An Analysis of As, Pb, Fe, and Co in the Rio Tinto Estuary in Southwest Spain

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ABSTRACT

Spurred on by the trace metal contamination in the Mediterranean Sea, a possible source of this has been pursued by examining the Rio Tinto estuary in the southwest of Spain. Using the AA and the ICPMS, five metals were investigated to observe mixing in the Tinto Estuary: arsenic, iron, lead, cobalt and thallium. If conservative mixing is observed in the estuary it can help prove that some trace metals may travel from the rivers Tinto and Odiel through the estuary, into the Atlantic coastal waters, and ultimately into the Mediterranean Sea. This would help to explain the high trace metal concentrations that are found in the Mediterranean.

After analyzing the concentrations for these five metals, it can be seen that some of the metals clearly do undergo conservative mixing in the estuary, with Pb and Co providing the best examples of conservative mixing. The other metals, As and Fe have straight mixing curves but seem to be affected by the two different water masses that empty into the estuary and provide separate sources of contamination of these metals. Lastly Tl was investigated and the results seem to correlate with the other metals; however, it should be kept in mind when looking at the data produced from the analysis of Tl, that the method used depends highly on the percent recovery and may not be very accurate.

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INTRODUCTION

High levels of certain trace metals have been known to exist in the Mediterranean Sea for many years, but the sources of this pollution has not been obvious. Open-ocean Atlantic Ocean waters entering the Mediterranean Sea through the Strait of Gibraltar and the Alboran Sea have been shown to be relatively metal-free. Testing of the waters of the Alboran Sea which is east of the Strait of Gibraltar has shown metal enrichments with concentrations of copper as high as 3.6 nmol/kg; nickel as high as 2.8 nmol/kg and cadmium as high as 120 pmol/kg (Boyle, et. al., 1985), while these metals are lower in the Atlantic Ocean (Cu: 1.5 nmol/kg; Ni: 2 nmol/kg; Cd: <10 pmol/kg).

At first glance one might be tempted to attribute the high metal levels to industry that resides along the Mediterranean Sea itself or to geochemical processes operating there naturally. It has been shown that trace metal concentrations in the deep waters of the Mediterranean Sea are comparable to the concentrations of trace metals of surface water samples (Boyle, et. al., 1985). Therefore, there is no major transport of metals from the deeper waters to the surface within the Mediterranean Sea. The source of the metals lies elsewhere. Discovering a plume of metal enriched waters entering the Alboran Sea, Boyle et. al. (1985) surmised that coastal waters that are very different from the "open ocean waters" were possibly the source of the high trace metal concentrations.

These coastal waters, which were later identified as Spanish Shelf water (van

Geen et. al., 1991), have been shown to flow into the Mediterranean Sea from studies based on conservative mixing models (van Geen et. al., 1991). These waters consist of a few percent of water that is contributed by rivers that flow into the ocean. These river waters may be polluted and thus may contribute pollution to the coastal waters that flow into the Mediterranean Sea. An examination of the area found a river that may support this scenario. Two inconspicuous but heavily polluted rivers in Spain flows into the Atlantic Ocean through the same estuary not far from the opening of the Strait of Gibraltar. These polluted waters flow along the shore of the Atlantic Ocean and into the Mediterranean Sea. These rivers are the Rio Tinto and Rio Odiel in Huelva, Spain which are contaminated by trace metals from acid mine drainage. These rivers join in the long and narrow Rio Tinto Estuary which is examined to see if the pollution in these waters are carried through to the coastal waters that ultimately flow into the Mediterranean Sea (see Figure 1 for a map of the area).

To better determine if the trace metals originating from the two rivers are a source of pollution to the Mediterranean Sea, metal concentrations are to be analyzed to determine the reactivity of metals within the estuary. Measurements of the trace-metals were made throughout the estuary to determine if they in fact "mixed out" travelling through the estuary and ultimately into the ocean, or if they were not noticeable as they travelled through the estuary because of chemical reactions which removed them from solution. For these metal enrichments to ultimately contribute to the high trace metal concentrations found in the coastal

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waters, conservative mixing should be observed throughout the estuary. The concentrations of the metals should correspond directly to the salinity of the water. However, if there are sinks or sources for these metals (such as precipitation, absorption to larger particles, or redissolution) conservative mixing will not be observed (see Figure 2 for an illustrative diagram).

HISTORY OF THE POLLUTION IN THE RIO TINTO ESTUARY

Water plays an important role in all our lives. The waterways of the world are the source for many things from bathing and cleaning to drinking and cooking. Interestingly though, even knowing of this importance, our waterways are also used as a general sewer where we are polluting our own vital resource. There are many industrial and municipal activities that pollute our waterways from industrial waste to agricultural runoff to wastewater from overflowing sewers during heavy rain events. With such a wide range of sources to pollute our water, one significant and extremely toxic source of pollution that directly affects the people living in an area is mining. The pollution in the rivers Tinto and Odiel have been polluted from a variety of activities, including industrial, but the dominant source is from mining (Dutrizac, et.al., 1983).

Many waterways, especially rivers, have been polluted because of mining activities. The pollution from the mines results in high trace metal concentrations in the water (Masters, 1991). These trace metals are potentially dangerous to the biota in the area, and some of these metals can also be carcinogenic. In fact, a listing called the "Consensus Ranking of Environmental Problem Areas on the Basis of Population Cancer Risk" listed mining wastes 18th on the list of pollution problems that can cause increased cancer rates (Masters, 1991). The increased rate of cancer is mostly attributed to arsenic which is at higher concentrations in waters that are polluted from mining wastes. Individual risk for cancer is very high and can be

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seen in the population of people who live in a remote area and are exposed to local

mining wastes in their drinking water. For this area it is not clear if the water from

these rivers are a drinking water supply for humans, but it is consumed by livestock

and is a source of contamination for other aquatic organisms which are a source of

food for the fishery industry (Nelson, et. al., 1993).

Waterways polluted by mines not only have high metal concentrations but

also become very acidic because of the acids that are discharged in the mining

drainage process. The lower pH levels in local waterways make it very difficult if

not impossible for a body of water to support aquatic life. Acid mine drainage

typically has a pH of approximately 2; the pH of rivers affected by these waters

depends on the relative contribution of mine drainage to more natural waters. The

aquatic life in a waterway with such a low pH cannot survive. In addition to the

problems with the sustainability of aquatic life, the lower pH also allows for toxic

minerals such as lead and mercury which are usually insoluble to enter solution,

which further contributes to the hostile environment for organisms. When levels

are not sufficient to poison aquatic organisms, these organisms can accumulate

metal levels that are harmful to animals that eat them.

The Rio Tinto and Rio Odiel in Huelva, Spain, with sizes that bely their

potency, are small rivers that flow through an area which has been mined

continuously since pre-Phoenician times and continues to be mined today. The Rio

Tinto ("tinto" is the Spanish word for red wine) was named due to its reddish color

from the large sulphide and iron-ore deposits (Nelson, et. al., 1993). The pyrite

reserves in this area is thought to be the largest reserve in the world (Dutrizac, et. al., 1983). The two rivers that flow through the mining area, form the Tinto estuary before entering the Atlantic Ocean.

The Pre-Iberians were the first to take advantage of the metal resources available in this area. Sometime before 2500 B.C. they found copper (Morral, et. al., 1990). Later silver resources were discovered by the Iberians from the processing of the jarosite ores. Mining in this area started out simply enough. Initial mining efforts consisted of no more than digging to the soft ores and the "iron capped" gossan and extracting the ore-laden metals.

The Phoenicians began trading in the area at about 1200 B.C. and exported silver, gold, tin, and tin ore, and much later, in 205 B.C., the Romans moved into the area and continued to mine extensively (Morral, et. al., 1990). They brought many skilled men solely for this purpose. The Romans, it has been found, used the jarosite formations for silver and the sulphide bodies for copper. As surface ores were used up, miners had to dig deeper and deeper requiring the dewatering of these mining areas. Drainage of the acidic mine water became a problem as mines were dug deeper. Eventually drainage channels were not adequate and pumping systems had to be set up bringing this polluted water up to the surface and discharging it elsewhere.

Mining declined when the barbarians, the Visigoths, moved into the area and did not resume intensively until the Moors came to the area (712 A.D.) and recovered copper from the acid drainage waters (Morral, et. al., 1990). After

searching for mines with precious metals King Phillip II, in 1637, directed that the Rio Tinto area was to be mined (Morral, et. al., 1990). The King granted a number of certificates to those who would mine the area, and mostly copper, silver, and gold were collected. A series of certificates were granted to different people over the following years.

In 1725 a Swede, Liebert Sjohjelm, was allowed to work a few of the mines in the area for gold and silver (Morral, et. al., 1990). Certificates were still being granted to mine this area, but occasionally the mines reverted to state control where different managers were appointed. In 1756, under Samuel Tiquet's management, a portion of the copper was produced from smelting ore and the rest was produced by cementation (Morral, et. al., 1990). The cemented ores were melted in blast furnaces. From 1788-1792, 185 tons of black copper and 132 tons of refined copper were produced per year (Morral, et. al., 1990).

When the French troops captured the area in 1810, mining activities stopped and did not begin again until 1814 (Morral, et. al., 1990). In 1845, the mines were leased to the Compania de las Planas and this company produced copper for 15 years; later, in 1873, the Rio Tinto Company (RTC) was set up to mine (Morral, et. al., 1990). This company was quite successful in the area for many years until control was reverted back to the Spanish government in 1956 (Morral, et. al., 1990). In 1962, RTC merged with the Consolidated Zinc Corporation becoming Rio Tinto Zinc Corporation Limited (RTZ) (Morral, et. al., 1990). Later in 1966, a new company Rio Tinto Patino S. A. came to the area and extracted gold and copper (Morral, et. al.,

1990). Since then more companies have been in the area, and it has been continued

to be mined up to the present day. This extensive and almost continuous mining

has caused the heavy pollution that is observed in the rivers that flow in the

Huelva area. Figure 3 is a plot of mining extraction (metric tons of Cu production)

versus time, between the years 1860 and 1960 (van Geen, et. al., 1996).

OTHER STUDIES OF THE POLLUTION

The Rio Tinto and Rio Odiel have both been greatly polluted over the centuries from industrial wastes and the extensive mining that has occurred for the last few thousands of years. These waters are, therefore, extremely polluted and unsuitable for aquatic life and unusable for the inhabitants of the area. The waters have been tested for pH and in previous studies the sediments have been studied to determine the heavy metal contamination.

The waters of the Rio Tinto just upstream from the mines has a pH typical of "neutral" water (a pH of about 7.2), but between the mine and estuary the pH is between 2.5 and 2.8 while in the estuary the pH returns to near neutral (about 6.2) (Nelson, et. al., 1993) as alkaline seawater neutralizes the acidity. The acidic waters of the rivers are toxic to any organism trying to survive in the area, and in fact no observable aquatic life seems to be present. However, not only is aquatic life affected by the waters, but so are the inhabitants that live in the remote mining area where these rivers are located.

Besides the low pH, the metal concentrations in the water are much higher than relatively unpolluted water. The exact levels have been tested for to determine the extent of pollution that has resulted from the long history of mining. Studies done by Nelson, et. al. (1993) and Respaldiza, et. al. (1993), have been performed on the sediments determining the metal concentrations of the Tinto and Odiel river sediments. These sediment studies have shown the extent to which the pollution

has resulted from the persistent mining, and the sediments have been shown to be a useful indicator of pollution and can provide the history of mining activity in an area. By using the sediment analysis a record of activity can be extracted and determined.

The Rio Tinto area seems to have much metal enrichment and contamination due to mine drainage. From a study that was published in 1993, sediment samples were analyzed from both the Tinto and Odiel rivers. Concentrations of 19 elements were obtained from each sample. The metal concentrations from each sample provides a guide for where the pollution may have originated, and studies have shown how industries have a direct effect on pollution in natural resources. Directly downstream from the Rio Tinto Mines, iron levels are extremely high (approximately 47% by weight) which is due to the extraction of iron and copper from pyrite at the mines, and iron levels elsewhere seem to decrease to approximately between 7-14% by weight (Respaldiza, et. al., 1993). The sulphur levels also seem to decrease along with the decreases in iron except for a site that has high levels of sulphur and calcium probably due to the proximity of gypsum piles where drainage from the piles directly flows into the river.

Travelling downstream phosphorus levels also increase due to the factories located along the Odiel river, and this contamination may affect Tinto levels due to the tides (Respaldiza, et.al., 1993). Heavy metals such as zinc, lead, and copper show dramatic increases as natural elements, such as aluminum and silicon, decrease

(Respaldiza, et. al., 1993). Arsenic shows the highest contrast, approximately $2.4x10^3$ ppm closest to the mines, and all arsenic levels are higher, between $0.7x10^3$ ppm and $1.83x10^3$ ppm, at each sample site (Respaldiza, et.al., 1993).

Most of the metal enrichment seen in the Rio Tinto come from mining activities, while the pollution found in the Rio Odiel comes from the UERT (Respaldiza, et.al., 1993), a minerals processing plant. It was seen in the study of sediments performed by Respaldiza that this leads to high levels of Fe (1.1% to 56%), Zn ($2.4x10^3$ ppm to $21x10^3$ ppm), Pb ($0.31x10^3$ ppm to $4.7x10^3$ ppm), Cu ($0.31x10^3$ ppm to $6.6x10^3$ ppm), as well as As ($0.07x10^3$ ppm to $2x10^3$ ppm). Therefore there are two sources of trace metals into the Tinto estuary, from pollution in both the Rio Tinto and the Rio Odiel.

Another study that was also published in 1993 also concurs with the previous study. Large anomalies of heavy metals derived from sulphide such as copper, zinc, lead, arsenic, and cadmium exceeded normal background concentrations usually by an order of magnitude or more (Nelson, et. al., 1993). The highest typical background levels for copper, lead, and arsenic are 50-100 ppm, 20-200 ppm, and 50-100 ppm respectively (Nelson, et. al., 1993). The highest levels of these metals found in the mud were 800-1500 ppm for copper, and 2000-3000 ppm for both lead and arsenic (Nelson, et. al., 1993). Cadmium levels in the mud were at 7 ppm which is a bit above the 0.2-1 ppm typical background range (Nelson, et. al., 1993). The levels of these heavy metals found in the Tinto-Odiel sediments all exceed the threshold sediment concentration levels which predict when the metal content in the water

will exceed the HDL which is the highest desirable level set by the World Health Organization for drinking water quality (Nelson, et. al., 1993).

Of chief concern is the arsenic levels which are the most toxic. Because arsenic is a carcinogen the large levels which are present are extremely dangerous. The maximum permissible limit for arsenic in a public water supply in the United States is 0.05 mg/L (Masters, 1991). From data that is found in Masters the number of cancers that results from just ingesting the maximum permissible limit can be estimated.

$$CDI = 0.05 \text{ mg L}^{-1} \times 2 \text{ L day}^{-1} / 70 \text{ kg} = 1.4 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1}$$
$$Risk = CDI \times Potency \text{ } Factor$$
$$= 1.4 \times 10^{-3} \text{ mg kg}^{-1} \text{ day}^{-1} \times 1.75 \text{ mg}^{-1} \text{ kg day} = 2.5 \times 10^{-3}$$

According to this calculation, a person who drinks water with the maximum permissible limit of arsenic over a lifetime (70 years) is subjected to a rate of 2500 cancers per million people. This is already a large number of people that can be affected by cancer due to arsenic. Increases in the level of arsenic greatly increases the risk of cancer for those living in an extremely contaminated area such as the Tinto-Odiel region. Further investigation of arsenic levels in the water will show whether arsenic is a main concern for the people in the area from their domesticated animals that may consume the water or the aquatic organisms that are a part of the food chain.

LABORATORY PROCEDURE

To determine whether or not the Rio Tinto may in fact be a source of pollution to the Mediterranean Sea, measurements of the trace-metals were made throughout the estuary. For these metal enrichments to ultimately contribute maximally to the high trace metal concentrations found in the coastal waters, conservative mixing should be observed throughout the estuary. The concentrations of the metals should correspond to the salinity of the water. However, if there are sinks or sources for these metals (such as precipitation, absorption to larger particles, or redissolution) conservative mixing will not be observed.

A mixing experiment was prepared to model what should be observed in the estuary which can be compared to what is actually measured for the estuary. The prepared mixing experiment graphs can be made for what should theoretically be seen for conservative mixing. If the salinities and the river end-member concentration are known the conservative mixing curve can be calculated. The plot of this graph (Figure 2) would follow the following equation:

$$C_x = C_d(S_o-S_x) / (S_o-S_d) \hspace{3cm} \text{Equation (1)}$$

C_x =Concentration at point x downstream
C_d = Concentration at discharge point or in this case the river end-member
S_o = Salinity or open ocean waters
S_x = Salinity at point x downstream
S_d = Salinity at discharge point or in this case the river end-member

For the mixing experiment, a river end member was chosen, estuary sample #9, as

well as an ocean sample, estuary sample #1. These were mixed in varying parts from all river end-member, #9, out of seven parts to all ocean member, #1, out of seven parts with varying mixes in between. Two sets of the mixing experiment samples were prepared: one set was filtered before mixing, and the other was unfiltered before mixing. Both sets were then filtered after mixing. The samples filtered before mixing would remove particles that may be needed for certain kind of precipitations. These nucleating particles once removed would inhibit some precipitation, and the resulting samples when filtered would subsequently have less of the metals removed. The unfiltered samples may have this precipitation which would be removed with the final filtering. For these metals differences in metal concentrations for the two sets of mixing experiment samples were not significant. The graphs of concentration versus salinity of the mixing experiment could then be compared with the graphs for the estuary itself to observe if the estuary behaves according to conservative mixing, or if there are other processes that act as the river water flows through the estuary and subsequently into the ocean.

To compute the concentrations of trace-metals, five metals were picked for analysis. These metals were chosen for two reasons: 1) it was known that these metals would have high concentrations in the Tinto Estuary and 2) most of these metals are well known for their significant toxic effects to human health and the environment. These five metals are arsenic (As), iron (Fe), lead (Pb), cobalt (Co), and thallium (Tl). Three of these metals (As, Fe, and Co) were analyzed by the method of standard additions using the atomic absorption spectrophotometer, and

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the other two (Pb and Tl) were analyzed using the ICPMS. Pb concentrations were computed using the isotope dilution method while Tl concentrations were computed using the standard addition method.

For As, Fe, and Co, the Hitachi Zeeman Atomic Absorption Spectrophotometer was used. As and Fe had Superlamps available while Co did not, and a regular cathode lamp was used. For all three of these metals, graphite pyrolitic tubes were used with As also using the platform method. As used a lamp current of 17.5 mA, with 20 mA boost current, and a wavelength of 193.7 nm. A 1.3 nm slit was used with a cuvette tube at optical temperature (see Figure 4 for the temperature program used for As). Each injection of the autosampler was 20 μL of solution. The mixing experiment, estuary, and Oceanus samples were analyzed.

For Fe a lamp current of 10 mA, with 25 mA boost current, and a wavelength of 248.3 nm. A 0.2 nm slit was used with a cuvette tube at optical temperature (see Figure 5 for the temperature program used for Fe). Each injection of the autosampler was also 20 μL of solution. The mixing experiment, estuary, and Oceanus samples were analyzed.

For Co a lamp current of 10 mA, with no boost current, and a wavelength of 240.7 nm. A 0.2 nm slit was used with a cuvette tube at optical temperature (see Figure 6 for the temperature program used for Co). Each injection of the autosampler was 20 μL of solution. The mixing experiment and estuary samples were analyzed. The Oceanus samples were not analyzed because of the very low levels presumed to be in the Oceanus samples.

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To prepare the samples, first three initial clean cups were prepared with differing amounts of spike. The spike concentration for As was approximately 0.7 μM, for Fe the spike was 7.07 μM, and for Co the spike was 8.4 μM for samples #8, #9, #10, and #13, and approximately 3.3 μM to 3.4 μM for the other samples. The variability is due to the differences in pipetting when mixing new standards. New standards were made for As and Co because of the instability of prepared standards over long periods of time. New standards were mixed at the start of each set of measurements.

To prepare the samples, the following procedure was followed: the first cup consisted of an amount of sample, dH_2O, no spike, and the same amount of NH_4NO_3 as sample for all samples except river samples #8, #9, #10, and #13. The second cup would be mixed in the same way as the first cup except that a metal spike was added. The amount of dH_2O was adjusted to result in all cups having the same resulting volume. Finally the third cup was also mixed similarly except double the metal spike was added. The volume was also adjusted accordingly. The solutions prepared in these three cups were then distributed among six cups mixed with a matrix of palladium nitrate to minimize interferences. The first solution was split among cups #1 and #6; the second solution was split among cups #2 and #5; the third solution was split among cups #3 and #4. This was done to observe any drift in the measurements produced by the machine.

For Pb, the isotope dilution method was used on the ICPMS. The mixing experiment, estuary, and Oceanus samples were analyzed. The mixing experiment

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samples and river samples #8, #9, #10, and #13 were prepared by adding an amount of sample, an amount of spike of comparable concentration as the sample, and HNO₃. Three replicates were prepared for each sample.

For the higher salinity Pb samples, low Pb levels necessitated a spearation from the salt matrix. To a large amount of sample (in this case 1mL of sample), spike, and ammonia were added. The ammonia caused $Mg(OH)_2$ to precipitate. After centrifuging, the precipitate was saved and the excess solution discarded. More concentrated 5% HNO_3 was then added to dissolve the precipitate. Three replicates of each sample were also prepared for these samples. The spike used for Pb was 92.29 nM for the high salinity samples and 3.1 nM for the mixing experiment and samples #8, #9, #10, and #13.

When running these samples on the ICPMS the peak jump method was used recording the counts per second for isotopes 204 and 208 for Pb. Mercury isotope 202 was recorded for some of the samples to monitor the amount of interference, and it was determined that Hg did not contribute significantly to the isotope counts in these samples. Knowing the counts per second and the amount of sample to spike ratio the following equation was used to determine the concentration of Pb in the sample:

$$C_{Pb} = C_{Sp} \ (\%204_{Sp} \ / \ \%204_S) * [(R_m\text{-}R_{Sp}) \ / \ (R_S\text{-}R_m)]$$ Equation 2

C_{Pb} = Concentration of Pb in sample

C_{Sp} = Concentration of spike

$\%204_{Sp}$ = Atomic abundance of isotope in spike

$\%204_S$ = Atomic abundance of isotope in sample

R_m = Ratio of counts per second of isotope 204 to 208

R_{Sp} = Ratio of isotopes (204/208) in spike

R_S = Ratio of isotopes (204/208) in sample

Tl was also analyzed using ICPMS; however, the standard addition method was used for calibration. Three cups were prepared using the precipitate method because of the lower amounts of this metal in the samples. To the sample ammonia was added in the first cup. In the second cup an amount of Tl spike was added, and to the third cup a larger amount of Tl spike was added. The spike used was 0.0479 μM for samples #2 through #7 and 0.0024 μM for the mixing experiment and the other estuary samples. Once again after centrifuging and concentrating the precipitate the precipitate was redissolved using 5% HNO_3. This method was not very accurate because it relies on the percent recovery of the thallium when using the ammonia to precipitate. Therefore the results are only general estimates. For Tl only the estuary and the mixing experiment samples were analyzed because of the very low levels of thallium presumed to be in the Oceanus samples.

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RESULTS AND ANALYSIS

Arsenic

Arsenic was the first metal to be tested for in the estuary and mixing experiment samples. Arsenic is a very toxic substance when ingested through drinking water and can also persist in the food supply. When consumed arsenic is not only toxic, with acute effects; it also has chronic effects. When chronically exposed to arsenic it acts as a carcinogen. The consumption of arsenic polluted water is the main source of possible carcinogenesis.

Workers in this industry are commonly exposed to high amounts of arsenic, and the additional arsenic released into the environment contributes to the possible ingestion of arsenic especially on local levels. Using a method devised by the EPA, calculations to determine cancer risk can be performed. It should be noted that since these calculations use the averages for all variables the cancer rate may be overestimated. The cancer rate due to occupational exposure (through inhalation) can be estimated by assuming a 60 kg worker is exposed 5 days per week, 50 weeks per year, over 20 years. The worker is assumed to breathe heavily 2 hours per workday at 1.5 m^3 per day and at a moderate breathing rate of 1 m^3 per day for 6 hours per workday. With a potency factor of 50 per mg/kg/day, an absorption factor estimated to be 80 percent , and the average concentration in the air thought to be about 0.05 mg/m^3 the rate of cancer can be estimated.

Daily Intake Rate $= 1.5 \text{ m}^3/\text{hr} \times 2 \text{ hr} + 1 \text{ m}^3/\text{hr} \times 6 \text{ hr} = 9 \text{ m}^3/\text{day}$

Total Dose $= 9 \text{ m}^3/\text{day} \times 5 \text{ days/week} \times 50 \text{ weeks/year} \times 20 \text{ years} \times 0.05 \text{ mg/m}^3 \times 0.8$
$= 1800 \text{ mg}$

Using a standard estimate of 70 years for a lifetime, the CDI is

CDI $= 1800 \text{ mg} / (60 \text{ kg} \times 70 \text{ yr} \times 365 \text{ days/year}) = 0.00117 \text{ mg/kg/day}$

Risk $= 0.00117 \text{ mg/kg/day} \times 50 \text{ (mg/kg/day)}^{-1} = 0.0585$

This calculation shows that the risk of cancer would be 58,500 chances in one million which is a devastatingly high rate. Besides worker exposure, arsenic can be ingested through drinking contaminated water, which was calculated previously.

With the known dangers of arsenic dissolved into a potential water supply as well as the possible effects on other organisms. Arsenic was one of the trace-metals that was especially interesting to test. The highest levels of arsenic were found in estuary sample #10 which has approximately 29.3 μM, and the sample used as the river end-member for the mixing experiment, estuary sample #9, has a concentration of 2.2 μM. The lowest values for arsenic concentration were found in the high salinity water samples with the lowest being about 0.045 μM in estuary sample #1.

Drinking water with a concentration of sample #10 will result in a risk of cancer. The following is the calculation of this risk.

CDI $= (29.3 \ \mu\text{mol/L} \times \text{mol}/1 \times 10^6 \ \mu\text{mol} \times 74.9 \text{ g/mol} \times 2 \text{ L/day}) / 70 \text{ kg} =$
$= 6.27\text{E-}5 \text{ mg/kg/day}$

Risk $= 6.27\text{E-}5 \text{ mg/kg/day} \times 1.75 \text{ (mg/kg/day)}^{-1} = 0.00011$

This would result in 110 per million people. This is a much lower rate of cancer, and since it is not clear if the people actually drink this water this is not a significant risk; however, the risk to animals and the risk of contamination of the food supply is still significant and cannot be overlooked. According to Nelson, et. al., (1993), this area is perhaps the most polluted in western Europe when compared to other river and estuarine systems, and the effects on the population from contamination that enters the food supply needs to be further investigated.

For As, the mixing experiment sample concentrations versus salinity was plotted in Figure 7. From this we can compare the mixing experiment graph (Figure 7) with the graph of the concentrations versus salinity found in the estuary (Figure 8). When comparing the mixing chart to what actually happens in the estuary it can be seen if there is indeed conservative mixing, if there are two or more water masses that are mixing, or if there are sources or sinks to the metals when mixed in the estuary with the increasing salinity waters.

Figure 7, shows the mixing curve that resulted from the mixing experiment that was simulated. When observing this graph it is obvious that the mixing experiment did not result in conservative mixing. In fact the graph shows that the simulated mixing experiment resulted in loss of arsenic, but Figure 8, which represents what was found in the arsenic or "real world observations", shows there is indeed linear mixing found in the estuary. This difference between the simulated mixing in the mixing experiment samples with the mixing that occurs naturally in the estuary, was possibly caused by additional precipitation occurring during the

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laboratory mixing of the mixing experiment samples. Because of the extreme salinity difference between the river water end-member, estuary sample #9, and seawater end-member, estuary sample #1, a salinity gradient is produced by mixing the two water samples. Before equilibrium was achieved in the mixed system, varying levels of pH and salinity were produced by the initial mixing as steady-state levels took time to occur. Therefore, precipitation could have occurred as the mixed samples reached equilibrium. These precipitates were then filtered out, and arsenic concentrations would be much lower for the mixing experiment samples.

Expanding the estuary graph of the higher salinity sample concentrations versus salinity in Figure 8b shows that there are two conservative mixing curves. This can be due to the two different waster masses that enter the estuary one from Rio Tinto and the other from Rio Odiel. Since there are two rivers that join and enter the estuary, the different mixing can be explained by these two different water masses that are entering the Tinto Estuary. In fact, looking at other studies that performed metal anomaly experiments on both rivers it can be determined whether there are metals that are unique to one or the other river or whether some metals are found in both rivers. According to Respaldiza et. al. (1993), As was found at appreciable levels in both rivers. This supports the theory that there is conservative mixing in the Tinto Estuary that occurs from two separate water masses. The fact that conservative mixing is observed also supports the theory that amounts of As enters the ocean coastal waters at detectable levels.

Iron

Although arsenic has negative effects on the environment, iron does not have carcinogenic effects; however, levels that are extremely high can be toxic to people as well as animals. This trace metal can also be studied to determine if this metal is "mixed out" and ends up in the Atlantic Ocean coastal waters. Iron levels were high throughout the estuary with once again the highest levels found at estuary sample #10 where Fe concentration was 25.5 mM. The chosen river end-member, estuary sample #9, has a concentration of about 12 mM. The lowest levels were found in the Oceanus samples as well as the high salinity samples in the estuary with the lowest being 26.4 μM in Oceanus sample (station) #0.1. This is higher than "normal" ocean waters which have Fe concentrations on the nM level. The higher Fe concentrations found in these samples; however, are not uncharacteristic due to the extensive pollution in this area.

Once again a mixing curve for the mixing experiment samples, Figure 9, was plotted. This indicates a somewhat conservative mixing curve for these samples; however, the higher salinity mixing experiment samples seem to have larger concentration values than expected. To explain this, it may be possible that the seawater end-member was contaminated for Fe. The actual measurements done for the estuary samples seems to also indicate conservative mixing, see Figure 10. However, when the cluster of low concentration values is expanded, in Figure 10b, there are not clear linear mixing curves to indicate conservative mixing, but again mixing is affected by different water masses. Referring to the study by Respaldiza, et.

al. (1993), appreciable levels of Fe were found in the sediments of both the Rio Tinto and Rio Odiel. This study again supports the theory that the different water masses from the Rio Tinto and Rio Odiel, containing Fe, enter the estuary and may result in the estuary data that are observed in Figure 10b.

Another important factor that affects the amount of soluble iron in the water samples is the speciation of iron. Morel, et. al., (1993), discusses the presence of iron as Fe(II) in waters affected by acid mine drainage. The oxidation of this form of iron has been shown to be slow in waters with low pH. Therefore, as discussed previously, the waters of the Rio Tinto has been measured to be between 2.5 and 2.8 from the mine to the estuary and increases to about 6.2 in the estuary (Nelson, et. al., 1993). Therefore, Fe(II) should persist in the river waters that enter the estuary and be further oxidized as this trace metal is carried through the Tinto Estuary. The rate of this oxidation of Fe(II), however, is greatly dependent on the pH, which is also related to salinity. To further understand the behavior of Fe in the estuary it was necessary to graph the pH relative to the salinity in the estuary (see Figure 11).

The graph was calculated assuming a mixing of 1.5 mM H_2SO_4 and seawater with a salinity of 36 containing 1900 μmol/kg ΣCO_2 and 2190 μeq/kg alkalinity. The behavior is greatly dependent on whether CO_2 is conservative in the estuary or not. CO_2 is believed to act fairly conservatively in the estuary because of the short residence times of the intermediate-salinity waters. Therefore, loss of CO_2 is thought to be small. Since it is fairly safe to assume that CO_2 is conservative, the estuary acts as a closed-system, the oxidation rate of the Fe(II) is slow in waters from

the river to waters with salinity of about 20-25. Again looking at Figure 10 and

Figure 10b modelling the estuary, this theory is indeed supported by the actual data

measured for the estuary system. In waters with salinity above 20-25 the rate of

oxidation is more rapid. Therefore mixing is conservative up to salinity 20-25.

Lead

Lead has toxic effects to humans especially children. Too much lead in the

blood effects the neurological system and can result in lowered IQ scores especially

in children who are most susceptible to lead exposure and are affected by much

lower levels. Pb has damaging affects to the nervous and peripheral systems with

additional damaging affects to the kidneys (Masters, 1991). Although this is mostly

documented in humans these affects can occur not from just drinking the

contaminated water, but also from eating contaminated foods. Since it is unknown

how children are exposed to the water and soils in this area, the effects of Pb could be

substantial especially to this extremely sensitive group.

The highest lead levels were again found in estuary sample #10 with a lead

concentration of about 7.2 μM. While estuary sample #9 was 0.42 μM, and the

lowest levels were found in the Oceanus samples as well as the high salinity estuary

samples with the lowest concentration of 0.00025 μM found in Oceanus sample

(station) # 2.0. The Pb mixing experiment sample concentration versus salinity was

graphed in Figure 12. This graph shows that conservative mixing should be

observed throughout the estuary. Comparing this to the graph of the estuary

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measurements (concentration versus salinity), in Figure 13, conservative mixing is also observed. Further investigation of the lower concentration levels in the high salinity samples, in Figure 13b, also reflects the linearity in the mixing. Pb is an excellent example of conservative mixing in the Tinto estuary, and is the best example of trace-metals being "washed out" and entering the coastal waters of the Atlantic Ocean.

Cobalt

Cobalt is also another trace metal that can be studied to observe the mixing that is undergone in an estuary. Cobalt was found at detectable levels throughout the estuary. The highest level of Co was found in estuary sample #9 with a concentration of 18.6 μM. The lowest levels found in the high salinity samples with the lowest measured at 0 μM in estuary sample #22.

The mixing experiment of Co was plotted in Figure 14. The simulated mixing experiment shows conservative mixing for Co that should be observed in the estuary if there are no other sink or source processes acting on this metal. Figure 15 of the estuary concentrations also reflects conservative mixing. Closely observing the graph of the estuary with particular attention to the lower level cluster, Figure 15b, also shows conservative mixing. Next to Pb, Co is also a good example of conservative mixing and should also result in contamination in the coastal waters leading to the Mediterranean Sea.

Thallium

Thallium is extremely toxic to the neurological system in people and probably has these same effects in animals. Because of the limiting effects of the method used to measure the Tl concentrations, it is hard to determine exactly how Tl behaves in the estuary. The measurements and subsequent graphs of thallium should, therefore, be analyzed with caution. Definitive conclusions on the behavior of thallium in this estuary should not be made without future study.

Figure 16 once again shows the mixing experiment, and indicates conservative mixing in these samples. The plot of the estuary measurements, in Figure 17, however, are inconclusive. It seems that conservative mixing may act in the estuary, but it is not clearly shown in this figure. Figure 17b does not provide any further insights into the mixing that is undergone in the estuary. With further measurements of Tl and perhaps with an alternative method, the behavior of Tl may be more conclusively understood. The results from the Tl measurements have to be used carefully and cautiously.

CONCLUSION AND FUTURE RECOMMENDATIONS

The results of the investigation into how the trace-metals, As, Fe, Pb, Co, and Tl, have shown that conservative mixing does act throughout the estuary for some metals. The study has been conclusive enough to show that the pollution found in the Rio Tinto and Rio Odiel can in fact contribute to the trace metal enrichments seen in the Mediterranean Sea. Future studies should be done to determine just what metals travel from the estuary into the Atlantic coastal waters and subsequently into the Mediterranean Sea. It may be possible to prove that these trace-metals originated in the Tinto estuary by performing analyses on the isotope ratios of the metals found in the Mediterranean Sea. Pb seems to be the most promising for a study like this. Pb from gasoline has a different ratio than Pb found from the pollution in the Tinto estuary. Co may also be another metal that future investigations can provide further insights whether these metals end up in the Mediterranean Sea. It may be possible to measure this in future studies. Another possibility may be to perform a tracer study of an isotope that is not found in either water body, either the estuary or the Mediterranean Sea. This tracer can be released as a river end-member, and its travel can be documented to observe the processes of metal transport from the Tinto estuary to the Mediterranean Sea.

Mining in any area can have disastrous effects on the natural water resources. Polluted water is an extensive problem throughout the world. Not only is it costly to clean it to make it usable, the polluted water is unable to sustain any aquatic life. Many organisms are affected by pollution including humans. Heavy metals persist

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for many years polluting the whole area travelling from the water into the sediments and beyond. These heavy metals, especially arsenic, are extremely hazardous to humans. It has been found that cancer risks to those who live in areas exposed to pollution from mines is extremely high. Another area of concern is how these metals may persist in the food supply. Further study of the effects of the pollution on human health and the food supply should be performed because of the extensive pollution in this area.

Since studies have been done, this area has been found to be the most polluted region in Spain, and its drinking water is unsuitable since the levels of metals in the sediments exceed all the limits set by the World Health Organization (Nelson, et. al., 1993). It is very important to ensure that safe, unpolluted water is available to everyone and that exposure to carcinogens is eliminated. Since the mining procedure produces wastes that have previously been discharged to the local waterways, it is obvious that this practice must stop. Although, it is not known whether the water in this area is regularly used for human consumption it is used for their livestock and grazing areas and affects the aquatic organisms that are part of the food supply. The acid drainage waters should be cleaned before it is introduced back to the environment. An even better alternative would be to require that mining operations recycle and reuse the water that they pollute. This would close the loop eliminating pollution to natural waters.

Although this solution seems pretty simplistic, it has only been recently that environmental issues have begun to be addressed. In the United States,

environmental policy has slowly evolved where now there are effluent standards to reduce the amount of pollution entering our waterways. However, many countries as of yet have little or no environmental concerns. This is especially problematic in remote areas where pollution and its effects on human health can easily be overlooked.

The problems of the Rio Tinto area have only been recently studied and understood even though this problem has persisted for thousand of years. Now that the pollution in the area has been studied and addressed, cleanup actions and changes to industries' procedures should be implemented. This, however, may not even happen anytime in the near future because environmental policy has to stimulate change away from the status quo.

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Figure 1

Concentration Versus Salinity
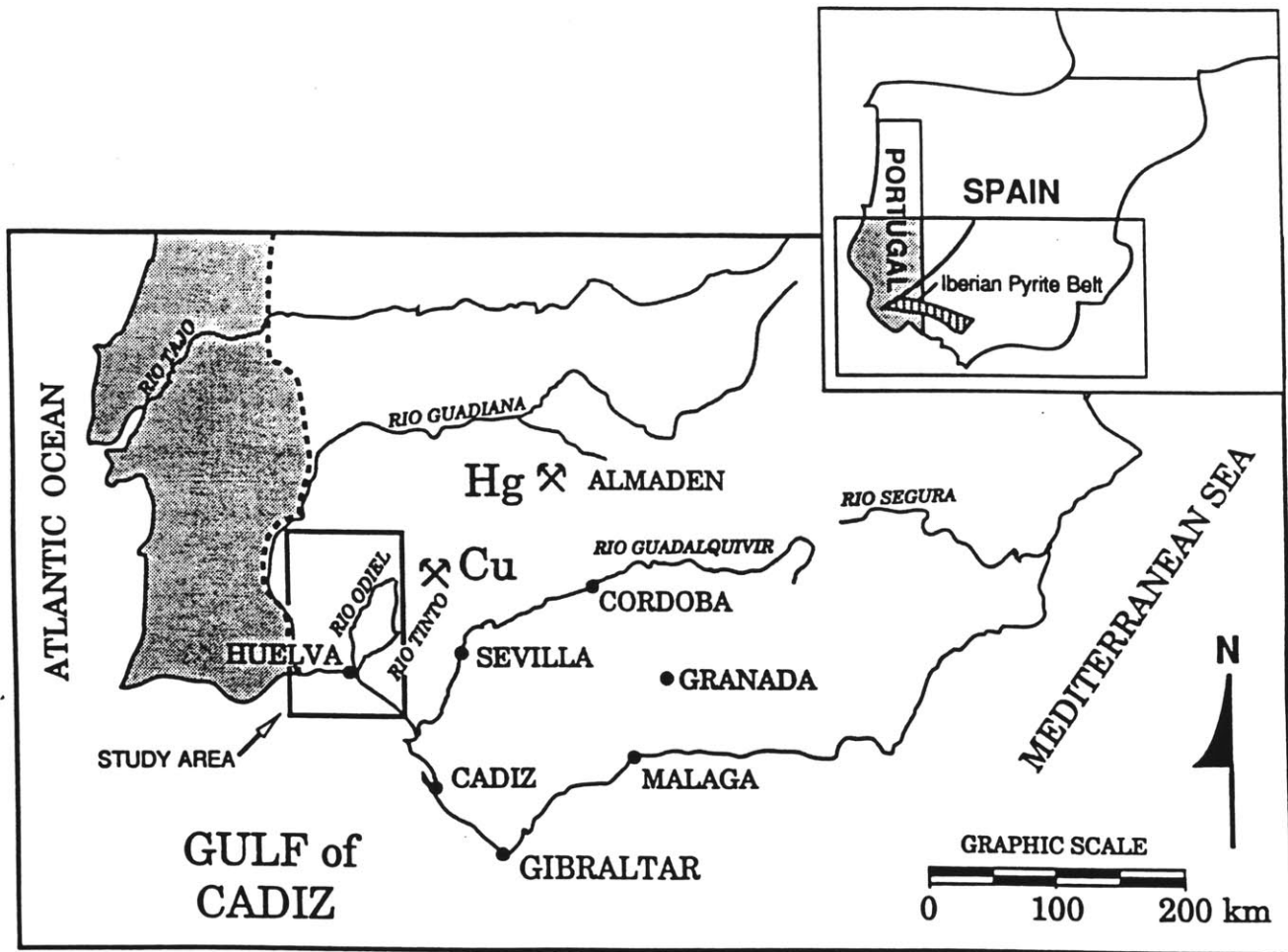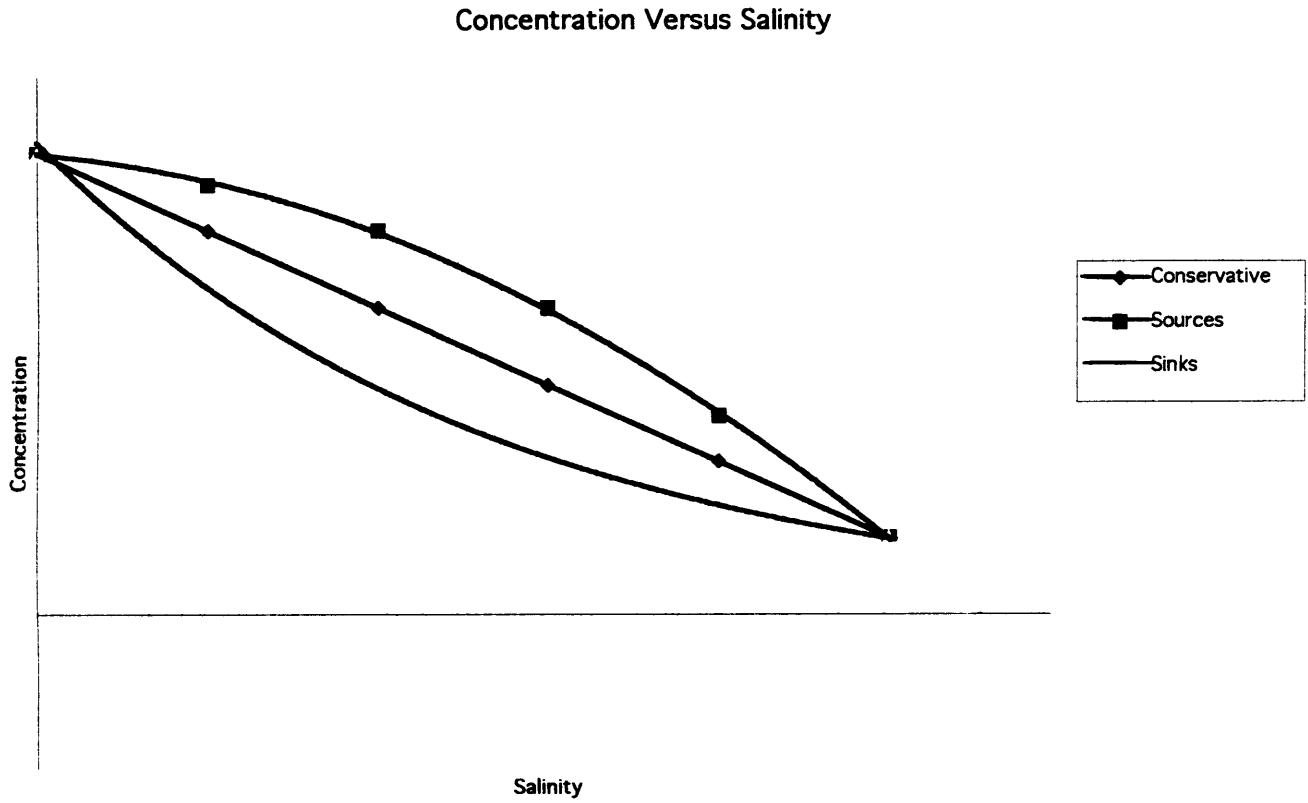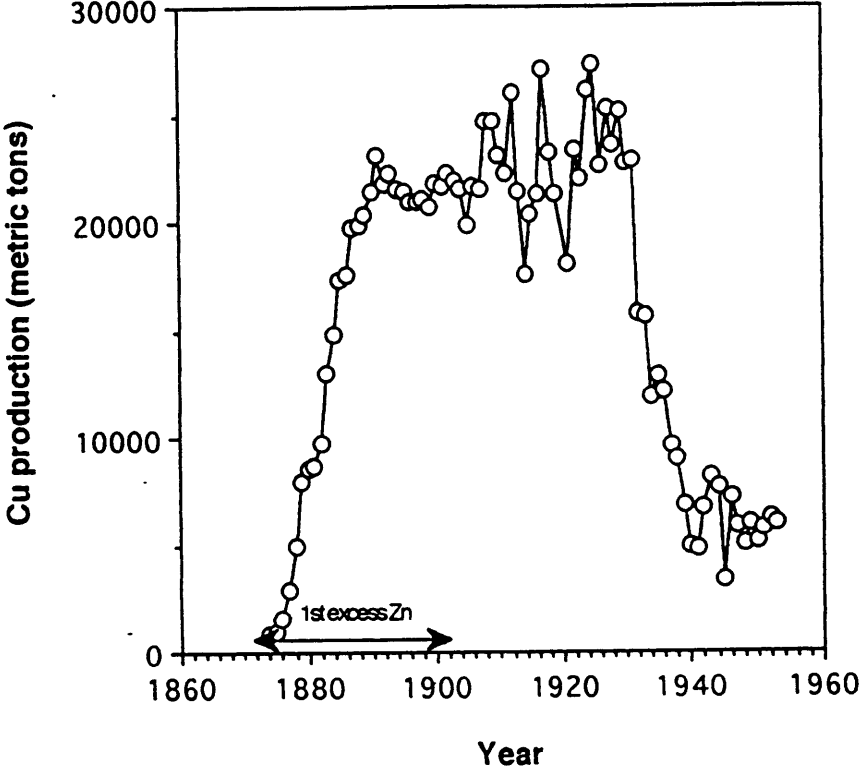
Figure 2

Figure 3

STAGE	As TEMPERATURE PROGRAM			
	START TEMPERATURE (C)	END TEMPERATURE (C)	TIME (sec)	CARRIER GAS (ml/min)
DRY	70	70	25	200
DRY	80	80	10	200
ASH	120	160	15	200
ASH	160	220	25	200
ASH	220	1400	15	200
ASH	1400	1400	15	200
ATOM	2700	2700	4	0
CLEAN	2800	2800	4	200

Figure 4

STAGE	Fe TEMPERATURE PROGRAM			
	START TEMPERATURE (C)	END TEMPERATURE (C)	TIME (sec)	CARRIER GAS (ml/min)
DRY	60	70	20	200
DRY	70	110	4	200
ASH	110	1100	15	200
ASH	1100	1100	10	200
ATOM	2400	2400	4	20
CLEAN	2800	2800	4	200

Figure 5

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STAGE	Co TEMPERATURE PROGRAM			
	START TEMPERATURE (C)	END TEMPERATURE (C)	TIME (sec)	CARRIER GAS (ml/min)
DRY	60	140	30	200
ASH	140	1200	15	200
ASH	1200	1200	10	200
ATOM	2700	2700	4	30
CLEAN	2800	2800	4	200

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Figure 6

As Mixing Experiment
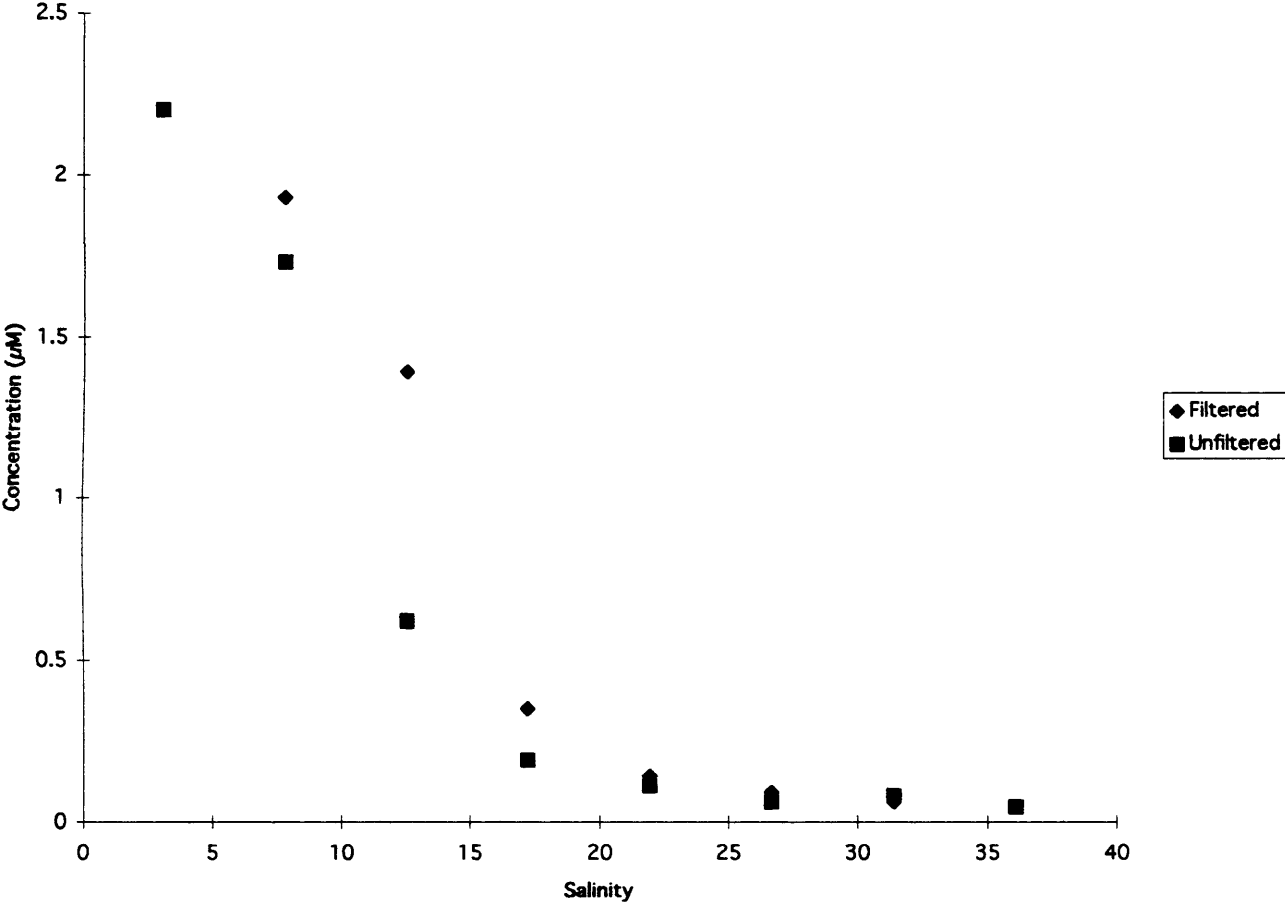
Figure 7

THE FIGURES

As Estuary

Figure 8
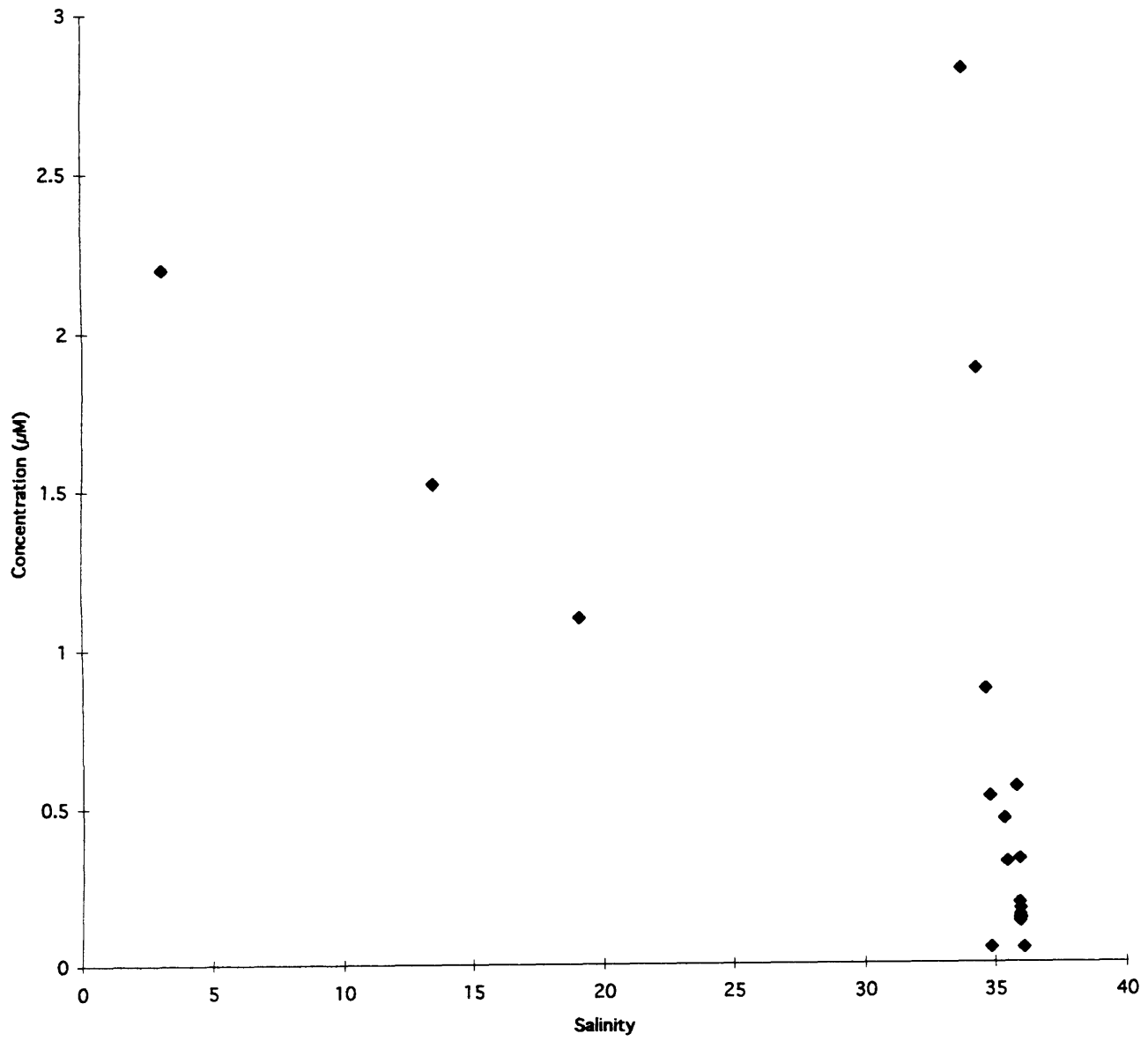
As Estuary

Figure 8b
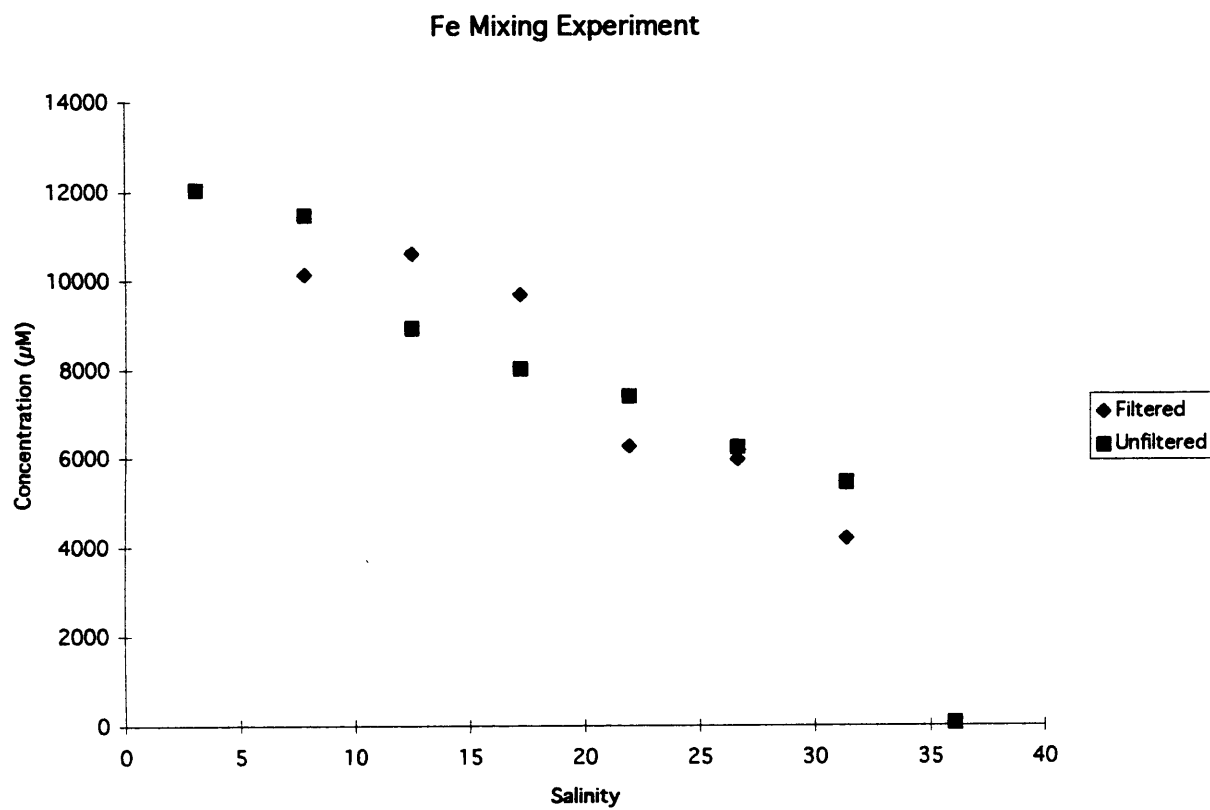
Figure 9

THE FIGURES
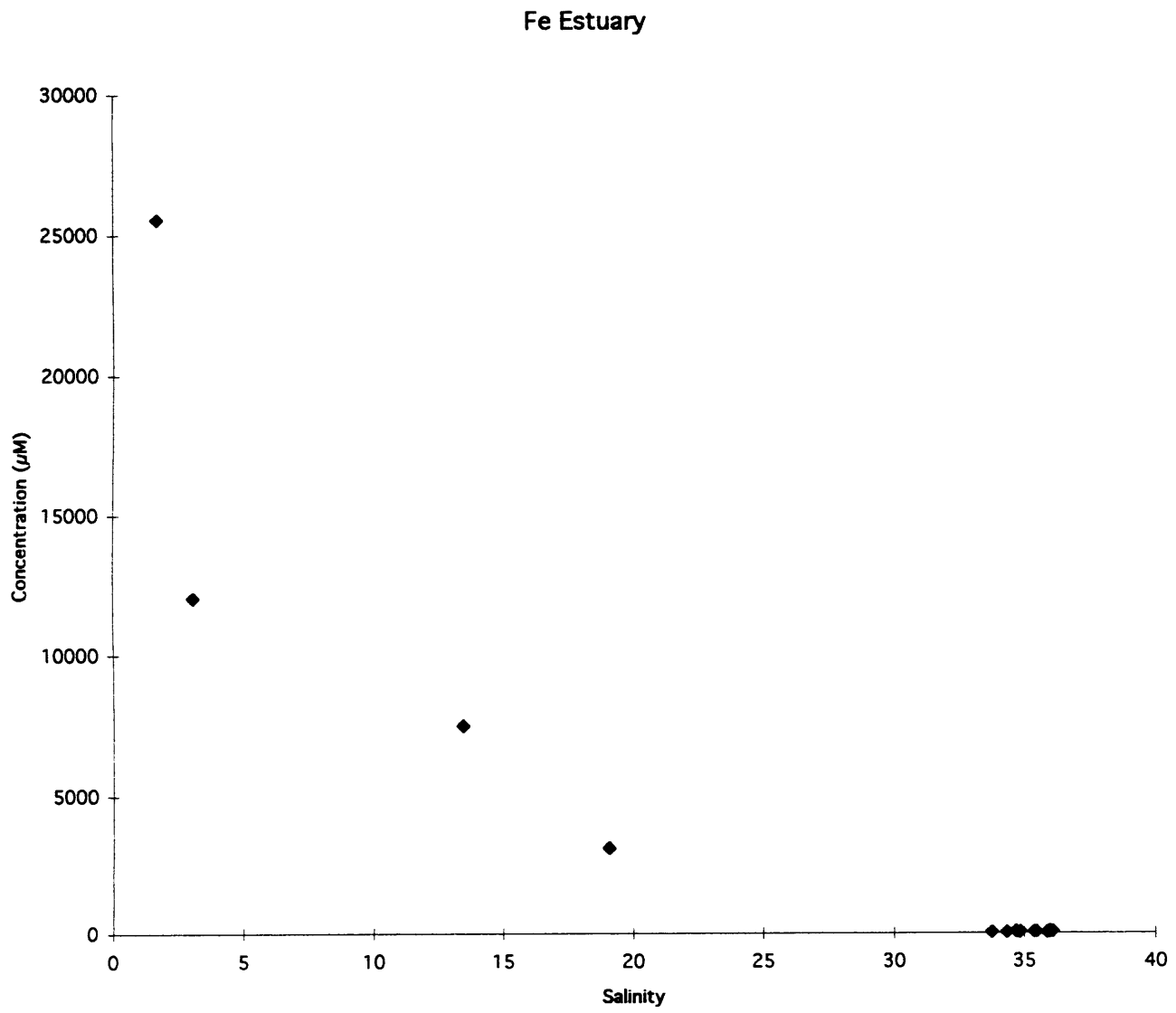
Fe Estuary
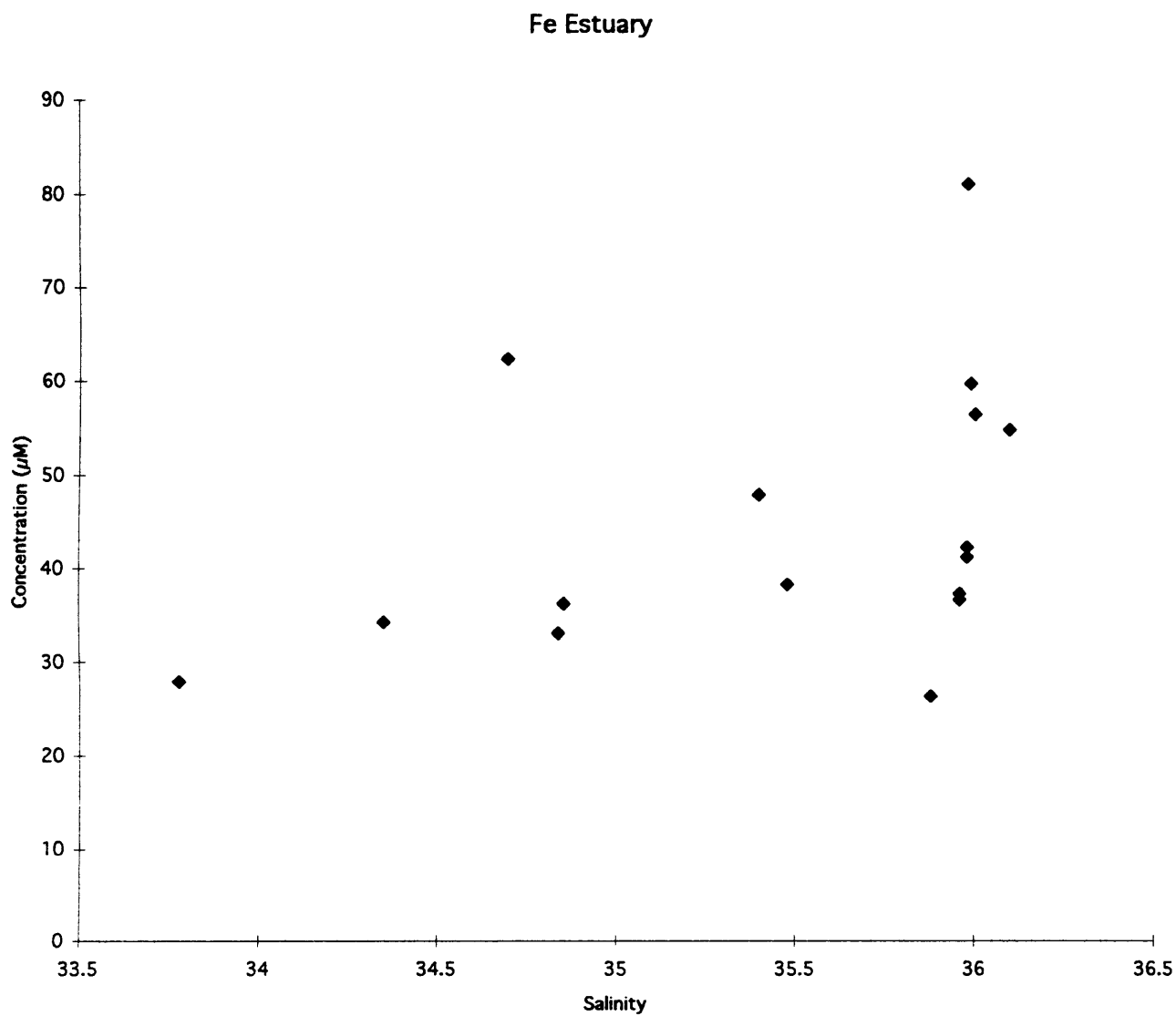
Figure 10

Fe Estuary

Figure 10b

Rio Tinto Estuary

Figure 11

Pb Mixing Experiment
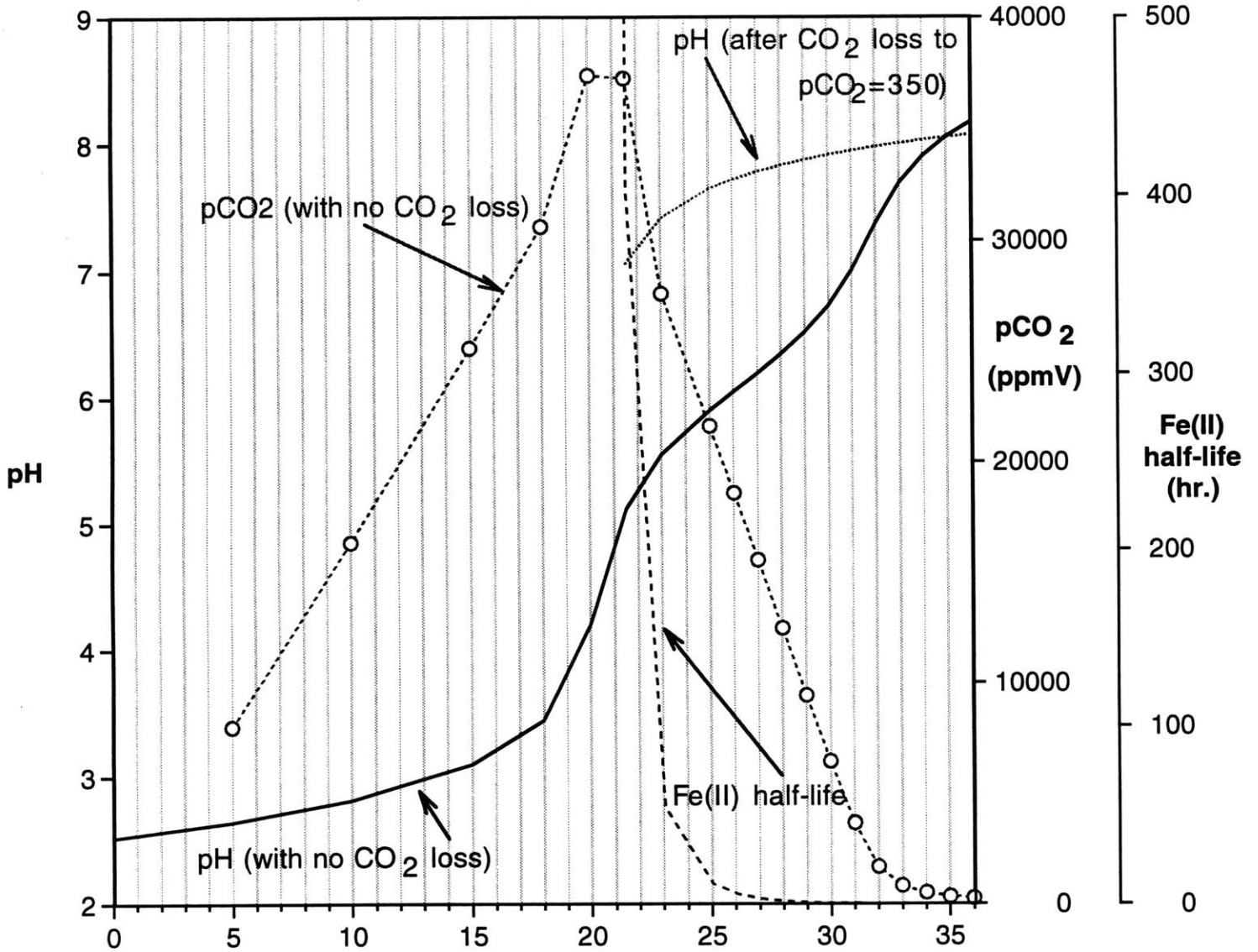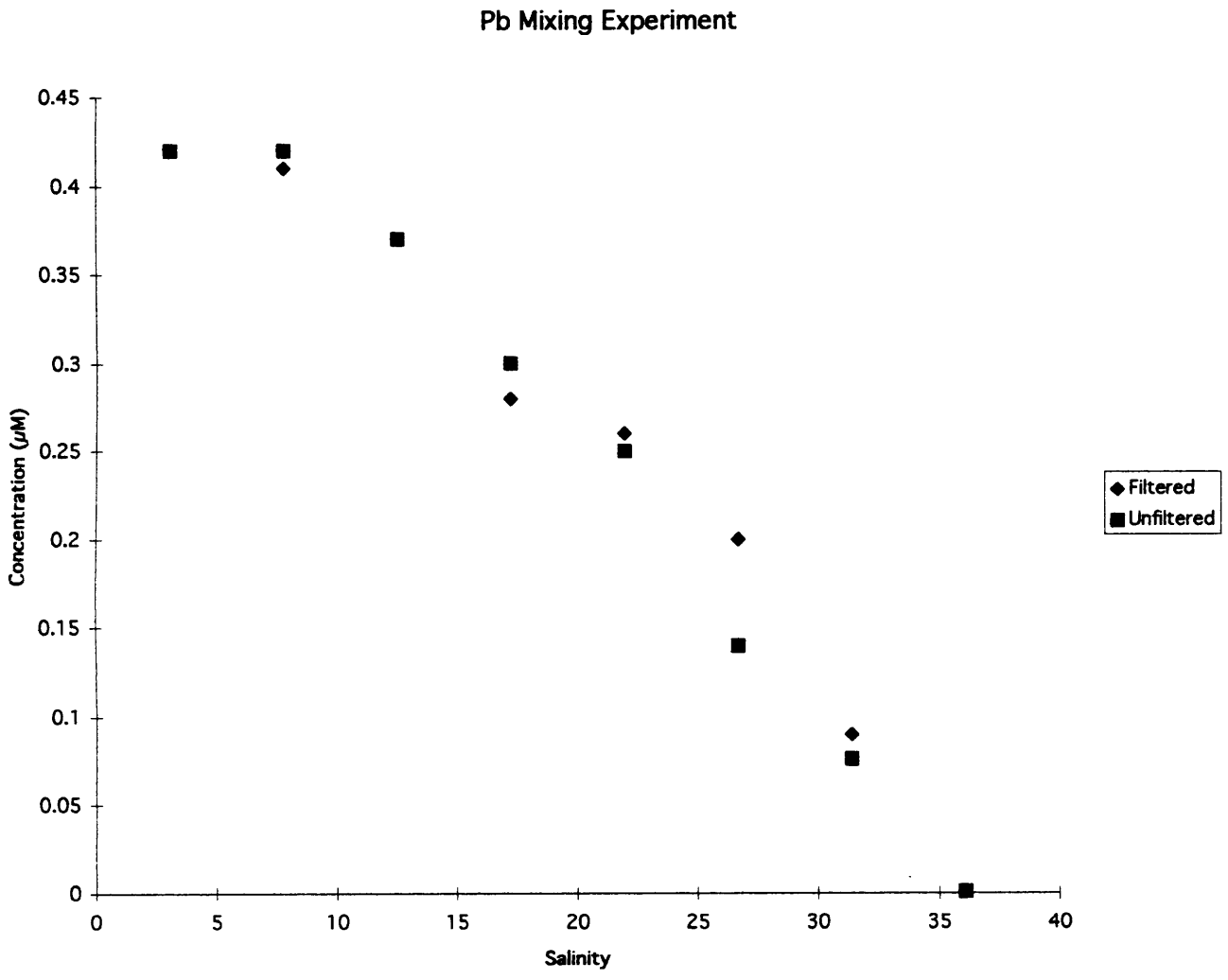
Figure 12

THE FIGURES

Pb Estuary

Figure 13

Pb Estuary

Figure 13b

Co Mixing Experiment
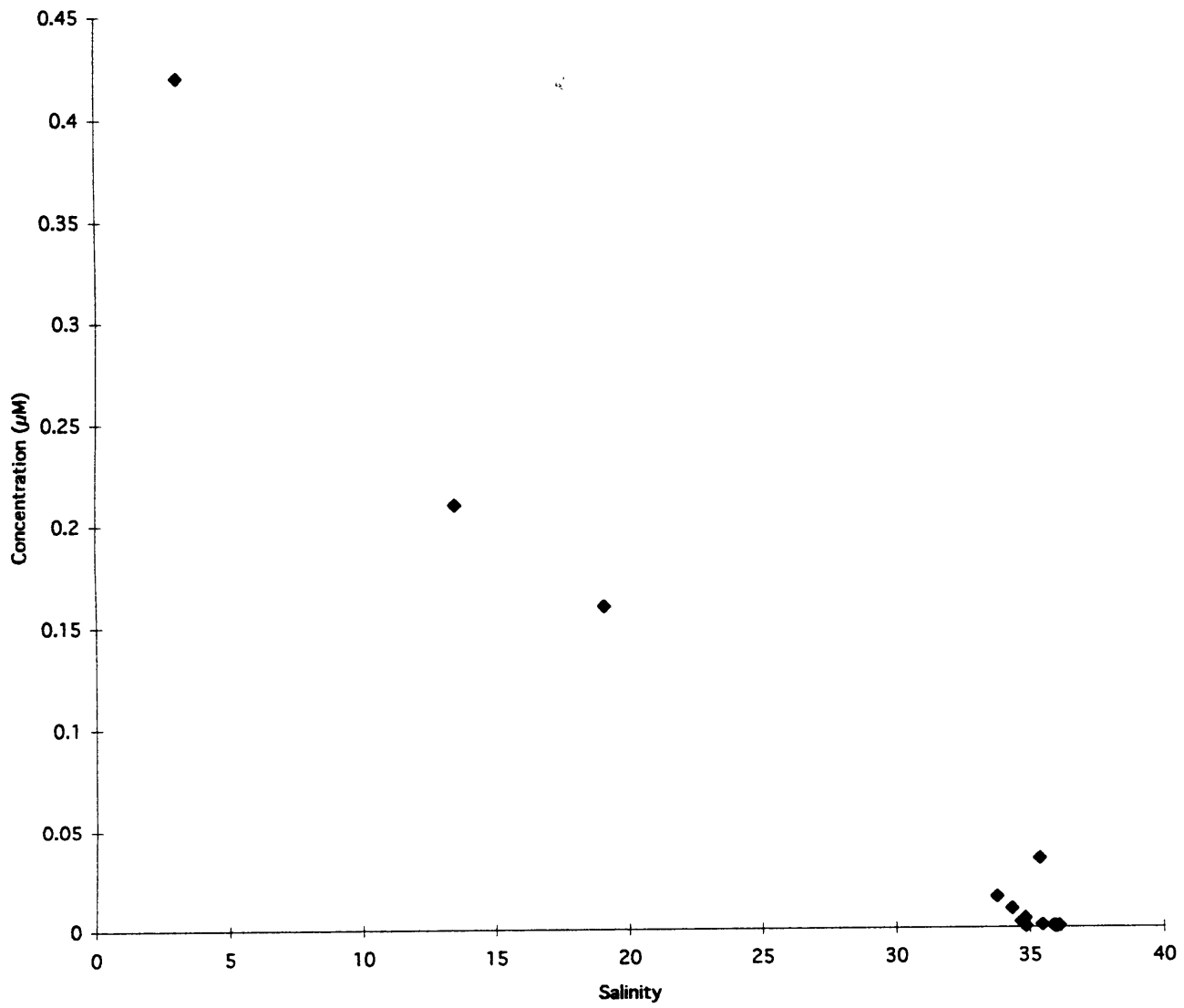
Figure 14
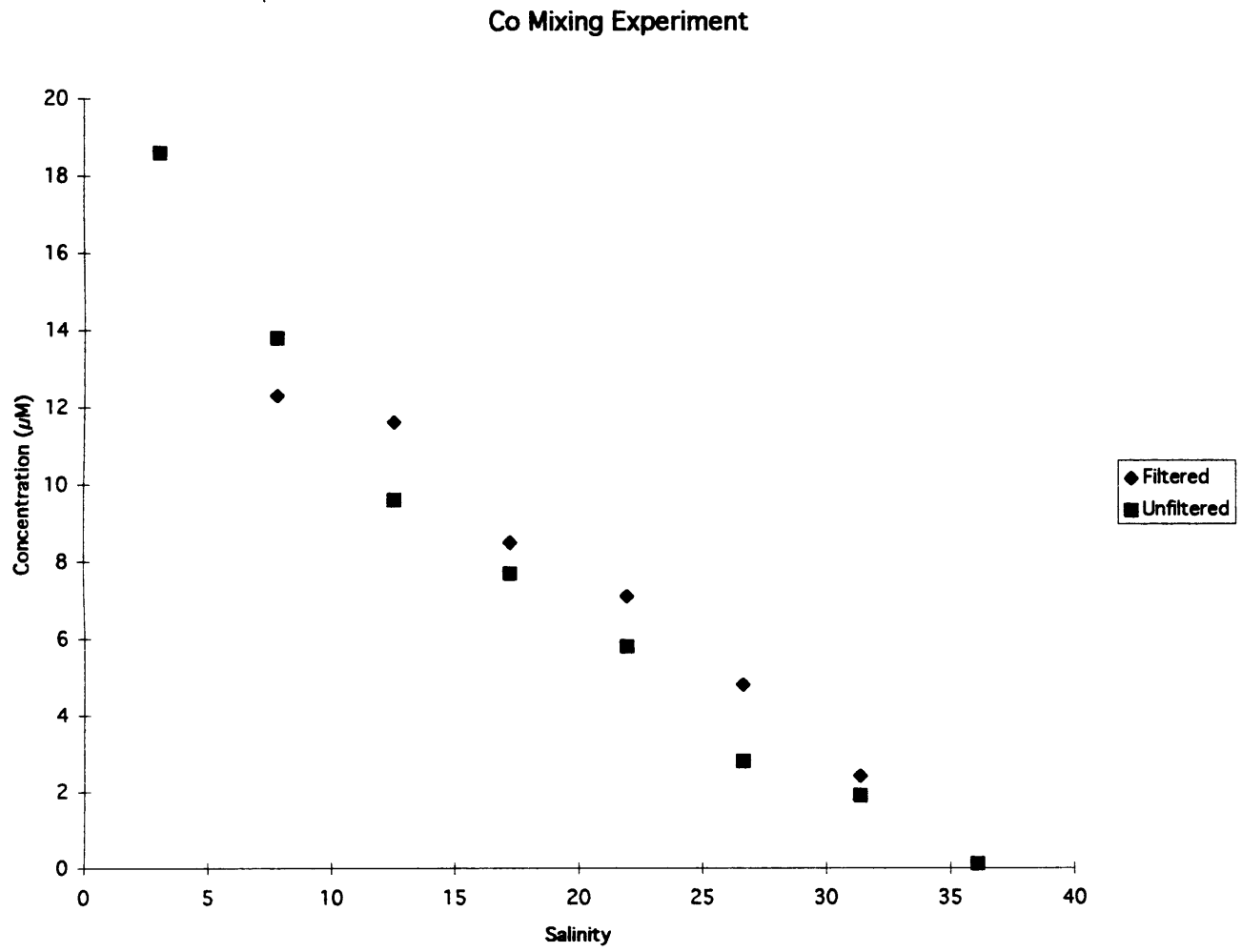
Co Estuary

Figure 15

THE FIGURES

Figure 15b

TI Mixing Experiment
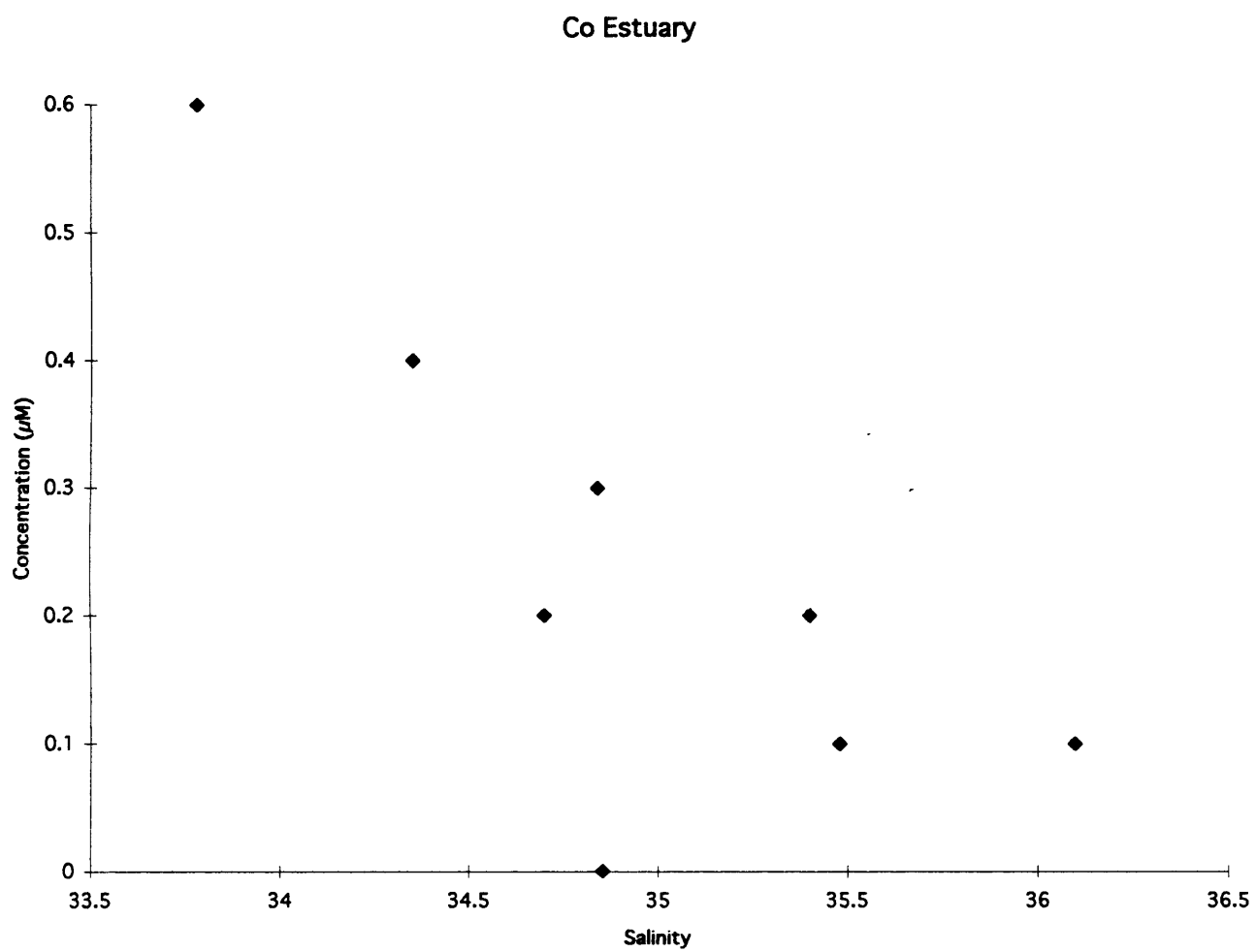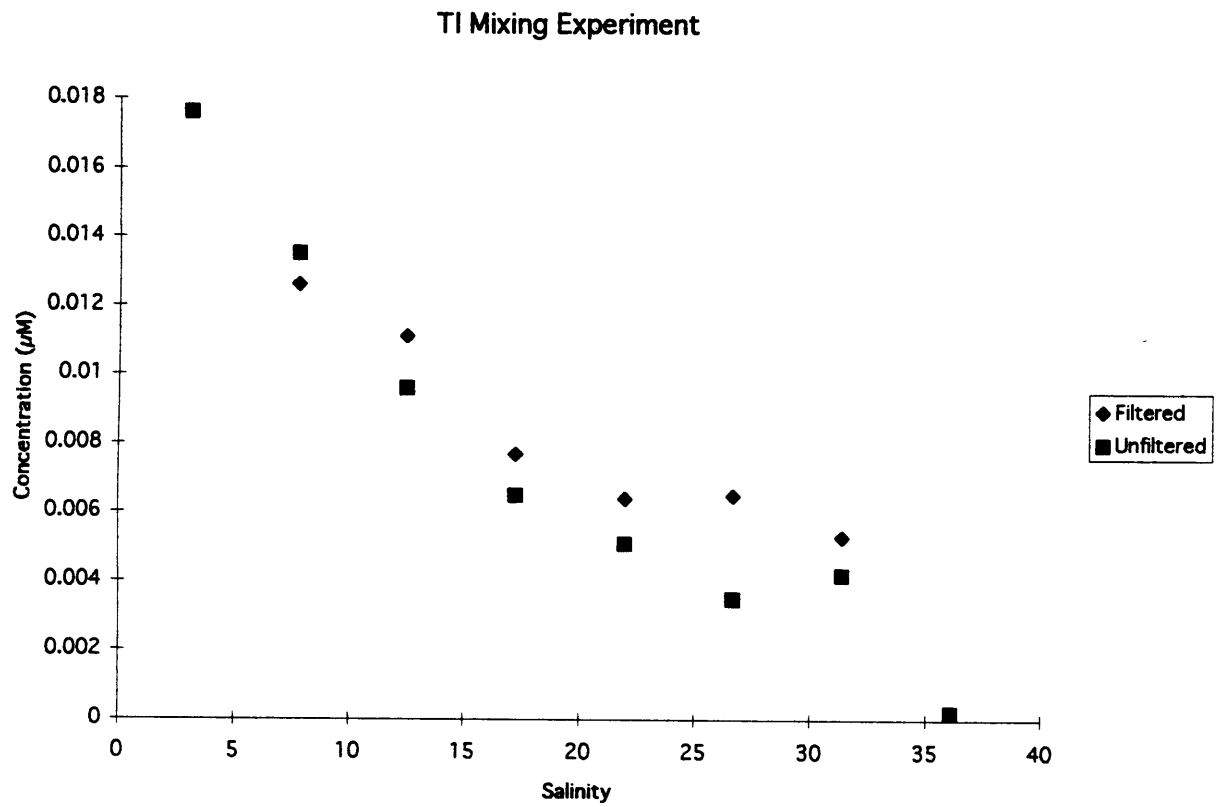
Figure 16

THE FIGURES

TI Estuary
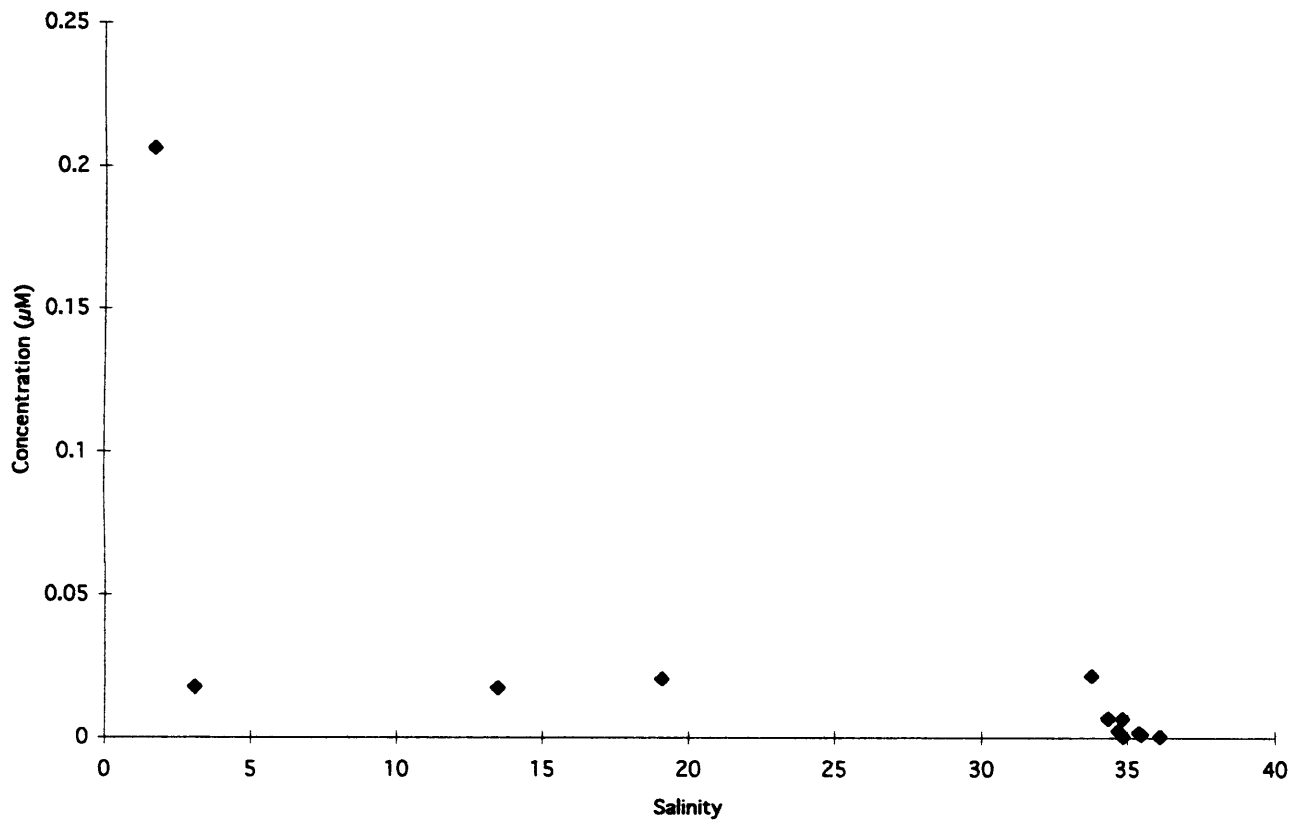
Figure 17

TI Estuary
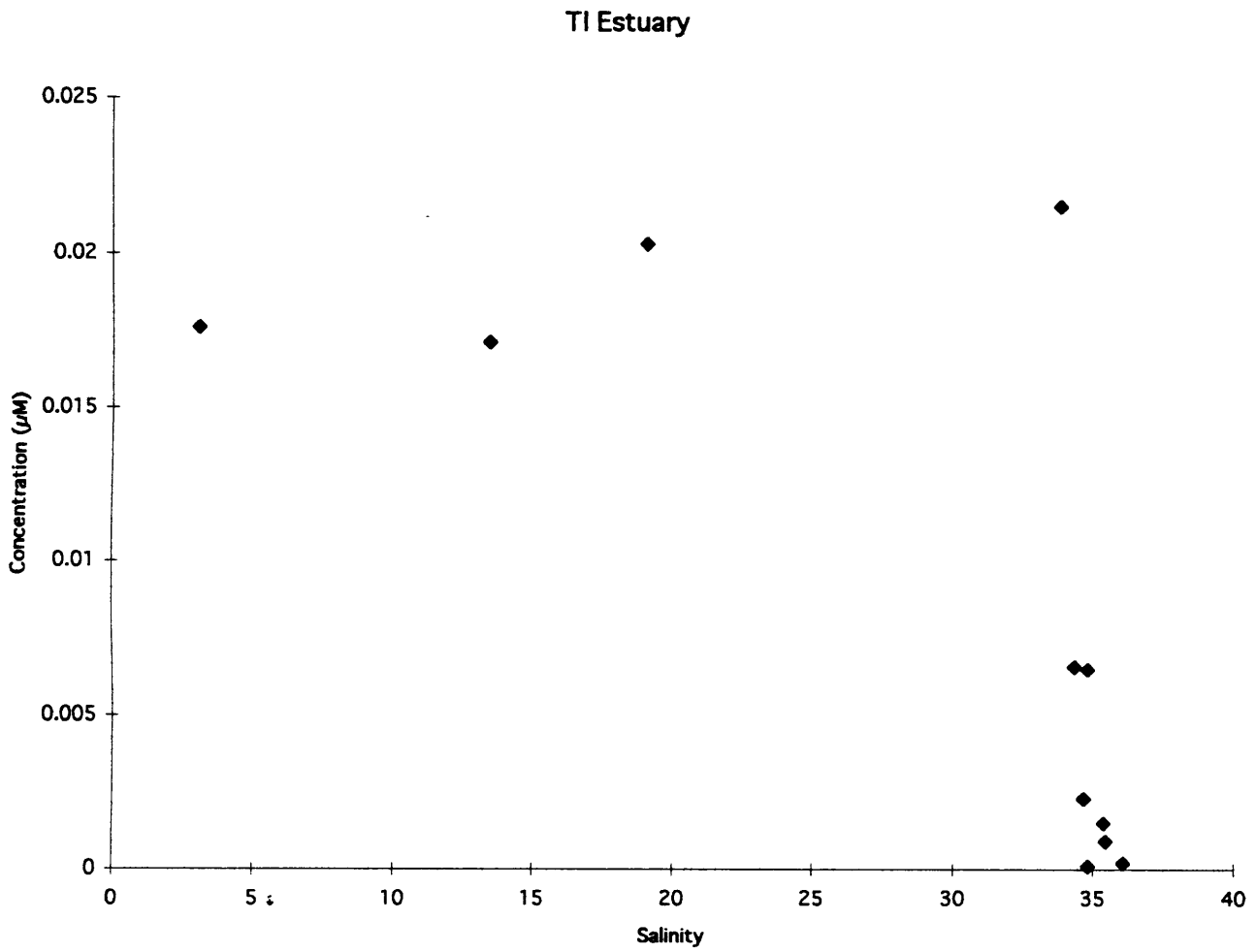
Figure 17b

APPENDIX: THE DATA

Sample	Salinity	As (μM)	Fe (μM)	Pb (μM)	Co (μM)	Tl (μM)
Estuary #1	36.1	0.045	54.9	0.00082	0.1	0.0002
Estuary #2	35.48	0.32	38.4	0.0012	0.1	0.0009
Estuary #3	35.4	0.46	48	0.03433	0.2	0.0015
Estuary #4	34.7	0.87	62.4	0.0027	0.2	0.0023
Estuary #5	33.78	2.82	27.9	0.01533	0.6	0.0215
Estuary #6	34.35	1.88	34.3	0.0093	0.4	0.0066
Estuary #7	34.84	0.53	33.2	0.0044	0.3	0.0065
Estuary #8	13.5	1.52	7509	0.21	9.4	0.0171
Estuary #9	3.1	2.2	12020	0.42	18.6	0.0176
Estuary #10	1.7	29.3	25545	7.2	13.1	0.2063
Estuary #13	19.1	1.1	3114.5	0.16	4.7	0.0203
Estuary #22	34.855	0.046	36.3	0.00031	0	0.0001
Mixing Exp. Filt. #9(7),#1(0)	3.1	2.2	12020	0.42	18.6	0.0176
Mixing Exp. Filt. #9(6),#1(1)	7.81	1.93	10113	0.41	12.3	0.0126
Mixing Exp. Filt. #9(5),#1(2)	12.53	1.39	10589	0.37	11.6	0.0111
Mixing Exp. Filt. #9(4),#1(3)	17.24	0.35	9672	0.28	8.5	0.0077
Mixing Exp. Filt. #9(3),#1(4)	21.96	0.14	6259.8	0.26	7.1	0.0064
Mixing Exp. Filt. #9(2),#1(5)	26.67	0.09	5963.7	0.2	4.8	0.0065
Mixing Exp. Filt. #9(1),#1(6)	31.39	0.06	4190.2	0.09	2.4	0.0053
Mixing Exp. Filt. #9(0),#1(7)	36.1	0.045	54.9	0.00082	0.1	0.0002
Mixing Exp. Unf. #9(7),#1(0)	3.1	2.2	26.4	0.42	18.6	0.0176
Mixing Exp. Unf. #9(6),#1(1)	7.81	1.73	36.8	0.42	13.8	0.0135
Mixing Exp. Unf. #9(5),#1(2)	12.53	0.62	41.3	0.37	9.6	0.0096
Mixing Exp. Unf. #9(4),#1(3)	17.24	0.19	59.8	0.3	7.7	0.0065
Mixing Exp. Unf. #9(3),#1(4)	21.96	0.11	56.5	0.25	5.8	0.0051
Mixing Exp. Unf. #9(2),#1(5)	26.67	0.06	42.4	0.14	2.8	0.0035
Mixing Exp. Unf. #9(1),#1(6)	31.39	0.08	81.2	0.076	1.9	0.0042
Mixing Exp. Unf. #9(0),#1(7)	36.1	0.045	37.4	0.00082	0.1	0.0002
Oceanus 0.1	35.88	0.56	26.4	0.0007		
Oceanus 1.1	35.96	0.14	36.8	0.0005		
Oceanus 2.0	35.98	0.13	41.3	0.00025		
Oceanus 3.1	35.99	0.17	59.8	0.00031		
Oceanus 6.0	36.003	0.14	56.5	0.00028		
Oceanus 14.2	35.98	0.15	42.4	0.00029		
Oceanus 14.4	35.98	0.33	81.2	0.00037		
Oceanus 14.6	35.96	0.19	37.4	0.00056		