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Metals loads into the Mediterranean Sea: estimate of Sarno River inputs and ecological risk

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Abstract The metals pollution in the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea) were estimated. Eight selected metals (As, Hg, Cd, Cr, Cu, Ni, Pb and Zn) were determined in the water dissolved phase (DP), suspended particulate matter (SPM) and sediment samples. Selected metals concentrations ranged from 0.32 to 1,680.39 μg l^{-1} in water DP, from 103.6 to 7,734.6 μg l^{-1} in SPM and from 90.7 to 2,470.3 mg kg^{-1} in sediment samples. Contaminant discharges of selected metals into the sea were calculated in about 13,977.6 kg $year^{-1}$ showing that this river should account as one of the main contribution sources of metals to the Tyrrhenian Sea.

Keywords Sarno River · Metals · River outflow · Contaminant transport processes · Contaminant loads

Introduction

Defined as "the most polluted river in Europe", the Sarno River originates in south-western Italy and has a watershed of about 715 km^2. It flows through the Sarno flatland, is delimited in the west by Mt. Vesuvius and in the east by the Lattari Mountains, and reaches the sea in the Gulf of Naples (Tyrrhenian Sea), flowing through the city of Pompei (Fig. 1). The Sarno watershed collects water from two important effluents, the Cavaiola and Solofrana torrents.

The Sarno flatland is one of the most fertile in Italy due to the high quality of the soil, constituted by layers of volcanic and alluvial origins. The high population density, the massive use of fertilisers and pesticides in agriculture and the industrial development represent the main causes of pollution of the Sarno River (Arienzo et al. 2001). The main agricultural activity is based on tomato production in the San Marzano area. In terms of industrial development, Solofra, a city on the Solofrana River, has a long-standing tradition in leather tannery that currently counts about 400 productive units and 3,500 workers. The pharmaceutical industry is represented principally by Novartis Pharma, whose plant is located at exactly 200 m from the river mouth and covers an area of about 201,000 m^2. This plant is one of the largest facilities of Novartis Pharma and one of the most important in the world. Another source of environmental pollution can be attributed to urban agglomerations and their wastewaters. Regarding the sewer system of the 39 towns of the Sarno area basin (with a population of about 1,300,635 and an average density of 1,818 inhabitants/km^2), the wastewater collection and treatment in the area is inadequate. Nineteen of the 39 towns collect between 0 and 33 % of the wastewater generated, 7 towns between 34 and 66 % and only 13 have a net which collects between 67 and 100 % of it. However, at present the administrations are trying to recover this heavily impacted area by means of investment policies aimed to improve the wastewater treatment systems (De Pippo et al. 2006; ISTAT 2007; Legambiente 2012; Novartis Pharma 2012).

This study is part of a large project aimed to contribute to the knowledge of the pollution affecting the Sarno River and its environmental impact on the Gulf of Naples. The

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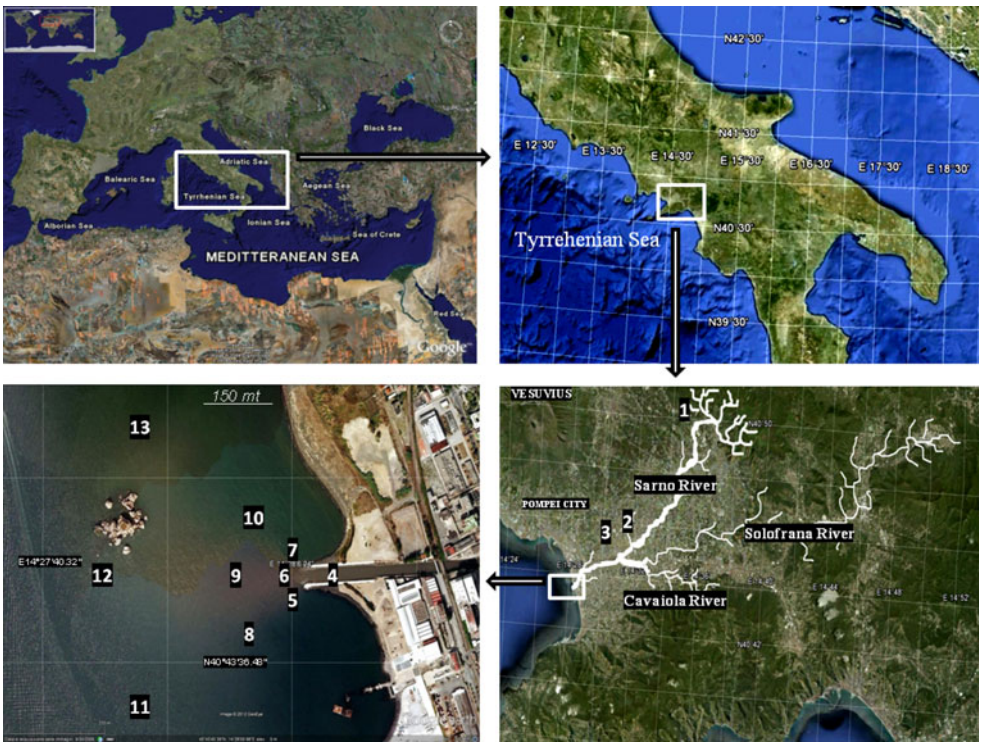

Fig. 1 Map of the study areas and sampling sites in the Sarno River and Estuary, Southern Italy (from Google Earth)

objective of this project is to assess the pollution due to effluents from local industries, agriculture and the urban impact by identifying several groups of organic and inorganic chemicals and some indicators of microbial pollution in water and sediments. This paper reports the data on the contamination caused by the metals drained into the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea).

Metals have been recognized as harmful for both environment and human health when present above certain levels. Exposure to metals has been linked to several human diseases such as developmental retardation or malformation, kidney damage, cancer, abortion, effect on intelligence and behavior (Homady et al. 2002; Banerjee 2003; Alomary and Belhadj 2007). As confirmed by numerous studies, the hydrographic basins appear to be one of the primary locations for metals (Uluturhan et al. 2011; Varol 2011; Kharroubi et al. 2012). They are carried from terrestrial sources through various pathways, such as atmospheric and river transports. The input pathways of heavy metals into aquatic environment include discharge of domestic sewage and industrial wastewater, runoff from non-point sources, and direct dumping of wastes (Abdallah 2007; Alomary and Belhadj 2007; Roig et al. 2011). Water could constitute a direct measure of the degree of aquatic environment. Sediments are natural sinks and environmental reservoirs for metals in the aquatic environment and they offer an irreplaceable aid in reconstructing the input and pollution of metals. Due to the high persistence, metals can accumulate and remain in the sediment for very long periods of time and may be a source of contaminants to aquatic biota. Thus, the assessment of metals in coastal environments is of great importance as these areas could receive considerable amounts of pollutant inputs from land-based sources through coastal discharges, which could potentially threaten the biological resources (Abdallah 2007; Alomary and Belhadj 2007; Accornero et al. 2008; Roig et al. 2011; Kharroubi et al. 2012).

Materials and methods

Sampling points and sample collection

Considering the seasonal variations of the Sarno flow, four intensive sampling campaigns have been conducted in the winter, spring, summer and autumn of 2008. In each campaign four locations were sampled (near the source of the Sarno River, just before and after the junction with Alveo Comune and at the river mouth) in order to have a proper idea of the evolution of the contamination along the river (Fig. 1). Also nine points in the continental shelf around the Sarno mouth were sampled in each campaign to assess the environmental impact of the Sarno River on the Gulf of Naples (Fig. 1). Three points were sampled 50 m from the Sarno River mouth, another three points 150 m away and, finally, another three points 500 m from the river mouth.

For metal analysis, the water samples were collected in an acid-washed cleaned polyethylene bottles. In each sampling point 2.0 L of water (two polyethylene bottles) were collected and transported refrigerated to the laboratory. Water samples were filtered through a previously kiln-fired (400 °C overnight) GF/F glass fiber filter (47 mm × 0.7 μm; Whatman, Maidstone, UK). Filters (suspended particulate matter, SPM) were kept in the dark at −20 °C until analysis. Dissolved phase refers to the fraction of contaminants passing through the filter. This includes the compounds that are both truly dissolved as well as those associated with colloidal organic matter.

Surface sediment (0–20 cm) samples were collected by using a grab sampler (Van Veen Bodemhappe 2 L) and put in aluminium containers. The sediments were transported refrigerated to the laboratory and kept at −20 °C before analysis.

Metal extraction and analyses

Dissolved samples (filtered samples) were immediately acidified with 0.1 N HNO_3 (Wilken and Hindelman 1991). Sediment samples were homogenized and reduced to a fine powder. Sediment and particulate matter (filters) samples were digested in microwave digestion system (Milestone 1200) with a HNO_3–HF–$HClO_4$ acid mixture solution in a three-step digestion process. Sample solutions and reagent blanks were analyzed for As (hydride vapour generation analysis method) and Hg (mercury reduction vapour atomization method) by atomic absorption spectroscopy (Shimadzu AA-6800) and Cd, Cr, Cu, Ni, Pb and Zn by graphite furnace atomic absorption with a Shimadzu ACS-6100 auto sampler. The instrumental conditions were those recommended in user's handbook of the instrument. To minimize the matrix effect, a second aliquot of prepared samples, spiked with the analyte of interest and analyzed exactly the same, and immediately after, the samples were carried out. All reagent blanks and matrix interference were monitored throughout the analyses, and were below the instrument detection limit. The detection limits for metals in the dissolved phase were As: 2.0 μg l^{-1}, Hg: 0.1 μg l^{-1}, Cd: 0.05 μg l^{-1}, Cr: 1.0 μg l^{-1}, Cu: 0.1 μg l^{-1}, Ni: 0.2 μg l^{-1}, Pb: 0.4 μg l^{-1} and Zn: 0.1 μg l^{-1}. The concentration were calculated from the calibration curves for the eight metals (Trace CERT-Fluka, Buchs, Switzerland) ($r^2 > 0.97$). Intercalibration sediment (SD-MEDPOL-1/TM) samples (from the International Laboratory of Marine Radioactivity, IAEA, Monaco) were used as a control for the analytical methods. The values obtained (in mg kg^{-1} dry wt.) for the analysis of six replicates of this sample were as follows: Hg (certified 0.168 ± 0.017; found 0.167 ± 0.015), As (certified 316. ± 16.0; found 322.4 ± 7.9), Cd (certified 0.153 ± 0.033; found 0.151 ± 0.021), Cr (certified 136.0 ± 10.0; found 139.5 ± 7.2), Cu (certified 30.8 ± 2.6 found 32.4 ± 1.8), Ni (certified 39.4 ± 3.1; found 38.7 ± 2.9), Pb (certified 26.0 ± 2.7; found 26.7 ± 1.82), Zn (certified 101.0 ± 8.0; found 99.3 ± 5.1).

Statistical analysis and calculation of metals inputs

Data analysis was performed with the statistical software SPSS, version 14.01 for Windows (SPSS Inc., Chicago, IL, USA). All data was presented as the mean ± SD. The level of significance was set at $p \leq 0.05$.

The method used to estimate the annual contaminant discharges (F_{annual}) was based on the UNEP guidelines (UNEP/MAP 2004) and has been widely accepted (Walling and Webb 1985; HELCOM 1993; Steen et al. 2001). A flow-averaged mean concentration (C_{aw}) was calculated for the available data, which was corrected by the total water discharge in the sampled period. The equations used were the following:

$$C_{aw} = \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \quad (1)$$

$$F_{annual} = C_{aw} Q_T \quad (2)$$

where C_i and Q_i are the instantaneous concentration and the daily averaged water flow discharge, respectively for each sampling event (flow discharge, section and bed elevation of river mouth were measured by manual probes). Q_T represents the total river discharge for the period considered (Feb 08–Nov 08), calculated by adding the monthly averaged water flow. River flow data was collected from the register of the Autorità di Bacino del Sarno to http://www.autoritabacinosarno.it (Campania Government for the Environment). Furthermore, to study the temporal contaminant discharge variation, C_i and Q_i were considered for each campaign and expressed as kg day^{-1}.

Results and discussions

Metals in the water dissolved phase, suspended particulate matter and sediment samples

As shown in Table 1, the concentrations of total selected metals obtained in the dissolved phase (DP) ranged from 0.32 (site 1) to 1680.4 (site 11) μg l^{-1} with a mean value of 311.78 μg l^{-1}. In detail, they ranged from 3.10 to 28.57 μg l^{-1} with a mean value of 11.32 μg l^{-1} for As, from 0.1 to 0.74 μg l^{-1} for Hg, from 0.03 to 0.79 μg l^{-1} for Cd, from 41.63 to 1669.84 μg l^{-1} for Cr, from 0.11 to 9.51 μg l^{-1} for Cu, from 0.47 to 22.11 μg l^{-1} for Ni, from 0.41 to 10.47 μg l^{-1} for Pb and from 0.14 to 5.17 μg l^{-1} for Zn. Many studies, and in particular the most recent, reported concentrations of metals found in the water as the

Table 1 Description of the sampling sites, concentration of metals in the water dissolved phase (DP) samples of the Sarno River and the continental shelf, Southern Italy, and USEPA water quality criteria values

Sampling location				Metals (μg l^{-1})								
Site number identification	Site characteristics	Site location	Campaigns	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Total
1 (River water)	Sarno River source	40°48′54.03″N 14°36′45.36″E	May	ND	ND	ND	ND	0.18	ND	ND	0.17	0.46
			Aug	ND	ND	ND	ND	1.02	0.71	0.62	0.69	3.04
			Nov	ND	ND	ND	ND	0.11	ND	ND	0.14	0.32
			Feb	ND	ND	ND	ND	1.25	0.81	0.56	0.97	3.58
2 (River water)	Upstream Alveo comune	40°46′42.73″N 14°34′00.48″E	May	11.03	0.12	0.10	86.35	1.35	0.86	0.50	1.13	101.44
			Aug	5.18	ND	0.12	263.76	2.24	8.60	1.28	4.15	285.38
			Nov	8.22	0.10	0.06	60.45	0.91	0.58	0.44	1.10	71.84
			Feb	5.75	0.11	0.10	340.38	1.99	5.96	0.84	2.10	357.25
3 (River water)	After Alveo comune	40°46′00.34″N 14°33′10.68″E	May	16.58	0.23	0.12	321.60	1.42	4.63	1.26	2.18	348.01
			Aug	10.27	0.18	0.57	358.44	6.41	9.98	9.42	4.45	399.71
			Nov	10.63	0.21	0.09	385.92	1.03	3.38	1.03	2.68	404.98
			Feb	5.32	0.18	0.42	257.29	3.79	12.11	6.98	2.37	288.45
4 (River water)	Sarno River mouth	40°43′42.62″N 14°28′07.89″E	May	15.44	0.19	ND	145.26	1.85	6.44	5.68	2.89	177.75
			Aug	8.06	0.23	0.38	377.08	9.51	10.98	3.31	3.92	413.49
			Nov	12.51	0.21	0.21	232.42	1.57	5.47	7.50	3.21	263.11
			Feb	20.02	0.23	0.31	243.31	5.16	12.55	2.51	3.36	287.46
5 (Sea water)	River mouth at 50 mt south	40°43′40.11″N 14°28′06.45″E	May	28.57	0.20	0.09	173.97	4.34	7.53	1.62	3.08	219.39
			Aug	8.49	0.46	0.45	813.98	9.10	22.11	10.47	1.27	866.33
			Nov	14.62	0.36	0.12	243.55	3.62	6.28	1.78	2.83	273.16
			Feb	13.16	0.29	0.79	1249.93	8.12	16.41	7.45	1.07	1297.21
6 (Sea water)	River mouth at 50 mt central	40°43′42.46″N 14°28′05.03″E	May	21.97	0.48	0.18	441.45	3.70	11.53	2.90	1.39	483.60
			Aug	17.08	0.26	0.17	96.68	3.17	7.39	9.87	1.66	136.28
			Nov	18.37	0.63	0.28	485.60	3.19	9.91	2.29	1.31	521.57
			Feb	22.04	0.74	0.30	187.15	2.54	5.91	7.70	2.18	228.56
7 (Sea water)	River mouth at 50 mt north	40°43′45.09″N 14°28′05.17″E	May	23.94	0.18	0.21	245.79	1.16	2.65	2.19	2.14	278.26
			Aug	12.14	0.53	0.03	383.61	4.91	2.94	3.38	2.43	409.95
			Nov	16.72	0.11	0.24	221.21	1.53	3.49	2.69	3.07	249.06
			Feb	13.38	0.10	0.07	250.58	4.38	2.64	4.33	2.45	277.91
8 (Sea water)	River mouth at 150 mt south	40°43′35.68″N 14°28′02.94″E	May	21.21	0.13	0.17	243.37	1.91	1.23	3.98	2.43	274.43
			Aug	11.27	0.26	0.50	41.63	4.46	2.42	2.14	0.66	63.33
			Nov	19.43	ND	0.11	194.70	1.59	1.02	3.14	2.21	222.29
			Feb	14.86	0.10	0.55	76.14	3.20	4.31	2.59	1.14	102.89
9 (Sea water)	River mouth at 150 mt central	40°43′42.25″N 14°27′59.97″E	May	10.09	0.16	0.14	162.46	1.77	2.89	1.27	1.43	180.21
			Aug	8.11	0.14	0.74	496.75	2.52	0.47	1.02	0.86	510.60
			Nov	11.86	0.14	0.25	97.48	1.61	2.63	1.09	1.60	116.65
			Feb	10.63	0.12	0.38	356.57	2.50	0.77	2.09	1.22	374.28
10 (Sea water)	River mouth at 150 mt north	40°43′49.26″N 14°27′59.82″E	May	14.67	ND	ND	127.98	2.26	0.78	1.53	1.77	148.99
			Aug	5.61	ND	0.26	93.89	1.25	1.92	2.51	1.32	106.85
			Nov	9.23	0.23	0.24	179.17	1.74	0.60	1.44	1.57	194.21
			Feb	7.99	0.22	0.15	81.88	1.39	1.71	1.52	1.37	96.24
11 (Sea water)	River mouth at 500 mt south	40°43′30.31″N 14°27′58.93″E	May	5.67	0.11	0.11	114.86	1.89	1.27	0.68	1.24	125.84
			Aug	4.38	ND	0.09	1669.84	0.56	2.76	1.11	1.58	1680.39
			Nov	6.52	0.17	0.09	102.23	1.59	1.07	0.97	1.62	114.26
			Feb	5.59	0.27	0.09	1002.85	1.13	2.52	1.11	1.55	1015.12

Table 1 continued

Sampling location				Metals (μg l^{-1})								
Site number identification	Site characteristics	Site location	Campaigns	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Total
12 (Sea water)	River mouth at 500 mt central	40°43′42.29″N 14°27′46.41″E	May	3.74	0.18	0.07	691.54	1.45	0.96	0.88	1.31	700.13
			Aug	5.65	0.19	0.09	59.86	1.68	1.22	1.20	0.51	70.40
			Nov	4.54	0.14	0.08	850.60	1.62	1.07	0.78	1.20	860.04
			Feb	3.16	0.14	0.08	53.38	1.09	1.06	0.60	0.57	60.07
13 (Sea water)	River mouth at 500 mt north	40°43′57.85″N 14°27′48.68″E	May	8.78	0.15	0.05	44.77	1.58	1.13	0.63	0.83	57.92
			Aug	3.87	0.42	0.08	128.02	0.69	7.29	1.74	2.87	144.97
			Nov	4.03	0.21	0.05	64.47	1.08	0.77	0.41	0.72	71.74
			Feb	3.10	0.19	0.11	257.22	1.06	4.38	1.76	5.17	272.98
USEPA water quality criteria value[a] (in μg l^{-1})		CMC = criterion maximum concentration a measure of acute toxicity		340 (69)	1.4 (1.8)	2 (40)	586[b] (1.1)	(4.8)	470 (74)	65 (210)	120 (90)	
		CCC = criterion continuous concentration a measure of chronic toxicity		150 (36)	0.77 (0.94)	0.25 (8.8)	85[b] (50)	(3.1)	52 (8.2)	2.5 (8.1)	120 (81)	
Samples percentage over the CMC for freshwater (site 1–4)				0	0	0	0	/	0	0	0	
Samples percentage over the CMC for saltwater (site 5–13)				0	0	0	100	8	0	0	0	
Samples percentage over the CCC for freshwater (site 1–4)				0	0	25.0	68.7	/	0	37.5	0	
Samples percentage over the CCC for saltwater (site 5–13)				0	0	0	94.4	30	11.0	5.5	0	

[a] Freshwater values and in parentheses saltwater values

[b] Cr(III) and Cr(VI) reference limits sum

sum of the DP and SPM, and not separately. Therefore, it's difficult to make a proper comparison between the concentrations of metals in DP samples found in this study and those from other polluted aquatic environments. Nevertheless, Table 3 shows that concentrations of metals in DP from the Sarno River and Estuary were higher than those found in the Ebro River (Spain), by Roig et al. (2011) for As, Hg, Cd, Cr and Ni, but lower for Pb and Zn. With the exception of Hg and Cu, metals levels in the Sarno River and Estuary were higher than those measured in the Gediz River (Eastern Aegean), by Kucuksezgin et al. (2008).

The concentrations of metals in the suspended particulate matter (SPM) samples range from 103.6 μg l^{-1} (15.9 mg kg^{-1} dry weight) in site 1 to 7734.5 μg l^{-1} (143.5 mg kg^{-1} dry weight) in site 4 (mean value of 2574.2 μg l^{-1}), as shown in Table 2. In detail, they ranged from 1.94 to 106.76 μg l^{-1} with a mean value of 31.83 μg l^{-1} for As, from 0.06 to 134.2 μg l^{-1} for Hg, from 0.03 to 0.62 μg l^{-1} for Cd, from 14.1 to 1149.7 μg l^{-1} for Cr, from 36.3 to 809.8 μg l^{-1} for Cu, from 3.3 to 1009.3 μg l^{-1} for Ni, from 1.02 to 4063.5 μg l^{-1} for Pb and from 59.4 to 3327.2 μg l^{-1} for Zn. Compared with other polluted rivers, estuaries and coasts in the Mediterranean Sea (Table 3), the concentrations of metals in the SPM samples from the Sarno River and Estuary were much higher than those found in the Ebro River (Spain) by Roig et al. (2011) and, with the exception of Hg, in the Gediz River (Eastern Aegean), by Kucuksezgin et al. (2008).

The concentrations of metals in the sediment samples are illustrated in Table 4 (relating to only 1 month of sampling: May 2008). Results ranged from 90.69 (site 1) to 2470.27 (site 4) mg kg^{-1} with a mean value of 1,257.65 mg kg^{-1}. The concentrations detected ranged from 0.24 to 69.30 mg kg^{-1} with a mean value of 22.44 mg kg^{-1} for As, from 0.2 to 1.02 mg kg^{-1} for Hg, from 0.39 to 2.92 mg kg^{-1} for Cd, from 23.77 to 514.40 mg kg^{-1} for Cr, from 33.64 to 580.18 mg kg^{-1} for Cu, from 1.58 to 651.70 mg kg^{-1} for Ni, from 0.47 to 1658.10 mg kg^{-1} for Pb and from 55.00 to 802.88 mg kg^{-1} for Zn. Compared with other polluted rivers, estuaries and coasts in the Mediterranean Sea (Table 3), the concentrations of As in the sediment samples from the Sarno River and Estuary were much higher than those found in the Ebro River (Spain), by Roig et al. (2011), in the Vlora Bay (Albania), by Rivaro et al. (2011) and in the Gulf of Naples (Italy), by Romano et al. (2004); but lower than those reported in the Naples Harbour (Italy), by Sprovieri et al. (2007). The concentration levels of Hg in the sediment samples were much higher than those found in the Gediz River (Eastern Aegean), by Kucuksezgin et al. (2008), in the

Table 2 Description of the sampling sites and concentration of metals in the water suspended particulate matter (SPM) samples of the Sarno River and the continental shelf, Southern Italy

Sampling location				Metals (μg l^{-1})										
Site number identification	Site characteristics	Site location	Campaigns	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Total (μg l^{-1})	Filter weight (mg)	Total (mg kg^{-1})
1 (River water)	Sarno River source	40°48′54.03″N	May	ND	ND	ND	ND	40	6	1	66	114	5.5	20.6
		14°36′45.36″E	Aug	ND	ND	ND	ND	65	3	2	61	132	7.3	18.1
			Nov	ND	ND	ND	ND	36	7	1	59	104	6.5	15.9
			Feb	ND	ND	ND	ND	59	5	3	72	139	6.3	22.0
2 (River water)	Upstream Alveo comune	40°46′42.73″N	May	9.6	0.07	0.06	78	293	86	71	487	1025	2.3	445.7
		14°34′00.48″E	Aug	11.2	101.43	0.05	59	489	87	45	348	1140	8.6	132.6
			Nov	18.8	8.02	0.06	69	407	68	93	586	1250	8.2	152.5
			Feb	17.2	7.35	0.06	63	501	68	102	595	1354	6.3	214.9
3 (River water)	After Alveo comune	40°46′00.34″N	May	11.2	0.12	0.14	611	334	364	746	839	2906	43.3	67.1
		14°33′10.68″E	Aug	21.5	132.65	0.62	610	547	1009	697	845	3864	47.4	81.5
			Nov	27.5	11.77	0.36	819	375	299	1671	1091	4294	5.0	858.9
			Feb	35.4	15.12	0.57	1150	629	835	1203	1732	5600	13.9	402.9
4 (River water)	Sarno River mouth	40°43′42.62″N	May	19.9	0.19	0.13	87	275	543	1673	870	3469	33.0	105.1
		14°28′07.89″E	Aug	76.5	134.20	0.50	248	687	496	1003	1634	4280	136.8	31.3
			Nov	44.2	18.91	0.23	247	370	733	3078	1045	5536	77.2	71.7
			Feb	99.1	42.35	0.42	440	810	661	2355	3327	7734	53.9	143.5
5 (Sea water)	River mouth at 50 mt south	40°43′40.11″N	May	31.9	0.11	0.09	157	375	652	218	1285	2719	66.4	41.0
		14°28′06.45″E	Aug	65.3	98.40	0.16	221	472	711	589	1278	3436	546.0	6.3
			Nov	58.7	25.09	0.20	323	505	920	343	1798	3973	99.1	40.1
			Feb	106.8	45.62	0.23	255	522	931	1211	2825	5896	88.0	67.0
6 (Sea water)	River mouth at 50 mt central	40°43′42.46″N	May	23.3	0.19	0.20	618	754	953	764	260	3372	42.9	78.6
		14°28′05.03″E	Aug	51.2	32.43	0.48	512	449	320	164	138	1668	160.2	10.4
			Nov	43.8	18.71	0.34	1081	664	829	1000	208	3843	126.0	30.5
			Feb	68.8	29.42	0.59	636	544	655	370	274	2577	85.2	30.2
7 (Sea water)	River mouth at 50 mt north	40°43′45.09″N	May	18.5	0.24	0.14	32	281	326	601	829	2087	49.8	41.9
		14°28′05.17″E	Aug	78.4	52.54	0.22	70	262	993	280	418	2153	181.3	11.9
			Nov	52.9	22.60	0.30	58	340	290	1290	580	2634	102.4	25.7
			Feb	61.4	26.24	0.42	77	351	910	527	480	2434	90.7	26.8
8 (Sea water)	River mouth at 150 mt south	40°43′35.68″N	May	21.8	0.20	0.15	219	83	321	2453	285	3385	80.1	42.3
		14°28′02.94″E	Aug	23.8	62.40	0.08	429	160	895	2525	306	4403	94.4	46.6
			Nov	39.6	16.93	0.15	393	73	421	2760	328	4033	60.2	67.0
			Feb	37.8	16.17	0.14	521	164	755	3091	361	4947	92.0	53.8

Table 2 continued

Sampling location				Metals (μg l^{-1})										
Site number identification	Site characteristics	Site location	Campaigns	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Total (μg l^{-1})	Filter weight (mg)	Total (mg kg^{-1})
9 (Sea water)	River mouth at 150 mt central	40°43′42.25″N 14°27′59.97″E	May	17.9	0.12	0.10	258	253	189	2188	419	3326	63.4	52.5
			Aug	41.1	57.60	0.31	459	414	208	1743	341	3264	128.8	25.3
			Nov	40.2	17.18	0.28	329	309	155	3122	524	4496	90.8	49.5
			Feb	48.6	20.77	0.51	788	426	287	4063	377	6012	78.7	76.4
10 (Sea water)	River mouth at 150 mt north	40°43′49.26″N 14°27′59.82″E	May	9.7	0.09	0.18	102	324	88	125	480	1129	64.1	17.6
			Aug	35.8	24.40	0.06	109	387	150	502	599	1808	142.9	12.7
			Nov	17.3	7.39	0.14	138	427	99	150	417	1257	84.3	14.9
			Feb	19.3	8.24	0.13	188	336	187	623	726	2087	91.1	22.9
11 (Sea water)	River mouth at 500 mt south	40°43′30.31″N 14°27′58.93″E	May	1.9	0.08	0.09	126	240	95	219	322	1004	65.2	15.4
			Aug	12.4	25.30	0.17	173	460	115	494	226	1505	94.1	16.0
			Nov	5.1	2.17	0.26	162	375	92	356	425	1416	45.2	31.3
			Feb	7.5	3.19	0.43	159	510	78	292	457	1508	82.3	18.3
12 (Sea water)	River mouth at 500 mt central	40°43′42.29″N 14°27′46.41″E	May	8.2	0.06	0.14	484	88	244	58	298	1180	62.3	18.9
			Aug	11.4	16.40	0.05	65	194	42	60	718	1107	91.8	12.1
			Nov	15.1	6.46	0.17	537	98	261	53	385	1356	48.7	27.8
			Feb	16.8	7.18	0.13	101	263	93	86	1237	1804	153.2	11.8
13 (Sea water)	River mouth at 500 mt north	40°43′57.85″N 14°27′48.68″E	May	9.5	0.12	0.06	85	275	106	84	447	1008	67.5	14.9
			Aug	5.7	27.60	0.03	14	99	29	87	111	373	92.6	4.0
			Nov	16.6	7.09	0.05	69	339	92	95	511	1128	43.3	26.1
			Feb	11.6	4.95	0.08	45	137	89	89	209	586	61.2	9.6

Table 3 Concentration ranges and mean value of metals in the sediments (mg kg^{-1}), in the water dissolved phase (DP) (μg l^{-1}), the suspended particulate matter (SPM) (μg l^{-1}) from recent studies of different rivers, estuaries and coasts in the Mediterranean Sea

Area	References	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn
Seyhan River, Turkey	Davutluoglu et al. (2011)	–	–	–	46–121[c]	6–57[c]	82–214[c]	11–74[c]	32.2–146[c]
Gediz River, Eastern Aegean	Kucuksezgin et al. (2008)	0.10–0.81[a]	0.10–0.81[a]	–	–	0.21–1.6[a]	0.39–9.0[a]	0.39–1.5[a]	0.19–2.9[a]
		–	120–430[b]	–	41–237[b]	30–180[b]	100–510[b]	190–8.100[b]	10–80[b]
		–	0.27–0.46[c]	–	59–494[c]	15–148[c]	35–175[c]	59–198[c]	34–196[c]
Tigris River, Turkey	Varol (2011)	–	–	0.7–4.9[c]	28–163[c]	11–5075[c]	74–288[c]	73–393[c]	60–247[c]
Homa Lagoon, Turkey	Uluturhan et al. (2011)	–	0.22–0.48[c]	0.06–0.19[c]	83–129[c]	10.3–25.8[c]	58–108[c]	2.4–17.2[c]	46.2–91.9[c]
Algerian Mediterrean sea	Alomary and Belhadj (2007)	–	–	0.1–2.3[c]	2.6–18.9[c]	1.1–10.4[c]	0.8–54.9[c]	1.3–11.5[c]	5.3–45.7[c]
Ebro River, Spain	Roig et al. (2011)	0.99[a]	0.22[c]	0.18[c]	8.84[a]	–	11.8[a]	16.3[a]	40.1[a]
		0.95[b]	–	–	0.37[b]	–	0.7[b]	1.5[b]	10.4[b]
		4.39[c]	–	–	0.18[c]	–	1.9[c]	3.1[c]	7.2[c]
Sea-Boughrara Lagoon, Tunisia	Kharroubi et al. 2012)	–	–	1.1–3.1[c]	–	14–56[c]	–	22–29[c]	39–160[c]
Berre Lagoon, France	Accornero et al. (2008)	–	–	6.2–60.2[c]	0.8–9.5[c]	0.3–1.4[c]	0.7–2.1[c]	17.4–78.9[c]	0.8–2.4[c]
El-Mex Bay, Egypt	Abdallah (2007)	–	–	3.8–8[c]	–	14–22[c]	–	–	64–305[c]
Vlora Bay, Albania	Rivaro et al. (2011)	9.0–32.6[c]	0.01–3.06[c]	0.06–0.29[c]	132–308[c]	22.3–46.1[c]	117–326[c]	9.6–20.1[c]	59.9–109[c]
Gulf of Naples, Italy	Romano et al. (2004)	33–66[c]	0.1–0.3[c]	0.01–0.90[c]	–	3–664[c]	0.01–26.70[c]	23–433[c]	77–1765[c]
Fratta -Gorzone, Italy	Giusti and Taylor (2007)	–	–	0.3–0.9[c]	64.5–2822[c]	13.3–65.5[c]	11.8–54.3[c]	9.0–46.4[c]	13–194[c]
Naples Harbour, Italy	Sprovieri et al. (2007)	1–1121[c]	0.01–139[c]	0.01–3[c]	7–1798[c]	12–5743[c]	4–362[c]	19–3083[c]	17–7234[c]
Venice Lagoon, Italy	Zonta et al. (2007)	–	0.5–4.8[c]	0.4–4[c]	14–66[c]	10–92[c]	8–59[c]	50–131[c]	97–524[c]
Po River, Italy	Farkas et al. (2007)	–	–	1.0–3.7[c]	–	31.7–187[c]	52.4–161[c]	32.0–98.5[c]	178–645[c]
Taranto Gulf, Italy	Annicchiarico et al. (2007)	–	0.1–11.5[c]	0.1–0.4[c]	–	5.7–149[c]	0.9–57[c]	10.6–137[c]	–
This study (mean + Sd)	DP	3.10–28.57[a]	0.05–0.74[a]	0.03–0.79[a]	42–1670[a]	0.11–9.51[a]	0.04–22.11[a]	0.03–10.47[a]	0.14–5.17[a]
		(11.3 ± 6.2)	(1.02 ± 0.14)	(0.21 ± 0.18)	(313.7 ± 326.1)	(2.51 ± 2.08)	(4.39 ± 4.13)	(2.59 ± 2.34)	(1.87 ± 1.10)
	SPM	1.9–106.8[b]	0.06–134.2[b]	0.03–0.62[b]	14–1150[b]	36–810[b]	3.3–1009.3[b]	1.0–4063.5[b]	59–3327[b]
		(31.8 ± 25.2)	(24.1 ± 32.7)	(0.2 ± 0.16)	(301.5 ± 276.0)	(343.8 ± 189.0)	(362.5 ± 329.3)	(873.5 ± 742.7)	(664.2 ± 644.9)
	Sediment	0.24–69.3[c]	0.19–1.02[c]	0.39–2.9[c]	24–514[c]	34–580[c]	1.6–651.7[c]	0.5–1658.1[c]	55–803[c]
		(22.4 ± 18.6)	(0.42 ± 0.23)	(1.23 ± 0.76)	(177.6 ± 138.2)	(235.3 ± 144.6)	(124.5 ± 180.6)	(335.8 ± 202.8)	(396.9 ± 190.7)

[a] DP

[b] SPM

[c] Sediment

Table 4 Description of the sampling sites (month of sampling: May 2008) and concentration of metals in the sediment samples (mg kg^{-1} dw) of the Sarno River and the continental shelf, Southern Italy

Sampling location			Metals								
Site number identification	Site characteristics	Site location	As	Hg	Cd	Cr	Cu	Ni	Pb	Zn	Total
1 (River water)	Sarno River source	40°48′54.03″N 14°36′45.36″E	0.24	<0.2	0.5	ND	33.64	1.58	0.47	55.00	90.69
2 (River water)	Upstream Alveo comune	40°46′42.73″N 14°34′00.48″E	34.35	0.31	1.75	174.27	172.44	37.93	57.13	324.90	768.42
3 (River water)	After Alveo comune	40°46′00.34″N 14°33′10.68″E	23.68	0.51	1.63	274.48	238.73	181.99	162.09	599.54	1458.46
4 (River water)	Sarno River mouth	40°43′42.62″N 14°28′07.89″E	16.94	0.45	1.02	161.46	171.99	19.58	1658.10	458.12	2470.27
5 (Sea water)	River mouth at 50 mt South	40°43′40.11″N 14°28′06.45″E	69.30	0.56	0.89	198.79	469.35	311.06	176.72	802.88	1959.70
6 (Sea water)	River mouth at 50 mt central	40°43′42.46″N 14°28′05.03″E	44.24	1.02	2.92	514.40	580.18	651.70	389.88	173.00	2312.07
7 (Sea water)	River mouth at 50 mt North	40°43′45.09″N 14°28′05.17″E	19.92	0.58	2.10	310.02	234.00	102.78	434.93	591.89	1675.70
8 (Sea water)	River mouth at 150 mt South	40°43′35.68″N 14°28′02.94″E	11.73	0.31	0.71	111.78	119.10	13.56	1147.91	317.16	1710.21
9 (Sea water)	River mouth at 150 mt central	40°43′42.25″N 14°27′59.97″E	30.13	0.24	0.39	86.43	204.07	135.24	76.83	349.08	852.04
10 (Sea water)	River mouth at 150 mt North	40°43′49.26″N 14°27′59.82″E	15.25	0.36	1.53	177.32	224.87	33.25	135.23	436.15	1008.35
11 (Sea water)	River mouth at 500 mt South	40°43′30.31″N 14°27′58.93″E	10.96	0.21	0.53	58.68	285.84	33.18	81.20	344.50	803.93
12 (Sea water)	River mouth at 500 mt central	40°43′42.29″N 14°27′46.41″E	6.77	0.23	0.60	40.40	141.48	64.40	18.12	347.80	612.80
13 (Sea water)	River mouth at 500 mt North	40°43′57.85″N 14°27′48.68″E	8.25	0.25	0.75	23.77	183.61	31.77	26.94	360.00	626.83
I_{geo}	Background values defined by Turekian and Wedepohl (1961)		5[a]	0.07[b]	0.05[c]	90	45	68	20	95	
	I_{geo} Max value computed		0.82	0.03	0.82	0.07	0.14	0.09	0.36	0.07	
	Quality of studied sediment according to Muller classes (1969)		From unpolluted to moderately polluted (0–1)								
TEL (mg kg^{-1} dw)[d]			7.2	0.13	0.6	52.3	18.7	15.9	30.2	124	
Samples percentage over the TEL			85	92	69	77	100	85	77	92	
PEL (mg kg^{-1} dw)[d]			42	0.49	3.50	160.4	108.2	42.8	112.2	271	
Samples percentage over the PEL			15.3	31	0	54	92	46	54	85	
ERL (mg kg^{-1} dw)[d]			8.2	0.15	1.2	81.0	43.0	20.9	46.7	150	
Samples percentage over the ERL			85	92	38	69	92	77	77	92	
ERM (mg kg^{-1} dw)[d]			70	0.71	9.6	370	270	51.6	218	410	
Samples percentage over the ERM			0	8	0	8	23	46	31	38	
Mean contamination factors (CFs) for all sites studied			4.49	5.51	23.0	1.82	5.23	1.83	16.79	4.18	

[a] Metal background values from Salomons and Forstner (1984) for shallow-water sediments

[b] Hg value from Buccolieri et al. (2006)

[c] European Union Risk Assessment Report (2007)

[d] MacDonald et al. (1996) and Long et al. (1998)

Homa Lagoon (Turkey), by Uluturhan et al. (2011), and in the Gulf of Naples (Italy), by Romano et al. (2004); but lower than those reported in the Vlora Bay (Albania), by Rivaro et al. (2011), in the Venice Lagoon (Italy), by Zonta et al. (2007), and in the Naples Harbour (Italy), by Sprovieri et al. (2007). At all sites, Ni concentration in the sediment samples of Sarno Rivers and its estuary exceeded the literature data reported in Table 3 (Romano et al. 2004; Abdallah 2007; Alomary and Belhadj 2007; Annicchiarico et al. 2007; Giusti and Taylor 2007; Farkas et al. 2007; Sprovieri et al. 2007; Zonta et al. 2007; Kucuksezgin et al. 2008; Davutluoglu et al. 2011; Roig et al. 2011; Rivaro et al. 2011; Varol 2011; Uluturhan et al. 2011; Kharroubi et al. 2012). Excluding Naples Harbour (Italy), Fratta-Gorzone (Italy) and Tigris River (Turkey), the concentrations of Cr, Cu, Pb and Zn in the sediment samples from the Sarno River and Estuary were higher than those in literature data reported in Table 3. On contrast, Cd contents in the present study were lower than those measured in the Tigris River (Turkey), by Varol (2011), in the Sea-Boughrara Lagoon (Tunisia), by Kharroubi et al. (2012), in the Berre Lagoon (France), by Accornero et al. (2008), in the El-Mex Bay (Egypt), by Abdallah (2007), in the Venice Lagoon (Italy), by Zonta et al. (2007), and in the Naples Harbour (Italy), by Sprovieri et al. (2007) and in the Po River (Italy), by Farkas et al. (2007).

Metals distribution in the water dissolved phase, suspended particulate matter and sediment samples in different seasons and loads into the Tyrrhenian Sea

The partition coefficients (Kp, defined as the ratio of the concentration of a chemical associated with sediment to that in the SPM: $Kp = C_{Sediment}/C_{SPM}$) showed an decreasing trend in the metals (C_M) partitioning from SPM to sediments ($C_{M\text{-}SPM}/C_{M\text{-}Sediment}$ mean value of 1.67 ± 0.727), and from SPM to DP ($C_{M\text{-}SPM}/C_{M\text{-}DP}$ mean value of 24.43). These results show that higher levels of selected metals were found in SPM samples than DP and sediment samples, which are an indication of fresh inputs of this metals in the Sarno River and its estuary. Moreover, higher levels of selected metals found in SPM samples than their corresponding sediment samples indicate that gravitational sedimentation and suspension processes are mainly in this area with subsequent transfer of metals between water bodies and sediment. This is also confirmed that the selected metals found in SPM samples were the same as those detected in sediment samples and generally reflected a similar pattern. Furthermore, more abundant metals in SPM samples than in DP and sediment samples lead use to consider that metals are principally transported by particulate matter during flood events (GESAMP/UNESCO 1987; GESAMP/UNESCO 1994; Dassenakis et al. 1995; Force et al. 1998).

The spatial distribution of selected metals in DP, SPM and sediment samples from the Sarno River and its estuary were studied by comparing the concentrations of metals in different sampling sites in dry and rainy seasons, respectively. The results, summarized in Fig. 2, show a similar trend. Indeed, the level of contamination of selected metals in the Sarno River clearly increases from location 1 to 4. In general, the upland part of the Sarno River was less contaminated by metals. Where the river flows through the Sarno flatland and through different urban agglomerations, the concentration of selected metals increased to 1,536.62 μg l^{-1} (DP + SPM mean value of four seasons) at location 2 (Upstream Alveo Comune). The concentration of selected metals then increased to 4,652.83 μg l^{-1} (DP + SPM mean value of four seasons) at location 3 (After Alveo Comune). This increase in metals concentrations resulted from the inflow from the Alveo Comune (30–50 m^3 s^{-1}), which carries the discharge of another industrial district. In the lower part of the Sarno River (location 4, Sarno Estuary), the concentration increased again, reaching 5,395.12 μg l^{-1}.

The metals loading into the Tyrrhenian Sea occurs through various transport pathways including storm water runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, atmospheric deposition, and dredged material disposal. The total selected metals loads contribution to the Tyrrhenian Sea from the Sarno River is calculated in about 13,977.53 kg $year^{-1}$. In detail, the load is about 186.6 kg $year^{-1}$ for As, 123.9 kg $year^{-1}$ for Hg, 1.38 kg $year^{-1}$ for Cd, 1274.47 kg $year^{-1}$ for Cr, 1362.56 kg $year^{-1}$ for Cu, 1556.97 kg $year^{-1}$ for Ni, 5126.04 kg $year^{-1}$ for Pb and 4345.54 kg $year^{-1}$ for Zn. Unfortunately, many studies don't report the annual loads of metals

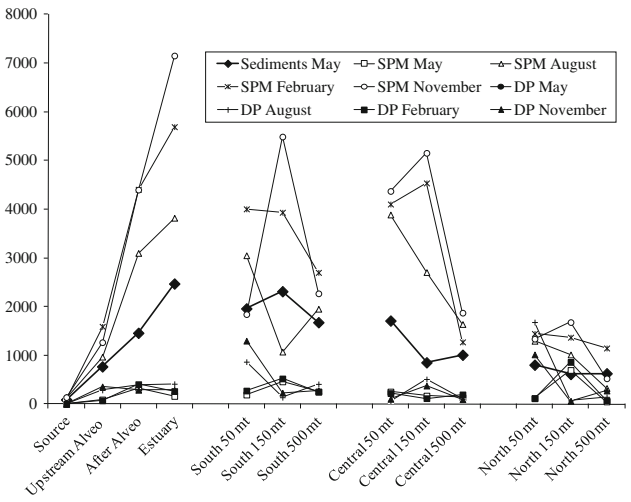

Fig. 2 Spatial and temporal concentration of total heavy metals in the water dissolved phase (DP, ng l^{-1}), the suspended particulate matter (SPM, ng l^{-1}) and the sediments (ng g^{-1} dry wt) of the Sarno River and the continental shelf, Southern Italy

from rivers. Therefore, it's difficult to make a proper comparison between the annual load of metals found in this study and those from other rivers. Nevertheless, Table 5 shows the annual loads of metals from some rivers along the Turkish Black Sea coast (Tuncer et al. 1998; Kucuksezgin et al. 2008). With the exception of Pb, metal loads from the rivers along the Turkish Black Sea coast are higher than Sarno River. In the Tyrrhenian Sea, around the Sarno plume, metals concentrations range in general from very low in offshore areas to very high in the vicinity of the river outflows. At 50 m of river outflow, the concentration of selected metals were close to those of the Sarno estuary. The concentrations at the sampling sites then increased at 150 m and less at 500 m of river outflows. Moreover, Fig. 2 shows that the concentration of selected metals at the central estuary were close to those at the southern estuary, decreasing northward. These results allow us to conclude that although some of the selected metals loads from the Sarno inputs are headed northwards, most of them move into the Tyrrhenian sea southward.

Quality guidelines and metals concentrations in the Sarno River and Estuary

In this work, the "National Recommended Water Quality Criteria" (USEPA 2009) to evaluate the quality of waters was used. In Table 1, the CCC (criterion continuous concentration—a measure of chronic toxicity) and CMC (criterion maximum concentration—a measure of acute toxicity) for Cr is Cr(III) and Cr(VI) sum due to the unavailability of CMC and CCC for total Cr in the criteria. It is shown in Table 1, As, Hg, Zn were the only metals which showed values below the CMC and CCC values. Cd was the metal which showed values below the CMC value, but a percentage of samples (25 %) presented values above the CCC for Freshwater. At all sites, Cr concentration in the water of Sarno Rivers and its estuary exceeded the CMC and CCC for Saltwater and CCC for Freshwater in 100, 94.4 and 69 % of samples respectively. Regarding Cu, the samples percentage over the CMC and CCC values was 8.3 and 81 %. A percentage of samples (11 %) above the CCC for Saltwater was observed for Ni. Pb concentration in the water of Sarno Rivers and its estuary exceeded only the CCC values in 37.5 and 5.5 % (Table 1). Therefore, it can be concluded from these results that, the most concerned metals in water body of Sarno Rivers and its estuary may pose some potential risks.

Table 5 Annual load of metals from rivers along the Turkish Black Sea coast and Sarno River (kg year^{-1})

Metals	Sakarya[a]	Fylios[a]	Kizilirmak[a]	Yesilirmak[a]	Sarno
Cd	110	240	300	190	1.38
Pb	2,400	4,400	8,500	5,800	5,126
Cu	70,000	139,800	31,100	11,100	1,362
Zn	11,000	155,600	231,000	186,900	4,345
Discarge (km^3 yt^{-1})	3.57	3.12	7.63	7.17	2.52

[a] From Tuncer et al. 1998

The Index of Geoaccumulation (I_{geo}), derived by Müller (1969), is a popularly method which was used to evaluate the degree of enrichment and pollution of sediment quantificationally. The I_{geo} value was calculated by the following equation:

$$I_{geo} = \frac{\mathrm{Log}_2(C_n)}{K(B_n)} \quad (3)$$

where C_n is the concentration of chemical element in sediment samples, the unit of C_n is mg/kg; K is the changing coefficient of background data which is related to the difference of rock component, the value of k is 1.5; B_n is global geochemistry background data of the specific element in viscidity deposit rock. According to Müller's research conclusion, the geoaccumulation index consists of seven classes (1969). Class 0 (practically unpolluted): Igeo $\leq$ 0; Class 1 (unpolluted to moderately polluted): 0 $<$ Igeo $<$ 1; Class 2 (moderately polluted): 1 $<$ Igeo $<$ 2; Class 3 (moderately to heavily polluted): 2 $<$ Igeo $<$ 3; Class 4 (heavily polluted): 3 $<$ Igeo $<$ 4; Class 5 (heavily to extremely polluted): 4 $<$ Igeo $<$ 5; Class 6 (extremely polluted): Igeo $>$ 5. In order to evaluate the studied sediment quality, the computed geoaccumulation index (Igeo) based on background values defined by Turekian and Wedepohl (1961) and by Buccolieri et al. (2006) showed similar values (Table 4). In both the Sarno River and estuary sediment areas, the computed Igeo values showed that metals are considered as unpolluted to moderately polluted.

Another assessment was made according to the sediment quality guidelines (SQGs), based on the total amount of contaminants, which was established for both freshwater and marine ecosystems in North America. To assess the ecotoxicological implications of the total metal concentrations in the sediments, two sets of SQGs developed for aquatic ecosystems were also considered in this study (Table 3) (MacDonald et al. 1996; Long et al. 1998). These sets are defined as: (i) effect range low (ERL)/effect range median (ERM) and (ii) the threshold effect level (TEL)/probable effect level (PEL). ERLs and TELs represent chemical concentrations below which the probability of toxicity and other effects are minimal. Differently, the ERMs and PELs represent mid-range above which adverse effects were more likely, although not always expected. ERLs-ERMs and TELs-PELs represent a possible-effects range, within which negative effects would occasionally

occur (Annicchiarico et al. 2007). The comparison of pollutants levels with SQGs, showed that As concentrations were above the TEL, PEL ERL and ERM values in 85, 15, 85 and 0 % respectively of all samples (Table 4). Regarding the Hg, the concentrations in these sediment samples were higher than their respective TEL, PEL ERL and ERM values in 92, 31, 92 and 8 % of all samples, respectively. The sediment concentrations of Cd at all sampling stations were below the PEL or ERM, but exceed TEL and ERL value in 69 and 38 percent of all samples, respectively. Also Cr content exceeds the TEL, PEL ERL and ERM values in 77, 54, 69 and 8 % respectively of all samples. TEL, PEL ERL and ERM values were exceeded for Cu in 100, 92, 92 and 23 % respectively of all samples, for Ni in 85, 46, 77 and 46 %, for Pb in 77, 54, 77 and 31 % and for Zn in 92, 85, 92 and 38 % (Table 4). Based on SQGs approach, therefore, the Sarno Rivers and its estuary would be considered as an area in which the ecological integrity is possibly at risk.

Finally, the Contamination Factor (CF) is the ratio obtained by dividing the concentration of each metal in the sediment by baseline or background value (concentration in uncontaminated sediment):

$$\mathrm{CF} = \frac{C_{Heavy\ metals}}{C_{Background}} \quad (4)$$

CF values were interpreted as suggested by Hakanson (1980), where: $\mathrm{CF} < 1$ indicates low contamination; $1 < \mathrm{CF} < 3$ is moderate contamination; $3 < \mathrm{CF} < 6$ is considerable contamination; and $\mathrm{CF} > 6$ is very high contamination. In this work, also the Contamination Factor to evaluate the quality of sediment samples was used. The results of contamination factors (CFs) are presented in Table 4. The mean CF values for Cd and Pb were >6, which denotes a "very high contamination" by these metals. The CF values for As, Hg, Cu and Zn showed a "considerable contamination", while the CF values for Cr and Ni indicated a "moderate contamination".

In summary, based on "National Recommended Water Quality Criteria" (USEPA 2009) approach, the results show that the concentrations of selected metals in water samples of Sarno Rivers and its estuary may pose some potential risks. About sediment samples, the computed Igeo values showed that Sarno river and its estuary is considered as unpolluted to moderately polluted. At same time, the comparison of pollutants levels with SQGs showed an area in which the integrity is possibly at risk. Finally, the CF approach denotes a "considerable contamination". Therefore, these dissimilar results suggest that the guidelines derived in one region will not be relevant for all regions, because, for example, biochemical reaction rates and biological activity increase exponentially with temperature (Chapman et al. 2006; Sánchez-Avila et al. 2010).

Conclusions

This study is the first to document a comprehensive analysis of metals levels in the Sarno River and its estuary; it has provided very useful information for the evaluation of trace metals levels in this river and its input into the Tyrrhenian sea, which is part of the Mediterranean sea. The results show that higher levels of metals were found in SPM samples than DP and sediment samples, which are an indication of fresh inputs of these compounds in the Sarno River and its estuary. Moreover, higher levels of selected metals found in sediment samples than their corresponding water bodies (DP and SPM samples) indicate that gravitational sedimentation are mainly in this area with subsequent transfer of the metals between sediment and water bodies. The results show that these areas are the main contribution sources of metals levels into the Tyrrhenian Sea and, although some of the metals levels from the Sarno River inputs move northwards, the majority of it moves into the Tyrrhenian Sea southward. In relation to the National Recommended Water Quality Criteria and sediment quality guidelines assessment (SQGs), the selected metals concentrations quantified in the water and sediments from the Sarno River and its estuary do not seem to cause immediate effects on the degeneration of the aquatic environment; but a relatively elevated level of contaminants suggest a best management to protect the river from further contamination. Consequently, periodical monitoring of the level of pollution, control the mixing of effluent of the concentration of metals, environmental remediation, treatment of industrial effluent and municipal wastewater are recommended.

References

Abdallah MAM (2007) Speciation of trace metals in coastal sediments of El-Mex Bay South Mediterranean Sea-west of Alexandria (Egypt). Environ Monit Assess 132:111–123

Accornero A, Gnerre R, Manfra L (2008) Sediment concentrations of trace metals in the Berre Lagoon (France): an assessment of contamination. Arch Environ Contam Toxicol 54:372–385

Alomary AA, Belhadj S (2007) Determination of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) by ICP-OES and their speciation in Algerian Mediterranean Sea sediments after a five-stage sequential extraction procedure. Environ Monit Assess 135:265–280

Annicchiarico C, Biandolino F, Cardellicchio N, Di Leo A, Giandomenico S, Prato E (2007) Predicting toxicity in marine sediment in Taranto Gulf (Ionian Sea, Southern Italy) using Sediment Quality Guidelines and a battery biomassa. Ecotoxicology 16:239–246

Arienzo M, Adamo P, Bianco MR, Violante P (2001) Impact of land use and urban runoff on the contamination of the Sarno River basin in southwestern Italy. Water, Air, & Soil Pollut 131: 349–366

Banerjee AD (2003) Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environ Pollut 123:95–105

Buccolieri A, Buccolieri G, Cardellicchio N, Dellatti A, Dilee A, Maci A (2006) Heavy metals in marine sediments of Taranto gulf, Ionian sea, Southern Italy. Mar Chem 99:227–235

Chapman PM, McDonald BG, Kickham PE, McKinnon S (2006) Global geographic differences in marine metals toxicity. Mar Pollut Bull 52:081–1084

Dassenakis M, Degaita A, Scoullos M (1995) Trace metals in sediments of a Mediterranean estuary affected by human activities (Acheloos river estuary, Greece). Sci Total Environ 168:19–31

Davutluoglu OI, Seckin G, Ersu CB, Yilmaz T, Sari B (2011) Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey. J Environ Manage 92:2250–2259

De Pippo T, Donadio C, Guida M, Petrosino C (2006) The case of Sarno River (Southern Italy): effects of geomorphology on the environmental impacts. Environ Sci Pollut Res Int 13:184–191

European Union Risk Assessment Report (2007) Cadmium oxide and cadmium metal Part I environment, 3rd Priority List Volume: 72

Farkas A, Erratico C, Vigano L (2007) Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. Chemosphere 68:761–768

Force MJL, Fendorf SE, Li GC, Schneider GM, Rsenzweing RF (1998) Heavy metals in the environment. A laboratory evaluation of trace elements mobility from flooding and nutrient loading of Coeur d'Alene river sediments. J Environ Qual 27:318–328

GESAMP/UNESCO (1987) Land/sea boundary flux of contaminants: contributions from rivers. Rep Stud 32:67–81

GESAMP/UNESCO (1994) Anthropogenic influences on sediment discharge to the coastal zone and environmental consequences. Rep Stud 52:4–20

Giusti L, Taylor A (2007) Natural and anthropogenic contamination of the Fratta-Gorzone river (Veneto, Italy). Environ Monit Assess 134:211–231

Hakanson L (1980) An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res 14:975–1001

HELCOM (1993) Second baltic sea pollution load compilation. Baltic Sea environment Proceedings No. 45, Baltic marine environment protection commission. Helsinki, Finland

Homady M, Hussein H, Jiries A, Mahasneh A, Al-Nasir F, Khleifat K (2002) Survey of some heavy metals in sediments from vehicular service stations in Jordan and their effects on social aggression in prepubertal male mice. Environ Res 89:43–49

ISTAT (2007) Bilancio demografico Anno 2007 e popolazione residente al 31 dicembre. http://demo.istat.it/. Accessed 12 May 2012

Kharroubi A, Gargouri D, Baati H, Azri C (2012) Assessment of sediment quality in the Mediterranean Sea-Boughrara lagoon exchange areas (southeastern Tunisia): GIS approach-based chemometric methods. Environ Monit Assess 184:4001–4014

Kucuksezgin F, Uluturhan E, Batki H (2008) Distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean). Environ Monit Assess 141:213–225

Legambiente (2012) Sarno, l'inquinamento preoccupa. Sondaggio di Legambiente sul disinquinamento del fiume. http://www.legambienteonline.it/news2001/sarno3.html. Accessed 12 May 2012

Long ER, Field LJ, MacDonald DD (1998) Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ Toxicol Chem 17:714–727

MacDonald DD, Carr RS, Calder FD, Long ER (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5:253–278

Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. GeoJournal 2:108–118

Novartis Pharma (2012) Salute, Sicurezza e Ambiente. http://www.novartis.it/downloads/media/salute2002. Accessed 12 May 2012

Rivaro P, Cullaj A, Frache R, Lagomarsino C, Massolo S, De Mattia MC, Ungaro N (2011) Heavy metals distribution in suspended particulate matter and sediment collected from Vlora Bay (Albania): a methodological approach for metal pollution evaluation. J Coast Res Special Issue 58:54–66

Roig N, Nadal M, Sierra J, Ginebreda A, Schuhmacher M, Domingo JL (2011) Novel approach for assessing heavy metal pollution and ecotoxicological status of rivers by means of passive sampling methods. Environ Int 37:671–677

Romano E, Ausili A, Zharova N, Magno MC, Pavoni B, Gabellini M (2004) Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. Mar Pollut Bull 49:487–495

Salomons W, Forstner U (1984) Metals in the hydrocycle. Springer, Berlin

Sánchez-Avila J, Quintana J, Ventura F, Tauler R, Duarte CM, Lacorte S (2010) Stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry: an effective tool for determining persistent organic pollutants and nonylphenol in coastal waters in compliance with existing Directives. Mar Pollut Bull 60:103–112

Sprovieri M, Feo ML, Prevedello L, Salvagio Manta D, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (Southern Italy). Chemosphere 67:998–1009

Steen RJCA, van der Baart M, Hiep B, van Hattum WP, Cono WP, Brinkman UATh (2001) Gross fluxes and estuarine behaviour of pesticides in the Scheldt estuary (1995–1997). Environ Pollut 115:65–79

Tuncer G, Karakas T, Balkas TI, Gokcay CF, Aygnn S, Yurteri C (1998) Land-based sources of pollution along the Black Sea coast of Turkey: concentrations and annual loads to the Black Sea. Mar Pollut Bull 36:409–423

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soc of Am Bull 72:175–192

Uluturhan E, Kontas A, Can E (2011) Sediment concentrations of heavy metals in the Homa Lagoon (Eastern Aegean Sea): assessment of contamination and ecological risks. Mar Pollut Bull 62:1989–1997

UNEP/MAP (2004) Guidelines for river (including estuaries) pollution monitoring programme for the Mediterranean Region. MAP technical reports series no. 151. UNEP/MAP, Athens

USEPA (2009) National recommended water quality criteria

Varol M (2011) Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J Hazard Mater 195:355–364

Walling DE, Webb BW (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Mar Pollut Bull 16:488–492

Wilken RD, Hindelman H (1991) Mercury in sediments and suspended particles from the river Elbe, North Germany. Water Air Soil Pollut 56:27–437

Zonta R, Botter M, Cassin D, Pini R, Scattolin M, Zaggia L (2007) Sediment chemical contamination of a shallow water area close to the industrial zone of Porto Marghera (Venice Lagoon, Italy). Mar Pollut Bull 55:529–542