Heavy metal and organic screen analysis of environmental and waste samples associated with industrial activities in Lebanon, September 1997.

Prepared by Angela Stephenson, Irina Labounskaia and Ruth Stringer
Greenpeace Research Laboratory, University of Exeter, UK
April 1998

Introduction

The Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention, 16 February 1976) was signed and ratified by all eighteen Mediterranean coastal states, and by the European Community, in June 1990. It stated that all Contacting Parties should take appropriate measures to “prevent, abate and combat pollution of the Mediterranean Sea caused by discharges from rivers, coastal establishments or outfalls, or emanating from any land-based sources within their territories (UNEP, 1982).

In 1992, as part of the United Nations Environment Programme for the Mediterranean Sea, a report was published assessing the state of the environment in Lebanon. It stated that “most industrial firms on the coast discharge their waste waters into the sea without any treatment” and “most inland industries discharge their waste waters generally into the nearest stream without any treatment”.

The main types of industry in Lebanon are food and beverage manufacture, tanneries, vegetable oil, soap and detergent production, paint manufacture, chemicals, paper, plastics, textiles, metal processing and petroleum refining. The industrial sector in Lebanon is relatively small, and the absence of many primary manufacturing industries, such as smelting, paper pulp bleaching, manufacture of PVC raw materials (chloralkali and oxychlorination processes) etc, leans to the assumption that much of the waste produced, could be managed and treated appropriately and effectively.

In October 1997, over 100 samples of industrial effluent and solid waste, raw sewage effluent and sludge, marine and freshwater sediment, soil, drinking water and plant tissue, were collected from industrialised coastal and inland sites in Lebanon. All accessible industrial and sewage coastal outfalls and dumpsites between Tripoli and Tyre were sampled, as were accessible industrial outflows discharging into the Ibrahim River, the Ghadir River, the Zaharani River, the Litani River, the Berdawni River, the Ghazayel River, and the Qarun Lake. The aims of this comprehensive scientific survey were as follows:

(i) To identify the main polluting industries in Lebanon.
(ii) To discuss the range and environmental significance of heavy metal contaminants and organic pollutants discharged, both directly and indirectly, into the Mediterranean Sea.
(iii) To propose appropriate and effective means of waste management and treatment.
(iv) To present potential alternatives to any toxic processing chemicals used.

Analytical Methodology

All samples were stored and transported to the Greenpeace Research Laboratory in analytically clean glass bottles (previously rinsed with nitric acid and pentane to remove all heavy metal and organic residues). The samples were kept cold during transit, and refrigerated immediately on arrival. Heavy metals were determined quantitatively using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Organic contaminants were identified using Gas Chromatography-Mass Spectrometry (GC-MS).

Heavy Metal Analysis

Analytical grade reagents and analytically clean glassware were used throughout sample preparation and analytical procedures.

1) Solid Samples

Samples of industrial waste, sewage sludge, soil, plant tissue, marine and freshwater sediment, were dried in an oven for 48 hours, until dry weight readings became constant. They were then crushed using a pestle and mortar until homogenous and sieved through a 2mm mesh. 0.5g of sample was weighed into a 120ml Teflon microwave vessel fitted with a screw cap and pressure relief valve. To this 10ml of deionised water was added followed by 7.5ml of concentrated hydrochloric acid and 2.5ml of concentrated nitric acid. The vessels were then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630W).

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50ml and mixed. Certified Reference Materials PACS-1 (trace elements in marine sediment, certified by the National Research Council, Canada), BEST-1 (mercury in marine sediment, certified by the National Research Council, Canada), and BCR-143 (trace elements in a sewage sludge amended soil, certified by the Commission of the European Communities, Community of Reference, Brussels, Belgium) were prepared with each batch of twenty samples, as was a blank sample. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

2) Aqueous Samples

All samples of industrial wastewater, sewage, sea and fresh water were preserved in 5% v/v nitric acid on arrival. 50ml was transferred to a 120ml Teflon microwave vessel and digested using the same procedure and programming conditions as described above. After cooling to ambient temperature, samples were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50ml and mixed. A quality control standard (internally prepared at a concentration of 8.0 mg/l, 0.08 mg/l for Hg) and a blank sample were prepared with every batch of twenty samples. Both were prepared in 5% v/v nitric acid.

3) ICP-AES Analysis

Following preparation all samples were analysed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese (Mn), chromium (Cr), aluminium (Al), iron (Fe), barium (Ba), vanadium (V), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). A multi-element instrument calibration standard was prepared at a concentration of 10.0mg/l (matrix matched to the samples). The calibration was validated using a quality control standard, prepared from different reagent stocks, at 8.0 mg/l. Samples exceeding the calibration range were diluted appropriately, in duplicate, and re-analysed. The spectrometer was re-calibrated after twenty samples to adjust for fluctuations in sensitivity. All other instrument and laboratory quality control procedures were adhered to.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (ii) was reduced to Hg (0) i.e. a vapour, following reaction of the sample with sodium borohydride (0.5% w/v), sodium hydroxide (0.6% w/v) and hydrochloric acid (10 molar). The 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). Samples exceeding this range were diluted and re-analysed. The quality control standard was again prepared from a different reagent stock at 80% of the calibration range (i.e. 80ug/l). The spectrometer was re-calibrated after every ten samples.

Organic Screen Analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and cleaning up procedures was cleaned in detergent, rinsed with tap water then deionised water, dried in the oven overnight at 105^0C, and rinsed tree times with low haloform pentane.

1) Solid Samples

For each sample, approximately 30g (wet weight) was weighed and transferred to a clean 100ml glass bottle. Samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 4.7mg/kg. 15ml of pentane was added, followed by 5ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid.

Following this, a second portion of 20ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume about 3ml. The concentrated extract was cleaned through Florisil column, eluted with 95:5 mixture of pentane:toluene, evaporated down to a volume 2ml under a stream of clean nitrogen, and 1-bromonaphthalene was added as a marker.

2) Aqueous Samples

Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150ug/l. 20ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. The same clean up procedure, as described above, was employed.

3) Chromatographic Analysis

Samples were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP ChemStation data system, and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of the compounds carried out by computer matching against a HP Wiley 275 library of 270 000 mass spectra. Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

Results

See appendices 1 and 2 for full sample descriptions, results, Certified Reference Material and quality control data.

Discussion

General: Environmental and Industrial Samples

Sewage

Over twenty samples of raw sewage and sludge were collected from pipes discharging directly, untreated, into the Mediterranean Sea. Many more samples were collected from waste channels discharging mixtures of domestic sewage and industrial effluent. Domestic sewage, with or without the presence of industrial wastes, probably represents the commonest and most widespread contamination of inshore and nearshore waters (UNEP, 1995; Harrison, 1996). Fishing was observed all along the Lebanese coastline, mostly on or close to sewage outfalls. Biodegradable organic matter and elevated nutrient levels an obvious attraction to fish and marine invertebrates. Sewage debris on beaches and in coastal waters was clearly an aesthetic problem, but its presence also poses significant health risks to both marine systems and human populations.

a) Pathogenic Microorganisms

There is not only a direct risk of infection by sewage derived pathogenic organisms (i.e. those capable of causing disease), but also considerable risks associated with the consumption of contaminated and improperly prepared sea food. Bacterial pathogens such as species of *Salmonella, Shingella, Staphylococcus* and *Pseudomonus* are all abundantly represented in the Mediterranean (UNEP, 1991). Together these bacterial pathogens are responsible for infections and intoxications such as typhoid and paratyphoid fevers, food poisoning and gastroenteritis, infections of the ear, eye and the urinary tract. Viral pathogens, (up to 120 different species of virus can be excreted in human faeces) present in polluted water, include enteroviruses, capable of inducing paralysis, fever, meningitis, respiratory disease and diarrhoea; gastroenteritis viruses, capable of inducing epidemic vomiting, diarrhoea and fever; and hepatitis virus, capable of inducing infectious hepatitis.

b) Biochemical Oxygen Demand (BOD)

Discharge of any biodegradable waste, such as raw sewage, into the marine environment will have an effect on the oxygen balance due to the exertion of immediate oxygen demand and biochemical oxygen demand (BOD). This can lead to significant oxygen depletion and, in extreme cases, total anoxia. The effects of oxygen depletion are much more marked in enclosed areas of the sea such as estuaries, lagoons, marinas, close narrow bays and sea-enclosures, and can result in substantial losses (in terms of both numbers and species diversity) to fish, and marine invertebrate populations (UNEP, 1995).

c) Nutrient Input

Sewage effluents contain large quantities of micronutrient elements such as nitrogen and phosphorus. Nutrient inputs to marine systems have been a matter for considerable concern because of the potential eutrophication effects that they may cause. A simple view of eutrophication is that additional nutrients lead to the formation of excess biomass, which, in turn, leads to an increase in BOD with subsequent oxygen depletion (UNEP, 1995).

Industrial Waste

Over forty samples of industrial effluent and solid waste were collected from pipes and waste channels, discharging directly into surface waters. Wastes sampled included those from tanneries, plastics, pesticide and fertiliser factories, paper mills, textile plants, cement, food and beverage manufacturers, and metal processors. The range of toxic substances present in industrial wastes is enormous. Some common toxins include acids from acid, battery, chemical and steel industries; alkalis from brewery, food, and textile wastes; heavy metals from metal processing and plating, tanneries and the chemical industry; solvents from pharmaceutical manufacture, tanneries and the chemical industry; detergents from detergent and textile manufacture, laundries and the food industry; ammoniacal nitrogen from coke production, fertiliser manufacture and the rubber industry; and pesticides, mostly chlorinated hydrocarbons, from the chemical industry.

As with the direct discharge of raw sewage, industrial effluents can effect the receiving ecosystem in a variety of deleterious ways. Often substances discharged are toxic at very low concentrations, they can also be persistent, bioaccumulative, alter the oxygen balance of receiving waters, and induce eutrophication. As treatment can often be technically difficult and expensive, or in cases of heavy metal treatment, mere segregation, the current and future emphasis must concentrate on the development of clean technologies and not merely end of pipe solutions.

Marine and Freshwater Sediment

At all sampling locations, the collection of sediment was considered to be of greatest importance. Analysis of sediment provides an excellent picture of the extent of pollution within a defined area. Water, due to fluctuations in emission and flow, follows a less well-defined pattern (Bryan and Langston, 1992). Heavy metals and many persistent organic pollutants, will bind predominantly to suspended material, and finally accumulate in the sediment, thus providing a reliable history of pollution. As concentrations in sediment can exceed those of the overlying water by between three and five orders of magnitude (Schuhmacher et al., 1995; Bryan and Langston, 1992), the bioavailability of even a minute fraction of the total sediment metal or organic pollutant assumes considerable importance.

Once contaminated, aquatic sediment poses a particularly pernicious form of pollution, acting as a long-term reservoir that can introduce toxins to the environment far from the original source and long after discharge activity has shut down. Polluted aquatic sediments can cause environmental damage by releasing toxins to surrounding waters, directly contaminating aquatic plants and animals living within and ingesting the sediments, and by introducing toxins into the food chain, which are then transferred up the trophic ladder to higher organisms, including humans (Marcus, 1991).

Over sixty samples of marine and freshwater sediment were collected as part of this survey, and over forty contained some degree of heavy metal / organic chemical contamination.

For the purpose of clarity, the report will discuss the range and environmental significance of heavy metal contaminants and organic pollutants according to area / region sampled:

1) Tripoli and North Lebanon
2) Selaata and Chekka
3) Jbeil and Halat

4) Junieh and the Antelias coast
5) Beirut
6) Saida
7) South Saida
8) The Beqaa Valley
9) Tyre.

1) Tripoli and North Lebanon (LN7069-LN7071; LN7109-LN7110)

Five samples were collected from this area. In Tripoli sediments were taken from the harbour and at positions north and south of the coastal dumpsite, approximately 10 metres from the shoreline. The coastal waste dump near the Abu-Ali River outflow receives domestic, industrial and hospital waste from Tripoli and the surrounding villages. In Abdeh Port, sewage effluent, discharging directly into the fishing area, was sampled; and in Akkar, sludge from the plastics factory “Future Pipe Industries”.

Heavy Metals

Sediments will always contain some levels of heavy metal ions, levels very much dependant on the natural geology of the area as well as anthropogenic input. However it is widely accepted that human activity has inevitably increased the levels of metal ions in many of our natural water systems. Mine drainage, industrial and domestic effluents, agricultural and urban runoff, have all contributed to the increase of metal loads in these waters (Samanidou and Fytianos, 1990). Comparison with much published data on background levels in oceanic and freshwater systems, should allow us to establish whether the metals found in coastal and inland waters in and around Lebanon, are elevated due to anthropogenic loading or not.

Uncontaminated marine and freshwater sediments will usually contain less than 0.5 mg/kg of Cd and Hg; less than 50 mg/kg of Pb, Cr, Cu, Co and Ni; less than 100 mg/kg of Zn and V; less than 500 mg/kg of Ba; and less than 1000 mg/kg of Mn (Salomomns and Forstner, 1984; Bryan and Langston, 1992; Palanques, 1994; Palanques et al., 1995).

a) Tripoli

Of the three sediments collected from Tripoli, sample LN7069 (collected south of the coastal dumpsite) contained elevated levels of heavy metals. Notably Zn, Cu and Pb. Similar concentrations of these metals are associated with other coastal urbanised and industrial sites in the Mediterranean Region, e.g. along the coast of Spain, Izmir Bay in Turkey, Haifa Bay in Israel, Gulf of Venice in Italy (UNEP, 1990).

It appears, due to the coastal currents, that contaminants from the dump are gradually being washed away and transported to the south side, where they are accumulating in the sediments. Levels of heavy metals are higher in sample LN7069 (south), compared to sample LN7070 (north), with levels of Cu, Zn and Pb found in sample LN7069 significantly higher than those usually found in unpolluted marine sediment (Salomons and Forstner, 1984; Bryan and Langston, 1992; Palanques, 1993). Many anthropogenic discharges could be responsible for elevated levels of these metals in the environment:

The most important discharges of Cu arise from mining, smelting and metal plating operations; agricultural runoff (Cu compounds are used as nutritional supplements in fertilisers and animal feed, fungicides and other agricultural chemicals) and domestic sewage effluents (ATSDR, 1997).
Anthropogenic releases of Zn result from electroplating, smelting and ore processing, as well as acid mine drainage, effluents from chemical processes (textiles, pigment and paint, fertiliser production), and discharges of untreated domestic sewage (ATSDR, 1997). It is often forgotten that the latter can be a significant source of heavy metals, with Zn being the most abundant heavy metal present, occurring at concentrations as high as 250 mg/kg (Stephenson, 1988).

Anthropogenic discharges of Pb again result from mining and smelting operations. With less direct, yet still significant sources, arising from urban runoff, domestic sewage discharges, and automotive emissions (ATSDR, 1997).

Studies on the bioavailability, bioaccumulation and effects of elevated levels of Cu, Zn and Pb in the aquatic environment are numerous (Bryan and Langston, 1992; Swartz et al., 1985; Di Toro, 1990; Schuhmacher et al., 1992; Auernheimer et al., 1996) and deleterious effects to aquatic biota have been reported.

Copper

Although essential for living organisms at very low concentrations, Cu is still one of the most toxic metals to aquatic organisms (Schuhmacher, 1995; Bryan, 1971). Generally speaking, but not a strictly rigid order of toxicity, Hg, Ag (silver) and Cu are considered more toxic than Cd, Zn and Pb, which in turn are considered more toxic than Cr, Ni and Co. There is considerable experimental evidence that a large number of species are sensitive to dissolved Cu in the range 1-10 ug/l. For example, it was observed that 2 ug/l Cu had significant effects of the survival of young bay scallops and clams (Nelson et al., 1988). Also, in the embryos of oysters and mussels, the 48 hour LC50 concentrations (i.e. the concentration required to kill half the exposed population), based on the production of abnormal embryos, were about 5 ug/l (Martin et al., 1981). A similar concentration resulted in increased mortalities in populations of isopod crustaceans (Giudici and Guarino, 1989).

There is a very significant relationship between Cu levels in aquatic biota and the levels found in sediments, with clear relationships found between animal and sediment concentrations from as little as 10 mg/kg to more than 2000 mg/kg (Bryan and Langston, 1992). The bioconcentration factor (BCF) of Cu in fish obtained in field studies is 10-100. The BCF is higher in molluscs, especially oysters, where it may reach 30,000 (Perwack et al., 1980). This may be due to the fact that they are filter feeders, and Cu concentrations are also higher in particulates than in water.

Mean and median Cu concentrations of 127 samples of edible fish from Chesapeake Bay and its tributaries were 1.66 and 0.36 ppm in 1978, and 1.85 and 0.61 ppm in 1979 (Eisenberg and Topping, 1986). Cu levels were increased in the livers and to a lesser degree, the gonads, compared with the flesh. The Cu content of muscle tissue of several species of fish collected from metal contaminated lakes near Sudbury, Ontario, ranged from 0.5 - 1.4 ppm (Bradley, 1986). Here the Cu concentration in the livers, ranged from 5-185 ppm. Thus, liver tissue appears to be a good indicator of Cu availability and bioaccumulation in these fish.

All of these studies indicate that aquatic organisms living within or ingesting sediments containing elevated levels of Cu, can be directly contaminated. As a result of such uptake, elevated levels of Cu are introduced into the food chain, where they can then be transferred up the trophic ladder to higher organisms, including humans (Marcus, 1991).

In terms of human health, Cu is an essential trace element. However very large single or daily intakes of Cu, or prolonged exposure to lower levels, can have adverse effects on health. Consumption of contaminated food or drinking water can result in vomiting, diarrhoea, stomach cramps and nausea (ATSDR, 1997).

Zinc

Evidence for the bioavailability of Zn in sediments comes from research on plants and deposit feeding invertebrates. Schuhmacher, 1995, found that Zn in molluscs and algae collected from the Ebro River reflected sediment concentrations. Although Zn actively bioaccumulates in aquatic systems, biota appears to represent a relatively minor sink compared to sediments. Steady-state Zn bioconcentration factors (BCFs) for 12 aquatic species range from 4 to 24,000 (EPA, 1987). Crustaceans and fish can accumulate Zn from both water and food. A BCF of 1,000 was reported for both aquatic plants and fish, and a value of 10,000 was reported for aquatic invertebrates (Fishbein, 1981). The order of enrichment of Zn in different aquatic organisms was as follows (Zn concentrations in mg/g dry weight appear in parentheses): fish (25), shrimp (50), mussel (60), periphyton (260), zooplankton (330), oyster (3,300) (Ramelow et al., 1989). The high enrichment in oysters may be due to their ingestion of particulate matter containing higher concentrations of Zn than does ambient water. Other investigators have also indicated that organisms associated with sediments have higher Zn concentrations than organisms living in the aqueous layer (Biddinger and Gloss, 1984).

Although Zn is not regarded as being especially toxic, it is sometimes released into the environment in appreciable quantities, and can thus have deleterious effects on certain species at specific concentrations. For example, effects on fertilisation and embryonic development have been observed in species of fish and harpacticoid copepods (Ojaveer et al., 1980; Verriopoulos and Hardouvelis, 1988).

Although most of the studies relating to the human health effects of Zn concentrate on exposure via inhalation (which can cause a specific short-term disease called metal fume fever) less is known about the long term effects of ingesting too much Zn, through food, *water or dietary supplements. Like Cu, it is an essential trace element, but ingestion of higher than recommended levels can have adverse effects on health. The Recommended Dietary Allowances for Zn are 15 mg/day for men and 12 mg/kg for women. If doses 10 – 15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur (ATSDR, 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (ATSDR, 1997).*

Lead

Even though Pb is not considered to be one of the most environmentally mobile metals, often heavily bound to suspended particulate and sediment material (Berg et al., 1995; Hapke, 1991), there is appreciable evidence showing that sediment Pb is available to deposit-feeding species (Bryan and Langston, 1992). In aquatic organisms, Pb concentrations are usually highest in benthic organisms and algae, and lowest in upper trophic level predators (e.g. carnivorous fish). High bioconcentration factors (BCFs) were determined in studies using oysters (6,600 for Crassostrea virginica), freshwater algae (92,000 for Senenastrum capricornutum) and rainbow trout (726 for Salmon gairdneri), although most median BCF values for aquatic biota are significantly lower: 42 for fish, 536 for oysters, 500 for insects, 725 for algae, and 2,570 for mussels (Eisler, 1988). Yet still indicative of the potential of Pb to bioconcentrate and bioaccumualte through the food chain. Pb is toxic to all aquatic biota, and organisms higher in the food chain may experience Pb poisoning as a result of eating Pb-contaminated food (ATSDR, 1997).

As well as occurring in its inorganic state, there is some evidence that even in the absence of organolead inputs, inorganic Pb may be alkylated, chemically or biologically, to produce mono-, di-, and trialkyl Pb compounds (Radojevic and Harrison, 1987). The chemical speciation of the Pb will often dictate the toxicity. Organolead compounds are more toxic than inorganic forms and have been shown to bioconcentrate in aquatic organisms. Tetraalkyl lead compounds are more toxic than trialkyl lead compounds, and ethyl forms are more toxic than methyl forms (Eisler, 1988).

Unlike some heavy metals, Pb is not required in trace amounts by animals (including humans) or plants for normal growth and development. It has no known nutritional or biochemical function and if present in sufficient quantities will inhibit animal and plant growth, development and health (Nriagu, 1988).

In terms of human health, the effects of Pb are the same irrespective of whether it is inhaled or ingested (ATSDR, 1997). Pb can cause irreversible central nervous system damage and decreased intelligence at extremely low doses (Needleman et al., 1990, ATSDR, 1997). At higher levels of exposure anaemia may result, along with severe kidney damage (ATSDR, 1997). Children are especially susceptible to Pb poisoning because they absorb and retain more Pb in proportion to their weight than adults (ATSDR, 1997).

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Cu, Zn and Pb in Annex 2. Whilst not considered as toxic, persistent and bioaccumulative as the metals listed in Annex 1 (Cd and Hg), they do exhibit similar characteristics. Therefore the directive does state that releases of Cu, Zn and Pb from land-based sources, whether directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be strictly limited, and continuously monitored.

In order to implement this Directive, far greater control on waste dumping is required. The disposing of potentially hazardous wastes must cease. Inert or non-hazardous wastes should be separated with a view to recycle and reuse wherever possible. Toxic wastes must be treated prior to disposal, again with a view to recycle and reuse all materials employed.

However long term and sustainable solutions to increased levels of hazardous waste generation, must concentrate on the development of cleaner technologies and not merely on end of pipe solutions. It must be remembered that as well as contaminating surrounding waters directly, i.e. runoff, there is also the more indirect, yet sinister threat of contaminated leachate migrating from the site. Leachate is composed of the liquid produced from the decomposition of the wastes, and liquids entering the site from external sources. Depending on ambient conditions, many organic and inorganic contaminants found in the leachate are present at high concentrations, and because of this, leachate formation and migration is often a threat to both groundwater and surface water quality (UNEP, 1991).

b) Abdeh Port

Sample LN7109, sewage effluent collected from an outlet discharging directly in the Abdeh Port fishing harbour, contained detectable, although not elevated, levels of Mn, Zn, and Pb. However, as discussed previously, untreated sewage contains a wide range of pathogenic organisms, biodegradable organic matter and nutrients, that can cause environmental harm. It is a complex mixture of suspended and dissolved materials, and both categories constitute organic pollution.

All sewage must be treated prior to effluent discharge. This requires preliminary treatment, to remove the larger floating and suspended materials; primary sedimentation, to settle out all the remaining suspended material and particles; and secondary (biological) treatment, the use of microorganisms to breakdown the biological solids. In some cases tertiary treatment may be required e.g. chemical flocculation or filtration. Only then should the liquid effluent be discharged. The remaining sludge can be dewatered and heat treated, and in the absence of any industrial contaminants, utilised on agricultural land.

c) Future Pipe Industries

Sample LN7110 was taken from the waste channel of “Future Pipe Industries”, manufacturers of PVC (polyvinylchloride), PET (polyethylene teraphthalate) and polypropylene plastics. The factory imports all raw materials (no manufacture occurs on-site). These raw materials are then mixed with any necessary additives, plasticisers, stabilisers, resins and pigments etc, to produce the final desired product.
Elevated levels of Zn and Pb were found in this sample. Both can be used in plastic materials as pigments or stabilisers (Vollrath et al., 1992). Metal pigments are used because at the temperatures employed to process plastic materials, organic pigments would often decompose. Metal stabilisers, traditionally Pb and Cd (although these metals are slowly being replaced by less toxic metals e.g. Zn, Ba and Ca) are used to prevent the decomposition of plastic polymers, notably PVC. PVC has a tendency to degrade upon heating or on prolonged exposure to light, due to loss of hydrogen chloride from the polymer. This leads to yellowing of the plastic and severe embrittlement. The addition of certain stabilising chemicals during the processing of PVC, inhibit this breakdown.

Zn and Pb can easily be removed from the waste stream. Treatment involves precipitation using lime (leading to the formation of insoluble hydroxides) or ion exchange, evaporative recovery and reverse osmosis (UNEP, 1995). Precipitation alone will result in the formation of metal containing sludges, which will then need to be disposed of. However in conjunction with the other treatment techniques listed, recover and therefore reuse of the metal is possible. Alternatively, non-toxic metals such as calcium could be used as stabilising materials.

Organic Chemicals

a) Tripoli

Dichlorobenzenes were reliably identified in samples LN7069 and LN7070.

Dichlorobenzenes

Leachates from chemical waste dumps, and manufacturing effluents, are reported to be the major anthropogenic sources of these compounds (Howard 1989). The major sources of atmospheric o-DCB emissions are solvent applications, which may emit 25% of annual production to the atmosphere. Use of m-DCB, as a fumigant, will release it directly to the atmosphere. The major source of p-DCB emissions to the atmosphere is volatilisation from use in toilet bowl deodorants, garbage deodorants, and moth flakes. It is worth noting that commercial applications of these compounds rely on their toxicity.

Sewage sludges collected from industrial areas will generally have higher chlorobenzene concentrations than those from rural areas. (Wang et al. 1994). If released to soil and sediment, all are moderately absorbed, and o-DCB in particular is reported as being a useful marker of the extent of contamination for untreated sewage discharges (Chapman et al. 1996). Chlorobenzenes which are present in sewage sludges, possess a range of properties which suggest that soil-borne chlorobenzenes may be susceptible to transfer to crops, grazing livestock and groundwater (Wang et al. 1994b).

In terms of human and animal health, o-DCB is known to cause injury to the liver and kidneys. High concentrations can also cause central nervous system depression (Merck, 1989). p-DCB is reported to cause headaches and dizziness, toxic effects in the liver and kidney, and increases in the rates of cancer among experimental animals (USPHS 1989, Bornatowicz et al. 1994). o-DCB has been classified as "possibly carcinogenic to humans" under the Canadian Environmental Protection Act (Meek et al. 1994).

The three dichlorobenzenes described above are listed in Annex 1D of the North Sea Ministerial declaration (MINDEC 1990), indicating that they should be considered for prioritisation as pollutants (both to air and water) in the future.

Monoaromatic hydrocarbons such as long-chain alkylbenzenes were tentatively identified in sample LN7070 together with linear alkanes.

Alkylbenzenes

The occurrence of these compounds in the environment is due to their presence in crude oil and petroleum products. Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chalaux et al. 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources. Monoaromatic and polyaromatic hydrocarbons are considered to be the most toxic, and are known to be present at the highest concentrations during the initial phase of a crude oil spill (Overton 1994).

b) Abdeh Port

Other chlorinated benzenes

Three chlorinated benzenes (1,4-dichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene) were identified in the sample LN7109, sewage effluent collected from an outlet discharging directly in the Abdeh Port fishing harbour. These compounds in effective concentrations are toxic to the marine invertebrates and were associated with a growth rate reduction of crabs (Mortimer et al. 1995).

Direct or indirect pollution from the land-based sources by the toxic, persistent and bioaccumulative organohalogen compounds and substances which may form such compounds in the marine environment has to be eliminated (European Community Environment Legislation, 1992a) according to the Council Decision 83/101/EEC.

c) Future Pipe Industries

Two phenols, bis (1,1-dimethylethyl) phenol and 2,6-bis (1,1-dimethylethyl)-4-methylphenol, were identified in this sample.

Butylated hydroxytoluene (BHT)

2,6-Bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), is frequently employed as an antioxidant in food products and in the production of plastics and other petrochemical products. It is also manufactured as an anti-skinning agent in paints, varnishes and other surface finishes. Its use in food has been associated with certain allergic reactions (Dean et al. 1986) and there is also some evidence that BHT can act as a promoter of liver cancer, in combination with other carcinogenic substances, through induction of abnormal liver metabolism (Williams et al. 1986).

2) Selaata and Chekka (LN7058-LN7068)

Both Selaata and Chekka are situated in the north of Lebanon, south of Tripoli. The “Lebanon Chemicals Company”, the largest chemical fertiliser factory, is located in Selaata. Whereas Chekka is home to two of the largest companies in Lebanon, “Cimenterie Nationale” (C.N.) and “Societe des Ciments Libanas” (S.C.L.), both cement factories. All three companies discharge liquid wastes directly into the Mediterranean Sea.

Heavy Metals

a) Lebanon Chemicals Company

Two samples were collected from the Lebanon Chemicals Company. One sample of industrial effluent (LN7058) discharging directly into the sea; and one sample of sediment collected in front of four discharging pipes (LN7059). Due to the rocky shoreline it was not possible to collect effluent samples from these pipes, and sample LN7059, as it was collected approximately 20 metres away from the discharge and was a very coarsely grained/rock-like sediment, did not contain elevated levels of heavy metals.

However, effluent sample LN7058 contained 4 mg/l of V. Zn and Cu were also detected, but at low concentrations. V is released primarily as a by-product or co-product during the extraction of other compounds, such as iron, titanium, phosphate, or petroleum. In this case, such significant releases of V are due to the processing of phosphate rock, which in turn is used to manufacture phosphoric acid and phosphate fertilisers. The pH of this effluent was found to be acidic (pH 4, measured using universal indicator paper pH1-pH14). This is usual for wastes resulting from phosphate rock/phosphoric acid processing.

<u>*Vanadium*</u>

Upon entering the ocean, V in suspension or sorbed onto particulates, eventually accumulates in seabed sediments (WHO, 1988). Some marine organisms, in particular filter feeders, e.g. the ascidians (sea squirts), bioconcentrate V very efficiently, attaining body concentrations approximately 10,000 times greater than the ambient sea water (Byerrum et al., 1974). Upon the death of the organism, the body burden adds to the accumulation of V in silt (WHO, 1988).

The essentiality of V for living organisms has yet to be established with certainty (Domingo, 1996). Research has concluded that the chemical form of V determines its toxicity. Vanadate (+5) and vanadyl (+4) forms may be reproductive and developmental toxicants in mammals for example. With decreased fertility, embryolethality, fetotoxicity, and teratogenicity reported to occur in rats, mice and hamsters following exposure (Domingo, 1996).

In certain fish species, overall general health conditions have been observed to be significantly hampered leading to deleterious alterations in the general metabolism of fish, following long term exposure to vanadate at concentrations ranging from 2 mg/l to 10 mg/l (Chakraborty et al., 1998).

Most studies relating to the human health effects of V concentrate on exposure via inhalation. Less is known about the long-term effects of ingesting too much V through contaminated food (in this case fish and marine invertebrates) or water. Animal studies using rats have shown that some minor birth defects (such as slightly smaller offspring, offspring with broken blood vessels on parts of their bodies or chemical changes in their lungs) occurred when pregnant females drank V contaminated water. In another study, rats exposed to sodium metavanadate in water developed minor kidney damage (ATSDR, 1997).

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists V in Annex 2. Therefore, as is the case with Cu, Zn and Pb, discharges released directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be strictly limited, and continuously monitored.

Also listed in Annex 2 of this directive, and of relevance to this discharge, are acid compounds and inorganic compounds of phosphorus and elemental phosphorus.

The levels of V in this wastewater, the acidic pH, and the potential release of significant levels of phosphorus warrant concern. Such uncontrolled and unmonitored discharges are in complete breach of EC Directive 83/101/EEC. Yet this effluent could easily be treated. pH can be adjusted (neutralised in this case) using calcium hydroxide, lime, sodium hydroxide, sodium carbonate or carbon dioxide. V may be removed by precipitation with ferrous sulphate under neutral (or slightly alkaline) conditions (UNEP, 1995). As V and its compounds are used widely (alloying agents in the steel industry, industrial catalysts, pigments, paints, varnishes, corrosion inhibitors), yet occur scarcely in the environment, there are economic benefits to be gained from its removal from the waste stream with a purpose to recycle rather than dispose (ATSDR, 1997).

b) Cimenterie Nationale (C.N.)

Five samples were collected from Cimenterie Nationale. One sample of industrial wastewater (LN7060), discharging into a small stream; two samples of sediment collected from the stream (LN7061-LN7062), upstream and in front of the discharging pipe, one sample of the final cement product (LN7063) collected from the loading bay; and one sample of dust (LN7064) collected outside the loading bay.

No elevated levels of heavy metals were found in the wastewater; slightly elevated levels of Zn and Hg were found in the sediment samples; and similar levels of metals were found both the cement dust and final cement product samples. None appeared to be present at anomalously high concentrations.

c) Societe des Ciments Libanas (S.C.L.)

Four samples were collected from Societe des Ciments Libanas. One sample of the final cement product (LN7065); one sample of dust (LN7066), collected from the klinker bay of the new plant; one sample of sediment (LN7067) collected from a waste channel running directly into the sea; and one sample of industrial wastewater (LN7068) discharging into this channel. No anomalously high levels of heavy metals were determined in any of the samples.

However of interest is the level of Ba found in sample LN7067 (sediment collected from the waste channel). The largest natural source of barium is barite ore which is composed largely of barium sulfate and found in beds or masses in limestone, dolomite, shales and other sedimentary formations (ATSDR, 1997). The level determined in this sample, and the elevated presence in the klinker and dust samples, relative to the other metals detected, suggest that Ba is present naturally in the raw cement materials.

Barium

As Ba appears to be naturally present in the cement product, exposure to Ba through inhalation of cement dust should be considered. There is little reliable information about the possible health effects in humans who are exposed to Ba by breathing or direct skin contact. However, many of the health effects might be similar to those seen after eating or drinking large amounts of Ba, i.e. breathing difficulties, increased blood pressure, changes in heart rhythm, stomach irritation, muscle weakness, liver and kidney damage etc. (ATSDR, 1997).

Thus to ensure human safety, facial protection, covering both the mouth and nose, should be worn by all workers exposed to the dust.

Organic Chemicals

a) Lebanon Chemical Company

Both samples contained long-chain alkylbenzenes and linear alkanes. The occurrence and toxicity of the alkyl benzenes is discussed above; linear alkanes are generally of petroleum origin; petroleum hydrocarbons are discussed below. Industrial wastewater sample LN7058, contained molecular sulphur and one phenolic compound, 2,4-bis (1,1-

dimethyl) phenol. Toxicological studies of sulphur rich phenolic leachate (Kahru et al. 1997) has shown that its toxicity was mainly caused by its phenolic and sulphuric compounds; luminescent bacteria were used as test organisms.

b) Cimenterie Nationale

Samples LN7060 and LN7064 contained cyclic or straight chain hydrocarbons, which might be of biogenic origin. Samples LN7061, LN7062 and LN7063 additionally contained different isomers of dichlorobenzene, the origin and toxicity of which are described above.

Samples LN7061 and LN7062 indicate possible oil and / or petroleum contamination.

Petroleum hydrocarbons

Petroleum is a complex mixture of hydrocarbons that is formed from the partial decomposition of biogenic material. Petroleum hydrocarbons are released into the environment through natural seeps, non-point source urban runoffs, and by large quantities of accidentally released oil. Petroleum substances can also be found, albeit at low concentrations, in sewage (Connel, 1974) but the total amount discharged is relatively high due to the large volumes involved. Refined petroleum products can contain the alkanes. It is often difficult to distinguish the origin of the hydrocarbons found in environmental samples. In cases of anthropogenic pollution, i.e. crude oil or petrol spills, alkanes are present together with monoaromatic hydrocarbons (benzenes) and polyaromatic hydrocarbons (naphthalene and others) compounds (Overton 1994).

The PAHs which were found in these samples were mainly naphthalene and its alkyl derivatives as well as phenanthrene, identified in the sample LN7061.

Polycyclic aromatic hydrocarbons (PAHs)

Exposure to PAHs can deleteriously effect human health. Individuals exposed to mixtures of PAHs, through inhalation or skin contact, for long periods of time, can cause cancer (USPHS, 1990). Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from an angular benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. In addition, substitution of methyl groups on specific carbons of the ring also enhances carcinogenicity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogens known (Williams 1986).

Among other compounds, responsible for the petroleum or creosote contamination of surface waters, soils, or groundwater (Johansen et al. 1997), one sulphur-containing aromatic compound - methylated dibenzothiophene- was identified in the sample LN7061.

Dibenzothiophenes

Several representative from this class of organic compounds including benzothiophene, benzothiophene sulphone, benzothiophene-2,3-dione, 3-, and 5- methylbenzothiophenes, 3-, and 5-methylbenzothiophene sulphones, 5-. and 7-methylbenzothiophene-2,3-diones, dibenzothiophene, dibenzothiophene sulphoxide, and dibenzothiophene sulphone have been found to be toxic by the Microtox(R) and Daphnia magna bioassays (Seymour et al 1997).

c) Societe des Ciments Libanas

No compounds were identified in the cement sample LN7065. 1,4-dichlorobenzene was identified in the dust sample LN7066, which as discussed above is very widely used. Consequently, there are a number of possible routes by which it could have entered this sample. Cement kilns are often used to burn hazardous wastes, and this is another possible route of contamination.

Sample LN7067 contained PAHs including alkylated naphthalene, phenanthrene and pyrene, all markers of oil contamination (see above).

Three representatives of phthalate esters were identified in the waste water sample LN7068: 1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester, known as DEHP; 1,2-benzenedicarboxylic acid, diisobutyl ester (DIBP), and 1,2-benzenedicarboxylic acid, butyloctyl ester.

Phthalate esters

Phthalate esters are bioaccumulative and moderately persistent in the environment. They are used in virtually every major product category, including construction, automotive, household products, apparel, toys, packaging, and medical products, resulting in the widest possible distribution of these materials. However, 90% is used in the production of soft PVC. 10-15 years before the two most abundantly produced phthalate esters were DEHP and DnBP (Menzert et al. 1986). DEHP can exert a number of chronic toxic effects following longer exposures and may be an important reproductive poison, (Life Systems, Inc. 1993). More recently, concern has been raised about the ability of DEHP and some other phthalates to interact with hormone receptors in animals. Jobling and coworkers (1995) demonstrated that DEHP was able to bind to the human estrogen receptor, although it showed no significant estrogenic activity. Its potential to interfere with other aspects of the hormone system has not been fully investigated. At present DEHP still used in greatest amount by industry together with other phthalates including DINP and DIDP (Harris et al. 1997). DINP is a long chain phthalate, which although extremely weakly estrogenic, is used in large quantities. BBP, DBP, and DIBP are used by industry in smaller quantities, but are more estrogenically active. Although less extensively studied, data currently available for DINP suggest that this isomeric phthalate may also carry many of the hazards associated with DEHP, impacting similar target organs in chronic studies (especially the liver, kidney and reproductive tracts) as DEHP. DINP, for example, has been shown to exhibit a range of toxic effects in laboratory animals. A wide range of toxic effects has been recorded in *mammals following acute and chronic laboratory exposures (KEMI 1994). Some, such as stress and damage to the liver, kidney, stomach and other organs and effects on blood and urine biochemistry (European Chemicals Bureau 1996, Myers 1991, USEPA 1991 & 1992), appear to be characteristic of many of the phthalates tested to date. Long-term exposure to DINP has been linked to gross changes in organ and body development in rodents. In addition, exposure to DINP appears to increase the incidence of certain cancers in rats, including liver, testicular and endometrial tumours, and lead to reduced survival from mononuclear cell leukemia (MCL) (Aristech 1995, KEMI 1994). Structural and functional changes in development of reproductive organs have also been reported following chronic exposure to DINP (European Chemicals Bureau 1996, Myers 1991, USEPA 1991), as well as some evidence for an increase in frequency of deformed and non-motile sperm in rats (USEPA 1992).*

A group of phthalate esters including dimethyl phthalate; diethyl phthalate; di-n-butyl phthalate; butyl benzyl phthalate; dihexyl phthalate; butyl 2-ethylhexyl phthalate; di-(n-hexyl, n-octyl, n-decyl) phthalate; di-(2-ethylhexyl) phthalate; diisooctyl phthalate; diisononyl phthalate; di-(heptyl, nonyl, undecyl) phthalate; diisodecyl phthalate; diundecyl phthalate; and ditridecyl phthalate has been found to have both acute (Adams et al. 1995) and chronic (Rhodes et al. 1995) toxicity to representative freshwater and marine species. There was a general trend for the lower-molecular- weight phthalate esters (C-1 to C-4 alkyl chain lengths) to seem less toxic with decreasing water solubility for all species tested. Phthalate esters with alkyl chain lengths of six carbon atoms or more were not acutely toxic at concentrations approaching their respective aqueous solubilities. The lack of toxicity observed for the higher-molecular-weight phthalate esters resulted from their limited water solubility.

3) Jbeil (Ibrahim River) and Halat (LN7048-LN7057)

Two paper mills, “Sanita” and “CPC”; “Adonis Pesticides” and “Elie Mwannes Plastics” were sampled in the areas of Halat and Jbeil, situated to the north of Beirut.

Heavy Metals

a) Sanita

Sanita is one of the three main tissue mills in Lebanon, situated in Halat. CPC one of the four main cardboard mills, close to Jbeil. The paper industry in Lebanon is limited to tissue and cardboard production. No paper pulp is produced from raw materials, thus heavy pollution by chlorine compounds, used to bleach the pulp, should be avoided. Relying on this assumption, little or no wastewater treatment is carried out by the paper industry in Lebanon (METAP, 1995).

Two effluent pipes belonging to Sanita were located. When operational, both discharge waste directly onto the beach and into the Mediterranean Sea. Only one pipe was discharging at the time of sampling, and as this was thought to be irrigation water, no

sample was collected. Instead, sediments in front of the pipes were taken (LN7048 and LN7050).
Elevated levels of Hg were found in both samples. Background levels of Hg in marine sediments are usually less than 0.5 mg/kg (Bryan and Langston, 1992; Salomons and Forstner, 1984). Levels of 1.4 mg/kg and 3.3 mg/kg were determined in these samples.

In addition, elevated levels of Cr were found in sample LN7048 (112.5 mg/kg); and elevated levels of Zn and Pb in sample LN7050 (424.5 mg/kg and 273.4 mg/kg respectively). Background levels of Cr and Pb are usually quoted as being less than 50 mg/kg, with Zn levels usually less than 100 mg/kg (Bryan and Langston, 1992; Salomons and Forstner, 1984;).

Sanita imports all the bleached pulp it uses, and no mixing with recycled paper is carried out on site. Thus the elevated presence of the heavy metals in sediments associated with wastewater discharges from the plant are difficult to explain. Certain trace metals, e.g. Zn will be present naturally in the wood, and thus remain in the pulp. However this is not likely to be the case for Cr, Hg and Pb. Alternatively, all these metals and their compounds are, to varying degrees, used as pigments, and if the tissue is being coloured, they may be employed. It is also possible that domestic and other industrial wastes are mixed with this industrial wastewater and discharged through the same channels. However in order to trace and source these metals fully, further investigation is required. The collection of effluent samples being a necessity in the future.

Environmental assessments of Zn and Pb are discussed above. Regarding the effects of elevated levels of Hg and Cr in the environment, the following is known:

Mercury

Hg concentrations associated with clean sediments are extremely low, with levels ranging from 0.03 mg/kg to 0.2 mg/kg (Bryan and Langston, 1992, Salomons and Forstner, 1984; Licheng and Kezhun, 1992). Elevated Hg concentrations in aquatic systems are primarily due to anthropogenic discharges of inorganic Hg. With sediments associated with gold mining sites and chlor-alkali discharges, the two major sources of anthropogenic Hg in the environment, containing levels ranging from 0.6 to over 150 mg/kg (Bryan and Langston, 1992; Reuther, 1994; Nriagu, 1992; Maserti and Ferrara, 1991).

Levels found in samples LN7048 and LN7050 are therefore between 5 and 100 times higher than background, depending on which data set is used for comparison

Hg is a non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and Hg is the only metal known to biomagnify i.e. progressively accumulate, through the food chain (WHO, 1989; ICME, 1995). It is extremely toxic to both animals and plants at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any exposed biota (ATSDR, 1997). Therefore environmental legislation exists in abundance to control and *monitor, and often prohibit, Hg discharges (e.g. 75/437/EEC; 82/176/EEC; 84/156/EEC; 85/513/EEC; 78/319/EEC).*

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Hg and its compounds in Annex 1. They are considered toxic, persistent and bioaccumulative, and thus their discharge, whether directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be eliminated.

Since "Minimata", the implementation of widespread regulations on Hg disposal has greatly reduced the threat of similar incidents. However the retention of Hg by benthic sediments may delay the elimination of contamination for many years. Thus for example, concentrations as high as 100 mg/kg were still present in sediments at certain sites in Minimata Bay ten years after discharges ceased (Bryan and Langston, 1992; Tsubaki and Irukayama, 1977).

Hg accumulation from sediments may be a dominant pathway for uptake in aquatic organisms and accounts for relatively high concentrations in deposit-feeders both in freshwater and estuarine systems (Bryan and Langston, 1992; Kiorboe et al., 1983). The most important factors affecting the toxicity of Hg to aquatic species are the concentration and chemical speciation of the Hg present. Other factors include the developmental stage of the organisms exposed, and physical-chemical parameters of the ecological system, such as pH, temperature, salinity, water hardness, oxygen levels etc.

Although there is evidence which links levels of total Hg in the environment with those in higher predators such as fish, concern centers on methylmercury (MeHg) accumulation. Inorganic Hg can be methylated by micro-organisms indigenous to soils, sediments, fresh water, and salt water, the process being mediated by various microbial populations under both aerobic and anaerobic conditions (ATSDR, 1997). It widely acknowledged that organic forms of Hg are even more toxic than inorganic forms.

The most common organic form of Hg is MeHg. It exhibits high lipid solubility, easily crossing cell membranes, and thus quickly enters the aquatic food chain. It also has a high biological half-life, and due to increased longevity of top predators in association with these other properties observed, it provides one of the rare examples of metal biomagnification in food chains. For example, MeHg concentrations in carnivorous fish at the tops of freshwater and salt water food chains (e.g., pike, tuna, and swordfish) are biomagnified on the order of 10,000 100,000 times the concentrations found in ambient waters (Callahan et al. 1979; EPA 1980, 1984; ATSDR, 1997).

Bioaccumulation of methylmercury in aquatic food chains is of interest because it is generally the most important source of non-occupational human exposure to the element (EPA 1984; ATSDR, 1997). As mentioned, Hg is a highly toxic, bioaccumulative, and persistent metal. It has no beneficial effects in humans, and there is no known homeostasis for it. Any long-term exposure may therefore be expected to progressively cause severe disruptions in the normal functioning of any accumulating organ (Nriagu, *1988). Such accumulating organs include the kidneys, liver and central nervous system. Exposure to high enough levels of metallic, inorganic or organic Hg can permanently damage these organs (ATSDR, 1997).*

Chromium

Background concentrations of Cr in sediment are usually less than 50 mg/kg (Salomons and Forstner, 1984, Bryan and Langston, 1992). Elevations above this background range are nearly always due to anthropogenic discharges, with three industrial sectors responsible for the majority of releases: metallurgical, chemical and refractory. In the metallurgical industry Cr is used in the production of stainless steel, alloy cast irons and non-ferrous alloys. In the chemical industry it is used primarily in leather tanning, in the production of pigments, metal finishing and wood treatment. Smaller amounts are used in water treatment, textiles and as catalysts.

Information on the effects of elevated levels on aquatic biota, fish, deposit feeding and wading birds is limited. How sediment-bound Cr reaches animal and plant tissues is uncertain, although it is recognised that the speciation of Cr determines its bioavailability. Cr (VI) will be accumulated more readily than Cr (III), as it has been shown to cross biological membranes more readily (Bryan and Langston, 1992). Whereas Cr (III) is a trace nutrient at low concentrations, Cr (VI) is non-essential and toxic. It's compounds being classified as carcinogenic by the International Agency of Research on Cancer (ATSDR, 1997). Most of the Cr associated with aquatic sediment will be in the trivalent form, and although not as environmentally mobile as Cr (VI), accumulation and movement up the food chain have been experimentally studied (Aislabie and Loutit, 1986; Bremer and Loutit, 1986. Accumulation of Cr in cockles, polychaetes and mud snails has been shown to occur following exposure to Cr contaminated sediments. The sediments became contaminated due to tannery waste (trivalent Cr) discharges in Sawyer's Bay, New Zealand (Aislabie and Loutit, 1986). Whether the tissue concentrations reported were sufficient to produce deleterious effects is not known.

For fresh water fish and shell fish, the uptake of metals through their food may be quite substantial (Heath, 1987; Dallinger et al., 1987), and metals taken up by plants can be an important route to make metals in the sediments bioavailable to herbivore species (Berg et al., 1995). Cr levels in edible oysters, mussels, clams and molluscs have been reported to range from <0.1 mg/kg to 6.8 mg/kg (Bryne and DeLeon, 1986; Ramelow et al, 1989). Fish and shellfish collected from ocean dump sites off New York City, Delaware Bay, and New Haven, Connecticut, contained <0.3 mg/kg to 2.7 mg/kg (ATSDR, 1997).

An average daily intake of 50-200 ug/day of Cr (III) is recommended for adults (ATSDR, 1997), Cr (III) being an essential nutrient, required for normal energy metabolism. However the consumption of contaminated fish, other foodstuffs and drinking water could increase the daily intake levels far beyond those recommended. Ingesting small amounts of Cr (both +3 and +6 forms) will generally not harm, however ingesting higher than *recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, kidney and liver damage (ATSDR, 1997).*

Dermal exposure to both Cr (III) and Cr (VI) can result in severe redness and swelling of the skin (ATSDR, 1997). Whereas breathing in high levels of Cr (far less likely in this case) can cause irritation of the nasal and respiratory membranes. These effects have primarily occurred in factory workers who make or use Cr (VI) for several months to many years. Long term occupational exposure to Cr (VI) is believed to be primarily responsible for the increased lung cancer rates (ATSDR, 1997).

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Cr in Annex 2. Therefore, as is the case with Cu, Zn, Pb and V previously discussed, discharges released directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be strictly limited, and continuously monitored.

b) CPC Paper

Two samples of river sediment were collected up and downstream of the CPC cardboard paper factory. Liquid wastes are discharged directly into the Ibrahim River. Similar levels of heavy metals were determined in both samples, and none were present at anomalously high concentrations. Therefore heavy metal usage does not appear to be associated with the cardboard manufacturing processes occurring in this plant.

c) Adonis Pesticides and Elie Mwannes Plastics

Adonis Pesticides and Elie Mwannes Plastics are situated next to each other on the bank of the Ibrahim River, upstream of the CPC cardboard producing plant. Both discharge untreated liquid waste directly into the river.

Five samples were collected. Two samples of industrial wastewater (LN7053 and LN7055), one from each factory; and three samples of river sediment (LN7051-LN7052, LN7054), two taken in front of the wastewater discharge channels, and one at the confluence of the two waste streams with the Ibrahim River.

The green effluent collected from the Adonis Pesticides (LN7053) waste channel contained detectable levels of Mn, Cr, Zn and V, none present at anomalously high concentrations. However the effluent collected from the plastics factory (LN7055) contained detectable levels of Mn, Cr, Zn, Cu, Pb, Ni, Co, Cd, V, Ba and Hg. Of these, Pb and Cd in particular, warrant concern. Their elevated presence in plastic processing waste is not unusual, as they can both be used as pigments, and in the manufacture of PVC, as polymer stabilisers.

Metal stabilisers, traditionally Pb and Cd (although these metals are slowly being replaced by less toxic metals e.g. Ca, Zn and Ba, also present in the effluent) are used to prevent the decomposition of PVC. It has a tendency to degrade upon heating or on prolonged exposure to light, due to loss of hydrogen chloride from the polymer. This leads to yellowing of the plastic and severe embrittlement. The addition of Pb, Cd, Ca, Zn and Ba stabilising chemicals inhibits this breakdown.

Sample LN7051, sediment collected from a waste channel running alongside the plastics factory, contained elevated levels of Cr, Zn, Cu, Pb, Cd, Ba and Hg. Of particular concern are the anomalously high levels of Zn, Pb, Cd and Hg.

Sample LN7052, sediment collected from a waste channel leading from the pesticide factory, contained elevated levels of Cr, Zn, Cu, Pb, Cd, Ba and Hg. Of particular concern are the anomalously high levels of Zn, Pb and Cd.

Sample LN7054, sediment collected at the confluence of the two waste streams with the Ibrahim River, contained elevated levels of Cr, Zn, Cu, Pb, Cd, Ba and Hg. Of particular concern are the levels of Zn, Pb, Cd and Hg. All are present at far higher concentrations than those usually associated with unpolluted river sediments, ten to fifteen times higher than background levels (Bryan and Langston, 1992; Salomons and Forstner, 1984; Licheng and Kezhun, 1992; Berg et al, 1995; Nelson and Lamothe, 1993; Goncalves, 1990).

As mentioned above, Pb, Cd, Zn and Ba are often used as stabilising chemicals, preventing the decomposition of PVC. The PVC raw materials are imported and not manufactured on site. However additives such as stabilisers, together with any necessary plasticisers, pigments and resins are added and mixed at the factory.

Cr, Hg and Cu compounds (as well as compounds of Pb, Cd, Zn and Ba) are all used, to varying degrees, as colouring agents, in dye formulations and in pigments. All could be employed in this capacity by the plastics factory.

Of the metals found in the sediments associated with releases from the pesticide factory, compounds of Cu, Zn, Ba and Hg are known to be used as fungicides, herbicides, algicides, animals repellants etc. (Agrochemicals Handbook, 1987; ATSDR, 1997). Examples of metal-containing pesticides include simple inorganic compounds such as zinc chloride, zinc sulphate, zinc phosphide, copper oxide, copper oxychloride, copper sulphate, mercury chloride, and barium carbonate. As well as more complex organic compounds such as copper naphthenate, methoxymethylmercury, phenylmercury acetate (banned in most countries), and the Zn containing fungicides Metirem, Mancozeb, Zinab and Zinab.

Although not as commonly used as those metals listed above, Cd, Cr and Pb compounds can also be used as pesticides. Examples include sodium dichromate, used as a defoliant of cotton and other plants and as a wood preservative; cadmium chloride, used as a fungicide; and lead arsenate, used for the control of moths, leaf rollers and other chewing insects (Hayes and Laws, 1991).

Environmental assessments of Cr, Cu, Pb, Zn and Hg are discussed above. Regarding the effects of elevated levels of Cd in the environment, the following is known:

Cadmium

Background levels of Cd in sediments are extremely low, with values less than 0.2 mg/kg, most commonly quoted (Bryan and Langston, 1992; Salomons and Forstner, 1984; Licheng and Kezhun, 1992; Goncalves et al., 1990). Levels of 10 mg/kg have been associated with contaminated sites in the UK (Bryan and Langston, 1992), with levels in Spain, i.e. the River Tinto and Odiel basin, cited as ranging from 0.1 mg/kg to 30 mg/kg (Nelson and Lamothe, 1993).

Levels of Cd in the sediments associated with discharges from Adonis Pesticides and Elie Mwannes Plastics into the Ibrahim river, range from 7.8 mg/kg to 20.3 mg/kg i.e. 40 to 100 times higher than levels associated with unpolluted river sediments. The most often mentioned sources of Cd entering the aquatic environment are industrial effluents and sewage (Butler and Timperley, 1995). Small amounts of cadmium enter the environment from the natural weathering of minerals, but most is released by human activities such as mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertiliser or sewage sludges (Elinder 1985).

Cd has no biological function, and is highly toxic to both animals and plants. The low concentrations of Cd usually encountered in the environment do not cause acute toxicity, however elevations above background concentrations can have deleterious effects on plant and animal health (Bryan and Langston, 1992; Alloway 1990). There is evidence to show that Cd can be absorbed from surface sediments, suspended particular matter and water (Bryan and Langston, 1992; Bryan and Humberstone, 1973; Ray et al., 1980; Schwartz et al., 1985). It is known to be one of the more mobile, and hence bioavailable, trace metals (Jensen and Bro-Rasmussen, 1990).

High tissue Cd concentrations are often associated with the presence of metallothionein (sulphur binding) proteins. The induction of these proteins in response to Cd is well established and is thought to afford protection against the toxic effects of the metal, at least until the system becomes saturated (Bryan and Langston, 1992). However deleterious effects have been reported. These include observed correlations between increased levels of Cd found in limpets and a reduced ability to utilise glucose (Shore et al., 1975). Reductions in reproduction rates and thus population numbers in copepods and isopods (Giudici and Guarino, 1989). The toxicity of low sediment-Cd concentrations was also suggested by observations showing that in San Francisco Bay, the condition of certain species of clam declined as Cd concentrations rose from 0.1 to 0.4 mg/kg (Luoma et al., 1990).

As mentioned above, Cd has no biochemical or nutritional function. It is highly toxic even at low concentrations, persistent in the environment, and has the potential to bioaccumulate. Along with Hg, Cd it is considered to be one of the most toxic metals, and *as such much legislation exists to control and monitor Cd discharged to the environment. Examples of European Environmental legislation include directives 75/437/EEC regulating pollution from land based sources; 76/464/EEC Dangerous substance Discharge; and 83/513/EEC on limit values and quality objectives for Cd discharges).*

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Cd and its compounds in Annex 1. They are considered toxic, persistent and bioaccumulative, and thus their discharge, whether directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be eliminated.

Regarding potential human exposure, food, water and cigarette smoke will be the largest sources of Cd for members of the general population. Eating food or drinking water with very high Cd levels can severely irritate the stomach, leading to vomiting and diarrhoea (ATSDR, 1997). Eating lower levels of Cd over a long period of time can lead to a build up of Cd in the kidneys. This Cd build-up causes kidney damage, and also leads to the weakening of bone (Nriagu, 1988). Studies concerned with the effects of eating and drinking high levels of Cd are not strong enough to show that such exposure can lead to an increased rate of cancer. However the U.S. Department of Health and Human Services and the U.S. Environment Protection Agency have both determined that Cd and Cd compounds may reasonably be anticipated to be carcinogens (ATSDR, 1997).

All of these heavy metals discharged can easily be removed from the waste stream. Treatment involves precipitation using lime (leading to the formation of insoluble hydroxides) or ion exchange, evaporative recovery and reverse osmosis (UNEP, 1995). Precipitation alone will result in the formation of metal containing sludges, which will then need to be disposed of. However in conjunction with the other treatment techniques listed, recover and therefore reuse of the metal is possible. Alternatively, non-toxic metals such as calcium could be used as stabilising materials.

Organic Chemicals

a) Sanita

Long-chain straight hydrocarbons were tentatively identified in the sample LN7048.

Sample LN7050 contained different representative of terpenoids such as alpha-amorphene, alpha-copaene, alpha- and beta-cubenene, alpha-humulene, delta- and gamma-cadinene and alpha-ylangene. These compounds are naturally occurring. The source of these sesquiterpenoids in the sediments could be of both a terrestrial and / or algal origin (Elias et al. 1997); in this case the source is probably the wood pulp.

b) CPC Paper

Two samples of river sediment were collected up and downstream of the CPC cardboard paper factory. Liquid wastes are discharged directly into the Ibrahim River. Several straight-chain hydrocarbons were tentatively identified in both samples.

c) Adonis Pesticides and Elie Mwannes Plastics

Adonis Pesticides and Elie Mwannes Plastics are situated next to each other on the bank of the Ibrahim River, upstream of the CPC cardboard producing plant. Both discharge untreated liquid waste directly into the river.

Compounds found in samples LN7051, LN7052, LN7054 and LN7055 all indicate a mixture of petroleum and creosote contamination. All samples contained variety of alkylated PAHs, alkylbenzenes and dibenzothiophenes which, as discussed above, are the typical compounds found in the samples of such contamination.

Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-, known as butylated hydroxytoluene (BHT) was identified in three samples from this area: LN7051, LN7052 and LN7055. As mention above, this compound is used in the production of plastics and other petrochemical products. It is also manufactured as an anti-skinning agent in paints, varnishes and other surface finishes. Its use in food has been associated with certain allergic reactions (Dean et al. 1986) and there is also some evidence that BHT can act as a promoter of liver cancer, in combination with other carcinogenic substances, through induction of abnormal liver metabolism (Williams et al. 1986).

In the industrial wastewater sample LN7053 from the "Adonis Pesticides" plant four compounds were reliably identified. Two of them, 1,2-benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP) and 1,4-dichlorobenzene, are discussed above.

Two other compounds of a particular interest were identified in this sample - 1,2,3,4,5,6-hexachlorocyclohexane and 2,4-dichlorophenol acetate.

<u>Hexachlorocyclohexane</u>

Lindane, is the gamma isomer of hexachlorocyclohexane (HCH) and is the coomercially produced isomer among the eight well-described stereoisomers. This compound is an insecticide and is used for the control of grasshoppers, cotton insects, rice insects, wireworms, and other soil pests. Lindane has been used for protection of seeds, for treatment of poultry and livestock, and for control of household insects. Direct human contact with lindane may result as it is still used as a scabicide and pediculocide, usually as lotions, creams, and shampoos.

Lindane is a bioaccumulative compound. It has been detected in air and water (Bildeman et al. 1995), plants (Strachan et al. 1994), birds and mammals (Smith 1991; Junqueira et al. 1994), and humans (Pesendorfer et al. 1973, Acker 1974, Inoue et al. 1974, Pramanik & Hansen, 1979). In humans lindane mostly concentrates in adipose tissue. Women chronically exposed to lindane or living in areas of intense usage, have *been found to contain residues of different chloroorganic compounds, including lindane, in breast milk (Larsen et al. 1994, Schlaud et al. 1995, Schoula et al. 1996).*

It was found that lindane and other organochlorine compounds can be transferred through the pathway soil-earthworm-bird/mammal (Romijn et al. 1994) causing secondary poisoning.

Lindane is toxic to animals, humans, and aquatic species. Acute animal poisoning by lindane causes increased respiratory rate, restlessness accompanied by increased frequency of micturition, intermittent muscular spasms of the whole body, salivation, grinding of teeth and consequent bleeding from the mouth, backward movement with loss of balance and somersaulting, retraction of the head, convulsions, gasping and biting, and collapse and death usually within a day (Smith 1991).

Human overexposure by skin contact or breathing can cause restlessness, insomnia, anxiety, irritability, poor appetite and/or headache. Higher exposures can also cause muscle twitching, seizures, convulsions or "fits" and even death.

The chronic (long-term) health effects can occur at some time after exposure to lindane and can last for months or years. Lindane may be a carcinogen in humans since it has been shown to cause liver, lung, endocrine gland and other types of cancer in animals (Bunton 1996, Smith 1991). Beta-hexachlorocyclohexane was reported as a possible representative of a new class of xenobiotic that produces estrogen-like effects through nonclassic mechanisms and, therefore, may be of concern with regard to breast and uterine cancer risk (Steinmentz et al. 1996). Many scientists believe there is no safe level of exposure to a carcinogen. Such substances may also have the potential for causing reproductive damage in humans. Several authors reported that the genotoxicity of lindane and other isomers of hexachlorocyclohexane is clearly established (Mattioli et al. 1996, Dubois et al. 1997).

Repeated overexposure may damage the liver or cause damage to the nerves of the arms and legs, possibly with weakness and poor co-ordination. The differential actions of hexachlorocyclohexane isomers may produce variable effects on different regions of the nervous systems and in different species of animals (Nagata et al. 1996). It is expected that humans chronically exposed to gamma-hexachloro-cyclohexane or similar insecticides and pesticides, are much more susceptible to liver damage when using paracetamol as a pain reliever (Itinose et al. 1995). Exposure may also cause a serious drop in the blood cell count (aplastic anemia) or in the white blood cell count (agranulocytopenia).

Hexachlorocyclohexane introduced to the environment from industrial discharges, insecticide applications, or spills, can cause significant damage. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants (Bunton 1996, Smith 1991). Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance.

Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Chronic effects can be seen long after the first exposure(s) to a toxic chemical. Lindane has high chronic toxicity to aquatic life. The insecticide load in surface waters does not ordinarily reach concentrations acutely toxic to aquatic fauna. The effects of the low insecticide concentrations often appear only after relatively long exposure times. Chronic exposure to insecticides, such as lindane, (Schulz et al. 1995) can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations. The low-concentration effects may depend on both species and substance and therefore cannot be predicted from toxicity data at higher concentrations.

Hexachlorocyclohexane is an organohalogen compound and is included in List I of the Dangerous Substance Discharges Directive (European Community Environmental Legislation, 1992). Therefore its discharge into the aquatic environment should be eliminated in view of its toxicity, persistence and bioaccumulation. If discharged into the aquatic environment, concentrations must be limited and regulated according to the Council Directive 84/491/EEC on limit values and quality objectives for discharges of hexachlorocyclohexane (European Community Environmental Legislation, 1992d).

Hexachlorocyclohexanes are included on a list of named pesticides currently banned in Lebanon. No importation or use of these pesticides are permitted (FAO, 1995).

2,4-dichlorophenol acetate, identified in the sample LN7053, has a very similar structure to the well-known pesticide 2,4-dichlorophenoxyacetic acid (2,4-D). It is possible that the occurrence of this substance in the wastewater of the pesticide factory is connected with the production of the 2,4-D pesticide, but this needs further investigation and confirmation. In general terms, all chlorinated phenols are toxic compounds, and they must not be discharged to the marine environment (European Community Environmental Legislation, 1992a, 1992b).

Chlorinated phenols

Chlorinated phenols, mainly used as biocides, are compounds with a wide spectrum of toxic effects including teratogenic (Zhao et al. 1995) and carcinogenic actions (Nagyova & Ginter 1995, Mehmood et al. 1997). Phenolic compound wastes from a large number of industries are highly toxic and pose a direct threat to human (Veningerova et al. 1994) and aquatic life (Ensley et al. 1994). 2,4-Dichlorophenol, one of the dichlorophenol isomers, is used in the manufacture of industrial and agricultural products such as pesticides, herbicides, soil sterilants, seed disinfectants and antiseptics.

Chlorine substitution increases the toxicity of phenolic compounds, for example, toxicity of 2,3-dichlorophenol to cells is 50 times higher than toxicity of pure phenol (Muller & Herbarth 1994). The level of chlorophenols toxicity depends upon the degree of chlorine substitution. The rank order of chlorophenols toxicity (i.e., pentachlorophenol >terachlorophenol > trichlorophenol >dichlorophenol > monochlorophenol > phenol) was confirmed in vitro and in vivo studies (Zhao et al. 1995).

4) Junieh / Nahr al-Kalb / Antelias Coast (LN7032-LN7047; LN7098-LN7100, LN7111)

Nineteen samples of sediment and industrial wastewater were collected from, or close to, sewage and industrial outfalls along the Antelias coastline, the highly popular tourist area of Junieh, and the Nahr al-Kalb “Dog River”. The latter receives a diverse mixture of industrial wastes from the Zuk Industrial Zone.

The Antelias coastal zone is an industrial and urbanised area situated to the north of Beirut. Factories discharging effluents through communal waste channels are common. In addition, domestic sewage is released, untreated, along the same channels. Industries of greatest importance along this coastline include petrochemical and pharmaceutical producers, tanneries, metal processors, oil refiners, and detergent, paint and paper manufactures. Untreated wastes from these processes, along with the discharges of raw sewage, could have an enormous deleterious effect on the surrounding shoreline. Both in terms of the toxic effects of the contaminants released in the industrial wastes and the potentially large number of pathogenic organisms, oxygen depleting materials, and high nutrient loads released in the raw sewage.

Uncontaminated sewage can be treated to produce non-toxic wastewaters and sludges. Sewage sludges can furthermore be composted to produce agriculturally valauble fertilisers. Therefore it is vital that wastes are separated and treated. Mixing industrial wastes with sewage not only renders it hazardous but can prevent it being treatable by the normal activated sludge process as the toxic components can kill the sludge bacteria.

Twelve samples were collected along this coastline. Directly from sewage and industrial outfalls (e.g. Daura, Oteri detergents, Hypco-COOP, Zouk Tanneries, Zouk Central), and close to fishing areas (e.g. Jal-el-Dib dumpsite, Zalka, north of Genayel Port). The majority of sediments collected were black and anoxic, liberating hydrogen sulphide gas, readily detected due to its characteristic “rotten egg” odour. Its presence is an indication that oxygen levels are low, possible non-existent, and potentially unable to sustain marine life.

There could be several possible sources of hydrogen sulphide. Hydrogen sulphide can be present, and continually produced, in sulphur containing waters under anaerobic (no oxygen) conditions. The discharge of oxygen depleting substances in both sewage (nutrients and biodegradable wastes) and industrial wastes will lead to an increased production of hydrogen sulphide. It is also the product of a bacterial reaction in the presence of sulphate. H_2S is produced by variety of bacteria including species of salmonella. The detection of H_2S in water can be indicative of their presence (Gawthorne et al., 1996). Other sources include industrial effluents, of particular importance are discharges from petrochemical industries and tanneries (Chirila et al., 1994; Sekaran, et al., 1996).

Hydrogen sulphide is poisonous to aerobic organisms (Heller, et al., 1995) and it is extremely hazardous to humans (Merck, 1986). In high concentrations it plays a major role in accidental deaths in the wastewater treatment and oilfield industries. Collapse, coma, and death from respiratory failure may result in a few seconds, after only one or two inspirations. In sufficiently high concentrations hydrogen sulphide will dull the sense of smell, preventing an unwary worker from detecting its presence. Low concentrations of hydrogen sulphide produce irritation in conjunctiva and mucous membranes. The reaction of hydrogen sulphide with fluids in the nose and lungs forms sulphuric acid.

Heavy Metals

a) Antelias

Heavy metal levels found in the majority of the sediment samples are not anomalously high. However Hg, Cr, Ni and Ba were present at elevated levels in some samples. For example, Cr and Ni are present at elevated levels in sample LN7111, collected from the "Oteri" detergents waste channel; four samples of marine sediment (LN7033, LN7039, LN7040, and LN7041) collected along the industrial zone contain slightly elevated levels of Hg; and sample LN7036 (Antelias Mazda), collected approximately 20 metres from the shore, at the edge of a fishing net, contained elevated levels of Ba.

Of even greater concern are the levels of metals being discharged in wastewaters from Zouk Tanneries and Zouk Central. In sample LN7043 (Zouk Central), 578 mg/l of Al was found, along with significant levels of Cr, Cu and Pb. This waste was sampled from a communal channel receiving discharges from Al and steel factories, pharmaceutical, detergent, paint and paper manufacturers Sample LN7044 (Zouk Tanneries) contained significant levels of Cr and Zn. Hg was also found at detectable concentrations.

Environmental assessments of Cr, Cu, Pb and Hg are discussed above. Regarding the effects of elevated levels of Al, the following is known:

Aluminium

Aluminum comprises approximately 8% of the earth's crust, making it the third most abundant element (ATSDR, 1997). It occurs ubiquitously in natural waters, however levels in surface waters can be increased directly or indirectly by human activity through surface run-off, tributary inflow, groundwater seepage, industrial and municipal effluents, and wet and dry atmospheric deposition (ATSDR, 1997).

The potential for accumulation of Al has been studied in several aquatic species, and it has long been recognised that when present in high concentrations, at low pH, it can exert toxic effects on aquatic organisms (Rosseland, 1990). Increased levels of Al in acidified natural waters is a primary cause of fish death from damage to gill epithelia and loss of osmoregulatory capacity (Birchall et al., 1989). Gill breathing invertebrates can also be effected (Rosseland, 1990). Al contaminated fish, invertebrates can thus be a link for Al to enter into terrestrial food chains (Rosseland, 1990).

Scientific opinion regarding the effects of exposure to Al in humans is divided. People have been eating it in their food for many years without any ill effects, however although there is no direct cause-and-effect proof that Al is toxic to humans, evidence is mounting to suggest that this element is somehow associated with several diseases. Its presence at many instances of toxic manifestation making it highly suspect (Krishnana, 1988). Factory workers who breathe large amounts of Al dusts can have lung problems such as coughing or changes that show up in chest x-rays. Patients suffering from kidney disease are treated with dialysis fluids that contain Al; because their kidneys are diseased, the Al may build up in their bodies and not pass out through the urine. Sometimes these patients have developed bone or brain diseases, which may be linked to the excess Al. Some studies show that people with Alzheimer's disease have more Al than usual in their brains. It is not known for certain whether Al accumulation is a result of the disease or its cause (ATSDR, 1997).

578 mg/l of Al was found in sample LN7043. As it known that an Al plant discharges into the communal waste channel from which this sample was collected, it is the obvious source. As is the case with most other metals, removal from the waste-stream involves precipitation using lime, to produce insoluble hydroxides. Followed by recovery techniques such as ion exchange and reverse osmosis. It is economically beneficial for an Al producing plant to remove and recover this amount of Al from its waste stream.

b) Zuk Industrial Zone

Two samples of sediment were collected from the Nahr al-Kalb (LN7042 and LN7098); Along with two samples of highly coloured industrial wastewater (LN7099 and LN7100), discharging directly into its waters from the Zuk Industrial zone. Possibly resulting from textile, dye or paint manufacture.

Sample LN7042, sediment collected downstream of paint, paper, solvent, petrochemical and metal processing discharges, contained an anomalously high level of Hg. 8.1 mg/kg was determined in this sample, far in excess of background concentrations, usually ranging from 0.03 mg/kg to 0.2 mg/kg (Bryan and Langston, 1992; Salomons and Forstner, 1984).

Hg is primarily used in the electrical industry, the medical industry, and the chemical and mining industry. Due to the high toxicity of Hg in most of its forms, many applications have been cancelled as a result of attempts to limit the amount of exposure to mercury waste. In this case, the level of Hg found in the Nahr al –Kalb sediment could be a result of Hg compounds (e.g. oxides and sulphides) being used as pigments in paints. Alternatively, as Hg compounds are quite often used as catalysts, factories producing organic polymers in particular, could result in Hg containing wastewaters being released to the environment.

There are many types of treatment technology available for Hg control. However alternatives to its use would be the most desirable and effective way of eliminating its release. Common methods of treatment include sulphide precipitation, ion exchange, adsorption, coagulation, and reduction followed by removal by filtration.

As discussed previously, Hg is a non-essential trace metal, having no biochemical or nutritional function. It is extremely toxic to both animal and plants at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any exposed biota (ATSDR, 1997). Also, as the retention of Hg by benthic sediments may delay the elimination of contamination for many years, much legislation exists to control, monitor and often prohibit its release.

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Hg and its compounds in Annex 1. They are considered toxic, persistent and bioaccumulative, and thus their discharge, whether directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be eliminated.

Sample LN7098, also collected from the Nahr al-Kalb, contained elevated levels of Zn and Pb. This sample was collected at the point where two highly coloured waste streams converged (see samples LN7099 and LN7100). These wastewaters also contained elevated levels of Zn , relative to the other metals present. Both effluents were alkaline (pH 9-10). These wastewaters are most likely to have resulted from textile, dye or paint manufacturing processes. Heavy metals, including Zn, are often used as dyeing agents, as their salts are often highly coloured. Wastes containing Zn are easily treated using technologies discussed previously; and wastes should be controlled and monitored in accordance with EC Directive 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources. This directive also implies the deleterious effects of alkaline discharges. With compounds of an acidic or alkaline nature listed in Annex 2.

c) Junieh Bay

Three samples of marine sediment were collected from the highly popular, tourist area of Junieh. Even here, where the economic reliance on tourism is high, and the coastal waters frequently used for bathing and fishing, raw sewage is being discharged directly into the sea. Swimmers could be directly exposed to pathogenic bacteria and viruses, and marine life could be harmed due to the elevated levels of nutrients and oxygen depleting substances discharged. One sample of sediment collected in front of the sewage outfall (sample LN7046) contained 2.5 mg/kg of Hg, between 10 and 80 times higher than background concentrations, depending on data set used (Bryan and Langston, 1992; Salomons and Forstner, 1984). This could be of industrial or domestic origin (batteries, pharmaceuticals, thermostats, cathode ray tubes etc.)

Another sample, LN7045, contained elevated levels of Cr, Zn, Pb and Hg. This sample was black and anoxic, liberating hydrogen sulphide gas. As discussed previously, this is an indication that oxygen levels are low, and potentially unable to sustain marine populations.

The third sample, LN7047, collected in front of the “Casino du Liban” also contained slightly elevated levels of Hg.

The sources of these elevated levels of Cr, Zn, Pb and Hg are anthropogenic in origin i.e. releases of domestic and possibly industrial untreated waste. The shallow and enclosed nature of the bay purposes that any contaminants released in raw sewage and industrial discharges will remain and accumulate in the sediment. The capacity of marine coastal sediments to assimilate anthropogenic pollutants is not infinite, and the continued, unregulated release of such contaminants, will result in further and more drastic decay of the bay.

Organic Chemicals

a) Antelias

Only one sample – LN7041 - from this area contained straight and branched aliphatic hydrocarbons, which are naturally occurring. All others showed a picture of contamination by one or several classes of organic pollutants:

m- and p-dichlorobenzenes (LN7035, LN7039, LN7043);
long-chain alkylbenzenes (LN7037, LN7033, LN7044);
phthalate esters including DEHP, DiBP, DnBP and dicyclohexyl phthalate (LN7034, LN7036, LN7040, LN7043);
polycyclic aromatic hydrocarbons (LN7033, LN7043 LN7044);
alkylated dibenzothiophenes (LN7033);
and phenolic compounds (BHT in samples LN7036 and LN7033; 4-methoxy-2,6-di-tert-butylphenol in sample LN7043; 2,4-dichloro-3,5-dimethylphenol in sample LN7043).

The occurrence and toxicity data of these compounds are discussed above.

One of the representative of N-heterocyclic polynuclear aromatic hydrocarbons, 7H-dibenzo[c,g]carbazole, was tentaively identified in the sample LN7043.

7H-dibenzo[c,g]carbazole (DBC)

N-Heterocyclic aromatics are by-products of incomplete combustion of organic materials.
7H-Dibenzo[c,g] carbazole is a potent liver and skin carcinogen following topical administration (Talaska G. 1994; Meier J.R. et al, 1994; Warshawsky D. et al, 1994). Several derivatives of this compound have shown large differences in enzymatic activation: N-acetyl-DBC was carcinogenic for several tissues; 5,9-dimethyl-DBC was exclusively hepatocarcinogenic; and N-methyl-DBC was exclusively sarcomagenic (Perinroussel et al. 1995). DBC has been found to have ability to induce genetic damage in human lymphocytes (Warshawsky et al. 1995).

In the sample LN7111 one of the representative of benzotriazoles, 1H-benzotriazole was tentatively identified. Benzothiazoles are widely used as corrosion inhibitors (Jinturkar et al. 1998, Ammeloot et al. 1997), as additive in copper chemical mechanical polishing (Wang et al, 1997), and as primary products in organic synthesis (Kang et al. 1997). Compositions containing benzotriazoles have been found toxic by Microtox-test (Cancilla et al. 1997).

Another compound identified in this sample was N,N'-bis(pentamethylene)thiuram tetrasulphide. This compound belongs to the family of dithiocarbamates, which are used as fungicides. There is no toxicity data on this particularly compound, but generally all dithiocarbamates have been found to be of moderate to extremely low acute toxicity to humans (Edwards et al. 1991). Relatively high proportions of the less toxic dithiocarbamates are eliminated unmetabolized in the faeces. Regardless of the underlying mechanism, the net acute toxicity is increased greatly by alcohol. A single dose of a dithiocarbamate can affect the thyroid, and repeated dosed of some cause goitres. Because they are metabolised to ethylene thiurea, the ethylenebisdithiocarbamates are suspected of being carcinogenic.

b) Zuk Industrial Zone

River sediment LN7042 contained straight and branched aliphatic hydrocarbons, which might be of sewage origin. Two industrial water samples LN7098 and LN7100 along with sediment sample LN7099 have shown a picture of mixed contamination by polycyclic aromatic hydrocarbons and their alkylated derivatives, long-chain alkylbenzenes, alkylated di- and benzothiophenes, and phenolic compounds (BHT). These contaminants, as was mentioned above, could indicate contamination associated with petroleum/oil and creosote processing and usage, they are molecular markers for the untreated sewage, and some of them are solvents which could be used in the textile, dye or paint manufacture. Toxicological data on these compounds is given above.

c) Junieh Bay

Two of these samples, LN7045 and LN7047, contained straight and branched aliphatic hydrocarbons, which might be of biogenic origin. Naphthalene, tentatively identified in the sample LN7047, can migrate along atmospheric or aquatic pathways from different land-based sources.

Sediment sample LN7046 collected in front of sewage channel, contained typical contaminants found in untreated sewage: m-dichlorobenzene, BHT, alkylbenzenes and DEHP. Occurrence and toxicity of these compounds are discussed above.

5) Beirut (coastal and inland sampling)

Heavy Metals

a) Borj-Hammud (LN7003-LN7006b, LN7101)

The coastal waste dump at Borj-Hammud, is a diverse mixture of untreated industrial (e.g. petrochemical and tannery), hospital and domestic waste. Plastics, tyres, scrap metal, clothing and animal carcasses are littered in abundance. Whilst this industrial and domestic waste is clearly an aesthetic problem, it also poses significant health risks to both marine systems and human populations.

Three samples were collected from communal waste channels running through the dumpsite. Two samples of sediment (LN7005 and LN7006b), and one sample of industrial wastewater mixed with seawater (LN7006a). In addition, two samples of marine sediment were collected approximately 10-20 metres away the dump (LN7003-LN7004).

Elevated levels of Cr, Zn, Ni, and Hg were found in the sediments collected from the waste channels; elevated levels of Cr, Zn, Cu, Pb and Hg were detected in the industrial wastewater mixed with seawater; and elevated levels of Cr, Zn, Cu, Pb, Ni and Hg were detected in marine sediments collected 10-20 metres away from the dump.

Of greatest concern are the levels of Cr and Ni determined, e.g. 5.5 mg/l of Cr was found in sample LN7006a, a sample of industrial waste diluted with seawater. The source of this Cr is untreated tannery waste. Cr salts are the most commonly used tanning agents. When an animal is killed and skinned, bacterial degradation starts immediately. The process of tanning, and the use of Cr, preserves the hide by stabilising the collagen proteins of which it is composed.

However, Cr is a controversial chemical on account of the persistence and potential toxicity of some of its chemical forms. Depending on its chemical state it has various levels of impact on humans, aquatic life and terrestrial plants, with some ability to move between media (UNEP, 1991). Cr can occur in oxidation states ranging from +2 to +6, however only the trivalent (+3) and hexavalent (+6) forms are of biological importance. The trivalent is the more common form and is considered an essential trace nutrient (but like any trace element, toxic effects can result form elevated concentrations). Hexavalent Cr is, on the other hand, non-essential and toxic, and compounds are classified as carcinogenic by the International Agency of Research on Cancer (IARC). They are corrosive and cause chronic ulceration and perforation of the nasal septum. They also cause ulceration of other skin surfaces. Allergenic Cr skin reactions readily occur with exposure and are independent of dose.

Both hexavalent and trivalent chromates are used in the tanning process. However due to the presence of other chemicals, particularly sulphides, most of the hexavalent Cr will be reduced to the trivalent state. Its potential for conversion to more toxic forms in the environment is low. However given the right physical and chemical conditions such as slight acidity (pH 5) and the presence of certain other metals e.g. manganese, conversion becomes a more likely occurrence.

A wide variety of alternative tanning materials, which have a lower acute toxicity than Cr are available. Examples include aluminium, titanium and zirconium salts, and vegetable tannins. It is the lack of familiarity with such alternatives, and the fact that they do not necessarily produce exactly the same leather product, that has inhibited their widespread adoption to date e.g.

Aluminium: gives a weaker chemical bond with collagen fibres than chromium. The leather produced is flat and hard, with a whitish colour.

Titanium: also gives a whitish appearance to the leather. It is an abundant element, which produces salts of generally low toxicity. Titanium sulphate can be used with existing conventional tanning equipment. In order to improve the reactivity of titanium with the hide, a pre-tanning step is employed, whereby the collagen matrix is first fixed with a polysaccharide (natural sugar, non-toxic) derivative. Following this step, titanium uptake is close to 100%; less than 50ppm is discharged in the effluent.

Leather quality is suitable for commercialisation. However the final properties may not correspond exactly to those achieved following chromium tanning. This is the dilemma. While environmentally preferable technical alternatives to current processes exist, much still depends on market acceptance. As stated in the UNEP Technical Guide on Tanneries "Those responsible for design, purchasing and product standard-setting can therefore do a great deal to assist the adoption of cleaner processes and products in the industry"

Zirconium: more expensive than chromium. Toxicological information on zirconium is scarce. Tanning operations are difficult to monitor.

Vegetable tanning agents: commercial tanning agents are extracted from the wood/bark of certain trees. The compounds have the general structure of polyphenolic compounds. There are generally two classes: derivatives of pyrogallol (tri-hydroxybenzene), and derivatives of catechol. The latter are non-toxic, however derivatives of pyrogallol can be if ingested. However they do biodegrade (hours/days) and are removed almost completely during secondary treatment processes.

The quality of vegetable (catechol) tanned leather is highly desirable. It can be mechanically shaped, is flexible and durable. It is often the leather of choice for handicraft and specialised work. However it is not as thermally stable as Cr tanned leather, and this can limit its use. Although heat resistance is not a property required of most leather.

Treatment of Cr wastes is usually a two stage process involving firstly the reduction of hexavalent Cr to the trivalent form (sulphur dioxide is commonly used), followed by precipitation of trivalent Cr in the form of an insoluble hydroxide (achieved by the addition of lime). However even though this is an efficient means of treating the effluent, is does generate a secondary waste in the form of chromium containing sludge, which is often landfilled or incinerated.

There is vigorous debate concerning the environmental hazard of landfilling Cr containing tannery sludge. Much of the debate centres on the potential conversion of trivalent Cr to the more toxic hexavalent form. Also, landfills that receive other industrial wastes, particularly acidic wastes, may not be suitable for receiving tannery wastes. Acidic industrial wastes can react with tannery wastes, perhaps liberating hydrogen sulphide gas. Cr sludges can also dissolve to liberate soluble chromium, which may escape from the site via leachate seepage to groundwater.

Similarly, the decomposition of domestic waste can lead to the formation of acidic conditions in the landfill.

Alternatively, incineration will not destroy / decompose the Cr present in the sludge. It will only be redistributed in the waste, releasing it in air emissions, fly ash, pollution control devices etc. The incineration of metal-containing sludges leads to problems with both air emissions and with soluble metals in the ash (UNEP, 1991).

Thus, as neither landfilling or incineration are suitable environmental options, recovery and recycling of the Cr must be considered. Given the wide disparity from country to country in the cost of chemicals, equipment, piping and civil engineering, it is impossible to accurately indicate the cost of recycling systems. However (as stated in the UNEP document) cost effective recycling can be readily achieved in most situations. The payback time for Cr recycling is given as less than one year. A communal plant for chromium recovery has been established in Tuscany, Italy. The plant treats both Cr containing liquors, and solid sludges. The incoming effluent is treated to produce chromium hydroxide (trivalent / insoluble). This is re-dissolved and polished and then passed back for use in the tanning process.

Also of concern, as mentioned above, are the elevated levels of Ni, found in the industrial wastewater, waste channel and marine sediments.

Nickel

Background concentrations of Ni are usually quoted as being less than 50 mg/kg (Bryan and Langston, 1992; Solomans and Forstner, 1984). The marine sediments contain between three and four times this background concentration. The most obvious anthropogenic source of Ni is scrap metal waste, notably alloyed metals including stainless steel. Ni is primarily used in alloys because it imparts desirable properties such as corrosion resistance, heat resistance, hardness, and strength to a product., and cast irons. Stainless steel may contain as much as 25-30% nickel, although 8-10% nickel is more typical. In addition to imparting characteristics such as strength, toughness, corrosion resistance, and machinability, some applications make use of nickel's magnetic characteristics. Most permanent magnets are made of alloys of iron and nickel (ATSDR, 1997).

Other industrial and domestic uses of Ni include applications in electroplating, ceramics, pigments, and as catalysts. Ni is also used in alkaline (nickel-cadmium) batteries.

Ni is considered an essential trace element at very low concentrations. It does bioaccumulate in aquatic systems, and as such elevations above normal concentrations can result in deleterious aquatic effects (ATSDR, 1997). The range of BCFs (bioconcentration factors) appears to be 40-100 in fish and 100-259 in invertebrates. As discussed previously regarding the environmental fate of other metals, consumption of contaminated fish and marine invertebrates can lead to increased exposure to Ni in human populations.

The most common adverse health effect of Ni in humans is an allergic reaction. People can become sensitive to Ni when jewelry or other things containing Ni are in direct contact with the skin. Once a person is sensitized to Ni, further contact with the metal will produce a reaction. The most common reaction is a skin rash at the site of contact. In some sensitized people dermatitis may develop at a site away from the site of contact. For example, hand eczema is fairly common among sensitised people. Less frequently, some people who are sensitive have asthma attacks following exposure. People who are sensitive to Ni have reactions when nickel is in contact with the skin, and some sensitized individuals react when they eat nickel in food or water, or breath dust containing Ni.

The most serious effects of Ni, such as cancer of the lung and nasal sinus, have occurred in people who have breathed Ni dust while working in Ni refineries or in Ni processing plants. Other lung effects include chronic bronchitis and reduced lung function. The levels of nickel in the workplace were much higher than background levels. The Department of Health and Human Services has determined that Ni and certain Ni compounds may reasonably be anticipated to be carcinogens. The International Agency for Research on Cancer (IARC) has determined that some Ni compounds are carcinogenic to humans and that metallic Ni may possibly be carcinogenic to humans. The EPA has determined that Ni refinery dust and Ni subsulfide are human carcinogens.

Much of our knowledge of Ni toxicity is based on animal studies. Rats and mice may die after eating large amounts of Ni. Eating levels of Ni very much greater than the levels normally found in food causes lung disease in dogs and rats and affects the stomach, blood, liver, kidneys, and immune system in rats and mice. Effects on reproduction and birth defects also were found in rats and mice eating or drinking very high levels of nickel (ATSDR, 1997).

Finally, of equal concern are the levels of hydrogen sulphide observed in the sediments surrounding the dump. Most of the sediment was black and anoxic, hydrogen sulphide bubbling to the seawater. Oxygen levels are thus poor, possibly none existent, The effects of oxygen depletion are much more marked in coastal areas of the sea, such as this, and can result in substantial losses (in terms of both numbers and species diversity) to fish and marine invertebrate populations (UNEP, 1995).

European Environmental Legislation Council Decision 83/101/EEC, for the protection of the Mediterranean against pollution from land-based sources, lists Cr and Ni in Annex 2, along with Pb, Zn, Cu and V. Thus releases from land-based sources, whether directly from outfalls discharging into the sea or through coastal disposal; or indirectly, through rivers, canals, other watercourses, or though runoff, should be strictly limited, and continuously monitored.

Dumping and landfill disposal of solid wastes and sludge always presents the potential problem of leaching. In most dumps and landfills, the leachate is composed of the liquid produced from the decomposition of the wastes and liquids entering the site from external sources. Depending on ambient conditions many organic and inorganic contaminants, reaching high concentrations, may be found in the leachate, and because of this its formation and movement is often a threat to both groundwater and surface water quality (UNEP, 1990).

In order to implement the Barcelona Convention, far greater control on waste dumping is required. The disposing of potentially hazardous wastes must cease. Inert or non-hazardous wastes should be separated with a view to recycle and reuse wherever possible. Toxic wastes must be treated prior to disposal, again with a view to recycle and reuse all materials employed. However long term and sustainable solutions to increased levels of hazardous waste generation, must concentrate on the development of cleaner technologies and not merely on end of pipe solutions.

Finally, one sample of sewage effluent was collected from an outfall discharging into the Bay of St George (LN7101). Elevated levels of Zn were detected.

b) Normandie (LN7001-LN7002b)

A second coastal dump receiving industrial and domestic wastes from Beirut and the surrounding areas is Normandie. Three samples were collected. Marine sediment collected approximately 10 metres offshore (LN7001); seaweed collected from a channel running through the dumpsite (LN7002b), and a seawater/sewage effluent collected from the same channel (LN7002a).

Elevated levels of Cr, Zn, Cu, Pb and Hg were found in the marine sediment. Anomalously high levels of Cr, Zn, Cu, Pb and Hg were found in the seaweed, a known and well-established bioaccumulator of heavy metals (Bryan and Langston, 1992). This sample contained nearly 20g/kg (2% w/w) of Cr, which can be anthropogenically sourced to tannery discharges. Nearly 10 mg/kg of Hg was also determined, undoubtedly of anthropogenic origin, as are the elevated levels of Zn, Cu and Pb found. All of these metals have the potential to bioaccumulate in aquatic plants and animals. With Hg there is the added danger of biomagnification. Fish, marine invertebrates and aquatic plants exposed to industrial and domestic wastes, as well as the leachate resulting from the solid waste dumping on this coastal site, could all be severely contaminated. The continued dumping and discharging will introduce ever increasing levels of anthropogenic toxins into the aquatic food chain, where they can then be transferred up the trophic ladder to higher organisms including humans (Marcus, 1991).

Sample LN7002a, a mixture of seawater and sewage effluent contained detectable levels of Mn, Cr, Zn, Pb, V, Ba and Hg. Of these V is present in the highest concentrations, 5.4

mg/l. V is a major trace metal in petroleum products, especially in heavier fractions. Concentrations in crude oil can range form 0.6 mg/kg to 1400 mg/kg (Alloway, 1990). V is present as an organometallic porphyrin complex of low volatility, in consequence it becomes concentrated during distillation, giving residual oils an elevated V concentration. As such it can act as a tracer of petroleum pollution. For it to be present in such high concentrations in this sample its release must be associated with untreated petroleum discharges.

c) South Beirut (LN7007-LN7011)

Three samples of sewage effluent, and two of marine sediment were collected from / close to sewage outfalls along the coastline south of Beirut. All were discharging untreated raw sewage directly into the sea.

Elevated levels of Mn, Cr, Zn, Cu, Pb, V, Ba and Hg were detected in sample LN7007 (Ras Beirut / Hotel Meridian). With discharged levels of Zn, Cu, Pb and Hg being of particular concern.

Elevated levels of Zn, Cu, Pb, Ni and Hg were found in marine sediment, collected in front of a sewage outfall (Ouzai / Khalde).

Theses levels of metals are most often associated with industrial discharges (metal processing, oil refining, chemical manufacture etc), and it is highly likely that such discharged are being mixed with domestic sewage and discharged, untreated, along the same channels.

Anthropogenic sources and consequent environmental assessments of such discharges are discussed above.

d) Southern Suburbs / Chuwaifat / Ghadir River (LN7087-LN7090)

Two samples were collected from “Seven Plastics Chemical Industries”, one of sediment (LN7087) collected from a waste channel running along an outside wall of the plant; and one of industrial effluent (LN7088), from the same channel. Elevated level of Zn were detected in the wastewater, with the sediment containing high levels of Zn, Pb, Cd and Hg. As discussed previously, Zn, Pb and Cd are all used as plastic (notably PVC) stabilisers and pigments. Hg oxides and sulphides are also used as pigments.

Two samples were collected from the Ghadir River. The river is constantly dredged to prevent blockage from discharged industrial waste (e.g. metal processing, textile, paint and dye manufacturing wastes). Sample LN7089, river water, contained anomalously high levels of Mn, Cr, Zn, Cu, Pb and Hg. The river sediment (LN7090), which liberated large quantities of hydrogen sulphide gas, contained elevated levels of Zn, Pb and Hg.

e) Sukomi Incinerator (LN7102)

One sample of black oily waste was collected from a pond into which liquid waste and leachate from the incinerator collect (LN7102). Anomalously high levels of Cr, Zn, Cu, Pb, Ni, Cd, Ba and Hg were detected in this sample. A perfect illustration that metals are never destroyed by incineration, only redistributed in the waste.

f) Nahr el-Mot (LN7091-LN7095)

Only one sample collected from this area contained elevated levels of heavy metals, notable Zn and Hg. Sample LN7095, solid waste collected from a lagoon in which over 100 barrels of quaternary ammonium salts, amines and amides had been dumped, all corrosive and inflammable. Thus, even though pollution from heavy metals may not be a significant problem, contamination of the area by other inorganic chemicals is potentially widespread.

g) Mazraat Yashuh Industrial Zone (LN7096-LN7097)

Effluent and sediment were collected from a communal waste channel, running through the site. Discharging industries include scrap metal, plastics, cement, marble and aluminium factories. No elevated levels of heavy metals were found in either sample.

h) Sibline Cement Factory, Iqlim al-Kkarrub (LN7103-LN7105)

Three samples were collected form the third largest cement company in Lebanon. Two of dust, and one of klinker. The klinker did not contain elevated levels of heavy metals. However dust collected by the kiln did. With high levels of Cr, Zn, Cu, Pb and Ba being determined. Cd and Hg were also present at detectable levels.

This dust is heavily contaminated and poses a serious occupation health risk if inhaled in large quantities. These materials are present as impurities in the raw cement materials, and as impurities in the fuel used, e.g. if tyres are being burned to fuel the kiln, this could explain the elevated levels of Zn found in the dust. It is imperative that workers exposed to this dust wear protective face masks which cover both the nose and face.

Organic Chemicals

a) Borj-Hammud (LN7003-LN7006b, LN7101)

Samples LN7004-7006b and LN7101 contained similar groups of compounds, typical of contamination resulting from industrial and domestic waste dumping. The following classes of organic pollutants were found:

m- and o-dichlorobenzenes (LN7005, LN7006b);
long-chain alkylbenzenes (LN7004, LN7005, LN7006a, LN7101);
DEHP (LN706b);
polycyclic aromatic hydrocarbons (LN7004, LN7005, LN706a, LN7006b, LN7101);
alkylated dibenzothiophenes (LN706a);
and phenolic compounds (BHT in samples LN706a)

The occurrence and toxicity of these compounds are discussed above.

The most polluted sample collected from this area was LN7003. In addition to the alkylated PAHs and DEHP, identified in this sample, the following chlorinated compounds were determined:

one isomer of dichloronaphthalene ;
three isomers of trichloronaphthalene;
three isomers of tetrachloronaphthalene;
one isomer of dichloroterphenyl;
trichlorinated derivative of 1H-indene

Polychlorinated naphthalenes (PCN)

PCNs were among the first synthetic chemicals and have been used continually for nearly 70 years in the United States and Europe. They were first used as flame retardants and dielectrics. Later PCNs were used as capacitor dielectrics, cutting oils, engine oil additives, die casting, ship insulation, wood, fabric and paper preservatives. Incineration and nonpoint sources, such as urban runoff and sewage sludge, may be the main contributors to current environmental levels (Nylund et al. 1992). PCN manufacture and commercial applications preceded the widespread use of PCBs and chlorophenols (both known now to be highly contaminated with PCDDs and/or PCDFs) by some 30 years. PCNs, PCBs, PCDDs, and PCDFs have all been associated with incidents of human and animal poisonings. These three classes of chemicals have similar physical properties and related toxicity. PCNs are generally considered hazardous at the trichalogenated level and higher.

Due to their hydrophobicity and low degradability, these compounds can accumulate to high concentrations in aquatic organisms and sediments relative to the concentrations found in the water (Larsen et al. 1992). They have been found in the soils, sediments and fish (Jarnberg et al. 1993, Falandysz et al. 1996), snapping turtle and bullfrog from the wetland located close to the industrial chemical disposal area (Watson et al 1985), rice oil (Haglund et al. 1995), and humans (Asplund 1994, Haglund et al. 1995, Weistrand et al. 1997).

Several of the polychlorinated naphthalene congeners exhibit similar toxic properties to 2,3,7,8-tetrachlorodibenzo-p-dioxin, i.e., chloracne (Hayward 1998), liver damage, and EROD (7-ethoxyresorufin-o-deethylase) and AHH (aryl hydrocarbon hydroxylase) enzyme induction (Hanberg et al. 1990). EROD and AHH induction by selected polychloronaphthalenes is only 2-3 times less than for 2,3,7,8-terachlorodibenzo-p-dioxin.

Polychlorinated naphthalenes are toxic to mammals, they have been associated with hyperkeratosis, lachrymation, conjunctivitis, and liver and kidney damage in domestic animals and humans (Hawley 1977, Hayward 1998).

b.) Normandie (LN7001-LN7002b)

One representative of phthalate esters, DEHP, was reliably identified in both sediment and seawater/sewage effluent. This probably confirms the source of this compound in the marine sediment. Sample LN7002a contained one of the dichlorobenzene isomers. These compounds, as mentioned previously, are commonly found in raw sewage effluents and sludges. Their toxicity is described above.

c) South Beirut (LN7007-LN7011)

Several groups of chemical pollutants considered as sewage markers (alkylbenzenes and dichlorobenzenes), creosote contaminants (dibenzothiophenes), and petroleum/oil contaminants (PAHs, alkylbenzenes) were identified in all but one sample (LN7009). As mentioned above, alkylbenzenes and PAHs are highly resistant to degradation and may accumulate in sediments. They can migrate long distances from their point sources this is why they have been found in the marine sediment LN7010, collected in front of the sewage channel.

The toxicity of these compounds is described above.

d) Southern Suburbs / Chuwaifat / Ghadir River (LN7087-LN7090)

Linear alkanes were identified in the sample LN7088. Sample LN7087 contained one representative of PAHs – trimethylnaphthalene - and one branched long-chain alkylbenzene together with chlorooctadecane. These samples are less contaminated than the samples collected from the river – LN7089 and LN7090 – in which wide range of different PAHs, alkylbenzenes, dibenzothiophenes and BHT (LN7089) were identified. There might be two explanations for this. On the one hand, it is known that waste channel has been periodically dredged, so contaminants could be removed from it at the time of sampling. The presence of pollutants in the river sediment indicates that they have been discharged from this factory in the past and have accumulated in the riverine sediment. On the other hand, the presence of the same pollutants in the river sample might mean that there is another source of contamination other than this waste channel.

e) Sukomi Incinerator (LN7102)

Several hydrocarbons and one PAH – naphthalene- were identified in this sample. In addition, the representative of sedimentary faecal stanols – cholestan-3-ol, 2-methylene – was identified. Sedimentary faecal stanols are the molecular markers for the tracing of deposited sewage contaminants in the vicinity of disposal sites (Chan 1998). 14.Beta.-H-Pregna, a short-chain sterane isomer which can be found in petroleum (Requejo et al. 1997), was also identified.

f) Nahr el-Mot (LN7091-LN7095)

Sample LN7092 collected from the communal waste channel, and solid waste sample LN7095, contained long-chain straight hydrocarbons and one PAH - naphthalene. Another sediment collected downstream of this channel (LN7093) and effluent collected from the channel (LN7091) contain pollutants typical of mixed industrial waste / sewage contamination, e.g. alkylated PAHs, alkylated benzenes and dibenzothiophenes. The toxicity of these compounds is described above.

Industrial wastewater sample LN7094 contained two chlorinated compounds – p-dichlorobenzene (see for the toxicity data and occurrence of it above) and 1-bromo-3,5-dichlorobenzene.

1-bromo-3,5-dichlorobenzene

1-bromo-3,5-dichlorobenzene is included in the Toxic Substances Control Act (TSCA, 1994). It is described as having low chemical toxicity to rats and rabbits. The estimated oral LD50 of bromodichlorobenzene in rats was 1213 mg/kg. Clinical signs included urine stained abdomens, hypoactivity, ataxia, diarrhoea, decreased limb tone, and prostration. The acute dermal LD50 was reported to be > 10,000 mg/kg. Instillation of the test material into the eyes of rabbits resulted in iridial irritation and slight-to-moderate conjunctival redness and very slight-to-moderate chemosis lasting < 7 days. Application of the material to the skin produced well-defined erythema, and very slight edema.

g) Mazraat Yashuh Industrial Zone (LN7096-LN7097)

Several hydrocarbons and one PAH – naphthalene – were identified in the sediment sample LN7097, collected from the communal waste channel. Effluent sample LN7096 collected from this channel contained pollutants typical of mixed industrial waste /sewage contamination, e.g. alkylated PAHs and alkylated benzenes. The toxicity of these compounds is described above.

h) Sibline Cement Factory, Iqlim al-Kkarrub (LN7103-LN7105)

All three samples collected from this area (LN7103, LN7104 and LN7105) were relatively clean in terms of the number of organic compounds identified. One representative of PAHs – naphthalene - was identified in the dust sample LN7105. 14.beta.-H-Pregna, a short-chain sterane isomer, was also identified. This compound can be used as a petroleum molecular marker (Requejo et al. 1997).

6) Saida (LN7012-LN7015, LN7017-7021; LN7108)

Ten samples were collected from sewage and industrial (e.g. associated with leather tanning and styrene manufacture) outfalls along the coast between Saida and South Beirut. Marine sediment was also collected from Saida harbour, and around the coastal waste dump.

Heavy Metals

Heavy metal contamination was significant in places. Cr levels were elevated due to tannery discharges and leather waste dumped on the beach; V levels are elevated due to

petroleum releases; Zn, Pb, Ni and Hg from domestic sewage and possibly chemical and metal processing activities.
Of huge interest and concern is the discharge from the styrene factory. The pH of this wastewater was measured as 14, strongly and corrosively alkaline. Also 5 mg/l of Ba was detected. Ba can be used as a fire retardant in PVC or as a stabiliser, it is possible it is being added to styrene for the same reasons. Ba containing wastewaters can be treated by precipitation (producing Ba hydroxides of sulphates) followed by ion exchange to recover and reuse the metal.

Environmental assessments of such releases, treatment of wastes and alternative to use are discussed above.

Organic Chemicals

Sediment sample LN7012 from the sewage channel and seawater/sewage effluent sample LN7013 from the same channel contained long-chain straight hydrocarbons and three compounds which can be associated with sewage pollution: dichlorobenzene (LN7012) and two alkylated benzenes (LN7013). Toxicity of these compounds is described above.

Several classes of environmental pollutants were identified in samples LN7014, LN7015, LN7017 and LN7019, including:

DEHP – LN7014, LN7018;
1,3-dichlorobenzene – LN7014, LN7018;
PAHs – LN7015, LN7017, LN7018.

Toxicity of these compounds is described above. In addition, two derivatives of alkylated phenols were identified, in all four samples:

2,4-bis(1,1-dimethylethyl)- in samples LN7014, LN7015 and LN7017;
2,6-bis(1,1-dimethyl)-4-methyl, methylcarbamate in samples LN7015 and LN7018.

Various phenolic compounds, normally presented as total phenols, have been found in the wastewater from several tanning-related operations (UNEP, 1991).

Alkylated phenols

Dimethylphenols (xylenols) represent an important component of the phenolic substances in coal tar creosote, a mixture used widely as a wood preservative (Terzian et al. 1995). Some of the phenolic compounds being used as antimicrobial preservative agents in pharmaceutical formulations. Unfortunately, these compounds often adversely affect proteins, triggering aggregation in particular. It has been found that the presence of a phenolic additive can cause conformational changes in recombinant human growth hormone structure (Maa et al. 1996).

Alkylated phenols are included in the Toxic Substances Control Act (TSCA, 1994) and are described as being toxic to animals. The toxicity studies (including neorotoxicity, *sensitisation and allergenicity) carried out on rabbits and guinea pigs indicate the high potential toxicity of these compounds. Toxic signs after oral administration included ataxia, piloerection, splayed hind-leg gait, lethargy, lacrimation and coma. Toxic signs after percutaneous application included irritations and ulcerations of the skin exposed.*

Sample LN7019, shredded leather waste, contained different terpenoids. These occur naturally, and are obviously derived in this case, from the spent animal carcasses.

Samples LN7021 and LN7108 contained long-chain straight hydrocarbons and one isomer of dichlorobenzene (LN7021 only), discussed above.

In the industrial wastewater sample LN7020, collected from a styrene factory, a wide range of aryl amines derivatives were identified. These compounds, together with other alkyl amines, amides and quaternary ammonium compounds, are known as antistatic agents. They are used in the polystyrene production to minimize primary dust-collecting problems during storage. (Platt et al. 1983). Styrene itself was not found in the samples taken at this site. However, it is to be expected that workers will be exposed to styrene through the air. Consequently, it is worth discussing briefly the toxic properties of styrene.

Styrene

Styrene is used extensively in the manufacture of numerous polymers and copolymers, including polystyrene, acrylonitrile-butadiene- styrene (ABS), styrene-acrylonitriie (SAN), styrene-butadiene latex, and styrene-butadiene rubber. Styrene is a component of cigarette smoke and automobile exhaust, and it may occur naturally at low levels in various types of foods (Miller et al. 1994).

The potential human carcinogenicity of styrene has been investigated mainly by epidemiological studies of occupationally exposed populations (Coogan 1994). Styrene is efficiently metabolised to styrene oxide, which is itself readily detoxified by the same enzymes. Styrene oxide is genotoxic and, if introduced directly into the stomachs of rodents in high doses/ concentrations, gives rise to cancers of the forestomach (Roe 1994). Exposing mice to doses of styrene high enough to overwhelm the capacity of the body to detoxify styrene oxide has been reported to increase lung tumour incidence in mice. Several cohort studies have suggested that workers exposed to styrene in the chemical industry have increased mortality from lymphatic and hematopoietic cancer (Kolstad et al. 1994). However, this finding has not been consistent and has not been reproduced in studies of reinforced plastics manufacturers, whose exposures to styrene are generally higher. The explanation for the observed associations may therefore be confounding by concomitant exposures to other chemicals such as benzene and butadiene, which are not used in the reinforced plastics industry. Despite their large size, the published studies of mortality and cancer incidence lack the statistical power to rule out an important hazard from long- term exposure to high (>50 ppm) airborne concentrations of styrene. However, they indicate that any risk of cancer from lower levels of exposure is likely to be small. Other studies showed that relatively low levels of styrene (250 to 500 ppm) can cause extensive mortality and hepatotoxicity for mice, *while rats and humans exhibit only nasal and eye irritations at exposure concentrations well above 500 ppm (Sumner et al. 1994).*

Diphenylamine derivatives.

Diphenylamine itself (Merck, 1986) is used in the manufacture of dyes, and as a stabiliser of nitrocellulose explosives. Diphenylamine can be irritative to mucous membranes. Methemoglobinemia has been produced experimentally. Symptoms are similar to those for aniline, but diphenilamine is less toxic.

Aqueous samples containing various nitrated and aminated diphenylamine derivatives were have been found to be "very toxic to aquatic organisms" in tests with the luminescent bacterium Vibrio fischeri NRRL-B-11177 (Drzyzga et al. 1995).

7) Ghazieh Industrial zone and South Saida (LN7016, LN7026-LN7030, LN7106-LN7107)

Eight samples were collected form this area. These included solid waste and effluent being discharged directly onto the beach; tannery waste discharged directly into the sea, sediments and effluents collected from sewage outfalls discharging directly into the sea; and river sediments collected from the Zahrani River, downstream of small factory and garage discharges;

Heavy Metals

White solid and liquid waste (LN7028-LN7029) was found to contain high levels of Al and Ba. This waste had the appearance of paint, and this is consistent with the levels of these metals found. Both Al powder and Ba sulphate are used in paint manufacture as white colorants.

Sewage discharges were found to contain high levels of Zn, Cu, Pb and Ba. The repeated presence of Ba suggests that industrial wastes generated by the Ghazieh industrial zone are being mixed with domestic wastes and discharged, untreated, along the same channels into the sea.

River sediments collected from the Zahrani River, which receives discharges from small factories (electroplating, ceramics, pigments, catalysts, alloys, batteries) and garages, contained elevated levels of Ni, Zn, Pb and Ba. Industrial waste flowing into the river, high in suspended solids and Ba, was also sampled.

Waste collected from the “Lebanese-Spanish Tannery SAL”, contained, as expected, high levels of Cr (2.9 g/kg in the effluent channel). Elevated levels of Zn, Cu, Pb and Ni were also found.

Environmental assessments of these discharges are discussed above.

Organic Chemicals

Samples LN7027, LN7029 and LN7030 contain pollutants typical of mixed industrial waste /sewage contamination, e.g. alkylated PAHs and alkylated benzenes, together with long-chain straight hydrocarbons. Toxicity of these compounds is described above.

Samples LN7016, LN7026, LN7028 and LN7106 contained long-chain straight hydrocarbons. Also, naphthalene was identified in sample LN7028 and m-dichlorobenzene in sample LN7016. Toxicity of these compounds is described above.

Industrial wastewater sample LN7107 contained alyphatic hydrocarbons, the sulphur-containing organic compound, 2-(methilthio)benzothiazole, and two phenolic compounds: octyl phenol and 4-(1-methylpropyl) phenol. As mentioned above, sulphur-containing and phenolic compounds are commonly found in wastewater effluents from tanneries. Toxicity of these compounds is described above.

Benzothiazoles.

Benzothiazoles appear in the environment mainly as a result of their production and use as rubber vulcanisation accelerators. One of the representatives of benzothiazoles, 2-(thiocyanomethylthio)benzothiazole (TCMTB), have been used as a wood preservative and as fungicide. Benzothiazole (BT), 2-mercaptobenzothiazole (MBT), and 2-(methylthio)benzothiazole (MTBT) were determined to be degradation products of the TCMTB in tannery wastewater (Reemtsma et al. 1995). Potential effects of benzothiazoles entering the aquatic environment was illustrated by luminescence inhibition of Vibrio fischeri (Photobacterium phosphoreum); EC(50) between 0.03 micro mol/L for TCMTB and 32 micro mol/L for BT) and growth inhibition of the same organism with TCMTB and MBT. MBT, BT, and MTBT at concentrations of 0.1- 0.2 micro mol/L inhibit nitrification on sediment columns and mixed culture respiration determined as BOD (0.6-11 micro mol/L). It was shown (Reemtsma et al. 1995, Paxeus et al. 1996) that 2-substituted benzothiazoles employed in industrial processes are not completely removable by biological wastewater treatment and are of concern for aquatic environment due to their limited biodegradability and potential toxicity (Nikl et al. 1993). Investigation of toxicity of tannery effluents (Walsh et al. 1997) has confirmed that fungicide 2-(thiocyanomethylthio)benzothiazole and its degradation products are the main compounds, among those found in the tannery effluents, causing toxic effects on the aquatic life. Toxic effects of MBT towards microorganisms have been studied and can be attributed to its metal chelating properties and/or its interference with membrane-bound (co)enzymes in particular (De Wever et al. 1997).

8) Beqaa Valley (LN7031, LN7072-LN7079)

Eight samples were collected from this area. These included waste discharges from the “Mimosa” paper factory, which discharges directly into the Berdawni River; sediment collected from the Berdawni River; sediment collected from the Berdawni / Litani River confluence; sediment collected from the Ghazayel River, up and downstream of the “Sugar Beet Factory”; and sediment from the Qarun Lake.

Heavy Metals

Relative to all the other areas samples, heavy metal pollution is at its lowest in these samples. With background levels of metals determined in most. However other contaminants are exerting deleterious effects on these riverine systems. For example, downstream of the “Sugar Beet Factory”, the Ghazayel River is turbid and brown. There are visible traces of oil in the water, and no plant life. Upstream the water is clear, oxygenated and there is an abundance of plant life. Oxygen depleting substances are being released from this factory and consequently the levels of oxygen in the downstream water of the Ghazayel are unable to sustain aquatic life. These substances are likely to be water soluble, thus it is not possible to detect them using standard organic solvent extraction procedures.

In addition, also as a result of oxygen depleting / high nutrient discharges e.g. sewage, algal blooms and turbid river water are observed in Litani River.

Thus even though anthropogenic heavy metal discharges seem to be non-existent, other pollutants are being released and are effecting water quality and aquatic life.

Organic Chemicals

Sample LN7031 contained m-dichlorobenzene, which can be associated with both industrial and sewage pollution. Toxicity data of this compound is presented above. Additionally wide range of terpenoids such as terpinene, ledene, humulene, cadinene and others were identified in this sample. The occurrence of these compounds might be of natural origin.

Three samples associated with “Mimosa” paper factory contained long-chain straight aliphatic hydrocarbons (all samples), alkylated PAHs (LN7072 and LN7073), dibenzothiophenes (LN7073), dichlorobenzenes (LN7072 and LN7074), alkylated benzenes (LN7074), and alkylated phenol (LN7074). Toxicity data and occurrence of these compounds are described above.

None of compounds were identified in the sediment sample LN7076 and only long-chain straight aliphatic hydrocarbons in the sediment sample LN7077. In the sediment sample LN7075, alkylated dibenzothiophenes were tentatively identified (see above for the toxicity data).

In two sediment samples LN7078 and LN7079 sulphur-containing compound – 1,1-dimethyl-decyl-mercaptane – was tentatively identified. Substituted alkyl mercaptans are included in the Toxic Substances Control Act (TSCA 1994) and are described as being toxic to experimental animals (rats and rabbits) and aquatic organisms.

9) Tyre (LN7022-LN7025)

Heavy Metals

Four samples were collected from Tyre. There is little industry in Tyre, but there are a number of small factories and garages, possibly dumping their waste into the sewage system. Sediment from the harbour, collected in front of the main sewage outfall, did contain elevated levels of Zn, Cu, Pb and Hg , thus suggesting this to be the case.

Soil collected from the waste dump at Tyre (scrap metal, tyres, household waste, plastics, batteries etc) contained high levels of Hg, probably resulting from battery disposal. 22.7 mg/kg was determined in one sample. Soil levels of Hg are usually less than 1 mg/kg (UK Department of the Environment, 1980). Using UK classifications for contaminated land, this soil would catagorised as "Heavily contaminated" with respect to Hg. Thus making it unsuitable for any urban, recreational or agricultural use.

Finally, a sample of drinking / irrigation water was collected from the Ras El-Ain fountains. Only Zn, V, Fe and Al were present at detectable levels. The level of Al in this sample is unusually high, in breach of the EC Directive 80/778/EEC on the quality of drinking water. This directive sets a Maximum Permissible Concentration (MAC) for Al in drinking water of 200 ug/l. 540 ug/l was determined in this sample.

Environmental assessments of Al and Hg are discussed above.

Organic Chemicals

Soil collected from the waste dump in Tyre contained a wide range of organic pollutants:

i) PAHs including individual compounds and derivatives of naphthalene, anthracene, fluorenechrysene, and phenanthrene (see above for the toxicity data);

ii) Alkylated benzenes (see above for the toxicity data);

iii) Polychlorinated benzenes including di-, tri- and pentachlorinated isomers. These compounds are toxic to the marine invertebrates. For example, they have been associated with a growth rate reduction of crabs (Mortimer et al. 1995).

iv) 1,1'-Biphenyl and its alkyl derivatives.

<u>1,1'-Biphenyl</u>

This compound, known as diphenyl, has been used to inhibit the mycelial growth and spore formation of citrus fruit rots. Diphenyl has low acute toxicity to laboratory animals (Edwards et al. 1991). Exposed animals showed increased respiratory rate, lacrimation, loss of appetite and weight, muscular weakness, respiratory distress, and death in coma. The most common complains of the workers involved in impregnating paper with diphenyl were headache, diffuse pain, nausea, indigestion, and numbness and aching in the limbs.

In the drinking water sample LN7022 p-dichlorobenzene was tentatively identified. The toxicity data on this compound is presented above. The source of this compound in the

fountains could be lechate from the waste dumpsite, which is situated about 500m from the fountains.
Sediment sample LN7025 has contains organic compounds typically associated with raw sewage, e.g. alkylated PAHs, phenolic compounds, m-dichlorobenzene and alkylated benzenes; together with long-chain straight hydrocarbons. The toxicity of these compounds is described above.

Conclusion

The aims of this study were to identify the main polluting industries in Lebanon, discuss the range and environmental significance of heavy metal and organic contaminants discharged; propose appropriate and effective means of waste treatment and present potential alternatives to all toxic processing chemicals used.

Many industries have been identified as being polluting. With waste from tanneries, plastic, pesticide and chemical manufacture, and textile, dye and cement factories all contributing heavily to a widespread and complex pollution inventory. In addition, untreated sewage discharges, domestic waste debris on the beaches and in coastal waters, and runoff from coastal waste dumps, are all responsible for widespread contamination of inshore and nearshore waters.

Over two thirds of the marine and freshwater sediments collected, contained elevated levels of heavy metals and organic pollutants. In some cases, levels far in excess of background concentrations. All resulting from the convenient surface water discharge of untreated industrial and domestic waste. Many economically beneficial and practical methods of wastewater treatment have been suggested as alternatives to this practice, and recovery and recycling technologies have been suggested in all appropriate cases. It is imperative to realise, that the decay of coastal and inland areas of Lebanon, resulting from anthropogenically derived waste, can be halted. Cleaner technologies and clean production are not utopian and unrealistic. The fact that the industrial sector in Lebanon is relatively small, is to its advantage. The absence of many primary-manufacturing industries, such as smelting and pulp bleaching, means that much of the waste produced could be managed and treated appropriately and effectively.

A recent UNEP report identifying pollution hot spots, and sensitive areas in the Mediterranean, listed Beirut, Junieh, Saida, Tripoli and Batroun-Selaata as priority coastal sites requiring immediate remedial action. Due to domestic and industrial discharges into these coastal areas, public health and aquatic life are being effected deleteriously, often severely (UNEP, 1997). At all of these sites, the report stresses the immediate need for WWTP (Wastewater Treatment Plants), with the ability to treat wastes to a secondary level (i.e. biologically) an imperative one.

A second (draft) UNEP report proposing strategic actions necessary to address pollution from land based activities in the Mediterranean Region, stipulates that, in order to comply with the legislation laid out in the Barcelona Convention, and the 1996 Land Based Sources (LBS) protocol, the following targets and activities, regarding industrial and domestic wastewater disposal, should be implemented:

At a National level, it will be necessary to prepare and adopt (over a period of two years) national regulations concerning sewage discharges into the sea and rivers, which takes into account the LBS Protocol and especially its Annex 2. By the year 2005, national plans and programmes for environmentally sound treatment and management of sewage discharges should have been fully installed and implemented.

Regarding all urban solid waste, plans and programmes for reduction and recycling of waste should be established, promoted, and legislatively implemented.

Regarding industrial pollution, at a National level it will be necessary to make, in as short a period as possible, and inventory of the point source discharges and emissions of pollutants from all industrial sectors, not just those discharging into priority pollution hot spots and other areas of concern. National regulations concerning such point source discharges should be prepared and adopted as soon as possible, which take into account the guidelines, common criteria and standards adopted by all the other parties and the European Community. Best Environmental Practices (BEP) and Best Available Techniques (BAT) should be applied to all industrial installations in order to reduce and treat all discharges and emissions and implement environmental audits as much as possible.

In real terms, these proposed targets are intended to phase out to the fullest possible extent, substances that are toxic, persistent and bioaccumulative e.g. persistent organic pollutants (pesticides, PCBs, other aromatically halogenated compounds e.g. hexachlorobenzene, dioxins and furans; PAHs, heavy metals, organometallic compounds, halogenated aliphatic hydrocarbons, chlorinated solvents etc)

It is vital that these recommendations, and all other environmental legislation regarding land based anthropogenic inputs of pollution to the Mediterranean Region, are strictly implemented by the Lebanese Ministry of the Environment. If not, further decay of inland, inshore and nearshore waters will be a certainty. The capacity of the aquatic environment to assimilate anthropogenic pollution is finite, and when this point is reached, rapid and probable irreversible environmental decay will result. The time to address the problems of waste production and disposal, and to prevent widespread environmental decay, is here, and governmental departments and industrialists alike must acknowledge this and act immediately.

References

1) Heavy Metals

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Nickel, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Aluminium, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Vanadium, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Barium, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Chromium, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Copper, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Lead, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Cadmium, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Zinc, 1997.

Agency for Toxic Substances and Disease Registry, U.S. Public Health Service. Toxicological Profile for Mercury, 1997.

Aislabie, J. and Loutit, M.W. (1986). Accumulation of Cr (iii) by bacteria isolated from polluted sediment. Marine Environmental Research 20, 221-232.

Alloway, B.J. (1990). Heavy metals in soils. ISBN 0-470-21598-4, Blackie and Son Ltd, Glasgow/London, UK.

Auernheimer, C., Chinchon, S. and Pina, J.A. (1996). Lead pollution in bivalve shells. Mar Menor, Spain. Archives of General Science 49, 87-98.

Berg, H., Kiibus, M., and Kautsky, N. (1995). Heavy metals in tropical Lake Kariba, Zimbabwe. Water, Air and Soil Pollution 83, 237-252.

Biddinger, G.R., Gloss, S.P. (1984). The importance of trophic transfer in the bioaccumulation of chemical contaminants in aquatic ecosystems. Residue Review 91, 103-145.

Birchall, J.D., Exley, C., Chappell, J.S. and Phillips, M.J. (1989). Acute toxicity of aluminium to fish eliminated in silicon-rich wtaers. Nature 338, 146-148.

Bradley, R.W. (1986). Heavy metals in fish from a series of metal contaminated lakes near Sudburry, Ontario. Water, Air and Soil Pollution 27, 341.

Bremer, P.J., and Loutit, M.W. (1986) Bacterial polysaccharide as a vehicle for entry of Cr (iii) to a food chain. Marine Environmental Research 20, 235-248.

Bryan, G.W. (1971). The effects of heavy metals (other than mercury) on marine and estuarine organisms. Proceeding from the Royal Society of London, B.177, 389-410.

Bryan, G.W. and Humberstone, L.G. (1973). Adaptation of the polychaete Nereis diversicolor sp. to estuarine sediments containing high concentrations of zinc and cadmium. Marine Pollution Assessment, UK 53, 839-857.

Bryan, G.W. and Langston, W.J. (1992). Bioavailabilty, accumulation and effects of heavy metals in sediments with special reference to United Kingdom Estuaries: a review. Environmental Pollution 76, 89-131.

Butler, C.A and Timperley, M.H. (1996). Fertilised farmland as a source of cadmium in oysters. The Science of the Total Environment 181, 31-44.

Byerrum, R.U., Eckardt, R.E. and Hopkins, L.L. (1974). Vanadium. Washington, D.C.: National Academy of Sciences, 1-117

Byrne, C.J. and DeLeon, I.R. (1986). Trace metal residues in biota and sediments from Lake Pontchartrain, Louisiana. Bulletin of Environmental Contamination and Toxicology 37, 151-158.

Callahan, M.A., Slimak, M.W. and Gabel, N.W. (1979). Water related environmental fate of 129 priority Pollutants, introduction and technical background, metals and inorganics, pesticides and PCBs. Washington, D.C: U.S. Environmental Protection Agency, Office of Water Waste and Management. Document no. EPA 440/4-79-029a., 14-1 - 14-15.

Chakraborty, A., Oinam, S. and Chatterjee, M. (1998). Vanadium toxicology – an assessment of general health, haematological aspects and energy response in an Indian catfish. Biometals 11, no. 2, 95-100.

Chirila E., Magearu V. (1994). Study concerning the analytical control in chemical treatment of the hydrogen-sulfide-containing and sulfides-containing waters discharged from the petrochemical units. Revista de Chemie, 1994, Vol.45, No.10, pp.908-911

Dallinger, R., Prosi, F., Segner, Back, H. (1987). Contaminated food and uptake of heavy metals by fish. A review and proposal for further research.Oecologia 73, 91-98

Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayr, S.M., and Redmond, M.S. (1990). Toxicity of cadmium in sediments: the role of acid-volatile sulphide. Environmental Toxicology and Chemistry 9, 1487-1502.

Domingo, J.L. (1996). Vanadium, a review of the reproductive and developmental toxicity. Reproductive Toxicology, vol. 10, no. 3, 175-182.

Eisenberg, M. and Topping, J.J. (1986). Trace metal residues in finfish from Maryland waters, 1978-1979. Journal of Environmental Science and Health 21, 87-102.

Eisler, r. (1988). Lead hazards to fish, wildlife, and invertebrates: A synoptic review. Laurel, MD: U.S. Department of the Interior, Fish and Wildlife Service. Biological Report 85 (1.14).

Elinder, C.G. (1985) Cadmium: Uses, occurrence and intake. In: Friberg L, Elinder CG, Kjellstrom T, Nordberg GF, eds. Cadmium and health: A toxicological and epidemiological appraisal. Vol. I. Exposure, dose, and metabolism. Effects and response. Boca Raton, FL: CRC Press, 23-64.

Environmental Protection Agency, Contract Laboratory Program. SOW number 784.
EPA, 1980. Ambient water quality criteria for mercury. Washington, DC: U.S.

Environmental Protection Agency, Office of Water Regulations and Standards. Document no. EPA 440/5-80-058.

EPA, 1984. Contract laboratory program statement of work. Washington, DC: U.S.

EPA, 1984. Mercury health effects update: Health issue assessment. Final report. Washington, DC: U.S. Environmental Protection Agency, Office of Health and Environmental Assessment. Document no. EPA 600/8-84-019F.

EPA. 1987. Ambient water quality criteria for zinc, 1987. Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards. EPA 440/5-87-003, PB87- 153581.

European Community Environment Legislation, Volume 7: Water. Council Decision 75/437/EEC of 3 March 1975 concluding the Convention for the prevention of marine pollution from land-based sources.

European Community Environment Legislation, Volume 7: Water. Council Decision 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.

European Community Environment Legislation, Volume 7: Water. Council Decision 83/513/EEC of 26 September 1983 on limit values and quality objectives for cadmium discharges.

European Community Environment Legislation, Volume 7: Water. Council Decision 82/176/EEC of 22 March 1982 on limit values and quality objectives for mercury discharges by the chlor-alkali electrolysis industry.

European Community Environmental Legislation Volume 7: Water. Council Decision 83/101/EEC of 28 February 1983 concluding the Protocol for the protection of the Mediterranean Sea against pollution from land-based sources.
European Community Environmental Legislation, Volume 6: Waste. Council Decision 78/319/EEC of 20 March on toxic and dangerous waste.

European Community Environmental Legislation, Volume 7: Water. Council Decision 80/778/EEC of 15 July relating to the quality of water intended for human consumption.

European Community Environmental Legislation, Volume 7: Water. Council Decision 84/156/EEC of 8 March 1984 on limit values and quality objectives for mercury discharges by sectors other than the chlor-alkali electrolysis industry.

Fishbein, L. (1981) Sources, transport, and alterations of metal compounds: An overview: 1. Arsenic, beryllium, cadmium, chromium, and nickel. Environmental Health Perspectives 40:43-64.

Gawthorne_T, Gibbs_RA, Mathew_K, Ho_GE (1996). H_2S papers as presumptive tests for Salmonella contamination in tropical drinking water. Water Science and Technology 34, no. 7-8, 187-194

Goncalves, E.P.R., Boaventura, R.A.R., and Mouvet, C. (1992). Sediments and aquatic mosses as pollution indicators for heavy metals in the Ave river basin, Portugal. The Science of the Total Environment 114, 7-24.

Guidici, M.N. and Guarino, S.M. (1989). Effects of chronic exposure to cadmium or copper on Idotea balthica sp. (Crustacea Isopoda). Marine Pollution Bulletin 20, 69-73.

Hapke, H.J. (1991). Metal accumulation in the food chain and load of feed and food. Metals and Their Compounds in the Environment, Merian, VCH, Weinheim, pp1438.

Harrison, R.M. (1996), Pollution: Causes, effects and control, 3rd Edition. ISBN 0-85404-534-1. The Royal Society of Chemistry Information Services, Cambridge UK.

Hayes, W.J. and Laws, E.R. (1991). Handbook of Pesticide Toxicology. Volume 2: Classes of Pesticides. Chapter 12: Inorganic and Organometallic Pesticides. ISBN 0-12-334161-2. Academic Press Inc., Harcourt Brace Jovanovich Publishers, USA.

Heath, A.G. (1987). The effects of waterborne copper or zinc on the osmoregularity response of bluegill to a hypertonic NaCl challenge. Comparative Biochemistry and Physiology 88, 307-311.

Heller J., Ehrlich S. (1995). A fresh-water prosobranch, melanoides-tuberculata, in a hydrogen-sulfide stream. Journal of Conchology 35, no. 3, 237-241.

Herr, C. and Gray, N.F. (1997). Metal contamination of riverine sediments below the Avoca mines, Southeast Ireland. Environmental Geochemistry and Health 19, 73-82.

I.C.M.E. (International Council on Metals and the Environment), 1995. Persistence, bioaccumulation and toxicity of metals and metal compounds. ISBN 1-895720-07-9, Paramex Inc., Washington.

Jensen, A. and Bro-Rasmussen, F. (1990). Review of environmental fate and exposure of cadmium in the European environment. EEC Contract no. B6614-35-89 and B6614-15-89. Report no. 90.102.

Kiorboe, T., Mohlenberg, F. and Riisgard, H.V. (1983). Mercury levels in fish, invertebrates and sediment in a recently recorded polluted area. Marine Pollution Bulletin 14, 21-24.

Krishnan, S. (1988). The case against aluminium. Canadian Research 21, no 3, 33-35.

Licheng, Z. and Kezhun, Z. (1992). Background values of trace elements in the source area of the Yangtze River. The Science of the Total Environment 125, 391-404.

Luoma, S.N., Dagovitz, R. and Axtmann, E. (1990). Temporally intensive study of trace metals in sediments and bivalves from a large river-estuarine system: Suisun Bay / Delta in San Francisco Bay. The Science of the Total Environment 97/98, 685-712.

Marcus, W.A. (1991). Managing contaminated sediments in aquatic environments: identification, regulation and remediation. Environmental Law Reported, News and Analysis, 21 ELR 10020.

Martin, M., Osborn, K.E., Billig, P. and Glickstein, N. (1981). Toxicities of ten metals to Crassostrea gigas sp. and Mytilis edulis sp. embryos and Cancer magister sp. larvae. Marine Pollution Bulletin 12, 305-308.

Maserti, B.E. and Ferrara, R. (1991). Mercury in plants, soil and atmosphere near a chlor-alkali complex. Water, Air and Soil pollution 56, 15-20.

Mediterranean Environmental Technical Assistance Program (METAP) 1995. Lebanon: Assessment of the State of the Environment.

Merck (1989) The Merck index: an encyclopaedia of chemicals, drugs and biologicals. 11th Edn.Budavari, S.M.J. O’Neil, A.Smith and P.E.Heckleman [Eds]. Merck and Co, Inc., New Jersey, USA, 1606p.

Needleman, H.L., Schell, A. and Bellinger, D. (1990). The long-term effects of exposure to low doses of lead in childhood. An 11 -year follow-up report. New England Journal of Medicine 322, 83-88.

Nelson, C.H. and Lamothe, P.J. (1993). Heavy metal anomalies in the Tinto and Odiel river and estuary system, Spain. Estuarine Research Foundation 16, no. 3A, 496-511.

Nriagu, J.O. (1988). A silent epidemic of environmental metal poisoning? Environmental Pollution 50, 139-161.

Nriagu, J.O. (1992). Mercury pollution in Brazil. Nature 356, 389.

Ojaveer, E., Annist, J., Jankowski, H., Palm, T. and Raid, T. (1980). Effects of copper, cadmium and zinc on the embryonic development of Baltic spring spawning herring. Marine Research 247, 135-140.

Palanques, A. (1993). Distribution and heavy metal pollution of the suspended particulate matter on the Barcelona continental shelf (North-Western Mediterranean). Environmental Pollution 85, 205-215.

Palanques, A., Diaz, J.I. and Farran, M. (1995). Contamination of heavy metals in the suspended and surface sediment of the Gulf of Cadiz (Spain): the role of sources, currents, pathways and sinks. Oceanologica Acta 18, no. 4, 469-477.

Perwak, J., Bysshe, S. and Goyer, M. (1980). Exposure and Risk Assessment for Copper. Cincinnati, OH: U. S. Environmental Protection Association. EPA 440/4-81-015. NTIS PB85-211985.

Radojevic, M. and Harrison, R.M. (1987). Concentrations and pathways of organolead compounds in the environment. The Science of the Total Environment 59, 157-180.

Ramelow, G.J., Webre, C.L., and Mueller, J. (1989). Variations of heavy metals and arsenic in fish and other organisms from the Calcasieu river and lake, Louisiana. Arch. Environmental Contamination Toxicology 18, 804- 818.

Ray, S., McLeese, D. and Pezzack, D. (1980). Accumulation of cadmium by Nereis virens sp. Archives of Environmental Contamination and Toxicology 9, 1-8.

Reuther, R. (1994). Mercury accumulation in sediment and fish from rivers affected by alluvial gold mining in the Brazilian Madeira Basin, Amazon. Environmental Monitoring and Assessment 32, 239-258.

Rosseland, B.O., Eldhuset, T.D. and Staurnes, M. (1990). Environmental effects of aluminium. Environmental Geochemistry and Health 12 (1-2): 17-27.

Salomons, W. and Forstner, U. (1984). Metals in the Hydrocycle. ISBN 3-540-12755-0, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo.

Samanidou, V. and Fytianos, K. (1990). Mobilisation of heavy metals from river sediments of Northern Greece by complexing agents. Water, Air and Soil Pollution 52: 217-225.
Schuhmacher, M., Domingo, J.L., Llobet, J.M., and Corbella, J. (1995). Variations of heavy metals in water, sediments and biota from the delta of the Ebro River, Spain. Journal of Environmental Science and Health, A30 (6), 1361-1372.

Schwartz, R.C., Ditsworth, G.R., Schults, D.W., and Lamberson, J.O. (1985). Sediment toxicity to a marine infaunal amphipod: cadmium and its interaction with sewage sludge. Marine and Environmental Research 18, 133-153.

Sekaran G., Chitra K., Mariappan M., Raghava K.V. (1996). Removal of sulfide in anaerobicaly treated tannery waste-water by wet oxidation. Journal of Environmental Science and Health. Part A – Environmental Science and Engineering & Toxic and Hazardous Substance Control 31, no.3, 579-598

Shore, R., Carney, G. and Stygall, T. (1975). Cadmium levels and carbohydrate metabolism in limpets. Marine Pollution Bulletin 6, 187-189.

Sola, M.J., Millan, E., Legorburu, I., Canton, L. (1991). Heavy metals in superficial river sediments, from Guipuzcoa (Spain). Environmental Technology 12, 441-445.

Stephenson, T. (1988). Heavy metals in wastewater and sludge treatment processes. Volume 1, sources, analysis and legislation. CRC Press Inc., Boca Florida.

The Agrochemicals Handbook, 3rd Edition (1991). ISBN 0-85186-416-3, The Royal Society of Chemistry Information Services, Surrey, UK.

Tsubaki, T. and Irukayama, K. (1977). Minimata Disease. Kodansha, Tokyo and Elsevier, Amsterdam.

UNEP (1982). Convention for the protection of the Mediterranean Sea against pollution and its related protocols. United Nations, New York, 1982.

UNEP (1990). State of the marine environment in the Mediterranean Region. UNEP Regional Seas Reports and Studies, no. 132. MAP Technical Reports Series, no 28. Prepared in co-operation with FAO, IOC and WHO, Athens 1989.

UNEP (1991). Tanneries and the Environment. A technical Guide. Technical report series no. 4.

UNEP (1992). Mediterranea Action Plan and Convention for the protection of the Mediterranean Sea against pollution and its related protocol. United Nations, Athens 1992.

UNEP (1995). Mediterranean Action Plan. Guidelines for treatment of effluents prior to discharge into the Mediterranean Sea. United Nations, Athens 1995.

UNEP (1991). Mediterranean Action Plan. Assessment of the state of pollution of the Mediterranean Sea by pathogenic organisms.

UNEP (DRAFT 1997). Mediterranean Action Plan. Strategic action programme to address pollution from land-based activities, Athens, 1997.

Verriopoulos, G. and Hardouvelis, D. (1988). Effects of sub-lethal concentrations of zinc on survival and fertility in four successive generations of Tisbe. Marine Pollution Bulletin 19, 162-166.

Volrath, A., Otz, T., Hohl, C. and Seiler, H.G. (1992). Comparison of dissolution procedures for the determination of cadmium and lead in plastics. Fresenius Journal of Alaytical Chemistry 344, 269-274.

WHO, 1988. Vanadium: Environmental health criteria 81. World Health Organization, Geneva, Switzerland.

World Health Organisation (1989). Environmental Health Criteria 86. Mercury: Environmental Aspects. ISBN 92-4-154286-1.

2) Organic Chemicals

Acker L., Schulte E. (1974). Organochlorine compounds in human fat. Naturwissenschaften no. 61, p32.

Adams W.J., Biddinger G.R., Robillard K.A., Gorsuch J.W. (1995). A summary of the acute toxicity of 14 phthalate esters to representative aquatic organisms. Environmental Toxicology and Chemistry, Vol.14, No.9, pp.1569-1574

Ammeloot F., Fiaud C., Sutter E.M.M. (1997). Application of photoelectrochemical methods for the characterization of Cu(I) oxide layers modified in the presence of corrosion inhibitors. Electrochimica Acta, Vol.42, No.23-24, pp.3565-3574

Aristech (1995) Arictech Chemical Corporation Material Safety Data sheet C1084E. Product Code 1564: Diisononyl phthalate.

Asplund L., Svensson B-G., Nilsson A., Eriksson U., Jansson B., Wideqvist U., Skerfving S. (1994). Levels of polychlorinated naphthalenes (PCN) in human blood plasma with reference to fish intake. In “Development and application of methods for determination of polychlorinated organic pollutants in biota”, [Ed] Asplund L., Institute of Applied Environmental Chemistry, Lab. Of Environ. Chem., Stockholm University, pp.1-10.

Bildeman T.F., Falconer R.L., Walla M.D. (1995). Toxaphehe and other organochlorine compounds in air and water at Resolute Bay, NWT, Canada. Science Of The Total Environment, Vol.161, pp.55-63.

Bornatowicz N., Antes A., Winker N., Hofer H. (1994). 2-generation reproduction toxicity study with 1,4-dichlorobenzene in rats. Wiener Klinische Wochenschrift, Vol. 106, No. 11, pp.345-353.

Bunton T.E. (1996). Experimental chemical carcinogenesis in fish. Toxicologic Pathology, Vol.24, No.5, pp.603-618.

Cancilla D.A., Holtkamp A., Matassa L., Fang X.C. (1997). Isolation and characterization of microtox(R)-active components from aircraft de-icing/anti-icing fluids. Environmental Toxicology And Chemistry, Vol.16, No.3, pp.430-434

Chalaux N., Takada H., Bayona J.M. (1995). Molecular markers in Tokyo Bay sediments – sources and distribution. Marine Environmental Research, Vol., 40, No.1, pp.77-92.

Chan K.H., Lam M.H.W., Poon K.F., Yeung H.Y., Chiu T.K.T. (1998). Application of sedimentary fecal stanols and sterols in tracing pollution in coastal waters. Water Research, Vol. 32, No.1, pp. 225-235.

Chapman P.M., Downie J., Maynard A., Taylor L.A. (1996). Coal and deodorizer residues in marine-sediments – contaminants or pollutants. Environmental Toixicology and Chemistry, Vol. 15, No.5. pp. 638-642.

Connell D.W. (1974). A kerosene-like taint in the sea mullet, *Mugil cephalus* (Linnaeus). I. Composition and environmental occurrence of the taining substance. Australian Journal of Marine and Freshwater Research, Vol. 25, pp. 7-24.

Coogan D. (1994). Epidemiologic studies of styrene exposed populations. Critical Reviews in Toxicology, Vol.24, No.1, pp.107-115.

De Wever H., Verachtert H. (1997).Biodegradation and toxicity of benzothiazoles. Water Research, Vol.31, No.11, pp.2673-2684

Dean J.H., Murrey M.J and Ward E.C. (1986). Toxic responses of the immune system. In Toxicology: the basic science of poisons. Klaasen C.D. Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 245-285.

Drzyzga O., Jannsen S., Blotelogel K.H. (1995). Toxicity of diphenylamine and some of its nitrated and aminated derivatives to the luminescent bacterium Vibrio fischeri. Ecotoxycology and Environmental Safety, Vol.31, No.2, pp.149-152

Dubois M., Grosse .Y, Thome J.P., Kremers P., Leszkowicz A. (1997). Metabolic activation and DNA-adducts detection as biomarkers of chlorinated pesticide exposures. Biomarkers, 1997, Vol.2, No.1, pp.17-24.

Edwards I.R., Ferry D.H., Temple W.A. (1991) Fungicides and related compounds. In: Handbook of pesticide toxicology. Volume 3. Classes of pesticides. [Eds] Hayes W.J. and Laws E.R. Academic Press, Inc., pp.1409-1470.

Elias V.O., DeBarros A.M.A., DeBarros A.B., Simoneit B.R.T., Cardoso J.N. (1997). Sesquiterpenoids in sediments of a hypersaline lagoon: A possible algal origin. Organic Chemistry, Vol.26, No.11-12, pp.721-730.

Ensley H.E., Barber J.T., Polito M.A., Oliver A.I. (1994). Toxicity and metabolism of 2,4-dichlorophenol by the aquatic angiosperm Lemna-Gibba. Environmental Toxicology And Chemistry, Vol.13, No.2, pp.325-331.

European Chemicals Bureau (1996) IUCLID: International Uniform Chemical Information Database. Existing Chemicals- 1996. Edition 1.

European Community Environmental Legislation (1992a), Volume 7: Water. Council Decision 83/101/EEC of 28 February 1983 concluding the Protocol for the protection of the Mediterranean Sea against pollution from land-based sources.

European Community Environmental Legislation (1992b), Volume 7: Water. Council Decision 75/437/EEC of 3 March 1975 concluding the Convention for the protection of marine pollution from land-based sources.

European Community Environmental Legislation (1992c), Volume 7: Water. Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community.

European Community Environmental Legislation (1992d), Volume 7: Water. Council Directive 84/491/EEC of 9 October 1984 on limit values and quality objectives for discharges of hexachlorocyclohexane.

Falandysz J., Strandberg L., Bergqvist P.A., Kulp S.E., Strandberg B., Rappe C. (1996). Polychlorinated naphthalenes in sediment and biota from the Gdansk basin, Baltic Sea. Environmental Science and Technology, Vol.30, No.11, pp.3266-3274

F.A.O. (1995). Obsolete, unwanted and banned pesticides in Lebanon.

Haglund P., Jakobsson E., Masuda Y. (1995). Isomerspecific analysis of polychlorinated naphtalenes in kanechlor KC 400, Yusho rice oil and adipose of Yusho victim. Organohalogen Compounds, Vol. 26, pp.405-410.

Hanberg A., Waern F., Asplund L., Haglund E., Safe S. (1990). Swedish dioxin survey:

determination of 2,3,7,8-TCDD toxic equvalent factors for some polychlorinated biphenyls and naphthalenes using biological tests. Chemosphere, Vol. 20, Nr.7-9, pp.1161-1164.

Harris, C.A., Henttu, P., Parker, M.G., & Sumpter, J.P. (1997). The estrogenic activity of phthalate esters *in vitro*. Environmental Health Perspectives 105(8):

Hawley G.G. (1977). The condensed chemical dictionary. Van Nostrand Reinhold Co., New York, 957pp.

Hayward D. (1998). Identification of bioaccumulating polychlorinated naphthalenes and their toxicological significance. Environmental Research, Section A, Vol.76, pp.1-18.

Howard Philip H. (1989). Handbook of environmental fate and exposure for organic chemicals. Volume I: Large production and priority pollutants. Lewis Publishers, Inc.,USA, 574 p.

Inoue Y., Takamatsu M., Aoki N. (1974). A study on the qualitative and quantitative ration of PCB and organochlorine pesticide residues in the blood and adipose tissue. Japanese Journal of Hygiene, Nr.29, p. 92.

Itinose A.M., Doisacuno M.L., Bracht A. (1995). Induction of parasetamol biotransformation in the rat-liver by gamma-hexachlorocyclohexane. Research Communication In Alcohol And Substances Of Abuse, Vol.16, No.4, pp.177-188

Jarnberg U., Asplund L., de Wit C., Grafstorm A-K., Haglund P., Jansson B., Lexen K., Strandell M., Olsson M., Jonsson B. (1993). Polychlorinated biphenyls and polychlorinated naphthalenes in Swedish sediment and biota: levels. Pattern, and time trends. Environmental Science and Technology, Vol.27, 1364-1374.

Jinturkar P., Guan Y.C., Han K.N. (1998). Dissolution and corrosion inhibition of copper, zinc, and their alloys. Corrosion, Vol.54, No.2, pp.106-114.

Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environmental Health Perspectives 103(6): 582-587

Johansen S.S., Hansen A.B., Mosbaek H., Arvin E. (1997). Identification of heteroaromatic and other organic compounds in ground water at creosote-contaminated sites in Denmark. Ground Water Monitoring And Remediation, Vol.17, No.2, pp.106-115.

Junqueira V.B.C., Bainy A.C.D., Arisi A.C.M., Azzalis L.A., Simizu K., Pimentel R., Barros S.B.M., Videla L.A. (1994). Acute lindane intoxication - a study on lindane tissue concentration and oxidative stress-related parameters in liver and erythrocytes. Journal of Biochemical Toxicology, Vol.9, No.1, pp.9-15.

Kahru A., Kurvet M., Kurvet I. (1997). Study of the toxicological impact of different components of ash-heap water (sulphur rich phenolic leachate) using luminescent bacteria as test organisms. Oil Shale, Vol.14, No.4 SISI, pp.469-475.
Kang Y.H., Kim K. (1997). Oxidation of 1-[(aryl)(phenyiseleno)methyl]-, 1-[(aryl)(arylthio)(phenylseleno)methyl]-, and 1-[(aryl)(diphenylseleno)methyl]benzotriazoles with m-chloroperbenzoic acid. Journal of Heterocyclic Compounds, Vol.34, No.6, pp.1741-1752

Kemi (1994) Phthalic acid esters used as plastic additives. Publ: Swedish National Chemicals Inspectorate; report 12/94, ISSN 0248-1185

Kolstad H.A., Lynge E., Olsen J., Breum N. (1994). Incidence of lymphohematopoietic malignancies among styrene exposed workers of the reinforsed plastics industry. Scandinavian Journal of Worh Environment & Health, Vol.20, No.4, pp.272-278.

Larsen B.R., Turriobaldassarri L., Nilsson T., Iacovella N., Didimenico A., Montagna M., Facchetti S. (1994). Toxic PCB congeners and organochlorine pesticides in Italian human-milk. Ecotoxicology and Environmental Safety, Vol.28, No.1, p.1-13

Larsen T., Kjeldsen P., Chriatensen T.H. (1992). Sorption of hydrophobic hydrocarbons on three aquifer materials in flow through system. Chemosphere, Vol.24, No. 4, pp.439-451.

Life Systems, Inc. (1993) Di (2-ethylhexyl) phthalate. Publ: US Department of Health and Human Services. Public Health Service Agency for Toxic Substances and Disease Registry.

Maa Y.F., Hsu C.C. (1996).Aggregation of recombinant human growth hormone induced by phenolic compounds. International Journal of Pharmaceutics, Vol.140, No.2, pp.155-168.

Mattioli F., Robbiano L., Adamo D., Federa R., Martelli A., Brambilla G.B. (1996). Genotoxic effects of alpha-hexachlorocyclohexane in primary cultures of rodent and human hepatocytes. Mutagenesis, Vol.11, No.1, pp.79-83.

Meek M.E., Giddings M., Gomes R. (1994). 1,4-dichlorobenzene – evaluation of risks to health from environmental exposure in Canada. Environmental carcinogenesis & ecotoxicology reviews – Part C of Journal of Environmental Sciences and Health, Vol. 12, No. 2, pp. 277-285.

Mehmood Z., Kelly D.E., Kelly S.L. (1997). Cytochrome P450 3A4 mediated metabolism of 2,4-dichlorophenol. Chemosphere, Vol.34, No.11, pp.2281-2291.

Meier J.R., Warshawsky D. (1994). Comparison of blood protein and target organ DNA and protein-binding following topical application of benzo[a]pyrene and 7H-dibenzo[c,g]carbazole to mice. Carcinogenesis, Vol.15, No.10, pp.2233-2240.

Menzert R.E., Nelson J.O. (1986). Water and soil pollutants. In Toxicology: the basic science of poisons. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 825-856.

Merck (1989) The Merck index: an encyclopaedia of chemicals, drugs and biologicals. 11th Edn.Budavari, S.M.J. O'Neil, A.Smith and P.E.Heckleman [Eds]. Merck and Co, Inc., New Jersey, USA, 1606p.

Miller R.R., Newhook R., Poole A. (1994). Styrene production, use and human exposure. Critical Reviews in Toxicology, Vol.24, No.1, pp.1-10.

MINDEC (1990). Final declaration of the Third Ministerial Conference on the Protection of the North Sea. Ministry of Transport and Public Works, The Hague, 36pp.

Mortimer M.R., Connell D.W. Effect of exposure to chlorobenzenes on growth-rates of the crab Portunus-Pelagicus (L). Environmental Science & Technology, 1995, Vol.29, No.8, pp.1881-1886.

Muller A., Herbarth O. (1994). Tetrahymena pyriformis – a cell test system for environmental medicine investigations into the effect of pollutants on cell-size of Tetrahymena pyriformis. Zentralblatt fur Hygiene und Umweltmedizin, Vol.196, No.3, pp.227-236.

Myers, B.A. (1991) 13-week subchronic dietary oral toxicity study with di(isononyl)phthalate in Fischer 344 rats (final report) with cover letter dated 05-20-92: Supplemental information. Hazelton Laboratories, Washington. EPA/OTS Doc # 89-920000224.

Nagata K., Huang C.S., Hamilton B.J., Carter D.B., Narahashi T. (1996). Differential-effects of hexachlorocyclohexane on the gaba receptor subunits expressed in human embrionic kidney-cell line. Brain Research, Vol.738, No.1, pp.131-137.

Nagyova A., Ginter E. (1995). The influence of ascorbic acid on the hepatic cytochrome-P-450, and glutatione in guinea pigs exposed to 2,4-dichlorophenol. Physiological Research, Vol.44, No.5, pp.301-305.

Nikl D.L., Farrell A.P. (1993). Reduced swimming performance and gill structural changes in Juvenile salmonids exposed to 2-(thiocyanomethylthio)benzothiazole. Aquatic Toxicology, Vol.27, No.3-4, pp.245-263

Nylund K., Asplund L., Jansson B., Jonsson P., Litzen K., Sellstrom U. (1992). Analysis of some polychlorinated organic pollutants in sediment and sewage sludge.

Chemosphere, Vol.24, pp.1721-1730.

Overton, 1994. Toxicity of petroleum. In: Basic Environmental Toxicology. Cockerham & Shane [Eds], Chapter 5, pp. 133-156.

Paxeus N., Schroder H.F.(1996). Screening for non-regulated organic compounds in municipal wastewater in Goteborg, Sweden. Water Science and Technology, Vol.33, No.6, pp.9-15.

Perinroussel O., Perin F., Barat N., Plessis M.J., Zajdela F. (1995). Interaction of 7H-dibenzo[c,g]carbazole and its organspecific derivatives with hepatic mitochondrial and nuclear DNA in the mouse. Environmental and Molecular Mutagenesis, Vol.25, No.3, pp.202-210.

Pesendorfer H., Eichler I., Glofke E. (1973). Informative analysis of organochlorine pesticide and PCB residues in human adipose tissue (from the area of Vienna). Wien. Klin. Wochenschr.. Nr. 85, pp. 218-222.

Platt A.E. Wallace T.C. (1983). In: Kirk-Othmer [Eds]: Encyclopedia of Chemical Technology, Vol.21, pp.801-847.

Pramanik A.K., Hansen R.C. (1979). Transcutaneous gamma benzene hexachloride absorption and toxicity in infants and children. Arch. Dermatology, Nr.15, pp.1224-1225.

Preston, M.R. & Raymundo, C.C. (1993) The associations of linear alkyl benzenes with the bulk properties of sediments from the River Mersey estuary. Environmental Pollution, Vol.81, pp. 7-13.

Reemtsma T., Fiehn O., Kalnowski G., Jekel M. (1995). Microbial transformations and biologival effectes of fungicide-derived benzithiazoles determined in industrial wastewater. Environmental Science and Technology, Vol.29, No.2, pp.478-485.

Requejo A.G., Hieshima B., Hsu C.S., McDonald T.J., Sassen R. (1997). Short-chain (C-21 and C-22) diasteranes in petroleum and source rocks as indicators of maturity and depositional environment. Geochimica et Cosmochimica Acta, Vol.61, No.13, pp.2653-2667.

Rhodes J.E., Adams W.J., Biddinger G.R., Robillard K.A., Gorsuch J.W. (1995). Chronic toxicity of 14 phthalate esters to Daphnia-Magna and Rainbow-Trout (*Oncorhynchus-Mykiss*). Environmental Toxicology and Chemistry, Vol.14, No.11, pp.1967-1976.

Roe F.J.C. (1994). Styrene – toxicity studies – what do they show. Critical Reviews in Toxicology, Vol.24, No.1, pp.117-125.

Romijn C.A.F.M., Luttik R., Canton J.H. (1994). Presentation of a general algorithm to include effect assessment on secondary poisoning in the derivation of environmental-quality criteria.2. Terrestrial food-chains. Ecotoxicology and Environmental Safety, 1994, Vol.27, No.2, pp.107-127.

Schlaud M., Seidler A., Salje A., Behrendt W., Schwartz F.W., Ende M., Knoll A., Grugel C. (1995). Organochlorine residues in human breast-milk – analysis through a sentinel practice network. Journal of Epidemiology and Community Health, Vol.49, No.S1, pp.17-21.

Schoula R., Hajslova J., Bencko V., Poustka J., Holadova K., Vizek V. (1996) Occurrence of persistent organochlorine contaminants in human-milk collected in several regions of Czech Republic. Chemosphere, Vol.33, No.8, pp.1485-1494

Schulz R., Liess M. (1995).Chronic effects of low insecticide concentrationson fresh-waterCaddisfly Larvae. Hydrobiologia, Vol.299, No.2, pp.103-113.

Seymour D.T., Verbeek A.G., Hrudey S.E., Fedorak P.M. (1997). Acute toxicity and aqueous solubility of some condensed thiophenes and their microbial metabolites. Environmental Toxicology and Chemistry, Vol.16, No.4, pp.658-665

Smith A.G. (1991). Chlorinated Hydrocarbon Insecticides. In: Handbook of pesticide toxicology. Volume 2. Classes of pesticides. [Eds] Hayes W.J. and Laws E.R. Academic Press, Inc., pp.731-860.

Steinmentz R., Young P.C.M., Caperellgrant A., GizeE.A., Madhukar B.V., Benjonathan N., Bigsby R.M. (1996) Novel estrogenic action of the pesticide-residue beta-hexachlorocyclohexane in human breast-cancer cells. Cancer Research, Vol.56, No.23, pp.5403-5409.

Strachan W.M.J., Eriksson G., Kylin H., Jensen S. (1994). Organochlorine compounds in pine needles - methods and trends. Environmental Toxicology and Chemistry, Vol.13, No.3, pp.443-451.

Sumner S.J., Fennell T.R. (1994). Review of metabolc fate of styrene. Critical Reviews in Toxicology, Vol.24, No.1, pp.11-33.

Talaska G., Reilman R., Schamer M., Roh J.H., Xue W., Fremont S.L., Warshawsky D. (1994). Tissue distribution of DNA-adducts of 7H-dibenzo[c,g]carbazole and its derivatives in mice following topical application. Chemical Research in Toxicology, Vol.7, No.3, pp.374-379.

Terzian R., Serpone N. (1995).Heterogeneous photocatalyzed oxidation of creosote components - mineralization of xylenols by illuminated TiO2 in oxygenated aqueous media. Journal of Photochemistry and photobiology, A - Chemistry, Vol.89, No.2, pp.163-175

TSCA, 1994. Section 8 (e) triage and Abstracts. October, 1994. U.S. EPA

UNEP (1991). Tanneries and the Environment. A technical Guide. Technical report series No.4.

USEPA (1991) Subchronic (4-week) dietary oral toxicity study of di(isononyl)phthalate in B6C3F1 mice (final report) with cover sheet dated 05-29-91. Hazelton Laboratories, Washington. EPA/OTS Doc # 86-910000793

USEPA (1992) 13-week subchronic dietary oral toxicity study with di(isononyl)phthalate in mice, with cover letter dated 07-06-92 and attachments: supplement. American College of Veterinary Pathology. EPA/OTS Doc # 89-920000303.

USPHS (1989). Toxicological profile for 1,4-dichlorobenzene. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service: 95p.

USPHS (1990). Toxicological profile for polycyclic aromatic hydrocarbons. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service: December 1990, 231p.

Veningerova M., Prachar V., Uhnak J., Lukacsova M., Trnovec T. (1994). Determination of chlorinated phenols and creosols in human urine using solid-phase extraction and gas chromatography. Journal of Chromatography B. Biomedical Applications, Vol.657, No.1, pp.103-110.

Walsh A.R., Ohalloran J. (1997). The toxicity of leather tannery effluent to a population of the blue mussel Mytilus edulis (L). Ecotoxicology, Vol.6, No.3, pp.137-152

Wang M.J., Jones K.C. (1994a) The chlorobenzene content of contemporary UK sewage sludges. Chemosphere, 1994, Vol.28, No.6, pp.1201-1210

Wang M.J., Jones K.C. (1994b).Behavior and fate of chlorobenzenes (CBs) introduced into soil-plant systems by sewage-sludge application – a review. Chemosphere, 1994, Vol.28, No.7, pp.1325-1360

Wang M.T., Tsai M.S., Liu C., Tseng W.T., Chang T.C., Chen L.J., Cheng M.C. (1997). Effects of corrosion environments on the surface finishing of copper chemical mechanical polishing. Thin Solid Films, Vol.308, pp.518-522

Warshawsky D., Barkley W., Miller M.L., Ladow K., Andringa A. (1994) Carcinogenicity of 7H-dibenzo[c,g]carbazole, dibenz[a,j]acridine and benzo[a]pyrene in mouse skin and liver following topical application. Toxicology, Vol.93, No.2-3, pp.135-149.

Warshawsky D., Livingston G.K., Fonounifard M., Ladow K. (1995). Induction of micronuclei and sister-chromatid exchanges by polycyclic and N-heterocyclic aromatic hydrocarbons in cultured human lymphocytes. Environmental and Molecular

Mutagenesis, Vol.26, No.2, pp.109-118.

Watson M.R., Stone W.B., Okoniewski J.C. Smith L.M. (1985). Tranactions of the Northeast Section of the Wildlife Society, 1985 northeast Fish and Wildlife Conference "Conflict and Communications in Natural Resource Management", May 508, 1985, Hartford, Connecticut.

Weistrand C., Noren K., Nilsson A. (1997). Organochlorine compounds in blood plasma from potentially exposed workers. Environmental Science and Pollution Research, Vol.4, Nr.1, pp.2-9

Williams G.M., Weisburger J.H. (1986). Chemical carcinogens. In Toxicology: the basic science of poisons. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 99-173.

Zhao F., Mayura K., Hutchinson R.W., Lewis R.P., Burghardt R.C., Phillips T.D. (1995).Developmental toxicity and structure-activity relationships of chlorophenols using human embryonic palatal mesenchymal cells. Toxicology Letters, Vol.78, No.1, pp.35-42.