

REPORT ON ARSENIC, COPPER AND ZINC IN COPPERHOUSE
POOL AND OTHER SITES IN HAYLE, CORNWALL.

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DISCLAIMER.

This report has been produced using the best information available to the author. Due to time constraints it has not been possible to complete a thorough survey of all relevant information which may be in existence at the time of writing. The main conclusions have been discussed with Professor Peter Evans of the University of Durham. Specialist advice in compiling the report has been received from Dr David Taylor of ICI Brixham, and Dr Alan Howard of the Chemistry Department, University of Southampton. Whilst the report is as up to date as possible, metal analyses and toxicity are rapidly expanding research fields, and most scientific papers and commissioned reports point to important gaps in our understanding of these topics.

This report concentrates on three elements which have high concentrations in Hayle compared with the rest of the UK (except some other parts of Cornwall). It is possible that as yet un-identified pollutants may be present in significant quantities.

Despite these reservations, I believe that the report will be sufficient for policy decisions regarding Copperhouse Pool, but it must be remembered that legislation may be either relaxed or made more stringent.

Legal advice should be obtained on the responsibilities of the developer in the special circumstances of Copperhouse Pool and the other developments at Hayle. I strongly advise that when final development proposals are prepared they should be accompanied by a report on the contaminated land issues and how they will be addressed. This report should be available to all interested parties.

1. EXECUTIVE SUMMARY.

From an initial study of metals in the sediments of Copper-house Pool in September 1988^ it was decided that arsenic, copper and zinc warranted a detailed investigation. Concern was focused on the arsenic concentrations, not only because of the high concentrations but also due to potential public misconceptions regarding arsenic.

ARSENIC.

Dissolved arsenic concentrations in the water of Copperhouse Pool range from 3.1 ug/l at the sluice gates at high water (ie diluted by seawater) to approximately 180 ug/l (high or low water) in Mill Leat at Black Road Bridge. These compare with an Environmental Quality Standard (EQS) of 25 ug/l for the protection of saltwater species, and a standard of 500 ug/l for bathing. The standard for bathing is in terms of total arsenic ('dissolved' plus particulate), but from the limited data available on particulate arsenic obtained by Southampton University at Hayle, I would expect the maximum total arsenic concentration in Copperhouse Pool to be approximately 195 ug/l at Black Road Bridge under the conditions at the time of sampling.

All of the 6 water samples from the canal (Angarrack River) in Copperhouse Pool were within the Environmental Quality Standard for protection of saltwater species (25 ug/l); but only 2 of the 6 water samples from the stream through Copperhouse Pool (Mill Leat) were within this standard. Highest arsenic concentrations within Mill Leat occurred during low water, when there was little dilution of the freshwater by seawater. If necessary this problem could probably be solved by preventing the most contaminated water from entering Mill Leat. At this stage it is thought that the main source of arsenic is probably adit mine drainage near Treeve Farm.

From the limited data available on arsenic concentrations in water I would expect Copperhouse Pool to be within the EQS for arsenic in bathing waters. Other sites around Hayle have much lower arsenic concentrations, and are likely to be within the EQS for saltwater species and bathing waters under all naturally occurring conditions. Operations such as dredging may of course mobilise arsenic and other metals from the sediments, resulting in higher concentrations in the water column.

Arsenic concentrations in the sediments of Copperhouse Pool were exceptionally high, ranging from 48 - 3830 ug/g in the 0 -10 cm layer, and 45 - 3400 ug/g in the 50 cm deep layer. There were often considerable differences between the arsenic concentrations in the 0-10 cm layer compared with the 50 cm deep layer, but there was no consistent increase or decrease 'with depth. The mean concentration of the 0-10 cm layer was 893 ug/g, compared with 846 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average arsenic concentration similar to that of the present surface.

The 'action trigger' concentration for arsenic in soils of redevelopment sites has not been determined yet; a decision is expected from the Department

of the Environment in spring 1989. It seems likely that the 'action trigger' concentration will be set quite high, possibly several hundred ug/g. Large tracts of Copperhouse Pool may therefore lie within this trigger level, and may not need to be removed. Other areas will almost certainly exceed the trigger level, and may need removal and/or treatment. The various options will need to be discussed with a consultancy specialising in land restoration and waste disposal/treatment. It should be noted that many garden soils in and around Hayle contain arsenic concentrations comparable with those of Copperhouse Pool. It also seems probable that the playing fields adjacent to the eastern edge of the saltmarsh contain very high concentrations of arsenic.

Calculations indicate that under the worst possible scenario 5.8 g of sediment would have to be ingested by a child of 2-3 years to give a fatal dose. Approximately 0.5 g of sediment would have to be ingested daily for periods of several days or more to give chronic arsenic poisoning. This is 5 times greater than the theoretical amount that could be eaten inadvertently by a child through eating dirty sweets, licking fingers etc.

Arsenic concentrations in the sediments at Lelant Water, Carnsew, Penpol Dock and the mouth of the estuary are much lower than those in Copperhouse Pool, and are in the normal range for estuaries in the most mineralised areas of Cornwall and Devon.

Arsenic concentrations in fish and shellfish caught off the coast near Hayle are unlikely to cause any health problems. This is because the sea rapidly dilutes the water from the Hayle estuary to concentrations which are only slightly above background concentrations. In addition, the form of arsenic in fish and shellfish (crabs, lobsters, prawns) is arsenobetaine, which is known to be of low toxicity and readily excreted by man.

COPPER.

Data from the survey by Berridge Environmental Laboratories suggest that copper concentrations in Copperhouse Pool are likely to be above the EQS for protection of saltwater species but below the EQS for bathing and contact. Unfortunately the data were virtually all less than the detection limit of 30 ug/l, so there is no information on the pattern of copper concentrations within Copperhouse Pool. It seems very likely that the highest concentrations in the water will occur at the freshwater end, especially in Mill Leat near Black Bridge at low water.

The low data produced by Berridge's are surprising and could be misleading. I believe that dissolved copper in Copperhouse Pool may be in the range 300 -400 ug/l, but this would need to be confirmed by further analyses. It is also possible that total copper concentrations may be above the EQS for bathing of 500 ug/l.

Copper concentrations in the sediments of Copperhouse Pool were exceptionally high, ranging from 108 - 9315 ug/g in the 0 -10 cm layer, and 30 - 4090 ug/g in the 50 - 150 cm deep layer. There were often considerable differences between the copper concentrations in the 0-10 cm layer compared with the 50

cm deep layer, but there was no consistent increase or decrease with depth. The mean concentration of the 0-10 cm layer was 1260 ug/g, compared with 1170 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average copper concentration similar to that of the present surface.

The maximum concentrations of copper in the sediments of Copperhouse Pool are higher than any other sediments analysed in the UK. However, due to the prompt emetic action of ingested copper it is unlikely that chronic or acute poisoning could occur through ingesting the sediment. The estimated quantity of sediment required to produce a lethal dose due to copper alone is over 300 g, well above the amount that could be ingested deliberately in a single incident.

ZINC.

Data from the survey by Berridge Environmental Laboratories suggest that zinc concentrations in Copperhouse Pool are likely to be within the EQS for protection of saltwater life, and well within the EQS for bathing and contact. Unfortunately the data were all below the detection limit of 30 ug/l, so there is no information on the pattern of zinc concentrations within Copperhouse Pool. It seems probable that the highest concentrations will occur at the freshwater end (Black Road) due to the inputs from the canal (Angarrack) and Mill Leat.

The low data produced by Berridge's are surprising and may be misleading. I believe that dissolved zinc in Copperhouse Pool may be in the range 200 - 300 ug/l; but this would need to be confirmed by further analyses. Even if the data are too low it seems highly likely that concentrations of zinc are below the EQS for bathing of 50,000 ug/l.

Zinc concentrations in the sediments of Copperhouse Pool range from 64 - 2880 ug/l in the 0 - 10 cm deep layer, and 150 - 3125 ug/g in the 50 - 150 cm deep layer. There were often considerable differences between the zinc concentrations in the 0-10 cm layer compared with the 50 cm deep layer, but there was no consistent increase or decrease with depth. The mean concentration of the 0-10 cm layer was 1020 ug/g, compared with 1120 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average zinc concentration similar to that of the present surface.

The highest concentrations of zinc are comparable with the most contaminated estuaries (eg Restronguet Creek in Cornwall) and the most contaminated dredge spoils (eg from the Tees estuary).

No data were available to me on the amounts of zinc required to produce chronic or acute poisoning. In view of the high concentrations of zinc in many molluscs and shellfish (eg up to 440 ug/g in mussels and 800 ug/g in whelks on a dry weight basis) the health risk from zinc in Copperhouse Pool sediments is probably insignificant.

2. INTRODUCTION.

This report was commissioned because of concerns about the high concentrations of arsenic, copper and zinc in Copperhouse Pool relative to many other estuarine sites in the UK. In order to determine the significance of the initial findings of high concentrations of these metals in surface sediments from Copperhouse Pool it was necessary to undertake a detailed sampling programme of metals in the sediments and water at Copperhouse Pool. This sampling was carried out by Berridge Environmental Laboratories from 25 - 27th October 1988. Due to the considerable differences between the toxicities of the various forms of arsenic that can occur in water a special study of arsenic was undertaken on 16th November 1988 by Dr Alan Howard of Southampton University, an acknowledged expert in arsenic speciation.

The main findings from these surveys are included in this report, but the original reports should be referred to for details.

This report attempts to put the results of these surveys into context, using data from other UK estuaries; legal limits and guidelines for metals; and calculations of the amounts of sediment that would have to be ingested to produce chronic or acute poisoning.

3. METAL ANALYSIS, SPECIATION AND TOXICITY.

Metals are analysed in a variety of environmental media, the most common subdivisions are water, sediments, air, and biota. Reasons for analysis include:

1. Monitoring of compliance with discharge consents
2. Monitoring of compliance with guidelines and legislation on metal concentrations in water, soils and biota
3. Scientific research on the behaviour of metals in water, sediments and biota.

Many fundamental questions relating to monitoring of metals in the environment have not been resolved yet. There are particular problems associated with determining whether to analyse the total amount of a metal present in say a water sample, or to analyse the filterable and non-filterable metal content. The filterable metal content is often referred to as dissolved, but it includes colloidal and dissolved metal.

There are further complicating factors, for example a particular metal may be present in different valencies and either as the free ion or in association with other ions or ligands. Complexation or chelation of by organic ligands nearly always reduces toxicity, and it appears that toxicity usually correlates best with the free metal ion concentration (Hunt, 1987)

Our understanding of the behaviour and toxicity of metals in the environment is still insufficient to be able to either predict or accurately analyse all of the various species that may be present, even for a single metal. For this reason most of the legislation and guidelines are in terms of the total amount of a metal. In the longer term it seems inevitable that these standards will have to become more sophisticated.

Arsenic is the 20th most abundant element in the earth's crust, with an average concentration of 3 - 5 ug/g (ppm) (Mance et al, 1984). The most commonly occurring ore is arsenopyrite (FeSAs), and it is in this form that most of the arsenic is present in the rocks of the mineralised areas of Cornwall. Arsenic compounds have been used as pigments and poisons for thousands of years, and more recently have been used as treatments and tonics for a variety of ailments. Most of the arsenic compounds used in medicine have been replaced by antibiotics.

Arsenic is a semi-metal (or metalloid) element in Group VB of the Periodic Table. In order of increasing atomic weight (and increasing metallic character) this group contains nitrogen, phosphorus, arsenic, antimony and bismuth. The chemistry of arsenic has many similarities with that of phosphorus and antimony, and antimony is often found associated with deposits of arsenic. Similarities between the phosphate ion and arsenate ion are probably responsible for many of the biological interactions of arsenate.

The valency states (number of bonds that the element can form) are -3, 0, +3, and +5. The -3 oxidation state and 0 oxidation state (ie pure metal) are extremely rare in natural conditions. This report therefore considers the valency states +3 and +5.

Arsenic III oxide is the most important arsenic compound in terms of industrial production, and is used to manufacture other arsenic compounds. These various compounds are used as pesticides, herbicides, wood preservatives, and in the manufacture of glass, ceramics, semiconductors and dyestuffs. Arsenic is also used in certain alloys to increase strength and hardness (World Health Organisation, 1986). In the UK the main use for arsenic is in wood preservatives (Mance et al, 1984). In 1975 the annual production of arsenic was 60,000 tonnes (WHO, 1986) and most of this was eventually deliberately released into the environment as pesticides, herbicides and wood preservatives.

Until the mid-nineteenth century arsenopyrite was regarded as a waste material from the copper and tin mines of Cornwall and Devon. Large quantities of arsenic-rich spoil were dumped in the vicinity of copper and tin mines. By 1870 arsenopyrite was regarded as a useful by-product, which found uses in medicines, insecticides and glass-making (Aston et al, 1975). Material from old arsenic-rich tips and newly mined arsenopyrite were roasted to obtain a crude form of arsenic III oxide (Aston et al, 1975).

There are several potential sources of arsenic in water, sediments and soils around Hayle:

1. Arsenic-rich spoil tips in the catchment basins of the tributaries.
2. Drainage from old adit mines.
3. Leaching from particles of arsenopyrite ore that may be present in the sediments of tributaries, Copperhouse Pool and Lelant Water.
4. Leaching from the blocks of foundry slag (scoria blocks) that were used in many buildings and walls in Hayle.
5. Previous atmospheric deposition from copper smelting (believed to have ended in 1820).
6. Previous atmospheric deposition from the iron foundries.
7. Previous atmospheric deposition from the tin smelter established at Angarrack in 1704 (Pascoe, 1981).
8. Previous atmospheric deposition from the coal-fired power station.
9. Sewage discharges.

The contributions from sources 8 and 9 are probably in-significant compared with the other sources, and will not be considered further.

Although part of the high concentrations in soils around Hayle could be due to natural weathering of underlying arsenic-rich rocks, it seems likely that atmospheric fall-out from the copper and tin smelters and the iron foundries was also an important source.

4.1 ARSENIC IN WATER.

4.1.1 Chemistry.

Arsenic undergoes a variety of chemical and biochemical reactions in water. The cycling of arsenic in freshwaters has been reviewed by Ferguson and Davis (1982). They estimated that human activities such as mining, burning of fossil fuels, and deliberate release of arsenic compounds has increased the amount of arsenic entering the oceans by at least a factor of three. In some locations the increase will be far higher.

The chemistry of arsenic in estuarine waters has been studied by several authors (Crecelius et al, 1975; Penrose et al, 1975; Waslenchuk and Windom, 1978; Howard et al, 1984; Knox et al, 1984; Howard et al, 1988) and there appear to be considerable differences between estuaries. This is partly due to variations in resuspension of sediments and in the amount of organic material present in the water column.

In some estuaries arsenic behaves conservatively, ie the concentration is simply a function of dilution by seawater (Waslenchuk and Windom, 1978).

Other studies have shown removal of arsenic during estuarine mixing (Howard, et al 1984) and strong seasonal variations in the appearance of arsenic (III) and methylated arsenic species (Howard et al, 1982).

Most detailed studies of arsenic in UK estuaries have shown that it can be present in the waters as arsenate ions, arsenite ions, monomethylarsonic acid and dimethylarsinic acid. It is generally thought that the methylated forms are produced by biomethylation, as they are usually only found in reasonable amounts during the summer months (Howard et al, 1982; Howard et al 1984). Arsenic (III) ions (eg arsenite) mainly occur under mildly reducing conditions and low pH, they are readily oxidised to arsenic (V) ions (eg arsenate) in estuarine waters. To complicate matters further, it has been shown that microorganisms can reduce arsenate to arsenite, and oxidize arsenite to arsenate.



4.1.2 Analytical results from Hayle compared with other sites in the UK.

The most detailed and recent data on arsenic concentrations in water are from the survey by Southampton University on 16th November 1988. Results for dissolved arsenic showed that approximately 10-20% was in the form of arsenite. Methylated arsenic species were below the detection limit, and probably comprised less than 5% of the dissolved arsenic. This result for methylated arsenic is not unexpected considering the time of year that the samples were taken. Methylation is generally believed to be primarily due to biological activity, and is greatest in the summer months.

Typical background concentrations of dissolved arsenic in rivers outside metalliferous zones are about 0.1 - 1.0 ug/l. Uncontaminated seawater has a very similar range, 0.2 - 1.2 ug/l. These figures compare with a range of 1.7 - 185 ug/l for the recent survey of the Hayle area by Southampton University. Aston et al (1975) reported that arsenic concentrations (presumably total arsenic) in the streams of the metalliferous areas of south west England ranged from 10 - >250 ug/l. Freshwater entering Restronguet Creek (a tributary of the River Fal in Cornwall) contained 33 - 209 ug/l (Langston, 1983). Restronguet Creek is widely regarded as one of the most contaminated estuaries in the UK, due to the metalliferous bedrock and mining activities. A survey of arsenic in UK estuaries was carried out by the Water Research Centre in from autumn 1981 to spring 1982 (Mance et al, 1984b). At most sites only dissolved arsenic was analysed. Results for the River Hayle at Carnsew Point were 12 - 13 ug/l, which compares very well with the results of 4.1 ug/l (high water) and 12.2 (low water) for a similar location in the study by Southampton University (1988). Dissolved arsenic concentrations at various sites are summarised in Table 1.

TABLE 1. CONCENTRATIONS OF DISSOLVED ARSENIC IN WATER.

	ug/litre		
Background cone, in rivers	0.1	-	1.0
Background cone, in seas	0.2	-	1.2
Copperhouse Canal (low water)	11.9	-	24.5 (Southampton University, 1988)
Copperhouse Canal (high water)	3.1	-	17.3 (Southampton University, 1988)
Copperhouse stream(low water)	114	-	169 (Southampton University, 1988)
Copperhouse stream(high water)	4.5	-	185 (Southampton University, 1988)
River Angarrack	11.5	-	17.3 (Southampton University, 1988)
Lelant Water at Carnsew Point	12	-	
Lelant Water (low water) Lelant	10.7	-	13 (Mance et al, 1984b)
Water (high water) Carnsew Pool	4.1	-	12.2 (Southampton University, 1988)
(low water) Carnsew Pool (high	3.9		(Southampton University, 1988)
water) River Hayle at St Erth	2.9		5.3 (Southampton University, 1988)
River Hayle at St Erth	8		3.8 (Southampton University, 1988)
		-	10 (Mance et al, 1984b)
Penpol Dock LW	4.2		5.7 (Southampton University, 1988)
Mouth of the Hayle estuary LW	8.2		
		HW	6.8 (Southampton University, 1988)
Restronguet Creek	3	HW	3.1 (Southampton University, 1988)
Restronguet Creek	1.8	-	
Freshwater entering Restronguet	33	-	28 (Mance et al, 1984b)
Red River at Gwithian Towans	12	-	42.1 (Klumpp and Peterson, 1979)
		-	209 (Langston, 1983)
Mersey (freshwater) Severn estuary	2	-	40 (Mance et al, 1984b)
Thames estuary			
			3 (Mance et al, 1984b)
			5 (Mance et al, 1984b)
			3 (Mance et al, 1984b)

Within Copperhouse Pool the highest concentrations of dissolved arsenic occurred in the stream (Mill Leat), where values of up to 185 ug/l were recorded. This compares with a maximum of 24.5 ug/l in the canal (Angarrack River). The course of Mill Leat upstream from Copperhouse Pool is rather complex (John Brown, pers. comm.). It rises in Trevarnon Moor then passes through Treeve Farm, where it picks up the flows from 3 adit mines. Further downstream it picks up adit mine drainage from the Boiling Well mine, which used to produce copper, lead zinc and silver (Dines, 1956). I understand that one of the adits from Boiling Well mine was also used as a land drain for the old dynamite works and munitions factory. Apparently there is a landfill site within the dynamite factory where waste was buried in the 1920s. Mill Leat then runs alongside Logans Road, and is joined by some of the flow from the Angarrack through a culvert at the location of the old grain mill (NE corner of the crossroads). Thereafter it flows past the nursery and then underground to the saltmarshes adjacent to Copperhouse Pool. It seems probable that most of the arsenic in Mill Leat comes from the adit mine drainage, but there are no data to confirm this. If there is a landfill site at the old dynamite

factory this may be producing a leachate containing chemicals for which we have not analysed. In my opinion this requires immediate attention.

In addition to arsenic concentrations in Mill Leat and the Canal, it is also helpful to determine the total amounts of arsenic entering from these two sources. Unfortunately this requires knowledge of flow rates and the arsenic concentrations under a variety of flows. Due to the higher flow rate of the Canal compared with Mill Leat it is certainly possible that the two inputs contribute a similar amount of arsenic to Copperhouse Pool.

4.1.3 Human health implications.

The relevant Environmental Quality Standards (EQS) for arsenic are shown in Table 2.

TABLE 2. SELECTED ENVIRONMENTAL QUALITY STANDARDS FOR ARSENIC.

USE	AVERAGE CONCENTRATION (ug/l)	95 PERCENT I LE CONCENTRATION (ug/l)	TOTAL OR DISSOLVED
Drinking water			
Treatment category A1		50*	TOTAL
A2		50*	TOTAL
A3		100*	TOTAL
Protection of salt- water life	25*		DISSOLVED
Bathing and contact		500 (note 1)	TOTAL

Notes: * Indicates a mandatory value (Department of the Environment Circular 18/85).

1. The standard for bathing water is based on the assumption that no more than one-tenth of the water consumed by an individual is likely to be accidentally swallowed during bathing or contact water sports. For most individuals the consumption of water by this route would be negligible.

Unlike mercury, where the methylated forms are more toxic than other mercury compounds, methylated arsenic is thought to be significantly less toxic than either arsenate or arsenite. Methylated forms of arsenic will be highest during the summer months as they are believed to be produced by bacteria and algae. At low concentrations of arsenic in the water they may form a significant proportion of dissolved total arsenic. In the River Beaulieu, Hampshire, methylated arsenic species accounted for up to 70% of dissolved arsenic, but were only found during summer months when the water temperature exceeded approximately 12 C (Howard et al, 1984). This compares with a maximum for methylated arsenic species of 36% in the River Tamar (Howard et al, 1988) which receives drainage from a metalliferous mining area, and may therefore be more similar to Copperhouse. During the summer months the proportion of arsenic present in methylated forms in the Tamar was about 15% of the total dissolved arsenic (Howard et al, 1988); this is probably a reasonable estimate of the methylated arsenic species in Copperhouse Pool during the summer.

The presence of methylated arsenic species may reduce the toxicity of the water in Copperhouse Pool in the summer months, but it is probably safer to assume that all of the arsenic is present as inorganic arsenic. This was the situation during the survey by Southampton University on 16 November 1988, when only arsenic (III) and arsenic (V) were detectable. Within Copperhouse Pool arsenic (III) comprised less than 25% of the dissolved arsenic during the survey (Southampton University, 1988).

Most of the analytical results from Southampton University are for dissolved arsenic in water, but three samples were also analysed for arsenic associated with suspended solids. This was not felt to be essential for all samples because of the low concentration of suspended solids in Copperhouse Pool and other areas. Total arsenic in water can be estimated by adding together the dissolved and particulate results. These are shown in Table 3.

 TABLE 3. CONCENTRATIONS OF DISSOLVED, PARTICULATE AND TOTAL ARSENIC IN THREE WATER SAMPLES OBTAINED ON 16 NOVEMBER 1988.

SITE	DISSOLVED ARSENIC (ug/l)	PARTICULATE ARSENIC (ug/l)	TOTAL ARSENIC (ug/l)	PERCENT DISSOLVED.
Copperhouse Pool Mill Leat. Site 5. Low water.	146	9.96	156	93.6
Copperhouse Pool Mill Leat. Site 5. High water.	7.4	0.44	7.8	94.9
Carnsew Pool at NE end. Site 11. Low water.	3.9	0.16	4.1	95.1

These results show that under the conditions at the time of sampling (neap tides therefore low energy and low concentrations of suspended solids) approximately 95% of the arsenic in the water is present in the dissolved form. Assuming that this percentage would be similar for other samples obtained during the survey on 16 November 1988, the highest total arsenic concentration can be estimated at 195 ug/l. This is well within the EQS for bathing and contact of 500 ug/l. However, it is unwise to place too much emphasis on spot samples of water quality.

Outside Copperhouse Pool the water quality in terms of arsenic should not present any problems under any naturally occurring conditions, but could potentially be adversely affected by disturbance of the sediments through dredging etc.

4.2 ARSENIC IN SEDIMENTS.

4.2.1 Chemistry.

Arsenic in sediments is present in a variety of forms, as mineral ore particles such as arsenopyrite, associated with iron and manganese oxides, and bound to clay particles and organic matter. In some estuaries arsenic in the water is readily precipitated with iron at the freshwater-seawater interface (Langston, 1983) and is retained by estuarine sediments. Other studies have shown very little removal of arsenic from water during estuarine mixing. In surface sediments which are well oxidised most of the arsenic will be present as arsenic (V), the less toxic form. In anaerobic (reducing) sediments the proportion of arsenic (III) will increase.

4.2.2 Analytical results from Hayle compared with other sites in the UK.

Results for arsenic concentrations in the soils and sediments of the Hayle area compared with other sites in the UK are shown in Table 4.

Arsenic concentrations in the sediments of Copperhouse Pool were exceptionally high, ranging from 48 - 3830 ug/g in the 0 -10 cm layer, and 45 - 3400 ug/g in the 50 cm deep layer. There were often considerable differences between the arsenic concentrations in the 0-10 cm layer compared with the 50 cm deep layer, but there was no consistent increase or decrease with depth. The mean concentration of the 0-10 cm layer was 893 ug/g, compared with 846 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average arsenic concentration similar to that of the present surface. I have not had time to consider the implications of removal of 1 metre or more of sediment, but would assume that more detailed data on arsenic concentrations below 1 metre will need to be collected.

TABLE 4. TOTAL ARSENIC IN SEDIMENTS (ug/g dry weight)

* = extractable by 6 molar HCl at 60 C for 4 hours

Background concentrations:

1. River sediments in SW England (unmineralised areas) <5 - 30 (Aston et al, 1975)
2. Estuarine sediments 3 - 20 (Various sources)

Lelant Water 550 (Langston, 1980)

Lelant Water 108 - 144* (Southampton University, 1988) 56 - 140* (Southampton University, 1988)

Penpol Dock Copperhouse Pool 93* (Southampton University, 1988)
 Copperhouse Pool (excl. canal) 410 950 (Langston, 1980) 1065 (Berridge Env. Labs., 1988a) 3830 (Berridge Env. Labs., 1988b) 3400 (Berridge Env. Labs., 1988b)

Copperhouse Pool (0-10 cm deep) 48 780* (Southampton University, 1988)

Copperhouse Pool (50 cm deep) 45 1030* (Southampton University, 1988)

Copperhouse Canal 172

Copperhouse stream (Mill Leat) 338

Mouth of the Hayle estuary Hayle (garden soils) 119 - 1130 (Grainger, 1988) versity, 1988)

Restronguet Creek (Fal) 12 - 2500 (Langston, 1980) 1975)
 90 ->5000 (Thornton et al, 1975)

Restronguet Creek 11 - 230 (Langston, 1980)

Gannel 42 - 131 (Langston, 1980)

Tamar, Tavy, Lynher 7 16 (Langston, 1980)

Loe 41 43 (Langston, 1980)

Plym 13 (Langston, 1980)

Avon (Devon) 12 74 (Langston, 1980)

Teign 7 12 (Langston, 1980)

Severn and Bristol Channel 5 28 (Langston, 1980)

Southampton Water 4 6 (Langston, 1980)

Thames 18 94 (Langston, 1980)

Humber 2 11 (Langston, 1980)

NW England (Morecambe Bay, Lune, Wyre, Ribble) 3 - 24 (Langston, 1980)

S Wales (Cleddau, Taf, Tywi, Gwendraeth, Loughor, Swansea Bay, Neath)

4.2.3 Human health implications.

The most relevant advisory limits for arsenic in soils are the ICRCCL (Interdepartmental Committee on the Redevelopment of Contaminated Land) Guidance Notes. The latest available edition (July 1987) only suggests tentative limits, and unfortunately only the threshold concentration has been determined so far. Results below the threshold concentration indicate that the site is uncontaminated with regard to that pollutant. Results above the action concentration (yet to be defined) show that remedial action will be required. In between the threshold and action concentrations is a grey area where expert advice will be necessary to determine the appropriate course of action. The threshold concentrations are shown below, neither of them are strictly applicable to the intertidal mudflats at Copperhouse.

ICRCCL Threshold Concentrations for Arsenic (ug/g air-dried soil)

Domestic gardens and allotments	10
Parks, playing fields and open space	40

Whilst the action concentrations have yet to be defined, it seems very likely that they will be below the maximum concentrations at Copperhouse and some other sites in Hayle. The Department of the Environment expect to publish a new edition of the Guidance Notes in spring/summer 1989. The new edition is being prepared by Professor Thornton from Imperial College, London. Professor Thornton has indicated (pers. comm.) that the Action Concentrations would have to be set at several hundred ug/g, due to the mineralised areas in Devon and Cornwall.

From the concentrations of arsenic in the sediments at Copperhouse Pool it is possible to calculate the amount of sediment that would have to be eaten to obtain a lethal dose. It is usual in this type of work to consider the maximum concentrations that have been recorded during a survey, rather than the mean or median concentration. All of the analytical results for the sediments are in terms of total arsenic per gram of dry sediment. It is likely that most of the arsenic will be in the less toxic arsenate form rather than arsenite. Under reducing (anaerobic) conditions it is possible that arsenite could be more prevalent. The worst possible scenario is that the ingested sediment is the most highly contaminated and all of the arsenic is present as arsenite.

The highest concentration of arsenic in Copperhouse Pool during the present study was 3830 ug/g in the 0 - 10 cm deep layer on transect 2, 60 metres out from the seawall on the NW side (Berridge Environmental Laboratories, 1988). In terms of wet sediment this would be approximately equal to 2500 ug/g (assuming approximately 35% water content of surface sediments). An ingested dose of 70-180 mg of arsenic (III) oxide has been reported to be fatal in man (WHO, 1981). Taking the lower figure of 70 mg (equivalent to 70,000 ug) this would be contained in

$$\begin{array}{r} 70,000 \\ 2,590 \end{array} = 27 \text{ g of wet sediment from the most contaminated area.}$$

These fatal doses of 70-180 mg of arsenic (III) oxide may have been for adults, and it is preferable to consider the lethal dose in terms of mg of arsenic per kilogram of bodyweight. This figure has been calculated to range from 1 to 2.5 mg of arsenic per kilogram body weight in man (WHO, 1981). For a 15 kg child (2-3 years old) the lethal dose may be as low as 15 mg of trivalent arsenic. Assuming that all the arsenic in the sediments was present in the trivalent form, a lethal dose could be obtained from approximately 5.8 g of sediment from the most contaminated part of Copperhouse Pool.

Toxicity studies on various laboratory animals including rats and mice have shown that ingestion of 11 - 293 mg of arsenic (as arsenic (III) oxide) per kilogram of body weight is sufficient to kill half the test animals (WHO, 1981). The lower figure of 11 mg per kg is more than ten times the lower estimate for humans, and therefore gives a correspondingly higher estimate of the amount of sediment that would have to be ingested to give a lethal dose.

The lethal dose from a single ingestion is the crudest measure of toxicity, and it is necessary to calculate other indices. It is possible that children may ingest moderate quantities of soil/sediment on a regular basis, either due to poor hygiene or deliberate soil eating. In recent years it has been discovered that soil eating is practiced by a small percentage of adults in most continents. In addition, children may eat non-food items (Pica) and this is not restricted to the better known examples of paint eating. It has been estimated that young children may inadvertently ingest up to 0.1 g of soil per day from finger-sucking, eating dirty sweets etc (Professor Thornton, pers. comm). I do not have any data for the amounts of sediment that may be deliberately eaten, but this would probably be extremely unlikely to occur for the wet intertidal sediments. There appear to be no reports of children or adults deliberately eating intertidal sediments (pers comm Prof. Barltrop, Westminster Hospital) although geophagy (soil-eating) could be a potential problem for garden soils. Professor Barltrop also indicated that the figure of up to 0.1 g of soil per day ingested inadvertently may be an overestimate.

A large scale contamination of dried baby milk with arsenic in Japan affected 12,000 babies. The babies ingested an estimated 1.3 - 3.6 mg of arsenic per day, over a period of several days; 130 deaths were reported. Symptoms usually appeared after a few weeks of exposure, and often included fever, insomnia and anorexia. Taking the lower figure of 1.3 mg per day, this would be present in about 0.5 g of the most contaminated sediment in Copperhouse Pool. This is approximately 5 times the likely maximum that could be ingested inadvertently.

4.3 ARSENIC IN BIOTA.

Because of the high concentrations of arsenic in the water and sediments of Copperhouse Pool and other sites around Hayle it is worth considering whether there may be any potential health problems from eating locally caught fish and shellfish.

Crustaceans (eg crabs and lobsters) have naturally high concentrations of arsenic, up to 200 ug/g (MAFF, 1982). However, most of this arsenic is in the form of arsenobetaine, which is of lower toxicity and is readily excreted by man. Earlier investigations had noted that the arsenic in fish and shellfish was present in an unusual form, and it now seems likely that arsenobetaine was involved. Experiments using human volunteers suggest that > 90% of arsenobetaine is excreted within 24 hours, largely via urine.

The arsenic content of the water at the mouth of the Hayle estuary ranged from 3.1 - 8.2 ug/l during the survey on 16th November 1988. Whilst these are above the normal for UK estuaries, they would not be expected to cause a significant increase in the arsenic content of the nearshore coastal zone, due to the considerable dilution that they receive. The only potential problem from seafood would be if substantial quantities were obtained from Copperhouse Pool or Hayle estuary. Surveys of arsenic in the clam *Scrobicularia piana* (not usually considered a food item) showed that concentrations were highest in Restronguet Creek (190 ug/g) and Copperhouse Pool (Langston, 1980). It is worth noting that Restronguet Creek is used as a holding area for oysters, which are then sold for growing-on (Thornton et al, 1975).

Although organisms such as crabs and lobsters bioaccumulate arsenic, there is no evidence for biomagnification of arsenic through a food chain.

Concentrations of arsenic in the soils around Hayle are very high by national standards (119 - 1130 ug/g, Grainger, 1988) and this may represent a more important source of arsenic, since it is present in the inorganic form. This point has been considered by the Ministry of Agriculture, Fisheries and Food (1982) who concluded that the occasional high results for vegetables were due to surface contamination from soils containing high concentrations of arsenic. Most of this is probably removed during washing and preparation for eating. MAFF further stated 'More work needs to be done to assess the true intake from this source of arsenic in areas with high soil arsenic levels derived from natural or industrial sources'.

Copper is an essential element for plants and animals, and occurs at an average concentration of about 4.5 ug/g in the earth's crust (Mance et al, 1984a). It is widely distributed as sulphides, oxides, carbonates, arsenides and chlorides; it also occurs as the pure metal. In the mines of south west England the main copper ores were sulphides (chalcopyrite and chalcocite') (Dines, 1956).

Copper is a metallic transition element in Group IB of the Periodic Table. Silver and gold are also in this group; all three elements are moderately soft, very ductile and malleable, and excellent conductors of heat and electricity.

There are four potential valency states for copper, 0 (ie the pure metal) +1, +2 and +3. The +3 valency has no stable aqueous chemistry and does not appear to occur in soils or sediments, and it is therefore not considered in this report. Although pure copper metal can occur naturally it is unlikely to be important in the copper cycle of water and sediments.

Systematic mining for copper in south west England started in about the 16th century and remained on a small scale until the 18th century. Thereafter the copper mining industry flourished in Devon and Cornwall, and for the first half of the 19th century Devon and Cornwall produced 40% of world output. The peak was reached in about 1860 when approximately 15,500 tonnes of metal were produced annually (Dines, 1956). A rapid decline followed, and by the end of the 19th century the output was negligible.

Annual world production of copper is now approximately 8 million tonnes. It is used in various alloys with zinc, nickel and tin, in metal plating and in the production of copper wire and pipes. Copper compounds are used in a variety of manufacturing industries, eg copper nitrate in plating and textile dyeing, and copper chloride in glass, ceramics and as a catalyst in the production of vinyl chloride. Other examples of the use of copper compounds include insecticides (copper fluoroarsenate), fungicides (copper sulphate and copper naphthanate) and algicides (copper pentachlorophenate and copper dimethylgloxime).

Copper also has medicinal applications, for example intrauterine contraceptives, some types of dental cement, and other dental materials (Nriagu, 1979b).

5.1 COPPER IN WATER.

5.1.1 Chemistry.

Copper (II) is the normal oxidation state for soluble aqueous complexes; insoluble aqueous complexes of copper (I) are also quite stable. In general terms only copper (II) compounds are important in terms of the aqueous chemistry and toxicity of copper in natural waters (Nriagu, 1979a). As with most metals, it has proved impossible to date to analyse the concentrations

of the various copper compounds that are present in fresh and marine waters, so most studies of copper speciation have relied on predictive methods. Although there are significant differences between the various predictions, it seems likely that copper (II) ions, carbonates and hydroxides are the main species in seawater at a pH of 8 - 8.2. Copper (II) also forms strong complexes with organic matter.

Copper in freshwater with very low organic content is predominantly as copper (II) ions below pH 6.0, and as carbonate complexes in the pH range 6.0 - 9.3. The presence of organic ligands alters the equilibrium considerably, so that most of the copper becomes organically complexed (Mance et al, 1984a, quoting various other sources). A considerable proportion (20 - 90%) of the copper entering estuaries may be in particulate form. In the River Hayle approximately 70% of copper is present in particulate form (Brown, 1977). As this enters the freshwater/saltwater mixing zone the increase in ionic strength probably causes some desorption of copper associated with clays, organic compounds and hydrous metal oxides (Mance et al, 1984a). However, the increased ionic strength also leads to flocculation of colloids and particulates, so that the associated copper tends to get deposited in estuarine sediments.

5.1.2 Analytical results from Hayle compared with other sites in the UK.

Copper concentrations in Copperhouse Pool water and other sites in the UK are shown in Table 5.

TABLE 5. CONCENTRATIONS OF DISSOLVED COPPER IN WATER.

	ug/litre		
Background cone, in rivers	<1.0	-	20.0
Background cone, in coastal seas	0.2	-	0.6
	<30		
Copperhouse Pool		-	30 (Berridge Envir. Labs., 1988b)
River Hayle	1	-	450 (Brown, 1977) (Boyden et al,
Restronguet Creek	5	-	26 1979) (Mance et al, 1979a)
Restronguet Creek	2.1	-	21 (Thornton et al, 1975)
Restronguet Creek	17	-	130 (Thornton et al, 1975) (Klumpp
Carnon River	20	-	900 & Peterson, 1979) (Bryan et al,
Carnon River	32.5	-	396 1987) (Boyden et al, 1979)
Carnon River	370	-	973 (Thornton et al, 1975)
Helford estuary	2	6	5 (Mance et al, 1984a)
Helford estuary	6	-	20 6 (Abdullah & Royle,
Severn	0.4	3	1974)
Bristol Channel	0.6	4	(Mance et al, 1984a)
Mersey Liverpool	2	8	3.0 (Abdullah et al, 1972)
Bay	0.9	3	

5.1.3 Human health implications.

The relevant Environmental Quality Standards (EQS) for copper are shown in Table 6.

TABLE 6. SELECTED ENVIRONMENTAL QUALITY STANDARDS FOR COPPER.

USE	AVERAGE CONCENTRATION (ug/1)	95 PERCENTILE CONCENTRATION (ug/1)	TOTAL OR DISSOLVED
Drinking water			
Treatment category A1		20*	TOTAL
A2		50*	TOTAL
A3		1000*	TOTAL
Protection of salt- water life	5*		DISSOLVED
Bathing and contact		500 (note 1)	TOTAL

Notes: * Indicates a mandatory value (Department of the Environment Circular 18/85). 1. The standard for bathing water is based on the assumption that no more than one-tenth of the water consumed by an individual is likely to be accidentally swallowed during bathing or contact water sports. For most individuals the consumption of water by this route would be negligible.

It is regrettable that the detection limits for dissolved copper in water obtained by Berridge Environmental Laboratories were so high. Only one result was at the detection limit of 30 ug/1, all the others were below. These results are lower than I would have expected from Copperhouse Pool, but unfortunately there are no other data on copper for this site.

From the results produced by Berridge Environmental Laboratories it seems likely that the water in Copperhouse Pool may be above the EQS of 5 ug/1 for protection of saltwater life, but would be within the EQS for bathing of 500 ug/1 (total copper) for bathing and contact. Further water analyses are needed to confirm these opinions. Any further surveys should ensure that the detection limit for copper is less than 1 ug/1, and both dissolved and particulate copper should be analysed. A consultancy which is familiar with the problems of analysing metals in water should be used.

In my opinion the results from Berridge Environmental Laboratories are probably too low by a factor of at least 10, either due to unusual conditions during sampling, or analytical errors. If these results are atypical then it is possible that total copper in Copperhouse Pool may exceed the EQS for bathing of 500 ug/l. The survey of the River Hayle by Brown (1977) showed that total copper concentrations at the site nearest to the estuary could reach 400 ug/l. More detailed information for the Hayle estuary should be available from South West Water, and should be obtained as a priority.

5.2 COPPER IN SEDIMENTS.

5.2.1 Chemistry.

The most important sinks for copper in sediments and soils are probably iron and manganese oxides, organic matter, sulphides and carbonates (Jenne and Luoma, 1976). Copper usually remains in estuarine sediments after deposition but mechanical disturbance or very low salinity of the overlying water could cause some desorption. These factors are potentially important in Copperhouse Pool.

5.2.2 Analytical results from Hayle compared with other sites in the UK.

Concentrations of total copper in sediments at Copperhouse Pool and other sites in the UK are shown in Table 7.

TABLE 7. TOTAL COPPER IN SEDIMENTS (ug/g dry weight)

Background concentrations:		
1. River sediments (unmineralised areas)	5 - 30	
2. Estuarine sediments	6 - 20	(Nriagu, 1979a)
Copperhouse Pool 0- 10cm	108 - 9315	(Berridge Envir. Labs., 1988b)
Copperhouse Pool 50-150cm	30 - 4090	(Berridge Envir. Labs., 1988b)
River Hayle (freshwater)	100 - 4900	(Brown, 1977)
Restronguet Creek	360 - 4500	(Thornton et al, 1975)
Restronguet Creek Humber estuary Southampton Water	- 2540	(Bryan et al, 1980)
Welsh coast	51 - 160	(Jaffa & Walters, 1977)
Dredged spoil from various UK coastal sites	18 - 110	(Romeril, 1979)
	1.5- 30	(Packer et al, 1980)
	2 - 700	(Murray & Norton, 1979)

Copper concentrations in the sediments of Copperhouse Pool were exceptionally high, ranging from 108 - 9315 ug/g in the 0 -10 cm layer, and 30 - 4090 ug/g in the 50 - 150 cm deep layer. There were often considerable differences between the copper concentrations in the 0-10 cm layer compared with the 50 cm deep layer, but there was no consistent increase or decrease with depth. The mean concentration of the 0-10 cm layer was 1260 ug/g, compared with 1170 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average copper concentrations similar to that of the present surface.

5.2.3 Human health implications.

The most relevant advisory limit for copper in soils are the ICRL (Interdepartmental Committee on the Redevelopment of Contaminated Land) Guidance Notes. The latest available edition (July 1987) only suggests tentative limits, and unfortunately only the threshold concentration has been determined so far. Results below the threshold concentration indicate that the site is uncontaminated with regard to that pollutant. Results above the action concentration (yet to be defined) show that remedial action will be required. In between the threshold and action concentrations is a grey area where expert advice will be necessary to determine the appropriate course of action. It is important to note that the standards for zinc and copper have been set due to potential toxicity for plants, rather than human health reasons. The threshold concentration is shown below, but is not really applicable to the intertidal mudflats at Copperhouse.

ICRCL Threshold Concentration for Copper (ug/g air-dried soil) Any

uses where plants are to be grown 130

Whilst the action concentration has yet to be defined, it seems very likely that it will be well below the concentrations regularly encountered at Copperhouse and many other sites in Hayle. The Department of the Environment expect to publish a new edition of the Guidance Notes in spring/summer 1989.

Fatalities from copper poisoning are extremely rare due to the prompt emetic effect of copper compounds (Nriagu, 1979b). The only known cases appear to be from deliberate suicide attempts in India (Chuttani et al, 1965 quoted in Nriagu, 1979b), where several grams of a copper salt are ingested. No definite figures are available, so the following calculation assumes that 2g (2,000,000 ug) of copper are required to give a fatal dose. It also assumes that the highest concentration is 9315 ug/g dry weight, equivalent to 6055 ug/g on a wet weight basis.

$$\frac{2.000.000}{6,055} = 330 \text{ g of wet sediment from the most contaminated area.}$$

Assuming that 0.1 g of sediment per day could be eaten by a child inadvertently, there is a safety factor of at least 3300. In addition, 330 g of sediment is well above the amount that could be ingested deliberately in a single incident.

ZINC.

Zinc is an essential element for plants and animals, and occurs at an average concentration of approximately 65 ug/g in the earth's crust. The main naturally occurring forms of zinc are sulphides (eg sphalerite or zinc blende), silicates (eg hemimorphite) and carbonates (eg smithsonite and calamine) (Mance and Yates, 1984). In the mines of south west England the main zinc ores were sphalerites (also known as zinc blende and 'black jack') with smaller amounts of calamine and hemimorphite (Dines, 1956). In south west England zinc sulphides are usually associated with the lead ore galena (dines, 1956).

Zinc is a metallic transition element in Group I IB of the Periodic Table. Cadmium and mercury are also in this group. There are only two stable valency states for zinc, 0 (ie pure metal) and +2. Only the +2 valency is considered in this report, since zinc does not occur naturally in the elemental state.

Until the early part of the 19th century in south west England it was normal practice to discard zinc ores. These old dumps were re-worked for the remainder of the 19th century, with maximum amounts being produced from 1850 to 1885. Production continued in a small way, mainly from dumps, until 1911 (Dines, 1956). Of the total production of 85,000 tonnes of zinc from the south west, 75% was produced in the St Agnes region. In most mines around Hayle zinc was less important than tin and copper, but at the small mine called Trungle (near Gwinear, therefore drainage probably passing to the Angarrack) zinc ore was the main product (Dines, 1956).

In 1981 the non-communist production of zinc ore was 4.4 million tonnes, and consumption of refined zinc in the UK was 0.2 million tonnes (Mance and Yates, 1984). The main uses of zinc are for the production of alloys such as bronze and brass, and for galvanising and electro-plating processes. Other uses include manufacture of rayon and paper, and in the production of fungicides, paint and ceramics (Mance and Yates, 1984).

6.1 ZINC IN WATER.

6.1.1 Chemistry.

Zinc exists in the +2 oxidation state in water and may form complexes with ammonia, amines, halides, cyanides, as well as other inorganic and organic ligands (Mance and Yates, 1984). In the absence of complexing or adsorbing agents the zinc ion co-ordinates 6 water molecules to form an octahedral ion with a charge of +2.

The speciation of zinc in natural waters has been the subject of numerous models, and there is considerable disagreement between various authors. It seems likely that in freshwater the octahedral aquo ion predominates at low alkalinity with the bicarbonate complex becoming significant at high alkalinity at pH greater than 7. In freshwater zinc is the least complexed of all the transition elements. Most of the zinc transported by rivers is

dissolved (dissolved plus colloidal) rather than in particulate form. In the River Hayle approximately 80% of zinc is transported in the dissolved form (Brown, 1977). Above pH 6 zinc can be adsorbed by iron and manganese oxides, clays, and humic materials; and then be deposited in sediments by coprecipitation (Mance and Yates, 1984). Precipitation of zinc sulphides may also be important in the rivers around Hayle, as they presumably have high sulphide concentrations.

Under estuarine conditions the proportion of the aquo ion decreases and chloro complexes become increasingly important with increasing salinity; hydroxo and carbonate complexes form a minor proportion of the dissolved zinc (Mantoura et al, 1978). At very low salinities (less than 2 ppt) zinc may be desorbed from particulate forms, especially when oxidising conditions increase. In the salinity zone 2 - 10 ppt flocculation of colloids and particulate matter occurs, and zinc is partially removed from the water to be deposited in the sediments (Mance and Yates, 1984). In full strength seawater most of the zinc is present in the dissolved form.

6.1.2 Analytical results from Hayle compared with other sites in the UK.

Zinc concentrations in Copperhouse Pool water and other sites in the UK are shown in Table 8.

TABLE 8. CONCENTRATIONS OF DISSOLVED ZINC IN WATER.

	ug/litre		
Background conc, in rivers	1 - 60		(Mance & Yates, 1984)
Background conc, in seas	0.5- 10		(various sources)
North Sea	0.8- 16		(Mance & Yates, 1984)
Copperhouse Pool	< 30		(Berridge Envir. Labs.,
River Hayle (freshwater)	40 - 1800		(Brown, 1977) (Mance &
Red River (freshwater)	9 - 5500*		Yates, 1984) (Boyden et al,
Restronguet Creek	17 - 300		1979) (Klumpp & Peterson,
Restronguet Creek	13 - 305		1979) (Thornton et al,
Restronguet Creek	180 - 2200		1975) (Thornton et al,
Carnon River	200 - 9400		1975) (Bryan et al, 1987)
Carnon River	3630 - 57230		(Klumpp & Peterson, 1979)
Carnon River	3692 - 22000		(Boyden et al, 1979)
Helford estuary	7 27		(Thornton et al, 1975)
Helford estuary	4 97		(Abdullah & Royle, 1974)
Bristol Channel	3 43		(Ireland, 1973) (Ireland,
Cardigan Bay	40 - 88		1973)
Rivers Rheidol & Ystwyth (draining lead & zinc mining area in North Wales)	180 - 250		

* These data are for total zinc in water.

The analyses of water from Copperhouse Pool by Berridge Environmental Laboratories were all below the detection limit of 30 ug/l. There is therefore no information on the pattern of dissolved zinc within Copperhouse Pool. In view of the high concentrations of zinc in the sediments it is perhaps surprising "that" concentrations in the overlying water were below 30 ug/l. If the data are correct they suggest that present-day inputs of zinc to Copperhouse Pool from Mill Leat and the Angarrack River are slight, and that most of the zinc in the sediments is derived from the active mining period in the mid to late 19th century. Atmospheric inputs from smelter emissions may also have been significant.

In my opinion the zinc analyses for Copperhouse Pool are probably too low by a factor of 10 or more; possibly due to unusual sampling conditions or analytical errors. I would expect dissolved zinc in the freshwaters entering Copperhouse Pool to be in the range 200 - 300 ug/l, ie comparable with results from Restronguet Creek and the rivers Ystwyth and Rheidol (see Table 8). Dissolved zinc in the water of the River Hayle at the site nearest to Hayle estuary was approximately 400 - 500 ug/l in the study by Brown (1977). It would not be surprising if similar concentrations were found in Copperhouse Pool.

6.1.3 Human health implications.

Table 9 gives the relevant Environmental Quality Standards for zinc.

TABLE 9. SELECTED ENVIRONMENTAL QUALITY STANDARDS FOR ZINC.

USE	AVERAGE CONCENTRATION (ug/l)	95 PERCENTILE CONCENTRATION (ug/l)	MAXIMUM ALLOWABLE (ug/l)	TOTAL OR DISSOLVED
<hr/>				
Drinking water				
Treatment category A1		3000*		TOTAL
A2		5000*		TOTAL
A3			7500*	TOTAL
Protection of salt- water life	40*			DISSOLVED
Bathing and contact		50000 (note 1)		TOTAL

Notes: * Indicates a mandatory value (Department of the Environment Circular 18/85). 1. The standard for bathing water is based on the assumption that no more than one-tenth of the water consumed by an individual is likely to be accidentally swallowed during bathing or contact water sports. For most individuals the consumption of water by this route would be negligible.

All of the data on dissolved zinc concentrations produced by Berridge Environmental Laboratories were below the detection limit of 30 ug/l. This result was somewhat unexpected, but if it is correct it suggests that the water is probably within the EQS of 40 ug/l for the protection of saltwater life, and well within the EQS for bathing and contact. Even if the results for Copperhouse Pool were considerably higher than those obtained by Berridge's it is highly unlikely that they would exceed the EQS for bathing and contact.

6.2 ZINC IN SEDIMENTS.

6.2.1 Chemistry.

Most of the zinc in estuarine sediments is probably associated with iron and manganese oxides, clays and organic matter. The particle size distribution of the sediment usually has a marked effect on zinc concentrations. Total zinc concentrations in sediments increase in the order:
gravels < sands < muddy sands < muds (assuming all other factors such as pH, salinity and concentration of zinc in the overlying water are identical).

6.2.2 Analytical results from Hayle compared with other sites in the UK.

Concentrations of total zinc in sediments at Copperhouse Pool and other sites in the UK are shown in Table 10.

TABLE 10. TOTAL ZINC IN SEDIMENTS (ug/g dry weight)

Background concentrations:			
1. River sediments (unmineralised areas)	43 -	98	(Taylor, 1976)
2. Estuarine sediments	25 -	65	(Taylor, 1976)
Copperhouse Pool 0- 10cm	64 -	2880	(Berridge Envir. Labs., 1988b)
Copperhouse Pool 50-150cm	150 -	3125	(Berridge Envir. Labs., 1988b)
River Hayle (freshwater)	100 -	1600	(Brown, 1977)
Restronguet Creek	540 -	3000	(Thornton et al, 1975)
Restronguet Creek Humber estuary Southampton Water	-	3515	(Bryan et al, 1980)
Welsh coast	53 -	519	(Jaffe & Walters, 1977)
Dredged spoil from various UK coastal sites	46 -	353	(Romeril, 1979)
	25 -	300	(Packer et al, 1980)
	11 -	3000	(Murray & Norton, 1979)

6.2.3 Human health implications.

The most relevant advisory limit for zinc in soils are the ICRCCL (Interdepartmental Committee on the Redevelopment of Contaminated Land) Guidance Notes. The latest available edition (July 1987) only suggests tentative limits, and unfortunately only the threshold concentration has been determined so far. Results below the threshold concentration indicate that the site is uncontaminated with regard to that pollutant. Results above the action concentration (yet to be defined) show that remedial action will be required. In between the threshold and action concentrations is a grey area where expert advice will be necessary to determine the appropriate course of action. It is important to note that the standards for zinc and copper have been set due to potential toxicity for plants, rather than human health reasons. The threshold concentration is shown below, but is not strictly applicable to the intertidal mudflats at Copperhouse.

ICRCL Threshold Concentrations for Zinc (ug/g air-dried soil) Any
uses where plants are to be grown 300

Whilst the action concentration has yet to be defined, it seems very likely that it will be well below the concentrations regularly encountered at Copperhouse and many other sites in Hayle. The Department of the Environment expect to publish a new edition of the Guidance Notes in spring/summer 1989.

Zinc concentrations in the sediments of Copperhouse Pool range from 64 - 2880 ug/l in the 0 - 10 cm deep layer, and 150 - 3125 ug/g in the 50 - 150 cm deep layer. There were often considerable differences between the zinc concentrations in the 0-10 cm layer compared with the 50 cm deep layer, but there was no consistent increase or decrease with depth. The mean concentration of the 0-10 cm layer was 1020 ug/g, compared with 1120 ug/g in the 50 cm deep layer. This suggests that removal of the top 50 cm would produce a new surface with an average zinc concentrations similar to that of the present surface. Zinc may be brought into the water column during excavating procedures, but this could be minimised by preventing seawater entering during the excavations.

The highest concentrations of zinc are comparable with the most contaminated estuaries (eg Restronguet Creek in Cornwall) and the most contaminated dredge spoils (eg from the Tees estuary).

No data were available to me on the amounts of zinc required to produce chronic or acute poisoning. In view of the high concentrations of zinc in many molluscs and shellfish in the UK (eg up to 440 ug/g in mussels and 800 ug/g in whelks on a dry weight basis) the health risk from zinc in Copperhouse Pool sediments is probably insignificant.

- 7 CONCLUSIONS.
- 7.1 Copperhouse Pool has been polluted with mining and smelting wastes to such an extent that there is only one other comparable estuary (Restronguet Creek) 'in the UK in terms of arsenic, copper and zinc concentrations in the sediments.
- 7.2 Arsenic, copper and zinc concentrations in the waters of Copperhouse Pool are probably within the Environmental Quality Standards for bathing and contact. This situation would be further improved if the freshwater inputs were diluted by seawater at all tidal states, ie if the water level in Copperhouse Pool remains high; presumably this would be the situation during the summer months if watersports are planned.
- 7.3 Concentrations of arsenic in the sediments are particularly high, and may be a health hazard. Under the worst possible scenario a 2 - 3 year old child may only have to ingest 5.8 g of sediment to obtain a lethal dose.
- 7.4 By comparison with arsenic concentrations, those of copper and zinc in the sediments are not considered significant. Over 300 g of sediment would probably have to be ingested to obtain a lethal dose of copper. Zinc concentrations do not pose a health hazard.
- 7.5 Removal of the top 50 cm of Copperhouse Pool sediments would produce a new surface with similar concentrations of arsenic, copper and zinc.
- 7.6 Any removal of sediments from Copperhouse Pool should be done under the supervision of environmentally qualified personnel, in order to minimise mobilisation of metals from the sediments.
- 7.7 None of the sediments in Copperhouse Pool could be used where plants are to be grown due to phytotoxicity of the arsenic, copper and zinc present.
- 7.8 A significant proportion of the arsenic entering Copperhouse Pool comes from Mill Leat. Due to the very low flow of Mill Leat it may be possible to divert the flow and/or treat the water to remove most of the arsenic. It is probable that most of the arsenic in Mill Leat is from adit mine drainage near Treeve Farm.
- 7.9 Arsenic concentrations in the waters of Copperhouse Pool exceed the EQS for protection of saltwater species, but this situation would be considerably improved if the freshwater inputs were diluted by seawater at all tidal states.
- 7.10 The EQS for copper and zinc to protect saltwater life are probably exceeded in Copperhouse Pool, but more data are required to confirm this view.

RECOMMENDATIONS.

- 8.1 Obtain data on water quality in the Hayle estuary from South West Water. Information on arsenic, copper, zinc, salinity of water samples and metals in sediments.
- 8.2 Obtain data from South West Water on metal concentrations (As, Cu, and Zn) in domestic water supplies.
- 8.3 Obtain details of reservoirs used to supply Hayle, including grid references, from South West Water.
- 8.4 Obtain any available information on flows in the Angarrack and Mill Leat.
- 8.5 Analyse adit mine drainage feeding into Mill Leat. Potential pollutants from the old dynamite works should also be considered.
- 8.6 Decide whether any of the polluted streams which eventually feed into Copperhouse Pool could be diverted or treated.
- 8.7 Consider whether to offer to sample the playing fields near Copperhouse Pool for arsenic, copper and zinc, and undertake remedial work if necessary.
- 8.8 Produce detailed plots of metals in the surface 0-10 cm, 50 cm and 100 cm depth if removal of some of the surface of Copperhouse Pool is planned.
- 8.9 Removal of just the top 50 cm of sediment will probably create additional problems, since metal concentrations do not decline significantly within this depth. This suggests that deeper, less contaminated sediments will have to be exposed.
- 8.10 Further sediment samples will be required from Copperhouse Pool if it is proposed to remove more than 50 cm of sediment.
- 8.11 Obtain expert advice on land restoration, preferably from a consultancy with experience of dealing with soils with a high arsenic content.
- 8.12 Analyse a wider range of soils in Hayle, especially for arsenic, zinc and copper. Sulphate levels will also be high, which may affect concrete structures.
- 8.13 Any remaining doubts about potential health hazards from arsenic in the soils, sediments and waters in Hayle could be answered by a proper epidemiological survey.

GLOSSARY.

Desorption	Transfer from the particulate to the dissolved phase.
Dissolved metal	This includes dissolved and colloidal forms, and is equivalent to the filterable fraction. The pore size of the filter is usually 0.45 urn
EQS Flocculation	Environmental Quality Standard. Similar to precipitation; process occurring in the freshwater/seawater mixing zone whereby particulate and colloidal matter aggregates and comes out of suspension.
ICRCL Action Concentration	Concentration above which a soil would require treatment before use in gardens, recreation areas etc.
ICRCL Threshold Concentration	Concentration below which a soil would be considered uncontaminated.
Metalliferous	Containing above average amounts of metal ores in the rocks. Usually associated with areas of metal mining activity.
Oxidation state	Number of positive or negative charges on an element or ion.
Particulate metal	Metals which are associated with material in suspension, and are retained on the filter paper. Also called the non-filterable fraction.
ppt	Parts per thousand (equivalent to grams per kilogram)
ug/g	Micrograms per gram; 1 mg/g is equivalent to 1 part in a million, or 1 ppm (part per million).
ug/l	Micrograms per litre; 1 ug/l is equivalent to 1 part in 1,000 million, or 1 ppb (part per billion).
Valency	Number of bonds which an element can form.

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A handwritten signature in black ink, appearing to read 'P R Smith'. The letters are cursive and somewhat stylized.

Report prepared by Dr P Smith, CChem, MRSC. 30th November 1988.