
NUTRIENT TRANSPORT BY INORGANIC COLLOIDS

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ABSTRACT

The availability of nutrients and other trace elements in natural systems is strongly influenced by the manner in which they are transported within the system. One mode of transport which is important in many environments involves adsorption onto colloidal particles, and subsequent desorption in response to changes in environmental conditions. Environmentally significant aspects of the chemistry of natural inorganic colloids are summarised, and two examples of their impact on biogeochemical processes in a marginal marine setting are presented. In the first example, colloidal iron-oxides acting as a chemical conveyor belt give rise to anomalously high heavy metal concentrations in marine bivalves, while in the second example, they are responsible for localised increases in phosphate concentrations in surficial marine sediments.

INTRODUCTION

When examining the dynamics of nutrients and trace elements in natural systems, emphasis is commonly placed on input concentrations and supply rates for the components of interest (e.g., the composition and discharge volumes of an industrial effluent), and on the effect of these 'diluted' reagents on selected target organisms or sediments elsewhere in the system. However, although it is frequently overlooked, it is equally important to determine how these reagents are moved around within the system. The mode of transport of a nutrient or trace element within the system will influence whether it is diluted and widely dispersed (e.g., dissolved ions), or it is concentrated by sedimentological, chemical, and biological processes at particular sites in the system and released slowly at that site only (e.g., chemicals transported as a component of suspended organic matter or clastic detritus, or chemicals adsorbed onto fine organic or inorganic particles). Clearly, each chemical constituent will have a differing environmental impact depending on whether it is transported in a manner which leads to dilution and dispersion, or it is transported in a manner which leads to localised accumulation of high concentrations. In practice, very few chemical reagents (including toxic chemicals in polluted systems) in natural systems are likely to have a seriously damaging environmental impact unless they are concentrated by some process at particular points in the system; concentration could involve selective sedimentation or bioaccumulation and biomagnification.

This paper examines the role of inorganic colloids in natural systems as a nutrient and trace element transporting agent which commonly causes localised accumulation of the transported reagents. The colloids can also influence the rate of release of adsorbed chemicals to other parts of the system in response to changes in biogeochemical conditions. Colloidal organic matter can also play a significant role in chemical transport in natural environments, but discussion of this group of substances is beyond the scope of this paper.

COLLOIDS AND THEIR BEHAVIOUR

In environmental analysis, particularly in relation to water samples, it is normal practice to filter samples through a glass fibre filter when determining total suspended solids, or a 0.45 μm filter as a preparation for water analysis; material passing through the filter is considered to be in solution while material retained by the filter is treated separately as suspended solids. However, this arbitrary boundary may often lead to an important sub-group of particles (the colloidal particles) being completely overlooked. Colloidal particles are generally considered to range in size between 0.1 μm and 0.1 nm (Krauskopf, 1979), and would pass through the filter, but their chemical and physical properties are quite distinct from those of ions in true solution (Yariv and Cross, 1979). The distinctive physical and chemical properties of colloidal particles confer on them an important role in many natural processes (e.g., McConchie, 1984; Lawrence, 1985; Martin et al., 1986).

A substance is colloidal if it consists of very fine particles (solid, liquid, or gas) dispersed in another substance. In this paper the term colloidal is confined to solids dispersed in water. Compositionally, a large range of compounds can form colloidal particles, but in natural waters the most common ones are clays, iron-oxides / -hydroxides, aluminium-hydroxides, manganese-oxides / -hydroxides, silicon-hydroxides, a variety of sulphides (primarily the hydrated iron-monosulphides, melnikovite and hydrotroilite), carbonates, and a variety of organic and organometallic compounds. Of these compounds, the clays and the iron-oxides / -hydroxides are the most important; although studies of Pre-Cambrian sedimentation (e.g., Ewers and Morris, 1981; McConchie, 1984) indicate that colloidal silicon-hydroxide may have been environmentally important in the past, it is now only significant, in relation to hydrothermal exhalations.

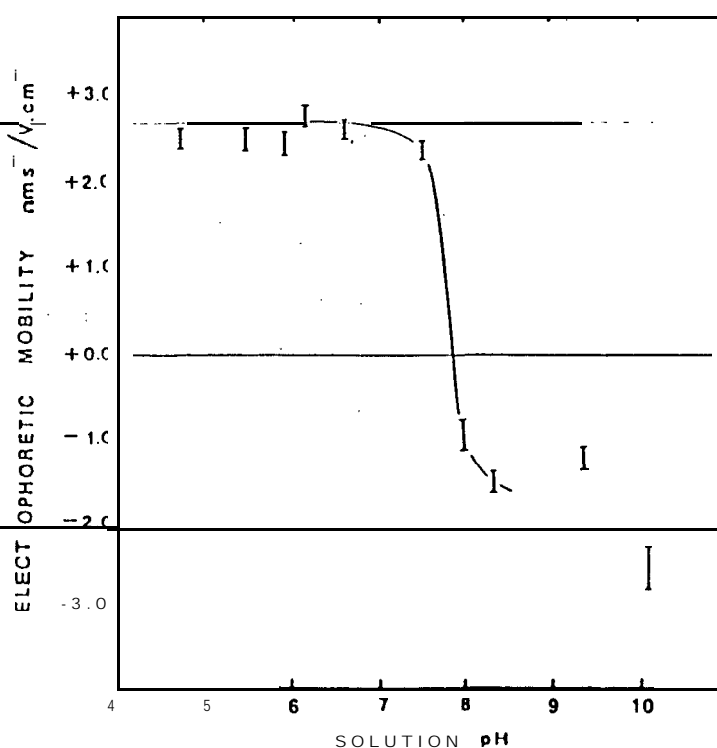


Figure 1. Plot of electrophoretic mobility against pH for colloidal hematite; note the isoelectric point at pH = 7.85,

Two properties of colloids are particularly important in an environmental sense; firstly their high surface area to volume ratio, and secondly their high charge to mass ratio. As a result of their high surface area to volume ratio, and because chemical reactions involving solids take place on surfaces, colloidal particles are very surface active (e.g., 1 gm of colloidal iron-oxides with a mean particle diameter of 10^{-2} μm will have an effective surface area of about 10^6 cm^2). The evaluation of surface charge density and sign is more complex (e.g., Yariv and Cross, 1979), because the sign and magnitude of the charge will depend on the composition of the particle, the pH of the solution, and the type and concentration of other ions present. Exactly how the charge develops is not well understood, but it is known to be strongly pH dependant (e.g., Krauskopf, 1979), and to have a major influence on the behaviour of colloids in natural environments. There are two ways in which the charge on colloidal particles is environmentally important a) it governs flocculation vs. dispersion processes, and b) it controls adsorption / desorption and ion exchange reactions.

Flocculation and dispersion

The dipolar water molecule orients itself in relation to the charges on colloidal particles to form a vicinal or oriented water layer (see Yariv and Cross, 1979) which prevents the colloidal particles from settling out unless the charge is cancelled. When the charge is cancelled by other ions in solution the colloidal particles may flocculate and settle out, but our knowledge of how the process works is very limited. Generally, if the colloidal particles are negatively charged, monovalent cations will tend to be dispersing agents while multivalent cations are flocculants; similarly monovalent anions will tend to be dispersants

TABLE 1

Isoelectric points for common colloidal materials

Compound	IEP
$\text{Al}(\text{OH})_3$ [amorphous]	7.1 - 9.4
$\alpha\text{-Al}(\text{OH})_3$ [gibbsite]	5.0
$\gamma\text{-Al}_2\text{O}_3$	8.0-8.5
$\text{Fe}(\text{OH})_3$ [amorphous]	7.1-8.5
$\alpha\text{-FeO}(\text{OH})$ [goethite]	3.2-6.7
$\gamma\text{-FeO}(\text{OH})$ [lepidocrocite]	5.4-7.4
$\text{FeO}(\text{OH})$ [limonite]	3.6
$\alpha\text{-Fe}_2\text{O}_3$ [Shark Bay hematite]	7.8
$\gamma\text{-Fe}_2\text{O}_3$ [maghemite]	6 . 7
MnO_2	4.0-4.5
$\text{Mn}(\text{OH})_2$	7.0
SiO_2 [quartz]	2.2
SiO_2 [amorphous]	1.8
Sulphides	<6.0
CaCO_3 [calcite]	9 . 5

for positively charged colloids, while multivalent anions are flocculants. Furthermore, whereas dilute electrolytes may be dispersive, the same electrolyte at higher concentrations may promote flocculation. Hence, $\text{Fe}(\text{OH})_3$ which is a common colloid in river systems, is virtually absent in normal seawater due to the higher electrolyte concentration; it is precipitated within estuaries as the electrolyte concentration rises. Colloid flocculation induced by a rise in electrolyte concentration is an important process in estuarine settings.

The charge on colloidal particles can also be neutralised by a small change in solution pH. The sign and magnitude of the charge may change significantly over a small pH range (Fig. 1) from strongly positive below the isoelectric point (IEP; the pH at which the charge on the particles is zero) to strongly negative above the IEP. The change in charge sign in natural environments is well illustrated by colloidal hematite which has an isoelectric point at pH 7.8 (Fig 1) such that it is negatively charged in normal marine waters where the prevailing pH is about 8.2 (Drever, 1982), but positively charged in non-marine systems where the pH tends to be < 7.5 . The isoelectric points for a selection of common colloid forming compounds in natural environments are summarised in Table 1.

The flocculation and precipitation of colloids (particularly iron-oxides and -hydroxides in estuaries) may also result in the precipitation of other chemical species in the water body by the process of co-precipitation. This process is sufficiently efficient (e.g., Harder, 1965; Yariv and Cross, 1979, McConchie, 1984) that precipitation of iron-oxides/-hydroxides, due to a rise in Eh and/or pH, can result in the co-precipitation of a mass of silica equivalent to 40% of the mass of the ferruginous precipitate, even if the silica was only at 10% saturation levels in the solution.

Adsorption / desorption, and ion exchange

Because colloidal particles carry an electrostatic charge under all pH conditions, except at the isoelectric point, positively charged colloids have a marked tendency to bind anions while negatively charged colloids bind cations. These adsorbed ions may be exchanged in response to changes in the activities of other ions in the solution, or they may be desorbed in response to a change in the solution pH; slow desorption during diagenesis will also accompany the ageing of any colloidal precipitate.

Clay minerals are a special case because they can carry both positive and negative charges simultaneously; the magnitude of the charge will depend on the type of clay mineral and the type and extent of isomorphous substitutions within the mineral lattice. Positive charges are centred on the crystal edges perpendicular to the '001' lattice plane and result from the isomorphous replacement of structural oxygen by hydroxyl groups leaving a negative charge deficiency. Residual positive charges are particularly noticeable in kaolinites (Grim, 1968) and can bind phosphate ions rather well because not only is the charge suitable but the atomic geometry of the phosphate ion is a good match for the silica-tetrahedral layer of the clay. Negative charges are centered on the '001' lattice plane and are largely due to the isomorphous replacement of structural silicon by aluminium or ferric iron, or the replacement of structural aluminium by magnesium or ferrous iron. The negative charges on clays are usually much greater than the positive charges and cations are readily bound by electrostatic attraction into interlayer positions on the '001' surfaces.

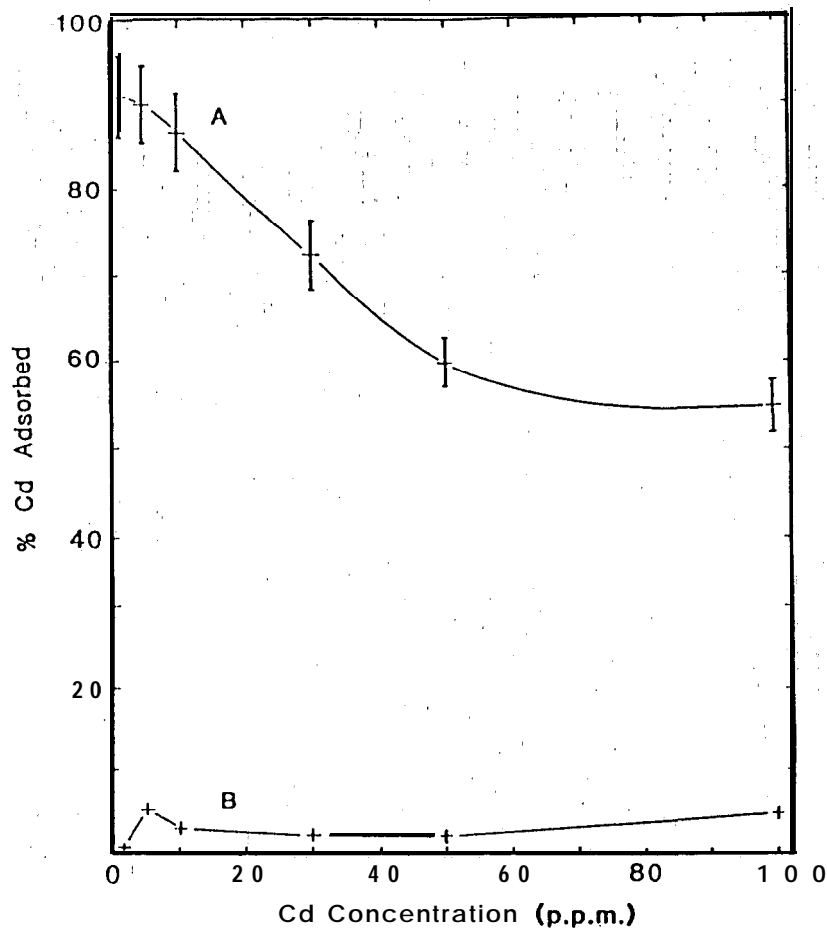


Figure 2. Plot of the percentage of cadmium adsorbed from spiked solutions of Shark Bay seawater by colloidal iron-oxides extracted from Shark Bay sediments. Curve A is the plot for tests involving the iron-oxides; plot B is for an identical experimental system in the absence of the iron-oxides.

Ions electrostatically bound to clay minerals and to other inorganic **colloidal particles** are not strongly fixed, and most can take part in ion exchange reactions in response to changes in the type and activity of ions in the associated solution. Thus, ions carried on colloidal **particles** can be released into the environment by a change in the ionic composition of the solution, and ions in the solution can be selectively bound to the colloidal particles. This process is environmentally important, particularly in estuaries where there are rapid changes in electrolyte concentrations; it is also important in the formation of many authigenic minerals (e.g., McConchie *et al.*, 1979; McConchie, 1984). Each clay or colloid will have its own total ion exchange capacity, but different ions will have differing tendencies to be adsorbed depending on **several** factors including::

- * The size and charge of the ion,
- * The pH of the solution,
- * The type and concentration of ions competing for the adsorption sites,
- * The total ionic strength of the solution, and
- * Temperature.

Because several of these factors vary widely within and between natural environments, it is not useful to generalise about preferential exchange sequences. However, it is significant to note that selective adsorption of ions can be extremely efficient, even at very low ionic strengths (e.g., the uptake of cadmium by colloidal iron-oxides in Shark Bay, Western Australia; Fig. 2).

There are several other properties of colloids (e.g., ageing, selective ion diffusion, crystal growth in gels, etc) which are environmentally significant, but discussion of these is beyond the scope of this paper; a good introduction to these aspects can be found in Yariv and Cross (1979).

ION TRANSPORT BY COLLOIDS IN NATURAL SYSTEMS

Substantial quantities of macronutrients including K^+ , NO_3^- , and PO_4^{3-} , and a wide range of trace elements can be transported in natural environments as ions adsorbed onto colloids and clay minerals (e.g., Grim, 1968; Yariv and Cross, 1979; see also several papers in Lasserre and Martin, 1986). K^+ in particular is moved in large quantities in natural environments as an ion bound into the interlayer position in clay minerals; it is not commonly transported by other colloidal particles. Hence, an influx of clay minerals as a result of a flood for example can substantially raise the potash availability for benthic flora in an estuary. Phosphate and nitrate are transported in small quantities by clay minerals where they are bound to crystal edges perpendicular to the '001' plane; they are also transported by colloidal particles under conditions where the pH is below the IEP for the colloid. In many non-marine settings, colloidal iron-oxides or -hydroxides are very efficient in transporting phosphate and nitrate because the pH is usually below the IEP, but under marine conditions where the pH is above the IEP anions are desorbed. Hence, colloidal iron-oxides and -hydroxides (possibly with adsorbed phosphate and nitrate), transported by fluvial systems, will flocculate in estuaries and other marginal marine settings due to the rise in electrolyte concentration, and the adsorbed anions will be desorbed due to the rise in pH. Thus, where anionic nutrients (e.g., from agricultural runoff) are adsorbed onto ferruginous colloids and transported by rivers, nutrient concentrations may rise in estuaries and other near-shore environments, but increases are unlikely to be detectable more than a few kms offshore. The efficiency of colloidal iron-oxides in transporting ionic species in marginal marine environments is well illustrated by the following two examples from Shark Bay, Western-Australia.

Colloids as a chemical conveyor belt

Shark Bay, Western Australia (Fig. 3), is a shallow marine embayment of about 8,000km² with an average water depth of 10m; over about 2,000km² the water depth is less than 1m. The topographic relief of the surrounding landmass is low and the area is exposed to strong winds which are very effective at resuspending fine sediments in the extensive shallow water parts of the embayment. Shark Bay is geographically remote from all known industrial and geological sources of heavy metals, but several species of mollusc found there have cadmium contents which exceed both the usual limits of 2ppm wet weight for molluscs taken for human consumption, and levels found in molluscs from areas of recognised heavy metal pollution (McConchie et al., 1988). The cadmium content of several species of Shark Bay molluscs frequently exceeds 10ppm wet weight, locally exceeds 20ppm, and shows substantial regional variation within the embayment (Fig. 4). Some regionally variable factors which could influence the rate of cadmium uptake include, an anthropogenic source, species variation, salinity variation, local groundwater influx, and variation in the dissolved cadmium concentration, but none of these possibilities are supported by the data of Lawrance (1985) and McConchie et al. (1988).

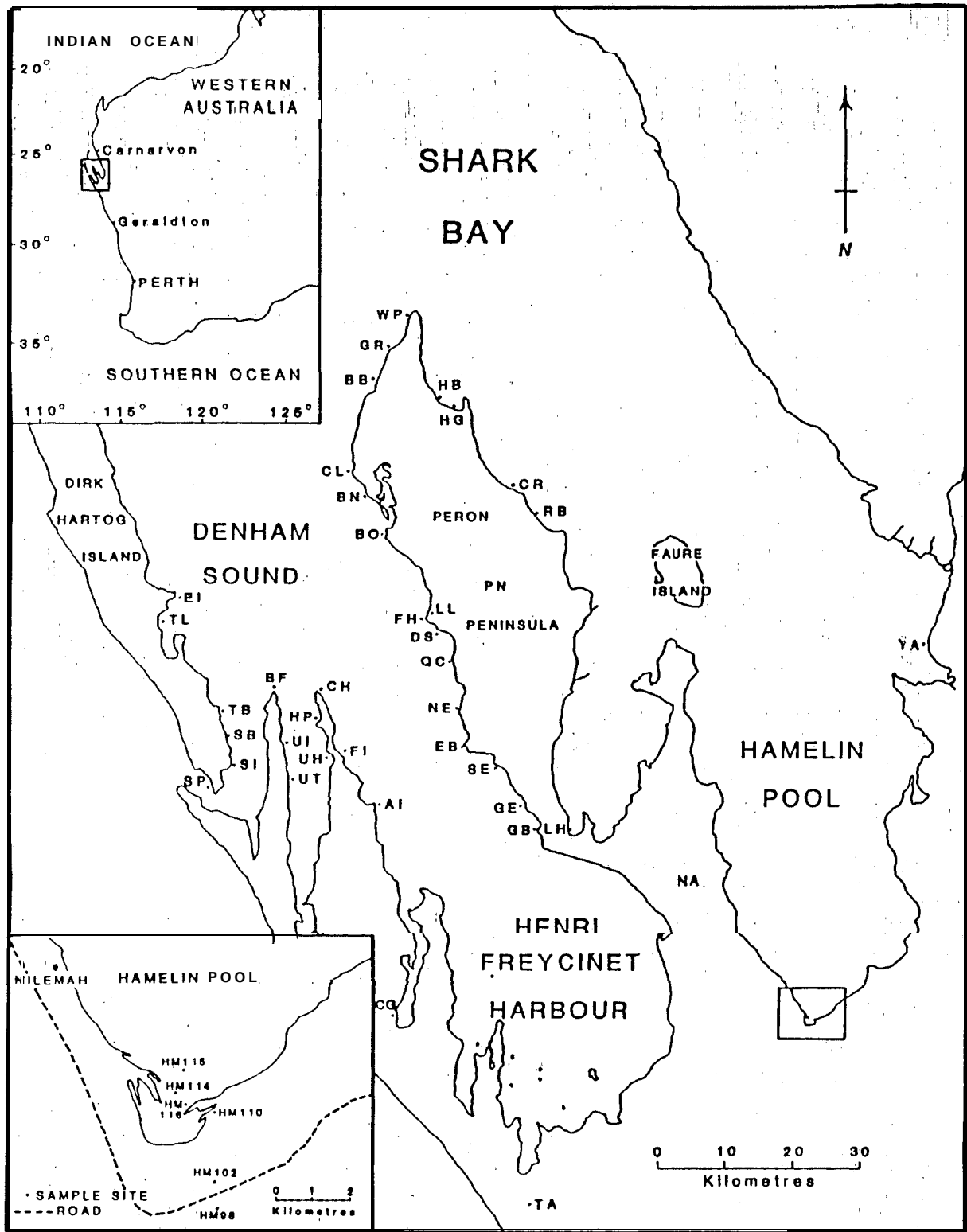


Figure 3. Map of the Shark Bay area showing sample sites examined during the 1984/5 phase of the project; after McConchie *et al.* (1988). Herald Bight is the embayment, toward the north of Peion Peninsula, which includes sites HB and HG

The concentration of dissolved cadmium in the waters of Shark Bay is not substantially different from that in normal oceanic water (0.06ppb), and the cadmium concentration in substrate sediment seldom exceeds 0.005ppm. Few viable explanations for the high cadmium concentrations in the Shark Bay molluscs were apparent until it was discovered that molluscs had their highest cadmium concentrations in areas of the bay where turbulence was high and the substrate sediment had a high iron-oxide content. The iron-oxides are derived from the ferruginous **Peron** Sandstone exposed in some coastal cliffs around the bay and constitute up to 2% of substrate sediments immediately offshore from these cliffs. It became clear, and was subsequently statistically confirmed, that cadmium in the water was adsorbing onto the surface of colloidal hematite, which was negatively charged at the prevailing pH of 8.15, and that these particles were suspended by turbulence and ingested by the organisms. The adsorption onto the iron-oxides is extremely efficient at low cadmium concentrations (e.g., Fig. 2). Once inside the organisms, lower pH conditions prevail, the iron-oxides become positively charged, and the cadmium is released in ionic form and accumulated within the organism. For areas with a similar turbulence the correlation between iron-oxides in the substrate sediment and cadmium in the molluscs is 0.87.

Further confirmation of the link between cadmium uptake and colloids can be found in the fact that bottom dwelling oysters have a substantially higher (up to 10 times) cadmium content than oysters grown in baskets suspended at the same site. The rate of cadmium uptake by oysters in an aquarium spiked with traces of cadmium was also found to be substantially enhanced by the addition of colloidal iron-oxide and sustained turbulence.

In this example, although the iron-oxides constitute only a small proportion of the substrate sediment, they carry most of the metal load, essentially they act as a chemical conveyor belt **preconcentrating** cadmium from the water, carrying it to the molluscs, *then* returning to the sediment as fecal matter to start the process again.

Phosphate transport in Herald Bight

The southern end of Herald Bight (sites HG and HB in Fig. 3) is unusual for Shark Bay because despite a very high iron-oxide concentration in the substrate sediment, molluscs in the area have relatively low cadmium concentrations by Shark Bay standards. The reason for this appears to be linked to the fact that seawater near the sediment/water interface has a pH of about 7.0 for much of the year (during and for several weeks after periods of high rainfall), which is below the IEP for the iron-oxides. The lower pH in this area of Herald Bight is due to a combination of the seepage into the bay of slightly acidic groundwater, bacterial decomposition of organic matter trapped by mangrove pneumatophores, and poor circulation.

The iron-oxides in sediments from the southern end of Herald Bight can be distinguished from those just 2km north and from those in all other sediments examined in Shark Bay by their high phosphate content. The phosphate content of these iron-oxides often exceeds 50ppm compared with concentrations of less than 1ppm further up the bight. The examination of a series of surface sediment samples taken at regular intervals along line transects perpendicular to the shore at the southern end of Herald Bight reveals a progressive northward decrease in the phosphate content of the iron-oxides. The decrease in the phosphate concentration correlates well with a progressive rise in the mean pH from 6.8 to 8.1 ($r = 0.78$ at the 95% confidence level); there is no matching shift in the dissolved phosphate concentration. It therefore appears likely that phosphate released during biotic decomposition in the mangrove zone is being adsorbed onto the colloidal iron-oxides, transported northward, and progressively desorbed as the pH rises and the charge on the oxides is reversed. It was also noted that benthic flora were more abundant and extended further seawards in this area of the bight than further north.

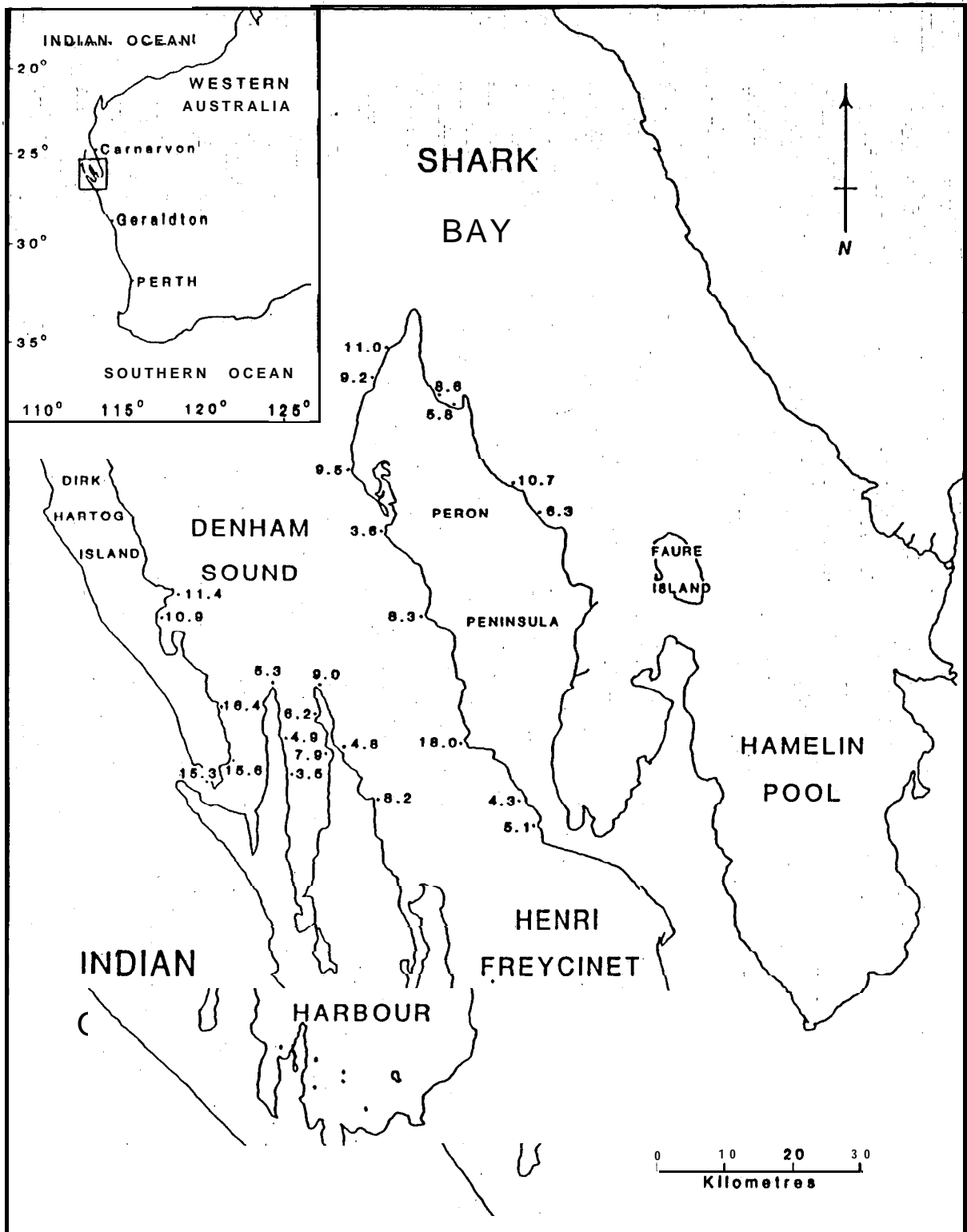


Figure 4. Map of Shark Bay showing regional variation in the geometric mean cadmium concentration (in ppm) for pooled samples of *the* pearl oyster *Pinctada curchariarum*; after McConchie *et al.* (1988).

CONCLUSIONS AND IMPLICATIONS FOR THE GREAT BARRIER REEF REGION

This paper has outlined some of the ways in which inorganic colloids are very effective agents in the transport nutrients and other trace elements in aquatic environments, and some of the ways in which their chemical behaviour responds to changes in environmental conditions. For Shark Bay it is clear that the ion transporting capacity of colloidal iron-oxides has a major influence on several biological processes in the embayment. Although colloids probably have their greatest impact in **estuarine** settings where changes in pH and electrolyte concentration are marked, the Shark Bay study indicates that they may also be important in fully marine settings.

In the Great Barrier Reef region, nutrients and other trace elements, derived from agricultural run-off or sewage disposal operations on the mainland, and adsorbed onto colloidal particles, are very unlikely to be transported far offshore. Rises in electrolyte strength and pH in oceanic waters are likely to restrict the dispersion of colloiddally transported ions to the nearshore zone, particularly to the major estuaries.

Although in offshore areas of the reef, colloidal material derived by continental runoff is not going to have a significant impact, any local accumulations of colloidal material on the reef may have an effect. A possible source of local accumulations of colloidal material on the reef involves the grounding and breakup of ships carrying iron- or aluminium-oxides. Both iron- and aluminium-oxides have IEPs in the pH range which would be expected in geochemical subenvironments on the reef. Hence, there may be a need for evaluation of the likely environmental impact of the accidental dumping of large quantities of these oxides on the reef, and some contingency planning to deal with such an eventuality. The hulks of wrecked ships may also constitute a source of colloidal iron-hydroxides during decomposition, and there is a tantalising link between this possibility and the commonly observed increase in algal growth around rusting ironware in marine environments (e.g., the wreck on Heron Island in the Capricornia section of the Great Barrier Reef). A further possible source of colloidal material which may affect nutrient cycling in the reef environment involves biogenic oxide or hydroxide production by the alga *Trichodesmium* (Jones *et al.*, 1986), and this possibility also warrants further investigation.

REFERENCES

- Drever, J.I., 1982: ***The geochemistry of natural waters***. Prentice-Hall, New Jersey.
- Ewers, W.E., and Morris, R.C., 1981: Studies on the Dales Gorge Member of the Brockman Iron Formation, Western Australia. *Econ. Geol.*, 76(7), 1929-1953.
- Grim, R.E., 1968: ***Clay mineralogy*** (2nd Ed.). McGraw-Hill, N.Y.
- Harder, H., 1965: Experimente sur "Ausfällung" der Kieselsäure. *Geochim. Cosmochim. Acta*, 29, 429-442.
- Jones, G.B., Thomas, F.G., and Burdon-Jones, C., 1986: Influence of *Trichodesmium* blooms on cadmium and iron speciation in Great Barrier Reef lagoon waters. *Estuarine, Coastal and Shelf Sci.*, 23, 387-401.
- Krauskopf, K.B., 1979: ***Introduction to geochemistry*** (2nd Ed.). McGraw-Hill, Tokyo.
- Lawrance, L.M., 1985: ***The role of iron-oxides in the concentration of heavy metals in marine sediment and biota of the Shark Bay area, Western Australia***. BSc honours thesis presented at the University of Western Australia, 114pp.
- Lasserre, P., and Martin, J.-M. (Eds.), 1986: ***Biogeochemical processes at the land-sea boundary***. Elsevier, Amsterdam.
- Martin, J.-M., Mouchel, J.-M., and Jednacak-Biscan, J., 1986: Surface properties of particles at the land-sea boundary. In P. Lasserre & J.-M. Martin (Eds.), ***Biogeochemical processes at the land-sea boundary***. Elsevier, Amsterdam, 53-71.

- McConchie, D.M., 1984: *The geology and geochemistry of the Joffre and Whaleback Shale members of the Brockman Iron Formation, Western Australia*. PhD thesis, presented at the University of Western Australia, 3 16pp.
- , McConchie, D.M., Ward, J.B., McCann, V.H., and Lewis, D.W., 1979: A Mössbauer investigation of glauconite and its geological significance.; *Clays, Clay Minerals*, 27(5), 339-348.
- McConchie, D.M., Mann, A.W., Lintern, M.J., Longman, D., and Talbot, V., 1985: *Heavy metals in marine biota, sediments, and waters from the Shark Bay area, Western, Australia*. W.A. Department of Conservation and Environment, Environmental Note, 175.
- McConchie, D.M., Mann, A.W., Lintern, M.J., Longman, D., Talbot, V., Gabelish, A.J., and Gabelish, M.J., 1988: Heavy metals in marine biota, sediments, and -waters from the Shark Bay area, Western Australia. *J. Coastal Res.*, 4(1), 5 1-72.
- Yariv, S., and Cross, H., 1979: *Geochemistry of colloid systems for earth scientists*. Springer Verlag, Berlin.