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Quality Evaluation of Sediments from 24 Tributaries of the Po River, Italy

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Abstract Sediment samples from 24 tributaries of the Po River (Italy) were screened for selected trace elements (Cd, Cu, Hg, Pb, and Zn) and extractable organic compounds; a proxy for contamination by organic microcontaminants. The toxicity of sediment extracts was evaluated using a battery of biotests (*Dugesia gonocephala*, *Paracentrotus lividus*, and *Tamnocephalus platyurus*). Contamination by trace elements (including very high Hg pollution – 4 to 16ppm total Hg – in one sub-basin) reached potentially harmful levels only in the sediments of four tributaries; while contamination by organic microcontaminants was present in most sub-basins. Sediments from most study sites did actually show signs of anthropogenic stress and were able to elicit a toxic response. A more detailed evaluation of sediment quality in the Po River tributaries seems to be urgently needed for developing the necessary remediation strategies. Research priorities should include more thorough testing of sediment toxicity, determination of metal background levels in the various sub-basins and a more detailed identification of the organic micropollutants of possible concern.

Keywords Extractable organic compounds · Metal background levels · Po River basin · Sediment contamination · Sediment toxicity · Trace elements

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1 Introduction

With a basin of over 70,000 km^2 and a length of about 650 km, the Po River is the largest Italian river flowing from West to East in the densely populated and agriculturally and industrially developed Padana plain (northern Italy). The characterization of sediment quality along the main channel of the Po River downstream from the confluence with selected tributaries has been studied in some detail during extensive field campaigns in the years 1994, 1996, and 1997 (IRSA 2000; Camusso et al. 2002; Viganò

et al. 2003; Vignati et al. 2003). These studies have identified the stretches downstream from the city of Turin and from the confluences with the rivers Lambro and Oglio as the most anthropogenically impacted zones of the Po River (see Fig. 1). However, to date, no systematic study of the sediment quality of the tributaries upstream from their confluences with the Po River has been published.

Given the presence of several industrial and agricultural activities in the Padana plain (Camusso and Pagnotta 1997 and Fig. 1), such assessment is needed to identify possible critical areas which may have been missed by the previous sediment quality assessment in the main channel of the Po River. This study investigates the concentration of selected trace elements and extractable organic compounds (a proxy for contamination by organic microcontaminants) in 24 tributaries of the Po River (Fig. 1) for the periods October 1996 and April 1997. The sediments' potential for toxicity has also been screened by testing sediment organic extracts with three standardized bioassays. The sampling periods correspond to those during which detailed sediment quality assessment has been performed along the main channel of the Po River. Apart from the coming into service of the wastewater treatment plant of Nosedo (in the basin of the Lambro tributary), no major changes in land use and industrial activities are known to have occurred. The results of this study should therefore be a useful complement to the information already available in the literature and should be sufficiently representative of the present situation to constitute guidance for future research and for the development of management strategies at the whole-basin scale of the Po River.

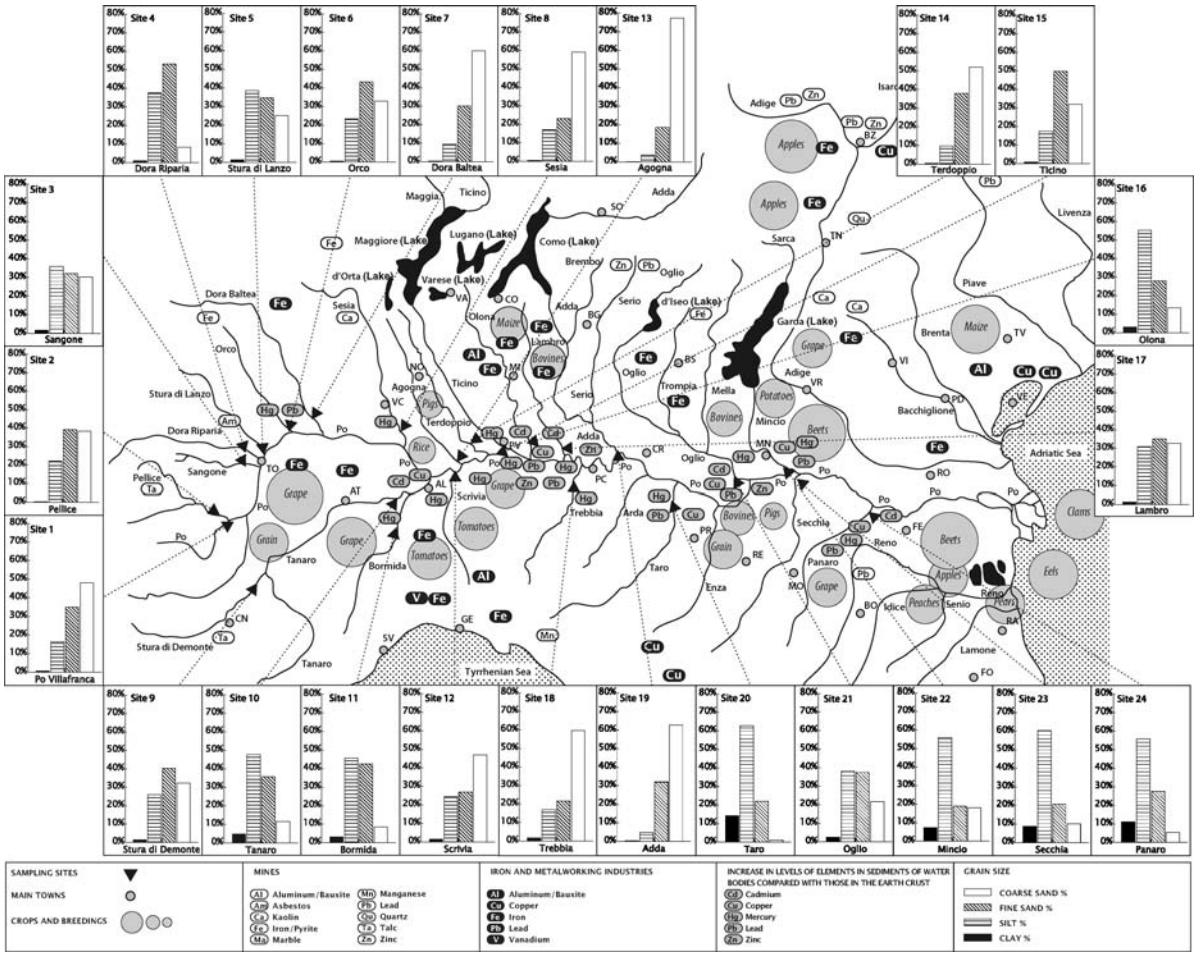

Fig. 1 Map of the Po River basin with sampling points and grain size characteristics of each site for the 1997 sampling period. Additional information about industrial, agricultural and stockbreeding activities is incorporated in the map

2 Material and Methods

2.1 Sampling and Physico-chemical Analyses

Bed sediments were collected in 22 first-order tributaries and 2 second-order tributaries of the Po River just upstream from their confluence with the Po River itself (first-order tributaries) or the higher order water course. Surface sediment samples (upper 5 cm) were collected manually from the rivers' bank, transferred into plastic containers, and transported on ice to the laboratory (University of Turin). Samples were decanted at 4°C for 72 h, sieved at 2 mm and then split for the various analyses.

Grain size distribution, organic matter content, and trace elements (Cd, Cu, Hg, Pb, and Zn) were determined according to the methods described in Vignati et al. (2003). For the quantification of extractable organic compounds (EOCs), an aliquot of wet sediment (corresponding to 90 g on a dry weight basis; water content determined on an independent sediment aliquot after drying at 105°C) was mixed with sodium sulphate, extracted for 6 hours with 225 ml of dichloromethane under agitation (180 tours min^{-1}), left to decant overnight and filtered (filter paper Whatman No 42) under conditions minimizing solvent evaporation. EOCs were then determined spectrophotometrically after Chiang et al. (1957).

2.2 Ecotoxicological Assays

For each sample, 50 ml of filtered dichloromethane extract (see Section 2.1) were treated with dimethylsulphoxide (DMSO), evaporated to near dryness by rotary evaporation at 37°C, and resolubilized in 20 ml of an adequate test medium (see below). Following this procedure, one millilitre of the raw, resolubilized extract contained the equivalent of the compounds present in 1 g of dry sediment. The presence of toxicity in the raw extract was assigned the value of 1 toxic unit (TU). Serial dilutions of toxic raw extracts were tested until no further toxicity was observed. Thus if a 200-fold dilution of one extract was the maximum dilution at which such extract could elicit toxicity, the sediment was assigned a value of 200 TU. Raw sediment extracts not eliciting toxicity were assigned a value of 0 TU. Control samples containing dimethylsulphoxide at the same concentration as in the raw extracts did not result in appreciable toxicity to test organisms.

The planarian *Dugesia gonocephala*, the sea urchin *Paracentrotus lividus*, and the crustacean *Tamnocephalus platyurus* (Thamnotoxkit) were used as test organisms (see Lagadic and Caquet 1998; Geffard et al. 2001; Latif and Licek 2004 for advantages and limitations of these types of tests). The evaporated sediment extracts (see above) were resuspended in mineral water for *D. gonocephala* (Arru et al. 1993a, b), filtered marine water for *P. lividus* (Arru et al. 1991a, b), and in the saline solution of the Thamnotoxkit for *T. platyurus* (Ugazio et al. 1998). Toxicity endpoints included mortality (daily observation for 8 days) and regeneration (daily observation for 15 days) for *D. gonocephala*, embryological development for *P. lividus* (48 hours) and mortality for *T. platyurus* (24 h). The number of organisms per test was 10 adult individuals of *D. gonocephala* (each individual exposed independently), 30 embryos for *P. lividus* and 30 eggs treated for hatching for *T. platyurus*.

2.3 Statistical Analysis and Data Evaluation

Since most variables showed a non-normal distribution (Kolmogorov-Smirnov test), seasonal variability and correlation among parameters were assessed by the Mann–Whitney Rank sum test and the Spearman correlation test respectively. All data were centred and reduced to avoid possible artefacts in the statistical results when comparing variables measured on different scales (Davis 1986).

The expected sediment toxicity arising from contamination by trace elements was estimated using the "Probable Effect Concentration Quotient" – PEC-Q_m (Wenning et al. 2005; Long et al. 2006):

$$\mathrm{PEC}-Q_m = \frac{\sum_{i=1}^{n} \mathrm{PEC}-Q_i}{n}$$

Where:

PEC-Q_m is the sum of the PEC-Q_i,

PEC-Q_i is the ratio between the concentration measured in sediments and the corresponding PEC value for each individual metal, and

n is the number of metals considered in the study.

Q-mode cluster analysis was used to group tributaries with similar characteristics in order to obtain some general conclusions about the extent of sediment pollution and potential toxicity at the different sites. Similarities between pairs of objects

were estimated using Euclidean distances and the weighed pair group average method was used to determine the final clusters.

3 Results and Discussion

3.1 Physico-chemical Measurements

All variables showed a marked spatial variability (Figs. 1 and 2; Table 1), but none of them had a definite longitudinal trend from the upper to the lower parts of the Po River catchment. For sediment characteristics such as organic carbon content (OC) and percentage of fine material (clay + silt), the lack of a clear trend is most likely due to the complex geology and mineralogy of the Po River basin (Amorosi et al. 2002). In both sampling periods, significant correlations ($p < 0.02$; Spearman correlation test) were observed among all the studied variables (OC, percentage fine material, and concentrations of trace elements and Extractable Organic

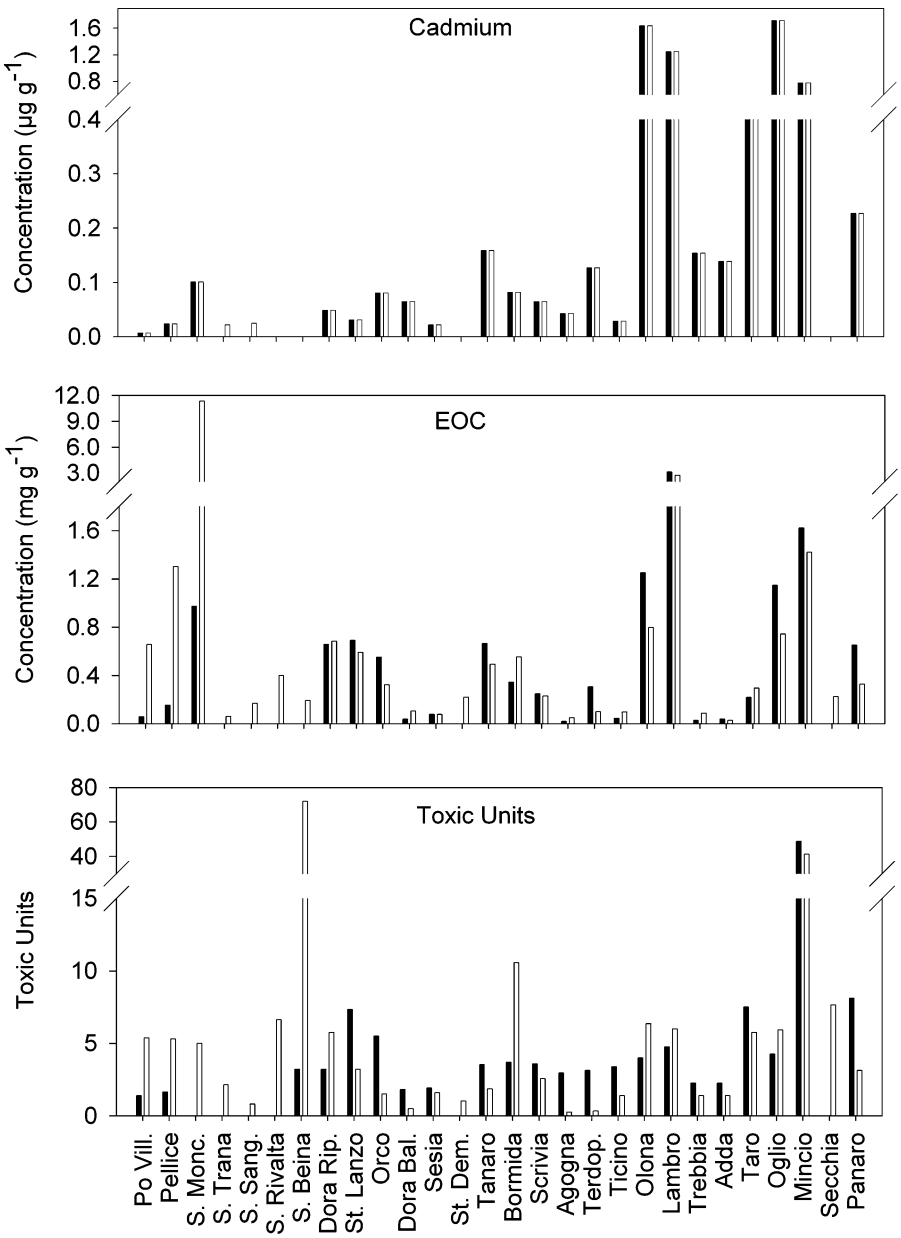

Fig. 2 Concentration of Cd and extractable organic compounds (*EOCs*) and toxic potential (toxic units) of sediments samples for 1996 (*black bars*) and 1997 (*white bars*). See Table 1 for complete results of trace elements and sediment characteristics and for the full names of the various tributaries

Table 1 River flow, percentage fine sediment (clay+silt), and trace metal and extractable organic compounds (EOCs) content for sediments from the various tributaries in the two sampling periods

Site (no.)	Site (name)	Q (m^3/s)	OC (%)	Grain size (%)	Cd (ug/g)		Cu (μg/g)		Hg (ng/g)		Pb (μg/g)		Zn (μg/g)		EOCs (μg/g)	TU (Units)
					Sites	Po River	Sites	Po River	Sites	Po River	Sites	Po River	Sites	Po River		
1996 Campaign																
1	Po Villafranca	200	0.73	10.3	0.007	0.328	2.9	63.0	21	119	1.6	32.0	5	192	57	1.4
2	Pellice	274	1.69	36.7	0.024		4.8		38		3.4		8		152	1.6
3	Sangone-Moncalieri	43.1	0.77	13.7	0.101		14.3		63		14.6		21		974	3.2
4	Dora Riparia	108	1.80	41.0	0.049	1.142	9.6	91.3	130	254	5.6	54.7	16	292	658	3.2
5	Stura di Lanzo	167	1.54	19.8	0.031		7.0		49		4.9		12		690	7.3
6	Orco		1.56	43.8	0.081		11.3		27		16.1		28		551	5.5
7	Dora Baltea		0.53	15.1	0.065	0.672	8.6	76.2	40	132	7.4	37.2	18	249	38	1.8
8	Sesia		0.58	15.9	0.022	0.341	3.1	64.5	62	97	3.3	23.4	14	199	77	1.9
10	Tanaro	104	2.29	56.4	0.159	0.351	22.4	55.9	40	92	14.2	25.4	35	177	664	3.5
11	Bormida	2.2	1.61	34.3	0.082		13.2		44		9.0		24		345	3.7
12	Scrivia	17.1	0.90	25.0	0.065		5.8		18		5.4		17		249	3.6
13	Agogna	32.4	0.63	0.9	0.043		3.0				3.5		24		19	3.0
14	Terdoppio	26.3	1.54	22.5	0.127		10.2		44		6.5		28		306	3.1
15	Ticino	212	1.04	35.1	0.029	0.317	2.7	47.0	132	93	4.3	19.1	12	145	45	3.4
16	Olona	10.4	6.73	61.1	1.640		123		221		52.0		222		1250	4.0
17	Lambro	66	3.50	35.2	1.248	0.886	118	99.9	247	320	52.0	39.0	303	263	3126	4.8
18	Trebbia	1.9	1.74	19.9	0.154		8.2		9		3.9		19		26	2.3
19	Adda	194	0.43	3.3	0.139	0.508	3.4	62.5	18	211	5.7	25.3	27	211	38	2.3
20	Taro	3.3	2.82	67.4	0.513		52.7		44		29.1		133		217	7.5
21	Oglio	162	4.96	45.4	1.718	0.720	228	89.7	132	203	80.4	35.4	984	302	1148	4.3
22	Mincio	2.3	4.50	58.2	0.778		34.0		4410		27.3		81		1621	49
24	Panaro	6.9	2.67	68.8	0.227	0.642	30.3	76.8	71	186	28.7	33.4	71	257	651	8.1

Table 1 (continued)

Site (no.)	Site (name)	Q (m^3/s)	OC (%)	Grain size (%)	Cd (ug/g)		Cu (μg/g)		Hg (ng/g)		Pb (μg/g)		Zn (μg/g)		EOCs (μg/g)	TU (Units)
					Sites	Po River	Sites	Po River	Sites	Po River	Sites	Po River	Sites	Po River		
1997 Campaign																
1	Po Villafranca	17.9	2.12	33.5	0.209	0.328	29.6	63.0	82	119	26.1	32.0	75	192	656	5.4
2	Pellice	12.6	4.15	43.2	0.103		21.9		65		17.0		44		1301	5.3
3	Sangone Moncalieri	6.8	12.80	62.4	3.389		200		206		71.3		416		11324	5.0
3a	Sangone Trana		0.41	6.3	0.022		2.9		33		4.0		15		60	2.1
3b	Sangone Sangano		0.65	5.1	0.025		4.7		37		5.7		22		169	0.8
3c	Sangone Rivalta		1.02	71.1			5.6		60		5.8		25		399	6.6
3d	Sangone Beinasco		0.52	2.3			9.3		65		8.3		32		191	72
4	Dora Riparia	61.5	1.77	41.9		1.142	36.9	91.3	76	254	21.8	54.7	76	292	683	5.8
5	Stura di Lanzo	28.6	1.27	66.2			13.9		43		12.9		34		590	3.2
6	Orco		0.87	27.5	0.147		8.6		43		8.0		30		322	1.5
7	Dora Baltea	30.1	0.29	0.8		0.672	6.9	76.2	11	132	4.0	37.2	20	249	104	0.5
8	Sesia	82.4	0.35	1.2	0.224	0.341	6.2	64.5	21	97	3.7	23.4	26	199	77	1.6
9	Stura di Demonte	36.3	0.80	13.3			6.8		33		8.0		33		219	1.0
10	Tanaro	58.3	1.33	61.4	0.322	0.351	17.7	55.9	274	92	14.9	25.4	48	177	492	1.9
11	Bormida	1	2.27	44.0	0.117		20.9		89		21.5		46		552	10.6
12	Scrivia	1	1.21	10.5	0.084		7.9		30		11.2		30		230	2.6
13	Agogna	3.7	0.68	2.7	0.135		4.3		23		6.7		34		49	0.3
14	Terdoppio	15.9	0.88	4.6	0.134		9.1		51		8.1		41		98	0.3
15	Ticino	151	0.69	5.4	0.112	0.317	5.7	47.0	30	93	5.5	19.1	30	145	97	1.4
16	Olona		5.49	60.7	0.747		53.6		344		36.5		143		798	6.4
17	Lambro	28.4	2.48	20.4	0.731	0.886	75.9	99.9	229	320	29.2	39.0	185	263	2711	6.0
18	Trebbia	1.9	1.93	5.5	0.096		16.4		33		6.1		42		87	1.4
19	Adda	121	0.42	7.5	0.131	0.508	4.8	62.5	25	211	7.8	25.3	34	211	27	1.4
20	Taro	1	2.63	80.9	0.160		20.5		41.2		21.4		57		295	5.8
21	Oglio	161	4.08	27.6	1.104	0.720	183	89.7	190	203	68.6	35.4	635	302	743	5.9
22	Mincio		5.23	68.3	0.617		41.2		16566		42.1		122		1421	41
23	Secchia	20.2	1.98	28.5	0.122		14.5		59		24.8		50		224	7.7
24	Panaro	20.6	2.12	92.3	0.147	0.642	26	76.8	778	186	14.7	33.4	74	257	328	3.1

Data for trace element concentrations in the Po River downstream from major tributaries are from Camusso et al. (2002) and Vignati et al. (2003). *TU* Average of the toxic units from the tests with *D. gonocephala*, *P. lividus* and *T. platyurus*. No sediment available for sites 3a–3d, 9, and 23 in 1996. Empty cells, values not available

Compounds). These correlations suggest a common entry-route, if not a common origin, of the investigated contaminants to the rivers' sediments and agree with the well-known importance of grain-size and OC content on contaminant concentrations. The widespread distribution of various anthropogenic activities throughout the Po River basin (Fig. 1; Camusso and Pagnotta 1997) can also contribute to the spatial variability in contaminant concentrations (Table 1, Fig. 2).

Part of the seasonal variability in the contaminants' concentration could actually be due to the variability in sediments' texture and organic carbon content (see Figs. 1 and 2, Table 1). Note however that overall differences between the sampling periods were not statistically significant except in the case of Zn (p = 0.019; Mann–Whitney test).

Compared with literature data (Camusso et al. 2002; Vignati et al. 2003), trace element levels in sediments from Lambro (site 17) and Oglio (site 21) were similar to (or higher than) those measured in the Po River main channel downstream from the confluences with these tributaries (Table 1). On the other hand, element concentrations measured for Adda and Panaro (sites 19 and 24) were generally lower than those measured in the corresponding stretches of the Po River main channel. The latter situation was also observed for the major tributaries in the upper Po River course: Dora Riparia (site 4), Dora Baltea (7), Sesia (8), Tanaro (10) and Ticino (15) (Table 1). To our knowledge, no data for comparison are published for the Po River sediments downstream from the other tributaries included in this study and for the period of interest.

The present study shows that sediments from Sangone Moncalieri (site 3), Olona (16) and Mincio (22) were also contaminated by trace elements. Contamination in the Olona sediments (site 16) was comparable to that in the chronically polluted Lambro river (site 17) on both sampling occasions. On the other hand, contamination at Sangone Moncalieri varied markedly between the two sampling periods suggesting a more episodic pollution from the industries present in the basin (Fig. 1; Camusso and Pagnotta 1997; Barbiero and Pagnotta in IRSA 2000).

Sediments from Mincio (site 22) had an extremely high Hg content (4 and 16ppm in 1996 and 1997 respectively), most likely due to the paper mills and industrial complexes located in the lower Mantua lake (Campanini and Morandi 1986; Cattaneo et al. 1988). Additional samples collected by the authors at this site in April 2006 contained about 4ppm of Hg; a value comparable to the 1996 sample. Furthermore, samples collected in 2006 upstream from the probable sources of pollution had an Hg content around 0.06ppm; corresponding to background levels observed in the upper part of the Po River basin and in the upper tributaries (Camusso et al. 2002; Vignati et al. 2003; Table 1). This analysis, although insufficient to appreciate the full extent of Hg contamination in the Mincio basin, confirms that high Hg levels still occurred in sediments from this tributary in 2006.

Joint examination of our original data and previously published ones (see Table 1) shows that, in the region between the city of Turin and the Ticino tributary (site 15), trace element concentrations in 1996–1997 were systematically higher in sediments from the Po River channel than in those from the tributaries. These observations confirm that the city of Turin constituted the major source of trace elements in the upper course of the Po River (Camusso et al. 2002; Vignati et al. 2003). Downstream from Turin, metallic contaminants undergo progressive dilution with relatively metal-poor material from the various upper tributaries (Dora Riparia to Ticino – sites 4 to 15; Table 1) as far as the confluence with the river Lambro (site 17). The Lambro and, further downstream, the Oglio (site 21) act as the principal sources of trace elements in the lower basin of the Po River; again in agreement with previous research (Camusso et al. 2002; Vignati et al. 2003). No data are available about the possible effect of sediment pollution in the Olona (site 16) onto the Po River sediments. On the other hand, metallic pollution at the sites Sangone Moncalieri (3) and Mincio (22) does not seem to influence the sediment quality of the Po River sediments, although it is clearly a problem in the specific sub-basins.

A conclusive evaluation of the severity of metallic contamination in the various sub-basins is prevented by the lack of adequate knowledge of the background levels of metals for the various tributaries. Concentrations of Cu, Pb, Zn, and, to a lesser extent, Cd in recent, unpolluted sediments from the upper part of the main channel of the Po River (Camusso et al. 2002; Vignati et al. 2003) and in quaternary deposits in the lower Po valley (Amorosi et al. 2002; Bianchini et al. 2002 – no results available for Cd in these

studies) agree fairly well with values reported by Salomons and Förstner (1984) for "mean sediment"; i.e., 33, 19, 95, and 0.170 μg g^{-1} for Cu, Pb, Zn, and Cd respectively. However, element concentrations much lower than "mean sediment" values have been measured in sediments from some rivers considered in this study (Table 1). Furthermore, background Hg concentrations measured in sediments from some upper Po tributaries were about two times lower than the corresponding value of 0.190 μg g^{-1} tabulated for the "mean sediment" (see again Table 1). Data about background element concentrations in the various sub-basins clearly represent a research priority to correctly estimate human-related metal enrichment in the River Po catchment.

The results for the Sangone tributary, which was sampled at different sites along its course in 1997, well illustrate this research need. Element concentrations in the upper part of this river (sites 3a–3d in Table 1) were five- to six- (Hg, Pb Zn) to tenfold (Cd, Cu) lower than those reported for "mean sediment". The contamination found at site 3 (Sangone Moncalieri) is then likely to be seriously underestimated if evaluated against "mean sediment" values instead of basin-specific ones (see Matschullat et al. 2000). Similar situations (but possibly also situations in which metal background values in the Po basin are higher than "mean sediment" ones) likely exist for several rivers examined in this study because of the complex lithology of the Po River basin (Amorosi et al. 2002).

The levels of Extractable Organic Compounds (EOCs) were significantly correlated ($p < 0.01$; Spearman correlation test) with those of trace elements. However, many sites with low levels of metallic contamination (e.g., Dora Riparia, Stura di Lanzo, Orco, and Scrivia – sites 4, 5, 6, and 12) had EOCs concentrations comparable with those of metal-polluted sites such as Olona (site 16) and Oglio (site 21; Table 1 and Fig. 2). While correlation might suggest a common origin for EOCs and trace element inputs, it is important to note that strong evidence of metal contamination (see above) appeared to be limited to four to five tributaries (i.e., sites 3, 16, 17, 21, and 22) where significant industrial activities are known to be present. On the other hand, the EOCs results suggest the presence of some input of organic contaminants (most likely from diffuse sources) for most sub-basins.

The actual environmental significance of EOCs results is rather difficult to determine. First, the non-selective nature of the EOCs extraction procedure does not give information about the specific organic chemicals contained in each sediment. Second, part of the natural organic compounds present in the sediments may be remobilized during the extraction (Guzzella et al. in IRSA 2000). Third, there are no accepted reference values or guidelines for EOCs to help with the environmental interpretation of the results. In such situation, interpretation of the environmental significance of EOCs concentrations can be best achieved by examining the results of toxicity tests and verifying whether trace elements (for which sediment quality guidelines are available) may explain the observed toxicity or not.

3.2 Toxicity of Sediment Extracts

The average toxicity of sediment extracts (expressed as the average toxic units measured for each organisms and for each endpoint – see Section 2) showed two distinct peaks for sediments from Oglio (site 22, both sampling periods) and Sangone Moncalieri (site 3, 1997 only; Fig. 2). Overall differences between the two sampling periods were not statistically significant (Mann-Whitney test), but average TU values correlated significantly ($p \leq 0.02$; Spearman correlation test) with PEC-Q_m values, individual element concentrations, and EOCs concentration.

The toxicity of a number of samples was comparable to that of the sediments from the Lambro (site 17), which are known for their high degree of contamination and toxic potential (Viganò et al. 2003 and references therein; Bettinetti et al. 2003). In the case of major tributaries (i.e., Dora Riparia, Dora Baltea, Sesia, Tanaro, Ticino, Lambro, Adda, Oglio, and Panaro – sites 4, 7, 8, 10, 15, 17, 19, 21 and 24), our results compared favourably with those previously reported for sediments collected in the corresponding areas of the Po River main channel. Viganò (2000) examined the toxicity of extracts from these sediments (1:1 mixture of n-hexane and acetone followed by rotary evaporation and recovery in DMSO) to *Ceriodaphnia dubia*. This author reported values of 1–2 TU for unpolluted sediments in the upper Po River stretches, 4–6 TU downstream from the confluence with Dora Riparia (site 4) and Oglio (site 21), and 12–14 TU for the Lambro (site 17).

Considering that contamination by inorganic and organic microcontaminants was studied more in depth for the sediments collected in the Po River main channel (Camusso et al. 2002; IRSA 2000; Viganò et al. 2003), the value of 2 TU is probably a reasonable threshold to distinguish between toxic and non-toxic sediments. Under this hypothesis, sediments from more than a half of the sites considered in the present study (see Fig. 2) would be potentially toxic to biota (i.e., showed a toxic potential higher than 2 TU); although differences surely exist in the relative sensitivity of *C. dubia* and the organisms used in the present study. Sediments from Olona, Lambro, Oglio, and Mincio (sites 16, 17, 21, and 22) would exhibit toxic potential on both sampling occasions; while sediments from several other sites would do so only on a seasonal basis (Fig. 2; Table 1). The number of sites showing toxicity lower than 2 TU (i.e., which can be considered non-toxic) was actually rather limited: 4 out of 22 in 1996 and 8 out of 28 in 1997 (Table 1 and Fig. 2).

The nature of the toxicity tests used in this study does not allow to precisely identify the elements and/or compounds specifically responsible for the observed effects. However, probable effect concentration quotients (PEC-Q_m; Wenning et al. 2005; Long et al. 2006) can provide a first indication on the amount of toxicity possibly caused by trace elements.

In agreement with raw results, the highest PEC-Q_m were calculated for the rivers Olona (site 16), Lambro (17), Oglio (21), Mincio (22), and, only in 1997, Sangone Moncalieri (3) (Table 2). According to Wenning et al. (2005), the probabilities of trace elements to elicit a toxic response from benthic organisms are as follows:

- 20% for PEC-Q_m <0.1 or in the range 0.1–0.5,
- 25–60% for PEC-Q_m in the range 0.5–1,
- 40–85% for PEC-Q_m >1.

Two caveats must be mentioned. Firstly, the correspondences between metal contamination and the probability of a toxic response have been established for *Chironomus riparius* and *Hylella azteca* (Wenning et al. 2005); which may have a different sensitivity to trace elements compared with the organisms used in this study. Secondly, the relationships between PEC-Q_m and expected toxic responses have been derived considering a set of trace elements (As, Cd, Cr, Cu, Pb, Ni, and Zn – Ingersoll et al. 2001) which is different from the elements analyzed here. However, with the possible exception of the Lambro (site 17; see Pettine et al. 1996), Cr and Ni in the river Po basin are largely of natural origin (Amorosi et al. 2002; Dinelli et al. 1999) and should not significantly contribute to sediment toxicity. Similarly, the levels of As contamination reported in the Po River mainstream are between 6 and 20 μg g^{-1} (Camusso et al. 2002). Compared with a PEC value of 33 μg g^{-1} (MacDonald et al. 2000), the contribution of As to sediment toxicity should not be too important. Finally, calculation of PEC-Q_m without Hg (which is not included in the original database of Ingersoll et al. 2001) clearly reduces the potential for

Table 2 Probable effect concentration quotients (PEC-Q_m) at the various sites for the two sampling periods

Site (no.)	Site (name)	PEC-Q_m 1996	PEC-Q_m 1997
1	Po Villafranca	0.01	0.14
2	Pellice	0.02	0.09
3	Sangone Monc.	0.07	0.74
3a	Sangone Trana	n.a.	0.02
3b	Sangone Sangano	n.a.	0.03
3c	Sangone Rivalta	n.a.	0.04
3d	Sangone Beinasco	n.a.	0.05
4	Dora Riparia	0.06	0.13
5	Stura di Lanzo	0.03	0.06
6	Orco	0.06	0.05
7	Dora Baltea	0.04	0.03
8	Sesia	0.03	0.04
9	Stura di Demonte	n.a.	0.04
10	Tanaro	0.08	0.13
11	Bormida	0.05	0.10
12	Scrivia	0.03	0.05
13	Agogna	0.02	0.04
14	Terdoppio	0.05	0.06
15	Ticino	0.04	0.04
16	Olona	0.45	0.29
17	Lambro	0.47	0.30
18	Trebbia	0.03	0.06
19	Adda	0.03	0.04
20	Taro	0.20	0.10
21	Oglio	0.95	0.71
22	Mincio	0.99	3.32
23	Secchia	n.a.	0.10
24	Panaro	0.14	0.24

See text for the details about the possibility of metal-induced toxicity for the various sites. Sangone Monc., Sangone Moncalieri.

n.a. Sediment samples not available

metal-induced toxicity in the Mincio (site 22); but does not alter the potential metal toxicity at the other sites. The PEC-Q_m values of Table 2 should therefore be sufficiently representative of the potential for metal-inducible toxicity of the various sediments. On these basis, metal-induced sediment toxicity would be expected only for Sangone Moncalieri, Olona, Lambro, Oglio, and Mincio (sites 3, 16, 17, 21, and 22); where the calculated PEC-Q_m approach or exceed 0.5 (Table 2). In the other cases, toxicity is more likely to be linked to various organic microcontaminants whose presence has already been documented in the Po River main stream (Calamari et al. 2003; Camusso et al. 2002; Viganò et al. 2003; Fattore et al. 2002; Guzzella et al. in IRSA 2000). A better characterization of the exact nature of these contaminants in the river Po tributaries then appears as a research priority in future studies.

3.3 Cluster Analysis

Cluster analysis was performed independently for the two sampling periods using the data contained in Table 1 for trace elements, EOCs, organic carbon, percentage of fine sediments, and TU values.

For 1996, four major groups are identified by cluster analysis (Fig. 3). Cluster A includes the tributaries Olona, Lambro, Oglio, and Mincio; char-

Fig. 3 Q-mode cluster analysis for all samples in 1996 (*top*) and 1997 (*bottom*). *Capital letters* identify the major clusters (see text for details). See Table 1 for the names of the tributaries corresponding to each "site number"

acterized by a marked contamination by trace element and EOCs accompanied by sediment toxicity. High contamination by trace elements is the most distinctive feature of these sites (see Tables 1 and 2). Sediments in cluster B (Dora Riparia, Orco, Tanaro, Taro, and Panaro) are characterized by a high content of fine sediments (approx. 40–70%), low metal contamination, and intermediate levels of EOCs and toxicity. Clusters C and D include the remaining tributaries with fine sediment content lower than 40%. These tributaries are further distinguished according to their organic carbon content (0.9–1.7% for cluster C vs 0.4–0.7% for cluster D) and toxicity. The latter is, on average, higher in cluster C than D. In cluster C, sites 3 (Sangone Moncalieri) and 5 (Stura di Lanzo) are separated from the other sites because of their higher EOCs' content. Cluster D (Po Villafranca, Dora Baltea, Sesia, Agogna, and Adda) can actually be considered as the group of the cleanest sites for the 1996 sampling period, although sediments from site 13 (Agogna) have 3 TU (Table 1); a value slightly higher than the hypothetical threshold of 2 TU assumed to be indicative of no toxicity (see Section 3.2).

For 1997, five major groups are identified by cluster analysis (Fig. 3). The most toxic sediments of the entire study (Sangone Moncalieri and Mincio; sites 3 and 22) form cluster A together with site 21 (Oglio). Sediments from this last site are actually much less toxic (Table 1 and Fig. 2), but all the sites have PEC-Q_m above 0.7 (see Table 2) and severe contamination by trace elements therefore seems the factor responsible for their separate clustering. Also note that, strictly speaking, site 3 is actually separated from sites 21 and 22; most likely because of its much stronger contamination by EOCs (Table 1 and Fig. 2). Sites 16 and 17 (Olona and Lambro) form a separate small cluster (B) because of their intermediate levels of contamination by trace elements (PEC-Q_m about 0.3; Table 2); which are higher than those observed at the remaining sites. Cluster C includes a large number of tributaries with low EOCs (27–230 μg g^{-1}) and low organic carbon content (less than 1% with the exception of sites 12 and 24). Some secondary subdivisions are actually present in the large cluster C. Sediments from sites 6, 9, 12, and 18 (Orco, Stura di Demonte, Scrivia, and Trebbia) have OC content higher than 0.8%; while OC for all other sites in cluster C is below this value. Sites 3a and 3d (Sangone Trana and Sangone Beinasco) are separated from the remaining locations because of their higher toxicity. Sites 3b, 7, 8, 13, 14, 15, and 19 (Sangone Sangano, Dora Baltea, Sesia, Agogna to Ticino, and Adda) are actually the "cleanest" sediments of the 1997 sampling period with TU below 2. Cluster D (Sangone Rivalta, Stura di Lanzo, Tanaro, Taro, and Panaro) and E (Po Villafranca, Pellice, Dora Riparia, Bormida, and Secchia) have OC content higher than 1% and EOCs ranging from 220 to 2,700 μg g^{-1} (Table 1). The subdivision between the two is made on the basis of fine sediment content (20–60% for cluster E and 60–90% for cluster D) and sediment toxicity (>5 TU for cluster E and less than 5 TU for cluster D). Site 20 (Taro) actually has 5.8 TU, but it is clustered with group D because of its high content of fine sediments (Table 1).

The results of cluster analysis support the hypothesis put forward during the discussion of the results of sediment toxicity about the limited extent of contamination by trace elements in the Po River tributaries. However, they also show that variations in basic sediment parameters such OC content and grain size markedly affect the differences and similarities among the various sites. Sub-clustering of sediments with similar basic characteristic is often made on the basis of the toxicity of sediment extracts. Because metal toxicity can be excluded in most cases, more information is needed on the exact nature of organic microcontaminants at the various sites to understand the observed toxicity patterns.

4 Conclusions

Only sediments from Dora Baltea, Sesia, Agogna, and Adda (sites 7, 8, 13, and 19) were "clean" and not toxic on both sampling occasions. At the opposite, sediments from Olona, Lambro, Oglio, and Mincio (sites 16, 17, 21, and 22) showed clear signs of contamination and toxicity in both campaigns. All the other sites had an unsatisfactory sediment quality (either chemical contamination or moderate to high toxicity) at least in one sampling period.

Trace element contamination was localized in Olona, Lambro, Oglio and Mincio (sites 16, 17, 21, and 22) because of inputs from the heavily populated and industrialized metropolitan area of Milan (sites 16 and 17) and, except for Hg, diffuse source from agriculture and stockbreeding at sites 21 and 22 (see

Camusso et al. 2002; Vignati et al. 2003). Mercury contamination at site 22 (Mincio) was probably of industrial origin and still remained a major problem, at least locally, in 2006. Fundamental studies on Hg cycle in this area are needed to better understand the environmental fate of this element in the region and as guidance for remedial action. Seasonal contamination by trace elements at site 3 probably has an industrial origin too.

Contrary to trace elements, contamination by organic microcontaminants (of which EOCs concentrations are a proxy) was rather widespread throughout the Po River basin and often seems to be the main cause of sediment toxicity at sites with low contamination by trace elements (for example cluster C in Fig. 3 for 1997).

With a few, already known exceptions (i.e., Lambro and Oglio – sites 17 and 21), the tributaries did not seem to act as major sources of either trace elements or organic micropollutants to the Po River main channel (see Table 1 and Viganò et al. 2003). However, the quality of sediments from most tributaries was indicative, at least seasonally, of anthropogenically-stressed ecosystems. Following the results presented here, more comprehensive investigations on the sediment quality of the Po River tributaries should be carried out; including (but not limited to) more ecologically relevant toxicity tests on whole sediments (laboratory-based and in situ) and more detailed identification of organic micropollutants. Better determination of background levels of element contamination is also needed for sediment quality assessment purposes in the various tributaries of the Po River.

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