Heavy metal contamination of Izmir Bay, Turkey

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1. Introduction

The bay of Izmir is one of the largest in the western part of the Aegean Sea, with the city of Izmir being one of Turkey's most important industrial centres. The harbour is the second largest port in Turkey, with an average of 2000 commercial ships visiting annually (1). The main types of industry in the region are: food and beverage manufacture, tanneries, vegetable oil and soap production, paint manufacture, chemicals, pulp and paper, textiles, metal processing, petroleum refining, and timber processing. There are also a large number of small scale manufacturers, producing a wide variety of goods.

Of all these industries, tanneries, textile plants and paint manufacturers are believed to be the most important contributors to the pollution of the bay (2). Discharges from such industries will, if untreated and released directly to surface waters, be a major source of heavy metal pollution. For example, wastes from tanneries will contain high levels of chromium, aluminium, manganese and copper; discharges from paint production, including manufacture of thinners, varnish and retarders etc, are known to contain high levels of cobalt, copper, iron, lead, manganese, nickel, zinc and antimony, and effluents from textile factories will contain significant levels of copper, chromium, mercury, nickel and zinc. Thus, the combined load of metals into the bay from these industries alone, could be considerable.

A recent UNEP technical report (Case Study of the Bay of Izmir, 1993) (3) concluded that the inner bay is heavily polluted by nutrients and organic material, but that metal concentrations were not high enough to indicate heavy metal pollution. The study concluded that pollution was spreading from the inner bay to the transitional middle bay, but that pollution in the outer bay was not significant. The aim of this investigation is to determine the extent of heavy metal pollution in both the inner and outer bays of Izmir harbour, and thus confirm or reject the findings of the UNEP technical report.

2. Sample collection

Samples of water and sediment were collected from a number of major streams flowing into Izmir bay: the Meles, Manda, Gediz, Halkapinar, Arap and Bornova. Sediment samples were also collected from the inner bay, an area being dredged for a new commercial harbour. Industrial discharges were taken from Henkel and Yapi Merkezi, manufacturers of vegetable oils and textiles respectively; and a sample of mussels was collected from the fishing harbour in the outer bay. See appendix (ii) for a map of sampling points.

3. Analytical Methodology

Sediment samples were dried in an oven for 48 hours, or until dry weight readings became constant. They were then crushed using a pestle and mortar until homogeneous. 0.5g of each sample was transferred to a 120ml teflon vessel fitted with a screw cap and pressure relief valve. To this 10ml of deionised water was added, followed by 7.5ml of concentrated hydrochloric acid and 2.5ml of concentrated nitric acid (both analytical grade). The vessels were sealed, placed on a rotating table in a microwave (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630W). After cooling to ambient temperature, the digests were diluted with deionised water, made up to a volume of 50ml, and mixed. With every batch of ten samples a blank and a certified reference material was prepared,with the same acid matrix as the samples. The certified reference material used was PACS-1 (trace elements in marine sediment), certified by the National Research Council, Canada.

The mussels were rinsed thoroughly with deionised water, and the flesh removed from the shells. They were then dried and digested in the same way as the sediments.

Water samples were preserved with 5% v/v concentrated nitric acid on arrival, and allowed to stand 24 hours prior to analysis.

Following preparation, the samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 spectrometer. The following metals were quantified: copper (Cu), zinc (Zn), lead(Pb), cadmium (Cd), Nickel (Ni), chromium (Cr), iron (Fe), aluminium (Al), manganese (Mn), cobalt (Co), vanadium (V) and beryllium (Be). Instrument calibration standards were matrix matched to the samples, and the calibration itself was validated using quality control standards at both 20% and 80% of the calibration range. Samples exceeding this range were diluted, in duplicate, appropriately. The spectrometer was recalibrated after every twenty samples to compensate for fluctuations in sensitivity. All other instrument quality control procedures were adhered to.

Mercury (Hg), arsenic (As) and antimony (Sb) were analysed by Cold Vapour Generation ICP-AES. Hg(ii) was reduced to Hg(0) vapour following reduction by sodium borohydride and hydrochloric acid (10M). As and Sb volatile, covalent hydrides (AsH3 and SbH3) were produced by preparing the samples in the absence of nitric acid, adding potassium iodide to the samples one hour prior to analysis (to ensure the +3 valence state was prevalent and not the +5), and then reducing any As and Sb present in the sample to the corresponding hydride by reduction with sodium borohydride and hydrochloric acid (10M).

4. Results

See appendix 1 for full sample descriptions and results.

5. Discussion

a) Sediment samples

Analysis of sediments provides an excellent picture of the extent of pollution within a defined area. Water, due to fluctuations in emissions and flow, follows a less well-defined pattern. Heavy metals bind predominantly to the suspended material (4), finally accumulating in the sediment, thus providing a reliable history of pollution.

Sediments from estuarine and coastal areas will always contain some levels of metal ions, levels very much dependent on the geology of the area. However the sediment samples collected from Izmir bay, indicate that elevated levels of metals, from anthropogenic sources are present. Uncontaminated marine sediments will generally contain less than 10 mg/kg dry weight of Pb, Cd, Ni, Cr, V, Co and As. Cu and Zn levels in pristine sediments are usually lower than 50 mg/kg; and Hg, Be, Cd and Sb will usually be present at levels less than 1mg/kg dry weight (5). Background levels of Al, Fe, and Mn will be higher and will vary widely, depending on geology as well as anthropogenic sources (6).

Sediment samples were collected from (i) the inner harbour, an area being dredged for a new commercial harbour, (ii) the Meles stream, (iii) the Manda stream, (iv) the Bornova stream, (v) the Gediz stream (which discharges into the outer bay), and (vi) the Halkapinar/Arap confluence. A sample was also collected near to the Yapi Merkezi factory, manufacturers of textiles and food.

(i) The inner harbour.

This appeared to be one of the most contaminated sites. Elevated levels of Cr, Ni, Hg, Zn, Pb and As were detected, with Al and Fe present at g/kg levels in all samples. The metal which warrants most concern is Cr, with concentrations ranging from 300 to 480 mg/kg. Uncontaminated sediments will generally, as stated earlier, contain less than 10 mg/kg dry weight of Cr, and although background concentrations can vary widely, the levels found in these samples are indicative of considerable anthropogenic loading, the sediments acting as a sink for Cr discharged in industrial effluents.

Three industries will be responsible for discharging Cr into the environment: metallurgical, chemical, and refractory. In the metallurgical industry Cr is used in making stainless steel, alloy cast irons and non-ferrous alloys. In the chemical industry it is used primarily in production of pigments, metal finishing, leather tanning, and wood treatment. Smaller amounts are used in water treatment, textiles and as catalysts. From previous case studies on Izmir bay, we know that the above stated industries are present in the vicinity of the harbour, and are likely to be discharging effluent directly into surface waters. We also know tanneries, paint, pigment, and textile factories are responsible for a large proportion of the pollution load into the bay. Cr is used in all of these processes, and it is evident that no wastewater treatment is being carried out prior to discharge.

As a comparison, Cr concentrations in UK estuarine sediments, collected from a number of industrially polluted sites including the Mersey, Tyne, Humber, and Severn, range from 30 to 200 mg/kg. The highest levels (207 mg/kg) being found in the Loughor Estuary in South Wales, a site of tin plate production (7). Thus the Cr levels detected in the inner bay are indicative of a substantial pollution load.

There is limited information on the effects of such levels on aquatic biota, fish and deposit feeding and wading birds. It is recognised that the speciation of Cr determines it's bioavaiability. The speciation will dictate the bioaccumulation of sediment bound Cr by marine and fresh water organisms (8).Cr(VI) will be accumulated more rapidly than Cr(III), as it has been shown to readily cross biological membranes (for this reason it is considered to be more toxic) (9). The results from this study are expressed as mg/kg aqua-regia extractable Cr, and thus the speciation of the Cr cannot be identified. However it has been shown that in many estuaries, anthropogenic Cr appears largely associated (adsorbed or coprecipitated) as Cr(III) with oxides of Fe, and thus will be the dominant species present here. However as levels are so high it would be naive to presume uptake from the sediment to aquatic organisms would not occur, as other metals eg Mn, and organic chelating agents can play a catalytic role in the oxidation of Cr(III) to Cr(VI).

Other metals of concern in this area are Ni, and Hg. Comparison with published data, both from pristine and polluted sites (10,11,12), show concentrations here to be indicative of anthropogenic pollution.

Hg, although noted for it's use in thermometers, barometers, and other pressure sensing devices, is utilised in many other products eg batteries, outdoor lighting, cameras etc. It is used as a catalyst in the chlorine and caustic soda industry, in the production of vinyl chloride monomer, urethane foam, anthraquinone, pharmaceuticals, pigments, lubrication oils, paints, anti bacterial and anti fungicidal agents. Although many of these uses are now banned, the retention of Hg by benthic sediments may delay the elimination of contamination for many years (13). Hg accumulation from sediments is considered a dominant pathway for uptake in aquatic organisms, and accounts for relatively high concentrations in deposit-feeders both in fresh water and estuarine systems (14).

Ni is primarily used in alloys, whilst Ni salts are used in electroplating, ceramics, pigments, and as catalysts.

Levels of both of these metals detected in the inner harbour allow us to assume that bioaccumulation in aquatic organisms will occur, with possible detrimental effects (15).

Levels of Pb, Zn and As although elevated and again indicative of anthropogenic pollution, do not appear as anomalous as the other results cited. Both Pb and Zn are used extensively in the metallurgical industry (alloying, plating etc), as well as in the manufacture of paints and pigments, indicating, in conjunction with the other results, that metal alloying and plating wastes, along with effluents from textile, paint and tanning factories are being discharged, untreated, into the surface waters flowing into Izmir bay.

A major source of As, along with paint and pigment production, is in the preparation of wood preservatives and agricultural chemicals. Again we know such industrial activities are occurring within the vicinity of the bay.

(ii) The Meles stream

The Meles stream has a basin area of 123 km^2 and a length of 16 km. More than 300 industries and companies are located on or near the stream (16). A 1985 study states that 60 million m^2 domestic wastewater and 15 million m^2 industrial wastewater are being discharged annually into the Meles.

Two samples were taken from this stream. One from the mouth, and one mid-stream, immediately before convergence with the Halkapinar. Elevated concentrations of trace metals were detected. The sample taken from the mouth of the Meles appears more contaminated than the sample collected before convergence with the Halkapinar and the Arap. It is evident, because of this, that both of these subsidiary streams are carrying polluted discharges from the Bornova industrial estate, into the Meles, and thus into the harbour.

Higher concentrations of Mn, Cr, Zn, Cu, Pb, As, and Sb are found at the mouth the stream. With levels of Cr, Zn, As and Sb appearing significant, on comparison with those detected in the sample taken further up stream. Again the Cr detected stands out as being anomalously high. Possible industrial sources of this metal have been stated above. What is obvious is that although the Meles, prior to confluence with the Halkapinar and Arap, is not exactly pristine, discharges from the Bornova industrial estate are increasing the anthropogenic load of metals into it's water, and thus into Izmir Bay.

The level of As detected at the mouth of the Meles is similar to that detected in the inner bay (the site of the new commercial harbour) and is again significant. Levels of As in the Manda, Bornova and outer bay will be discussed later, however levels are lower than those detected in the mouth of the Meles and the inner bay, indicating that the Bornova industrial estate is the most probable source of contamination. It appears that the Meles stream, due to the waste that is deposited and carried in it, is responsible for off loading most of the metallic pollution into the bay.

(iii) The Manda Stream

The Manda stream flows into the inner bay. It's source being south east of Izmir, before the Pinarbasi region. It is one of the most important pollution carriers in the bay. Almost all of the industrial sites located in Pinarbasi discharge their wastewaters into a small stream which meets with the Manda. The stream flows through industrial sites located in Bornova and receives a high amount of industrial and domestic waste water before flowing into the inner bay. Trace metal levels detected in the following samples are indicative of this.

Four samples were taken from the Manda stream. One from the mouth, one further up stream by the second bridge (see map for location), and two slightly north of the Bornova industrial estate. Levels are generally higher in the sample taken from the mouth of the stream. With levels of Cr, Zn, Cu, Pb, Ni, As, and Hg being significant.

Hg is present at elevated levels in all of the Manda stream samples, with a maximum of 14.1 mg/kg being detected in one of the samples north of the Bornova industrial estate (MI5102, see map). High sediment concentrations are usually associated with inputs from the chloralkali industry. Whilst inputs from the chemical manufacture and sewage sludge may further enhance contamination. Whatever the source, the level of Hg detected (exceeding that detected in the most pollute estuary in the UK, the Mersey, receiving discharged waste from the chloralkali industry) is of great concern, because as previously noted, Hg accumulation from sediments may be a dominant pathway for uptake in aquatic organisms, accounting for relatively high concentrations in deposit-feeders both in freshwater and estuarine systems (17).

(iv) Bornova stream

One sample was collected from the Bornova. Mid stream, under the fourth bridge (see map for location). Trace metals levels are generally lower than those detected in the other samples, with one exception: Hg, present at 15.0 mg/kg. This was the highest level of Hg found in any of the samples analysed. The source of such contamination is difficult to identify. Industrial sources are listed above, however many small factories discharge into the Bornova, and thus individual industrial activities cannot be identified. All other metals are present close to, or below, background levels, and because of this we can use the results from this sample to assess the degree of pollution in the rest of the bay.

(v) Gediz stream

The Gediz stream, which flows to the outer bay, is the second largest river in the Aegean region Three samples were taken from the mouth of the Gediz, which discharges into the outer bay (not shown on the map). The stream receives waste effluents from an industrial estate which lies to the north.

This outer bay area is also a site being proposed as a dumpsite for dredged spoils. The results from these three samples are, as expected, very similar. The following pattern is identified:

Fe > Al > Mn > Zn Cr Ni > V > Cu > Pb > Co As > Hg > Be > Sb > Cd

Most of the metals are present at relatively low concentrations compared to those found in the inner bay. However levels of Cr and Ni are elevated from those levels expected in uncontaminated sediments, and again Hg levels are indicative of a considerable pollution load.

(vi) Halkapinar / Arap confluence

One sediment sample was collected from the point where the Halkapinar joins the Arap. Both streams run close to the Bornova industrial estate, and thus one would expect to find significant levels of metals present in both. Indeed this is the case. Elevated levels of Cr, Zn, Cu, Pb, and Ni are found. The most anomalous being Cu, present at 498 mg/kg. A UK study which involved measuring Cu levels in the most polluted estuaries, found Cu levels were generally lower than 100 mg/kg, with the exception of Restronguet Creek, the Fal estuary, and the Tamar. All sites of present and past mining the estuaries, thus receiving or once having received acidic drainage from such activities. For Cu levels to be detected at levels greater than 100 mg/kg is significant and worrying, as there is experimental evidence that a considerable number of aquatic species are sensitive to both dissolved and sediment bound Cu, with concentrations of Cu in benthic species from contaminated areas being present one to two orders of magnitude higher than normal (18).

(vii) Yapi Merkezi

One sediment sample was collected from this location, an area both the site of food and textiles production. Relative to the other samples, levels of metals found here are low. However again levels of Cr and Hg are significant. Cr is used in the textile industry, and in the chemical industry in pigments (both Cr(vi) and mixed metal, Cr(iii) and Cr(iv), oxides), and although, a significant amount of solid Cr waste from plating operations will be recovered, relatively large amounts of Cr containing wastewaters from plating, finishing, and textile manufacture will be discharged into surface waters, as appears to be the case here.

The elevated level of Hg in this relatively clean site also reinforces the problem of Hg contamination within the entire bay.

b) Water samples

Whereas the sediment provides a clear picture of the on going pollution of waters, over a relatively long period of time. Heavy metal analysis of the waters may be used to pinpoint specific discharge points.

Seven samples of surface water were collected from the following points: The mouth of the Manda; the mouth of the Meles; the Halkapinar, immediately before confluence with the Meles; the bank of the Meles, before confluence with the Halkapinar; the Yapi Merkezi site; Henkel; and lastly from a partially blocked stream, north of the Bornova industrial estate. Be, Cd and Sb were not detected in any of the samples.

Three of the samples collected were relatively clean: the sample from the mouth of the Meles; the sample from the Halkapinar, before confluence with the Meles; and the discharge from Henkel. However in the latter levels of Zn and Hg are significant. Henkel produces vegetable oils and soaps, thus Zn, which is widely used to catalyse a whole variety of organic reactions, could easily be present in the discharges from this plant. However the Hg level, based on the known processes being utilised in the manufacture of oils and soaps, warrants further investigation.

The other samples are more contaminated. The sample collected from the Meles, before confluence with the Halkapinar and the Arap, appears to be the most polluted. Levels of Al, Mn, Fe, Cr, Zn, Pb and Ni are significant. All of these metals are present at levels many times greater than expected in fresh surface water systems, for example Zn is present at 26 g/l which is an anomalous level when one considers that Zn is generally found at concentrations less than 50 ug/l (US EPA 1980). Cr, Pb, Mn and Ni again are typically present at levels ranging from 10-50 ug/l, levels greatly exceeded in this sample.

The sample collected from the mouth of the Manda is also contaminated. Elevated levels of Mn, Cr, Zn, and Cu are present, and Al and Fe were found in g/l quantities. In the case of Zn, Cr, and Cu, levels up to ten times greater than expected in fresh surface waters (US EPA 1984) are found. Such increased levels of Cu, Cr, and Zn must, in this case be correlated with urban and industrial runoff.

Concentrations of Pb, Ni, Co,Cd, Be, Hg and Sb in the sample from Yapi Merkezi are below instrument detection limits. Levels of Al, Fe, Cu, V, and As are all typical of fresh surface water systems. Zn is present at a slightly elevated level, however Cr is present at 8 mg/l. Yapi Merkezi, as stated earlier, is a site of textile and food production. Cr is used in the textile industry, extensively as a catalyst and a complexing agent for the synthesis of dye and dye intermediates. Wastewaters from such operations are often discharged directly into receiving surface waters, as seems to be the case here.

The final sample of surface water was taken from a partially blocked stream, north of the Bornova industrial estate. In this sample Hg, Cr, and Zn concentrations are significant. The level of Hg detected in this sample is the highest found in any of those collected, 72 ug/l. Levels of Hg found in fresh surface water system are generally lower than 1 ug/l. Industrial sources of Hg contamination are cited above. Hg is largely associated with the sediment, and for such a large amount to be found in the surface water is indicative of serious Hg pollution.

c) Mussels

Most aquatic organisms are able to incorporate and accumulate heavy metals introduced into their environment. Although aquatic organisms in Izmir bay were not extensively studied, one sample of mussels was collected: from the pier in the fishing harbour, located in the outer bay. Concentrations of Pb, Ni, Co, Cd, Be and Sb were below instrumentation detection limits. Detectable levels of Al, Mn, Fe, Cr, Zn, Cu, V and As were found. Compared with published data on levels of trace metals found in mussels from uncontaminated sites only Hg levels detected here exceeded such values. Cr is very close to the top of the range quoted. These two results do seem to illustrate that, even in the outer bay, Cr and Hg pollution, from industrial sources, is significant.

6. Conclusion

To say the bay of Izmir does not show signs of heavy metal pollution is incorrect. Only one of the sediment samples collected contains levels of metals that would be associated with pristine, unpolluted environments. If we then use the results from this sample to be indicative of ""background" levels for the area, we find that all the other sites sampled contain elevated concentrations of heavy metals. Even Al and Fe levels, which are difficult to assess (as natural inputs are often greater than anthropogenic ones), are higher than one would expect.

The UNEP case study report, written in 1993, states the following: "Scientific evidence suggests if no pollution control measures are taken immediately pollution in the bay will reach a critical level by 1995 leading to a collapse in the ecosystem starting in the inner bay and gradually reaching the Aegean coast". Based on this limited study of heavy metal contamination, largely centred on the inner bay, results do suggest that if discharging of untreated industrial effluents, directly to surface waters flowing into the bay, continues, then severe, detrimental effects on ecosystems existing within the bay will be observed.

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