Pu isotopes in surface and subsurface waters

M.H. Dai(1), J.M. Kelley(2), K. O. Buesseler(1), R. A. Belastock(1), D. J. Repeta(1), T. C. Maiti(2), J.F. Wacker(2) and J. E. Andrews(1) ((1)MS 25, WHOI, Woods Hole, MA 02543; (2)PNNL, PO Box 999, Richland, WA 99352)

A. Introduction

This study is designed to study the association of plutonium with dissolved organic complexes in surface and subsurface waters. To investigate this, we are developing techniques to sample and identify aquatic organic constituents, and to measure the Pu isotopes associated with different fractions of organic matter. In this presentation, we are focusing on: 1) sampling techniques to minimize contamination and artifact formation; 2) to establish mass balances of cross-flow ultrafiltration(CFF) that represents the major fractionation technique in this study; 3) application of thermal ionization mass spectrometry (TIMS) for the detection of Pu isotopes in different size fractions (dissolved, colloidal and particulate phases) and in various oxidation states; 4) preliminary results on Pu isotopes in various surface and ground waters including the Savannah River Site (SRS) and the Hanford Site (HS). TIMS is not only providing us the sensitivity (fg level) needed to make measurements on small samples at ambient fallout levels and in the far field migration of groundwater Pu; it also provides the ability to use isotopic ratios to distinguish between fallout and other possible sources.

B. Methods

The prefiltered water samples (0.2 µm Nuclepore) were processed with a CFF system equipped with Millipore Prep-scale CFF 1 kD membranes in order to separate the colloidal fraction from the dissolved phase. Detailed CFF processing procedures have been described in Dai *et al.* (1998). Size fractionated samples were then radiochemically purified and Pu isotopes were analyzed using a three stage TIMS. The final efficiency of TIMS measurements was 1-3 %.

C. Performance of CFF

C.1. Blank

Sample	Vol(liter)	Concentration (fg/l). ^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Q-water 1	4	0.01985	0.00997	0.01001	0.00804
Q-water 2	4	0.069477	0.00399	0.004	0.00301
Q-water 3	4	0.009925	0.00598	0.00701	0.00502
Q-water 4	4	0.009925	0.00698	0.005	0.00502
CFF blank (Retentate)	2	0.198505	0.09967	0.1201	0.00804
CFF blank total	4	0.008933	0.00399	0.002	0.00402

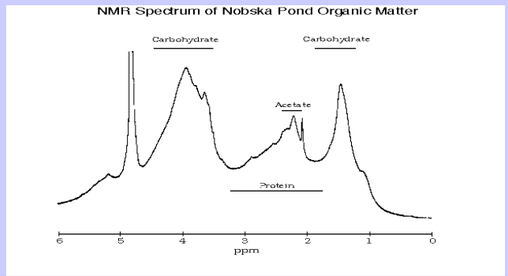
C.2. CFF Mass Balance

Size fractionated ^{239}Pu and the CFF mass balance

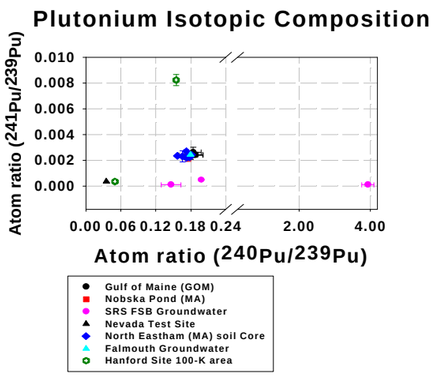
	Dissolved (< 1 kD) dpm/1000kg	% of Total	Colloidal (1 kD - 1 µm dpm/1000kg	% of Total	Particulate (> 1 µm) dpm/1000kg	% of Total	CFF Recovery (%)
GOM (1m)	0.2205	92.0	0.0099	4.1	0.0094	3.9	99
GOM (15 m)	0.1462	58.5	0.0206	8.2	0.0832	33.3	99
GOM (37m)	0.2106	85.7	0.0165	6.7	0.0187	7.6	87
GOM (65 m)	0.3492	92.1	0.0149	3.9	0.0152	4.0	110
GOM (200 m)	0.4442	88.3	0.0142	2.8	0.0447	8.9	103
GOM (250 m)	0.4512	85.6	0.0003	0.1	0.0758	14.4	96
Nobska Pond	0.04259	0.20	21.3544	99.8	N/A	N/A	110
Falmouth groundwater	0.00105	10.1	0.00592	57.1	0.00341	32.9	71

In light of our previous studies on Th isotopes and other trace elements, we carefully evaluated two possible CFF artifacts, namely the system blank and mass balance issues. After careful cleaning, we achieved a very low blank for all of the Pu isotopes (total CFF blank < 0.008 fg/l for ^{239}Pu and < 0.004 fg/l for ^{240}Pu), and the CFF mass balance for Pu was within (100+/-10%), indicating that no significant losses or contamination occurred. Furthermore, the isotope ratio (^{240}Pu/^{239}Pu) remained constant in all fractions suggesting that no isotopic fractionation occurred during CFF processing. Also shown in the above table is the size fractionated Pu. In seawater, the majority of Pu was found in the low molecular fraction (<1 kD). Colloidal Pu varied from 8 % of the total in surface waters to <1% in the deepest (250m) seawater sample. In contrast, in a freshwater pond at Woods Hole, all of the Pu was found associated with the high molecular weight fraction, most likely due to complexation with organic material. In the groundwater in Falmouth, colloidal Pu represents 57% of the total Pu.

D. Characterization of the high molecular weight organic matter



The above figure shows the proton NMR spectrum of the >1kD dissolved organic matter (DOM) fraction from Nobska Pond. This fraction of DOM was found to bind with 99% of the Pu in the solution. Based on the NMR spectrum, major classes of biochemicals in the sample include polysaccharides and proteins, with smaller contributions from lipids. Humic substances, as determined by aromatic resonances, are nearly absent from our sample. Monosaccharide analyses shows the presence of seven major neutral sugars: glucose, galactose, mannose, xylose, rhamnose, arabinose, and fucose in approximately equimolar abundances. The potential metal binding properties of this polymer are currently under investigation.



E. The isotopic composition indicates Pu in GOM, Falmouth goundwater and Nobska pond at Woods Hole originated from global fallout. The Hanford site has a local Pu source while the abnormal Pu isotopic composition at SRS indicates sources have not been fully unidentified.

F. Preliminary results on Pu isotopes in the groundwater of Savannah River Site and Hanford Stie

F.1 SRS F-area Seepage Basin

Well #	^{240}Pu/^{239}Pu atom ratio	error(+/-)	^{239}Pu fg/l	error(+/-)	^{240}Pu fg/l	error(+/-)
FSB103C	0.1460	0.0170	0.09	0.00	0.014	0.002
FSB78	3.9300	0.1700	3.59	0.36	14.16	1.52
FSB92D	0.1981	0.0007	75.8	1.07	15.06	0.22

Results from unfiltered groundwater samples taken in August 1997 at F area Seepage Basin showed ^{240}Pu/^{239}Pu ratios ranged from 3.9 to 0.18, signifying various sources at this one site. The excessively high ratio at well FSB 78 may be related to the decay of Cm-244 and Cm-243. This high ^{240}Pu/^{239}Pu ratio was confirmed in our recent study in May 1998. Oxidation speciation study showed even higher enrichment of ^{240}Pu (^{240}Pu/^{239}Pu=11.42) at higher valence states (V, VI) in the dissolved fraction (< 1 kD). Further data interpretation is in progress.

F.2 Hanford 100-K area

Preliminary results for Pu isotopic composition in the ground water samples taken from Hanford Site 100-K area in Oct. 1997

Well#	^{240}Pu/^{239}Pu atom ratio	error (+/-)	^{241}Pu/^{239}Pu atom ratio	error (+/-)	^{239}Pu fg/l	error (+/-)	^{240}Pu fg/l	error (+/-)
199-K-107A	0.081	0.017	N/A	N/A	0.150	0.013	0.012	0.003
199-K-30	N/A	N/A	N/A	N/A	0.155	0.007	0.006	N/A
199-K-106A	N/A	N/A	N/A	N/A	0.026	0.002	0.002	N/A
199-K-28	0.0498	0.0038	N/A	N/A	1.567	0.045	0.078	0.006
199-K-27	N/A	N/A	N/A	N/A	0.222	0.011	0.041	N/A
199-K109A	0.1549	0.0021	0.0082	0.00044	1.870	0.035	0.291	0.007

Pu isotopes were detected in groundwater from the 100-K area for the first time samples by using TIMS technique which is much more sensitive than the alpha spectroscopy analytical method typically used previously. The likely source of the Pu is past operations at the K-Basins where 2,100 metric tons of spent nuclear fuel is stored in concrete pools of water. The high ^{241}Pu/^{239}Pu in the well#199-K109A likely signified that there were leaks of the material from N-reactor. This might relate to the fact that the K-East reactor basin is currently being used to store irradiated fuel from the N-reactor. The isotopic ratio in other wells reflect the K-reactor signals, possibly mixed with fallout signials.

G. Summary

- *CFF performance*
  - *– Reasonable mass balance for Pu isotopes*
  - *– No isotope fractionation*
  - *– No observable blank from the CFF system.*
- *Colloidal Pu (% of total dissolved)*
  - *– 0-8% in GOM, equivalent to the particulate fraction in surface*
  - *– 99% in a fresh water pond. The organic matter associated with Pu in this Pond is comprised of specific biochemical with very low amounts of humic materials.*
  - *– 57% in Falmouth groundwater*
- *^{239}Pu/^{240}Pu*
  - *- in GOM, Nobska Pond & Falmouth groundwater reflect global fallout*
  - *- At SRS : non-weapon or reactor signals, **decay from Cm-243 and Cm-244??***
  - *- At Hanford Site 100-K area: shows for the first time detectable Pu isotopes. Different isotopic ratio in various wells might indicate leaks from the wastes originated from different reactors*

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