Bull. Environ. Contam. Toxicol. (1994) 52:13–18
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Bulletin of Environmental Contamination and Toxicology

Distribution of Inorganic and Organic Pollutants in River Sediments in Campania, Italy

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The aim of the present study was to investigate the pollution status of sediment in two Campania rivers, by focusing both on chemical analysis of some major contaminants, and on sediment-induced toxicity in sea urchin fertilization and embryogenesis. Here we report the data of pollutant distribution in a number of selected sampling sites, whereas toxicity data are reported elsewhere (Pagano et al. 1993). The rivers investigated were the Sarno River and its tributary, the Solofrana Stream, and the Volturno River and its drainage system, the Regi Lagni, as depicted in Figure 1. The Sarno River and Solofrana Stream are affected by multiple pollution sources of industrial, domestic and agricultural origin, and are located in a densely populated area. The Volturno River was expected to be less polluted, since wastewater from the Volturno River lowland is disposed of in its drainage system, the Regi Lagni. An earlier report by Amodio-Cocchiari and Arnese (1988), however, provided evidence for chemical pollution in the Volturno River; thus it appeared worthwhile to extend available information on the pollution status of these water bodies. In particular, the study was both aimed at providing comparative information on pollution and toxicity of water and sediment in the two rivers, and to obtain up-to-date information that could be used as a reference for future clean-up interventions.

MATERIALS AND METHODS

A total of ten sampling sites in the Volturno (V) and the Sarno (S) River were located in the Campania region (Southern Italy) in the provinces of Naples, Salerno and Caserta; the sites were the following: 1) Ciorlano (V.1, a relatively "pristine" site); 2) Alife (V.2); 3) Capua (V.3); 4) Grazzanise (V.4); 5) Castelvolturno (V.5, Volturno River estuary); 6) Villa Literno (V.6, Regi Lagni mouth); 7) Mercato S. Severino (S.1, a very polluted site in the Solofrana Stream); 8) Nocera Inferiore (S.2); 9) S. Marzano (S.3, an agricultural site), and 10) Castellammare di Stabia (S.4, Sarno River mouth). Topographic details and pollution sources of sampling sites have been described by Pagano et al. (1993).

Water samples were collected year-round, biweekly (1 July 1988 to 30 June 1989) by using an iron sampler (made in the workshop of GM's institute). The sampler, containing 0.5-L polypropylene bottles, was immersed midstream at a 20- to 50-cm depth (except for sites S.1 and S.2). Sampling bottles were washed in hot tap water, soaked in distilled water overnight and rinsed 3x in river water just prior to sampling. Samples were carried at 4°C to the laboratory and processed within 5 hr upon arrival.

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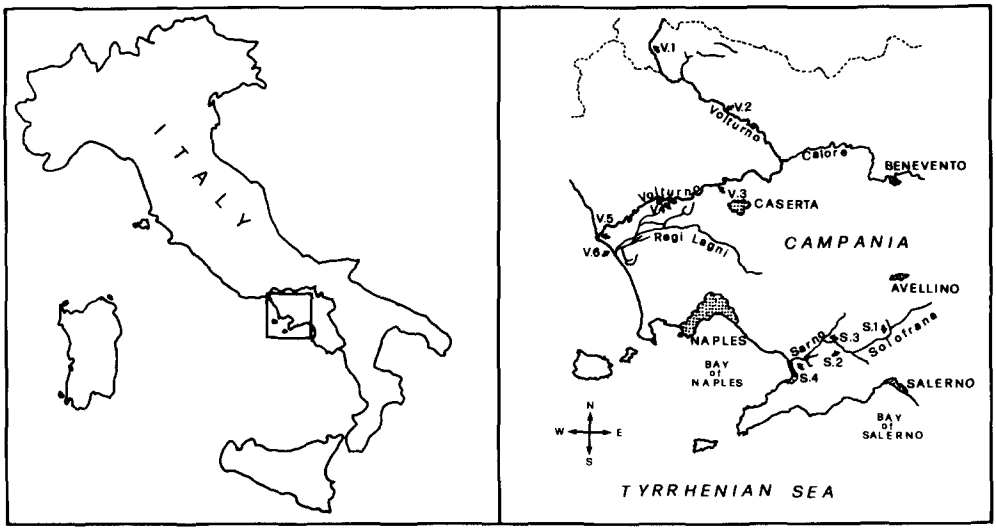

Figure 1. Location of sampling sites (from Pagano et al. 1993, reproduced with permission of Springer Verlag)

Sediment samples were collected with a bucket, drawing an approx. 3-cm layer; they were maintained at approx. 4°C and processed upon arrival at the laboratory. Each water sample was analyzed for COD and BOD_5, according to Standard Methods (APHA 1989); other water analyses, such as nitrogen content and microbial flora will be reported elsewhere; early determinations of inorganic contaminants failed to show any relevant data and were discontinued. Sediment samples were subjected to the following analyses: a) inorganic contaminants; b) organic contaminants (organochlorine, organophosphate and organonitrogen pesticides) (Luke et al. 1981; Osselton and Snelling 1986; Stan 1989), and c) domestic sewage microflora (to be reported elsewhere). Appropriate standards were run along with environmental samples for each determination of both inorganic and organic contaminants. In all cases, analytical data were referred to on a dry weight basis (following a 48-hr dehydration at 60°C). For inorganic analysis (As, Cd, Cr, Cu, Mn, Pb, and Zn), 50-g aliquots of dry sediment samples were extracted by acid mineralization (in sulfuric, perchloric and nitric acids, 7:3:1); extracts were air-dried at 180°c, and dissolved repeatedly in bidistilled water up the disappearance of acid fumes; eventually, the extracts were resuspended in 20 mL bidistilled water, and pH was adjusted at approx. 5.5; inorganics were then analyzed by plasma emission atomic spectrophotometry (Beckman, USA). To analyze pesticide residues, 50-g aliquots of sediment samples were homogenized in acetonitrile 1:5 (wt/vol) with 10 g NaCl; homogenates were centrifuged at 3,600xg for 10 min, and supernatant was filtered whereas sediment was soaked in acetonitrile 1:5 for 24 hr. The soaked sediment was spun again at 3,600xg for 10 min and the two supernatants were pooled. Acetonitrile extracts were vacuum-concentrated by Rotavapor at 40°C, re-extracted in toluene, dehydrated with anhydrous sodium sulphate, and filtered with a 0.45 μm nylon filter. Eluates were concentrated under a N_2 flow, and the residues were redissolved in 1 mL hexane and analyzed by gas chromatography (DANI mod.5000, Italy), capillary column ultra 1HP in He 2 mL/min at 100°C for 4 min, 100°C to 150°C for 30°C/min, and thereafter up to 260°C for 3°C/min, injector at 250°C and detector at 275°C. The following detectors were used: a) ECD; b) NPD, and c) FID detectors (DANI). Residue recovery was evaluated by adding a known amount (final concentration

3 μg/g) of Alachlor, Methoxychlor and Dichlorvos (Riedel de Haen, Netherlands) to each sample; these chemicals were used as internal standards, and their recovery was approx. 65 to 70%. The choice of these standard residues was due to the lack of any positive finding for these pesticides in test samples; other residue levels were then referred to the above standards. Each sediment sample was subjected to five consecutive extractions, and the eluate of the last extraction was referred to as the blank.

RESULTS AND DISCUSSION

The results of BOD_5 testing in water samples showed that upper Sarno River sites (S.1 and S.2), and the Regi Lagni mouth (V.6) displayed very high BOD_5, as shown in Table 1; the data of these sites exceeded the limit of 20 mg/L BOD_5 for surface water in 42 out 50 determinations. Both the Sarno River mouth (S.4) and the Volturno River estuary (V.5) failed to display any excess BOD_5. COD values paralleled BOD_5, pointing to a hypoxic status for 3 out of 4 Sarno River sites and for V.6 site; however, some discrepancies were observed as, e.g., for V.5 site, suggesting the occurrence of non-biodegradable organic contaminants (Table 1).

Table 1. Water sample determinations of BOD_5 (mg/L) and COD (mg/L) in four Sarno River and six Volturno River sampling sites (depicted in Figure 1). Analyses were carried out 1 July 1988 through 30 June 1989. (n) = number of replicates for BOD_5 (n_1) and COD (n_2); data are reported as means ± SD *[range]*.

Sites	(n_1)	BOD_5	(n_2)	COD
S.1	(17)	192.4 ± 139.3 *[60 - 535]*	(18)	647.2 ± 439.8 *[300 - 1700]*
S.2	(17)	84.4 ± 72.5 *[30 - 300]*	(18)	300.6 ± 193.1 *[60 - 750]*
S.3	(17)	7.1 ± 11.0 *[0 - 30]*	(18)	39.2 ± 44.3 *[10 - 200]*
S.4	(17)	22.1 ± 14.9 *[0 -60]*	(18)	89.2 ± 40.3 *[60 - 240]*
V.1	(5)	12.0 ± 13.0 *[0 - 30]*	(9)	10.0 ± 9.7 *[0 -30]*
V.2	(6)	18.3 ± 25.6 *[0 - 60]*	(11)	15.2 ± 7.1 *[0 -25]*
V.3	(5)	23.0 ± 19.2 *[0 - 45]*	(15)	26.3 ± 21.5 *[10 - 90]*
V.4	(8)	8.1 ± 15.6 *[0 -45]*	(18)	33.9 ± 20.6 *[10 - 100]*
V.5	(15)	7.0 ± 7.0 *[0 -20]*	(18)	75.8 ± 95.2 *[10 - 430]*
V.6	(16)	36.2 ± 17.2 *[10 - 60]*	(18)	131.4 ± 30.5 *[75 - 210]*

As reported in Table 2, the analysis of 7 inorganic contaminants in sediment samples showed a dramatic excess of chromium in site S.1 (8.2 μg/g, as expected from the

presence of leather tanneries) and, quite surprisingly, an even higher Cr level in S.3 sediment (27.3 μg/g); this site also showed excess Zn levels (14.2 μg/g), as well as the highest As and Cu levels among the 6 sampling sites.
The results of pesticide analysis in sediment samples are shown in Tables 3 and 4, and refer to 9 organochlorine and 12 organophosphate/organonitrogen residues, respectively. The sediment samples from the Sarno River and Regi Lagni sites S.1, S.3, S.4 and V.6 showed detectable levels of 11 to 14 out of 21 pesticide residues; on the other hand, sites V.3 and V.5 displayed detectable, but low, levels for only 3 pesticide residues. Furthermore, some residue levels appeared to be highest in some of the most polluted sites, e.g., furalaxyl at sites S.4 and V.6, malathion at sites S.3 and S.4, sethoxidym at site V.6 and endosulfan at site S.1.

Table 2. Inorganic contaminant levels in sediment samples from six sites at the Sarno and the Volturno River. Means from five determinations ± SD. Detection limits (DL) were referred to extracts from 50-g aliquots of dry sediment samples; the following DL's were recognized (expressed as ng/g dry weight; wavelengths are reported as nm in square parenthesis): As 32 [193.7]; Cd 2 [228.8]; Cr 2.8 [285.0]; Cu 0.8 [324.7]; Mn 0.24 [280.3]; Pb 4 [368.3]; Zn 4 [206.2].

Contaminants	Sampling Sites					
(μg/g dry wt)	S.1	S.3	S.4	V.3	V.5	V.6
Arsenic	3.2 ± 1.9	5.5 ± 2.2	4.7 ± 1.7	3.7 ± 1.4	3.6 ± 1.6	3.4 ± 1.9
Cadmium	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
Chromium	8.2 ± 3.4	27.3 ± 9.8	0.8 ± 0.2	3.3 ± 1.6	1.4 ± 0.6	2.1 ± 1.1
Copper	1.8 ± 0.7	5.6 ± 1.3	5.3 ± 2.0	4.5 ± 1.8	2.1 ± 1.1	1.9 ± 0.8
Lead	0.4 ± 0.2	0.5 ± 0.2	0.5 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	0.5 ± 0.3
Manganese	21.9 ± 9.6	25.6 ± 9.2	46.9 ± 10.5	19.1 ± 7.3	31.2 ± 9.5	32.6 ± 11.6
Zinc	2.0 ± 0.8	14.2 ± 2.1	5.2 ± 1.4	6.6 ± 2.1	2.8 ± 0.7	2.6 ± 0.9

Table 3. Organochlorine pesticide levels in sediment samples from six sites at the Sarno and the Volturno River. Means from five determinations ± SD; bdl = below detection limit. The following DL's were recognized (reported as pg/g dry wt): Aldrin 1.5; p,p'DDD 0.7; p,p'DDE 0.6; p,p'DDT 0.6; Dieldrin 0.5; Endosulfan 0.3; Endrin 0.4; Heptachlor 2; Lindane 7.

Contaminants	Sampling Sites					
(ng/g dry wt)	S.1	S.3	S.4	V.3	V.5	V.6
Aldrin	45.5 ± 7.9	1.0 ± 0.7	1.3 ± 0.6	0.4 ± 0.1	1.3 ± 0.9	bdl
p,p'-DDD	36.0 ± 8.8	bdl	bdl	bdl	bdl	bdl
p,p'-DDE	28.0 ± 8.3	6.5 ± 0.9	2.6 ± 0.7	bdl	bdl	6.0 ± 0.6
p,p'-DDT	52.0 ± 8.6	11.0 ± 5.6	bdl	bdl	bdl	bdl
Dieldrin	58.0 ± 7.4	5.2 ± 3.2	3.9 ± 2.5	bdl	bdl	bdl
Endosulfan	164.0 ± 12.3	73.0 ± 9.5	54.0 ± 5.4	65.0 ± 9.4	110.0 ± 11.7	39.0 ± 6.2
Endrin	36.0 ± 8.9	3.9 ± 4.1	0.6 ± 0.6	bdl	bdl	11.0 ± 3.1
Heptachlor	25.0 ± 9.2	bdl	bdl	0.6 ± 0.9	bdl	bdl
Lindane	26.0 ± 8.8	bdl	bdl	bdl	bdl	bdl

The above analytical information on the Sarno/Solofrana and Volturno/Regi Lagni systems appears to be consistent with the bioassay toxicity data reported by Pagano et al. (1993) who tested the same samples as in the present study, using sea urchin embryos and sperm (Pagano et al. 1986; 1989). In particular, significant toxicity

Table 4. Organophosphate and organonitrogen pesticide levels in sediment samples from six sites at the Sarno and the Volturno River. Means from five determinations ± SD; bdl = below detection limit. The following DL's were recognized (reported as pg/g dry wt): Dimethoate 9.5; Diphenamid 186; Folpet 122; Furalaxyl 196; Linuron 24; Malathion 240; Metalaxyl 320; Methamidophos 30; Methylparathion 90; Metribuzin 100; Pirimicarb 146; Sethoxidym 30.

Contaminants	Sampling Sites					
(ng/g dry wt)	S.1	S.3	S.4	V.3	V.5	V.6
Dimethoate	13 ± 8	32 ± 9	33 ± 7	bdl	bdl	12 ± 6
Diphenamid	bdl	bdl	bdl	bdl	bdl	1,170 ± 16
Folpet	bdl	bdl	bdl	bdl	bdl	bdl
Furalaxyl	bdl	1,235 ± 26	4,225 ± 37	bdl	bdl	3,120 ± 25
Linuron	bdl	bdl	bdl	bdl	bdl	bdl
Malathion	104 ± 17	1,950 ± 26	1,430 ± 25	bdl	208 ± 19	780 ± 16
Metalaxyl	bdl	1,560 ± 25	bdl	bdl	bdl	bdl
Methamidophos	117 ± 20	130 ± 18	200 ± 15	bdl	bdl	130 ± 16
Methylparathion	6 ± 9	23 ± 7	33 ± 6	bdl	bdl	13 ± 5
Metribuzin	bdl	bdl	12 ± 6	bdl	bdl	220 ± 16
Pirimicarb	bdl	bdl	bdl	bdl	bdl	bdl
Sethoxidym	26 ± 9	13 ± 5	64 ± 8	bdl	bdl	130 ± 17

outcomes were observed for sediments from sites S.1, S.3, S.4 and V.6, coinciding with pollution data reported here; *vice versa*, sediment samples from V.3 and V.5 both displayed scanty pollutant levels and failed to result in any significant toxic outcomes both to sea urchin embryogenesis and to fertilization success.

An important point to note is the excellent correlation between analytical and sea urchin bioassay data. Precisely which toxic agents are responsible for the toxicity manifested in the sea urchin bioassay system is unknown. However, it is most likely that the total toxicity is either the sum or interactions of separate toxicities exerted by the individual components. The parallel between analytical and toxicity data is not surprising in that both organochlorine compounds and inorganic contaminants have all displayed toxic outcomes both in sea urchin embryogenesis and fertilization success (Pagano et al. 1985; 1986; 1988).

It is interesting to note that the water column both showed scanty, if any, detectable contaminant levels and was almost invariably non-toxic to sea urchin embryos and sperm, as reported by Pagano et al. (1993). Regarding BOD_5 and COD data, these are measures of organic content of water, although BOD_5 is a direct measure of oxygen depletion (Marrack 1980). Thus, BOD_5 and COD can be viewed as indirect indicators of toxic pollution, with an inconsistent result in the case of site S.3, showing relatively low BOD_5 and COD levels in the water column, in contrast to a definite sediment toxicity.

The present study points to the possible environmental hazards associated with sediments from the Sarno River and the Regi Lagni drainage system, but not from the Volturno River. Whether these potential hazards may be substantiated in coastal sediments nearby the mouths of the Sarno River and the Regi Lagni is an open question that requires further investigations. The need for a multi-disciplinary approach, involving analytical and toxicological methods appears to be mandatory for future investigations on the environmental impact of sediment and other complex mixtures.

Acknowledgments. This study was performed with partial support of WHO/EURO, Mediterranean Action Plan [ICP/CEH 039 - ITA 127 (G)]. Thanks are due to the following river agencies for support in water sampling: 1) Consorzio di Bonifica (CdB) Agro Nocerino-Sarnese, Nocera I. (Salerno); 2) CdB Sannio Alifano, Piedimonte M. (Caserta), and 3) CdB Bacino Inferiore del Volturno, Caserta.

REFERENCES

American Public Health Association (1989) Standard methods for the examination of water and wastewater, 18th ed. APHA, New York, New York

Amodio-Cocchiari R, Arnese A (1988) Organochlorine pesticide residues in fish from Southern Italian rivers. Bull Environ Contam Toxicol 40:233-239

Luke MA, Froberg JE, Doose GM, Masumoto HT (1981) Improved multiresidue gas chromatographic determination of organophosphorous, organonitrogen and organohalogen pesticides in produce, using flame photometric and electrolytic conductivity detectors. J Ass Off Anal Chem 64:1187-1195

Marrack D (1980) Water and health. In: Trieff NM (ed) Environment and Health. Ann Arbor Science Publ., Ann Arbor, Michigan, p 163

Osselton MD, Snelling RB (1986) Chromatographic identification of pesticides. J Chromat 368:265-271

Pagano G, Cipollaro M, Corsale G, Esposito A, Ragucci E, Giordano GG, Trieff NM (1985) Comparative toxicities of chlorinated biphenyls on sea urchin egg fertilisation and embryogenesis. Mar Environ Res 17:240-244

Pagano G, Cipollaro M, Corsale G, Esposito A, Ragucci E, Giordano GG, Trieff NM (1986) The sea urchin: Bioassay for the assessment of damage from enviromental contaminants. In: Cairns J, Jr (ed) Community Toxicity Testing. American Society for Testing and Materials, Philadelphia, Pennsylvania, p 67

Pagano G, Cipollaro M, Corsale G, Esposito A, Giordano GG, Ragucci E, Trieff NM (1988) Comparative toxicities of benzene, chlorobenzene and dichlorobenzenes on sea urchin embryos and sperm. Bull Environ Contam Toxicol 40:481-488

Pagano G, Corsale G, Esposito A, Dinnel P, Romaña LA (1989) Use of sea urchin sperm and embryo bioassay in testing the sublethal toxicity of realistic pollutant levels. In: Grandjean E (ed) Carcinogenic, Mutagenic, and Teratogenic Marine Pollutants: Impact on Human Health and the Environment. Gulf Publ. Co., Houston, Texas, p 153

Pagano G, Anselmi B, Dinnel PA, Esposito A, Guida M, Iaccarino M, Melluso G, Pascale M, Trieff NM (1993) Effects on sea urchin fertilization and embryogenesis of water and sediment from two rivers in Campania, Italy. Arch Environ Contam Toxicol 25:20-26

Stan HJ (1989) Application of capillary gas chromatography with mass selective detection to pesticide residue analysis. J Chromat 467:85-98

Received January 7, 1993; accepted June 30, 1993.