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Pb, Cu and Cd distribution in five estuary systems of Marche, central Italy

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Abstract

Heavy metals are subjected to monitoring in estuarine and marine water by the European Union Water Framework Directive, which requires water body health to be achieved by 2021. This is the first survey of heavy metals content in five estuaries of Marche, a region in central Italy. Results showed that total Pb and Cu concentrations decreased by 70-80 %, from 1000-2000 to 100-200 ng L^{-1} (Pb) and from 2000-3000 to 500-1000 ng L^{-1} (Cu) from river to sea. Cd was consistently 20-40 ng L^{-1}. Dissolved Pb and Cu concentrations declined by 50% and 70 % respectively passing from oligohaline to euhaline water, from 150 to 70 ng L^{-1} and from 2000-1000 to 600-400 ng L^{-1}. Cd decreased slightly from ~20 to ~10 ng L^{-1}. Although such concentrations are in the range allowed by the Water Framework Directive, they far exceed (up to 10x) the ground content ceiling set for 2021.

Rivers are major sources of marine pollution. The industrialization of coastal and estuarine areas, especially over the past few decades, has increased the amount of contaminants that flow into rivers and the sea. A number of pollutants pose considerable health risks due to their toxicity, persistence, bioaccumulation, and biomagnification in the food chain (Papagiannis et al., 2004). Heavy metals released into rivers by fertilizers, mining tailing, and industrial and urban wastewater raise special concerns because they are non degradable. They accumulate in sea sediment and may be released overlying water, during re-mobilisation events or due to changes in the physico-chemical characteristics of water (McAlister and Orians, 2012; Annibaldi et al., 2009). In addition, heavy metals taken up by marine organisms can move to higher trophic levels and enter the human food chain through contaminated seafood (Pan and Wang, 2012). In estuaries a variety of inputs (rivers, benthic zone, atmosphere) and physicochemical processes (mixing, adsorption, desorption, sedimentation) affect trace metal distribution in coastal areas (Buffle, 1988; Waeles et al., 2005). Analysis of the distribution of their dissolved and particulate fraction is important to understand the toxicity, bioavailability and mobility of trace metals (Tessier and Turner, 1995; Mota et al., 2005).

The European Union (EU) Water Framework Directive (WFD) (European Parliament and Council, 2000) set ambitious goals to improve aquatic ecosystems and ensure the health and sustainable use of water. Member States were required to set up river basin management plans (RBMP) by 2009 (European Commission, 2009). The key WFD objective is for all water bodies to achieve a healthy state, entailing a good ecological and chemical status of surface water, by 2015. It envisages improved and expanded monitoring and assessment tools to obtain a statistically robust and comprehensive picture of the status of the aquatic environment for the purpose of further planning.

The chemical status of a large proportion of water bodies is unknown because chemical monitoring is poor in many Member States, either because not all priority pollutants (PP) are monitored or because few water bodies are monitored (EEA, 2012).

With regard to chemical pollutants, heavy metals such as Pb, Cu and Cd are of interest because of their toxicity. Cd and Pb are toxic even at low levels, whereas Cu toxicity requires high doses (for example the value of 4.8 ug L^{-1} is the maximum concentration fixed by EPA for aquatic life) (Pan and Wang, 2012). Pb, and Cd are considered as PP; for this reason the Italian government (Ministero dell'Ambiente e della Tutela del Territorio e del Mare, 2010) has set a maximum value for dissolved metal concentration for water standard quality to be reached by the end of 2015, to reduce the level of contaminants at ground level by 2021.

In this study the speciation (distribution) of Pb, Cu and Cd was investigated in the estuarine system of Marche, an Adriatic region in central Italy. Their total, dissolved and particulate concentrations were determined at three stations with different salinity values (from ~0 ppm to ~35 ppm) in the five principal rivers of Marche, to determine the level of contamination of each estuarine area and to evaluate the possible effect of river water on surface marine water along the region's coastline. Because the distribution of the different fractions is essential to understanding metal availability to biota and their mobility in the aquatic environment (Wen et al., 2011), the study investigated not only the dissolved concentration, as required by the law, but also total and particulate concentrations.

Marche's RBMP (Regione Marche, 2010) classifies the five rivers assessed in this paper as significant water bodies; as a consequence they must achieve a good quality status by the end of 2015. Pb, Cu and Cd concentrations were determined by square wave anodic stripping voltammetry (SWASV), an ultrasensitive technique, in line with WFD quality objectives (Coquery et al., 2005; Tueros et al., 2008).

The study was carried out inform 15 to 18 June 2004, after several days of rain. Sampling was conducted at the estuaries of the 5 rivers, which course from West to East crossing the whole region from the mountains to the Adriatic sea (Fig. 1). Sampling sites were as follows: river Foglia, Pesaro; river Esino, Falconara Marittima; river Potenza, Porto Recanati; river Tenna, south of Porto Sant'Elpidio; and river Tronto, Porto d'Ascoli, listed from North to South.

The Foglia estuary lies in a densely populated area close to Pesaro harbour; it is surrounded by bathing establishments and hotels and provides mooring for small boats. The Esino estuary is near an oil refinery, a train line and an airport. The river Potenza crosses densely populated areas and industrial sites, whereas the river Tenna courses mostly through farmed fields and sparsely populated areas. The river Tronto is heavily influenced by human activities all along its course.

Surface water (depth, 0.2 m) was collected along the transect of 3 stations (A, the closest to the river, B, intermediate, and C, the farthest from the river) at different values of salinity (A, freshwater-oligohaline, ~0-1 psu; B, mesohaline, ~15-20 psu; and C, euhaline, ~35 psu) (Tab. 1) (Fig. 2). The estuaries of rivers Foglia and Esino have a longer transect (~3 km) than those of rivers Potenza, Tenna and Tronto (~200 m). Samples were collected from the river directly into polyethylene bottles using an in house developed telescopic plastic barrel fitted with an adaptor into which a sampling bottle can be inserted. Immediately after collection, a fraction of each sample was used to measure temperature, salinity and turbidity. Samples were taken to the clean room laboratory within ~ 1 h of collection. Here each sample was divided into two aliquots; the first was acidified with ultrapure HCl (2 mL acid in 1000 mL seawater, pH ~1.5) to determine total extractable metal concentrations (raw solution). The second aliquot was filtered (0.45 μm pore size) and acidified with ultrapure HCl (2 mL acid in 1000 mL seawater, pH ~1.5) to determine dissolved metal content (filtered solution). The raw and filtered solutions were kept at room temperature for at least 2 days and then stored at 4 °C until analysis (1–3 months).

Immediately before voltammetric analysis acidified samples were added with 9 μL superpure H_2O_2 and UV-irradiated for 12 h. Determinations of Pb, Cu and Cd were carried out by the Square Wave Anodic Stripping Voltammetry (SWASV) in background-subtraction mode, following a procedure set up and optimized in our previous work (Truzzi et al., 2002). The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyser, equipped with a 747 VA Stand, a Teflon PFA cell, which includes an epoxy-impregnated graphite (Ultra Trace) rotating disk

working electrode, an Ag/AgCl/3 M KCl reference electrode (to which all potentials are referred throughout) and a glassy carbon rod counter electrode.

Laboratory, apparatus, reagents and procedures used in this work were described in detail elsewhere (Truzzi et al., 2002; Annibaldi et al., 2007; Annibaldi et al., 2009, Annibaldi et al., 2011). Briefly the parameters of the voltammetric procedure were as follows: deposition potential −975 mV; deposition time 1–10 min; SWASV scan from −900 mV to 0 mV with SW amplitude 25 mV, frequency 100 Hz, step height 8 mV, step time 150 ms, pulse time 5 ms, current sampling time the last 3 ms of the pulse. Quantification was obtained by multiple standard addition method. The mean of at least 3 determinations was used for subsequent analyses; the relative standard deviation was consistently < 10%. Total and dissolved metal content was determined directly. The particulate concentration was the difference between total and dissolved concentration, as described in an earlier work (Annibaldi et al., 2011).

The accuracy of the analytical procedure was checked by analysing certified National Council of Research Canada reference materials for trace metals in seawater, i.e. CASS 4 (National Research Council of Canada, 1999) for coastal seawater, and SLEW 3 (National Research Council of Canada, 2000) for estuarine water. As shown in Table 2, Pb, Cu and Cd concentrations were in line with the reference values within experimental errors (no statistically significant differences between certified and measured values, p-values generally <0.05), showing good accuracy (STATGRAPHICS, 2000).

In the following section we explored the metal concentrations (in order Pb, Cu and Cd) passing from river to sea, in the five estuaries studied. Data are reported in Table 3 and graphically in Figures 3 and 4.

Total Pb content decreased significantly and linearly with increasing salinity (Fig. 4). Values decreased by about 80 % from ~ 1000 ng L^{-1} (station A) to ~ 200 ng L^{-1} (station C). The values measured in the estuary of river Foglia show the highest value in station A (1870±70 ng L^{-1}).

The decline of Pb values was related to the dilution effect (McAlister and Orians, 2012; Tueros et al., 2008), i.e. the mixing of river water with high metal content with seawater with low metal

content, and was most evident in rivers Foglia, Potenza Tenna and Tronto. In fact dilution of trace metal concentrations sourced from a river results in conservative mixing and it is exemplified by linear elemental concentration as a function of salinity (McAlister and Orians, 2012).

Deviation from linearity (concave curve) is clearly visible in river Esino; this trend indicates removal processes of trace metal during mixing of river and seawater endmembers (Boyle et al., 1974, 1977; Liss, 1976; Officer, 1979; Rattray and Officer, 1979) probably due to the removal of Pb from water to sediment (Idriss and Ahmad, 2012).

The dissolved Pb content was similar in 4/5 estuaries (all but the one of river Foglia), with comparable and consistent concentrations that are quite constant passing from station A to B (~150 ng L^{-1}) and decreased by about 50 % at station C (~50 ng L^{-1}). This trend confirms that dissolved Pb concentrations seem to be influenced more by river water and inputs than by salinity distribution in the estuary, as also reported by other authors (Monbet, 2006). In the Foglia estuary Pb concentrations were much higher than the ~150 ng L^{-1} of the other estuaries in stations A (586±33 ng L^{-1}) and B (251±18 ng L^{-1}), and fell to a concentration similar to those of the other estuaries in station C (66±1 ng L^{-1}).As regards the particulate fraction, it was dominant at all stations (except the Esino station B) with values around 80-90% and decrease linearly with increasing salinity as total content. It is evident that the dilution effect is the principal physicochemical process affects this trend in the rivers studied.

As in the case of lead, total Cu content decreased with salinity except at the Foglia site, with a negative deviation from linearity (Fig. 3), except for Potenza river. Excluding the data from the Foglia estuary, total Cu concentrations fell by approximately 70 % from ~3000 ng L^{-1} at station A to ~700 ng L^{-1} at station C. The removal process of this metal, from water to sediment, is not the only reason for the decline; in fact we had to consider that Cu is an essential element for all living organism; so copper speciation is strongly influenced by biological and geological processes (Hasle and Abdullah, 1981; Saad and Hassan, 2002; Little et al., 2013). Phytoplankton, for example contributes to trace metal removal through both cellular uptake and sorption onto cell surfaces;

scavenging of trace metal in the surface are is therefore enpowered by increased particulate surface area given by phytoplankton.Cu removed from the surface (fall down to bottom bounded to particulate matter) could be remineralized during heterotrophic respiration, returning to the dissolved phase, and therefore accumulating as a function of increasing water mass age (McAlister and Orians, 2012) or if maintaining association with the particulate phase, could be removed by settling through the water columnExcepting the Foglia stations, a concave curve was also observed for dissolved Cu, which decreased from ~1000-2000 ng L^{-1} at station A to ~400-600 ng L^{-1} at station C: this fraction accounted for 30 % of the total in station A of rivers Esino and Foglia and for 50-70 % at the other three sites, and rose up to 65-95 % for all sites in station C. It has been suggested that desorption of trace metals from suspended matter may occur once in contact with seawater due to decreasing concentrations seaward (De Groot, 1973; Saad and Hassan, 2002). The dissolved Cu profile was described (Bruland and Lohan, 2003) as hybrid between nutrient and scavenged type; so it is both biologically active and particle reactive

The high metal content in the particulate fraction at station A is mainly due to adsorption enhanced by high values of suspended matter from river water. The elevated turbidity recorded at all stations A (Tab. 1) confirms this. At intermediate salinity values, higher concentrations (in terms of fraction) of dissolved compared with particulate fraction (Fig. 4 and Tab. 3) are due to desorption from particulate matter, in line with earlier studies (Moore and Burton, 1978; Saad and Hassan, 2002). At seawater station dissolved and particulate fractions do not show particular changes in distribution, with a predominance of dissolved one, fraction more available for uptake by organisms.

A separate discussion is required for river Foglia, where Cu shows peak total and dissolved concentrations at the mid salinity point (~ 4500 ng L^{-1} and ~ 4000 ng L^{-1} respectively). These are probably to be ascribed to the fact that the area around station B is the mooring site of a large number of small craft whose hulls are coated with Cu-rich antifouling paint (Haynes et al., 2002; Smith et al., 2003). The paint is designed for slow Cu release in the dissolved and most toxic form,

to delay the growth of algae and other encrusting organisms and maintain a smooth underwater surface (Schiff et al., 2004). This is reflected by the fact that the highest value of dissolved Cu is found at station B. From B to C total and dissolved Cu fell respectively by 80 % and 20 % to 786 ng L^{-1} and 620 ng L^{-1}, respectively, which are comparable to the other sites.

Total Cd concentrations were roughly similar along the transect (20-40 ng L^{-1}), considering the low content of this metal respect to others studied in this paper. Once again the exception was river Foglia, where at 81 ng L^{-1} the value at station A was twice that of the corresponding stations; it then decreased by about 60 % to around 35 ng L^{-1} at stations B and C.

Dissolved Cd decreased along the transect from 20-30 ng L^{-1} to 10-20 ng L^{-1}: this fraction is generally dominant at all sites and accounts for 50-80 % of total content. This trend confirms the low tendency of Cd to associate with suspended matter (Balls, 1988; Saad and Hassan, 2002). For this reason the dissolved fraction is generally used to monitor environmental changes and for identifying contaminated area (Mart et al., 1985). Again the river Foglia values were the highest, with 36 ng L^{-1} at station A and ~25 ng L^{-1} at station B and C.

Particulate Cd concentrations, except at the Foglia and the Tenna sites, showed a parabolic trend, with a minimum (between 4-9 ng L^{-1}) at intermediate station B, (Fig. 3): Esino and Tronto show same particulate content, too, with maximum values at point A and B of about 18 ng L^{-1} whereas Potenza displayed similar trend but with half value in station A and C (~ 10 ng L^{-1}) . A concave trend is clearly visible in river Foglia where Cd particulate concentration reached the highest value in station A (45 ng L^{-1}) and decreased by about 90% in station B (6 ng L^{-1}) and by about 70% in station C (14 ng L^{-1}). Tenna river displayed a singular trend, with Cd particulate concentration that increase by 2 fold passing from station A and B (7 and 9 ng L^{-1} respectively) to station C (20 ng L^{-1}).

In the following section we compared the metal contents in the different rivers in relation to the salinity parameter (freshwater-oligohaline water, mesohaline water, euhaline estuary water).

Total Pb content in river water (station A, salinity <2 psu) was similar in rivers Esino, Potenza and Tronto; the river Foglia showed 2-fold higher values than other sites, and river Tenna the lowest value, ~700 ng L^{-1}.

Dissolved Pb was about 150 ng L^{-1} in all rivers except river Foglia, where concentrations were again highest, ~ 600 ng L^{-1}, or 5 times those found at the other sites.

Differences in total Cu concentrations were found between the northernmost rivers (Foglia, Esino, and Potenza) and those to the South (Tenna and Tronto). Values were in the range of 3200-3800 ng L^{-1} in the former rivers and were approximately 30 % lower in the latter (~ 2300 ng L^{-1}).

An opposite trend was found for dissolved Cu, which from North to South rose from 885 ng L^{-1} in river Foglia to 1080 ng L^{-1} in river Esino and 1680 ng L^{-1} and 1900 ng L^{-1} in rivers Potenza and Tenna, respectively. Instead the value in river Tronto was the lowest in this area, around 950 ng L^{-1}. Obviously this trend involves an increase of dissolved percentage of dissolved Cu in south of Marche, around 50% for Tronto and Potenza, and 73% for Tenna.

The values of total Cd were around 35 ng L^{-1} in all rivers except in river Foglia, where it was 2-fold greater (81 ng L^{-1}). The same was true for dissolved Cd, whose values were around 20 ng L^{-1} in all rivers except the Foglia (36 ng L^{-1}). Dissolved Cd accounted for 44 % in river Foglia and for 50-74 % in the other rivers.

Overall these data show that river Foglia is the most polluted, with a total PP content (Pb and Cd) that is twice that of the other rivers. High Cu concentrations were also found. Although not a PP, high levels may be toxic for many organisms (Haynes et al., 2002; Smith et al., 2003; Schiff et al., 2004).

At intermediate salinity values (station B) total Pb was around 600 ng L^{-1} in rivers Foglia, Potenza and Tenna and exactly half (~300 ng L^{-1}) in the Esino and Tronto. Dissolved Pb was ~200 ng L^{-1} except in river Potenza, which showed the lowest value (78 ng L^{-1}), possibly because of its high turbidity, which is related to a high value of the particulate fraction (85 %).

Total Cu content was ~800-1000 ng L^{-1} in all estuaries; dissolved Cu was ~500-600 ng L^{-1} at all sites except river Tenna (~ 900 ng L^{-1}).

A separate discussion is again required for river Foglia, where Cu at this station was very high both as regards total (~ 4.5 μg/l) and dissolved Cu (~ 3.5 μg/l). As noted above, this site is a mooring area for small craft, whose antifouling hull paint involves slow and continuous Cu release. These paints contain large amounts of Cu and sometimes co-biocides whose function is to delay the growth of algae and other organisms (Schiff et al., 2004). Cu is found in these paints as CuO_2 (primary biocide); it is released into seawater as Cu^{+}, and is then rapidly converted to Cu^{++} (Morel and Hering, 1993; Valkirs et al., 2003), as confirmed by the high value of dissolved Cu found here.

The Potenza river shows the lowest values of total and dissolved Cd, whereas the Esino has the lowest content of Pb; rivers Esino and Tronto have the lowest Cu values.

In euhaline water total Pb (between 100 ng L^{-1} and 300 ng L^{-1}) is lowest in the two rivers at the ends of Marche (Foglia, 145 ng L^{-1}; Tronto, 116 ng L^{-1}) compared with the three rivers in between (Esino, 223 ng L^{-1}; Potenza, 241 ng L^{-1}; and Tenna, 293 ng L^{-1}). Values of dissolved Pb ranged from 44 ng L^{-1} to 66 ng L^{-1} with percentages ~50%, in rivers Foglia and Tronto (46% and 49%, respectively) and ~20% in the rivers in between (Esino, 24%; Potenza, 20%; Tenna, 15%). Total Cu was fairly similar in all rivers (600-800 ng L^{-1}); the dissolved fraction was predominant and was highest in river Esino (96 %).

Total Cd was about 30 ng L^{-1} in all five rivers. Dissolved Cd was highest in rivers Foglia and Potenza (~18-20 ng L^{-1}) and lowest in the Esino (9.4 ng L^{-1}).

The data found in this study are compared in Table 4 with literature data from other estuaries and seas; with Italian legal water quality standards (Ministero dell'ambiente e della tutela del territorio e del mare 2010, DM 260/2010, in line with European Directive EC/2000/60, 2000); with UK Department of the Environment standards (Smith, 1993); and with USEPA standards (Federal Register, 1998). A comparison with background values according to the WFD directive (Tueros et al., 2008), one of whose aims is to reduce metal concentrations in marine environment to pristine

content by 2021, is also reported. Only the dissolved metal fractions are considered in each case, as provided by Italian law.

As regards the literature data, available data for estuarine stations A and B are insufficient for comparisons, but our findings are in line with them for all three metals. For stations C, Cu and Cd generally showed values of the same order of magnitude as those reported for other seas (Baltic, Vigor Ria, Mediterranean Sea). We found slightly higher Pb values than those reported in the Baltic and Celtic seas and, especially, in the central Adriatic, the same area we studied. This highlights a direct effect of river water on dissolved Pb concentrations in seawater.

As regards background values, which are available only for seawater, Pb and Cu values in station C were higher than those reported in the literature. We found fivefold higher values for Pb and tenfold values for Cu, reflecting a high level of heavy metal pollution. Only Cd values at stations C agree with the background values reported in Table 4, reflecting the low human impact on this concentration.

As regards the comparison with legal limits, the dissolved content of these metals was well below Italian DM 260/2010 (Ministero dell'ambiente e della tutela del territorio e del mare, 2010) and international limits (Smith, 1993; Federal Register, 1998). However the re-suspension of sediments, which are often highly contaminated by heavy metals, has the potential to increase the dissolved fraction of contaminants (Annibaldi et al., 2009), bringing values closer to the allowed limits.

In summary the data collected in the study show a generally good quality level of the waters that is in line with WFD goals for 2015. However the input of contaminants carried by the rivers is clearly evident everywhere, especially in river Foglia, where the levels of all three metals were highest. In particular copper released by antifouling ship paint in this area involves high levels both of dissolved and particulate concentrations.

Even though all values are well below national and EU legal limits, comparison with background levels demonstrate that Pb and Cu are up to 5 and 10 times higher, reflecting strong anthropogenic pollution.

SWASV accurately determined PP content and enabled to carry out speciation studies, because it can detect ultra-trace amounts of heavy metals. The method thus proved to be a useful tool to monitor water quality in view of the WFD 2021 goals of achieving metal concentrations close to background values in estuarine and marine environments.

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Figure captions

Fig. 1. Map of the Marche region with the five rivers studied.

Fig. 2. . Representative transect (Tronto river) with the three sampling stations and corresponding salinity values.

Fig. 3. Metal concentrations along the river transects (Stations from A to C) of total (black circle), dissolved (white circle) and particulate (grey circle) fractions.

Fig. 4. Metal distribution along the river transects (Stations from A to C) of dissolved (white box) and particulate (cross-lined) concentrations.

Table 1
Estuarine sampling stations and salinity and turbidity field data.

Site	Stn.	Salinity(psu)	Turbidity (NTU)
Foglia	A	1.35	14.5
	B	20.2	7.3
	C	34.4	0.55
Esino	A	0.3	53.8
	B	19.2	11.3
	C	33.4	3.3
Potenza	A	0.38	58.5
	B	21.6	33.8
	C	35.2	15.1
Tenna	A	0.3	22.3
	B	13.3	21.7
	C	35.0	14.1
Tronto	A	0.3	19.9
	B	18.8	12.9
	C	33.9	7.7

Table 2. Results (ng L^{-1}) of the analysis of two water reference materials by means of SWASV (n=8). Mean ± SD.

		Pb	Cu	Cd
CASS-4	Analyzed	9.6±0.5	594±10	26±1
	Reference	9.8±3.6	592±55	26±3
SLEW-3	Analyzed	8.9±1.7	1535±131	50±2
	Reference	9.0±1.4	1550±120	48±4

Table 3. Analytical results of total, dissolved and particulate concentrations.

St.	Salinity	Metal concentration (Mean±SD)								
		Pb			Cu			Cd		
		Total ng L^{-1}	Dissolved ng L^{-1}	Particulate ng L^{-1}	Total ng L^{-1}	Dissolved ng L^{-1}	Particulate ng L^{-1}	Total ng L^{-1}	Dissolved ng L^{-1}	Particulate ng L^{-1}
Foglia										
A	1.35	1870±70	586±33 [31%]	1280±80 [69%]	3200±260	885±98 [28%]	2320±280 [72%]	81±5	36±4 [44%]	45±6 [56%]
B	20.2	685±36	251±18 [37%]	434±40 [63%]	4710±270	3950±120 [84%]	760±295 [16%]	36±1	30±1 [82%]	6±1 [18%]
C	34.4	145±6	66±1 [46%]	79±6 [54%]	786±24	620±4 [79%]	166±24 [21%]	34±2	20±1 [58%]	14±2 [42%]
Esino										
A	0.3	1030±20	127±17 [12%]	903±26 [88%]	3810±100	1080±160 [28%]	2730±190 [72%]	36±2	18±2 [50%]	18±3 [50%]
B	19.2	263±16	152±11 [58%]	111±19 [42%]	716±35	627±44 [88%]	89±56 [12%]	20±4	15.7±0.4 [78%]	4±4 [22%]
C	33.4	223±10	54±3 [24%]	169±10 [76%]	626±66	598±17 [96%]	28±68 [4%]	29±3	9.4±0.5 [32%]	20±3 [68%]
Potenza										
A	0.38	1110±100	152±12 [14%]	960±100 [86%]	3340±140	1680±130 [50%]	1660±190 [50%]	32±5	21±2 [66%]	11±5 [34%]
B	21.6	503±18	78±6 [15%]	425±19 [85%]	1120±130	479±47 [43%]	641±138 [57%]	18±4	11.6±0.8 [64%]	6±4 [36%]
C	35.2	241±16	49±3 [20%]	192±16 [80%]	835±13	539±17 [65%]	296±21 [35%]	27±2	17.3±0.7 [64%]	10±2 [36%]
Tenna										
A	0.3	756±2	114±15 [15%]	642±15 [85%]	2620±190	1900±100 [73%]	720±210 [27%]	27±4	19.9±0.4 [74%]	7±4 [26%]
B	13.3	635±20	155±7 [24%]	480±21 [72%]	1060±30	928±13 [88%]	132±33 [12%]	26±2	17.3±0.6 [67%]	9±2 [33%]
C	35.0	293±19	44±8 [15%]	249±21 [75%]	775±38	624±10 [81%]	151±43 [19%]	33±5	13±2 [39%]	20±5 [61%]
Tronto										
A	0.3	980±30	170±8 [17%]	810±30 [83%]	2180±70	960±90 [44%]	1220±110 [56%]	40±4	22±1 [55%]	18±4 [45%]
B	18.8	375±25	158±6 [42%]	217±26 [58%]	767±20	476±23 [62%]	291±30 [38%]	23±1	14.3±0.7 [62%]	9±1 [28%]
C	33.9	116±6	57±6 [49%]	59±8 [51%]	635±16	416±34 [66%]	219±38 [34%]	33±2	15±2 [45%]	18±3 [55%]

Table 4
Selection of literature data and water quality standards for dissolved metal concentrations in surface seawaters (depth ≤100 m).

Location	Methodology	Pb, μg L^{-1}	Cu, μg L^{-1}	Cd, μg L^{-1}	Reference
This study					
Stations A	Min-max	0.114-0.586	0.885-1.90	0.018-0.036	This study
Stations B	Min-max	0.078-0.251	0.476-3.95	0.012-0.030	This study
Stations C	Min-max	0.044-0.066	0.416-0.620	0.009-0.020	This study
Nervion, BC- estuary	Mean	n.d.	33.5	n.d	Fernandez et al., 2008
Hudson Estuary	Min-Max	n.d.	1-7	0.1-0.5	Klinkhammer et al., 1981
Seine Estuary	Min-max	n. d.	1.5-2.5	n.d	Chiffoleau et al., 1999
Baltic Sea	Median	0.03	0.55	0.014	Dippner et al., 2004
Taiwan	Min-max	0.02-0.09	0.02-0.1	0.003-0.016	Fang et al., 2006
Vigo Ria (Atlantic)	Mean	0.1	0.3	0.008	Prego et al., 2006
California	Median	n.d.	1.3	n.d.	Buck et al., 2007
Celtic Sea	Mean	0.03	0.07	0.007	Cottè-Krief et al., 2002
Mediterranean Sea					
Central Adriatic Sea, 2004	Mean	0.028	0.599	0.015	Annibaldi et al., 2009
Open Mediterranean Sea, 1983	Mean	0.057	0.136	0.006	Béthoux et al., 1990
North Adriatic Sea, 1990	Mean	0.023		0.016	Scarponi et al., 1995
Venice lagoon, 1992	Min- max	0.033-0.290	0.330-0.521	0.007-0.020	Cescon et al., 2000
Background values (seawater)					
Atlantic ocean	Min-max	0.005-0.020	0.050-0.100	0.005-0.025	Helcom, 2000
Northern North Sea	Min-max	0.010-0.020	0.050-0.090	0.008-0.025	Helcom, 2000
English Channel Southern North Sea	Min-max	0.010-0.017	0.140-0.360	0.009-0.012	Helcom, 2000
Celtic sea	Min-max	0.010-0.020	0.060-0.080	0.004-0.012	Helcom, 2000
Water quality standards					
Internal surface water (i.e. rivers, lakes)	Annual mean	7.2	0.08-0.25		DM 260/2010
Marine coastal water	Annual mean	7.2	0.2		DM 260/2010
Seawater[a]			5		EQS U.K. (Smith, 1993)
Saltwater CMC[b] acute			4.8		USEPA, 1998
Saltwater CMC[c] chronic			3		USEPA, 1998

[a]Designed to protect all salt water life
[b]Criterion maximum concentration for aquatic life
[c]Criterion continuous concentration for aquatic life

Adriatic
Sea
Italy
S. MARINO
PESARO
FANO
Foglia
Urbino
Fossombrone
Senigallia
Montemarciano
Falconara
Marittima
ANCONA
Chiaravalle
Esino
Osimo
Castelfidardo
Loreto
Porto Recanati
Recanati
Potenza Picena
Cingoli
MACERATA
Civitanova
Marche
Potenza
Corridonia
Sant'Elpidio a Mare
Porto S. Giorgio
Tolentino
Camerino
PERUGIA
Lago
Trasimeno
Tenna
Pedaso
Sarnano
Amandola
Grottammare
Offida
S. Benedetto
del Tronto
ASCOLI PICENO
Tronto
Appennino Umbro-Marchigiano

Fig. 1

Fig. 2

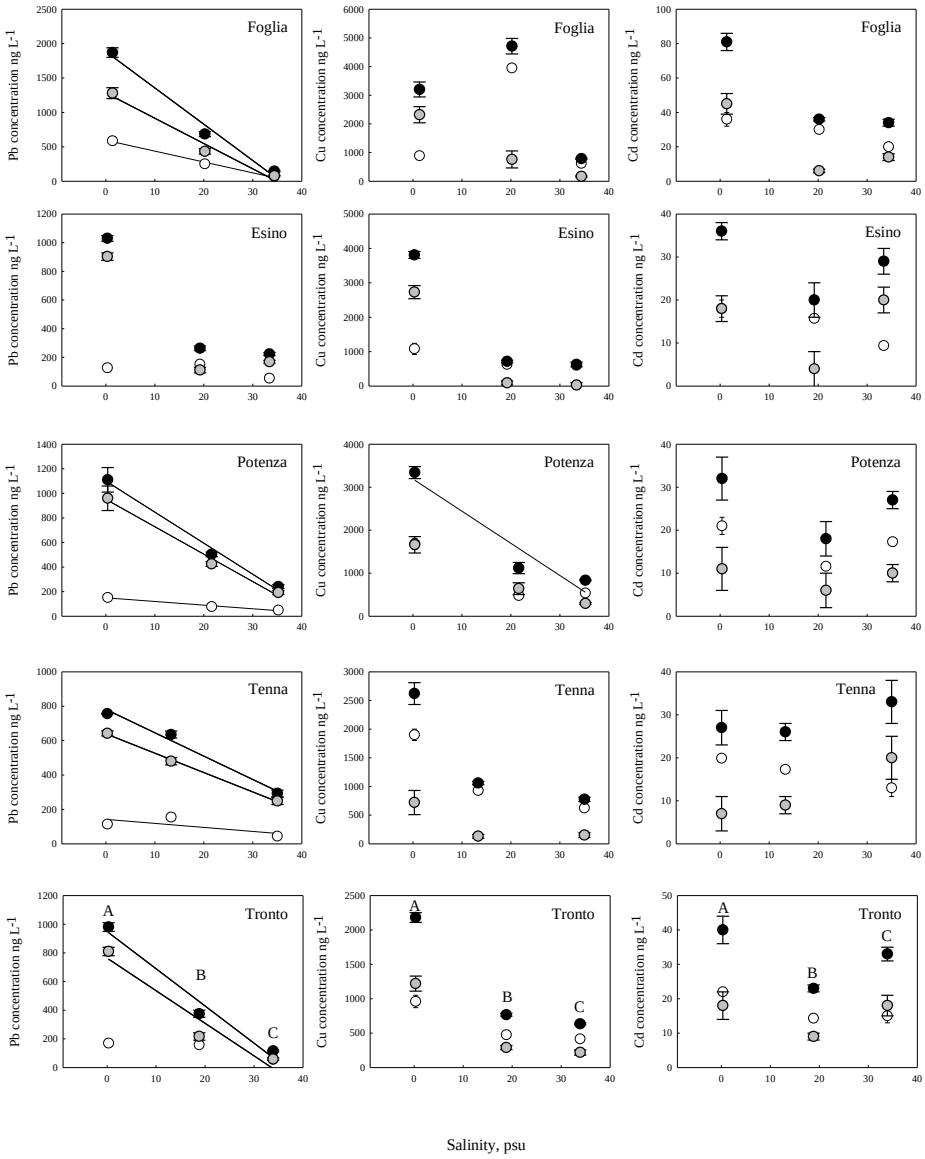
Foglia
Esino
Potenza
Tenna
Tronto
Pb concentration ng L-1
Cu concentration ng L-1
Cd concentration ng L-1
A
B
C
Salinity, psu

Fig. 3

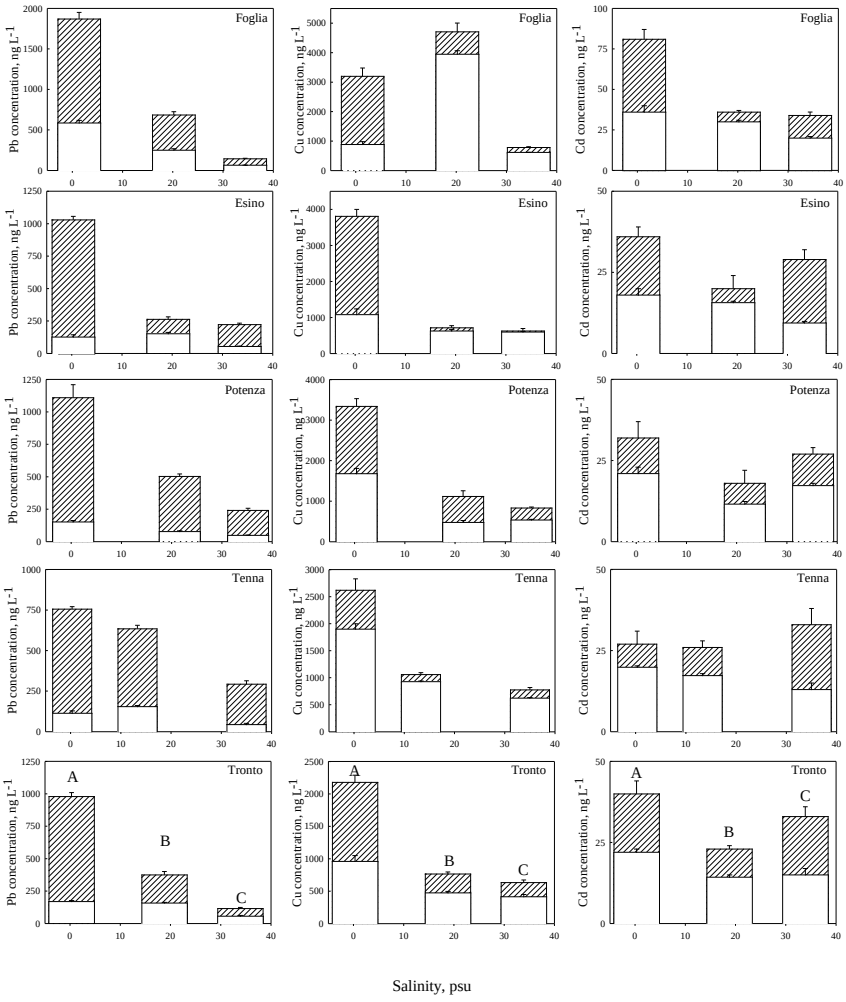
Foglia
Esino
Potenza
Tenna
Tronto
Pb concentration, ng L-1
Cu concentration, ng L-1
Cd concentration, ng L-1
A
B
C
Salinity, psu

Fig. 4