EXPERIMENTAL STUDIES ON Cu UPTAKE AND RELEASE BY Fe-Mn PRECIPITATES IN AQUATIC ENVIRONMENT

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TO

MA and BABUJI

for many personal reasons

PREFACE

The research work embodied in this dissertation has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted so far, in part or full, for any other degree or diploma of any University.

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CONTENTS

ABSTRACT

Copper was coprecipitated with Fe and Mn as hydroxide at room temperature and pressure. The uptake and release of copper by hydrous Fe-Mn-oxide precipitate was investigated. The variables studied were pH, ionic strength and initial copper concentration.

The results indicate that the uptake of copper by hydrous Fe-Mn-oxide precipitate depends on the pH and the initial copper concentrations of the solution but is independent of the ionic strength of the media. As the initial copper concentration in the solution increases, the Cu uptake at lower pH values (< 3) increases.

The desorption experiments show that copper is present both as exchangeable and non-exchangeable "fixed" fraction in the coprecipitate. The relative proportions of these fractions in the precipitates vary with the ionic strength of the preci-pitating medium. In fresh water, the desorption is higher if the initial copper concentration is higher. Trace elements such as Co and Ni in the aqueous media can occupy these exchange sites.

Calculations based on solubility product data suggest that Cu does not precipitate as a separate copper phase and hence it will, somehow or other, be associated with the hydrous Fe-Mn-oxide precipitate.

The nature of the coprecipitate indicates the probability for it being a solid solution. This could not be confirmed because of the unavailability of IR and Mossbauer Spectra at the moment.

The experimental results can be used to explain the presence of heavy metals in natural ferromanganese materials. It can also be used for studies of pollution of the aquatic environment by trace metals.

INTRODUCTION

The behaviour of trace elements in natural aqueous
system is attracting researchers because of environmental
issues and yet this subject is not well understood. One of
the first step in any systematic study of the aquatic chemistry
of a potential contaminant is an elucidation of the principal
modes of transport and reservoirs for the contaminant. For
heavy metal contaminants such as Cu, Cd, Pb, Zn, Ni, Hg, Fe
and Mn, the hydrous oxides of Al, Fe and Mn may play dominant
roles in determining reservoirs and modes of transport of these
metals.

While the role of clays and biota in affecting the
transport of radionuclides and other pollutants is commonly
recognised, the significance of Fe and Mn among the factors
that are involved is frequently overlooked. Cation exchange
capacities of sea water and fresh water sediments are in the
range of 30-60 meq/100 gm. It has been shown by Goldberg (1954)
that the amounts of trace elements in sea water sediments are
proportional to the iron or manganese content of the sediments.
The observations by Mortimer (1941, 1942), Hutchinson (1957)
and others that oxidised sediments have much greater adsorptive
powers than reduced sediments lend support to the idea that
Fe and Mn play a significant role in influencing the distribution

and the transport of a variety of metal ions of both the
naturally occurring and polluted kinds.

It has been known for a long time, that metal ion
hydrolysis species are strongly adsorbed at solid-solution
interfaces (Stumm & Morgan, 1962). This tendency to be adsorbed
is especially pronounced for polynuclear poly hydroxo species.
No adequate theory for this enhanced adsorption by hydrolysis
is available, but few qualitative reasons can be:

a) Hydrolyzed species are larger and less hydrated
   than non-hydrolysed species,

b) The enhancement of adsorption is apparently due
   to the presence of a coordinated OH^- group.

Simple OH^- ions are bound at many solid surfaces and are
frequently potential determining ions, hydroxo metal complexes
may similarly or to an even larger extent be adsorbed to the
solid surface (O'Melia and Stumm, 1967). Finally, adsorption
becomes especially pronounced for poly hydroxo-poly metal
species because more than one hydroxide group "per molecule"
can become attached at the interface. Most species containing
OH-groups, cationic as well as anionic hydroxo-complexes, have
been observed to be adsorbed at solid-solution interfaces.

It is interesting that adsorption of poly hydroxo metal
complexes can occur against electrostatic repulsive forces, i.e.,

the chemical adsorption energy can outweigh the electro-
chemical work involved in the adsorption.

Co-agulation as practiced in water treatment is
brought about by metal ion hydrolysis species and not by free
multivalent metal ions (Matijevic et. al., 1961). These
hydrolysis species also can play a significant role in flotation
processes.

Considerable emphasis has been placed thus far on hydroxo-
complexes; this is amply justified by the omnipresence of OH^-
in water and by the strong affinity of many metal ions to
OH^- ions.

OH^- ligand is selected over others because metal ions
in solution in natural waters are not appreciably complexed by
ligands other than H_2O or OH^- due to the fact that most bases
indigenous to natural waters are unidentate ligands. And
unidentate ligands form less stable complexes than multidentate
ligands, especially in dilute solutions. And also in natural
waters the concentrations of the ligands and the affinity of
the ligands to the metal ion, with the exception of H_2O and OH^-,
are usually sufficiently small so that at best a one ligand
complex may be formed.

The role of metal hydroxides coatings in controlling trace element chemistry in fresh water environments has been investigated primarily by soil chemists. Coatings can be formed in two ways: while the hydroxides are precipitated, suspended grains offer a nucleus for coating; or, the negatively charged suspended clay surfaces attract the positively charged hydroxide sols to form coatings. Metallic coatings are generally 10% to 20% of the sediment grains by weight and seldom cover more than 40% of the grain surface (Sumner, 1964). The ability of the metallic hydroxide coatings to act as sinks for various trace metals is well known (Turekian & Scott, 1969; Jenne, 1968; Kharkar et. al., 1968; Gibbs, 1973; Martin et. al., 1973); these sinks are comparable to the ferro-manganese nodules in marine environment. These hydroxides and oxides readily sorb or coprecipitate cations and anions; even a low percentage of $Fe(OH)_3$ and MnO_2 has a controlling influence on the heavy metal distribution in an aquatic system. Practical application of the sorption ability of hydrous metal oxides has been made in water and waste water treatment, particularly by the use of iron and aluminium salts for the removal of phosphorus compounds, organic contaminants and heavy metals. Under reducing conditions the sorbed heavy metals are readily mobilised; accumulations of hydrous Fe/Mn oxides can therefore act as a major source of dissolved metals in natural waters. The latter mechanism is particularly

effective in the presence of higher concentrations of
dissolved organic material. The chemistry of Fe and Mn in
natural aqueous system have been studied in detail by Hem and
Crooper (1959); Hem (1972) and Stumm & Morgan (1970).

While studies of hydroxides in fresh water systems are
relatively few, hydroxide concretions have been studied in
considerable detail in marine environments (Goldberg, 1954; Manhin,
1965; Cronan, 1969; Glasby, 1971). Hydroxide complexes in lakes
have been studied by Dean (1970); Cronan (1972) and, in some
mine drainage, by Dyck (1971).

Fe is the dominant trace element in natural aqueous
system; Mn is the next most important element — its chemistry
is closely related to that of Fe (Krauskopf, 1957); Cu is
considered in the present study as an example of other (minor)
trace element. In coatings and other ferromanganese materials,
significant quantities of Fe and Mn occur as hydroxides (Gibbs,
1973). In order to understand the behaviour of Fe, Mn and Cu in
hydroxide precipitates, laboratory experiments were performed
which involved the coprecipitation of hydroxides of Fe, Mn and
Cu and the study of the properties of the aqueous media and also
of the precipitates.

Previous Work

Fe and Mn have a mutual catalytic effect in the co-precipitation of their hydroxides (Hem, 1963; Morgan & Stunn, 1965). It is known through the works of Krumbein and Garrels (1952), Garrels and Christ (1965), Stumm and Morgan (1965), Langmuir and Whitmore (1971) and Subramanian (1973) that the pH is primarily the potential determining factor for hydrous oxide precipitates. The uptake of metals by hydrous oxide precipitates has also been found to be strongly dependent on pH (Murray et. al. 1968; Anderson et. al. 1973; Guy et. al. 1975; Loganathan et. al. 1977; Davis and Leckie, 1978). It could then be expected that partitioning of Fe, Mn and Cu between river water and Fe-Mn precipitate would also be influenced by pH. The chemistry of Fe, Mn and Cu in natural water systems can be considered in three parts: the dissolved phase, water-precipitate interaction and the inter elemental relationship within the solid precipitate.

River Water Characteristics

Wagemann, R. (1978) has summarized the data for average concentrations (μg/l) in different fresh waters and estimated "typical" fresh water concentrations of some trace metals(total (dissolved) (Table 1). Zirino,A. et. al. (1978) measured dissolved Cu in San Diego Bay and found copper concentration less than 0.1 μg/l at the mouth of the bay and increased toward the centre

of the bay to approximately 2.5 μg/l. Andrew Eaton (1979)
reported that dissolved Cu concentrations in estuaries varies
from the values as low as 1 μg/kg to as high as 37 μg/kg (Tees).
Goldberg (1954) has cited the data for Fe, Mn and Cu concen-
tration in sea water and manganese nodules (Table 2).

Due to their low solubilities, the hydroxides of the
transition elements are precipitated from the river water when
even a small change in the composition of the solution occurs.
This will leave an insignificant amount of Fe, Mn and Cu in
solution in the river water. Because of the importance of
hydroxide ligand in these precipitates, pH (related to the con-
centration of hydroxyl ions in solution) should be related to
the amount of Fe, Mn and Cu in solution.

Data for total dissolved Fe and pH were collected from
several publications. The analyses were representative at several
fresh water environments. The above data were combined in a
single plot involving pH and total dissolved Fe and the plot is
shown in Fig. 1. A negative relationship between pH and Fe
concentrations is seen although there is scatter in the data.
The scatter could reflect analytical errors or be an inherent
relationship between the two variables. Gibbs (1972) has shown
the effect of salinity on the concentration of major ions in

Table 1: Concentrations of Fe, Mn and Cu
in some fresh waters.

Location	(ug/l)		
	Fe	Mn	Cu
North West Territories (NWT) Rivers, Canada	260	56	8
Lake Ontario	5	0.5	6
Tributaries of Lake Michigan	40	12	3
Rivers and Lakes of the U.S.A.	52	56	15
Large rivers of North America	300	20	5
Typical fresh water values	50	20	7

(Typical values are a compromise between different
concentrations for different fresh waters.)

Table 2: Fe, Mn & Cu in sea water and Mn-nodules.

Metal	Weight per cent in Mn-nodules	Abundance in sea water (µg/l)
Fe	6.18 – 20.27	10 – 100
Mn	10.8 – 24.15	1 – 10
Cu	0.17 – 1.81	4

river water. With this help a plot of salinity vs pH for the
same points were made (Fig. 2). The total dissolved Fe was now
normalised by dividing with salinity and this ratio (Fe/salinity)
was plotted against pH as shown in Fig. 3. A good negative co-
relation is evident which suggests the importance of ionic strength
and pH in controlling the conc $_n$ of Fe in natural waters. So it
can be expected that these can also be important variables for
controlling Mn and Cu in natural waters.

Andrew Eaton (1979), from the studies of the San Francisco
Bay estuary, indicated that the behaviour of Fe and Cu may be
related.

Water - Precipitate Interaction

The understanding of exchange processes occurring at the
sediment-water interface is important in the transport of heavy
metals. The sediment is a complex mixture, with four main compo-
nents: silica, clays, organic matter, and oxides of iron and
manganese. The association of heavy metals with sediments can
range from weak Vander Walls forces to strong covalent bonding,
coprecipitation with ferromanganese oxides, and incorporation
within crystal lattices. The release of sorbed heavy metals into
the bulk water is dependent on partition coefficients, which in
turn are related to sediment characteristics, the type of heavy
metal, and other environmental parameters. As several of the

FIG. 1

RELATIONSHIP BETWEEN TOTAL DISSOLVED
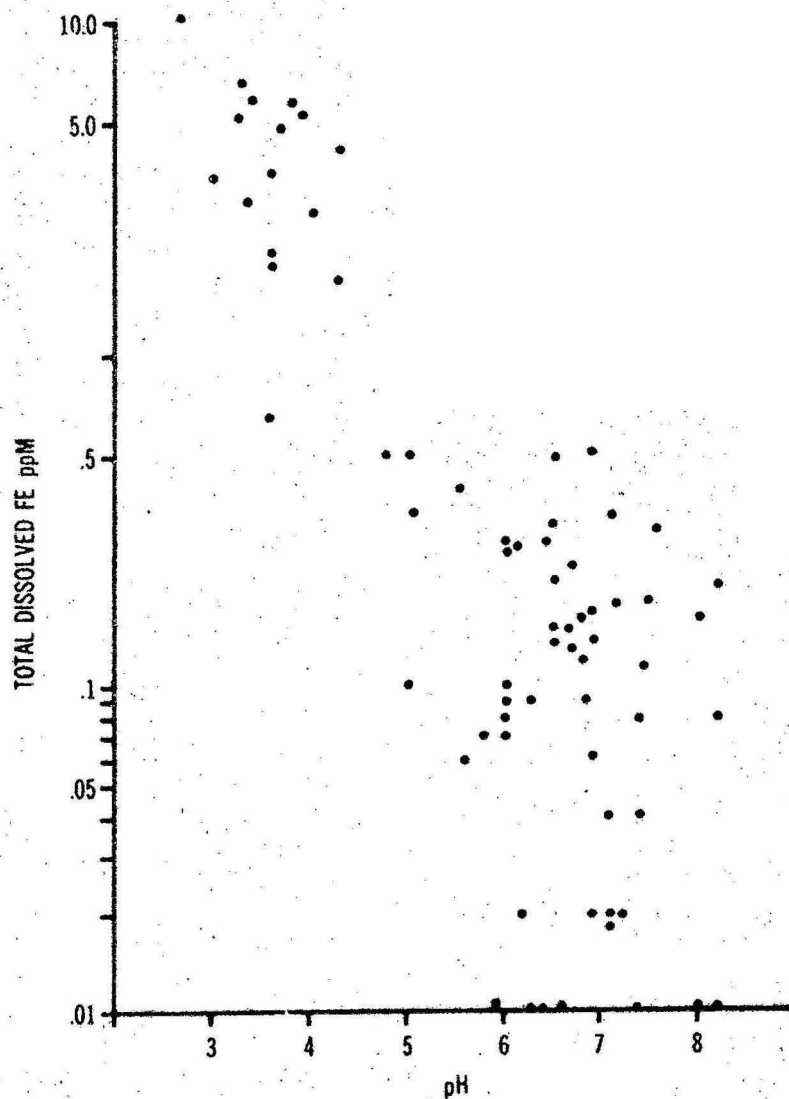Fe (ppm) AND pH FOR VARIOUS RIVER WATERS.

FiG. 2
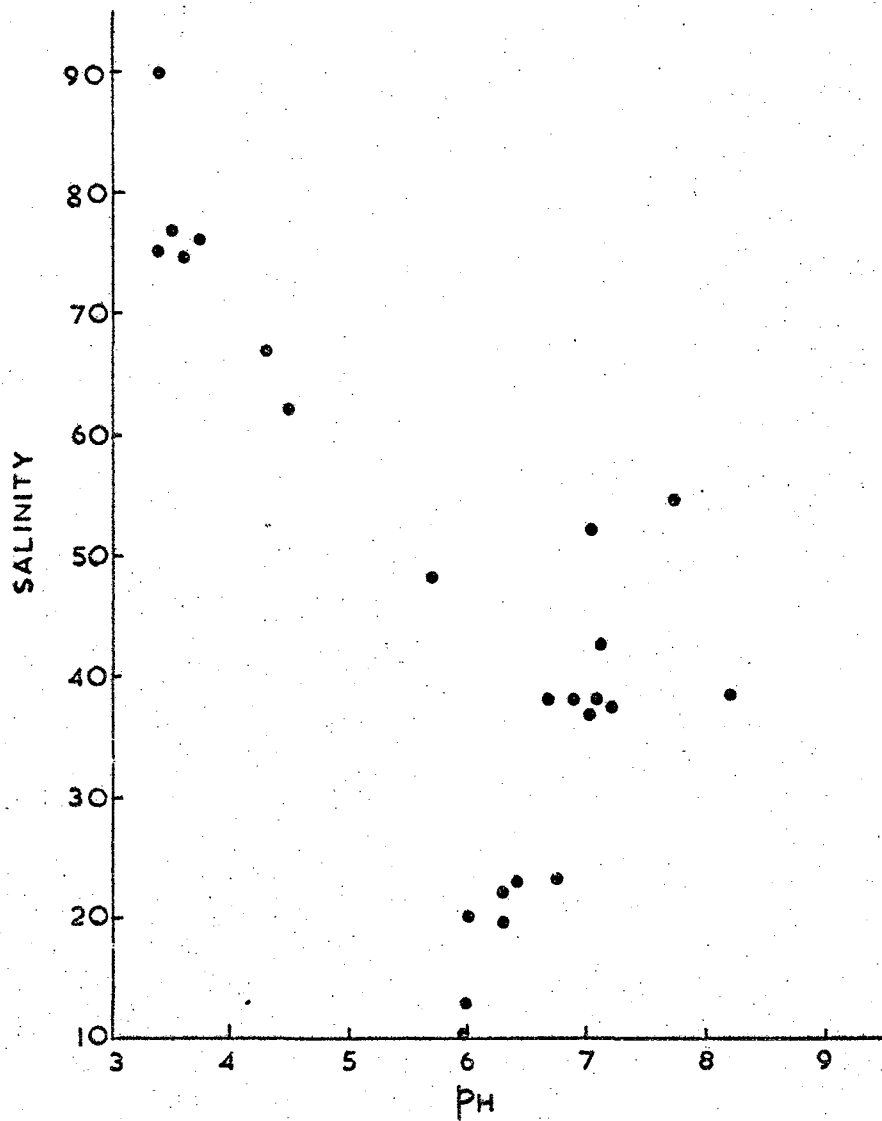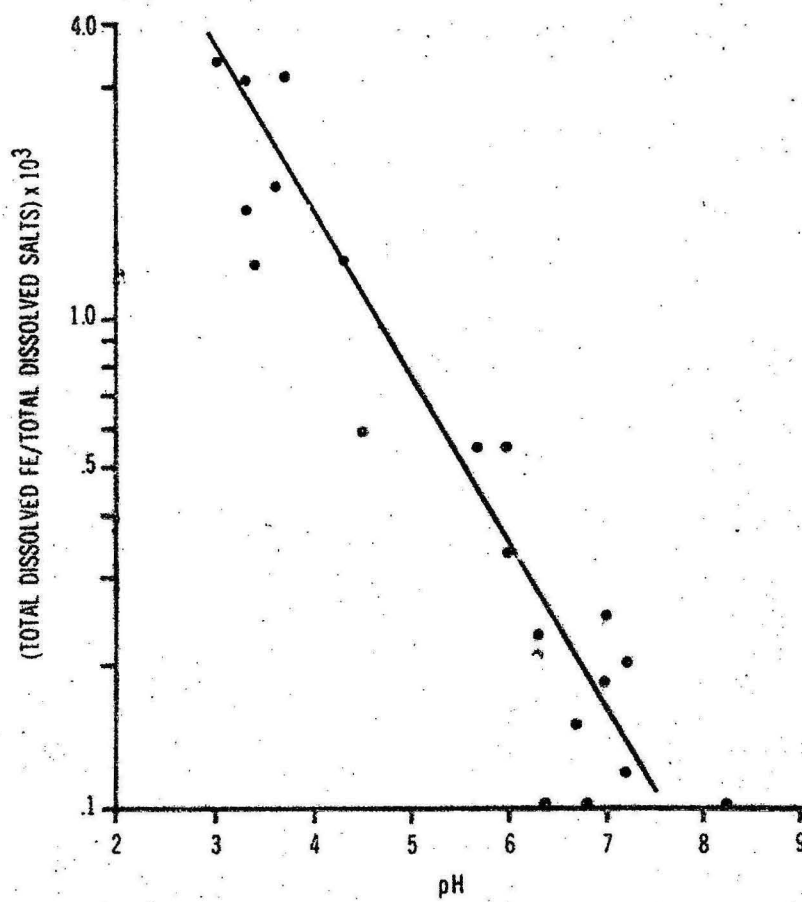RELATIONSHIP BETWEEN SALINITY (ppm)
AND Pн FOR VARIOUS RIVERS.

Fig. 3

INFLUENCES OF SALINITY ON THE pH AND TOTAL
DISSOLVED Fe RELATIONSHIP.

metals concerned are potentially toxic pollutants, much
interest is concerned with the chemical-composition of the
sediment-water interface. At this boundary several chemical and
biochemical transformation reactions occur, involving fluxes of
mobile constituents from the sediment to the water (Lu and
Chen, 1977).

Goldberg (1954) has given some data on the partition co-
efficients of some elements in marine waters. For Fe, maximum
ionic concentration is 0.5 μg/l and particulate concentration
range is 1 to 100 μg/l, so the partition coefficient for Fe will
be 2-200. Ionic Cu amounts to around 4 μg/l. The Cu adsorbed to
Mn, which contains about one-thirtieth of its weight in Cu,
would be 0.03 - 0.30 μg/l. So the partition coefficient for Cu
is 0.01 to 0.1. The partition coefficient of Mn is 0.7.
De Groot et. al. (1973) calculated the discharge of heavy metals
by the water and by the suspended matter of the Rhine and the ratios
metal in water /metal in sediments (Table 3) and concluded that
Cu will be present mostly in the suspended material. So the transport
of these metals mainly takes place in a solid form.

Similar results have been found by Gibbs (1973) for the
Amazon and Yukon rivers, where the ratios were even more extreme.
Some observations from Strakhov's (1965) data and that of Cronan
(1972) can be summarised as follows:

Table 3: Discharge of heavy metals by the water and
by the suspended matter of the Rhine.

Metal	In the water (tons/yr)	Fixed to sediments fraction 16 um (tons/yr)	Metal in water/Metal in sediments
Pb	695	1830	1:2.6
Cr	1250	2820	1:2.3
Cu	765	1355	1:1.8
Zn	11380	6705	1:0.6

Variables	Correlation Coefficients
Dissolved Fe-Dissolved Mn	- 0.7632 (Data from Strakhov)
Dissolved Fe-pH	- 0.7551 (-do-)
Fe-Mn in suspension	- 0.5784 (-do-)
Fe-Mn in coatings	- 0.989 (Data from Cronan)

Ramamoorthy, S and Rust, B.R. (1978) observed that for a given
heavy metal, the partition coefficient between sediment and solution
is not greatly changed by the presence of another cation, provided
the latter has the same order of concentration. If the concentra-
tion of one cation exceeds another by more than 10, however,
significant desorption of the less concentrated ion takes place
on a mass action basis.

Natural hydroxides, Coatings and Concretions

Numerous studies of river, lakes, estuarine and marine
sediments have shown that many trace metals are concentrated in
sedimentary material in natural aquatic systems (Turekian & Scott,
1967; Bower et. al. 1978; Andrew Eaton, 1978/79; Ramamoorthy &
Rust, 1978; Griggs, 1978; Hamilton - Taylor, 1979). Because
Fe and Mn hydroxides are more common in nature (Jenne, 1968;
Turekian & Scott, 1967; Gibbs, 1973), it is worthwhile to look
into the data collected by other workers. Fresh water ferro-
manganese rich materials have been reported by several workers

(Strakhov, 1965; Dean, 1970; Cronan and Thomas, 1972; Rossman et. al., 1972; Martin et. al., 1973). Data of Cronan and Thomas, Martin et. al. and Strakhov represent wide ranges in Fe and Mn values. Their Fe and Mn analysis are plotted in Fig. 4. Since their data differ by several orders of magnitude and also for clarity, scales have been purposely omitted from the figure. It appears that Fe and Mn are negatively related; since the total analyses by these authors include other metals, the observed negative relationship is not due to Fe and Mn complimenting each other; rather, certain genetic considerations concentrate Mn in Fe-deficient materials and vice-versa. Fixation of Mn by $Fe(OH)_3$ and Fe by hydrous MnO_2 is one possible explanation of the above relationship. Covariance of Fe in the Mn in natural waters, could in effect, reflect a common source for them, such as ferro-manganese nodules and hydroxide coatings in the drainage basin (Subramanian, 1975; Subramanian, 1976).

Since hydroxide coatings and concretions are commonly reported to contain other elements besides Fe and Mn, the total trace metal content has been plotted against the total (Fe+Mn) in Fig. 5. A positive relationship between the trace element content and the (Fe+Mn) content is observed. Several workers have shown the existence of positive or negative relationship involving Fe or Mn on one hand and trace metals on the other (Goldberg, 1954; Hawkes, 1965; Cronan and Thomas, 1972; Rossmann et. al., 1972).

Fig. 4

CONCENTRATION OF Fe   Vs. CONCENTRATION
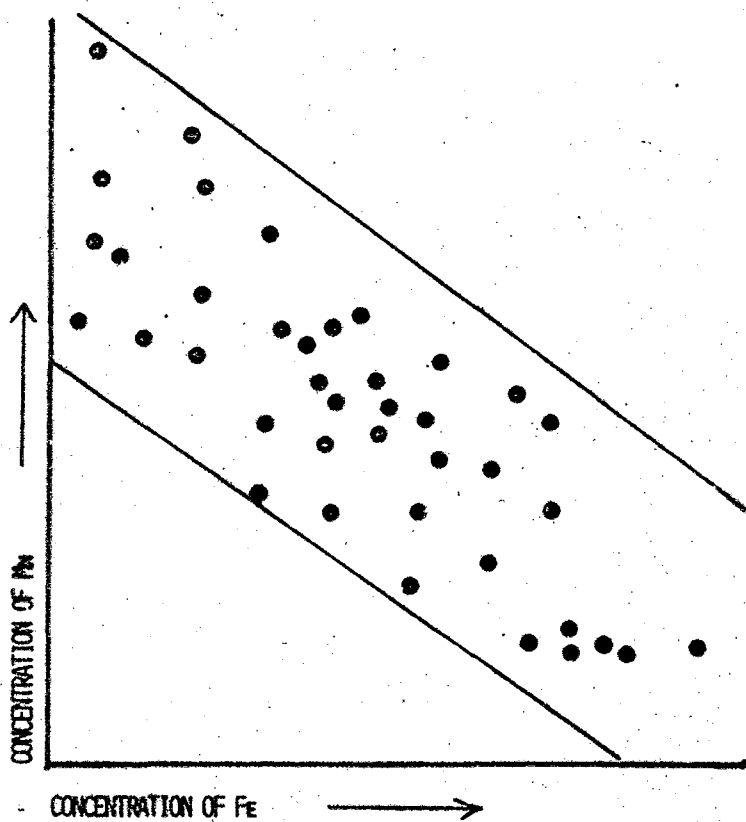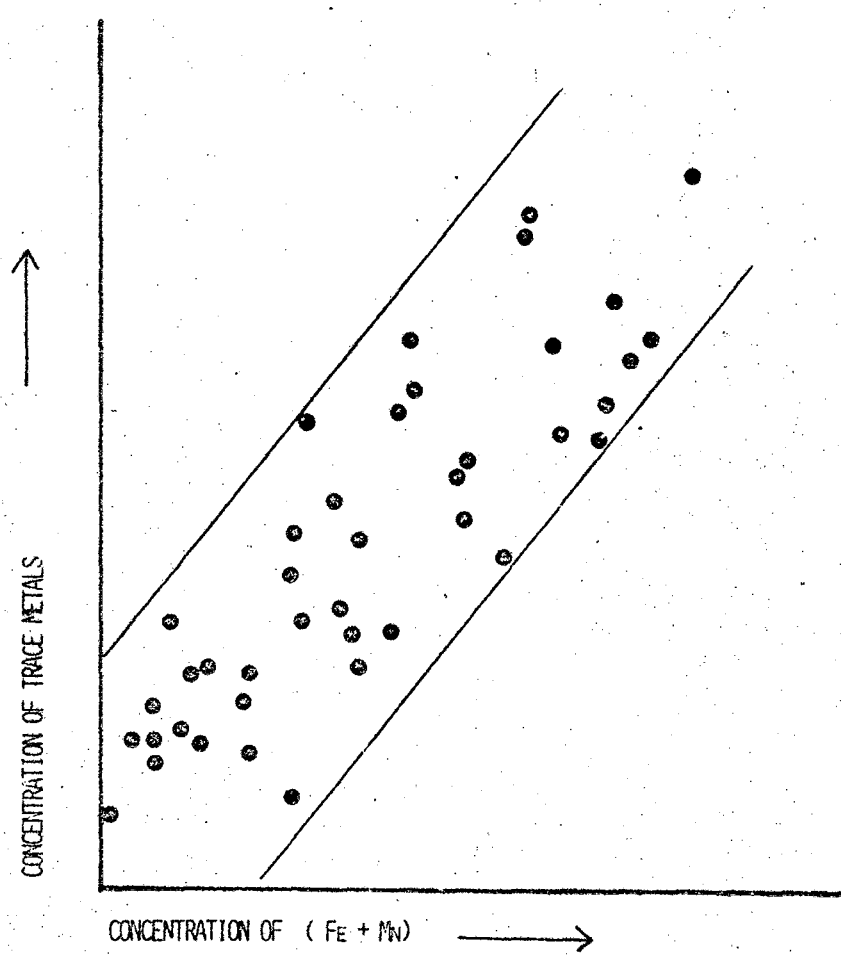OF Mn IN FERROMANGANESE RICH MATERIALS

CONCENTRATION OF Mn

CONCENTRATION OF Fe

Fig. 5.

CONCENTRATION OF (Fe + Mn) Vs. CONCENTRATION
OF TRACE METALS IN FERROMANGANESE RICH MATERIALS.

CONCENTRATION OF TRACE METALS

CONCENTRATION OF (Fe + Mn) ⟶

This suggests the combined role of Fe and Mn in the trace element fixation phenomenon.

Andrew Eaton (1978/79) when analysing the trace elements in San Francisco Bay sediments obtained the following mean concentrations of trace metals (Table 4). He concluded from his experiment that Fe and grain size variations are more important in explaining variance of elemental concentration in this estuarine system than Mn is. This indicates that Fe is a much more important geochemical agent than Mn in this system.

The baseline concentration of Cu in the sediments of Windermere England is about 24 ppm whereas Fe and Mn are 5.9% and 1.45% respectively (John Hamilton-Taylor, 1979). From the leaching experiments he found that the concentrations of Cu associated with the resistate faction is constant at all depths with mean of 13 ppm. Thus, even where the metals are at their base line levels, the labile fraction constitutes 50% of the Cu.

Skei and Paus (1979) analysed metals in the sediment from Ranafjord, Northern Norway and found the enrichment of metals in surface sediment. He attributed it partly to organic matter diagenesis and scavenging on to freshly precipitated manganese oxide and mainly to anthropogenic inputs of metals.

Collin Neal et. al. (1979) found that anthigenic As in North Atlantic deep-sea sediments is associated with anthigenic iron in the same proportion as in ferromanganese nodules. He

Table 4: Mean concentrations of trace metals
in San Francisco Bay Sediments.

Location	Fe (%)	Mn (ppm)	Cu (ppm)
South Bay	4.0	365	55
Central Bay	3.2	380	50
San Pablo Bay	4.5	460	65
North Bay	4.1	515	54
Average Shale (Krauskopf, 1967)	4.7	850	57

attributed it to the fact that As is scavenged from sea water
by an iron-bearing phase present in both sediments and nodules.

On the basis of his experimental studies, Subramanian
(1976) could explain the negative inter elemental relationship
between Fe and Mn and also the positive relationship between
(Fe + Mn) and the trace elements in natural ferromanganese
materials.

Hydrous Fe-Mn-oxide: Heavy Metal Associations

It has been reported that the concentrations of Co, Zn
and other agriculturally important heavy metals in the soils are
quite high in the hydrous manganese oxides (Taylor and Mackenzie,
1966; Taylor, 1968; Saures and Langmuir, 1975). Also large
amounts of Co, Ni, Cu and other heavy metals occur in manganese
nodules in the ocean (Willis and Ahrens, 1962; Mero, 1965; Burns
and Fueretenau, 1966; Barnes, 1967; Crerar and Barnes, 1974).
Heavy metals are common constituents of nodules and other sediments
in rivers, lakes, estuary and ocean (Krauskopf, 1956; Cronan,
1969/70; Cronan and Thomas, 1972; Griggs, 1976; Bower, 1976;
Andrew Eaton, 1978/79; John Hamilton-Taylor, 1979).

Jenne (1968), in reviewing the available information on
the controls on Mn, Fe, Co, Ni, Cu and Zn in soils, sediments and
fresh water, concluded that the hydrous oxides of Mn and Fe were

the major control on these heavy metals in soils and freshwater
sediments. Zn was scavenged from waters of the Fraser river
estuary by hydroxides of Fe and Mn, but disorption occur in the
lower estuary and ocean (Grieve and Fletcher, 1977). Iron
hydroxide, along with detritus and clay, were largely responsible
for trapping many metals in pre-delta areas of the Ando River
(Monaco, 1977). A practical example from the Arctic areas of
Canada showing the dominant role of Fe and Mn oxides in the distri-
bution of trace metals in fluviatile systems is described by
Cameron and Co-workers (Cameron, 1974; Cameron and Ballantyne,
1975; and Jonasson, 1977).

The sorption of heavy metals on hydrous Mn and/or Fe-oxides
has been reported by many researchers (Morgan and Stumm, 1964;
Posselt et. al., 1968; Murray et. al., 1968; Mckenzie, 1970; Anderson,
et. al., 1973; Loganthan and Bureau, 1973; Lockwood and Chen, 1973;
Guy et. al., 1975; Burns, 1976; Loganathan et. al., 1977;
Inone Y. and Munemori, M.,1979).

Loganathan and Bureau (1973), Subramanian (1975) and
Burns (1976) proposed that heavy metal ions are structurally bound
in hydrous oxide of Fe or/and Mn.

Murray et. al. (1968) reported that group one and two
cations are strongly sorbed on manganese dioxide. They found that
the sorption was independent of small pH changes at high

concentrations of the cations and was highly pH dependent at low concentrations of the cations. They propose that in dilute solutions, the adsorption occurs as counter ions in the diffuse double layer, while in the high concentration, the sorption occurs within the manganite lattice. They also reported that Ni^{2+}, Cu^{2+} and especially Co^{2+} exhibited marked specific adsorption on the MnO_2.

The uptake of Co^{2+}, Zn^{2+} and Ca^{2+} by $\delta-MnO_2$ at $24 \pm 0.5°C$ as a function of pH and salt concentration was investigated by Loganathan, Burau, Fuerstenau (1977). At pH values < 5, there is not much change in the sorption of these cations with increase in pH. At pH values above 6, there is an abrupt increase in the uptake of Co^{2+} and Zn^{2+} within narrow pH ranges which depend on the equilibrium concentrations of the metal ion whereas no such marked increase of Ca^{2+} sorption was found upto pH 9.2. They proposed that this type of sharp increase in sorption is due to specific adsorption and is related to hydroxylation of the metal ions.

Guy et. al. (1975) studied the sorption of Cu(II), Cd(II) and Zn(II) on to potassium bentonite, hydrous MnO_2, and solid humic acid and found that Cu distribution depends on the pH of the suspension. Above pH 6, 50% of the copper is sorbed on to the particulates whereas the Cu in solution is in a complexed form;

between pH 6 and 3.8 the soluble Cu is distributed between organic complexes and "free" copper ion; between pH 4.2 to 2.5 copper is being desorbed from the particulates; and below pH 2.5 all the Cu is present in solution as "free" Cu ion.

Davis and Leckie (1978) investigated the adsorption of Cu(11) and Ag(1) on $Fe(OH)_3$ (amorphous) as a function of pH. He took the dilute total metal concentrations typically found in natural waters and an intermediate ionic strength between the extremes of fresh waters and marine systems. They found that Cu(11) and Ag(I) adsorption increases from 0 to nearly 100% adsorbed within a narrow pH range. The adsorption edge for Cu(11) is in the pH range 5-6. They also studied the effect of adsorbed complexing ligands on trace metal uptake by $Fe(OH)_3$(am) and found that despite the large amount of organic material present at the surface in the pH range 4-6, Cu(11) uptake by $Fe(OH)_3$ (amorphous) is not significantly affected by the addition of these ligands to the system or by 10^{-3}M added sulphate.

Experiments conducted by Kharkar et. al. (1968) on the adsorption of Co, Ag, Sc, Cr and Mo on various mineral phases in distilled water, and on desorption of adsorbed metals in sea water show that where a trace metal is adsorbed from fresh water solution, it is always released — to a greater or lesser degree — upon contact with sea water due to displacement by Mg and Na ions.

An experimental study was performed by Rohtagi and Chen (1975) on the effects of sea water on the concentrations of trace metals in waste water particulates. Samples of primary effluents, digested sludge, and mixtures of primary and secondary effluents were obtained from the Hyperion Treatment plant of Los Angeles, California. In most cases, Cd, Cu, Ni, Pb and Zn were found to be released to a greater extent than the other metals. Cr, Fe and Mn were not released except in the case of digested sludge, in which 9% of Cr and 36% of Mn was released from solid phases. However, upto 96% of Cd was released from suspended particulates. At different dilution rates of waste water effluents and digested sludge with sea water, no significant difference in the release of Cd was observed. On the other hand, the dilution ratio seems to play an important role in the release of Ni and Zn from suspended particulates.

Thus the analysis of the previous work indicates that hydrous Fe and Mn oxide is an effective sink for trace metals. It also indicates the combined role of hydrous Fe and Mn-oxide in controlling heavy metals in natural waters. In all the previous works, either iron hydroxide or manganese oxide was used as adsorbant except Subramanian's (1973), who studied the combined role of Fe and Mn in the fixation of Ni.
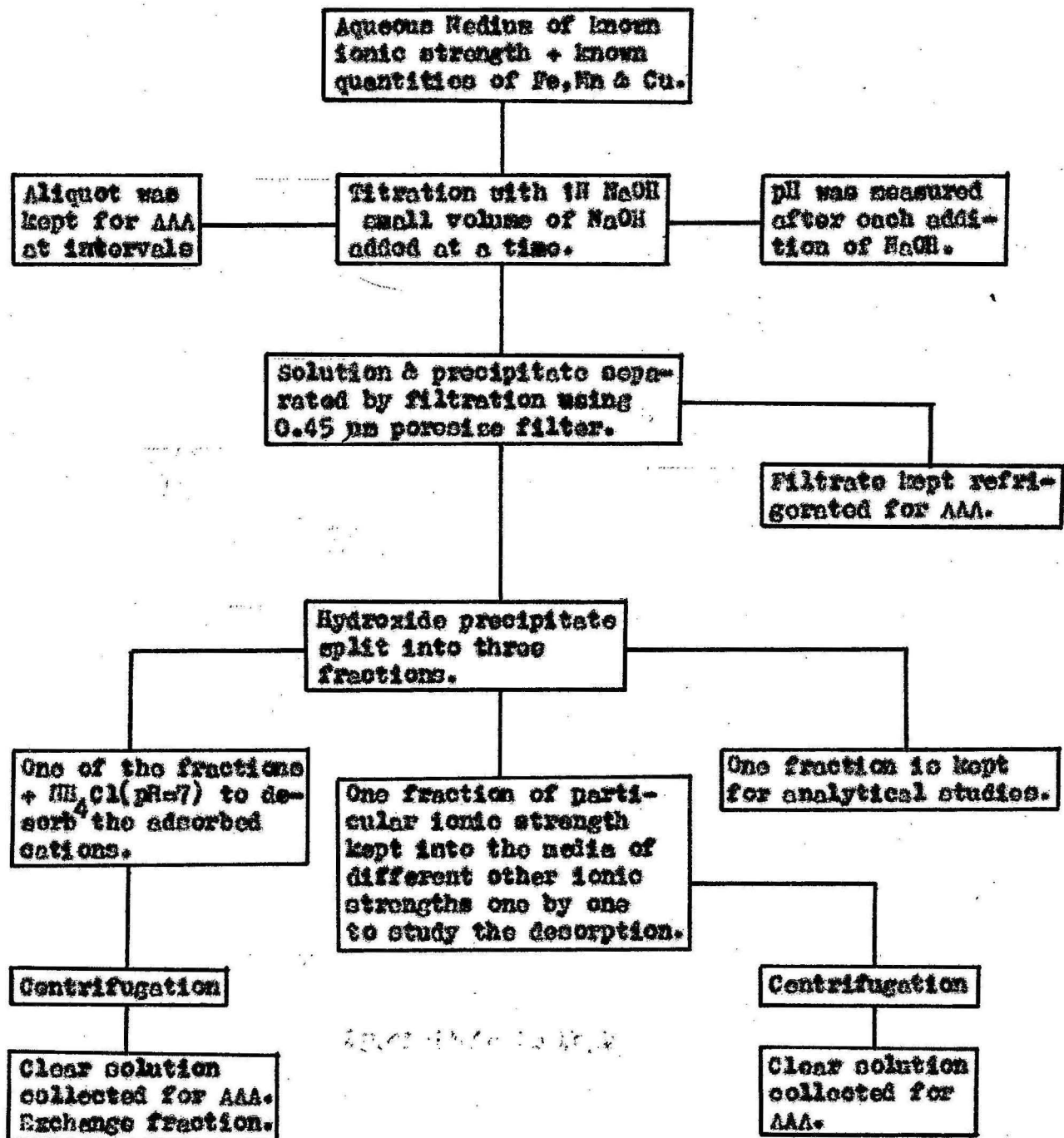
In the present work, an attempt is made to study the combined role of hydrous Fe & Mn oxide in controlling copper in the aquatic environment.

28

Description of Experimental Set Up

All analytical grade reagents were used. Aqueous NaCl solution having ionic strengths .01, .1, .3, .5 and .7 (ranging from river water to sea water) were prepared in the laboratory. Fe, Mn and Cu were added from stock solutions kept refrigerated in the amount required for individual experiments. Coprecipitation of hydroxides of Fe, Mn and Cu was effected by titrating the aqueous medium containing known quantities of Fe, Mn and Cu with NaOH. Desorption was done in a medium of 1 NH_4Cl solution adjusted to pH = 7.0. Desorption was also done by putting the precipitate of one ionic strength medium to the medium of different other ionic strengths one by one. Dissolved species were separated from solid suspensions or precipitates by filtration using 0.45 µm pore size filter.

All experiments were done at room temperature and pressure. Elemental analyses were done with an AAS-1 model Atomic Absorption Spectrophotometer following procedures in its manual of instructions. Solutions of these species were acidified and kept refrigerated. pH measurements were done by a digital pH meter. The laboratory work is schematically illustrated in Fig. 6. Brief descriptions of individual experiments are as follows:

Fig. 6: A generalised flow-chart for the experimental work. (AAA - Atomic Absorption Analysis)

Aqueous Medium of known ionic strength + known quantities of Fe, Mn & Cu.

Aliquot was kept for AAA at intervals

Titration with 1N NaOH small volume of NaOH added at a time.

pH was measured after each addition of NaOH.

Solution & precipitate separated by filtration using 0.45 μm porosize filter.

Filtrate kept refrigerated for AAA.

Hydroxide precipitate split into three fractions.

One of the fractions + NH$_4$Cl(pH=7) to desorb the adsorbed cations.

One fraction of particular ionic strength kept into the media of different other ionic strengths one by one to study the desorption.

One fraction is kept for analytical studies.

Centrifugation

Centrifugation

Clear solution collected for AAA. Exchange fraction.

Clear solution collected for AAA.

Coprecipitation Experiments

1.   100 cc of 200 ppm Fe, 100 cc of 200 ppm Mn and 100 cc of 100 ppm Cu were added simultaneously to 100 cc aqueous solutions of different ionic strengths (.01, .1, .3, .5 and .7) in different 500 cc pyrex beakers. Hydroxides were precipitated by titration with 1 N NaOH. After every addition of NaOH, pH of the solution was measured. Aliquot were kept at intervals for AAA. After complete precipitation, the solution and the precipitate were separated by filtration. The solution was kept refrigerated after acidification for elemental analysis. Desorption experiment was done with one portion of the precipitate and another portion kept for IR analysis.

2.   100 cc 200 ppm each of Fe and Mn and 100 cc of different concentrations of Cu (4 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm, 120 ppm) were added in different beakers containing 100 cc aqueous solution of ionic strength 0.01. Coprecipitation, separation and analysis were done as above.

Desorption Experiments

1. In 1 NH_4Cl

A portion of the precipitate obtained from above experiments was suspended in 50 cc 1 NH_4Cl maintained at pH 7 and kept for 1 hour. The aqueous portion was then separated and kept refrigerated after acidification for elemental analysis.

2. In different ionic strength media

Precipitate from one ionic strength media was suspended in 25 cc aqueous solution of different ionic strengths successively for an hour in each. The aliquot was then kept refrigerated after acidification for elemental analysis.

Results and Discussions

Subramanian (1975) stated that adsorption is not pertinent to understanding the nature of Fe-Mn-hydroxide precipitate. It is not important whether adsorption or co-precipitation actually occurs in natural conditions because the inter elemental relationships within the hydroxide is not altered by the method of introducing Mn and Ni into $Fe(OH)_3$. In this study, Fe, Mn and Cu have been coprecipitated as hydrous oxide. In response to changes in pH, or other factors such as changes in total dissolved Fe, Mn and Cu in water, their hydrous oxides would be precipitated from natural aqueous system.

In the present system anions present are OH^-, SO_4^{--}, NO_3^- and Cl^-. SO_4^{--}, NO_3^- and Cl^- will not affect the co-precipitation, as Cu (II) uptake by $Fe(OH)_3$ (am.) is not significantly affected by sulphate ligand (Davis and Leckie, 1978), nitrate ion is a very weak complexing agent (Ramamoorthy and Rust, 1978) and chloride is not an important complexing agent at room temperature. Above all, NaCl is used to represent different water bodies. To represent ocean system, Na^+ and Cl^- ions are very important. The solubility of OH^- is very low, so hydroxide will precipitate readily. Thus only OH^- ions are effective, others are not. Hence it may be assumed that the precipitate formed will be some form of hydrous oxide.

In the case of coprecipitation, the mixture formed
can be physical with the micro-component adhering to the
surface of the major component or it can be structural with
the microcomponent free to diffuse through the interior of the
solid phase or it can be occlusion. Thus, coprecipitation can
take place in a system of equilibrium or non-equilibrium involving
miscible or immiscible components.

Jenne (1968), Allen et. al. (1970) have pointed out
that the uptake or release of heavy metals from Fe and Mn
oxides is a function of the type of heavy metal and its concen-
tration, pH etc. The variables studied here are pH, ionic
strength of the media and heavy metal concentration.

Here the results of uptake and release of copper by
hydrous Fe-Mn-oxide precipitate are presented.

<u>Uptake of Cu by Hydrous Fe-Mn-oxide Precipitate</u>

In the laboratory experiment, Fe, Mn and Cu were
completely precipitated as hydroxides. At that point, almost
100% of these go to solid phase irrespective of the ionic
strength of the media in one case and different copper concen-
trations in the other (Table 5 and 6).

Fig. 7 shows the uptake of Cu(II) by hydrous Fe-Mn-oxide
precipitate as a function of pH in different ionic strength media.
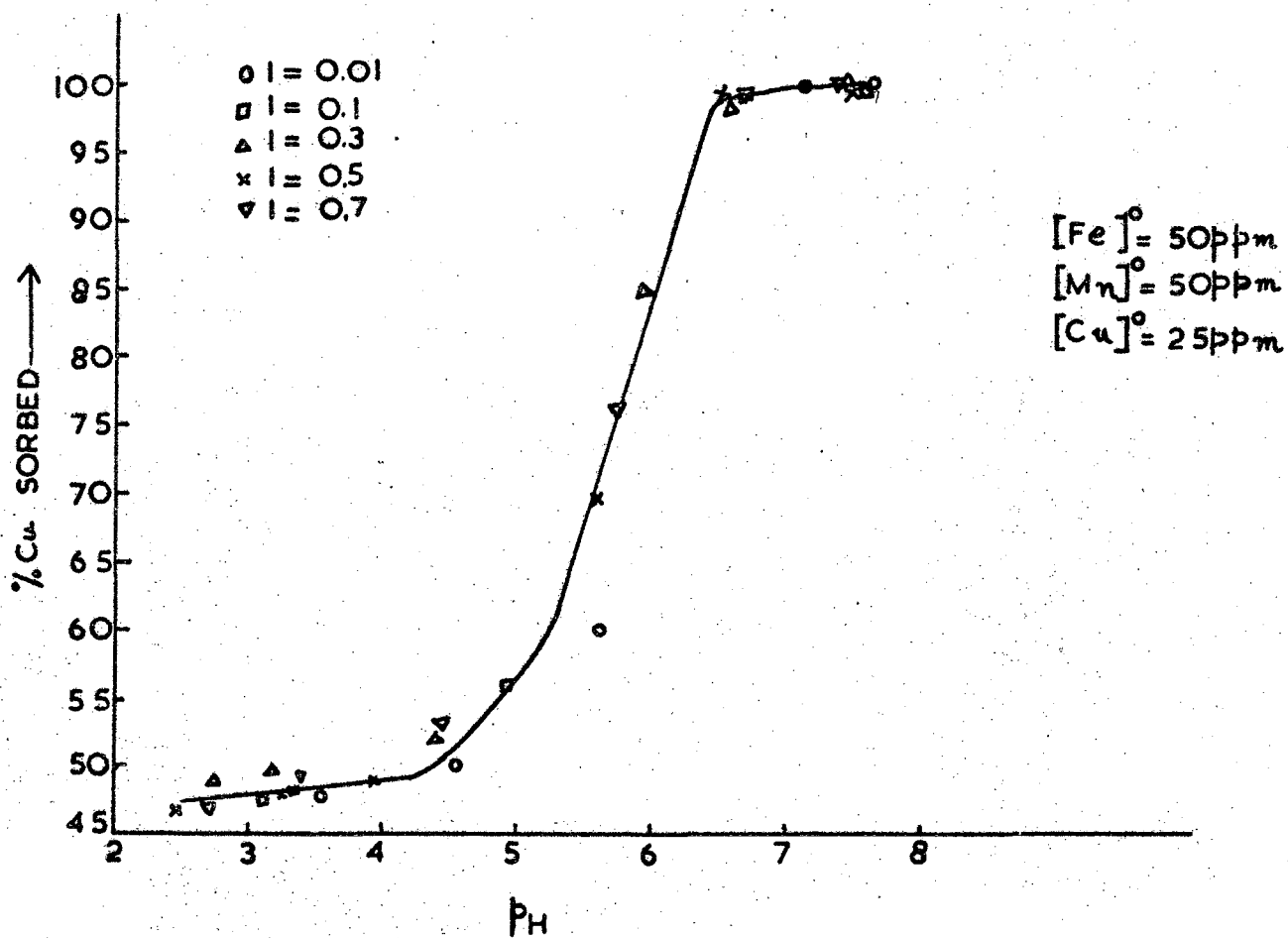The copper concentration is 25 ppm in all cases.

Table 5: % Uptake at different ionic strengths and same Cu concentration (25 ppm).

Ionic strength	Initial concentration in ppm			Final concentration in ppm			% uptake		
	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu
0.01	50	50	25	0.1	0.1	0	99.8	99.8	100
0.1	50	50	25	0.0	0.0	0.0	100.0	100.0	100
0.3	50	50	25	0.0	0.5	0.05	100.0	99.0	99.8
0.5	50	50	25	0.0	0.7	0.05	100.0	98.6	99.8
0.7	50	50	25	0.1	2.0	0.0	99.8	96.0	100

Table 6: % uptake at different Cu concentrations and same ionic strength (0.01).

Ionic strength	Initial ppm			Final ppm			% Uptake		
	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu
0.01	50	50	1	0	1.0	0	100	98	100
0.01	50	50	5	0	1.0	0.02	100	98	99.6
0.01	50	50	10	0.1	0.1	0.05	99.8	99.8	99.5
0.01	50	50	15	0	3.2	0	100	93.6	100
0.01	50	50	20	0	0.5	0	100	99.0	100
0.01	50	50	30	0	2.0	0	100	96.0	100

FiG.7

CuⅡ UPTAKE BY Fe-Mn PPT AS A FUNCTION
OF Pн AT DIFFERENT IONIC STRENGTHS

o I = 0.01
▫ I = 0.1
▲ I = 0.3
× I = 0.5
▽ I = 0.7

$[Fe]^o = 50ppm$
$[Mn]^o = 50ppm$
$[Cu]^o = 25ppm$

% Cu SORBED

PH

Similar to the results of many other investigations
of hydrolysable metal ion adsorption (Schindler et. al., 1976;
Guy et. al., 1975; Loganathan et. al., 1977; and Davis &
Leckie, 1978), it is seen that most of the Cu (II) uptake takes
place within a narrow pH range. The adsorption edge for Cu(II)
is in the pH range 5.25 to 6.4 irrespective of the ionic strength
of the media, which is approximately the same as observed by
Davis and Leckie (1978) (Fig. 8) but in the present case about
48% Cu is sorbed at pH $<$ 3 whereas sorption at lower pH is very
small in Davis and Leckie's experiment. This may be due to
the difference in different factors in the two experiments.
1)   Adsorbent used by Davis & Leckie was $Fe(OH)_3$ (amorphous)
whereas in this case the adsorbent is hydrous Fe-Mn-oxide.
2) Concentration of copper used by him was very low, 10^{-6}M
(i.e. 0.0635 ppm) whereas the concentration of copper in this
experiment is 25 ppm. Second factor seems to be very strong for
higher sorption of Cu at pH $<$ 3 as is clear from Fig. 12 which
shows that the sorption of Cu is zero at pH $<$ 3 for lower copper
concentration in the solution (here 1 ppm and 5 ppm) and it
goes on increasing as the copper concentration in solution
increases. For 30 ppm copper in solution, the sorption below
pH 3 is about 52%. Using 10 μg/ml copper, Guy et. al. (1975)
found that sorption of copper on MnO_2 was zero below pH 1.5 (Fig.9).
Both Fe and Mn oxide are present in the natural system, so the

FIG. 8
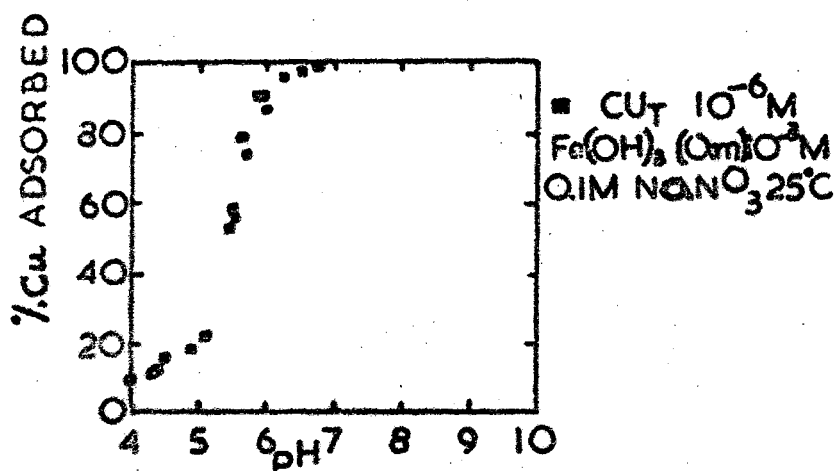
ADSORPTION OF COPPER (II) ON AMORPHOUS
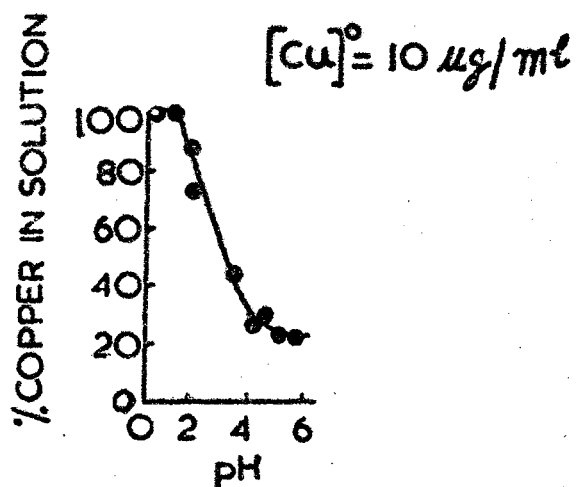IRON OXIDE AS A FUNCTION OF pH

FIG.9: COPPER SORPTION ON $Mn O_2$
AS A FUNCTION OF PH

present study is better representative of natural system than that of Guy et. al. (1975), Davis & Leckie (1978) and others because they have considered either only $Fe(OH)_3$ or MnO_2 as adsorbent. Though this system deviates from the natural system, as the copper concentrations used are higher. But it can well represent a polluted natural system.

To know, whether the copper precipitated in the pH range studied is a separated copper phase or it is associated with the hydrous Fe-Mn-oxide phase, theoretical calculation was done at different pH to know the amount of copper which must be present in the solution in order to get the two probable solid copper compounds precipitates in this system: $CuO(s)$ and $Cu(OH)_2(s)$. The calculations were done on the basis of solubility product data. Table 7 shows these values. Comparing this copper concentration value at particular pH with the copper concentrations present in the experimental system at that pH (Fig. 7), it is concluded that copper is not precipitated as a separate copper phase but somehow or other it is associated with hydrous Fe-Mn-oxide precipitate.

As the uptake of Cu takes place even at lower pH, it can be speculated that the surface charge of hydrous Fe-Mn-oxide precipitate is negative at all pH values studied, though surface charge is not determined in this study. Loganathan et. al. (1977) has reported that the surface charge of δ-MnO_2 was

Table 7: Calculated Cu concentrations (total dissolved) required to precipitate CuO(s) and Cu(OH)$_2$(s) at different pH at 25°C.

pH	Concentration of Cu required to precipitate CuO(s). (ppm)	Concentration of Cu required to precipitate Cu(OH)$_2$(s). (ppm)
2.5	87.63×10^6	63.5×10^7
3.0	87.63×10^5	63.5×10^6
3.5	87.63×10^4	63.5×10^5
4.0	87.63×10^3	63.5×10^4
4.5	87.63×10^2	63.5×10^3
5.0	8.763×10^2	63.5×10^2
5.25	2.78×10^2	19.05×10^2
5.5	87.63	6.35×10^2
6.0	8.763	63.5
6.4	1.397	10.16
6.5	0.8763	6.35
7.0	0.08763	0.635

*Corresponding Cu^{+1} compounds, cuprous oxide and cuprous hydroxide are unstable in aqueous solution.

negative at all pH values, even at very low pH. Metal

ions can then interact with the negatively charged particle

in two ways:

i) formation of a counter-ion layer.

ii) specific sorption of ions on to the surface, as shown

for copper sorption on to MnO_2 surface by Guy et. al. (1977).
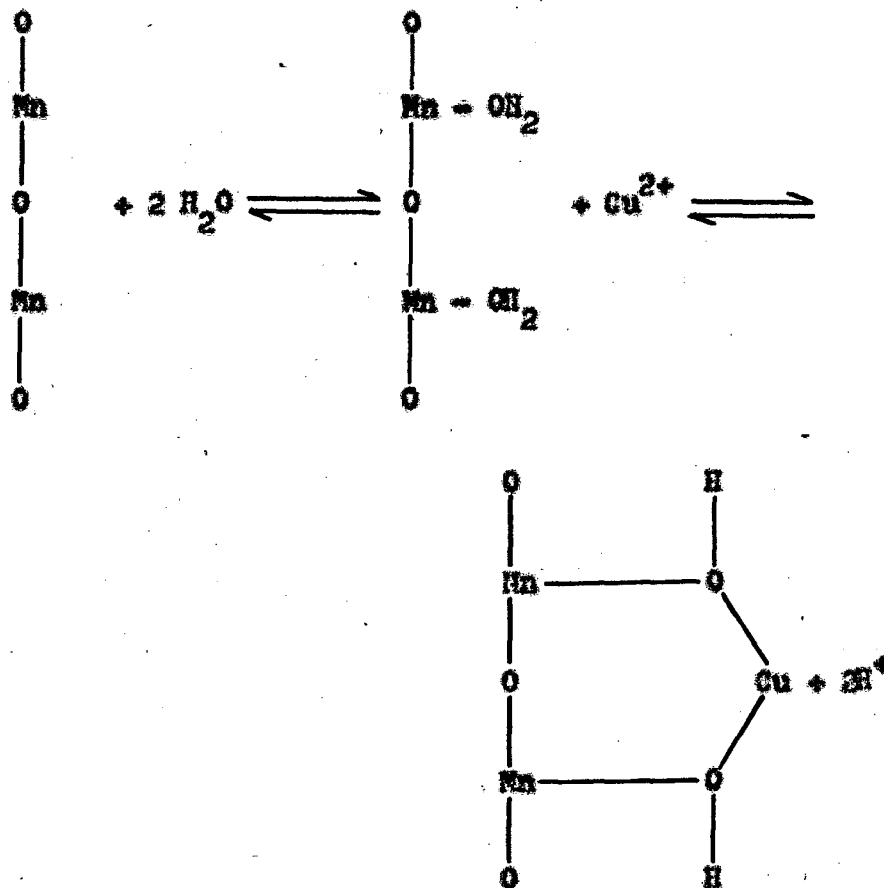
It is also likely that adsorbed $CuOH^+$ is the predominant

Cu(II) surface species, since it has been shown that adsorption

of metal ions on various oxide surfaces increases abruptly in

the pH range where hydrolysis products become a significant fraction of the dissolved metal (Leckie and Janes, 1975).

Fig. 10 relates the uptake of Mn to pH which shows that about 50% Mn is coprecipitated at pH < 2.5, then there is almost no increase in Mn uptake till pH 6.95 and again there is abrupt increase in the uptake within narrow pH range (6.95 - 7.55). The uptake of Fe increases with increasing pH till pH 5.25 where the sorption is almost 100% (Fig. 11).

So the Figs. 7, 10 and 11 indicate that at higher pH, there is competition between Mn and Cu for $Fe(OH)_3$ but copper is preferred by Fe over Mn.

Fig. 12 relates the uptake of copper by hydrous Fe-Mn-oxide precipitate to pH at different copper concentrations. The nature of the plot is very much the same as it is in Fig. 7 except the plot of 1 ppm Cu. This may be due to less number of data points taken in the experiment. But one thing is very clear from the figure that as the concentration of Cu(II) in solution increases, the % uptake of Cu by hydrous Fe-Mn-oxide precipitate at lower pH also increases. The Cu uptake is zero below pH 2.75 when the Cu(II) concentration in solution is 1 ppm and 5 ppm, whereas Cu uptake is about 18% at pH 2.75 when the Cu concentration is 10 ppm, 25% when Cu concentration is 15 ppm, 36.5% when Cu concentration is 20 ppm and 52% when

FIG. 10

Mɴ UPTAKE AS A FUNCTION OF Pʜ

FIG 11

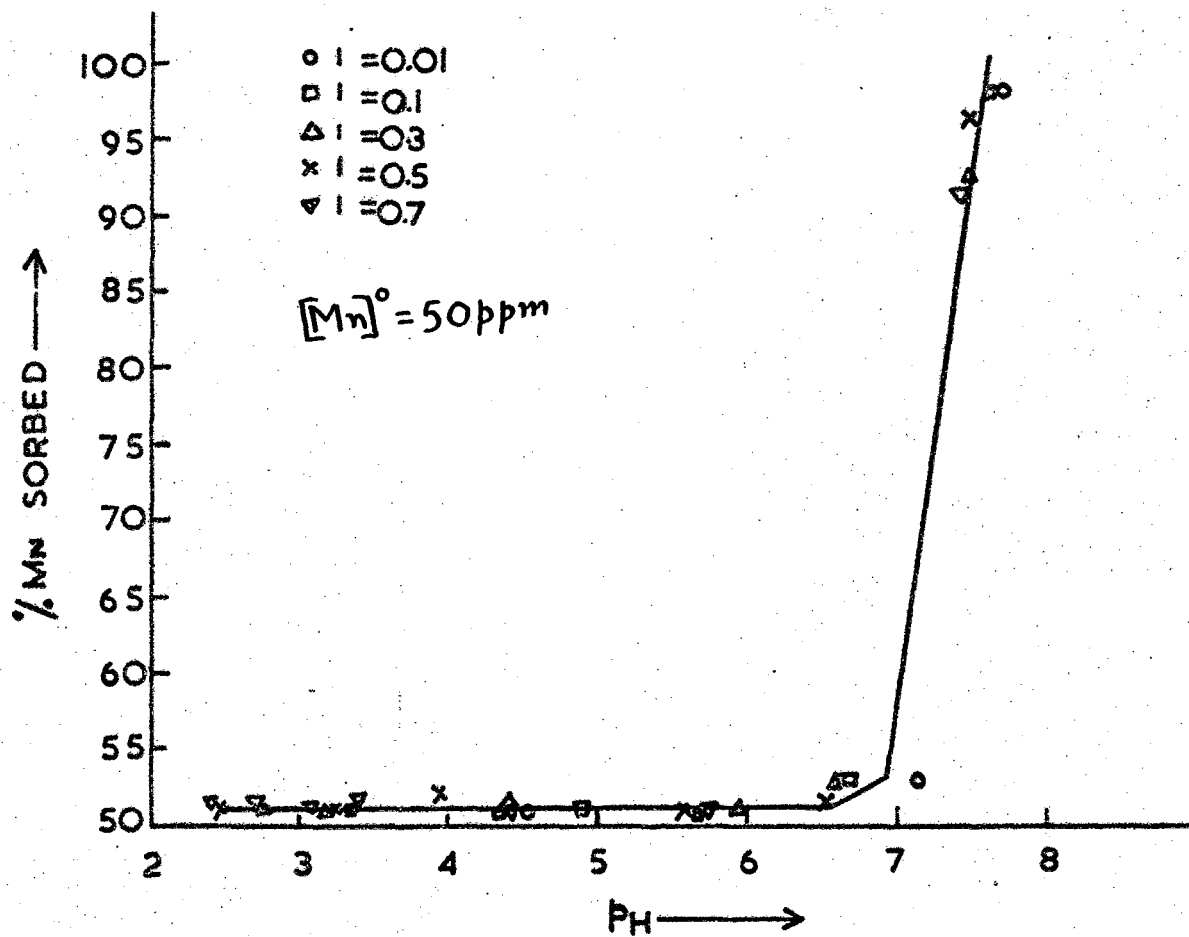FE UPTAKE AS A FUNCTION OF PH

%.FE SORBED →

PH ——→

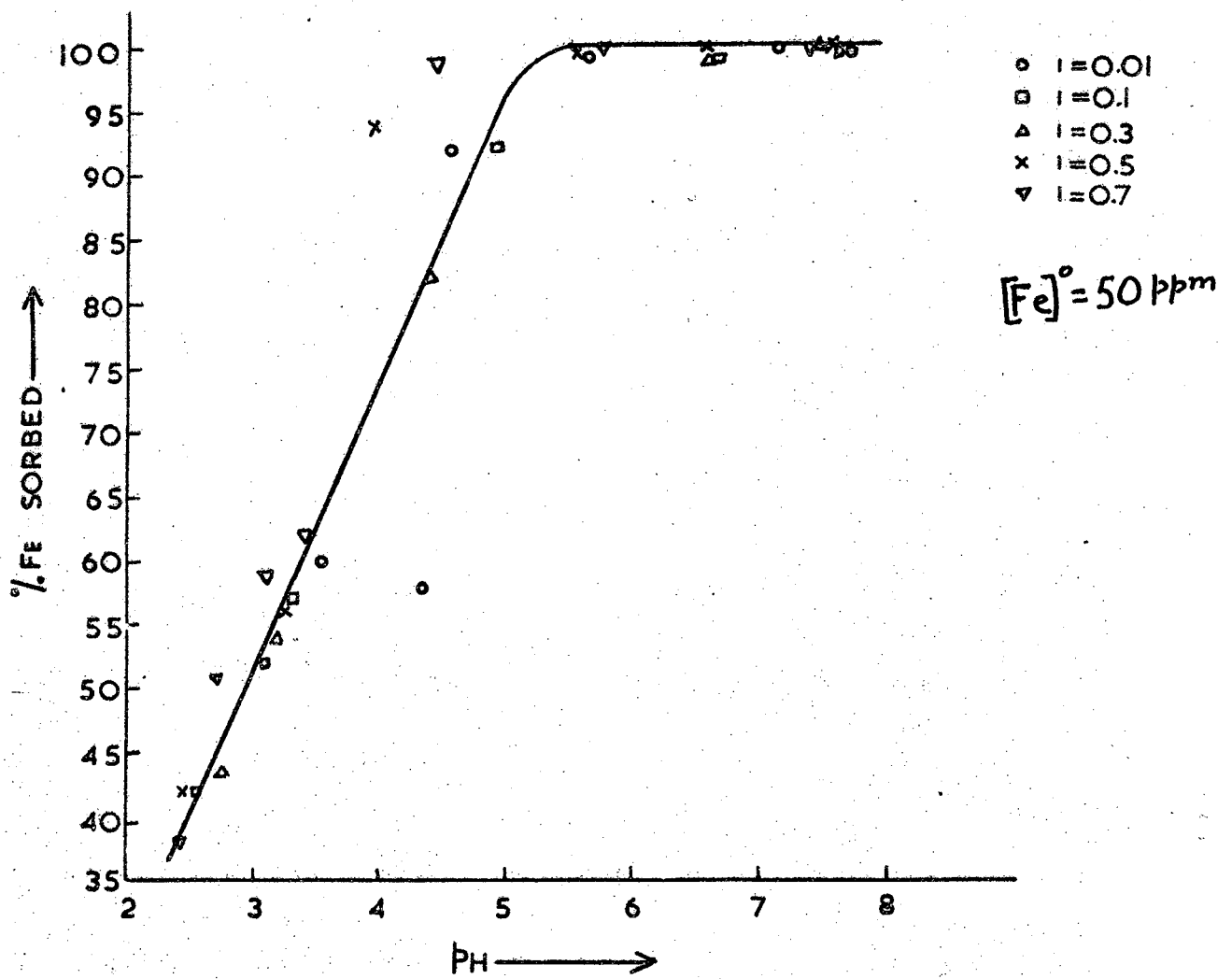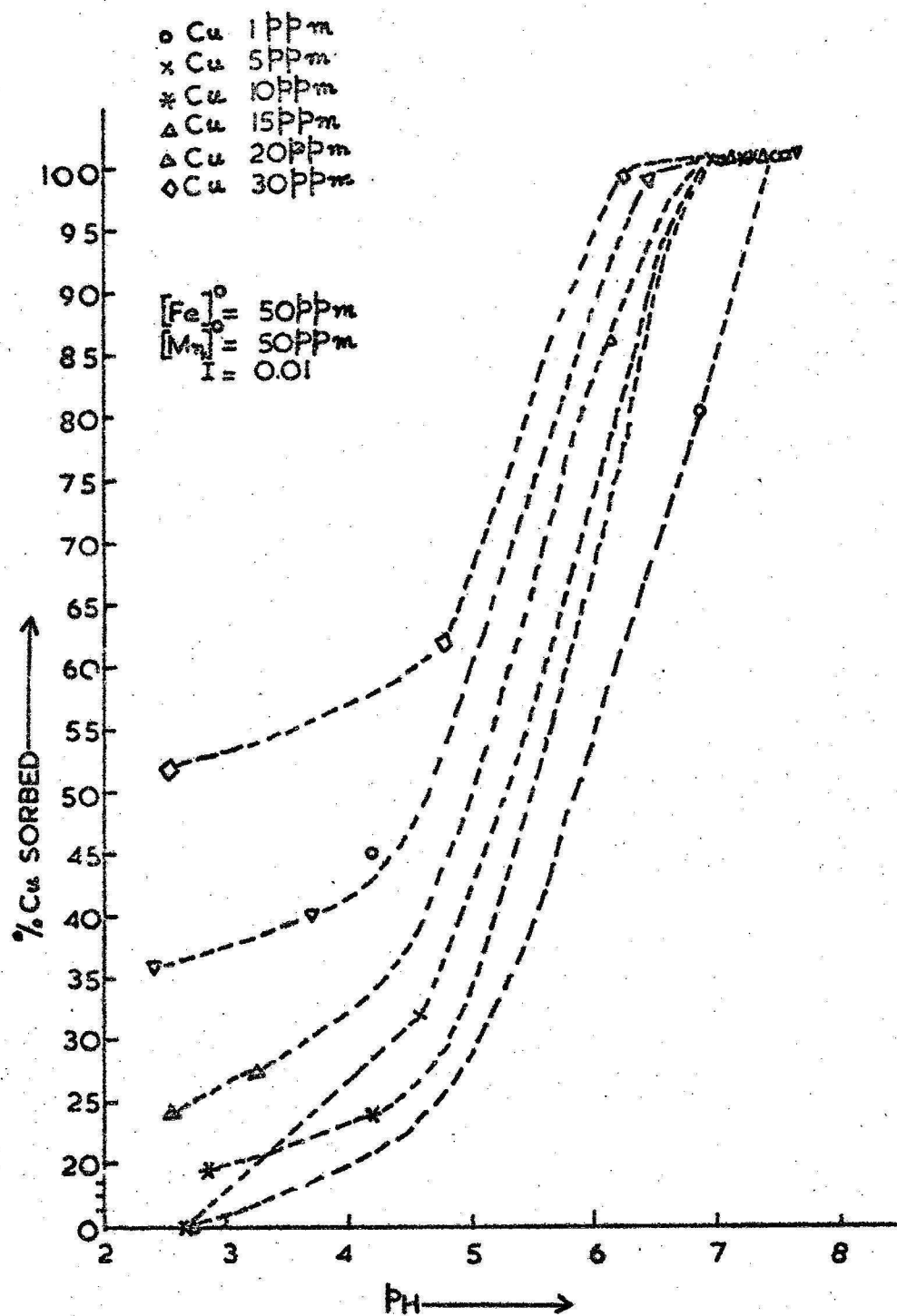|	
o	I=0.01
□	I=0.1
△	I=0.3
×	I=0.5
▽	I=0.7

$[Fe]^\circ = 50 \, ppm$

FIG. 12

Cu(II) UPTAKE BY Fe-Mn-PPT. AS A FUNCTION OF pH AT DIFFERENT Cu CONCENTRATIONS

the copper concentration is 30 ppm. In all concentrations, the Cu uptake increases with increasing pH.

Fig. 7 shows that the uptake of Cu by hydrous Fe-Mn-oxide precipitate is independent of the ionic strength of the media.

Now it can be inferred that pH and concentration of copper are important factors in controlling the sorption of Cu by hydrous Fe-Mn-oxide precipitate. It is also clear from above that copper is not precipitated in the system as separate Cu-phase but it is somehow associated with hydrous Fe-Mn-oxide. This association may be sorption, occlusion or/and solid-solution. Subramanian (1975) has proposed a solid solution model for Fe-Mn-Ni-hydroxide.

Sorption can be considered as an exchange reaction and is related to the structure of the host material. Chemisorption is generally reversible but may eventually lead to incorporation of minor elements (here Cu) in the structure of the host. On the other hand, coprecipitation of Fe-Mn-Cu hydroxide incorporates all of the above functions in a single step. Such a relationship between the trace metals and host materials may lead to occlusion or solid solution. Occlusion is a process in which the trace metals are locally distributed in the host so that the trace metal/host mixture cannot be considered as a single

homogeneous phase. In the case of a solid solution, the trace metals would be uniformly distributed over the host substance so that the precipitate could be considered as a single homogeneous substance.

Desorption is a method of determining the nature of the precipitated mixture within the framework of the above mechanisms. Desorbable cations from a precipitate are a measure of its exchange capacity. In addition a small amount of the precipitate will dissolve in the medium in which desorption takes place. Thus the precipitate looses its exchange fraction, and also the soluble fraction, to the aqueous media.

Release of Copper from the Precipitate

Fig. 13 and Table 8 relate the per cent release of Fe, Mn and Cu from the mixed precipitates obtained from solutions of different ionic strength media. The desorption experiment was done in 1 NH_4Cl solution to show the exchangeable fraction of Fe, Mn and Cu in the precipitate. Figure shows that the desorption of Fe is negligible from all the precipitates formed from different ionic strength media, even the desorption of Mn is smaller. But the desorption of Cu is significant. The desorption of copper is around 40 to 47.5 % depending upon the ionic strength of the media. This shows the fraction of Cu in the exchangeable part of the precipitate. This desorption

FIG. 13

IONIC STRENGTH AS A FUNCTION
OF DESORBABLE Fe,Mn AND Cu IN
PRECIPITATES

△ Fe   ▽ Mn   O Cu
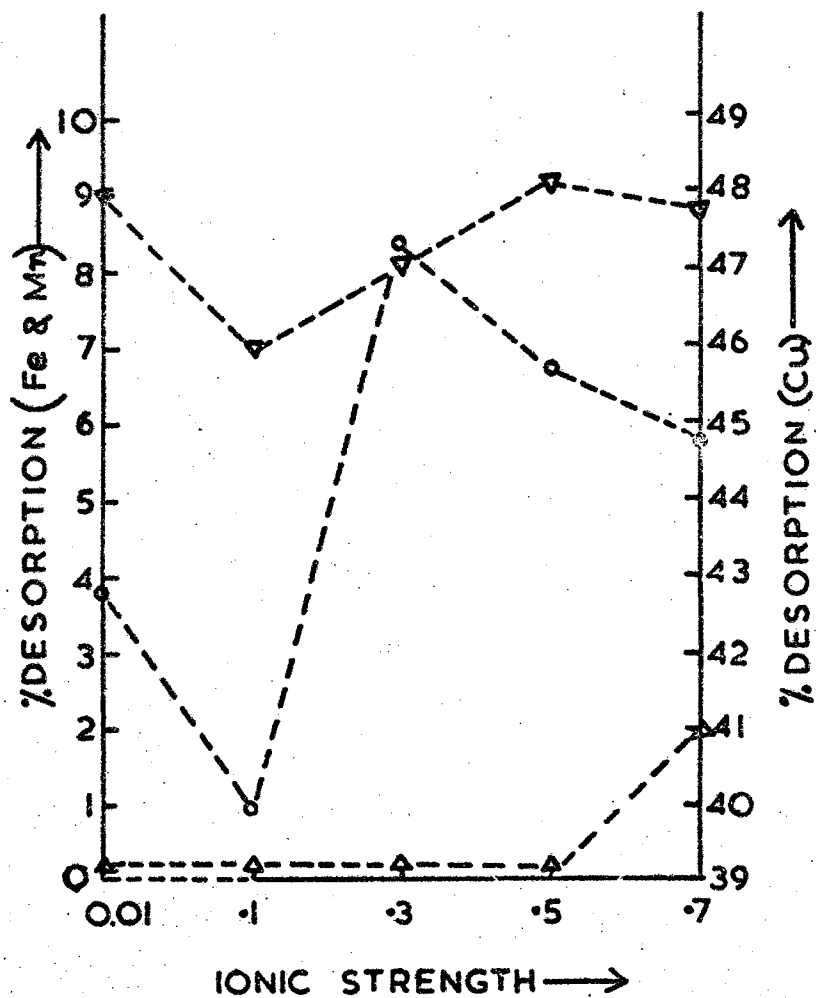
might then represent the amount of Cu truly adsorbed, i.e., held on to the surface of hydrous Fe-Mn-oxide. Remaining amount of copper, which is more than 50%, must then be in the fixed portion of the precipitate, i.e., entered into the structure of the host. So this plot suggests that there is a large quantity of copper in the surface or exchange sites of the hydroxide precipitate and that most of the Mn and Fe are held together in the structure of the hydroxide. Thus the precipitates can be considered to contain two fractions -- the exchangeable fraction and the nondesorbable "fixed" fraction. The relative proportions of these fractions in the precipitates vary with the ionic strength of the precipitating medium.

The presence of cations other than Fe, Mn and Cu in the coatings and other ferromanganese materials can be explained as follows: coprecipitated hydroxides contain some percentage of exchangeable fraction; the amount of this fraction varies depending on the ionic strength of the aqueous media. Cations such as Ni^{2+}, Co^{2+} and other compatible ions in the solution can replace the exchangeable Fe, Mn and Cu from the adsorption sites and thereby become part of the mass of the ferromanganese materials.

Initial copper concentration as a function of % copper desorption from the precipitates formed from solutions having

the same ionic strength (0.01, similar to a river water)
is plotted in Fig. 14. The plot shows that the copper de-
sorption increases with increasing initial copper concentration
which is natural because copper will first enter into the
structure of the Fe-Mn-oxide precipitate and then the excess
copper will undergo surface adsorption. The Figure also shows
a decrease in desorption when Cu is 30 ppm. This is inexpli-
cable at the moment. It might be an analytical error.

Tables 8 and 9 show the percentage desorption of Fe, Mn
and Cu under various experimental conditions. Precipitates
formed from different ionic strength media having the same
initial copper concentrations is desorbed into the media of
another ionic strengths (Table 8). And precipitates having
different initial copper concentrations formed from the same
ionic strength (0.01) media is desorbed into different other
ionic strength media (Table 9). In both the cases, the results
show that the desorption of Fe, Mn and Cu is very small. Three
values are higher, which might be due to analytical errors. So
the desorption of Fe, Mn and Cu from the precipitates does not
take place simply by change in media of the precipitate (i.e.,
river to estuary to sea) but it occurs when the compatible ions,
like Ni^{2+}, Co^{2+} etc. are present in the medium which can exchange
with the exchangeable fraction of Fe^{2+} or Fe^{3+}, Mn^{2+}, and Cu^{2+}
from the adsorption sites.

FiG.14

INITIAL Cu CONCENTRATIONS
AS A FUNCTION OF Cu
DESORPTION FROM PRECIPITATES
(I=0.01)
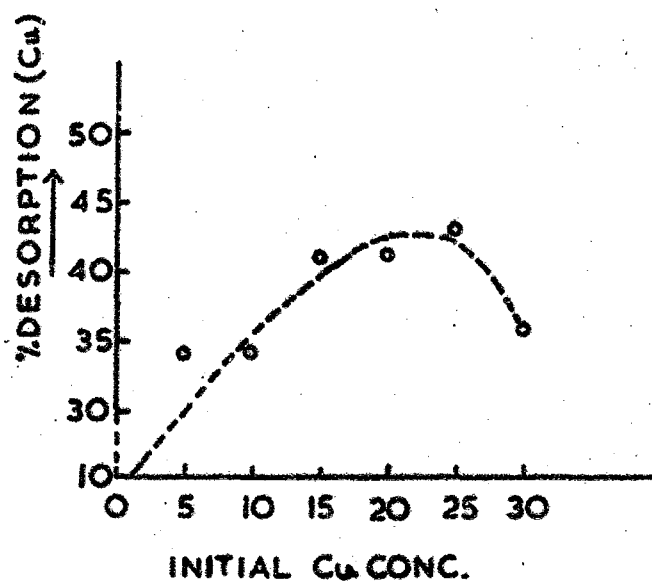
INITIAL Cu CONC.

Ionic strength of the media in which precipitate is formed	% Release in NH_4Cl			% Release in different ionic strength														
				0.01			0.1			0.3			0.5			0.7		
	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu
0.01	0.22	9.02	42.8	-	-	-	0.2	1.0	0	1.0	2.0	0.8	1.0	1.2	0.2	1.0	1.2	0.8
0.1	0.2	7.0	59.2	0	2	0.8	-	-	-	0.6	1.2	0.2	0.2	1.8	0.8	6.2	3.4	1.6
0.3	0.2	8.08	47.32	0	2.02	0.8	0	4.68	1.6	-	-	-	1.0	3.03	2.8	2.0	1.0	0.8
0.5	0.2	9.13	45.69	0.6	3.45	3.2	0	1.22	0.2	0.2	4.05	0.2	-	-	-	2.0	1.62	0.8
0.7	2.0	8.75	44.8	0.2	1.875	0.4	1.0	4.375	4.0	2.0	2.709	3.2	22.0	7.292	3.6	-	-	-

Table 9: % Release from the precipitates having different Cu concentrations and formed from same ionic strength media (0.01).

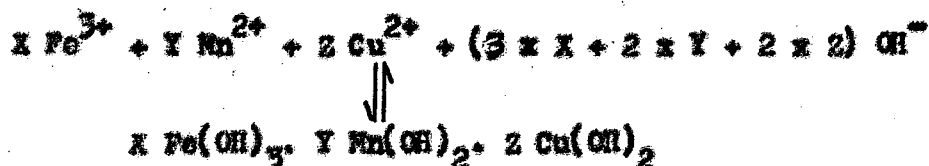| Initial Cu concentration (ppm) of the precipitate	% Release in NH_4Cl			% Release in different ionic strength											
				0.1			0.3			0.5			0.7		
	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu	Fe	Mn	Cu
1	5	5.71	10	1.0	2.24	5	17.8	5.71	5	6.4	2.04	25	-	-	-
5	2	10.0	34	5.0	1.22	1	1.0	1.22	2	3.2	5.92	5	-	2.45	1.0
10	0.2	1.8	34	1.0	4.0	1	3.2	3.0	1	1.0	1.6	-	6.2	3.4	7.0
15	0.2	5.98	40.7	2.6	9.82	2.89	3.2	6.41	2	2.0	6.41	1.7	1.0	4.1	3.3
20	5.8	1.1	41	0.2	6.06	6.5	4.0	7.475	4.5	1.0	5.253	1.5	2.0	4.24	2.5
30	2.0	8.125	35.7	2.0	5.416	4.7	8.2	3.95	3.0	6.0	2.3	1.0	8.2	3.54	2.3

Thus the exchangeable fraction of the copper in the precipitate varies with the ionic strength of the media and the initial copper concentration in the solution.
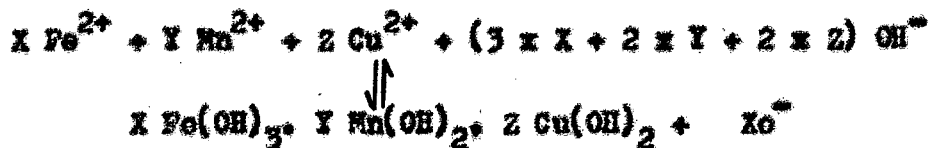
Nature of the Precipitate

The nature of the precipitate formed by the coprecipitation of Fe-Mn-Cu-hydroxide can be viewed upon the basis of experimental results. Comparison of Figs. 7, 10 and 11 shows that the precipitation might be taking place in three phases when the concentration of Cu in the system is higher (25 ppm), i.e., approaching towards the concentration of major component Fe and Mn. First phase is below pH 3, where the hydrous Fe-Mn-Cu-oxide might be precipitating. The second phase is between pH 3 and 6.5, where the precipitate might be dominating in hydrous Fe-Cu-oxide. The third phase is above pH 6.5, where Mn might be precipitating above as manganese oxide, because firstly, sufficient quantity of Mn (about 25 ppm) is still present there which is enough for manganese oxide precipitation and secondly Fe and Cu are completely precipitated below pH 6.5. It is already seen in this work that copper cannot precipitate as separate copper phase. So it suggests that Cu and Mn are in competition for $Fe(OH)_3$ and Cu is preferred over Mn by $Fe(OH)_3$. The ionic radii of Fe^{3+} is 0.64 Å, of Fe^{2+} is 0.74 Å, of Mn^{2+} is 0.80 Å and that of Cu^{2+} is 0.70 Å. The ionic radii value supports the fact that Fe prefers Cu than Mn.

On analysing the plot of % Cu sorbed vs. pH for 1 ppm Cu, it can be speculated that in addition to the above probable precipitates, hydrous Mn-Cu-oxide precipitate is also possible.
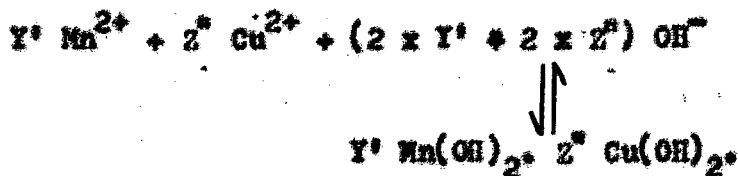
The probable reactions of the precipitate formation can be:

$$X \ Fe^{3+} + Y \ Mn^{2+} + Z \ Cu^{2+} + (3 \times X + 2 \times Y + 2 \times Z) \ OH^-$$

$$\Updownarrow$$

$$X \ Fe(OH)_3 \cdot Y \ Mn(OH)_2 \cdot Z \ Cu(OH)_2$$

If the iron be in the ferrous state, then the above reaction can be written as

$$X \ Fe^{2+} + Y \ Mn^{2+} + Z \ Cu^{2+} + (3 \times X + 2 \times Y + 2 \times Z) \ OH^-$$

$$\Updownarrow$$

$$X \ Fe(OH)_3 \cdot Y \ Mn(OH)_2 \cdot Z \ Cu(OH)_2 + \ Xe^-$$

Reactions between Fe-Cu and Mn-Cu can be as follows:

$$X' \ Fe^{3+} + Z' \ Cu^{2+} + (3 \times X' + 2 \times Z') \ OH^-$$

$$\Updownarrow$$

$$X' \ Fe(OH)_3 \cdot Z' \ Cu(OH)_2$$

$$Y' \ Mn^{2+} + Z'' \ Cu^{2+} + (2 \times Y' + 2 \times Z'') \ OH^-$$

$$\Updownarrow$$

$$Y' \ Mn(OH)_2 \cdot Z'' \ Cu(OH)_2.$$
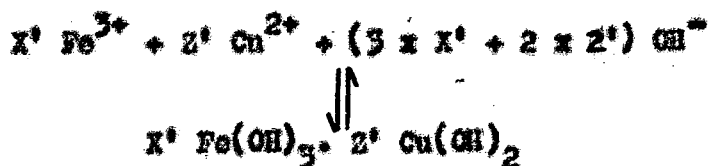
So the precipitate obtained may not be homogeneous. In sea water, Fe equilibrium is governed by systems such as $FeOOH - Fe(OH)_2^+$ rather than $Fe^{+++} - Fe(OH)_3$ (Kester & Byrne, Jr., 1972).

Similarly for Mn and Cu, the equilibria may be $MnOOH - Mn^{++}$
and $CuOOH - Cu^{++}$. Hence the coprecipitated hydroxides may
represent,particularly in high ionic strength,composition such
as (Fe, Mn, Cu)OOH.

Desorption experiments show that these mixed hydroxides
have certain exchange capacity. Fig. 15 shows that Fe and Mn
desorption is poor and Cu desorption is higher upto 47.4% at
0.3 ionic strength. This shows that copper is present both
in "exchangeable" and the "fixed" fraction of the precipitate.
If the desorption of Fe and Mn is compared, Mn is found to
desorb much more than Fe in different ionic strength media. It
again supports the fact that Mn might be precipitating in a
separate phase as manganese oxide at pH above 6.5. Since mixed
hydroxides have certain exchange capacity, cations such as Co,
Cr etc. from the water can be adsorbed on to these sites, thus
making the precipitate a chemically complex substance. Most
ferro-manganese nodule and metallic hydroxide coatings represent
such a complex system.

So the present results suggest that the coprecipitate
might have different phases like hydrous Fe-Mn-Cu oxide,
hydrous Fe-Cu-oxide and hydrous Mn-Cu-oxide. Any one or all of
the phases might be dominating in the precipitate. Except some
amounts of desorption observed, it may be said that each phase
might be occlusion or solid solution. Whether it is occlusion
or solid solution, it is iso-structural or non-isostructural, can
be made known by IR and Mossbauer Spectra, which are yet to get.

Applications to Natural Systems

Both Fe and Mn are present in abundance in the
natural system and their chemistry is closely related to each
other (Krauskopf, 1957), so their hydrous oxides must be acting
in combination in deciding the fate of trace metals in natural
waters. Cronan (1972) found a positive relationship between
(Fe + Mn) and the trace element content of hydroxide coatings
and concretions which stresses the importance of combined role
of Fe and Mn in the trace element fixation phenomenon. The
present work studies the importance of hydrous Fe-Mn-oxide in
the uptake and release of copper, hence it is more closer to the
natural system than the study done by others (Guy et. al., 1975;
Davies & Leckie, 1978), because they have either used manganese
oxide or ferric hydroxide as adsorbant. Though the concentra-
tions of copper in this study is higher which may represent a
polluted system.

In natural suspended sediments, coatings are common
because of electrostatic attraction between the negatively charged
clay surface and the positively charged hydroxide solids. 10-20%
by weight of the sediment could be the hydroxides. Although
Fe and Mn can be coprecipitated as Fe-Mn hydroxides, they develop
surface charges because of their finely divided nature. Generally,
40% of the particle surfaces are covered with coatings and the

excess negative charges in the particles would be satisfied only by successive layers of coatings. If the available positively charged hydroxide sols exceed that needed for coating formation, the excess sols may remain in colloidal suspension or attract anions such as HCO_3^-, Cl^- and SO_4^{-2} from the aqueous phase and form soluble or insoluble complexes. Thus, the coating process does not have to be a single-stage process. There could be successive homogeneous distribution of Fe, Mn and Cu in each layer but the overall coating process may be heterogeneous.

Though there are other sinks for Fe, Mn and Cu, such as oxide minerals and clay minerals, coating is the largest sink in natural aqueous system for these elements. Since they are transported along with the suspended sediments from rivers to oceans, the coatings can be considered as carriers of several elements from fresh water to saline water.

Coprecipitated Fe, Mn and Cu hydroxide can be considered as a natural hydroxide coatings, because Subramanian (1975) has pointed out that the experimental results in which the hydroxides were coprecipitated as coatings on suspended sediments does not differ with the results in which suspension was not used.

In aquatic systems where oxidizing occurs, hydrous iron and manganese oxides constitute a highly effective sink for heavy metals (Lee, 1975). Experiments by Groth (1971) show that the

metals Co, Zn and Cu coprecipitated from natural inland
lake water with Fe/Mn hydroxides at a rate of 67%, 86% and
98% respectively. These findings are very much in conformity
with the present finding for Cu.

Since the pH of river water does not vary appreciably
in nature, coatings formed would be chemically stable as long
as they remain suspended. Upon accumulation of suspension as
bottom sediments, the pH and E_h of the environment changes
from an oxidizing environment to a reducing environment. Such
a change may dissociate the coatings and release the elements,
such as Fe, Mn and Cu, to the surrounding waters. Bonatti (1971),
Cronan (1972) and Subramanian & d'Anglejan (1975) have shown
that interstitial waters of bottom sediments are enriched in
these elements. Of course, there are other sources, such as
pyrite, for Fe in the reducing environment, but the coating can
be a single source for several elements and only such an assumption
can explain the generally high concentration of transition elements
in interstitial waters of bottom sediments everywhere.

Experiments by Subramanian and Gibbs (1972) show that
coatings act as inert but permeable membrane during exchange
reactions. This is possible only if the hydroxide coating is
structurally stable; the impurities (Mn and Cu) probably stabilize
the hydroxides. The inert behaviour of coatings can then be
thought of as suggesting that coatings are homogeneous multi-
component phases, rather than simply Fe-hydroxide.

A remobilisation of heavy metals from suspended
material and sediments is potentially hazardous not only for
the aquatic ecosystem, but also for the drinking water supply.
Remobilisation is mainly caused by four types of chemical
changes in waters:

1. Elevated salt concentrations, whereby the alkali and
   alkaline earth cations can compete with the metal ions
   sorbed on to solid particles.

2. Lowering of pH which leads to dissolution of hydroxides,
   as well as to increased desorption of metal cations due
   to competition with H^+ ions.

3. Changes in the redox conditions, usually in conjunction
   with a decrease in the oxygen potential due to advanced
   eutrophication. Iron and manganese hydroxides are partly
   or completely dissolved, part of the incorporated or
   sorbed heavy metal load being released.

4. Increased use of natural and synthetic complexing agents,
   which can form soluble metal complexes sometimes of high
   stability with heavy metals that are otherwise adsorbed
   to solid particles.

In addition to these four processes, there are other bio-
chemical transformation processes, by means of which heavy metals
are either transferred from the sediment to animal or plant

organisms - possibly to be further enriched along the food chain - or are discharged directly or via decomposition products into water.

The present work studies the effect of elevated salt concentrations, increasing trace metal (Cu) concentration and pH on the remobilisation of heavy metals. Some amounts of desorption from the hydroxide take place in different ionic strength media, though some irregular pattern is there which may reflect the problem estuarine zone. At lower pH, Cu is desorbed completely when the copper concentration is lower. Since some amount of desorption from the hydroxides takes place, the exchange reaction can introduce Na, Mg and other cations into the coatings upon contact with a saline aqueous medium, such as sea water. The presence of cations other than Fe, Mn and Cu in the coatings and other ferromanganese materials can be explained as follows: coprecipitated hydroxides contain some percentage of exchangeable fraction; the amount of this fraction varies depending on the ionic strength of the aqueous media. Cations such as CO^{2+}, Zn^{2+}, Mg^{2+}, Na^+ ions etc. can replace the exchangeable Fe^{2+}, Mn^{2+} and Ni^{2+} from the adsorption sites and thereby become part of the mass of the ferromanganese materials.

Application to Pollution Studies

In addition to the natural inputs, anthropogenic inputs (like, industrial effluents, sewage disposal, agricultural runoff, mining activities etc.) are the major source of pollution of the aquatic environment. Among the pollutants, heavy metals is of grave concern. Sometimes, the establishment of metal levels in sediments can play a key role in detecting sources of pollution in aquatic systems. Metals such as Cr, Co, Ni, Cu, Zn, Cd, Hg and Pb have become enriched in sediments chiefly as a result of man's activities. Turekian and Scott (1967) were able to determine a distinct accumulation of Ag, Ni and Co in suspended material from eighteen rivers, particularly in the case of Susquehana River, which they ascribed to industrial contamination. He concluded that "the annual transport of trace elements by the Susquehana River as suspended material is sufficiently large to be of possible economic interest if the demand for some of the metals increases and the metals are present in an easily reversible form." De Groot and Allersma (1973) calculated the discharge of heavy metals by the water and by the suspended matter of Rhine. They found that 765 tons/year of Cu is discharged in water and 1355 tons/year fixed to sediments. So the metal in water to metal in sediments ratio come to 1:1.8. Hence the transport of Cu and any other

metal mainly takes place in solid form. Among other
substances, sediment contains hydrous Fe and Mn oxides.
So hydrous Fe and Mn oxide carries heavy metal with them in
the solid form. Saures, D.L. and Langmuir, D. (1976) studied
the soil samples from 70 ft. beneath a municipal waste land-
fill in Central Pennsylvania and determined Mn, Fe, Ni, Co,
Cu, Zn, Cd, Pb, and Ag in exchangeable and nonexchangeable
forms. They found that heavy metals, Co, Ni, Pb, Zn, Cu, Cd,
and Ag were associated with Fe and Mn oxides. It is in
agreement with the present work that Cu uptake is very significant
by hydrous Fe-Mn-oxide. The sorbed copper is desorbed depending
upon the ionic strength of the media. The desorption increases
with the increasing initial copper concentration.

Sitasawad, R.L. (1980) reported the metal content of
Jamuna river water around Delhi (Table 10). Mn content of the
river is almost zero. The Fe content of the river remains the
same (0.36 ppm) both when Jamuna enters Delhi at Wazirabad and
leaves at Okhala, irrespective of the fact that drains are
contributing the metals to the river in between. This excess
Fe then must have gone to the sediments, may be in the form of
hydrous Fe-oxide. Cu concentration in the river has increased
slightly at Okhala, obviously due to the contribution by drains.
This does not agree with the proposed mechanism for the Cu uptake

Table 10: Average Metal Concentration in River Jamuna (in ppm)

S.No.		Cr^{+6}	Mn^{++}	Fe^{++}	Ni^{++}	Cu^{++}	Zn^{++}	Pb^{++}
1.	Upstream of Najafgarh drain mixing at Wazirabad	0.40	0	0.36	1.05	0.038	0.16	0.25
2.	Average concentration of metals in drains	0.39	0.028	0.37	0.59	0.064	0.22	0.35
3.	Weighted discharge of average drains	0.0028	0.0002	0.0026	0.0042	0.0005	0.0016	0.0025
4.	Expected concentration of metals if drains are polluting at Okhla	0.4028	0.0002	0.3626	1.0542	0.0385	0.1616	0.2525
5.	Observed concentration of metals at Okhla	0.40	0.017	0.36	0.86	0.056	0.17	0.33

by Fe-Mn-precipitates in the present study. It may be due
to the fact that Cu concentration even at Okhala is very small
(0.056 ppm) which may be lower than the solubility product of
any probable Cu compound in the system whereas the minimum Cu
concentration used in the present study is 1 ppm. The proposed
mechanism can be used to explain the decrease in Ni content
of the river from 1.05 ppm at Wasirabad to 0.86 ppm at Okhala.
So one possibility is that Ni might have gone to sediment in
association with hydrous Fe-oxide. Ni uptake by hydrous Fe-Mn-
oxide precipitate has been proposed by Subramnian (1973).
Similarly the same concentration of Cr (0.40 ppm) at Wasirabad
and Okhala inspite of the contribution by drains in between
the two points can be explained on the basis of present study.

The present work represents the polluted environment
more closely as the Cu concentration in the experiment is higher.

Limitations of the Experiment

Hydrous Fe-Mn-oxide is used in the present work to study
the uptake and release of copper. Organics, clay minerals etc.
are present in the natural system along with Fe/Mn hydroxide
which can affect the sorption and desorption of heavy metals by
Fe/Mn hydroxide. Moreover, inorganic and organic complexing
ligands can increase or decrease the uptake of heavy metal by
by Fe-Mn hydroxides which are not considered here. The

artificial river, estuarine or sea water used in the present work approximates a world average composition, extension of the results to any specific sites should take into consideration local conditions.

Analyses of natural nodules and hydroxide coatings by various workers have shown the presence of several elements correlated to either Fe or Mn. It was shown earlier that Fe and Mn together can be correlated to all other elements taken together. This is possible because Fe-Mn together form a stable double hydroxide and this hydroxide adsorbs other elements or exchanges with aqueous medium.

Now it is evident that while there is no doubt that hydrous metal oxides are important sinks and modes of transport for heavy metals in the environment, the quantitative magnitude of this role cannot be estimated at the present stage for a variety of natural water conditions.

Thus, it can be stated here that within the limitations of experimental conditions, the observations made can be used to explain the nature of hydroxide coatings and their ability to fix trace metals.

Conclusions

The hydrous Fe-Mn-oxide can be an effective sink for copper in the aquatic environment. The results of uptake and release of copper can be concluded as follows:

1) pH and copper concentration are two important factors in controlling the Cu-uptake by the hydrous Fe-Mn-oxide precipitate. The Cu-uptake takes place within a narrow pH-range depending upon the concentration of Cu(II) in solution. The ionic strength of the media does not matter appreciably in the uptake.

2) Copper is not precipitated as a seperate copper phase, rather it is associated with the hydrous Fe-Mn-oxide. The precipitate formed may be hydrous Fe-Mn-Cu-oxide, hydrous Fe-Cu-oxide and/or hydrous Mn-Cu-oxide.

3) Copper is present both in exchangeable and fixed fraction of the precipitate. Almost 50% of copper is fixed in the structure of the host. Whether this fixed fraction is uniformly distributed in the host or not, is not established in this work.

4) Release of copper from the host is not affected by simply changing the media of the precipitate, but it is the presence of exchangeable cation in the media which cause the release of copper from the precipitate.

5)   The results can be used to explain the presence of heavy metals in natural ferromanganese materials. It can also be used for studies of pollution of the aquatic environment by trace metals.

References

Allen, H.E., Matson, W.R. & Mancy, K.H. (1970): J. Water Pollution Control Federation, 42, 573.

Anderson, B.J., Jenne, E.A. & Chao, T.T. (1973): The sorption of Ag by poorly crystallized manganese oxides. Geochim. Cosmochim. Acta. 37, 611-622.

Andrew Eaton (1978/79): Leachable trace elements in San Francisco Bay Sediments: Indicators of sources and estuarine processes. Environmental Geology 2, 6, 333-339.

Andrew Eaton (1979): Observations on the geochemistry of soluble Cu, Fe, Ni and Zn in the San Francisco Bay Estuary. Environ. Sci. Technol. 13, 4, 425.

Barnes, S.S. (1967): Minor element composition of ferromanganese nodules. Science 158, 63-65.

Bonnatti, E. (1971): Post depositional mobility of some transitional elements, P, U, and Th in deep-sea sediments: Geochim. Cosmochim. Acta. V. 35, P.3-24.

Bothner, M.H. & Carpenter, R. (1973): Sorption-desorption reactions of Hg with suspended matter in Columbia river; Vienna, Austria. Radioactive Contamin. Mar. Environ. Proc. Symp., I.A.E.A., P.73-87.

Bower, P.M., Simpson, H.J., Williams, S.C. & Li, Y.H. (1978): Heavy metals in the sediments of Foundry Cove, Cold Spring, New York. Environ. Sci. Technol. 12, 6, 683.

Burns, R.G. (1976): The uptake of Co into ferromanganese nodules, soils and synthetic Mn (IV) oxides. Geochim. Cosmochim. Acta. 40, 95-102.

Burns, R.G. & Fuerstenau, D.W. (1966): Electron-probe deter-
mination of inter-element relationships in manganese
nodules. Amer. Mineral. 51, 895-902.

Cameron, E.M. (1974): Geochemical methods of exploration for
massive sulphide mineralisation in the Canadian shield.
In: Geochemical Exploration - Proc. 5th Int. Geoch.
Expl. Symp. Vancouver. Elliott, I.L.,Fletcher, W.K. (eds).
PP 21-49.

Cameron, E.M. & Ballantyne, S.B. (1975): Experimental hydrogeo-
chemical surveys of the High Lake and Hackett River areas,
Northwest territories. Geol. Surv. Can. Pap. 75/29, 19P.

Collin, N., Elderfield, H. & Cheater, R. (1979): Arsenic in sedi-
ments of the North Atlantic Ocean and the Eastern Medi-
terranean Sea. Marine Chemistry 7, 207-219.

Crerar, D.A. & Barnes, H.L. (1974): Deposition of deep sea Mn-
nodules. Geochim. Cosmochim. Acta. 38, 279-300.

Cronan, D.S. (1969): Inter-element association in some pelagic
deposits. Chemical Geology 5, 93-106.

Cronan, D.S. & Thomas, R.L. (1972): Geochemistry of Ferromanganese
oxide concretions and associated deposits in Lake Ontario.
Geol. Soc. America Bull. 83, 1493-1502.

Davis, J.A. & Leckie, J.O. (1978): Effect of adsorbed complexing
ligands on trace metal uptake by hydrous oxides. Environ.
Sci. Technol. 12, 12, 1309.

Dean, H.W. (1970): Fe-Mn oxydate crusts in Lake Oneida. Proc. 13th
Conf. Great Lakes, 217-226.

DeGroot, A.J. & Allersma, E. (1973): Field observations on the
transport of heavy metals in sediments: in Heavy metals
in the Aquatic Environment, edited by P.A. Krenkel, Proc.
of the International Conf. held in Nashville, Tennessee.

Dyck, W. (1971): Adsorption and Coprecipitation of Ag on hydrous Fe and Mn oxides. Geol. Surv. Canada Paper 70-64, P. 1-23.

Garrels, R.M. & Christ, C.L. (1965): Solutions, Minerals and Equilibria. Harper & Row, New York, 450 P.

Gibbs, R.J. (1972): Water Chemistry of Amazon River. Geochim. Cosmochim. Acta. V. 36, P.785.

Gibbs, R.J. (1973): Mechanisms of trace metals transport in rivers. Science V. 180, P. 73.

Glasby, G.P. (1971): Distribution of organic pigments in marine manganese nodules from Northwest Indian Ocean. Geochim. Cosmochim. Acta. V. 35, P.845-861.

Goldberg, E.D. (1954): Marine Geochemistry. Jour. Geology. V. 62, P.249-265.

Grieve, D. & Fletcher, K. (1977): Interactions between Zn and suspended sediments in the Fraser River Estuary, British Columbia. Estuarine and Coastal Marine Science, V. 5, P.415-419.

Griggs, G.B., Grimanis, A.P. & Grimani, M.V. (1978): Bottom sediments in a polluted marine environment, Upper Saronikos Gulf, Greece. Environmental Geology. V. 2, No.2, P.97-106.

Groth, P. (1971): Untersuchungen über einige Spurenelemente in Seen. Arch. Hydrobiol. 68, 305-375.

Guy, D.R., Chakrabarti, C.L. & Schramm,B.L. (1975): The application of a simple chemical model of natural waters to metal fixation in particulate matter. Can. J. Chem. V.53,P.661-669.

Hawkes, A.E. (1965): Exploration Geochemistry. Harper and Row Pub., N.Y.

Hem, J.D. (1963): Coprecipitation of Fe and Mn oxides. Amer. Chem. Soc. Div. Water Waste Chem., Preprint 7-10.

Hem, J.D. (1972): Chemical factors that influence the availability of Fe and Mn in natural aqueous systems. Bull. Geol. Soc. Am. V. 83, P.443-450.

Hem, J.D. & Crooper, W.H. (1959): Survey of ferrous-ferric equilibria. U.S.G.S.W.S.P. 1459A, 31 Pages.

Hutchinson, G.E. (1957): A Treatise of Limnology. V.1, Wiley, New York.

Inoue, Y. & Munemori, M. (1979): Coprecipitation of Hg(11) with Fe(111) hydroxide. Environ. Sci. Technol. V.13, No.4, P.443.

Jenne, E.A. (1968): Controls on Mn, Fe, Co, Mi, Cu and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. In Trace Inorganics in Water (editor, R.F. Gould), Adv. Chem. Ser. 73, 337-387.

Jenne, Skei & Por, E. Pana (1979): Surface metal enrichment and partitioning of metals in a dated sediment core from a Norwegian Fjord. Geochim. Cosmochim. Acta. V.43, No. 2, P.233-246.

John Hamilton-Taylor (1979): Enrichments of Zn, Pb and Cu in recent sediments of Windermere, England, Environ. Sci. Technol. V. 13, No. 6, P.693.

Jonasson, I.R. (1977): Geochemistry of sediment/water interactions of metals, including observations on availability. In: The Fluvial Transport of Sediment-Associated Nutrients and Contaminants, IJC/PLUARG. Shear, H., Watson, A.E.P. (eds.), Windsor/Ont.: 1977, PP.255-271.

Kester, D.A. & Byrne, Jr., R.H. (1972): Chemical forms of Fe in sea-water. In: Ferromanganese Deposits on the Ocean Floor. ed: D.R. Horn, P.107-113.

Kharkar, K., Turekian, K.K. & Bertin, K. (1968): Stream
        supply of dissolved Ag, Mo, Sb, Se, Cr, Co, Rb and Cs
        to the oceans. Geochim. Cosmochim. Acta. V. 32, P.285-298.

Krauskopf, K.B. (1956): Factors controlling the concentrations
        of thirteen rare metals in sea water. Geochim. Cosmochim.
        Acta. V. 9, P.1-32 B.

Krauskopf, K. (1957): Factors affecting the concentrations of
        13 rare elements. Geochim. Cosmochim. Acta. V.12, P. 61.

Krauskopf, K. (1967): Introduction to geochemistry: New York,
        McGraw Hill, 721 P.

Krumbein, W.C. & Garrels, R.M. (1952): Importance of Eh and pH
        in sedimentary processes. Jour. Geology, V. 60, P.1-32.

Langmuir, B. & Whitmore, D. (1971): Precipitation of Fe oxy-
        hydroxides. Amer. Chem. Soc. Spec. Paper 106, 207-223.

Leckie, J.O. & James, R.O. (1975): In "Aqueous Environmental
        Chemistry of Metals". A.J. Rubin, Ed., Chap. 1, Ann. Arbor.
        Science, Ann Arbor, Mich.

Lee, G.F. (1975): Role of hydrous metal oxides in the transport
        of heavy metals in the environment. In: Heavy Metals in
        the Aquatic Environment. Krenkel, P.A. (ed.). Oxford:
        Pergamon Press, PP.137-147.

Lockwood, R.A. & Chen, K.Y. (1973): Adsorption of Hg(11) by hydrous
        manganese oxides. Environ. Sci. Technol. V.11, P.1028-1034.

Loganathan, P. & Burau, R.D. (1973): Sorption of heavy metal
        ions by a hydrous manganese oxide. Geochim. Cosmochim. Acta.
        Vol. 37, P.1277-1293.

Loganathan, P., Burau, R.G. & Fuerstenau, D.W. (1977): Influence
        of pH on the sorption of Co^{2+}, Zn^{2+} and Ca^{2+} by a hydrous
        manganese oxide. Soil. Sci. Soc. Am. Journal. V. 41,
        No. 1, P.57-62.

Lu, J.C.S. & Chen, K.Y. (1977): Migration of trace metals in interfaces of sea-water and polluted surficial sediments. Environ. Sci. Technol. V. 11, 174-182.

Manheim, F.T. (1965): Mn-Fe accumulation in the shallow marine environments. In: Geol. Publ. No. 3, University Rhode Island. P. 217-226.

Martin, J.M., Kulbicki, G. & De Groot, A.J. (1973): Terrigenous supply of radioactive and stable elements to the oceans. Hydrogeochemistry. V.1, P.443-463.

Matijovic , E. et.al. (1961): J. Phys. Chem. 65, 826.

McKenzie, R.M. (1970): The reaction of Co with manganese dioxide minerals. Aust. J. Soil Res. V.8, P.97-106.

Mero, J.L. (1965): The mineral resources of the sea. 312 PP. Elsevier.

Monaco, A. (1977): Geochemistry of the estuarine environment: Comparison between Fluviatile suspensions and prodelta deposits of the Ande (Langedoc). Chem. Geol. V.20, P.45.

Morgan, J. & Stumm, W. (1964): Colloid chemical properties of manganese dioxide. J. Colloid Interface. Sci. V.19, P.347-359.

Morgan, J. & Stumm, W. (1965): Role of multivalent metal oxides in limnological transformations as exemplified by Fe & Mn: Adv. in Water Poll. Res. V.1, P.195.

Mortimer, C.H. (1941): J. Ecol. V. 29, P. 280.

Mortimer, C.H. (1942): J. Ecol. V. 30, P. 147.

Murray, D.J., Healy, T.W. & Fuerstenau, D.W. (1968): The adsorption of aqueous metal ion on colloidal hydrous manganese oxide. In: Adsorption from aqueous solution, Adv. in Chem. Ser. V.79, P.74-81, American Chemical Society, Washington, D.C.

O'Melia, C.R. & Stumm, W. (1967): J. Coll. Interface. Sci. V.23, P.457.

Posselt, H.S., Anderson, F.J. & Weber, W.J. (1968): Cation sorption on colloidal hydrous manganese dioxide. Environ. Sci. Technol. V. 2, No. 2, P. 1087-1093.

Ramamoorthy, S. & Kushner, D.J. (1975a): Binding of mercuric and other heavy metal ions by microbial growth media. Microb. Ecol. V. 2, P. 162-176.

Ramamoorthy, S. & Rust, B.R. (1978): Heavy metal exchange processes in sediment-water systems. Environmental Geology, V. 2, No. 3, P. 165-172.

Rohatgi, N.K., Chen, K.Y. (1975): Transport of trace metals by suspended particulates on mixing with sea water. J.W.P.C.F. 47, 2298-2316.

Rossmann, R., Callender, C. & Bowser, C. (1972): Inter elemental geochemistry of trace metals in Ferromanganese nodules. Proc. 24th Inter. Geol. Cong. V. 10, P.336-341.

Sauron, L.D. & Langmuir, D. (1975): Heavy metal relationships in a Pennsylvania soil. Geochim. Cosmochim. Acta. V. 40, P.589-598.

Schindler, P.W., Furst, B. et. al. (1976): J. Colloid Inter. Sci. 55, 469.

Sitasawad, R.L. (1980): M.Phil. Dissertation. Jawaharlal Nehru University, New Delhi-110067.

Strakhov, N.M. (1965): Principles of lithogenesis, V. 1, Plenum Press, New York.

Stumm, W. & Morgan, J.J. (1962): J. Amer. Water Works Assoc. 54, 971.

Stumm, W. & Morgan, J.J. (1970): Aquatic Chemistry. Wiley
Interscience, N.Y. 583 pages.

Subramanian, V. (1973): Mechanisms of fixation of the trace
metals Mn and Ni by ferric hydroxide. 121 pages, Ph.D.
thesis, Northwestern University, N.Y.

Subramanian, V. (1975): Water Chemistry of the St. Lawrence River,
Maritime Sediments. V. 11, P.97-105.

Subramanian, V. (1976): Experimental modelling of interelemental
relationship in natural ferromanganese materials. Canadian
Mineralogists V. 14, P.32-39.

Subramanian, V. & d'Anglejan, B. (1976): Water Chemistry of the
St. Lawrence Estuary. Jour. Hydrology, 29: 341-354; 30:310.

Sumner, K.E. (1964): Effects of iron oxides on positive and
negative charges in clays and soils. Clay and Clay Minerals.
V.5, P.218-226.

Taylor, R.M. & Meckenzie, R.M. (1966): The association of trace
elements with Mn-minerals in Australian soils. Aust. J.
Soil Res. 4, 29-39.

Turekian, K. & Scott, M. (1967): Suspended matter in various
rivers. Environ. Sci. Technol. V.1, P.915-317.

Wagemann, R. (1978): Some theoretical aspects of stability and
solubility of inorganic As in the Fresh water environment.
Water Research. V. 12, P.139-145.

Willis, J.P. & Ahrens, L.H. (1962): Some investigations on the
composition of Mn-nodules, with particular reference to certain
trace elements. Geochim. Cosmochim. Acta. 26, 751-764.

Zirino, A., Libermann, S.H. & Clavill, C. (1978): Measurement
of Cu and Zn in San Diego by Automated Anodic Stripping
Voltammetry. Environ. Sci. Technol. V.12, No.1, P.73.