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Environmental Behaviour of Transuranium Actinides: Availability to Marine Biota*

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In general, transuranium elements form relatively insoluble compounds in the marine environment and therefore are not considered biologically mobile. Their interaction with biological systems is largely passive and they tend to attach, sometimes strongly, to the external surfaces of marine organisms.

Although concentration factors are usually low and decrease with trophic level, seaweed represents the critical pathway for their transfer from the marine environment to man.

Introduction

Commercial power production and the fabrication of nuclear weapons in the last few decades have produced large quantities of radioactive wastes that, if handled incorrectly, could cause serious health and safety problems for future generations.

The disposal of such wastes is a problem of considerable scientific and technological interest, and one of some public concern. Transuranium nuclides produced by neutron absorption in the reactor core and their decay products are the group of most concern, because of the high radiotoxicity and the abundance in waste materials. The phrase 'transuranic waste' is used in the nuclear field to define waste material containing one or more long-lived alpha-emitting radionuclides of atomic number greater than 92, in quantities above limits established by an operating organization or a regulatory agency, based upon an assessment of the risk posed by those waste materials [1].

Disposal of transuranic waste by burial in the sea floor may be technically and environmentally feasible and could represent a 'safe' solution [2]. The research approach used in subseabed disposal programmes includes the development of mathematical models to evaluate the risk to man, and thus a good knowledge of the biogeochemical behaviour of transuranium actinides is necessary before a disposal plan can be implemented.

In radioecological studies concerning isotopes of naturally occurring elements, it can be assumed that they are very near a steady state condition in the environment. Therefore, information on long-term cycling in the biosphere can be acquired from the behaviour of the corresponding stable isotopes. This is not the case for man-made elements such as transuranium actinides, and a much better understanding of their biogeochemical behaviour is required to make predictions on the long-term distribution and thus on their potential hazard to man.

Information on the behaviour of transuranium elements in marine ecosystems has been obtained from environmental data and laboratory investigations. Advantage has been taken of the world-wide fallout from nuclear weapon tests to determine concentrations of plutonium and, to a very limited extent, of americium in seawater, sediments and several species of marine organisms. Data on neptunium, plutonium, americium and curium have been collected in localized areas receiving wastes from nuclear fuel reprocessing plants or involved in accidental releases.

Environmental investigations have been integrated with laboratory studies, in which short-lived photon-emitting isotopes of transuranium elements have also been used.

Research on the long-term environmental behaviour of actinides is considered to be of high priority in the Radiation Protection Programme of the European Communities [3], and several studies are in progress with the aim of providing a solid scientific background to the management of transuranic wastes.

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TABLE I. Inventory of Transuranium Nuclides by the Year 2000.

Radionuclide	Bq	%	kg	%
^{237}Np	5.18×10^{15}	0.02	1.94×10^{5}	68.00
^{238}Pu	1.48×10^{18}	4.29	2.27×10^{3}	0.80
^{239}Pu	2.37×10^{16}	0.07	1.02×10^{4}	3.57
^{240}Pu	6.66×10^{16}	0.19	7.93×10^{3}	2.78
^{241}Pu	4.81×10^{18}	13.94	1.13×10^{3}	0.40
^{242}Pu	1.04×10^{14}	–	7.16×10^{2}	0.25
^{241}Am	2.37×10^{18}	6.87	1.97×10^{4}	6.90
^{242}Am	5.92×10^{16}	0.17	1.94×10^{-3}	–
^{243}Am	2.66×10^{17}	0.77	3.89×10^{4}	13.63
^{242}Cm	4.81×10^{16}	0.14	3.93×10^{-1}	–
^{243}Cm	6.66×10^{16}	0.19	3.89×10^{1}	0.01
^{244}Cm	2.52×10^{19}	73.04	8.30×10^{3}	2.91
^{245}Cm	4.07×10^{15}	0.01	6.96×10^{2}	0.24
^{246}Cm	8.88×10^{14}	–	9.02×10^{1}	0.03
^{251}Cf	8.88×10^{16}	0.26	1.34×10^{3}	0.47
^{252}Cf	1.11×10^{16}	0.03	5.25×10^{-1}	–

Natural Radioactivity in the Marine Environment

The natural baselines of marine radioactivity, excluding the contribution from early nuclear weapons fallout, have been reported in detail in a recent publication [4] and can be summarized as follows.

Total radioactivity of seawater is approximately 12.6 Bq/L, but less than 1% is due to alpha-emitting nuclides. The global inventory of beta-gamma emitters is 1.7×10^{11} Bq and that of alpha-emitters 1.6×10^{9} Bq. Although the major radionuclides in marine sediments have highly variable distributions, of the 1.15×10^{4} Bq/kg mean specific activity of dry sediment approximately 50% is due to alpha-emitters. Thus, relative to seawater, sediments show an enrichment of actinides and daughter nuclides. The inventory of natural radioactivity in deep-ocean sediments is 6.3×10^{23} Bq, considering the upper 200 m of the pelagic sediment cover.

Inventory of Transuranium Nuclides

Predictions on future trends of nuclear energy production and weapon material fabrication are subject to important uncertainties. However, taking into account only the fuel cycle and assuming that the global nuclear capacity reaches 2500 GW, Grimwood and Webb [5] made an estimate of the waste which is expected to accumulate by 2000 AD, and thus to be available for disposal at that time after a storage period of 10 years. The most relevant data concerning transuranium actinides are reported in Table I.

The mass of alpha-emitting nuclides included in transuranic waste represents only a part of the total world-wide inventory of these radionuclides. Plutonium is the element of major concern, and most of it is contained in spent fuel and weapons material.

It has been estimated [6] that less than 2% of the plutonium and all neptunium, americium and curium appear in waste streams during fuel reprocessing.

It is worthwhile mentioning that all the transuranium nuclides listed in Table I are classified by the Nuclear Energy Agency as having seaweed as their critical pathway for transfer from the environment to man [7].

Considering as waste material the totality of radionuclides present in spent fuel, at the disposal time the gobal activity of actinides accounts for less than 1%, the major contribution (97%) being due to the short-lived fission product pairs ^{137}Cs/^{137m}Ba and ^{90}Sr/^{90}Y. The radioactivity of high-level wastes decreases rapidly, reaching less than 10% of the initial value after 100 years: taking into consideration both the ingrowth of decay series daughter species and the decay of parent nuclides, the activity of each radioisotope can be calculated at different time points after disposal.

Radioactivity of total waste, fission products and actinides are listed in Table II.

The fractional contribution of long-lived actinides, and particularly of the transuranium nuclides ^{243}Am, ^{239}Np, ^{240}Pu, to the total radioactivity of high-level wastes becomes more important with time. The aim in presenting these data on radionuclide

TABLE II. Activity (Bq) of High-Level Waste after Disposal.

Products	Time (years)		
	0	10^2	10^4
Total waste	4.47×10^{21}	4.11×10^{20}	5.59×10^{17}
Fission products	4.44×10^{21}	4.07×10^{20}	2.48×10^{17}
Actinides	3.45×10^{19}	4.44×10^{18}	3.11×10^{17}
Percent contribution of actinides	0.77%	1.08%	55.63%

inventory is to show the relevance of actinides in waste material and thus the need of improving our understanding on their long-term behaviour in the environment. This knowledge is required to make predictions on movement and distribution of transuranium nuclides as well as to identify and quantify the most important pathways responsible for their transfer from the environment to man.

Physico-chemical Characteristics in Relation to Bioavailability

Before reviewing the most recent data on the concentration of transuranium nuclides in marine organisms, it may be useful to give some information on the relevance of their physico-chemical properties for biological accumulation, and thus the potential contamination of marine food chains.

Chemical forms which are soluble in seawater would be more widely dispersed in marine ecosystems and less adsorbed to particulate material and surfaces of biota; however, they can be easily absorbed, particularly through the gills and the gastro-intestinal tract, by invertebrates and fish.

Hydrolyzed and colloidal species are likely to be adsorbed onto fine particulate material and be present in filter-feeding organisms. Such physicochemical forms are also expected to be adsorbed by benthic algae and by small planktonic organisms having a relatively large surface area.

In good agreement with their enrichment in bottom sediments, actinides have been observed to be largely insoluble in seawater. However, the marine chemistry of transuranium elements is largely unknown. Neptunium is most likely to exist in seawater as Np(V) and, to a limited extent, as Np(IV) within interstitial water. Plutonium is the element for which more information is available. It is largely adsorbed onto suspended particulate material and thus removed from the water column to bottom sediments. A small fraction which remains soluble has been identified [8] as Pu(V+VI), whereas that associated with particulate material is mainly Pu(III+IV). A theoretical evaluation [9] of the chemical forms of plutonium in seawater provided results compatible with experimental data. The removal of reduced species from the water column is in good agreement with hydrolysis and polymerisation of $Pu(OH)_4$, determining its adsorption on negatively-charged particulate material present in seawater.

The oxidation states of other transuranium elements in the marine environment have not been investigated in detail, but americium, curium and californium are generally considered to be present in seawater in trivalent forms.

Data on chemical forms occurring in settled sediments are almost totally lacking, but some useful information can be obtained by the determination of distribution coefficients between solid and liquid phases.

An indirect approach to the understanding of long-term behaviour of transuranium elements is based upon the distribution of natural elements having similar physico-chemical characteristics, which are supposed to be very near biogeochemical equilibrium in the environment ('analog' element approach).

Lanthanides are similar to the actinides, in that electrons are successively added to the 4f rather than the 5f orbitals. Since these electrons are less effectively shielded than the 4f electrons and the differences in energy between adjacent orbitals are smaller, the transuranium elements have more complex chemical properties, particularly in relation to their oxidation-reduction behaviour. However, lanthanides can be considered as 'analog' elements of the trivalent actinides [10].

The most important aspects of actinide chemistry pertinent to their environmental behaviour have been recently reviewed [11, 12]. More sparse is the information on the distribution of transuranium nuclides in marine organisms and their transport to man through the food chains.

Transuranium Elements in Marine Organisms

An excellent review on the biological availability to marine organisms of transuranium and other long-lived radionuclides has been prepared by Pentreath [13].

Further information has been acquired, in particular from laboratory studies facilitated by the use of photon-emitting radiotracers such as ^{235}Np and ^{237}Pu.

Neptunium

The isotope ^{237}Np (half-life: 2.1 × 10^6 y) is released to the environment mainly from nuclear detonation tests and fuel reprocessing facilities. Since ^{237}Np is the daughter of ^{241}Pu (half-life: 14.4 y) and ^{241}Am (half-life: 433 y), it is considered to be a problem for the disposal of transuranic wastes. The long-lived products in the decay chain of ^{237}Np (such as ^{233}U and ^{229}Th) play an important role in the same sense.

Neptunium-237 can only be measured in marine samples contaminated with levels higher than global fallout using reasonable sample sizes and work effort. In the Sellafield area, the concentration of ^{237}Np in seaweed is 0.14–0.40 Bq/kg, in comparison to seawater and sediment concentrations of 0.001 and 1.4 Bq/kg, respectively [14]. These results indicate that neptunium should have a considerable mobility in the marine environment and low concentration factors for biota. Fowler and Aston [15] applied ^{235}Np in experiments on neptunium behaviour in seawater, sediments and zooplankton. The ion NpO_2^+, which is the chemical form of neptunium expected to occur in well-oxygenated seawater remains in solution without the tendency to form particulate or colloidal species. However, in the presence of near-shore and deep-sea sediments, adsorption of NpO_2^+ can occur, with distribution coefficient values which reach the same order of magnitude as those observed in areas contaminated with ^{237}Np. Pentavalent neptunium is rapidly accumulated and released by marine zooplankton, but is less available than either plutonium or americium. Previous experimental studies had shown that accumulation of ^{237}Np from water by selected species of crustaceans was largely due to surface adsorption [16, 17].

Plutonium

This element is the most studied transuranium actinide. In general, it is fairly highly accumulated by benthic algae, planktonic organisms, and a variety of benthic invertebrates. Fish usually have lower concentrations [13].

In consideration of the complex chemistry of plutonium in the marine environment, the existing data are of limited value in assessing biological availability. Furthermore, contamination with sedimentary materials tends to obscure the effects of biological assimilation. Guary and Frazier [18] attempted to relate plutonium concentrations to trophic levels in marine organisms collected near the reprocessing plant of Cap La Hague. Since a marked decrease of concentration factor was observed with increasing trophic level, contamination of marine food chains should not represent a critical pathway for the transfer of plutonium to man.

The distribution of $^{239+240}Pu$ and ^{238}Pu in environmental samples of starfish tissues is identical to the tissue distribution observed in experimental animals following uptake of ^{237}Pu(III + IV) directly from seawater [19].

Transfer of plutonium to starfish via food also occurs; however, the resultant tissue distribution is not consistent with that found in the natural environment, where plutonium is available from both contaminated food and seawater [19].

These recent observations indicate that in the marine environment the water pathway predominates in the accumulation of plutonium by asteroids. The high levels of plutonium which have been noted in starfish result from the strong affinity of colloidal, particulate or soluble plutonium for the animal's mucus covered epidermal layer which is in contact with seawater.

Americium

There are fewer data on the occurrence of americium in the marine environment. Attempts have been made to compare its behaviour with that of plutonium [13].

Vangenechten *et al.* [20] studied the uptake of ^{241}Am from marine sediments by benthic organisms. Transfer factors for a bivalve mollusc, a polychaete and an isopod were lower than 0.1 and most of the radionuclide was fixed to the shell or to the body walls of the animals. Transfer of americium was 2–5 times higher from Atlantic carbonate rich (83%) sediments in comparison to Pacific sediments containing only 7.6% total carbonate.

In a series of laboratory experiments on the biokinetics of americium in euphausiids [21] it has been shown that accumulation of ^{241}Am from water occurs by passive adsorption onto the exoskeleton, achieving concentration factors after one-week exposure of the order of 10^2. Essentially all of the americium taken up from water was associated with the exoskeleton, so that a negligible amount of radionuclide was retained by the euphausiids after moulting. Americium ingested with Am-labelled diatom cells was not assimilated and was excreted within a few days.

These results underscore the importance of sinking biogenic debris from zooplankters in mediating the vertical transport of americium in the sea. Because of the relatively high retention half-time of americium and their rapid sinking rates, fecal pellets and discarded moults have the potential to transfer americium from the seawater column to bottom sediments.

The difficulty in assessing the biological availability of americium from environmental samples is that ^{241}Am detected within an organism could arise either from *in situ* production (grow-in from ^{241}Pu) or from external sources, or from both.

Curium

From the review of Pentreath [13] it appears that curium in marine biological samples has only been reported in samples collected in the Irish Sea, near the reprocessing plant of Sellafield.

Invertebrates and algae have higher concentrations than do the edible parts of commercial fish. Nothing is known on the rates of accumulation and loss of curium by marine organisms. To our knowledge, there are no published data of laboratory experiments using curium isotopes.

Californium

Preliminary observations on the behaviour of ^{252}Cf in seawater, sediments and zooplankton have been published recently [22].

Californium introduced into seawater as a trivalent cation partially associates with the particulate fraction. Adsorption onto coastal and deep-sea sediments is rapid with distribution coefficients in the range 10^4–10^5. As with other transuranium nuclides, ^{252}Cf is readily accumulated from water by marine zooplankton: the relative degree of uptake by euphausiids is Cf(III) $\geqslant$ Am(III) $>$ Pu(V+VI) $>$ Np(V). Surface adsorption is the most likely mechanism responsible for the uptake process. Assimilation and accumulation of ^{252}Cf is extremely low in these organisms. As with americium and curium, biogenic particulates produced by zooplankton have the potential to redistribute californium in the marine environment, removing these elements from the water column.

Conclusions

In marine ecosystems, transuranium nuclides are readily adsorbed on the surface of plants and small animals such as zooplankton, and thus may enter the food chain.

Concentration factors for plutonium decrease with trophic level and, for all the elements studied, are lower in the internal as compared to the external tissues of marine organisms.

Adsorption on planktonic organisms and fecal pellets may result in a redistribution of transuranium elements by removal from the water column and transfer to bottom sediments, which ultimately represent the storage reservoir.

Further information on the long-term environmental behaviour of transuranium nuclides is necessary before disposal plans for radioactive wastes can be implemented.

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