

A study of the speciation of ^{60}Co added to coastal pore-water

Cobalt
Cobalt-60
Sea-water
Pore-water
Estuary

Cobalt
Cobalt-60
Eau de mer
Eau interstitielle
Estuaire

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ABSTRACT

The speciation of soluble ^{60}Co in oxic estuarine pore-waters is described. Anionic, cationic and neutral forms are present in approximately equal amounts, but about 50% is in another indeterminate form, from which it may be partially released by addition of acid. Similar speciation has been observed in sea-water. The half-value time for formation of this speciation is 125 days, equivalent to that in sea-water, and there is a large change in speciation with time from an initial predominantly cationic form. Humic and fulvic acids are probably involved. Short-term model systems studied in the laboratory are therefore likely to be seriously misleading.

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RÉSUMÉ

Une étude de la spéciation du ^{60}Co ajouté aux eaux interstitielles côtières

Les formes chimiques du ^{60}Co ont été étudiées dans l'eau interstitielle anoxique d'estuaire. Les formes anioniques, cationiques et neutres se trouvent dans des proportions approximativement égales, mais environ 50 % sont sous une forme indéterminée qui pourrait être libérée par acidification. Une répartition analogue a été observée en eau de mer. La demi-durée (ou la demi-période) nécessaire à la formation des formes chimiques est de 125 jours; un résultat similaire a été observé dans le cas de l'eau de mer. Pour une forme à prédominance initiale cationique le changement de forme est très grand. Les acides humiques et fulviques sont probablement mis en cause. Une expérience de courte durée peut induire sérieusement en erreur dans un modèle étudié en laboratoire.

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INTRODUCTION

The fate of ^{60}Co released from nuclear power plants into the aqueous environment is still a matter of investigation (Olsen *et al.*, 1981, Mahler 1984). The speciation of the ^{60}Co will influence its subsequent behaviour, especially whether it is fixed to sediment or free to interact with the biosphere, but there is still uncertainty about the exact nature of the speciation (Frazier, Ancellin, 1975).

Such study is also relevant in the context of sea disposal of nuclear wastes when information is needed on the likelihood of diffusion of ^{60}Co within oxic burial sediments.

Information already gathered shows that only about 0.1% of total Co in marine sediments is in soluble form

(*e.g.* Huynh-Ngoc *et al.*, 1989; Santschi *et al.*, 1983). However this fraction deserves study because it exists as soluble compounds and may diffuse to the overlying water (Huynh-Ngoc *et al.*, 1989; Santschi *et al.*, 1983). There exist no detailed previous studies on Co speciation in oxic pore-waters, but by analogy with sea-water studies (Nishiwaki *et al.*, 1981; Frazier, Ancellin, 1975) it was suspected that speciation might change significantly over time.

Very few previous studies have taken any care to avoid possible contamination from environmental stable cobalt, which may have invalidated their results because the absolute amount present may influence the speciation and change it from the natural type.

Given all these factors it was thought worthwhile to continue to study coastal and estuarine pore-water.

The aim of the study was therefore to determine the percentages of different charge forms of Co present in pore-water and how they changed with time.

METHODS AND SAMPLES

Sea water was obtained from the supply in the laboratory housed in the Musée Océanographique, and is routinely filtered through a battery of 0.4 µm filters.

Separated pore-water was used in experiments. An alternative might have been to add ^{60}Co to sediment containing pore-water, and after a period of equilibration to express the pore-water. However calculation shows about 400 MBq would have been needed and the uncertainty about equilibrium would have needed to be the subject of a separate study. Such studies are interesting, and in the longer term should be undertaken as an extension of the present work.

Pore-water was obtained from sediments taken by box-corers. The pore-water used in most of the studies in this paper was obtained from Roustan in the Estuary of the Rhône, 43°19'02"N and 5°49'90"E. Another two samples were obtained from the inlet of Villefranche, and off Cannes both of which are to the East of the Rhône on the Côte d'Azur. The samples were all from oxic sediments, which were brown and the layer taken was the top 30 mm. They were put in the refrigerator at 4° as soon as possible.

The day of collection was taken to be day 0, and other days were referenced to it.

The characteristics of the sediments and the interstitial waters contained in them may be found in Fernex *et al.* (1984). Sediments from the Rhône contained 1.5-2% Total Organic Carbon, whereas those from Villefranche contained 9%. Both contained approximately 50% CaCO_3 and had pH's of 8 as for sea-water (the Rhône waters have a pH similar to that of sea-water because of previous passage through limestone-rich country). The organic fractions consist largely of humic and fulvic acids.

Other details of typical mineral compositions of similar sediments from the region are in Aston and Duursma (1973). Briefly, calcite predominates followed by illite and quartz.

Analysis of the interstitial waters themselves showed those from the Rhône estuary typically contained 5-35 $\mu\text{M}\cdot\text{l}^{-1}$ Fe and 25-30 $\mu\text{M}\cdot\text{l}^{-1}$ Mn. Those from Villefranche contained 5 $\mu\text{M}\cdot\text{l}^{-1}$ Fe and 2-2.5 $\mu\text{M}\cdot\text{l}^{-1}$ Mn. For the Villefranche interstitial water also present are 10 $\mu\text{M}\cdot\text{l}^{-1}$ NH_4^+ , 1-3 $\mu\text{M}\cdot\text{l}^{-1}$ NO_2^- and NO_3^- and 2-4 $\mu\text{M}\cdot\text{l}^{-1}$ PO_4^{3-} (Fernex *et al.*, 1984). All these figures are from the top 30 mm oxic zone. Results for the Cannes location should be similar to those from Villefranche.

Extraction of pore-water was on day 2. All samples were obtained from the sediments using a "squeezer" which pressurizes the sediments under pure nitrogen and forces the pore-water out through 0.22 µm filters. Throughout the period of the experiment the water

was kept in dark conditions and at 4°C. No other precautions were taken to avoid growth of bacteria or other biological changes. It was hoped that these conditions would approximate those found in the original locations of the sediments.

The special precautions for avoiding heavy metal contamination as used for previous analyses of metals in sea-water are described in Fowler *et al.* (1984). Non-porous plastic surfaces were used whenever possible both during collection and analysis. All apparatus was pre-washed with Suprapur Nitric acid, and careful reagent blanks performed during the experiments. The techniques have been shown to avoid metal contamination for sea-water analysis, and specifically for cobalt because the results accord very closely with those of other laboratories (Huynh-Ngoc and Whitehead, 1986). The analysis technique as described by Huynh-Ngoc and Whitehead (1986) was Differential Pulse Cathodic Stripping Voltammetry (DPCSV).

Some of the test solutions were used for determination of stable cobalt by DPCSV using pore water obtained at the beginning of the experimental series. Others were examined by a radiometric technique in which ^{60}Co was added. Test specimens were counted in standard geometry in a NaI(Tl) well crystal and compared with standards where appropriate.

The technique used to determine speciation, was designed to detect the amounts of cationic, anionic and neutral species present by use of cationic, anionic and neutral resins, respectively, and is an extension of similar work by Nishiwaki *et al.* (1981), Frazier and Ancellin (1975), Isshiki and Nakayama (1987) and Marchand (1974) who used these resins only for sea-water, not pore-water. In addition, Chelex resin was used which is supposed to be a rather specific chelator of first transition series elements. Because MnO_2 has been frequently used in the past for speciation studies, it was also included in the present study.

A batch technique was used rather than a column technique because of the quite limited amounts of pore-water available.

To 5 ml portions of aqueous test phase were added an appropriate quantity of resin as found in preliminary experiments, *i. e.* 0.14 g Chelex (chelator), 0.24 g Biorad 1X8 (anionic), 0.20 g Biorad 50X8 (cationic), 1g XAD-4 (neutral), and 0.3 g MnO_2 . Resin types were never combined in the same test vial.

From the known properties of these resins it was expected that the forms Co^{2+} and CoCl^+ would attach to Biorad 50X8 and the forms CoCO_3^0 and CoSO_4^0 would attach to XAD-4. Chelex resin was expected to adsorb all types. Any negatively charged forms were expected to attach to Biorad 1X8.

Since addition of the resins in some cases caused significant pH changes even with washed resins, the pH was immediately adjusted with NaOH back to 8 which was the pore-water pH. We do not believe permanent changes were caused to the system by this brief pH perturbation of 3 pH units. Even for the sensitive case of protein denaturation in biochemical studies such a change would be reversible.

The vials were shaken for 1 hour, allowed to equilibrate for 6 hours, then 1.0 ml of supernatant liquid (containing no resin) was taken for analysis, which was either in a NaI(Tl) assembly for ^{60}Co or by the voltammetry technique.

In a time-series experiment (the plan of which should be consulted in figure 1) we took a stock solution of the pore-water, at day 60, added a small quantity of ^{60}Co , and at subsequent times took a subsfraction. The ^{60}Co added was from a CEA solution purchased in 1971 which contained Co in inorganic form only. Sampling dates were days 67, 74, 88, 123, 180. From the subsfraction 5 ml portions were taken, filtered through a $0.22\mu\text{m}$ filter and a quantity of absorbing reagent was added to each. Because of the filtration the experiments always took place with any colloidal material present having the same upper size limit. Amounts of radioactivity present in each 5 ml aliquot were about 52 kBq ($1.4\mu\text{Ci}$) and also contained $1.7\mu\text{g}$ of stable Co from the original ^{60}Co solution and $1.8\mu\text{g}$ of stable Co from the pore water. In all vases analysis of the ^{60}Co content of the liquid in the vials was done in duplicate and sometimes triplicate.

In another experiment the pore-water in contact with ^{60}Co for 180 days was acidified and allowed to sit for two days to see whether ^{60}Co was released from its chemical complexation in solution.

In a further experiment ^{60}Co was added to 180-day old pore-water free of ^{60}Co for 180 days to see whether the results were the same as those for ^{60}Co exposed to pore-water constituents for 180 days. Additionally a subsample was filtered before addition of ^{60}Co .

Unfortunately UV-irradiation apparatus was not available during the experiments. It would have been very useful to check whether changes occurred on destruction of the organic matter. Interpretation might however have been complicated by photochemical reduction of Fe^{3+} present. Similarly Dissolved Organic Carbon measurements were not possible.

RESULTS

0.5 l of pore-water was obtained from the Roustan site, and half used for the time-series experiments. It was somewhat brown, suggesting the presence of organic compounds and/or iron compounds. Though filtered, the pore-water showed a tendency to produce a slight light-coloured precipitate with time. This precipitate cannot have been the normally red-brown ferric hydroxide nor does calculation show its solubility product was exceeded, but may have been humic acids. Other pore waters obtained from different locations differed in colour. For all sites combined, a total of 1 liter of pore-water was expressed from 6.2 kg of oxic sediment.

^{60}Co attached to the walls of experimental containers proved to be an insignificant percentage of the total.

The pore-waters from different locations gave significantly different results, as shown in table 1, regardless of whether the analysis technique uses ^{60}Co or DPCSV. It is not clear whether this is due to differences in the cobalt speciation detected by the DPCSV technique but inherent variability in the pore-waters is probably a factor.

The results of the long-term study (Fig. 2, Tab. 2) show some irregularities and are best interpreted in terms of the long-term trends. The ^{60}Co present in the pore waters attached less and less readily to added Chelex or MnO_2 whereas no clear long term trend was noted for attachment to the AG 50WX8 and AG 1X8 and XAD-4 resins. It will be noted that the amounts absorbed by cationic, anionic and neutral resins do not add to 100% at 180 days.

Initially the Chelex resin was by far the most efficient at absorbing the ^{60}Co under these experimental conditions. MnO_2 was generally less efficient but more efficient than the other resins.

Figure 1 shows the results of the various experiments at 180 days.

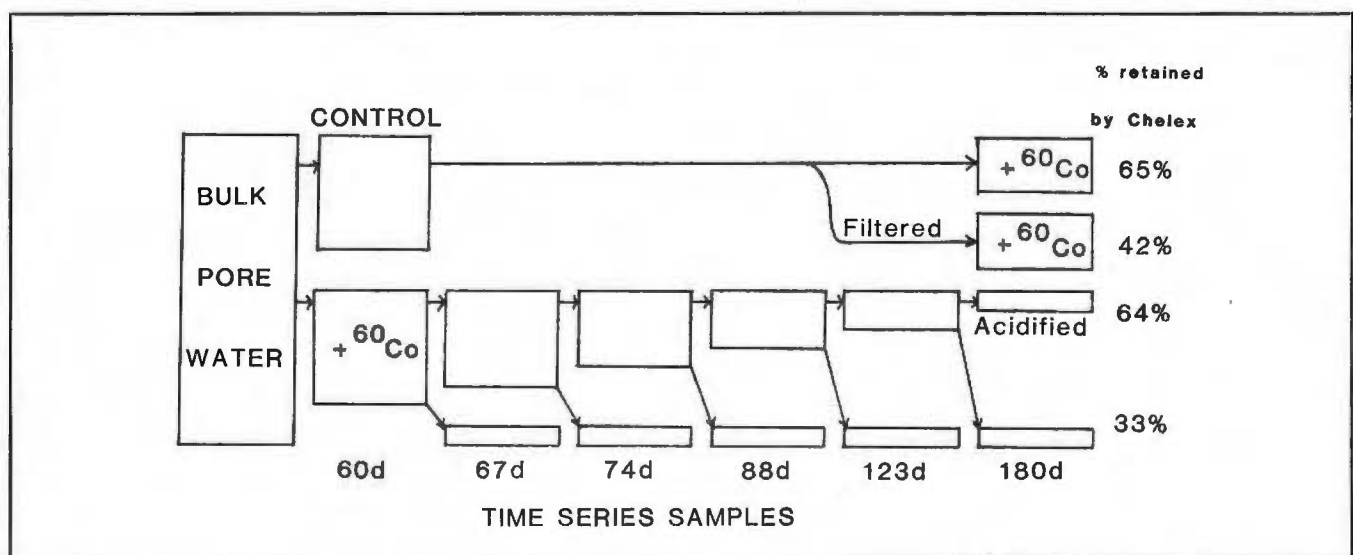


Figure 1.

Plan of experiment for time series samples, with results at day 180.

Schéma de l'échantillonnage en séries temporelles et résultats au 180^e jour.

Table 1

Relative initial speciation of Cobalt in different pore-waters. % absorbed.
Spéciation initiale du cobalt dans les eaux interstitielles. % absorbés.

Sample	Technique	Chelex	Cationic	Anionic	Neutral
Sea-water	^{60}Co	98.8	63.1	17.3	20.5
Villefranche	DPCSV	90.9	68.0	30.1	0
Roustan	^{60}Co	90.4	29.9	25.8	44.3
Cannes	^{60}Co	58.2	14.9	6.2	29.1

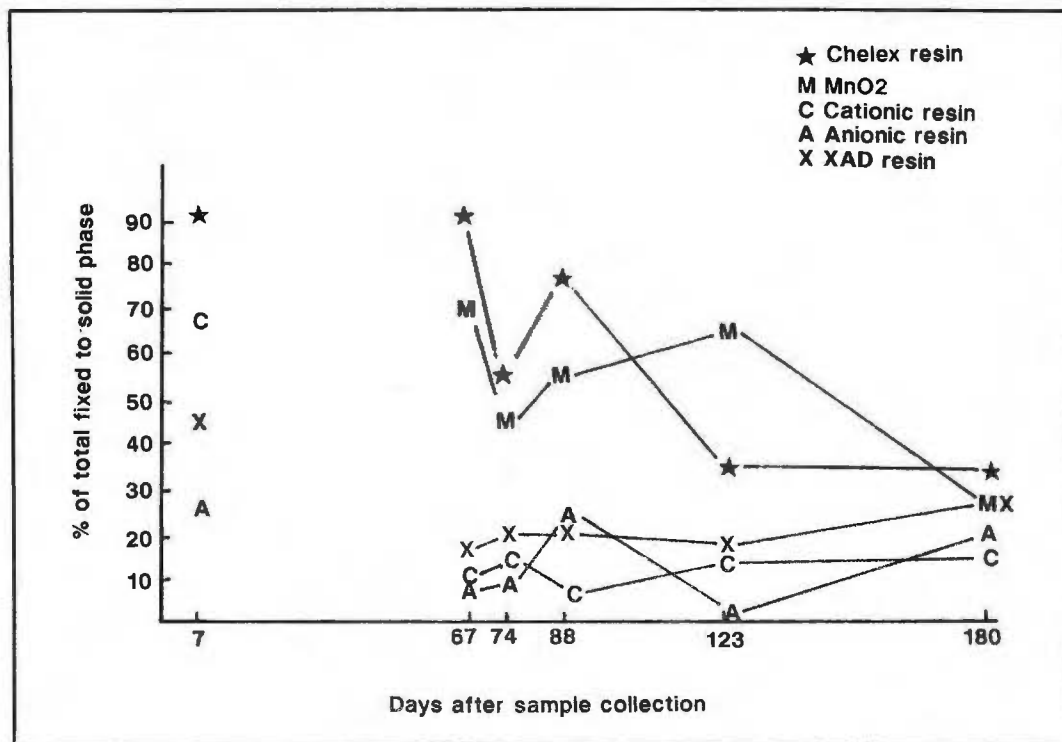


Figure 2.

Percentage ^{60}Co retained by various resins with time.

Pourcentage du ^{60}Co retenu par différentes résines en fonction du temps.

Table 2

Speciation of ^{60}Co in Roustan pore-water with time. % absorbed by different resins.

Spéciation du ^{60}Co dans l'eau interstitielle de Roustan en fonction du temps. % absorbés par différentes résines.

Date	Day 67	Day 74	Day 88	Day 123	Day 180
AG 50WX8 Cationic	8.8	15.4	6.2	15.9	9.8
AG 1X8 Anionic	8.2	8.4	23.6	0	15.7
XAD-4 Neutral	14.7	20.5	23.6	17.2	22.8
(Total)	31.7	44.3	53.4	33.1	48.3
Chelex	88.8	54.9	85.7	35.2	33.4
MnO_2	70.7	43.6	53.6	61.4	20.9

DISCUSSION

Speciation in seawater

For comparison with the pore-water results the literature on speciation of ^{60}Co in sea-water will be described first, for useful background.

Amdurer *et al.* (1983) cite several theoretical studies on cobalt speciation in sea-water. These showed that in the absence of organic fractions the expected distribution is Co^{2+} 54%, CoCl^+ 31%, which suggests that as much as 85% should be in cationic form. Neutral forms expected are CoCO_3^0 7% and CoSO_4^0 7%. The percentages found in the same paper from actual

experiments on sea-water corresponded moderately well with those found in the theoretical treatment.

Earlier work by Marchand (1974) using resin columns showed that 55-68% of cobalt in sea-water was cationic and only 0.5-3% was neutral or anionic. The missing material was not accounted for. Over the course of 5 weeks the cationic fraction diminished a great deal.

In contrast, Sugimura *et al.* (1978) found that 75-95% of stable cobalt in sea-water was neutral or anionic, and only 5-10% cationic. Their results seem different from most others in the literature, and assuming there were no gross experimental errors in their work the results can be reconciled with the other literature by invoking the presence of variable amounts of minor constituents which are likely to be organic.

In table 1 it can be seen that 98.8% of ^{60}Co added to sea-water can be chelated by Chelex, and that 63.1% is in cationic form. These results correspond with the theoretical results of Amdur *et al.* (1983) and the experimental results of Marchand (1974), but not with those of Sugimura *et al.* (1978).

Occurrence in sediments

Anoxic conditions give rise to very ready diffusion of ^{60}Co within the sediments (Kremling 1983, Heggie *et al.*, 1986), a situation quite different from that described here.

The Co content of the estuarine sediment was 3.9 mg kg^{-1} and the mean pore-water concentration about 1800 ng.l^{-1} of water (Huynh-Ngoc *et al.*, 1989). This shows that more than 99.9% of the Co in sediments is therefore found in the insoluble particles as also found by Fukai and Murray (1973).

The work of Added *et al.* (1983) showed that stable cobalt is associated with the organic fraction but only for recent sediments such as those studied in the present work. Hirata (1985) similarly showed that organic matter was enriched near the surface of sediments, and in the surface layers Co was bound to organic matter with a molecular weight greater than 5000 Dalton.

These data suggest most Co is attached to the organic solids within sediments. The small soluble fraction is also likely to be influenced by the soluble organics.

Speciation in pore water

Data on ^{60}Co speciation in pore-water are few.

Huynh-Ngoc *et al.* (1989) in preliminary work, showed that the absolute levels of stable cobalt in their coastal oxic pore-waters were 30 times those in open ocean sea-water, and nearly half of pore-water cobalt was present as a very strong complex suspected to be organic.

Table 1 shows that in some fresh pore-waters the Chelex resin is able to chelate almost 100% of the added ^{60}Co . The sum of the amounts adsorbed by the different forms of resin is often in the vicinity of 100%. This confirms the chosen conditions were adequate to detect the different forms.

XAD-4 has a low but significant cation absorption capacity (Mackey, 1982). The figure given for "neutral" could contain a cationic contribution as well. In that case however the percentage of radionuclide which has not attached to any of the resins is even higher than the percentages given in Tables 1, 2.

Cationic forms predominate (58-90.9%) but significant percentages of anionic (14-68%) and neutral forms (0-44%) are present. The pore-water results bracket the sea-water results and cannot be said to be different as studied so far.

Change of speciation with time

The work of Nishiwaki *et al.* (1981) showed that ^{60}Co added to sea-water became progressively altered over 36 days into a form in which it could not be chelated by

Chelex resin. Gel filtration showed that the molecular weight of the ^{60}Co -containing compounds increased markedly. The authors thought that amino acid complexing might be responsible.

Similarly Frazier and Ancellin (1975) found for ^{60}Co added to sea-water that after two months only 48% was still cationic, 33% was anionic or neutral and 5% was in an indeterminate form. Both these papers show strong changes of speciation in Co with time and the kinetics were quite slow.

Previous work therefore suggests changes in Co speciation in sea-water are slow. The present experiments show that the above changes in sea-water speciation also occur in pore-waters and the cationic form of Co disappears preferentially. A strong difference from starting conditions is already apparent at 60 days. The anionic, cationic and neutral forms fall far short of a total of 100% which indicates a transformation into some forms very weakly absorbed on any of the resins. The half-life for this process appears to be about 125 days for our samples, which corresponds well with what others have reported for sea-water, taking into account the fact that the experiments of other authors were at 15°C while ours were at 4°C , hence an approximate halving of rate is expected.

The acidification experiment (exposure to pH 2 for two days and the normal assay technique applied thereafter) showed that under the experimental conditions the percentage absorbed on Chelex was 64% which is much higher than the 33% at day 180 in Table 2 from a sample which was not acidified. However acidification did not restore the 90% chelating ability of Chelex seen on day 0. This shows that the changes which have occurred are only partially reversible by acid. The ^{60}Co has been transformed into a form which is relatively inaccessible.

The explanation of the test results is almost certainly not due to bacterial absorption. The initial filtration of the pore-water at day 2 should have removed most bacteria. Also before adding test resins the pore-water was again filtered which would have removed any bacteria which had grown in the mean time. The tests were therefore on soluble complexes. In addition the experiment in which 180-day pore-water was filtered and then ^{60}Co added, suggested that the component of interest is soluble.

Ferric iron was present in these pore-waters but its solubility product was not exceeded. $\text{Fe}(\text{OH})_3$ was not present even as a colloidal suspension and cannot therefore have contributed to the speciation.

The aged and filtered pore-water containing ^{60}Co added at day 180 did not contain a form of ^{60}Co which could be easily chelated by Chelex. It is not easy to account for this observation in detail, though it again confirms that changes take place in the pore-water with time.

There are three consequences of the changes that take place with time. First, the speciation observed using ^{60}Co at day 180 is much more likely to represent the true Co speciation in pore-water samples as found in the environment than the apparent speciation at day

0. Short-term studies with added ^{60}Co are therefore likely to yield misleading results unless samples are aged for some months. It is obviously important to check if this finding for ^{60}Co applies to other radionuclides. Second, if inadequate precautions are taken to prevent contamination of pore-water samples with stable Co, subsequent analysis is likely to suggest a distribution of the Co present which is likely to be misleading, because the distribution of the accidentally added Co will not reflect the true distribution in aged samples. Third, since most surfaces in the marine environment have an outer layer which is negatively charged, any change to negatively charged complexes with time will promote diffusion out of a sediment.

The inability of Chelex to chelate added ^{60}Co or aged ^{60}Co in aged pore-water samples is either an indication of extremely strong chelation by a component in the solution or physical removal from solution.

The few other data available support this conclusion.

Koshy *et al.* (1969) found when they added ^{60}Co to humic acids isolated from a marine sediment that initially the ^{60}Co was 100% in cationic form, but the percentage decreased to 28% after 28 days, the remaining 72% being neutral (*see also Pillai et al.*, 1971). The complexation of cobalt with the humic acids was about as strong as a Co-EDTA complex.

It was shown in a previous paper by Huynh-Ngoc *et al.* (1989) that most stable cobalt in the fresh pore-water studied was extremely strongly bound by soluble components with an effective dissociation constant stronger than that for the dimethylglyoxime complex, *i. e.*, about 10^{22} . Acid treatment moved the equilibrium towards dissociation of the complex. The quantitative shift was close in magnitude to the change found when samples in the present experimental series were acidified.

All available data therefore suggest either strong chelation or physical sequestration of added Co with time. It seems rather unlikely that a true chelating agent exists naturally which is more efficient than EDTA or dimethylglyoxime so alternative explanations are preferable. An explanation such as physical isolation from the environment by humic acids coagulating to a colloidal size is persuasive, but needs confirmation with further work.

REFERENCES

- Added A., J. Cenciariini, F. Fernex, C. Serra and D. Span (1983). La situation des métaux dans les sédiments marins en des zones plus ou moins polluées de la Méditerranée Nord-Occidentale. *VI^{es} Journ. Etud. Pollut. C.I.E.S.M.*, Cannes, 377-383.
- Amdurer M., D. Adler and P. H. Santschi (1983). Studies of the chemical forms of trace elements in sea-water using radio-tracers. 1983. In: *Trace Elements in Seawater*, edited by C. S. Wong *et al.*, Plenum Press, N.Y., 537-562.
- Aston S. R., E. K. Duursma (1973). Concentration effects on ^{137}Cs , ^{65}Zn , ^{60}Co and ^{106}Ru sorption by marine sediments with geochemical implications. *Neth. J. Sea Res.*, **6**, 225-240.
- Emeleus H. J. and J. S. Anderson (1938). In: *Modern Aspects of Inorganic Chemistry*, Routledge, London, p. 151.
- Fernex F. E., D. Span, G. N. Flatau and D. Renard (1984). In: *Sediments and water interactions*, Springer-Verlag, Berlin, p. 353-369.
- Fowler S. W., L. Huynh-Ngoc and R. Fukai (1984). Dissolved and particulate trace metals in coastal waters of the Gulf and Western Arabian Sea. *Deep-Sea Res.*, **31**, 719-729.
- Frazier A. and J. C. Ancellin (1975). Study of the contamination of constituents of the marine milieu by soluble and insoluble forms of radionuclides. In: *Impacts of Nuclear Releases into the Aquatic Environment*, I.A.E.A., Vienna, p. 49-62.
- Fukai R. and C. N. Murray (1973). Environmental behaviour of radiocobalt and radiosilver released from nuclear power stations into aquatic systems. In: *Environmental Behaviour of Radionuclides released in the Nuclear Industry*, I.A.E.A., Vienna, p. 217-242.
- Heggie D., D. Kahn and K. Fisher (1986). Trace metals in metalliferous sediments. MANOP Site M: interfacial pore water profiles. *Earth. Pl. Sci. Lett.*, **80**, 106-116.

We also cannot rule out an explanation of the results in terms of conversion of Co to strongly bound Co^{3+} (*e. g.* Emeleus, Anderson, 1938).

CONCLUSIONS

Cobalt in coastal pore-waters or sea-water may exist initially mainly in the cationic form, as theoretical models would suggest, but after a few months the amounts of cationic, anionic and neutral forms are almost equal. The speciation found in different pore-waters varies probably due to differing organic content. Much more work would be necessary to clarify the factors involved.

^{60}Co added to estuarine pore-water behaves similarly to ^{60}Co added to some sea-waters, becoming progressively isolated from further chemical reactions and this is only partly reversed by acid treatment. The process in the present environment is slow, and has a half-time of about 125 days. The precise explanation of this still awaits further work, though there is some evidence humic and fulvic acids may be involved, but the present work shows that laboratory contamination of samples with stable Co may yield results which do not reflect the true metal distribution at all, and therefore greater care should be exercised.

The transformation to neutral and negatively charged forms means that diffusion of Co out of oxic sediments is more likely with time.

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- Hirata S.** (1985). Phosphorus and metals bound to organic matter in coastal sediments—an investigation of complexes of P, Cu, Zn, Fe, Mn, Ni, Co and Ti by inductively coupled plasma—atomic emission spectrometry with Sephadex gel chromatography. *Mar. Chem.*, **16**, 23-46.
- Huynh-Ngoc L. and N. E. Whitehead** (1986). Nickel and Cobalt determination in the North Western Mediterranean by differential pulse cathodic stripping Voltammetry. *Oceanologica Acta*, **9**, 433-438.
- Huynh-Ngoc L., N. E. Whitehead, M. Boussemart and D. Calmet** (1989). Dissolved Nickel and Cobalt in the Aquatic Environment around Monaco. *Mar. Chem.*, **26**, 119-132.
- Isshiki K. and E. Nakayama** (1987). Selective Concentration of cobalt in Sea-water by complexation with various ligands and sorption on macroporous resins. *Anal. Chem.*, **59**, 291-295.
- Koshy E., M. V. M. Desai and A. K. Ganguly** (1969). Studies on organo-metallic interactions in the Marine Environment. Pt. 2. Interaction of Metallic ions with humic acid from a marine sediment. *Curr. Sci.*, **24**, 582-586.
- Kremling K.** (1983). Behavior of Zn, Cd, Cu, Ni, Co, Fe and Mn in anoxic waters. *Mar. Chem.*, **13**, 87-108.
- Mackey D. J.** (1982). Amberlite XAD-2 and XAD-4 as cation-exchange resins of low capacity. An investigation using an atomic fluorescence detector directly coupled to a liquid chromatograph. *J. Chromatogr.*, **237**, 79-88.
- Mahler P.** (1984). The nature of occurrence of Cesium-137, Chromium-51, Cobalt-60, Manganese-54, Sodium-22 and Zinc-65 in simulated estuary environments. Influence of mineral particles in suspension and dissolved organic matter. *Doctoral Thesis, University of Nice*, 179 pp.
- Marchand M.** (1974). Consideration of the physico-chemical forms of cobalt, manganese, zinc, chromium and iron in a sea-water enriched or not in organic mater. *J. Cons. Int. Explor. Mer.*, **35**, 130-142.
- Niskiwiki Y., Y. Kimura, Y. Honda and K. Katsurayana** (1981). Possible formation of organic cobalt complexes with amino acids and uptake by marine bivalve. In: *Impacts of radionuclide releases into the marine environment*, I.A.E.A. Vienna, p. 401-419.
- Olsen C. R., H. J. Simpson and R. M. Trier** (1981). Plutonium radiocesium and radiocobalt in sediments of the Hudson River estuary. *Earth. Pl. Sci. Lett.*, **55**, 377-392.
- Pillai T. N. V., M. V. M. Desai, E. Mathew, S. Ganapathy and A. K. Ganguly** (1971). Organic materials in the marine environment and their associated metallic elements. *Curr. Sci.*, **4**, 75-81.
- Santschi P. H., Y. H. Li, P. O'Hara and M. Amdurer** (1983). Sediment-water exchange under oxic and anoxic conditions in a coastal marine ecosystem (MERL): results from radiotracer experiments. *EOS Trans. Am. Geophys. Union.*, **64**, 716.
- Sugimura Y., Y. Suzuki and Y. Miyake** (1978). Chemical forms of minor metallic elements in the ocean. *J. Oceanogr. Soc. Jap.*, **34**, 93-96.

