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DETERMINATION OF THE DISTRIBUTION COEFFICIENTS FOR ^{134}Cs, ^{60}Co AND ^{234}Th IN THE PINHEIROS RIVER SEDIMENT-WATER

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The distribution coefficients (Kd) for ^{134}Cs, ^{60}Co and ^{234}Th were determined experimentally in order to foresee the fate of these radionuclides discharged to Pinheiros River by IPEN's facilities. The parameters studied in the laboratory were the effect of pH, aerobic condition and the time of contact. The results obtained experimentally confirm the predictions that the cesium is slowly retained by the sediment along the Pinheiros River. The retention of cobalt, which is an unstable element, is affected by variations in the pH. Thorium is almost completely retained in the vicinity of the discharge point.

In order to control the discharges of radioactive material generated by the nuclear installations at "Instituto de Pesquisas Energeticas e Nucleares" (IPEN), an effluent monitoring program was established on a routine basis. The nuclear installations which contribute to the liquid source term are: a swimming pool research reactor IEA-R1, a center for production of radioisotopes and a center for development of the main steps of the nuclear fuel cycle. The control of the emission of such installations is carried out by measuring the activity of the radionuclides present in the effluents. The results obtained are compared with the operational limits adopted, before a decision is made to discharge the effluents into the environment. The effective dose to the critical group is then evaluated by using this source term and a generic model which describes the transfer of the radionuclides into the ecosystem. All the liquid effluents discharged from IPEN's facilities flow to Pinheiros River through the sewage system.

In this paper the distribution coefficients (Kd) are determined for the most critical radionuclides (Cs, Co and Th) present in the source term released by IPEN's facilities during 1988[3], according to the radiological protection standards[1,2]. The solid/liquid distribution coefficient is often used in transport models for the purpose of predicting the environmental behavior of radionuclides.

The distribution coefficient quantifies the overall distribution of a given element between the solid and liquid phases, according to the equation:

$$Kd(ml/g) = \frac{\text{Total element concentration in solid phase}}{\text{Total element concentration in solution}}$$

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Experimental

The distribution coefficient is a measured quantity determined experimentally using a variety of techniques, under specific conditions[4,5,7,9]. Since there are a variety of environmental parameters which can affect the distribution coefficient, the laboratory experiments were carried out by considering temperature, pH, sediment mass/water volume ratio and the main ionic species found in the Pinheiros River. The method used for estimating the distribution coefficients was to add radioactive tracers to laboratory samples to simulate the real water-sediment system.

The experiments were carried out by collecting 10 L of Pinheiros River water with the characteristics shown in Table 1. The sample was passed through a 0,45 um filter to separate the particulate from the soluble matter and then stored in polyester tanks at 4°C. The sediment was sampled from the Pinheiros River at the same point as the water. Its characteristics are shown in Table 1. All the sediment samples collected were oven-dried at 110°C for one week, mixed, and passed through a 200 mesh sieve.

Effect of the pH on the distribution coefficient

Small quantities of the sediment (10 and 50 mg, dry weight) were added to 90 ml of river water treated with 25 ug of tetracycline to prevent microbial activity. The pH was adjusted by the addition of HCl and NaOH and the sample was allowed to hydrate for seven days. The tracer solution (^{234}Th, ^{134}Cs or ^{60}Co) was added and the final volume was adjusted to 100 ml. After fifteen days the solution was passed through two 0,45 um filters, the first one to separate the solid phase (sediment) and the second one for checking the residual activity level of the nuclides in the water absorbed in the filter. The filtered water was collected and the activity of the particulate and soluble matter were determined using a HpGe detector coupled to a 4096 channel analyzer interconnected to a micro computer. The results obtained from these experiments were determined by comparing the activity present in the solid and liquid phases to calculate Kd and by calculating the percentage of ^{134}Cs, ^{60}Co or ^{234}Th present in the solution. All the experiments were carried out in triplicate.

Effect of the aeration on the distribution coefficient

This experiment was carried out under the same conditions as described above but using 50 mg of the sediment and 500 ml of the river water. The water sediment system was aerated for 45 hours by a glass capillary tube connected to a compressor. The same experiment was also repeated without aeration by bubbling gaseous nitrogen into the system in order to obtain an anaerobic condition. The separation of the solid phase from the solution and the corresponding activity measurements were carried out as described previously.

TABLE 1

Characteristics of Sediment and Water Sampled from the Pinheiros River at Jaguare Stream, July 1988.

SEDIMENT

Mineral Analysis of Clay	quartz illite chlorite halloysite	
Granulometry (%)	>250 um 10% 50-250 um 49% <50 um 40%	
Elemental Macroanalysis (%)	Si-39 Al-9.86 Fe-3.82 Mg-2.12	K-1.65 Li-0.53 Na-1.82
Elemental Microanalysis (%)	Mn-336 Cl-248 V-102 La-41.3 Co-32.8	Th-16.8 Sc-13.4 U-4.54 Sb-3.30 Cs-4.25
Exchangeable Cations (meq/100g)	11 ± 3	
Activity Measured by a HpGe Spectrometer (Bq/100g)	Cs-134 < 2x10-3 Co-60 < 3x10-3 Th-234 < 8.1	

WATER

pH	5.5 - 6.0	
Ions (mg/l)	Fe-12.9 P-1.08 Mn-0.27 Ni-0.05	Pb-0.10 Cu-0.07 Cr-0.05 Zn-0.27
Activity Measured by a HpGe Spectrometer (Bq/l)	Cs-134 < 0.17 Co-60 < 0.21 Th-234 < 8.1	

Effect of the time of contact on the distribution coefficient

Following the same procedure, the sediment samples weighing 50 mg were added to 500 ml of the river water and the final system was aerated for 15 days. At fixed time intervals two samples of the solution were removed. The first one (3 ml) was passed through two 0,45 um filters to separate the solid phase activity from that present in the solution. The filtrate was also measured for the determination of the radionuclides concentration present in the solution. The second one (1 ml) was used for the determination of the total radionuclides concentration present in the sediment-water system.

Results and Discussion

The results obtained for the distribution coefficients and for the percentage of ^{234}Th, ^{134}Cs and ^{60}Co as a function of pH are presented in Figure 1 and Figure 2. The results concerning the effect of the aeration in the distribution coefficients are presented in Table 2, and finally, the results given as a function of the time of contact are presented in Figures 3 and 4.

The distribution coefficients obtained in this work for ^{60}Co, ^{234}Th and ^{134}Cs were lower than those reported in the literature for the same type of sediment, mainly for cesium and cobalt[5,6,9,10].

These differences can be explained by the fact that the sediment was dried at 110°C. At this temperature changes can be observed in the structure of the mineral clays which can affect the absorption of the radionuclides.

For the cesium no considerable changes were observed for the Kd with the variation pH and aerobic condition. The Kd values ranged from 21±7 ml/g to 33±4 ml/g. The study of the time of contact showed that the equilibrium between the cesium concentration in the water and sediment was achieved in a few days.

In the pH range considered (between 4 and 8), the cesium is most likely present in the water in the ionic form Cs^+ [12]. Therefore, any changes in the retention of such cation should be attributed to changes in the structure of the mineral clay and in the concentration of H^+ in the solution[10,11].

The pH effect for the cobalt was considerable since the Kd increased from 46.9±2,1 ml/g for pH 4 to $(1.66\pm0,15)10^3$ ml/g for pH 8. The Kd observed with the agitation with air was 424±26 ml/g, rising to 666±32 ml/g with the agitation with N_2. The time of contact study showed that the equilibrium between the cobalt concentration in water and sediment was not achieved even after 15 days. Serne[8] believes that this behavior is a consequence of the hipolimium condition, since the sediment characteristics cause the pH to drop, thus allowing the solubilization of several transition metals such as cobalt.

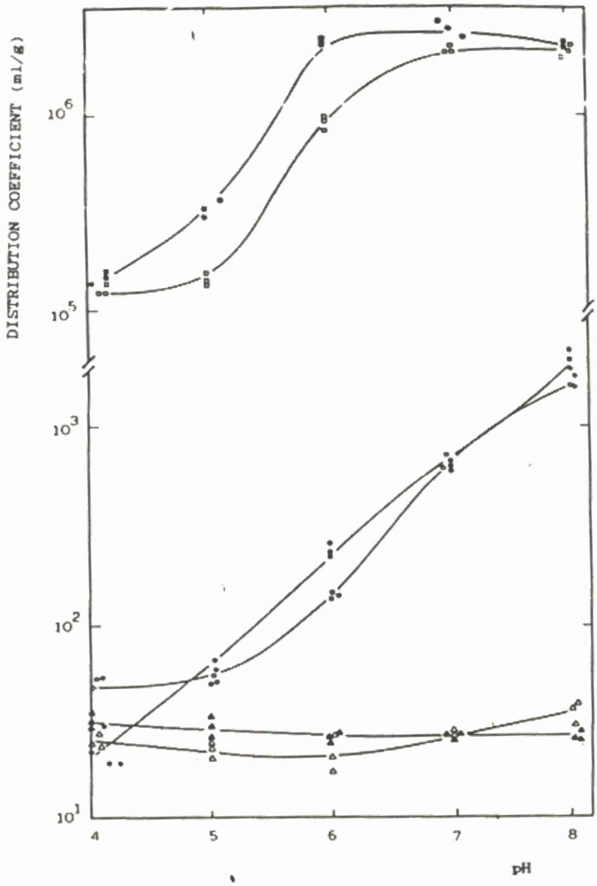

Figure 1. Distribution coefficients (Kd) as a function of pH for Cs.
for Cs: △ 10 mg/100 ml mass ratio and
▲ 50 mg/100 ml mass ratio;
for Co: ○ 10 mg/100 ml mass ratio and
● 50 mg/100 ml mass ratio;
for Th: □ 10 mg/100 ml mass ratio and
■ 50 mg/100 ml mass ratio.

The Co^{++} is a small ion and therefore can penetrate easily into the structure of any mineral clay expanded. However, its retention is affected by the pH, which besides changing the mineral clay structure may also alter its ionic form. For pH 4 to 6, the ionic form prevails[13]. Above this range the cobalt can form complexes with other ions present in the solution. In the complex form, cobalt tends to bind only with the external layers of the mineral clay structures, thus preventing the remotion of the cobalt ions still present in the solution.

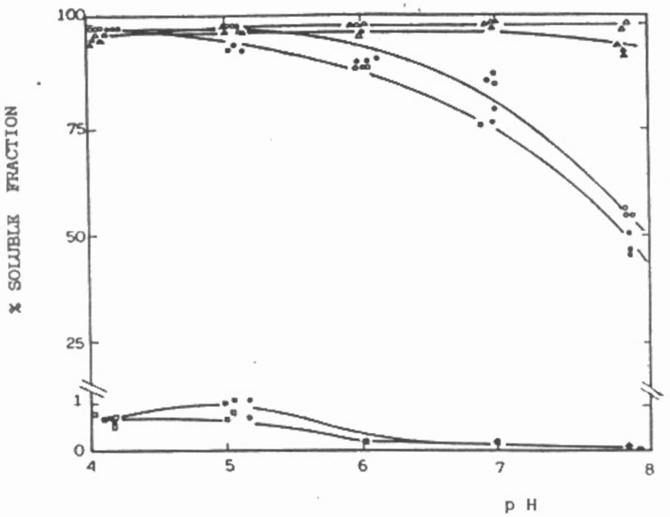

Figure 2. Percentage of radionuclides present in the soluble form as a function of pH.

for Cs: △ 10 mg/100 ml mass ratio and
▲ 50 mg/100 ml mass ratio;
for Co: ○ 10 mg/100 ml mass ratio and
● 50 mg/100 ml mass ratio;
for Th: ☐ 10 mg/100 ml mass ratio and
■ 50 mg/100 ml mass ratio.

TABLE 2

Distribution coefficients (Kd) and percentage of radionuclides present in the soluble form for Cs, Co and Th as a function of aeration condition.

Treatment	Radionuclide	Kd (ml/g)	Concentration in the soluble form (%)
Bubbling of air	Cs-134	21.3 ± 1.6	98.2 ± 0.1
	Co-60	424 ± 26	66.9 ± 7.6
	Th-234	$(2.61 \pm 0.11)\times10^6$	0.05 ± 0.01
Bubbling of N_2	Cs-134	22.2 ± 1.0	98.5 ± 0.7
	Co-60	666 ± 32	75.4 ± 1.9
	Th-234	$(2.78 \pm 0.25)\times10^6$	0.06 ± 0.01

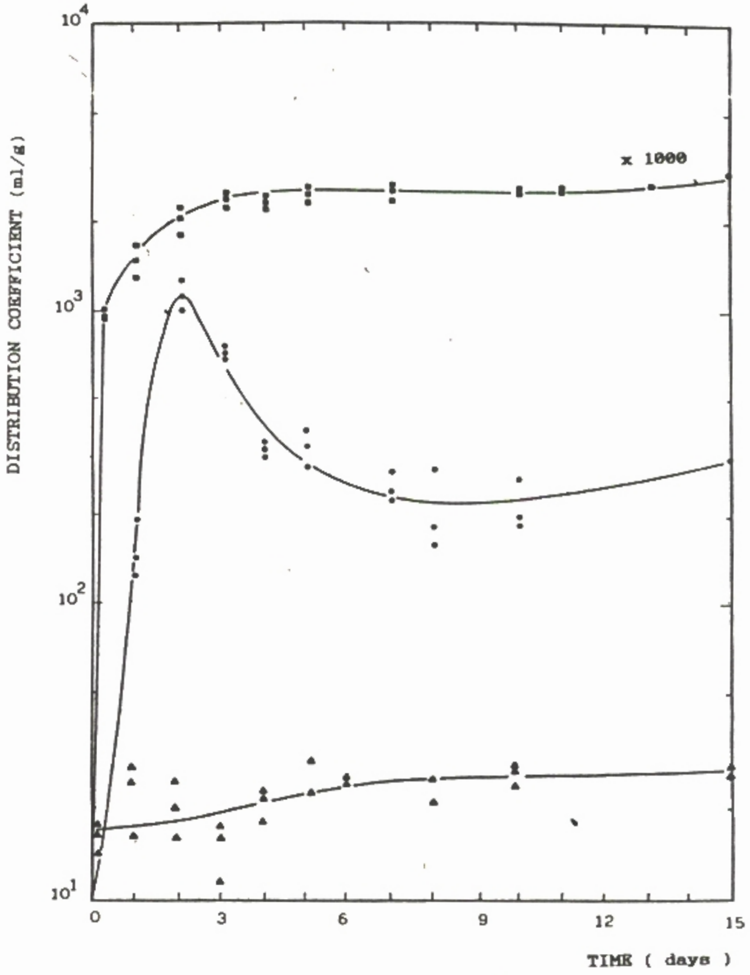

Figure 3. Distribution coefficients (Kd) as a function of the time of contact for Cs ▲, Co ● and Th ■.

According to Chester, cited in Madruga[7], the cobalt would be absorbed in the form of a monovalent cation $Co(OH)^+$. Sorathesn[10] states that cobalt absorption is mainly due to its affinity with organic matter. For pH 6 to 9, cobalt can react with the humic and phulvic acids and may even precipitate. This phenomenon prevails in the Pinheiros River, as can be seen from Figure 1 and Figure 2, where the affinity of the sediment by the cobalt increases with the increase of pH and does not seem to be affected by the sediment weight/volume of the solution ratio studied.

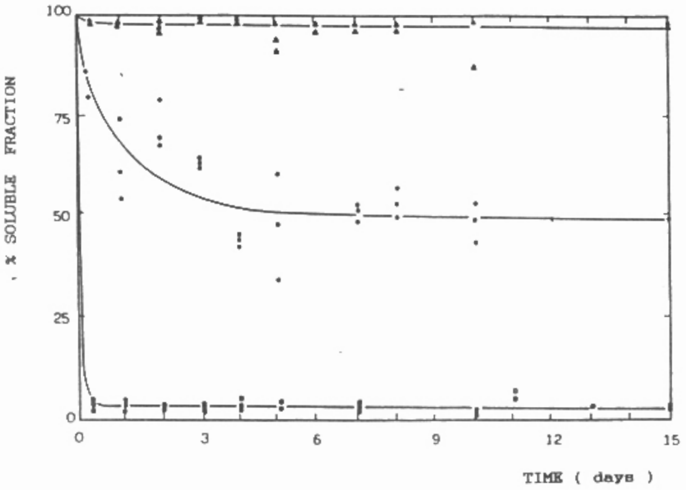

Figure 4. Percentage of radionuclides present in the soluble form as a function of the time of contact for Cs ▲, Co ● and Th ■.

For the thorium, the pH effect was also considerable, since the Kd increased from $(147\pm9)10^3$ ml/g for pH 4 to $(2.33\pm0.09)10^6$ ml/g for pH 8. No effect was observed for the Kd values obtained in the experiment carried out with aeration of N_2 bubbling. The time of contact study showed that the equilibrium between the thorium concentration in the water and sediment was achieved after the first hours of contact.

Due to the large Th^{4+} charge/ionic radius ratio, it can be easily hydrolyzed at pH > 3. In the soluble form, $Th(OH)^{+4}$ form complexes with humic and phulvic acids so stable as those formed with hydroxides and carbonates. In this process the pH affects the Th hydrolysis and the dissociation of acids present in the organic macromolecules[14]. Therefore, the higher the pH, the greater the probability of Th retention by the sediment.

Conclusions

Summarizing, the results obtained can be better understood if the severe pollution present in the Pinheiros River is considered. This pollution may cause the formation of a variety of complexes and precipitates which prevent the mobilization of the convention pollutants and the radionuclides, interfering in the retention of these elements by the sediment. Therefore, the results obtained experimentally for the Kd confirm the predictions that: the cesium is slowly retained by the sediment along the Pinheiros River; the cobalt is an unstable element, its retention by the sediment being affected by variation in the pH values; and finally, the thorium is almost completely retained in the vicinity of the discharge point.

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