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Interactions between Thorium and Humic Compounds in Surface Waters*

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As a result of their close chemical similarities to Pu(IV) and trivalent transuranics (Am, Cm), thorium and rare earth elements can be useful 'chemical analogues' for the study of interactions of critical radioactive nuclides with the near- and far-field of nuclear waste repositories. Utilizing a thorium–rare earth deposit [Morro do Ferro (MF)] in the State of Minas Gerais, Brazil, a site with unusual high levels of natural radioactivity (1–3 mR/h), a systematic investigation is being carried out to obtain fundamental information about the environmental behavior of these transuranium analogues [1–4]. This paper reports data on Th and dissolved organic carbon (DOC) concentrations in surface waters from this site, which confirm the importance of humic compounds, especially humic acids, on thorium 'solubilization'. Although humic compounds have been identified as efficient complexing media for polyvalent metal ions for more than twenty years, their influence on actinide mobilization is little known. The progress achieved so far has been reviewed by Choppin and Allard [5].

Experimental

Water Sampling and Analysis

Water samples were collected in a near-surface mine gallery and in a trench, located in the region of highest radioactivity of the deposit. This zone is mainly composed of a deeply weathered stockwork of hydrothermally altered alkalic igneous rocks, anomalously enriched in thorium and rare earth elements (> 10 000 ppm) [6]. Immediately after collection, the water samples were filtered through a 0.45 μm membrane and the filter kept for sediment analysis. An aliquot of the filtrate (10 to 20 l) was acidified and stored for Th analysis by α-spectroscopy. A second aliquot (20–40 l), preserved with NaN_3 against bacterial growth, was stored for DOC analysis and sequential ultrafiltration, using stirred pressure cells (400 ml capacity) and flat membranes with different molecular weight cuttoff limits (Amicon XM-300, PM-10/UM-10 and YM-2). A separation flow-sheet is shown in Fig. 1, details of the analytical procedure for Th determination by α-spectroscopy are presented elsewhere in this volume [7]. Analysis of DOC was performed by means of a Total Carbon Analyser (Beckman Mod. 915B).

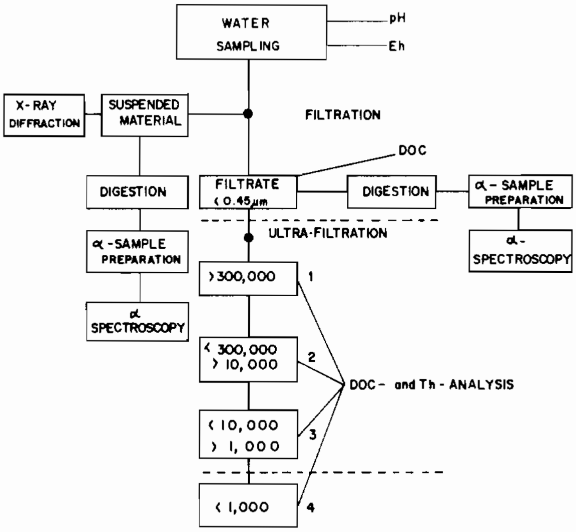

Fig. 1. Flow-sheet of the procedure for ultrafiltration and analysis of thorium and DOC.

Distribution of Thorium Between Water and Sediments

50 mg aliquots of a composite sample of particulate material, obtained by filtration of ground waters, were equilibrated by shaking in polyethylene bottles for 24 h with 10 ml of radioactively labelled solutions (^{234}Th) of commercial humic acid (Aldrich) of different concentrations and pHs. The aqueous phase was then separated by centrifugation and membrane filtration (0.45 μm) and the non-adsorbed ^{234}Th fraction determined by γ-counting of a solution aliquot. Similar experiments were performed with ultraconcentrates from MF waters.

Results and Discussion

Thorium and DOC Concentrations in Surface Waters (SW)

Table I summarizes Th isotopic data and DOC concentrations determined in natural SW from the MF region, as well as in ultraconcentrates (UC) of different molecular weight exclusion limits obtained

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TABLE I. Concentrations/Activities of Th Isotopes and DOC in Surface Waters from the Morro do Ferro Region and in Ultraconcentrates (sample code: GA = percolation water from the mine gallery; TR = water from a trench; A: <0.45 μm; B: >300 000 M_r; C: 300 000 > M_r > 10 000; D: 10 000 > M_r > 1000; E: <1000 M_r)

Sample	^{232}Th		^{228}Th		DOC	
	[μg/l ± (σ)]	[% T][a]	[Bq/l ± (σ)]	[% T]	[mg/l ± (σ)]	[% T]
GA1-A	17(1)	100	2.4(0.1)	100	12(2)	100
GA1-B	172(6)	69	20.0(0.3)	57	62(6)	19
GA1-C	82(4)	26	14.0(0.2)	34	92(3)	24
GA1-D	12(1)	5	1.06(0.02)	3	68(3)	22
GA1-E	<0.08	<1	0.12(0.01)	6	5.5(0.7)	35
GA2-A	14(1)	100	1.8(0.1)	100	13(2)	100
GA2-B	261(10)	53	32.2(0.4)	44	111(3)	14
GA2-C	205(9)	44	32.0(0.4)	46	201(8)	27
GA2-D	<2.4	<1	7.5(0.3)	4	163(2)	10
GA2-E	0.38(0.06)	3	0.120(0.006)	6	11(3)	49
GA3-A	15(1)	100	2.4(0.1)	100	10.0(0.2)	100
GA3-B	168(7)	56	21.0(0.3)	48	96.5(0.4)	16
GA3-C	138(9)	44	21.1(0.3)	46	258(3)	40
GA3-D	<2.6	<1	0.93(0.03)	1	98(2)	12
GA3-E	<0.02	<1	0.054(0.003)	5	5.7(0.3)	32
GA5-A	0.13(0.02)		0.030(0.002)		3.8(0.4)	
GA5-B	<0.9		0.28(0.02)		7.0(0.4)	
GA5-C	<2.2		0.29(0.02)		5.5(0.4)	
GA5-D	<0.8		0.43(0.02)		15.5(0.9)	
GA5-E	<0.06		0.017(0.006)		N.A.[b]	
TR1-A	1.4(0.2)	100	0.34(0.02)	100	3.8(0.2)	100
TR1-B	40(6)	75	5.0(0.1)	21	18.1(0.9)	8
TR1-C	4.3(1.5)	15	5.1(0.1)	45	56(2)	47
TR1-D	<0.7	<1	1.96(0.06)	15	37.0(0.6)	32
TR1-E	0.09(0.03)	10	0.067(0.003)	19	N.A.	
TR448-A	12.5(0.5)		0.88(0.04)		8.2(0.2)	
TR469-A	<0.05		0.032(0.002)		6.1(0.2)	
TR485-A	5.2(0.3)		0.32(0.02)		6.0(0.5)	
TR490-A	5.6(0.3)	100	0.39(0.02)	100	N.A.	100
TR490-B	<2.2	<1	0.39(0.02)	6	11.6(0.3)	5
TR490-C	11(2)	15	1.53(0.05)	11	21(2)	6
TR490-D	87(11)	81	6.6(0.6)	32	223(3)	32
TR490-E	0.08(0.04)	4	0.16(0.02)	51	6.0(0.2)	57

[a] [% T] = percentage of the total. [b] N.A. not analysed.

from these waters. Highest concentrations of ^{232}Th (and activities of ^{228}Th) were analysed in waters with high DOC content. These concentrations seem to be the highest ever reported for natural waters [8] and are greater by a factor of about 170 (>2500 in some of the ultraconcentrates), when compared with the solubility of $Th(OH)_4^0$ (0.1 ppb), the predominant Th species in pure water of pH > 5 [8]. Similar high concentrations of Th to those of the ultrafiltration (UF) fractions were determined in leachates of soils and weathered ore material from the same region of the MF, with solutions of 10 ppm of commercial humic acid [3]. These observations about the very high solubility of Th in the presence of humic compounds are in accordance with the high stabilities of Th–humate complexes ($\log \beta_1$ [HA]: 10.74–13.18 [9]), which are very similar to those of strong synthetic complexants (e.g. $\log \beta_1$ NTA: 12.4 [10]).

The fact that thorium concentrates together with a portion of the DOC mainly in the >1000 M_r UF-fraction (see Table I and Figs. 2a, b), excludes significant 'inorganic' complexing of Th and may be caused, in part, by the relatively low concentrations of potential inorganic ligands in these waters ($\Sigma F \leqslant 0.5$ ppm; $\Sigma PO_4 \leqslant 0.1$ ppm; $\Sigma SO_4 \leqslant 0.5$ ppm; $\Sigma CO_3 \leqslant 2$ ppm; pH = 3 to 6; E_h = 530 to 580 mV) and also of other competing major cations ($\Sigma Fe \leqslant 0.03$ ppm; $Al \leqslant 0.01$ ppm; $Ca \leqslant 5$ ppm; $Mg \leqslant 0.3$

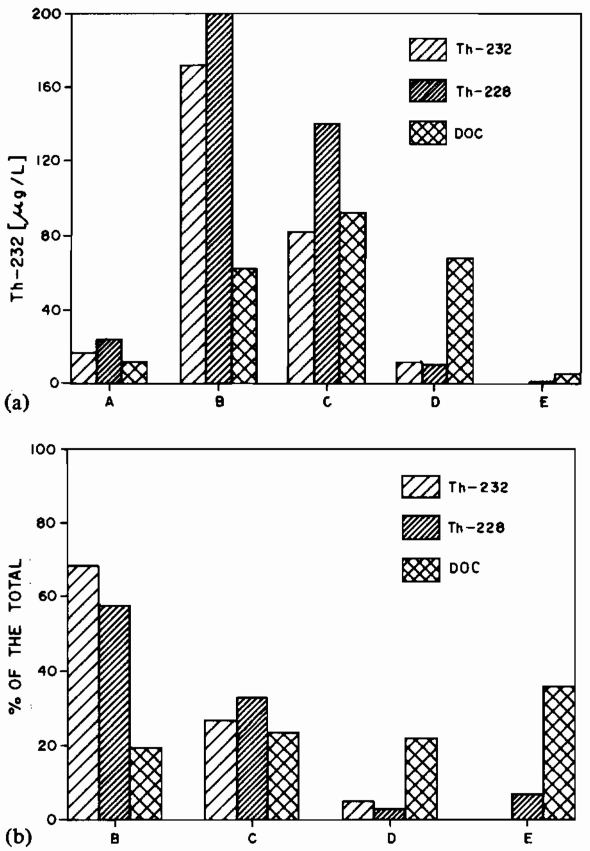

Fig. 2. (a) Concentrations/activities of Th isotopes and dissolved organic carbon (DOC) in a surface water sample (GA1) and in ultraconcentrates from this sample. (Letters after sample number refer to molecular weight cutoff limits. A: <0.45 µm; B: $>300\,000\ M_r$; C: $300\,000 > M_r > 10\,000$; D: $10\,000 > M_r > 1000$; E: $<1000\ M_r$; concentrations of DOC in [mg/l] and activities of ^{228}Th in [Bq/l × 10].) (b) Relative distribution (% of the total) of Th isotopes and DOC in ultraconcentrates from sample GA1. (Meaning of the letters as in Fig. 2a.)

ppm; Mn $\leqslant 0.2$ ppm). As theoretically predicted by Langmuir and Herman [8], 'organic' complexation can predominate over 'inorganic' by orders of magnitude, even when the concentrations of organic ligands are low as compared with inorganic ones. This may be expected also for high molecular weight organic ligands such as HA and FA, however, at low concentrations of these compounds (e.g. in deep ground waters), adsorption of Th organic complexes on solid/liquid interfaces can oppress the 'solubilizing' effect.

Figure 2 and Table I show also that a considerable part of the DOC, apparently less effective in Th complexing, is concentrated in the $<1000\ M_r$ fractions, and whose chemical identity has still to be investigated: low molecular weight (LMW) fulvic acids (FA), LMW decomposition products of soil organic matter, citric and oxalic acid are the likely compounds. Excluding this portion of DOC and plotting Th concentrations against 'humic carbon' (operationally defined as [DOC] $>1000\ M_r$), correlation ($r = 0.92$) between both parameters is indicated (Fig. 3). From the above it becomes evident that direct plotting of 'total' DOC concentrations of the waters against [Th] would be less meaningful.

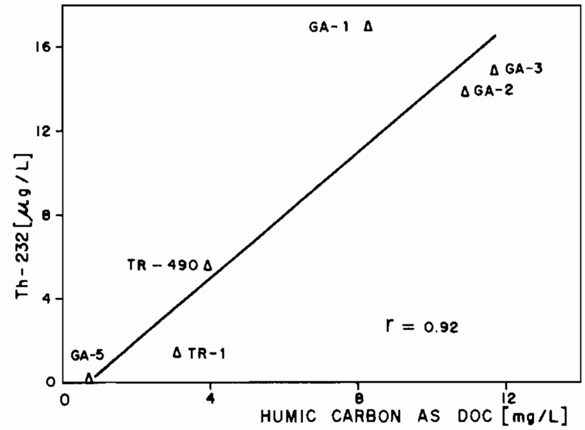

Fig. 3. Relationship of the concentration of Th(IV) to 'humic carbon' (DOC > 1000 M_r) in surface water from the Morro do Ferro region.

It is interesting to mention that the original surface waters containing Th organic colloids, as well as their UC, are very stable when kept under natural pHs (4 to 6) and properly preserved with NaN_3 (10 ppm). Acidification (pH <2; HCl) of the UC $>1000\ M_r$ but, especially, those of $>300\,000\ M_r$, causes precipitation of brown humic acids (HA) and coprecipitation of thorium. In UC of similar DOC content, partitioning of thorium during precipitation of HA is more pronounced in the $>300\,000\ M_r$ fraction (distribution ratio [solid/liquid]: 3.0) than in the 10 000 to 300 000 M_r fraction (ratio: 1.3), indicating a higher content of HA as compared to FA in the first fraction. Although the 'actual' M_r ranges of HA are still a matter of discussion, it can be mentioned that up to 70% of the total organic matter in lake sediments was determined in the HA fraction $>100\,000\ M_r$, by means of a different method [11].

Humic acids isolated from the $>300\,000\ M_r$ fraction showed spectroscopic patterns and chemical composition (54.2% C; 5.5% H; 3.5% N; 37% O) similar to those reported for soil humic acid [12].

The Influence of Humic Compounds on the Sorption of Thorium

To verify the influence of HA complexing on adsorption/desorption equilibria, which are of primary importance for predicting the migration behavior of a nuclide, laboratory K_D experiments were performed with clay material, representing particulate matter from ground water of the MF region. This material was mainly composed of illite, kaolinite and gibbsite and minor portions of goethite. To simulate as closely as possible 'natural' conditions (e.g. the competing influence of other cations (REE), which are much more abundant than Th in the MF region and/or the other inorganic or organic complexants) HA solutions of different concentrations were prepared by dissolving HA in aliquots of the UF $<1000\,M_r$ (sample GA4-E, 7.5 ppm DOC) considered to be essentially 'free' of humic acids. The pH of the solutions was adjusted to the natural pH of the percolation waters (pH 4 to 5). Preliminary experiments have shown that in the pH range of 4.2 to 9.6 sorption of thorium by the particulate matter is nearly independent of pH [13]. Lower pH causes precipitation/adsorption of HA with a 40% loss of the 'dissolved' Th, present in the solution phase at higher pH (>4.2). This is worthwhile to mention as it indicates, once more, the predominating effect of HA on Th(IV) adsorption/complexation.

Figure 4(a) shows, as is usually presented in a log–log graph, the relationship of the experimentally determined K_D values (ml/g) to HA concentrations (as DOC (mg/l)). An inverse correlation is obtained ($r = -0.93$), indicating complexation of Th(IV) by 'dissolved' HA and/or competition between Th(IV) and HA for sorption sites on the particulate material (formation of clay–humate complexes [14]). As the ^{234}Th tracer was present in 'infinite' low concentration as compared to the complexant (HA), the second mechanism is more convincing. This is supported by laboratory observations that 100 mg of suspended material can adsorb quantitatively at least 500 μg of HA from the ultrafiltrate, observable by a complete decoloration of the initially brown solution. This process causes also quantitative loss of Th tracer from solution. Under the experimental conditions used for the determination of K_D (see Fig. 4), HA concentrations of <10 ppm result in 'infinite' high K_D. Replotting the data in a log–linear graph, 'saturation' of clay binding sites with HA at higher concentrations (>90 ppm; >0.9 mg of HA per 10 mg of suspended material) is indicated (see Fig. 4(b)). Figure 4(a) includes data points of K_D determined with UF of different M_r cutoff limits. (In this series commercial HA was not added.) Under the necessary restrictions imposed by having only 4 data points available until now, the K_D determined with UF (GA2-B, GA2-C) containing the major fraction of HA (range >10 000 M_r) are similar to those obtained with commercial HA, confirming indirectly the predominance of Th complexation by HA in surface waters of the MF region.

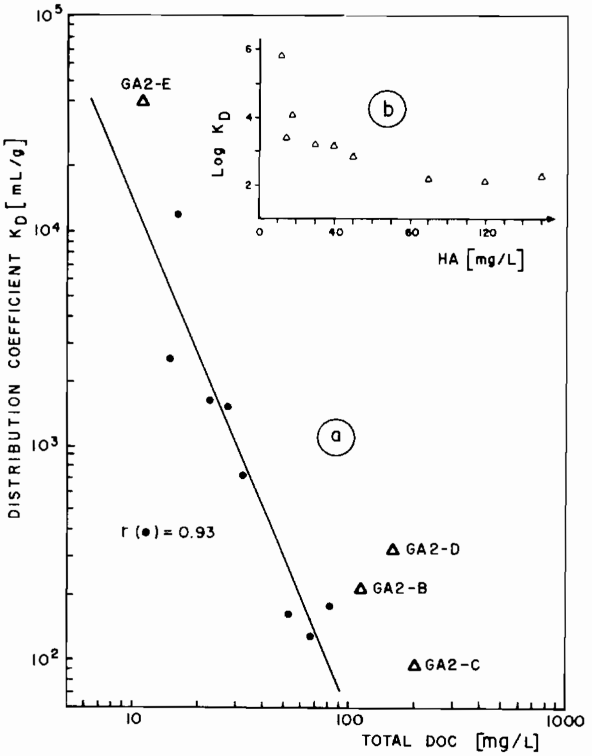

Fig. 4. (a) Relationship of the distribution coefficient K_D to the concentration of humic acids expressed as total DOC (HA as DOC (mg/l) + 7.5 mg/l of DOC) and to the concentrations of DOC in ultrafiltrates of sample GA2. (Experimental conditions: equilibrium time 24 h, ambient temperature 25 °C, solvent for HA: 10 ml of sample GA4-E (7.5 mg/l DOC), particulate matter: 10 mg.) (b) Relationship of K_D to humic acid concentration (mg/l) in a log–linear graph.

Similar relationships between K_D and DOC have been observed for Th(IV) and Pu(IV) in North American lake sediments (Wahlgren and Orlandini [15]) and for Pu(IV) in laboratory experiments by Nelson *et al.* [16] and others.

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