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Forms of Iron in River Waters

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Abstract

Iron complexes with humic substances isolated from river sediments and decomposition products of phytoplankton were investigated with an anion exchange column. It was found that iron complexed only with humic substances and the complexes had negative charges. Dissolved, particulate (0.45-0.025 μ) and particulate ($\geq 0.45 \mu$) iron in river waters were 25, 35 and 41% in total iron, respectively. Dissolved iron existed in river waters as complexes with humic substances and the residues were particulates of iron hydroxide or colloidal humic substances.

Introduction

The forms of trace metals in the aquatic ecosystem are crucially important in studies of metal toxicity, biogeochemical pathways and the growth of aquatic organisms. Iron and manganese are considered to be very important elements for the growth of phytoplankton. In aqueous system, dissolved trace metals are present in the form of cations or as complexed compounds with miscellaneous organic and inorganic ligands. Undissolved trace metals are present in the form of particulates, that is, particulate metal hydroxide or metals adsorbed on organic or inorganic particulate materials. In river water it is assumed that most heavy metals exist in complexed forms with various ligands, mainly humic substances.

The chemical or biochemical nature of humic substances has been studied from the nineteenth century. Humic substances make up the bulk of organic matter in soils and river waters, and play a major role in leaching cations from rocks and soil.

Sharpiro¹⁾ assumed that metals are transported by humic substances as peptized colloids. Drozdova²⁾, Khan³⁾ and Rashid⁴⁾ point out the presence of strongly chelating groups in the structure of humic acids. They assumed that metal forms complex compounds with substances of this type. Binding capacity of heavy metal in river water was measured by using ion specific electrode^{5,6)}. The molecular weight distribution of humic substances of the peat type and their complexes with bivalent and trivalent metals was investigated with gel filtration⁷⁾.

Iron concentrations are commonly several orders of magnitude higher than the equilibrium solubility of iron hydroxide. Two of the chemical species postulated to account for this phenomenon are fine colloidal organic matter

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(possibly associated with colloidal organic matter) and dissolved complexes of iron with naturally occurring substances. Perdue et al.⁸⁾ have found a fairly good correlation between dissolved organic matter and the sum of iron and aluminium concentrations in the Satilla River.

In this paper, the forms and the charges of iron in natural rivers are investigated with an anion or cation exchange column.

Experiment

Laboratory experiment: Humic substance was isolated from river sediment by extraction with 0.5 M sodium hydroxide solution by usual method. Humic and fulvic acids were separated by adjusting pH of the solution to 3 with a sodium hydroxide solution. The precipitated humic acid was then resolved with a sodium hydroxide solution. These separated solutions were used for the chelation of iron.

To the humic or fulvic acid solutions including three different carbon contents (50–250 mg/l) was added a ferrous or ferric chloride solution and the solutions are adjusted to pH 6–7, and then filtered with HA type (0.45 μ) or VS type (0.025 μ) Millipore filters. The filtrates were passed through both chloride type anion exchange resin (Dowex 1 \times 8, 50–100 mesh) and sodium type cation exchange resin (Dowex 50 W \times 8, 50–100 mesh) columns at the flow rate of 2 ml/min. After washing the columns with distilled water, the iron organic complexes in the columns were eluted with 2 M nitric acid. Iron in the filtrates and the elutions was determined with an atomic absorption spectrophotometer. The analytical error was about 5% at 0.5 ppm of iron level.

Natural river sample: River water samples were collected in polyethylene bottles, which are pre-rinsed with hydrochloric acid, by hand dipping. The samples were filtered in a nitrogen atmosphere with both HA type and VS type Millipore filters. The filtrates that passed through the later filters were passed through the both columns and then eluted with 2 M nitric acid. Iron in river samples, filtrates and elutions was determined with the atomic absorption spectrophotometer.

Results and discussion

Laboratory experiment: The results of the iron (III) concentrations in the filtrates and the elutions are shown in Table 1. Iron particulates, with diameters between 0.45 and 0.025 μ , exist in both the humic and fulvic acid solutions. Iron concentrations in the filtrates passed through VS type filters are consistent with the elutions from the anion exchange resin columns. However, iron in the elutions from the cation exchange resin columns was not detected. Thus, it was found that iron chelates with humic or fulvic acids and produces iron humate complexes with negative charges. In Figs. 1 and 2, the relations between ferrous or ferric concentration and carbon content in humic substance are shown. It was assumed that the ferrous humate complex would have one order higher stability constant than the ferric humate complex.

Other metals are also presumed to chelate with humic substances, for example,

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Table 1. Iron in filtrates and in elutions (Fe: ppm).

	Filtrate (HA type)	Filtrate (VS type)	Elusion (Anion type)	Elusion (Cation type)
Fulvic acid	0.25	0.20	0.18	0
	0.05	0.05	0.04	0
	0.21	0.20	0.18	0
Humic acid	0.52	0.47	0.50	0
	0.08	0.06	0.06	0
	0.16	0.14	0.15	0

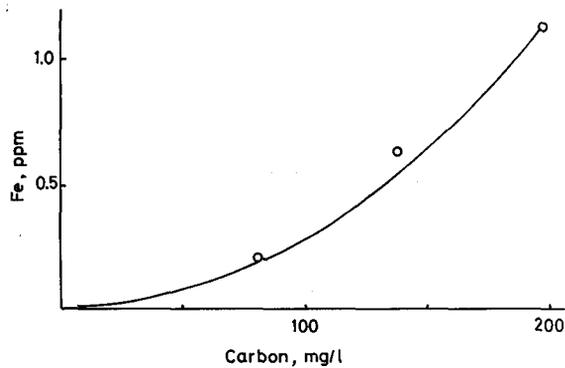


Fig. 1. Complex of ferric iron with humic substance.

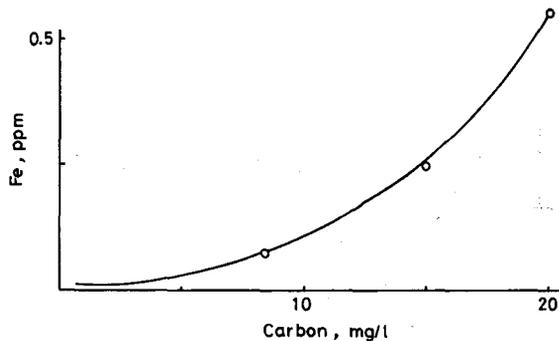


Fig. 2. Complex of ferrous iron with humic substance.

the relationship between manganese and carbon content is shown in Fig. 3. An iron inorganic complex with a negative charge was not detected using anion exchange resins. Iron does not chelate with the decomposition products of phytoplankton, which were produced under an aerobic condition by bacterial decomposition. Iron complexes only with humic substances.

Natural river samples: The results of the laboratory experiments and of river

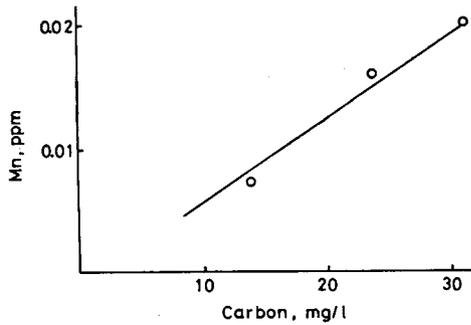


Fig. 3. Complex of manganese ion with humic substance.

samples (Table 2) show that dissolved iron made particulate complexes with negative charges with humic substances. Dissolved, particulate ($>0.45 \mu$) and particulate iron ($0.45-0.025 \mu$) are about 25, 41 and 35% of the total iron, respectively. Iron was not detected in the elutions from the cation columns. This fact is thermodynamically reasonable because the samples have high oxidation reduction (redox) potentials and the pH was a range from 6 to 7.

Iron hydroxide is included in the particles ($>0.45 \mu$) and the chemical forms of iron included in the particles

($0.45-0.025 \mu$) are not clearly known.

In conclusion, dissolved iron makes complexes with negative charges with humic substances naturally existing in river waters.

Table 2. Iron in river waters, filtrates and elutions (Fe: ppm).

River Date	Natural Sample	Filtrate (HA type)	Filtrate (VS type)	Elution (Anion type)
Samekawa				
Dec. 13, 1976	0.58	0.33	0.17	0.15
Dec. 16, 1976	0.53	0.32	0.12	0.10
Dec. 17, 1976	0.65	0.41	0.20	0.23
Dec. 20, 1976	0.55	0.34	0.17	0.16
Jan. 7, 1977	0.47	0.33	0.12	0.12
Jan. 8, 1977	0.52	0.38	0.15	0.17
Matsukura				
Dec. 13, 1976	0.08	0.04	0.01	0.01
Kunebetsu				
Jun. 3, 1977	0.91	0.51	0.11	0.12
Jun. 4, 1977	0.28	0.10	0.04	0.04
Jun. 6, 1977	0.47	0.28	0.15	0.13

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