Processes Influencing the Fate of Trace Metals in Torres Strait: A Review of Current Data and Concepts

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Abstract

In this presentation, the exisiting data on trace metals concentrations in Torres Strait waters and sediments is compiled, methods reviewed and the data briefly discussed. Physico-chemical processes likely to be important in the supply to and mobilization within Torres Strait are then reviewed and, on the basis of exisiting data, attempts are made to refine the range of possibilies for source, transformation processes and fate of heavy metals in the Torres Strait system. A brief compilation of additional data requirements to satisfactorily develop predictive modelling capability is also included.

Introduction

Assessment of the fate of trace metals introduced by natural or anthropogenic activities to the marine environment is often exceedingly complex and requires an understanding of the chemical, physical and biological processes influencing the forms and amounts of trace metal species. Typically, a spatial and temporal description of the inter-dependence of chemical, physical and biological processes, unique to each system, is ultimately required. Such an interplay of processes is certainly appropriate to the Torres Strait system.

While hypotheses regarding the source, mobilisation processes and subsequent transport of metals in a system such as Torres Strait can easily be formulated, the hypotheses must be tested against actual data for the system of interest. In addition, assessment of the importance of certain processes may require parameters such as rates of metals release and rates of transformation of sediments. Once feasible models

of potential metals fate have been constructed for the elements of interest, they must be tested against actual water column and benthic sediment data.

Existing data on trace metals content of waters and sediment may be adequate for model development and testing. However, experience shows that historic chemical data, particularly at the trace level, suffers seriously from deficiencies in sampling and analysis methodologies and statistical veracity.

In this presentation, the exisiting data on trace metals concentrations in Torres Strait waters and sediments is compiled, methods reviewed and the data briefly discussed. On the basis of exisiting data, attempts are made to refine the range of possibilies for source, transformation processes and fate of heavy metals in the Torres Strait system. Physico-chemical processes likely to be important in the supply to and mobilization within Torres Strait are then reviewed in more detail and a brief compilation of additional data requirements to satisfactorily develop predictive modelling capability is noted.

Review of Trace Element Concentration Data for Waters and Sediments of Torres Strait

While extensive monitoring of waters and deposited and suspended sediments in the Ok Tedi and Fly River systems is undertaken by the mining industry for assessment of compliance with regulatory limits, very few broader scale studies of the trace element composition of waters and sediments throughout Torres Strait have been undertaken. Much of the data that is available has been collected with a view to assessing the extent of transport of the riverine metals load through the estuarine region to the Gulf of Papua. The scope of relevant documented studies, the methods used and results obtained are summarised below.

Ok Tedi Mining Limited Environmental Investigations

Environmental investigations have been undertaken by Ok Tedi Mining Lmited (OTML) since 1981 when the Ok Tedi Environmental Study was commenced (Maunsell and Partners, 1982) and an environmental monitoring program has been in place since 1983. The initial study was focussed particularly on the immediate environment of the Ok Tedi and Fly Rivers but was broadened considerably in 1986 following abandonment of construction of a tailings dam by OTML due to structural geologic problems (Eagle and Higgins, 1991). The study was completed in 1989 and the results presented in a Final Draft Report (OTML, 1988) and in a Supplementary Investigations Report (OTML, 1989).

As part of the ongoing environmental monitoring program, surface sediment samples were collected at intertidal mangrove sites and at locations on reefs in the northern Torres Strait (see Figure 1) and analysed for particle size distributions and copper fractionation between the various size classes. Samples were collected from the following locations:

- Dibiri Island
- Puruto Island
- Kiwai Island

Table 1. Copper concentrations in various size classes of sediments obtained from intertidal mangrove sites and at locations on reefs in the northern Torres Strait (from OTML, 1989)

Location	Size (μm)	Weight (g)	% Wt	Copper Assay (μg/g)
1. Dibiri Island	<10	18.874	57.8	39
	<20	25.972	79.6	28
	<63	31.252	95.7	26
	<100	32.052	98.2	26
	Total	32.658	100	
2. Puruto Island	<10	17.359	36.1	51
	<20	24.656	51.2	45
	<63	39.249	81.6	34
	<100	47.655	99.0	38
	Total	48.122	100	
3. Kiwai Island	<10	0.794	1.4	71
	<20	1.094	1.9	53
	<63	1.459	2.6	45
	<100	6.906	12.1	48
	Total	56.968	100	
4. Sigabadiri (11 km west)	<10	2.120	4.2	41
	<20	3.464	6.9	33
	<63	39.679	59.3	22
	<100	48.338	96.6	34
	Total	50.028	100	
5. Bristow Island	<10	0.747	1.7	92
	<20	0.968	2.2	86
	<63	1.209	2.7	69
	<100	19.438	44.0	10
	Total	44.138	100	
6. Parama Island	<10	3.095	6.1	53
	<20	3.701	7.3	48
	<63	5.056	10.0	31
	<100	17.488	34.6	35
	Total	50.597	100	
7. Sagero Village	<10	0.702	1.2	65
	<20	0.928	1.6	65
	<63	1.117	2.0	54
	<100	16.547	29.2	15
	Total	56.739	100	

sites available for binding of copper and any other surface reactive species increase on decreasing particle size. Concentrations of copper in sediments of the Warrior Reefs complex are relatively low with values in the 16-28 μg/g range in the <10 μm fraction. Concentrations are significantly higher in the intertidal and mangrove sites with values in the range 39-92 μg/g in the <10 μm fraction. Highest values are reported at Kiwai Island (71 μg/g) and Bristow Island (92 μg/g).

Pore water dissolved metal concentrations were, in all cases, very low with dissolved copper at or below detection limit (0.01μg.mL^{-1}). Concentrations of particulate metals were determined in all cases as a function of depth however significant variations or trends with increasing depth were not generally observed. From the surface (0-2 cm) sediment concentrations reported in Table 3, it can be seen that particulate copper concentrations were generally higher in the delta than in the Gulf of Papua and were highest at delta stations D4 and D5. At these stations, some depth dependence of particulate copper concentration was observed while at other sites, the copper concentration was relatively uniform with depth (Figure 3). As so clearly shown by the OTML results, significantly higher concentrations of copper (in mass of copper per unit mass of sediment) than reported for the bulk sediment are likely to be associated with the finer sediment fractions.

Table 3. Concentrations of particulate iron (% dry weight), manganese (μg/g) and copper (μg/g) in the top 2 cm of cores obtained at various locations. Values are mean ± 1σ (from Robertson *et al.*, 1990).

Station	Fe (% DW)	Mn (μg/g)	Cu (μg/g)
D1	9.83±0.83	1100±82	10±2
D2	4.65±0.08	535±27	12±1
D4	5.07±0.19	725±50	71±10
D5	5.53±0.10	794±38	48±7
D9	6.74±0.34	1600±282	30±3
D7	5.56±0.16	819±29	40±2
D10	4.68±0.33	523±34	8±3
GP1	5.17±0.09	587±18	22±1
GP3	4.69±0.08	551±9	13±1
GP4	4.28±0.03	435±10	7±1
GP5	5.08±0.07	570±21	22±1
GP6	5.96±0.20	1004±69	10±1
GP7	5.58±0.12	741±22	19±1
GP8	5.53±0.09	825±22	24±1

Ocean Sciences Institute Studies of Torres Strait Benthic Sediment Metals Content

As reported by Schneider (1990), sediment samples at 20 locations in Torres Strait (see Figure 4) were collected using either a Van Veen grab or a Shipek sediment sampler. At one site (Site 1), subsamples from a vibrocore were obtained for metals analysis. Sediment samples were analysed for gravel (>2.00 mm), sand (< 2.00 mm and > 0.063 mm) and clay (< 0.063 mm) content with the clay and sand fractions being further analysed for carbonate content (the gravel fraction was assumed to be formed entirely of carbonate). Metals content of complete sediment samples was determined by atomic absorption spectrometry (Cu, Zn - flame AAS; Cd - graphite furnace AAS) following homogenisation and acid digestion.

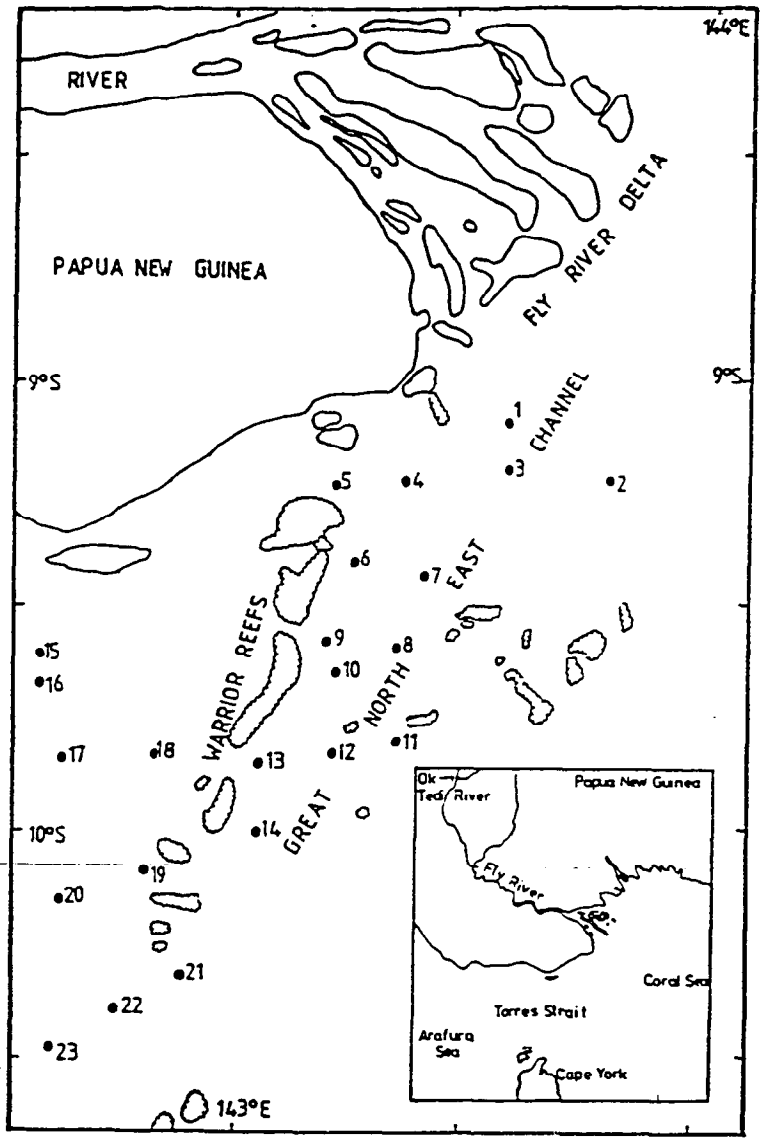

Figure 5. Locations at which water samples obtained for separation of suspended sediment and subsequent analysis of particulate copper and cadmium by Baker (1990).

Ocean Sciences Institute Studies of Torres Strait Suspended Sediment Metals Content

Studies of the concentration of copper and cadmium associated with suspended matter obtained at locations in the northeastern section of Torres Strait and the mouth of the Fly River delta during March 1989 have been undertaken by Baker (1990a, 1990b). At each location (see Figure 6), 250 mL of seawater was filtered through 0.80 µm membrane filters within 3 minutes of collection and stored for later analysis. The particulate matter and filter membranes were digested using high purity acids and analysed by carbon furnace AAS. The grain size and mineralogical composition ofsuspended matter were determined and extensive studies of the mineralogy and possible source of surficial sediments at a wider range of locations were also undertaken by Baker (1990a).

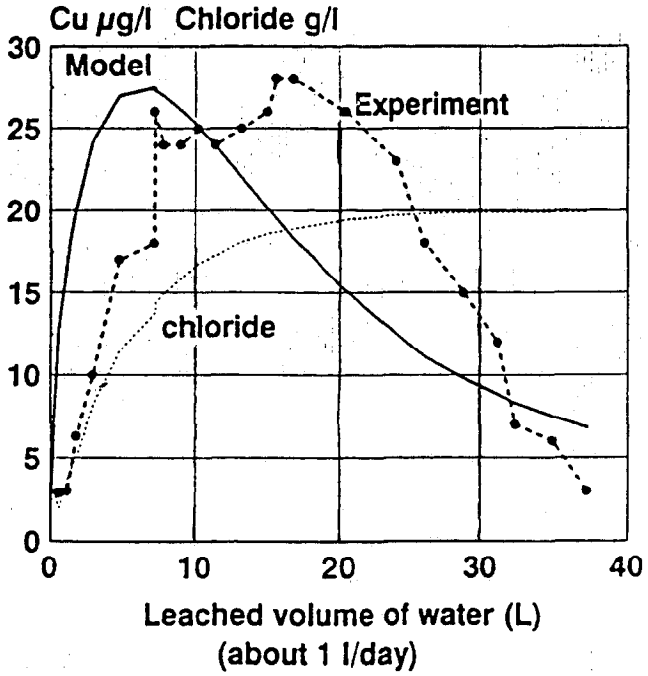

Figure 6. Release of copper from contaminated sediments from the Middle Fly in a salinity gradient. The results of a model assuming instantaneous cation exchange (equilibrium conditions) is shown by the solid line (after Salomons and Eagle, 1990).

The concentrations of copper and cadmium retained on the 0.80 µm pore size filters (per litre of seawater) are given in Table 6. While highest concentrations of metals are observed at stations closest to the Fly River, the lack of information on relative suspended sediment concentrations or on extent of mixing of fresh and saline waters renders interpretation difficult. Waters near the mouth of the Fly River contained subrounded to subangular particles of detrital kaolinite clays and occasional crystals of sucrosic gypsum and rutile needles similar to surficial sediments of the delta. Samples taken from west of Warrior Reefs also corresponded to surficial sediments from that region and were typically comprised of abraded skeletal fragments, conglomerate clays and plankton. A small quantity of fine clays (< 10%), either as discrete particles or as surface coatings on other particles were also detected. These fine clays were concluded to originate from erosion and resuspension of earlier seafloor deposits by tidal currents.

A number of conclusions based on the mineralogical identity of suspended and surficial sediments have been noted by Baker (1990):

- persistently turbid water located west of the Warrior Reefs is caused by the erosion and resuspension of local carbonate deposits and not by terrigenous material from the Fly River;

- most of the suspended sediment output of the Fly River (much of which comes from the Strickland River arm) appears to be retained within the delta area though some evidence suggests the occurrence of tidally driven sediment transport in a westerly direction along the coast and east into the Gulf of Papua, and

- monsoonal activity may extend the influence of the Fly River southwards into the Great North East Channel.

Table 6. Mean copper and cadmium concentrations associated with particulate matter in Torres Strait sea water collected in March, 1989. Mean values are based on two determinations for Cu and three for Cd. (After Baker, 1990b).

Sample No.	Mean Cu (µg/L)	Mean Cd (µg/L)
1	13.3	0.80
2	2.4	0.03
3	4.2	0.15
4	3.5	0.09
5	6.8	0.06
6	0.9	0.16
7	5.8	0.16
8	2.0	0.06
9	3.4	0.09
10	3.0	0.06
11	3.0	0.20
12	2.5	0.16
13	2.6	0.04
14	1.8	0.07
15	1.6	0.10
16	1.4	0.20
17	0.9	0.05
18	1.5	0.08
19	3.1	0.03
20	1.6	0.08
21	3.4	0.04
22	2.7	0.23
23	3.3	0.01

Review of Data on Processes Controlling Trace Element Composition of Waters and Sediments of Torres Strait

Overview of Processes

The sources of metals to the waters and sediments of Torres Strait will be dominated by the large riverine inputs to this relatively wide but shallow connection between the Gulf of Papua and the Gulf of Carpentaria to the west. In addition it should be noted that the Gulf of Papua is also the receiving basin for a number of other significant streams and rivers other than the Fly including the Purari, Pie, Era, Kikori Turama and the Bamu. Obviously, mining operations in the headwaters of these rivers increases the sediment and metals load of these rivers with the potential for increased input to the marine environment.

Studies of the Fly River system by Salomons *et al.* (1988) and Salomons and Eagle (1990) indicate that the bulk of copper, a metal that is significantly enriched in the area (and obviously for that reason mined by OTML), is associated with particulate matter. A significant portion of this particle bound copper represents mine-derived ore residues and overburden. Copper is not distributed uniformly over the various

size ranges of ore residues. For example, the very fine grained < 2 μm fraction, whilst constituting only 5% of the total ore residue tonnage, contains 25% of the total copper. Approximately 70% of the copper load is associated with the < 100 μm fraction. Given the flow characteristics in the river system, most of this material will ultimately be transported to the estuary and delta front and Gulf of Papua (Salomons and Eagle, 1990).

On reaching the more saline estuarine environment, the fine colloidal particles carrying the bulk of the metals will be destabilised by the high ionic strength medium (mainly as a result of double layer compression) and will begin to flocculate and settle out of the water column. The extent of sedimentation within the estuarine and deltaic environment will be determined by the energy of mixing and dispersal and will obviously be influenced significantly by riverine flow, tidal regime, large scale circulation patterns and wind mixing effects.

In addition to the processes of flocculation, sedimentation and dispersal of particles in the estuarine environment, the marked difference in water chemistry between the fresh and estuarine environments may result in significant redistributions of metals between particulate and solution phases. In particular, the concentrations of magnesium, calcium and sodium are much higher in the estuarine than freshwater system and may lead to release of metal to solution phase as a result of cation exchange processes. Higher chloride and carbonate concentrations may also lead to a change in speciation of both disolved and particulate metal and, in the latter case, increase the solubility of the metal. The results of preliminary experimental studies of such processes conducted by OTML are discussed briefly below.

Transformations in Trace Metal Partitioning in the Estuarine Environment

The effects of increasing admixtures of seawater on potential copper releases have been studied in a series of flow-through experiments by OTML (1988). The admixtures comprised copper enriched sediments obtained from the river system, ore residues from the OTML copper circuit and mixtures of ore residues and river sediments. The experimental method was designed to simulate the transport of particulates through a salinity gradient, and thus simulate likely estuarine processes. A simultaneous and identical experiment using freshwater was carried out for control purposes.

The control experiment showed little release of copper from the admixtures with concentrations of dissolved copper in the test solution remaining within the range of 1-5 μg/L. Lower concentrations of dissolved copper were evident where the admixtures contained proportionally higher concentrations of river sediments, due to the presence of adsorbing clay fractions. In the experiments with seawater, the release of copper increased significantly and in proportion to increased chlorinity.

Results of such studies indicated that only a portion (9-14%) of the total copper was released from the sediments tested. An attempt was made to simulate the results of the experiments using an estuarine numerical modelling technique based on assumptions of chemical equilibrium, however, as shown in Figure 7, this model did not reproduce the shape of the release curve well owing to the relatively slow kinetics of the reactions involved. Salomons and Eagle (1990) note that an understanding of the chemical kinetics of such release processes is important in assessing the likely impact of

deposition of copper enriched sediments in the estuarine environment. For example, if the release mechanisms are slow, copper enriched particulates entering the estuarine environment will be subject to a high rate of dispersion prior to significant copper mobilisation. A present lack of information on the kinetics involved precludes reliable numerical assessment of dissolved copper levels in this environment.

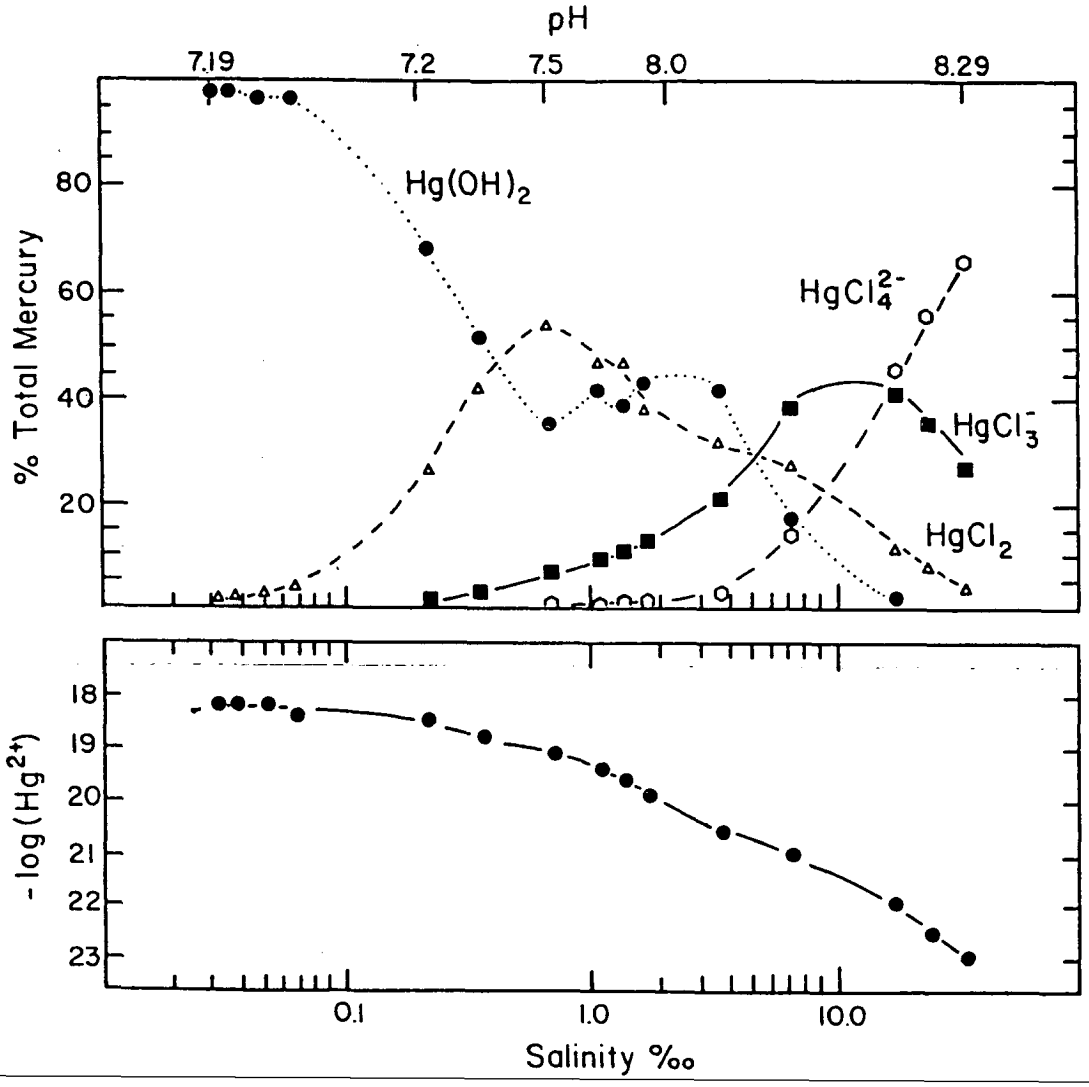

Figure 7. Inorganic speciation of mercury in an estuary as a function of salinity. Example calculated by considering the mixture of a freshwater ($[Cl^-]=5x10^{-4}M$, $Alk=1.3x10^{-4}M$, pH=7.2) with seawater (salinity=36‰, pH=8.20) and maintaining the total mercury concentrations at 1 nM (after Morel, 1983).

A variety of chemical reactions may be involved in release of copper from such sediments including ion exchange, desorption of specifically bound metal and oxidation of sulfide minerals with subsequent possible release of copper. A model suitable for prediction of release rates must incorporate kinetic expressions for these processes (or, at least, justify why certain processes should be excluded). Other particle-associated trace elements, if present, may also be released on changing from a freshwater to a high ionic strength marine environment though the driving forces for transformation and the rates of associated chemical processes will be element specific (Salomons, 1980; Li *et al.*, 1984; Ackroyd *et al.*, 1986; Davies-Colley *et al.*, 1984).