Reports

Plutonium in Drinking Water: Effects of Chlorination on Its Maximum Permissible Concentration

Abstract. *Soluble plutonium is oxidized to the Pu(VI) oxidation state by chlorine during water treatment. Under certain conditions Pu(VI) is readily absorbed from the gastrointestinal tract. It appears that due consideration has not been given to the effect that the presence of plutonium in this oxidation state may have on the maximum permissible concentration of plutonium in drinking water.*

We have established that Pu(IV) is oxidized to Pu(VI) by chlorine in water treatment plants and distribution systems. The consequence of this observation is that the present values for the maximum permissible concentration (MPC) of plutonium in drinking water (5 pCi/ml for the general public) (*1*) appear to be too high by several orders of magnitude. The gastrointestinal absorption factor used to calculate the MPC is based on the results of experiments in which solutions of Pu(III) or Pu(VI), or both, were fed or administered intragastrically to animals. It is our view that, in deriving this factor, due consideration was not given to evidence in the literature that the absorption of Pu(VI) is higher by three orders of magnitude than that for Pu(IV) or to the possibility the Pu(VI) could be formed during water treatment (*2*).

The experiments were carried out under the conditions that exist in the water treatment plants and distribution system for the city of Chicago. The water chlorination process begins immediately after intake from Lake Michigan, and the chlorine concentration is maintained at about 1 part per million (ppm) throughout the treatment plant and in the distribution system. The average elapsed time from initial chlorination to consumption is 24 hours. (In other water treatment plants, the average chlorine concentration during treatment is frequently higher, by as much as a factor of 10, and the elapsed time is generally longer.)

We used two kinds of water in the experiments: Chicago drinking water (*3*) and a synthetic Chicago drinking water. We prepared the synthetic drinking water by adding sufficient potassium bicarbonate to distilled water to make the bicarbonate ion concentration and the *p*H the same as they are in Chicago drinking water. The plutonium stock (*4*) was a dilute potassium bicarbonate solution with more than 99 percent of the plutonium in the Pu(IV) state. The chlorine stock was a dilute sodium hypochlorite solution. Portions of the plutonium and chlorine stock solutions were added to the waters, and these solutions were analyzed for Pu(IV) and Pu(VI) (see below) immediately and after 24 hours. The ^{239}Pu concentrations were 2.0 and 0.002 pCi/ml, the chlorine concentrations were 1.0 and 9.8 ppm, and the *p*H of the solutions was 8.6.

We used the classical lanthanum fluoride method to determine the amount of plutonium in each oxidation state (*5*, p. 12). In this method, Pu(IV) is coprecipitated with lanthanum fluoride whereas Pu(VI) is not. From measurements of the amount of plutonium in the precipitate and in the supernatant solution, the percentage of plutonium in each oxidation state can be calculated. We confirmed the results by analyzing some of the water samples by a method in which Pu(IV) is separated from Pu(VI) by ion exchange (*5*, p. 84); in strong nitric acid, Pu(IV) is strongly absorbed onto Dowex-1 anion resin whereas Pu(VI) is not.

Table 1. Oxidation of Pu(IV) to Pu(VI) by chlorine in two types of drinking water.

Chlorine concentration (ppm)	Time (days)	Percentage* of Pu(IV)	Percentage* of Pu(VI)
Chicago drinking water			
1.0	0.01	98	1
1.0	1.0	28	69
9.8	1.0	4	92
Synthetic Chicago drinking water			
1.0	0.01	97	1
1.0	1.0	25	72

*The uncertainty in each of these values is ± 3.

From the results obtained with the lanthanum fluoride method for those samples in which the ^{239}Pu concentration was 0.002 pCi/ml (Table 1) it can be seen that the chlorination of drinking water results in the oxidation of Pu(IV) to Pu(VI). The results obtained from the analysis of the water samples in which the ^{239}Pu concentration was 2.0 pCi/ml were not significantly different from those given in Table 1, that is, the oxidation rate is independent of the plutonium concentration in this concentration range.

The use of chlorine in water treatment plants to destroy harmful bacteria, and in water distribution systems to prevent bacterial growth, is standard practice; hence, the effect of chlorine on the oxidation state of plutonium must be considered. Hamaker (*6*) has shown that in acetate-buffered solutions (*p*H 4.5 to 8.4) Pu(IV) is completely oxidized to Pu(VI) by chlorine in 15 minutes at 80°C. However, his data could not be extrapolated to a water treatment and distribution system. The concentrations of plutonium and chlorine in his experiments were higher by orders of magnitude, and the temperature was 80°C rather than 10° to 20°C. These factors are offset by the increase in reaction time, from minutes to days. (In the absence of experimental evidence, oxidation would be predicted from the standard oxidation potentials. In acidic solution the Cl(0)-Cl(−I) and Pu(VI)-Pu(IV) couples are −1.36 and −1.04 V, respectively, whereas in basic solution they are −0.89 and −0.51 V, respectively.)

In 1965, Committee 2 of the International Commission on Radiological Protection (ICRP) established a task group on the metabolism of plutonium and related elements. One of the conclusions drawn by this task group was that the current value for the gastrointestinal absorption factor, 3×10^{-5} appears to be reasonable for soluble plutonium compounds (*7*, p. 49). In drawing this conclusion, the task group either did not consider the possibility that Pu(VI) would be formed during water treatment or, if they did, they concluded either that the data obtained by Weeks *et al.* (*2*) on the absorption of Pu(VI) were invalid or that Pu(VI) would be rapidly reduced to Pu(III) or Pu(IV), or both, in the gastrointestinal tract.

Weeks *et al.* (*2*) studied the effect of oxidation state on the absorption and retention of plutonium by rats after intragastric administration. When all the plu-

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Scoreboard for Reports. The acceptance rate for Reports during the last year has been about 25 percent. The number accepted has exceeded the number published and publication delay has increased to about 4 months. For the next few months, our acceptance rate will be about 15 percent, or ten Reports per week.

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tonium in the administered solution was in the Pu(III) state, the retention (the percentage of the administered dose) in the skeleton and liver after 4 days was 0.006 percent, in the Pu(IV) state 0.001 percent, and in the Pu(VI) state 1.75 percent. After 80 days the retentions were 0.010, 0.001, and 1.57 percent, respectively. Each value is the average for six rats. The results they obtained for Pu(III) and Pu(IV) were in close agreement with those of many other investigators. For those experiments in which the plutonium administered was a mixture of Pu(IV) and Pu(VI), the correlation between the percent Pu(VI) and the percent plutonium absorbed was high.

The authors of the task group's report were aware of the work by Weeks *et al.* (*2*), as they refer to it in the section on gastrointestinal absorption (*7*, p. 10). However, the nature of their statement suggests that there was doubt in their minds about the validity of the data: "Although the evidence is meager, Pu(VI) appears to be absorbed more readily than Pu(IV)." As published, the study that Weeks *et al.* carried out appears to be quite definitive.

The gastrointestinal absorptions of Np(VI) by the rat and of U(VI) by man substantiate the absorption of Pu(VI) found by Weeks *et al.* (*2*). [Both Np(VI) and U(VI) are very close chemical analogs of Pu(VI). The compounds formed when each is precipitated from solution by a particular reagent are isomorphous, they form complexes with the same ligands and to a comparable degree, and they are extremely difficult to separate from each other when they are all in the VI state.] Ballou *et al.* (*8*) found that the gastrointestinal absorption of Np(VI) by the rat was 2 percent. From measurements of uranium in man and his diet, Hursh and Spoor (*9*) estimated that the gastrointestinal absorption of U(VI) is between 10 and 30 percent. The absorption of Pu(VI) in man should not differ significantly, that is, by more than a factor of 10, from that of U(VI).

The fact that conditions within the gastrointestinal tract are reducing in nature may lead to the reduction of Pu(VI) to Pu(IV) shortly after water has been consumed. In this case, the gastrointestinal absorption factor for Pu(IV) rather than for Pu(VI) should be used to calculate MPC's. In reviewing the paper of Weeks *et al.* (*2*) with one of its authors (*10*), we learned that in their experiments (i) the rats were food-deprived both before and after the administration of the plutonium and (ii) the solutions that contained Pu(VI) were about 0.01*M* in dichromate. Thus, at the time of administration, the gastrointestinal tracts of the animals may have been devoid of those constituents that could reduce Pu(VI) or, if these constituents were present, they may have reacted with the dichromate and this forestalled plutonium reduction. At this time we know of no information about the reduction of Pu(VI) to Pu(IV) during the period when digestive processes are occurring.

Our study shows that plutonium in drinking water will be in the Pu(VI) state, but it remains to be shown whether or not Pu(VI) will be reduced to Pu(IV) immediately after ingestion. In establishing this, consideration must be given to the fact that water and food consumption are not necessarily related temporally; Pu(VI) may be rapidly reduced when food is being digested but not when the digestive tract is empty.

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References and Notes

1. *Standards for Radiation Protection* (Energy Research and Development Administration Manual, Washington, D.C., April 1975), chap. 0524.
→ M. H. Weeks *et al.*, *Radiat. Res.* **4**, 339 (1956).
3. The major cationic impurities in Lake Michigan are calcium (30 ppm) and magnesium (10 ppm), the major anionic constituent is bicarbonate (200 ppm), the *p*H is about 8.3, and the water is saturated with atmospheric oxygen. The composition of Lake Michigan is quite similar to that of the resources for other metropolitan water systems.
4. The plutonium used was a mixture of ^{239}Pu (half-life, 24,000 years) and ^{237}Pu (46 days) in which the atom ratio of ^{239}Pu to ^{237}Pu was about 100. Plutonium measurements were based on the detection of the neptunium K x-rays that are emitted in the decay of ^{237}Pu.
5. G. H. Coleman, *The Radiochemistry of Plutonium* (Publication NAS-NS-3058, National Academy of Sciences–National Research Council, Washington, D.C., 1965).
6. J. W. Hamaker, in "Report CN-239" (Department of Energy Technical Information Center, Oak Ridge, Tenn., 1942), part 2, p. 22.
7. A. Lindenbaum *et al.*, *The Metabolism of Plutonium and Other Actinides* (ICRP Publication 19, Pergamon, New York, 1972).
8. J. E. Ballou *et al.*, *Health Phys.* **8**, 685 (1962).
9. J. B. Hursh and N. L. Spoor, in *Uranium, Plutonium, and Transplutonic Elements*, H. C. Hodge, J. N. Stannard, J. B. Hursh, Eds., vol. 36 in *Handbook of Experimental Pharmacology* (Springer-Verlag, New York, 1973), p. 234.
10. R. C. Thompson, personal communication.
11. Work was performed under the auspices of the U.S. Department of Energy.

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Venus: Further Evidence of Vortex Circulation

Abstract. *A space-time composite of polar stereographic ultraviolet images of Venus from Mariner 10 shows a remarkable circumpolar vortex. The vortex is characterized by a cloud which appears similar to dense terrestrial stratus having an albedo that is 50 percent higher. Spiral streaks converge into it from low latitudes, akin to the spiral bands of a hurricane. The bright visible polar cloud is not axisymmetric but has roughly an elliptical shape. The high brightness of the polar cloud suggests that it has a different origin from the rest of the Venus cloud cover.*

Soon after the Mariner 10 encounter with Venus, the Mariner Venus Mercury-73 imaging team (*1*) presented a preliminary view of the atmospheric circulation on Venus as revealed by the ultraviolet (UV) markings. In particular, Murray *et al.* made the following comments about the polar region (*1*, p. 1312): "Our preliminary impression is that the pole of atmospheric rotation is on the terminator. . . . There is an indication of vortex structure in the streaks emanating from the poleward side of the edge of the polar region. Indeed, the entire polar region may be a vortex fed by meridional flow from the equatorial regions." Subsequently Suomi (*2*) and Suomi *et al.* (*3*) tracked the motions of UV features of a few Mariner 10 UV frames taken over a small time interval compared to the total Venus encounter. These observations showed highly zonal motion with maximum speeds near ± 50° latitude suggestive of the conservation of angular momentum in the outer zone of the vortex. We have completed another analysis of Mariner 10 images that covers almost the entire period of the Venus encounter, about 7 days, using an extension of the basic technique. The new approach has produced striking evidence of a global circumpolar vortex in the stratosphere of Venus.

First, all of 22 frames spanning 6.85 days were normalized to a standard scattering geometry. The normalization was performed in order to remove shading due to scattering geometry variation over the planet. The images were normalized to a standard sun-planet-observer geometry as described by Limaye and Suomi (*4*). Second, the images were remapped into a polar stereographic projection to give a better view of the high-latitude regions of Venus. Third, several separate polar stereographic projections spanning several days were made into a composite for the whole polar region. This procedure simulates the view that would be obtained from a flight over the pole.

The polar projection has the advantage that it is easier to discern motion patterns in the high latitudes than in the

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