0.11	0.87	32.3	12.3	22.2	24.3	40.5	25.0	–
V08-17		–	–	–	–	4.52	14.3	169	49.6	107	34.7	159	103	98.5
V08-66		–	–	–	–	0.26	14.5	132	24.7	80	34	117	104	99.2

[a] Calculated with data from AAL86 (-13; -18; -27) and NAR88 (-4; -5; -6; -7; -13; -14; -15; -16).
[b] Calculated with data from AAS87 (-3; -10; -15; -16; -19; -30; -34; -37) and V08-17.
[c] Not enough data available.

data to limit computing to only to the study area. A Universal Transverse Mercator projection was applied to the map with scale and isotropy grid spacing of 0.25 min.

The minimum Latitude and Longitude were computed for each compartment to determine the Elemental Area of each grid node, which was multiplied by the grid node number to obtain the area.

Descriptive statistics, scale factor for median value and standard deviation on grid interpolations were calculated by "grdinfo", a tool from "Generic Mapping Tools" open source software (Wessel and Smith, 1991).

Scale factors were calculated by multiplying 1.4826 by Median Absolute Deviation (MAD) that is a robust measure of the variability of an univariate sample of quantitative data. It is a measure of statistical dispersion. In other words, it is the average distance of the data set from its median. The multiplication of MAD with 1.4826 to obtain scale factor makes the result comparable with the standard deviation.

4. Results

4.1. Sediment characteristics

1986–88 Sediments cores were mainly taken from the mud belt that extends along the Italian coast following the main Adriatic cyclonic current (Brambati et al., 1983; Correggiari et al., 2001; Frignani et al., 2005). Therefore as showed from the analyses of selected samples (Fig. 1b), these materials are mostly clayey silt and silty clay (NAR88-3, -4, -5, -6, -7, -15; AAL86-13, -18; AAS87-3, -10, -15, -16-, 30, -34, -37; AMA88-34, -37). A few samples (NAR88-13, -14, -16; AAL86-27; AAS87-16, -19; AMA88-39) were taken also from the transition areas where sediments are mainly sand and loam according to Shepard's classification.

Cores sampled in 2008 show predominance of fine fractions: 79.3–99.3 and 93.9–99.1% for V08-17 and V08-66, respectively. No significant variations were observed along the sedimentary column, thus accounting for a constancy of both sources and sedimentary conditions.

4.2. Metal concentrations

Table 1 shows the interval values of trace metals in surficial sediment of the three compartments and the median level calculated by gridding interpolation.

Minimum values of all metals were found in compartments 1 (Al, Cr, Cu, Ni, Pb, Zn, V). On the other hand, maxima (Cr, Cu Ni, Pb, Zn) belong to compartment 2, with the exception of Al and V that peaked in compartments 1 and 3, respectively.

The median values (calculated averaging surficial concentrations by gridding interpolation) confirming their maximum for Cr, Cu, Ni, Pb and Zn in compartment 2, whereas Al highest were located south of it as for V. Values obtained from surficial layers of sediment cores taken in 2008 provide consistent information (Table 1).

In general, mean values were always higher than median for all metals and compartments but showed the same distribution. Furthermore, the scale factor, which reports dispersion around median values, showed a larger dispersion of data in the study area and compartments.

4.3. Chronologies and mass accumulation rate

The quantitative estimate of MARs (g cm^{-2} y^{-1}) based on both $^{210}Pb_{ex}$ and ^{137}Cs activity-depth distributions in cores sampled from the study area was discussed in Frignani et al. (2005); Palinkas and Nittrouer (2006, 2007); Alvisi (2009). The median MARs for the three compartments were calculated from a grid based on the 136 dated cores out of the 231 taken into account by Tesi et al. (2013). With respect to these authors, the attention was focused on the Northwestern Adriatic coastal area with a southern limit in correspondence of Ancona (latitude 43.9°N). Moreover, the southern limit in the three compartments are different and are comparable to those used by Frignani et al. (2005) for the box 3.

Median MARs in the study area were 0.52, 0.85, and 0.27 g cm^{-2} y^{-1} in compartments 1, 2 and 3, respectively (Table 1). Scale factors (Table 1) shows a large dispersion around the median as also indicated by the grid intervals in compartments.

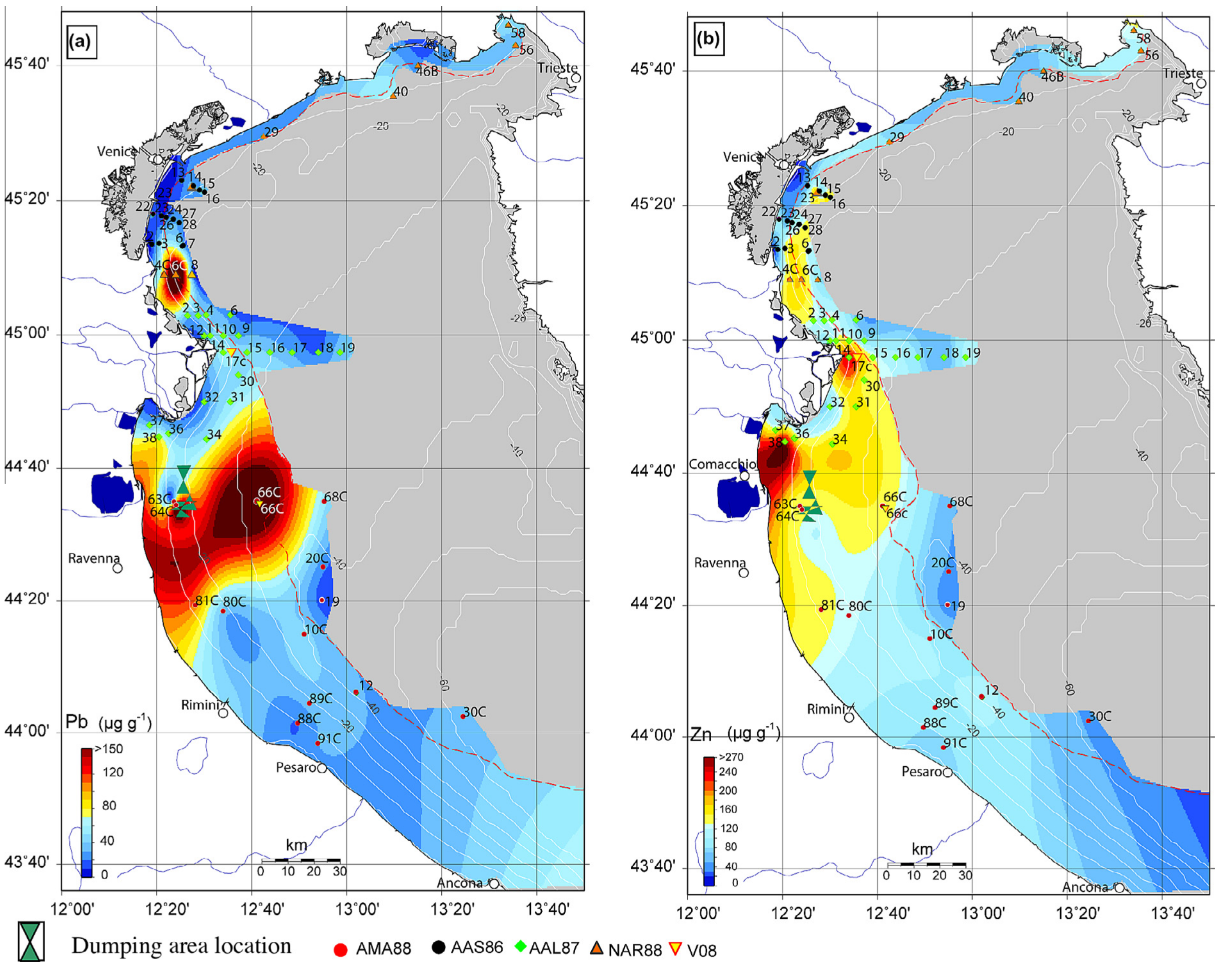

Fig. 2. Areal distributions of Pb (a) and Zn (b) in surficial sediments.

V08-17, collected in front of the main Po River outflow, showed a MAR as high as 4.52 g cm^{-2} y^{-1}.

5. Discussion

5.1. Areal distributions between 1986 and 88

To build maps of sediment and metal accumulations it was necessary to define the eastward boundary, where the values become negligible. The red lines in Figs. 1 and 2 and Fig. S1 (Supplementary material) mark the boundary between the area where modern sediment is accumulating and the one where accumulation of fine material is assumed to be null because of the predominance of relict sands (Frignani et al., 2005). This is obviously an approximation, because Fig. 2 and Fig. S1 (Supplementary materials) shows a low level of excess metals and fine sediment accumulation (and MARs) even beyond that limit.

MAR spatial interpolation (Figs. 1b and S1f) identified five areas of sediment accumulation in proximity of the coastline as discussed in Frignani et al. (2005). There is strong evidence of the dominance of inputs from the Adige River and, mostly, the Po delta system.

The distribution of trace metals in the study area (Figs. 2 and S1 in Supplementary material) were very similar and related to MAR patterns. Metal concentrations were significantly affected by the presence of relict sands. As found before by Donazzolo et al. (1984) and successively largely confirmed by Dolnec et al. (1998); De Lazzari et al. (2004), the fine grain size fraction is the primary carrier of contaminants and the main link between chemical and physical processes in the Adriatic Sea.

Pb and Zn areal distributions (Fig. 2) clearly identify the main sources of these elements to the study area.

The role of both Po, Adige and Brenta rivers, and Venice Lagoon in supplying anthropogenic Zn to the Adriatic shelf is clear. According to Donazzolo et al. (1984), the Zn levels in front of the Venice Lagoon were 200–840 μg g^{-1} in the late 70s and were distributed off the main inlets and southward, due to industrial tailings and wastes that were dumped in the area or transported associated with particulate matter across the lagoon by tidal movements (Donazzolo et al., 1984). Red deposits of industrial wastes have been noticed in this area when both cores and surficial sediment samples were collected in 1977–79 (Colantoni et al., 1980; Bellucci et al., 2002).

Our samples, collected in the late 80s, showed again high Zn values (up to 219 μg g^{-1}; AAS86-26) outside the Venice Lagoon, also in the transition area (e.g. AAS86-15; -16). However, the maximum values were located in front of the tip of the Po delta, and close to the mouth of Po di Volano (240 and 269 μg g^{-1}, respectively). South of the delta, concentrations decreased to a minimum of 76.7 μg g^{-1} (AMA88-91).

Pb distribution was rather different in that maximum concentrations (up to 234 μg g^{-1}) characterized the prodelta of the rivers Adige and Brenta (NAR88-4, -6). Those rivers drain one of the most heavily industrialized and intensely cultivated areas of Italy (Di Silvio, 1975). Moreover, the system is the second most important supplier of freshwater to the Adriatic Sea (Boldrin et al., 1989).

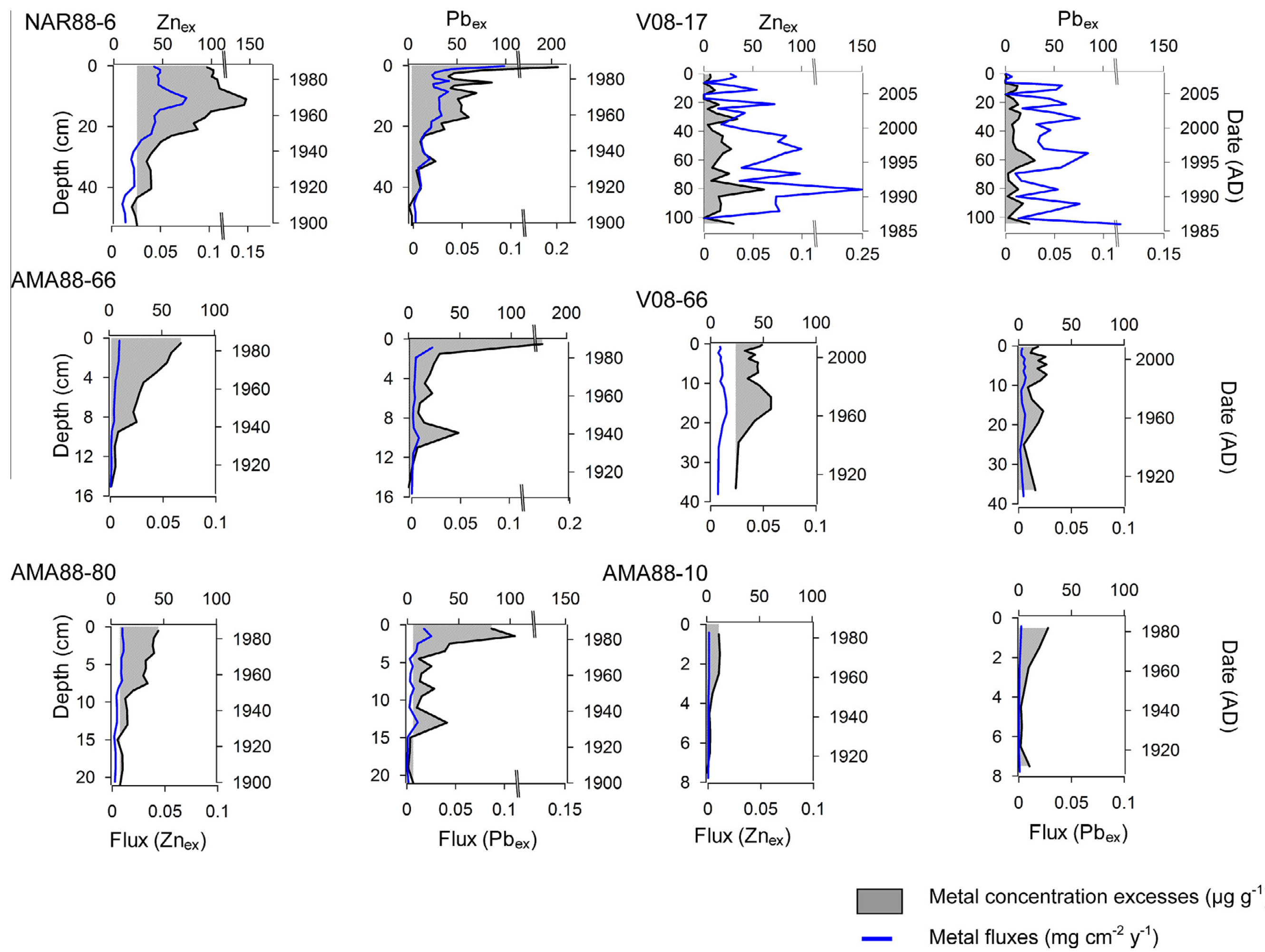

Fig. 3. Dated concentration-depth profiles and fluxes of excess Zn and Pb in selected cores.

South of the Po delta, high concentrations (up to 184 μg g^{-1}) were locally found (AMA88-64; -66, Fig. 2a) only in the most surficial levels. These values were linked to the influence of a dumping area off Comacchio and Ravenna. Located in proximity of AMA88-64, the area was used from 1986 to 1990 as disposal site for dredged materials from the Ravenna Port (Giani et al., 1994). The highest concentration at the top of AMA88-66 suggests that a significant fraction of the metal was disposed or exported eastward by currents. Anyway, as these were local values, not representative of compartment 3, the grid interpolation was calculated using the sub-surficial concentrations in cores AMA88-64 (Fig. S2) and -66 (Fig. 3).

Concentrations along shore-normal transects probably depend on the relative importance of the nearby sources and the pattern of sediment grain size (Brambati et al., 1983), which in turn is a function of the strength and direction of currents. Particularly in compartment 1, low values usually characterized distal samples in transitional areas while high concentrations were found at intermediate distances. In the second compartment, the distribution shows a rapid decrease in front Po della Pila and then a gradual decrease of values from the coast towards the zone of relict sands offshore. An eastward gradual decrease of concentrations it is also observed in compartment 3.

The interpolation of late 1980s data is consistent with both previous studies and more recent point measurements (2008 data, Table 1). This result may be partially due to the use of MAR from the literature. Both scale factors and standard deviations indicated that the error associated with the interpolation of these datasets was not negligible. However, these errors can be considered typical of the nature of data that are not uniformly distributed.

5.2. Mass budgets

Ideally, a sediment budget should be based on accurate data for both the supply of each source and the accumulation rates in all parts of the receiving area. Also, the incoming and outgoing transport by the main current system should be well known. These conditions could be only partially met in this work. In spite of the approximations, however, calculating a budget is important because quantitative estimates are needed for a better understanding of the system characteristics. In this study, the advective transport to and from the eastern side of the basin were considered negligible, as Frignani et al. (2005) did for the particulate mass budget.

Results of the gridding procedure for each compartment are listed in Tables 1 and 2 as surface (km^2), median MARs, median concentrations (μg g^{-1}) of Zn and Pb and yearly accumulation of Pb and Zn with sedimentary materials. Moreover, budgets are graphically summarized in Fig. S3 (Supplementary materials). These estimates were obtained by multiplying the median surficial concentrations (μg g^{-1}) for each compartment by the corresponding median MARs (g cm^{-2} y^{-1}). Then resulting metal fluxes

Table 2
Pb an Zn fluxes from northwest Adriatic rivers and budget for the Adriatic shelf calculated by median gridding interpolation. Exports occur through the southern boundaries.

Compartments	Sediment mass accumulation per area (10^6 t y^{-1})	Pb flux (µg cm^{-2} y^{-1})	Zn flux (µg cm^{-2} y^{-1})	River load contributions (%)	Pb atmosphere input[a] (t y^{-1})	Zn atmosphere input[a] (t y^{-1})	Pb river input (t y^{-1})	Zn river input (t y^{-1})	Pb accumulation (t y^{-1})	Zn accumulation (t y^{-1})	Pb exported (t y^{-1})	Zn exported (t y^{-1})	Pb_{ex} (µg g^{-1})	Zn_{ex} (µg g^{-1})
1	3.19	8.25	30.4	11.8	0.05	0.04	170	531	50.6	186	120	345	–	39.6
2	7.64	38.9	126	39.3	0.07	0.06	498	1540	349	1127	269	757	12.7	109
3	13.6	8.82	23.2	49.0	0.39	0.36	621	1921	445	1327	445	1352	49.9	20.0
Total	21.6	8.53	23.2	100	0.50	0.47	1290	3992	845	2641	445	1352	26.5	41.4

[a] Max atmosphere dry deposition calculated from Correggiari et al., 1989.

(µg cm^{-2} y^{-1}) were multiplied by the compartment area (km^2) to obtain the quantity of metal yearly accumulating in each compartment (t y^{-1}).

According to the values listed in Table 2, the maximum fluxes were observed in compartment 2, whereas the minima characterized compartments 1 and 3 for Pb and Zn, respectively.

The comparison of Pb and Zn accumulation in sediments with the inputs from land and atmosphere (Table 2) provides further information.

Sediment riverine inputs were taken from Boldrin et al. (1989); Frignani et al. (2005); Syvitski and Kettner (2007), whereas metal data were those published by Boldrin et al. (1989); Mantovan et al. (1985); Sommerfreund et al. (2010); Tankèré et al. (2000).

The partitioning of contaminants between water and particles adds extra complexity to the estimates. However, Zn and Pb appear to be transported predominantly by the particulate (Vignati et al., 2005; Provini and Binelli, 2006), with dissolved concentrations variable over time. In addition, dissolved concentrations are not always available. Therefore, river contributions to the system were calculated multiplying mean suspended loads (t y^{-1}) by particulate metal concentration in rivers, neglecting dissolved metals. Consequently, the results can be underestimated.

Table 2 summarizes atmospheric dry depositions of metals over the study area (Correggiari et al., 1989; Guerzoni et al., 1989) that appear negligible in comparison with other contributions.

Metal accumulations are not consistent with inputs: both Pb and Zn show an increasing accumulation trend toward the southern compartment, where maxima were observed. This pattern is strongly influenced by compartment dimensions.

As already said, compartment 1 did not show significant accumulation of Pb and Zn (50.6 and 186 t y^{-1}, for Pb and Zn input, respectively) in spite of the contribution from the Venice Lagoon (Donazzolo et al., 1984; Boldrin et al., 1989; Sommerfreund et al., 2010). This means that the most part (70% and 65%, of Pb and Zn, respectively) is exported southward. The second compartment receives a very significant contribution from land, atmospheric deposition and first compartment (Table 2) but considering the accumulation in sediments it is evident that a great part is moved southward (43% and 40% t y^{-1} for Pb and Zn, respectively).

In compartment 3, 445 and 1327 t y^{-1} of Pb and Zn, respectively, were accumulated. The amounts were comparable to compartment 2, and very low considering the dimension and the higher input. The amounts of Pb and Zn exported from compartment 3 are double than those coming from compartment 2% and 35% and 34% of Pb and Zn total input, respectively. The evidence that input of Apennine rivers was as much as 49% of total with the lower MAR per area in compartment 3 and metal fluxes lower than in compartment 2 despite the larger size of the compartment, suggest that the southward metals transport is effective. This means that, in late 80s the study area has worked as a metals source, and 445 and 1352 t y^{-1} for Pb and Zn respectively were moved toward the southern Adriatic basin. Moreover, results confirm that sediment particles were the main driving system for metal accumulation; and the area in front the Po delta was characterized by significant accumulation of both sediments (Frignani et al., 2005) as for metals.

5.3. Downcore metal distribution

Concentration-depth profiles in sediment cores present interesting features that are dependent on both metal inputs and sampling locations (Fig. 3). However, sediment accumulation is the net result of processes of deposition and resuspension (Alvisi et al., 1996; Frignani et al., 2005) that may also lead to an irregular distribution downcore of both sedimentary material and trace metals.

Usually, a background level is identified from pre-industrial sediments, and in metal/Al ratios can be applied to determine metal excesses or to account for natural changes. However, since Al and V in samples showed a very significant correlation and a similar areal pattern distribution (Fig. S1, Supplementary material), following Price et al. (1996) we chose V as representative of natural fluctuations. Also, it is principally contained in clay minerals that are the main scavenger of anthropogenic contaminants. We calculated excess metals through the formula $Me_{ex} = Me–[V\ (Me/V)_{bg}]$ (Price et al., 1996), where Me is the total concentration at depth z, V is vanadium concentration at the same depth, and $(Me/V)_{bg}$ is the ratio relative to pre-industrial sediments, obtained for each core and also applied to the nearby surficial samples. To calculate excess metal levels in cores sampled in 2008, the same background ratios $(Me/V)_{bg}$ previously identified for nearby areas were applied.

Fig. 3 shows different types of concentration-depth/time profiles for Pb_{ex} and Zn_{ex}. Because the grain size depth profiles did not show significant variations (between 96% and 100% of fines) metal downcore patterns in the study area seem to depend mainly on inputs and the observed variations were entirely due to the history of delivery and flooding events.

In some sectors of the northern area, we had no cores, and excess metal values were obtained by subtracting backgrounds (i.e., the nearly constant values at the base of concentration-depth profiles) reported by Donazzolo et al. (1984); Guerzoni et al. (1984) from surficial concentrations.

The patterns of Zn represent three different situations: (1) in core NAR88-6, located in front of Adige River mouth, there is a constant increase from the mid-1920s to the late 1960s-mid 1970s when the maximum was reached, then it decreased. This is consistent with what was found in sediment cores from the Venice Lagoon by Frignani et al. (1997); Cochran et al. (1998); (2) an oscillation of values due to some peak inputs, with highest concentrations linked to contributions from the Po river and historical flooding events for V08-17 (Fig. 3), whereas V08-66 showed the topmost 10 cm totally bioturbated (XR in Fig. S4, Supplementary material), (3) core AMA88-80; -10, shows a nearly constant increase starting from the early 1920s.

Pb_{ex} profiles were similar to the trends of Zn_{ex} with two exceptions: AMA88-66 where the abrupt increment in the topmost level, representing the 1980s, was due to a local event (as above mentioned) and AMA88-80 that shows an oscillation of values from 1920s to 1965 and a successive maximum in 1980s. These are probably linked to both the sediment delivery, because the 20 m bathymetry may be affected by flooding events of Apennine rivers, and the significant growth rate of Italian industries in those years (Felice and Carreras, 2012; Fig. S5 Supplementary material).

In Italy, the modern stage of industrial development can be traced back to the years of the so called "Economic Miracle" (1945–63) after the Second World War. These years saw the birth of the mechanical, chemical, ceramics industries, and the switch from coal to oil with the new productions of all its plastic derivatives. The 1970s-early 1980s also saw the beginning of environmental awareness. In 1972 the Paris Summit Meeting of European Economic Community (EEC) can be considered the beginning of the EU's environmental policy. One of the most important consequences in Italy was the law 319/76, also known as "Merli law", which contained the guidelines to regulate the concentrations of chemicals in wastewaters even if it was only in the late 1990s that the Italian Ministry of Environment and the regional agencies for environmental protection and control (ARPAs) were established. Therefore, it was expected that our profiles followed the logic of environmental Kuznet Curve with an inverse U-shaped pattern. I.e., in the beginning, when natural resources are degraded intensely, environmental pollution grows rapidly; only successively, technological improvement, increasing knowledge, economic growth and impact on people health result in an increase of attention to the environment that could lead to the turning point between environmental degradation and economic growth (Gürlük, 2009). However, the concentration patterns in many cases showed upward increases along the cores, which imply that at the time of collection the supply of anthropogenic metals was still significant, probably reaching its maximum in some cases, and that the metal contamination of the river sediment had not been abated in the years preceding the sampling. In some cases, sub-surficial peaks were present such as in core AMA88-66. Similar situations are more numerous for Zn than for Pb due to the different sources (see below).

In addition, Italian industrial sectors have faced alternative stages of development and rapid decline (see Fig. S5, Supplementary material) that can have caused variation of the inputs, so as the effect of sediment input seasonality.

5.4. Fluxes

Fluxes, obtained from excess metal concentrations and mass accumulation rates, quantify metal delivery in the unit time and area. The comparison between flux-depth profiles is most reliable than that of concentration-depth profiles because they take into account the sediment compaction (Bellucci et al., 2005). However, Fig. 3 shows the strong similarity between these patterns, thus confirming that depth-profiles are not dependent on changes of sediment compositions. Furthermore, some considerations are possible comparing trends and the three Italian economic steps suggested by the Italian economic history (Gürlük, 2009; Pistoresi and Rinaldi, 2012; Felice and Carreras, 2012): (i) liberal age (1861–1911), (ii) interwar period (1913–1945), and (iii) economic miracle (1945-early-mid 1970s).

Zn higher fluxes and excess metal concentrations characterized NAR88-06, located in front of Adige and Brenta river mouths, between 1940 and 1960. A strong decrease followed in 1975–88 (Fig. 3). On the contrary, Pb shows a constant increase of fluxes and excess concentrations from 1911. Probably due to the prolonged use of leaded gasoline that was banned in Italy at the beginning of 2000. Zn and Pb showed a similar increasing constant trends in cores AMA88-66, -80, -11 and V08-66, located in compartment 3. In these cases, while excess metals were higher than median values in the area, fluxes are less significant that in cores located in the northern compartments.

Because of the high sediment accumulation rate, V08-17 profile represents only the last 22 years. It is expected that the sites off Po River branches, such as Po della Pila and Po di Volano, are characterized by higher concentrations of anthropogenic metals than other places but probably the large sediment discharge has a diluting effect. On the contrary, profiles show high fluxes, combination of concentrations and sediment accumulation rates, with maxima in correspondence of historical flooding events.

Inventories, i.e. the amounts of excess metals stored in the sediment column per unit area, depend on both concentrations and accumulation rates and are particularly suited to understand where metals are distributed and accumulated. Inventories were calculated by integrating bulk dry densities with excess metal concentrations for four dated sediment representing the above mentioned Italian economic steps. Table 3 reports fluxes calculated from inventories normalized to the time intervals of the correspondent Italian economic steps. Both Pb and Zn show a general increasing trend from 1913 to recent time, with some exceptions for the second (NAR88-6 and AMA88-68). In general, the larger increase occurred in 1975–1988, with values even double in some cases (AMA88-80, Table 3).

Table 3
Fluxes (μg cm^{-2} y^{-1}) calculated from inventories normalized to time intervals correspondent to Italian economic phases in selected cores.

Sediment core	1913–1945	1945–1975	1975–1988	1988–2008	
NAR88-6	6.2	22.3	35.0	nd	Pb
	14.8	51.3	49.5	nd	Zn
	14	18	8		Sediment thickness
V08-17	nd	nd	48.6[a]	41.2	Pb
	nd	nd	59.3[a]	69.8	Zn
			12	93	Sediment thickness
AMA88-68	–[*]	0.85	3.75	nd	Pb
	1.48	1.29	0.77	nd	Zn
	5	4	1		Sediment thickness
AMA88-66	2.23	2.74	10.3	nd	Pb
	1.53	5.45	6.86	nd	Zn
	8	6	2		Sediment thickness
V08-66	3.2	4.1	3.6	4.9	Pb
	8.4	11.9	11.1	10.1	Zn
	13	10	4.5	7.5	Sediment thickness
AMA88-63	0.71	1.32	4.61	nd	Pb
	1.24	2.12	4.80	nd	Zn
	8	7	3		Sediment thickness
AMA88-64	3.68	3.43	12.2	nd	Pb
	4.96	2.24	5.44	nd	Zn
	8	7	2		Sediment thickness
AMA88-81	0.84	0.87	3.61	nd	Pb
	–[*]	0.51	–[*]	nd	Zn
	9	6	3		Sediment thickness
AMA88-80	3.98	5.14	17.3	nd	Pb
	3.63	7.74	9.64	nd	Zn
	8	7	3		Sediment thickness
AMA88-10	0.51	1.05	1.87	nd	Pb
	0.27	0.90	0.77	nd	Zn
	4	3	1		Sediment thickness

nd: No data available to calculate inventories.
[*] Dashes line represent no excess metals for those sediment thickness to calculate inventories.
[a] It is referred to time interval 1985–1988.

Actually, it was since the mid-1970s that Italian export became polarized in two categories: the so called "Made in Italy" (textile, clothing, leather, footwear, jewellery, cosmetics, furniture, and so on) and engineering products. Moreover, also the imports of manufactured goods boomed and, in particular, starting from 1980s Italy became a consumer of imported vehicles, chemicals, and high-tech products (Federico and Wolf, 2011). As a consequence, the discharge of contaminants into the sea significantly increased.

After 1988, V08-66 and V08-17, showed contrasting patterns, however, because the slight negative inflection of values. In addition, a bioturbation of top sediment (Fig. S4, Supplementary material) may have confused the most recent trends.

6. Conclusions

Pb and Zn areal distributions (Fig. 2) clearly identify the main sources of these elements to the study area. The role of both Po, Adige and Brenta rivers, and the Venice Lagoon in supplying anthropogenic Zn to the Adriatic shelf is evident, whereas Pb distribution points out mainly the role of Adige–Brenta rivers and the influence of Apennine rivers along the western Adriatic coast.

1988 surficial concentrations, together with the annual sediment input to the area, results in an accumulation of 845 and 2641 t y^{-1} of Pb and Zn, respectively. The comparison among metal fluxes from land, metal accumulations, exportation rates per compartment, and compartment dimensions showed that large amounts of Pb and Zn (445 and 1352 t y^{-1}, 34% and 35% of total river and atmosphere dry deposition inputs, respectively) is exported outside the study area to the southern Adriatic. The sediment particles were the main driving system for metal distributions in the Northwest Adriatic basin, where the Po delta represents an area of favored accumulation as for sediments as for metals.

Sources of error in sediment mass accumulation and in metal interpolated data are essentially linked to both the estimate of median values due to non-uniform data distributions and large concentration intervals both at compartment and study area levels. Moreover, a lack of data about the riverine input of metals, severely affected the budget estimates. In spite of this, the present study is the most complete concerning historical patterns and mass balance of trace metals in sediments of the northwestern Adriatic Sea, the area that collects the inputs of rivers draining the zones where industrial activity in Italy first began. Furthermore, these results can be used as a benchmark, for comparison with new evidence, to reveal and quantitatively assess recent environmental changes.

Depth profiles of concentrations and fluxes from selected sediment cores were used to enlighten the environmental changes that took place before the dates of collection. Pb and Zn trends were compared to Italian industrial–economic phases. It would be expected that our profiles followed an environmental Kuznet Curve (Gürlük, 2009) with an inverse U-shaped curve. In fact, the patterns in many cases show a constant upward increase along the cores, with the supply of anthropogenic metals in 2008 still more significant than in the past.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2013.09.034.

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