ORGANOCHLORINE AND METAL POLLUTION AT RIA DE PONTEVEDRA, NORTHWEST SPAIN

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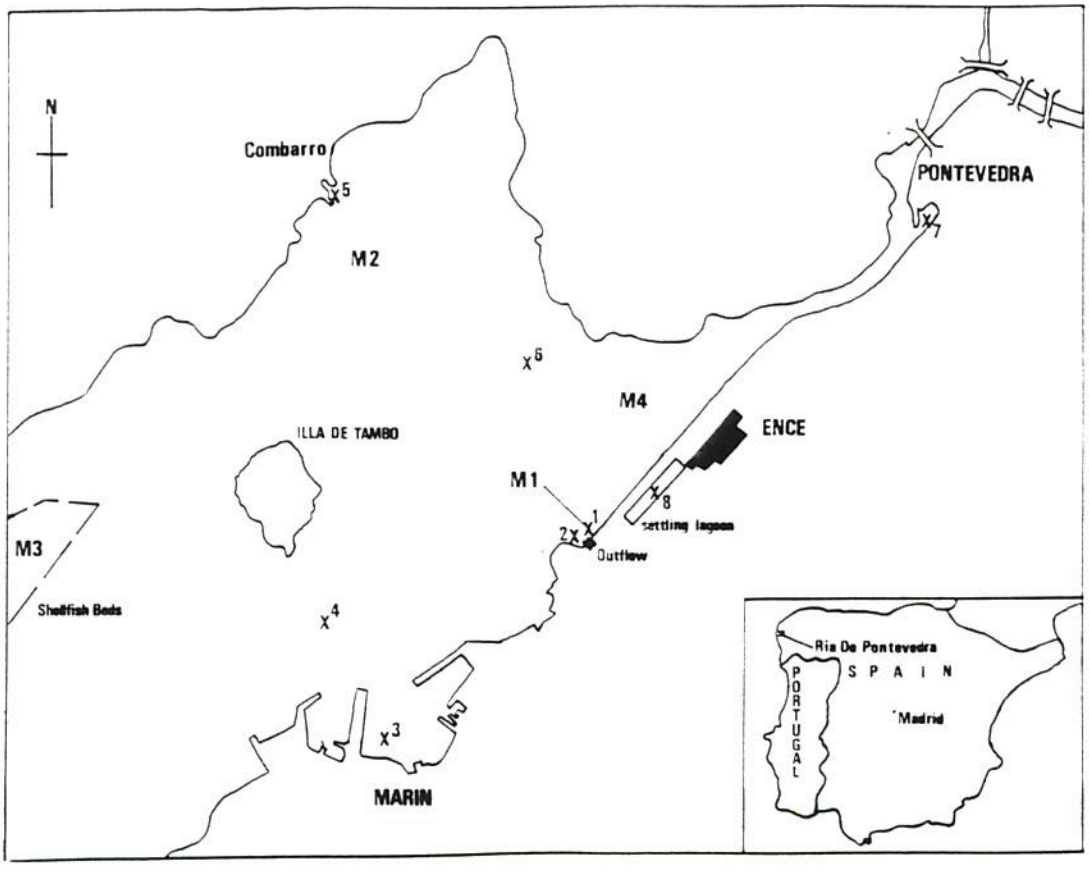
INTRODUCTION

The Ria de Pontevedra is an estuary situated on the Northwest coast of Spain (see insert Figure 1) into which the Rio Lerez flows. The estuary supports a thriving shellfishery despite the presence of the ENCE pulp and paper industrial complex which discharges large volumes of effluent into the bay. Chlorine for the pulp bleaching process is produced within the ENCE complex using the mercury cell process.

The bleached chemical pulp industry of the world consumes considerable quantities of chlorine and discharges large 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 as many of them are toxic, show considerable resistance to biological and chemical degradation, and are prone to bioaccumulation. 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's list of priority pollutants. This study investigated EOCl and metals in the sediments of Ria de Pontevedra. Shellfish from the bay and the effluent from the ENCE complex were sampled and analysed for a variety of parameters.

FIGURE 1: Ria de Pontevedra and sampling positions



METHODS

An effluent sample was obtained directly from the outfall into the estuary, the position of which is marked in figure 1. The effluent was collected in a glass sample bottle which had been prepared by acid- and hexane-washing.

Sediment samples were obtained in the estuary with the use of a 15x15x17cm Ekman grab operated from a small vessel. The location of these samples is shown in figure 1; the sediments were labelled PV1-PV8. Samples were only taken where the substrate consisted of fine muds and areas of sandy sediment were not sampled. A further sediment sample was obtained from the settling lagoons of the factory with a pipe dredge. All sediments were collected in Nalgene bottles which were kept chilled during transport to the analysing laboratories.

Shellfish were collected from points in the bay and represent the three main species which are commercially fished in the estuary. These samples were labelled M1-M4, figure 1 illustrates where they were taken.

EXTRACTABLE ORGANIC CHLORINE

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

TOTAL MERCURY

Shellfish were transported frozen 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), analysed on a Thermoelectron 151 AAS.

HEAVY METALS

The effluent and sediments were analysed for heavy metal content at Queen Mary and Westfield College, London. A range of seven metals was investigated, these being Cu, Cd, Cr, Pb, Ni, Zn & Ag. Sediments were oven-dried and their moisture content thereby 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 thus obtained. Analysis was by Thermoelectron IL157 AAS calibrated against known standards and background corrected for all the metals except Cr.

RESULTS AND COMPARISONS

EXTRACTABLE ORGANIC CHLORINE (EOCl)

TABLE 1.

	EOCl mg/kg wet weight	EOCl mg/kg dry weight	EOCl mg/l
SEDIMENT			
PV1	44	65	
PV2	14	33	
PV3	6	26	
PV4	6	26	
PV5	<4	<8	
PV6	38	133	
PV7	12	31	
PV8	12	41	
MEAN	17	44	
RANGE	<4-38	<8-133	
BACKGROUND LEVEL FOR SEDIMENT[1]		1-6	
EFFLUENT			3.04

[1]Hakanson *et al* (1988)

TABLE 2.

STANDARDS ADOPTED IN THE NETHERLANDS FOR SOIL AND GROUNDWATER CONTAMINANTS (in Bridges 1989)

A = reference value
B = value above which there is a need for further investigation
C = value above which a clean-up is required

	EOCl in soil mg/kg dry weight	EOCL in groundwater mg/l
A	0.1	0.001
B	8	0.015
C	80	0.070

METALS IN SEDIMENTS

TABLE 3.

METAL	SAMPLE NUMBER PV1	PV2	PV3	PV4	PV5	PV6	PV7	PV8	MEAN	BACK-GROUND[2]
CADMIUM (ppm)	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	0.3
LEAD (ppm)	14.9	97.6	76.4	63.2	19.0	48.8	109.5	8.6	54.8	30
COPPER (ppm)	24.4	171.6	98.3	56.6	19.2	32.6	59.1	33.5	61.9	20
SILVER (ppm)	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	1.0	<0.25	<0.25	
ZINC (ppm)	68.2	233.8	236.4	192.4	76.8	194.9	240.2	98.7	167.7	76
CHROMIUM (ppm)	12.5	36.2	46.7	38.2	14.5	34.9	22.5	30.8	29.5	73
NICKEL (ppm)	4.0	11.8	16.1	17.0	3.6	10.7	7.8	50.0	15.1	26

[2] in Driel and Nijssen (1988)

MERCURY IN SHELLFISH

TABLE 4.

	Shellfish type	mercury content dry wt. mg/kg	wet wt. mg/kg
M1	blue mussels	5.53	0.65
M2	small clam	0.82	0.15
M3	blue mussels	0.52	0.09
M4	cockles	1.25	0.16
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

Metals

Sediment levels of Pb, Cu, Cd, Cr, Zn, Ni, & Ag are not exceptional. The high levels of mercury, however, found in shellfish are of obvious concern. The European and Paris Commissions have adopted an Environmental Quality Standard (EQS) for mercury, which requires that the mean concentration of mercury in the flesh of a representative sample of fish, locally caught from areas receiving significant inputs of mercury, shall not exceed 0.3 mg/kg on a wet weight basis. The mussels collected beside the outfall (M1) contained 0.65 mg/kg wet weight, thus exceeding this standard.

Organics

The EOCl levels range from <8 to 133 mg/kg dry weight in Pontevedra 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 due to anthropogenic input but are not as high as found in the vicinity of pulp and paper plants in Sweden. Hakanson *et al* (1988) 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 however. The Ria de Pontevedra has a tidal range of 2.9 metres during spring tides and also will experience net outflow of sediment because of the flow of water from the Rio Lerez. Therefore it would not be expected that the sediment levels of EOCl would be as high as those in the relatively low energy areas of the Baltic and Bothnian Seas. In fact, in areas of erosion and transportation identified by Hakanson *et al* (1988) low EOCl levels of <1 mg/kg dry weight were reported. The high level of sample 6 in this study can be accounted for by the local hydrographical conditions which result in a back-eddy where the river flows into the estuary. The level of EOCl found in the effluent from ENCE is about half that found in spent bleach liquor from a kraft mill using a spruce and pine mixture (Carlberg *et al* 1988). This reflects the lower quantities of chlorine generally used in manufacture of eucalypt pulp.

Dilution effects are unlikely to play a large role in this particular case. The chlor-alkali effluent mixed with the process waters at ENCE is thought to be around 2% of the total flow. It is also to be expected that a number of the more volatile components will have escaped to the atmosphere, as the effluent is warmer than ambient and appears to be discharged via a settling lagoon. This is another route by which chlorinated organics enter the workplace and the wider environment and may constitute a health hazard.

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), these effluents are also implicated in spinal damage to fish.

There is some regulation of organochlorines in the Netherlands and control levels have been set for soils and groundwater (see table 2). There are no regulatory levels for EOCl in sediments although the issue of pollutants in dredging spoils is a subject of considerable debate. The groundwater of the area may be at risk of organochlorine pollution. ENCE effluent passes through settling lagoons and there may be some leaching from these into the groundwater.

The ENCE plant utilises eucalypt wood as feedstock. Chlorinated thiophenes are a group of compounds which have been identified in the spent bleach liquor from kraft pulp when eucalyptus was used as the raw material (Carlberg *et al* 1988). Thiophenes have been shown to bioaccumulate in fish and some of them demonstrate mutagenic activity.

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 represent significant implications for human health and aquatic life.

It is likely also that the organic chlorine compounds are being concentrated in the shellfish as this phenomenon has been reported from the vicinity of pulp and paper plants in Finland (Herve 1988).

It is clear that there are elevated levels of organically bound chlorine in the sediments of the Ria de Pontevedra and entering the Ria via ENCE's effluent. For humans there are several routes of exposure of these chlorinated organics, one such route being the ingestion of contaminated shellfish. Given that it is widely accepted that chlorinated organics pose a threat to human health, the pulp and paper plant at Pontevedra must be regarded as posing a potential health risk to the local population as well as to the receiving ecosystem.

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