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INFLUENCE OF THE PHYSICO-CHEMICAL FORMS OF RADIONUCLIDES
AND STABLE TRACE ELEMENTS IN SEAWATER IN RELATION
TO UPTAKE BY THE MARINE BIOSPHERE^(a)

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INTRODUCTION

Artificial radionuclides enter the oceans from four main sources:

(1) atmospheric fallout from nuclear weapons testing, (2) discharges from nuclear processing plants, (3) discharges from power reactors, and (4) releases from nuclear powered ships (see Figure 1). Future uses of reactors for desalination and the use of nuclear explosives for excavating harbors and canals may represent additional sources of radioactivity entering the oceans. Considerable attention has been given to the possibility of utilizing the continental shelf for future power reactor sites (Anderson, 1971). Both floating and undersea nuclear stations have been considered for offshore siting.

Atmospheric fallout introduces approximately three orders of magnitude more artificial radioactivity to the oceans than both reactors and nuclear fuel reprocessing combined (see Table 1). Assuming, however, that nuclear weapons testing in the future does not exceed the 1968-70 rate, the future discharges of radioactivity into coastal waters from power reactors and fuel reprocessing plants will contribute a much greater fraction of the total radioactivity entering the oceans. A comparison of the radioactive releases from eleven power reactors in the U.S. during 1968 with the annual releases at Windscale and Hanford and the annual deposition of ^{90}Sr in fallout from nuclear weapons testing is shown in Table 2.

Whereas fallout from nuclear weapons testing is dispersed in the atmosphere and deposited over the entire ocean, discharges from reactors and nuclear fuel reprocessing plants are usually point source releases into coastal waters. Atmospheric fallout enters the ocean as a very finely divided aerosol, whereas discharges from reactors and nuclear fuel reprocessing plants may be in the form of primary or secondary cooling waters, treated low level wastes, or accidental releases from ruptured fuel elements. The physico-chemical forms of the artificial radionuclides entering the oceans from these various sources are diverse, and generalizations concerning their behavior and fate in the marine environment are not applicable for all marine regimes. For example, the physico-chemical forms of many radionuclides discharged in coastal waters containing relatively high concentrations of suspended sediments, plankton and dissolved and particulate organic carbon would be grossly different than the same radionuclides deposited into very clean open ocean waters.

Often these radionuclides enter the oceans in forms completely different from that of their stable isotopes naturally present in the oceans. If the equilibration between these different forms is slow, the uptake, distribution and behavior of the radionuclides and their naturally occurring stable isotopes by the marine biosphere could show significant anomalies.

Probably the best known example of different rates of biological uptake and retention for different physico-chemical species of the same element is that of the mercury-methylmercury pair, which does not even involve radioactivity. Studies resulting from the Minamata Bay incident have estimated that methylmercury is accumulated in fish from seawater by a factor of about 50,000 to 500,000 (Ui and Kitamura, 1971), whereas inorganic mercury is apparently accumulated in marine fish by a factor of about 1000 (Beasley, 1971). This

difference in chemical speciation results in methylmercury being assimilated 50-500 times more efficiently than inorganic mercury by marine organisms. Analogous situations involving radionuclides and their stable isotopes have frequently been observed in the marine environment or in laboratory studies. This paper reviews some of the more obvious examples of dissimilar behavior between some of the important artificial radionuclides and their stable isotopes in the marine environment due to differences in their physico-chemical speciation.

PHYSICO-CHEMICAL SPECIATION OF RADIONUCLIDES AND TRACE ELEMENTS IN THE OCEANS

The possible physico-chemical forms which may occur in the oceans are summarized in Table 3. These forms are usually classified into three categories: (1) species in true solution, (2) colloidal species, and (3) particulate forms.

Species in True Solution

Constituents which may be classified in true solution, with a somewhat arbitrary maximum size limit of less than 0.001 microns diameter (Horne, 1969) include (1) simple hydrated ions, (2) inorganic complex ions, (3) organic chelates, (4) molecules and polymeric species, and (5) ion pairs. Simple hydrated ions are the most predominant species of the alkali and alkaline earth metals and some divalent transition metal ions (Goldberg, 1963). Thermodynamic calculations and recent experimental evidence indicate that inorganic metal complexes with Cl^- , OH^- and $\text{CO}_3^{=}$ form major dissolved species of metals such as Ag, Au, Cd, Hg, In, U, V and Zn (Anonymous, 1966; Baric and Branica, 1967; Goldberg, 1963). An increasing amount of evidence indicates that significant fractions of the Zn, Fe and Cu in the oceans are present as soluble metal chelates (Barber and Ryther, 1969; Barber, et al, 1971; Corcoran and Alexander, 1964; Martin, et al, 1971; Rona, et al, 1962; Slowey and Hood, 1971; Steeman-Nielsen and Wium-Anderson, 1970; Torti, 1969, Williams, 1969. However, no naturally

occurring metal chelates have ever been isolated from seawater, and some investigators believe that the concentrations of natural chelating compounds present in the dissolved organic matter in the oceans are too low to permit extensive organic complexing of most trace metals (Duursma and Sevenhuysen, 1966; Duursma, 1970). Clearly, more definitive work is needed in this area.

Very little is understood concerning the soluble uncharged molecular and polymeric trace metal species present in the oceans. However, certain elements such as ruthenium (as nitrate complexes) have been observed to hydrolyze and form polynuclear species such as $\text{Ru} \cdot \text{NO} \cdot \text{NO}_3 \cdot \text{OH} \cdot \text{H}_2\text{O} \begin{smallmatrix} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{smallmatrix} \text{RuNO}(\text{OH})_2\text{H}_2\text{O}$ (Wyatt and Rickard, 1961). Several transition metals, such as iron and manganese, may also exist in solution in the oceans in significant fractions as uncharged molecules or polymeric species (Martin, 1967). Ion-pairing has been shown to be significant for the major divalent cations Mg, Ca and Sr (Garrels and Thompson, 1962), but at the concentrations of the trace metal constituents in seawater, the ion pairing effect should be greatly minimized.

Colloidal Species

Colloidally dispersed aggregates exist in all natural waters and are important major species of several trace elements in the ocean (Stumm and Morgan, 1970). Colloids composed of terrestrial minerals or resuspended sediments, hydrolysis and precipitation products, and biopolymers and detritus probably all exist in the oceans. However, little experimental confirmation or actual observations of the presence of colloids in seawater have been reported. The reason for this lack of information is obvious: how does one isolate colloids from seawater for physico-chemical characterization? Available methods for filtration or centrifugation are not adequate or convenient for separating trace quantities of colloids from large volumes of seawater. Electromigration techniques, such as zeta potentiometry, are useful methods for in situ characterization of colloids in fresh waters, but are ineffective for studying ocean

colloids due to the high ionic strength of seawater. Dialysis techniques have been used to study the physico-chemical speciation of Zn, Mn and Cu in seawater (Slowey and Hood, 1971), and these results indicated that only Zn was present in significant non-dialyzable forms. About 40% of the total zinc was found to be non-dialyzable. Slowey and Hood did not determine the nature of the non-dialyzable Zn, but presumed it to be organically bound. Dialysis techniques may prove useful for separating ocean colloids from seawater, but several complications associated with this method will require very careful evaluation of this procedure and interpretation of results.

Iron is the prime example given in treatises on chemical oceanography emphasizing the occurrence of colloids in the ocean (Horne, 1969; Riley and Skirrow, 1965). The maximum concentration of dissolved, cationic, uncomplexed ferric iron that can exist at equilibrium at the pH of seawater is about 5×10^{-7} $\mu\text{g/l}$ (Cooper, 1937). However, iron concentrations in the open ocean range from about 1 to 10 $\mu\text{g/l}$ (Spencer, et al, 1970). Therefore, the iron in the oceans has been assumed to be present as colloidal ferric hydroxide or ferric phosphate, although no experimental or field observations have directly confirmed the actual nature of the non-filterable fraction of iron in seawater.

Colloidal material is undoubtedly much more abundant in coastal waters than in the open ocean and probably plays an important role in the behavior of radionuclides discharged into coastal waters. There is an obvious need for a better understanding of the occurrence and behavior of colloidal material in coastal waters and in the open ocean.

Particulate Speciation in the Oceans

The filterable suspended matter in seawater is of complex composition and contains both inorganic and organic compounds. Organic particles are

composed of plankton, detritus, fecal remains, bacteria and other micro-organisms. Inorganic particles may consist of terrestrially derived mineral substances and resuspended sediments, and precipitated and coagulated particles. Recent studies (Chesselet, 1971) indicate that the ratio of inorganic/organic content of particulate matter in the deep open sea is about 1:1. Modern refinements in sampling and analytical techniques have indicated that the filterable particulate matter in the open ocean is significantly lower than previously believed (Strickland, 1965; Chesselet, 1971; Spencer, et al, 1970). A very significant recent observation is that the filterable ($> 0.5\mu$) iron concentrations in the open oceans are about ten times lower than previously believed (Betzer and Pilson, 1970), being present at an average concentration of about 0.1-0.2 $\mu\text{g/l}$. Spencer, et al (1970) observed that filtration of open N.E. Pacific Ocean seawater samples through 0.5μ membrane filters did not significantly alter the total concentrations of the trace elements Ni, Cu, Zn, Co, Sb, U, Cs, Sr and Sc in the seawater. They did find that filtration slightly decreased the total iron concentrations in the seawater. However, it is difficult to ascertain whether the decreased iron concentrations were the result of removal of particulate iron or adsorption of colloidal or soluble iron on the filtration apparatus. Slowey and Hood (1971) reported average particulate/total concentration ratios for Cu, Mn and Zn in open Gulf of Mexico waters of 0.39/1.3, 0.03/0.31 and 0.4/3.5, respectively, indicating about 30% of the Cu and approximately 10% of the Mn and Zn are associated with particles greater than 0.45μ diameter. For the size range $10\text{ m}\mu - 0.45\mu$, they reported particulate/total concentration ratios for Cu, Mn and Zn of 0.15/1.3, $< 0.01/0.31$ and 0.1/3.5, respectively.

The physical states of the fallout radionuclides $^{95}\text{Zr-Nb}$, ^{106}Ru , ^{137}Cs and ^{144}Ce in open ocean waters have been studied by Silker (1971) using large

volume sampling techniques. Contrary to the 1954 laboratory simulation results of Greendale and Ballou (1954), Silker found the filterable ($> 0.3\mu$) fractions of $^{95}\text{Zr-Nb}$, ^{106}Ru , ^{137}Cs and ^{144}Ce to average only 8, 2, <1 and 21 percent of their total concentrations in open ocean waters (see Table 4). These findings are opposite to the reported behavior of $^{95}\text{Zr-Nb}$, ^{106}Ru and ^{144}Ce discharged into Irish Sea coastal waters at Windscale (Templeton and Preston, 1966), where concentrations of detritus, suspended sediments and plankton are much higher than in the open ocean. In addition, the effluent from Windscale injects these radionuclides into the ocean mainly in particulate forms, being carried on a neutralized $\text{Fe}(\text{OH})_3$ suspension (Wilson, 1968).

Several studies of the abundance and chemical composition of suspended matter in coastal waters showed much higher concentrations of trace metals associated with particulates in coastal waters relative to the open ocean (Atkinson and Stefansson, 1969; Joyner, 1964; Spencer, et al, 1970; Williams and Chou, 1966).

The concentrations and suspected physico-chemical states of some of the important stable isotopes of abundant fission and neutron activation products are presented in Tables 5 and 6. It should be emphasized that these concentrations represent values reported for open oceanic waters which are not directly affected by river discharges or coastal disturbances. Likewise, the distribution between various physico-chemical states of these constituents would undoubtedly be much different in coastal versus open ocean waters. Fukai and Huynh-Ngoc (1968) have summarized recent data available in the literature concerning the different states of trace metals in seawater which can be separated by filtration. However, the concentration ranges of trace metals in filterable matter were so great that the most useful feature of the data is to indicate the extreme variability of trace metals in coastal waters versus the open ocean.

IMPORTANT ARTIFICIAL RADIONUCLIDES IN THE MARINE ENVIRONMENT

The most important radionuclides entering the marine environment are those with relatively long half-lives and the ability to be rapidly and efficiently taken up and retained by the marine biosphere. Most fission products (see Table 7 for major fission products in reactor fuel wastes) do not fall in this category. Strontium-90 ($t_{1/2} = 28.8\text{y}$) and ^{137}Cs (30y) have very long half-lives and long residence times in the ocean, but are not accumulated by marine organisms to any great extent, except for the reconcentration of ^{90}Sr by the marine plankton *Acantharia*, whose skeletons are formed of strontium sulfate crystals (Schreiber, 1968). However, *Acantharia* are rather scarce in the oceans and do not form a large base in the marine food chain. Strontium-90 and ^{137}Cs , plus minor amounts ^{154}Eu and ^{134}Cs are the fission products with sufficiently long half-lives to remain in nuclear wastes after many decades (see Table 8). Plutonium-239, ^{238}Pu and ^{240}Pu are the major radionuclides which will be present in nuclear wastes several hundred years after processing, assuming that a small fraction of the plutonium is not recovered during processing of fuels.

Neutron activation products of biologically essential transition elements (see Table 9) are important radionuclides in the marine environment because they are frequently accumulated to very high degrees by the biosphere. The most predominant activation products which have been observed in fallout and effluents from nuclear power reactors include ^{55}Fe , ^{65}Zn , ^{60}Co and ^{54}Mn . These elements are all biologically essential to marine organisms and are accumulated from seawater by factors ranging between 10^3 to 10^5 .

The major radionuclide constituents of Hanford origin in Columbia River sediments after the closure of the last plutonium production reactor in January, 1971 are ^{65}Zn , ^{54}Mn , ^{46}Sc , ^{60}Co , ^{152}Eu , ^{154}Eu (see Figure 2). Cesium-137, ^{144}Ce and ^{155}Eu are also present, but have originated from both the Hanford reactors

and atmospheric fallout. These radionuclides are very tightly bound to the sediment particles in the river bed and dissolution from the sediments is extremely slow. The Columbia River now presents a unique opportunity to study the radionuclide behavior and depletion processes as the river cleanses itself of its radionuclide inventory.

SPECIFIC ACTIVITY AND ITS LIMITATIONS

There are many factors that determine the food chain reconcentration of radionuclides by marine organisms. The most important is the stable-element chemistry of the organism and its environment. The most useful approach taken by marine radioecologists for predicting maximum allowable concentrations and biological accumulations of radioactivity in the marine environment is the specific activity concept. Specific activity refers to the ratio of radioactive atoms to total atoms of the same element in any environmental media. By using the stable-element distribution in environmental samples as a chemical analog for the radionuclide, it is possible to predict the dispersion of long-lived radionuclides through the marine food chain if we know: (1) the stable element chemistry of organisms constituting the links in the marine food chain, and (2) the specific activity ratio of the element at the source of its entry into the food chain.

$$\frac{\text{Radionuclide in Source}}{\text{Total element in Source}} = \frac{\text{Radionuclide in organism}}{\text{Total element in organism}}$$

The reasoning behind this approach is that organisms will ingest all isotopes of an element in the same proportion as they occur in the water or food source of the organisms, that is, isotopic fractionation will not occur. For example, if the total uptake on an element by a human organ comes from eating seafood, the specific activity in the organ should not exceed the specific activity in the ocean.

The basic assumption required for the application of the specific approach is that all isotopes (both radioactive and stable) of the same element be in identical chemical and physical forms and that equilibrium exist between the organisms and their environment. If a radionuclide is present in the ocean in a different physico-chemical form than its stable isotope(s), the biogeochemical behavior of the radionuclide could not be expected to parallel the behavior of the stable isotope(s). Kaye and Nelson (1968) have analyzed the specific activity concept as related to environmental reconcentration of radionuclides and stressed some of the assumptions and factors which should be considered in applying various specific activity modeling. Important assumptions and factors to be considered are: (1) stable and radioactive atoms of the element are in the same physico-chemical forms, are completely mixed and behave similarly, (2) biological half-time is known, (3) organisms are in equilibrium with their environment, (4) concentrations of the stable elements are known, (5) rates of growth of the organisms are known, and (6) rates of input of radioactive atoms are constant.

In laboratory experiments and in actual field studies, gross differences in the biological uptake between radionuclides and their stable isotopes from seawater have been observed and attributed to differences in physico-chemical forms. The major differences have occurred with elements which are present in the oceans in more than one form, i.e., Fe, Zn, Ru, etc., whereas no differences have been reported for the very conservative elements Sr and Cs. However, an interesting specific activity anomaly for ^{90}Sr in humans has been reported when human blood plasma contained consistently higher specific activities than human hair (Magno, et al, 1966). In this study it was suggested that the hair may have adsorbed stable strontium from some environmental source, or from sweat or from soaps or shampoo. However, in aquatic environments ^{90}Sr and ^{137}Cs follow

the behavior of their naturally occurring stable isotopes. Close agreement has been observed between the specific activities of ^{90}Sr and ^{137}Cs in Clinch River water and fish (Nelson, 1967; Nelson and Griffith, 1966), and for ^{137}Cs in the N.E. Pacific Ocean and its fish (Robertson, et al, 1968).

Specific activity differences have been observed between organisms and water in two Italian lakes during uptake of ^{54}Mn by mollusks (Merlini, 1967), by estuarine scallops and surrounding water (Schelske, et al, 1966), in the N.E. Pacific Ocean for ^{65}Zn and ^{60}Co in pelagic fishes and shrimp (Robertson, et al, (1968)(see Tables 10 and 11), and for salmon and other marine organisms (Palmer, Beasley and Folsom, (1966) (see Table 12). The anomalies observed in all of these studies have been attributed to differences in physico-chemical forms between the radionuclides and their stable isotopes. In order to examine such anomalies in more detail, several case studies are presented in the following section which illuminate the importance of understanding the speciation of trace constituents in the marine environment.

CASE STUDIES OF THE INFLUENCE OF PHYSICO-CHEMICAL FORMS OF RADIONUCLIDES AND TRACE ELEMENTS IN RELATION TO BIOLOGICAL UPTAKE

Iron- ^{55}Fe

Since the 1961-62 nuclear tests, ^{55}Fe increased from a minor fraction of fallout to the most abundant of all fallout radionuclides during the mid-1960's (Palmer and Beasley, 1967). Iron-55 is formed as a neutron activation product from the structural iron components used in nuclear weapons testing and has a half-life of 2.7 years. It is a very important fallout radionuclide in the marine environment because its stable isotopes are biologically essential and ^{55}Fe and stable iron are rapidly assimilated to great extents by marine organisms. The energy of the radiation emitted (5.9 keV X-rays) is small, but is of great interest since most of the radiation dose is absorbed by the red blood cells

of the body where ^{55}Fe is concentrated (Wrenn and Cohen, 1967). Iron-55 is also associated with stable iron requirements in porphyrins, cytochromes and certain enzymes (Davies, 1970).

Iron-55 is one of the most widespread radioactive contaminants in marine organisms, especially in high northern latitudes where it is deposited mainly as tropospheric fallout from USSR weapons testing at Nova Zemlya (75°N) and Central Asia (52°N). The greater ^{55}Fe deposition at high northern latitudes is opposite to the deposition patterns of stratospheric fallout where maximum deposition occurs in the middle latitudes. The deposition pattern of ^{55}Fe is reflected by the higher specific activities of fish taken off Iceland (65°N) and in the Bering Sea compared with the same species taken in the North Sea (52°N), and off the west coast of the United States (Palmer and Beasley, 1966; Jennings, 1968; Preston, 1970). The ^{55}Fe is transferred to human populations who consume large quantities of fish. Alaskan Eskimos whose major diet was fish contained ^{55}Fe body burdens about four times higher than Alaskan natives whose major diet was caribou (Palmer and Beasley, 1967). Because of the importance of ^{55}Fe in the marine biosphere, it is of great interest to understand the biogeochemical and physical oceanic processes which govern the ^{55}Fe and stable iron distribution in the oceans. Of particular concern is the role of the physico-chemical speciation of ^{55}Fe and stable iron in relation to biological assimilation by marine organisms.

The specific activity (ratio of radioactive atoms/total atoms of the same element) approach to predicting maximum allowable concentrations and biological accumulation of radioactivity in the marine environment assumes that the physico-chemical states of ^{55}Fe and stable iron in the oceans are identical, are in equilibrium, and behave similarly (Anonymous, 1967). Intuitively, this assumption appears reasonable, since the initial uptake, distribution and biological elimination should be the same for the radionuclide as for the stable form of the

same element. However, experimental and field data indicate that large differences exist between the behavior of ^{55}Fe and stable iron in the marine environment (Palmer et al, 1968). The first indication of these differences was observed by Palmer and Beasley (1968) who found that specific activities of ^{55}Fe in N.E. Pacific Ocean salmon were 1000 to 10,000 times greater than the seawater from which they were taken. This indicated that the ^{55}Fe entering the ocean from atmospheric fallout was in a different physico-chemical form than the stable iron in seawater, and that marine organisms preferentially accumulated ^{55}Fe compared to the stable iron.

In studying the uptake of iron from seawater by the marine diatom *Phaeodactylum tricornutum*, Davies (1967) observed some highly significant results which provide some explanation of the behavior of ^{55}Fe in the marine environment. He found that freshly formed hydrous ferric oxides were rapidly sorbed onto the surface of the diatoms. However, when the hydrous ferric oxides were allowed to "age" in seawater, they were rendered unreactive and were not taken up as rapidly by the diatoms. It was also observed that freshly hydrolyzed ferric oxides could build layers of iron oxide on diatom surfaces, whereas "aged" hydrous ferric oxides could not form sorbed layers. The majority of atmospheric fallout is associated with particles of sub-micron diameters (Drevinsky and Pecci, 1965), and ^{55}Fe is probably deposited at the sea surface in particles of similar size. The residence time of sub-micron sized particles in the surface layers of the ocean is long and mixing with deep waters will be governed by ordinary turbulent and thermohaline mixing processes, or biological processes. As these particles enter the ocean from the atmosphere, the ^{55}Fe will form freshly hydrolyzed ferric oxides which have been shown to be preferentially sorbed onto diatoms and plankton, relative to the "aged" hydrous iron oxides naturally present in seawater.

The ^{55}Fe specific activity of the diatoms and plankton will then be much greater than the surrounding seawater. This high specific activity ^{55}Fe will then be transferred up the food chain to higher trophic level marine organisms. It would then be expected that filter-feeding marine organisms feeding on diatoms and plankton would contain higher ^{55}Fe specific activities than more predaceous organisms, and this has actually been observed for various species of N. Pacific Ocean salmon (see Table 12). The ^{55}Fe specific activities of Sockeye salmon, which are greater filter-feeders than Chinook salmon, were observed to be 13-38 times higher than Chinook salmon. Unfortunately, no ^{55}Fe specific activity measurements of diatoms and phytoplankton have been made to compare with seawater and other marine organisms.

It now appears evident that a significant fraction of iron in oceanic waters is meteoritic in origin and is deposited from the atmosphere at rates of between 120-250 $\text{mg}/\text{m}^2/\text{year}$ (Labeyrie, 1968). Such iron will be deposited in the oceans in very small particles which will react with seawater to form hydrous ferric oxides. Labeyrie (1968) has measured the ^{55}Fe specific activity of this meteoritic iron and Preston (1970) has extrapolated this specific activity back to the period of maximum ^{55}Fe fallout in 1963. The specific activity of ^{55}Fe deposited at latitudes 60 - 70°N in 1963 probably amounted to about 1.8-3 $\text{nCi } ^{55}\text{Fe}/\text{mg Fe}$ and could have reached as high as 9 $\text{nCi } ^{55}\text{Fe}/\text{mg Fe}$. These values match the order of magnitude of the maximum ^{55}Fe specific activities found in marine organisms.

Jennings and Osterberg (1971) stress caution in interpreting differences in specific activities between marine organisms and their surrounding water. Because of local variations in fallout and stable element concentrations, and variations in the physical hydrography, the specific activity in a water mass

at one location would not necessarily equal the specific activity of an organism taken from another location, or for that matter from the small water mass. For example, if an organism accumulated most of its ^{55}Fe from relatively undisturbed surface waters and was then caught while temporarily residing in coastal waters during a period of intense upwelling of deep waters, the specific activity of the surrounding water would undoubtedly be much lower than the specific activity of the organism. The time that the organism accumulated most of its ^{55}Fe in relation to its growth period is also an important consideration. It has been suggested that salmon retain most of the iron they take up (Palmer and Beasley, 1967). Thus, rather than compare specific activities of salmon and water collected simultaneously, it would be more reasonable to compare the specific activity of ^{55}Fe in salmon with the specific activity of ^{55}Fe in seawater collected during the time of the salmon's period of most rapid growth, being one to six years before maturity, depending on the species (Jennings and Osterberg, 1971). Since ^{55}Fe input to the oceans has been decreasing since 1963, it would not be surprising to find mature salmon with a specific activity higher than the waters from which they were caught. However, this consideration does not appear to fully account for the very large specific activity differences observed by Palmer, et al (1968), and rates of biological uptake of various forms of radio and stable iron appears to be an important mechanism.

PHYSICO-CHEMICAL STATE OF STABLE IRON IN THE OCEANS

Since Cooper's (1948) original treatment of the possible forms of iron in the oceans, surprisingly little reliable data have become available to quantitatively characterize the various forms of iron. Most of the early iron measurements in seawater were for coastal waters which were greatly influenced by terrestrial runoff and resuspended sediments. However, recent data of Spencer,

et al (1970) indicate that the majority of iron in oceanic waters exists in a non-filterable ($< 0.45\mu$) form. Betzer (1970), in very careful work, has shown that the filterable fraction ($> 0.45\mu$) of iron in Atlantic oceanic waters averaged approximately $0.2 \mu\text{g/l}$. Betzer and Robertson (1971) have observed similar concentrations in a Pacific oceanic water column. These values are over ten times lower than most previously reported concentrations of filterable iron. In coastal waters the filterable fraction of iron increases significantly and is extremely variable (Atkinson and Stefansson, 1969; Joyner, 1964; Williams and Chan, 1966). Thermodynamic considerations indicate that ferric iron is by far the dominant oxidation state present in normal ocean conditions (Horne, 1969). Only in anoxic waters would ferrous iron be expected to be present in appreciable amounts. The most dominant ferric species in seawater probably exists as dispersed, colloidal $\text{Fe}(\text{OH})_3$ (Horne, 1969). Since the solubility product of $\text{Fe}(\text{OH})_3$ is 10^{-37} , negligible amounts of Fe^{+3} ion should exist in seawater. The most abundant ionic species is probably the hydroxy complex $\text{Fe}(\text{OH})^{+2}$, although $\text{Fe}(\text{OH})_2^+$, $\text{Fe}_2(\text{OH})_2^{+4}$ and ferric phosphate complexes may also be present (Sillen, 1961). Soluble, organically chelated iron is believed to play an important role in the marine environment, especially for converting iron to a form more available for planktonic organisms (Barber, et al, 1971; Desai and Ganguly, 1970; Ingle and Martin, 1969; Johnston, 1964; Koshy and Ganguly, 1969). However, no iron chelates have ever been isolated from seawater, although several organic compounds have been detected which possess the ability to form chelates with a large number of transition metals (Duursma, 1965). However, these naturally occurring organic compounds are present in the oceans in very low concentrations and their ability to chelate with metal ions at such low concentrations has been minimized (Duursma and Sevenhuysen, 1966).

There remains an obvious need for further research aimed at elucidating the physico-chemical forms of iron and ^{55}Fe in the marine environment. Of immediate concern is the characterization of colloidal and organic iron species, especially in relation to biological uptake. The behavior of hydrous ferric oxides in the marine environment is also of immediate interest since they may control the apportionment of many other trace metals in the ocean.

Zinc - ^{65}Zn

Zinc-65 is produced during nuclear weapons testing and is deposited in the oceans from atmospheric fallout. Increasing amounts of ^{65}Zn are reaching the oceans in liquid effluents from power reactor operations, although present levels in discharges are very low. Zinc-65, which had originated from the Hanford reactors, is still the predominant radionuclide in Columbia River sediments (Robertson, 1971; see Figure 2), and ^{65}Zn was the limiting radionuclide governing discharges from the Bradwell Power Station in the U.K. (Preston, 1961). Zinc-65 is widespread in the marine environment and has been detected in various organisms by many investigators (Robertson, 1968; Folsom, et al, 1963; McCauley, 1971; Nagata and Folsom, 1964; Osterberg, et al, 1964; Perkins, et al, 1960; Watson, et al, 1961; Wolfe, 1970; Young and Folsom, 1967).

A close examination of the behavior of ^{65}Zn in the marine environment and in laboratory studies indicates that it is not always in the same forms as the stable zinc naturally occurring in the oceans. Bernard and Zattera (1969) observed that the uptake of zinc and added ^{65}Zn by diatoms and Chelex-100 chelating resin occurred at different rates, and that equilibration between the zinc and the ^{65}Zn was slow relative to biological uptake (see Figure 3). The obvious explanation is that the zinc and ^{65}Zn were present in the seawater culture medium in

different physico-chemical forms, and that the ^{65}Zn was not diluted in the entire pool of the stable zinc, but only in that fraction which had the same physico-chemical form.

Kane, et al (1969) in studies of ^{65}Zn uptake by crabs found that the biological elimination of the ^{65}Zn was much different when crabs were placed in laboratory seawater compared with seawater from the open ocean (see Figure 4). The temperature, salinity and total zinc concentrations of the two seawaters were the same, and stable zinc additions of 0.1 and 1.0 mg Zn/l to the open ocean seawater did not affect the rates of ^{65}Zn elimination from the crabs. It appeared that some constituent in the laboratory seawater retarded the elimination of ^{65}Zn from the crabs. No explanation of this unusual behavior has been given.

Wolfe (1970b) reported that the "ecological" half-life of fallout ^{65}Zn in oysters was higher than the physical half-life of ^{65}Zn . He attributed this to the fact that ^{65}Zn in fallout is not equilibrated with the stable zinc in the environment and that the ^{65}Zn was taken up by oysters more efficiently than stable zinc. Possibly oysters have the ability to filter particulate fallout material directly from seawater which represents a source of ^{65}Zn at a very high specific activity. Continuous ingestion of particulate fallout could help to provide the ^{65}Zn necessary to prolong the "ecological" half-life.

Robertson, et al (1968) observed that the specific activities of ^{65}Zn in several N.E. Pacific Ocean pelagic organisms were approximately two orders of magnitude higher than in the surrounding seawater. It is difficult to assess whether these anomalies were due to differences in physico-chemical forms, or whether this was an artifact due to ^{65}Zn and ^{60}Co contributions from the Columbia River.

Larson, et al (1971) reported that ^{65}Zn specific activities in mussels living along the Pacific Northwest coast were approximately 10 times higher than

could be attributed to linear mixing of Columbia River water with the Pacific Ocean water at the sampling locations. A likely explanation which they offer for this observation is that the relatively high-specific activity of ^{65}Zn from the Columbia River may be in a physico-chemical form that is more readily assimilated by mussels than the form of zinc naturally occurring in seawater.

In studies of the accumulation and distribution of ^{65}Zn and ^{54}Mn in the freshwater clam, *Anodonta*, (Harrison, 1969), specific activity measurements indicated that in all parts of the body, a large fraction of the zinc and manganese was in pools with which the radionuclides did not exchange. Thus, evidence from both laboratory experiments and ocean observations indicate differences in biological uptake between ^{65}Zn and stable zinc.

A literature review of the occurrence of zinc in the marine environment indicates the complexity of its distribution among various physico-chemical forms. Slowey and Hood (1971) and Rona, et al (1962) have separated zinc in Gulf of Mexico waters into three forms: (1) extractable zinc, being that fraction removed by solvent extraction with diethyldithiocarbamate and assumed to be soluble ionic or weakly complexed zinc, (2) non-dialyzable zinc, which was assumed to be bound organically, and (3) particulate zinc. The average concentrations of zinc in these three fractions from open seawaters were $2.6 \mu\text{g}/\ell$, $1.5 \mu\text{g}/\ell$ and $0.4 \mu\text{g}/\ell$, respectively. About 75% of the particulate zinc was associated with particles greater than 0.45μ diameter. Torti (1969) found that the ionic zinc in the Ligurian Sea and Gulf of Spezia was consistently only 10% of the total zinc. Baric and Branica (1967), using polarographic techniques to study the speciation of zinc in seawater, concluded that the major inorganic species present is the simple aquo ion Zn^{+2} , and smaller amounts of the monohydroxo complex ZnOH^+ . Spencer, et al (1970), during a pre-GEOSecs intercalibration exercise

in the open N.E. Pacific Ocean found that filtering the seawater through 0.45 μ membrane filters did not significantly alter the total zinc concentration in the water. In fact, the concentrations of total suspended matter in the 4000 meter water column averaged only 20 ug/l, and assuming an average zinc concentration of 200 ppm for suspended matter in the open ocean (Chesselet, 1971), the particulate zinc concentrations must have been about 0.004 μ g/l. Compared to an average total zinc concentration of 3.5 ug/l for the water column, the fraction of zinc in a particulate form would be about three orders of magnitude lower than the soluble forms. Spencer, et al (1970) found that if the seawater samples were not acidified to a pH of about 1.7, approximately half of the total zinc was lost by adsorption onto the container surfaces (see Figure 5). These results were contrary to tracer experiments with ^{65}Zn , which indicated that no zinc was lost by adsorption on container walls even at pH 8.0 (Robertson, 1968). Apparently, this was another case where the inorganic ^{65}Zn tracer (added as soluble nitrate) behaved much differently than the naturally occurring zinc in seawater and equilibration between the two forms was very slow. This observation increases the circumstantial evidence that a large fraction of the soluble zinc in seawater is in a form other than ionic or inorganic complexes, and is probably organically bound. If we assume that the zinc in the unacidified seawater samples of Spencer, et al (1970) (avg. conc. 1.7 ug/l) represented only ionic or inorganic complexed zinc and the total zinc in the acidified seawater samples (avg. conc. 3.5 ug/l) represented both ionic zinc and organically complexed zinc, then the total zinc appeared to be distributed as 50% inorganic ions and 50% organically complexed. This distribution would be very similar to the results of Slowey and Hood (1971).

Kuenzler (1969) during studies of uptake of ^{65}Zn by marine zooplankton found that significant fractions of the ^{65}Zn in excreta was in the form of a non-ionic soluble species, presumably being organically complexed.

Zinc is biologically essential in the marine environment and is a constituent of several important enzymes (Fowler and Small, 1969; Pequegnat, et al, 1969; Wolfe, 1970b). Wolfe (1970b), in studies of the zinc enzymes in oysters, found nearly all of the zinc bound, either to high molecular weight proteins, or to structural cellular components such as cell membranes. The main zinc enzyme in the oysters was alkaline phosphatase. Dialysis of the oyster soluble tissue extracts at pH 7-9 removed up to 96% of the total zinc without affecting the alkaline phosphatase, indicating that the zinc enzymes account for only a small portion of the total zinc in oysters. The remaining zinc is probably accumulated coincidentally with other ions such as Ca. Perhaps the oyster has a poor ionic discrimination capacity at its environmental interface and an efficient discriminating capacity at the mantle-shell boundary, so that the Ca is assimilated and deposited in the shell, whereas Zn remains loosely bound to the tissue proteins. Pequegnat, et al (1969) confirmed the observation that zinc is accumulated by marine organisms far in excess of the zinc enzyme requirements of the organism. Fowler, et al (1969), from studies of ^{65}Zn uptake by euphausiids, concluded that the accumulation and loss of ^{65}Zn apparently is largely non-metabolically controlled. They found that ^{65}Zn was taken up more efficiently by sorption onto dead organisms than was assimilated by live euphausiids, and that most of the ^{65}Zn activity was on the molted exoskeleton. In a later study Fowler, et al (1971) postulated that zinc attached to euphausiid molts would be 87% lost by dissolution by the time the sinking molts reached a depth of slightly over 400 meters. Such a process could explain the depth distribution at the N.E. Pacific Ocean pre-GEOSECS station, where the presumed organic zinc appeared to increase with depth.

Ruthenium - ^{106}Ru

Ruthenium 103-106 enter the oceans in atmospheric fallout from nuclear weapons testing and in a more concentrated form as point source discharges from

nuclear fuel reprocessing plants at Windscale, U.K. and the La Hague area of France. Because of its longer half-life, ^{106}Ru is the principle ruthenium radionuclide in the oceans. Ruthenium-106 constituted 90-98% of the total radioactivity of the fission products discharged at Windscale in the 1950's (Jones, 1960), and is still a major component of Windscale discharges (Preston and Jeffries, 1969). Ruthenium-106 is also a major constituent in radioactive wastes discharged into the Bay of Ec lgrain in the La Hague region (Guegueniat and Lucas, 1969). The limiting radionuclide for safe releases of nuclear wastes at Windscale was found to be ^{106}Ru . The critical pathway for this radionuclide is through the seaweed, *Porphyra umbilicalis*, used to make laverbread, which is eaten by a small number of people in South Wales. The critical group concept of the limiting human radiation exposure pathway of ^{106}Ru via laverbread is discussed in detail by Preston and Jefferies (1969).

The ^{106}Ru released at Windscale is in both particulate and soluble forms since the discharged effluent consists of a very dilute aqueous solution of pH about 8-9, carrying a suspension of ferric hydroxide (Wilson, 1968). Studies of the physico-chemical states of ^{106}Ru in the Windscale effluent disclosed the following forms (Wilson, 1968):

Solid	55 ± 10	} % of total Ru
Colloidal	7 ± 3	
Dissolved	38 ± 10	
Anionic	51.2 ± 5.1	} % of dissolved Ru
Cationic	13.0 ± 1.4	
Neutral	45.8 ± 5.3	

The particulate ^{106}Ru is nearly irreversibly bound to the $\text{Fe}(\text{OH})_3$, whereas the dissolved species are present as nitrosylruthenium complexes. The nitrosylruthenium grouping is extremely stable and probably remains in that state in the oceans.

The nitrosylruthenium in the Windscale effluent is considered to be mainly complexed with the more labile nitro and nitrate groups, but the complex speciation undoubtedly changes upon dilution in seawater, and Jones (1960) reported that the nitrate complexes convert to nitrosylruthenium chloride in the ocean.

In neutral solutions nitrosylruthenium hydrolyzes and gradually polymerizes and converts to a colloidal form, but upon further dilution the colloids appear to slowly break down (Wilson, 1968). The equilibrium between nitrate-nitrosyl complexes of ruthenium in aqueous solution is extremely complex and a simplified review of some of the various forms has been reported by Wyatt and Rickard (1961). Guegueniat (1970) has reported on the complex physico-chemical speciation of ruthenium in seawater.

The biological uptake of ^{106}Ru is complicated by the diverse physico-chemical species present in seawater. In coastal waters where concentrations of suspended sediments are high, ^{106}Ru exists predominantly in a particulate form (Templeton and Preston, 1966). However, in open ocean waters, where suspended matter is low and ^{106}Ru originates from atmospheric fallout, the ^{106}Ru is mainly in a non-filterable form (Silker, 1971; see Table 4). In coastal discharges the ^{106}Ru becomes attached to fine silt or sand particles and the presence of ferric hydroxide coatings on these particles enhances the ^{106}Ru adsorption. Bottom feeding fish accumulate ^{106}Ru in the gut, gills and skin by ingesting bottom organisms containing sediments and by direct contact with the sediments (Jones, 1960).

The adsorption of ^{106}Ru on the edible seaweed *Porphyra* appears to be a surface phenomena involving complexation with the extra-cellular polysaccharide material (Jones, 1960). Wilson (1968) believes that the uptake of ^{106}Ru by *Porphyra* also involves a cation exchange mechanism. Porphyran, a sulfated polysaccharide which forms much of the extra-cellular material of the seaweed *Porphyra*, is essentially a chain of galactose units with $-\text{OSO}_3\text{H}$ groups at frequent, but irregular intervals (Wilson, 1960). This structure is analogous

with the sulfonated polystyrene type of cation exchange resins, and the porphyrin is probably capable of acting as a cation exchanger. Although ^{106}Ru is initially present mainly as an anionic complex, the equilibrium between anionic, neutral and cationic species appears to be fairly rapid, so that a cation exchanger can be a fairly effective adsorbant for ^{106}Ru .

Soluble species of ^{106}Ru in different chemical forms are accumulated by the marine biosphere at grossly different rates. Keckes, et al (1967) observed that the uptake of ^{106}Ru in chloride complex forms by the mussel, *Mytilus galloprovincialis* Lam., was ten times greater than for ^{106}Ru in nitrate complex forms (see Figure 6). These investigators and Marazonic and Pucar (1967) investigated the chemical speciation of the chloride and nitrate complexes of the ^{106}Ru using a two-dimensional electrochromatographic technique. They found that the distribution of ^{106}Ru in seawater involved a great number of well-defined species which they classified as anionic, cation, electroneutral and particulate (see Figure 7). The ^{106}Ru in the chloride complexed form occurred mainly as a neutral species, with smaller fractions of both cationic and anionic forms. The ^{106}Ru in the nitrate complexed form occurred mainly as anionic species with lesser fractions of cationic and electroneutral forms. Kimura and Ichikawa (1970) observed similar, but less pronounced behavior of ^{106}Ru in chloride and nitrate forms in uptake by the short-necked clam, *Tapes japonica*. These experiments clearly illustrate the great importance of the physico-chemical speciation of ruthenium and other trace constituents in bioaccumulation processes.

Plutonium

Plutonium is an artificial radioelement with no stable isotopes, but it is of considerable interest in the marine environment and possesses some interesting physico-chemical characteristics in the ocean. Approximately 5000 kilograms

(300 kilo-curies) have been deposited over the earth in fallout from nuclear weapons testing (Harley, 1971). Miyake, et al (1970) estimate a total release of 3700 kilograms of $^{239,240}\text{Pu}$. The majority of this fallout has entered the oceans. It has been estimated that by 1980 the U.S. alone will be producing 15,000 - 20,000 kg of Pu each year (Andelman and Rozzell, 1970). Its uses as reactor fuels and power sources will increase the probability of environmental contamination.

The most abundant plutonium nuclide is ^{239}Pu , but ^{238}Pu and ^{240}Pu have also been detected. In 1966 the $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio over Tokyo, Japan averaged 0.018. However, the accidental release of 17,000 curies of ^{238}Pu during a SNAP-9A nuclear power source burnup in 1964 increased this ratio to about 0.16 during 1967-1969 (Miyake, et al, 1970). Plutonium-239 concentrations in ocean surface waters range from $0.11 - 3.0 \times 10^{-15} \text{ Ci/kg}$ ($1.8 - 48 \times 10^{-15} \text{ g/kg}$) (see Table 1). Miyake and Sugimura (1968) have observed characteristic surface concentrations of ^{239}Pu down to a depth of 3000 meters in the Pacific Ocean and Bowen, et al, (1971) have observed penetration of ^{239}Pu to a depth of 2200 meters in the Atlantic, although not to the extent observed in the Pacific by Miyake and Sugimura. This deep penetration of the oceans by plutonium indicates that a large fraction of plutonium must be present in the oceans in a particulate form which can sink at a fairly rapid rate. An examination of the ratios of $^{239}\text{Pu}/^{90}\text{Sr}$ and $^{239}\text{Pu}/^{137}\text{Cs}$ in fallout or ocean aerosols and in the oceans tends to verify the particulate nature of plutonium in the oceans. The $^{239}\text{Pu}/^{90}\text{Sr}$ ratio in fallout over the Atlantic Ocean averages 0.013, whereas the ratio in surface seawater averages 0.0056. The ratio in seawater increases to about 0.013 in waters below a depth of 500 meters (Bowen, et al, 1971). The $^{137}\text{Cs}/^{239}\text{Pu}$ ratio exhibited similar behavior. It thus appears that plutonium separates from the more soluble radionuclides ^{90}Sr and ^{137}Cs in the surface waters and settles downward through the water column.

Bowen, et al (1971) observed a ^{239}Pu maximum concentration at a depth of about 500 meters and suggested that bacterial degradation of biogeneous particles containing plutonium occurs as these particles settle in the oceans; a process similar to regeneration of nutrients in deep waters. Thus, biological sedimentation appears to be an important mechanism for the removal of plutonium from the oceans. Unfortunately, none of the investigations of plutonium in the oceans characterized the physical state by utilizing membrane filtration.

The concentrations of ^{239}Pu in marine organisms varies widely (see Table 15). Plutonium obviously serves no useful function in the biochemistry of marine organisms and is co-accumulated by ingestion of food, water or sediments, or is adsorbed on the outer surfaces of organisms. Considering the generally higher concentration factors of ^{239}Pu compared to ^{90}Sr and ^{137}Cs , and the relative biological effectiveness of alpha vs beta or gamma radiation, ^{239}Pu appears now to contribute more than ^{90}Sr and ^{137}Cs to the artificial radiation exposure of marine invertebrates (Wong, et al, 1970). The data in Table 15 indicate that physical adsorption onto organisms and plants is an important mechanism. Indeed, in ^{239}Pu uptake, experiments with the lobster, *Homarus vulgaris*, Ward (1966) found that 89.5% of the ^{239}Pu was associated with the shell of the lobster. Plutonium concentrations in muscle tissue were always very low, representing accumulation factors of only 1-5. Highest concentrations were normally found in the gut of fishes where it was ingested with the food of the fishes.

The physico-chemical behavior of plutonium in very dilute aqueous solutions would indicate that sorption on inorganic particulate matter in the oceans may also be an important process in removing plutonium from the oceans. Plutonium hydrolysis products in natural waters exhibit colloidal behavior and these hydrolyzed forms possess the ability to easily adsorb onto minerals and other

surfaces (Andelman and Rozzell, 1970; Sheidina and Kovarskaya, 1970). The most stable oxidation state expected for plutonium in natural waters is the tetravalent species (Andelman and Rozzell, 1970). At pH's greater than 7, very low concentrations (10^{-9} to 10^{-10} M) of plutonium exist in aqueous solutions as $\text{Pu}(\text{OH})_4$ colloids of negative charge (Sheidina and Kovarskaya, 1970). These colloids are too small to be centrifuged at 3000 rpm, but they form pseudocolloids by adsorption onto impurities in the solution. Aging of plutonium colloids in natural waters increases the aggregate size, as does increasing the ionic strength of the solution. These aggregates can be sorbed onto silica surfaces (Andelman and Rozzell, 1970). It seems likely that the plutonium deposited in the oceans from fallout would rapidly sorb onto inorganic (as well as organic) particles present in the seawater.

Lai and Goya (1966) conducted a series of informative experiments by reacting plutonium metal with seawater. Plutonium metal reacts completely with seawater to form solid reaction products of two types: (1) a black solid believed to be PuO and (2) a greyish-green gelatinous material composed of Pu (IV) hydroxide or oxides. Once formed, the rate of dissolution of these reaction products is slow (1.5-2 $\mu\text{g/day}$ per 50-70 mg of solids). The equilibrium concentration of dissolved plutonium, (or more appropriately, the species passing a 0.45 μ filter) in seawater was about 67 $\mu\text{g/l}$ and was attained after 25 to 40 days. Since the solubility product of $\text{Pu}(\text{OH})_4$ in water is 7×10^{-56} , it is obvious that the equilibrium concentrations in "solution" must either be present as colloidal or complexed species of plutonium. Lai and Goya (1966) observed that greater than 90% of the plutonium aggregates formed by plutonium reaction products in seawater are less than 0.01 μ in diameter. These investigators have studied the effects of natural complexing anions in seawater with the solid plutonium reaction

products formed in seawater and concluded that carbonate, sulfate, borate and possibly phosphate ions could form stable plutonium complexes in seawater. At least by gradually increasing the amounts of these anions in natural seawater, they were able to increase the equilibrium concentration of the "soluble" plutonium species. Carbonate ion exhibited the greatest complexing ability. In addition, they found that the combined effect of these anions was additive. Therefore, the dissolution of plutonium reaction products in seawater may be controlled by the formation of soluble anionic complexes. However, in view of the apparent particulate behavior of plutonium in the oceans, it appears that the complexing reactions leading to the solubility of plutonium particles must either be slower than demonstrated in the laboratory by Lai and Goya, or that these species also attach to suspended matter in the oceans and settle to the ocean floor. Also, the physico-chemical forms of plutonium entering the oceans as atmospheric fallout are undoubtedly different from the fresh reaction products generated by Lai and Goya, and would be expected to behave much differently in the oceans.

Kubose, et al (1968) have studied the behavior of plutonium dioxide in seawater in connection with programs involving SNAP fuel materials. These investigators exposed plutonium dioxide microspheres to seawater at a depth of 50 feet off San Clemente Island for a period of 5 months to determine the effects of in situ exposure. Their most significant finding was that approximately 70 percent of the microspheres became encrusted with marine growth! This phenomena was beneficial in the sense that it significantly retarded the dissolution rates of the microspheres, but on the other hand this could increase the probability of a microsphere's entering the marine food chain. Microscopic examination of the microspheres showed no visible evidence of surface chemical or structural changes. X-ray diffraction results indicated single phase stoichiometric $\text{PuO}_{2.00}$.

Their studies indicated that contamination of the marine environment from a point source addition of PuO_2 would be very localized. The dissolution rate of PuO_2 microspheres in seawater is much lower than that observed for fresh plutonium metal reaction products formed in seawater by Lai and Goya (1966).

In summary, it appears that the majority of the plutonium present in the oceans is available for biological assimilation mainly in a particulate form. For seaweeds and certain crustaceans, the relatively high accumulation of plutonium appears to be a surface adsorption process, probably not unlike that observed for ruthenium.

Teresi and Newcombe (1966) indicate that the critical pathway of plutonium from the oceans to man may be by uptake by the alga, *Porphyra* and subsequent transfer through the seaweed products agar and alginic acid.

The concentration of plutonium from a single release in the sea that would lead to the permissible body burden through a fish food chain was calculated on the basis of published concentration factors. The value of the concentration of plutonium to give this body burden was found to be $6.4 \times 10^{-2} \mu\text{Ci/ml}$, assuming a single intake of 200 gms of fish per individual. Present levels of plutonium-239 in oceanic waters (see Table 14) are about 10^{10} lower than the estimated maximum permissible concentration for seawater.

In studying the behavior of plutonium in an arctic marine environment after the U.S. B-52 crash at Thule, Greenland, Aarkrog (1971) observed no strong evidence for solubilization of particulate plutonium in the marine environment. The plutonium was released as PuO_2 with a mean diameter of 2μ and its subsequent movement through the marine food chain indicated no major changes in physico-chemical forms.

REFERENCES

- Aarkrog, A. Radiological investigation of plutonium in an Arctic marine environment. *Health Physics* 20, 31-47 (1971).
- Alexander, G. V. and R. H. Rowland. Estimation of zinc-65 background levels for marine coastal waters. *Nature* 210, 155-157 (1966).
- Andelman, J. B. and T. C. Rozzell. Plutonium in the water environment. I. Characteristics of aqueous plutonium. pp. 118-137. in Radionuclides in the Environment. *Advances in Chemistry Series* 93, American Chemical Society, Washington, D. C., 1970.
- Anderson, T. D. Offshore Siting of Nuclear Energy Stations, *Nuclear Safety* 12, 9-14 (1971).
- Anonymous. Disposal of low-level radioactive waste into Pacific Coastal Waters. *NAS-NRC Publication* 985. National Academy of Sciences, National Research Council, Washington, D. C., 1962.
- Anonymous. Polarographic investigations of cadmium, zinc and indium. Annual Report on Research Contract No. 201/R2/RB July 1965 - June 1966. Institute Ruder Boskovic, Rovinj and Zagreb, Yugoslavia, 68-82, 1966.
- Anonymous. Report of the seminar on methods of detection, measurement and monitoring of marine pollutants. Panel 7: Radioactivity. *FAO Fisheries Reports*, No. 99, (suppl. 1)FAO, Rome, August, 1971.
- Atkinson, L. P. and U. Stefansson. Particulate aluminum and iron in seawater off the southeastern coast of the United States. *Geochim. Cosmochim. Acta* 33, 1499-1453 (1969).
- Barber, R. T., et al. Variations in phytoplankton growth associated with the source and conditioning of upwelling water. *Investigacion Pesquera* 35, Publicado en febrero de 1971, Barcelona, 1971.
- Barber, R. T. and Ryther, J. H. Organic chelators: factors affecting primary production in the Cromwell Current upwelling. *J. exp. mar. Biol. Ecol.* 3, 191-199 (1969).
- Baric, A. and M. Branica. Polarography of sea water. I. Ionic state of cadmium and zinc in sea water. *J. Polarographic Society* 13, 4-8 (1967).
- Beasley, T. M. Mercury in selected fish protein concentrates. *Environ. Sci. Technol.* 5, 634-635 (1971).
- Bernhard, M. and A. Zattera. A comparison between the uptake of radioactive and stable zinc by a marine unicellular alga. In Symposium on *Radioecology*, (editors D. J. Nelson and F. C. Evans), University of Michigan, Ann Arbor, Michigan, March 1969.
- Betzer, P. R. and M. E. Q. Pilson. Concentration of particulate iron in Atlantic open-ocean water. *J. Mar. Res.* 28, 251-267 (1970).

- Betzer, P. R. and D. E. Robertson. (1970). Unpublished work.
- Bowen, V. T., et al. Plutonium-239 in and over the Atlantic Ocean. *J. Mar. Res.* 29, 1-9 (1971).
- Cooper, L. H. N. Some conditions governing the solubility of iron. *Proceedings of the Royal Society of London* 124B, 299-307 (1937).
- Cooper, L. H. N. Some chemical considerations on the distribution of iron in the sea. *J. Mar. Biol. Ass. U.K.* 27, 314-321 (1948).
- Corbit, C. D. Reactors, radiation and risk, The three Rs of public concern. *Proc. Fifth Annual Health Phy. Soc. Midyr. Topical Symp, Health Physics Aspects of Nuclear Facility Siting*, Vol. 111. Idaho Falls, Idaho, Nov. 3-6, 1970.
- Corcoran, E. F. and J. E. Alexander. The distribution of certain trace elements in tropical seawater and their biological significance. *Bull. Mar. Sci. Gulf & Carib.* 14, 594-602 (1964).
- Chesselet, R. Oral communication at the 1971 *Gordon Res. Conf. on Chemical Oceanography*, Santa Barbara, California, January 1971.
- Davies, A. G. Studies of the accumulation of a radio-iron by a marine diatom. In *Radioecological Concentration Processes*, 983-991 (editors B. Aberg and F. P. Hungate) Pergamon Press, Inc., New York, 1967.
- Davies, A. G. Iron, chelation and the growth of marine phytoplankton. *J. Mar. Biol. Ass. U.K.* 50, 65-86 (1970).
- Desai, M.V.M. and A. K. Ganguly. Interaction of trace elements with the organic constituents in the marine environment. *BARC-488*. Government of India Atomic Energy Commission. Bhabha Atomic Res. Center, Bombay, India, 1970.
- Drevinsky, P. J. and J. Pecci. Size and vertical distributions of stratospheric radioactive aerosols. pp. 158-182. In *Radioactive Fallout from Nuclear Weapons Tests*, (editor W. W. Klement) USAEC November, 1965.
- Duursma, E. K. The dissolved organic constituents of sea water. In *Chem. Oceanography* (editors J. P. Riley and G. Skirrow) Academic Press, London, 1965.
- Duursma, E. K. Organic chelation of ^{60}Co and ^{65}Zn by leucine in relation to sorption by sediments. In *Organic Matter in Natural Waters*, (editor D. W. Hood) Univ. of Alaska, June 1970.
- Duursma, E. K. and W. Sevenhuysen. Note on chelation and solubility of certain metals in sea water at different pH values. *Netherlands J. of Sea Res.* 3, 95-106 (1966).
- Folsom, T. R., et al. Manganese-54 and zinc-65 in coastal organisms of California. *Nature* 200, 327-329 (1963).
- Fowler, S. W. and L. F. Small. Metabolism of zinc-65 in euphausiids. In *Symp. on Radioecology* (editors D. J. Nelson and F. C. Evans) Univ. Michigan, Ann Arbor, Michigan, pp. 399-411, (1969).

- Fowler, S. W. et al. Experimental studies on elimination of zinc-65 cesium-137 and cerium-144 by euphausiids, *Marine Biol.* 8, 224-231 (1971).
- Fukai, R. and L. Huynh-Ngoc. Studies on the chemical behavior of radionuclides in seawater. I. General consideration and study of precipitation of trace amounts of chromium, manganese, iron, cobalt, zinc and cerium. *IAEA Radioactivity in the Sea* No. 22 (1968).
- Garrels, R. M. and M. E. Thompson. A chemical model for sea water at 25°C and one atmosphere total pressure, *Am. J. Sci.* 260, 57 (1962).
- Goldberg, E. D. The oceans as a chemical system. In *The Sea* (editor M. N. Hill), Interscience Pub., New York, pp. 3-25 (1963).
- Greendale, A. E. and N. E. Ballou. Physical state of fission product elements following vaporization in distilled water and seawater. *USNRDL-436*, U. S. Naval Radiological Defense Laboratory, San Francisco, Calif., 1954.
- Guegueniat, P. Etude sur la physico-chimie du ruthenium dan l'eau de mer. *CEA-R-4125*, Centre de la Hague, December, 1970.
- Guegueniat, P. and Y. Lucas. Observations sur la contamination in situ de quelques especes marines. *CEA-N-1185*, Centre d'Etudes Nucleaires de Fontenay-aux-Roses, September 1969.
- Harley, J. H. Worldwide plutonium fallout from weapons tests. In preprints of *Environmental Plutonium Symposium*, Los Alamos Scientific Lab., Los Alamos, N. Mexico, August 1971.
- Harrison, F. L. Accumulation and distribution of ⁵⁴Mn and ⁶⁵Zn in freshwater clams. In *Symp. on Radioecology*, (editors D. J. Nelson and F. C. Evans) Univ. of Michigan, Ann Arbor, Mich. pp. 198-220, March 1969.
- Horne, R. A. *Marine Chemistry* pp. 181-184, John Wiley & Sons, Inc. New York 1969.
- Ingle, R. M. and D. F. Martin. Prediction of the Florida Red Tide by means of the iron index. *Environ. Letters* 1, 69-74 (1971).
- Jenkins, C. E., et al. Iron-55 concentrations in Columbia River estuarine and Pacific Ocean marine organisms. BNWL-1051, Part 2, pp. 69-72. Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, Washington, June 1969.
- Jennings, C. D. Iron-55 in Pacific Ocean organisms. Ph.D. Thesis, Oregon State University, June, 1968.
- Jennings, C. D. and C. L. Osterberg. Specific activity of iron-55 in Pacific salmon. pp. 104-117. In Progress Report *Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean* (editor J. E. McCauley), July, 1971.
- Johnston, R. Sea water, the natural medium of phytoplankton II. Trace metals and chelation, and general discussion. *J. Mar. Biol. Ass. U.K.* 44, 87-109 (1964).

- Jones, R. F. The accumulation of nitrosyl ruthenium by fine particles and marine organisms. *Limnol. Oceanogr.* 5, 312-325 (1960).
- Joyner, T. The determination and distribution of particulate aluminum and iron in the coastal waters of the Pacific Northwest. *J. Mar. Res.* 22, 259-268 (1964).
- Kane, J., et al. Errors in the extrapolation of laboratory experiments to field observations. *Rapp. Comm. Int. Mer. Medit.* 20, 1969.
- Keckes, S., et al. The influence of the physico-chemical form of ^{106}Ru on its uptake by muscles from seawater. pp. 993-994. In *Radioecological Concentration Processes*. (editors B. Aberg and F. P. Hungate) Pergamon Press, Inc., New York, 1967.
- Kimura, K. and R. Ichikawa. Uptake of ruthenium-106 by short-necked clam. *Bull. Japan Soc. Sci. Fish.* 36, 653-660 (1970).
- Koshy, E. and A. K. Ganguly. Organic materials in the marine environments and their interactions with some metal ions BARC-402, Government of India Atomic Energy Commission, Bhabha Atomic Research Centre, Bombay, India, 1969.
- Kubose, D. A., et al. Radioactivity release from radionuclide power sources IIIa. Dissolution studies of plutonium dioxide in the ocean - 5 months exposure. USNRDL-TR-88-74. U. S. Naval Radiological Defense Laboratory, San Francisco, Calif., April 1968.
- Kuenzler, E. J. Elimination of iodine, cobalt, iron and zinc by marine zooplankton. In *Symp. on Radioecology*. (editors D. J. Nelson and F. C. Evans), pp. 462-473. University of Michigan, Ann Arbor, Michigan, March 1969.
- Labeyrie, J. Le fer dans la mer. *Revue int. Oceanogr. med.* 11, 129-140 (1968).
- Lai, M. G. and H. A. Goya. Radioactivity release from radionuclide power sources. III. Release from plutonium metal to seawater. USNRDL-TR-1050. U. S. Naval Radiological Defense Lab., San Francisco, Calif. July 1966.
- Larson, I. L., et al. Zinc-65 specific activity in *Mytilus californianus* tissues. In Progress Report *Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean*, (editor J. E. McCauley), Oregon State Univ., Corvallis, Oregon, July 1971.
- Marazovic, L. J. and Z. Pucar. Two-dimensional electrochromatography of ruthenium-106 and some other radiomicroconstituents in sea water. *J. Chromatography* 27, 450-459 (1967).
- Martin, D. F. Coordination chemistry of the oceans. pp. 255-269. In *Equilibrium Concepts in Natural Water Systems. Advances in Chemistry Series* 67, American Chem. Soc., Washington, D.C. 1967.
- Martin, D. F., et al. Distribution of naturally occurring chelators (humic acids) and selected trace metals in some west coast Florida streams, 1968-1969. *Professional Papers Series Number Twelve*, April, 1971. Florida Department of Natural Resources, Marine Res. Lab., St. Petersburg, Florida, 1971.

- McCauley, J. E. (editor) Progress Report. *Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean*. Oregon State Univ., Corvallis, Oregon, July 1971.
- Merlini, M. The freshwater clam as a biological indicator of radio-manganese. In *Radioecological Concentration Processes* (editors B. Aberg and F. P. Hungate) pp. 977-982, Pergamon Press, Inc., New York, 1967.
- Miyake, Y. and Y. Sugimura. Plutonium content in the western North Pacific waters. *Papers in Meteorology and Geophys.* 19, 481-485 (1968).
- Miyake, Y., et al. A study of plutonium fallout. *J. Geophys. Res.* 75, 2329-2330 (1970).
- Nagata, Y. and T. R. Folsom. Zinc-65 and other fallout nuclides in marine organisms of the California coast. *J. Rad. Res.* 5, 82-89 (1964).
- Nelson, D. J. The prediction of ⁹⁰Sr uptake in fish using data on specific activities and biological half-lives. In *Radioecological Concentration Processes* (editors B. Aberg and F. P. Hungate) pp. 843-851. Pergamon Press, Inc., New York, 1967.
- Nelson, D. I. and N. A. Griffith. Cesium and potassium in white crappie and other Clinch River fish. USAEC Report ORNL-4007, pp. 84-87, Oak Ridge National Lab., Oak Ridge, Tennessee, October 1966.
- Osterberg, C. L., et al., Zinc-65 in euphausiids as related to Columbia River water off the Oregon coast. *Limnol. Oceanogr.* 9, 249-257. (1964).
- Palmer, H. E. and T. M. Beasley. Iron 55 in the marine environment and in people who consume ocean fish. In *Radioecological Concentration Processes* (editors B. Aberg and F. P. Hungate) Pergamon Press, Inc., New York, 1967.
- Palmer, H. E. and T. M. Beasley. Iron-55 in man and the biosphere. *Health Phys.* 13, 889-895 (1967).
- Palmer, H. E., et al. Iron-55 in marine environment and in people who eat ocean fish. *Nature* 211, 1253-1254 (1966).
- Palmer, H. E., et al. Levels of iron-55 in humans, animals and food, 1964-1967. *Radiolog. Health Data and Reports* 9, 387-390 (1968).
- Pequegnat, J. E., et al. Estimates of the zinc requirements of marine organisms. *J. Fish. Res. Bd. Canada* 26, 145-150 (1969).
- Perkins, R.W., et al. Zinc-65 and chromium-51 in foods and people. *Science* 132, 1895-1897 (1960).
- Pillai, K. C., et al. Plutonium in the marine environment. *Nature* 203, 568-571 (1964).
- Preston A. The concentration of ⁶⁵Zn in the flesh of oysters related

- to discharge of cooling pond effluent from the C.E.G.B. nuclear power station at Bradwell-on-Sea-Essex. pp. 995-1004. In *Radio-ecological Concentration Processes* (editors B. Aberg and F. P. Hungate) Pergamon Press, Inc., New York, 1967.
- Preston, A. Concentrations of iron-55 in commercial fish species from the North Atlantic. *Marine Biol.* 6, 345-349 (1970).
- Preston, A. and D. F. Jefferies. The I.C.R.P. critical group concept in relation to the Windscale sea discharges. *Health Phys.* 16, 33-46 (1969).
- Riley, J. P. Analytical chemistry of seawater. In *Chemical Oceanography* (editors J. P. Riley and G. Skirrow), Vol. 2, Academic Press, London, pp. 295-411, 1965.
- Robertson, D. E. Unpublished data. Battelle, Pacific Northwest Laboratory, Richland, Washington, 1971.
- Robertson, D. E., et al. Multielement analysis of seawater, marine organisms and sediments by neutron activation without chemical separations. In *Proc. of the Int. Symp. on the Application of Neutron Activation Analysis in Oceanography*. Institute Royal des Sciences Naturelles de Belgique, Brussels, Belgium, June, 1968.
- Rona, E., et al. Activation analysis of manganese and zinc in sea water, *Limnol. Oceanogr.* 7, 201-206 (1962).
- Schelske, C. L., et al. Radioassay, pp. 12-14, In: Annual report of the Bureau of Commercial Fisheries Radiobiological Laboratory, Beaufort, N.C., for the fiscal year ending June 30, 1965. *Circ. U.S. Fish Wildl. Serv.* 244, 1966.
- Sheidina, L. D. and E. N. Kovarskaya. Colloidal state of Pu (IV) in aqueous solutions. *Radiokhimiya* 12, 253-259 (1970).
- Silker, W. B. Unpublished data. Battelle, Pacific Northwest Laboratory, Richland, Washington, 1971.
- Sillen, L. G. The physical chemistry of sea water. In *Oceanography* (editor M. Sears) Am. Assoc. Advance Sci. Publ. No. 67 (1961)
- Slowey, J. F. and D. W. Hood. Copper, manganese and zinc concentrations in Gulf of Mexico waters. *Geochim. Cosmochim. Acta* 35, 121-138 (1971).
- Spencer, D.W., et al. Trace element calibrations and profiles at the GEOSECS test station in the Northeast Pacific Ocean. *J. Geophys. Res.* 75, 7688-7696 (1970).
- Spencer, D.W. et al. The distribution of some chemical elements between dissolved and particulate phases in the ocean. AEC Report No. NYO-4150-9, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, 1970.

- Steeman-Nielsen, E. and F. Wium-Andersen. Copper ions as poison in the sea and in freshwater. *Marine Biol.* 6, 93-97 (1970).
- Strickland, J.D.H. Production of organic matter in the primary states of the marine food chain. In *Chemical Oceanography* editors J. P. Riley and G. Skirrow), Academic Press, London, 1965.
- Stumm, W. and J. J. Morgan. *Aquatic Chemistry*, Wiley-Interscience, New York, pp. 445-565, 1970.
- Templeton, W. L. and A. Preston. Transport and distribution of radioactive effluents in coastal and estuarine waters of the United Kingdom. In *Proc. of Symp. on The Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters*. IAEA, Vienna, May, 1966, pp. 276-289.
- Teresi, J. D. and C. L. Newcombe. An evaluation of hazards from immersion of plutonium in the marine environment. pp. 673-680. *Proc. of First International Congress of Radiation Protection* (editor W. S. Snyder) Pergamon Press, Oxford, 1966.
- Torti, E. Chemical environmental factors in marine radiocontamination. In *Studies on the Radioactive Contamination of the Sea* (editor M. Bernhard), Annual Report 1967 CNEN Report No. RT/B10 (68)60. CNEN-EURATOM, Fiascherino, La Spezia, Italy, pp. 5-11, 1969.
- Ui, J. and S. Kitamura. Mercury in the Adriatic. *Mar. Pollution Bull.* 2, 56-58 (1971).
- Ward, E. E. Uptake of plutonium by the lobster *Homarus vulgaris*. *Nature* 209, 625-626 (1966).
- Watson, D. G., et al. Zinc-65 in marine organisms along the Oregon and Washington coasts, *Science* 133, 1826-1828 (1961).
- Williams, P. M. The association of copper with dissolved organic matter in seawater, *Limnol. Oceanogr.* 14, 156-158 (1969).
- Williams, P. M. and K. S. Chow. Distribution and speciation of iron in natural waters: transition from river water to a marine environment, British Columbia, Canada, *J. Fish. Res. Bd. Canada*, 23, 575-593 (1966).
- Wilson, P. D. Some aspects of the chemistry of ruthenium in sea water, *PG Report* 819 (w), United Kingdom Atomic Energy Authority, 1968.
- Wolfe, D. A. Levels of stable Zn and ⁶⁵Zn in *Crassostrea virginica* from North Carolina. *J. Fish. Res. Bd. Canada* 27, 47-57 (1970a).
- Wolfe, D. A. Zinc enzymes in *Crassostrea virginica*. *J. Fish. Res. Bd. Canada* 27, 59-69 (1970).
- Wong, K. M., et al. Plutonium concentrations in organisms of the Atlantic Ocean. pp. 529-539. In *Proc. Fifth Annual Health Physics Society Midyear Topical Symposium-Health Physics Aspects of Nuclear Facility Siting*, Vol. 11, Idaho Falls, Idaho, November 1970.

Wrenn, M. E. and N. Cohen. Iron-55 from nuclear fallout in the blood of adults: dosimetry implications and development of a model to predict levels in blood, *Health Phys.* 13, 1075-1082 (1967).

Wyatt, E. I. and R. R. Rickard. The radiochemistry of ruthenium. NAS-NS 3029. National Academy of Sciences, National Research Council, Washington, D. C., February, 1961.

Young, D. R. and T. R. Folsom. Loss of ^{65}Zn from the California sea mussel *Mytilus californianus*. *Biol. Bull.* 133, 438-447 (1967).

TABLE 1

TOTAL CONTENT OF ARTIFICIAL RADIONUCLIDES
IN THE WORLD OCEANS
(ADAPTED FROM FAO FISHERIES REPORTS, NO. 99, SUPPL. 1, AUGUST, 1971)

	<u>YEAR 1970</u>	<u>YEAR 2000</u>
<u>NUCLEAR EXPLOSIONS</u>		
FISSION PRODUCTS (EXCLUSIVE OF TRITIUM)	$2-6 \times 10^8 \text{ Ci}$	$? \times 10^8 \text{ Ci}^*$
TRITIUM	10^9 Ci	$? \times 10^9 \text{ Ci}^*$
<u>REACTORS AND REPROCESSING OF FUEL</u>		
FISSION AND ACTIVATION PRODUCT (EXCLUSIVE OF TRITIUM)	$3 \times 10^5 \text{ Ci}$	$3 \times 10^7 \text{ Ci}$
TRITIUM	$3 \times 10^5 \text{ Ci}$	$? \times 10^8 \text{ Ci}$
TOTAL	10^9 Ci	10^9 Ci
POTASSIUM-40	$5 \times 10^{11} \text{ Ci}$	$5 \times 10^{11} \text{ Ci}$

* ASSUMED THAT ATMOSPHERIC NUCLEAR TESTING WILL CONTINUE
AT ABOUT THE RATE OF 1968-1970

TABLE 2

COMPARISON OF RADIONUCLIDE DISCHARGES FROM
POWER REACTORS, NUCLEAR PROCESSING PLANTS
AND ATMOSPHERIC FALLOUT

(RELEASES IN Ci/YEAR, 1968)		
<u>POWER REACTOR</u>	<u>MIXED FISSION AND CORROSION PRODUCTS</u>	<u>TRITIUM</u>
1	7.9	34.0
2	3.2	7.2
3	5.97	2.9
4	3.8	1735.0
5	0.074	NEG.0
6	1.5	2353.0
7	0.009	7.5
8	34.6	787.0
9	0.2	8.2
10	0.00035	NEG.0
<u>11</u>	<u>0.009</u>	<u>1170.0</u>
TOTALS 11	57.26	6104.8
ANNUAL DISCHARGE AT WINDSCALE (EARLY 1960'S)	- 90,000	
ANNUAL DISCHARGES FROM COLUMBIA RIVER (EARLY 1960'S)	- 350,000	
ANNUAL DISCHARGES FROM COLUMBIA RIVER (1971)	- ~350	
GLOBAL ⁹⁰ Sr DEPOSITION (1967)	- 270,000	

TABLE 3

POSSIBLE PHYSICO-CHEMICAL FORMS OF RADIONUCLIDES
AND TRACE ELEMENTS IN THE OCEANS

TRUE SOLUTION
<0.001 MICRONS

- 1) SIMPLE HYDRATED IONS
- 2) INORGANIC COMPLEX IONS
- 3) ORGANIC CHELATES
- 4) MOLECULES AND POLYMERIC SPECIES
- 5) ION PAIRS

COLLOIDAL
0.001 - 0.10 MICRONS

- 1) MINERAL SUBSTANCES
- 2) HYDROLYSIS AND PRECIPITATION PRODUCTS
- 3) BIOPOLYMERS AND DETRITUS

PARTICULATE
0.1 - 50 MICRONS

- 1) ORGANIC PARTICLES
 - A) PLANKTON
 - B) DETRITUS
 - C) BACTERIA AND MICROORGANISMS
- 2) INORGANIC PARTICLES
 - A) MINERAL SUBSTANCES
 - B) PRECIPITATED AND COAGULATED PARTICLES

TABLE 4

COMPARISON OF PRESENT PHYSICAL STATES OF RADIOELEMENTS
IN OCEANIC WATERS WITH DATA OF GREENDALE AND BALLOU

RADIOELEMENT	PERCENT PARTICULATE IN SEAWATER	
	PRESENT OCEANIC WATERS (SILKER, 1969)	GREENDALE AND BALLOU 1954 LABORATORY SIMULATION
ZIRCONIUM-NIOBIUM	1-13 (8)*	96 - 100
RUTHENIUM	1-3 (2)	95
CERIUM	1-54 (21)	94
CESIUM	< 1	23

* AVERAGE VALUE IN PARENTHESES

TABLE 5

CONCENTRATIONS AND PHYSICO-CHEMICAL
STATES OF TRACE ELEMENTS WITH FISSION
PRODUCT COUNTERPARTS IN OPEN OCEANIC WATERS

<u>ELEMENT</u>	<u>ABUNDANCE ($\mu\text{g/l}$)</u>	<u>PRINCIPLE SPECIES</u>
RUTHENIUM	4-7 ($\times 10^{-4}$)	ANIONIC, CATIONIC, NEUTRAL, PARTICULATE
CESIUM	0.28	Cs^+
STRONTIUM	8000	Sr^{+2} , SrSO_4
NIOBIUM	0-0.005 (FILTERED); 0.01-0.1 (UNFILTERED)	Nb (COLLOIDAL HYDROXIDE)
ZIRCONIUM	0.01-0.04	?
CERIUM	8.5-42 ($\times 10^{-4}$)	Ce^{+4} , Ce^{+3} , COLLOIDAL, PARTICULATE
EUROPIUM	0.95-1.4 ($\times 10^{-4}$)	Eu^{+3} , COLLOIDAL, PARTICULATE

TABLE 6

CONCENTRATIONS AND PHYSICO-CHEMICAL STATES OF TRACE
ELEMENTS WITH ACTIVATION PRODUCT COUNTERPARTS IN
OPEN OCEANIC WATERS

<u>ELEMENT</u>	<u>ABUNDANCE [*]($\mu\text{g/l}$)</u>	<u>PRINCIPLE SPECIES</u>
IRON	1-20 (5)	$\text{Fe}(\text{OH})_3$ COLLOIDAL, Fe CHELATED, $\text{Fe}(\text{OH})_2^+$
COBALT	0.005-0.5 (0.03)	Co^{+2} , CoSO_4
MANGANESE	0.01-0.88 (OPEN SEA)	Mn^{+2} , MnSO_4
ZINC	1-10 (4)	Zn^{+2} , ZnOH^+ , Zn CHELATED
NICKEL	0.5-3 (1)	Ni^{+2} , NiSO_4
CHROMIUM	0.01-0.8	Cr^{+6} , Cr^{+3}
SCANDIUM	0.0001-0.001	Sc^{+3} , COLLOIDAL, PARTICULATE
EUROPIUM	0.95-1.4 ($\times 10^{-4}$)	Eu^{+3} , COLLOIDAL, PARTICULATE
TANTALUM	< 0.02	?
SILVER	0.002-0.04 (0.01)	AgCl_2^- , $\text{AgCl}_3^{=}$

*AVERAGE VALUES IN PARENTHESIS

TABLE 7

FISSION PRODUCTS IN LIGHT WATER
MODERATED REACTOR FUEL WASTES*
180 DAYS OLD

<u>RADIONUCLIDE</u>	<u>CONTENT (KILOCURIES)</u>	<u>HALF-LIFE (YEARS)</u>
Ru-106	864	1.0
Nb-95	365	0.1
Pm-147	214	2.6
Cs-137	209	30
Zr-95	188	0.2
Sr-90	152	28.8
Ce-144	119	0.8
Ru-103	100	0.1
Sr-89	41	0.1
Cs-134	36	2.1
Y-91	34	0.2
Ce-141	26	0.1
Eu-154	12	16
Kr-85	11	10.3

* BASIS: ONE METRIC TON OF FUEL AT 33,000 MWD
BURNUP AND 24.5 MW SPECIFIC POWER

TABLE 8

FISSION PRODUCTS IN WASTES^{*} 50 YEARS AFTER PROCESSING

<u>RADIONUCLIDE</u>	<u>CONTENT (KILOCURIES)</u>	<u>HALF-LIFE (YEARS)</u>
Cs-137	84.7	30
Sr-90	45.6	28.8
Eu-154	0.25	
Cs-134	1×10^{-6}	

WASTE CONTENT^{**} 500 YEARS AFTER PROCESSING

<u>RADIONUCLIDE</u>	<u>CONTENT (CURIES)</u>	<u>HALF-LIFE (YEARS)</u>
Pu-240	4	6,580
Pu-239	4	24,300
Pu-238	0.5	86.4
Sr-90	1.5	28.8
Cs-137	2.1	30

^{*} BASIS: ONE METRIC TON OF FUEL AT 33,000 MWD
BURNUP AND 24.5 MW SPECIFIC POWER

^{**} SAME AS ^{*} ; ONE PERCENT OF FUEL PLUTONIUM
CONTENT LOST TO WASTE

TABLE 9

IMPORTANT NEUTRON ACTIVATION PRODUCTS
ORIGINATING FROM NUCLEAR WEAPONS TESTING,
POWER PRODUCTION AND WASTE DISCHARGE

<u>RADIONUCLIDE</u>	<u>HALF-LIFE (YEARS)</u>	<u>SOURCE</u>
IRON-55	2.4	W.T. AND P.O.
IRON-59	0.12	P.O.
COBALT-57	0.74	W.T.
COBALT-58	0.19	W.T.
COBALT-60	5.3	P.O. AND W.T.
MANGANESE-54	0.76	P.O. AND W.T.
ZINC-65	0.67	P.O. AND W.T.
EUROPIUM-152	12.5	W.D.
EUROPIUM-154	16.0	W.D.
TANTALUM-182	0.32	P.O.
SCANDIUM-46	0.23	W.D.
NICKEL-63	92	W.T.
CHROMIUM-51	0.08	P.O. AND W.T.
SILVER-110M	0.69	W.T. AND W.D.

W.T. - NUCLEAR WEAPONS TESTING

P.O. - NUCLEAR POWER OPERATIONS

W.D. - WASTE DISCHARGES

TABLE 10

COMPARISON OF SPECIFIC ACTIVITIES OF ^{60}Co , ^{65}Zn AND ^{137}Cs IN SURFACE SEA WATER AND IN MARINE ORGANISMS

SEA WATER		SPECIFIC ACTIVITY (d/m/gram OF ELEMENT)	
$^{60}\text{Co-Co}$		1×10^4	
$^{65}\text{Zn-Zn}$		$< 1 \times 10^2$	
$^{137}\text{Cs-Cs}$		4×10^6	
	SPECIFIC ACTIVITY (d/m/gram of element)	RATIO OF: SPECIFIC ACTIVITY IN ORGANISMS SPECIFIC ACTIVITY IN SEA WATER	
1. <u>Colalabis saira</u> (saury)			
$^{60}\text{Co-Co}$	$\sim 1 \times 10^6$		~ 100
$^{65}\text{Zn-Zn}$	$\sim 1 \times 10^4$		> 100
$^{137}\text{Cs-Cs}$	$\sim 6 \times 10^6$		~ 1.5
2. <u>Diaphus theta</u>			
$^{60}\text{Co-Co}$	4×10^5		40
$^{65}\text{Zn-Zn}$	3.4×10^4		> 340
$^{137}\text{Cs-Cs}$	$\sim 4 \times 10^6$		~ 1
3. <u>Lampanyctus ritteri</u>			
$^{60}\text{Co-Co}$	$\sim 4 \times 10^5$		~ 40
$^{65}\text{Zn-Zn}$	$\sim 6 \times 10^3$		> 60
$^{137}\text{Cs-Cs}$	2×10^{-6}		0.5
4. <u>Sergestes similis</u>			
$^{60}\text{Co-Co}$	1×10^6		100
$^{65}\text{Zn-Zn}$	3×10^4		> 300
5. <u>Tactostoma macrurus</u>			
$^{60}\text{Co-Co}$	$\sim 7 \times 10^5$		~ 70
$^{65}\text{Zn-Zn}$	$\sim 2 \times 10^3$		> 20

TABLE 11

RADIONUCLIDE CONCENTRATIONS AND SPECIFIC ACTIVITIES IN SILVER SALMON LIVERS

ISOTOPE	HALF-LIFE	ACTIVITY (dis/min/kg Wet Tissue)			SPECIFIC ACTIVITY (nCi/g ELEMENT)	SPECIFIC ACTIVITY OF SEA WATER (nCi/g ELEMENT)
		SAMPLE A	SAMPLE B	AVERAGE		
^{40}K	$1.3 \times 10^9 \text{ Y}$	6600 ± 100	6700 ± 100	6600 ± 100	0.81 ± 0.14	0.81
^{60}Co	5.2 Y	28 ± 1	26 ± 1	27 ± 1	360 ± 180	4.5
^{65}Zn	243 D	8900 ± 100	7800 ± 100	8300 ± 100	220 ± 30	<0.05
$^{110\text{m}}\text{Ag}$	260 D	7.0 ± 0.5	6.6 ± 0.5	6.8 ± 0.3	100 ± 60	-----
^{137}Cs	30 Y	40 ± 10	30 ± 10	35 ± 15	1800 ± 600	~1800

TABLE 12

IRON-55 IN THE MARINE ENVIRONMENT OFF THE WEST COAST
OF THE UNITED STATES

SAMPLE	LOCATION	SAMPLE DATE	SPECIFIC ACTIVITY (nCi ⁵⁵ Fe/mg Fe)
SEAWATER* (1)	15 MI. OFF N. CALIF.	1965	< 0.02 (ADAPTED)
SEAWATER* (2)	350 MI. OFF ORE.	1967	0.005
SALMON(1)	WASH. COAST	1965	2.4
ALBACORE TUNA(1)	N. PAC. OCEAN	1965	2.2
SAURY(1)	WASH. COAST	1965	2.0
CHUM SALMON(3)	JAPAN HIGH SEAS	1965	7.0
CHINOOK SALMON(3)	ASTORIA, ORE.	1967	0.18
COHO SALMON(3)	ASTORIA, ORE.	1967	0.29
COHO SALMON	EUREKA, CALIF.	1965	1.6
COHO SALMON	JAPAN HIGH SEAS	1965	4.9
SOCKEYE SALMON(3)	ASTORIA, ORE.	1967	1.2
SOCKEYE SALMON	JAPAN HIGH SEAS	1965	5.2
EUPHAUSIA PACIFICA(3)	OFF COL. RIVER EST.	1967	0.051 (AVG)
SEA CUCUMBER(3) (Paelopatides Sp.)	ORE. COAST	1965-1967	0.003-0.007
SEDIMENTS	ORE. COAST (600 M)	1965	4.7x10 ⁻⁴
	ORE. COAST (2800 M)	1966	0.92x10 ⁻⁴

*PARTICULATE IRON COLLECTED BY FILTRATION THROUGH 0.3 μ MEMBRANE FILTERS

(1) PALMER, BEASLEY AND FOLSOM, 1966

(2) ADAPTED FROM LANGFORD, 1969

(3) JENNINGS, 1968

(4) PALMER, et. al, 1968

TABLE 13

SPECIFIC ACTIVITY OF ^{55}Fe (nCi/mg Fe) IN THREE SPECIES OF SALMON (AFTER JENNINGS, 1968)

STRAIT OF JUAN de FUCA, 1964		
SPECIES	NUMBER INDIVIDUALS	SPECIFIC ACTIVITY 1964
CHINOOK (PREDACEOUS)	2	0.75
COHO	2	1.57
↓		
SOCKEYE (FILTER-FEEDER)	2	28.7
PETERSBURG, ALASKA, 1964		
CHINOOK (PREDACEOUS)	4	1.2
PINK	2	7.7
COHO	6	11.8
CHUM	1	15.1
↓		
SOCKEYE (FILTER-FEEDER)	2	15.4

TABLE 14

Plutonium-239 Concentrations in the Oceans

<u>Location</u>	<u>Date</u>	<u>Depth (m)</u>	<u>Pu²³⁹ Concentrations</u>	
			<u>Ci/kg (x10⁻¹⁵)</u>	<u>g/kg (x10⁻¹⁵)</u>
N.E. Pacific (coastal) ⁽¹⁾	1964	Surface	0.35-0.47	5.6-7.5
N.E. Pacific (oceanic) ⁽¹⁾	1964	Surface	1.9 -3.0	30.4-48
N.W. Pacific (oceanic) ⁽²⁾	1967	Surface	0.11-1.4	1.8-22.6
"		0	0.30	4.8
"		1000	0.31	4.9
"		3000	0.24	3.9
N. Atlantic ⁽³⁾	1963-1969	Surface	0.32-1.2	5.1-19
"	1968-1969	100	0.22-3.5	3.5-56
"	"	400-500	0.32-2.4	5.1-38
"	"	700-1000	0.09-1.8	1.4-29
"	"	1500-2200	0.09-0.27	1.4-4.3
S. Atlantic ⁽³⁾	1968	Surface	0.18	2.9
"	1968	100	0.32	5.1
"	1968	500	1.9+1.9	30.4+30.4
N. Atlantic ⁽⁴⁾	1968	Surface	2.5-26* (3.2 avg)	40-420*

* Possible contamination from Thule, B-52 crash.

⁽¹⁾Pillai, et al., 1964

⁽²⁾Miyake and Sugimura, 1968

⁽³⁾Bowen, et al., 1971

⁽⁴⁾Aarkrog, 1971

TABLE 15

Plutonium-239 Concentration in Marine Organisms

<u>Organism</u>	<u>Location</u>	<u>²³⁹Pu Concentration pCi/kg wet wt.</u>	<u>Concentration Factors</u>
<u>Pelagic fishes</u>			
muscle	Atlantic, 1970 ⁽¹⁾	0.001-0.003	1-5
bone	"	0.01 -0.36	18-570
liver	"	0.01 -0.13	14-200
gut	"	0.02 -0.67	36-1060
gill	"	0.01	14
whole	Pacific, 1964 ⁽²⁾	0.0014±0.0018	3
mussels	Atlantic, 1970	0.10 - 0.26	160-290
mussels	Pacific, 1964	0.096- 0.12	230-290
zooplankton	Atlantic, 1970	1.5	2300
zooplankton	Pacific, 1964	0.023- 1.08	2600
sargassum	Atlantic, 1970	5.8	9000
kelp	Pacific, 1964	0.32- 0.65	770-1600
clam	Atlantic, 1970	0.18	380
starfish	"	0.50- 0.64	760-1000
salpa	"	0.60- 1.6	900-2400

⁽¹⁾Wong, et al., (1970)⁽²⁾Pillai, et al., (1964)

FIGURE 1

SOURCES OF ARTIFICIAL RADIOACTIVITY IN THE OCEANS

FIGURE 2

COLUMBIA RIVER SURFACE SEDIMENT-McNARY DAM

FIGURE 3

UPTAKE OF ^{65}Zn AND STABLE ZINC BY
Phaeodactylum tricornutum IN SUCCESSIVE DAYS
AND GENERATIONS FROM NATURAL SEAWATER MEDIUM.
EXPRESSED IN FRACTIONS (F) OF TOTAL ^{65}Zn AND
TOTAL STABLE ZINC. AFTER BERNHARD AND ZATTERA (1969)

FIGURE 4

RELATIVE BIOLOGICAL LOSS OF ^{65}Zn FROM Pachygrapsus KEPT IN RUNNING LABORATORY SEA WATER (L.S.W.) AND IN RUNNING SEA WATER FROM OPEN SEA (O.S.W.) WITH NATURAL AND INCREASED ZINC CONCENTRATIONS. (AFTER KANE, et.al, 1969)

FIGURE 5

ZINC

FIGURE 6

THE UPTAKE RATE OF ^{106}Ru IN CHLORIDE AND
NITRATE FORM IN SHELLS AND SOFT PARTS
OF MUSSELS

(AFTER KECKES, et. al, 1966)

FIGURE 7

SCHEMATICALLY REPRESENTED RADIOAUTOGRAMS OF TWO-DIMENSIONAL ELECTROCHROMATOGRAMS OF ^{106}Ru IN SEA WATER. BACKGROUND ELECTROLYTE: 30% SEA WATER OF ORIGINAL SALINITY 37.56%. LEFT: ^{106}Ru IN CHLORIDE FORM; RIGHT: ^{106}Ru IN NITRATE FORM. (AFTER KECKES, et.al, 1966).