# SEVERE HEAVY METAL AND PAH CONTAMINATION IN BILBAO, NORTHERN SPAIN

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### INTRODUCTION

Bilbao is an industrialised city on the Northern coast of the Basque region of Spain (see fig 1) with a population of approximately 1 million. It has been an important port in the region for many years, heavy industry having been present since the turn of the century. Because of the many ferrous mines in the area, trade in heavy metals through the port has been significant in the twentieth century. The Ria del Nervion, the estrary of the Bilbao river (Ria de Bilbao) which flows through Bilbao (see figs 1 & 2) receives wastes from these industries as well as the more recent industries which include chemical manufacturing, a coal fired power station, upriver pulp and paper mills and boat building. The inner harbour area, El Abra, has a marina complex at its eastern side and a dockyard on the west. Because of the presence of these industries some pollution of the river and surrounding area is likely but very little work has been done to assess the extent and type of contamination in the area. The harbour of Bilbao at Santurce is well protected from onshore winds by an inner and outer harbour wall system. Therefore the area within the inner harbour is a relatively low energy area where fine silts accumulate. Hence the main river channel is regularly dredged to a depth of 6 metres with the dredgings being dumped offshore in the Cantabrian Sea. There is no specified or designated dumpsite for these dredgings. Previous studies have shown elevated levels of heavy metals in sediments, water and biota in the outer harbour and beyond (Perez et al 1988 and Gobierno Vasco 1988) but to date no studies have been published which give levels for the Ria itself.

The treatment and recycling of metal wastes has become more prevalent in Bilbao in latter years. Several plants associated with this industry are situated on and discharge into the Rio Asúa which in turn discharges into the Ria del Nervion. (see fig 3)

Soil levels of heavy metals and organic pollutants have been shown to be elevated in the vicinity of smelters and metals reclamation plants. Martin and Coughtry (1987) document a case of heavy metal contamination from a smelter in Avonmouth, U.K. and there are numerous other examples (Asami 1985, Riss et al 1988, Blake et al 1987 and Buchauer 1973).

The area around Bilbao including the Asúa valley is used extensively for forestry and agriculture and many inhabitants grow their own crops on whatever land is available. Bilbao is situated in a valley, therefore air emissions will have a tendency to be wet deposited into the catchment of the Ria del Nervion and the adjacent sea area. This study investigates heavy metal levels in soils from the Asúa valley and in sediments from Rio Asúa and Ria del Nervion.

There are a number of uncontrolled hazardous waste dumps in the vicinity of Bilbao. Villanueva et al 1991 in their recent study of one such dump found strong contamination of nearby aquifers by polynuclear aromatic hydrocarbons (PAHs). PAHs are of increasing concern as environmental pollutants and as human toxins. Epidemiological studies of some occupation-associated skin cancers in humans provide strong presumptive evidence of the role of PAH in certain kinds of cancers (Fawell & Hunt 1988). Some PAHs have been shown to be mutagens and carcinogens in various laboratory experiments (Hawkins et al 1990, Rice 1989, Payne & Fancey 1989) and this has prompted many studies of the

distribution of these hydrocarbons in the environment (Marcus et al 1988, Al-Saad & Al-Timari 1989, Kayal & Connell 1989 and Villanueva et al 1991). This study investigates PAHs in the sediments of Rio Asúa and the length of Ria del Nervion.

### SAMPLING AND ANALYSIS

An extensive sediment sampling programme was carried out on the Ria del Nervion in November 1990 (sites illustrated in figs 1 & 2). Samples were obtained from the length of the river between the city centre and the inner harbour wall. The location of these samples is shown in the figures and the samples are numbered 1-23. The sediments of the outer harbour were not investigated in this study as this has already been sampled and reported on (Gobierno Vasco 1988). Rio Asúa and the valley through which it passes (fig 3) was also investigated because of the adjacent scrap metal recovery plants. Surface sediment samples were obtained from the river as were a limited number of soil samples from the valley. Sediment samples from Rio Asúa were labelled A1-A4 and the soil samples denoted with a letter.

Sediment samples were obtained using a 15x15x17cm Ekman grab operated from a small vessel on the Ria del Nervion. Sediments in Rio Asúa were obtained with a pipe dredge operated from the river bank. Soils were collected from the surface 3-4cms. The sediments were collected in polypropylene bottles which were kept chilled during transport to the analysing laboratories. All samples were analysed for heavy metal content at Queen Mary and Westfield College, London. A range of seven metals was investigated, these being Cu, Cd, Cr, Pb, Ni, Zn & Ag. Polynuclear aromatic hydrocarbons (PAHs) and hexachlorobenzene were investigated in some of the sediments by Clayton Environmental Consult ants, Birmingham.

## Heavy metals

All soils and sediments were oven-dried and their moisture content thereby determined. The sediments were qualitatively examined for sand/shell/clay content. While analytical measurements of particle size distribution would have been preferable, this method of macroscopic rating of sediment composition was justified since the only intent was to separate sand/shell-dominant samples from clay-dominant samples. In fact all of the sediments in this study were dominated by clay. Soils were sieved through a 2mm stainless steel sieve, the retained portion being discarded. Preparation of the sample digests was by microwave digestion in a CEM MDS2000 sample preparation system. Approximately 1 gram of sample was weighed accurately into an acid washed teflon sample vessel and 20mls of 1:1 nitric acid:double distilled water added. The samples were microwaved at full power for one hour and pressure controlled to a maximum of 150psi. Duplicate samples were analysed for each sampling location and an average value thus obtained.

A blank and a sample of PACS-1 marine sediment was included in each sample run of twelve individual sealed teflon vessels. This reference material is certified by the National Research Council of Canada for six of the metals investigated in this study.

Nitric acid was used for the digestion although this method does not produce a complete digestion of the sediment as it has been shown by Pavoni et al (1987) to be satisfactory in determining heavy metal concentrations for environmental investigations. The remaining metals are more firmly bound to the mineral matrix of the sediment and therefore less bioavailable. Analysis was by Thermoelectron IL157 AAS calibrated against known standards and background corrected for all the metals except Cr. The results are shown as table 1 for sediments and table 3 for soils.

### PAHs and hexachlorobenzene.

About 5 grams of sample was accurately weighed into a vial and 15ml of distilled water added. The sample was extracted with 1ml of toluene to which internal standards of deuterated naphthalene, acenaphthene, phenanthrene, chrysene and perylene at 40 micrograms per litre had been added. Samples were extracted by vigorous shaking followed by centrifuging. 1 microlitre of supernatent was taken for GC/MS using a 12M BP-1 column, film 1 micron, from 100 o C to 310 o C at 10 o C/min and then held for 4 minutes. Column effluent was monitored by low resolution mass spectrometry from m/z 120 to m/z 300. From suitable standards, retention times and relative response factors were calculated. Quantification was by internal standard method, with the required peaks being monitored at the molecular ion (normally the base ion for each compound of inter est). The results are shown as table 5.

# THE ASÚA VALLEY

Severe point source contamination of the Rio Asúa by heavy metals and PAHs has obviously occurred. Levels of these contaminants in sediments are lowest (with the exception of Chromium in sample A1) upriver of samples A2 and A3 (tables 1 & 5). The fine surface sediments of the Rio Asúa are likely to be highly mobile in periods of heavy rainfall. The scouring action of the swollen river would remove most of these sediments, preventing accumulation over many years. Even if the sediments were immobile, it would take a considerable period of time for the metals under investigation to accumulate to the concentrations found at points A2, A3 and A4 if they were being discharged at low levels from industrial sources. The most likely explanation is that the heavy metals found at A2 and downstream thereof were discharged over a fairly short time period prior to sampling in November 1990.

Soil levels of Cd, Pb, Cu and Zn exceed levels above which, in the Netherlands, a soil clean-up would be required (see tables 3 & 4). The levels found in the Asúa valley are consistent with a prolonged regular input of heavy metals into the environment from the adjacent metals industries, the most likely route into the soil being that of atmospheric deposition. The levels of the heavy metals investigated in this study, with the exception of chromium, are well above those occurring naturally in soils (see table 5) The only possible explanation for these high levels at Asúa is anthropogenic input.

Several sources of PAH contamination are suggested by the results. Naphthalene and fluorene were found in significant quantities downriver of sample A1. Benzo[a]pyrene

(BaP), fluoranthene, pyrene, benz[a]anthracene, chrysene and benzo(k&a)fluoranthenes were found to be elevated downriver of sample A2. The total PAH loading of sample A3 is comparable to that found in the contaminated estuary of Brisbane (see table 6). Netherlands standard soil levels, although not directly comparable to sediment levels, would suggest that a further investigation is needed in the Rio Asúa. BaP and total PAH levels in samples A3 and A4 are particularly noteworthy.

### RIA DEL NERVION

In general the heavy metals levels in the Ria del Nervion are much elevated, with different metals predominating in different parts of the river system. Silver and chromium levels are elevated in samples 1-3. There are exceptionally high lead levels in samples 12-16. In Canal de Deusto sample 6 shows elevated levels of all metals analysed in this study.

Heavy metal levels in Ria del Nervion exceed that of dredged material from Rotterdam and Hamburg harbours (see table 2). Most of the sediments sampled in Bilbao are highly contaminated and probably compare with Rotterdam's Class 4 dredgings. The majority of Rotterdam dredgings are considered to be too polluted to dump in the sea or to spread on agricultural land and are therefore treated as toxic waste by the Netherlands authorities (Nijssen 1988). The dredgings are grouped into four classes according to contaminant levels. Class 4 waste, being the most polluted, is disposed of in a specially designed and lined site. The long term policy for these dredgings is to reduce pollutant loading of the sediments from source so that Class 4 waste is no longer produced. Hamburg dredgings are disposed of in upland sites.

Several sources of PAH contamination are suggested by the results; these represent very high concentrations in comparison to surface sediments from different geographical regions (Kayall & Connell 1989). The total PAH loading of several samples exceed that found in the contaminated estuary of Brisbane (see table 6). The high level of naphthalene and other PAHs in sample 11 at the mouth of the Rio Galindo suggests a point source upriver.

### DISCUSSION

### Metals

Cadmium levels in the soil and sediments of the Rio Asúa are unusually high. Elevated Cadmium levels in soils are a cause for concern as this metal is easily mobilised into crops. Cadmium does not occur freely in nature and there are no specific ores from which it is mined. The soil levels of cadmium and other metals indicate that there has been a large amount of atmospheric deposition in the valley probably arising from the metals recycling facilities. Cadmium is of concern to human health and has been demonstrated to have several adverse effects. It has been shown to cause an increased number of deaths due to chronic bronchitis and lung cancer in cadmium exposed workers (Kazantzis 1990) a problem which may be confounded by cigarette smoking (because of

the high absorption of cadmium from tobacco) and exposure to other potential carcinogens in the workplace, in particular arsenic, nickel, asbestos and PAHs. Occupational exposures are almost invariably multiple, and such exposures may act in an additive, synergistic, or in an antagonistic manner. Other workers have reported effects of cadmium inhalation on male rat reproductive systems, effects observed were loss of libido, lowered sperm count and total sterility. Some other recorded effects of exposure to cadmium in laboratory animals include renal tubular damage, placental and testicular necrosis, structural and functional liver damage, osteomalacia, testicular tumours, teratogenic malformations, anaemia, hypertension, pulmonary oedema, chronic pulmonary emphysema and induced deficiencies of iron, copper and zinc. Some of these effects have also been observed in humans after accidental exposures to cadmium oxide fumes (Ragan & Mast 1990). In work on kidney damage to seabirds and mice, nephrotoxic lesions were found in individuals contaminated with cadmium and mercury at levels considered as relatively safe for humans by the World Health Organisation (Nicholson et al 1983).

High levels of lead were found in the soils of Asúa and sediments of Rio Asúa and Ria del Nervion. Lead in soil is not generally as available to plants as is cadmium, but at high levels there is some translocation of lead to plants. Lead poisoning causes derangement of the central nervous system, gastrointestinal tract, muscular coordination and red blood cell synthesis (in Neathery & Miller 1975). Generally lead enters the body through the gastrointestinal and respiratory tracts and occasionally through the skin.

The levels of nickel found in the soil around Asúa were not exceptionally high but the low recovery of this metal from the PACS-1 standard used may mean that this study is under-reporting these levels. The nickel level in Rio Asúa sediments however is a cause for concern. Many aspects of the ill-effect on human health caused by nickel in its various forms have been studied. Nickel-containing dusts are carcinogenic in humans where roasting of nickel subsulphide at high temperatures occurs (Morgan 1989). Nickel and nickel compounds have been classified as human carcinogens by IARC. Nickel also causes contact dermatitis.

Zinc and copper are also elevated in all soils and sediments analysed in this study, exceptionally so in the sediments of Rio Asúa. Elevated levels of mercury would be expected in the environment of the Asúa valley as they are often associated with high levels of zinc. Zinc minerals and wastes often contain a high concentration of mercury. Mercury was not investigated in this study. A further investigation into levels of this EEC regulated metal in this area and that of Bilbao as a whole would be desirable in the future.

Chromium and silver are elevated in sediments of Ria del Nervion which were sampled adjacent to the city centre. Hexavalent chromium possesses carcinogenic properties and silver has been shown in laboratory experiments to be one of the most toxic elements to microorganisms and biochemical processes in the soil (Jones et al 1990).

## **Organic Chemicals**

The levels and distribution of PAHs found in this study indicate several diverse sources of pollution. The elevated levels of benzo[a]pyrene, benz[a]anthracene and dibenz[a,h]anthracene are of concern because these compounds are known to be carcinogenic (Williams and Weisburger 1986). Benzo[a]pyrene is also a mutagen (Thilly & Call 1986), is reported to alter fertility after prenatal exposure (Dixon 1986) and to depress immune responses (Dean et al 1986). Other PAHs have been shown to exhibit similar effects. Exceptionally high levels of naphthalene were found at the mouth of the Rio Galindo. Villannueva et al in their study of uncontrolled hazardous waste dumps in the catchment of Rio Galindo also found elevated levels of PAHs in core samples from the dumps and in groundwater. However the level of naphthalene found in this study is higher than that found in these dumps and indicates that there are probably other sources. In comparison to standards adopted in the Netherlands for soil levels of PAHs the levels found in the sediments of Bilbao warrant further investigation, the extremely high level of naphthalene in sample 11 is of particular concern. Naphthalene has been shown to cause cataracts and is retinotoxic (Potts et al 1986).

The highly toxic polychlorinated dibenzo-p-dioxins and dibenzofurans are almost certainly being emitted by the metals reclamation plants in Asúa. Heavy metals, particularly copper, catalyse reactions which have these substances as an end product (Gullet et al 1990) and the presence of plastics in metals wastes results in greater production of dioxins and furans. Several researchers have reported elevated levels of these substances in the vicinity of such plants. Riss et al 1988 report elevated levels in soil, grass, cow's milk, human blood and spruce needles in the vicinity of a metals reclamation plant. The plastics present in this operation caused increased emissions. Oehme et al 1989 report on the formation of PCDFs and PCDDs by production processes for magnesium and nickel. Antonsson et al 1989 and Tysklind et al 1989 report scrap metal processing in steel mills to be a significant source of these substances.

### **Health Effects**

A study by Neuberger et al 1990 on health problems at a heavy metal mining site subject to government clean-up found statistically significant, or borderline excess, reported prevalence of chronic kidney disease, heart disease, skin cancer and anaemia. Also found was a statistically significant excess of deaths from hypertensive disease, ischemic heart disease and stroke. The environmental exposures included lead and cadmium in drinking water, mine wastes and surface soils.

A 188 page report has been published under a World Health Organisation's Healthy Cities Programme, on the health conditions in the towns on the left bank of the Bilbao estuary. This shows that tumourous diseases affect the population in a significantly higher proportion than the average population of the autonomous Basque country as a whole (Dirección de Salud Publica Gobierno Vasco 1990, hereafter referred to as the Bilbao left bank report). The report establishes cancer as the first cause of death among men and as the second among women. The study links the cases of cancer that are cause of death to the conditions of the environment at the work sites and to environmental

conditions. It is likely that the health of the local population of Asúa and of the rest of Bilbao is being adversely affected in a similar manner to that indicated in these reports. An investigation into occupational exposure within the industries at Asúa would be desirable. There are likely to be several routes of exposure to the cocktail of chemicals being released into the environment of Bilbao and Asúa and a variety of health effects.

One such route is by inhalation and ingestion of polluted aerosols. Sediment samples obtained from near the centre of Bilbao (samples 1-3) were anoxic, with bubbles of gas carrying portions of sediment to the surface to produce black circles on the surface. Heavy metals and PAHs have been shown to accumulate in the sea surface microlayer (Hardy 1982) and aerosols of seawater may contain enriched levels of toxins (Blanchard 1989). Therefore aerosols produced by turbulence in the river and by bubbles rising to the surface from anaerobic sediments are likely to contain enriched levels of heavy metals and PAHs. This combined with enriched levels of bacteria and viruses from any existing sewage pollution may present a major health hazard to inhabitants of Bilbao.

### CONCLUSION

From the results of this study it is clear that the city and environs of Bilbao are suffering a high level of pollution due to insufficient regulation of industrial inputs into the environment. Soil and sediment levels of heavy metals in the Asúa valley are exceptionally high. There is an obvious health risk from these pollutants and it is clear from the Bilbao left bank report that a substantial proportion of the local population is suffering ill effects. The presence of many uncontrolled waste dumping sites is of great concern because these represent a source of contaminants entering the environment in an unpredictable manner. The ground water in the area is already polluted by PAHs and this pollution is likely to continue unless remedial action is taken urgently.

It is clear that there is substantial variation in sediment and soil contamination levels, indicative of point source discharges. However the overall level of contamination is alarmingly high. A comprehensive audit of pollutants and their method of entry into the Bilbao environment is required in order to implement a progressive control and protection programme. There is an obvious need for investigations into the health status of workers in the industrial sectors of Bilbao.

Effects on the wider ecosystem warrant further investigation. Bird populations are just one component of the both terrestrial and marine ecosystems that are likely to be adversely affected. No studies have been published on the effects of the dumping of dredge spoils into the Cantabrian Sea or of levels of pollutants in fish caught in this area.

The practise of dumping dredgings from the river into the Cantabrian Sea is clearly not acceptable as long as the pollutant loadings in the sediment remain so high. Many industries discharge directly into harbours and estuaries only for their waste to be dumped at sea adsorbed onto the fine sediment in dredging spoils. This gives industry a back door route to cheap and easy waste removal and provides no incentive for waste reduction. Industrial pollutants therefore continue to accumulate in the marine environment. Adopting the precautionary principle and implementing clean production would eventually solve this problem. Meanwhile the dredging spoils from Bilbao should be treated as toxic waste.

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### REFERENCES

Al-Saad, H.T. & Al-Timari, A.A. (1989) Distribution of polycyclic aromatic hydrocarbons (PAH's) in marsh sediments Iraq. Bull. Environ. Contam. Toxicol. 43: 864-869.

Antonsson, A.-B., Runmark, S., Mowrer, J. (1989) Dioxins in the work environment in steel mills. Chemosphere 19(1-6): 699-704

Asami, T. (1985) Soil pollution by metals from mining and smelting in Chemistry & Biology of Solid Waste. Ed. Salomons, W & Rorstner Pub. by Springer-Verlag.

Blake, P., Chamberlain, C.S., Chambers, D., Clarke, B. & Mendham, J. (1987) Heavy metal contamination near scrap metal yards and car breakers yards. Sci. Total Environ. 59: 9-18

Blanchard, D.C. (1989) The ejection of drops from the sea and their enrichment with bacteria and other materials: a review. Estuaries 12(3): 127-137.

Bridges, E.M. (1989) Polluted and contaminated soils. In: Annual report 1989, international soil reference and information centre. Wageningen - The Netherlands.

Brown, S.S. & Kodama, Y. (1987) Toxicology of metals. Publ. Ellis Horwood. pp. 448.

Buchauer, M.J. (1973) Contamination of soil and vegetation near a zinc smelter by Zinc, Cadmium, Copper, and Lead. Env. Sci. Technol. 7(2): 131-135

Dean, J.H., Murray, M.J. & Ward, E.C. (1986) Toxic responses of the immune system. Chapter 9. Casarett and Doull's toxicology ed. Klaassen, C.D., Amdur, M.O. & Doull, J. pub. Macmillan pp. 974

Dirección de Salud Publica Gobierno Vasco. (1990) Ciudades saludables: margen Izquierda, Departmento de Sanidad y Consumo, Dirección de Salud Publica Gobierno Vasco, Servicio Central de Publicaciones. First edition, November 1990.

Dixon, R.L. (1986) Toxic responses of the reproductive system. Chapter 16. Casarett and Doull's toxicology ed. Klaassen, C.D., Amdur, M.O. & Doull, J. pub. Macmillan pp. 974

Driel, van W, & Nijssen, J.P.J. (1988) Development of dredged material disposal sites: implications for soil, flora and food quality. Chapter in: Salomons, W. & Forstner, U. (eds.) Chemistry and biology of solid waste. Publ. Springer-Verlag. pp. 305.

Fawell, J.K. & Hunt, S. (1988) Environmental Toxicology, organic pollutants. Pub. Ellis Horwood. pp. 440

Gobierno Vasco (1988) Tratamiento conjunto de aguas residuales urbanas e industriales. Limites de inhibición de los procesos biologicos. pp. 24. In: Control de la contminación en origin en la industria de galvotecnia. Seminar 1987. Pub. Gobierno Vasco.

Gullett, B.K., Bruce, K.R. & Beach, L.O. Formation of chlorinated organics during solid waste combustion. Waste Management and Research 8: 203-214.

Hardy, J.T. (1982) The sea surface microlayer: biology, chemistry and anthropogenic enrichment. Prog. Oceanog. 11: 307-328.

Hawkins, W.E., Walker, W.W., Overstreet, R.M., Lytle, J.S. & Lytle, T.F. (1990) Carcinogenic effects of some polycyclic aromatic hydrocarbons on the Japanese medaka and guppy in waterborne exposures. Sci. Tot. Environ. 94:155-167.

Jones, D.C., Lepp, N.W. & Obbard, J.P. (1990) Other metals and metalloids. Chapter 13, Heavy Metals in soils. ed. Alloway, B.J., pub. Blackie. pp.339

Kayal, S.I. & Connell, D.W. (1989) Occurrence and distribution of Polycyclic aromatic hydrocarbons in surface sediments and water from the Brisbane river estuary, Australia. Est. Coast. Shelf. Sci. 29: 473-487.

Kazantzis, G. (1990) The mortality of cadmium exposed workers. Toxicol. Environ. Chem. 27: 113-122

Marcus, J.M., Swearingen, G.R., Williams, A.D. & Heizer, D.D. (1988) Polynuclear aromatic hydrocarbons and heavy metal concentrations in sediments at coastal South Carolina Marinas. Arch. Environ. Contam. Toxicol. 17: 103-113.

Martin, M.H. & Coughtrey, P.J. (1987) Cycling and fate of heavy metal transfers following application of sewage sludge. p. 319-336 in: Pollutant transport and fate in ecosystems. eds. Coughtrey, P.J., Martin, M.H. & Unsworth, M.H. pub. Blackwell Scientific pp. 414

Moen, J.E.T., Cornet, J.P., and Evers, C.W.A. (1986) Soil protection and remedial actions: criteria for decision making and standardization of requirements. p. 441-448 in: Contaminated Soil eds. Assink, J.W. & Van den Brink, W.J. Martinus Nijhoff, Dordrecht.

Morgan, L.G. (1989) Nickel toxicology. Environ. Geochem. & Health 11(3/4): 75-75.

Neathery, M.W. & Miller, W.J. Metabolism and toxicity of Cadmium, Mercury, & Lead in animals: A review. J. Dairy Sci. 58(12): 1767-1781

Neuberger, J.S., Mulhall, M., Pomatto, M.C., Sheverbush, J. & Hassanein, R.S. (1990) Health problems in Galena, Kansas: a Heavy metal mining superfund site. Sci. Total Environ. 94: 261-272.

Nicholson, J. K., Kendall, M.D. & Osborn, D. (1983) Cadmium and mercury nephrotoxicity. Nature 304: 633-635.

Nijssen, J.P.J. (1988) Rotterdam dredged material: approach to handling. Chapter in: Salomons, W. & Forstner, U. (eds.) Environ mental Management of solid waste. Publ. Springer-Verlag. pp. 396

Oehme, M., Mano, S. & Bjerke, B. (1989) Formation of polychlorinated dibenzofurans and dibenzo-p-dioxins by production processes for magnesium and refined nickel. Chemosphere 18(7/8): 1379-1389

Pavoni, B., Donazzolo, R. & Marcomini, A. (1977) A comparison between two analytical methods for the determination of copper, cobalt, nickel, cadmium, lead, zinc, iron and chromium in marine sediments. Annali di Chemica 77:551-562.

Payne, J.F. & Fancey, L.F. (1989) Effect of aromatic hydrocarbons on immune responses in fish: change in melanomacrophage centers in flounder (Pseudopleuronectes americanus) exposed to hydrocarbon-contaminated sediments. Marine Environ. Res. 28: 431-435.

Perez, J.G., Puente, C.R. & Sancho, A.J. (1988) Estudio de metales pesados en aguas y sedimentos superficiales en las costas Cantabrica y Gallega. Informes Tecnicos instituto español de oceanografía. Ministerio de agricultura, pesca y alimentación No. 64

Potts, A.M. (1986) Toxic responses of the eye. Chapter 17. Casarett and Doull's toxicology ed. Klaassen, C.D., Amdur, M.O. & Doull, J. pub. Macmillan pp. 974

Ragan, H.A. & Mast, T.J. (1990) Cadmium inhalation and male reproductive toxicity. Rev. Environ. Contam. Toxicol. 114: 1-22.

Rice, J.M., Kovatch, R.M. & Anderson, L.M. (1989) Intraperitoneal mesotheliomas induces in mice by a polycyclic aromatic hydrocarbon. J. Toxicol. Environ. Health. 27:153-160.

Riss, A., Hagenmaier, H., Weberuss, U., Schlatter, C. & Wacker, R. (1988) Comparison of PCDD/PCDF levels in soil, grass, cow's milk, human blood and spruce needles in an area of PCDD/PCDF contamination through emissions from a metal reclamation plant. Poster presented at DIOXIN 88, Umea, Sweden.

Thilly, W.G. & Call, K.M. (1986) Genetic toxicology. Chapter 6. Casarett and Doull's toxicology ed. Klaassen, C.D., Amdur, M.O. & Doull, J. pub. Macmillan pp. 974

Tysklind, M., Soderstrom, G. & Rappe, C. (1989) PCDD and PCDF emissions from scrap metal melting processes at a steel mill. Chemosphere 19(1-6): 705-710

Villanueva, J., Rosell, A. & Grimalt, J.O. (1991). Chemical characterisation of polycyclic aromatic hydrocarbon mixtures in uncontrolled hazardous waste dumps. Chemosphere 22(3-4): 317-326.

Williams, G.M. & Weisburger, J.H. (1986) Chemical Carcinogens, Chapter 5. Casarett and Doull's toxicology ed. Klaassen, C.D., Amdur, M.O. & Doull, J. pub. Macmillan pp. 974



TABLE 1

HEAVY METALS IN SEDIMENTS FROM RIA DE BILBAO AND RIO ASUA

[mg/kg dry weight]

Sample	e Cd	Pb	Cu	Ag	Zn	Cr	Ni
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 A1	5.89 10.4 10.4 0.25 3.71 53.6 7.98 28.8 13.4 38.8 10.3 114 37.9 73.0 63.6 18.8 11.7 4.64 25.6 17.0 6.92 35.8 39.7 1.42	267 298 275 62.4 143 876 184 683 371 623 211 1800 1310 1060 885 1390 759 444 511 412 377 399 538 106	342 372 244 85.1 117 562 171 450 300 537 328 1990 965 916 667 501 542 257 441 309 211 417 467 132	5.29 5.42 7.31 <0.20 0.81 3.63 0.94 1.27 0.79 1.74 0.50 2.73 1.21 1.19 0.96 0.79 1.07 0.74 0.97 0.76 0.67 1.14 2.01 0.46	2180 2430 1600 424 678 5260 978 1850 1480 2720 1330 5160 3680 3140 3370 1850 1910 1070 1500 1170 1280 2020 2660 477	924 782 157 23.1 13.8 340 166 128 179 136 145 315 244 194 211 166 199 111 176 134 91.0 207 152 1006	60.0 57.8 33.8 20.4 28.1 61.8 28.9 41.3 31.1 22.2 35.3 52.0 46.6 29.5 29.5 19.5 14.3 21.7 17.3 15.8 28.5 240
A2 A3 A4	304 139 142	7590 2273 1600	11400 1460 1070	<0.20 1.10 <0.20	19100 5490 2380	606 524 100	$\begin{array}{r} 781 \\ 139 \\ 33.4 \end{array}$
mean S.D.	45.1 64.1	942 1415	936 2100	1.61	2860 3460	275 257	71.7
I	percenta	age recov	ery of	PACS-1 r	eference	sediment	
	68.4	79.3	80.6	n/a	79.7	61.9	51.6

Figures  $\underline{\text{underlined}}$  indicate maximum levels found in this study S.D.= standard deviation

TABLE 2
HEAVY METALS IN SEDIMENTS FROM OTHER HARBOURS COMPARED TO BILBAO

	Rotterdam#	Hamburg\$*	Background* level	Bilbao mean	
	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	
Pb	80-240	268	30	942	
Cd	3-13	9	0.3	45.1	
Cr	97-187	90	73	275	
Cu	39-142	237	20	936	
Ni	24-63	45	26	71.7	
Zn	256-1079	1238	76	2860	

<sup>#</sup> figures are for 1984 dredged material, here the heavy metals have been extrapolated to a 50% fraction smaller than 16 micrometres. [Nijssen (1988)]

<sup>\$</sup> concentration in dredged material disposal site

<sup>\* [</sup>Driel & Nijssen (1988)]

TABLE 3

HEAVY METALS IN SOILS FROM THE ASUA VALLEY

[mg/kg dry weight]

Sample	Cd	Pb	Cu	Ag	Zn	Cr	Ni
A	4.09	283#	240#	0.96	590#	64.3	23.3
В	7.68#	377#	241#	n/d	1110#	30.1	27.7
C	2.43	459#	238#	n/d	685#	51.1	29.6
D	1.28	89.0	71.7	n/d	426	55.9	18.7
E	20.1*	696*	537*	n/d	1470#	113	47.5
F G	12.0#	304#	331#	n/d	1130#	73.5	33.5
	24.8*	1520*	1200*	n/d	3720*	98.1	63.9
H	48.8*	1930*	2460*	n/d	3610*	148	91.4
I	4.71	323#	288#	0.95	644#	58.4	27.1
average	14.0	665	624	<0.4	1490	77.0	40.3
S.D.	14.5	595	721	n/a	1200	34.5	22.3

Figures underlined indicate maximum levels found in this study.

TABLE 4
STANDARDS ADOPTED IN THE NETHERLANDS FOR SOIL CONTAMINANTS
Concentration in soil (mg/kg dry weight)

METAL	Α	В	C	background
Cr	100	250	800	5 <b>-</b> 500
Ni	50	100	500	5 - 500
Cu	50	100	500	2 - 100
Zn	200	500	3000	10 - 300
Cd	1	5	20	0.01 - 1.0
Pb	50	150	600	2 - 200

A = reference value

<sup>#</sup> corresponds to level B of the standards adopted in the Netherlands for soil contaminants.

 $<sup>^{\</sup>star}$  corresponds to level C of the standards adopted in the Netherlands for soil contaminants. (SEE BELOW)

B = value above which there is a need for further investigation

C = value above which a clean-up is required (Moen et al 1986)
= range of heavy metals in uncontaminated soils (Bridges 1989)

TABLE 5

PAHS IN SEDIMENT FROM RIA DE BILBAO AND RIO ASUA

PAHS mg/kg dry weight

	1	4	6	11	13	16	17	19	22	A1	A2	A3	A4
NAPHTHALENE	<0.12	<0.04	<0.19	418	1.26	0.12	0.19	<0.06	<0.06	<0.04	1.30	0.46	<0.04
ACENAPHTHYLENE	<0.12	<0.04	0.28	2.00	0.41	0.26	0.17	0.14	0.12	<0.04	0.05	0.25	0.14
ACENAPHTHENE	<0.12	<0.04	<0.19	5.74	<0.07	<0.05	<0.06	<0.06	<0.06	<0.04	0.10	0.14	<0.04
LUORENE	<0.12	<0.04	<0.19	8.20	0.33	0.21	0.06	0.06	0.06	<0.04	1.40	0.35	<0.04
HENANTHRENE	0.12	<0.04	1.03	17.8	1.59	1.75	0.31	0.48	0.26	0.04	1.05	1.24	0.36
NTHRACENE	<0.12	<0.04	1.12	4.65	1.37	1.27	0.31	0.43	0.35	<0.04	0.17	0.74	0.40
LUORANTHENE	0.18	0.04	4.94	6.01	3.47	5.19	1.09	1.45	0.99	0.06	0.83	3.50	1.63
YRENE	0.12	0.04	3.54	3.28	2.62	4.01	0.92	1.08	0.81	0.04	0.76	2.76	1.59
BENZ[A]ANTHRACENE	<0.12	<0.04	2.52	1.67	3.21	3.54	0.47	1.45	0.81	<0.04	0.54	2.23	1.36
HRYSENE	<0.12	<0.04	3.08	1.86	2.88	2.24	0.78	1.14	1.14	<0.04	0.17	3.11	1.32
BENZO[B]FLUORANTHENE}	<0.12	0.04	3.17	1.18	6.65	5.19	1.28	2.67	2.81	<0.04	1.03	2.16	2.53
BENZO[K]FLUORANTHENE}													
BENZO[A]PYRENE	<0.12	<0.04	2.05	0.27	4.06	4.01	0.97	1.84	2.31	<0.04	0.64	1.49	1.99
NDENO[123,CD]PYRENE	<0.30	<0.07	<0.47	<0.14	0.92	1.35	<0.14	0.17	0.23	<0.10	<0.12	<0.18	0.23
DIBENZ[A,H]ANTHRACENE	<0.30	<0.07	<0.47	<0.14	0.18	0.52	<0.14	<0.14	<0.15	<0.10	<0.12	<0.18	<0.09
BENZO[GHI]PERYLENE	<0.30	<0.07	<0.47	<0.14	1.59	1.44	<0.14	0.14	0.15	<0.10	<0.12	<0.18	0.42
TOTAL PAHs	0.42	0.12	21.7	470	30.5	31.2	6.55	11.1	9.99	0.10	8.04	18.4	12.0
MOISTURE CONTENT %	83.4	27.5	89.3	63.4	72.9	57.6	64.1	64.8	65.8	51.4	59.2	71.7	44.8

Figures <u>underlined</u> indicate maximum levels found in this study

TABLE 6
COMPARATIVE LEVELS OF PAHS
mg/kg dry weight

Bris	sbane sediment a	Soil st A	andards B	С
NAPHTHALENE	0.16	0.1	5	50
ACENAPHTHENE FLUORENE PHENANTHRENE ANTHRACENE	0.07 0.33 1.49 0.39	0.1	10 10	100 100
FLUORANTHENE PYRENE BENZ[A]ANTHRACENE	2.34 2.26 0.89	0.1	10	100
CHRYSENE BENZO[A]PYRENE INDENO[123,CD]PYRENE	0.97 1.06	0.05	1	10
DIBENZ[A,H]ANTHRACENI BENZO[GHI]PERYLENE				
TOTAL PAHS	16.11	1	20	200

a Mean concentration of PAHs in surface sediment samples from the Brisbane River estuary. Kayal & Connell 1989.

# STANDARDS ADOPTED IN THE NETHERLANDS FOR SOIL CONTAMINANTS

A = reference value

 ${\tt B}$  = value above which there is a need for further investigation

C = value above which a clean-up is required (Moen et al 1986)



