ORGANOCHLORINE AND HEAVY METAL CONTAMINATION.

TORRELAVEGA
RIO SAJA, NORTHERN SPAIN

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INTRODUCTION

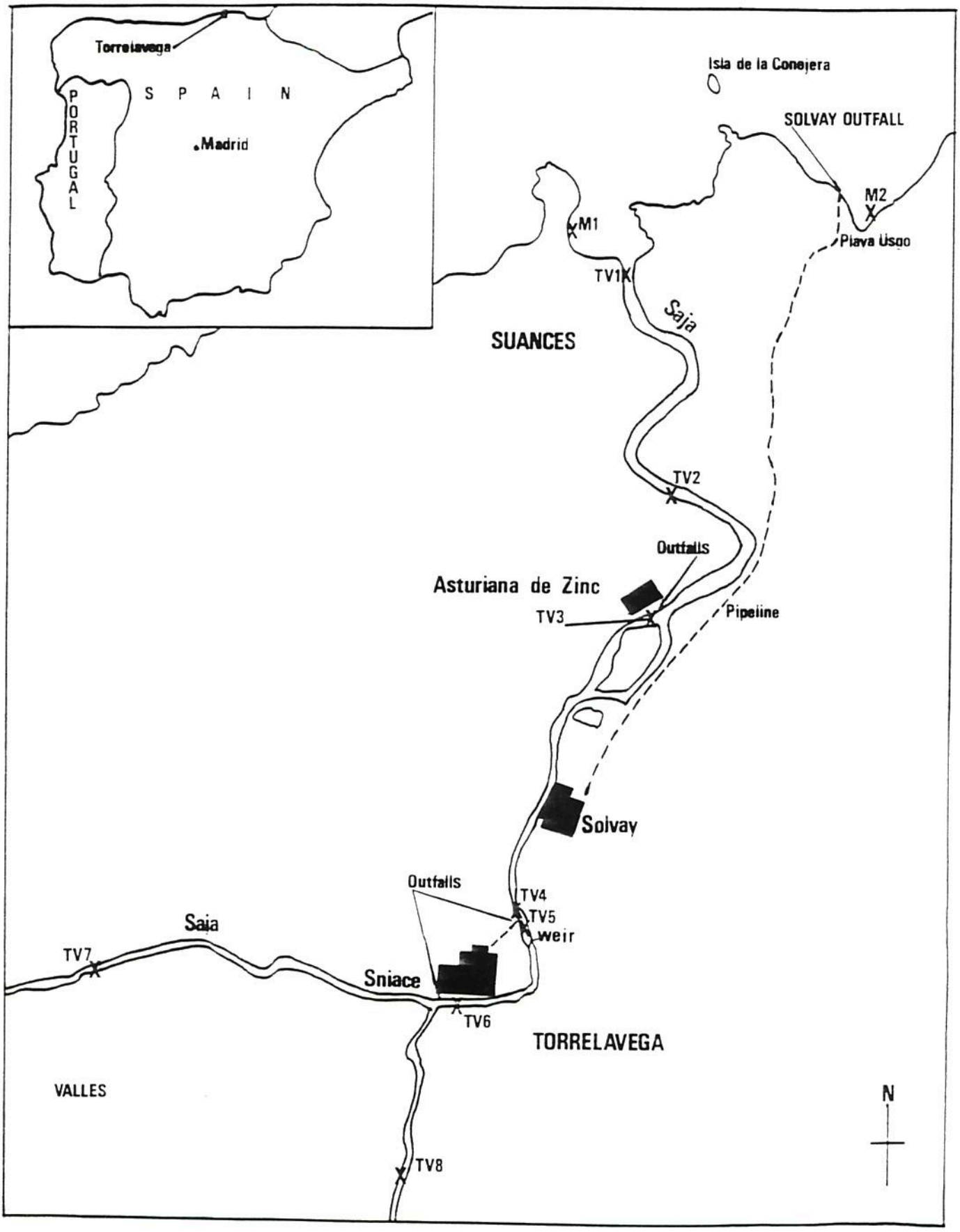
The Rio Saja is a small river on the northern coast of Spain (see insert Figure 1) which passes through the town of Torrelavega and discharges into the sea at Suances, a coastal tourist resort. Several industries are situated on this river, the most notable of these being the Sniace pulp and paper plant, Solvay's chlor-alkali complex and Asturiana de Zinc metals processing. Sniace and Asturiana de Zinc discharge directly into the river. The Solvay plant pipes effluent 9km to the sea at Playa Usgo.

The bleached chemical pulp industry consumes considerable quantities of chlorine and as a result, discharges appreciable quantities of chlorinated organic matter into rivers, lakes and oceans (Kringstad and Lingstrom 1984). There is growing concern about the release of halogenated organic compounds into the environment since many are toxic, show considerable resistance to biological and chemical degradation and are prone to bioaccumulate. Bleach plants have been found to affect the diversity, biomass and distribution of invertebrates and plants within the receiving body of water (Sodergren *et al* 1988). Extractable organic chlorine (EOCl) levels in effluents, biota and sediments from the vicinity of pulp and paper mills have been reported by several workers (Hakanson *et al* 1988, Sodergren 1989).

Mercury, cadmium, chromium, lead and soluble copper compounds are included in the EEC list of priority pollutants. The toxicity of these metals is well documented (Brown & Kodama 1987) and this has prompted many investigations into their distribution in the environment (Bridges 1989, Nriagu 1990). Many workers have reported elevated levels of heavy metals, particularly zinc, cadmium, lead and mercury, in the vicinity of zinc smelting and refining industries (Spierenburg *et al* 1988 & Buchauer 1973, Martin & Coughtry 1987, Moore & Luoma 1990).

A sampling programme was carried out in the Rio Saja to investigate the levels of industrial contaminants in sediments and biota. Samples of effluent, sediments and shellfish were collected in November 1990 and analysed for a variety of parameters. The results of these analyses are presented in this report.

FIGURE: Rio Saja and Sampling positions



SAMPLING

A sediment sampling programme was carried out on the Rio Saja (sites illustrated in figure). Sediments were obtained from the river with the use of a pipe dredge except for sample TV4 which was collected using a hexane-washed spatula into a hexane- and acid-washed glass container. Sample TV4 was collected immediately downstream of the discharge from Sniace and was found to consist almost wholly of wood pulp and particulates originating from the outfall. Sediments TV6 and TV2 consisted of fine muds only, others were composed of a range of particle sizes including small stones. All sediment samples were collected in Nalgene bottles and kept chilled during transport to the analysing laboratory.

Effluent samples (three in total) were obtained directly from outfalls or from channels discharging into the river and were collected in acid- and hexane-washed sample bottles.

In the case of Sniace there were two visible outfalls into the river. One of these was not discharging on the day of sampling and was located just upstream of sediment sample TV6 (see figure). The other was a flume discharge and is indicated by a broken line in the figure. Two separate effluent streams converge into the flume and the mixed discharges to the river. Two effluent samples were obtained, one from the channel upstream of the convergence and one of mixed effluent downstream. It was impossible to obtain a sample of the other upstream effluent as it was caged in. A weir just downriver of sample TV6 and upriver of the channelled outfall which results in a low energy area of fine sediment deposition. The quality of the river is visibly degraded. In the case of the Asturiana de Zinc plant, an effluent sample was obtained from the one outfall to which it was possible to gain access (the location of this outfall is indicated in the figure). There were several other outfalls which were impossible to access directly.

It was not possible to sample the Solvay discharge at Playa Usgo directly on this occasion, since it discharges at low tide level and sea conditions thus prevented access. The effluent from the Solvay plant is piped for several kilometres and is marked on the figure by a broken line.

Shellfish (blue mussels) were collected at low tide from the bay at Suances and from Playa Usgo (these are designated M1 & M2).

ANALYSIS

EXTRACTABLE ORGANIC CHLORINE

The effluent and sediments were analysed for extractable organic chlorine (EOCl). Due to lack of a defined method no EOCl analysis of the shellfish samples was made. A subsample of each sediment was extracted with ethyl acetate. The organic chlorine extracted was then determined using a Dohrmann DX20A microcoulometer with a high temperature combustion furnace and a microcoulimetric titration cell specific to halides.

TOTAL MERCURY

The shellfish and sediments were transported, suitably chilled, to the analysing laboratory. Total mercury analysis was by cold vapour generation using stannous sulphate reduction according to the method of Hatch and Ott (1968), using a Thermoelectron 151 AAS.

HEAVY METALS

The effluent and sediments were analysed for heavy metal content at Queen Mary and Westfield College (QMW), London. A range of seven metals was investigated, these being copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), zinc (Zn) and silver (Ag). Sediments were oven-dried and their moisture content determined. Preparation of the sample digests was by microwave digestion in a CEM MDS2000 sample preparation system. Approximately 1 gram of sample was weighed accurately into an acid washed teflon sample vessel and 20ml of 1:1 nitric acid:double distilled water added. The samples were microwaved at full power for one hour and pressure controlled to a maximum of 150psi. Duplicate samples were analysed for each sampling location and an average value obtained. Analysis was by Thermoelectron IL157 AAS calibrated against known standards and background corrected for all the metals except Cr. Recovery was checked against known reference sediments.

ORGANIC SCREEN

An organic screen was carried out on the effluents and one of the sediments (TV4) at QMW. 1ul of a 10ml hexane extract of the samples were analysed using a Hewlett-Packard 5890 gas chromatograph fitted with a 5970 mass selective detector. The column used was an Ultra-1, 25m in length, internal diameter 0.2mm and phase thickness 0.33um. The stationary phase is cross-linked methyl silicone.

RESULTS

METALS

	SEDIMENT SAMPLE NUMBER								EFFLUENTS		
METAL	TV1	TV2	TV3	TV4	TV5	TV6	TV7	TV8	A	B	C
CADMIUM (ppm)	1.91	20.5	19.5	<0.5	6.7	12.9	<0.5	8.7	0.01	<0.01	<0.01
LEAD (ppm)	138	1360	3170	164	1400	3540	29.8	708	0.08	<0.04	<0.04
COPPER (ppm)	102	111	321	54.9	71.7	846	19.1	94.2	<0.02	0.02	0.03
SILVER (ppm)	<0.25	<0.25	0.44	<0.25	<0.25	<0.25	<0.25	<0.25	<0.01	<0.01	<0.01
ZINC (ppm)	1290	13500	22800	680	4880	226	11000	3800	3.2	4.9	0.16
CHROMIUM (ppm)	16.2	60.6	21.3	15.9	36.0	285	35.7	48.5	<0.05	<0.05	<0.05
NICKEL (ppm)	4.19	23.1	34.6	4.43	12.8	40.7	14.4	24.6	<0.02	<0.02	<0.02
MERCURY (ppm)	0.56	3.63	4.66	0.08	0.22	0.08	0.04	0.11	N/A	N/A	N/A

A = effluent from Asturiana de Zinc, Hinojedo.
B = mixed effluent from channel below convergence at Sniace pulp mill.
C = effluent from above convergence at Sniace pulp mill.

HEAVY METALS FROM OTHER HARBOURS

	Rotterdam# [mg/kg]	Hamburg$* [mg/kg]	Background* [mg/kg]
As	13-38	122	13
Pb	80-240	268	30
Cd	3-13	9	0.3
Cr	97-187	90	73
Cu	39-142	237	20
Ni	24-63	45	26
Hg	0.8-3.8	8.7	0.2
Zn	256-1079	1238	76

#figures for 1984 dredged material in, here the heavy metals have been adjusted to conform to a nominal 50% fraction fines fraction of size 16 micrometres. (from: Nijssen 1988)
$concentration in dredged material disposal site
*in: Driel & Nijssen (1988)

EXTRACTABLE ORGANIC CHLORINE (EOCl)

	EOCl mg/kg wet weight	EOCl mg/kg dry weight	PERCENTAGE WATER
SEDIMENT			
TV1	26	33	22
TV2	30	96	69
TV3	8	19	57
TV4	<4	<22	82
TV5	6	11	47
TV6	32	105	69
TV7	<4	<20	80
TV8	8	18	56
RANGE	<4-32	11-105	
BACKGROUND LEVEL FOR SEDIMENT[1]		1-6	

[1]Hakanson *et al* (1988)

EFFLUENT	EOCl mg/l
B(Sniace mixed)	1.24
C(Sniace)	0.74

MERCURY IN SHELLFISH

SHELLFISH

	Shellfish type	mercury content dry wt. mg/kg	mercury content wet wt. mg/kg
M1	blue mussels	0.48	0.09
M2	blue mussels	1.46	0.23
FRANCE[3]	blue mussels	max. 0.83	

[3]This is the maximum level found in a total number of 1341 samples taken from 153 sites around the coast of France (in Claisse 1989).

DISCUSSION

EOCl

The EOCl levels range from 11 to 105 mg/kg dry weight in Rio Saja sediments (Table 1). Hakanson *et al* (1988) analysed sediments from a total of 16 lakes and coastal areas far from paper and pulp industries and found a 'background' range of 1-6mg/kg EOCl dry weight. The levels of EOCl found in this study must therefore be regarded as elevated. Since there are few examples of natural organochlorines, this elevation must be attributable to anthropogenic input.

The highest level of 105 mg/kg dry weight was found in sample TV6. This is not as high as that found in the vicinity of pulp and paper plants in Sweden. For example, Hakanson *et al* (1988) have found EOCl levels in sediment to be as high as 903 mg/kg dry weight in the sediments of the Bothnian Sea and the northern part of the Baltic. All of these sediments were from accumulation bottoms. In areas of erosion and transportation identified by Hakanson *et al* (1988) low EOCl levels of <1 mg/kg dry weight were reported. The distribution of EOCl in the Rio Saja sediments can be partially explained in relation to the local deposition patterns for fine sediments and possible seasonal mechanisms of sediment removal. The relatively high level of 96 mg/kg recorded as site TV2 is probably due to depositional patterns influenced by the estuarial salt/fresh water interface. In addition, the relative intensity of pulping activities on the Rio Saja is much less and this would be expected to result in somewhat lower levels of EOCl than is common in the areas of the Baltic highly impacted by this industry.

The values of EOCl recorded suggest a possible point source discharge upriver of sample TV6 and downriver of sample TV7 together with an appreciable input upriver of sample TV8 on the Rio Besaya. Possible sources are unknown. It is possible too, that the weir in place below the plant may act to partially impound effluents discharged above it. The relative pattern of metal contamination (See eg cadmium) evident in these samples strongly suggests the presence of individual point sources impacting site TV8. Similarly, the highly elevated level of zinc present at site TV7 suggests a source of this metal upstream of the Sniace plant. The elevated levels of metals present in the sediments at site TV6 can be then regarded as due to the deposition of particulate bound metals from both upstream sources in the low energy area behind the weir. Nonetheless, the possibility that this enrichment is due to a local source cannot be dismissed. The existence of such a point source is indicated by the high (105 mg/kg) EOCl level at site TV6 in comparison to that from both upstream sites. The analysed discharges from Sniace contain significant levels of organically bound chlorine and there is no doubt that this outfall is contributing to the organochlorine pollution of the Rio Saja.

EOCl discharges are of great environmental significance. Martinsen *et al* (1988) suggest that sediments play a part in the fish bioaccumulation of organochlorine compounds discharged from bleach plants. Serious disorders in vital physiological functions (gonad development, liver function, immune defence, metabolization and ionic balance) have been caused by pulp mill effluents (Sodergren 1989) and these effluents have also been implicated in spinal damage to fish.

Numerous studies have confirmed the formation of chlorinated dibenzo-p-dioxins and dibenzofurans in the paper making process when chlorine is used as a bleaching agent for wood pulp (Keleda 1990, Koistinen *et al* 1990). Kroner & Zacherle (1990) have concluded that predicted exposures of these substances near chlorine-bleaching pulp and paper mills could have significant implications for human health as well as aquatic for aquatic organisms.

It seems probable that organochlorine compounds are being concentrated in the shellfish as this phenomenon has been reported on in the vicinity of pulp and paper plants in Finland (Herve 1988).

Metals

The effluent from Asturiana de Zinc contains an appreciable concentration of zinc as does the mixed effluent from Sniace. The presence of silver in the sediment at site TV3 serves, however, as a unique indicator of the introduction of the smelter effluent as does the sharp elevation in levels of sediment bound mercury recorded at this point. In general, the heavy metal levels in the Rio Saja sediments are much elevated. Different metals predominate in different parts of the river system, reflecting the impact of individual sources. Several sources of contamination are indicated. Site TV3 and TV6 are of particular note and elevated levels of zinc were found at site TV7.

Concentrations of mercury, zinc, silver and cadmium are highest in sample TV3 adjacent to the metals processing facility. Concentrations of nickel, chromium, copper and lead are highest in sample TV6, adjacent to the Sniace complex. Many of these levels exceed those found in dredged material from the highly polluted estuaries of Rotterdam and Hamburg (see table, page 5). Most of the sediments sampled in Rio Saja are highly contaminated and probably compare with Rotterdam's Class 4 dredgings. The majority of Rotterdam dredgings are considered to be too polluted to dump in the sea or to spread on agricultural land and are therefore treated as toxic waste by the Netherlands authorities (Nijssen 1988). The dredgings are grouped into four classes according to contaminant levels. Class 4 waste, being the most polluted, is disposed of in a specially designed and lined site.

The presence of these metals in the river sediments is of concern because many of them are known to have adverse effects on the wider ecosystem. In addition many are associated with possible human health impacts. Lead poisoning is known to cause derangement of the central nervous system, gastrointestinal tract, muscular coordination and red blood cell synthesis and also to affect cognitive development in the young (in Neathery & Miller 1975). Nickel and nickel compounds have been classified as human carcinogens by IARC and also causes contact dermatitis.

Hexavalent chromium possesses carcinogenic properties and silver has been shown in laboratory experiments to be one of the most toxic elements to microorganisms and biochemical processes in the soil (Jones *et al* 1990). Mercury has long been recognised as toxic to humans in the organic form and affects the central nervous system. Other, more subtle, effects on enzyme systems, cardiovascular function, blood parameters, the immune response, kidney function and structure, and behaviour have been reported (WHO 1989).

Zinc minerals and wastes often contain a high concentration of mercury and it would appear that Asturiana de Zinc is a point source for this metal. It is also likely that the area is being contaminated with atmospheric emissions.

The high levels of mercury found in shellfish are of obvious concern. The mussels collected at Playa Usgo, not far from the Solvay outfall (M2) contained 0.23 mg/kg mercury wet weight. This is approaching the 0.3mg/kg WHO/FAO advisory value. Emissions from the chlor-alkali plant are probably responsible although it is not possible to differentiate between the separate sources of this metal impacting Playa Usgo.

In conclusion, the river systems associated with Torrelavega are subject to diverse inputs of metals which are reflected in elevated levels in the sediments and which conform in the main to identified inputs.

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