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Nutrient, heavy metal and organic pollutant composition of suspended and bed sediments in the Rhone River

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Key words: River quality, sediment-bound contaminants, ecotoxicity, statistical relationships.

ABSTRACT

The environmental quality of the Rhone River (Switzerland-France) has been assessed with a geochemical survey of the pollutants bound to suspended sediments. Ten samples were collected between Lake Geneva and the Mediterranean Sea in Nobember 1989 by continuous flow centrifugation and analysed for grain size distribution, carbonate, organic C, N, forms of particulate P, trace metals, and organic compounds (chlorobenzenes, organochlorine pesticides, PCBs, and PAHs). Four bed sediment samples were also studied for comparative purposes. The suspended solids provide lower variance by parameter than the bed sediments and are clearly most suitable for synoptic monitoring.

The Upper Rhone River carries a glacial derived sediment with a low nutrient content, the stretch from Geneva to Lyon provides a sediment dominated by carbonate, and in the Lower Rhone the organic matter and phosphorus are relatively increased, mainly due to wastewater effluents and to an industrial P source. High concentrations of metals and organic micropollutants downstream of Lyon indicate a multiple contamination in the Lower Rhone, whereas more specific inputs are located downstream of Geneva and Arles.

The comparison with data from other polluted major systems, the Rhine, the Niagara and the Detroit rivers, shows on overall similarity confirming that the Rhone quality is degraded downstream of Lyon. The levels of particular concern are for Hg, DDT metabolites which reveal a recent release in the basin, PCBs with a likely high chlorine content, and PAHs.

The statistical evaluation of the compositional variables indicates a limited number of well defined associations, suggesting that the contamination of the suspended sediments results from the combination of numerous and intermittent point and diffuse sources in the Rhone River basin.

Introduction

River sediments are known to play a key role in the adsorption, transport and deposition of contaminants in the environment (Golterman et al. 1983). Bed sediments have been used as integrators of pollution episodes to point out the sources in the Rhone basin (Vernet et al. 1976, Thomas et al. 1984, André and Lascombe 1988, Corvi et al. 1991, Favarger et al. 1991a). Suspended sediments from a variety of river systems have been analysed to study the real time transport of nutrients, metals and organic pollutants and to determine the loading of sediment bound contaminants (Shear and Watson 1977, Frank et al. 1981, Thomas and Frank 1982, Burrus et al. 1990b, Favarger et al. 1991b)

A multi-agency collaborative study was developed to evaluate the toxicity associated with the sediments in the Rhone River between Lake Geneva and the Mediterranean Sea. This survey was intended to provide a "snapshot" of the environmental quality according to physical, chemical and ecotoxicological characteristics. Major emphasis was placed on the evaluation of total suspended solids (SS), though for comparative purposes a number of bed sediments were collected. Grain size analyses of the samples have shown the homogeneous texture of the suspended solids (Santiago et al. 1992). Toxicity bioassays with sediment extracts on *Daphnia magna*, Microtox® and natural phytoplankton demonstrated that toxic acute impacts occur downstream of the urban industrial centres (Geneva, Lyon and Arles), with major inhibitory effects occurring downstream of Lyon (Santiago et al. 1993).

The rough characteristics were shown to change with land physiography. The sediment from the mouth of the Upper Rhone at Bouveret reflects its glacial origin from an alpine watershed (Figure 1). The sediment upstream from Lake Geneva has recently been subjected to detailed textural and geochemical evaluation (Burrus et al. 1989, 1990a, 1990b) and to algal bioassays (Santiago et al. 1989, Santiago and Thomas 1992). The outlet of Lake Geneva is the source of the Lower Rhone, which flows some 540 kilometres through mountainous landscapes and a flood plain to discharge into the Mediterranean, via the delta system in the Camargue. The Saône River, a major tributary, joins the Rhone at Lyon. Main urban centres are Geneva (350 000 inhabitants) and Lyon (1.7 million inhab.) which

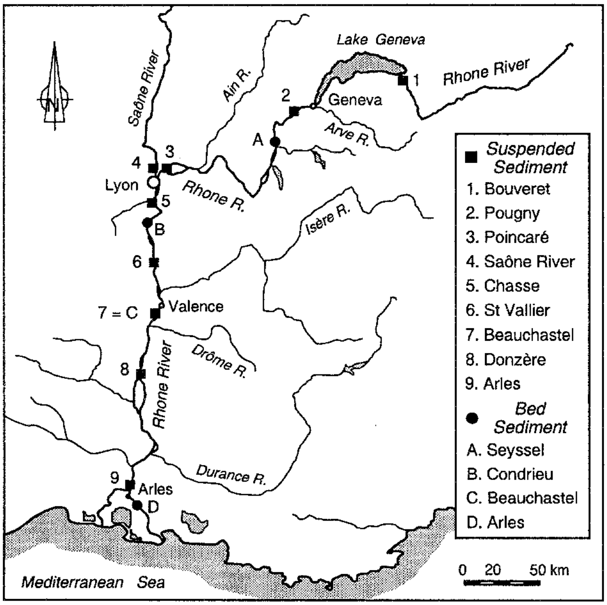


Figure 1. Location of sampling sites in the Rhone River basin

also comprises downstream to Chasse one of the most heavily industrialised zones in France. Additional industrial complexes occur at Roussillon-Péage (upstream from St Vallier) and Tarascon (upstream from Arles). Elsewhere the region is under intense agriculture, mainly cereals upstream from Lyon and arboriculture and viticulture downstream. The river has been harnessed with 20 hydrelectric power plants with associated structures for navigational purposes (André and Lascombe 1988).

In this paper we present the results of a wide range of analyses carried out on both suspended and bed sediment in order to evaluate the status of the Rhone River quality, to obtain some insight into sediment processes based on chemical composition and to make some inferences on the major sources of toxic contaminants.

Materials and methods

Sediment sampling

Bed sediments were sampled during low water flow on July 5th 1989 at Seyssel, Condrieu, Beauchastel and south from Arles, designated as locations A to D respectively (Fig. 1). Near-shore sampling was selective in that finer grained sediments were collected from natural particle traps, between large boulders or downstream of obstructions, on the left river bank other than for D. The samples were kept in a cooler with ice-packs (<12°C) in the field.

Suspended sediments were collected at 9 locations in November 1989, from the 13th to the 16th, with the station at Bouveret and a second sampling at Pougny being taken one week later. Stations are numbered 1 to 9 in a downstream sequence (Fig. 1) and are concordant with those periodically monitored by the French "Agence de l'Eau Rhône-Méditerranée-Corse". For the recovery of the particles, water samples were pumped through 2 continuous flow centrifuges, an Alfa-Laval (Sedisamp system II, Envirodata) and a Westphalia (type KA2-06-175) mounted in the back of a Ford transit bus and operating in parallel. Flow rate for each machine was maintained at 5–6 L/min. Since SS were generally low throughout the river, water processing was carried out for 4 hours at each station, giving a total volume of 2400–2900 litres, to provide sufficient sediment to carry out the total array of required analyses. The dewatering efficiency in these machines is known to be greater than 90% for incoming particles over 0.25 μm (McMillan and Thomas 1977, Ongley and Blachford 1982, Horowitz et al. 1989, Ongley and Thomas 1989, Burrus et al. 1989). A comparative evaluation indicates high similarity in the performance of both centrifuges, as the recovered samples show comparable grain size distributions and heavy metal concentrations (Santiago et al. 1990).

Sediment analysis

On return to the laboratory (<48 hours) subsamples were immediately prepared for the chemical analyses and freeze-dried. Grain size distribution was determined by laser diffraction using a Coulter LS100 particle size analyser following ultrasonic dispersal in distilled water (Loizeau et al. 1994).

Carbonate was measured by CO_2 volumetry after HCl digestion (Jaquet et al. 1971), organic carbon by titrimetry following acid oxidation (Gaudette et al. 1974), and total nitrogen after the method of Kjeldahl (1883). The forms of particulate phosphorus were determined following the fractionation scheme of Williams et al. (1976) as modified by Burrus et al. (1990a, 1990b). Th P bound to organic matter (OP) is obtained by HCl extraction after calcination (at 550°C) following an acid extraction of inorganic P. The procedure used for the P adsorbed to hydrated non-crystalline oxides and defined as non-apatite inorganic P (NAIP) differs from the scheme of Williams et al. (1976) in that the CDB (Na-citrate-dithionite-bicarbonate) extraction is omitted. Only a NaOH extraction is used to estimate the NAIP, which provides a better estimate of the fraction bioavailable to phytoplankton than the complete procedure (Williams et al. 1980, Sonzogni et al. 1982, Young et al. 1985). Finally the P incorporated in the mineral apatite (AP) and occluded forms of inorganic P are extracted with HCl after the NAIP procedure.

The metals Cr, Cu, Fe, Mn, Ni, Pb and Zn were analysed by multi-channel inductively coupled plasma/atomic emission spectroscopy on an ARL 3400 instrument, following digestion in teflon bombs heated to 150 °C in a perchloric, hydrofluoric and hydrochloric acid mixture (Favarger 1982). Arsenic was measured by ICP/AES with an hydride generator. Cadmium was determined by graphite furnace atomic absorption spectrometry and mercury by cold vapour AAS (Hach and Ott 1968), after digestion of the sediment at 95 °C with concentrated HNO_3 and HCl.

For the organic analysis, a 10 g sample of wet sediment was extracted twice with 100 mL pesticide grade hexane/acetone (1 : 1) solution by sonication for 3 minutes. After settling, the extract was passed through a prewashed celite column, reduced to 100 mL on a rotary evaporator and mixed with 100 mL reagent water. After shaking of the 2 phase mixture and separation, the water layer was back extracted with 200 mL methylene chloride (DCM), and this latter combined with the hexane isolate. The resulting extract was dried with anhydrous sodium sulfate, exchanged with 50 mL iso-octane as the keeper solvent, concentrated to 4 mL on the rota-evaporator and finally diluted to 10 mL with iso-octane. A 5 mL aliquot was then fractionated on 3 % deactivated silica gel into fractions A (elution with 40 mL hexane) and B (60 mL of 1 : 1 DCM/hexane). After elution, 10 mL of iso-octane were added to each fraction, the solutions concentrated to 2 mL and diluted back to 5 mL of iso-octane. The organic sulfur in fraction A was removed with 0.2 mL of distilled mercury.

Chlorobenzenes and organochlorine pesticides were analysed by gas chromatography (GC) with ^{63}Ni electron capture detectors and dual capillary columns (phases SPB1 and SPB5). The injected sample was split after 0.5 min onto the two columns. The initial oven temperature of 80 °C was maintained for 2 min, then programmed at 4 °C/min to 280 °C and holding for 16 min. Injector and detector temperatures were 250 °C and 300 °C respectively. The carrier gas was hydrogen (column head pressure of 13 p.s.i.) and with argon/methane as the makeup gas (flow rate of 30 L/min). Polychlorinated biphenyls were determined as total PCBs by packed column GC. The samples were analysed isothermally at 190°C, argon/methane being used both as the carrier gas and the makeup gas (flow rate of 30 L/min). A 1 : 1 : 1 by volume mixture of Aroclors 1242 : 1254 : 1260 served as the standard, giving 24 distinct peaks. In order to report PCBs it was necessary to qualitatively observe a pattern of peaks similar to the standard with a minimum of 8 matching peaks required for quantification. The polynuclear aromatic hydrocarbons (PAHs) were determined by GC with electron impact, multiple ion monitoring mass spectrometric detection. The identification was based on both the retention time and the ratios of the selected ions characteristic of the analyte. The initial oven temperature of 70 °C was held for 3 min, programmed at 10 °C/min to 300 °C and holding for 10 min. The ion source of the mass spectrometer was maintained at 150 °C. The carrier gas was helium with a column head pressure of 10 p.s.i. Detection limits for the various compounds

Table 1. Grain size characteristics, nutrient and heavy metal concentrations (dry weight) in the suspended and bed sediments of the Rhone River

Station	1	2-A	2-B	3	4	5	6
Location	Bouveret	Pougny	Pougny	Poincaré	Saône Riv.	Chasse	St Vallier
KD[*]	−286.0	−185.5	−185.5	−7.3	−6.5	+19.0	+75.3
Sampling date in 1989	21-Nov	13-Nov	20-Nov	13-Nov	14-Nov	14-Nov	15-Nov
Flow discharge[**] (m^3/s)	126	184	185	285	250	590	590
Conductivity (µS/cm)	274	301	315	334	454	405	456
Suspended solids (mg/L)	34.7	6.0	8.2	12.0	40.1	23.2	13.6
Mean grain size (µm)	17.7	7.5	7.8	9.3	8.5	11.6	8.2
clay (0.4–4 µm) (%)	16.9	30.7	27.7	24.9	22.4	21.7	25.6
silt (4–63 µm) (%)	64.7	64.6	68.9	68.9	75.5	65.9	71.2
sand (>63 µm) (%)	18.4	4.7	3.4	6.2	2.1	12.4	3.2
Carbonate (%)	5.3	25.1	23.8	35.0	15.0	24.4	13.8
Organic carbon (%)	1.8	3.1	3.5	3.6	5.7	5.8	4.6
Total nitrogen (%)	0.11	0.31	0.46	0.33	0.72	0.58	0.30
C/N ratio	15.9	9.9	7.7	10.8	7.9	9.9	15.3
Total phosphorus (mg/kg)	848	1654	1835	1443	2125	2459	2788
Organic P (mg/kg)	160.2	376.4	482.6	448.2	804.6	772.8	613.1
Apatite P (mg/kg)	519.0	635.5	587.6	544.4	546.3	1029.4	988.5
NAIP (mg/kg)	168.5	623.9	764.5	450.4	774.1	657.2	1186.1
As (mg/kg)	2.46	2.30	1.76	1.41	2.95	3.12	2.66
Cd (mg/kg)	0.28	1.48	2.80	0.75	1.73	1.92	4.19
Cr (mg/kg)	178	120	132	87	118	130	217
Cu (mg/kg)	59	88	107	197	103	175	156
Hg (mg/kg)	0.30	0.20	0.23	0.89	0.44	0.49	0.45
Fe (mg/kg)	41450	27430	31300	22370	35980	23570	20020
Mn (mg/kg)	724	672	702	963	1076	583	1008
Ni (mg/kg)	151	74	71	58	67	63	61
Pb (mg/kg)	55	67	95	76	90	122	88
Zn (mg/kg)	132	241	309	219	293	325	318

[*] KD: kilometric distance to the Rhone River – Saône River confluence in Lyon.

[**] Mean daily discharge: the decrease at Arles is due to the "Petit Rhone" derivation.

ranged as follows: 1–18 µg/kg for chlorobenzenes and organochlorine pesticides, 80 µg/kg for total PCBs and 0.2–0.5 mg/kg for PAHs. Typical analytical recoveries were known to average 63% (±32%) for CBs, 98% (±11%) for OCs, 99% (±8%) for PCBs and 94% (±9%) for PAHs. Mean reproducibility was 16% for CBs, 8% for OCs and PCBs and 23% for PAHs. Further details on analytical methods are given by Afghan and Forbes (1987).

For the statistics, a Pearson correlation matrix was computed to evaluate the relationships amongst the textural and composition variables of the samples. When a "lower than detection or quantification" value was reported for organic pollutants, then a single digit was entered at the last decimal place used for that parameter. The best associations were computed by a principal component analysis with varimax rotation of the component loading using the software Systat®.

Table 1 (Continued)

7 Beauchastel +119.7	8 Donzère +170.4	9 Arles +282.3	(2–9; n=9) Lower Rhone	A Seyssel –148.5	B Condrieu +43.6	C Beauchastel +119.7	D Arles +295.2
15–Nov	16–Nov	16–Nov	13/20–Nov	5–Jul	5–Jul	5–Jul	5–Jul
800	760	712					
468	440	455	403±68				
11.6	61.2	10.2	20.7±18.4				
8.0	8.0	10.7	8.8±1.4	22.4	46.6	20.6	40.8
23.6	30.1	21.3	25.3±3.5	9.7	6.7	13.2	9.9
74.6	67.0	69.1	69.5±3.7	67.6	44.9	63.2	38.3
1.8	2.9	9.6	5.1±3.6	22.7	48.4	23.6	51.8
16.7	32.7	21.9	23.2±7.4	25.6	24.4	25.2	21.3
5.7	2.0	4.1	4.2±1.3	2.3	2.3	1.9	1.2
0.60	0.15	0.35	0.4±0.2	0.30	0.20	0.20	0.10
9.6	13.4	11.8	10.7±2.5	7.7	11.5	9.5	12.0
3107	1081	1890	2042±649	682	1304	1104	953
818.6	150.1	483.6	550±224	75	50	167	96
980.2	431.0	635.2	711±226	423	1010	644	558
1308.5	499.9	771.0	782±290	184	244	293	299
1.35	0.71	0.10	1.82±1.03	0.25	0.83	2.85	1.41
1.21	0.56	0.62	1.70±1.18	1.01	0.95	1.03	0.87
197	85	141	136±45	91	66	98	75
173	49	133	131±48	36	46	51	36
0.63	0.13	0.39	0.43±0.24	0.10	0.24	0.25	0.20
28700	23660	27920	26770±4950	22890	14400	26650	23450
925	298	729	773±246	445	273	504	523
74	38	63	63±11	54	33	51	40
120	60	106	92±22	57	53	74	53
374	119	325	280±76	193	131	167	137

Results and discussion

Particle size characteristics

As a consequence of the low flow period in November 1989, the concentration of suspended sediment in the Rhone downstream of Lake Geneva was generally low, ranging from 6 to 23 mg of SS/L (Table 1). The station at Donzère showed a temporally increased turbidity which is believed due to high particle loading derived from tributary rivers (i.e. Drôme or Isère, Fig. 1). The instantaneous flux of SS downstream of Lyon was fairly constant, other than at Donzère, and averaged 9.6 kg/s (±2.9).

The mean grain size and the proportions of clay and silt show a remarkable consistency in the particle size distribution. One major population with an averaged mean diameter of 8.8 μm (±1.4) and a mode of 9 – 11 μm is characteristic of the suspended material all along the river from Geneva to Arles, including the Saône River (Tab. 1). Slight increases in the sand population at Chasse and Arles are ascribed to the resuspension of coarser bed particles due to the wakes of passing vessels. The Upper Rhone at Bouveret differs in the sense that the water is of glacial origin with relatively high turbidity and carries a sediment with a bimodal distribution. Despite the effort to find fine bed sediment, the size parameters of the collected samples indicate variable bimodal distributions. The grain size characteristics have been described in detail by Santiago et al. (1992). Additional data from other Swiss rivers indicate that the mean grain size of SS varies only from 6.0 μm during low flow to 19.4 μm during a run-off, with an overall average of 10.3 μm (±2.6 μm, n = 63; Santiago, unpubl.). All distributions are skewed towards the medium silts and moderately platykurtic. These observations clearly confirm the consistent texture of the various samples and support the high suitability of fluvial suspended sediments for comparative geochemistry purposes.

Carbonate

The inorganic carbon content is low for SS at Bouveret, higher for the samples from Geneva to Lyon, and intermediate between the Saône River and Arles except Donzère (Tab. 1). Increases of carbonate content due to precipitation in the water column have been described for the "Petit Lac" of western Lake Geneva by Vernet et al. (1972). Clearly the higher values downstream of Geneva reflect the transport of carbonate rich fine silts from the lake, supplemented by sediment from tributaries draining limestones in the Prealps and Jura mountains (Arve and Ain rivers, Fig. 1). At Lyon, dilution of the carbonate by sediment from the Saône is taking place.

Organic carbon and nitrogen

Organic carbon in SS shows a small spread in concentration but from the Saône to Arles (Donzère left apart) significantly higher values are observed (Figure 2a). The total nitrogen concentrations for suspended and bed sediments provide some similar trend to the organic C but may in general be considered to be low throughout.

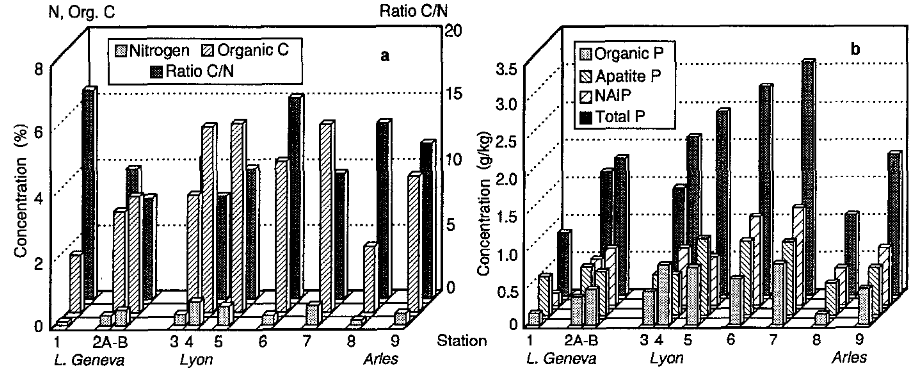


Figure 2. Concentration of nutrients (2a) and forms of phosphorus (2b) bound to the suspended sediment

The C/N ratio of organic matter has been effectively utilised by a number of authors in evaluating the source of organic carbon in sedimentary environments (Damiani and Thomas 1974, Kemp et al. 1977). Sediments in which terrestrial plants and macrophytes are the major source of organic matter have a C/N ratio around 15–20, whereas wastewater treatment plants (WWTP) produce a sludge effluent ratio of about 4 (Stumm and Morgan 1981). The high ratio for the Bouveret (Fig. 2a) clearly indicates that the particles are predominantly of terrestrial origin, in accord with the interpretation given by Burrus et al. (1990a) and Thomas et al. (1992). All the other values fall between 7.7 and 15.3, concordant with organic matter derived either from WWTP, macrophyte production in the river or diffuse loadings from the basin. However the ratios are not sufficiently characteristic to provide a clear origin and the source may be regarded as mixed.

Phosphorus and organic matter

Many studies have analysed phosphorus associated with sediments in an effort to determine its role in phytoplankton production and freshwater eutrophication. Williams et al. (1976) defined a chemical fractionation scheme in which particulate P is described as bound to organic matter (OP), incorporated in the mineral apatite (AP) or absorbed to hydrated non-crystalline oxides (in particular iron hydroxides). This latter fraction defined as non-apatite inorganic P (NAIP) is known to be the form bioavailable to phytoplankton (Williams et al. 1980, Sonzogni et al. 1982, Young et al. 1985, Santiago and Thomas 1992).

Total particulate P shows high concentrations at Pougny and from the Saône to Beauchastel (Figure 2b). The speciation of the P forms indicates that OP, AP and NAIP all increase from upstream to downstream of Lyon. The major change occurs for NAIP, also well correlated to the trend of soluble P in water samples ($r = 0.82$). Soluble P concentration increases between Chasse (0.13 mg/L) and St Vallier (0.33 mg/L), and then decreases consistently from Beauchastel (0.25 mg/L) downstream to Arles (0.11 mg/L). The main source of this P is an industrial effluent located at Condrieu (André and Lascombe 1998). The bed sediments are less enriched, particularly in OP and NAIP (Tab. 1). The high values in the Lower Rhone for total P and the forms of P compare with the range obtained in watersheds under intensive land use due to agriculture, population density and WWTPs (Thomas et al. 1992). Also the average proportions of OP (26.9% of total P), AP (34.8%) and NAIP (38.3%) are close to those observed for WWTP effluent solids.

Thomas et al. (1992) have utilised the relationships between the P forms and the C/N ratio as diagnostic tools in the determination of the major sources of particulate nutrients. In order to diminish the variability in the sedimentary environment due to different watersheds, the concentrations of OP and NAIP have been normalised to the content of AP used as a geological background. The relationship between the ratios C/N and OP/AP is given in Figure 3a. The diagram clearly shows the organic rich nature of samples 4 and 2-B, whereas stations 8, 6 and 1 are comparatively deficient in OP. This trend and the good correlation coefficient ($r = 0.73$; $n = 10$) for SS both agree with the observations of Thomas et al. (1992) on various surficial sediments from Lake Geneva and its tributaries. The increasing proportion of OP as the C/N ratio declines is ascribed to increasing contribution of WWTP in the basin. This being the case, the particulate organic matter in the Saône appears to be mainly derived from domestic point sources. The sediments from Donzère, St Vallier and Bouveret show characteristics of more terrestrial material from diffuse

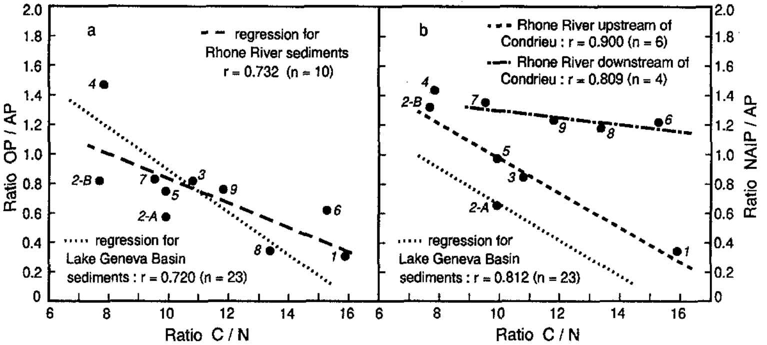


Figure 3. Relationships of the forms of particulate phosphorus to the carbon/nitrogen ratio

sources. The other samples fall in an intermediate field compatible with organic matter derived from mixed sources.

The relationship for the ratios NAIP/AP and C/N is presented in Figure 3b. The Rhone sediment shows 2 separate trends which can be distinguished according to the location of the sample upstream or downstream of the industrial P input at Condrieu. Firstly, the samples from Bouveret to Chasse follow a trend parallel to that described by Thomas et al. (1992), with increasing content of NAIP as the C/N ratio decreases. When these samples upstream of Condrieu are compared to the regression line for Lake Geneva, a shift appears which is believed to be due to the greater P removal in WWTPs in Lake Geneva basin. The samples downstream from Condrieu indicate a linear relationship yet have higher NAIP/AP ratios with little variation regardless of a changing C/N ratio. Thus the NAIP content is no longer mainly affected by inputs from WWTP and all the samples show the direct influence of the industrial source of inorganic P.

On the basis of the nutrient and carbonate composition of the sediment, the Rhone River can be divided into 3 principal sections; the first is the Upper Rhone with low content in all nutrients due to the predominant glacial origin of the particles; the second stretches from Lake Geneva to the confluence with the Saône at Lyon showing a carbonate dominated sediment; and the third section is from the Saône to the river mouth, where major inputs of organic matter and P occur from Lyon to Beauchastel, followed by dilution taking place at Donzère and to a lesser extent at Arles.

Heavy metals

Results for heavy metals are listed in Table 1 and illustrated in Figure 4. The highest concentrations in SS are found as follows: arsenic in samples 4 and 5; cadmium in stations 2, 4, 5 and particularly in 6; chromium in 1, 6 and 7; copper in 3, 5, 6, and 7; mercury in samples 3 and 7 and lead in 5 and 7. These results based on a point sampling agree with the data gathered from longer term monitoring using aquatic mosses (bryophytes) and bed sediments along the Rhone (André and Lascombe 1988). The longitudinal pattern for each element is concordant, with overall concentrations in SS being generally in the same order of magnitude as in the other monitored compartments. For example the high Cu and Hg concentrations at Poincaré (Tab. 1) correspond to the maximum values in bryophytes

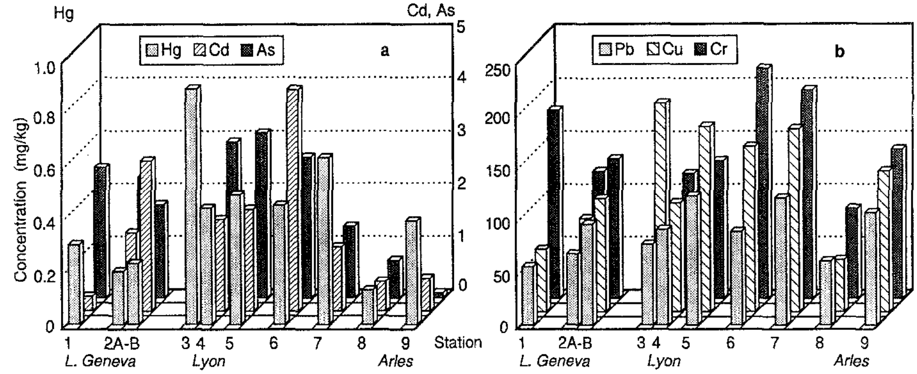


Figure 4. Concentration of heavy metals bound to the suspended sediment

(748 mg/kg for Cu and 0.49 mg/kg for Hg) found in 1986 downstream of the industrial plain of the Ain River. The peaks of Cd, Cr and Pb in SS downstream of Lyon are comparable to the maxima found at St Vallier in deposited sediments (7.0, 212, and 280 mg/kg respectively) and in aquatic mosses (22.5, 69, and 216 mg/kg resp.; André and Lascombe 1988).

As a general conclusion, the samples downstream of Lyon show a relatively high polymetallic contamination; some monometallic inputs can be seen between Geneva and Lyon, while medium levels in contamination are observed in the Saône River and at Arles. The sample at Donzère indicates low concentrations as a result of dilution due to the temporally increased turbidity, whereas the sample at Bouveret generally provides lower levels other than for As, Cr, Hg and Ni. This intermediate contamination in the Upper Rhone is confirmed by Favarger et al. (1991b) on samples collected every two months at this latter station. The metal concentrations in bed sediments remain fairly constant from Seyssel to Arles and show lower values than for SS at the closest corresponding stations, except for As at Beauchastel and As and Cd at Arles (Tab. 1). This may result from a temporal variation in the contamination level of the river between July and November 1989 but is more likely due to the different grain size characteristics as noticed earlier.

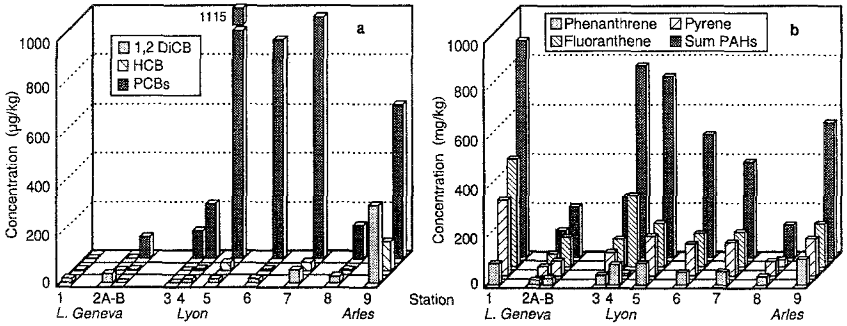


Figure 5. Concentration of chlorobenzenes and PCBs (5a) and PAHs (5b) bound to the suspended sediment

Table 2. Concentration of organic contaminants (dry weight) in the suspended and bed sediments of the Rhone River

	Station	1	2-A	2-B	3	4	5	6
	Location	Bouveret	Pougny	Pougny	Poincaré	Saône R.	Chasse	St Vallier
1,3 DiCB	(μg/kg)	ldl	ldl	ldl	ldl	ldl	60.4	ldl
1,4 DiCB	(μg/kg)	ldl	ldl	ldl	ldl	ldl	ldl	ldl
1,2 DiCB	(μg/kg)	19.5	37.6	ldl	ldl	16.3	16.6	18.7
1,3,5 TriCB	(μg/kg)	ldl	ldl	ldl	ldl	9.7	475	5.3
1,2,4 TriCB	(μg/kg)	ldl	ldl	ldl	ldl	6.8	22.0	ldl
1,2,3 TriCB	(μg/kg)	ldl	ldl	ldl	ldl	ldl	4.4	ldl
1,2,3,4 TetraCB	(μg/kg)	ldl	ldl	ldl	ldl	1.6	9.9	ldl
PentaCB	(μg/kg)	ldl	ldl	ldl	ldl	13.3	19.9	ldl
HexaCB	(μg/kg)	3.8	ldl	2.8	ldl	6.7	33.1	6.1
ΣCBs	(μg/kg)	23.3	37.6	2.8	ldl	54.4	641	30.1
γ-HCH	(μg/kg)	ldl	ldl	ldl	ldl	ldl	ldl	ldl
Aldrin	(μg/kg)	ldl	14.7	ldl	ldl	ldl	ldl	3.5
γ-Chlordane	(μg/kg)	ldl	ldl	ldl	ldl	6.6	ldl	5.5
α-Chlordane	(μg/kg)	ldl	ldl	ldl	ldl	ldl	7.0	2.4
p,p'-DDE	(μg/kg)	2.6	ldl	ldl	ldl	20.9	16.4	12.2
Dieldrin	(μg/kg)	ldl	ldl	ldl	ldl	5.2	7.1	3.7
β-Endosulfan	(μg/kg)	ldl	ldl	ldl	ldl	ldl	49.1	19.4
Total PCBs	(μg/kg)	ldl	ldl	90	114	226	1115	893
2-Methylnapht.	(mg/kg)	ldl	ldl	ldl	ldl	ldl	26.2	13.8
1-Methylnapht.	(mg/kg)	ldl	ldl	ldl	ldl	ldl	16.2	ldl
Acenaphthene	(mg/kg)	ldl	ldl	ldl	ldl	ldl	12.0	ldl
Phenanthrene	(mg/kg)	84.7	19.6	27.8	39.1	83.3	89.3	51.5
Pyrene	(mg/kg)	312	39.4	61.1	96.4	9.1	164	130
Fluoranthene	(mg/kg)	441	53.0	122	114	294	180	137
Benzo(k)fluor.	(mg/kg)	int	int	int	int	int	int	int
Benzo(b)fluor.	(mg/kg)	int	int	int	int	int	int	int
Benzo(a)pyrene	(mg/kg)	45.3	int	ldl	int	144	78.7	57.2
Indeno(1,2,3)pyr.	(mg/kg)	ldl	int	ldl	int	106	73.2	47.6
Benzo(g,h,i)peryl.	(mg/kg)	ldl	int	ldl	int	147	99.7	67.0
ΣPAHs	(mg/kg)	883	112	211	250	783	739	504

ldl = lower than the method detection limit; int = interference; tr = the mean is lower than the detection limit or the occurence is ≤ than 50%.

Undetected compounds = α-HCH, Heptachlor, Heptachlor epoxide, α-Endosulfan, Endrin, p,p'-DDT, o,p'-DDT, p.p'-DDD, Mirex, Methoxychlor, Indene, 1,2,3,4 Tetrahydronaphthalene, β-Chloronaphthalene, Acenaphthylene, Fluorene.

Organic micropollutants

The results for organics are given in Table 2 and illustrated in Figure 5. The occurrence of detected compounds in SS between Bouveret and Poincaré (mean = 5.3) represents 12.2% of the total array of analysed pollutants (n = 43), whereas from the Saône to Arles the average occurrence (mean = 17.2) increases to 39.9% with a maximum at Chasse (51.2%). The main pollution upstream of Lyon is due to PAHs at Bouveret. Organics do not decrease from Pougny to Poincaré. The Saône sediment has relatively high levels of p,p'-DDE and

Table 2 (Continued)

7 Beauchastel	8 Donzère	9 Arles	(2–9; n = 9) Lower Rhone	A Seyssel	B Condrieu	C Beauchastel	D Arles
ldl	14.5	ldl	tr	ldl	ldl	22.3	38.3
ldl	ldl	340	tr	ldl	ldl	ldl	ldl
53.0	26.4	321	54.4±101	ldl	ldl	99.6	100
28.7	8.8	220	83.1±163	ldl	9.3	11.4	16.2
76.7	27.7	676	89.9±221	ldl	5.4	72.4	90.0
21.8	9.9	252	tr	ldl	ldl	21.7	26.7
11.2	3.6	107	14.8±34.8	ldl	ldl	7.0	9.3
12.0	3.4	97.8	16.3±31.4	ldl	ldl	7.4	13.3
34.3	5.4	120	23.2±38.7	ldl	13.2	28.3	41.0
238	99.7	2134	360±696	ldl	27.9	270	335
ldl	5.1	ldl	tr	ldl	ldl	ldl	ldl
1.3	ldl	ldl	tr	ldl	ldl	ldl	ldl
ldl	2.6	ldl	tr	ldl	ldl	ldl	ldl
ldl	ldl	ldl	tr	ldl	ldl	ldl	ldl
19.8	5.1	94.7	18.8±29.7	ldl	ldl	20.9	63.9
ldl	ldl	ldl	tr	ldl	ldl	ldl	ldl
ldl	ldl	ldl	tr	ldl	ldl	ldl	ldl
986	139	631	466±440	73	271	473	840
15.3	12.1	18.9	9.6±9.9	ldl	ldl	ldl	ldl
ldl	ldl	10.0	tr	ldl	ldl	ldl	ldl
ldl	ldl	ldl	tr	ldl	ldl	ldl	ldl
55.2	34.7	106	56.3±30.1	32.3	35.9	50.8	78.6
138	60.4	153	94.6±54.8	40.5	54.8	80.5	71.7
143	29.4	178	139±77	71.0	82.3	114	97.4
int	int	int	int	int	30.4	int	int
int	int	int	int	int	ldl	int	int
41.7	ldl	49.6	41.2±48.9	ldl	ldl	20.6	ldl
ldl	ldl	ldl	tr	ldl	ldl	ldl	ldl
ldl	ldl	38.4	tr	ldl	ldl	ldl	ldl
393	137	554	409±252	144	203	266	248

Table 3. Concentration of DDT and metabolites (dry weight) in the bed sediments of the Rhone River

Station Location	A Seyssel	B Condrieu	C Beauchastel	D Arles
p,p'-DDT (μg/kg)	ldl	ldl	8.6	15.5
o,p'-DDT (μg/kg)	ldl	ldl	ldl	ldl
p,p'-DDD (μg/kg)	ldl	ldl	19.0	26.4
p,p'-DDE (μg/kg)	ldl	ldl	20.9	63.9
ΣDDT (μg/kg)	ldl	ldl	48.4	105.8
p,p'-DDE/ΣDDT	–	–	43%	60%

ldl = lower than the method detection limit

PAHs. Contamination by the chlorobenzenes including hexachlorobenzene is taking place from Chasse downstream, with a major input localised upstream of Arles (Fig. 5a). This latter source may be related to the "Cellulose du Rhône" pulp and paper mill. The concentration of PCBs is particularly high at Chasse. This impacts on all subsequent stations downstream and suggests a main origin likely related to the "chemical corridor", discharging wastes from the heavily industrialised zone in Lyon. The longitudinal distribution of PAHs shows that major inputs occur in the Upper Rhone, in the Saône and downstream of Lyon (Fig. 5b).

The results for the bed sediment samples agree with the analyses mentioned above (Tab. 2). Concentrations of chlorobenzenes are similar in both bed and suspended sediments at Beauchastel, and they persist at the same level in the bed sediments at Arles. The occurrence of p,p'-DDE in SS downstream of the Saône River is further confirmed by the levels of DDT metabolites in the bed sediments, as listed in Table 3. Whereas only the final degradation product p,p'-DDE was detected in SS, the parent p,p'-DDT and p,p'-DDD are found at both stations Beauchastel and notably Arles (ΣDDT = 48.4 and 106 µg/kg resp.). These data clearly indicate that atmospheric deposition is not the only source of DDT, and they reveal that recent releases of this prohibited pesticide still occur in the basin. The longitudinal distribution of PCBs and PAHs in bed sediments corresponds to the general picture given by SS, but is more difficult to distinguish due to the low and varying content of clay and organic matter in the deposited sediments.

These results again agree with the survey of André and Lascombe (1988). For instance the contamination by DDT metabolites downstream of the Isère River (Beauchastel) and particularly at Arles is corroborated by bryophyte and bottom sediment analyses (ΣDDT = 145 and 1760 µg/kg resp.; André and Lascombe 1988). The high PCB content in the suspended matter downstream of Lyon (Tab. 2) can be compared to their results on bed sediments (4500 µg/kg). A known point source of PCBs upstream of Poincaré, due to a waste treatment and incineration plant, was highlighted only with bryophytes and in fish tissue (2390 and 4390 µg/kg resp.; André and Lascombe 1988) but not in SS, probably due to their relatively low organic carbon content and/or to an intermittent release of the pollutant. This temporal limitation of the SS representativity may also apply to lindane (γ-HCH). Indeed lindane was detected in only 1 sample, whereas maxima of 600 µg/kg in deposited sediments and 68 µg/kg in bryophytes are reported by André and Lascombe (1988).

The ecotoxicity of contaminants associated with the suspended sediments

These observations on the chemical pollution agree with the general trend in acute ecotoxicity inferred from bioassays on natural phytoplankton, luminescent bacteria (Microtox® test) and zooplankton (*Daphnia magna* test). The combined results of this battery of bioassays with sediment extracts are summarised in Figure 6 and compared to the relative contamination of the Rhone River as depicted by metal and organic analyses. According to the sample rankings, both approaches indicate that SS downstream of Lyon are the more toxic, followed by Pougny and the Saône River. Intermediate toxicity occurs at Arles as a consequence of generally reduced pollutant concentrations, whereas better sediment quality is found at Bouveret, Poincaré and Donzère. The bioassay results have been discussed in detail by Santiago et al. (1993).

Chemical analyses

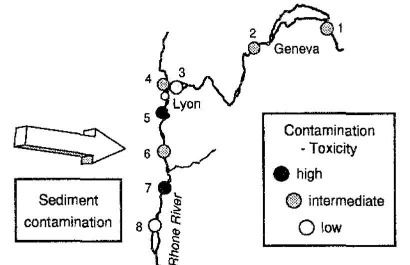
Analysis	Heavy metals		Organic pollutants		Combined ranking
Sample	Contamination	Ranking	Contamination	Ranking	
1. Bouveret	+	9	+ +	7	**7**
2-A. Pougny	+ +	8	+	8	**8**
2-B. Pougny	+ +	4	+	10	**6**
3. Poincaré	+ +	7	+	9	**9**
4. Saône River	+ +	5	+ +	4	**5**
5. Chasse	+ + +	1	+ + +	1	**1**
6. St Vallier	+ + +	3	+ +	5	**3**
7. Beauchastel	+ + +	2	+ + +	3	**2**
8. Donzère	-	10	+ +	6	**10**
9. Arles	+ +	6	+ + +	2	**3**

Relative contamination : + + + high + low
+ + intermediate - nil

Bioassays

Bioassay	Natural phytoplankton		*Daphnia magna*		Microtox®		Combined ranking
Sample	Toxicity	Ranking	Toxicity	Ranking	Toxicity	Ranking	
1. Bouveret	-	9	-	9	+	9	**9**
2-A. Pougny	+ + +	2		[4]	+ +	6	**[4]**
2-B. Pougny	+ + +	1	+ +	4	+ +	7	**4**
3. Poincaré	+	6	-	9	+	8	**8**
4. Saône River	+	7	+ +	3	+ +	4	**6**
5. Chasse	+ +	4	+ +	6	+ + +	1	**2**
6. St Vallier	+ +	3	+	7	+ + +	2	**3**
7. Beauchastel	+ +	4	+ + +	1	+ + +	3	**1**
8. Donzère	-	9	-	9	-	10	**10**
9. Arles	-	9	+ +	2	+ +	5	**7**

Relative toxicity : + + + high + low
+ + intermediate - nil



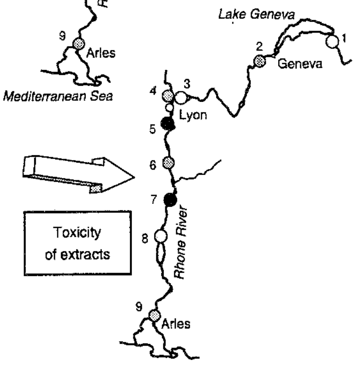


Figure 6. Summary of the contamination and the ecotoxicity associated to the Rhone suspended sediments.
The samples are ranked according to heavy metal, organic pollutant concentrations and to acute toxicity on natural phytoplankton, Microtox® and *Daphnia magna*

Contaminants in the Lower Rhone compared to other major rivers

In order to qualitatively assess the level of pollution in the Lower Rhone, the average contaminant concentrations at the 5 stations downstream of Lyon may be compared with those from suspended sediments collected close to the mouth of other major rivers. The comparison given in Table 4 is made with the monthly sampling of the Rhine River (Germany-Netherlands; IKSR 1990, 1991), with the extensive monitoring of the Niagara River (USA-Canada) based on biweekly samples (Kuntz 1984), and with two separate surveys on the Detroit River (USA-Canada; Comba et al. 1985, Johnson and Kauss 1987). Despite the variation in the analytical methods and the temporal limitation of the sampling in some surveys, particularly for the Detroit and the Rhone rivers which negates a meaningful computation of loadings, many interesting observations can be drawn regarding the transport of contaminants in these important fluvial systems.

The Rhine River provides the major discharge of toxicants to the North Sea, as does the Niagara River into Lake Ontario. The Niagara River is known to be highly contaminated by heavy metals (Hg, Cd, Pb) and organic pollutants (PCBs), originating from point sources (steel and petrochemical industries and municipal WWTP) and from disposal dumpsites and active leaching landfills through groundwater migration (Environment Canada et al. 1991). The Detroit River is used extensively for shipping, commercial, industrial and domestic purposes. It is polluted by metals and organics from industrial out-

Table 4. Average concentrations of heavy metals and organic contaminants in the suspended sediments of the Lower Rhone (stations downstream of Lyon), the Rhine, the Niagara, and the Detroit rivers (closest stations to the river mouth)

		Rhone River	*Rhine River*	*Niagara River*	*Detroit River*	
	Stations	Chasse to Arles	Bimmen and Lobith	Niagara-on-the-Lake	210–231/DTW.7W-DT9.3	
	period	November 1989	1989–1990	1981–1982	June 1983/1984	
	n	5	42/47 unless specified	53/56 unless specified	4/16	
	reference	this work	IKSR (a)	CCIW (b)	CCIW (c)/OMOE (d)	
Water discharge	(m^3/s)	690	1850	6262	6282	(d)
Suspended solids	(mg/L)	24.0±21.4	41.0(1976–88; n = 13)	8.8	16.2±6.9	(d)
Organic carbon	(%)	4.4±1.5	6.6±2.2 (n = 24)	6.7±3.2 (n = 23)	4.3±1.4	(d)
As	(mg/kg)	1.59±1.28	18.2±2.8	12.0±2.3 (n = 20)	–	
Cd	(mg/kg)	1.70±1.50	2.71±1.12	5.6±4.8 (n = 41)	–	
Co	(mg/kg)	–	19.7±1.8 (n = 11)	37.0±20.0	–	
Cr	(mg/kg)	154±53	105±32	132±63	–	
Cu	(mg/kg)	137±52	101±48	64.0±33.0	–	
Hg	(mg/kg)	0.42±0.18	0.94±0.35	1.57±1.52 (n = 20)	0.46±0.15	(d)
Ni	(mg/kg)	59.8±13.2	52.3±6.5 (n = 25)	67.0±29.0	–	
Pb	(mg/kg)	99.2±25.8	129±41	93.0±59.0	–	
Zn	(mg/kg)	292±99	588±119	313±219	–	
HexaCB	(µg/kg)	39.8±47.0	53.7±92.3	42.9±68.2	13.2±9.0	(d)
α-HCH	(µg/kg)	ldl	tr	9.5±14.3	ldl	(c)
γ-HCH	(µg/kg)	tr	3.1±3.3	tr	ldl	(c)
p,p'-DDE	(µg/kg)	29.6±36.8	5.8±4.6	10.9±24.6	ldl	(c)
p,p'-DDT	(µg/kg)	ldl	2.5±3.0	tr	ldl	(c)
Dieldrin	(µg/kg)	tr	tr	3.1±3.7	ldl	(c)
Mirex	(µg/kg)	ldl	–	11.9±21.9	ldl	(c)
Total PCBs	(µg/kg)	753±386	110±68*	533±651	79.1±90.5	(d)
Benzo(a)pyrene	(mg/kg)	45.5±28.9	0.5±0.2 (n = 22)	0.3±0.2 (1988–89)	0.8±1.4	(c)
ΣPAHs	(mg/kg)	465±222	–	2.4±0.2 (n = 81)	45.0±44.7	(c)

ldl = lower than the method detection limit

tr = the calculated mean is lower than the detection limit or the occurence is ≤ than 40%

– = not analysed

* Sum of PCB-28, 52, 101, 118, 138, 153, and 180.

References:

(a) Int. Kommission zum Schutze des Rheins 1990, 1991. Koblenz, Germany.

(b) Kuntz 1984. Canada Centre for Inland Waters, Burlington, Ontario.

(c) Comba et al. 1985. Canada Centre for Inland Waters, Burlington, Ontario.

(d) Johnson and Kauss 1987. Ontario Ministry of the Environment, Toronto.

falls, hydro facilities, waste disposal sites, WWTP and combined sewer overflows with the majority of the sources being located along the United States shore. This river represents a major source of Hg, PCBs, DDT and metabolites to Western Lake Erie (Frank et al. 1977, Oliver and Bourbonniere 1985, UGLCCS 1989).

With respect to the general sediment characteristics (Tab. 4), the mean concentration of suspended solids varies between a low 8.8 mg/L in the Niagara River, due to the proximity of the source in Lake Erie, and to a high 41 mg/L in the Rhine due to the length of this river (865 km). The organic carbon concentrations range only from 4.3% to 6.7%, further corroborating the good homogeneity of fluvial SS not only in their grain size parameters as presented above but also in their organic matter content. Total Cr and Cu in the Rhone surpass the respective concentrations in the other rivers, whereas values for As, Cd, Ni, Pb and Zn are similar or lower. Mean Hg concentration is the lowest in the Rhone, however it still indicates a certain contamination because the maximum in the Niagara River, as observed in 1982, has been significantly reduced by 1988–1989 to 0.16 mg/kg (±0.08, n = 77; Kuntz, pers. comm.). Indeed the long term monitoring data reveal that the point source loading of many priority contaminants have decreased by up to 60–80% in the Niagara River (Environment Canada et al. 1991).

Hexachlorobenzene data show a high range of variation but provide similar averages for 3 of the 4 rivers. The HCB in the Detroit River is known to partially originate upstream in the Sarnia petrochemical area discharging into the St. Clair River (UGLCCS 1989). Hexachlorocyclohexanes were high in the Niagara River in the recent past but have decreased by 1988–89 to levels close to the detection limit as observed for the other rivers (Kuntz, pers. comm.). Concentrations of p,p'-DDE are comparatively higher in the Rhone by a factor of 3 or more, further suggesting as discussed above recent or continuing inputs in the basin in addition to any residual level.

High concentrations of total PCBs are also found in the Lower Rhone, particularly when comparing to the Detroit River. The low average in this latter is nevertheless confirmed by Frank et al. (1977) on 5 SS along the Detroit River (72.0±28.0 µg/kg) and by Comba et al. (1985) on 4 samples at a river mouth transect (93.0±125 µg/kg). Oliver and Bourbonniere (1985) have demonstrated that PCB in bed sediments increase from the head to the mouth of the Detroit River (660 µg/kg), due to WWTP and combined sewer overflows. The sediment contamination increased quantitatively in concentration and qualitatively in the proportion of high congeners and the total chlorine content. Figure 7 illustrates the distribution of PCB homologs (same number of chlorines per biphenyl molecule) in the sample from Poincaré, reanalysed by gas chromatography with mass spectrometer detector, and in a bottom sediment close to the Detroit River mouth (Oliver and Bourbonniere 1985). Both samples have very similar compositions, resulting in an identical average of chlorine content (56.8%). Though the total PCB concentration at Poincaré is low compared to the other samples, the homolog distribution reveals the presence of high PCB congeners. By analogy, the homolog composition in the contaminated SS downstream of Lyon may provide high chlorine toxic contents certainly of concern.

The partitioning of organics between the aqueous and particulate phases in the Rhone needs to be assessed. For instance in the Niagara River, most of the organics are generally in the aqueous phase which has a low concentration of suspended solids (5–10 mg/L). Kuntz and Warry (1983) found that only 40 percent of the annual loading of DDE, mirex and PCBs were in the particulate phase.

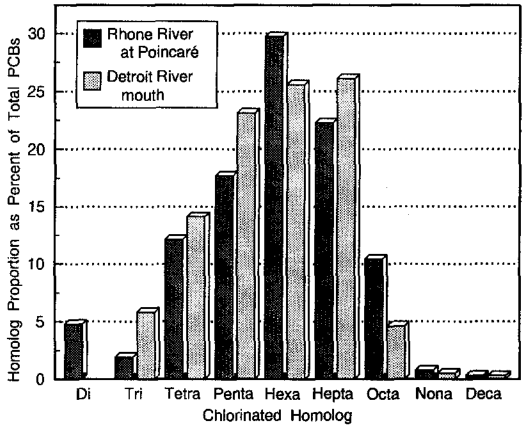


Figure 7. Homolog composition of PCBs in the Rhone suspended sediment (station Poincaré) and in the bed sediment from the Detroit River mouth (from Oliver and Bourbonniere 1985)

Relationships between the compositional variables

In order to assess these relationships for the Rhone SS, a Pearson correlation matrix was computed between the grain size parameters and the nutrient, heavy metal and organic pollutant concentrations. Since the sediment from Bouveret has very different characteristics due to its glacial origin, the computation was run on the 9 samples from Pougny to Arles. Only the variables showing significant relationships are reported in Table 5 with the corresponding coefficients of correlation. Both the mean grain size and the carbonate are negatively or weakly correlated to the other parameters, since the changes in the grain size affect the surface area and the inorganic C content serves as a diluter of the fractions to which the toxic chemicals are bound. An exception is provided by the relationship between the mean grain size and fluoranthene ($r = 0.785$), also observed by Kaiser et al. (1985) in the Detroit River for PAHs which can be absorbed onto particulate matter of both inorganic and organic nature.

The organic C is strongly related to OP and N, Pb and Zn, PAHs, and PCBs (Tab. 5). The P forms show overall interrelations which consequently result in high coefficients with total particulate P. The correlations of total P with the other variables are due more specifically to OP closely following the trend of organic C, to AP being related to PCBs and to NAIP being associated with Cr. No relationship significant at the 95% confidence level is found for As, Cd, Fe, Mn and Ni with the other variables. Mercury is strongly related to Cu and Pb to Zn, whereas Cr shows a intermediate coefficient with Zn. Hexachlorobenzene is statistically related to dichlorobenzene and DDE ($p < 0.01$) and to phenanthrene, whereas total PCBs show a broader association encompassing organic C, apatite, some metals and pyrene. Pyrene seems to differ from the other PAHs which are mainly associated with the organic matter.

To improve the level of resolution and understanding of these relationships, the best associations were statistically evaluated with a principal component analysis (PCA). Since the number of sediment samples is small, caution must be exercised in the interpretation

Table 5. Correlation coefficients for the compositional variables of the suspended sediments in the Rhone River (n = 9)

	Organic C	N	Organic P	Apatite p	NAIP	Total P	Cr	Cu	Hg	Pb	Zn	HexaCB	Total PCBs	Phenanthrene	Pyrene	Σ PAHs
Organic C	1.000															
Nitrogen	0.871 **	1.000														
Organic P	0.990 **	0.899 **	1.000													
Apatite P	0.689 *	0.348	0.671 *	1.000												
NAIP	0.580	0.352	0.604	0.691 *	1.000											
Total P	0.840 **	0.588	0.847 **	0.887 **	0.895 **	1.000										
Cr	0.536	0.223	0.548	0.785 *	0.957 **	0.889 **	1.000									
Cu	0.596	0.330	0.586	0.623	0.316	0.560	0.383	1.000								
Hg	0.474	0.307	0.474	0.298	0.144	0.331	0.127	0.895 **	1.000							
Pb	0.831 **	0.690 *	0.800 **	0.706 *	0.546	0.765 *	0.529	0.602	0.351	1.000						
Zn	0.821 **	0.677 *	0.832 **	0.715 *	0.736 *	0.864 **	0.744 *	0.569	0.308	0.874 **	1.000					
HexaCB	0.217	0.045	0.120	0.135	0.150	0.156	0.181	0.170	0.038	0.520	0.405	1.000				
Total PCBs	0.715 *	0.344	0.651	0.900 **	0.642	0.824 **	0.702 *	0.595	0.318	0.804 **	0.671 *	0.421	1.000			
Phenanthrene	0.638	0.472	0.539	0.280	0.154	0.352	0.164	0.304	0.223	0.654	0.486	0.750 *	0.581	1.000		
Pyrene	0.377	-0.016	0.296	0.705 *	0.369	0.512	0.490	0.680 *	0.403	0.676 *	0.497	0.599	0.839 **	0.482	1.000	
Σ PAHs	0.838 **	0.696 *	0.780 *	0.437	0.282	0.547	0.290	0.365	0.278	0.653	0.572	0.369	0.608	0.875 **	0.309	1.000

* $p < 0.05$ ($r \geq 0.666$)

** $p < 0.01$ ($r \geq 0.798$)

Table 6. Eigenvalues and rotated loadings of the principal component analysis (n = 9) with selected variables

Component	n° 1	n° 2	n° 3	n° 4	n° 5
Eigenvalues	8.15	1.90	1.56	1.29	0.56
Percent of total variance	58.2	13.6	11.1	9.2	4.0
Cumulative percent	58.2	71.8	82.9	92.1	96.1
Organic C	0.86	0.33	0.27	0.06	0.25
Nitrogen	0.95	0.16	0.13	−0.03	−0.12
Organic P	0.86	0.39	0.29	−0.02	0.17
Apatite P	0.31	0.58	0.22	−0.02	0.69
NAIP	0.24	0.93	0.05	0.04	0.16
Cr	0.15	0.92	0.06	0.06	0.32
Cu	0.24	0.20	0.88	0.10	0.33
Hg	0.22	0.00	0.96	−0.01	0.06
Pb	0.64	0.36	0.25	0.44	0.34
Zn	0.59	0.65	0.23	0.33	0.12
HexaCB	0.11	0.05	-0.01	0.97	0.14
Total PCBs	0.36	0.42	0.19	0.26	0.76
Pyrene	−0.02	0.25	0.40	0.52	0.71
ΣPAHs	0.85	−0.02	0.03	0.21	0.34

of the PCA. The associations relative to each component axis should be supported by the *r* values in the correlation matrix. The retained variables are the same as in the matrix other than total P becoming redundant and phenanthrene strongly related to the sum of PAHs. The loadings following varimax rotation for the first 5 components, which account for some 96% of the total problem variance, are given in Table 6. Each component may be described as follows, with the proposed name indicating the dominant group of variables rather than the highest component loading.

Component 1: organic matter (Tab. 6)

This component accounting for 58% of the total variance has high positive loadings on N, organic C, OP and PAHs. It shows intermediate loadings on Pb and Zn with lower values for apatite P and PCBs. Clearly this component relates to the content of organic matter in the sediment, the strong relationship between C, N, and P resulting from the stochiometric composition of the organic matter. The association of PAHs and partly of Pb, Zn, and PCBs with this component reflects the adsorption by organic matter of these pollutants. The loading on apatite P is probably due to auto-correlation since any direct relationship is unlikely.

Component 2: adsorbed elements

This component accounting for some 14% of the variance shows high loadings on NAIP and Cr, with intermediate loadings for Zn and apatite P. NAIP is known to be mainly associated to hydrated oxides of iron probably as adsorbed phosphate ions (Williams et al.

1976). The coefficients on Cr and Zn indicate that these elements are similarly bound, though a Zn fraction is organic bound as shown above. The loading on AP is again due to auto-correlation with NAIP.

Component 3: Hg and Cu

High loadings are observed for Hg and Cu with a moderate loading on pyrene. These seemingly unrelated elements show no affinity to any other used variable and hence are construed to be acting independently. They are rather believed to be linked by the similarity of the sources, a major one being located in the industrial plain of the Ain River (André and Lascombe 1988).

Component 4: organochlorine contaminants

High loadings for HCB, which is strongly correlated to 1,2-dichlorobenzene and pp'-DDE. Clearly the organochlorines form a distinct component which surprisingly is associated neither with the organic matter nor with the PCBs, but likely reflects the water solubility and vapour pressure characteristics of these compounds. Moreover, the important contamination by CBs occurring upstream of Arles suggests a point source of concern which must be clearly identified.

Component 5: municipal-urban point sources (?)

This low eigenvalue component gives high loadings on PCBs, pyrene and "apatite P". It may be interpreted as the influence of municipal and/or urban wastewater point sources, though no clear insight is provided by this component.

Conclusions

This geochemical study provides a "snapshot" of the sediment quality in the Rhone River. The representativity of the suspended sediments, particularly under low flow conditions as was the case in November 1989, is only valid for the short duration of the sampling. Despite the temporal limitation of the small number of samples collected in this rapid assessment procedure, the environmental quality as described along the river is in good agreement with the longer term monitoring conducted with bryophyte and bed sediment analyses (André and Lascombe 1988). On the basis of the SS composition, a number of specific conclusions can be derived as follows:

1) The grain size characteristics and the organic carbon content are fairly consistent all along the Rhone downstream of Geneva. This enables an improved comparison of the chemical results and highlights the varying sources of current pollution in the river.
2) High concentrations of particulate phosphorus are due to two distinct causes: point sources related to wastewater treatment plants and a major industrial outfall at Condrieu which impacts on all the subsequent downstream samples.

3) Heavy metal contamination is found in the whole watershed. The sediments from Lyon to Beauchastel show high polymetallic concentrations, which then decrease to the river mouth. Monometallic inputs occur at Pougny and downstream of the Ain River industrial plain, whereas generally dilution due to increased turbidity takes place in the Upper Rhone and at Donzère.
4) The occurrence of organic pollutants increases dramatically downstream of Lyon and shows contamination by chlorobenzenes, PCBs, and PAHs. The high levels of DDT metabolites in bed sediment clearly suggest continuing or recent release in the basin of this prohibited pesticide.
5) The comparison of the Rhone sediment composition with the Rhine, the Niagara and the Detroit rivers indicates that an overall contamination with similar high levels is occurring in these major fluvial systems. This confirms that the quality of the Rhone River is as degraded as for two of the most heavily polluted areas of concern in the Great Lakes basin and the major carrier of toxic chemicals to the North Sea. The poor environmental quality of the Rhone sediments, also demonstrated by toxicity bioassays (Santiago et al. 1993), needs to be further evaluated with a more frequent sampling in order to get an improved temporal representativity.
6. The statistical evaluation indicates that only a few associations exist amongst the contaminants, suggesting that some anthropogenic inputs originate from very specific sources, as for Hg and Cu and for the organochlorines. Other pollutants, such as Zn and PCBs, provide intermediate loadings on several components probably resulting from a combined mixture of point and diffuse sources and/or from a better defined affinity to organic matter.

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