

Fig. 5. Percent Removal of Americium by Filter in Several Experiments

The left-hand bar with vertical stripes shows the particulate formation of americium in Hudson River water. The particulate formation of americium in Ob River water is shown in the bar with horizontal stripes. The remaining two bars show particulate formation of americium in UV-irradiated Ob River water. The right-hand most bar is for a 1.0 micron filter; all the other bars are for a 0.2 micron filter.

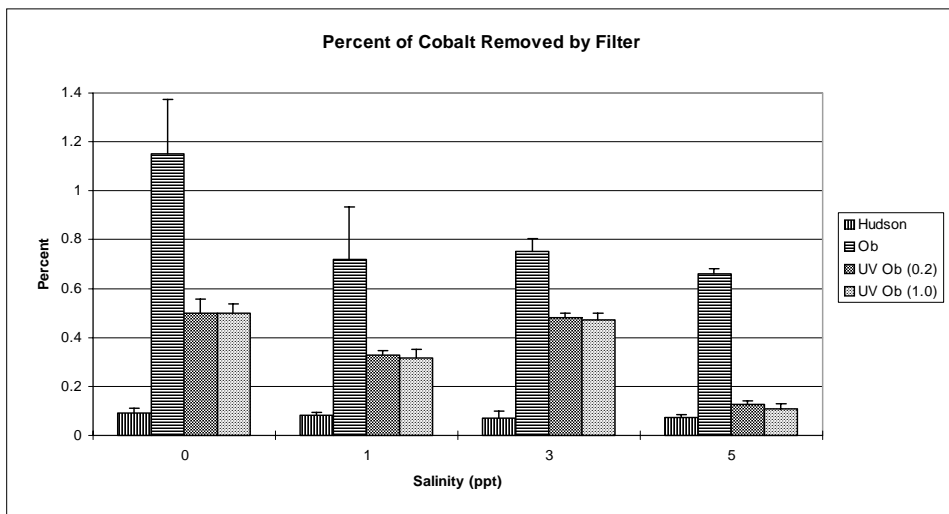


Fig. 6. Percent Removal of Cobalt by Filter in Several Experiments

The left-hand bar with vertical stripes shows the particulate formation of cobalt in Hudson River water. The particulate formation of cobalt in Ob River water is shown in the bar with horizontal stripes. The remaining two bars show particulate formation of cobalt in UV-irradiated Ob River water. The right-hand most bar is for a 1.0 micron filter; all the other bars are for a 0.2 micron filter.

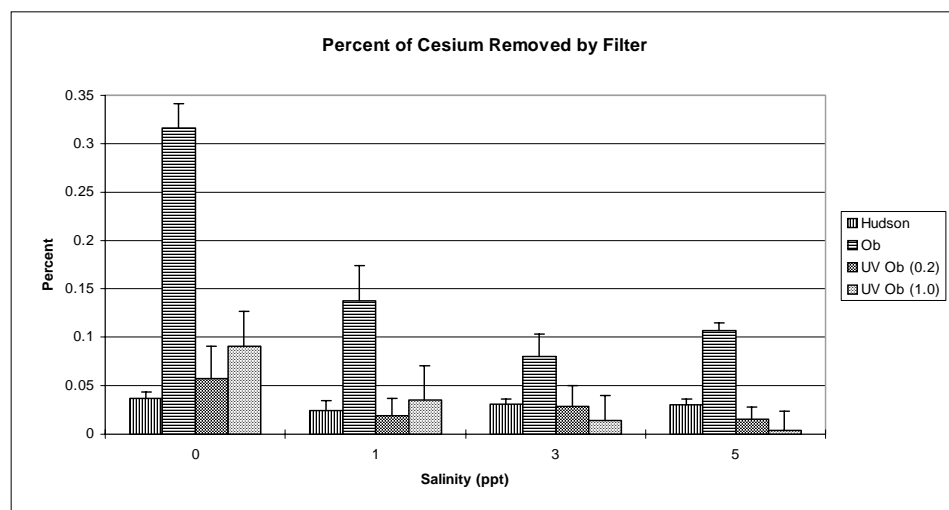


Fig. 7. Percent Removal of Cesium by Filter in Several Experiments

The left-hand bar with vertical stripes shows the particulate formation of cesium in Hudson River water. The particulate formation of cesium in Ob River water is shown in the bar with horizontal stripes. The remaining two bars show particulate formation of cesium in UV-irradiated Ob River water. The right-hand most bar is for a 1.0 micron filter; all the other bars are for a 0.2 micron filter.

ages of removal were down by a factor of 10 in Hudson River water compared to Ob water.

Following the suggestions of Sholkovitz, it is presumed that the difference in dissolved organic carbon material is responsible for the different behavior of the water from the two rivers in regard to americium ions. The water from the Ob River is quite yellow in color and is presumed to contain large amounts of dissolved organic matter.

The important role played by dissolved organic matter seems to be confirmed by the studies of UV-irradiated water. Irradiation of the water, which should oxidize the organic matter, completely removes the yellow color of the river water. It also leads to a sharp increase in removal of americium by filtration, over 80% even at 0 salinity as seen in Fig. 5.

This same qualitative increase at 0 salinity was found by Hudson Rhoditi of the Stony Brook Marine Radioecology Laboratory in his (unpublished) experiments on americium in freshwater Hudson River water. In his experiments, irradiation of the freshwater Hudson River water led to sharply increased removal of americium by filtration. On the other hand, his UV irradiation of South Hampton seawater (where dissolved organic matter is believed small) made no significant change in the removal of americium by filtration.

Cobalt with a principal oxidation number of +2 and cesium with a valence of +1 did not show the same behavior as americium. Indeed, there was less removal of these metal ions by filtration when the salinity was increased, which is the opposite of the behavior found for americium. Also, interestingly, there was the same reverse behavior in UV-irradiated Ob water; whereas americium had its filtration removal greatly increased, cobalt and cesium had their filtration removal decreased. Presumably, the low polarizing power of cesium and cobalt makes them unable to compete with the sodium and magnesium ions which are present.

The qualitative ideas regarding polarizing power of the ions, and therefore the likelihood of the ions forming

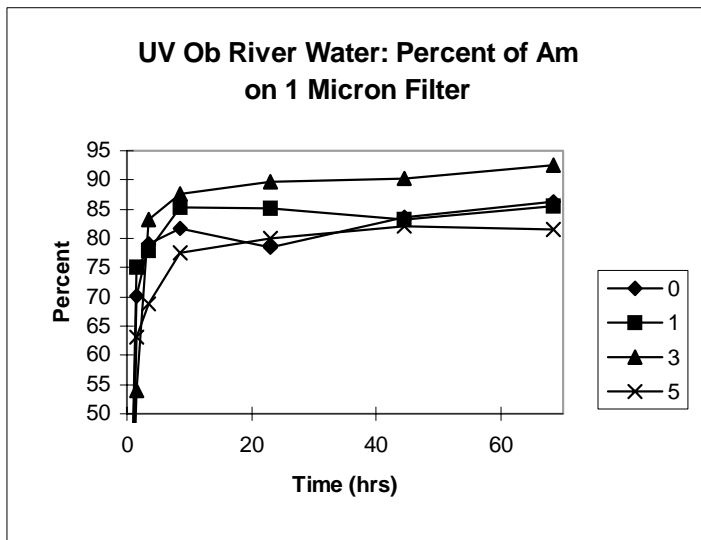


Fig. 4a

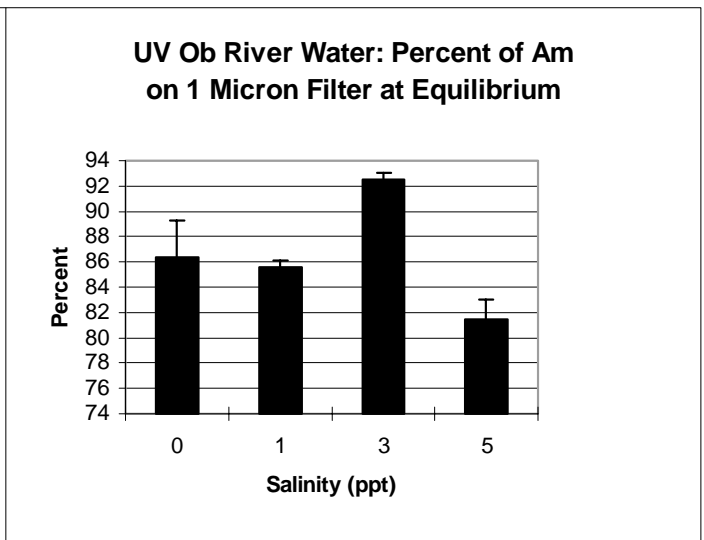


Fig. 4b

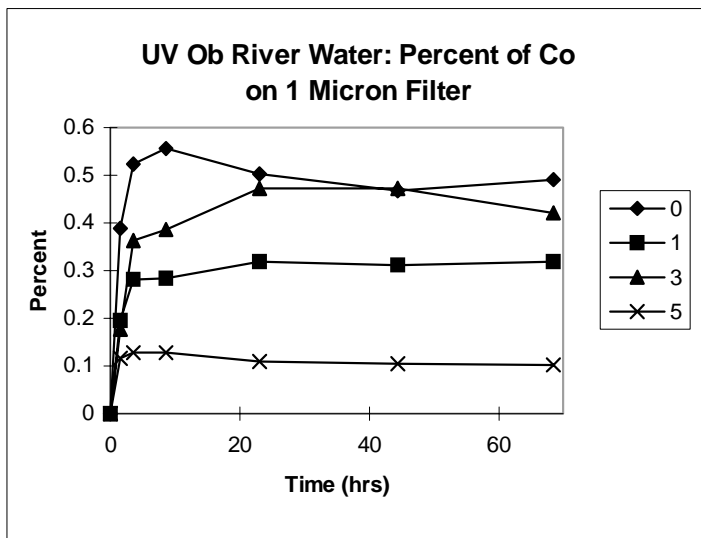


Fig. 4c

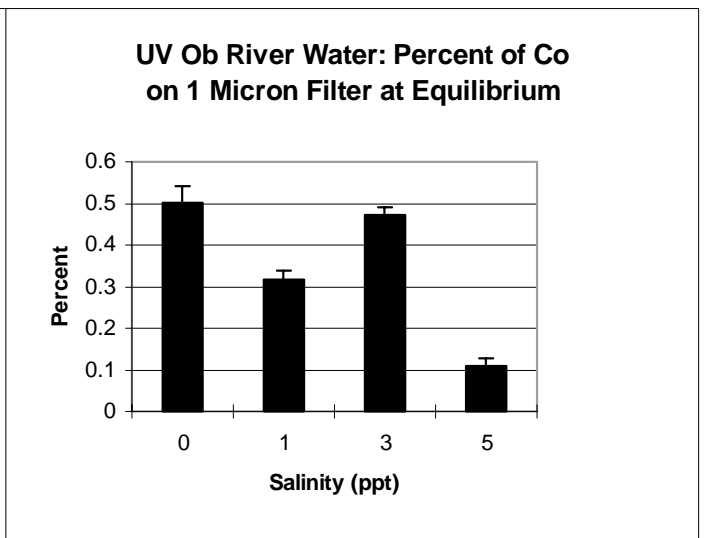


Fig. 4d

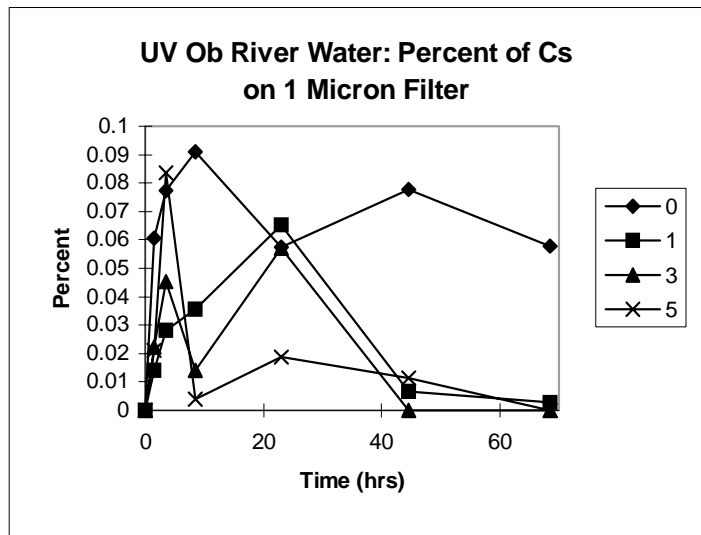


Fig. 4e

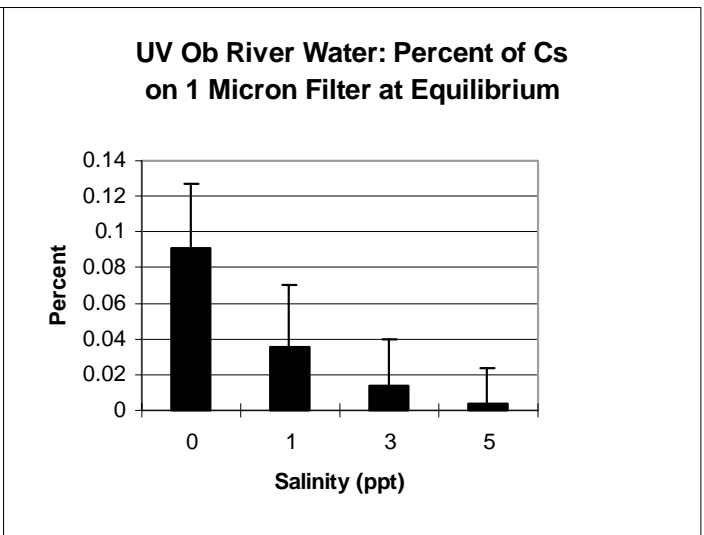


Fig. 4f

Fig. 4. Data from UV OB River Water Experiment (1 Micron Filter)

The three graphs on the left show the percentages of the metal ions caught on the filter as functions of time. The four curves correspond to the four salinities 0 ppt, 1 ppt, 3 ppt, and 5 ppt. Where the time-curves become flat is the equilibrium point; the percentages at the equilibrium time are used to plot the bar graphs at the right.

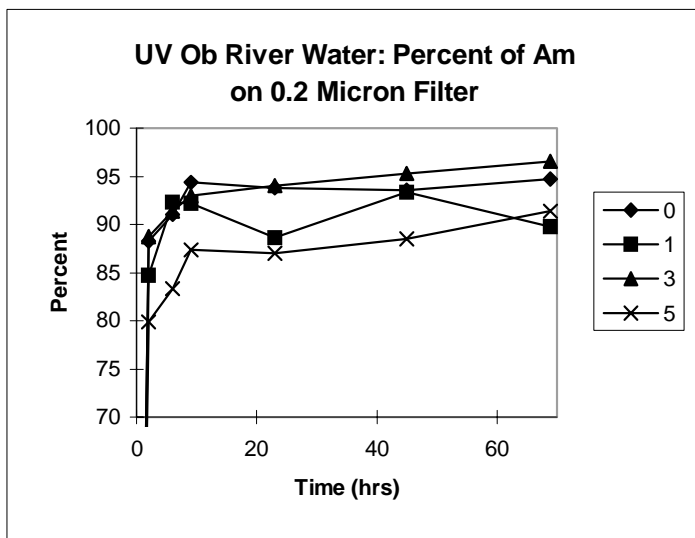


Fig. 3a

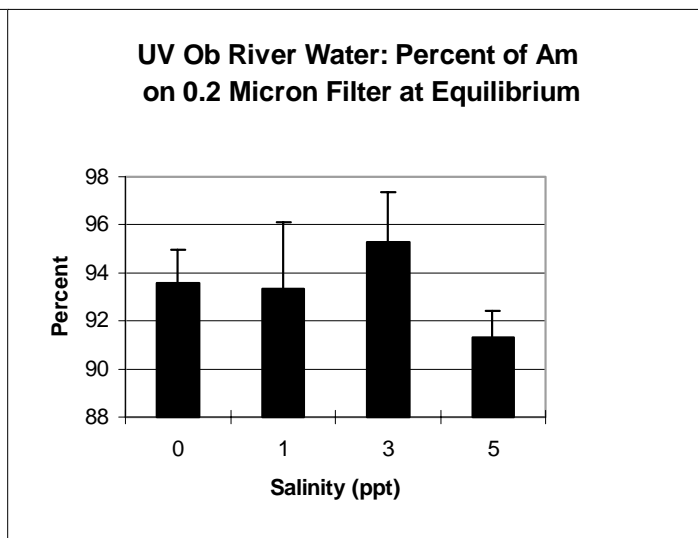


Fig.3b

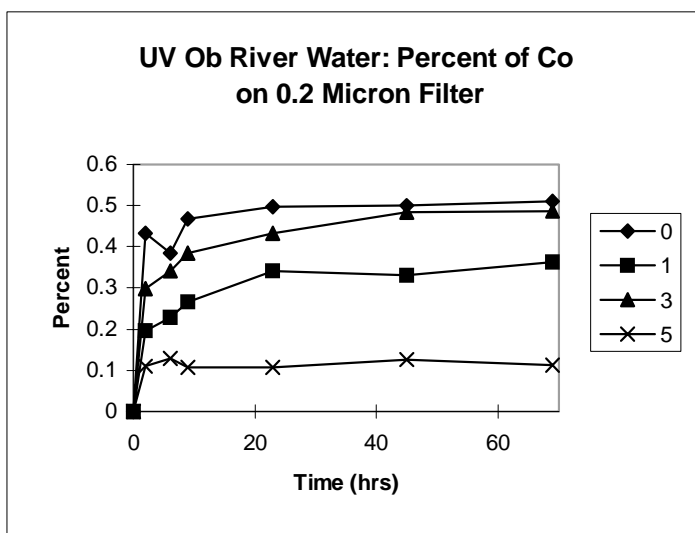


Fig. 3c

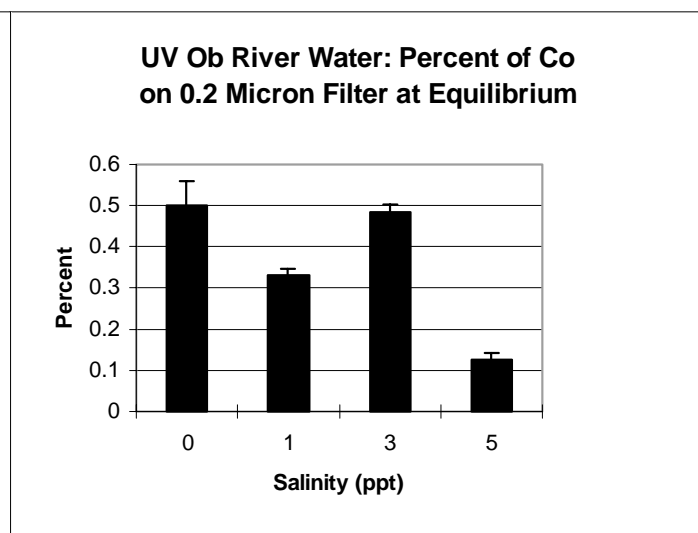


Fig. 3d

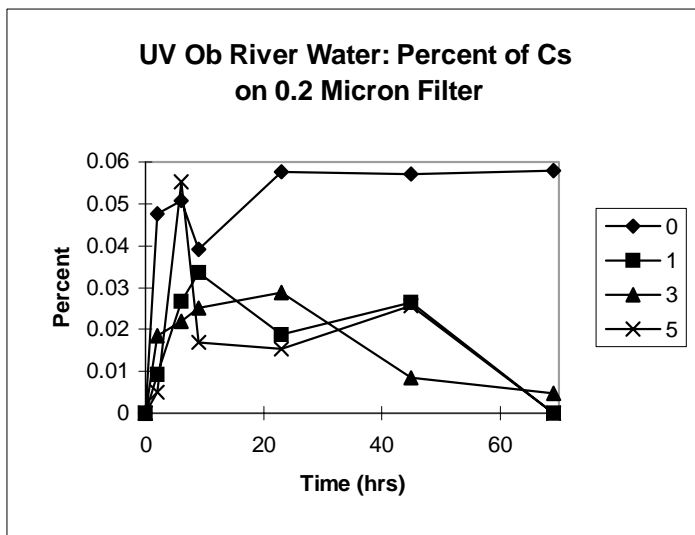


Fig. 3e

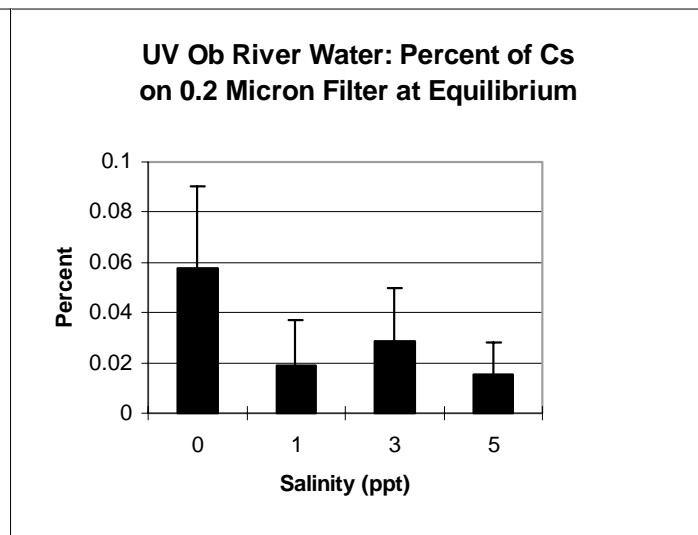


Fig. 3f

Fig. 3. Data from UV OB River Water Experiment (0.2 Micron Filter)

The three graphs on the left show the percentages of the metal ions caught on the filter as functions of time. The four curves correspond to the four salinities 0 ppt, 1 ppt, 3 ppt, and 5 ppt. Where the time-curves become flat is the equilibrium point; the percentages at the equilibrium time are used to plot the bar graphs at the right.

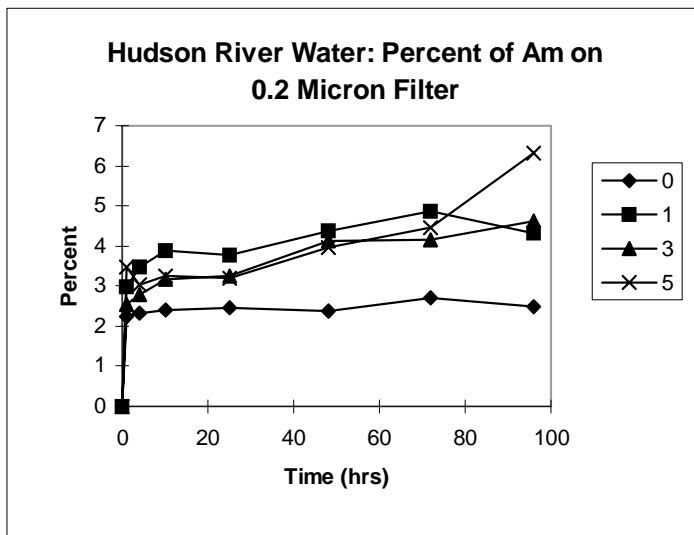


Fig. 2a

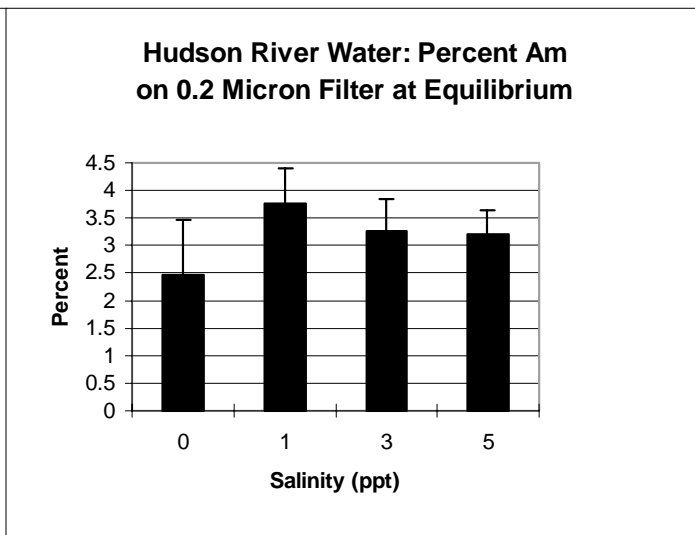


Fig. 2b

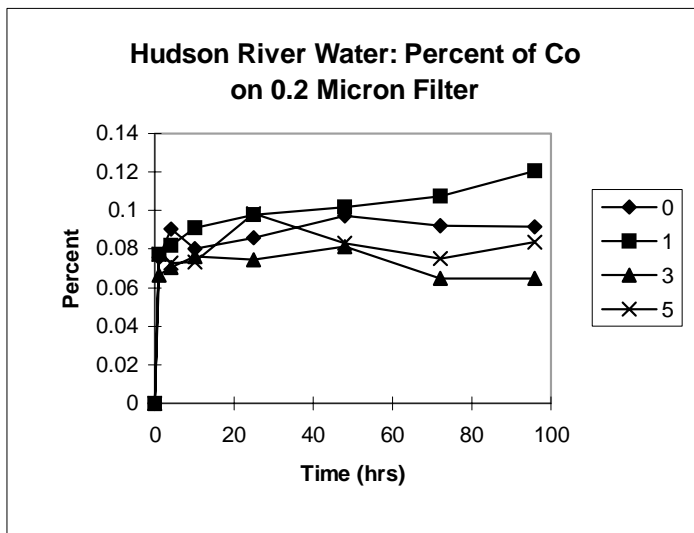


Fig. 2c

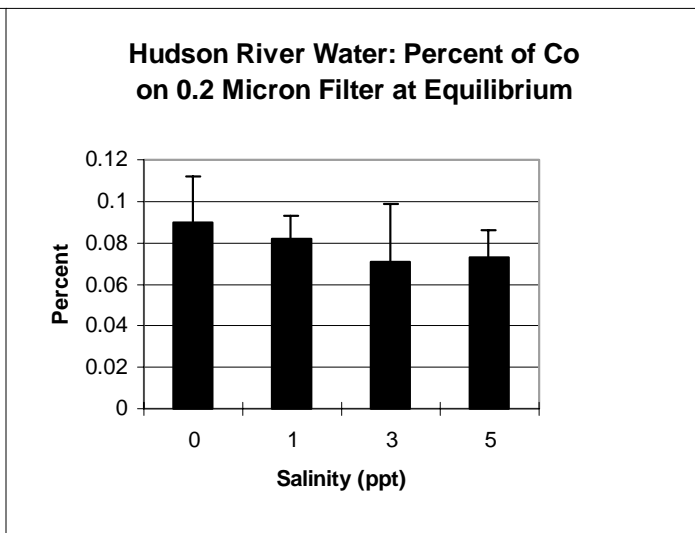


Fig. 2d

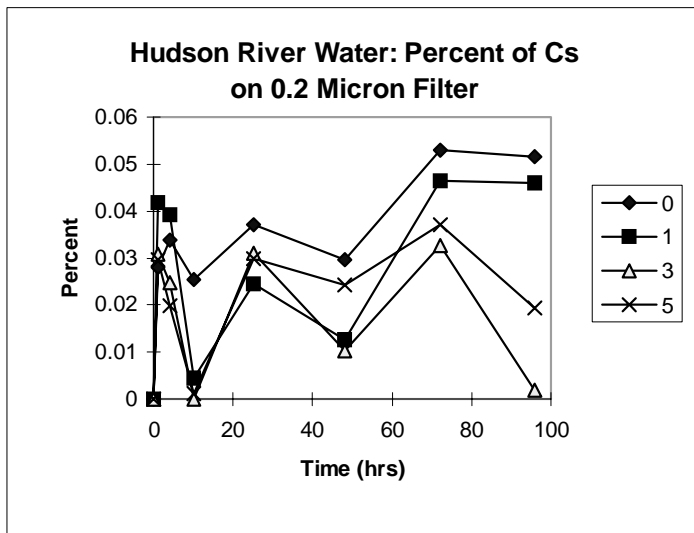


Fig. 2e

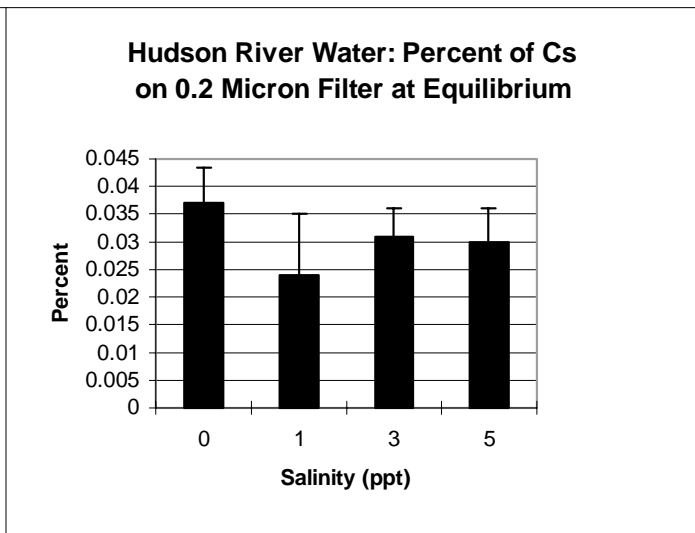


Fig. 2f

Fig. 2. Data from Hudson River Water Experiment

The three graphs on the left show the percentages of the metal ions caught on the filter as functions of time. The four curves correspond to the four salinities 0 ppt, 1 ppt, 3 ppt, and 5 ppt. Where the time-curves become flat is the equilibrium point; the percentages at the equilibrium time are used to plot the bar graphs at the right.

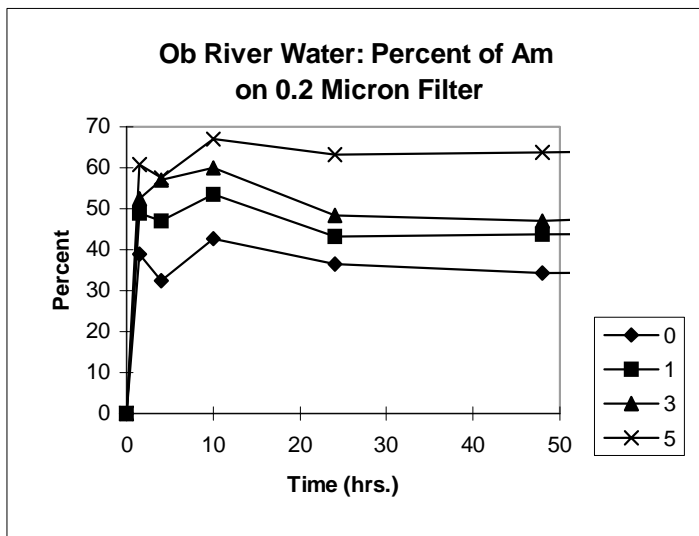


Fig. 1a

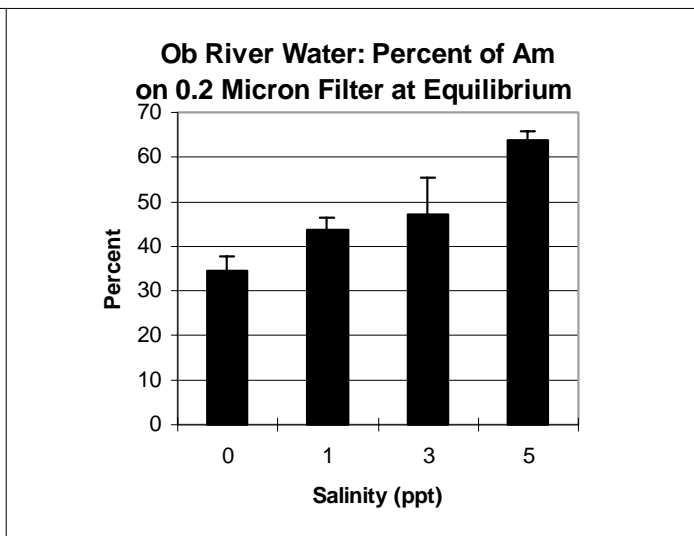


Fig. 1b

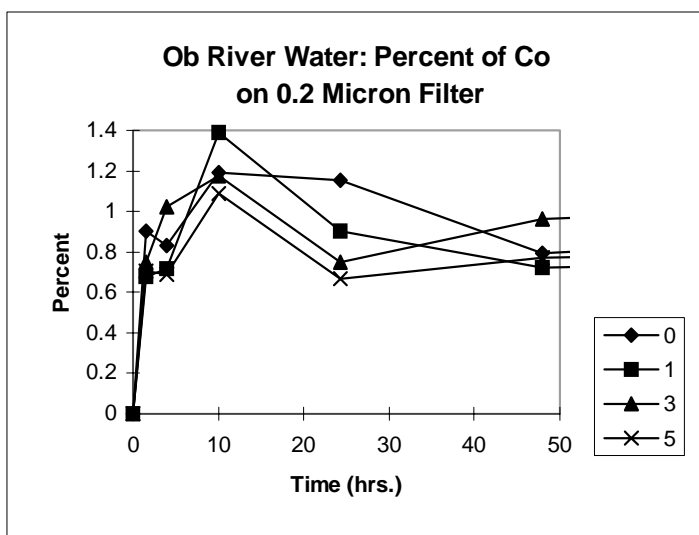


Fig. 1c

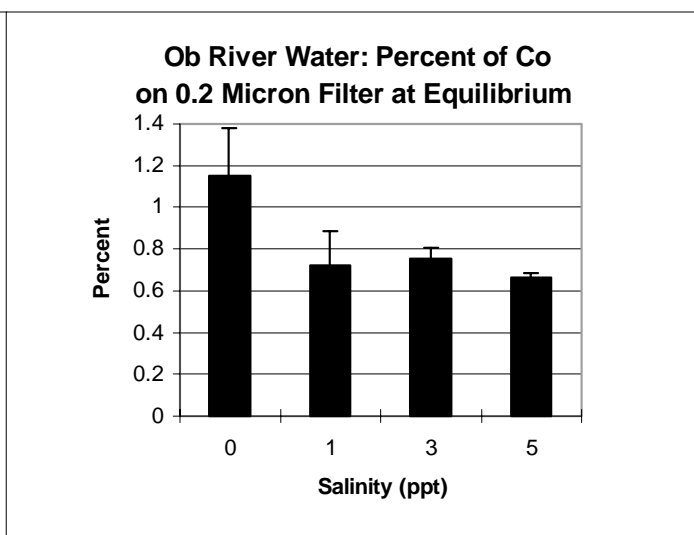


Fig.1d

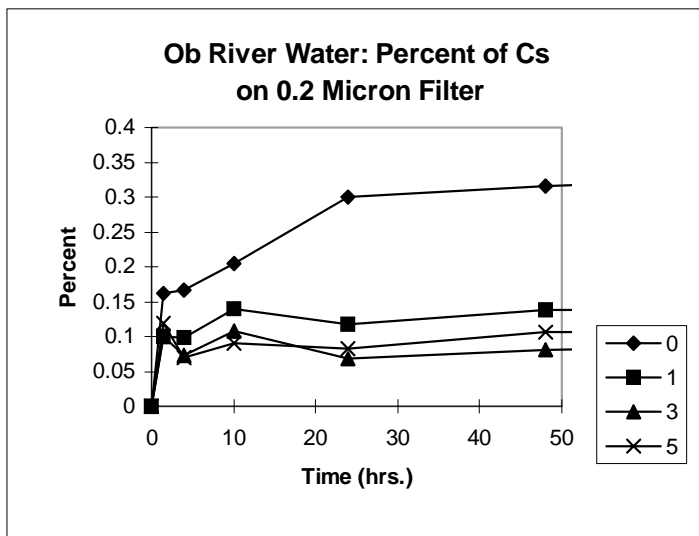


Fig. 1e

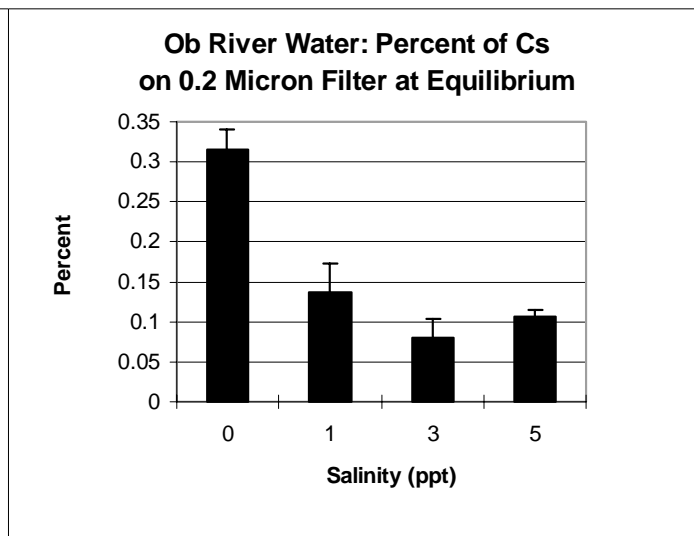


Fig. 1f

Fig. 1. Data from Ob River Water Experiment

The three graphs on the left show the percentages of the metal ions caught on the filter as functions of time. The four curves correspond to the four salinities 0 ppt, 1ppt, 3 ppt, and 5 ppt. Where the time-curves become flat is the equilibrium point; the percentages at the equilibrium time are used to plot the bar graphs at the right.

filter as was placed directly into a counting tube, the fraction of ions collected by the filter was the ratio of the retentate (filter) activity divided by ten and then divided by the solution activity. Finally, this fraction was multiplied by 100 to give the result in terms of a percentage. The mean and standard deviation for the three replicates for each salinity were determined, and the results were graphed as functions of time.

Because the percentage of americium removed by filtration was unexpectedly high, the experiment was repeated, yielding consistent results.

## II. Hudson River Water Experiment

In order to compare the results for Ob River water with water from a more familiar temperate-zone river, the same experiment was repeated using water from the Hudson River. The only change in procedure from the protocol was the readjustment of the pH to 8.05 which is the normal pH of the Hudson River water at the collection point.

## III. UV Ob River Water Experiment

Because dissolved organic carbon is suspected of being important in holding some metal ions in solution, the same experiment was repeated using UV-oxidized water. The UV treatment was intended to remove the dissolved organic molecules. The Ob River water was irradiated by ultraviolet light after 30 mL of hydrogen peroxide were added for every liter of Ob River water. The experiment using UV-oxidized water was run twice, and in the second run, the solution was filtered through both 0.2  $\mu\text{m}$  and 1.0  $\mu\text{m}$  filters.

## Results

The data from the series of experiments are shown in Figures 1-4. Each of these four Figures has six graphs. The three line graphs at the left show the percentage of the metal ions (americium, cobalt, and cesium respectively) caught on the filter as a function of time; the four curves in each line graph correspond to the four salinities (0 ppt, 1 ppt, 3 ppt, and 5 ppt). The point where the time-curves become flat is taken as the equilibrium point in the interaction of the ions with the river water; the data at that point in each time graph was used to plot the bar graph to the right. In some cases there is ambiguity as to what is the appropriate equilibrium point. The raw

data in Figs. 1-4 was used to prepare the comparison graphs in Figs. 5-7.

### Americium

As shown in Figure 5, about 35% of the americium was removed by a 0.2 micron filter at 0 ppt salinity. Increasing amounts of americium were removed when the river water was mixed with seawater so as to increase its salinity. At 1 ppt salinity the removal increased to about 45%. At 5 ppt salinity, nearly 65% of the americium was removed by the 0.2  $\mu\text{m}$  filter. Repetition of the experiment produced consistent results.

For the Hudson River water, only a few percent of the americium was removed by filtration through a 0.2  $\mu\text{m}$  filter. Again the graphs suggest that increasing salinity did increase the percentage of americium removed by the filter.

For UV-irradiated Ob River water, over 80% of the americium introduced into the water was removed by both the 1.0 micron and 0.2  $\mu\text{m}$  filters even at 0 salinity, and increasing the salinity of the water seemed to make little difference in removal of the americium by filtration. The use of the larger 1.0  $\mu\text{m}$  filter decreased the amount of americium on the filter by about 5% in comparison with the 0.2  $\mu\text{m}$  filter.

### Cobalt

The removal of cobalt by filtration is shown in Fig. 6. Note the change in scale at the left compared to the previous Figure. In untreated Ob water, about 1% of the cobalt was removed by filtration of the fresh water. With increasing salinity the removal of cobalt by the filter was even smaller dropping to about 0.6% removal for a salinity of 5 ppt. This decreasing trend with increasing salinity is the opposite of that found for americium.

By comparison, the Hudson River water results involved removal of cobalt by filtration which was about 10 times smaller, involving about 0.09% removal at 0 salinity and 0.07% removal at 5 ppt salinity.

For UV-irradiated Ob River water, increasing salinity involved smaller (not larger) removal of cobalt by the filter. The results were similar for both the 0.2 and 1.0  $\mu\text{m}$  filters, with the smaller filter giving a slightly higher removal of cobalt.

### Cesium

The results for cesium are shown in Fig. 7. Again note that the percentage scale has been decreased. In untreated Ob River

water, about 0.4% of the cesium was removed by the 0.2 micron filter at 0 salinity and the removal decreased with increasing salinity, dropping to 0.1% at 5 ppt salinity.

In Hudson River water, the percentage removal by the filter, was one tenth as large, about 0.04% removal at 0 salinity with the suggestion of decreasing removal with increasing salinity.

The experiment involving UV-treated Ob River water showed removal of cesium decreased with increasing salinity. The removal was about 0.06% for 0 salinity. In connection with cesium it seems interesting in Figs. 3e and 4e that although the percentage removal of the cesium in 0 salinity UV-irradiated Ob water held fairly steady after 10 hours, the filtration removal of cesium in higher salinity water decreased after about 20 hours.

## Discussion

Metal ions in natural waters form complexes with the material in the water. The term "dissolved" is defined operationally as involving particles which pass through a 0.2  $\mu\text{m}$  filter.<sup>13</sup> The material which is removed by such a filter is regarded as particulate. Writing in 1993, Morel notes: "The transport of colloidal iron and aluminum in rivers and their deposition within estuaries is strongly influenced by sorbed humic substances. In freshwaters, colloids are stabilized by sorbed organics which impart to them a large negative charge; flocculation and coagulation occur in estuaries where the ionic strength and the concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (which may partly neutralize the negative surface charge) are higher."<sup>14</sup>

The behavior of the metallic ions is pictured as involving a competition between the dissolved condition, perhaps complexed with dissolved organic carbon, and the attachment to the particles through the organic ligands. Only those ions attached to the particles are removed by filtration.

The americium ions, which have a lowest oxidation state of 3+, are 35% removed from solution in Ob River water by filtration through a 0.2  $\mu\text{m}$  filter at zero salinity, as seen in Fig. 5. With increasing salinity, increasing amounts of americium are removed by filtration with 70% removed at a salinity of 5 ppt. This is in agreement with the flocculation comments of Morel. The increasing removal of americium under conditions of increasing salinity was also indicated in the experiment with Hudson River water. However, the percent-

precipitation of iron ions in conjunction with dissolved organic matter forms the basis for economically important iron deposits such as those of the Massabi range.<sup>7,8</sup>

The distribution of various metal ions among several possible complexes in freshwater and seawater is largely dependent upon the polarizing power of the ions.<sup>9</sup> Cesium, cobalt, and americium, the elements chosen in the present experiments, have ionic charges  $Z$  of +1, +2, and +3 respectively and should represent a wide variation in  $Z^2/r$  polarizing power in solution. Cesium has the smallest possible ionic charge +1 and the largest ionic radius (0.169 nm) of all the metals, giving a  $Z^2/r = 5.92/\text{nm}$ . Corresponding to this small polarizing power, cesium is listed as remaining mainly as a free ion without complexing.<sup>9</sup> Cobalt with a +2 ionic charge and smaller ionic radius (0.072 nm) has a ten times larger value of  $Z^2/r = 55.6/\text{nm}$ , and complexes with various ions, depending sharply on the pH of the water. Literature searches failed to produce information regarding either the polarizing power of americium or its ionic radius. However, americium has a +3 ionic charge (therefore a large value of  $Z^2$ ); also, the trend across the periodic table suggests a very small ionic radius.<sup>10</sup> These considerations suggest the possibility of a very large value of  $Z^2/r$  for americium and the likelihood of strong complexing by this ion.

The apparent chemistry of natural waters is extraordinarily complex.<sup>6,11</sup> In some cases metal ions are held in solution to an unexpectedly high degree by dissolved organic material.<sup>7,12</sup> This organic material is hard to characterize and is specific for each body of natural water.<sup>6</sup> Thus, the precipitation of metal ions cannot, unfortunately, be predicted by simple chemical analysis of river water. At present, questions such as the likelihood of deposit of dissolved radioactive materials when rivers enter saline estuaries can be answered only by studies involving the water from each individual river. This is just what has been done in the present study using water taken from the Ob River. The study attempted to analyze the removal of the radioactive metal ions from solution by particle formation over a period of several days. The experiments were performed in the Marine Radioecology Laboratory of Dr. Nicholas S. Fisher at the State University of New York at Stony Brook. Information of the sort obtained in this study will be important in the selection of sites to monitor Arctic pol-

lution from radioactive nuclei.

## Methodology

The study here involved three basic experiments, some of which were repeated: I. Ob River Water Experiment, II. Hudson River Water Experiment, and III. UV Ob River Water Experiment.

### Water Sample Collection

Samples of water from the Ob River in Russia were collected at several locations in the fresh water portions of the estuary during a cruise in 1995 by Dr. Brad Moran of the University of Rhode Island. Some of the water taken was sent to the Marine Radioecology Laboratory of Dr. Nicholas Fisher at SUNY. Seawater was collected from the Atlantic Ocean near South Hampton, Long Island, in 1995, and Hudson River water was collected near Poughkeepsie during 1995.

I. Ob River Water Experiment  
Sample Preparation. The study attempted to emulate the conditions existing in the Ob River as it enters the saline portions of the Gulf of Ob on its way to the Kara Sea.

Before the samples were prepared, water from each of the three sources was filtered through 0.22 micron Millipak filters to eliminate all particles in the water.

The South Hampton seawater had a salinity of 34 ppt (parts per thousand) and so could be combined with the fresh water from the Ob River to create four 600 mL aliquot water mixtures and four 200 mL aliquot mixtures with salinities of respectively 0, 1, 3, and 5 ppt. These salinities were chosen because Sholkovitz<sup>6</sup> reported little increase in flocculation above these values for rivers in temperate regions. The Ob River water and the South Hampton Seawater were held separately and not mixed together until the start of the experiment.

Radioactive nuclides were added to each of the four 600 mL aliquots with Ob River water (0.75 microCi americium-241, 0.375 microCi cobalt-57, and 0.375 microCi cesium-137 in each) while the four 200 mL aliquots had no radioactivity introduced. The addition of radioactive nuclides held in acidic solutions, in general, altered the pH of the water in the aliquots. Therefore, the pH of each of the aliquots was readjusted to 7.10 ( $\pm 0.1$ ), so as to match the pH of the Ob River, by adding 4M HCl or 4M NaOH.

The measured Ob River water and the South Hampton Seawater was mixed together to create the desired salinities of 0, 1, 3, and 5 ppt., and the total radioactivity of each solution was taken. Each of the four 600 mL solutions was then separated into three replicates (200 mL in each replicate), giving a total of 12 samples with radioactivity; in addition, there were also four 200 mL samples without radioactivity. While conducting the study, the replicates were kept in an incubator at 2 degrees Celsius, the temperature of the Ob River in the arctic region near the Kara Sea.

Filtration. At regular time intervals, part of the water in each replicate at each salinity was run through a filter so as to measure the filtration removal of the radioactive ions. The radioactivity of the retentate material on the filter was compared to the radioactivity of the solution to determine the percent of metal ions that were in particulate form and hence were removed by filtration. Specifically, 20 mL of solution from each replicate was filtered through a 0.2 micron filter while 2 mL of solution was pipetted directly into a counting tube. Then 10 mL of solution, with the same components and salinity as the replicate (but with no radioactive ions) was filtered through the same filter to wash through any radioactivity that might have been adsorbed onto the filter without being held in particle form. After the filtration, the filter holding the radioactive retentate was crumpled up and placed in a counting tube. Both this counting tube and the counting tube holding the 2 mL of the corresponding unfiltered radioactive solution were set aside for analysis.

Analysis of Radioactivity. The samples were analyzed by radiation detection techniques. All of the counting tubes were placed in a 1282 Compugamma Cs Universal Gamma Counter. This counting machine contains a multichannel analyzer which can analyze the gamma emissions corresponding to their energies. Thus, the counts due to each of the three radioactive isotopes could be separated because the energy spectra for americium, cesium, and cobalt are all different. Each of the counting tubes was moved automatically into the counting chamber and then counted to determine the amounts of radioactive americium-241, cobalt-57, and cesium-137.

The desired results represented the percentage of radioactive ions removed from solution by filtration. Since 10 times as much solution had been run through the

# Filtration Removal of Americium, Cobalt, and Cesium in Ob River Water Under Conditions of Increasing Salinity

MICHAEL BOYER

Water from the Ob River of central Russia was used in a series of laboratory experiments to determine the precipitation of dissolved americium, cobalt, and cesium under conditions of increasing salinity. The conditions of the experiment tried to emulate those of the Ob River where it flows into the saline Kara Sea near the Arctic Circle. It was found that americium introduced into fresh Ob water solution and allowed to stand was 35% removed by filtration through a 0.2  $\mu\text{m}$  filter. When the Ob water was mixed with seawater, increasing percentages of americium were removed with increasing salinity, reaching 65% removal at a salinity of 5 ppt. Cobalt and cesium remained in solution with only small fractions of a percent removed by filtration through a 0.2  $\mu\text{m}$  filter; the removal by filtration decreased with increasing salinity. The general trends with increasing salinity matched those found in a parallel experiment using water from the Hudson River, but the removal of americium by filtration in Hudson River water was only one tenth that found for Ob River water. Experiments were repeated when the Ob River water was exposed to ultraviolet radiation to break up the dissolved organic molecules. The filtration removal of americium exceeded 90% in this UV-treated Ob water. These results are of interest in anticipating the transport of nuclear waste pollutants from the area drained by the Ob to the Arctic Ocean. They suggest that americium may precipitate as the Ob flows into the saline Kara Sea while dissolved cobalt and cesium will continue on to pollute the Arctic Ocean.

The Ob river is located east of the Ural Mountains in the central section of the former Union of Soviet Socialist Republics. It drains a vast area of central Russia where large amounts of radioactive material are deposited and stored. There are major radioactive dumps containing hundreds of millions of curies associated with nuclear reprocessing for the military in the watershed of the Ob.<sup>1</sup> In addition, there are nuclear power plants along the shores of the Ob and radioactive soil contamination originating from years of fallout (particularly cesium-137) from atmospheric nuclear testing and also from industrial production which concentrates radioactive material of natural origin. The industrial city of Tomsk-

7 is a source for relatively high background radioactivity levels. There has been a measurable increase in background radioactivity at the mouth of the Chernilshchikova Channel where water originating from the Tomsk-7 area flows into the Ob River. The levels now read 30-35 micror/hr for the general background and 30 micror/hr in the water.<sup>2</sup>

There is the threat that increasing amounts of radioactive contamination will be introduced into ground water and will eventually reach the Ob River where it will be transported into the arctic regions. Although there has been significant work on the transport of metallic ions in rivers of the temperate zone,<sup>3,4</sup> data on how Arctic

ecosystems function in transforming and transporting radioactive nuclides are scant.<sup>5</sup> The fresh water Ob flows into the Gulf of Ob (Obskaya Guba) at the Arctic Circle, and the Gulf empties into the saline Kara Sea some 800 km farther north.

One obvious concern is the effect that increasing salinity would have on the dissolved metal ions as the fresh water Ob mixes with the saline waters coming from the Kara Sea. It has been observed in rivers of the temperate zone that colloidal material tends to flocculate with increasing salinity.<sup>6</sup> Thus it is possible that dissolved metals complexed with organic material may be precipitated and deposited by the Ob as it moves through the Gulf. Such pre-

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