Characterisation of wastewater discharges from chloralkali plants and associated chlorinated chemical production facilities in Spain

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Executive Summary

Eight of the nine chloralkali plants located in Spain continue to use outdated 'mercury-cell' technology for the manufacture of chlorine, accounting for more than 90% of national chlorine production capacity and representing almost a fifth of all mercury cell plants remaining across the whole of Europe. Despite improvements in performance and reductions in mercury discharges and losses to air in recent years, these plants still account for hundreds of kg of mercury inputs to Spain's environment every year (an estimated 713 kg in total in 2005). While other sources of mercury dominate national mercury emissions budgets, chloralkali plants nonetheless represent significant point sources of pollution of air and water at local and regional levels, arising both from historic and current discharges.

Mercury is a very mobile pollutant which can be transformed rapidly into its most toxic organic forms (especially methyl mercury) once released to the environment. These organic forms can accumulate in animals, including fish and, ultimately, humans and can cause damage to the nervous system, even in the unborn child.

In addition to mercury, chloralkali plants can also be significant sources of other pollutants, arising from the electrolysis of concentrated brines. Furthermore, much of the chlorine they manufacture is commonly used in industrial facilities located close to the chloralkali plants, including the manufacture of the chlorinated plastic PVC (polyvinyl chloride, the single greatest use of chlorine) and chlorinated solvents, manufacturing processes which themselves generate waste streams rich in harmful substances.

Although some information on total mercury losses to air and water from chloralkali facilities is regularly reported under international conventions and published by the industry, few further details are openly available concerning the chemical characteristics of waste streams discharged to water and their impacts on the receiving environment. At the same time, while international regulations place certain limits on industrial discharges from PVC manufacturing facilities, these limits cover only a small fraction of the substances of concern which such waste streams may contain. The current study was therefore intended to provide a snapshot of the chemical characteristics and complexity of wastewater discharges from chloralkali and associated chlorinated chemical manufacturing facilities located in Spain, insofar as those waste streams could be accessed, as well as an indication of the extent to which such discharges have contributed to pollution of waters and sediments in the receiving environment.

A total of 43 samples were collected (from 22 locations) in June and July 2007, including (where accessible) wastewaters, river waters, sediments and wastes from settlement or evaporation ponds used for effluent treatment. Given the inaccessibility of discharge pipes at several of the facilities (especially those which are now released via sub-sea pipelines) and the nature of the receiving environments in some other cases, it was not possible to collect a comprehensive set of samples (i.e. upstream, downstream and from the discharge points themselves) from all nine facilities. Nonetheless, the samples which were collected provide a unique insight into discharges to water from this sector.

All samples were returned to the Greenpeace Research Laboratories (University of Exeter, UK) for analysis, including quantitative analysis for mercury and other toxic metals and for a range of volatile organic compounds (VOCs), and qualitative analysis of other, semi-volatile (solvent-extractable) organic compounds. Metal analyses were conducted using ICP-Atomic Emission Spectrometry, other than for mercury in water which was determined using ICP –

Mass Spectrometry by an independent accredited laboratory. All organic analyses were conducted using gas chromatography-mass spectrometry (GC-MS).

Key findings from the study can be summarised as follows:-

1. For the two chloralkali/chlorinated chemical manufacturing facilities at which it was possible to collect a comprehensive sample set (Monzón and Sabiñánigo), characteristic contaminants which could not be detected in upstream samples of water and/or sediment were readily detectable in samples collected downstream from the facilities.

    a. in the case of Monzón, for example, vinyl chloride monomer (VCM, the toxic precursor of PVC) was detectable in water collected from the Cinca River 200m downstream, despite the high flow of water and the volatility of this compound. A sample of wastewater from the PVC plant's discharge contained over 3 mg/l of VCM, three-times higher even than the limit imposed by OSPAR Decision 98/5 for process wastewater <u>before</u> secondary treatment. Mercury was detected in discharges from both the PVC and chloralkali plants and was present also in sediments collected adjacent to the discharge pipes (at up to 11 mg/kg) and from the downstream site.

    b. at Sabiñánigo, the sub-surface wastewater discharge to the Gallego River from the chloralkali plant was clearly adding a range of chlorinated and brominated VOCs to the river, which were again detectable downstream. Discharges of mercury at the time were 2.6 ug/l, the highest recorded for effluents in this study, and undoubtedly contributing further to the substantial existing burden of historic mercury contamination (5.6 mg/kg adjacent to the discharge pipe). The presence of over 300 ug/l of hexavalent chromium, the most toxic form of this metal, in this same discharge is currently unexplained but clearly demands urgent investigation.

2. Although fewer samples could be collected from other sites, evidence of mercury accumulation as a result of current and/or historical discharges could be found in sediments collected adjacent to the Flix plant (Ebro River, 144 mg/kg), as well as (at far lower levels), in sediments close to the former discharge pipes for the Martorell facility (Llobregat River, 0.8 mg/kg) and the Elnosa facility at Lourizan (Ria de Pontevedra, 1.5 mg/kg), despite their replacement by sub-sea outfalls in 2003. Contaminated sediments from these locations may be expected to act as significant sources of ongoing contamination to the downstream environment for years or even decades after the reduction or cessation of actual discharges.

3. At Torrelavega, discharges from the chloralkali plant are carried by pipeline to a sea outfall some distance to the plant, the discharge from which could not be sampled at the time of this investigation. In the Saja River itself, on which the Solvay plant is located, the pattern of sediment contamination is complex, largely as a result of the presence of numerous other industrial facilities on the same stretch of the river. No specific chemical 'signal' relating to the chloralkali facility could be detected in the river sediments in the vicinity of the Solvay plant and the origins of an effluent pipe found at this location could not be reliably traced. In the case of the Hernani facility, the one plant in Spain converted entirely to membrane technology (but which at one time did discharge effluents from a mercury cell process to the Urumea River), the extent to which the river bed has since been 'restored' by the local authorities, coupled with the very sandy nature of the

sediment now present in the river, meant that the samples collected were unlikely to give a representative picture of contamination from former discharges.

4. Aside from mercury, sediments collected adjacent to the Flix chloralkali and chlorinated solvent plants revealed a substantial 'footprint' of other hazardous chemicals, including cadmium (34 mg/kg), hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD). While a large part of this footprint may be a legacy of past production, wastewater being discharged at the time of sampling revealed ongoing inputs of a range of volatile chlorinated and brominated VOCs (at a total of over 150 ug/l) as well as tetrachlorobutadiene and a bromochlorobenzene derivative.

5. Samples of liquid and solid (sludge) wastes collected from treatment plants (settlement lagoons/evaporation ponds) at two facilities for which discharge points could not be identified (Palos de la Frontera, Huelva, and Vila-seca, Tarragona) showed high levels of contamination with metals and chlorinated organics.

    a. at Palos de la Frontera, for example, liquid collected from the last pond in the treatment plant prior to discharge contained 2.77 mg/l of the harmful solvent dichloromethane (methylene chloride), as well as chloroform, 1,2-dichloroethane (otherwise known as ethylene dichloride, or EDC, the precursor in the production of VCM and, hence, PVC) and traces of VCM itself. Given the volatile nature of these contaminants, it is likely that discharge of such contaminated effluents to this pond results routinely in significant losses to air in the vicinity, as well as to water should effluent of this nature be discharged. Levels of mercury (5.6 mg/kg), copper and zinc were notably high in the solid materials sedimenting out in this pond, though the ultimate fate of these sludges is not known.

    b. chlorinated VOCs were also prominent in liquid samples collected from two settlement ponds located in front of the chloralkali, PVC and chlorinated solvents plants at Vila-seca, and known to be receiving effluents from these facilities. These included 58 ug/l of VCM, 42 ug/l EDC and 25 ug/l chloroform.

Taken together, the results from this study confirm that discharges from many of the chloralkali and associated PVC and chlorinated chemical manufacturing facilities in Spain have not only created a substantial legacy of environmental contamination and complex hazardous wastes, but in several cases continue to act as significant point sources of mercury and harmful chlorinated substances to the receiving freshwater environment. Although a comprehensive survey of all discharges was simply not possible, not least because of the trend over the last decade towards the construction of sub-sea outfalls to replace historic discharges to rivers, the results nonetheless provide a unique and valuable snapshot of the quality and complexity of discharges to water from this sector.

While reliance on mercury-cells continues for the manufacture of chlorine in Spain, despite the clear decision under the IPPC Directive that Best Available Techniques (BAT) for the sector is conversion to membrane cells, some level of mercury discharges and losses to water and air remain inevitable. Likewise, the generation and release of harmful product residues and by-products from the synthesis of chlorinated organic chemicals, including PVC, is also unavoidable for as long as such products continue to be manufactured.

Meanwhile, PARCOM Decision 90/3, which recommended phase-out of mercury cells throughout the North-East Atlantic region (including Spain) as soon as possible, with the target of 2010, is very much in force and remains to be implemented. In setting its own, more relaxed timetable of 2020, the chloralkali industry has clearly signalled its intention to try to sidestep international law and, as a result, has been reluctant to invest the funds necessary to achieve an early phase-out, even though that would be both technically feasible and consistent with legislative pressure. In Western Europe as a whole, the industry in Spain appears to have been particularly slow in this regard.

Further tightening of end-of-pipe treatment technologies could result in additional reductions in discharges and losses of mercury, EDC, VCM and other hazardous substances to the environment, but can never eliminate such releases and will not address the substantial legacy of pollution which remains in many areas. Spain, along with other Contracting Parties to the OSPAR Convention (1992), made the commitment ten years ago to make "*every endeavour to move towards the target of the cessation of discharges, emissions and losses of hazardous substances by the year 2020*". Since then, a similar cessation objective has been agreed for a range of 'priority hazardous substances' under the EU Water Framework Directive (2000/60/EC), including *inter alia* mercury (and of direct relevance to this study) and its compounds, cadmium and its compounds, hexachlorobenzene and hexachlorobutadiene.

In order to meet these commitments, and to provide for a high level of protection for Spain's environment (whether in relation to freshwater or marine ecosystems and resources), there is an urgent need for a more fundamental rethink not only of the manner in which chemicals are manufactured, but also more fundamentally of the chemicals themselves which are being produced and on which society has come ever increasingly to rely. The fact that so much of the chlorine produced is directed towards manufacture of PVC, a plastic which could be readily replaced with non-chlorinated alternative materials, indicates that such a fundamental re-evaluation and redirection of industrial enterprise may by no means be unthinkable.

Introduction

Despite its hazards and those of many of the chemicals it is used to manufacture, chlorine remains a key commodity for the chemical industry worldwide, including in Europe. According to industry estimates, European producers manufactured 10.7 million tonnes of chlorine in 2007 (approximately 20% of global production), from a total installed capacity of around 12.6 million tonnes distributed between 76 plants in 20 EU countries (Eurochlor 2007a). Although chlorine is used in a wide array of organic and inorganic chemical synthesis applications, as well as in water disinfection, the largest single use sector remains the production of the chlorinated plastic polyvinyl chloride, or PVC. Demand for PVC and polyurethanes (the latter manufactured using chlorinated intermediates), as well as for a host of chlorinated substances for use as solvents, industrial chemicals, pesticides and pharmaceuticals (among others), supported a rapid increase in the production of chlorine from the 1940s onwards (EC 2001). Manufacture of PVC is the main driver of continued expansion of the chlorine production sector globally, with markets for this plastic expanding at an estimated 5% per year. Although there is no significant growth in production in Europe, PVC manufacture nonetheless still consumes around 35% of all chlorine manufactured in the EU (Eurochlor 2008).

There are three main industrial processes in use for the manufacture of chlorine, all involving the electrolysis of brine (concentrated salt solutions), namely the mercury cell, diaphragm and membrane processes. Together, these account for 95% or more of global chlorine production (Stringer & Johnston 2001). Because of the electrochemistry involved, all yield both chlorine and caustic soda (sodium hydroxide) in roughly equal proportions. The mercury cell, so called because of its use of elemental mercury as a cathode, has long been the dominant process in Europe, since the construction of the first Castner-Kellner mercury cell in the UK in the 1890s (with the demand for chlorine at that time largely for bleaching applications) (EC 2001). In 2006, mercury cells still accounted for 43% of all chlorine production capacity in Europe (down from roughly 60% in 1997), compared to 39% for membrane cells and 15% for diaphragm cells (Eurochlor 2007b).
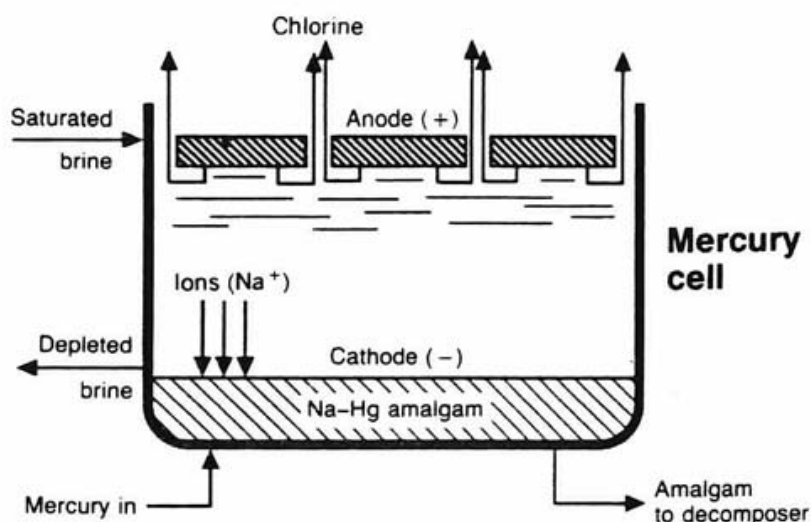

Figure 1: Mercury electrolysis cell (after Curlin *et al.* 1993)

A key driver for the closure or conversion of mercury cell plant to membrane cells around the world has been the health and environmental concerns associated with the inevitable releases of mercury and its compounds from the mercury cell process. Severe pollution of the environment surrounding and downstream from chloralkali plants, including contamination of workers and individuals from nearby communities, has been recorded in many countries, including the USA, UK, Sweden, Spain, Portugal, Italy and India (Duarte *et al.* 1991, Maserti & Ferrara 1991, Stringer & Johnston 2001). Although technical developments have resulted in a substantial reductions in routine mercury losses from existing facilities in Europe, from levels associated with early facilities as high as 135-225g mercury per tonne of chlorine (Leddy *et al.* 1978) to the figures closer to 1g per tonne now reported (Eurochlor 2007a, OSPAR 2007a), mercury losses to air, water and solid wastes remain a significant concern given the scale of chlorine production.

Moreover, the balance of production processes in Europe is by no means typical of the global situation. In the USA, for example, the diaphragm process (which uses no mercury and is more energy efficient, but for which concerns remain around the use of asbestos in older facilities) has for many years accounted for around 75% of national chlorine production. In Japan, where mercury pollution has long been recognised as a priority issue following the severe pollution of Minimata Bay (though not in itself related to a chloralkali facility) and resulting poisoning of thousands of people through consumption of contaminated seafood (Davies 1991, Grandjean *et al.* 1996, Kudo *et al.* 1998), membrane cells comprise 90% of production capacity. Membrane cells are not only less polluting, but also far more energy efficient than mercury cells.

For these reasons, the definition of BAT (Best Available Techniques) for mercury cell plants under the European Directive on Integrated Pollution Prevention and Control (IPPC) is conversion to membrane cells (EC 2001). However, the fact that much of the chlorine production capacity in Western Europe was installed in the 1970s and with expected plant lifetimes of 40-60 years, combined with the lack of the same legislative drive which influenced the industry in Japan, has meant that the dominance of the mercury cell process has been slow to decline.

Under the auspices of the former Paris Convention (1974) on land-based sources of marine pollution (amalgamated with the 1972 Oslo Convention to become the OSPAR Convention in 1992), and recognising the ongoing threat of mercury pollution to the environment and living resources of the North-East Atlantic region, many governments in Western Europe agreed on a recommendation to phase-out of mercury cell technology as soon as possible, with the objective that this should be completed by 2010 (PARCOM 1990). Despite this commitment, and the more recent call from the European Parliament for the European Commission to take action to implement PARCOM Decision 90/3 (EP 2006), the chlorine industry in Europe has long resisted pressure for conversion within this timeframe, citing the high economic cost and efforts made to reduce mercury emissions from existing facilities in recent decades. Instead, the industry federation Eurochlor has set its own 'voluntary commitment' to phase-out mercury cell plants from Europe by 2020 (Eurochlor 2007a).

Although the number of mercury cell plants has undoubtedly declined under this programme, 43 such facilities, spread over 14 countries, remained in operation within Europe at the start of 2007, containing a total quantity of mercury in cathodes of around 9 600 tonnes. Among these 43 facilities are 8 of the 9 chloralkali plants located in Spain (Eurochlor 2007a). One relatively small facility, in Hernani in the north-east of the country (production capacity 15 000 tonnes of chlorine per year), has converted completely to a membrane cell process while another, at Vila-seca on the Mediterranean coast near Tarragona (total capacity 190 000 t Cl/a), has undergone partial conversion, with membrane cells now providing around 30% of capacity. Together with the 7 other plants, this means a total mercury cell chlorine production capacity for Spain of 755 000 tonnes per year, more than 90% of the national total of 827 000 tonnes. Further details of all Spanish chloralkali facilities are provided in Table 1, and their locations shown in Figure 2.

Figure 2: Locations of the nine chloralkali facilities in Spain

Site	Operator	Location	Established	Type of chloralkali cell	Chlorine production capacity 2007 (kt)	Associated chemical production facilities
Flix	Ercros	Flix, Tarragona	1899	Hg	150	Chlorine derivatives solvents, dicalcium phosphate
Hernani	Electroquimica de Hernani	San Sebastián, Gipuzkoa	1948	M	15	PVC
Martorell	SolVin	Martorell, Barcelona	1972	Hg	218	PVC
Monzón	Quimica del Cinca	Cinca Media, Aragon	1952	Hg	31	PVC
Huelva (Palos de la Frontera)	Ercros	Huelva	1973	Hg	101	Chloromethanes, dichloroethane, PVC
Lourizan	Elnosa	Pontevedra, Galicia	1966	Hg	34	Pulp and paper
Sabiñánigo	Ercros	Huesca, Aragon	1921	Hg	25	VCM, PVC, chloroisocyanurates, chlorine derivatives
Torrelavega	Solvay	Cantabria	1904	Hg	63	Hydrochloric acid, soda ash, sodium hypochlorite
Vila-seca	Ercros	Tarragona	1970	Hg, M	190	VCM, PVC, dichloroethane, chlorine derivatives

Table 1: overview of chloralkali facilities and chlorine production capacity in Spain as of 2007

In Spain, as in most other countries, emissions of mercury to the environment (predominantly to the atmosphere) from human activities are dominated by combustion sources, including coal-fired power plants, cement kilns and solid waste incinerators. Overall, anthropogenic sources in Spain contribute just over 9 tonnes of mercury per year to the atmospheric burden (roughly doubling the baseline from natural sources), the fourth largest national contribution within the Mediterranean region, after France, Turkey and Italy (Pirrone *et al.* 2001). Emissions from chloralkali plants may, along with other industrial sources, make a relatively small contribution to this overall burden, but are nonetheless significant point sources, especially at local and regional scales. The most recently available figures reported to OSPAR indicate that, in 2005, Spanish chloralkali facilities accounted for total losses to air, water and waste of 713 kg mercury, the majority of which (613 kg) was emitted to air

(OSPAR 2007a). These losses are lower than those reported a decade ago (1057 kg), but are by no means insubstantial given the toxicity of mercury (see Box 1 for background information on mercury toxicity). Furthermore, there are significant uncertainties associated with these reported losses as they do not account fully for the 'difference to balance' between mercury consumption and mercury inventories, and concerns remain that actual emissions, discharges and losses, whether from routine operations or periodic incidents, may be considerably higher in some cases.

In addition to well-publicised studies showing mercury contamination of workers and local children in the vicinity of the Ercros chloralkali plant at Flix on the Ebro River in eastern Spain (Batista *et al.* 1996, Montuori *et al.* 2006), hotspots of mercury pollution have also been recorded downstream of the Quimica del Cinca facility in Monzón (Raldua *et al.* 2007)

Box 1: Mercury

Mercury and its compounds have used in numerous products and industrial processes, including the chloralkali mercury cell process (ATSDR 1999, UNEP 2002). Many historical uses of mercury are, however, being increasingly restricted or phased out due to environmental and health concerns (UNEP 2002). Mercury compounds are also present as trace components in coal, the burning of which constitutes the main source of mercury emissions to the environment from human activities (Pacyna *et al.* 2006).

Mercury is generally found in the environment at extremely low levels. Level in uncontaminated river sediments can vary, but levels are typically below 0.4 mg/kg. In Spain, levels are commonly below 0.2 mg/kg (EuroGeoSurveys 2005, Salomons & Forstner 1984). Surface freshwaters without known sources of mercury contamination generally contain less than 1ng/l (0.001ug/l) of total mercury (Hope & Rubin 2005).

Mercury can exist in a number of forms; metallic mercury (including mercury vapor), inorganic mercury compounds and organic mercury compounds. The toxicity of mercury is dependant on the form (Clarkson & Magos 2006, Eisler 2006). For a metal, mercury is highly volatile and upon release to the atmosphere metallic mercury can travel globally and impact far from the source of its release (UNEP 2002). Where mercury enters the aquatic environment (either through direct input or through deposition from the atmosphere), mercury and its compounds can become transformed into organic mercury (methyl-mercury) by micro-organisms, a highly toxic form that can bioaccumulate and biomagnify (progressively concentrate) to high levels in food chains, particularly in fish (Harris *et al.* 2007). For humans, this is the major route of exposure for the general public (Mahaffey *et al.* 2004). Methylmercury can accumulate in the body and its main impact is damage to the nervous system. Being able to pass through the placental barrier and the blood-brain barrier, methylmercury can have adverse effects on the developing brain and central nervous system in foetuses and children (Axelrad *et al.* 2007). Recent research also indicates that exposure can increase cardiovascular and heart disease (Virtanen *et al.* 2005). Where used in the industrial setting, such as in chloralkali mercury cells, workers may also be exposed to mercury, primarily through inhalation (Lopez-Colon & Lozano 2006). This route of exposure can also cause effects on the nervous system and damage to the kidneys (Clarkson & Magos 2006).

Mercury is a recognised priority pollutant under many national and international laws and conventions. For example, mercury and its organic compounds have been listed as Chemicals for Priority Action under the OSPAR Hazardous Substances Strategy since its inception in 1998 (OSPAR 2007b). In addition, mercury and its compounds (in general) are listed as 'priority hazardous substances' under the EU Water Framework Directive (EU 2000, EC 2006), and are therefore subject to requirements for phase-out or cessation of emissions, discharges and losses within a certain timeframe.

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and in sediments from the inner Ria de Pontevedra in Galicia (north-west Spain), close to the Elnosa plant (Beiras *et al.* 2003). In the latter case, mercury contamination of the marine environment, readily detectable in sediments, mussels and algae in the area, has led in turn to mercury accumulation in yellow-legged gulls (*Larus cachinnans*), and the presence of high levels of mercury in debris surrounding their nesting sites on Las Islas Cies some way off the coast (Otero *et al.* 2000). Furthermore, samples of moss collected from uncontaminated 'control' sites rapidly accumulate mercury residues when transplanted close to the Elnosa chloralkali plant (Fernandez *et al.* 2004). More recently, spot-checks of mercury concentrations in air around three Spanish chloralkali plants, at Monzón, Torrelavega in the north and Huelva (Palos de la Frontera) in the south, revealed highly variable levels, but with maximum values well above health benchmarks set for mercury exposure by the US Environmental Protection Agency (EEB 2006).

While the majority of reported losses of mercury from chloralkali plants are to air, direct discharges also occur to water. Mercury contamination of waste waters can occur from a number of sources, including purification wastes, leakage and condensates from the electrolysis process itself, wash water from cell cleaning operations and rinse water from the periodic cleaning of floors, tanks, pipes, dismantled apparatus and surfaces of areas beyond the cell room (EC 2001). However, despite the obvious concerns arising from inputs of mercury to freshwater environments, there are remarkably few data freely available on the concentrations of mercury in effluents discharged from chloralkali facilities, in Spain or elsewhere. Where limits are set, both nationally and internationally, they tend to be defined in relation to installed chlorine production capacity, i.e grammes of mercury per tonne of capacity. In a similar way, PARCOM Decision 90/3 set emissions limits for mercury to atmosphere of 2 g mercury per tonne of installed chlorine capacity (PARCOM 1990). In recognition of impending permitting requirements under the IPPC Directive, the industry continues to pursue a target set in 1998 of 1 g/t for all emissions, whether to air, water or product (Eurochlor 2007b). In that year, Eurochlor reported that mercury releases specifically to water from Western European plant fell in the range 0.01 to 0.28 g/t (EC 2001). On the basis of total losses reported to OSPAR for 2005 (OSPAR 2007a), it is possible to estimate that combined losses to water and to products (i.e. chlorine and caustic) from all eight chloralkali plants in operation in Spain were in the range of 100 kg, or around 0.13 g/t. What this means in terms of the mercury concentrations of waste waters discharged from individual plants, however, and the resulting accumulation of mercury in the receiving environment, remain poorly described.

At the same time, while most attention has understandably focused on mercury losses, chloralkali facilities make routine use of a wide range of other chemical substances, and generate waste by-products from these chemicals and from the brines themselves, residues of which may well be released to atmosphere and/or appear in effluents discharged to surface waters. For example, these can include metals other than mercury, sulphates, chlorides and chlorates and a range of volatile chlorinated (and sometimes brominated) organic compounds (EC 2001). The generation of chlorinated organic compounds has declined substantially over time, from a high of tens of thousands of tonnes per year released to air and water when records began in the mid-1980s (Eurochlor 2007b), not least because of the switch from graphite to titanium-based anodes. Nonetheless, it is possible that emissions of such compounds remain a significant issue in some facilities.

One of the purposes of this study, therefore, was the collection and chemical characterisation (to the extent possible) of effluent discharges from as many as possible of the nine chloralkali plants operating in Spain in order to provide further background information on the nature of these point source industrial discharges. At the same time, and especially in cases in which collection of effluents was not possible for practical reasons, samples were collected from the aquatic environment receiving the effluents in order to determine the current nature and scale of contamination of waters and sediments with mercury and other pollutants arising from these facilities.

As noted above, both the chlorine and caustic manufactured serve a wide array of demands from the chemical industry, though in quite different market sectors, with the manufacture of PVC plastic taking the largest single share of the chlorine manufactured in Europe. Because of the substantial hazards involved in transport of elemental chlorine, industries which make use of it have tended to become established in close proximity to the chloralkali plants themselves, resulting in large industrial complexes engaged in both chlorine and chlorinated chemical production. It is, therefore, not uncommon to find a chloralkali plant closely associated with a facility manufacturing PVC or, at least, the ethylene dichloride (EDC) and vinyl chloride monomer (VCM) from which PVC are subsequently produced. This is the case, for example, at the Monzón, Sabiñánigo, Vila-seca and Martorell facilities in Spain, among others. In the case of the Flix chloralkali plant, much of the chlorine produced has been directed to the synthesis of other chlorinated materials, most recently chlorinated solvents, though there are reports that the plant has manufactured PCBs and pesticides in the past (de Voogt & Brinkman 1989, Montanes *et al.* 1990). Similarly, chlorine from the plant at Palos de la Frontera (Huelva) in Andalucía on the southern Atlantic coast is used to make chlorinated solvents, including chloromethanes and dichloroethane, as well as polymer chemicals.

Because of the nature of the chemical reactions involved, the manufacture of chlorinated organic compounds tends to generate substantial quantities of harmful wastes and result in releases of both volatile and non-volatile organochlorine chemicals to the surrounding environment. In the case of PVC, for example, the manufacture and purification of ethylene dichloride and, subsequently, vinyl chloride results not only in fugitive losses of these harmful chemicals but also in the generation of highly contaminated distillates and tarry wastes (Stringer & Johnston 2001). As well as providing almost ideal conditions for the formation of chlorinated dioxins and furans (ICI 1994), the standard oxychlorination reactions employed can also generate a wide range of other chlorinated contaminants, some of which may inevitably be released to air or in liquid effluents to receiving waters. Similarly, the chlorination reactions used in the manufacture of solvents can generate a complex range of harmful chlorinated by-products, leading to contamination of the environment, workers and local populations.

Perhaps the most widely recognised case of pollution resulting from the activities of the chlorine industry in Spain is that relating to the Flix chlorinated chemical plant, at which past production had led to extensive releases to air of hexachlorobenzene (HCB) which could, as a result, be detected at far higher levels in the blood of local residents than in individuals from other communities (Herrero *et al.* 1999, To-Figueras *et al.* 2000, Ozalla *et al.* 2002, Eljarrat *et al.* 2008). Although these high exposures do not seem to have led to one of the most commonly recognised symptoms of HCB-poisoning, namely *porphyria cutanea tarda* (PCT, detectable from the excretion of porphyrins in urine), some observations suggest more subtle effects on thyroid hormone systems may be significant (Sala *et al.* 2001). At the same time,

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contamination of water, sediments and soil organisms with HCB and other chlorinated organic chemicals associated with past and/or ongoing production activities at the Flix plant has been described (Swindlehurst *et al.* 1995, Ramos *et al.* 1999). As a 'hotspot' of environmental pollution, its contribution has also been recognised in relation to increased prevalence of both male and female reproductive disorders in fish in that stretch of the Ebro river (Lavado *et al.* 2004).

Under the OSPAR Convention, some limits values have been set for releases to air and water from facilities manufacturing EDC, VCM and PVC, but these cover only a very limited range of contaminants and only in relation to specific parts of the waste management process. For example, OSPAR Decision 98/4 sets limits for releases of EDC, VCM, dioxins and hydrogen chloride (HCl) to air, and of chlorinated hydrocarbons (in general), copper, dioxins and chemical oxygen demand (COD) to water but, other than for COD, discharge limits are defined once again in terms of g/t of manufacturing capacity, and not in more empirical concentration terms (OSPAR 1998a). Absolute concentration limits for VCM are set for both suspension- and emulsion-PVC plants, but then only in relation to partially treated wastewaters, after stripping but before secondary treatment (OSPAR 1998b, 2000). At the final point of release of effluent to surface waters, limits are set for COD and suspended solids only. It is possible, therefore, that the discharge of a range of other potential pollutants may routinely be overlooked.

On the whole, therefore, discharges of waste water from PVC and chlorinated solvent manufacturing plants in Spain are, once again, relatively poorly characterised. For this reason, efforts were also made in the current study to collect and analyse such effluents or, at least, to characterise the extent of contamination of water and sediment samples with chemicals of concern. In some cases, where waste waters are now discharged from inaccessible sub-sea outfalls, samples of waste were instead collected from accessible areas of treatment facilities, as close as possible to the final point of release of treated wastes to the environment.

While by no means a comprehensive survey of waste discharges from the chloralkali and chlorinated chemical manufacturing sector in Spain, the current study should, nonetheless, provide a useful snapshot of effluent quality and its consequences for the downstream environment.

Site	Date	Sampling location	Co-ordinates	Sample types	Sample codes
Flix (Ebro River)	27/06/07	Approximately 7km upstream from plant, at Riba Roja dam	N 41°14.995' E 00°28.911'	River water and sediment	SP07001-3
	28/06/07	Discharge channel serving pipes '12' and '13' from plant	N 41°13.886' E 00°32.236'	Effluent and sediment from channel	SP07004-6
Hernani (Urumea River)	05/07/07	Upstream from former discharge pipes	N 43° 15.208' W 01° 56.957'	Sediment	SP07007
		Adjacent to former discharge from chloralkali plant	N 43° 15.276' W 01° 56.921'	Sediment	SP07008
		Adjacent to former discharge from PVC plant	N 43° 15.265' W 01° 56.950'	Sediment	SP07009
Martorell (Llobregat River)	28/06/07	Upstream from plant, under road bridge	N 41°29.713' E 01°55.349'	Sediment	SP07010
		Downstream from chloralkali and PVC plant, close to suspected former (pre-2003) discharge pipe	N 41°29.122' E 01°55.919'	Sediment	SP07011
Monzón, (Cinca River tributary of Ebro River)	27/06/07	Approximately 1km upstream from plants	N 41° 56.329' E 00° 10.051'	River water and sediment	SP07015-17
		Downstream from plants, 200m from road bridge	N 41° 55.020' E 00° 10.563'	River water and sediments	SP07012-14
		Discharge to river from chloralkali plant	N 41° 55.513' E 00° 10.348'	Effluent and sediment from end of channel	SP07018-20
		Discharge to river from PVC plant	N 41° 55.432' E 00° 10.388'	Effluent and sediment from end of channel	SP07021-23

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Site	Date	Sampling location	Co-ordinates	Sample types	Sample codes
Palos de la Frontera	10/07/07	Sediment from estuary close to Odiel River	N 37° 10.673' W 06° 55.134'	Sediment	SP07024
		Waste from the last open lagoon/evaporation pond of the chloralkali and PVC wastewater treatment plant	N 37° 10.709' W 06° 55.103'	Effluent and solid waste	SP07025-27
Lourizan (Ria de Pontevedra)	04/07/07	Sediment from the banks of the Ria de Pontevedra, opposite the chloralkali plant	N 42° 25.471' W 08° 40.076'	Sediment	SP07028
		Sediment from the Ria de Pontevedra collected adjacent to former discharge pipe (disused since 2003)	N 42° 24.449' W 08° 40.910'	Sediment	SP07029
Sabiñánigo (Gallego River)	26/06/07	Approximately 1km upstream from plants	N 42°31.171' W 00°20.556'	River water and sediment	SP07033-35
		Downstream from plants, before confluence with Tulivana River	N 42°30.623' W 00°21.469'	River water and sediment	SP07030-32
	27/06/07	Sub-surface discharge to river from chloralkali plant	N 42°30.769' W 00°21.112'	Effluent and sediment from end of pipe	SP07036-38
Torrelavega (located on Saja River, discharging *via* a subsea outfall)	05/07/07	Upstream from chloralkali plant, paper mill and other chemical plants	N 43° 21.345' W 04° 03.608'	Sediment	SP07039
		20m from unidentified discharge pipe adjacent to chloralkali plant	N 43° 22.650' W 04° 02.650'	Sediment	SP07040
Vila-seca	28/06/07	Western-most of two wastewater lagoons/evaporation ponds serving chloralkali and PVC plants	N 41° 06.176' E 01° 09.846'	Wastewater	SP07041
		Eastern-most of two wastewater lagoons/evaporation ponds serving chloralkali and PVC plants	N 41° 06.168' E 01° 09.893'	Wastewater	SP07042-43

Table 2: summary of sampling sites and samples collected in the 2007 study

Materials and Methods

Sample collection

A total of 43 samples (including sediments, waters and waste waters) were collected during June and July 2007, from a total of 22 different locations in the vicinity of the nine chloralkali facilities in operation in Spain and, where relevant, their associated chemical production facilities. The number and types of samples which could be collected varied from site to site, depending on the practicality of access to discharge pipes, treatment facilities and/or appropriate stretches of the receiving water systems. Therefore, despite initial intentions to collect environmental samples from both upstream and downstream locations and samples of the effluents being discharged from all nine facilities, it was not always possible to do so. Table 2 provides a summary of all of the samples collected

In all cases, samples were collected in pre-prepared (acid washed and pentane rinsed) glass bottles. For sites at which liquid (water or wastewater) samples were collected, two such samples were collected at each location, one in a 100ml amber vial with ground glass stopper (filled to leave no headspace) for volatile organic compound (VOC) analysis, and the other in a 1 litre screw-cap bottle for use in the quantitative analysis of metals and qualitative analysis of solvent extractable (semi-volatile) organic compounds. Sediment samples were collected in 100ml screw-cap bottles. Upon collection, samples were immediately chilled and kept cool and dark during transit to our laboratory.

Upon reception at the Greenpeace Research Laboratories, individual samples were homogenised before being sub-sampled for metals analysis, the remainder being used for organic analysis. All samples were stored refrigerated until analysis.

Analysis for Volatile Organic Compounds (VOCs)

Method

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 35^0C (held for 4min), rising to 55^0C at 5^0C/min, and then to 210^0C at 15^0C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method.

Halogenated VOCs quantified in the water samples:

Vinyl chloride	Chloroform	Propene, 1,3-dichloro-,
Ethane, chloro-	Ethane, 1,1,1-trichloro-	trans-
Ethene, 1,1-dichloro-	Methane, tetrachloro-	Ethene, tetrachloro-
Methane, dichloro-	Ethane, 1,2-dichloro-	Methane, dibromochloro-
Ethene, 1,2-dichloro-,	Ethene, trichloro-	Bromoform
trans-	Methane, dibromo-	Ethane, 1,1,2,2-tetrachloro-
Ethane, 1,1-dichloro-	Methane, bromodichloro-	Ethane, hexachloro-
Ethene, 1,2-dichloro-, cis-		Butadiene, hexachloro

Not all of the VOCs were detected in the samples. Therefore reported results only present information for those compounds identified and quantified.

Quality control

Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated using data from the analysis of seven replicates of a standard mixture of commonly occurring VOCs, containing 1ppb of each analyte. Limits of quantification (LOQ) were determined as the lowest concentration in the linear regression used for quantification. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analysing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Analysis for extractable organic compounds

Preparation

20 μg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. For sediment samples, approximately 30 g of each sample (wet weight) was extracted for two hours using a mixture of 15ml pentane and 5ml acetone, at a temperature of 69°C with sonication to increase solvent contact with the sediment. After cooling and decanting off the solvent fraction, the samples were acidified to a pH of approximately 2 using nitric acid (10% v/v) and the heated, sonicated extraction process repeated with fresh solvent, following which the two portions of solvent extract were combined. Water samples (approximately 1000ml) were also extracted twice, both before and after acidification to pH 2, using 20ml portions of pentane and a bottle roller to ensure efficient contact between the solvent and the sample.

Clean-up procedures were the same for the crude extracts from both aqueous and sediment samples. For each sample, the two extracts obtained were combined, concentrated to 3ml under a stream of analytical grade nitrogen, shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 2ml as before. Particularly oily extracts were treated with concentrated sulphuric acid sufficient to

obtain a translucent extract prior to treatment with TBA-reagent. 20 µg of bromonaphthalene was added to each extract as a second internal standard (see below) prior to GC-MS analysis.

Analysis

Samples were analysed using an Agilent 6890 Series gas chromatograph with a Restek Rtx-XLB column (30m , 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed an initial temperature of 35^0C, raised to 260^0C at 10^0C/min, then to 295^0C at 50^0C/min (held for 5min), then to 325^0C at 50^0C/min (held for 12min), and finally to 330^0C at 50^0C/min (held for 4min). The carrier gas was again helium, supplied at 2ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory.

Analysis for metals and metalloids

Preparation

A representative portion of each sediment sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5g of each sample was digested with 7.5ml concentrated hydrochloric acid, 2.5 ml concentrated nitric acid and 10 ml deionised water, firstly overnight at room temperature, then for 4 hours under reflux at 130^oC. Digests were filtered and made up to 50ml with deionised water.

Two samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China, and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

For water samples, a representative portion of each sample (90ml) was acidified by the addition of concentrated nitric acid (10ml) to give a final concentration of 10% v/v. 50ml of each acidified sample was refluxed at 130^oC for 4 hours. Cooled digests were filtered and made up to 50ml with deionised water. Two samples were prepared in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water) and a mixed metal quality control solution of 8 mg/ l. These control samples were prepared in an identical manor to the samples.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 1 mg/l and 10 mg/l, and matrix matched to the samples, were used for instrument calibration. Calibration of the ICP-AES was validated by the use of quality control standards at 8 mg/l and 0.8 mg/l prepared from different reagent stocks to the instrument calibration standards. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Analysis of the mercury content in the samples was carried out separately. For the digest solutions from the sediment samples and associated quality control digest solutions, mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l, matrix matched to the samples. The calibration was validated using two quality control standards (10 ug/l and 80 ug/l), prepared internally from different reagent stock. Analysis of water samples for mercury content was carried out at an external accredited laboratory using Inductively Coupled Plasma Mass Spectrometry (ICPMS).

Results

The results obtained from the analyses are presented and discussed below for each site in turn. For water and wastewater samples analysed for both volatile and semi-volatile (extractable) organic compounds, results for both types of analysis are reported together.

Flix (Ebro River, Tarragona)

Samples of both sediment and river water collected from the Ebro River approximately 7km upstream from the Flix chloralkali and chlorinated solvent plants, close to a small landing stage by the Riba Roja dam, showed evidence of only background levels of a range of metals (see Table 3). In the water samples (SP07002-3), only iron was found at levels above detection limits. In addition, no residues of any volatile organic compounds (VOCs) were detected in the water sample from this location. Although a reasonable number of individual organic chemicals could be isolated from both water and sediment (SP07001) samples, of which only between 15 and 30% could be reliably identified, those substances which could be identified were dominated by linear alkanes and alkenes, with no evidence for the presence of chlorinated organic compounds. Those compounds identified, including a small number of polycyclic aromatic hydrocarbons (PAHs) in the sediment, may indicate a low background of contamination from urban and/or industrial inputs, though some may also arise from natural sources.

Unfortunately, it was not possible at the time to collect water or sediment samples from a location downstream from the Flix plant. Nevertheless, samples of effluent and associated sediment collected directly from a discharge channel carrying wastewaters from the plant (identified as the combined effluent streams from pipes numbered '12' and '13'), contained a wide range of metal and organic compounds, including a diversity of chlorinated organics.

For example, the effluent itself (SP07005-6) contained 0.2 ug/l of mercury, almost certainly arising from the chloralkali process, as well as a total of over 150 ug/l of chlorinated and brominated VOCs. Among the VOCs detected, those in greatest abundance were chloroform (40.9 ug/l), trichloroethene (63.9 ug/l) and tetrachloroethene (25.5 ug/l), though lower levels of dichloroethenes and mixed chloro- and bromo-methanes were also found, as well as traces of vinyl chloride monomer (VCM), tetrachloromethane and hexachloroethane. Also present in the effluent were tetrachlorobutadiene, a bromochlorobenzene derivative, a range of substituted naphthalenes and two phthalate esters, di-n-butyl and di-iso-butyl phthalate (DnBP and DiBP).

Chloroform (trichloromethane) is identified as a priority pollutant under the EU Water Framework Directive (EU 2000), with a proposed Annual Average Environmental Quality Standard (AA-EQS) for internal surface waters of 2.5 ug/l (EC 2006). Although the concentration recorded in the wastewater at the time of sampling was substantially above this standard, it is important to note both that the standards apply to the quality of receiving waters rather than quality of discharges and that it is not possible to extrapolate from a single sample to estimate an annual average. This is also the case for the two other substances found for which such quality standards have been set (under other legislation), namely trichloroethene and tetrachloroethene (AA-EQS of 10 ug/l in both cases). Nonetheless, the fact that this effluent discharge is a point source of such pollutants indicates the importance of careful monitoring to ensure EQS are not exceeded.

Sample code	SP07002-3	SP07001	SP07005-6	SP07004
Sample description	Approximately 7km upstream from plant, at Riba Roja dam	Approximately 7km upstream from plant, at Riba Roja dam	Discharge channel serving pipes '12' and '13' from plant	Discharge channel serving pipes '12' and '13' from plant
Matrix	water	sediment	water	sediment
Metals	ug/l	mg/kg	ug/l	mg/kg
Cadmium	<10	<0.5	<10	34
Chromium	<30	14	<30	208
Cobalt	<10	4	<10	2
Copper	<20	12	<20	50
Iron	63	12	29	11
Lead	<30	n/a	<30	n/a
Manganese	<10	183	141	52
Mercury	<0.02	<0.1	0.2	144
Nickel	<20	11	96	55
Zinc	<5	50	<5	450
Halogenated VOCs, ug/l				
Vinyl chloride	<0.4	n/a	1.0	n/a
Ethene, 1,1-dichloro-	<0.4	n/a	0.7	n/a
Methane, dichloro-	<0.5	n/a	1.9	n/a
Ethene, 1,2-dichloro-, trans-	<0.2	n/a	1.5	n/a
Ethene, 1,2-dichloro-, cis-	<1.3	n/a	7.2	n/a
Chloroform	<0.4	n/a	40.9	n/a
Methane, tetrachloro-	<0.4	n/a	2.1	n/a
Ethene, trichloro-	<3.7	n/a	63.9	n/a
Methane, bromodichloro-	<0.5	n/a	3.8	n/a
Ethene, tetrachloro-	<0.4	n/a	25.5	n/a
Methane, dibromochloro-	<0.7	n/a	2.9	n/a
Bromoform	<1.3	n/a	1.6	n/a
Ethane, hexachloro-	<0.5	n/a	1.2	n/a
Organic qualitative results				
No. of organic compounds isolated	68	46	94	116
No. of reliably identified compounds	10(15%)	15(33%)	31(33%)	21(18%)
Chlorinated benzenes	n/d	n/d	n/d	2
Chlorinated butadienes	n/d	n/d	1	2
Bromochlorinated benzenes	n/d	n/d	1	n/d
Phthalate esters	1	n/d	2	n/d
PAHs & derivatives	n/d	3	8	2
Dibenzyl toluenes	n/d	n/d	n/d	5
Alkanes & alkenes	9	11	4	10
Heterocyclic aromatic compounds	n/d	1	n/d	n/d
Other hydrocarbons	n/d	n/d	1	n/d

Table 3: Summary of analytical results for samples collected in the vicinity of the Flix chloralkali plant

Sediment collected from the same channel (SP07004) reaffirmed the presence of a wide range of toxic and persistent chemicals in wastes discharged from the plant. As well as very high levels of mercury (at 144 mg/kg, by far the highest recorded in this study), the sediment contained elevated levels of cadmium (34 mg/kg), chromium (208 mg/kg) and zinc (450 mg/kg) in particular. The levels of mercury and cadmium in this sediment far exceeded typical background levels of these metals in sediments from freshwater systems, which in

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Box 2: Cadmium

Cadmium and its compounds have numerous industrial uses which include metal plating, as pigments for glasses and plastics, as stabilisers in polyvinyl chloride (PVC), in the manufacture of nickel-cadmium rechargeable batteries and increasing as a component of certain solar cells (ECB 2007, OSPAR 2004). Many historical uses of cadmium are, however, being increasingly restricted or phased out due to environmental and health concerns. Cadmium compounds are also present as trace components in bulk raw materials, including coal and phosphate ores used to produce fertilizers, and use of these materials can result in substantial releases of cadmium to the environment (OSPAR 2004).

Cadmium is generally found at very low levels in unpolluted environments, with concentrations in unpolluted soils and sediment typically below 1 mg/kg (Alloway 1990, Salomons & Forstner 1984). In Spain, levels in stream sediments are commonly 0.1-0.3 mg/kg (EuroGeoSurveys 2005). In the aquatic environment cadmium compounds are generally more mobile than most other metals (ECB 2007).

Cadmium is highly toxic to a wide range of aquatic organism, particularly when present in dissolved forms. Effects on fish and aquatic invertebrates can occur at levels as low as 1 ug/L, with effects being dependant on other water quality factors such as hardness, acidity and the presence of other pollutants (ECB 2007). In addition, many aquatic organisms can bioaccumulate cadmium from water and sediments (Ankley *et al.* 1994, ECB 2007). Cadmium is also toxic to humans and can accumulate in the body over time, with exposure being primarily through diet for the general population. Long-term exposure can cause damage to the kidneys and bone structure (ECB 2007, Hellstrom *et al.* 2001). Recent studies indicate impacts due to cumulative low level exposure (Satarug & Moore 2004). Cadmium is listed as a Chemical for Priority Action under the OSPAR Hazardous Substances Strategy (OSPAR 2007b). Cadmium and its compounds are known human carcinogens, though primarily through inhalation of contaminated fumes and dusts (DHSS 2005), and have been identified as 'priority hazardous substances' under the European Water Framework Directive (EU 2000, EC 2006), such that a target of phase-out or cessation of emissions, discharges and losses will apply.

Spain are typically below 0.2 mg/kg for mercury, and in the range 0.1-0.3 mg/kg for cadmium. Additional information on mercury and cadmium is provided in Boxes 1 (above) and 2 (below) respectively.

Among the 116 organic compounds isolated, of which only 21 (18%) could be identified reliably, were tetra- and hexachlorobutadiene, hexachlorobenzene and the strongly irritant compound chlorodiphenylmethane. Hexachlorobutadiene is a highly toxic, persistent and bioaccumulative compound, generated as a common unintended by-product of organic chlorine chemistry for the manufacture of solvents and other products. Further details on this chemical are provided in Box 3 below.

Although downstream samples were not available in this case, it is nonetheless clear that the discharge channel sampled, which carries effluent from the Flix plant directly to the Ebro River without further treatment, is acting as a significant point source of heavy metals, especially mercury, and a complex array of toxic and, in some cases, persistent chlorinated organic compounds. The extent to which the presence of HCB and the chlorinated butadienes in sediment from the channel reflects ongoing, or only historic, releases cannot be determined from these results, but clearly such contaminated sediments can be readily remobilised and are likely to act as a legacy source of persistent organic pollutants, and additional mercury, to the downstream environment for some time to come.

Box 3: Hexachlorobutadiene (HCBD)

Hexachlorobutadiene (HCBD) is a synthetic chemical that is not found naturally in the environment. HCBD is mainly produced as a by-product during the manufacture of certain chlorinated hydrocarbons such as tetrachloroethylene, trichloroethylene, carbon tetrachloride and related products (van der Gon *et al.* 2007). Commercially manufactured HCBD has several minor uses, e.g. chemical intermediate in the manufacture of rubber compounds, solvent and fluid for gyroscopes (Lerche *et al.* 2002). HCBD residues have been detected in many environmental compartments including river water (Fatta *et al.* 2007), sediments (Lee *et al.* 2005, Schwarzbauer *et al.* 2000), fish tissues (Pere-Trepat   *et al.* 2006) and soils from industrial sites contaminated with chlorinated hydrocarbons (Röhrs *et al.* 2002).

Hexachlorobutadiene toxicity has extensively studied on rats and to a lesser degree on other laboratory animals. It has been shown that HCBD is toxic to the kidneys in rats, causing damage to the proximal tubules (US EPA 2003, Pahler *et al.* 1997, Rosner *et al.* 1998, Nakagawa *et al.* 1998). Several oral studies in rats have suggested that HCBD-induced cytotoxicity may lead to the kidney tumor formation (US EPA 2003). There is limited evidence for the genotoxicity of HCBD in animals, and insufficient evidence for its classification in humans. HCBD has been classified by IARC as Group 3 carcinogen (IARC 1999). Limited information is available on human health effects associated with exposure to HCBD. However, human *in vitro* data suggest that the metabolism of hexachlorobutadiene in humans is similar to that observed in animals (Green *et al.* 2003, WHO 1994). HCBD vapour is considered to be irritating to the mucous membranes of humans, and the liquid is corrosive. It has also been generally observed that existing nephropathy or age-related kidney degeneration can increase the risk of renal injury or exacerbate nephrotoxicity of HBCD in humans (WHO 1991).

Environmental toxicity of HCBD has mainly been described in aquatic organisms, with crustaceans and fish the most sensitive groups. An environmental concern level of 0.1 µg/litre was established for HCBD by the World Health Organisation (WHO 1994), and the same value has since been proposed as an Annual Average Environmental Quality Standard (AA-EQS) for internal waters under the EU Water Framework Directive (EU 2000, EC 2006), as well as a maximum allowable concentration at any one time of 0.6 ug/l. In common with mercury and cadmium, HBCD is also identified as a 'priority hazardous substance' under this Directive, such that a target of phase-out or cessation of emissions, discharges and losses will apply. HBCD is highly bioaccumulative, such that the consumption of benthic or aquatic organisms in polluted surface water by other species may give cause for concern.

It is worth noting that only one of several discharge channels leading from the plant could be sampled on this occasion and that the contamination of sediments contained therein cannot be considered indicative of the nature and level of contamination over the entire area adjacent to the industrial site. Previous studies have reported the presence of high concentrations of PCBs in sediments collected close to the Flix plant (e.g. Fernandez *et al.* 1999), as well as the same chlorinated butadiene and HCB residues reported here and high concentrations of the banned pesticide DDT (Swindlehurst *et al.* 1995).

Hernani (Urumea River, San Sebastián)

Three samples of sediment were initially collected from the river channel in the vicinity of the Electroquimica de Hernani chloralkali and PVC plants (SP07007-9), including two samples collected close to former discharge pipes from these plant. However, as the samples

Sample code	SP07010	SP07011
Sample description	Upstream from plant, under road bridge	Downstream from chloralkali and PVC plant, close to suspected former (pre-2003) discharge pipe
Metals, mg/kg		
Cadmium	<0.5	<0.5
Chromium	20	19
Cobalt	8	8
Copper	15	23
Lead	11	14
Manganese	330	358
Mercury	0.2	0.8
Nickel	20	20
Zinc	73	94
Organic qualitative results		
No. of organic compounds isolated	19	49
No. of reliably identified compounds	6(32%)	11(22%)
Chlorinated benzenes	n/d	(1)
Phthalate esters	1	n/d
Diisopropylnaphthalenes	n/d	4
Alkyl benzenes	n/d	n/d
Alkanes & alkenes	4	6
Heterocyclic aromatic compounds	1	n/d

Table 4: Summary of analytical results for samples collected in the vicinity of the Martorell chloralkali plant

consisted primarily of coarse sand and gravel, and information available suggested that the river bed had been substantially modified by the local authorities as part of a restoration programme in recent years, it was judged that analysis of these samples was unlikely to yield results representative of either historic or ongoing industrial inputs. Therefore, no results are available for the Hernani site.

Martorell (Llobregat River, Barcelona)

Only sediment samples from two locations could be collected in the vicinity of the Martorell site, one upstream from the plant under a road bridge (SP07010) and the other downstream from the chloralkali and PVC plants, close to what is thought to be the site of the previous effluent discharge point, prior to the opening of a sub-sea outfall in 2003 (SP07011). Results for both samples are given in Table 4.

Concentrations of most metals were very similar in the two sediment samples. The one exception was mercury which, though far less abundant here than in sediments from the Flix site, was nevertheless present at levels four times greater in the downstream than in the upstream sample (0.8 mg/kg compared to 0.2 mg/kg). Although no firm conclusions can be drawn from this observation, it is clearly possible that the enrichment of the sediments with mercury close to the Martorell SolVin plant may be the legacy of previous discharges to the river. It is also significant that the range of extractable organic compounds present in the

sediment adjacent to the plant was more complex and extensive than in the upstream sample, including traces of dichlorobenzene and four isomers of diisopropylnaphthalene, compounds which find use in the polyester, paper and pesticide manufacturing industries, among others. Further investigations would be necessary in order to identify possible sources in the area.

Monzón (Cinca River, Aragon)

At Monzón, it was possible to collect representative samples from locations both upstream and downstream of the chloralkali and PVC plants, as well as from the discharge channels serving these two facilities. Both channels carry the final treated effluents from pipelines originating within the plants directly to the Cinca River, a tributary of the Ebro. Results for all water and waste water samples are given in Table 5a and for all sediment samples in Table 5b.

Once again, water samples collected (approximately 1km) upstream from the plants (SP07016-17) contained relatively low levels of most contaminants, aside from a range of alkanes and alkenes (which may reflect a combination of natural occurrence and urban/industrial run-off and discharges). Traces of the phthalate esters DiBP and DnBP were also found. Further studies may well be justified to trace the possible sources of these contaminants. No volatile organic compounds were detected.

While river water collected 200m downstream from the facility (SP07013-14) appeared to have a rather similar profile, it did also contain 3.1 ug/l of vinyl chloride monomer, or VCM (10 times the World Health Organisation drinking water Quality Guideline Value of 0.3 ug/l, WHO 2006), a compound which was not detectable in the upstream sample and which undoubtedly arose from the PVC plant. Indeed, analysis of effluent collected from the channel carrying wastewater from the Martorell PVC plant (SP07022-23) revealed the presence of more than 3 mg/l (3324 ug/l) of VCM, the highest recorded in this study, as well as lower ug/l levels of chloroethane and dichloroethanes (including 3.5 ug/l of the compound 1,2-dichlorethane, or ethylene dichloride (EDC), used in the manufacture of VCM). The concentrations of VCM recorded in the final discharge to water were more than three times greater than the limit set by OSPAR Decision 98/5 (OSPAR 1998b) for waste exiting from the solvent stripper on site, even before any secondary treatment has taken place. VCM is a highly toxic chemical, which has long been classified as carcinogenic to both animals and humans. Further details of the properties and toxicity of VCM are given in Box 4 below. This effluent also contained a chlorinated butane, the antioxidant butylated hydroxytoluene (BHT) and several cyclohexanol and cyclohexanone derivatives which may arise from a specific synthesis reaction conducted within the plant at that time. Traces of mercury were also detectable in this discharge (0.15 ug/l).

Significantly higher mercury concentrations, at 0.68 ug/l, were present in the wastewater being discharged from the chloralkali facility (SP07019-20), as well as 1.4 ug/l of chloroform, recognised as a common contaminant from side reactions which occur in chloralkali electrolysis cells (EC 2001).

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Sample code	SP07016-17	SP07013-14	SP07019-20	SP07022-23
Sample description	Approximately 1km upstream from plants	Downstream from plants, 200m from road bridge	Discharge to river from chloralkali plant	Discharge to river from PVC plant
Metals, ug/l				
Cadmium	<10	<10	<10	<10
Chromium	<30	<30	<30	<30
Cobalt	<10	<10	<10	<10
Copper	<20	<20	<20	<20
Iron	284	628	516	227
Lead	<30	<30	<30	<30
Manganese	<10	22	26	34
Mercury	<0.02	<0.02	0.68	0.15
Nickel	<20	<20	<20	<20
Zinc	<5	<5	8	39
Halogenated VOCs, ug/l				
Vinyl chloride	<0.4	3.1	<0.4	3324
Ethane, chloro-	<0.9	<0.9	<0.9	9.9
Ethane, 1,1-dichloro-	<0.4	<0.4	<0.4	3.1
Ethane, 1,2-dichloro-	<0.2	<0.2	<0.2	3.5
Chloroform	<0.4	<0.4	1.4	<0.4
Organic qualitative results				
No. of organic compounds isolated	71	66	51	63
No. of reliably identified compounds	11(15%)	11(17%)	7(14%)	21(33%)
Chlorinated butenes	n/d	n/d	n/d	1
Phthalate esters	2	2	1	1
BHT & related compounds	n/d	n/d	n/d	2
Alkyl cyclohexanols & cyclohexanones	n/d	n/d	n/d	4
Alkanes & alkenes	9	8	5	9

Table 5a: Summary of analytical results for water and wastewater samples collected in the vicinity of the Monzón chloralkali plant

Although it was not possible to detect the impact of ongoing mercury discharges in the downstream water samples, presumably due to the rapid adsorption of mercury to particulate matter that usually occurs following its discharge to aquatic systems, mercury was present at above limits of detection in the sample of sediment collected 200m downstream (SP07012), at 0.2 mg/kg, while concentrations of all other metals in the sediment were remarkably similar to those in the sample collected 1km upstream (SP07015, in which mercury was undetectable, at levels below 0.1 mg/kg) (Table 5b). Once again, however, it is possible that this small increase is the result of more substantial historic inputs of mercury than currently measured discharges. In the early 90s, Raldúa & Pedrocchi (1996) reported substantially higher concentrations of mercury in river sediments collected close to the chloralkali plant, in the range of 2.69 mg/kg. By 2002, however, concentrations immediately downstream from the plant had fallen to around 0.4 mg/kg, though elevated mercury levels were still detectable (0.25 mg/kg) as far as 30km downstream from Monzón (Raldúa *et al.* 2007).   Our data, for sediments collected just downstream of the plant in 2007 (0.2 mg/kg), suggest some further dilution of mercury-contaminated sediments may have taken place in the last five years.

Nonetheless, the long-term significance of historic pollution, along with the potential for ongoing redistribution of mercury contaminated sediments from the two discharge channels sampled (SP07018 and SP07021, which contained mercury residues at 11 mg/kg and 7.3 mg/kg respectively) must not be overlooked. It is likely that the mercury footprint of Monzón will be present in the Cinca River for some time to come, as suggested by the substantial body burdens of mercury and evidence of liver damage in locally caught freshwater fish, including, in the case of one species (barbel, *Barbus graellsii*), when collected 30km downstream from the plant (Raldúa *et al.* 2007).

Box 4: Vinyl chloride monomer (VCM)

Vinyl chloride, also known as vinyl chloride monomer (VCM), is among the highest production volume chemicals in the world (ATSDR 2006). The majority of the VCM produced is used in the production of the polyvinyl chloride (PVC), which is used extensively in construction materials, packaging, electrical and electronic equipment, textiles, coatings, furniture and many other products. Recently some interest was expressed for the use of PVC in the production of nano-composites (Mamunya *et al.* 2008, Rodríguez-Fernández *et al.* 2008).

The main sources of the VCM in the environment are VCM and PVC production facilities, as well as plants where PVC products are manufactured (WHO 2000). Other sources included storage and handling facilities for VCM and PVC as well as formation of VCM as a result of microbial degradation of chlorinated ethenes (Nijenhuis 2007). Most VCM released into environment will eventually partition to air. Nonetheless, it is highly mobile in the soil and can reach groundwater reserves. Contamination of groundwater by VCM has been observed in industrialized areas involved in the production or use of VCM and PVC and also around facilities with known contamination by chlorinated solvents (e.g. chlorinated ethenes) (Kistemann *et al.* 2008, Imfeld *et al.* 2008, Conant *et al.* 2004, WHO 2006). Furthermore, relatively high levels of VCM have been also detected in soil, groundwater, aquifers, and wells near landfill and industrial waste disposal sites that were not located near VCM/PVC production facilities (Kielhorn *et al.* 2000). Concentrations up to 10µg/l of VCM have also been detected in drinking water (WHO 2006), with a possible significant contribution from older PVC piping.

VCM is highly toxic chemical with a wide spectrum of toxic effects, including carcinogenicity in both humans and animals, established many years ago (IARC 1979). DHHS classified VCM as known to be a human carcinogen (DHHS 2005), with the liver being the primary target. A rare type of liver tumor, angiosarcoma, has been strongly associated with occupational exposure to VCM (WHO 1999, DHHS 2005). Several studies also have reported that exposure to vinyl chloride causes cancer at other tissue sites including brain, lung, lymphatic system, hematopoietic system (organs and tissues involved in production of blood) (IARC 1998), skin (WHO 1999) and thyroid (Rhomberg *et al.* 2004). Abdominal pain, weakness, fatigue, and weight loss are the most prominent clinical symptoms of VCM poisoning, and hepatosplenomegaly, ascites and jaundice are the most common clinical signs (WHO 1999).

Because of its toxicity, VCM has been a subject to many regulations (DHHS 2005), including the US EPA's Clean Air Act, Clean Water Act (Water Quality Criteria: based on fish/shellfish and water consumption - 2 µg/l; based on fish/shellfish only - 530 µg/l) and Safe Water Drinking Act (Maximum Contaminant Level - 2 µg/l). However, the WHO drinking water Quality Guideline Value for VCM is 0.3 µg/l (WHO 2006). Under a US FDA regulation (FDA 2006), aerosol drug products containing VCM have been withdrawn from the market and may not be compounded and VCM is also banned from use in cosmetic aerosol products because of its carcinogenicity. OSHA's Permissible Exposure Limit (OSHA 2008) is set to 1ppm (over any 8-hour period) and ceiling concentration to 5ppm (over any period not exceeding 15 min).

Sediment collected from the PVC plant effluent channel (SP07021) also contained concentrations of lead and manganese that were significantly higher than the background for sediments in the river.

Both discharge channel sediments were also of significance in terms of their burden of chlorinated organic compounds. Sediment from the channel carrying waste water from the chloralkali plant (SP07018) contained a range of chlorinated benzenes, including di-, tri- and tetrachlorinated forms and pentachlorobenzene. Although chlorinated benzenes are not specifically listed as potential by-products of brine electrolysis in the IPPC BREF (EC 2001), they are nevertheless included among the 23 so-called CoCs (chlorinated organic compounds) for which Eurochlor requires its companies to monitor emissions on a routine basis (Eurochlor 2007a).

DDT and its metabolites were also detected in the sediment sample SP07018 with the *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT, being the most abundant. This fact may suggest a historic or chronic source of contamination in this place. Another reason for the presence of DDT residues in the sediment from the wastewater channel of the chloralkali plant could be the re-distribution of contaminated sediments from the river itself during period of floods, which could possibly cause migration of the sediments from the River Cinca into the channel. The contamination of the River Cinca sediments by DDT has been known since 1999 when the industry Montecinca SA, which produced the pesticide dicofol using DDT as an intermediate, was accused of exceeding its authorized discharge of DDT to the river (de la Cal *et al.* 2008).

Most notable among the 85 organic compounds isolated from the sediment in the PVC plant effluent channel were 20 congeners of polychlorinated biphenyls (PCBs), including di-, tri-, penta- and hexachlorinated congeners and one tetrachlorinated congener present at levels high enough to be detected even in a low sensitivity scan analysis. The possible origin of these highly toxic and persistent organic pollutants clearly warrants further investigation, not least because their manufacture and use has been prohibited for well over two decades.

Palos de la Frontera (Huelva)

A single sediment, collected under the jetty serving the Ercros chloralkali and chlorinated chemical synthesis plant at Palos de la Frontera (SP07024), consisted largely of coarse sand. As it was also not possible to identify the location of any discharge pipes or channels originating from the site in this area, this sediment was not subjected to further analysis.

Instead, attention was directed to samples of waste water (SP07026-27) and sediment/solid waste (SP07025) collected from the final settling lagoon of the treatment plant serving both plants, located very close to the jetty and presumably representing the final stage in any treatment of effluents before discharge (though this could not be confirmed). Analytical results for these samples are reported in Table 6 below.

Sample code	SP07015	SP07012	SP07018	SP07021
Sample description	Approximately 1km upstream from plants	Downstream from plants, 200m from road bridge	Discharge to river from chloralkali plant	Discharge to river from PVC plant
Metals, mg/kg				
Cadmium	<0.5	<0.5	<0.5	<0.5
Chromium	37	35	32	20
Cobalt	8	6	7	4
Copper	10	9	14	12
Lead	10	8	11	28
Manganese	298	297	476	1340
Mercury	<0.1	0.2	11	7.3
Nickel	21	16	19	10
Zinc	59	48	53	59
Organic qualitative results				
No. of organic compounds isolated	42	37	51	85
No. of reliably identified compounds	14(33%)	13	21(41%)	36(42%)
Chlorinated benzenes	n/d	1	1(8)	1
PCBs	n/d	n/d	n/d	1(19)
DDTs & metabolites	n/d	n/d	4(1)	n/d
PAHs & derivatives	1	n/d	2	1
BHT & related compounds	n/d	2	1	1
Alkyl benzenes	n/d	n/d	n/d	1
Alkanes & alkenes	13	9	4	11
Other hydrocarbons	n/d	1	n/d	1

Table 5b: Summary of analytical results for sediment samples collected in the vicinity of the Monzón chloralkali plant

As well as traces of mercury (0.17 ug/l), the wastewater in the lagoon (SP07026-27) contained very high levels of volatile organic compounds, dominated by 2.77 mg/l of dichloromethane (2772 ug/l), as well as lower (though substantial) levels of chloroform (85.1 ug/l) and 1,2-dichloroethane (25.9 ug/l) and traces of bromodichloromethane and vinyl chloride. Dichloromethane, also known as methylene chloride, is classified as harmful if swallowed, inhaled or absorbed through the skin (which it penetrates readily), as a possible mutagen and possible human carcinogen. As noted above, 1,2-dichloroethane is more commonly known as ethylene dichloride, or EDC, the first intermediate in the manufacture of VCM and, ultimately, PVC. EDC is a skin irritant, mutagen and probable human carcinogen, which can cause damage to the liver and other organs following ingestion and/or long-term inhalation.

In common with chloroform, both dichloromethane and EDC are listed as priority substances under the EU Water Framework Directive (EU 2000, EC 2006), such that Environmental Quality Standards (EQS) for surface waters will be applied. Given the volatile nature of these contaminants, it is likely that discharge of such contaminated effluents to this pond results routinely in significant losses to air in the vicinity. Nevertheless, should any effluent of this nature be discharged to surface waters, it would clearly represent a highly significant

point source of such contaminants. For example, the concentration of dichloromethane recorded in this sample was more than 100 times higher than the Annual Average EQS proposed for this substance (20 ug/l) in inland surface waters, estuary waters, inland coastal waters and territorial waters under the Water Framework Directive (EC 2006). Concentrations of EDC and chloroform were also significantly higher than the AA-EQS proposed for these substances under the same Directive (10 and 2.5 ug/l respectively).

In contrast, no chlorinated organic compounds could be reliably identified in the sediment/solid waste collected from the same lagoon (SP07025), although 2,4,5-tribromotoluene was present, as were two additional, but so far unidentified, polyhalogenated compounds. As is commonly the case with complex wastes of this nature, of more than 90 individual organic compounds which could be isolated from both wastewater and sediment samples, only between 15 and 20% could be identified with any degree of reliability. In

Sample code	SP07025	SP07026-27
Location	Palos de la Frontera	
Sample description	Waste from the last open lagoon/evaporation pond of the chloralkali and PVC wastewater treatment plant	
Matrix	sediment	water
Metals	mg/kg	ug/l
Cadmium	1	<10
Chromium	30	<30
Cobalt	2	<10
Copper	117	<20
Iron	n/a	48
Lead	11	<30
Manganese	18	80
Mercury	5.6	0.17
Nickel	63	<20
Zinc	565	20
Halogenated VOCs, ug/l		
Vinyl chloride	n/a	1.3
Methane, dichloro-	n/a	2772
Chloroform	n/a	85.1
Ethane, 1,2-dichloro-	n/a	25.9
Methane, bromodichloro-	n/a	1.0
Organic qualitative results		
No. of organic compounds isolated	92	92
No. of reliably identified compounds	14(15%)	18(20%)
Brominated toluenes	1	n/d
Phthalate esters	n/d	1
PAHs & derivatives	5	n/d
Alkanes & alkenes	7	12

Table 6: Summary of analytical results for wastewater samples collected from the treatment plant of the Palos de la Frontera chloralkali facility

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addition, concentrations of mercury (5.6 mg/kg), copper (117 mg/kg) and zinc (565 mg/kg) were also notably high in the sediment from this lagoon.

Lourizan (Ria de Pontevedra, Galicia)

Unfortunately, sampling opportunities in the vicinity of the Elnosa chloralkali plant near Pontevedra were very limited. Until 2003, this mercury cell plant discharged effluent via a pipeline which terminated close inshore around the low tide mark. Effluents are now discharged further offshore in the Ria de Pontevedra via a sub-surface pipeline, but it was not possible to collect samples from the new discharge pipe on this occasion.

A sample of sediment collected from the beach adjacent to the disused pipeline (SP07029) contained 1.5 mg/kg mercury, probably resulting from historic inshore discharges, but was otherwise unremarkable. A second sample, collected from the northern banks of the Ria de Pontevedra, was once again considered too coarse to act as a representative control for comparative purposes and was not analysed.

Sabiñánigo (Gallego River, Aragon)

A total of three sites were sampled in the vicinity of the Sabiñánigo chloralkali, chlorine derivatives and PVC facilities, one approximately 1km upstream, one at the end of the waste water discharge pipe and another around 500m downstream from the plants. All results are presented in Tables 7a and b.

Samples of river water collected from the upstream site (SP07034-35) contained more than 60 individual organic compounds, including traces of DiBP and a diverse array of branched alkanes of unknown origin. Mercury was present at a level marginally above detection limits (0.02 ug/l), higher than usual background levels in surface waters, suggesting some significant upstream inputs. However, no chlorinated VOCs were detected. Once again, the sediment collected from this site (SP07033) was judged to be too coarse to provide a representative upstream control for comparative purposes as the sediments from the slower flowing downstream sites were characteristically much finer.

River water collected from the downstream site, after the dam but before the confluence with the Tulivana River (SP07031-32), contained similar trace levels of mercury (0.023 ug/l) but, more significantly, also contained residues of five halogenated VOCs, with a combined concentration of just over 10 ug/l. Of those compounds identified, dibromochloromethane and bromodichloromethane were the most abundant (3.3 and 2.5 ug/l respectively), with chloroform (trichloromethane), bromoform (tribromomethane) and dichloromethane at slightly lower levels. Both chloroform and dichloromethane are well recognised as possible by-products from brine electrolysis (EC 2001, Eurochlor 2007a), though the mixed bromo- and chloro- derivatives found to be most abundant here do not seem to be included in regular monitoring programmes or, therefore, voluntary commitments for reductions in VOC emissions.

Sediment collected from the same downstream location (SP07030) contained mercury at a concentration of 0.6 mg/kg, suggesting historic and/or ongoing mercury emissions from the Sabiñánigo facility. Indeed, effluent collected from the end of the discharge pipeline from the plant (SP07037-38), despite being located underwater, was found to contain 2.6 ug/l of mercury, the highest level recorded for a wastewater sample in this study, far exceeding

levels typically seen in uncontaminated surface waters which are commonly below 1 ng/l (0.001 ug/l).

This effluent sample was interesting for other reasons also. In particular, chromium was present at a markedly high concentration of 388 ug/l, of which more than 80% (325 ug/l) was in the most toxic form, hexavalent chromium (VI). While the process origin of this material within the Ercros facility is not clear, such high discharges of a highly toxic and recognised carcinogenic substance clearly demand urgent investigation. Further details on the toxicity of chromium, and of hexavalent chromium (VI) in particular, are given in Box 5.

The effluent also contained the same range of chlorinated and brominated VOCs as were found in the water sample collected 500m downstream, though in this case at an overall concentration of more than 70 ug/l. Bromoform (tribromomethane) was by far the most abundant, at 58.8 ug/l. Among other, less volatile organic compounds identified were a dimethylated phenyl ethanone derivative, a tributyl ester of phosphoric acid (known to be used in some polymer applications as a flame retardant) and a number of poorly identified compounds with characteristics suggesting they may well be polybrominated alkane and benzene derivatives.

Box 5: Chromium

Chromium is primarily used in the metallurgical industry (stainless steel and other alloys), as well as refractory, leather and chemical industries. Hexavalent chromium compounds are used in metal finishing (chrome plating), in wood preservatives and as corrosion inhibitors (ATSDR 2000).

In the environment, chromium normally exists in either trivalent Cr(III) forms, which are generally insoluble in water, or hexavalent Cr(VI) forms, most of which are readily soluble in water. In the aquatic environment, trivalent forms tend to precipitate rapidly or to adsorb onto suspended particles and bottom sediments (ATSDR 2000, DeLaune *et al.* 1998). Due to their reactivity, hexavalent compounds rarely occur naturally, as these are converted to trivalent Cr(III) compounds by reducing compounds (Lin 2002).

Chromium (III) is an essential nutrient for animals and plants, though large doses may be harmful. In contrast, hexavalent chromium is highly toxic even at low concentrations. Hexavalent chromium compounds are also corrosive, and in humans allergic skin reactions readily occur following exposure, independent of dose (ATSDR 2000). Furthermore, hexavalent chromium is a known human carcinogen under some circumstances (IARC 1990). Hexavalent chromium is toxic to a wide range of aquatic organisms, with effects reported at levels below 50μg/l (Kimbrough et al 1999, Baral et al. 2006). The World Health Organization (WHO) has set a drinking water guideline value for chromium of 50μg/l (Total chromium) (WHO 2006).

Sample code	SP07034-35	SP07031-32	SP07037-38
Sample description	Approximately 1km upstream from plants	Downstream from plants, before confluence with Tulivana River	Sub-surface discharge to river from chloralkali plant
Metals, ug/l			
Cadmium	<10	<10	<10
Chromium	<30	<30	388
Cobalt	<10	<10	<10
Copper	<20	<20	<20
Iron	72	126	700
Lead	<30	<30	<30
Manganese	<10	<10	75
Mercury	0.02	0.023	2.6
Nickel	<20	<20	<20
Zinc	<5	<5	48
Halogenated VOCs, ug/l			
Methane, dichloro-	<0.5	1.1	1.0
Chloroform	<0.4	1.8	1.5
Methane, bromodichloro-	<0.5	2.5	2.6
Methane, dibromochloro-	<0.7	3.3	7.9
Bromoform	<1.2	2	58.8
Organic qualitative results			
No. of organic compounds isolated	66	46	86
No. of reliably identified compounds	13(20%)	11(24%)	18(21%)
Halogenated VOCs	n/d	5	5
Phthalate esters	1	1	1
Acetophenone derivatives	n/d	n/d	1
Phosphoric acid, tributyl ester	n/d	n/d	1
Alkanes & alkenes	12	5	10

Table 7a: Summary of analytical results for water and wastewater samples collected in the vicinity of the Sabiñánigo chloralkali plant

Sediment collected from the river immediately adjacent to the subsurface discharge contained substantial levels of mercury (5.6 mg/kg) but no traces of chlorinated or brominated organic compounds. The high mercury level, at over twenty times background levels, indicates the accumulation of mercury in the sediment as a result of historic and ongoing discharges in the wastewater.

Sample code	SP07030	SP07036
Sample description	Downstream from plants, before confluence with Tulivana River	Sub-surface discharge to river from chloralkali plant
Metals, mg/kg		
Cadmium	<0.5	<0.5
Chromium	33	56
Cobalt	7	8
Copper	12	16
Lead	13	22
Manganese	288	361
Mercury	0.6	5.6
Nickel	22	24
Zinc	73	128
Organic qualitative results		
No. of organic compounds isolated	42	40
No. of reliably identified compounds	14(33%)	17(43%)
PAHs & derivatives	4	2
Alkyl benzenes	n/d	2
Alkanes & alkenes	10	13

Table 7b: Summary of analytical results for sediment samples collected in the vicinity of the Sabiñánigo chloralkali plant

Torrelavega (Saja River, Cantabria)

Effluents from Solvay's chloralkali plant at Torrelevega in northern Spain are carried via pipeline to a sub-sea outfall some distance away. For this reason, it was possible only to collect and analyse sediment samples in the immediate vicinity of the plant itself, both from a site upstream from some of the largest industrial facilities in the area (including Solvay and a paper mill) and from a site approximately 20m from an unidentified discharge pipe located adjacent to the Solvay plant. It was not possible to collect samples of effluent from the subsea outfall as part of this investigation. Results are reported in Table 8.

Interestingly, concentrations of mercury, lead and cadmium, elevated in both samples, were higher in the upstream sample (SP07039) than in that collected adjacent to the Solvay plant (SP07040) (e.g. 0.6 mg/kg compared to 0.2 mg/kg in the case of mercury). This high background of contamination is probably indicative of the general industrial nature of the lower reaches of the Saja River and reflects the fact that any mercury contaminated discharges arising from the Solvay plant have been discharged remotely to sea rather than to the river itself. Among the organic compounds present, the sample collected in front of the Solvay plant, close to the so far unidentified discharge pipe, did contain residues of compounds tentatively identified as tri- and tetrachlorobutadiene, indicative of some former or ongoing organic chlorine chemistry along this stretch of the river. However, without further, more detailed and extensive sampling within, above and below this stretch of the river and investigations into the possible origins of the unidentified pipeline, it is not possible to draw any firm conclusions regarding likely sources of pollution, past or present. Furthermore, evaluation of the quality of current effluents discharged by Solvay's plant would clearly require the far more challenging sampling of a sub-sea outfall.

Sample code	SP07039	SP07040
Sample description	Upstream from chloralkali plant, paper mill and other chemical plants	20m from unidentified discharge pipe adjacent to chloralkali plant
Location	Torrelavega	
Metals, mg/kg		
Cadmium	2.2	1.7
Chromium	19	15
Cobalt	5	4
Copper	21	16
Lead	157	116
Manganese	160	91
Mercury	0.6	0.2
Nickel	15	10
Zinc	1020	852
Organic qualitative results		
No. of organic compounds isolated	19	22
No. of reliably identified compounds	8(42%)	15(68%)
Alkanes & alkenes	8	14
Other hydrocarbons	n/d	1

Table 8: Summary of analytical results for sediment samples collected in the vicinity of the Torrelavega chloralkali plant

Vila-seca (Tarragona)

In the case of Ercros' plant at Vila-seca, which (as well as chlorine and caustic) manufactures dichlorethane, VCM and PVC, it was once again not possible to locate and sample the final effluent discharge as effluents are now carried to a sub-sea disposal point. Instead, sample collection was restricted to three waste water samples from two open settling lagoons (identified as west and east wastewater pools) located on open ground to the south of the production facilities and receiving effluents from the chloralkali and PVC plants. Analytical results for these samples are presented in Table 9.

As may be expected, waste water samples from both lagoons contained significant concentrations of a number of chlorinated VOCs. By far the higher concentrations were found in the eastern pool (SP07042-43, total VOCs 125 ug/l), including 58.4 ug/l VCM and 42.8 ug/l EDC. Concentrations on the western pool (SP07041) were an order of magnitude lower, perhaps reflecting differences in the process origin of the wastes directed to these two lagoons or the length of time for which the effluents had been settling and evaporating, since VOCs will inevitably be lost to atmosphere over time, especially at high ambient temperatures. Significant differences were also evident in the range of less volatile, extractable organic compounds present in samples from the two lagoons. For example, waste water from the eastern pool contained conspicuous residues of 2,4,6-trichlorophenol, as well as two compounds tentatively identified as chlorinated ether derivatives.

In terms of metal contamination, wastewater from the western pool contained the higher concentrations of mercury, at 0.14 ug/l compared to relative traces of 0.021 ug/l in the eastern

pool. In this context, it is worth noting that high levels of mercury (76.9 mg/kg) were found in a sludge sample (MI5059) collected 12 years before from a dry evaporation pond located just to the west of the two lagoons sampled in the current investigation, but now no longer identifiable. This material also contained very high concentrations of chlorinated dioxins and a wide array of other toxic and persistent polychlorinated organic compounds. What has been done with these highly contaminated solid wastes in the intervening period, and any relationship there may be with sludges contained within the lagoons remaining on site, are simply not known.

Sample code	SP07041	SP07042-43
Location	Vila-seca	
Sample description	Western-most of two wastewater lagoons/evaporation ponds serving chloralkali and PVC plants	Eastern-most of two wastewater lagoons/evaporation ponds serving chloralkali and PVC plants
Matrix	water	water
Metals	ug/l	ug/l
Cadmium	<10	<10
Chromium	<30	<30
Cobalt	<10	<10
Copper	37	52
Iron	135	246
Lead	<30	<30
Manganese	<10	<10
Mercury	0.14	0.021
Nickel	<20	<20
Zinc	47	128
Halogenated VOCs, ug/l		
Vinyl chloride	<0.4	58.4
Ethane, chloro-	<0.9	0.9
Methane, dichloro-	<0.5	1.2
Chloroform	2.5	25.8
Ethane, 1,2-dichloro-	4.4	42.8
Methane, bromodichloro-	1.1	<0.5
Organic qualitative results		
No. of organic compounds isolated	44	34
No. of reliably identified compounds	11(25%)	13(38%)
Chlorinated phenols	n/d	1
Phthalate esters	1	2
Alkyl cyclohexanols & cyclohexanons	1	2
Alkanes & alkenes	6	2
Other hydrocarbons	n/d	1

Table 9: Summary of analytical results for wastewater samples collected from settling lagoons / evaporation ponds of the Vila-seca chloralkali plant

Conclusions

Taken together, the results from this study confirm that discharges from many of the chloralkali and associated PVC and chlorinated chemical manufacturing facilities in Spain have not only created a substantial legacy of environmental contamination and complex hazardous wastes, but in several cases continue to act as significant point sources of mercury and harmful chlorinated substances to the receiving freshwater environment. Although a comprehensive survey of all discharges was simply not possible, not least because of the trend over the last decade towards the construction of sub-sea outfalls to replace historic discharges to rivers, the results nonetheless provide a unique and valuable snapshot of the quality and complexity of discharges to water from this sector.

While reliance on mercury-cells continues for the manufacture of chlorine in Spain, despite the clear decision under the IPPC Directive that Best Available Techniques (BAT) for the sector is conversion to membrane cells, some level of mercury discharges and losses to water and air remain inevitable. Likewise, the generation and release of harmful product residues and by-products from the synthesis of chlorinated organic chemicals, including PVC, is also unavoidable for as long as such products continue to be manufactured.

Meanwhile, PARCOM Decision 90/3, which recommended phase-out of mercury cells throughout the North-East Atlantic region (including Spain) as soon as possible, with the target of 2010, is very much in force and remains to be implemented. In setting its own, more relaxed timetable of 2020, the chloralkali industry has clearly signalled its intention to try to sidestep international law and, as a result, has been reluctant to invest the funds necessary to achieve an early phase-out, even though that would be both technically feasible and consistent with legislative pressure. In Western Europe as a whole, the industry in Spain appears to have been particularly slow in this regard.

Further tightening of end-of-pipe treatment technologies could result in additional reductions in discharges and losses of mercury, EDC, VCM and other hazardous substances to the environment, but can never eliminate such releases and will not address the substantial legacy of pollution which remains in many areas. Spain, along with other Contracting Parties to the OSPAR Convention (1992), made the commitment ten years ago to make "*every endeavour to move towards the target of the cessation of discharges, emissions and losses of hazardous substances by the year 2020*" (OSPAR 1998c). Since then, a similar cessation objective has been agreed for a range of 'priority hazardous substances' under the EU Water Framework Directive (EU 2000, EC 2006), including *inter alia* (and of direct relevance to this study) mercury and its compounds, cadmium and its compounds, hexachlorobenzene and hexachlorobutadiene.

In order to meet these commitments, and to provide for a high level of protection for Spain's environment (whether in relation to freshwater or marine ecosystems and resources), there is an urgent need for a more fundamental rethink not only of the manner in which chemicals are manufactured, but also more fundamentally of the chemicals themselves which are being produced and on which society has come ever increasingly to rely. The fact that so much of the chlorine produced is directed towards manufacture of PVC, a plastic which could be readily replaced with non-chlorinated alternative materials, indicates that such a fundamental re-evaluation and redirection of industrial enterprise may by no means be unthinkable.

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