AN ABSTRACT OF THE THESIS OF

Peter James Hanson   for the   M. S.
_____   _____
(Name of student)   (Degree)

in   Oceanography   presented on   May 11, 1967
                                                        (Date)

Title: Vertical Distribution of Radioactivity in the Columbia River

Estuary
_____

Abstract approved: _____
                              Charles L. Osterberg

_____
                              William O. Forster

In situ salinity, turbidity and temperature were measured at

discrete depths and water samples for radioanalysis were simultan-

eously collected in the Columbia River Estuary using a specially de-

signed instrument package.

Particulate radioactivity was concentrated by filtration and the

dissolved radioactivity by evaporation or ferric oxide bulk precipi-

tation. Radioanalysis was by gamma-ray spectrometry and data

reduction by computer. Chromium-51 was mostly dissolved and

conservative in brackish water, while zinc-65 was mostly particu-

late and non-conservative. The intrusion of salt water into the estu-

ary was seen to greatly increase the concentrations of particulate

chromium-51, zinc-65 and scandium-46 near the bottom.

The fall and rise in estuarine radioactivity levels were followed during an infrequent pause in Hanford reactor operations. Changes in radioactivity levels of up to three orders of magnitude were recorded at Astoria, Oregon, some 380 miles from the reactors. The pause in reactor operations enabled the determination of river flow times from the reactors to Astoria. Flow times of 12 and 19 days were measured for average river discharges of 290,000 and 130,000 c.f.s., respectively.

Vertical Distribution of Radioactivity
in the Columbia River Estuary

by

Peter James Hanson

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1967

APPROVED:

Redacted for Privacy

Professor of Oceanography

In Charge of Major

Redacted for Privacy

Assistant Professor of Oceanography

In Charge of Major

Redacted for Privacy

Chairman of Department of Oceanography

Redacted for Privacy

Dean of Graduate School

Date thesis is presented ___May 11, 1967___

Typed by Opal Grossnicklaus for ___Peter James Hanson___

Acknowledgments

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

LIST OF FIGURES

LIST OF TABLES

Vertical Distribution of Radioactivity
in the Columbia River Estuary

INTRODUCTION

General Statement

With the use of atomic energy for both weapons and power generation, artificial radioactivity is being introduced into the environment in increasing quantities. Since many radionuclides eventually end up in natural waters, it is necessary to understand their complex pathways through a water system in order to protect humans and other life forms from radiation exposure. Processes which concentrate and dilute radionuclides are not completely understood, and until these processes are quantified a radioactivity budget cannot be completed.

Several equations of varying forms and notation for the radioactivity budget in natural waters have been proposed (Waldichuck, 1961; Sayre, Guy and Chamberlain, 1963; Reynolds, 1963; Haushild et al., 1966) and all can be summarized by the following simplified version:

$$r_i + r_b - r_d - r_{pd} = r_s + r_{sp} + r_{bp} + r_o$$

For any given period

r_i = the radioactivity discharged into the system,

r_b = the background radioactivity,

r_d = the radioactivity discharged from the system,

r_{pd} = the radioactivity loss from physical decay,

r_s = the radioactivity in solution,

r_{sp} = the radioactivity sorbed by particulate matter in suspension,

r_{bp} = the radioactivity sorbed by particulate matter in place on the bottom, and

r_o = the radioactivity sorbed by biological systems.

The budget equation provides an overview of the ubiquitous nature of radioactive wastes.

Two problems pointed out by Reynolds (1963) are 1) the complexity and interdependency of many of the variables in the equation make its application difficult and 2) the present lack of necessary data and knowledge makes its complete evaluation impossible. As an example of the first point, radioactivity levels associated with the biota (r_o) are dependent on the radioactivity dissolved in the water (r_s), sorbed on sediments in transport (r_{sp}) and sorbed on sediments in place (r_{bp}). With regard to the second point, it is hoped that this work will contribute to the knowledge and methods necessary for evaluation of the radioactivity budget in streams and estuaries. Specifically, the levels of dissolved and suspended particulate radioactivity, r_s and r_{sp} respectively, are investigated in this study.

Statement of the Problem

This is a preliminary investigation of certain gamma emitting radionuclides in the Columbia River Estuary. As the river enters the estuary, changes in the environment occur which may cause changes in the behavior of radionuclides. The Columbia River Estuary is a zone of transition between fresh river water and solute-rich ocean water. The confluence of tides and river produce a complex distribution of energies resulting in an unstable physical and chemical environment. It would seem logical that changes in radionuclide distribution may occur here.

The immediate goals of this research are 1) to develop a system for the collection of water samples and the simultaneous, in situ measurement of salinity and light transmission (i.e. turbidity), 2) to make preliminary measurements of dissolved and suspended particulate radioactivity in the estuary and 3) to correlate the radioactivity data with salinity and turbidity measurements, to interpret results when possible and to suggest areas in need of study.

Few reports have been published on the levels of radioactivity dissolved in water and sorbed to suspended particulates in the Columbia River Estuary. Seymour and Lewis (1964) gave values for samples taken mostly in 1961 and 1962. Toombs and Bailey (1963) also reported for June 1961 through July 1963. Perkins,

Nelson and Haushild (1966) published data on the Columbia River between

Hanford (CRM 361)[1] and Vancouver (CRM 106), Washington for 1964.

Haushild et al. (1966) reported for the same stretch of the river for

the period July 1963 to September 1963. It is hoped that this research

will add to the existing data for the estuary and extend the upstream

data into the estuary.

---

[1]CRM denotes Columbia River Mile. Columbia River Mile
zero (CRM0) is at the river mouth in the center of the channel due
north from the original end of south jetty (Columbia Basin Inter-
Agency Committee. Hydrology Subcommittee. 1962).

BACKGROUND LITERATURE

Columbia River

The Columbia River originates at Columbia Lake, British Columbia, Canada, at an elevation of 2,652 feet, and flows for some 1,210 miles through British Columbia, Washington and Oregon, before reaching the Pacific Ocean. The discharge of the Columbia River is subject to seasonal variation. High water flow occurs during May, June and July as a result of melting snows in the high Rocky Mountain head waters. Low water occurs from September through March (Figure 1). Superimposed on the average annual flow are local increases in discharge during the winter months due to heavy rains. The average discharge ranges from 70,000 to 660,000 c.f.s. (Hickson and Rodolf, 1951), with a maximum of 1,300,000 c.f.s. and a minimum of 59,000 c.f.s. (Lockett, 1963). Numerous multipurpose dams, both completed and proposed, are expected to limit the discharge to a maximum of 600,000 c.f.s. and a minimum of about 150,000 c.f.s. (Lockett, 1963).

Columbia River Estuary

The limits of the estuary, especially the upstream boundary, vary depending on the basis of definition. If flow characteristics
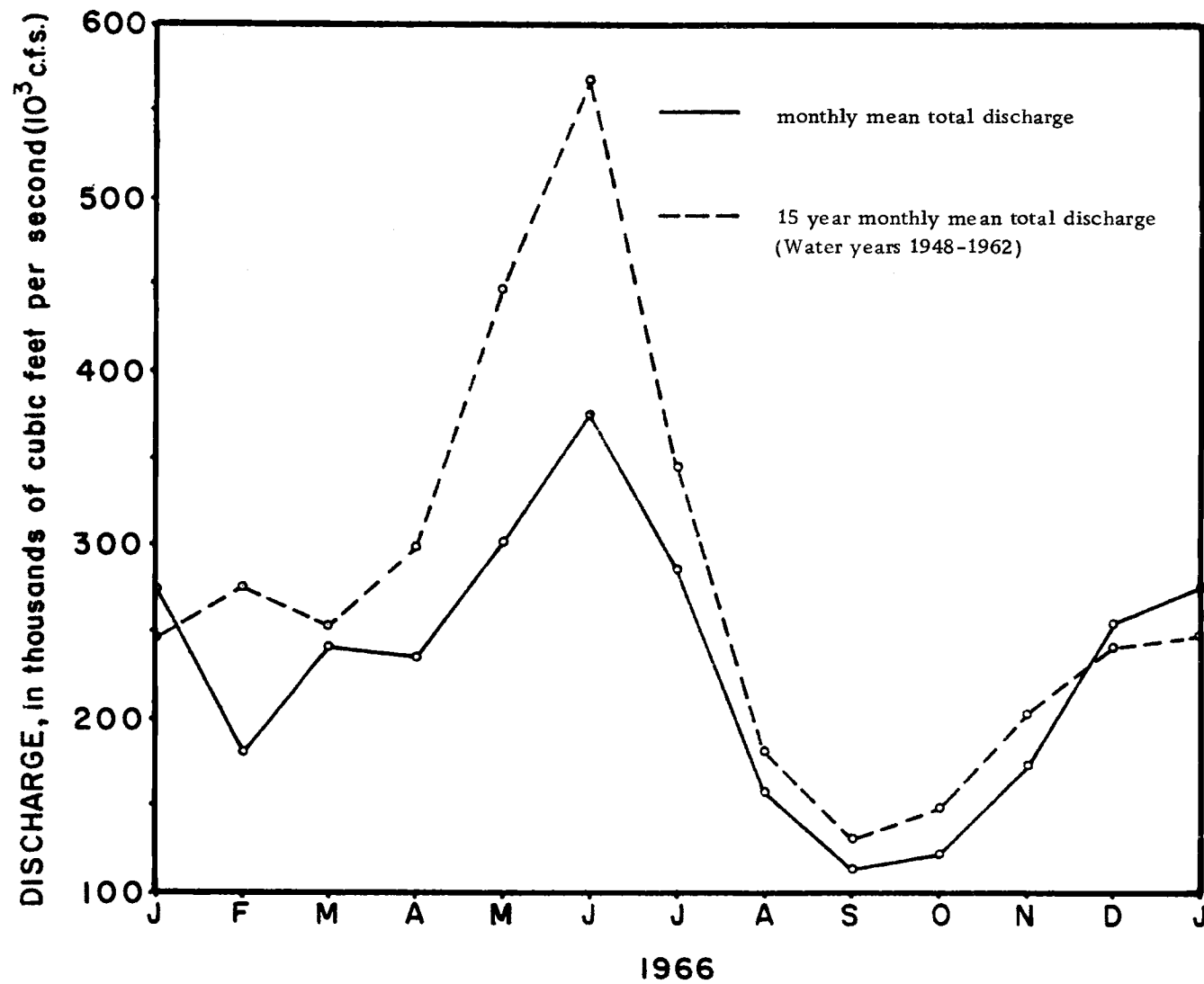
Figure 1. Estimated mean total monthly discharges at the mouth of the Columbia River for 1966 (discharges are not adjusted for storage or diversion). (Data prepared by U.S. Geological Survey, Portland, Oregon)

are the criteria, the upriver extent of the estuary varies depending on river discharge and tide level. During low flow, tidal effects can extend upstream to Bonneville Dam on the Columbia River (CRM 146) and to Oregon City on the Willamette River (Lockett, 1963). Upstream from Oak Point, Washington (CRM 52), however, river influence predominates the flow regime, while downstream of this point, tidal fluctuations predominate (Lockett, 1963). Salinity can also be used as a basis of definition. Examination of salinity profiles of the estuary (Lockett, 1963; Neal, 1965; Burt and McAlister, 1959) shows the maximum intrusion of salt water to be approximately Harrington Point (CRM 23.5). The extent of salt water intrusion is governed by river discharge and tidal energy, being inversely proportional to the former and directly to the latter. During stages of high river flow and lower low tide the maximum salinity intrusion is often limited to the first five nautical miles of the estuary (Neal, 1965).

Tides in the estuary are of the mixed semidiurnal type typical of the Pacific coast. At the mouth of the estuary the tides show a mean range of 6.5 feet, a high mean range of 8.5 feet and an extreme range of 14.2 feet (Lockett, 1963).

Using the methods of Pritchard (1952), the Columbia River Estuary may be classified as a positive coastal plain estuary (Neal, 1965). This implies that the estuary is a drowned river valley with precipitation and runoff in excess of evaporation. Applying the

further classification of coastal plain estuaries devised by Pritchard (1955), Neal (1965) shows the estuary to a partly mixed type (type B) the majority of time. During high river flow and low tide level the estuary may become a two layered type (type A), while with low river flow and high tide level the estuary may become a mixed type (type D). Partly mixed is the best over-all classification for the estuary.

Hansen and Rattray (1966) have developed a two parameter system of estuary classification based on relative stratification and circulation parameters. According to these authors the estuary can at most times be described as having a net flow seaward at the surface reversing at depth, while retaining appreciable stratification (type 2b). Upstream salt flux is by both advection and diffusion in this type 2b. At times of maximum discharge the estuary may have net flow seaward at all depths, still retaining appreciable stratification (type 1b). Upstream salt flux is by diffusion in this type 1b. With the normalizing effect on river discharge predicted with the completion of all the dams on the Columbia River and its tributaries (Lockett, 1963), the estuary may permanently become a type 2b. The existence of a permanent net flow upstream at depth may have pronounced effects on sedimentation and flushing times in the estuary.

Radioactivity in Columbia River and Estuary

Sources and Concentrations of Radionuclides

The Columbia River contains the largest concentrations of radioactivity of any river in the United States and probably of any river in the world. The use of Columbia River water as a coolant for the Hanford nuclear reactors near Richland, Washington, provides the principal source of radioactivity (Figure 2). Natural radioactivity and fallout from weapons tests are secondary contributors. River water passes once through the reactors before rejoining the river. More than 100 radionuclides are added to the Columbia River from reactor effluent (Nielson, 1963). Many of these are of such short half life or low concentration that processes of natural decay and dispersion make them of little importance downstream. Silicon-31 ($T_{\frac{1}{2}}$=2.6s) and manganese-56 ($T_{\frac{1}{2}}$=2.58h) are examples of short lived radionuclides which are relatively abundant immediately after irradiation, but not downstream. Chromium-51($T_{\frac{1}{2}}$= 27.8d) becomes relatively more abundant downstream partly due to its longer half life. Of a total radioactivity concentration of 4.4×10^4 picocuries per liter (pCi/l) at Hanford Ferry (CRM 361.7), manganese-56 and chromium-51 make up 21 and 17 percent, respectively. At Pasco, Washington (CRM 330.0), 32 river miles downstream, manganese-56

WASHINGTON

COLUMBIA ESTUARY

OCEAN

PACIFIC

Astoria

OREGON

1	Point Adams Station	8	Hood River
2	Astoria Station	9	The Dalles Dam
3	Astoria	10	John Day Dam
4	Harrington Point	11	McNary Dam
5	Oak Point	12	Pasco
6	Vancouver	13	Hanford Reactors
7	Bonneville Dam		
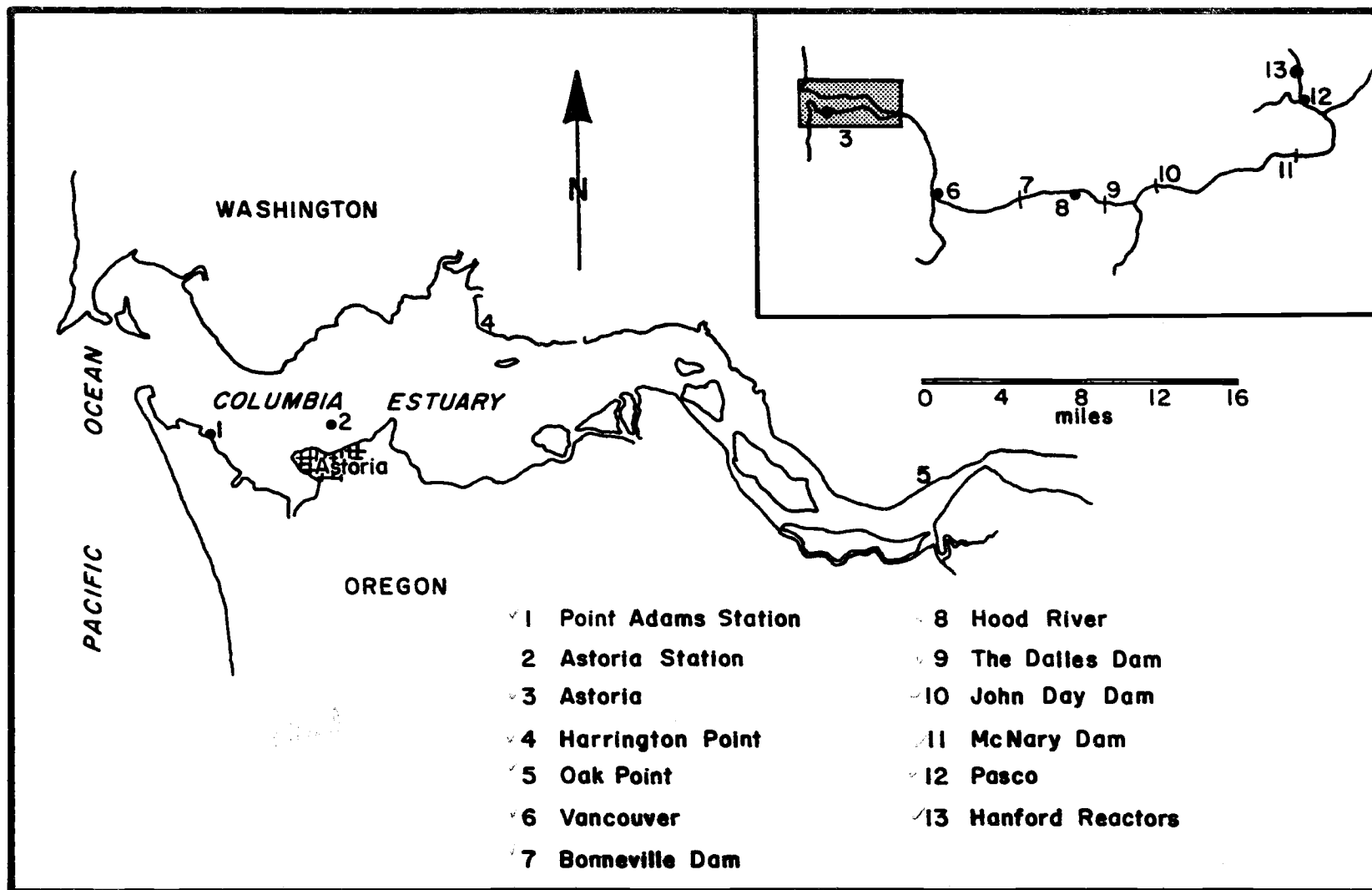
Figure 2.   Map of the Columbia Estuary and River downstream from the Hanford reactors.

is less than 2. 7 percent and chromium-51 is 42 percent of a total

concentration of 1×10^4 pCi/l. At Vancouver, Washington (CRM

106), some 275 river miles downstream from the reactors, mangan-

ese-56 is undetectable while chromium-51 increased to 78 percent of

a total concentration of 2.3×10^3 pCi/l. The above data are 1962

annual averages of unfiltered river water (Wilson, 1963). The total

radionuclide concentration in the river at Vancouver is decreased

by a factor of 19 from its outfall. Processes other than physical

decay which act to reduce the radioactivity carried by the river in-

clude sedimentation, biological uptake and infiltration. The relative

importance of each process can vary for different radionuclides.

Perkins, Nelson and Haushild (1966) list concentrations for

several of the more abundant gamma emitting radionuclides in the

Columbia River for the year 1964. Zinc-65 and chromium-51 con-

centrations at Vancouver agree closely for the years 1962 and 1964.

This indicates that levels of radioactivity have remained within the

same order of magnitude for these years. More recent values for

zinc-65 and chromium-51 also indicate no major deviations in the

levels of radioactivity up to June 1965 (Wilson, 1965). The Hanford

reactors add radioactivity to the river at essentially a constant rate

(Perkins, Nelson and Haushild, 1966) providing a quasi steady-state

input (Barnes and Gross, 1966).

Production of Radionuclides

Most of the radionuclides present in Hanford reactor effluent water are produced by neutron activation of stable nuclides. Sources of stable nuclides for activation are 1) trace elements naturally present in the river, 2) chemicals added in water treatment processes, and 3) corrosion products from the reactor components. Most of the radionuclides are formed by (n, γ) reactions on natural trace elements; Zn-65, Sc-46 and Co-60 are examples. Manganese-54 may be formed at Hanford by an (n, p) reaction with naturally occurring Fe-54, but fallout appears to be its main source. Silker (1964) showed seasonal variations in concentrations of elements in the Columbia River to correlate with variations in tributary discharges. While this is true for most trace metals, chromium-51 results from the addition of sodium dichromate to the reactor coolant water as a corrosion inhibitor. Potassium-40 is a long lived natural radionuclide, while Zr:Nb-95, Ce-144 and Cs-137 are fission products derived in part from the Hanford reactors and from fallout.

Important Gamma Emitting Radionuclides

Gamma-ray spectrometry and a computer program for data reduction have been developed in this laboratory to measure Cr-51, Zn-65, Sc-46, Co-60, Mn-54, Cs-137, Ce-144 and K-40. These

eight radionuclides were initially chosen because of their presence

in the Columbia River Estuary and adjacent Pacific Ocean.

Distribution of Radioactivity

Radioactivity in the Columbia River is distributed throughout

the fluvial environment. Biota, bottom sediments, and dissolved,

suspended and bed loads of the river have all been shown to be active

sinks for various radionuclides. The different radionuclides are by

no means partitioned similarly into these divisions of the river sys-

tem. When radioactivity enters any environment its subsequent

affinities are dependent on its initial physical and chemical proper-

ties and on changes in these properties that the environment itself

may affect.

Tracer Role of Radionuclides

The basic working assumption is that radionuclides behave

identically to their stable isotopes (i.e. no isotope effect). The iso-

tope effect so prominent between hydrogen and deuterium decreases

with mass, becoming negligible for heavier elements. (Wang and

Willis, 1965). Gamma-emitting radionuclides measured in this study

are of sufficient mass (all greater than 40) for the isotope effect to

be negligible.

	PARTICULATE			0·45μ		DISSOLVED	
SIZE	10^5	10^4	10^3	10^2	10	1	Å
	10	1	0·1	0·01	0·001	0·0001 microns, μ	
STATE	suspension	colloidal solution			atom molecule		

Figure 3. Division of radionuclides into particulate and dissolved phases (modified from van Olphen, 1963, p. 5).

Physical Form of Radionuclides

The physical form of a radionuclide can be defined as dissolved or particulate depending primarily on size, Since the boundary between dissolved and particulate form is gradational, the distinction between the two forms is entirely arbitrary. Small particle sizes are usually computed from their settling velocities by applying Stokes law. Particle sizes calculated by Stokes law are equivalent spherical diameters, and thus the calculation gives a truer value for particle size the closer the natural particles approach sphericity. Usually the divisions are made as shown in Figure 3.

Particles dispersed in a suspension are large enough to settle rapidly, while those in a colloidal solution do not. The gradation of particles from particulate to dissolved is obvious.

The division between particulate and dissolved form is defined for this study as 0.45 microns. Actual separation of the two forms is carried out by filtration through a 0.45 micron pore diameter membrane filter (Gelman (GA-6).

Perkins, Nelson and Haushild (1966) determined the physical form of several of the more important radionuclides originating from the Hanford reactors (Table 1). It is seen that all these radionuclides tend to increase in association with the particulate phase with distance downstream. Chromium-51 and antimony-124 increase but remain mostly dissolved. Zinc-65, scandium-46, manganese-54 and cobalt-60 increase becoming largely associated with particles. Osterberg, Carey and Curl (1963) and Freiling and Ballou (1962) indicate cerium-141 and cerium-144 to be readily absorbed on particulate matter, and the latter authors find cesium-137 mainly in soluble form. Zinc-65, Sc-46, Ce-144, Co-60 and Mn-54 appear to be largely in particulate form, while Cr-51, Sb-124 and Cs-137 are largely dissolved.

Processes Affecting Radionuclide Pathways Through Fluvial and Estuarine Environments

Figure 4 visually traces the various processes acting on a radionuclide which affect its distribution upon entering a fluvial or estuarine environment. The pathway for a particular radionuclide may lead to increased dilution and dispersion until its presence may

RADIONUCLIDE	HALFLIFE	Effluent Water	Pasco	Hood River	Vancouver	LOCATION
		0	50	210	275	RIVER MILES FROM REACTORS
Cr-51	27. 8d	2. 4	6. 4	4. 0	7. 6	
Zn-65	243d	1. 8	14	64	76	
Sc-46	83. 8d	36	74	85	89	PERCENT
Mn-54	312d	2. 6	20	88	88	IN
Co-60	5. 24y	1. 8	26	80	91	PARTICULATE
Sb-124	60. 2d	1. 1	3. 4	--	ca. 5. 9	PHASE
Ce-144	285d	see text p. 15				
Cs-137	30y	see text p. 15				

Table 1.   Percent of radionuclides in the particulate phase in the effluent and at downstream locations (modified from Perkins, Nelson and Haushild, 1966.   p. 238)
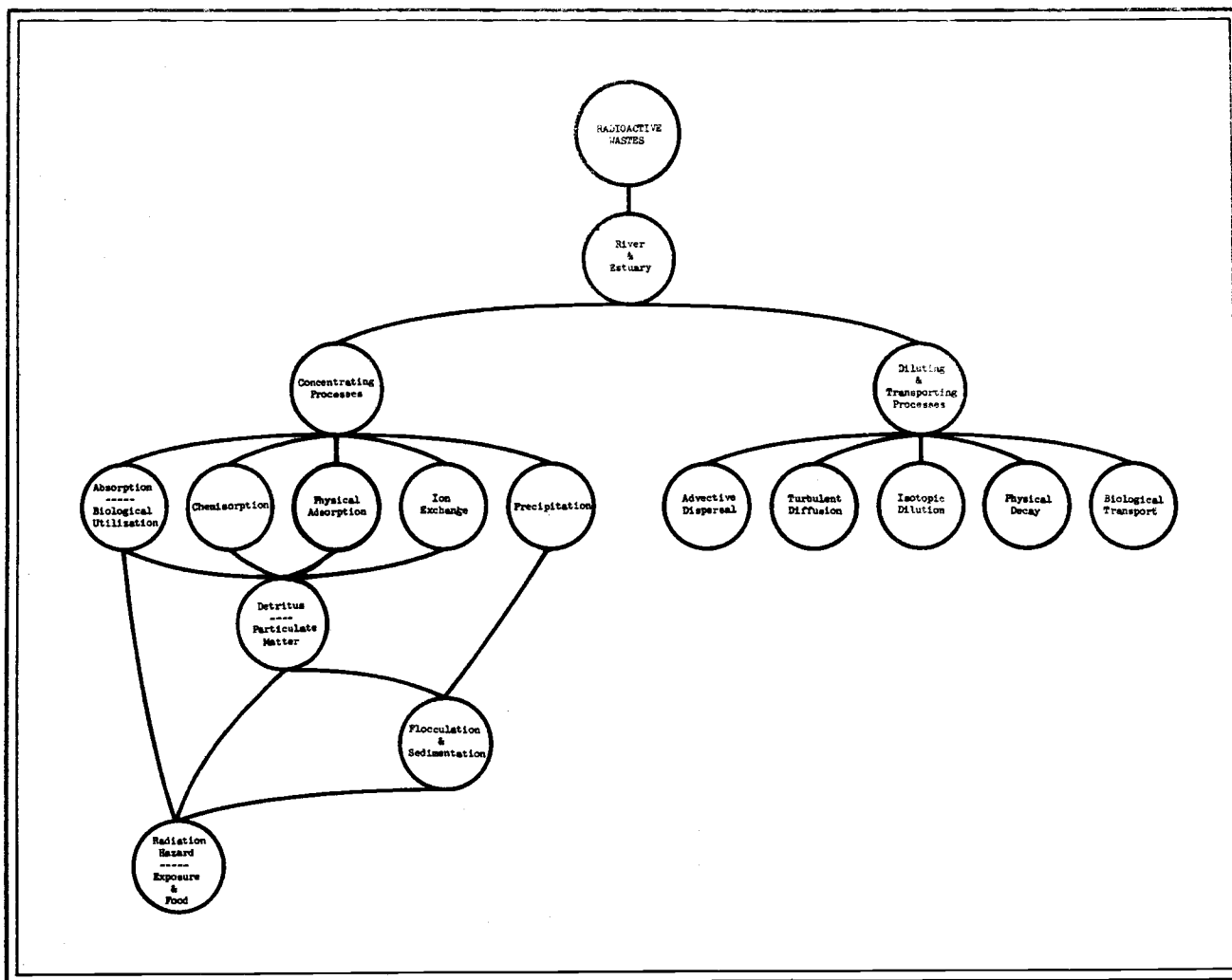
Figure 4. Diagram of important processes diluting, transporting and concentrating radionuclides

be disregarded, or to increased concentration until a radiation
hazard exists. Radionuclide pathways depend on complex relation-
ships involving the physical, geological, chemical, and biological
characteristics of the environment.

Physical Processes

The physical and chemical properties of a radionuclide deter-
mine its interactions with the environment. Particle size, specific
gravity, temperature, viscosity and surface tension are important
physical properties affecting the dispersion of radioactive waste in
a stream or estuary. In a flowing stream the major dispersive
process is longitudinal downstream advection, with turbulent and
molecular diffusion of secondary importance. Turbulent diffusion
is primarily generated by channel-boundary shear and wind shear.
Density currents caused by the introduction of waste products can
also produce turbulence especially near the source of outfall. Mole-
cular diffusion is usually negligible compared to advection and tur-
bulent diffusion. Physical dispersion plays the largest part in dilu-
tion in radioactive wastes. Glover (1964) shows that in flowing
streams longitudinal diffusion is 300 times more important as a
dispersal mechanism than is lateral diffusion.

Physical-chemical Processes

Many physical-chemical processes affect the association of dissolved species with particles. Physical adsorption is the association of dissolved and solid phases via electrostatic attraction (van der Waals forces); chemical bonds are not involved. Chemisorption is a similar, but stronger, association resulting from chemical bond formation. Ion exchange may be characterized as a process similar to physical adsorption in that electrostatic attraction is the binding force, but also similar to chemisorption in that the ionic bonding forces are much stronger than van der Waals forces. It is easy to visualize that radionuclides could be concentrated on particulate matter. Sayre, Guy and Chamberlain (1963) state that the concentration of radionuclides on the surface of suspended and deposited sediment particles may be thousands of times greater than in the surrounding solution. That radionuclides do become associated with particulate matter is quite evident from the data in Table 1.

Absorption, the penetration of a solute into a sorbent, is often confused with adsorption, the attachment of a solute onto a sorbent. In practice it is usually very difficult to distinguish between the two; thus, the noncommittal term sorption is generally used (Adamson, 1960).

Flocculation or coagulation is a process of agglomeration of

dispersed colloidal particles due to a chemical change in the environment. Suspended river sediments of the fine silt and clay size can be in colloidal suspension. With transport into brackish water, as into an estuary, flocculation and subsequent sedimentation can occur. Flocculation of clays by sea water is usually reversible, thus with the return of fresh water flocculated sediments can be redispersed. Flocculation is important in an estuary as the bulk of the silt and clay load in a river appears to be deposited there (Waldichuk, 1961). Radionuclide sorption onto particulate matter, followed by flocculation in brackish water, could lead to a large concentration of radioactivity in estuarine sediments.

The Columbia River Estuary is described as being a vast sediment trap due to 1) the normalizing effect on river flow of the numerous upstream dams combined with 2) the energetic tidal prism which causes a predominance of upstream flow at the bottom and lower levels of the estuary. These two factors preclude, except during rare occasions of extreme discharge, the seaward movement of bottom sediments and enhance the movement of sediments into the estuary from adjacent ocean areas. As a result the estuary is gradually becoming shallower (Lockett, 1963). Nelson, Perkins and Nielsen (1964) found sediments behind McNary Dam, the first reservoir below Hanford, to have higher concentrations of radioactivity than sediments under normal river flow. Preliminary measurements

show the estuary to be second to McNary Reservoir in total activity

inventory (ibid.). Jennings (1966) identified Cr-51, Mn-54, Zn-65,

Co-60, and K-40 in sediments of the lower estuary with Cr-51 and

Zn-65 most abundant. This agrees with values found by Nelson,

Perkins and Nielsen (1964). Radioactivity from both fallout and

nuclear installations appears to be concentrated in fluvial, estuarine

and oceanic sediments (Friend, 1963; Kaufman and Klingerman, 1963;

Osterberg, Kulm and Byrne, 1963; Toombs and Bailey, 1963; Clanton

and Gloyna, 1964; Friend et al., 1965; Gross, 1966; Kautsky, 1966;

Pickering et al., 1966).

Chemical Processes

Chemical precipitation is a possible method of removing dis-

solved radionuclides from solution and concentrating them as solids

in the sediment. A precipitate will form when the product of the

ionic concentrations exceeds the solubility product constant of a

given compound. This is likely to occur in an estuary where rela-

tively concentrated sea water and river water mix, especially if the

river water were heavily loaded with dissolved wastes. Waldichuk

(1961) notes that lack of data for the ionic thermodynamic activities

of ions in fresh and marine waters makes prediction of the extent

of precipitation impossible.

Radionuclides added to an environment rich in stable isotopes

are subjected to isotope dilution. The result is a reduction in the radioisotope to stable isotope ratio of the concentrated radioactive waste. As long as the radioisotope to stable isotope ratio remains low in the environment, those systems in equilibrium with the environment will also remain low in radioactivity.

Biological Processes

A radionuclide may become associated with the biota as a result of one or both of two processes 1) absorption through biological assimilation and utilization and 2) adsorption to external and internal surfaces as a result of contact from the media or food. Biota tend to absorb and concentrate certain elements through metabolic use, thus concentrating radioisotopes.

Although it is possible for radionuclides to be transported due to association with organisms, biological transport in rivers is insignificant when compared to other mechanisms of dilution and dispersion. Considering the organisms that most accumulate radionuclides, it is evident that sessile and planktonic forms are important. Sessile forms would act as concentrators rather than dispersing agents. Dispersion of radioactivity accumulated by plankton would be the result of advective and diffusive processes rather than actual transport by the organisms. The biota and organic detritus, therefore, are more important as concentrators of radioactivity than as

dispersive agents.

Zinc-65 has been found by many investigators to be concentrated to high levels in aquatic and marine organisms. Zinc-65 appears to be the gamma emitting radionuclide of greatest biological importance in the Columbia River and adjacent ocean. Chromium-51, on the other hand, has not been found to be as concentrated. The concentration of Cr-51 in the estuary is greater than that of Zn-65 by a factor of about 20 (Seymour and Lewis, 1964) to 50 (Foster and Jenkins, 1960). The factor of 50 agrees with the findings of this author. The relative concentration of Cr-51 and Zn-65 in organisms, however, is reversed indicating a high biological demand for zinc. Chromium-51 is also found in organisms, particularly in the high concentrations of the Columbia River and Estuary. This association appears to be the result of adsorptive processes. Seymour and Lewis (1964) point out that Cr-51 is mostly associated with organisms having a high potential for adsorptive uptake, or, in other words, a high surface to volume ratio. Algae, beach diatoms with mucilagenous sheaths, and Oikopleura, which possess a good potential for adsorptive uptake, were found to have adsorbed Cr-51 (ibid.).

EXPERIMENTAL METHOD

Sampling Stations

Two sampling stations were selected (Figure 2). Astoria station (CRM 14) was chosen because the vertical salinity gradients vary from zero (i.e. salinity constant with depth) to slightly positive (i.e. salinitity increasing with depth). Thus it was frequently possible to find a zero gradient during a low tide followed by a positive gradient at the next high tide. Point Adams station (CRM 8) was chosen be-cause of its strong positive salinity gradients due to greater tidal influence. A zero gradient of zero salinity was not observed at Point Adams, while this is common at Astoria station. Together, these two stations can be used to indicate the effect of salt water influx and tidal energy on the behavior and transport of the various radionuclides entering the estuary.

Sampling Equipment

An instrument package was designed to collect river water samples at any depth while simultaneously recording salinity, tem-perature (not reported), and light transmission (i.e. turbidity) data at the same depth (Figure 5). The sampling system was made to take water samples and other measurements in vertical profile at
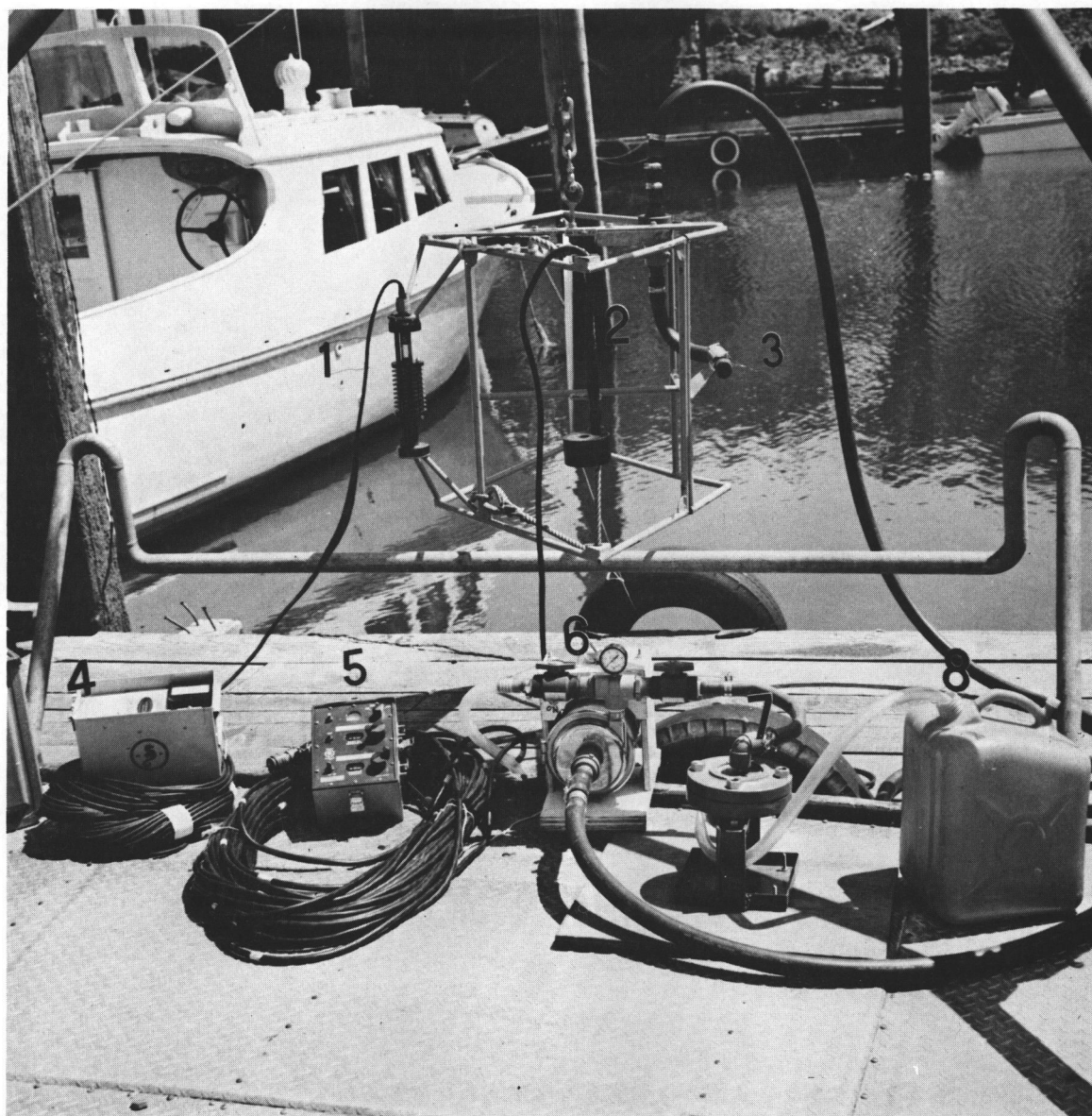
Figure 5. Instrument package ready for sampling: (1) Transmissometer underwater sensor; (2) Conductance-Temperature cell; (3) water intake for pumping; (4) Transmissiometer unit; (5) Conductance-Temperature unit; (6) stainless steel pump; (7) filter unit; (8) polyethylene storage container.

any point in the Columbia River and Estuary (depths to about 100 feet). Samples can be taken afloat or from piers.

The instrument package is constructed from common 3/8 inch steel tubing welded together. Lead weights were added to increase stability when submerged. Two 5/32 inch stainless steel wires are used with the system. One wire, wound on a handwinch, raises and lowers the package. The other wire, attached to a low speed electric winch, is used as a tether line on which the instrument package can slide vertically in the water. The tether line is kept vertically taut by means of a 200 pound lead weight. When working from a boat the anchor is set and the vessel is allowed to become adjusted to the surface current before the tether line is set out. A vane fixed on the instrument package enables the pump intake, salinometer cell and transmissometer sensor to be orientated into the current. This provides unobstructed sampling of the river water. Depth of sampling is determined with a meter wheel.

Water samples are obtained by pumping. Water enters through an intake and PVC footvalve on the instrument package and is lifted through a one inch ID rubber hose by a stainless steel electric pump. With the instrument package on the bottom the water intake is 12 inches above the sediments. Power for the 115V pump is provided by a portable gasoline-engined generator.

Salinity and temperature data are measured by a portable

battery-operated induction salinometer. The conductance-temperature cell is mounted on the instrument package and is connected by electric cable to surface battery supply, electronics and salinity and temperature indicators.

Water turbidity is measured by a portable self-contained transmissometer indicating percent light transmission from 0% to 100%. An underwater sensor mounted on the instrument package is connected by electric cable to ship board battery supply, electronics and percent transmission meter.

Sampling Procedure

Water samples (4-12 liters) are pumped through a 0.45 micron pore diameter membrane filter (Gelman GA-6) with a glass fiber prefilter (Gelman Type E). The prefilter catches the larger sized particles and enables larger water volumes to pass through the membrane filter before clogging. The filtering step divides the sample into dissolved and particulate fractions. Filtered water samples are temporarily stored in plastic containers until the dissolved radionuclides can be concentrated by precipitation or evaporation. The membrane and prefilter are removed as a unit from the filter holder, drained of excess water, rolled into a cylindrical shape, placed in a plastic counting tube, and counted without further processing.

Concentration of Dissolved Radionuclides

The various radionuclides are in such low abundance that a method of concentrating them is necessary before radioanalysis. Concentration by evaporation is feasible in river water, but with increasing salinity the relatively large quantity of sea salts in the residue after evaporation makes this method undesirable for two reasons. First, the amount of evaporation residue large enough to contain a measurable amount of a radionuclide is too large for counting in the well detector. Secondly, such large volumes of sea water are required that evaporation would be impractical.

Evaporation is a laboratory process. Filtered water samples are acidified with HNO_3 and evaporated on a hot plate under a heat lamp to near dryness. The liquid-solid residues are quantitatively transferred into plastic counting tubes. Further evaporation, if necessary, is carried out in a waterbath under a heat lamp. The residue salts are suspended in agar-agar gel to provide standard counting geometry.

Concentration of dissolved radionuclides can also be carried out by a precipitation method. Amorphous precipitates, such as ferric oxide and aluminum hydroxide, when formed with an excess of ammonia are active adsorbents for trace metals, such as zinc, copper and others (Kolthoff

and Sandell, 1952).[2] Iron III (45 mg per liter of sample) and car-
riers of chromium III, zinc II, cobalt II and manganese II (5. 3 mg
each per liter of sample), all as chloride salts, are added to each
water sample. Tin II (5. 3 mg per liter of sample) is added as the
chloride salt to reduce Cr IV to Cr III thus insuring greater recov-
ery of chromium (Cutshall, Johnson and Osterberg, 1966). After
mixing for several minutes, sufficient aqueous ammonia to cause
flocculation of colloidal hydrous ferric oxide (pH 9. 0-9. 5) is added
dropwise with continual mixing. Separan (Dow Chemical) in concen-
tration sufficient to give a total of 1 to 2 ppm in the sample, is added
as a flocculant when more rapid setting is desired. In this process
ferric oxide acts as a bulk precipitate which can coprecipitate var-
ious trace metals present (ibid.).

Chakravarti et al. (1964) used a similar precipitation method
differing in that iron was added as a carrier, thus no bulk precipi-
tate was formed. Manganese, cobalt, zinc and chromium were also
added as carriers, but no reducer was used. The same authors re-
ported the chemical yields by ammoniacal precipitation for

---

[2]The precipitation of the hydrous metal oxides of Fe^{3+} is
commonly written $Fe(OH)_3$ and termed ferric hydroxide. This is
not rigorously correct, but often appears in the literature. In fact,
the process shows ion adsorption selectivity and flocculation rever-
sibility characteristic of hydrophobic colloidal systems. The term
precipitation is used in this paper for the lack of a better word (see
appendix).

manganese-54, cobalt-60, iron-59, zinc-65 and chromium-51 to be

in the range of 89 to 100 percent. Silker (1965) has shown the hydrol-

ysis of ferric sulfate and aluminum sulfate in natural waters to be

effective in removing the fission products cerium, ruthenium and

zirconium-niobium from solution by flocculation and settling. Cer-

ium-141, zirconium-niobium-95 and ruthenium-103 can be removed

from solution in percents greater than 98, greater than 99 and 70 to

80, respectively (ibid.). This process is essentially the same as

used in this study. Cutshall, Johnson and Osterberg (1966) report

recovery of chromium-51 spikes by ferric oxide bulk precipitates

formed in the laboratory to be greater than 99 percent when a reduc-

ing agent is added to insure that all chromium is in the III oxidation

state.

A system has been developed for carrying out the precipitation

in the field. Filtered water samples are placed in one of the four

18 liter graduated plastic precipitating vats (Figure 6). The pre-

cipitate is formed and allowed to settle. The supernatant liquid is

siphoned off and the precipitate is transferred to a 500 ml plastic

bottle for transport to the laboratory. In the laboratory the precipi-

tate is filtered onto number 42 Whatman filter paper, rolled into a

cylindrical shape, and placed in a plastic tube for radioanalysis.

Concentration was carried out by the bulk ferric oxide precipitation

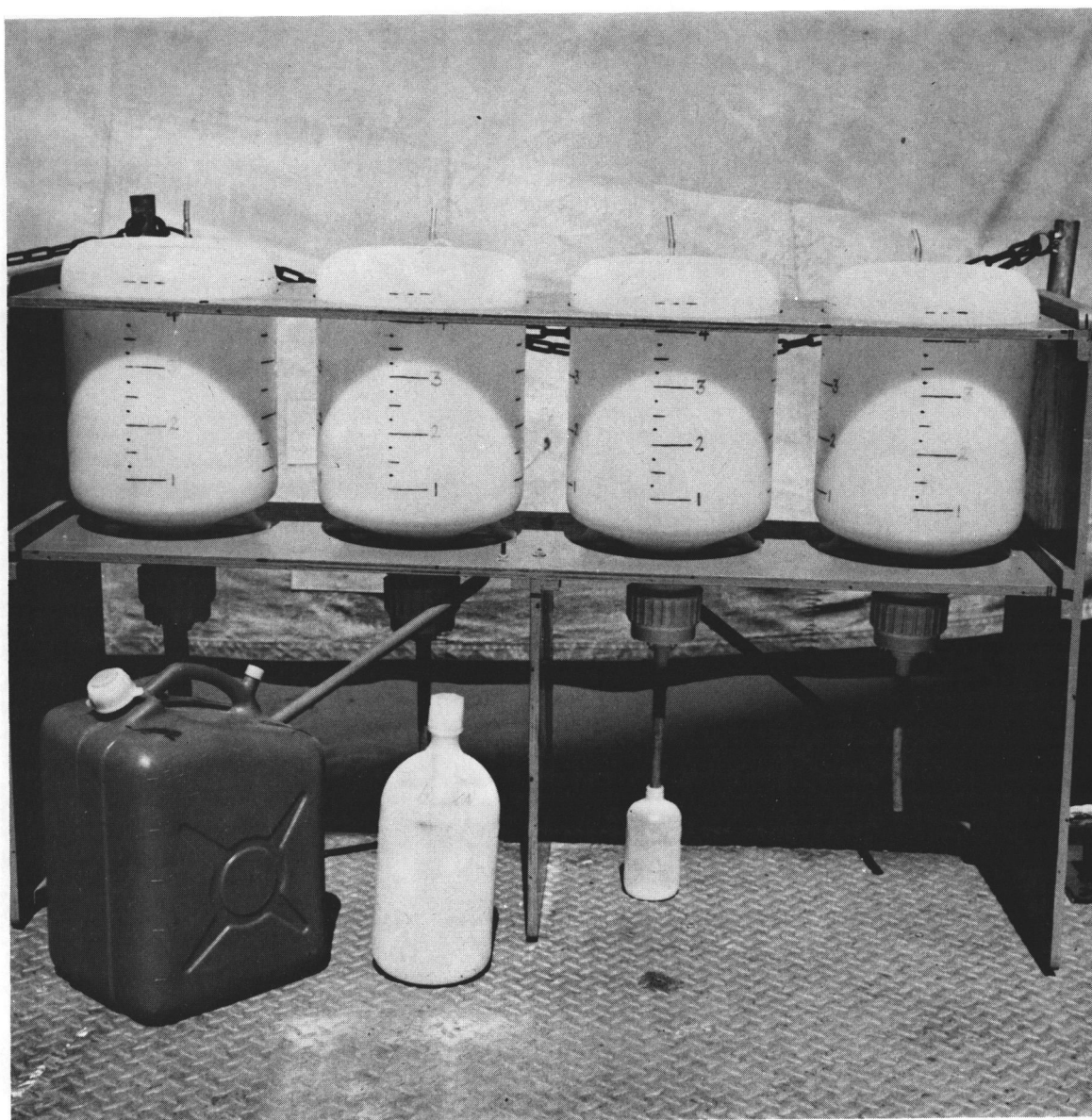method for all samples except where otherwise noted.

Figure 6. Precipitating containers. Precipitates are formed
in the calibrated containers. The supernatant liquid
is siphoned off and precipitate is washed down into
small polyethylene bottles for transport to the labor-
atory. Air is bubled through the containers to assure
good mixing during precipitation.

Radioanalysis

Counting

Identification and measurement of gamma emitting radio-nuclides recovered by filtration, precipitation and evaporation is carried out with gamma-ray spectrometry. Plastic tubes (ca. 12 ml) containing membrane filters, precipitates or agar-agar suspensions of river salts are counted for 100 minutes in the well of a 5 × 5 inch NaI(Tl) detector coupled to a Nuclear Data ND-130 AT 512-channel analyser. Background is subtracted from each count. Data read-out is by punch tape, x-y recorder and typewriter.

Data Reduction

Spectrum analysis is by IBM 1410 computer with a least squares program. The program, developed at this laboratory, will yield results accurate to ±5% of the standards (Frederick, Larsen and Borden, 1965). An explanation of the program, its mathematical deviation and the errors involved in its use are given by Frederick (1967). Data on punch tapes are directly punched into computer cards by an IBM 870 Document Writing System. Header cards containing individual sample information are punched by hand. The program yields a print out containing the activity of each radionuclide

and its counting standard deviation expressed in picocuries per unit sample size. The program corrects for decay to the day of sampling.

Typical spectra are shown in Figure 7. The upper spectrum is the precipitate from a 9.5 liter sample and the lower spectrum is the particulate matter filtered from the same volume. Both are 100 minute counts minus background (sample spectra from Figure 9b; profile P-3, depth 9 feet).
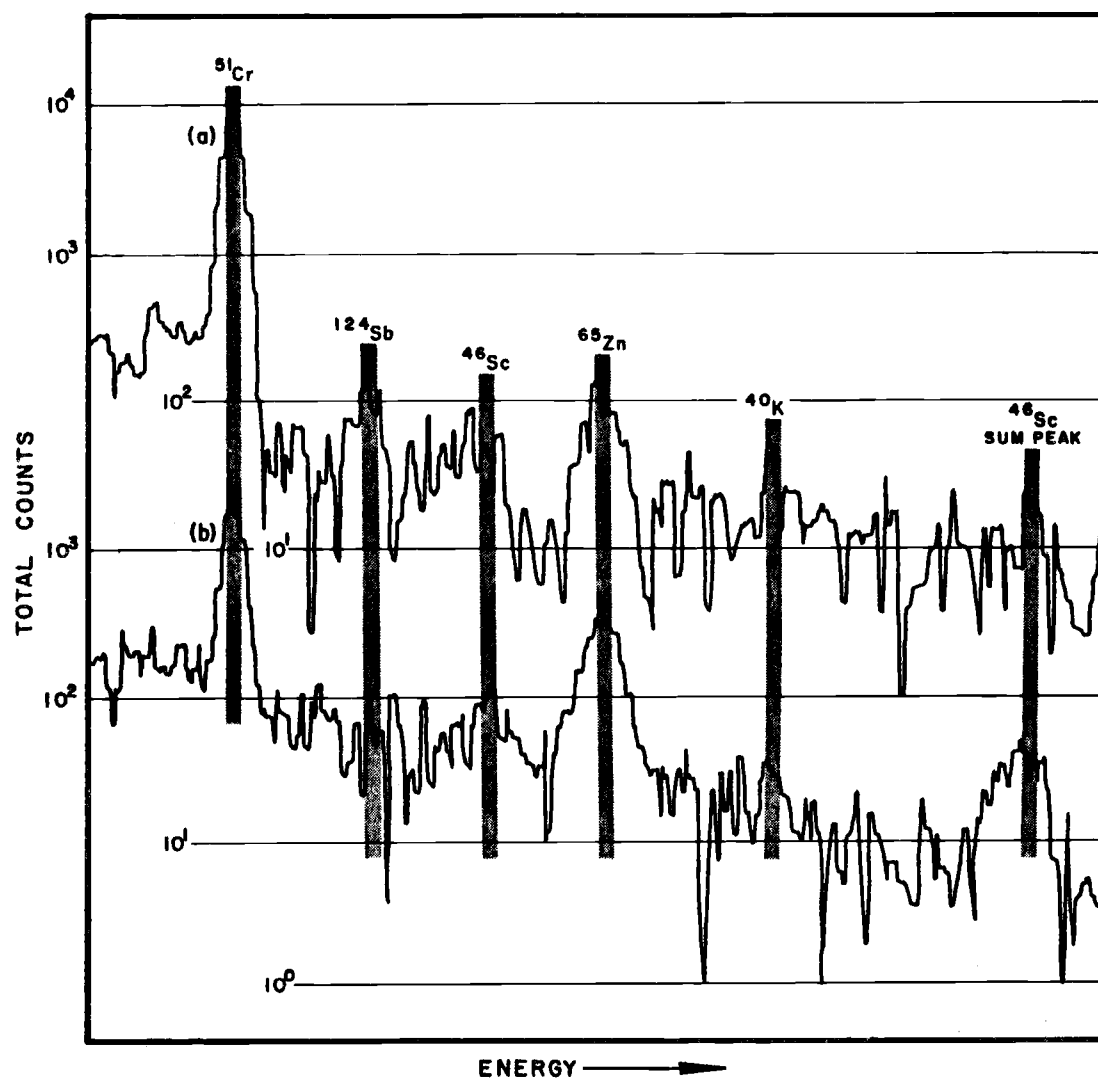
Figure 7. Typical spectra of Columbia River Estuary water. Upper spectrum (a) is the dissolved phase. Lower spectrum (b) is the particulate phase filtered from (a).

RESULTS AND DISCUSSION

Astoria Station

Two vertical profiles at Astoria station were taken in April 1966; one during lower low tide and the other on the following lower high tide. Figure 8a-b shows plots of the Astoria Station data with depth. Salinity, percent light transmission, and concentrations of certain radionuclides are included. Salinity measured with the conductance cell is accurate to within $\pm$ 0.3‰. Light transmission data, after correction for instrument drift, are accurate to $\pm$ 3.8%. Percent light transmission gives a measure in percent of the turbidity relative to distilled water. Light transmission decreases as turbidity, the amount of light scattering matter in the water, increases. Chromium-51 and zinc-65, both dissolved and particulate, and scandium-46, particulate only, were measurable in the 4 to 12 liter samples obtained. Sample size was determined by the volume of water which passed before clogging the filter.

The vertical profile at lower low tide is shown in Figure 8a. Salinity is zero at all depths while turbidity increases with depth. Chromium-51 and zinc-65 in the dissolved fraction vary with depth, but show no definite trends. Chromium-51, zinc-65 and scandium-46 in the particulate fraction increase with depth and turbidity.

		$\dfrac{F}{}$			
cd	Dissolved ^{51}Cr	10^2		S	Salinity
cp	Particulate ^{51}Cr	10^2		LT	Light Transmission
zd	Dissolved ^{65}Zn	1		pCi/l	picocuries per liter
zp	Particulate ^{65}Zn	10		‰	parts per thousand
sp	Particulate ^{46}Sc	1			

LEGEND: Figures 8a-b, 9a-i, 11, 12a-c, and 13

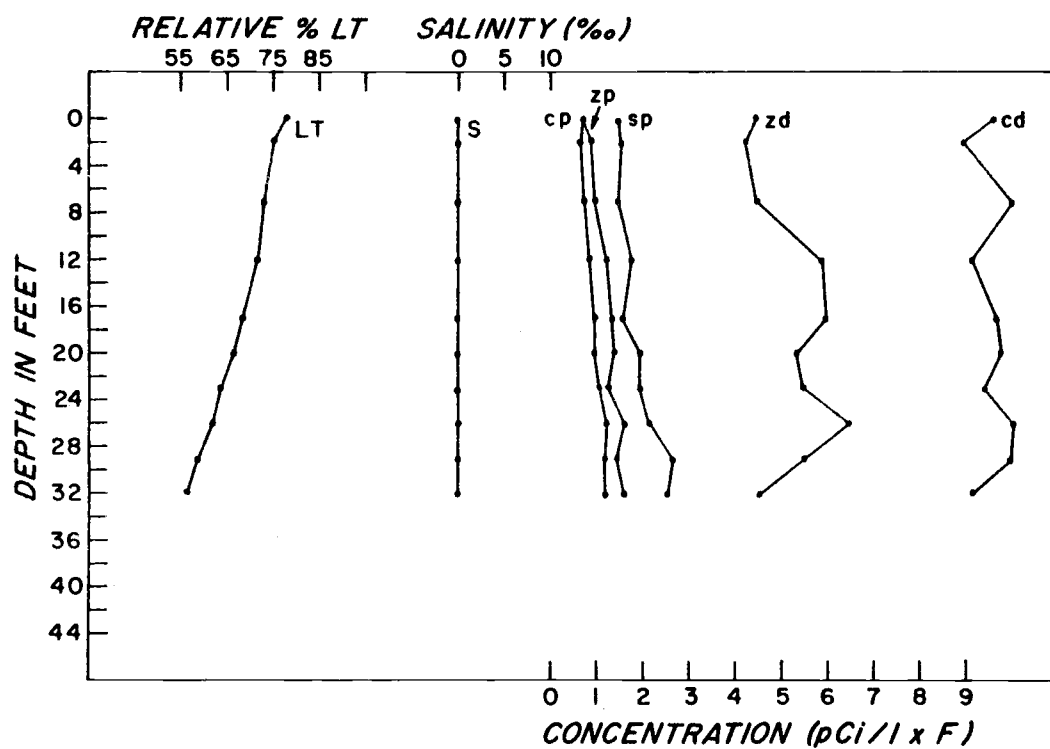Table 2.   Legend for Figures 8a-b, 9a-i, 11, 12a-c and 13

Figure 8a. Astoria station vertical profiles (legend is in Table 2, p. 36).
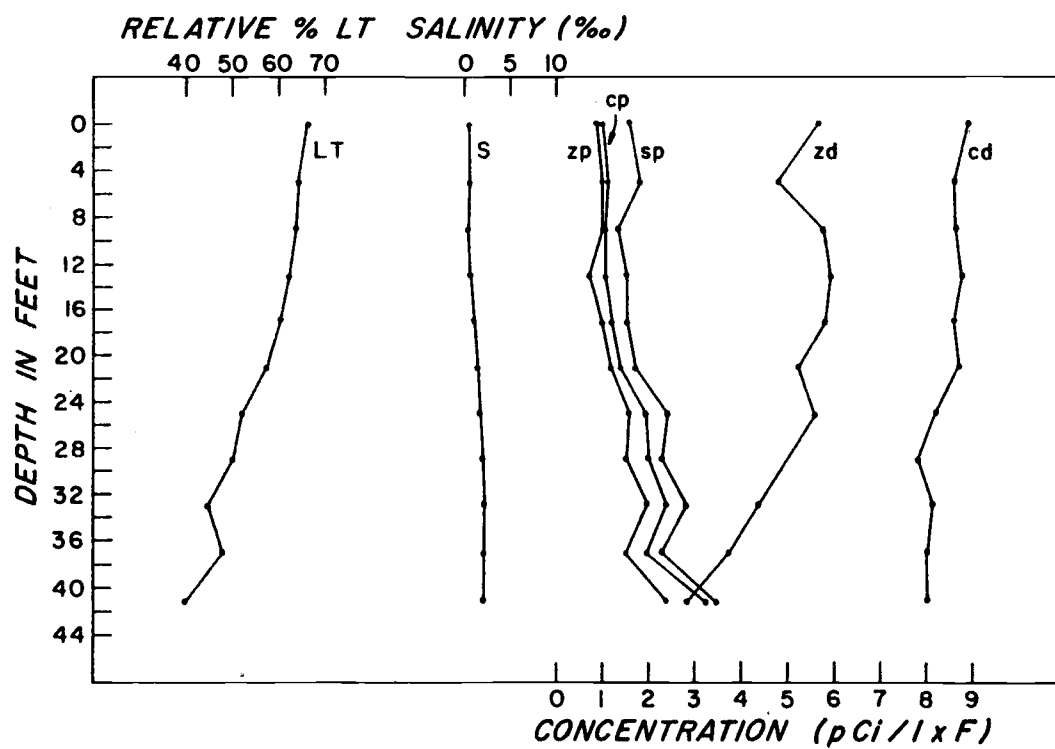

Figure 8b. Astoria station vertical profiles (legend, p. 36).

In the vertical profile at lower high tide (Figure 8b), salinity
increases with depth due to the higher tidal stage. Turbidity increas-
es with depth but to a greater extent than in the lower tide profile.
Chromium-51 and zinc-65 in the dissolved fraction vary with depth.
It should be noted that the greater variations in dissolved zinc-65
compared to dissolved chromium-51 probably result from the much
lower concentration of zinc-65 in the water. Particulate chromium-
51, zinc-65 and scandium-46 concentrations increase with depth, as
does turbidity, but both increase to a greater extent than in the lower
low tide profile.

Point Adams Station

Sixteen vertical profiles distributed over a complete tidal cycle
(ca. 25 hours) were taken at Point Adams station in May 1966. Eight
profiles included salinity, light transmission, and radionuclide meas-
urements. The other eight profiles included salinity and light trans-
mission measurements. Unfortunately, a malfunction in the trans-
missometer rendered the turbidity data meaningless.

The 16 profiles are plotted in Figure 9a-1. Salinity gradients
through the complete tidal cycle vary from strongly positive to zero,
thus reflecting different stages of the tide. Surface salinities range
from 0.5 to 0.5‰ bottom salinities from 0.5 to 25.7‰. Radio-
nuclide concentrations in the Point Adams and Astoria profiles show
similar trends with depth. Notably, dissolved chromium-51
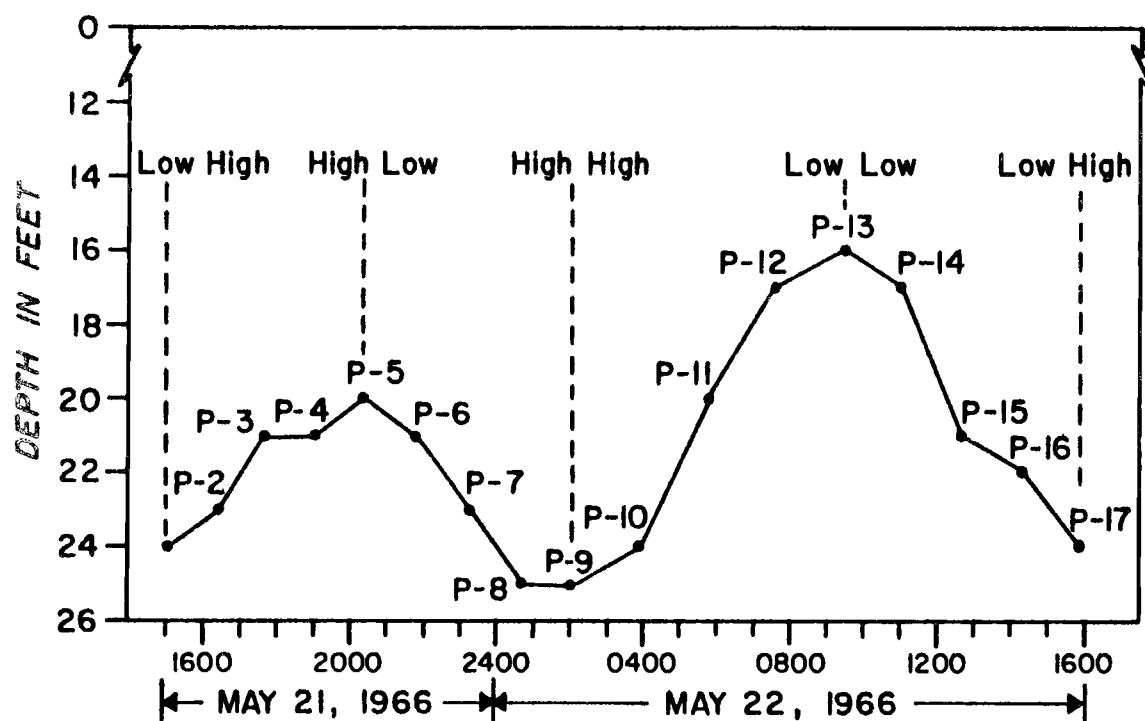
Figure 9a. Point Adams station vertical profiles. Figure shows the relationship of time, depth and tide stage to the 16 vertical profiles, P-2 through P-17.

Figure 9b. Point Adams station vertical profiles (legend, p. 36).

Figure 9c. Point Adams station vertical profiles (legend, p. 36).

SALINITY (‰)

0 5 10   0 5 10

DEPTH IN FEET

0
2
4
6
8
10
12
14
16
18
20
22
24

S

P-6

S   zp cp   zd   cd
sp

cp zp
P-7

CONCENTRATION (pCi/l x F)

0 1 2 3 4 5 6 7 8

Figure 9d. Point Adams station vertical profiles (legend, p. 36).

SALINITY (‰)

0 5 10 15 20   0 5 10 15 20 25

DEPTH IN FEET

0
2
4
6
8
10
12
14
16
18
20
22
24

S

P-8

S   zp cp   sp   zd   cd

cp   cd   sp
P-9   zp   zd

CONCENTRATION (pCi/l x F)

0 1 2 3 4 5 6 7

Figure 9e. Point Adams station vertical profiles (legend, p. 36).

Figure 9f. Point Adams station vertical profiles (legend, p. 36).

Figure 9g. Point Adams station vertical profiles (legend, p. 36).
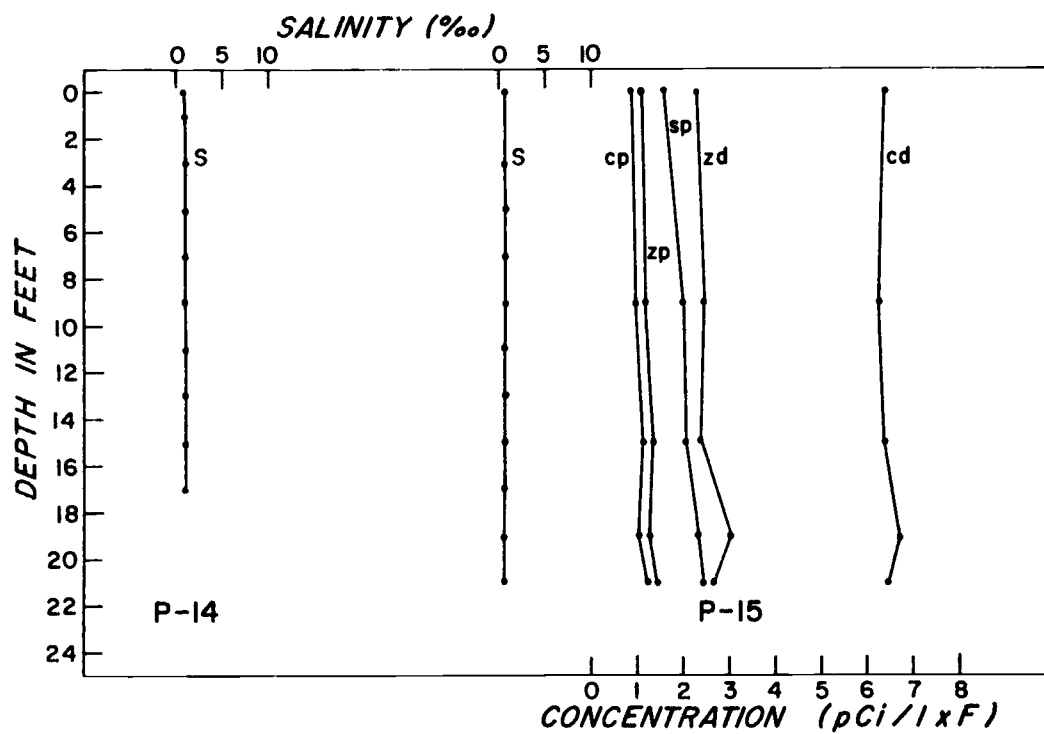
Figure 9h. Point Adams station vertical profiles (legend, p. 36).

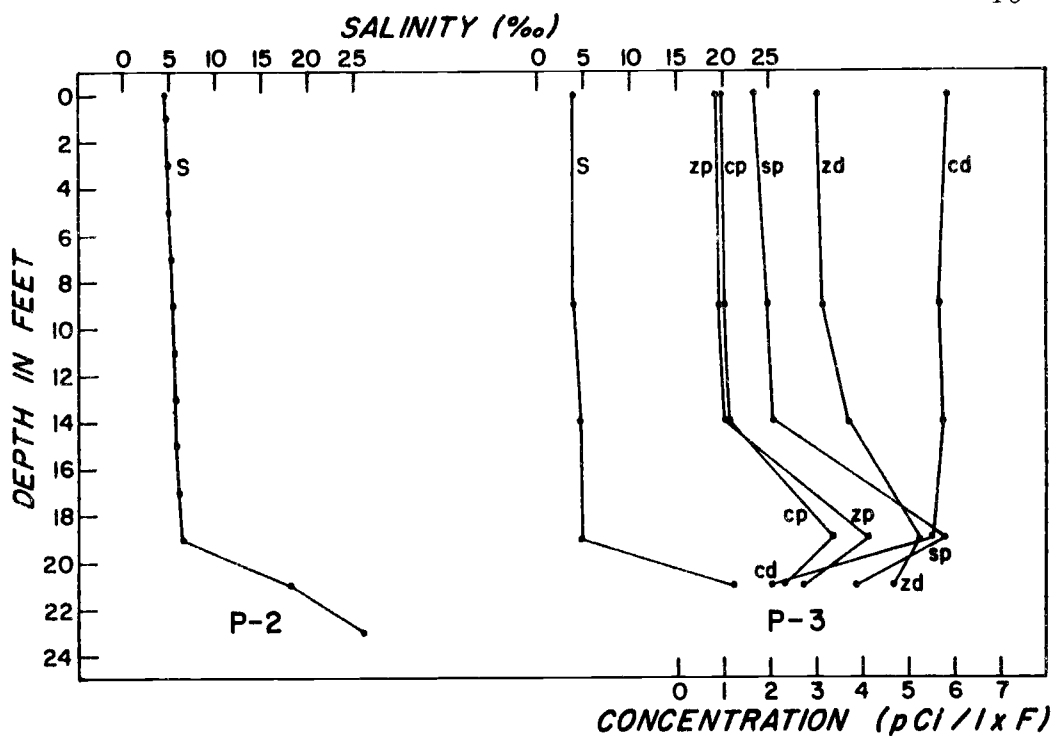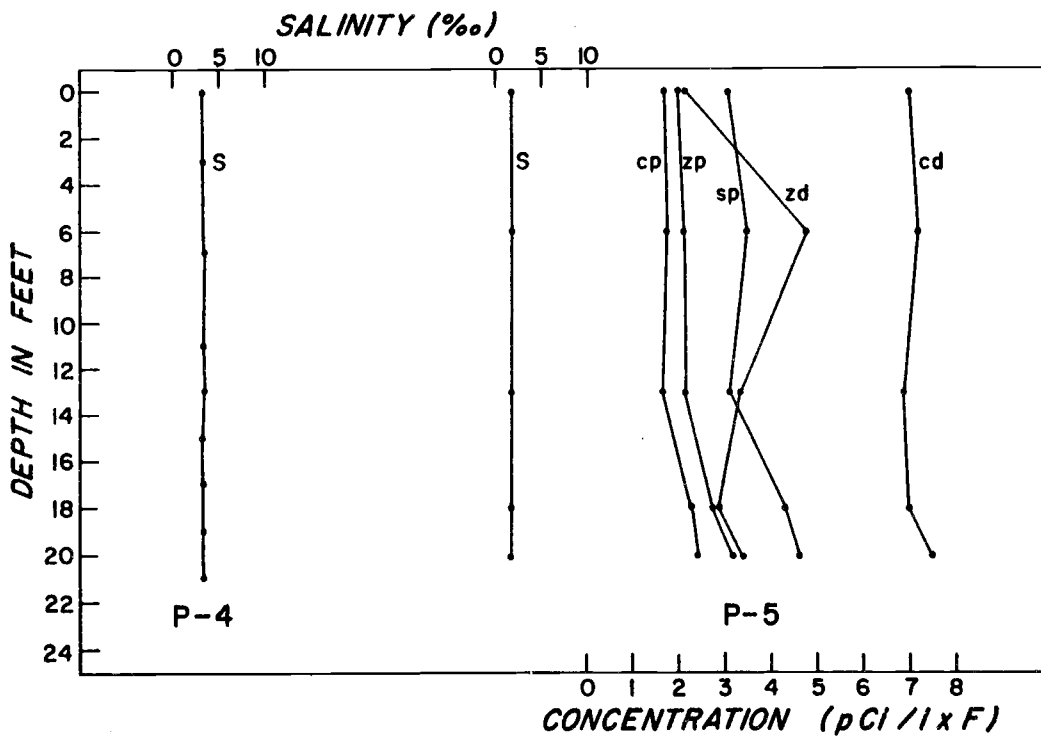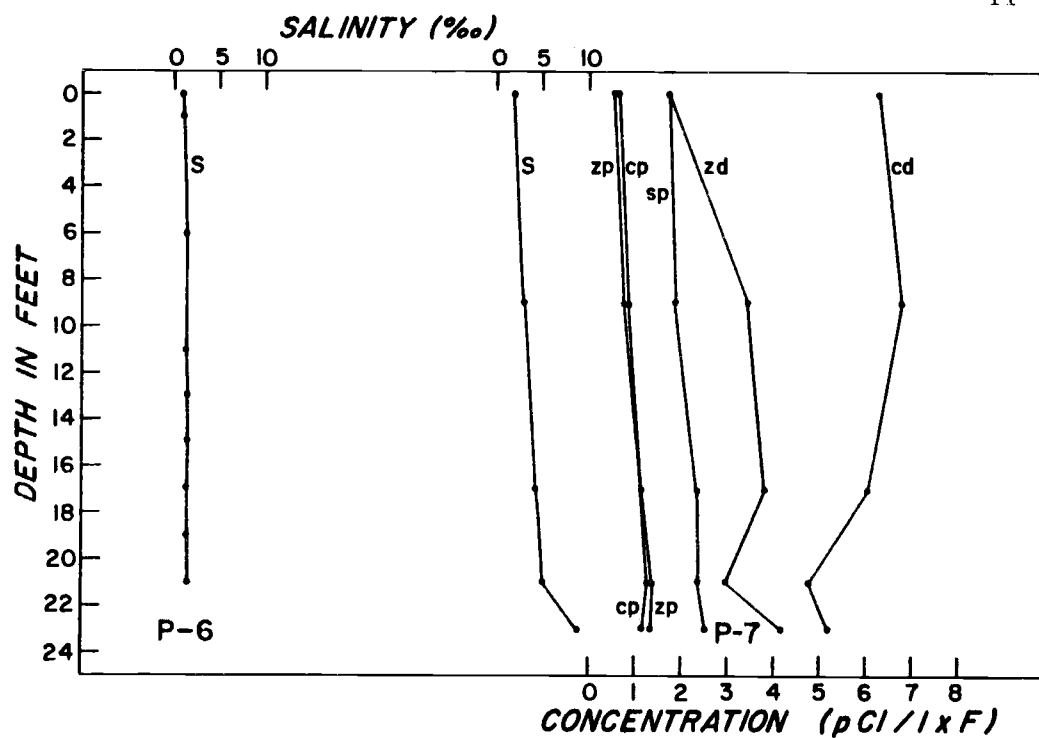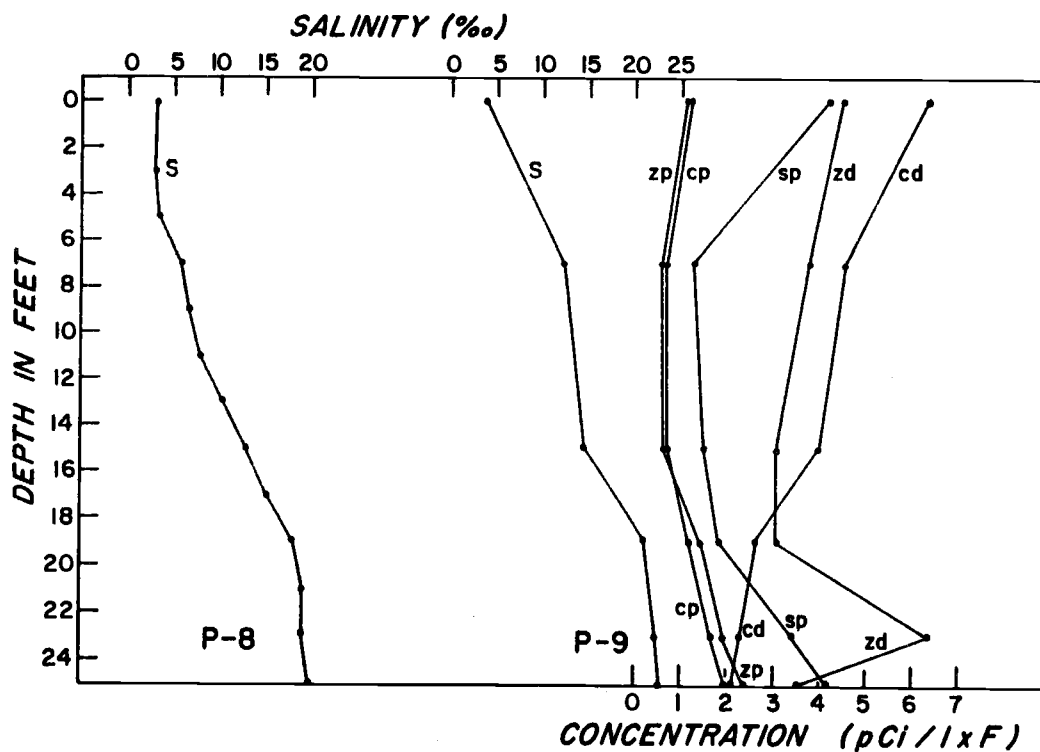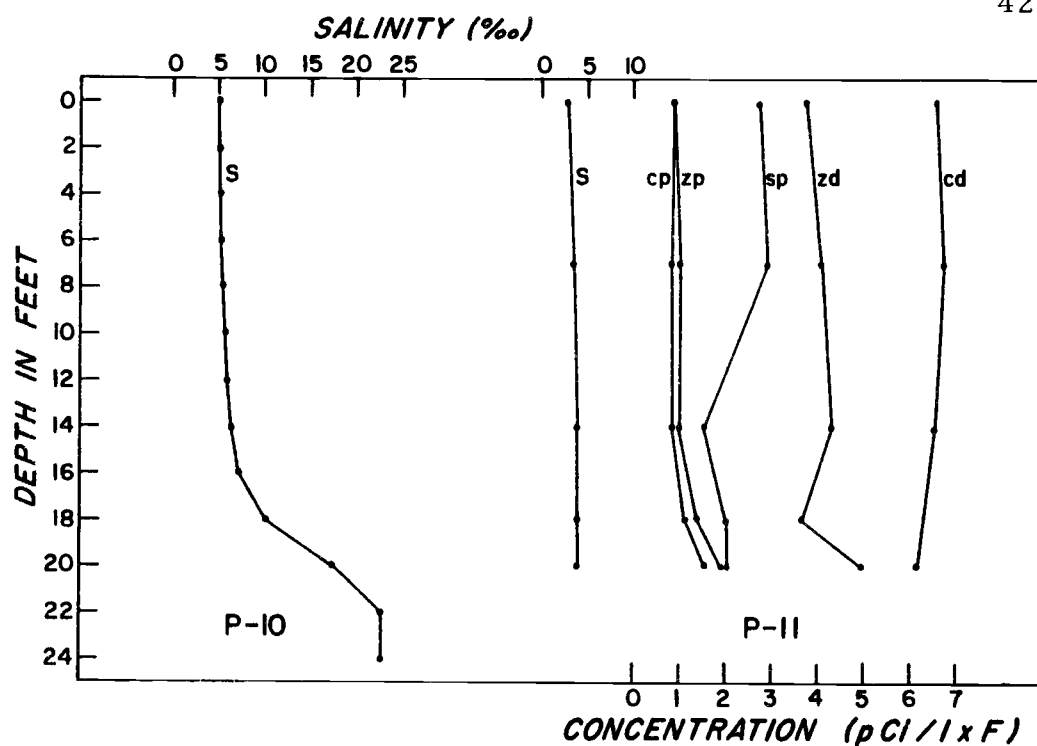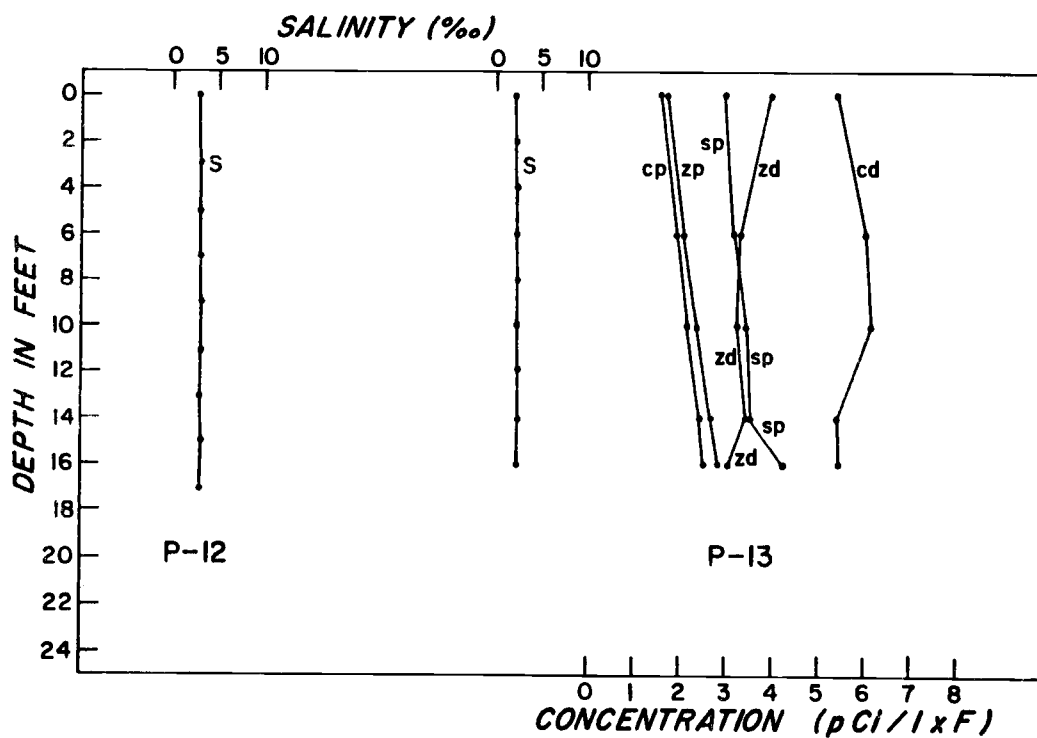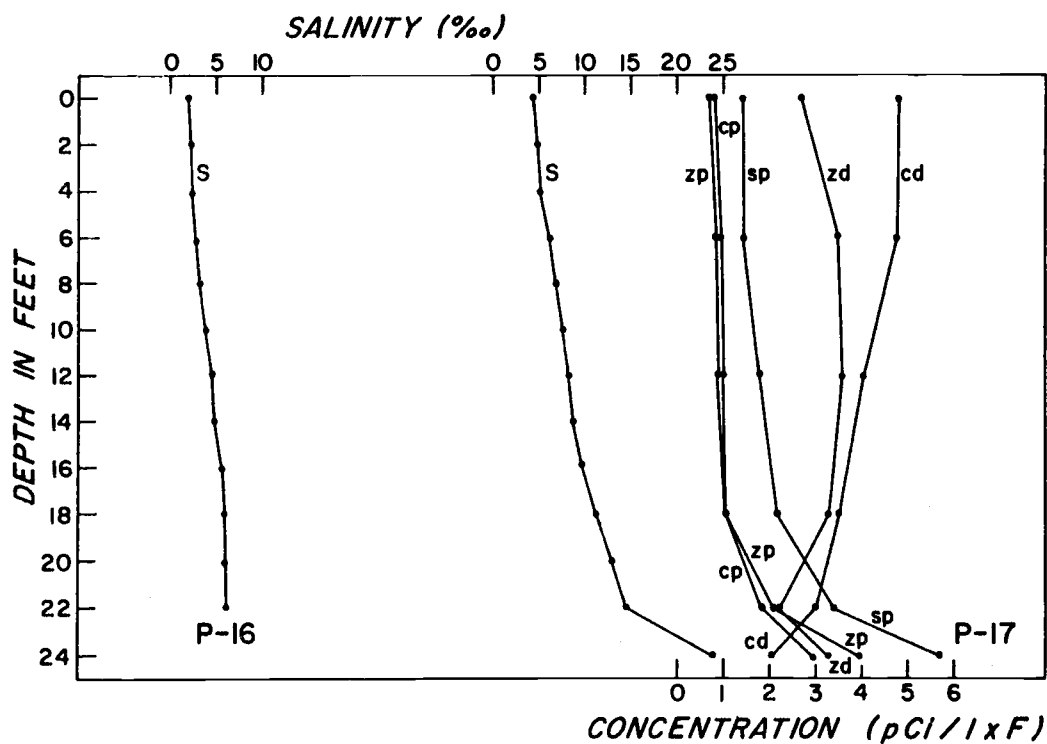
Figure 9i. Point Adams station vertical profiles (legend, p. 36).

concentrations appear to decrease linearly with increasing salinities.
Dissolved zinc-65 concentrations vary with depth, showing no definite
trend. Particulate chromium-51, zinc-65 and scandium-46 tend to
increase with depth. Since turbidity data are not available, the
correlation between particulate radionuclide concentration and turbid-
ity cannot be made directly as in the Astoria profiles. Salinity and
turbidity values increase with depth to their greatest values during
higher tidal stages. High salinity reflects the influx of sea water
and increased turbidity reflects tidal energy lifting sediments into
suspension and/or flocculation of suspended and colloidal radionu-
clides. Thus in those areas of the estuary which show a large range
in salinity, high salinity values should indicate increased turbidity
in the lower depths.

Dissolved Radionuclides

Dissolved chromium-51 appears to vary inversely with salinity.
This suggests that low dissolved chromium-51 concentrations in high
salinity water may be the result of sea water dilution of radioactive
river water. If the above supposition is correct, then a graph of
salinity versus dissolved chromium-51 concentration should show a
linear relationship. Such a plot is shown in Figure 10 for all samples
taken at Point Adams. By the method of least squares, the regres-
sion line which was fitted to the set of points showed a correlation
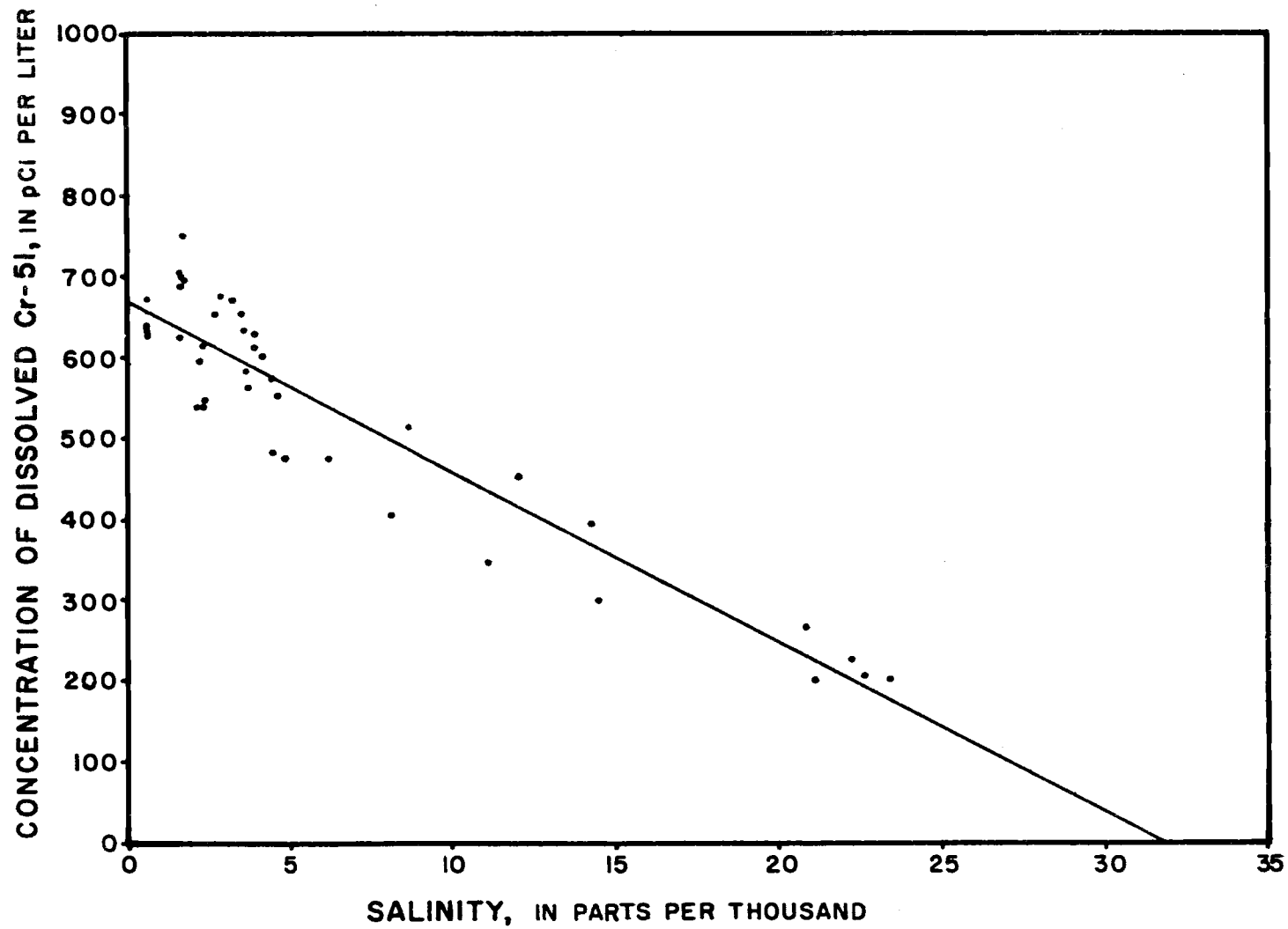
Figure 10. Least squares analysis for salinity of mixing sea water.

coefficient of 0.94. This suggests a strong linear relationship, but its value near unity cannot be interpreted as implying, in itself, a cause and effect relationship. More significant is the x-intercept of the regression line. The x-intercept gives the salinity of water which would have zero dissolved chromium-51 concentration or, in other words, it represents the salinity of the sea water which is mixing with river water. The salinity of the mixing sea water given by the x-intercept should agree with actual values. Neal (1965) used 32.0‰ as the salinity of the sea water entering and mixing in the estuary for the purpose of calculating flushing times. Gross, Barnes and Riel (1965) found the ambient sea surface salinities near the mouth of the Columbia River to be variable but generally greater than 32.5‰. Pattullo and Denner (1965) found the most prevalent type of sea water along the Oregon coast to have a salinity varying from 33.0 to 33.5‰. From the above data, it appears that the salinity of the sea water entering the estuary would be between 32 and 33‰. The salinity extrapolated from Figure 10 is 31.7‰.

It must be mentioned that three factors would affect the validity of the argument. First, the salinity of the sea water entering the estuary may vary. Second, the amount of chromium-51 added to the river at Hanford may vary. Third, the discharge of the river basin may change, thus causing the concentration of chromium-51 to vary. Since all the samples at the Point Adams station were taken

in less than 25 hours, the data should be relatively unaffected by these factors. The close agreement between the predicted and extrapolated salinity values plus the close linear correlation of the data strongly suggest that dilution by sea water is the process reducing the chromium-51 concentration in saline, estuarine waters. This is not to imply that chemical changes may not occur, but only that chromium-51 remains in solution and is largely conservative in sea water.

The conservative nature of chromium-51 in sea water is indicated by its presence in the Columbia River plume. Gross, Barnes and Riel (1965) detected chromium-51 in surface sea water up to 115 km south of the river mouth in August 1963. Osterberg, Cutshall and Cronin (1965) traced the plume 350 kilometers to sea using chromium-51 as a radioactive tag. In February 1966 the author took part in a cruise of the R/V Yaquina in search of the Columbia River plume off the Washington coast. The sensitivity of the chromium-51 detection system allowed the plume to be followed 260km north from the river mouth to Cape Flattery at the entrance of the Strait of Juan de Fuca.

Dissolved zinc-65 shows no linear relationship with salinity. Its non-conservative nature is indicated in the next section by large percent particulate values, especially in more saline waters.

Particulate Radionuclides

The percentage of chromium-51 and zinc-65 in the particulate phase was calculated for each sample; results are shown in Figures 11 and 12a-c. Particulate chromium-51 increases with depth. Zinc-65 shows a similar, but not so regular trend.

At Astoria station the average values over all depths for chromium-51 and zinc-65 are 13.1 and 70.7 percent particulate, respectively. The same average values at Point Adams station are 21.6 and 79.6 percent for chromium-51 and zinc-65, respectively. The average surface values at Astoria station for chromium-51 and zinc-65 are 8.3 and 61.6 percent, respectively and for Point Adams station 14.7 and 76.6 percent, respectively. The average bottom values at Astoria station for chromium-51 and zinc-65 are 20.3 and 83.7 percent, respectively; those for Point Adams station are 31.7 and 86.2 percent, respectively.

Percent particulate values at Astoria station correlate well with turbidity (Figure 11). At Point Adams station percent particulate values are highest when salinities are at a maximum. The increase in percent particulate appears to be the result of tidal action working on the bottom and lifting sediments into suspension and/or flocculation of suspended and colloidal radionuclides.

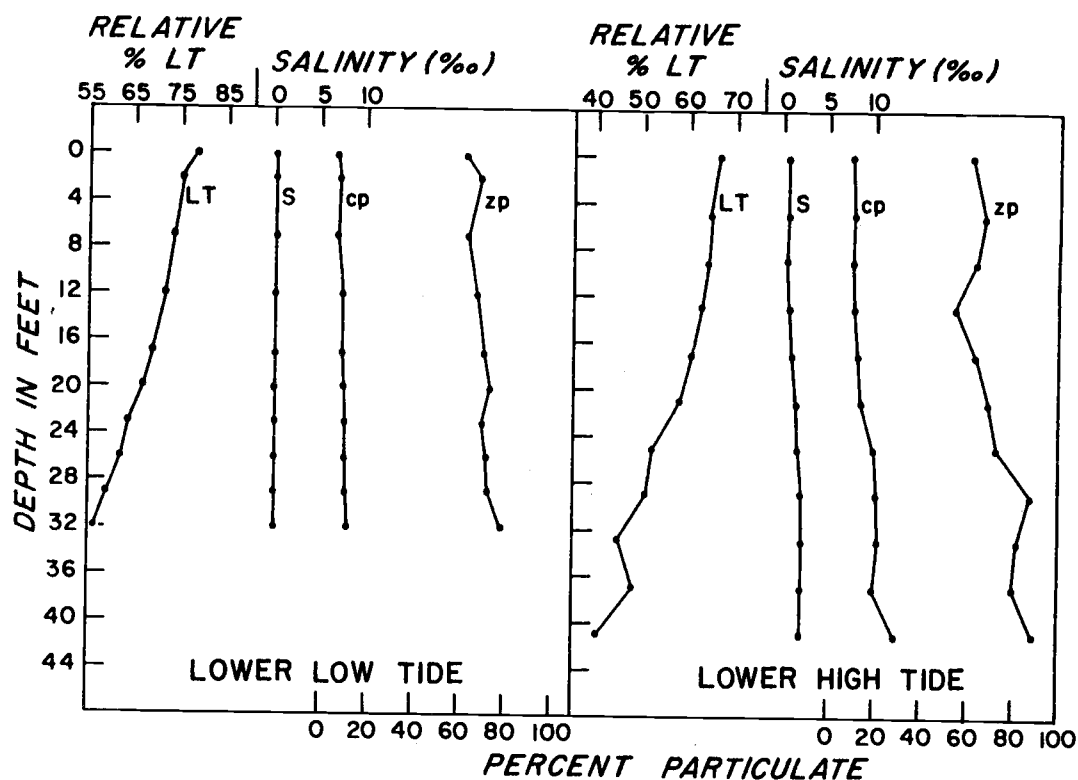Seymour and Lewis (1964) report average values of 19 and 69

Figure 11. Astoria station percent particulate profiles (legend, p. 36).
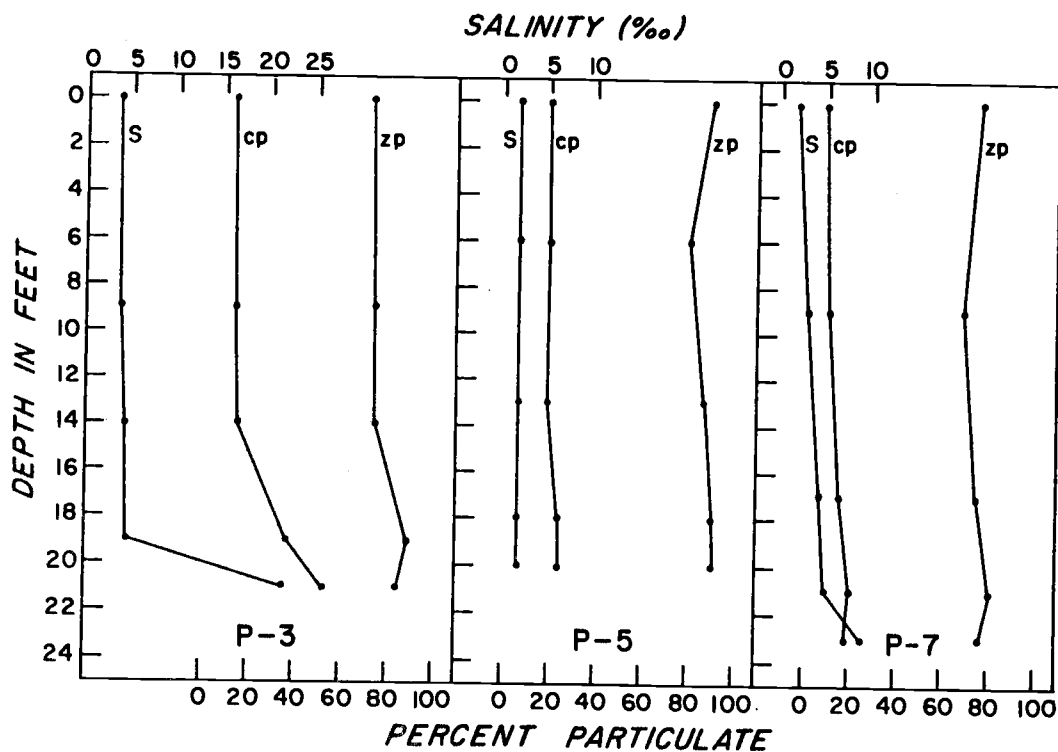
Figure 12a. Point Adams station percent particulate profiles (legend, p. 36).
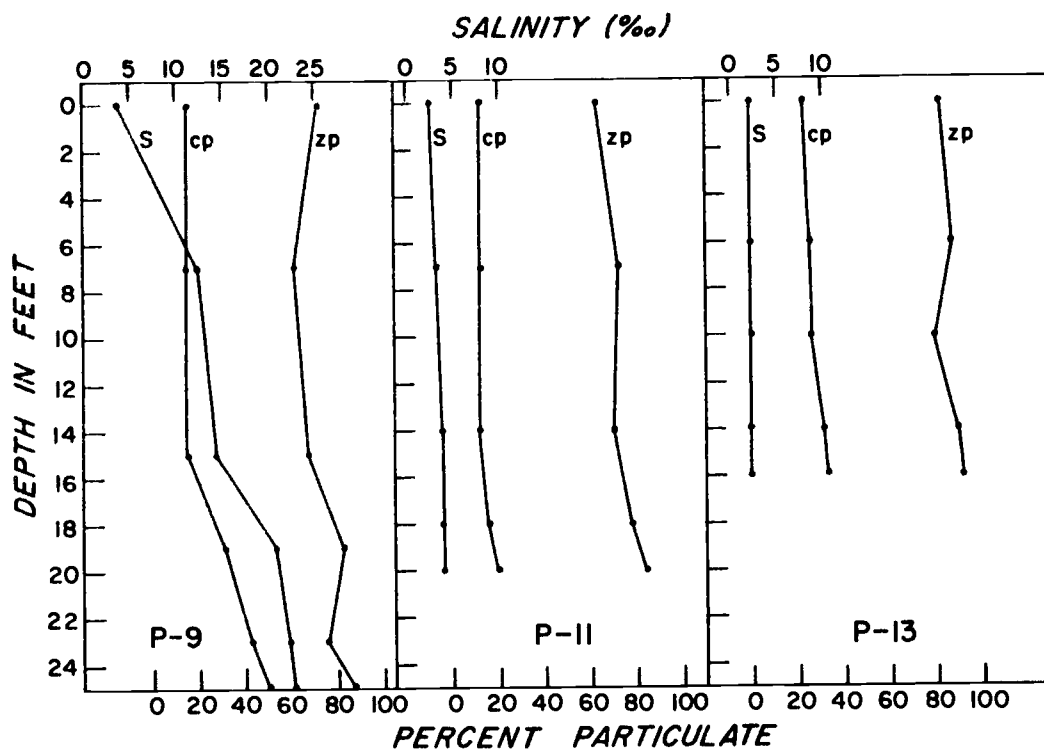
Figure 12b. Point Adams station percent particulate profiles (legend, p. 36).
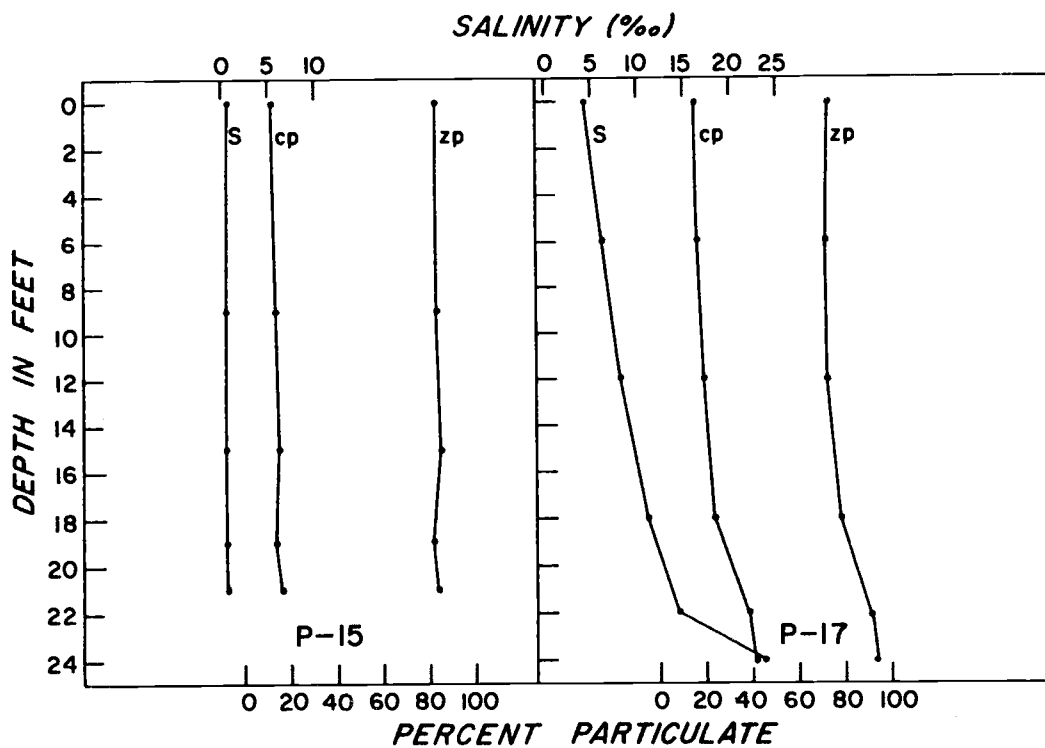
Figure 12c. Point Adams station percent particulate profiles (legend, p. 36).

percent particulate chromium-51 and zinc-65, respectively, in the

Columbia River Estuary. A 0.45 micron filter was used to separate

the particulate and dissolved fractions; this is the same size used

in this study. Particulate values reported in this study and those

reported by Seymour and Lewis (1964) are not directly comparable,

however, because depths are not indicated and their values are aver-

ages from the mouth upstream to Westport, Oregon (CRM 43.1).

Significant variations in chromium-51 and zinc-65 percent particulate

values do occur with depth and tidal stage (Figures 11 and 12a-c).

Even so, both studies show chromium-51 to be mostly dissolved and

zinc-65 mostly particulate in the river and estuary. Both chromium-

51 and zinc-65 appear to become more particulate with transport

downstream (Table 1). However, Perkins, Nelson and Haushild

(1966) report chromium-51 and zinc-65 to be 7.6 and 76 percent

particulate, respectively, at Vancouver compared to 13.1 and 70.7

percent, respectively at Astoria station as determined in this study.

The apparent loss of zinc-65 and gain of chromium-51 in the particu-

late phase is probably dependent on several factors which are not

necessarily of the same importance for different radionuclides.

The apparent loss of zinc-65 from the particulate phase with

transport downstream from Vancouver may be explained by a differ-

ence in filtering procedure. Perkins, Nelson and Haushild (1966)

used a 0.30 micron filter, thus their values of percent particulate

would tend to be higher than those reported by Seymour and Lewis

(1964) and those reported in this study. The depth average percent

particulate value of 13.1 for chromium-51 at Astoria station is not

characteristic of a fluvial system, but rather of an estuarine system.

This is evident from examination of depth profiles in Figure 11. The

depth average is greatly influenced by the larger percent particulate

values at lower depths which correlate with high salinities and thus

sea water influx. The average surface value of 8.3 percent at

Astoria is more comparable with Vancouver values as it more nearly

reflects a fluvial environment. The percent particulate values at

Point Adams (Figure 12a-c) are even more characteristic of an

estuarine environment as would be expected due to the station's closer

proximity to the ocean.

As will be seen in the next section, particulate radionuclides

are not distributed evenly through the particle size range, and

chromium-51 is more concentrated than zinc-65 in the surface sedi-

ments of the estuary. These facts make questionable the comparison

of depth average percent particulate values determined with different

filter pore sizes.

Zinc-65 to Chromium-51 Ratios

Zinc-65 to chromium-51 ratios were calculated for both sta-

tions. Two ratios were calculated for each sample: 1) the zinc-65

to chromium-51 ratio for the dissolved fraction and 2) the same ratio

for the particulate fraction. The ratios for Astoria station are listed

in Table 3 from surface to bottom down the column; salinities are

included. Figure 8a-b shows the data from which these ratios were

calculated. The dissolved ^{65}Zn to ^{51}Cr ratios show no significant

change with depth or tidal stage; the average value in both profiles

is the same. On the other hand, the particulate ratios in the high

tide profile tend to be smaller than in the low tide profile; the de-

crease is especially noticeable at lower depths. The ratios from

Point Adams show the same trends.

The particulate ^{65}Zn to ^{51}Cr ratio can be changed by two

processes, 1) physical decay in which the ratio increases and 2)

relative increase in concentration of one radionuclide in which case

the ratio either increases or decreases.

Increased salinity and turbidity at high tide reflect the influx

of sea water and an increase in particulate matter, respectively.

Increased turbidity may be accounted for by scouring of bottom sedi-

ments and/or flocculation by sea water. Both scouring and floccula-

tion could alter the particulate ^{65}Zn to ^{51}Cr ratio. Scouring would

cause an increase in the ratio if aged sediments were being sus-

pended. However, scouring could produce either an increase or a

decrease in the ratio by selective resuspension of zinc-65 or

chromium-51 rich sediments, respectively. The effect of

LOW TIDE PROFILE			HIGH TIDE PROFILE		
S‰	Particulate $\dfrac{Zn-65}{Cr-51}$	Dissolved $\dfrac{Zn-65}{Cr-51}$	S‰	Particulate $\dfrac{Zn-65}{Cr-51}$	Dissolved $\dfrac{Zn-65}{Cr-51}$
0	0.10	0.0046	0.50(sfc)	0.093	0.0064
0	0.13	47	0.60	0.091	55
0	0.13	55	0.37	0.10	66
0	0.14	65	0.68	0.071	67
0	0.15	62	0.98	0.081	68
0	0.15	54	1.38	0.084	60
0	0.12	58	1.62	0.081	68
0	0.14	63	1.90	0.076	28
0	0.12	55	2.04	0.082	53
0(btm)	0.13	0.0050	2.04	0.075	46
			2.10(btm)	0.072	0.0035
	$\overline{av}$ 0.13	av 0.0056		$\overline{av}$ 0.0806	av 0.0056

Table 3. Astoria station zinc-65 to chromium-51 ratios.

flocculation on the ratio is not known. The important role of floccu-
lation in estuarine shoaling processes and the need for further re-
search in this field are pointed out by Lockett (1963). Harris (1963)
concluded that 22 percent and possibly more of the total sediment
load of the Savannah River (South Carolina-Georgia border) is com-
pletely flocculated by a salinity of about 5‰ in from three to 12 hours.
The same author also pointed out that in addition to the colloidal
sediment load, flocculation may hasten the deposition of fine grained
suspended sediments.

By the decrease in the ratio it would appear that scouring of
aged sediments is not important here. Table 3 shows that the de-
crease in the ratio was caused by a large relative increase of par-
ticulate Cr-51 over Zn-65. This suggests that either colloidal and/
or suspended Cr-51 rich particles experienced flocculation and/or
Cr-51 rich sediments were resuspended. Nelson, Perkins and
Nielsen (1964) show Cr-51 concentrations to be 100 times that of
Zn-65 in Columbia River Estuary bottom sediments. Jennings (1966)
found Cr-51 to be more concentrated than Zn-65 in bottom sediments
of the same estuary. Particle size fractions of McNary Reservoir
(CRM 297.0) sediments show finer particle sizes (fine silt, 20
microns, to fine clay, 0.2 microns) have relatively high concentra-
tions of Cr-51 while the coarser particles (sand plus organic, > 62
microns) have high concentrations of Zn-65 (Nelson, Perkins and

Nielsen, 1964). Jennings (1966) found finer sediments more radio-active than coarser sediments in the estuary.

Influx of sea water near the bottom at high tide may cause resuspension of finer sediments, thus higher turbidity and a decrease in the particulate ^{65}Zn to ^{51}Cr ratio. Flocculation of fine suspended sediments and colloidal particles may also increase the turbidity and reduce the particulate ^{65}Zn to ^{51}Cr ratio. Fine sediments appear to be richer in Cr-51 than Zn-65, but the relative concentrations of these radionuclides are unknown in the colloidal sediment load.

Pause in Reactor Operations

Estuarine Radionuclide Levels

The quasi steady-state input of radioactivity from the Hanford reactors was interrupted by a temporary reactor operations shutdown during July and August 1966. Six reactors of varying radioactivity output were in operation when the three-day shutdown period began (Jaske, 1967). All six reactors were inoperative by July 9 and remained so until normal operations were resumed over a three-day period ending August 25 (ibid.). The exact levels of radioactivity released into the river during the shutdown period are not available; however, it can be said that shutdown levels were several orders of magnitude less than during normal operation (ibid.).

The interruption of the quasi steady-state input raised several questions which in turn prompted the sampling program. The rate of response of individual radionuclide levels in the estuary to the pause in input and the levels to which they might readjust were of interest. This information would also be of potential value for correlative purposes with radioactivity levels found in organisms routinely sampled in the estuary by other workers at this laboratory.

Sampling was begun on July 17 in Astoria, Oregon, from a pier immediately downstream from the interstate bridge. The position of the pier provided access to actively flowing river water rather than slack, tidal water. Samples were taken one foot below the surface twice a day at low tide in order to sample as pure river water as possible without picking up floating debris. Salinities ranged from 0 to 6.11‰ with an average of 2.27‰. Sampling continued on a twice daily basis until August 3. Sampling was resumed, as before, on August 30 and continued to September 23.

Samples were taken, prepared for counting, analyzed, and reduced in the same way as the Astoria and Point Adams samples (see p. 27-33).

Figure 13 is a plot of dissolved and particulate Cr-51 and Zn-65 concentrations versus time during and after the reactor shutdown period. The sampling began 8 days after all reactor operations
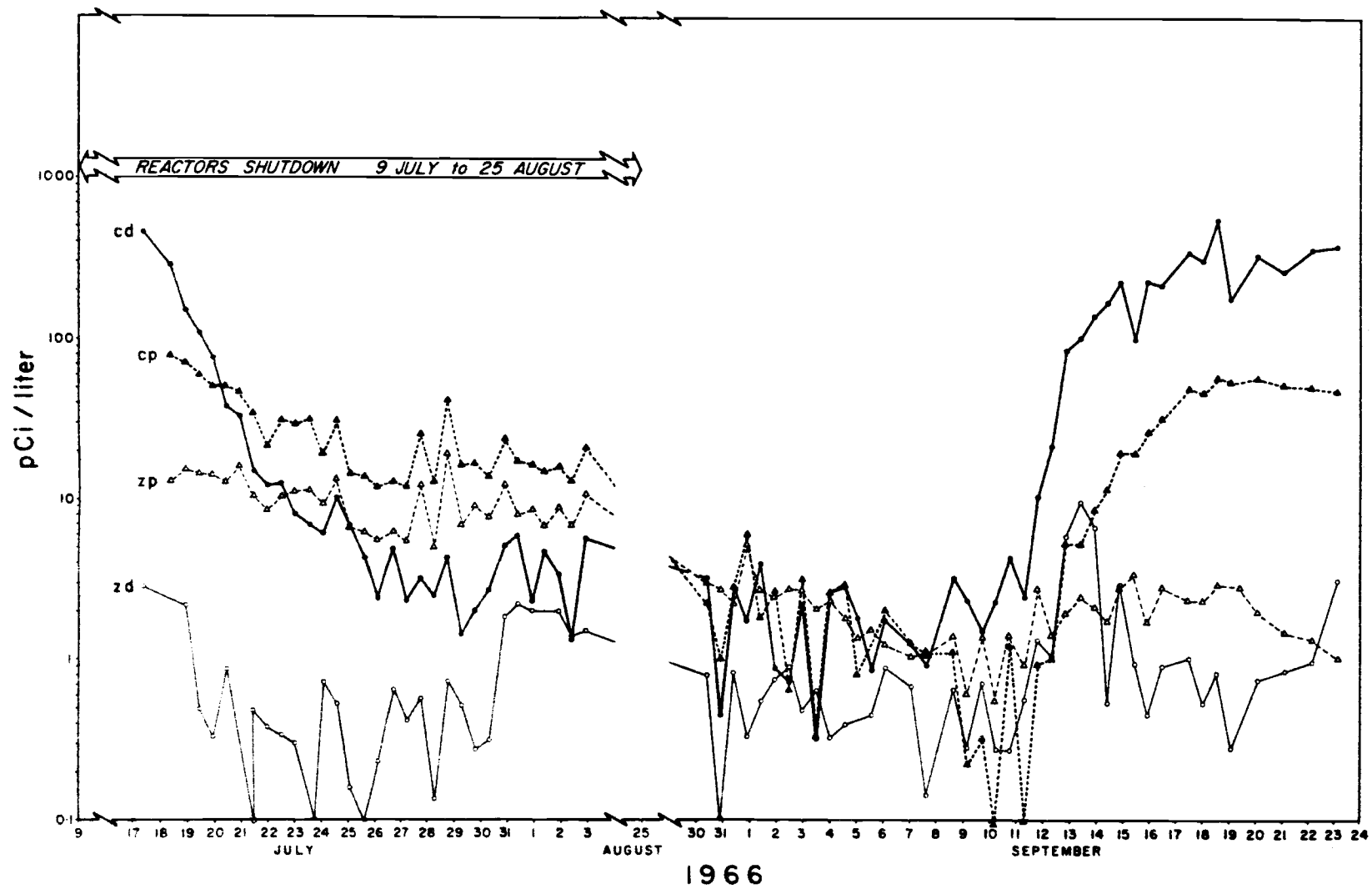
Figure 13. Radionuclide concentrations at Astoria, Oregon during pause in Hanford reactor operations (legend, p. 36).

had ceased. Radionuclide concentrations were already on the decrease when sampling was begun. Using dissolved Cr-51 values from the Astoria station (Figure 8) and river discharge values from Figure 1, along with the assumption of a steady state, the expected concentration of dissolved Cr-51 in early July can be calculated to be 700-800 pCi/liter. Extrapolation of the dissolved Cr-51 curve (cd) back to this expected range of concentration indicates that the curve began its descent about two days before sampling began. The normal decrease in river discharge during this period (Figure 1) would tend to increase the concentration of dissolved radionuclides; its effect on the suspended particulate phase would probably be to decrease its concentration due to decreased mean river velocity. These effects are thus superimposed on the shutdown curve.

Dissolved Cr-51 showed the greatest rate and relative magnitude of decrease in concentration. Dissolved Zn-65 showed a marked decrease followed by fluctuating levels of concentration. Particulate Cr-51 and Zn-65 concentrations decreased more gradually. Approximately 17 days after resumption of normal reactor operations particulate and dissolved Cr-51 concentrations rapidly began increasing from low "shutdown" levels. Dissolved Zn-65 showed an initial rapid increase followed, again, by fluctuation levels of concentration. Particulate Zn-65 increased gradually.

Temporary reductions in the radioactivity levels caused by the

approximately 47 day pause in reactor operations were of the order

of 1000 for dissolved Cr-51, 100 for particulate Cr-51, 10 for dis-

solved Zn-65 and 10 for particulate Zn-65. Both phases of Cr-51

and Zn-65 were approaching normal levels when sampling was com-

pleted.

The rapid rates of response of dissolved Cr-51 to the pause in

reactor operations is understandable considering its conservative

nature. The gradual decrease in both particulate Zn-65 and Cr-51

concentrations can be accounted for by mechanical equilibrium between

suspended sediments and bottom sediments, the latter possessing an

inventory of both Zn-65 and Cr-51 (Perkins, Nelson and Haushild,

1966, p. 247). The fact that dissolved concentrations dropped below

particulate concentrations in the case of Cr-51 also indicates the

conservative nature of Cr-51 and that the particulate levels were

maintained by resuspension of radioactive sediments.

Measurement of Flow Times

The flow time of the river from the reactors to Astoria can be

estimated from Figure 13 by considering the difference in time be-

tween the shutdown and the final passage of radioactivity past Astoria.

A similar estimate can be made by considering the difference in time

between the resumption of reactor operations and the initial passage

of radioactivity past Astoria. Chromium-51 should provide the

better estimate due to its low particulate association and conservative nature. Thus, further discussion will be limited to the dissolved Cr-51 curve (cd) in Figure 13.

Nelson, Perkins and Haushild (1966) used radionuclides introduced into the Columbia River by the Hanford operations to time the river flow between the reactors and Astoria. The only value given for the flow time to Astoria was 5.7 days during a period of very high discharge (657, 000 c.f.s.). This represents a minimal value of flow time.

The effects of longitudinal dispersion and changes in river discharge due to dams and natural variation, plus the fact that the reactors are spaced over a 15-mile reach of river, must be considered when estimating flow times (ibid.). The reactors were shutdown and reactivated over three-day periods. Thus, longitudinal concentration gradients were initially introduced into the river which were further modified by longitudinal dispersion. For these reasons the midpoints of the rapidly falling and rising portions of the dissolved Cr-51 curve in Figure 13 were chosen as the dates on which to base the flow time estimates. These dates are July 20 and September 12 for the falling and rising portions of the curve, respectively. Since all reactors were inoperative by July 9 after a three day shutdown period, July 8 was chosen as the average shutdown date. With similar reasoning, August 24 was chosen as the average resumption

date.

Using the above dates, the estimated flow times for the river between the reactors and Astoria are 12 days for the period July 8 to July 20 and 19 days for the period August 24 to September 12. The average discharge at Astoria during the period July 8 to July 20 was approximately 290,000 c.f.s. and during the period August 24 to September 12 it was approximately 130,000 c.f.s. (Figure 1). Direct comparison of the flow times estimated here and those of Nelson, Perkins and Haushild (1966) cannot be made due to large differences in discharge. As mentioned above, only one value of 5.7 days at 657,000 c.f.s. discharge was measured (ibid.). However, flow times extrapolated to Astoria from Vancouver data (ibid.) and those estimated here agree closely considering the numerous variables mentioned above. Twelve and nineteen days appear to be credible estimates of the flow times for the Columbia River under the prevailing discharges.

SUMMARY

Method Evaluation

The integration of salinometer, transmissometer and pump intake onto a rigid framework is a useful and convenient method for sampling the river at any desired depth. The unitized approach provides quick, precise, in situ measurement of salinity, temperature and turbidity while also providing a water sample for radio-analysis. Concentration of the radioactivity by precipitation in the field reduces the volume of each sample from several liters to less than 500 ml. Immediate storage and transportation of samples to the laboratory are greatly facilitated by the reduction in sample size. Except for the transmissometer failure at Point Adams the system worked without difficulty. Keeping the tether line vertical was not the problem it was anticipated to be. The taut, weighted tether line actually acts as a second anchor and provides extra stability to the boat. As mentioned previously, sample sizes are determined by the maximum volume of water filterable before clogging of the filter. Sample sizes varied from 4 to 12 liters in the estuary; the average sample is between 6 and 7 liters. Of the dissolved radionuclides, only chromium-51 and zinc-65 are in sufficient concentration to be measured with any precision in samples

of this size range. Of the particulate radionuclides, only chromium-51, zinc-65 and scandium-46 are easily detectable. Particulate manganese-54 and cerium-144 are at the limits of measurement. Sample sizes of 18 to 20 liters in fresh water and up to 25 liters in saline water are indicated for the future. Larger sample sizes could be achieved by using two successive filters or a single filter of larger diameter.

Recovery of dissolved chromium-51 by the precipitation method has been shown to be quantitative (Cutshall, Johnson and Osterberg, 1966). In several large estuarine water samples the dissolved radionuclides were concentrated from paired aliquots by both the evaporation and precipitation methods. The evaporation method can be assumed to be quantitative for the gamma emitting radionuclides of interest in this study. Comparing the activity of each radionuclide in the precipitate to that in the evaporation residue allows the calculation of an efficiency factor for each radionuclide. Actual estuarine water samples, instead of spiked samples, were used to avoid any question as to the comparability of laboratory and field conditions. It is obvious that to duplicate field conditions in the laboratory the chemical form of each radionuclide in the environment must be known. Even if such information were available the direct approach of using unspiked estuarine water is more valid. The calculated efficiency factor for chromium-51 was greater than 98%. The

samples used for determining efficiency factors were taken in mid

July 1966 during the period when the Hanford reactors were shut-

down. The concentration of dissolved zinc-65, along with the other

radionuclides, dropped below accurately measurable values. Effi-

ciency factors for zinc-65 and other radionuclides were not obtain-

able. Future sampling will allow calculation of efficiency factors

for zinc-65 and other radionuclides.

It is possible that pumping water samples through an impeller

type pump may introduce a bias into the samples. Dissolved species

would be unaffected, but the distribution of particles could conceiv-

ably be altered by radial acceleration in the pump or by turbulence

generated at the surfaces of the intake, hosing, pump, etc. How-

ever, samples pumped in succession as fast as the filters could be

changed indicate that significant variations in particulate radionuclide

concentration do not occur.

<center>Experimental</center>

Dissolved zinc and chromium show homogenous vertical con-

centrations in the fluvial estuary. However, with the intrusion of

sea water at lower depths followed by mixing at the sea water-river

water interface a pronounced, negative concentration gradient is

developed due to replacement and dilution by sea water.

Particulate zinc, chromium and scandium normally show a

positive concentration gradient which is increased by sea water

influx. The spacial distribution of suspended river sediments is

anistropic, this condition being most pronounced with larger sized

sediments. Colloidal, clay and silt sized sediments (diameters less

than 62 microns) can be considered in most streams to be uniformly

distributed (Sayre, Guy and Chamberlain, 1963). Sediments of sand

size and larger show an increase in concentration with depth, the

gradient increasing sharply near the bottom (Gilluly, Waters and

Woodford, 1959; ibid.). Thus, a positive gradient of particulate

radionuclides would be expected in the estuary. The increase in

particulate radioactivity near the bottom during periods of sea water

intrusion can result from at least two processes, scouring and re-

suspension by the tidal prism and/or flocculation of colloidal and

very fine sediments by saline water. Most likely both processes are

acting, but their relative magnitudes are unknown. Flocculation is

inhibited while resuspension of bottom sediments is enhanced by

turbulence. Thus, the turbulence generated near the bottom by

tidal energy may favor scouring and resuspension in this area while

flocculation may be more important in less turbulent regions.

While the lateral, as well as vertical, distribution of dissolved

radioactivity is characteristically uniform upstream from the estu-

ary (Perkins, Nelson and Haushild, 1966), this appears not to be

so in the estuary. Neal (1965) found that the greater flood flow

occurs on the Washington side, while the greater ebb flow occurs on the Oregon side of the estuary. It could be expected from this situation that the Washington side of the estuary would have higher salinities and lower radioactivity concentrations than the Oregon side. However, Seymour and Lewis (1964) found higher concentrations of dissolved and particulate zinc-65 and chromium-51 on the Washington side of the estuary. Further study of the lateral distribution of dissolved and particulate radioactivity is indicated, and could be accomplished by the methods used in this study.

The river discharges, during the two periods in which flow times were measured, were, at 290,000 c.f.s., 17% lower than the 15 year mean and, at 130,000 c.f.s., 13% lower than the 15 year mean. Thus, the 19 day flow time measured at 130,000 c.f.s. is a maximal value. The projected normalization of river discharge with the completion of all feasible storage in the Columbia River basin (Lockett, 1963) would also tend to normalize flow times. The normalization of flow times and the increased sedimentation behind dams should tend to increase the radioactivity inventory in the river system. The knowledge of flow times could be important in the event of an accidental release into the river of extremely hazardous levels of radioactivity. Such countering measures as impoundment of the radioactivity in a reservoir would be greatly facilitated by such knowledge.

Chromium-51 is largely conservative in both fresh and marine water, becoming associated with particles to a relatively small extent. Due to its conservative nature, low biological utilization and comparatively short half-life, the majority of chromium-51 should respond to the diluting processes of advection, diffusion and time which tend to reduce its potential as a radiation hazard. However, the portion of chromium-51 which is particulate, although a small part of the total, has a significant activity due to the high concentration of chromium-51 released into the river. Thus, in areas of sedimentation such as reservoirs, estuaries and quiet water, a radiation hazard from chromium-51 may exist. Chromium-51 is most concentrated on finer sediments which tend to remain in suspension longer; this fact tends to reduce the radiation hazard of chromium-51 due to concentration by sedimentation and counterbalances the greater sorption capacity of finer sediments.

Zinc-65 is largely particulate in both fresh and marine water. Desorption of zinc-65 from particulate matter upon entering saline water is unimportant (Johnson, Cutshall and Osterberg, 1967). Due to its non-conservative nature, high biological utilization and comparatively long half-life, zinc-65 possesses a high potential as a radiation hazard. The particulate nature of zinc-65 suggests its concentration in areas of sedimentation. Concentration of zinc-65 by food organisms provides radiation exposure not only to themselves

but to predators, including man. Biological concentration of radio-

activity tends to increase many fold the hazard as would exist from

only external exposure to, or even ingestion of, contaminated water

or sediments.

BIBLIOGRAPHY

Adamson, Arthur W. 1960. Physical chemistry of surfaces. New York, Interscience. 629 p.

Barnes, C. A. and M. G. Gross. 1966. Distribution at sea of Columbia River water and its load of radionuclides. In: Symposium on the disposal of radioactive wastes into seas, oceans and surface waters, Vienna, 1966. p. 291-302. (International Atomic Energy Agency. STI/PUB/126)

Burt, Wayne V. and W. Bruce McAlister. 1959. Recent studies in hydrography of Oregon estuaries. Research Briefs of the Fish Commission of Oregon 7:14-27.

Chakravarti, D. et al. 1964. Analyses of radionuclides of biological interest in Pacific waters. Nature 203:571-573.

Clanton, U.S. and E. F. Gloyna. 1964. Radioactivity transport in water. Sorption and release of radioactivity by sediments of the Guadalupe River. Austin. 62 p. (Texas. University of Texas. Department of Civil Engineering. Technical report-6)

Columbia Basin Inter-Agency Committee. Hydrology Subcommittee. 1962. River mile index-main stem Columbia River. Portland. 17 p.

Cotton, F. Albert and Geoffrey Wilkinson. 1966. Advanced inorganic chemistry. New York, Interscience. 1136 p.

Cutshall, Norman, Vernon Johnson and Charles Osterberg. 1966. Chromium-51 in sea water: chemistry. Science 152:202-203.

Foster, R. F. and R. L. Junkins. 1960. Off-project exposure from Hanford reactor effluent. 45 p. (U.S. Atomic Energy Commission. HW-63654 Rev.)

Frederick, Lawrence C., I. Lauren Larsen and Susan Borden. 1965. Radionuclide spectrum analysis. In: Ecological studies of radioactivity in the Columbia River Estuary and adjacent Pacific. Corvallis. p. 120-129. (Oregon. State University. Dept. of Oceanography. Progress report 1 March 1964 through

1 July 1965 submitted to the U. S. Atomic Energy Commission contract AT(45-1) 1750)

Frederick, Lawrence Churchill. 1967. Dispersion of the Columbia River plume based on radioactivity measurements. Ph. D. thesis. Corvallis, Oregon State University. 134 numb. leaves.

Freiling, E. C. and N. E. Ballou. 1962. Nature of nuclear debris in sea-water. Nature 95:1283.

Friend, Albert G. 1963. The aqueous behavior of strontium-85, cesium-137, zinc-65 and cobalt-60 as determined by laboratory type studies. In: Transport of radionuclides in fresh water systems. p. 43-60. (U.S. Atomic Energy Commission. TID-7664)

Friend, Albert G. et al. 1965. Behavior of certain radionuclides released into freshwater environments--annual report 1959-1960. Washington. 90 p. (U.S. Public Health Service. Publication no. 999-RH-13)

Gilluly, J., A. C. Waters and A. O. Woodford. 1959. Principles of geology. 2d ed. San Francisco, Freeman. 534 p.

Glover, Robert E. 1964. Dispersion of dissolved or suspended materials in flowing streams. Washington. 32 p. (U.S. Geological Survey. Professional paper 433-B)

Gross, M. Grant, Clifford A. Barnes and Gordon K. Riel. 1965. Radioactivity of the Columbia River effluent. Science 149: 1088-1090.

Gross, M. Grant. 1966. Distribution of radioactive marine sediments derived from the Columbia River. Journal of Geophysical Research 7:2017-2021.

Hansen, Donald V. and Maurice Rathay, Jr. 1966. New dimensions in estuary classification. Limnology and Oceanography 11: 319-326.

Harris, R. W. 1963. Hydraulics of the Savannah Estuary. In: Studies of the fate of certain radionuclides in estuarine and other aquatic environments, ed. by Julius J. Sabo and Paul H. Bedrosian. Washington. 10 p. (U.S. Public Health Service. Publication no. 999-R-3)

Haushild, W. L. et al. 1966. Radionuclide transport of the Columbia River. Portland, Oregon, U. S. Dept. of the Interior, Geological Survey. 188 p.

Hickson, R. E. and F. W. Rodolf. 1951. History of Columbia River jetties. In: Proceedings of the First Conference on Coastal Engineering, Long Beach, California. p. 283-298.

Jaske, Robert T. 1967. Research Associate, Battelle Memorial Institute, Environmental and Radiological Science Department. Personal communication.

Jennings, Charles David. 1966. Radioactivity of sediments in the Columbia River Estuary. Master's thesis. Corvallis, Oregon State University. 62 numb. leaves.

Johnson, Vernon, Norman Cutshall and Charles Osterberg. 1967. Retension of Zinc-65 by Columbia River sediments. Water Resources Research 3:99-102.

Kaufman, Warren J. and Peter C. Klingerman. 1963. Nature and disposition of sediment sorbed radionuclides entering San Francisco Bay. In: Transport of radionuclides in fresh water systems. p. 149-159. (U. S. Atomic Energy Commission. TID-7664)

Kautsky, H. 1966. Possible accumulation of discrete radioactive elements in river mouths. In: Symposium on the disposal of radioactive wastes into seas, oceans and surface waters, Vienna, 1966. p. 163-175. (International Atomic Energy Agency. STI/PUB/126)

Kolthoff, I. M. and E. B. Sandell. 1952. Textbook of quantitative inorganic analysis. 3d ed. New York, Macmillan. 759 p.

Lockett, John B. 1963. Phenomena affecting improvement of the lower Columbia Estuary and entrance. Portland, Oregon. U. S. Army Engineer Division, North Pacific. 51 p.

Neal, Victor T. 1965. A calculation of flushing times and pollution distribution for the Columbia River Estuary. Ph. D. thesis. Corvallis, Oregon State University. 82 numb. leaves.

Nelson, J. L., R. W. Perkins and J. M. Nielsen. 1964. Progress in studies of radionuclides in Columbia River Sediments. 21 p. (U. S. Atomic Energy Commission. HW-83614)

Nelson, Jack L., R. W. Perkins and W. L. Haushild. 1966. Determination of Columbia River flow times downstream from Pasco, Washington, using radioactive tracers introduced by the Hanford reactors. Water Resources Research 2:31-39.

Nielsen, J. M. 1963. Behavior of radionuclides in the Columbia River. In: Transport of radionuclides in fresh water systems. p. 113-125. (U.S. Atomic Energy Commission. TID-7664)

Osterberg, Charles, Andrew G. Carey and Herbert Curl. 1963. Acceleration of sinking rates of radionuclides in the ocean. Nature 200:1276-77.

Osterberg, Charles, L. D. Kulm and John V. Byrne. 1963. Gamma emitters in marine sediments near the Columbia River. Science 139:916-917.

Osterberg, Charles, Norman Cutshall and John Cronin. 1965. Chromium-51 as a radioactive tracer of Columbia River water at sea. Science 150:1585-1587.

Pattullo, June and Warren Denner. 1965. Processes affecting seawater characteristics along the Oregon coast. Limnology and Oceanography 10:443-450.

Perkins, R. W., J. L. Nelson and W. L. Haushild. 1966. Behavior and transport of radionuclides in the Columbia River between Hanford and Vancouver, Washington. Limnology and Oceanography 11:235-248.

Pickering, R. J. et al. 1966. Radioactivity in bottom sediments of the Clinch and Tennessee Rivers. In: Symposium on the disposal of radioactive wastes into seas, oceans and surface waters, Vienna, 1966. p. 33-35. (International Atomic Energy Agency. STI/PUB/126)

Pritchard, D. W. 1952. Estuarine hydrography. In: Advances in geophysics. New York, Academic Press. p. 243-280.

_____. 1955. Estuarine circulation patterns. Proceedings of American Society of Civil Engineers 81 (separate 717): 1-11.

Reynolds, Tom D. 1963. Sorption and release of radionuclides by sediments. In: Transport of radionuclides in fresh water

systems. p. 127-148. (U.S. Atomic Energy Commission. TID-7664)

Sayre, W. W. H. P. Guy and A. R. Chamberlain. 1963. Uptake and transport of radionuclides by stream sediments. Washington. 35 p. (U.S. Geological Sruvey. Professional paper 433-A)

Seymour, Allyn H. and Gary B. Lewis. 1964. Radionuclides of Columbia River origin in marine organisms, sediments, and water collected from the coastal and offshore waters of Oregon and Washington, 1961-1963. Seattle, University of Washington, Laboratory of Radiation Biology. 69 numb. leaves. (Mimeographed)

Silker, W. B. 1964. Variations in elemental concentrations in the Columbia River. Limnology and Oceanography 9:540-545.

_____. 1965. Removal of fission products from contaminated water by flocculation methods. In: III. Radiological chemistry Hanford radiological sciences research and development annual report for 1964. p. 3.47-3.50. (U.S. Atomic Energy Commission. BNWL-36 III)

Toombs, George L. and John G. Bailey. 1963. Lower Columbia River environmental radiological survey in Oregon, 1961-1963. Portland, Oregon, State Board of Health, Division of Sanitation and Engineering. 48 p.

van Olphen, H. 1963. An introduction to clay colloid chemistry. New York, Interscience. 301 p.

Waldichuk, Michael. 1961. Sedimentation of radioactive wastes in the sea. Nanaimo, B. C. 24 p. (Canada. Fisheries Research Board, Circular 59)

Wang, C. H. and David L. Willis. 1965. Radiotracer methodology in biological science. Englewood Cliffs, New Jersey, Prentice Hall. 382 p.

Wilson, R. H. (ed.) 1963. Evaluation of radiological conditions in the vicinity of Hanford for 1962. 186 p. (U.S. Atomic Energy Commission. HW-76526)

Wilson, R. H. (ed.) 1965. Evaluation of radiological conditions
in the vicinity of Hanford, January-June 1965. 29 p. (U.S.
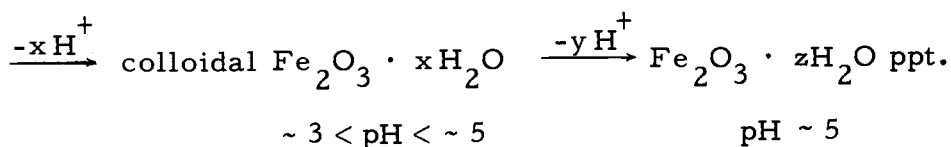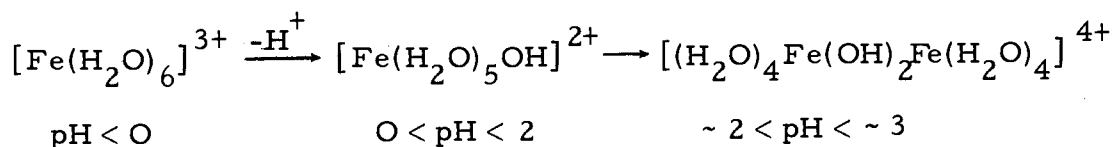Atomic Energy Commission. BNWL-165)(Microfiche)

APPENDIX

APPENDIX

The precipitation of Fe^{3+} from ammoniacal medium is commonly written:

$$Fe^{3+} + 3\ OH^- \longrightarrow Fe(OH)_3$$
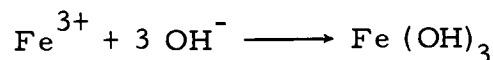
This formulation and the term ferric hydroxide precipitate is not rigorously correct. Strictly speaking, the precipitation of Fe^{3+} is by the formation of the hydrous oxide $Fe_2O_3 \cdot xH_2O$ through the stages (Cotton and Wilkinson, 1966):

$$[Fe(H_2O)_6]^{3+} \xrightarrow{-H^+} [Fe(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$$

$$pH < O \qquad\qquad O < pH < 2 \qquad\qquad \sim 2 < pH < \sim 3$$

$$\xrightarrow{-xH^+} \text{colloidal } Fe_2O_3 \cdot xH_2O \xrightarrow{-yH^+} Fe_2O_3 \cdot zH_2O \text{ ppt.}$$

$$\sim 3 < pH < \sim 5 \qquad\qquad pH \sim 5$$

Accordant with the existence of ferric oxide at pH greater than 5 is its extremely small solubility product of 10^{-36} or less (Kolthoff and Sandell, 1952). The above formulation elucidates many of the phenomena associated with the formation of hydrous ferric oxide. The precipitate is an amorphorous, highly voluminous, flocculated colloid possessing no definite stoichiometric composition. It consists of the metal oxide with variable amounts of water. As shown in the

above equation, hydroxo bridges form during the precipitation.

The colloidal nature of ferric oxide is a result of its extremely small solubility. The pronounced adsorptive properties of hydrous ferric oxide can be explained by the formation of colloidal particles with the associated large surface area development and electrical double layer. In weakly acid medium the colloid particles have a positive surface charge due to the adsorption of protons. With an excess of ammonia the particles would be negative due to adsorption of hydroxyl ions. Thus in acid medium adsorptive coprecipitation of anions is observed, and in basic medium cations are coprecipitated. It is by these adsorptive processes that hydrous ferric oxide can act as a scavenger for both types of dissolved ionic species.