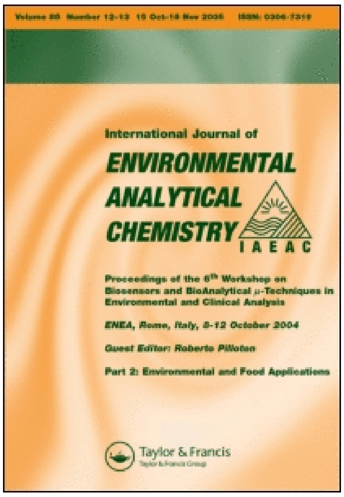

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Manganese in Natural Waters
I. Speciation of Manganese in Running Waters and Sediments

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Manganese speciation in natural waters and sediments has been investigated. Size distribution studies coupled with differential pulse polarography (DPP) showed that manganese in water is present either as Mn^{2+}_{aq} or as a labile Mn(II) complex. The speciation of manganese in the sediments were done by sequential extraction. The exchangeable fraction showed the same pattern at the cross section of the river as for dissolved manganese and total organic carbon (TOC) indicating that all these have a common origin, i.e. anthropogenic input.

KEY WORDS: Manganese speciation, natural waters, DPP, size fractionation, sediments.

INTRODUCTION

The distribution of manganese in marine and lacustrine waters have been extensively studied, however there are only a few reports on the speciation of this metal in running waters.[1−9]

In general, manganese enters natural waters from a variety of sources:[1]

1) The rocks directly exposed to carbonated waters are the chief natural source of Mn in geochemical cycle.

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2) Drainage of forest floors contribute small amounts of metals to adjacent waters, particularly the coniferous trees accumulate this metal and are rained out into the river.

3) Man's activities (e.g. industrial activities) can introduce significant quantities of manganese to natural waters.

Typical mean concentration of soluble form of manganese found in natural waters [2–5] is 5 $\mu g.l^{-1}$. It should be noted that this value must be used with caution as the concentration of manganese in waters strongly depends on the geochemical environment.

The manganese speciation studies in aquatic environments have shown that the metal is primarily found in the particulate form.[7–9] In contrast to other metals, a fairly large fraction of manganese ($>18\%$) is metal exchangeable.

In this paper, the speciation of manganese in a fluvial till of river Rhône in Geneva has been investigated because water quality determination in the downstream of Geneva city revealed high manganese content.

PRELIMINARY STUDIES: WATER QUALITY OF RHONE RIVER

Matarial and methods

Total metal concentrations were determined in water samples acidified with nitric or hydrochloric acid (reagent grade) to $pH=2$. The samples were filtered to remove suspended matters which might interfere in their determination. For this purpose, the samples were filtered successively through fibre glass filters ($\leq 40\,\mu m$ pore size), Schleicher and Schull filters of porosities: 8 μm and 0.45 μm.

The water samples were collected in polythene containers prewashed with 2 M HNO_3, rinsed with demineralised water and rinsed with sample before filling. The samples were stored at $7.0 \pm 0.5°C$ in case where they were not immediately analysed.

The major elements (Ca, Mg, Mn) and the alkali metals were determined by flame atomic absorption spectrometry (AAS) and emission spectrometry (ES) respectively using a Pye UNICAM SP 1900 atomic absorption spectrometer.

The total organic carbon (TOC) concentration was determined with a Beckman total organic carbon analyser (Model 915). The samples for this analysis were stored in glass bottles. The inorganic carbon was removed by treating the sample with HCl ($pH \leq 2$) and degassing it with nitrogen gas (99.999% purity) to remove CO_2.

The alkalinity of the sample which was solely due to the presence of bicarbonate ions under our conditions was determined by acid titration using potentiometric end point detection. NH_3, NO_2^- and PO_4^{3-}, were determined by Hach method using Hach Dr—EL/2 Kit.

The chloride, nitrate and sulphate concentrations were determined by anion chromatography as described previously.[10] The sampling location and dates of collection are indicated in Table I and Figure 1.

TABLE I

Water quality (μg/ml) of Rhône river water at Geneva compared with Lake Léman (station du Prieuré, GE). Sampling date: 24.11.81.

Constituents	Site 3R	Site 4R	Lake Léman
Na	4.2	3.9	3.9
K	1.6	1.6	1.3
Ca	50.0	52.5	45.6
Mg	7.0	7.0	6.4
Si	0.55	0.54	0.8
Fe	0.03	0.04	0.03
Mn	0.44	0.14	0.003
Cu	0.003	0.002	0.004
Cr	0.002	0.002	0.003
Ni	0.002	0.002	0.003
Cd	0.0004	0.0003	0.0004
Zn	0.005[a]	0.004[a]	0.012
Pb	0.002[a]	0.002[a]	0.001[b]
Ag	0.0001	—	0.0007
HCO_3^-	117	117	—
COT	1.6	1.3	1.5[b]
NH_3	0.23	0.24	0.008
NO_3^-	1.4	1.4	1.9
NO_2^-	0.02	0.01	0.02
F^-	0.19[a]	0.18[a]	0.24
SO_4^{2-}	48.0	46.0	48.2
Cl^-	4.6	4.4	4.6
PO_4^{3-}	0.38	0.36	0.20

[a] Sampling date: 8.12.81.

[b] Maximum value observed.

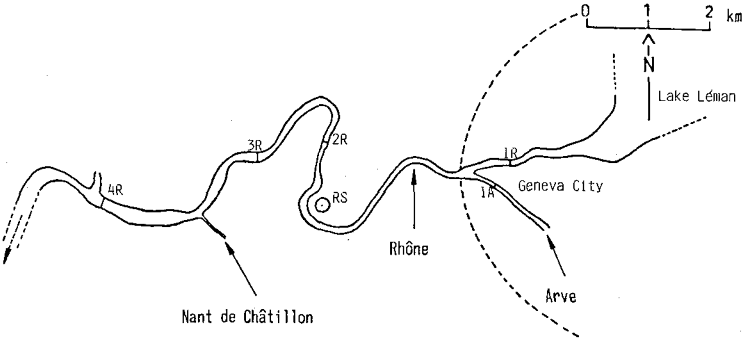

FIGURE 1 Location of sampling sites: 1R:Pont Sous-Terre; 1A:Passerelle du Bois de la Bâtie; 2R:Passerelle du Lignon; 3R:Passerelle de Chèvres; 4R:Pont de Peney; RS:Aire water treatment plant.

Results and discussions

The results of analyses of samples at various sites are summarized in Table I. The Rhône being an effluent of Lake Léman these results were compared with the water quality of the Lake provided by the Geneva city water authorities (Prieuré Domestic Water Supply Station).

The chemical composition of both river and lake waters are similar with the exception of NH_3 and manganese concentrations (Table I).

The endogenic influence of NH_3 is usually rather small whereas the discharge of waste water effluents into the river increases the concentration of NH_3 appreciably. Thus the increase in NH_3 concentrations from 0.008 to $0.24\,mg.l^{-1}$ (Table I) is consistent with results obtained by other investigators[11] suggesting the existence of exogenic source.

The variations in dissolved manganese concentrations observed with samples collected at sites 4R and 3R (Table I, Fig. 1) seem to indicate that there is a concentration gradient between the upstream and downstream samples. However, contrary to this assumption, the manganese concentration of 0.014, 0.13 and $0.004\,mg.l^{-1}$ were found in samples collected at sites 2R, 1A and 1R.

The decrease in the dissolved manganese concentrations between sites 1A and 2R may be due primarily to two factors:

a) The dilution of the metal due to high flow rate of Rhône River (average annual flow rate 293 $m^3.s^{-1}$ in 1980) compared to River Arve (97 $m^3.s^{-1}$).[11]

b) Transport of dissolved manganese by forming solid phase by the oxidation of Mn(II) to Mn(IV) and adsorption on suspended particulates. It must be noted that the total manganese concentration is not affected by the discharge of effluent from water treatment plant. The effluent of water treatment plant contained $<0.01\,\mu g.ml^{-1}$ of Mn. The relatively high proportion of manganese found at site 3R suggests that there is an influx of manganese into the water from the neighbouring area on site 3R. The abnormally high manganese concentration found in this water led us to investigate speciation of manganese in both surface water and sediments in more detail.

DISTRIBUTION OF MANGANESE AT SITE 3R

The water was sampled along the cross-section of site 3R from right bank (RB) to left (LB): 5, 35, 55, 75 and 175 m.

The samples were analysed for dissolved manganese concentration and TOC (Figure 2). The results show the following:

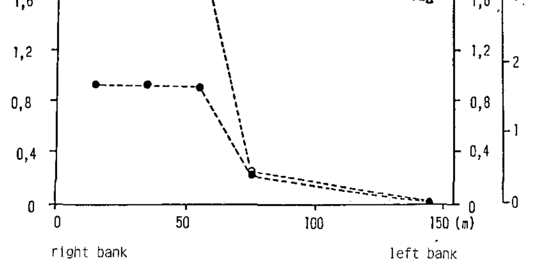

FIGURE 2 Variations of total organic carbon (TOC) and dissolved manganese(II) at site 3R from right bank (RB) to left bank (LB). Sampling date: 4.2.82. △ TOC(16h00–16h30). ⊙ : Mn^{2+}_{aq} (10h30–11h00). ● : Mn^{2+}_{aq} (16h00–16h30).

1) The dissolved manganese concentration is localised mainly in the first one thirds of the river.

2. The manganese concentrations in the samples left of site 3R and 2R which is located upstream are virtually the same.

3) The TOC follows the same pattern as the dissolved manganese. It should be noted that the values of TOC found in the second half of the river (Figure 2) are in good agreement with those found for lake waters.

These results tend to suggest that:

1) The temporal variations in Mn(II) results from anthropogenic influence.

2) The spatial and probably the temporal variations in TOC which show trends similar to manganese imply that both Mn and TOC have a common origin.

The spatial distribution of manganese in samples at site 4R is uniform. The Mn(II) concentrations in samples collected at distances of 45, 80 and 116 m from the right bank (RB) of site 4R were virtually the same ($0.05\,mg.l^{-1}$). This shows a better homogeneity of the samples between sites 3R and 4R.

SPECIATION OF MANGANESE IN WATER

The fraction passing through $0.45\,\mu m$ filters has been considered as dissolved manganese and that retained being particulate.

The speciation studies of manganese in Rhône River were carried out by means of ultrafiltration and differential pulse polarography.

Size fractionation

The water sample was acidified with HNO_3 to pH 2 and filtered successively through Schleicher and Schull filters of porosity: 8, 0.45 and $0.2\,\mu m$ and Amicon PM10 ($\simeq 2.10^{-3}\,\mu m$ pore size) and UM05 ($\simeq 10^{-3}\,\mu m$ pore size). The manganese concentration in the unfiltered sample and the UM05 filtrate were determined by AAS and were found to be 8.0×10^{-6} M and 8.2×10^{-6} M respectively. These results show that virtually all the manganese is present in the smallest size fraction ($\emptyset < 10^{-3}\,\mu$m) implying the presence of ionic form at site 3R.

Differential pulse polarography (DPP)

The DPP measurements were performed with untreated samples at $\mathrm{pH} = 7.34 \pm 0.03$. The pH of the sample was adjusted with CO_2/N_2 mixture. The measurements were made at the natural ionic strength of the sample ($I \simeq 5 \times 10^{-3}$ M). The results (Figure 3) show that the peak potential Ep (Ep = 1.446 vs Ag/AgCl/KCl 3 M) is unaffected by successive additions of metal standards.

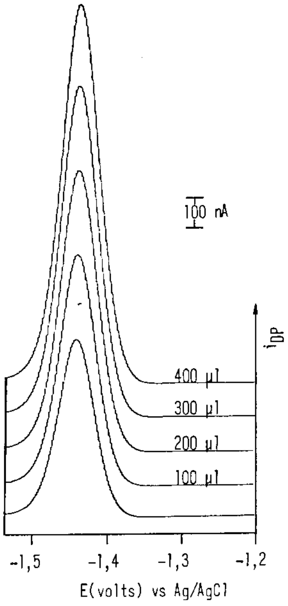

FIGURE 3 Speciation of manganese in Rhône River water by differential pulse polarography (DPP). $E_{\mathrm{pulse}} = 60$ mV; sample volume: 10 ml, concentration of Mn^{2+}_{aq} standard added: 9.1×10^{-4} M; $\mathrm{pH} = 7.34 \pm 0.03$; $T = 23.0 \pm 0.5$°C; $I = 5 \times 10^{-3}$ M.

Thus Mn at site 3R is present either as Mn^{2+}_{aq} or as labile Mn(II) complex which is in accordance with the findings of size fractionation.

It is not surprising that Mn(II) occurs as Mn^{2+}_{aq} since in general, Mn(II) forms weak complexes. This view is supported by the fact that inorganic ligands (Cl^-, SO_4^{2-}, NH_3, etc.) as well as organic ligands (TOC) are found at low concentration (Table I). In addition the presence of competing cations (e.g. Mg^{2+}, Ca^{2+}) at relatively high concentration (Table I) would favour the existence of Mn_{aq}^{2+}.

SPECIATION OF MANGANESE IN THE SEDIMENTS

Material and methods

Sediment samples were collected using a grab (Büchi). Sampling was done at 4 cm depth. The samples were homogenised and stored at 7.0 ± 0.5°C in polyethene bottle prewashed with 1 M HNO_3 and rinsed with demineralised water.

At site 3R, four samples were collected between the right bank and the centre of the river. One sample was collected at site 2R.

The speciation of manganese in the sediments was determined using a slightly modified Tessier *et al.*'s sequential extraction procedure.[8] The schematic representation of this method is summarized in Table II. The interstitial water was removed by centrifu-

TABLE II

Sequential extraction of manganese in the sediments.

Extracted fraction		Experimental conditions; quantity used; 1 g of wet sediment
I	Exchangeable	1 M NH_4OAc[a] (10 ml); pH 7.0; 20°C; continuous stirring; 1 h
II	Carbonate	1 M NaOAc (20 ml); pH 5.0; 20°C; continuous stirring; 5 h
III	Fe–Mn oxide	0.04 M $NH_2OH.HCl$ in CH_3COOH 25% (20 ml); 96°C; occasional stirring; 6 h
IV	Organic	0.02 M HNO_3 (5 ml) + H_2O_2 30% (5 ml); pH 2.0 85°C; occasional stirring; 2 h; + H_2O_2 30% (5 ml); pH 2.0; 85°C; periodical stirring; 3 h; + 3.2 M NH_4OAc in HNO_3 20% (10 ml); 20°C; continuous stirring; 30 min
V	Residual	HNO_3 65% (3 ml) + HCl 37% (2 ml); 95°C; periodical stirring

[a] $OAc = CH_3COO^-$.

gation and its manganese content was found to be <0.1% of the manganese concentration in the sediment. The manganese concentrations in various fractions were determined by AAS.

Results and discussions

The manganese contents in the sediment samples were evaluated with reference to dry samples for comparison purposes as the water contents of sediments vary from one sample to another depending on the sampling site selected. The dry samples were obtained by lyophilisation.

The manganese concentrations in various fractions are shown in Figures 4 (site 3R) and 5 (sites 4R, 2R and RS).

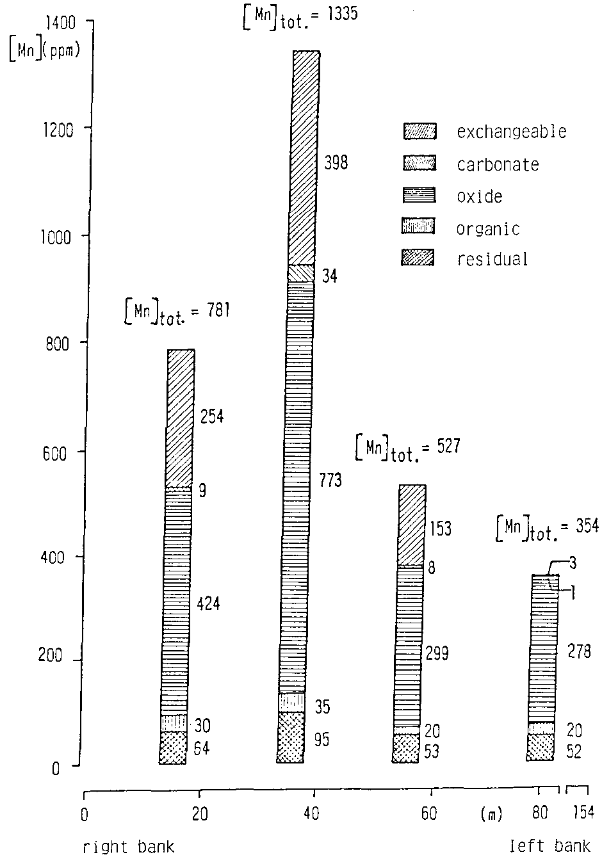

FIGURE 4 Speciation of manganese in the sediments at site 3R.

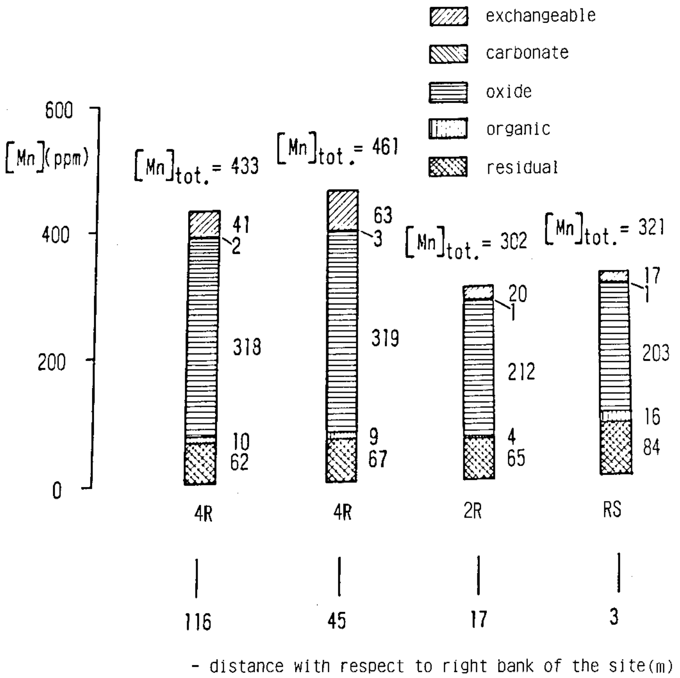

FIGURE 5 Speciation of manganese in the sediments at sites 4R, 2R and RS.

Fractions I and II: Exchangeable and carbonate

The trace metals which are either adsorbed electrostatically or specifically on to sediments are readily desorbed by increasing the ionic strength of the medium and are considered as exchangeable metals.

The exchangeable manganese in the samples collected at the RB of site 3R were found to be much higher than those found at other sites studied. Furthermore, a higher concentration of manganese was observed at 35 m from RB than the other points of site 3R, with regards to both exchangeable and other fractions. This point is characterized by the presence of vegetation all the year round. Because of this vegetation, the water probably stagnates for a longer time than at other points and as a result increased amounts of manganese is transported in the solid form.

Although the exchangeable manganese concentration in the upstream sample (site 4R, Figure 1) is much lower than at site 3R, at least its concentration on the RB is about 2 to 3 times more than at sites 2R and RS. A lower concentration of manganese in the sediments of site 4R than at site 3R is reflected by the distribution of this metal in the aqueous phase. The spatial distribution of the dissolved manganese at site 4R is found to be uniform. In the sediments, the exchangeable manganese concentration at the RB is slightly more than at the LB (Figure 5), the Mn in other fractions being identical on both the banks of the river.

The exchangeable manganese concentration at 75 m of RB of site 3R (3 ppm) is lower than those found upstream (2R:20 ppm; RS:17 ppm). This decrease in Mn content between upstream and downstream samples (2R to 3R) leads to the supposition that Mn_{aq}^{2+} is being oxidised to MnO_2 during the passage between these two sites. This assumption can be ruled out as the oxidation of Mn_{aq}^{2+} under these conditions was found to be a slow process with a half life of more than 200 hrs. The cause for this 6 to 7 fold decrease in Mn concentration is at present obscure since losses during the extraction alone would not account for such a behaviour.

The concentration of Mn bound to the carbonate fraction is negligible (Figures 4 and 5) in contrast to the findings of other investigators.[9,13] Tessier *et al.*[9] reported that 20% of total Mn was found in this fraction whereas up to 60% of total Mn in this fraction have been found in the Villefranche Bay.[13] The maximum Mn content found in this study was c.a. 3%. The pH of the sediment was in the range 7.0–7.4 (pH of water: 8.0–8.2). At this pH, HCO_3^- is the predominant form of carbonate and it might be the reason why Mn is deficient in this fraction. For comparison purpose the distribution of Fe in these sediments were also studied and like in the case of Mn, the Fe content in this fraction was found to be low.

The speciation studies of metal ions in aquatic systems[9] have shown that the anthropogenic input of Mn affects only the first four fractions viz: exchangeable, carbonate, oxide and organic. We observe that the manganese content in samples at sites 3R and 4R are much higher than in the upstream samples (Figures 4 and 5). A similar trend for the spatial distribution of exchangeable manganese is found (sites 3R, Figure 6). Like in the case of Mn_{aq}^{2+}, virtually all exchangeable manganese is localised within the first 50 m of the river, undoubtedly indicating an anthropogenic input into the water body.

Fractions III to V: Oxide, organic and residual

The oxide fractions follows the same pattern as the exchangeable fraction. For instance, at site 3R, the RB samples contains higher manganese concentration than the LB. Moreover, the Mn concentration found in fraction III at site 4R was higher than at sites 2R and RS. This is to be expected as the dissolved manganese concentration at site 4R is 10 times greater than at site 2R. The fact that the oxide and exchangeable fractions show similar trends supports the view that the anthropogenic contribution of metal to water is non negligible. These observations are in accordance with the findings of Tessier *et al.*[9]

The chemical composition of sediment of Rhône River was found to be different from Lake Léman. In Lake Léman sediments, at 0–2 cm level, the manganese content was found to be highest ($\simeq 65\%$) in the carbonate fraction[14] whereas the Rhône River samples contained negligible amount of this metal in this fraction. In contrast the Mn content in the oxide fraction of Rhône River is significantly higher (54 to 79%) than that found in Lake Léman ($\simeq 17\%$).[14] Although the organic and residual fractions show similar trends, they are poor in manganese (Figures 4 and 5). These results are in agreement with those reported in the literature.[7,9,13] The maximum amount of Mn found in these fractions was 6%.

The residual fraction which is generally considered to be free from anthropogenic influence[7,9] contain practically the same amount of manganese in all the sites (Figures 4–5). However, variations in the manganese concentrations up to a factor of 2 between different sampling points were observed. These differences may be attributed to the change in the geochemical composition of the sediment. The manganese were extracted with aqua regia which does not attack the silicates.

The relative manganese content at site 3R shows exactly the opposite result to those found for exchangeable metal. The higher concentrations of manganese found on the LB compared with RB confirms the absence of anthropogenic influence in this fraction. Although the oxide fraction follows the general trend, it is more rich in manganese than the corresponding organic or residual fractions. The higher manganese content observed suggests a partial anthropogenic influence in this fraction.

The distribution of relative amounts of manganese in the various

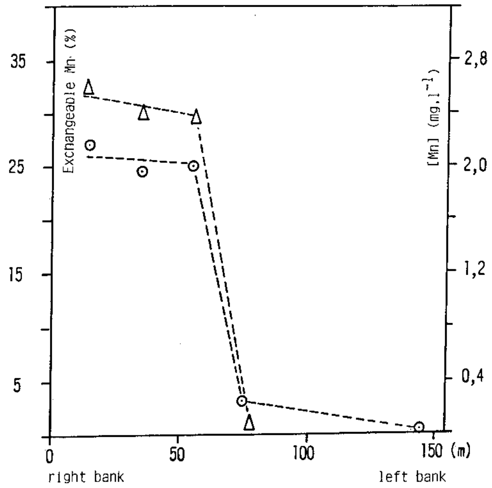

FIGURE 6 Distribution of dissolved and exchangeable manganese at the cross section of site 3R: △, exchangeable; ⊙, dissolved.

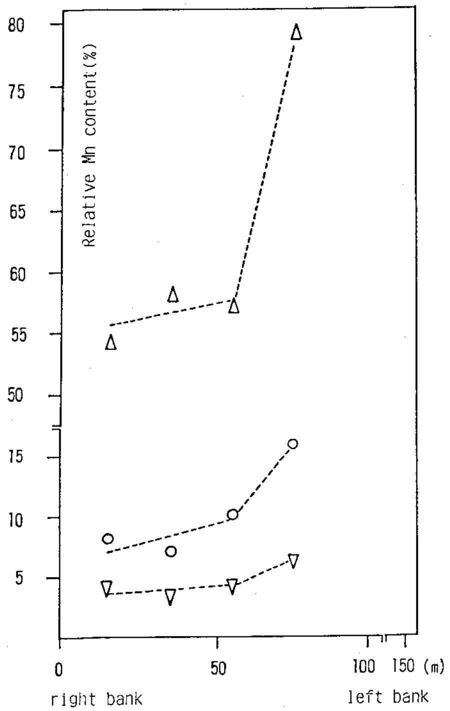

FIGURE 7 Relative amounts of manganese in the sediments at the cross section of site 3R: △, oxide fraction; ○, residual fraction; ▽, organic fraction.

fractions of samples collected at various collection points are represented in Figures 6 and 7. The results show that the Rhône River can be divided into 2 zones (viz: left half and right half) according to its chemical composition. The right half of the river is exposed to anthropogenic activities and this results in a high local concentration of manganese in this portion of the river, the Mn being mainly present in the dissolved and exchangeable forms. The TOC in the right half is higher than in the other half of the river. The left half of the river in contrast contains practically no exchangeable manganese and its Mn concentration and TOC are similar to lake water (Table I). The organic and residual fraction which are virtually free from anthropogenic influence (left bank) have a high relative Mn content.

CONCLUSION

In conclusion, the speciation studies of manganese have shown that in aquatic system studied in this work, manganese is found in the aqueous phase as aquo complex or labile complex, these two forms being indistinguishable by polarographic technique. At site 3R, the spatial distribution of the exchangeable form in the sediment phase reflects that found in the aqueous one which would suggest that input source is common to both phases, namely an anthropogenic origin.

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