The decline of radioactivity in the Columbia River and estuary was followed in water, sediment and biota after closure of the last of the single-pass plutonium production reactors at Hanford, Washington.

Rates and Patterns  The relative levels and rates of decline of Zn-65 specific activities were similar among several different species examined. Half-times of decline for this radionuclide, after correction for physical decay, were closely grouped at 350-400 days, and were similar to that found for water just upstream from the estuary. The close correspondence between the rate of decline of Zn-65 in water and estuarine biota was explained using an input-output model with an exponentially declining source term. It was shown that when
the rate of decline of the source is long relative to the turnover rate in the receptor, species with different biological half-lives have similar rates of decline as well as similar activity levels.

Zinc-65 specific activities in biota from different locations were found to change less than expected from dilution of river water alone. This was explained by a combination of non-conservative particle transport and sediment isotope dilution. The latter process results from mixing of Zn-65 labeled, high-zinc sediment of Columbia River origin with unlabeled, low-zinc sediment from downstream tributaries. The above explanation requires that a significant portion of the zinc in the food web of the species examined be derived from sediment and/or detritus.

Decay-corrected residence times of Zn-65 in water, sediment and biological phases ranged from 500 to 1000 days. Because virtually all of the Zn-65 in water was particulate, the residence time for this phase may also represent the residence time of suspended sediment in the system (~600 days).

Recovery times for hypothetical soluble and particulate contaminant phases in the river system were calculated and suggest several years would be required to significantly reduce particulate contaminant levels following a chronic input.

**Sediment-Water Transfer Mechanisms**  
Manganese-54 was found to decline two to three times faster than Co-60, Zn-65, Cs-137 and Eu-152 in surface sediment. This was attributed to the isotopic exchange-ability of the sediment-bound radionuclide. Slight evidence of solubilization of Zn-65 was noted in McNary reservoir water while
clear evidence of solubilization was found in the estuary. Soluble and particulate Zn-65 specific activities in river water indicated that once this nuclide is taken up by sediment, it is no longer isotopically exchangeable with stable zinc in solution. This result stands in contrast to predictions based on laboratory studies of Zn-65 exchange in pure mineral-solution systems.

Sedimentary processes considered included: 1) erosion of bed sediment, 2) particle exchange or diffusion, 3) deposition and 4) benthic mixing. Ratios of Co-60/Eu-152 and Eu-154/Eu-152 were used to evaluate sedimentation rates and benthic mixing in sediment at a fluvial and an estuarine depositional site. Sedimentation rates of 2-4 cm/year were estimated from this evaluation. It did not appear that reworking or mixing of deposited sediment was a significant process in transporting deeper, contaminated sediment to the surface. This was in part attributed to a relatively shallow mixed-layer depth.

The correlation between river discharge and the corresponding increase in transported radioactivity illustrated the importance of this major variable in mobilizing stream-bed contaminants. While it was not possible to distinguish between simple resuspension and particle-exchange or diffusion, it seems likely that both processes are involved in dispersing sediment-bound contaminants from the riverbed.
DECLINE OF RADIOACTIVITY IN THE COLUMBIA RIVER AND ESTUARY: RATES AND MECHANISMS

by

Vernon Gene Johnson

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Karen Johnson typed the manuscript.

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DECLINE OF RADIOACTIVITY IN THE COLUMBIA RIVER AND ESTUARY: RATES AND MECHANISMS

INTRODUCTION

An understanding of the behavior of trace substances in ecosystems is essential in assessing their potential hazard as contaminants (Eberhardt et al., 1976). Basic to this understanding is a knowledge of rates and mechanisms of contaminant interaction with ecosystem components. Rates can be used to estimate recovery times for a contaminated system. While such information is needed, few opportunities have occurred for determining such parameters for major natural systems. This work deals with one such opportunity where it was possible to directly measure the clearance times for trace substances in a major aquatic ecosystem.

Hanford and the Columbia River

In January 1971 the last of the eight single-pass plutonium production reactors near Richland, Washington was phased out of operation. This event marked the end of a quarter century of input to the Columbia River of a variety of radioactive contaminants. With no new input it became possible to directly measure the rate of decline or "wash out" of selected radiocontaminants in the major components of a previously labeled system. This unique opportunity to determine the time scale for natural purging in a major ecosystem was the primary objective for this study.
Specific Objectives

Primary emphasis is on Zn-65 in this study because of its ubiquitous occurrence in all components of the system, and because of its ease of measurement. Other long-lived radionuclides, however, will be included for analysis in selected components.

The specific goals of this study were:
1. To determine the rate of decline of Zn-65 in water, sediment and biota in portions of the Columbia River and estuary,
2. To analyze observed patterns and dynamics of decline, and
3. To test some hypotheses concerning mechanisms of sediment-water transfer of selected radionuclides.

While the primary focus is on Zn-65, the processes and rates of decline for other heavy metals are expected to be similar to the metal under study for this thesis. The fundamental question being addressed is, "What controls the response time of a major ecosystem when contaminant input is terminated?"

Theory

The conceptual framework for most of this study can be succinctly represented by a single box model:
Where \( A(t) \) represents the current burden or content of the tracer or contaminant at time \( t \), \( R \) is the input rate (assumed to be constant over time) and \( \mu \) is the fraction of compartment content loss per unit time. This simple compartmental model results in the first order differential equation known as the "uptake and retention" equation:

\[
dA/dt = R - \mu A
\]

During steady state when \( dA/dt = 0 \), the loss rate coefficient is simply:

\[
\mu = \frac{R}{A}
\]

Another means of expressing the loss rate constant involves the concept of residence time. This parameter is simply the inverse of the loss rate constant:

\[
T = \frac{1}{\mu}
\]

The residence time \( T \) represents the time required to replace the contents, \( A \), of the reservoir at rate \( R \). The residence times for the elements in lakes and oceans have been calculated based on estimates of the input rates and on the present content of the water body. Few such calculations, however, have been made for large river systems (Bowen, 1975).

One of the primary difficulties in making loss rate or residence time estimates under the steady state condition is the great uncertainty in the reservoir size. The analytical burden necessary to define the total reservoir contents is prohibitive for most large ecosystems.
This is especially true for a large, dynamic river system. When an ecosystem has been labeled, however, with a tracer and the input terminated, the loss rate can be determined comparatively easily. For this case, \( R = 0 \), the relationship becomes:

\[
\frac{dA}{dt} = -\mu A
\]

which yields exponential decline. For this case a plot of \( \ln(A) \) against time produces a straight line with slope equal to the loss rate constant, \( \mu \). Thus the residence time or loss rate can be determined by measuring the concentration in samples of the component of interest with time; i.e., it is not necessary to know the total content of the reservoir. The freedom from the burden of determining total reservoir content is the principal advantage of the terminated contaminant or tracer input case. Indeed, for a large dynamic river system, this may be the only way in which such information can be obtained.

For tracers with an appreciable radioactive decay rate, an additional allowance for loss by physical decay must be made. The basic form of the equations, however, remain the same. Derivation of the mathematical relations covering this situation for the present study as well as the case for recycled source, will be presented later.
BACKGROUND

Geology of the Drainage Basin

The Columbia River Drainage Basin enjoys a rich heritage of geological history. The region contains rock units representing the Pre-Cambrian eras through most of the geological time scale. The diversity of geological regimes represented throughout the basin is probably unequalled and adds to the unique character of the Columbia among the rivers of the world.

In the headwaters region high in the Canadian and northern U.S. Rockies, the river courses through Cambrian limestone/mudstone interspersed with granitic intrusives and metamorphic rock units. Zones of mineralization are encountered in northeastern Washington and the Panhandle region of northern Idaho. From near the Canadian border nearly to the ocean, the geology is dominated by extensive basalt flows and glacial/fluvial deposits. The Snake River, the largest and most important tributary, has a similar geology although the basalt flows are cut through in places exposing ancient Cambrian limestone. Other tributaries of the Snake drain regions of exposed evaporite deposits such as the famous Phosphoria formation which supplies the major portion of the western U.S. phosphate production.

Below the confluence of the Snake with the Columbia, large portions of the regional geology of the Cascades and vicinity are dominated by volcanic rocks. The Cascade mountain peaks stand as silent sentinels to a past history of violent eruptive activity that
Figure 1. Geologic map of the Columbia River drainage basin. (from Whetten et al., 1969).
dispersed pumice, volcanic ash, and andesitic rock fragments over extensive areas now eroded by tributaries of the lower Columbia. Further downstream in the Coast range, yet another geological regime is represented by the marine Miocene and Oligocene sandstones, siltstones and interbedded volcanics.

Understandably, the mineralogy of the stream bed sediments in the Columbia varies along the course of the river reflecting in part the diversity of the rock types and erosive forces in the drainage basin. Whetten, Kelly and Hanson (1969) conclude that the upstream drainage basin sources produce primarily fine-grained, nonvolcanic sediments (presumably glacial flour carried in suspension). Downstream sources add coarse sediment of andesitic volcanic origin considerably different from upper Columbia sediment. The basalt underlying much of the drainage basin is poorly reflected in the mineralogy of the bed sediments.

Montmorillonite, illite and chlorite-kaolinite are the principal clay minerals in the clay size fraction. In the clay mineral suite, montmorillonite shows a progressive relative increase downstream from the Grand Coulee region of the river while illite shows the reverse trend and kaolinite remains consistently low (Knebel, Kelly and Whetten, 1968). Quartz and feldspars make up a major portion of the fine silt and coarse to medium clay size fraction (Glenn, 1973).

With the exception of the lower reach of the Grand Coulee and McNary reservoirs, Whetten et al. (1969) report that very little fine-grained sediment has accumulated on the streambed.
Hydrology

The dominant hydrologic feature of the main stem of the Columbia is its high discharge. The mean annual discharge is 7200 \( m^3/sec \) and is second only in flow to the Mississippi among rivers of the U.S. The second most distinctive feature is the seasonal high discharge period in the spring resulting from snow melt in the interior regions, followed by a minimum in the fall. The lower river is subject to a secondary maximum during high winter runoff from the Coast range and western slope of the Cascades. The extent and duration of the second peak, however, is highly variable.

The estuary is much more river dominated than most other estuaries. Tidal forces and seasonally variable river flow interact to produce complex circulation patterns. The major features of these interactions are that during low flow, a general clockwise lateral circulation exists while an opposite circulation pattern occurs during high river flows (Lutz, Hubbell and Stevens, 1975). Maximum salt water intrusion occurs during low flow periods in the fall and extends as far upstream as Harrington Point at river mile 21. During periods of high river flow as during the spring freshet, salt intrusion is limited to only the lower 5-10 miles of the estuary. Vertical circulation is of the type characteristic of salt wedge estuaries with an associated turbidity maximum. The significance of this type of circulation is that suspended material brought into the estuary by the river is retained for a longer period of time, thus extending the influence of the river in the estuary.
Livingstone (1963) has referred to the Columbia as a dilute calcium bicarbonate solution. In comparison to other rivers the Columbia is approximately a factor of two more alkaline and has a high pH, often close to eight. Storm activity in the fall and early winter, of course, modify this picture bringing acidic flood waters from the Cascades and Coast Range into the lower river. The high pH of the river is due to dissolution of limestone or carbonate sedimentary rocks in the headwater region. Thus, this major variable is set early in the river's history. The elevated bicarbonate acts as a buffer to maintain the pH near eight. The Cascade and Coast Range tributaries as well as the Spokane River all have pH values below seven, presumably reflecting the absence of the influence of limestone on their water quality.

The suspended solids content of the Columbia is remarkably low in comparison to other major rivers. Weyl (1970), for example, lists the average suspended solids concentration for the Columbia as 30 mg/liter. In contrast, the Mississippi and Pacific Slope rivers have average values of 560 and 870 mg/liter, respectively, while the average for all U.S. rivers is 530 mg/liter. Thus, while the Columbia is second in flow, the low suspended load results in very low total solids transported. The low suspended sediment concentration may be significant in solute-particle equilibria considerations. In addition, particle-bound contaminants would undergo minimal sediment dilution as compared to other rivers having high suspended solids contents. Table 1 shows the average chemical composition of the Columbia River.
Table 1. Average concentrations of major and trace constituents of Columbia River water in relation to world average values.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Columbia A (mg/liter)</th>
<th>World Ave. (mg/liter)</th>
<th>Ratio (A/B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃</td>
<td>108</td>
<td>58.4</td>
<td>1.8</td>
</tr>
<tr>
<td>SO₄</td>
<td>19</td>
<td>11.2</td>
<td>1.7</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>4.9</td>
<td>7.8</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.3</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca</td>
<td>23</td>
<td>15</td>
<td>1.5</td>
</tr>
<tr>
<td>Mg</td>
<td>6.2</td>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Na</td>
<td>16</td>
<td>6.3</td>
<td>2.5</td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.28</td>
<td>0.67</td>
<td>0.4</td>
</tr>
<tr>
<td>Al</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13</td>
<td>13.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>191</td>
<td>120</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Trace metals (dissolved) (ug/liter)

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<tr>
<th></th>
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<tr>
<td>Zn</td>
<td>22</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>Mn</td>
<td>2.7</td>
<td>7</td>
<td>0.4</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>9</td>
<td>7</td>
<td>1.3</td>
</tr>
<tr>
<td>Pb</td>
<td>27</td>
<td>3</td>
<td>9.0</td>
</tr>
</tbody>
</table>

1 major constituent data from Krauskopf (1967) based on analyses below the Dalles Dam.

2, 3 world average trace metal data from Goldberg et al. (1971); Columbia River data from Kopp and Kroner (1968) for Clatskanie, Oregon station.
Radioactivity in the Columbia River System

The Hanford story in relation to radioactivity in the Columbia River has been told in numerous theses and publications. Robertson et al. (1973) provide a succinct general account that can be little improved upon and will therefore be quoted directly.

"The discharge of reactor effluent water from the Hanford reactors to the Columbia River began with the first reactor operation in 1944 and ended with the closure of XE reactor in January, 1971. During much of this period, eight nuclear reactors were in operation and treated Columbia River water was used as a primary, one-pass coolant, which after a few hours of holding time was returned to the river. During passage through the reactors, the cooling water was subjected to the ambient neutron flux which resulted in neutron activation of the various trace elements present in the water. In addition, occasional fuel element failures occurred and trace amounts of irradiated fuel were leached by the cooling water and carried into the river. The radionuclides discharged to the river in reactor effluent water included neutron activation products, fission products, and traces of Pu-239. Upon entering the Columbia River, the radionuclides were rapidly dispersed in the river water, sorbed onto detritus and inorganic particulates, or incorporated into aquatic biota."

See Figure 1 for a summary of reactor operating history.

Chemical Characterization of Effluent Radionuclides

The radionuclides of interest to this study (Zn-65, Mn-54 and Co-60) were shown to leave the reactors as soluble species that passed through an 0.45 μm membrane filter and were retained on cation exchange resins (Nelson et al., 1966). While not all eight reactor effluent waters were tested in this manner, it is assumed that the chemical nature of the radionuclides produced was similar since all of the reactors were of similar design. Ultracentrifuge analysis of the
Figure 1. Operating history of the plutonium production reactors at Hanford, Washington. ("N" is a closed loop reactor in contrast to the older single-pass reactors).
effluent also demonstrated the soluble or solute nature of the radionuclides in the effluent (Lammers, 1968). These observations imply that the divalent, soluble radiocations were in a chemical form that would mix isotopically with the ecosystem components of the river.

**Transport and Behavior**

While most of the radionuclides in effluent left the reactors in solution, the cationic transition metals rapidly reacted with the suspended material in transport by the river. Zinc-65, Mn-54 and Co-60, for example, were shown to be nearly 100% soluble near the reactor area and 20-30% soluble within 100 miles downstream (Perkins et al., 1966; Nelson et al., 1966; Hanson, 1967). This same approximate soluble-particulate distribution prevailed until mixing with seawater in the estuary released the ion-exchangeable fraction of the suspended load. In view of the relatively high pH of the river, it is at first surprising that even a 20-30% soluble state existed since sorption on solid phases is dramatically increased with increasing pH for metals such as zinc. However, when it is recognized that the suspended load is so low, it may be reasonable to expect this relatively high soluble fraction to exist for transition metals (O'Connor and Renn, 1964).

The soluble fraction in transport was further characterized at various locations downstream to Vancouver by passing membrane-filtered water through anion and cation exchange resins (Nelson et al., 1966). These studies showed that nearly all the Zn-65, Mn-54 and Co-60 passing through 0.3 µm filters was retained on the cation resin. There was a trace of an uncharged or anionic metal fraction. However, the manner
in which this fraction was estimated was not clear from the report cited above. While the above would be compatible with the currently held view of the existence of both organic and inorganic metal-ligand complexes in natural waters, it is important to note that most of the soluble fraction was retained by the cationic resin. While this is not unequivocal evidence that metal-ligand complexes such as ZnCO\(_3\) or organic-metal complexes do not exist, the data do suggest that if such complexes are present, they must be nearly all positively charged or are easily dissociated by the functional groups of the cation resin used (i.e. outcompeted).

Evans (1977) recently reviewed the chemistry of zinc in river and seawater and pointed out that this metal has only one stable valence state (\(\text{II}\)), greatly simplifying its chemistry. He further reviewed the possible chemical controls on the solubility of zinc with respect to various solid phases and concluded that most rivers and seawater would be undersaturated with dissolved zinc.

The above and foregoing discussion add support to the assumption that Zn-65 released to the river from the Hanford Operations was free to undergo isotopic equilibration with the stable zinc present in the receiving water during the quasi-steady state input period.

**Radionuclide Depletion and Streambed Inventory.** As a result of radionuclide association with suspended material, a significant portion of cationic radionuclides were removed by deposition on the streambed. Since previously deposited inventory is the source in the present study, it is important to review past information relating to the
disposition of the streambed inventory as well as factors influencing its mobilization.

Perkins et al. (1966) periodically measured soluble and particulate radionuclides near the reactors and at various downstream locations over a one year period. By computing input to and output from various reaches of the river, inventories of stored radionuclides in the river were calculated. This study showed that during low flow periods radionuclides with a high affinity for particles were depleted by a factor of five to ten between Pasco and Vancouver. During high river flow, the transport of these radionuclides was equal to or exceeded the transport at Pasco. This observation suggested that resuspension of previously deposited inventory occurs during increased river flow.

Other studies attempted to determine the bed sediment inventory directly by measuring radionuclide content in streambed samples. This approach was used in the estuary and for the reach between McNary Dam and the reactors (Nelson and Haushild, 1970; Hubbell, Glenn and Stevens, 1971). By combining these data and the input-output inventory estimates for the year 1965, an approximate picture of the relative distribution of the stored inventory can be obtained from the reactor area to the river mouth. Figure 2a displays this data as a cumulative distribution as a function of river mile and shows the gross position of the bed inventory during steady state conditions. These data show that over half of the total inventory in the river and estuary occurs above McNary Dam with most of this concentrated in the McNary to Pasco reach. Within this reach, the major portion occurs
Fig. 2a. Cumulative Zn-65 inventory in the riverbed as a function of distance from the mouth to the reactor area during 1965.
in the lower half where fine sediment is known to accumulate. The reach just upstream from McNary Dam is one of the few places where fine sediments accumulate in the river system outside the estuary. Figure 2b illustrates the non-uniform distribution of the inventory from the reactor area to the mouth. For example, of the total in the 375 miles of river below the reactors, almost half is in one 35 mile reach and nearly half the remainder is in another 35 mile reach at the mouth (the estuary). It is reasonable to expect that the estuary and McNary reservoir are the principal sites of radionuclide accumulation since these are the principal locations in the river system that accumulate fine sediment. An important difference between the two sites, however, is that radionuclide concentrations in estuarine sediments are 10 to 15 times lower than in McNary sediments. This is presumably due to dilution by non-labeled sediment added by tributaries and to radioactive decay.

**Biological Reactions** Some of the earliest studies of the interaction of Hanford radioactivity with Columbia River biota showed that direct uptake from the water was minor compared to ingestion of contaminated food. For example, fish collected downstream from the reactors were approximately 100 times as radioactive as fish maintained in a laboratory exposed to equivalent dilutions of effluent but fed uncontaminated food (Davis and Foster, 1958).

Cushing and Watson (1968) showed that living and killed phytoplankton were equally effective accumulators of radiozinc. They concluded that adsorptive uptake is the primary means of association
Figure 2b. Relative Zn-65 inventory in various reaches of the streambed of the Columbia River from the reactor area to the mouth.
with phytoplankton and periphyton. Cushing (1970) further noted that Zn-65 uptake is significantly reduced when the magnesium ion level of the uptake medium is doubled and suggested there was competition for binding sites by divalent cations. This would be reasonable since the polysaccharide gel associated with phytoplankton is rich with cation exchange sites. Other environmental variables that influenced uptake included: 1) temperature; 2) river flow (i.e., during the spring freshet near the reactors plankton have lower radioactivity levels in response to increased dilution of the reactor effluent; 3) pH (between a pH of six and eight adsorption of zinc increases with increasing pH of the water); 3) isotopic dilution by changes in metal levels in the receiving water (Cushing, 1970).

Aquatic studies during a brief shutdown of all the plutonium production reactors in 1966 for a six week period indicated rapid declines in biota for which adsorption is thought to play an important role in uptake (Watson et al., 1968). There was only slight evidence of recycling from sediments during the shutdown. However, the period was too brief to make firm conclusions. The transport rate of Zn-65 and Mn-54 below the reactor area was found to be greater than could be accounted for from reactor effluent releases during the shutdown (during shutdown, water was circulated through the reactors and some radioactivity continued to "bleed" from reactor components; release rates from this source, however, were less than 5% of the input during operation). It was concluded that Zn-65 and Mn-54 were released from the sediments during the shutdown.
Losses of Zn-65 in algae and caddis fly larvae were about an order of magnitude while the flesh of suckers appeared unaffected during the shutdown. This is reasonable in view of later work showing effective Zn-65 half lives of approximately 15 days for periphyton and of the order of 100 days for fish (Cushing and Watson, 1971).

The radioactivity relationships are important clues to dynamics. Seasonal variations of Zn-65 specific activity in fish and crustaceans were very similar for the estuary proper and the slough. The seasonable trends showed increases in the spring which fell off in the mid-summer and continued at a more or less low-level during the winter (Renfro, 1967; Renfro, Forster and Osterberg, 1972). This general pattern is in contrast to the studies of Zn-65 in the river below the reactors where decreases, especially in plankton, were noted in the spring in response to increased dilution of the effluent from the spring freshet. It appears that part of the radionuclide inventory stored in bed sediment in reservoirs below the reactors is resuspended during the spring freshet, thus increasing transported activity levels which compensates for the effects of freshet dilution in the estuary. The seasonal increases in activity levels in the estuarine biota were attributed to increased metabolic activity and
tissue elaboration (Renfro, Forster and Osterberg, 1972).

In both the estuary and slough studies the smaller, more rapidly growing animals had higher specific activities than the larger biota captured at the same locations. This was true for juveniles and adults of the same species as well as for prey and predator species. The higher specific activity of prey or smaller animals is a natural consequence of food chain kinetics of radioactivity released into an ecosystem under continuous conditions (steady state). That is, under the steady state case, specific activity will decrease with successive steps along the food chain (Reichle, Dunaway and Nelson, 1970).

An additional important aspect of the slough study was the measurement of rates of decline during the brief reactor shutdown in 1966 mentioned previously. It was found that organisms in the lower trophic levels (algae, amphipods, etc.) exhibited the shortest half-times while each succeeding trophic level appeared to have longer half-times of decline (Renfro, 1967). The loss rate under the conditions where additional activity was available for uptake following termination of input was termed "ecological half-life" to indicate the contribution from the ecosystem; i.e., additional activity stored in food, sediment, detritus, etc.

The algae in the Alder Slough shutdown study showed a half-time of decline of eight days, very similar to the experimental rates of decline observed by Cushing and Watson (1971) for algae-periphyton in the Columbia River water near the reactor area.
Such rapid rates of decline are reasonable if zinc is primarily associated with algae by ion-exchange bonding at surface sorption sites. Such bonding on algae surfaces would allow radiocations to readily equilibrate with the water, resulting in more rapid decline than for biota in which the metal is incorporated into various tissues.

In addition to algae, Renfro (1967) also measured Zn-65 specific activities in emergent vegetation in the slough study site. These measurements showed that levels in algae and emergent vegetation were similar, and not appreciably different than the surficial sediment. It may be that emergent vegetation, plentiful in the upper estuary, is a significant source of detrital zinc and other nutrients to the estuary. Unfortunately, there appear to be no tidal marsh productivity data for the Columbia River estuary with which to assess the role of macrophytes as a food source. The fact that they have been shown to accumulate Zn-65 and the extensive occurrence of marsh lands in the upper estuary, demands attention in the context of the present study (See Appendix F).

Summary and Synthesis of Background Information

The Columbia River is a large, relatively swift, free flowing body of oligotrophic, cold, clear, slightly alkaline water. Compared to other rivers, the Columbia is very low in suspended material.

The characteristic spring freshet from snow melt in the Rocky Mountains coupled with the winter flow maximum of lower river tributaries, lend to the unusual hydrologic regime and complex estuarine
Circulation. Circulation patterns in the estuary are a complex product of tidal forces and river flow.

In general, due to the high river flow, the system can be regarded as "open" or once through in terms of element pools; i.e., rather than as a true cycle as in a lake or pond. Thus, as an ecosystem, reliance is made on import of minerals and energy from the upstream drainage basin. On-stream primary production due to phytoplankton probably supplies most of the food energy input to the estuary as well as the river. The occurrence of extensive beds of intertidal marsh grasses, however, require that this assumption be checked.

Radioactive transition elements added to the riverine ecosystem during reactor operations rapidly associated with plankton and sediments. Biota near the reactor source showed seasonal decreases due to dilution caused by the spring freshet while the opposite picture occurred in the estuary. This is in part attributed to the resuspension of sediment from behind downstream reservoirs in response to increased water velocity during the spring freshet.

Radioecological studies during reactor operating years showed decreasing specific activities with increasing trophic level. Algae and smaller animals showed shorter half-times of decline than larger fish and predator species during a brief reactor shutdown.
EXPERIMENTAL

Study Sites and Sample Collection

McNary Dam and vicinity and the estuary were the study sites for the field work. These sites were chosen because they were known to contain the majority of the bed sediment radionuclide inventory in the river. Sample site locations are shown in Figure 3. A daily composited water sample was taken at Prescott to evaluate input to the estuary.

McNary Dam Site

Water, sediment and biota were collected near McNary Dam. Biological collections included carp (Jones, 1975), freshwater mussels (Harney, 1974) and rooted plants.

Samples of water were taken for both soluble and particulate radioactivity as well as for soluble and particulate stable zinc. Samples were collected from the surface at mid-channel approximately 1.6 km below the dam. Water for radioactivity analysis was collected in 50 liter plastic garbage cans and was processed on shore. It was necessary to process 50 to 200 liters of water during the sample period to obtain sufficient radioactivity for radioanalysis. On shore the samples were filtered through 0.45 μm membrane filters with glass fiber pre-filters. The filtrate was further treated by performing a ferric hydroxide precipitation to concentrate the Zn-65 and other radionuclides. Stable carriers were added for yield determination. The supernate from the ferric hydroxide treatment was siphoned off
Figure 3. Study sites and sampling station locations. Fig. 3C shows the reservoir and estuary sites in relation to major geographic features of the region. Fig. 3A shows trawl stations in the estuary designated H, A and C, and S is the sediment sampling station. Fig. 3B is an enlargement of McNary Dam and vicinity showing water, sediment and biological sampling stations.
and the remaining precipitate returned to the laboratory.

Samples for stable zinc analysis were collected at the same time as the water for radioanalysis. This water was collected in a separate acid cleaned 25 liter polyethylene container by holding the opening of the bottle beneath the surface. The sample was taken with the boat underway and oriented in the upstream direction to avoid contamination from the outboard motor. The water samples from the 25 liter container were filtered immediately after collection using a five liter PVC pressure filtration apparatus. The 0.45 \( \mu m \) membrane filters were pre-rinsed with six liters of deionized distilled water to minimize the zinc blank correction. Both an unfiltered and filtered water sample were taken. (At the time of the study, zinc-free membrane filters were not available; thus particulate zinc could not be determined by direct digestion of the filter media. Instead, particulate zinc was estimated by taking the difference between the filtered and unfiltered sample). Great care was taken throughout the entire process to prevent contamination of the sample. A three liter portion of deionized distilled water was filtered in the field as a system blank. The three liter samples were stored in four liter polyethylene bottles to which was added 15 ml of concentrated \( \text{HNO}_3 \) to stabilize the sample. In addition, two 500 ml samples were taken for suspended sediment determination. These were kept cold and in the dark until final processing in the laboratory.

Sediment was collected along two transects of six stations each (see Figure 3B). One transect was approximately 0.8 km upstream
from the dam face and the other approximately 3.2 km upstream.

Samples collected at these sites consisted of both grab and core samples. Only one or two cores could be obtained in any one trip and these were not always successfully recovered. The grab samples were taken with a Dietz-Lafond snapper type grab. Approximately 250 cc of wet sediment were transferred to a plastic container with 500 ml of 0.05 M CuSO₄ solution immediately upon collection (Cutshall et al., 1971). Samples were stored for at least a week before the solids were separated from the leachate. This separation technique was used to both concentrate the sample and separate the radionuclides of interest from potential gamma-emitting spectral interferents, thus simplifying the data reduction of the spectra. The cores were frozen in the field with dry ice and stored frozen until they could be sectioned into 1.5 cm sections. It was subsequently discovered that the Phieger corer used for collection of most of the cores distorts the sediment column. Only the top portions of these cores provided reliable samples for this study. Near the end of the investigation a specially designed, large-diameter corer was fabricated to take "undisturbed" cores (Appendix A). With this device relatively undisturbed cores could be obtained of 60-70 cm lengths in soft, fine textured sediment. These cores were sectioned in the field immediately after recovery.

Fish were captured with a 15 meter beach seine on the Oregon side of the river near the upper sediment transect (Figure 3B). Fish were frozen until final processing. Freshwater mussels and rooted aquatic plants or macrophytes were collected by free diving near shore
in the same area. Details of the carp and mussel sampling efforts and handling procedures are recorded in Jones (1975) and Harney (1974).

**Estuary**

A water sample was taken daily and composited every two weeks at the National Marine Fisheries Service (NMFS) floating laboratory located just downstream from the Trojan Nuclear Power Plant site near Prescott, Oregon. Water was dipped from the surface and stored in a 200 liter barrel lined with a polyethylene bag and covered with a lid. Initially water was removed from the barrel at two-week intervals and later at monthly intervals. A ferric hydroxide precipitation was made in the barrel after a 15 minute period of agitation to resuspend settled sediment. Agitation was accomplished by air mixing using a portable air pump and plastic hose-diffuser positioned near the bottom of the barrel. The supernate from the barrel was siphoned off after approximately one hour of settling. The 5-10 liters of precipitate was returned to the laboratory for further processing where the slurry was allowed to stand for another day, further reducing the volume. This supernate was then siphoned off and the remaining precipitate placed on a Buchner filter funnel and filtered through a Whatman #41 filter paper. The precipitate so obtained was air dried, ground and packed into a 13 cc counting tube for radioanalysis.

In addition to the composite water samples, grab samples were taken at the time the composite sample was collected. These were processed in the same manner as described above. Occasionally a
filtered sample was collected to check the soluble-particulate status of the radionuclides in transport and to compare with soluble-particulate distribution of the radionuclides after mixing with sea water further down in the estuary. Estuarine water samples were taken so as to have a salinity at approximately mid-range to ensure completion of ion-exchange reactions but at a minimum of dilution to preserve analytical sensitivity. Recovery or yield was checked as described for the McNary samples.

Sediment was collected from Alder Slough and treated by CuSO₄ leaching (Renfro, 1973). Here, the top 1-2 cm of fine sediment was scooped from the surface and added to 0.05 M CuSO₄ solution as described for the McNary grab samples. The sample site was adjacent to the main flow channel of the estuary and was protected from strong wind-wave mixing and tidal currents. In addition, cores were taken in the Youngs Bay region in 1974 using the large diameter corer. It was intended that analysis of radionuclide depth distribution patterns would provide some insight to sedimentation, bioturbation, etc. Extensive biological investigations were also made adjacent to these sites as part of another ecological assessment of the Bay (Higley and Holton, 1975).

Biological collections were made at three stations in the estuary representing the freshwater, mid-estuary and lower, marine-dominated portion of the estuary. These sites are referred to in this study as Harrington Point (H); Astoria (A) and Chinook Point (C). Samples were taken with an otter trawl fished on or near the bottom for 15-30 minutes. Trawls near the shipping channel were made at
the edge of the channel to avoid interference from ship traffic. Samples so collected were placed in plastic containers and preserved with formalin solution. Samples were stored in this condition for one to two weeks before further processing. Flesh and soft tissue were analyzed from the fish and shrimp collected. Fish lengths were measured and the individuals were grouped into size classes for analysis. Other biological collections in the estuary included freshwater mussels in the upper estuary and marine mussels at both the north and south jetty (Harney, 1974; Nelson and Seymour, 1973; Larsen, 1977).

Laboratory Methods of Analysis

Sample analyses required special techniques as well as methods common to all samples. In the latter category, radioanalysis was common to all samples analyzed for radionuclide content. Consequently, this technique will be described as a unit and will apply to all radioanalyses performed for this study unless otherwise indicated.

Radioanalysis

Most samples for radioanalysis were packed into 13 cc plastic counting tubes. Where not enough material was available to fill the tube, sugar was added to maintain a constant sample counting geometry. Samples were analyzed in the well of a 12.7 x 12.7 cm lead shielded NaI(Tl) detector coupled to a Nuclear Data ND-130 AT 512 channel analyzer. Samples were counted for 100 to 800 minutes depending on activity levels. Punched paper tape output from the analyzer was used as data file for batch processing of the spectra on the OSU CDC 3300 computer. Gamma-ray spectra were resolved using a least squares
computer program. Two such programs were used in the course of the study. During the first phase of the study, a program known as GAMMA (Frederick, 1967) was used. Later, degradation of the counting equipment and increasing complexity in the gamma-ray spectra necessitated use of a program that could adjust for gain shift and electronic drift of the analyzer. For this purpose, a program known as ALPHA (Schonfeld, 1966), was used. ALPHA includes a subroutine to correct spectral data for drift and gain shift occurring during analysis. All of the standard spectra in the library used with the program were individually adjusted to their proper positions on the energy-channel axis. Both standards and sample spectra were automatically aligned by the program subroutine prior to spectral analysis by the least squares technique. Both of the above programs required the use of a library of standard spectra and a judicious selection from the library to be used in each data reduction run. Up to 14 standard spectra were used in this study to resolve gamma-ray spectra from sediment and water samples. This was required because in addition to the various major radionuclides of Hanford origin (Zn-65, Co-60, Mn-54, Eu-152, Eu-154, Cs-137), fallout from Chinese testing added to the complexity of the spectra with Ce-141,144, ZrNb-95, Ru-103,106. It was also necessary to allow for K-40 and uranium and thorium daughter activities. Spectra for thorium and uranium plus their daughters were prepared by counting equilibrium ore mixtures. Some of the samples were also allowed to decay for nearly a year to remove spectral interferents such as Sc-46.
Radionuclide identifications and accuracies were checked by comparing with high resolution counting system results (described below) and by interlab exchange of samples (Battelle Northwest Laboratories). The interlab comparisons were excellent with the exception of Zn-65. For this nuclide the OSU results were approximately a factor of two higher than the Battelle results for the same samples. The difference was not, however, a consistent factor of two. The system employed for this study was checked by using new calibrated standards and by preparing mixed solutions containing known amounts of the isotopes in the approximate proportions thought to be present in the real samples. The Zn-65 levels in these mixtures were varied as well. When the mixtures prepared as described above were counted and processed using the data reduction methods previously described, the proper amount of Zn-65 was reported. As a result of these checks, it is felt that the Zn-65 reported using the methods employed in this study were accurate. The source of the difference between the Battelle results and ours is still an enigma (See Appendix D).

Gamma-ray spectra of biological samples were uncomplicated, commonly consisting of only two radionuclides, K-40 and Zn-65.

In addition to radioanalysis by NaI(Tl) systems, some of the later sediment cores were analyzed using a high resolution low-level, gamma-ray counting system. This system included an 85 cc Ge(Li) detector coupled to a Canberra model 8100 analyzer and a computer system for data reduction and calibration. A PDP 11/05 computer operating under the RT 11 disc based system with 28K memory core and
associated programs was used for determining peak locations, areas, energies and calculated activities. A DEC LA 36 Decwriter was used for hardcopy output of results. The greater energy resolution and use of larger sample sizes allowed greater sensitivities and the ability to measure radionuclides to a greater depth in sediment cores. Zn-65 analyses made with the high resolution system agree well with the results of NaI(Tl)/ALPHA determinations.

Sediment Sample Processing

Sediments for radioanalysis were air dried, weighed and packed into counting tubes or 125 cc jars. A few sediments were also analyzed in Marinelli beakers.

Copper sulfate leachates from the grab samples were filtered on a Buchner funnel, a one ml sample of the filtrate saved for stable metal analysis, and the remaining volume evaporated to dryness. The dry residue was then packed into 13 cc counting tubes. The 1 ml portion was diluted to 25 ml for stable metal analysis.

Sediment samples for total metal content were dried, ground to pass a 63 μm stainless steel screen and digested in a mixture of concentrated HNO₃ and HF. One hundred milligrams of sediment in 3 ml of HNO₃ and 1 ml of HF in a 50 ml capped polyethylene bottle were heated in a hot water bath at 60°C for 24 hours to effect complete dissolution of the sediment sample. The resulting solutions were clear indicating complete dissolution of the sediment. Analysis of geochemical reference rock standards showed good recovery.
Filters and Precipitates for Radioanalysis

The large masses of filter media from the filtered water samples were added to 500 ml Erlynmeyer flasks and digested with 200 ml of aqua regia on a hot plate at approximately 100°C for two to three hours. After cooling, the slurry of acid and filter media were separated on a Buchner funnel. The filter media was washed with 0.36 N HCl and the washings added to the leachate. This mixture was evaporated to dryness on a hot plate and the resulting dry solids ground and packed into 13 cc counting tubes.

The ferric hydroxide precipitates were filtered on a Buchner funnel, the filter cake air dried, and then ground to a powder in a mortar and pestle. One hundred milligrams of the powder were taken for stable metal analysis for yield determination. The bulk of the ground precipitate was packed into counting tubes for radioanalysis.

Water Sample Processing for Zinc Analysis

Both the filtered and unfiltered water samples were processed by solvent extraction using methyl isobutyl ketone (MIBK) as the solvent and ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent. The organic extracts of the water were back extracted into 0.36N HCl and the resulting solution analyzed by flame atomic absorption spectrometry. Distilled water as well as filtered water blanks were carried through the process to correct for any contamination from the filter media or reagents. The mean difference between duplicate values for soluble and particulate zinc concentration (determined by difference between filtered and unfiltered) was 1 μg/liter and 2
μg/liter, respectively.

**Biological Sample Preparation**

Soft tissue or flesh separated from biological specimens was first oven dried at 90°C. The dried tissue was then placed in crucibles and ashed in a muffle furnace at 450°C until the white ash stage. The ash was then removed and a small portion weighed into 25 ml volumetric flasks. Five ml of concentrated HNO₃ were added and the ash digested on low heat for 24 hours. The acid was taken to dryness and the residue brought up in 0.36 N HCl as a final running solution for stable zinc analysis. The bulk of the ash was packed into counting tubes for radioanalysis. Sugar was added when necessary to maintain the 13 cc volume.

**Stable Element Analysis**

The solutions prepared as described above were analyzed by aspiration into the flame of an atomic absorption spectrophotometer (Perkin Elmer model 303). Standards and blanks were prepared with the same reagents as used for the final run solutions used in sample preparation.
RESULTS AND DISCUSSION

Biokinetics and Specific Activity Relationships

Specific activities were calculated by dividing the radio-nuclide concentration of the sample by the corresponding stable element concentration. A graphical display of the Zn-65 specific activity data as a function of time post shutdown is shown in Figure 4. The plotted points each represent pooled samples. Error bars about data points are analytical uncertainties expressed as a pooled standard deviation resulting from both radioactive counting statistics and element analysis uncertainties.

Linear least squares analysis of the data was performed with the OSU statistical code SIPS on the CDC 3300. The natural logarithm (ln) of specific activity was regressed on time. Biological data were weighted in proportion to the number of individuals comprising a sample. The regression was restricted to data collected between June 1971 and December 1972. The June 1971 starting data was chosen because some collections were not routine until then. Intercepts were arbitrarily taken to 16 March 1971.

For the McNary sediment grab samples, data from the 12 stations were pooled on each collection date and the mean value regressed on time.

The time series water data required slightly different techniques. The composited water sample data for Prescott was graphically paired with mean monthly river discharge and a multiple regression of
Figure 4. Zinc-65 specific activities in estuarine sediment and biota versus time post-shutdown (Pooled grab data for McNary sediment also shown for comparison).
ln(activity) and ln(discharge) on time was performed. Since it has been shown that ln(discharge) is correlated with ln(sediment concentration) in transport for many rivers (Graf, 1971), this assumed relationship was used to smooth the seasonal peaks in the water data which occurred in response to the increased velocities associated with the spring freshets. Simple linear regression of activity on time produces slightly shorter half-times but larger errors of regression.

The numerical results of the regression analyses for the various components sampled are shown in Table 2. The loss rates are expressed in half-times as well as in residence times. The specific activity intercepts are also tabulated so that comparisons of relative levels from one location to another and among sample types can be made.

Specific Activity Intercept Data

There are several points of interest concerning the intercept data of Table 2. First, the rather narrow range of values is rather striking, considering there is approximately 500 km between McNary Dam and the south jetty. Due to dilution by mixing with tributaries and with seawater in the estuary, one might expect to see a much greater difference than the factor of two to three in the specific activity intercepts between McNary biota and estuarine biota. Within the estuary itself, the specific activity intercept of the marine mussels at the south jetty is only 30 percent lower than the mean of the values for freshwater biota at Harrington Point.

Water Isotope Dilution Model An attempt was made to explain the narrow range in specific activity data by using a simple conservative
Table 2. Half-times of decline of Zn-65 in water, sediment, and biota at McNary Reservoir and in the Columbia River estuary during June 1971 through December 1972.

<table>
<thead>
<tr>
<th>Location</th>
<th>Phase</th>
<th>$\text{decay-corrected Intercept, } \text{nCi}^{65}\text{Zn/gZn}$</th>
<th>half-time, days</th>
<th>$4E$</th>
<th>$5E - L$</th>
<th>Residence time, days</th>
</tr>
</thead>
<tbody>
<tr>
<td>McNary Reservoir</td>
<td>Sediment (pooled grabs)</td>
<td>269</td>
<td>181 ± 11</td>
<td>700 ± 159</td>
<td>1010 ± 229</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td></td>
<td>146 ± 40</td>
<td>361 ± 99</td>
<td>521 ± 143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clams (soft parts)</td>
<td>230</td>
<td>189 ± 9</td>
<td>827 ± 166</td>
<td>1190 ± 240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carp (flesh)</td>
<td>194</td>
<td>174 ± 56</td>
<td>600 ± 660</td>
<td>866 ± 950</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Macrophytes (Potamogeton)</td>
<td>297</td>
<td>57 ± 7</td>
<td>75 ± 9</td>
<td>108 ± 13</td>
<td></td>
</tr>
<tr>
<td>Estuary</td>
<td>Sediment (Prescott composite)</td>
<td>58</td>
<td>177 ± 14</td>
<td>639 ± 181</td>
<td>922 ± 261</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (&lt;10 cm)</td>
<td>130</td>
<td>131 ± 9</td>
<td>281 ± 43</td>
<td>405 ± 62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (10-20 cm)</td>
<td>110</td>
<td>149 ± 8</td>
<td>378 ± 49</td>
<td>545 ± 71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sculpin (C. asper 5-10 cm)</td>
<td>122</td>
<td>176 ± 12</td>
<td>631 ± 151</td>
<td>910 ± 218</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sculpin (C. asper 10-20 cm)</td>
<td>89</td>
<td>212 ± 18</td>
<td>1600 ± 1030</td>
<td>2310 ± 1490</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clams (Anodonta soft parts)</td>
<td>100</td>
<td>149 ± 9</td>
<td>380 ± 61</td>
<td>548 ± 88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (10-20 cm)</td>
<td>137</td>
<td>145 ± 5</td>
<td>354 ± 31</td>
<td>511 ± 45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (&lt;10 cm)</td>
<td>101</td>
<td>152 ± 6</td>
<td>400 ± 45</td>
<td>577 ± 65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sculpin (L. armatus 10-20 cm)</td>
<td>82</td>
<td>144 ± 13</td>
<td>351 ± 78</td>
<td>506 ± 113</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shiner perch (&lt; 10 cm)</td>
<td>109</td>
<td>138 ± 7</td>
<td>316 ± 38</td>
<td>456 ± 55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tom cod (10-20 cm)</td>
<td>87</td>
<td>149 ± 9</td>
<td>382 ± 58</td>
<td>551 ± 84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lemon sole (10-20 cm)</td>
<td>86</td>
<td>158 ± 18</td>
<td>448 ± 144</td>
<td>646 ± 208</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sand shrimp</td>
<td>101</td>
<td>143 ± 6</td>
<td>341 ± 37</td>
<td>492 ± 53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shiner perch (&lt;10 cm)</td>
<td>119</td>
<td>156 ± 13</td>
<td>430 ± 99</td>
<td>620 ± 143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sculpin (L. armatus 10-20)</td>
<td>82</td>
<td>150 ± 19</td>
<td>386 ± 123</td>
<td>557 ± 180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (&lt;10 cm)</td>
<td>132</td>
<td>145 ± 13</td>
<td>354 ± 80</td>
<td>511 ± 115</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Starry flounder (10-20 cm)</td>
<td>118</td>
<td>156 ± 9</td>
<td>431 ± 72</td>
<td>622 ± 104</td>
<td></td>
</tr>
<tr>
<td>North Jetty</td>
<td>Mussels (M. edulis)</td>
<td>136</td>
<td>120 ± 11</td>
<td>237 ± 44</td>
<td>342 ± 63</td>
<td></td>
</tr>
<tr>
<td>South Jetty</td>
<td>Mussels (M. californianus)</td>
<td>77</td>
<td>159 ± 7</td>
<td>453 ± 57</td>
<td>654 ± 82</td>
<td></td>
</tr>
</tbody>
</table>

1 See Figure 3 for station locations.
2 See Appendix B for species names and feeding habits of animals.
3 Specific Activity (SA) intercepts from linear regression of ln (SA) on time are all adjusted to 16 March 1971.
4 (E) designates the half-time computed from the regression slope.
5 (E-L) designates half-time computed after subtracting the radiological decay constant (L) from the regression slope.
6 Residence time = $T_{\frac{1}{2}} (E-L) / 0.693$. 
isotope dilution model for mixing of seawater with river water. The approach and model used by Cutshall, Renfro and Larsen (1975) was used to generate hypothetical curves for mixing seawater with river water. A ratio of 0.2 for stable zinc in seawater and river water was considered to be the most appropriate based on the analysis by Cutshall, Renfro and Larsen (1975). Curves for concentration ratios of 1.0 and 0.02 were also generated for comparison. These theoretical curves are shown in Figure 5 together with the mean specific activity intercepts for the three estuarine stations. In addition, Zn-65 specific activity data for marine mussels from the south jetty (south side) and shrimp collected in March 1971 on the continental shelf near the river mouth are plotted. The specific activity data were plotted using near-bottom average salinities at collection sites.

If the stable zinc ocean/river concentration ratio of 0.2 is valid for the estuary, the isotopic mixing model does not appear to account for the observed specific activities in the estuary. On the other hand, if the ratio of 0.2 is in error, and the true seawater value is much lower, then it may be possible to explain the observed data with the simple isotopic mixing model. Cutshall, Renfro and Larson (1975) based their analysis on analytical data for the Columbia River and coastal region off Oregon available at the time of their analysis. The only new data for this region of which I am aware at the time of this writing, is the stable zinc levels in Columbia River water at McNary Dam reported in this thesis. These data show an average soluble zinc concentration of approximately 7 µg/liter as compared to the 26 µg/liter for river water and 5 µg/liter in coastal
Figure 5. Comparison of observed and predicted Zn-65 specific activities in estuarine biota as a function of salinity. The solid triangles and error bars are the means and standard errors of the means of the intercept values listed in Table 2; the open triangle is the marine mussel (*M. californianus*) specific activity intercept for the collections from the south side of the South Jetty (Table 2). The open square is the specific activity of a single collection of the sand shrimp (*Crangon fransiscorum*) collected on March 1971 near the river mouth on the continental shelf (taken from Carey and Cutshall, 1973). The predicted values are shown as continuous lines for three different ocean/river stable zinc ratios and are based on the isotopic dilution model used by Cutshall et al., (1975). The mean specific activity value for station H was used as the starting point (100% river water) in the computation. The application of the model in the above case assumes only simple mixing of river and ocean water in the estuary influences the specific activity of the animals at a given salinity; i.e., conservative mixing is assumed.
seawater used to establish the ratio of 0.2. There appears to be no new zinc data available for the Oregon coast with which to update the ratio. Bowen (1975) lists an average seawater value of 4.9 μg/liter and 10 μg/liter for average river water. Recent data from the California coast, however, include exceptionally low soluble zinc levels (Bruland, et al., 1978). If true soluble zinc levels in seawater are, as their data suggest, as low as 0.1 μg/liter or less, then an analytical ocean/river water ratio of 0.02 might be more appropriate. Since the mixing model is so sensitive to the ocean/river stable zinc ratio and stable zinc data are in doubt, no firm conclusions can be drawn. Oceanic zinc measurements are needed off Oregon before the estuarine isotope dilution hypothesis for water can be tested.

An alternate explanation for the apparent uniform Zn-65 specific activities in the estuary is that most of the species comprising the mean specific activities at each collection site are migratory. For example, 0-1 year class flounder reside in the strictly freshwater portion of the estuary during their first year and then gradually migrate into more saline water as they mature. This type of "biological" mixing could blur the apparent relationship between salinity at the collection site and the measured specific activity. A more ideal test organism would be stationary. Filter feeding molluscs would be ideal for this test both because they are stationary and because they are more closely linked to the water through the rather direct water-phytoplankton-consumer food chain. The latter characteristic would remove the additional uncertainty concerning varied food sources of
the estuarine fishes (see Appendix B for feeding habits of the estuarine biota examined in this study). Only limited data for filter feeders exist from the collections made for the present study. Mussel data, however, for various locations along the Oregon coast are available. Even though there is apparently some question concerning the seawater/riverwater zinc ratio \( Z_o/Z_r \), the observed specific activities should at least follow the appropriate theoretical specific activity-salinity curve for a given \( Z_o/Z_r \). Zinc-65 specific activities in *Mytilus californianus* from the Oregon coast during 1965 (Larsen, 1977) are also plotted against salinity (Figure 6). Curves for various \( Z_o/Z_r \) ratios are superimposed on the observed specific activity-salinity plot. The observed specific activities are plotted as relative values referenced to Harrington Point juvenile flounder as the starting point specific activity of the undiluted source water. These specific activities cut across lines of equal \( Z_o/Z_r \) at low salinities and then approach the 0.2 ratio line at higher salinities. This implies the water-phytoplankton-*Mytilus* food chain is out of equilibrium with the isotope dilution model from the mouth of the river to near Cannon Beach, some 38 km south of the estuary. It also suggests that a \( Z_o/Z_r \) ratio of 0.2 as used by Cutshall, Renfro and Larsen (1975), is at least reasonable in spite of the uncertainties in zinc levels in ocean water. If the 0.2 ratio is valid, as suggested by Figure 6, then the data near the river mouth clearly are too high to be accounted for by conservative mixing and isotope dilution. Some mechanism must exist for supplying Zn-65 at relatively
Figure 6. Comparison of observed (▲) and predicted (solid lines) relative Zn-65 specific activities in Mytilus californianus along the Oregon coast, 1965. Theoretical curves are for various ocean/river stable zinc ratios as a function of salinity (Mytilus data from Larsen, 1977).
high specific activity. At any rate, the water model does not yield an adequate description of specific activities near the river mouth. It may be necessary to also consider particulate matter in the isotope dilution model for the estuarine zone.

**Sediment Isotope Dilution**

The specific activity of sediment mixtures can be modeled similarly to water. A mixture of two sediments has a specific activity that depends upon the specific activities of the components, the relative proportions of the components, and the relative amounts of the stable element in the components. Thus, mixing of contaminated sediment that is high in zinc with non-contaminated sediment that is low in zinc results in very little change in specific activity except for mixtures that are almost pure non-contaminated sediment. Since Columbia River water appears to be considerably higher in zinc content than seawater, it might also be expected that Columbia River sediment would be rich in zinc. This too appears to be the case.

However, direct comparisons of metal concentrations in different sediment samples is inappropriate since zinc concentrations in sediments are surface area dependent. For spherical particles the relationship is linear with a slope of 1 on a log-log plot of diameter and concentration (Glenn, 1973; Sayre, 1963). This relationship was used to adjust the zinc concentrations of the <63 μm fraction of the sediment samples collected for this test. The particle median diameter of the <63 μm was determined by the dispersed-pipet method (Guy, 1965). The average of all the median diameters of the samples used in the test was calculated and the measured concentration at
each sample location adjusted to this particle size using the relationship described above. Adjusting all the samples to the average of the median diameters minimizes error in the adjustment procedure. Results from Priest Rapids Dam just upstream from the reactor area, down to Youngs Bay near Astoria are shown in Table 3. Zinc content increases with each upstream location on the main stem of the river. The maximum or highest value is nearly ten times higher than the crustal average for zinc while the tributary values are near the crustal average of 70 µg/g and 95 µg/g for average shale (Bowen, 1966). Therefore, during mixing of low zinc sediment from the tributaries into Zn-65 labeled, high-zinc sediment of the Columbia, the specific activity of the mixture is affected less than if the two sediments had the same stable zinc content.

In order to make a quantitative assessment of the sediment isotope dilution model, I have estimated the relative proportions of sediment from the tributary sources in Columbia River sediment. This was done using the two component mixing relationship:

\[ C_m = aC_1 + (1-a)C_2 \]

where \( C_m \) represents the mixed concentration, \( C_1 \) is the concentration in component 1 and \( C_2 \) the concentration in component 2; \( a \) is the fraction of \( C_1 \) in the mixture, and \( (1 - a) \) is the fraction of \( C_2 \) in the mixture.
Table 3. Stable zinc content of Columbia River and tributary sediment samples.

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>1Distance from mouth, km</th>
<th>2Median diameter, phi units</th>
<th>3Un-adjusted ng/g</th>
<th>Mean phi adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main stem locations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Priest Rapids Dam</td>
<td>640</td>
<td>6.07</td>
<td>844</td>
<td>863</td>
</tr>
<tr>
<td>McNary Dam</td>
<td>500</td>
<td>6.35</td>
<td>553</td>
<td>494</td>
</tr>
<tr>
<td>Miller Sands</td>
<td>37</td>
<td>5.65</td>
<td>227</td>
<td>285</td>
</tr>
<tr>
<td>Astoria (Youngs Bay)</td>
<td>19</td>
<td>5.70</td>
<td>149</td>
<td>182</td>
</tr>
<tr>
<td><strong>Tributary locations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Snake River at Ice Harbor Dam</td>
<td>523</td>
<td>7.63</td>
<td>94</td>
<td>45</td>
</tr>
<tr>
<td>Willamette River</td>
<td>164</td>
<td>5.60</td>
<td>101</td>
<td>130</td>
</tr>
<tr>
<td>Youngs River</td>
<td>20</td>
<td>6.80</td>
<td>90</td>
<td>65</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>6.12</td>
</tr>
</tbody>
</table>

1 Distances entered for tributaries are for the approximate location at the confluence of the tributary with the Columbia River.

2 Phi units = log2(median diameter, μm)

3 Unadjusted values are the actual concentrations of the < 63 μm fractions. The adjusted values are the concentrations obtained after allowing for the effect of particle diameter on metal concentration. The mean phi of the median diameters of 6.12 was used for this estimate.
When the above equation is solved for $a$, the following relationship results:

$$a = \frac{(C_m - C_2)}{(C_1 - C_2)}$$

I have computed $a$ using the stable zinc data below each tributary (Table 4).

Table 4. Sediment mixing fractions for Columbia River and tributary combinations.

<table>
<thead>
<tr>
<th>Mixture location</th>
<th>Columbia River (source 1)</th>
<th>Tributary (source 2)</th>
<th>$a$ (fraction of 1 in mixture)</th>
</tr>
</thead>
<tbody>
<tr>
<td>McNary Dam</td>
<td>Priest Rapids</td>
<td>Snake River</td>
<td>0.548</td>
</tr>
<tr>
<td>Miller Sands</td>
<td>McNary Dam</td>
<td>Willamette River</td>
<td>0.426</td>
</tr>
<tr>
<td>Youngs Bay</td>
<td>Miller Sands</td>
<td>Youngs River</td>
<td>0.535</td>
</tr>
</tbody>
</table>

Assuming the only influence on the sediment specific activity is dilution by tributary sediments, a relationship between sediment specific activity and mixing fraction can be expressed as:

$$S_{A_m} = S_{A_S} \times \frac{aC_s}{C_m}$$

where $a$ is the mixing fraction of the sediment from the labeled source and $s$ designates source values while $m$ designates mixture values. Using the above relationship with the mixing fractions in Table 4, the sediment specific activity during mixing can be calculated (Figure 7). Between the reactor area and McNary Dam
Figure 7. Relative change in Columbia River sediment Zn-65 specific activity due to hypothetical mixing with tributary sediment. Dotted line represents expected relationship when source and diluting sediment have the same stable zinc content. Numbers in parentheses are distances from mouth in river miles.
the sediment specific activity declines very little even though a
two-fold dilution of the sediment has occurred due to mixing with
Snake River sediment. Even though the sediment from near the reactor
area comprises only approximately 10 percent of the estuarine
sediment, the specific activity would theoretically decrease by only
about a factor of two. This may explain why the specific activities
of the McNary biota were only a factor of two or three higher than
specific activities of the estuarine biota. These considerations
imply that sediment particles play a significant role in uptake of
zinc by biota in the Columbia River and estuary.

Rates and Patterns of Decline

It has been common practice in modeling radionuclide turnover
in organisms to treat the biological system under study as an individual. The procedure used in this study involved compositd samples
of predetermined size classes. That is, a discrete size or age-class
was followed in time. Alternatively, in a laboratory study, it would
have been conventional to study a group of individuals in time. The
distinction between these two approaches is that the constant size-
class population view does not consider animal growth during the
period of interest since the same size-class is always sampled.
Growth merely causes the individuals in any size-class to change from
time to time. In the other approach, the interpretation of kinetic
relationships involves a term to account for growth. This distinction
is necessary since data from both approaches will be compared.
Half-lives from Linear Regression Analysis  The most striking feature of the biological rate data (Table 2) is the similarity of half-lives for all the estuarine species. This is especially surprising when it is realized that the list of species represented includes animals of very divergent feeding habits, trophic position, habitat, size, etc. This grouping of half-lives is dramatically illustrated in Figure 8. The weighted mean of the decay corrected half-lives is 370 days. Rates of decline of sediment from both the estuary and McNary were significantly slower than for biota.

Furthermore, rates of decline in water appear to bracket the rates of decline in the biota. This observation suggested that the rate of decline of the primary source (in this case the water) drives the receptor organisms during a decline period.

Kinetic Model for Declining Source  From the input-output model referred to in the introduction, a simple source-receptor relationship can be considered in order to simplify the mathematics and thereby focus on the response functions. For this model we treat a single declining source and a receptor. In terms of specific activity, the approach and nomenclature used by Foster (1959) and Vanderploeg (1973) will be used. The basic equation describing input and output to a receptor is:

\[ \frac{dS}{dt} = BC(t) - (\Lambda + B)S \]

Where  
- \( S \) = specific activity of the receptor  
- \( C(t) \) = specific activity of source as a function of time, \( t \)  
- \( \Lambda \) = physical decay constant of radionuclide  
- \( B \) = biological rate constant of radionuclide in receptor organism
Figure 8. Frequency plot of half-times of decline of Zn-65 specific activity in estuarine biota, Columbia River estuary, 1971-72. The above half-times were computed after subtracting the radiological decay constant from the slopes of regression (The terms half-time and half-life are used interchangeably in this thesis).
For the terminated input case, the uptake term is modified to allow for a declining source. Including this modification the equation becomes:

\[
\frac{dS}{dt} = B C e^{-Kt} - (A + B)S
\]

where \( K \) is the loss rate constant of the source which includes the radiological decay constant \( A \).

Integration of the above equation requires the boundary condition that the specific activity of the organism is equal to its steady state specific activity just prior to termination of input. The steady state source and receptor relationship is:

\[ C = \frac{(A + B)S_0}{B} \]

With the above boundary condition integration results in the following:

\[
S = S_0 \left[ \frac{\mu}{\mu - K} e^{-Kt} + \left(1 - \frac{\mu}{\mu - K}\right) e^{-\mu t} \right]
\]

where \( \mu = (A + B) \)

\( S_0 \) = steady state specific activity in organism

and with the limitations: \( K \neq \mu \)

In the present study \( K \) is considered to be the loss rate of the Zn-65 in river water.

From inspection of the above equation(s) it is evident that \( K \) is an important variable influencing the specific activity. This is dramatically illustrated by performing sensitivity plots for hypothetical cases where it is assumed organisms or receptors having
different Zn-65 biological half-lives all derive radioactivity from the same source (Figure 9). Specific activity varies with $T_K$ ($0.693/K$) and with the biological half-life. As $T_K$ increases, the slopes of the curves for the three different biological half-lives approach the same approximate value. In the jargon of modelers, $e^{-0.693/T_K}t$ is a "forcing function". Another way of illustrating this is to plot the ratio of the slopes of linear regressions of the straight-line portions of the curves. The time interval between 200 and 700 days is used for this purpose. When this is carried out a curve of the type shown in Figure 10 is obtained. This curve shows that as $T_K$ reaches a value of approximately 150 days the slope ratio approaches unity and changes very little with increasing values of $T_K$.

While this model is highly simplified compared to an estuarine ecosystem, it does suggest an explanation for the similarity in observed rates of decline in the water and in the estuarine biota. It appears that $T_K$ is large enough that the terms containing $K$ dominate the calculation regardless of the biological half-life.

Another application of the model was made using two species for which biological half-lives had been determined in the laboratory (Renfro, 1967). Sand shrimp, *Crangon franciscorum*, has a much shorter biological half-life (30 days) than starry flounder, *Platichthys stellatus* (200 days). Making the same assumptions used to generate the time-response curves in Figure 9, i.e., both species having the same source of activity, and using the biological half-lives from Renfro (1967), a comparison is made between the observed specific activity ratio of these two species and the theoretical ratio based on
Figure 9. Theoretical Zn-65 specific activity-time response curves. Based on equation for source-receptor model, p. 53, assuming the same intake source to each hypothetical receptor. Individual curves for each fixed value of $T_K$ are for biological half-lives ($T_B$) of 30, 300 and 3000 days respectively. $T_K$ is the effective half-time of the source term (i.e., it includes the physical half-life of Zn-65 as well as the half-time of the source).
Figure 10. Ratio of Zn-65 specific activity loss rate constants for two hypothetical species as a function of the half-time of decline of the source. Prepared from data used in Figure 9 for 30 and 300 day biological half-lives.
the simple input-output model (Figure 11). The half-time of decline of the source was obtained from the Prescott water data. Figure 11 illustrates that during the steady-state period the specific activity of the species with the shorter biological half-life is higher than the species with the longer half-life. This difference diminishes during the post-shutdown period so that estuarine species with widely different biological half-lives have similar specific activities during the post-shutdown period. This stands in contrast to the noticeable differences observed during steady-state operation. Thus, specific activities of these animals decline in a predictable manner.

The foregoing evaluation suggests that simple input-output models are useful for describing decline in even a very complex ecosystem. This lends support to the use of such models for planning sample collection and for estimating dose levels from hypothetical contamination incidents.

Another important conclusion is that where the rate of decline or "washout" of a previously contaminated ecosystem is slow with respect to the biological turnover of the receptor organisms, it may not be necessary to know all the individual biological half-lives in order to predict time-dependent activity levels in biota following a chronic contamination incident. It appears that major emphasis should be placed instead on contaminant-sediment interactions and sediment transport mechanisms (this will be the subject of the following chapter).
Figure 11. Theoretical and observed Zn-65 specific activity ratios ($S_1/S_2$) versus time for sand shrimp (Crangon franciscorum) and flounder (Platichthys stellatus), Columbia River estuary.
The foregoing evaluation focused on the similarities among the half-times of decline of the estuarine biota. However, there were some marked differences in half-times of biota at the McNary site. The most striking of these was the very rapid rate of decline exhibited by the pond weed, Potamogeton (Table 2). This can be explained by the fact that: 1) this macrophyte absorbs a major portion of its nutrients by direct absorption through its leaves (1Schults and Malueg, 1971) and 2) as will be shown in the next section, little, if any, soluble Zn-65 was in transport during the post-shutdown period. Thus, the direct absorption route of uptake by this plant was blocked during the decline period. As the pond weed grew during the first year post-shutdown, little, if any, Zn-65 from solution was available for incorporation in its tissue. As a result, the Zn-65 specific activity appeared to drop rapidly in comparison to other biota. This observation points further to the importance of sediment particles as an important mode of transfer of zinc to consumers (presumably by incidental ingestion of sediment particles). If the primary route of entry of Zn-65 to the food web for the riverine and estuarine species examined was via the soluble zinc route, then the rates of decline of other biota examined would have been dissimilar as well as more rapid for certain species than was observed (This situation can be illustrated with the most rapid source rate of decline as shown in Figure 9, $T_{50} = 50$).

Sediment-Water Exchange and Transport

Because the predominant portion of the bed sediment inventory was concentrated in the upper river behind McNary Dam, most of the study effort was centered there. One site in the estuary, however, was included in order to compare an estuarine with a fluvial depositional environment. The McNary sediment sample site locations and station numbers to be referred to in this study are shown in Figure 12.

Ion-Particle Interactions

Yousef and Gloyna (1970) used a reversible exchange model to describe the sorption-release function in a radionuclide transport model for fluvial systems. According to their model radionuclides in a flowing stream will be taken up by bottom sediment until a saturation point is reached. If the concentrations in the water subsequently decline, the model predicts release of the isotopes from the sediment (Figure 13). Under ideal conditions, isotope exchange would be completely reversible. However, in simulated stream experiments, Yousef and Gloyna (1970) found that the isotope exchange reaction was only partially reversible depending on both substrate and radionuclide. They concluded there were stronger bonds than simple ion-exchange (electrostatic) bonds.

Based on the above findings, it appeared likely that those radionuclides that are adsorbed to a large extent by simple ion-exchange bonding would be likely to undergo isotope exchange reversal in a system where the input of new tracer is terminated.
Figure 12. Sediment sample station locations in McNary Reservoir.
Figure 13. Open, two compartment tracer system illustrating the interaction of labeled bed sediment with an infinite stable element reservoir (water). The water compartment represents either water behind a dam, a section of river or the estuary. $Q$ is the flow rate of water through the system (the star denotes the direction of movement of the radioactive label).
Radionuclides adsorbed by stronger bonding mechanisms would be lost more slowly.

Columbia River radionuclides are frequently bound by more complex interactions than simple ion-exchange bonds (Johnson, Cutshall and Osterberg, 1967; Cutshall, 1967; Nelson et al., 1966 and Robertson et al., 1972). The general order of chemical exchangeability found from these studies was:

\[ ^{54}\text{Mn} > ^{60}\text{Co} > ^{137}\text{Cs} > ^{65}\text{Zn}, \quad ^{51}\text{Cr}, \quad ^{55}\text{Fe}, \quad ^{46}\text{Sc}, \quad ^{152}\text{Eu} \]

**Isotope Exchange Loss from Bed Sediment**

It was hypothesized that relative loss rates following terminated input should parallel the order of chemical exchangeability. To test this hypothesis, decay-corrected radionuclide ratios and specific activities in sediment over time were evaluated. Decay-corrected specific activities should show a rate of decline in the same order shown above. Changes in activity ratios would suggest a chemical loss mechanism since chemical dissolution would affect radioactive and stable metals equally and would not result in a change in specific activity. Sediment dilution would affect specific activities but would have the same influence on all the radionuclide specific activities, assuming no major change in sediment composition occurred during the period of consideration.

Samples consisted of the top 1.5 cm sections of Phleger cores collected periodically at stations 5, 9, 10 and 12 (Figure 12). Radioanalysis was performed by gamma-ray spectrometry. Metal analyses for specific activity determinations were performed by flame atomic
absorption following complete dissolution of the sample with concentrated HNO₃/HF in a bomb.

Decay-corrected radionuclide ratios were regressed on time using a linear model (Table 5). Regressions of decay-corrected activity ratios on time should have a slope of 0 if changes in one radionuclide relative to another have not occurred. Mn-54 appears to be lost from sediment relative to the other radionuclides, Zn-65, Co-60, Eu-152 and Cs-137. Specific activities of Zn-65, Mn-54 and Co-60 were also regressed on time (Table 6). The decay-corrected half-times computed from the slopes show an order reflecting the general order of exchangeability previously noted for Columbia River sediment; that is, Mn-54 specific activity declines nearly twice as rapidly as Co-60 and nearly three times as rapidly as Zn-65.

In terms of the isotope exchange hypothesis, radionuclides bound by ion-exchange bonds more readily undergo isotope exchange reversal following terminated input and are thus lost more rapidly from the substrate. These considerations are concordant with the radionuclide transfer function of the transport model proposed by Gloyna and co-workers (Yousef and Gloyna, 1970).

It is concluded from the above considerations that Mn-54 is mobilized more readily than either Co-60, Zn-65, Eu-152 and possibly Cs-137. This is attributed to the fact that divalent manganese behaves more like an alkaline earth than a transition metal and forms relatively weak coordinate-convalent bonds. This allows isotope exchange to occur more readily with the unlabeled manganese in
Table 5. Regression parameters for radionuclide ratios versus time in surficial sediment, McNary Reservoir, 1971-72.

<table>
<thead>
<tr>
<th>Radionuclide Ratio</th>
<th>N</th>
<th>slope</th>
<th>$t_0$</th>
<th>95%</th>
<th>99%</th>
<th>99.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{54}\text{Mn}/^{65}\text{Zn}$</td>
<td>13</td>
<td>-7.69E-5 ± 1.55E-5</td>
<td>4.95</td>
<td>2.201</td>
<td>3.106</td>
<td>3.497</td>
</tr>
<tr>
<td>$^{152}\text{Eu}/^{65}\text{Zn}$</td>
<td>19</td>
<td>1.91E-6 ± 9.16E-6</td>
<td>0.21</td>
<td>2.11</td>
<td>2.898</td>
<td>3.22</td>
</tr>
<tr>
<td>$^{60}\text{Co}/^{65}\text{Zn}$</td>
<td>19</td>
<td>6.73E-6 ± 2.23E-5</td>
<td>0.30</td>
<td>2.11</td>
<td>2.898</td>
<td>3.22</td>
</tr>
<tr>
<td>$^{137}\text{Cs}/^{65}\text{Zn}$</td>
<td>19</td>
<td>1.03E-5 ± 5.05E-6</td>
<td>2.04</td>
<td>2.11</td>
<td>2.898</td>
<td>3.22</td>
</tr>
</tbody>
</table>

The above test statistics show that only the Mn-54 ratio data has a slope different from zero. It furthermore shows that it is significantly different even at the 99.5% confidence level. The hypothesis that the slopes are equal to zero cannot be rejected for the other nuclides except for $^{137}\text{Cs}$ data at the 90% level of confidence.

Table 6. Rates of decline of radionuclide specific activities in surficial sediment of McNary Reservoir, 1971-72.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>N</th>
<th>Slope</th>
<th>$T_0$ days</th>
<th>$R^2$</th>
<th>intercept</th>
<th>Decay Corrected $T_0$ days</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{65}\text{Zn}$</td>
<td>12</td>
<td>-1.09E-3</td>
<td>$178 ± 9.1$</td>
<td>0.9838</td>
<td>5.86 ± 0.3700</td>
<td>645 ± 95</td>
</tr>
<tr>
<td>$^{54}\text{Mn}$</td>
<td>10</td>
<td>-4.81E-3</td>
<td>$144 ± 9.4$</td>
<td>0.9673</td>
<td>3.426 ± 0.105</td>
<td>269 ± 33</td>
</tr>
<tr>
<td>$^{60}\text{Co}$</td>
<td>10</td>
<td>-1.91E-3</td>
<td>$360 ± 99$</td>
<td>0.6238</td>
<td>7.407 ± 0.177</td>
<td>455 ± 150</td>
</tr>
</tbody>
</table>
the ambient water. Cesium, although not subject to strong coordinate bonding, is specifically trapped in layer silicate minerals (Grim, 1953). Cobalt is intermediate between manganese and zinc in its coordinate bond strengths and would be expected to exhibit intermediate exchange tendencies.

**Isotope Dilution** The intercept data in Tables 5 and 6 show some interesting effects of relative isotope dilution. For example, a comparison of activities and specific activities of selected pairs (Table 7) show that while Co-60 activity is seven times lower than Zn-65, its specific activity is nearly five times higher. This is due to the unusually high stable zinc and the naturally low stable cobalt levels in sedimentary materials (see Table 8 for a comparison of metal levels in McNary sediments with world averages). This type of information is important in assessing radiological impact based on the specific activity approach.

**Suspended Sediment-Water Isotope Exchange** The previous analysis implies that tightly bound transition metal radiocations on sediment may not undergo isotopic exchange with their stable metal counterparts in the water. Specific activities in the "soluble" and particulate phases of the river water should also reflect this condition. The particulate specific activity below McNary Dam is generally more than 10 times higher than the filtered water specific activity (Figure 15 and Table 9). These results also show little tendency for the particle-bound Zn-65 to equilibrate with the stable
Table 7. Comparison of activity and specific activity ratios. (based on Y intercepts of regressions at 0 time)

<table>
<thead>
<tr>
<th>Radionuclide Pair</th>
<th>Ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activity</td>
<td>Specific Activity</td>
<td></td>
</tr>
<tr>
<td>$^{54}\text{Mn}/^{65}\text{Zn}$</td>
<td>0.084</td>
<td>0.088</td>
<td></td>
</tr>
<tr>
<td>$^{60}\text{Co}/^{65}\text{Zn}$</td>
<td>0.142</td>
<td>4.70</td>
<td></td>
</tr>
</tbody>
</table>
Table 8. Comparison of average trace element abundances in McNary sediment with world averages (all values in µg/g).

<table>
<thead>
<tr>
<th>Metal</th>
<th>McNary Reservoir</th>
<th>Average Shale</th>
<th>Igneous Rock</th>
<th>Ratio (1)/(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>537 ± 33</td>
<td>95</td>
<td>70</td>
<td>5.6</td>
</tr>
<tr>
<td>Mn</td>
<td>557 ± 30</td>
<td>850</td>
<td>950</td>
<td>0.66</td>
</tr>
<tr>
<td>Co</td>
<td>17 ± 1</td>
<td>19</td>
<td>25</td>
<td>0.89</td>
</tr>
</tbody>
</table>

(1) Values are standard errors of the means of the stable element values used for the specific activity determinations in surface sediments.

(2) Average shale and igneous rock values from Bowen (1966).

Note: the median particle diameter for sediment in the vicinity of the McNary sample sites was 20 microns which should be comparable to the particle size of average shale.
Figure 15. Soluble and particulate: Zn-65, stable Zn, and Zn-65 specific activity; suspended load, and river discharge in the Columbia River at Umatilla, Oregon, 1971-72.
<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Stable % Soluble Particulate</th>
<th>Stable % Particulate</th>
<th>Activity, pCi/L</th>
<th>Specific Activity nCi/gZn</th>
</tr>
</thead>
<tbody>
<tr>
<td>170271</td>
<td>--</td>
<td>--</td>
<td>0.73 ± .11</td>
<td>55 ± 11</td>
</tr>
<tr>
<td>120371</td>
<td>(total = 28)</td>
<td>--</td>
<td>0.78 ± .08</td>
<td>--</td>
</tr>
<tr>
<td>170471</td>
<td>18</td>
<td>14</td>
<td>0.46 ± .079</td>
<td>26 ± 4.4</td>
</tr>
<tr>
<td>300471</td>
<td>4.6</td>
<td>11</td>
<td>0.14 ± .046</td>
<td>30 ± 10</td>
</tr>
<tr>
<td>160571</td>
<td>4.6</td>
<td>17</td>
<td>0.11 ± .13</td>
<td>24 ± 28</td>
</tr>
<tr>
<td>010671</td>
<td>15</td>
<td>7.4</td>
<td>0.053 ± .077</td>
<td>146 ± 20</td>
</tr>
<tr>
<td>150671</td>
<td>6.3</td>
<td>10</td>
<td>0.049 ± .053</td>
<td>154 ± 22</td>
</tr>
<tr>
<td>010771</td>
<td>5.7</td>
<td>10</td>
<td>0.022 ± .050</td>
<td>104 ± 11</td>
</tr>
<tr>
<td>190771</td>
<td>4.8</td>
<td>8.9</td>
<td>0.018 ± .026</td>
<td>80 ± 10</td>
</tr>
<tr>
<td>020871</td>
<td>2.5</td>
<td>9.6</td>
<td>0.030 ± .046</td>
<td>80 ± 10</td>
</tr>
<tr>
<td>040971</td>
<td>1.4</td>
<td>4.5</td>
<td>0.016 ± .024</td>
<td>113 ± 4.2</td>
</tr>
<tr>
<td>270971</td>
<td>2.8</td>
<td>4.5</td>
<td>0.51 ± .035</td>
<td>----</td>
</tr>
<tr>
<td>191171</td>
<td>3.6</td>
<td>7.1</td>
<td>0.18 ± .016</td>
<td>113 ± 7.8</td>
</tr>
<tr>
<td>140172</td>
<td>7.2</td>
<td>4.7</td>
<td>0.11 ± .010</td>
<td>23 ± 2.2</td>
</tr>
<tr>
<td>280372</td>
<td>12</td>
<td>22</td>
<td>0.19 ± .019</td>
<td>--</td>
</tr>
<tr>
<td>180572</td>
<td>4</td>
<td>21</td>
<td>0.19 ± .019</td>
<td>9.0 ± 0.9</td>
</tr>
</tbody>
</table>
zinc in solution. Again there appears to be little if any isotopic exchange of the suspended sediment-bound Zn-65.

In general, suspended sediment concentrations and Zn-65 specific activities correlate with river discharge, and stable and radioactive zinc levels (Figure 15). Careful inspection of the data, however, reveals a lag in the specific activity, relative to discharge. There also appears to have been a significant soluble fraction of Zn-65 during the first two to three months following shutdown which rapidly diminished after that time. The percent soluble Zn-65 also seemed to increase during the fall and winter. This increase is manifested by an increase in soluble specific activity. These observations suggest dissolution of sediment-bound zinc and Zn-65. Dissolution could result from a decrease in pH or microbial decomposition of organically bound forms. While microbial decomposition release would occur during all seasons, it should be more noticeable during the fall and early winter in the upper Columbia due to the greatly diminished suspended sediment in transport at this time and to the large amounts of decaying macrophytes (Potamogeton).

Another possibility is that N reactor could have released low levels of Zn-65 during this period. Release records for this closed-loop reactor, do not suggest such a release occurred (appendix E). In addition, the same type of fall-winter increase in soluble Zn-65 was noted by Perkins et al. (1966) at a time when all of the single pass reactors were in operation. Thus, there seems to be some evidence for solubilization of sediment-bound Zn-65.
Soluble and Particulate Zn-65 in River and Estuarine Water

Filtered water data for the Prescott, Clatskanie and estuary sample sites are shown in Table 10. The weighted mean percent particulate Zn-65 activities of these samples and the McNary water data are given in Table 11. Zn-65 is predominantly particulate in the river water samples. Robertson, et al. (1973) reported 99 percent particulate Zn-65 activity in water samples from McNary and The Dalles over the same time period. In contrast, the estuarine samples show a significant increase in the soluble fraction occurs upon mixing of ocean water with river water. This observation is in agreement with earlier work in the estuary during the period when reactors were still in operation (Evans and Cutshall, 1973). However, the apparent solubilization of Zn-65 in the present study was completely unexpected. For example, the Evans and Cutshall (1973) data were acquired when a continuous supply of soluble Zn-65 was being added to the river. A significant portion of the suspended matter in the Columbia is biogenic, consisting primarily of freshwater diatoms. Indeed, during the bloom periods of spring and summer, the particulate count is dominated by diatoms (Haertel, 1970). The cation exchange properties of the polysaccharide coatings associated with these freshwater algae are well known. Furthermore, a large portion of the Evans and Cutshall data was acquired during the season when diatom levels could have been at a maximum. Thus, the steady-state data can be explained in terms of a significant exchangeable fraction associated with the biogenic component of the suspended load. The lack of
Table 10. Soluble and particulate Zn-65 in river and estuarine water.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling Date</th>
<th>Load, mg/L</th>
<th>( ^{65} \text{Zn}, \text{pCi/Liter} )</th>
<th>Soluble</th>
<th>Particulate</th>
<th>Percent Particulate</th>
</tr>
</thead>
<tbody>
<tr>
<td>River</td>
<td>(da/mo/yr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prescott</td>
<td>050671</td>
<td>53</td>
<td>0.030 ± 0.048</td>
<td>0.74 ± 0.068</td>
<td>96 ± 14</td>
<td></td>
</tr>
<tr>
<td>Clatskanie</td>
<td>240671</td>
<td>56</td>
<td>0.056 ± 0.016</td>
<td>0.60 ± 0.051</td>
<td>91 ± 9</td>
<td></td>
</tr>
<tr>
<td>Clatskanie</td>
<td>220771</td>
<td>--</td>
<td>0.0 ± 0.028</td>
<td>0.62 ± 0.049</td>
<td>100 ± 12</td>
<td></td>
</tr>
<tr>
<td>Clatskanie</td>
<td>050871</td>
<td>16</td>
<td>0.026 ± 0.009</td>
<td>0.23 ± 0.026</td>
<td>88 ± 13</td>
<td></td>
</tr>
<tr>
<td>Prescott</td>
<td>190971</td>
<td>19</td>
<td>0.008 ± 0.016</td>
<td>0.23 ± 0.037</td>
<td>96 ± 18</td>
<td></td>
</tr>
<tr>
<td>Clatskanie</td>
<td>020971</td>
<td>13</td>
<td>0.0 ± 0.008</td>
<td>0.16 ± 0.018</td>
<td>100 ± 17</td>
<td></td>
</tr>
<tr>
<td>Prescott</td>
<td>160971</td>
<td>8.2</td>
<td>0.0 ± 0.007</td>
<td>0.14 ± 0.013</td>
<td>100 ± 14</td>
<td></td>
</tr>
<tr>
<td>Prescott</td>
<td>071071</td>
<td>9.1</td>
<td>-</td>
<td>0.12 ± 0.009</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Prescott</td>
<td>041171</td>
<td>8.0</td>
<td>0.006 ± 0.019</td>
<td>0.098 ± 0.020</td>
<td>94 ± 21</td>
<td></td>
</tr>
</tbody>
</table>

| Estuary   | Sta. (°/oo)   |            |                                      |         |             |                     |
|-----------|---------------|------------|--------------------------------------|         |             |                     |
| B14(3.28) | 070771        | 19         | 0.070 ± 0.016                        | 0.20 ± 0.023 | 74 ± 11     |                     |
| PA (1.92) | 210771        | --         | 0.068 ± 0.009                        | 0.25 ± 0.020 | 78 ± 8      |                     |
| B14(11.7) | 040871        | 13         | 0.057 ± 0.010                        | 0.043 ± 0.012 | 43 ± 14    |                     |
| AST(8.96) | 010971        | 10         | 0.10 ± 0.014                         | 0.099 ± 0.013 | 49 ± 8      |                     |
| PA (18.1) | 210971        | 5.8        | 0.052 ± 0.007                        | 0.062 ± 0.010 | 54 ± 10     |                     |
| AST(8.43) | 071071        | 56         | 0.16 ± 0.019                         | 0.48 ± 0.034 | 75 ± 7      |                     |
| B19(12.7) | 051171        | 10         | 0.025 ± 0.008                        | 0.081 ± 0.007 | 76 ± 10     |                     |
| PA (4.06) | 031271        | 13         | 0.00025 ± 0.008                      | 0.034 ± 0.011 | 100 ± 50    |                     |
| CP (20.0) | 260672        | 15         | 0.025 ± 0.008                        | 0.022 ± 0.008 | 47 ± 20     |                     |

1 The Clatskanie station was located approximately 20 miles downstream from Prescott at the Beaver Army Terminal docks on the Oregon side of the river at approximately river mile 53.

2 Station codes in the estuary refer to various landmarks; i.e., Pa = Point Adams, AST = Astoria, CP = Chinook Point and B refers to buoy locations. The numbers in parentheses following station codes are the salinities of the water samples.

3 Yield-corrected (based on recovery of stable zinc carrier added to the filtered water at time of collection).

\( \pm \) Standard deviations due to spectral resolution and counting uncertainties.

<table>
<thead>
<tr>
<th>Location</th>
<th>N</th>
<th>( \bar{x}_w \pm \sigma_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>River (Prescott and Clatskanie)</td>
<td>8</td>
<td>94.8 ( \pm ) 4.7</td>
</tr>
<tr>
<td>Estuary</td>
<td>10</td>
<td>72.3 ( \pm ) 3.5</td>
</tr>
</tbody>
</table>

\( \bar{x}_w \) weighted mean defined as: 

\[
\bar{x}_w = \frac{\sum (x/\sigma^2)}{\sum (1/\sigma^2)}
\]

where \( x \) designates each individual value in the average and \( \sigma \) is its standard error. This procedure gives greater weight to those values having the lowest standard errors.
a significant exchangeable Zn-65 component in bottom sediment as previously discussed, can be explained by a difference in sorptive properties of suspended material and bottom sediments. That is, the bottom sediment consists primarily of crystalline and amorphous inorganic phases while the suspended sediment is enriched in biogenic matter. This difference in sorptive status of Zn-65 on suspended and bottom sediment ought to disappear during the post-shutdown period since the only Zn-65 available for transport would be the non-exchangeable form on resuspended bottom sediment. The filtered water data for McNary and Prescott-Clatskanie samples suggest no solubilization occurred during transport. Therefore, since virtually no soluble Zn-65 was available to occupy cation-exchange sites on the particulate material in transport, the rationalization used for steady-state data (Evans and Cutshall, 1973) cannot be used to explain the desorption in the estuary after shutdown.

An alternative explanation for post-shutdown solubilization of particle-bound Zn-65 might be that freshwater diatoms are capable of dissolving metals directly from sediment particles. Subsequently, upon mixing with seawater, the cells could release metals to solution. There appears to be no information with which to confirm or deny such a mechanism.

Another possible mechanism involves release of hydrous oxide coatings and associated metals under reducing conditions. If this occurred in the presence of the abundant divalent cations in seawater,
there would be less tendency for sorption back onto particles and, as a result, the apparent soluble fraction of estuarine water would increase. Coupling the reduction-release scheme with the estuarine recycling model for manganese proposed by Evans et al. (1977) would allow buildup of elevated metal levels without violating mass balance considerations. In this scheme, metals associated with manganese oxide particles or coatings would settle from the outward moving surface layer of river water and would be transported upstream as bed load in the salt wedge. After deposition, reduction would occur to release divalent manganese and associated metals. Upon mixing into the outward flowing river water the divalent manganese would eventually be reoxidized and again settle with adsorbed metals to complete the cycle.

Sedimentary Processes

Processes acting on the sediment particles themselves include: 1) erosion, 2) particle exchange, 3) deposition and 4) benthic mixing. Particle exchange is an active interchange between suspended sediment in transport and the bed sediment over which the stream or river is flowing. The concept has been developed theoretically in sediment transport models (Sayre, 1969; Graf, 1971). It is significant here as a mechanism by which bed sediment-associated contaminants can be dispersed or mobilized.
Erosion and Particle Exchange  A comparison of Zn-65 levels in the Prescott composite water samples and mean monthly discharge is shown in Figure 17. The correlation between the peaks in activity levels and the peaks in discharge for the years 1971 and 1972 shown the effects of streambed erosion in response to increased water velocity. It is evident that resuspension of bottom sediment must be a dominant process involved in the transport and dispersion of the radionuclides in the bed sediment. While it is not possible to determine the particle exchange or diffusion contribution to the transported load, some simple considerations may provide some qualitative insight. For example, if only erosion is responsible for dispersion of sediment-associated radionuclides, then one would expect that following the characteristic spring freshet the transported activity should cease. As both Figures 15 and 17 show, significant Zn-65 levels persisted during the low flow period. Decay-corrected monthly estimates of Zn-65 transported past Prescott are shown in Figure 18. The exceptionally high transport for the month of May, 1971 resulted from a combination of flow manipulation in the reservoirs and a rapid, early spring snow melt in the Rocky Mountains. Near the end of April water was held behind the dams to improve survival of downstream migrating salmon smolts. Consequently, the water level rose rapidly in all the reservoirs. When the spill gates were subsequently opened, the river flow rate nearly doubled overnight. The rapid increase in stream velocity probably resuspended more sediment-associated activity than would have occurred if a more gradual increase in flow had been allowed.
Figure 16. Comparison of dilution-corrected total Zn-65 content of estuary water samples with total Zn-65 content of river water collected upstream from the estuary. The apparent "spike" in the estuary sample collected on day 250 was due to abnormally high suspended sediment content presumably resuspended from the bottom.
Figure 17. Zinc-65 concentration in Prescott composite water samples and mean monthly Columbia River discharge at the mouth versus time post-shutdown.
Figure 18. Monthly estimates of Zn-65 in transport past Prescott, Oregon during 1971 and 1972 (decay corrected to time of shutdown, January 28, 1971).
Considerably smaller but measurable transport is shown for the low flow period of August through February. While the relative amounts transported during this period are minor, it is significant that any activity at all was in transport. This is taken as evidence that particle exchange was responsible for mobilization of the sediment-bound activity during this period. Particle exchange is a diffusion-like process where labeled bed sediment particles are exchanged for non-labeled suspended sediment. This type of dispersion occurs even during periods of net deposition. During erosion it is supplemented by net transfer from the bottom to suspension.

Scour or resuspension of bed sediment is implied by a linear relationship between ln(discharge) and ln(suspended sediment concentration), Graf (1971). This appears to be the case (Figure 19).

**Deposition**  It should be possible to make some inferences concerning depositional conditions during the post-shutdown period by examining depth profiles of radionuclides in sediment cores. Primary focus for this analysis will be on two large-diameter cores collected in June 1974 and January 1975, (other cores collected with a Phleger coring device were found to be distorted by the coring device and are thus unreliable for this analysis).

Theoretically, sedimentation rates and thus a time scale can be obtained by making use of the ratio of two different radionuclides of known half-lives. A regression of the ratio on depth yields a slope from which sedimentation rate can be extracted. The mathematical relationship relating these variables is as follows:
Figure 19. Suspended sediment concentration in Columbia River water versus discharge, Umatilla, Oregon, 1971-72. The straight line represents the least squares fit of ln(conc.) on ln(discharge); $r=0.98$, open triangle not included in fit.
\[ \ln(R_X) = \left( -\frac{\Gamma}{s} \right) X + \ln R_0 \]

where: 
- \( R_X \) is the ratio at depth \( X \)
- \( R_0 \) is the ratio at the surface of the core
- \( \Gamma \) is the combined physical decay constants
  \( (\Gamma_1 - \Gamma_2, \text{for } R = \frac{A_2}{A_1}) \)
- \( s \) is the sedimentation rate, cm/yr
- \( X \) is the depth in the core in cm

(Derivation of the above equation is given in Appendix C).

Ideally, one would choose an isotopic pair of nuclides in order to minimize chemical fractionation after deposition. The choice of radionuclides in the cores, however, is limited to Eu-152, Eu-154 and Co-60. Plots based on ratios of these radionuclides are shown in Figures 20 and 21 for the McNary core. The Co-60/Eu-152 plot shows an interesting inflection at mid-depth while the Eu-154/Eu-152 does not. Either the latter is less sensitive to changes in depositional conditions owing to the longer half-life of Eu-154 than Co-60, or the inflection is a result of changes in production conditions; i.e., in relative proportions of the stable target nuclides, in reactor neutron spectra, etc. Changes in neutron spectra seem unlikely since the Eu-154/152 ratio is so uniformly linear with depth over the entire core (Figure 21). On the other hand, alterations in cooling water treatment or in fuel cladding could easily change the relative amounts of different elements activated without changing the ratio of isotopic pairs.
Figure 20. Co-60/Eu-152 ratio versus depth in McNary core, station 5, 16 January 1975.
Figure 21. Eu-154/Eu-152 ratio versus depth in McNary core, station 5, 16 January 1975.
When all of the Co-60/Eu-152 data points are used in a regression of $\ln(R)$ on depth for the McNary core, a sedimentation rate of 2.1 cm/yr is obtained. Using the Eu-154/152 ratio data for the same core, a sedimentation rate of 3.8 cm/yr is obtained. If the Co-60/Eu-152 ratio plot is broken into three recognizable linear segments, sedimentation rates of 1.3, 4.4 and 1.5 cm/yr for the top, mid and bottom sections are obtained. From the depth profiles shown in Figure 22, it appears that a sharp decrease in activity occurs at approximately the 60 cm level. If this represents the completion of McNary Dam in 1953 and, therefore, the time when fine sediment began to accumulate, we can check the reasonableness of the above sedimentation rates. For example, the time since dam completion to the core sampling date is approximately 22 years. Using the average sedimentation rate from the Co-60/Eu-152 data, a time interval of 28 years is obtained (60 cm/2.1 cm/yr). Using the Eu-154/Eu-152 data, a time interval of only 16 years is obtained.

Other authors have estimated sedimentation rates in the lower portion of McNary Reservoir using different nuclide pairs. For example, Robertson et al. (1973) reported a value of 10 cm/yr near the same location as the station 5 core used in the present work. They also determined sedimentation rates from several other core locations further up in the reservoir. The average of these was 13 cm/yr, considerably greater than estimated for the core used in the present study. If sedimentation rates are of the magnitude reported by Robertson et al. (1973), then there is a serious error in assumptions, calculational technique, etc. in the approach used
Figure 22. Radionuclide-depth profiles in a McNary core, station 5, 16 January 1975 (shaded zone in upper right indicates surface concentration of Co-60 measured in 1971 decayed to collection date above).
in the present work.

To check the reasonableness of the above sedimentation rates, mass balance can be estimated. The pool behind McNary Dam has an area of $1.57 \times 10^{12} \text{ cm}^2$ but the fine sediment accumulates only in the lower third of the reservoir, so I estimate a depositional area of $5.2 \times 10^{11} \text{ cm}^2$. Then assuming one gram of dry sediment per cc of wet sediment, and taking the average sedimentation rate of $13 \text{ cm/yr}$ from above, I estimate $6.7 \times 10^{12} \text{ grams/yr}$ of sediment would be required to maintain the above sedimentation rate. Whetten et al. (1969) indicate an average sediment discharge in the vicinity of McNary Dam of $4 \times 10^{12} \text{ grams/yr}$. Thus, average sedimentation rates of the order $10 \text{ cm/yr}$ would require more sediment than the river could supply. Clearly, the actual sedimentation rates must be only a few cm/yr.

**Benthic Mixing** In addition to mixing of bottom sediment by wind-waves, currents, etc., it is possible that benthic fauna can exert a significant mixing action in the benthic boundary layer. The significance here is that this type of action represents a mechanism by which deeper, labeled strata are transported to the surface thereby maintaining contaminants in the surface active layer for a longer period of time. By comparing expected sedimentation rates with observed values, it should be possible to make some qualitative inferences concerning this type of mixing. The Youngs Bay site is ideal for this type of test.

A core was taken from a location in Youngs Bay where fine sediment has been accumulating since completion of a causeway in 1964. The solid fill of the causeway acts as a breakwater that
protects the zone from the strong wind-wave mixing. Thus, an average accumulation rate based on the historical record can be compared with a radionuclide ratio-determined sedimentation rate. If either physical mixing or bioturbation has had a significant effect on transport of sediment-associated radionuclides from deeper strata up into surface sediment, the slope of a regression of ln(R) on depth will yield a sedimentation rate that is greater than that estimated from net accumulation.

Activity levels were too low for reliable analysis of Eu-154 at this site so that only the Co-60/Eu-152 ratio can be used. The completion date of the causeway is represented by a marked textural inflection at a depth of 40 cm. The average accumulation rate for this interval is 4 cm/yr. The ratio-estimated sedimentation rate for the same interval is 3.9 cm/yr. Closer inspection of the ratio-depth plot suggests an inflection at the 35 cm level above which a more linear fit would be obtained. If this were used for the the ratio-estimated sedimentation rate, an even smaller sedimentation rate would be obtained than when all the ratio data over the 40 cm interval is used. Since the analysis of the McNary core data suggested the Co-60/Eu-152 method yielded rates that were approximately 20 percent too low, the corrected values for the above consideration would be very close to the historical value of 4 cm/yr. This suggests that either bioturbation is not important at this site or that the sedimentation rate is rapid with respect to the mixing depth. In the latter case mixing could occur at even a very rapid rate but would
not be detected by the method used. While it is not possible to
distinguish between these two possibilities, the latter seems more
likely in view of the biological data for this site. For example,
a survey of benthic fauna in Youngs Bay (Higley and Holton, 1975)
showed animal densities of >60,000/m² occur adjacent to the coring
station used in the present study. Oligochaetes, amphipods, and
nematodes accounted for more than 98 percent of the individuals
present at the time of collection. A study of the vertical distri-
bution of these animals showed they were nearly all confined to the
top 1-2 cm layer, although a few individuals were found at greater
depths. Their predominance in the surface sediment may in part be
due to the presence of reduced sediment that commonly occurs 1-2 cm
below the sediment-water interface at this location. Since the
benthic infauna at this site are all known to be highly active in
mixing sediment, it seems more likely that the method used to test
for benthic mixing in this case is insensitive to a shallow mixing
depth coupled with a high sedimentation rate.

Evaluation of mixing or bioturbation at the McNary core site
is more difficult because there is no unique historical event marker
with which to compare ratio-estimated sedimentation rates. Some
qualitative inferences may be possible, however, by inspecting the
radionuclide-depth profiles. For example, if biological mixing is
responsible for the activity present in the surface layers of sediment,
the activity would have to be supplied from the deeper strata. This
would require that the deeper strata radionuclide concentrations
decrease in time to supply the upward mixed radioactivity. To test this, we can compare the surface sediment radionuclide concentrations that existed at station 5 in 1971 with the maximum in the depth profile for the core taken at station 5 in 1975. After allowing for radioactive decay, the concentration in the region of the maximum should be significantly lower than the surface activity at this site in 1971 if upward mixing of the sediment has occurred during the interim period of approximately four years. Figure 22 shows the depth profiles of Co-60, Eu-152 and Cs-137 of the 1975 core at station 5. Radionuclide concentrations in the surface sediment at station 5 from the core taken in 1971 were decayed for the appropriate time between 1971 and 1975 and are superimposed on the concentration axis of the 1975 depth profiles. This comparison suggests that little upward mixing occurred since the decay-corrected surface activity levels in 1971 are nearly identical to the subsurface maxima in the 1975 profiles. However, the same alternative mechanism used in the Youngs Bay core could be applied here as well. If the sedimentation rate is high relative to the mixing depth, the effect would be undetected in the radionuclide profiles. In any event, the above considerations suggest benthic mixing may not have been a significant factor in supplying the radionuclide levels observed in surface sediment during the post-shutdown period.

**Fallout Observations**

The intermittent presence in the samples of fallout radionuclides complicated data reduction and fallout was considered a
contaminant. Fallout data, however, provides some interesting observations. $^{95}$Zr-Nb concentrations, like those of other radio-
nuclides, vary with mean monthly river discharge (Figure 23). 
Presumably this activity came from Chinese nuclear test debris 
transported across the Pacific by the prevailing westerly winds. 
Two tests were conducted 100 and 150 days before maximum river 
discharge in 1972. Transport time across the Pacific is only of the 
order of a week yet the maximum in $^{95}$Zr-Nb activity did not occur 
until some 100-150 days later. This suggests the fallout nuclides 
had been "washed" out of the atmosphere and stored with the snow 
pack. In the spring the snow melt released the residual fallout 
to the drainage system. This may have significance with respect 
to water quality in the Pacific Northwest. Maximum contaminant 
concentration coincides with the beginning of the growing season 
when irrigation water is withdrawn from the upper Columbia. Tests 
conducted in late summer would have less impact on water quality.
Figure 23. Fallout $^{95}$Zr-Nb in Prescott composite water samples, 1971-72. Upper figure is mean monthly discharge of the Columbia River at the mouth.
SUMMARY AND CONCLUSIONS

Specific Activity Relationships

Two dominant conclusions emerge from evaluation of the Zn-65 specific activities in this study: 1) sediment particles and particle concentrating processes are important in transferring this radionuclide to biota and 2) the effect of sediment dilution on Zn-65 specific activity was minimized because sediment zinc concentrations near the reactor area are ten times higher than in sediment from downstream tributaries. It is concluded that the interplay of these two processes resulted in specific activities in biota that were higher than expected from river water dilution alone.

Circumstantial evidence suggests the elevated sediment zinc levels in the Columbia result from mining activities in the upper drainage basin (Campbell, 1961; Maxfield et al., 1974). The influence of this heavy metal contaminant in maintaining higher-than-expected Zn-65 specific activities is a classic example of the interaction of two environmental contaminants.

Rates and Dynamics of Zn-65 Decline

Half-times of decline (corrected for physical decay) in estuarine biota were closely grouped at 350-400 days. The rate of decline in water upstream at Prescott, Oregon was conspicuously close to this same value. Evaluation of a simple source-receptor
kinetic model showed this observation could be rationalized because the loss rate of the source is long relative to the loss rate in the receptor. Under these conditions, the loss rates for different species with widely ranging biological half-lives all exhibit similar rates of decline. It was concluded that the response time of the biotic ecosystem component is controlled by the rate of decline of the source where the source rate is sufficiently long. The rate of decline in the river water, assumed to be the source in the present study, is a unique property of the water course and will vary depending on the hydrologic regime(s). It is further concluded that where the rate of decline or washout of a previously contaminated system is slow with respect to the biological turnover of receptor organisms, it may not be necessary to know all the individual biological half-lives to predict time-dependent levels in biota following termination of chronic contaminant input. In these cases, greatest emphasis should be placed on sediment water transfer and transport.

The analysis presented here also suggests simple input-output kinetic models are adequate for describing radionuclide kinetics in a very complex riverine-estuarine ecosystem. This means that such models can be used to plan sample collection and for environmental safety analyses.

**Residence Times**

The residence times (Table 12) illustrate the relative response times of the different phases sampled. The estimated residence time
Table 12. Residence times of Zn-65 in water, sediment and biota in the Columbia River, 1971-72.

<table>
<thead>
<tr>
<th>Component</th>
<th>Conditions</th>
<th>Residence time, Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>estuarine biota</td>
<td>based on weighted mean of all estuarine species sampled</td>
<td>540 ± 60</td>
</tr>
<tr>
<td>river water</td>
<td>Prescott composite sample</td>
<td>640 ± 80</td>
</tr>
<tr>
<td></td>
<td>Umatilla grab samples</td>
<td>520 ± 140</td>
</tr>
<tr>
<td>sediment</td>
<td>top 1-½ cm core samples at McNary Dam</td>
<td>930 ± 140</td>
</tr>
<tr>
<td></td>
<td>pooled grab data, McNary Dam</td>
<td>1010 ± 270</td>
</tr>
<tr>
<td></td>
<td>estuarine sediment, Alder Slough site</td>
<td>920 ± 260</td>
</tr>
<tr>
<td>hypothetical solute</td>
<td>based on estimate of instantaneous</td>
<td>10 - 20</td>
</tr>
<tr>
<td></td>
<td>river-reservoir volume for the Prescott to reactor area reach and mean flow</td>
<td></td>
</tr>
</tbody>
</table>

of the solute phase as estimated from the reservoir-river volume and mean discharge, shows the soluble form would flush rapidly from the system. This is due to the high discharge rate and low river-reservoir volume. The residence time computed for the Zn-65 in transport in river water represents the residence time of suspended sediment or particle-bound form. In this case, the Zn-65 is essentially a suspended sediment/particle tracer in the river system and thus, may represent the residence time of suspended sediment in the reach under study. The similar rates for the Umatilla and Prescott sites suggest the reach above McNary Dam controls the rate for the rest of the river. This view is compatible with the known locations of fine sediment accumulation below the reactor area.
The noticeably longer residence times in surficial sediment, which are remarkably similar for both the fluvial and estuarine sites, suggests these are primarily depositional sites. If so, the primary supply of resuspended sediment-bound Zn-65 must be further upstream in the reservoir.

The close correspondence between residence times in the estuarine biota and water at Prescott has already been noted. Since specific activities were measured, the residence times for the Zn-65 may have significance in the biogeochemistry of stable zinc, a well acknowledged, important micronutrient for nearly all life forms. In this sense, the radioisotope-measured residence time may represent the ecological residence time of this metal in the system studied.

Inasmuch as the Zn-65 is representative of particle-bound contaminants in general, the above residence times suggest several years would be required to reduce contaminant levels, in at least water and sediment, by an order of magnitude or more following a chronic input (Figure 24).

**Sediment-Water Transfer Mechanisms**

Sediment-water transfer involves a combination of ion-particle interactions and resuspension as well as transport of the particles themselves. Ion-particle interactions evaluated included isotope exchange and solubilization. While Zn-65 was predominantly particulate in water samples, there was some evidence of slight solubilization in the water from McNary Dam during the fall-winter period. Clear evidence of resolubilization was apparent for this radionuclide in the estuary. Two explanations were attempted for this unexpected
Figure 24. Recovery times for hypothetical soluble (S) and particulate (P) contaminant phases in the lower Columbia River and estuary. 1) Particulate phase estimates based on rates of decline of decay-corrected Zn-65 in surficial and suspended sediment; upper dashed line based on the mean rate of decline of Zn-65 in Umatilla and Prescott water samples while the lower dashed line is based on the mean rate of decline in McNary and estuarine surficial sediment. Solid line is based on overall mean rate of decline. 2) Soluble phase estimates of recovery times are based on the residence time of water in the Hanford-to-the-mouth reach of the river; solid line is for mean flow conditions (250,000 cfs) and dashed line is for low flow (125,000 cfs).
occurrence: 1) direct uptake from sediment particles by freshwater phytoplankton followed by release in the estuary, and 2) a redox-solubilization scheme tied to estuarine recycling of manganese.

Isotope exchange loss from bed sediment was examined in surface sediment from McNary reservoir. Co-60, Mn-54, Cs-137 and Eu-152 as well as Zn-65 were included in this evaluation. It was concluded that radionuclides bound by electrostatic bonds more readily undergo isotope exchange and were lost more rapidly from sediment whereas radionuclides that form strong coordinate covalent bonds with the substrate undergo isotope exchange reversal only very slowly or not at all. Consequently, Mn-54 declined at a rate two to three times more rapidly than Co-60 and Zn-65. Further support for this conclusion was provided by the specific activity measurements of Zn-65 in the soluble and particulate phases of river water below McNary Dam. It was found that particle-bound specific activity was at least 10 times greater than the soluble fraction (0.45 μm filtered). Thus, once Zn-65 is taken up by the sediment it does not appear to re-equilibrate with stable zinc in the water. The isotope exchange loss evaluation represents a large-scale field verification of a portion of the sediment-water transfer function in the radionuclide transport model for streams proposed by Yousef and Gloyna (1970).

The correlation between discharge and activity levels in Columbia River water clearly indicate the role of stream velocity in mobilization of much if not most of the bed sediment radionuclide inventory. The "spike" in the radionuclide discharge record that occurred for the month of May 1971 was related to hydraulic shock
in the river system which resulted from retention and release of water in the reservoirs. The sudden increase in stream velocity probably provided additional energy for resuspension that resulted in transport of more of the streambed inventory than would have occurred if a more gradual buildup in flow had been allowed. Because of this perturbation in the "normal" hydraulic regime, the residence times and rates of decline may be somewhat shorter than they would have been otherwise. The hydraulic shock effect on resuspension of particle-bound contaminants represents a potential impact of reservoir flow manipulation on downstream water quality.

Radionuclide ratios and a simple mass balance of sediment for McNary reservoir were used to evaluate sedimentation rates. It was concluded that sediment accumulation rates in McNary reservoir are only a few cm/year.

An attempt was made to evaluate effects of benthic mixing in sediment at an estuarine and reservoir site. It is concluded that sedimentation rates were too rapid relative to the mixing depth for processes such as bioturbation to have had a significant impact on transferring deeper contaminated layers into surface sediment.
Water Resource Management Considerations

The Columbia River ranks high among the most important natural resources in the Pacific Northwest. It provides irrigation water for seven million acres of crop land, serves as an inland waterway for major shipping, provides for millions of kilowatts of generating capacity, sustains a valuable fishery, and provides drinking and industrial process water. Because of the wide range of multiple-use activities, careful consideration must be given to potential contamination from new or existing industrial activities along the river. This is especially significant in view of the relatively long "natural" recovery time required as found in the present study.

Priority planning and management strategies for future use(s) should consider the impact of new or intensified uses on the abatement or enhancement of potential pollutants in the river system. For example, increased diversions of water and expanding agricultural withdrawals, could increase the time to flush the system. Flow regulation that smooths out the characteristic high flows during the spring freshet have the same effect. If hypothetical contaminants were stored in the bed sediment of the river, a hydraulic perturbation such as might occur from manipulation of flows for out-migrating smolts, could mobilize excessive amounts of sediment-bound contaminants at a time when downstream biota are in a maximum growth phase and more susceptible to damage.

As conflicting and increasing demands are made on the Columbia River, the potential for serious damage from contamination may also
increase. Hopefully, this work will provide perspectives for long-range planning and management where potential contamination is involved.


The large diameter corer used in this study is shown in Figure A-1. The essential design and operational features involved: 1) a 15 cm diameter core barrel (standard 6 inch aluminum irrigation pipe), 2) no core catcher or bottom closure at the cutting edge of the barrel, and 3) the use of sufficient weight (100-150 kg) to allow slow substrate penetration in order to minimize disturbance of the surface sediment.

Cores were sectioned immediately after recovery. The collar and attached core barrel were removed from the corer frame and the cutting end of the barrel positioned over a vertical extruder. (The core was maintained in the vertical position at all times). The valve was removed and the sediment extruded through the top of the core barrel into a 3 cm ring positioned at the top of the collar. A thin sheet of stainless steel was inserted between the bottom of the 3 cm ring and the top of the collar to remove the sections from the sediment column. The outer 1 cm rind was trimmed and the samples placed in plastic bags and frozen for storage.
Figure A-1. Large diameter coring device (Not shown are the lead rings which are placed over the vertical stand of pipe on the yoke).
Feeding habits of most of the estuarine species used in the present study are summarized in Table B-1. Assignments for the benthic fishes were based on stomach content analyses of specimens collected at the same stations used in the present study and reported as an annual average percentage in Haertel and Osterberg (1967).

It should be noted that Table B-1 is a summary of average conditions and that marked seasonal variations occur in the diets of some of the benthic fishes. For example, very young flounder (0-1 year class) shift from a diet of copepods to benthic amphipods (mostly Corophium salmonis) after reaching a length of 5-6 cm. In addition to this growth-related shift in food preference, starry flounder, at least in the estuary, appear to cease feeding during winter months as evidenced by the high incidence of empty stomachs during this period. (Starry flounder are "sight" feeders and are presumably less able to locate prey during the turbid winter months). In contrast to starry flounder, tom cod appear to feed through all seasons on a variety of prey dominated by fish, small molluscs and polychaetes during the winter, and amphipods, copepods and shrimp in the summer. The staghorn sculpin appear to prey more consistently on fish the year round and on shrimp when available (Haertel and Osterberg, 1967).
TABLE B-1

List of common species in the Columbia River estuary and their feeding habits, (after Haertel and Osterberg, 1967).

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Scientific Name</th>
<th>Food Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shiner perch</td>
<td>Cymatogaster aggregata</td>
<td>P, B</td>
</tr>
<tr>
<td>Pacific staghorn sculpin</td>
<td>Leptocottus armatus</td>
<td>F, B</td>
</tr>
<tr>
<td>Prickly sculpin</td>
<td>Cottus asper</td>
<td>B, F</td>
</tr>
<tr>
<td>Starry flounder</td>
<td>Platichthys stellatus</td>
<td>B, P</td>
</tr>
<tr>
<td>Pacific tomcod</td>
<td>Microgadus proximus</td>
<td>P, B, F</td>
</tr>
<tr>
<td>Sand sole</td>
<td>Psettichthys melanostictus</td>
<td>B, P</td>
</tr>
<tr>
<td>Lemon sole (or English sole)</td>
<td>Parophrysvetulus</td>
<td>B, P</td>
</tr>
<tr>
<td>Sand shrimp</td>
<td>Crangon franciscorum</td>
<td>P</td>
</tr>
<tr>
<td>Freshwater clam</td>
<td>Anodonta oregonensis</td>
<td>FF</td>
</tr>
<tr>
<td>Marine mussel</td>
<td>Mytilus californianus</td>
<td>FF</td>
</tr>
<tr>
<td>Marine mussel</td>
<td>Mytilus edulis</td>
<td>FF</td>
</tr>
</tbody>
</table>

*symbols:  B = benthos  
P = plankton  
F = fish  
FF = filter feeder

where more than one food type is indicated, the more dominant form is underlined.

APPENDIX C

Equation Relating Radionuclide Ratio, Sediment Depth, and Sedimentation Rate.

Beginning with the standard equation for radioactive decay,
\[ A = A_0 e^{-\lambda t} \]
, a relationship between sediment depth, sedimentation rate and the activity ratio of two different radionuclides can be derived. In the above equation, radionuclide activity in surface sediment is taken as \( A \) and at some depth, \( X \), as \( A \). Letting "1" and "2" designate two different radionuclides, an expression relating the ratio of the two nuclides is obtained by dividing the standard equation for one by the standard equation of the other:

\[ \frac{2A}{1A} = \frac{2A_0}{1A_0} \cdot e^{(\lambda_1 - \lambda_2)t} \]  

(i)

Then, letting \( R \) equal the activity ratio, equation (i) becomes:

\[ \ln(R) = \sqrt[\lambda]{t} + \ln(R_0) \]  

(ii)

where \( \lambda \) is the combined radiological decay constants, \( (\lambda_1 - \lambda_2) \). Then by equating sediment depth with time, \( t = X/s \), (where \( X \) is depth and \( s \) is sedimentation rate), and assuming a constant sedimentation rate over the interval of interest, equation (ii) can be modified to express the radionuclide ratio as a function of depth and sedimentation rate. Substituting \( X/s \) for \( t \) in equation (ii):

\[ \ln(R) = \sqrt[\lambda]{\frac{X}{s}} + \ln(R_0) \]  

(iii)
A regression of $\ln(R)$ on depth yields a slope of $\Delta \theta / s$ from which sedimentation rate is calculated:

$$s = \frac{\Delta \theta}{(\text{slope})}$$

This method allows the use of all the depth-ratio data over a given interval to estimate sedimentation rate and/or the average time represented by the depth interval chosen.

The radiological decay constants used in applying equation (iii) in the present study were as follows:

<table>
<thead>
<tr>
<th>nuclide</th>
<th>$\lambda$, yr$^{-1}$</th>
<th>$T_\lambda$, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{152}\text{Eu}$</td>
<td>0.055887</td>
<td>12.4</td>
</tr>
<tr>
<td>$^{154}\text{Eu}$</td>
<td>0.088662</td>
<td>8.0</td>
</tr>
<tr>
<td>$^{60}\text{Co}$</td>
<td>0.13150</td>
<td>5.27</td>
</tr>
</tbody>
</table>

More recent information suggests the half-times for $^{152}\text{Eu}$ and $^{154}\text{Eu}$ should be 13.6 and 8.6 years, respectively (Cutshall, 1978)

Cutshall, N. C. 1978. Personal communication, Oak Ridge National Laboratory, Isotopes Division, Union Carbide Corporation.
APPENDIX D

Quality Control Check of Radionuclide Measurements in Columbia River Sediment

An inter-laboratory comparison of gamma-emitting radionuclides in a sediment sample from McNary Reservoir was made with Battelle Northwest Laboratories, Richland, Washington. Results of this comparison are shown in Table D-1. This comparison shows that reasonable agreement was obtained for all but the Zn-65. Analysis of six other sediments collected and analyzed by Battelle confirmed the discrepancy for Zn-65; the OSU results were an average of 1.7 times higher than the Battelle values.

In order to check the accuracy of the OSU system a mixture of radionuclides of known amounts was prepared that contained the approximate proportions of radionuclides present in the sediment sample analyzed for the interlaboratory comparison. In addition, the Zn-65 level was varied in three separate mixtures to check for spectral interferences with the Zn-65 photopeak. The Zn-65 added in the mixture of isotopes was a new calibrated source (Gamma Industries) and was not used in preparation of the standard spectra and conversion factors used in the data reduction program. This served as an additional outside check of the accuracy of the Zn-65 standard that had been in use.
Table D-1. Comparison of OSU and Battelle results for gamma-ray spectrometric analysis of a McNary sediment sample.
(Battelle sample ID M-3-1 collected 15 April 1971, top 2.5 cm section).

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Physical half-life</th>
<th>pCi/gram</th>
<th>OSU</th>
<th>Battelle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>5.27 years</td>
<td></td>
<td>29.9 ± 0.4</td>
<td>27.0</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>30 years</td>
<td></td>
<td>5.4 ± 0.2</td>
<td>4.1</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>310 days</td>
<td></td>
<td>9.6 ± 0.5</td>
<td>11.3</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>8.0 years</td>
<td></td>
<td>4.4 ± 0.3</td>
<td>5.9</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>12.4 years</td>
<td></td>
<td>15.6 ± 0.7</td>
<td>17.0</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>245 days</td>
<td></td>
<td>170 ± 3</td>
<td>108</td>
</tr>
</tbody>
</table>

a Physical half-lives used in the data reduction for present study.
b Analyzed with NaI(Tl) well detector and spectra reduced with the computer program ALPHA.
c Analyzed with high resolution Ge(Li) detector and analyzer system.
d Half-life used for data reduction of above sample was 16 years. Later information updated the half-life for this nuclide. Since the above sample was reduced using the old half-life, the decay correction may have resulted in a slight under estimate of the amount present on date of collection (sample was analyzed in March 1972).
The mixture of isotopes used for this test was as follows:

<table>
<thead>
<tr>
<th>nuclide</th>
<th>amount added, pCi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-60</td>
<td>254</td>
</tr>
<tr>
<td>Cs-137</td>
<td>41</td>
</tr>
<tr>
<td>Mn-54</td>
<td>139</td>
</tr>
<tr>
<td>Eu-154</td>
<td>72</td>
</tr>
<tr>
<td>K-40</td>
<td>193</td>
</tr>
<tr>
<td>Eu-152</td>
<td>176</td>
</tr>
<tr>
<td>Thorium (equilib.)</td>
<td>16</td>
</tr>
<tr>
<td>Uranium (equilib.)</td>
<td>13</td>
</tr>
<tr>
<td>Zn-65 I (the above plus):</td>
<td>1400</td>
</tr>
<tr>
<td>II (the above plus):</td>
<td>280</td>
</tr>
<tr>
<td>III (the above plus):</td>
<td>70</td>
</tr>
</tbody>
</table>

The Zn-65 reported from analysis of these mixtures using the same counting system and data reduction procedures and parameters as used in the inter-laboratory comparison are shown in Table D-2.

Table D-2. Comparison of amount added and amount found of Zn-65 in mixtures of radionuclides in the proportions and levels similar to McNary sediment.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Amount added, pCi</th>
<th>amount found, pCi</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1400</td>
<td>1435 ± 12</td>
</tr>
<tr>
<td>II</td>
<td>280</td>
<td>297 ± 5</td>
</tr>
<tr>
<td>III</td>
<td>70</td>
<td>94 ± 4</td>
</tr>
</tbody>
</table>
During the period when analyses were performed for the present study, Zn-65 levels were similar to mixtures I and II. For these two cases the counting system and data reduction process used appeared to be capable of reporting accurate amounts of Zn-65 present in a fairly complex mixture. For mixture III, however, it appears that as the amount of Zn-65 becomes small compared to the other long-lived components present, a slight over estimate occurs. Alternatively, it is also possible that a combination of pipetting errors associated with preparing the mixture could account for the difference. In any event, the above comparisons show that the system used during the present study was capable of producing reasonably accurate Zn-65 data.
Radioactive Waste Releases to the Columbia River from N Reactor

N reactor released small amounts of various radionuclides to the Columbia River during this study (Table E-1). This was apparent in the surface sediment at McNary Dam (Figure E-1) when Mn-54 and Co-60 levels began to increase approximately 600 days following shutdown. Zn-65, on the other hand, exhibited a continuous and regular decline through the same period which is concordant with the absence of Zn-65 in N reactor effluent (Table E-1). Because of the sharp upward inflection in the Mn-54 surface sediment curve only data obtained prior to the inflection were used in computing the half-times of decline and decay-corrected radionuclide ratios (text Tables 5 and 6). (Analysis of Zn-65 in water and biota involved only the 1971 and 1972 data). If additional input from N reactor occurred during the first 600 days post-shutdown, the rates of decline of these nuclides would be slower than expected. Mn-54 in surface sediment, however, clearly declined more rapidly than Zn-65 or Co-60. Thus, the general conclusion concerning the greater mobility of Mn-54 would not be altered by possible additional inputs from N reactor for the time period between shutdown and 600 days thereafter. (Mn-54 would have actually declined even more rapidly than observed if significant N reactor releases of this nuclide occurred during the first 600 days post-shutdown).
Figure 1. Surface sediment radionuclide concentrations versus time post shutdown, McNary Reservoir, August 1971 to August 1973, Station 9 (Hatched lines indicate suspected excess levels from N reactor waste release).
### TABLE E-1

100-N RADIOACTIVE MATERIAL RELEASES TO THE COLUMBIA RIVER--1972

Via 102 inch Discharge Line

<table>
<thead>
<tr>
<th>Gross Volume</th>
<th>Nuclide</th>
<th>Curies</th>
<th>Conc. (μCi/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.7 \times 10^{11}$</td>
<td>$^{140}$BaLa</td>
<td>10</td>
<td>$2.7 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{58}$Co</td>
<td>2</td>
<td>$5.4 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>20</td>
<td>$5.4 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{51}$Cr</td>
<td>20</td>
<td>$5.4 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{134}$Cs</td>
<td>0.5</td>
<td>$1.4 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$^{137}$Cs</td>
<td>5</td>
<td>$1.4 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{59}$Fe</td>
<td>10</td>
<td>$2.7 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{131}$I</td>
<td>40</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{54}$Mn</td>
<td>40</td>
<td>$1.1 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{56}$Mn</td>
<td>600</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$^{99}$Mo</td>
<td>20</td>
<td>$5.4 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{24}$Na</td>
<td>500</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$^{239}$Np</td>
<td>90</td>
<td>$2.4 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{124}$Sb</td>
<td>0.8</td>
<td>$2.2 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$^{95}$ZrNb</td>
<td>8</td>
<td>$2.2 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{103}$Ru</td>
<td>0.4</td>
<td>$1.1 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$^{106}$Ru</td>
<td>4</td>
<td>$1.1 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{133}$Xe</td>
<td>10</td>
<td>$2.7 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Via Seepage Springs on Riverbank

<table>
<thead>
<tr>
<th>Gross Volume</th>
<th>Nuclide</th>
<th>Curies</th>
<th>Conc. (μCi/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.8 \times 10^{9}$</td>
<td>$^{140}$BaLa</td>
<td>0.5</td>
<td>$1.8 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>0.01</td>
<td>$3.6 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$^{51}$Cr</td>
<td>5.3</td>
<td>$1.9 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$^{137}$Cs</td>
<td>0.05</td>
<td>$1.8 \times 10^{-8}$</td>
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<tr>
<td></td>
<td>$^{3}$H</td>
<td>7000</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$^{131}$I</td>
<td>1.9</td>
<td>$6.8 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{99}$Mo</td>
<td>1.1</td>
<td>$3.9 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{89}$Sr</td>
<td>0.05</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{90}$Sr</td>
<td>0.95</td>
<td>$3.4 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

[a] Significant reduction of the activity in this stream is expected following the post-1972 rerouting of radioactive liquid waste streams feeding into the 102 inch discharge line.

The predominantly particulate nature of Zn-65 in transport during the period of this study is further evidence that significant N reactor release of this nuclide did not occur; i.e., a noticeable increase in the soluble fraction in transport would have occurred. With the exception of the late Fall samples, this was not observed. Furthermore, the absence of Eu-152 and Eu-154 in N reactor effluent (Table E-1) suggests another check on possible N reactor Zn-65 in the system. For example, if new or additional Zn-65 were added during the period of study, the decay-corrected Eu-152/Zn-65 ratios would have decreased in time in the surface sediment at McNary Dam. Since the ratio remained constant over time (text Table 5), it is unlikely that significant additional Zn-65 was added from N reactor operations.
Estimates of Inter-tidal Marsh and On-stream Primary Production in the Columbia River and Estuary

In order to assess the possible significance of the inter-tidal marsh areas of the lower Columbia River as a source of detrital zinc and Zn-65 to the estuary, it is first necessary to estimate the potential contribution of marsh detritus to the overall energetics of the estuary.

Because the Columbia River estuary is so river dominated, the inter-tidal marsh areas are more often than not fresh-water. This is especially so for the areas upstream of Tongue Point near Astoria. The large freshwater inter-tidal area of the Columbia is a unique feature of this ecosystem. The significance to the present study is that Zn-65 accumulated by macrophytes in fresh and brackish water represent a relatively "undiluted" source of potential importance in the food web of the estuarine species examined in this study. A fresh-water-derived detrital pathway could have supplied relatively undiluted Zn-65 to animals in the lower marine dominated portion of the estuary as well as to animals in the upper, fresh-water dominated portion. This type of non-conservative transfer of Zn-65 could help to explain the uniform specific activities observed among all the estuarine species.
Plants Biomass Estimates

Little, if any, marsh production data exist for the Columbia. Thus, it is necessary to use information from nearby estuaries where such measurements have been made. Eilers (1976) measured intertidal marsh production in the Nehalem just south of the Columbia. He reports a mean fresh-water marsh production rate of 1.39 kg (dry) /m²/yr. The net aerial inter-tidal salt marsh production rate for the same estuary was 1.714 for low marsh (Carex lyngbyei) and 1.710 for the high marsh which consisted primarily of Juncus balticus and Aster subspicatus. These same species are also members of the intertidal plant communities in the Columbia estuary. Assuming the production rates in the Columbia are the same as in the Nehalem, it seems appropriate to use the average of the fresh and salt marsh production rates; i.e., 1.5 kg(dry)/m²/yr. Not all of the net aerial production would, however, be available for transport. Eilers (1976), for example, estimated that 72 percent of the net production is exported from the site of production (based on an average of the Nehalem plant communities). Applying this estimate of export to the above average production rate estimate, a corrected value of 1.1 kg/m²/yr is obtained. Combining the aerial production rate estimate with the estimated inter-tidal marsh area in the Columbia River estuary (11,457 acres up to river mile 50, Seamen, 1975), a total plant biomass potentially available to the estuarine ecosystem is computed at $4.4 \times 10^{10}$ grams (dry)/year. To put this estimate into perspective a comparable estimate of the on-stream
primary production from the river is needed. (While import of oceanic phytoplankton due to tidal exchange may also be important, the extensive occurrence of fresh-water diatoms in the estuary suggest river-derived phytoplankton would be the most important of the two sources, Haertel, 1970). Surprisingly, little primary productivity data exist for the lower Columbia River and estuary. Thus, it will be necessary to use a value derived indirectly from nutrient utilization considerations. For example, Park et al. (1970), estimate 0.08 mg of carbon/day/liter for the lower Columbia during the growth period between April and August. The mean flow of the river during this time period is $1.12 \times 10^{12}$ liters (from Park et al., 1972). The total carbon produced would be $9 \times 10^9$ grams. In order to compare this estimate with that from inter-tidal macrophytes, it is necessary to convert to a common unit of comparison. Using kilocalories as a common basis the following is obtained.

<table>
<thead>
<tr>
<th>Source</th>
<th>Annual Estimated Production</th>
<th>Caloric Conversion Factor</th>
<th>Equivalent Kcal/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>inter-tidal macrophytes</td>
<td>$4.4 \times 10^{10}$ grams (dry tissue)</td>
<td>5 Kcal/g dry</td>
<td>$2.2 \times 10^{11}$</td>
</tr>
<tr>
<td>fresh-water phytoplankton</td>
<td>$9.9 \times 10^{9}$ grams carbon</td>
<td>10 Kcal/g C</td>
<td>$9 \times 10^{10}$</td>
</tr>
</tbody>
</table>

The above estimates suggest that inter-tidal plant production cannot be rejected as a significant source of primary production for the estuary. The above estimates of plant production, however, are only a gross estimate of total production. The utilization by the food web serving the estuarine species examined in this study, however, is not known. One might reason that if these inter-tidal macrophytes play a significant role in the energetics of the food web, then the rate of decline of Zn-65 in estuarine biota should reflect the rate of decline in this source. Renfro (1967) showed that *Scirpus* and *Carex* in Alder Slough, just off the main shipping channel near Astoria acquired Zn-65 levels not significantly different than the sediment in which they grew. The rate of decline of Zn-65 observed in the sediments of Alder Slough during the post-shutdown period was significantly longer than the mean rate of decline observed in estuarine fish and shrimp. Assuming these macrophytes derive their zinc from the sediment and would decline at the same rate as the sediment, and assuming the other marsh areas respond similarly, the discrepancy in rates of decline suggests macrophytes may not be an important component in the food web of at least the species examined in this study. This view would be compatible with some recent studies suggesting that phytoplankton rather than plant detritus is the major source of carbon to estuarine consumers in Spartina-salt marsh ecosystems (Haines, 1976). (These conclusions were based on differences in $^{13}\text{C}/^{12}\text{C}$ ratios in algae, *Spartina* and consumers. Similar measurements would be needed to verify this in
the Columbia River estuary).

If inter-tidal macrophytes are not a major source of primary production for the Columbia estuary, they may be utilized instead on the continental shelf near the river mouth. If so, this estuary would be a net exporter of carbon.

The foregoing discussion is very speculative concerning the relative contribution of inter-tidal marshes of the Columbia to estuarine energetics. However, it does identify an important potential recycling pathway for sediment bound zinc regardless of whether the detritus resulting from the annual production of these plants is utilized within the estuary or in the adjacent coastal zone.


