

AN ABSTRACT OF THE THESIS OF

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Title: ANTIMONY-124 IN THE LOWER COLUMBIA RIVER

Abstract approved: Redacted for Privacy  
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Water samples were collected in the Columbia River from Bonneville, Oregon, to Pt. Adams, Oregon, in early spring 1969. After filtration, the radioactivity was concentrated by ferric hydroxide scavenging. Antimony-124 activity was determined by well detection system and by coincidence counting, a system assembled for this research. Chromium-51, scandium-46, and zinc-65 activities were determined by well detection also.

Most of the  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  activity was associated with the soluble phase, while most of the  $^{65}\text{Zn}$  and  $^{46}\text{Sc}$  activity was associated with the particulate phase. The concentration of activity did not vary appreciably on any one date.

Although the coincidence system had a lower minimum detection level and less sample standard deviation than the well detection system, the low levels of  $^{124}\text{Sb}$  activity precluded precise

determination of its activity with counting precision less than 20%.

The ratio of soluble  $^{51}\text{Cr}$  to soluble  $^{124}\text{Sb}$  did not vary significantly in the region that was studied. However, flow rate determination of the Columbia River would be unreliable during the summer freshet because of the large uncertainty in time due to the standard deviation of the  $^{51}\text{Cr}$  to coincidence counted  $^{124}\text{Sb}$  ratio. Flow rate of the Columbia River summer plume should be possible to estimate using  $^{51}\text{Cr}/^{124}\text{Sb}$  ratios.

The average transport rate past Vancouver, Washington was calculated to be 1.5 curies per day (Ci/d) for  $^{124}\text{Sb}$ , 200 Ci/d for  $^{51}\text{Cr}$ , 11 Ci/d for  $^{46}\text{Sc}$ , and 10 Ci/d for  $^{65}\text{Zn}$ ; the corresponding oceanic equilibrium activities were 140 Ci of  $^{124}\text{Sb}$ , 8000 Ci of  $^{51}\text{Cr}$ , 1300 Ci of  $^{46}\text{Sc}$ , and 3500 Ci of  $^{65}\text{Zn}$ .

Antimony-124 in the  
Lower Columbia River

by

Stephen Van Wyck Pope

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# ANTIMONY-124 IN THE LOWER COLUMBIA RIVER

## INTRODUCTION

With the advent of nuclear testing and reactors, the environmental level of radioactivity has increased, not only in amount but also in variety of radionuclides. This higher level of radioactivity can be utilized to trace the movement of an element through the different parts of the environment, depending on the particular radioisotope. Marine radioecology is concerned with the dispersion and interaction of radionuclides in and with the total marine environment. This includes not only the behavior of the radionuclides but also the effect of their radiations upon the individual organisms and communities (Mauchline and Templeton, 1964). The dispersion and interaction are manifested by the different amounts accumulated in the various individual environments, as represented by organisms, sediments, and soluble and particulate phases in the hydrosphere.

Antimony-124 is believed to remain primarily in the soluble phase of the aqueous environment. With this property, it could be used as a tracer of water mass movements. Another radionuclide, chromium-51, is also soluble. The half-lives of  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  are 27.8 and 60 days, respectively. If both could be measured precisely, then a value of elapsed time could be given to the water from which they were sampled, based on a changing ratio that is a function of

their different decay rates. However, Frederick (1966) states that  $^{124}\text{Sb}$  is not as conservative as  $^{51}\text{Cr}$  in the Columbia River plume in the open ocean, based on a difference in velocity computed between two stations with each radionuclide. This conclusion may not be valid, since  $^{124}\text{Sb}$  is present in such small amounts that precise measurements of its activity is a major problem. Because only one pair of measurements was made, the low velocity computed from  $^{124}\text{Sb}$  by Frederick may have been due to counting statistical variation and not physical effects.

The purpose of this thesis is to adapt a method of analysis that will determine the radioactivity of  $^{124}\text{Sb}$  more precisely, and to contrast its physical behavior with other radionuclides in different aquatic environments.

## BACKGROUND

### The Columbia River

The source of the Columbia River is Lake Columbia in British Columbia, Canada, about 780 m above sea level. It merges with the Pacific Ocean approximately 1950 km downstream. The Columbia and its principal tributaries, the Snake, Pend Oreille-Clark Fork, Kootenai, and Willamette Rivers, drain an area of about 671,000 square kilometers, 85% of which is in the United States. This area includes most of Idaho, Washington, and Oregon, a large part of western Montana, and British Columbia, and small portions of Utah, Nevada and Wyoming.

The Columbia River Basin is a region of many geological formations, ranging in age from Pre-Cambrian to Recent. The major framework is divided into four primary features; in the east are the Rocky Mountains and their northwest-southeast trend and narrow cut valleys in Canada. Next are the basaltic plateaus, which include the crescent-shaped Snake River Plain and the Columbia Plateau. These were formed by lava flows and are deeply cut by gorges of major streams and rivers. The Cascade Mountains are west of the Columbia Plateau. Finally, there is the southern part of the Puget Trough between the Cascade and Coastal Ranges, which is drained by the Willamette and Cowlitz Rivers. The mineral resources are associated

mainly with the igneous formations. The sites of the principal mineral resources are in the Coeur d'Alene Mountains in northern Idaho and the copper-producing area near Butte, Montana. Some minerals that are mined include copper, lead, zinc, gold, silver, and antimony.

### Occurrence of Antimony

Antimony is present in very small amounts in various portions of the earth's crust. In limestone, sandstone and igneous rocks the concentration is around 0.2 parts-per-million (ppm); in some shales and oceanic red clays it may be as high as one to two ppm. Slates may vary from 0.3 to 1.9 ppm (Onishi and Sandell, 1955). Soils may range from two to ten ppm (Bowen, 1966). The crustal average is about 0.2 ppm (Taylor, 1964).

Of the approximately 112 minerals of antimony, stibnite ( $\text{Sb}_2\text{S}_3$ ) is the principal mineral for mining. Other sulfides, principally tetrahedrite ( $\text{Cu}_8\text{Sb}_2\text{S}_7$ ) and the five oxidation products of stibnite, are less important. The antimony content of ores ranges from 20% to 50%. Tetrahedrite is the main antimony ore in the Coeur d'Alene region. Stibnite is usually found in veins of quartz and is associated with many minor antimony-bearing minerals. Antimony often occurs in some localities associated with ores of copper, lead, mercury, tungsten, silver or gold and is recovered

from the milling or smelting of these ores. Its presence can interfere with efficient separation of the desired metal.

### Solubility and Aqueous Chemistry of Antimony Compounds

The inorganic compounds of antimony are generally insoluble in water. Antimony trioxide is the most soluble compound that occurs naturally and does not decompose in water; it has a solubility of  $1.6 \times 10^{-2}$  g/l (Fairhall, 1947); stibnite, the principal mining mineral, has a solubility of  $1.75 \times 10^{-3}$  g/l in cold water and decomposes in hot water. The other chloride and oxide compounds are either very slightly soluble or insoluble. The SbIII ion has a great tendency to hydrolyze, and cationic compounds are mostly antimonyl,  $\text{SbO}^+$  (Cotton and Wilkinson, 1962). Antimony salts form complexes with various acids in which the Sb forms the nucleus of an anion, such as  $\text{Sb}(\text{SO}_4)_2^-$ , or  $\text{SbCl}_6^-$ .

An Eh-pH diagram shows mineral stability relations of an element for a range of oxidation potentials and hydrogen ion concentrations. According to an Eh-pH diagram, one could assume Sb in a natural aqueous environment with a pH range of six to eight to be either anionic or uncharged. By using a series of anion, cation and anion-cation exchange resins, Nelson, Perkins and Nielson (1966) found these two chemical forms are predominant in the Columbia River. Nelson and his co-workers hypothesized that uncharged

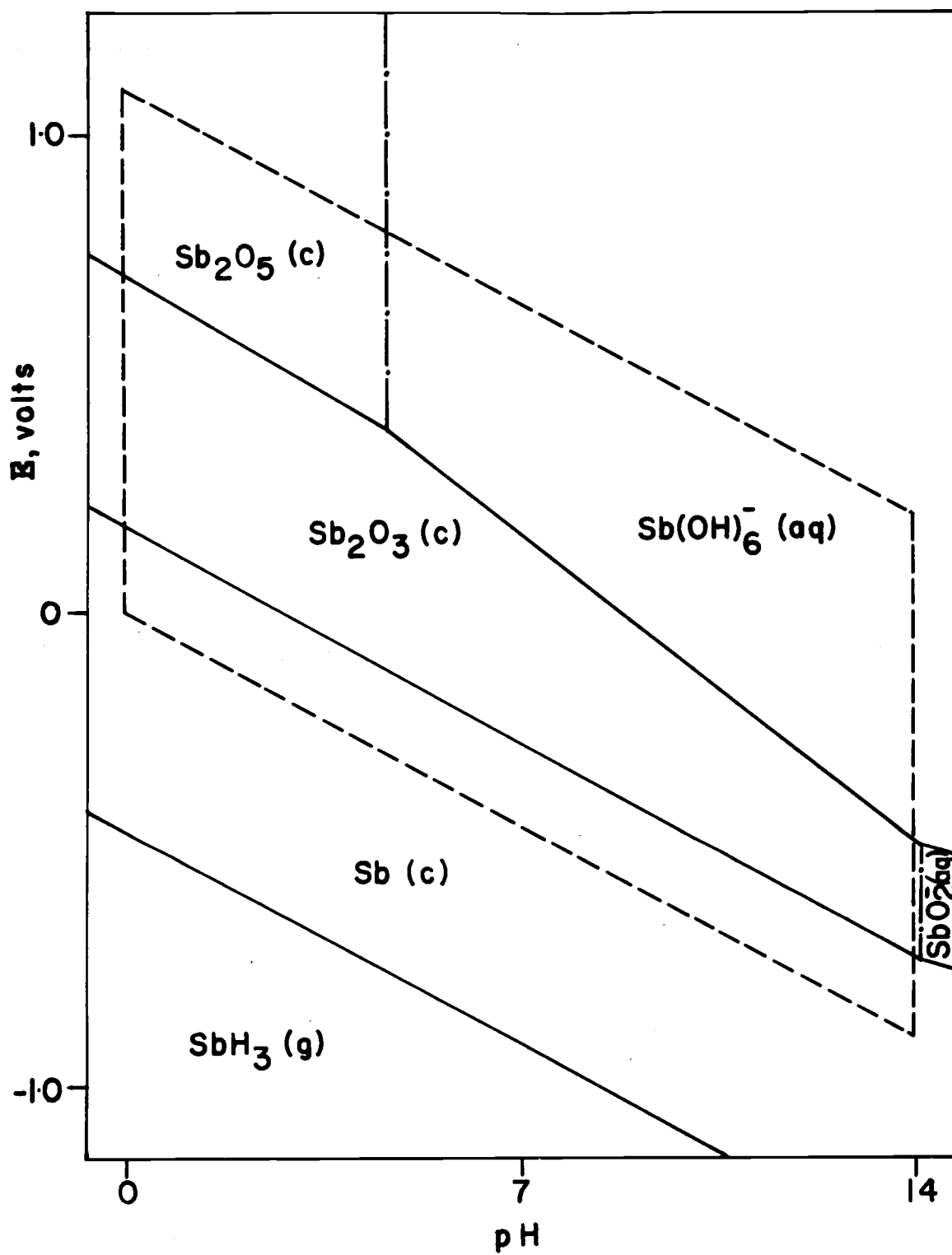


Figure 1. Eh-pH diagram for antimony (Campbell and Whitaker, 1969).

radionuclides are possibly complexed species, either associated with biota and/or organic derivatives of biota in the river. From the Eh-pH diagram, uncharged antimony could also be  $\text{Sb}_2\text{O}_3$ .

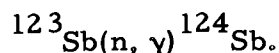
Trace elements in natural water may be associated with either or both the soluble or particulate fractions that are suspended in the water. A molecule can be physically classified according to size as particulate, colloidal, or soluble. The intermediate colloidal size range is between 10 and  $10^4$  Angstroms ( $\text{\AA}$ ). Sizes larger than  $10^4 \text{\AA}$  are particulate and those smaller than  $10 \text{\AA}$  are soluble. In this research, an arbitrary division is made at  $4500 \text{\AA}$ , or 0.45 microns, that separates the soluble and particulate. In the soluble phase, the element may be anionic, cationic or uncharged. In the particulate phase, it is adsorbed to material suspended in the water.

#### Antimony-124

There are several radioactive isotopes of antimony ranging in mass from 115 to 135. The stable isotopes are  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ ; they are 57.25% and 42.75% abundant, respectively. Most of the radionuclides have relatively short half-lives; two long-lived radionuclides are  $^{125}\text{Sb}$  and  $^{124}\text{Sb}$ . The source of  $^{124}\text{Sb}$  is the nuclear reactors at Hanford, Washington. The water from the Columbia River is diverted for coolant, and is returned to the river. Some of the stable elements are neutron activated when in close proximity to

the fuel cells and re-enter the river as radioactive nuclides.

Antimony-124 is created by



The half-life of  $^{124}\text{Sb}$  is 60 days, so it is detectable long distances downstream.

The decay scheme of  $^{124}\text{Sb}$  is very complex. In addition to having three isomeric transitions, it also emits a number of beta particles, followed by several gamma photons of different energies and abundances. These disintegrations are listed in Table 1. The relative abundance refers to nuclear emissions of the same species. Some of the gamma photons occur in coincidence; that is, their decay is a cascading process with one photon immediately following another. There is also a  $\gamma - \gamma$  angular correlation as to the direction in which the cascading photons are emitted. The two coincident gamma rays used in this research have energies of 0.603 million electron volts (MeV) and 1.69 MeV. They are emitted at an angle of approximately  $180^\circ$  of each other with the 1.69 MeV photon preceding the 0.603 MeV photon (Kloepper, 1952). They are the most abundant of all the gamma photons for this radionuclide, and are best suited for coincidence counting, a method of radioanalysis that is described later. Darby (1951) could not find any  $\beta^- - \gamma$  angular correlation, but Langer (1953) found that the 0.603 MeV gamma photon is coincident with the 49%  $\beta^-$  group.



Table 1. Disintegrations of  $^{124}\text{Sb}$ .

Type of decay	Energy (MeV)	Relative abundance
Beta	2.317	21.0
"	1.60	7.0
"	0.97	9.0
"	0.61	49.0
"	0.24	14.0
Gamma	0.603	100.0
"	0.644	7.5
"	0.714	4.0
"	0.722	10.0
"	0.967	2.5
"	1.048	2.4
"	1.298	1.3
"	1.326	2.0
"	1.361	4.7
"	1.37	
"	1.45	2.1
"	1.50	1.1
"	1.54	0.6
"	1.692	51.0
"	2.088	7.0

(From: Lederer, Hollander and Perlman, 1967; p. 268).

Antimony-124 from the Hanford reactors was included in a study of the Columbia River sediments and water by Nelson, et al. (1966). Twenty-two liters of sample were filtered through a 0.3 micron pore membrane filter and evaporated to 13 ml. The sample was counted in a well crystal with shielding that electronically reduced the background level. It was found that most of the  $^{124}\text{Sb}$  between Pasco and Vancouver, Washington in 1964 was not depleted from the water and that approximately 90% of it was soluble. As of January 1965, Nelson et al. estimated the inventory of Sb-124 deposited between

Pasco and Vancouver to be five curies, which was less than  $2 \times 10^{-2}\%$  of the total estimated deposited radioactivity of ten nuclides.

### Region of Study

The area of study in this thesis includes the lower Columbia River extending from Bonneville Dam to the Columbia River estuary. The drainage area covers about 41,000 sq. km and is drained primarily by the Cowlitz and Willamette Rivers, plus other tributaries such as the Sandy and Youngs Rivers in Oregon and the Lewis River from Washington. The valley rests between the Cascade and Coastal ranges and consists of alluvial material. Most of the economy of the area involves agriculture and forest products. Since the mineral resources are not important compared to the rest of the Basin, no large amounts of antimony should be added to this portion of the river.

The sampling stations were chosen to be representative of four conditions that may influence the aqueous environment of the radio-nuclides. They were dams, paper and pulp mills, rivers and salt water. These conditions may or may not contribute to the depletion of activity in the water by causing the separation of particulate activity or by increasing the particulate activity which may settle from the river further downstream.

The stations behind the powerhouse and downstream near Tanner Creek around Bonneville Dam were designated 1U and 1D

respectively. The discharge from the dam should reflect the concentration and distribution of the physical forms of radionuclides behind the dam. However, the existence of a thermocline in the reservoir behind the dam could inhibit vertical mixing of soluble activity and some particulate activity. A difference downstream in concentration and form could indicate that upper and lower layers of the thermocline were sampled, since surface water behind the dam was sampled while water downstream of the dam is mainly from the depths of the reservoir. A difference in radioactivity levels could reflect different ages of the layers.

Sulfite liquor wastes from the Crown Zellerbach plant in Camas, Washington, are released to the river once a week after being stored in a pond. Water samples were taken upstream from and downstream in the middle of the sulfite effluent at stations 2U and 2D, respectively. The contents of the sulfite liquor may alter the physical form of a radionuclide by forming a stable complex that either competes with the particulate matter for the radionuclide or adsorbs readily to the particulate matter. Another possibility is that the sulfite liquor has no effect.

The rivers that empty into the Columbia may not only dilute the radioactivity but may also introduce particulate matter that could adsorb the soluble radioactivity. Stations 3U and 3D were chosen above and below the entrance of the Willamette River into the Columbia

to examine this possibility.

The station at Point Adams, Oregon, was chosen to observe the behavior of radioactivity in estuarine water at high and low tides. The concentration of activity would be diluted by more saline water, and the physical form may become more or less particulate due to its presence.

Based on work by Nelson and his co-workers, soluble  $^{124}\text{Sb}$  is conservative, and the different conditions should have no significant effect on it. However, due to its low concentration in the river, small changes in the relative amounts of soluble and particulate  $^{124}\text{Sb}$  may not be adequately detected by the methods of radioanalysis used in this research.

## METHODS

### Collection and Preparation of Samples

Samples of surface water were taken at the different stations from Bonneville Dam to Point Adams, Oregon, during the months of February, March, and April of 1969. Most of them were obtained with a plastic bucket. The samples at depth were obtained with a Van Dorn bottle. The samples were transported to the laboratory in five-gallon plastic containers for processing.

To separate the soluble and particulate phases, the samples were filtered by using a stainless steel pump to force the water through a 0.45 micron pore membrane filter (Gelman GA-6). A pre-filter trapped large particles and allowed greater volumes of water to pass through before clogging of the membrane filter occurred. Thirty to thirty-eight liters of sample were forced through each filter. The filter and prefilter were air-dried, cut into squares four cm on a side, and stacked and wrapped in Saran Wrap for coincidence counting.

The method used for concentrating the soluble fraction of radio-nuclides was described by Hanson (1967). The process involves adsorption of trace metals on an amorphous precipitate of ferric hydroxide. Chloride salts of iron III (45 milligrams per liter of sample) and chromium III (1.4 mg per l), zinc II (3.4 mg per l), manganese II (2 mg per l), and cobalt II (1.8 mg per l) carriers were

added to the water sample. Stannous ion (4 mg per l of sample) was added to reduce the chromium VI in the water to chromium III and enhance its recovery (Cutshall, Johnson and Osterberg, 1963). One milliliter of aqueous ammonia (18%) was added per liter of sample to bring the pH to approximately ten. This was followed by the addition of one ml of a 0.05% solution of Separan, a flocculant, per liter of sample. The Separan enhances the precipitation of the ferric hydroxide.

The precipitation was done in an inverted plastic carboy. The maximum volume processed was 16.8 l per sample. Air was bubbled through the carboy to mix the sample. After settling for one and one-half hours, the supernatant was decanted and the precipitate was drained through the bottom. Centrifuging further reduced the volume of the sludge. The sample was transferred to a beaker lined with Saran Wrap and dried in an oven for 48 hours. The resulting pellet was powdered and placed in a one inch aluminum planchet for coincidence counting. The powder was later transferred to a counting tube and was mixed with sugar to attain proper counting geometry for the well detector.

### Radioanalysis

#### Scintillation Detection

The amount of radionuclide in a sample spectrum is determined

from the area under the photopeak. In scintillation counting a gamma ray (electromagnetic radiation originating in the nucleus) passes through a crystal of sodium iodide that is activated by a trace amount (approximately 0.1%) of thallium. This is denoted as NaI(Tl).

Depending on the energy of the gamma ray, three processes may occur, the photoelectric effect, the Compton effect, or pair production. The photoelectric effect occurs when a gamma photon collides with a bound K or L electron. The electron is ejected with an imparted energy of  $h\nu - b$ , where  $b$  is the binding energy of the electron. This electron may cause ionizations and excitations in other atoms. The gamma photon transfers all its energy in this reaction. The Compton effect occurs when there is an interaction between a gamma photon and an electron in the outer orbitals of an atom. The photon does not lose all of its energy, but may cause subsequent ionizations or excitations. The ejected electron may also interact with other atoms. The energy of a Compton interaction varies with the angle of scattering, the binding energy of the electron and the energy of the incident gamma photon. Pair production occurs when the gamma photon interacts with the field of the nucleus to produce an electron and a positron. The required energy must exceed 1.02 MeV. The electron may have subsequent interactions. The lifetime of the positron is very short. After it has been slowed by ionization processes, it is annihilated when it combines with an electron. Simultaneously, two

quanta of radiation, each with an energy of 0.51 MeV, are emitted in opposite directions.

Scintillation counting is the product of the conversion of gamma photons to visible light. For the NaI(Tl) crystal, the photoelectric effect is the predominant interaction for gamma energies up to 1 MeV. The primary and secondary ionizations caused by the photoelectric effect excite orbital electrons in the NaI(Tl) crystal. Flashes of light are produced by the decay of the excited state. The intensity of the flashes is proportional to the energy of the incident gamma photons. A photomultiplier tube amplifies the signal by a factor of about one million, but the uncertainty of multiplication of electrons from the dynodes causes the pulses to form a bell-shaped curve about the mean energy. A linear amplifier further amplifies the signal. The signal is routed to an analyzer (Nuclear Data, Model ND 130 A) where it is sorted according to its voltage and stored in a specific energy channel. After a predetermined counting time, the resulting spectrum can be read out or displayed on an oscilloscope. The crystal used for this type of counting was a 12.7 cm x 12.7 cm diameter NaI(Tl) well crystal (Harshaw).

The amount of activity determined by scintillation counting will vary with different counting geometry, a function of the construction of the crystal and of the size and shape of the sample. A sample resting on top of a crystal is counted by  $2\pi$  geometry. More gamma photons



are detected by  $4\pi$  geometry than by  $2\pi$  geometry. Due to a delocalization of detection area in the crystal, a sample covering a larger area of the crystal will have more gamma photons detected than a confined source.

### Coincidence Counting

The coincidence method employed in this project involves using one gamma photon to allow another one of different energy to be counted. Equipment included a 7.6 cm x 7.6 cm NaI(Tl) crystal (Harshaw) placed above a 12.7 cm x 12.7 cm NaI(Tl) crystal (Harshaw) in an acrylic holder that could be adjusted to separate the crystals a desired distance. Figure 2 illustrates the schematic design of the system. When an atom of  $^{124}\text{Sb}$  decays, the 0.603 MeV and the 1.69 MeV photons may be emitted. When the 1.69 MeV photon was detected by the larger crystal, a negative pulse was sent to side B of the dual amplifier (Nuclear Data, Model ND500). The coincidence output of the dual amplifier was positive and was routed to the coincidence input on the analyzer. If the smaller crystal simultaneously detected the 0.603 MeV photon, a negative pulse was sent to side A of the dual amplifier. The output signal from side A was delayed two microseconds before a negative pulse was routed to the negative zero to three volt input on the analyzer. The positive coincidence pulse opened a "gate" for the negative pulse to be counted. After the latter

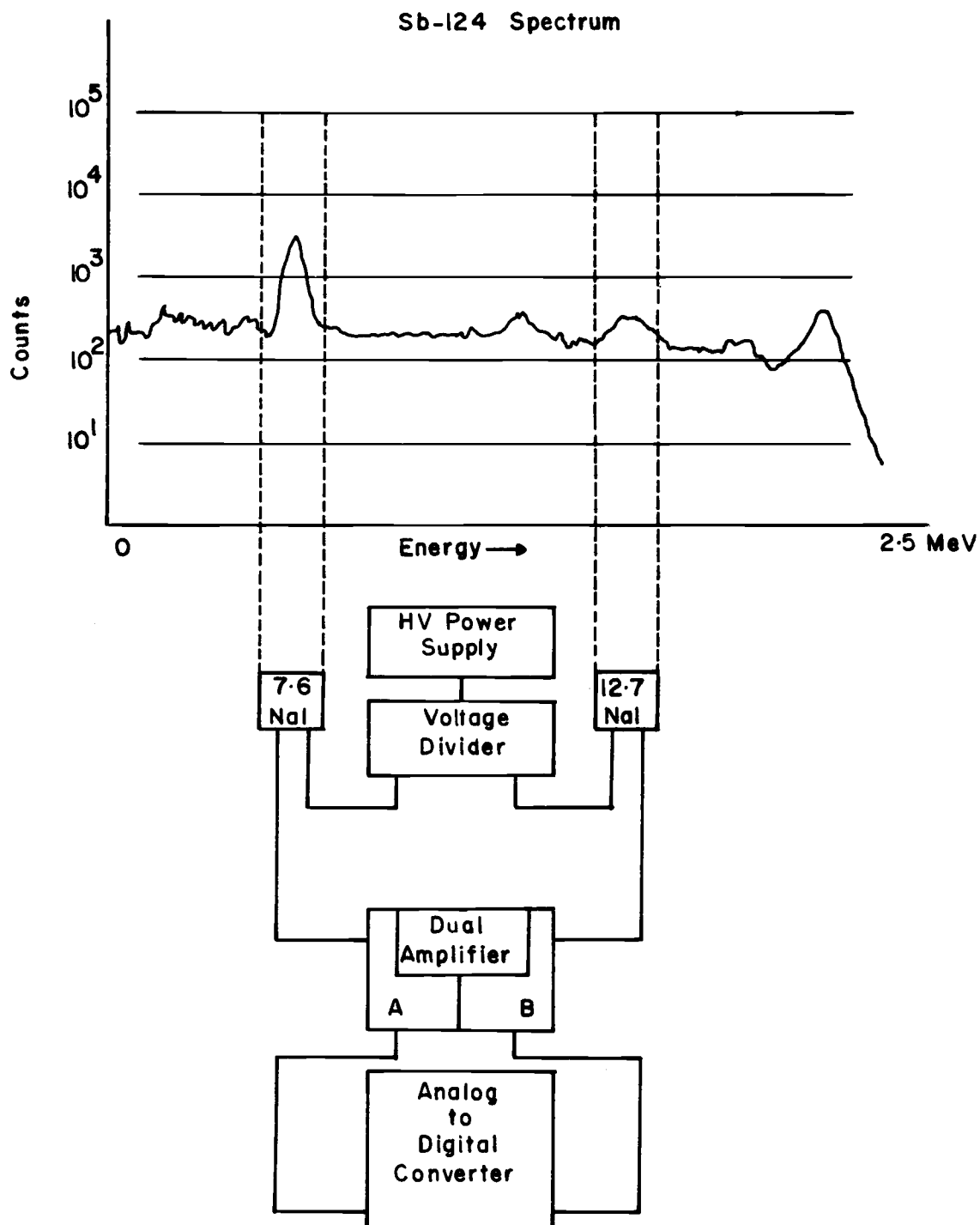


Figure 2. Coincidence counting system schematic diagram.

signal entered, the "gate" closed. Figure 3 illustrates the apparatus that was used. Upper and lower discrimination levels were set by dials on side B of the dual amplifier to detect only the 1.69 MeV photon; side A did not have any discrimination levels.

Some of the experimental conditions to be considered when a coincidence system is assembled are the distance between the crystals, the angular correlation of the emitted photons, and the delay time for the coincidence and signal pulses. The detection efficiency of coincidence counting decreases rapidly with increasing distance between the crystals. For this system, this may be due to the decreased detection of photons not emitted nearly perpendicularly to the crystals. The distance of nine millimeters between the crystals in this work minimized this condition. The angular correlation varies for coincident photons of other radionuclides. Photons that are emitted at right angles to each other would be detected better by a different crystal arrangement. The 0.603 MeV and 1.69 MeV photons of  $^{124}\text{Sb}$  are emitted in opposite directions and are best detected by the directional arrangement of this system. The delay time of a coincidence system should be adjusted so the coincidence pulse arrives at the analyzer just before the signal pulse. If the delay time is too short, the signal pulse will arrive at the analyzer before the coincidence pulse and will not be counted. If the delay time is too long, a signal pulse whose source is not a coincident photon could enter the



A. Coincidence crystals

B. Dual amplifier

C. Analyzer

Figure 3. Coincidence counting system apparatus.

analyzer before the signal pulse of the coincident photon and could be counted. The delay time of the dual amplifier was inherent at two microseconds. The system apparently functioned properly at that delay time, so no attempt was made to alter it.

The 1.69 MeV photon was chosen as the coincidence pulse because it was located in a region of the sample spectrum isolated from other photopeaks and not subject to much Compton interference from other gamma photons. Background radiation is not abundant in the 1.69 MeV region; thus, the background levels of the coincidence system were lower than if the 0.603 MeV photon were the coincidence pulse.

The background level of the coincidence system used in this project was much lower than the background level from a well detector. The levels were about 0.05 counts per minute (cpm) and 38 cpm, respectively. Because of the lower background level, the minimum detectable level (MDL) of the coincidence system was also lower. The MDL for this research was considered to be the distribution of sample count rates that was greater than 99% of the background count rates for 97.5% of the samples. The MDL of coincidence counting was nine picocuries (pCi) and eleven pCi for soluble and particulate samples, respectively. The difference probably was due to the larger surface area of the particulate sample available for detection. The MDL for well counting was 67 pCi. The coincidence system also had a much

lower detection efficiency than the well detector. The efficiencies were about 0.61% and 45%, respectively. The lower detection efficiency of coincidence counting is due largely to the timing and directional requirements of the coincident photons.

The coincidence counting system in this research increased the counting precision of  $^{124}\text{Sb}$  values by reducing the Compton interference from other radionuclides and the background radiation level.

## RESULTS

The sources of errors for a value of activity in the soluble fraction of a water sample were considered to be from estimation of sample volume, yield of the concentration process, counting errors of the sample, background and standard, and the total uncertainty of the activity of the standard. This was termed the experimental standard deviation. For the average of duplicate values, the standard deviation of the mean of the two values was calculated. The standard deviations of the soluble activities (Figures 4a and 4b and Table 2) were calculated as the square root of the sum of the squares of the experimental and duplicate standard deviations.

The mean and standard deviation of the percent standard deviations for all the individual samples of  $^{124}\text{Sb}$ ,  $^{51}\text{Cr}$ ,  $^{46}\text{Sc}$  and  $^{65}\text{Zn}$  are shown in Table 2. The average percentages of experimental standard deviation and the total standard deviation were lower for coincidence counting than for well counting despite the imprecision of coincidence counting for  $^{124}\text{Sb}$ . Figures 4a and 4b show that the total standard deviation of coincidence counted  $^{124}\text{Sb}$  is usually less than the total standard deviation of well counted  $^{124}\text{Sb}$ , except for station 4 on 7 March. The large standard deviation here is due to a large difference between the duplicates. Chromium-51 had the lowest percent total standard deviation.

The levels of soluble activity of each radionuclide in Figures 4a

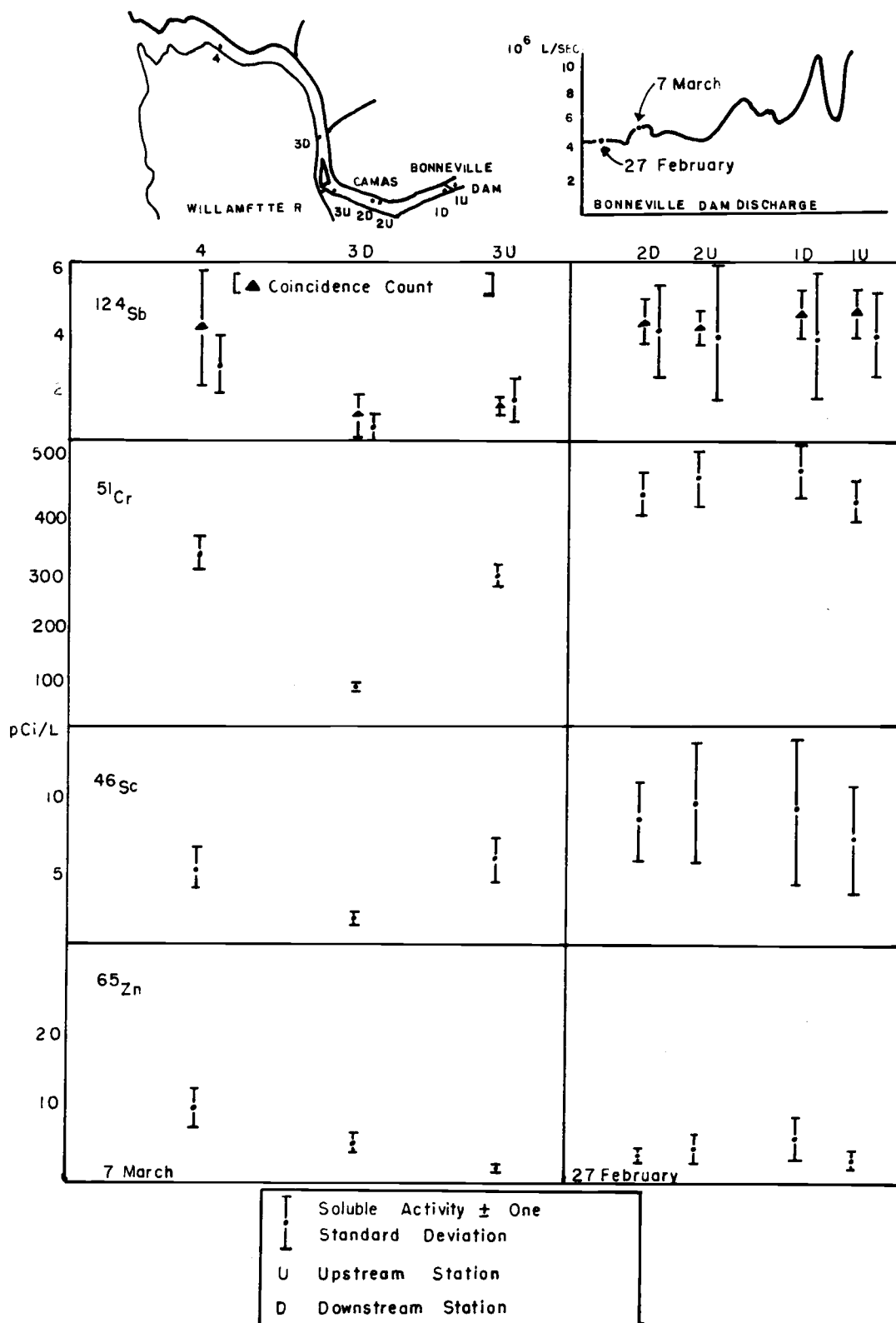


Figure 4a. Soluble activity for four radionuclides in the Columbia River at several stations on two collection dates.



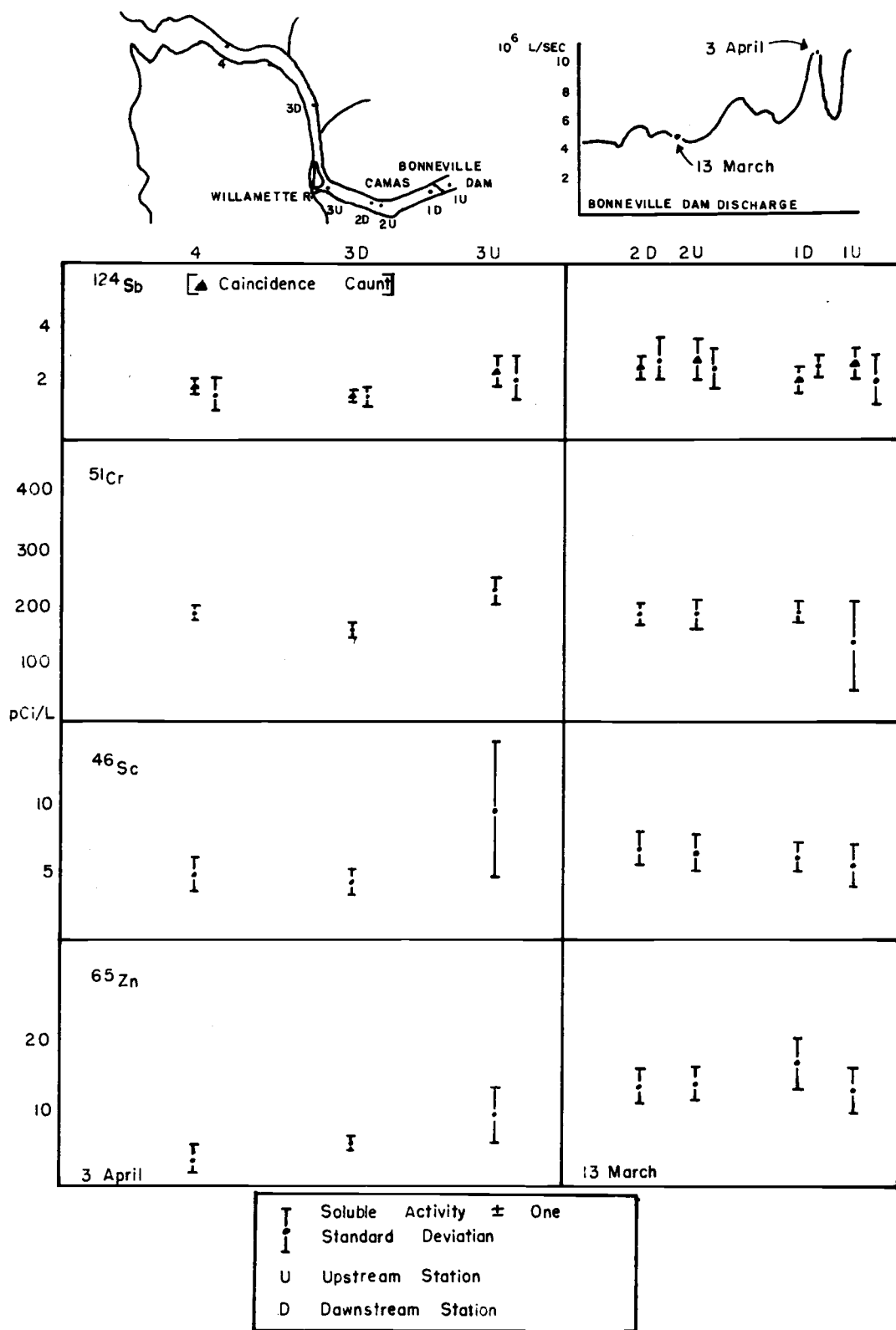


Figure 4b. Soluble activity for four radionuclides in the Columbia River at several stations on two collection dates.

Table 2. Summary of soluble standard deviations.

	$^{124}\text{Sb}$ (coincidence)	$^{124}\text{Sb}$ (well)	$^{51}\text{Cr}$	$^{46}\text{Sc}$	$^{65}\text{Zn}$
<u>Experimental</u>					
Range	13%-24%	30%-121%	7%-14%	18%-46%	13%-92%
Mean, $\bar{x}$	17%	49%	9.3%	29%	30%
$\sigma$	$\pm 4\%$	$\pm 22\%$	$\pm 1.8\%$	$\pm 8\%$	$\pm 18\%$
$\frac{\sigma}{\bar{x}} \times 100$	24%	45%	19%	28%	60%
<u>Duplicate</u>					
Range	1%-7.2%	0%-76%	0%-54%	2%-48%	2%-37%
Mean, $\bar{x}$	17%	13%	6%	17%	13%
$\sigma$	$\pm 18\%$	$\pm 16\%$	$\pm 12\%$	$\pm 13\%$	$\pm 11\%$
$\frac{\sigma}{\bar{x}} \times 100$	106%	123%	200%	76%	85%
<u>Total</u>					
Range	16%-76%	31%-122%	7%-55%	22%-56%	15%-92%
Mean, $\bar{x}$	27%	52%	12%	35%	34%
$\sigma$	$\pm 14\%$	$\pm 24\%$	$\pm 11\%$	$\pm 11\%$	$\pm 19\%$
$\frac{\sigma}{\bar{x}} \times 100$	52%	46%	92%	31%	56%

and 4b do not vary to a large extent for the stations around Bonneville Dam and Camas, Washington, nor does the Willamette River decrease the levels significantly. The level of  $^{124}\text{Sb}$  for all stations and dates was between one and five picocuries per liter (pCi/l). The apparently large decreases of soluble  $^{51}\text{Cr}$  and  $^{46}\text{Sc}$  on 7 March was probably due to different activity levels in two different water masses sampled.

Figures 5a and 5b illustrate the percent particulate activity of the four radionuclides. The sources of the individual standard deviation of particulate activity were the same as those for the soluble standard deviation except for the yield of the concentration process. Only those values of  $^{124}\text{Sb}$  that were greater than their experimental standard deviation were plotted. Percent particulate  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  varied more than percent particulate  $^{46}\text{Sc}$  and  $^{65}\text{Zn}$ . The variation of percent particulate  $^{124}\text{Sb}$  is an indication of detection difficulty of particulate  $^{124}\text{Sb}$  rather than environmental effects. The standard deviation in these figures is not analogous to the standard deviation of Figures 4a and 4b since duplicate particulate values were not obtained. The denominator of total activity was the average soluble value plus the particulate value. The standard deviation of Figures 5a and 5b is largely a reflection of the uncertainty of the calculations, not of the measurements. Table 3 shows the average of the particulate values for all stations. The variance of particulate  $^{46}\text{Sc}$  and  $^{65}\text{Zn}$  is less than the variance of particulate  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$ .

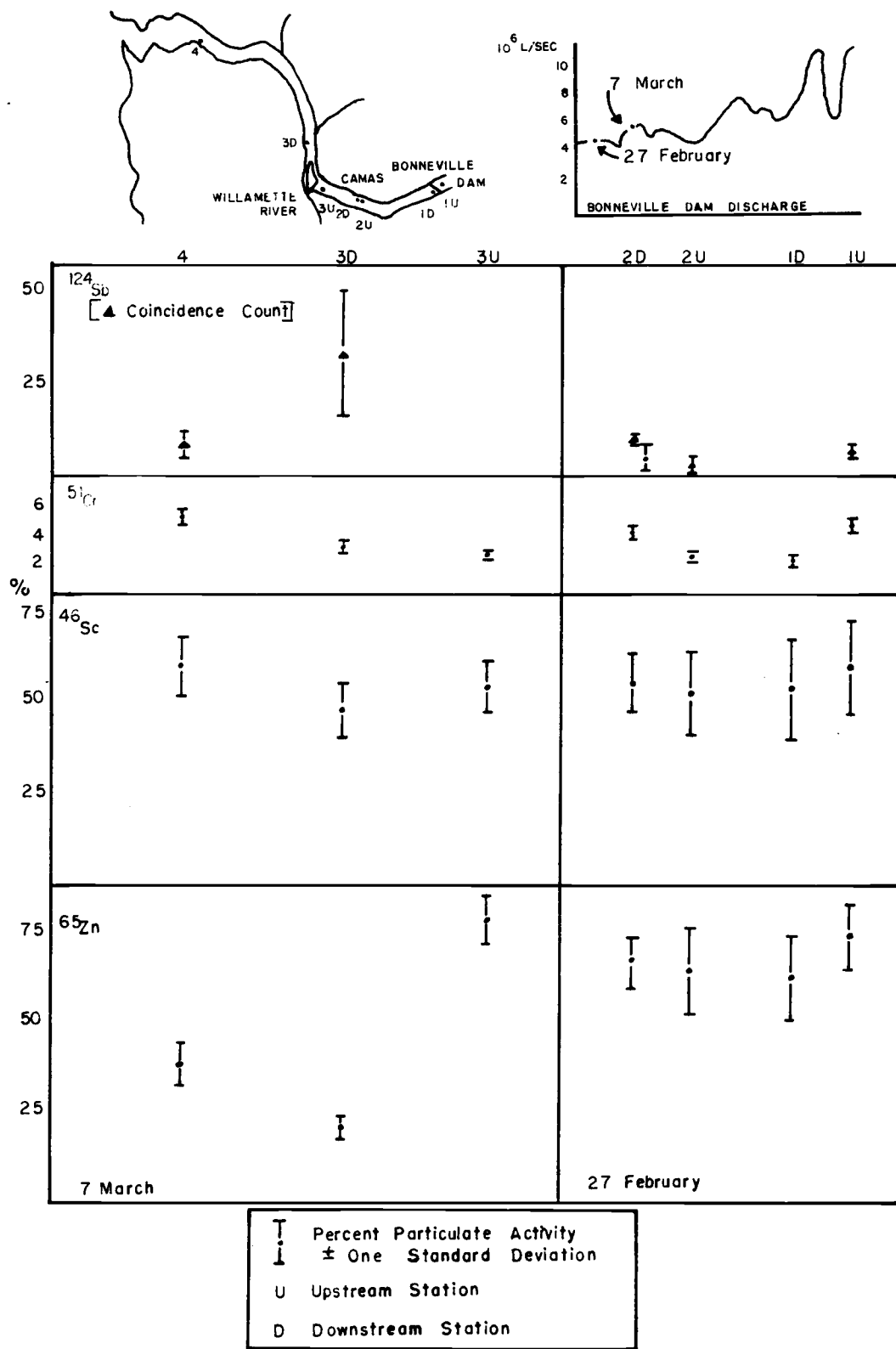


Figure 5a. Percent particulate activity for four radionuclides in the Columbia River at several stations on two collection dates.

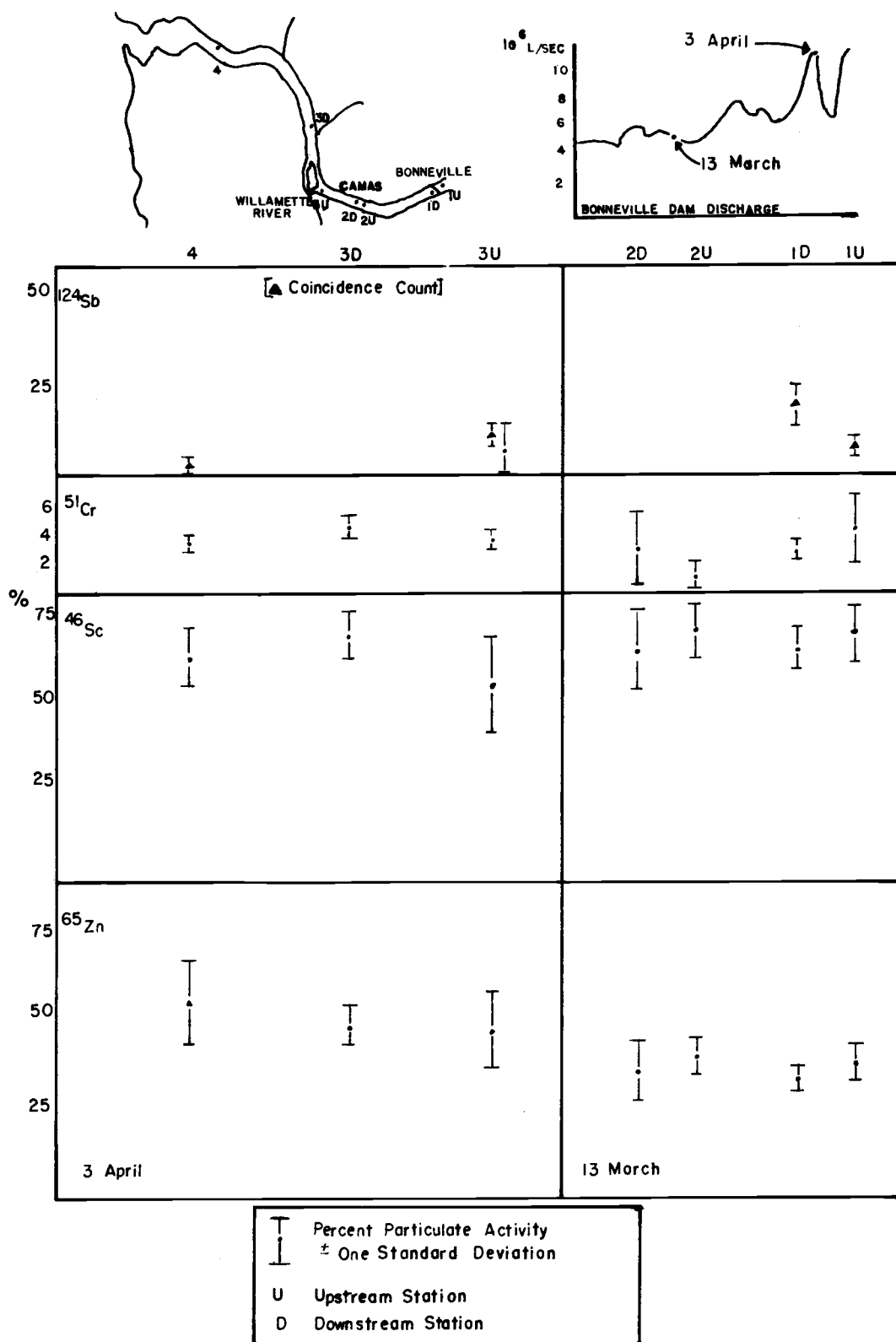


Figure 5b. Percent particulate activity for four radionuclides in the Columbia River at several stations on two collection dates.

Table 3. Average of particulate activities (pCi/l).

	Range	Mean $\bar{x}$	$\sigma$	$\frac{\sigma}{\bar{x}} \times 100$
Sb-124* (coincidence)	0.14-0.46	0.25	$\pm 0.16$	64%
Sb-124** (well)	0.13-0.19	0.16	$\pm 0.03$	19%
Cr-51	2-22	11	$\pm 6$	55%
Sc-46	1.5 -13	8.8	$\pm 2.4$	27%
Zn-65	1.2 -9.9	6.1	$\pm 2.2$	36%

\* Represents 10 values.

\*\* Represents 3 values.

On 7 March, station 4 appears to have higher levels of soluble and percent particulate activity than station 3D upstream. The samples were taken in the Prairie Channel, on the Oregon side of the Columbia River. The ship channel runs along the Washington side. The samples from station 4 were probably from a different water mass containing more activity.

On 7 March, soluble  $^{65}\text{Zn}$  increased downstream from station 3U to 3D despite the dilution effect of the Willamette River. The percent particulate activity also decreased about 400%. The samples were taken from the St. Helens, Oregon, boat dock. About 50 meters upstream liquid wastes from a paper mill were being dumped into the river. The waste possibly contained chemicals that caused the release of  $^{65}\text{Zn}$  adsorbed to particulate matter.

On 27 February, the levels of soluble  $^{51}\text{Cr}$  appear higher than on

13 March at the Bonneville Dam and Camas, Washington, stations. The soluble  $^{65}\text{Zn}$  levels were higher on 13 March than on 27 February at the same stations, although the levels of particulate  $^{65}\text{Zn}$  did not appear to change.

The data from Point Adams, Oregon, are listed in Table 4. Samples taken at depth during high tide probably were not within the salt wedge so the effect of saline water upon the physical distribution of the radionuclides was not observed. The values only indicate typical estuarine data. The levels of percent particulate  $^{51}\text{Cr}$  appear higher at low tide than at high tide. This could be due to resuspension of particulate matter by river flow at low tide.

Table 4. Activity at Point Adams, Oregon, on 10 April, 1969.

Tidal cycle	Depth	Salinity	$^{124}\text{Sb}$ (coincidence count)	$^{124}\text{Sb}$ (well count)	$^{51}\text{Cr}$	$^{46}\text{Sc}$	$^{65}\text{Zn}$
<u>Averages of soluble activity (pCi/l)</u>							
High	0	1.00%	$1.1 \pm 0.3$	$1.0 \pm 1.2$	$166 \pm 24$	$5.2 \pm 1.9$	$3.6 \pm 3.3$
High	3.4 m	1.78%	$1.2 \pm 0.3$	$1.4 \pm 0.7$	$164 \pm 17$	$3.1 \pm 1.3$	$3.4 \pm 1.6$
Low	0	1.80%	$1.2 \pm 0.2$	$1.4 \pm 0.4$	$150 \pm 11$	$2.8 \pm 0.7$	$3.1 \pm 1.0$
Low	8 m	1.95%	$1.1 \pm 0.3$	$1.3 \pm 0.6$	$146 \pm 13$	$3.0 \pm 1.0$	$3.6 \pm 1.5$
<u>Averages of percent particulate activity (pCi/l)</u>							
High	0	1.00%	-	-	$7.4 \pm 1.2$	$59 \pm 9$	$48 \pm 24$
High	3.4 m	1.78%	$4.3 \pm 3.2$	$8.5 \pm 7.9$	$5.9 \pm 0.8$	$69 \pm 10$	$55 \pm 13$
Low	0	1.80%	-	-	$12 \pm 1$	$76 \pm 6$	$60 \pm 9$
Low	8 m	1.95%	-	-	$13 \pm 1$	$74 \pm 8$	$56 \pm 13$



## DISCUSSION

The data from this research appear to indicate that different environmental influences affect  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  to the same degree. The similar behavior was investigated by plotting the ratio of soluble  $^{51}\text{Cr}$  to soluble  $^{124}\text{Sb}$  against the distance of a station from the mouth of the Columbia River (Figure 6). The ratios from coincidence counted and well counted  $^{124}\text{Sb}$  were plotted separately. The soluble  $^{51}\text{Cr}/^{124}\text{Sb}$  ratio appears to increase downstream. The slope of the ratio of soluble  $^{51}\text{Cr}$  to coincidence counted soluble  $^{124}\text{Sb}$  was  $-0.16 \text{ km}^{-1}$  while the slope of the ratio of soluble  $^{51}\text{Cr}$  to well counted soluble  $^{124}\text{Sb}$  was  $-0.11 \text{ km}^{-1}$ . The correlation coefficient (r) denotes degree of linear correlation between two functions; it ranges from negative one to positive one. The correlation coefficients were low, being  $-0.30$  for coincidence counted  $^{124}\text{Sb}$  and  $-0.15$  for well counted  $^{124}\text{Sb}$ . The error terms of the slopes were  $0.10 \text{ km}^{-1}$  for coincidence counted  $^{124}\text{Sb}$  and  $0.15 \text{ km}^{-1}$  for well counted  $^{124}\text{Sb}$ . These slopes were tested by the "t" distribution test to ascertain whether they were significantly different than zero at the 95% confidence level. The formula was

$$t = \frac{b - B}{s_b}$$

where "t" represents the "t" distribution, b is the sample slope,  $s_b$  is the standard deviation of the sample slope, and B is the actual slope

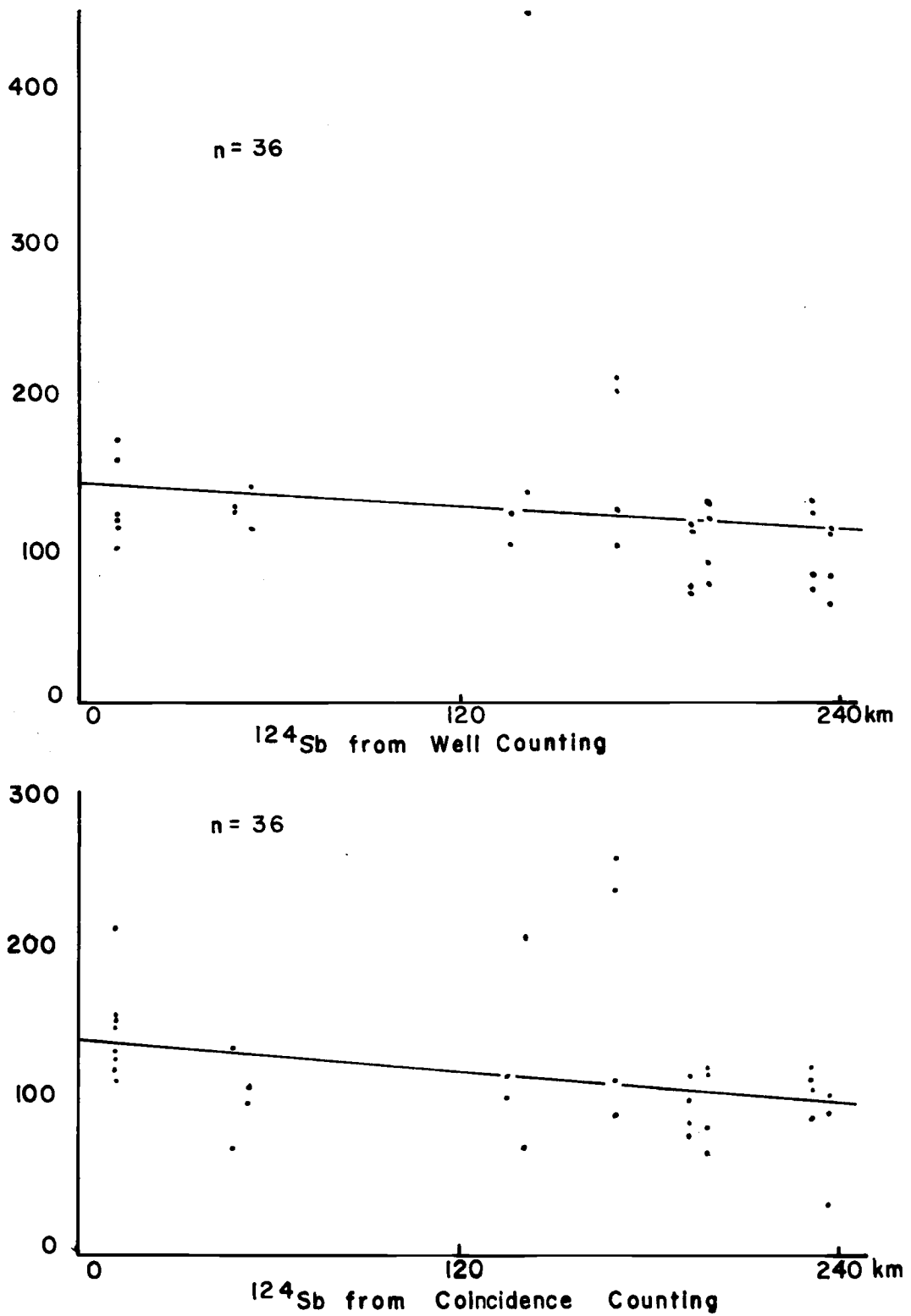


Figure 6. Regression analysis of soluble  $^{51}\text{Cr}$  to soluble  $^{124}\text{Sb}$  ratio vs. distance upstream from the mouth of the Columbia River.

of the entire population of  $^{51}\text{Cr}/^{124}\text{Sb}$  ratios in the region studied. B was assumed to be zero. The value of "t" was 1.60 for the graph with coincidence counted  $^{124}\text{Sb}$ , and 0.79 for the graph with well counted  $^{124}\text{Sb}$ . The value of "t" at the 95% confidence level for the number of samples used was 2.03. Neither of the experimental "t" values exceeded 2.03. Thus, the slopes are not significantly different from zero, indicating that no systematic change with distance should appear in the measurement of  $^{51}\text{Cr}$  to  $^{124}\text{Sb}$  ratios. Thus, they appear to be conservative in a fresh water environment; that is, their activities per unit volume are altered locally by diffusion and advection only.

If the ratio decrease were due essentially to the faster decay rate of  $^{51}\text{Cr}$ , conceivably it could be used to measure flow times. However, the range of plus or minus one standard deviation of the ratio at a station may be larger than the difference between ratios at upstream and downstream stations, thus casting doubt upon the precision of the calculated flow time.

Flow time (t) may be determined from the ratio in the following manner. The  $^{51}\text{Cr}/^{124}\text{Sb}$  ratios from an upstream station (U) and from a downstream station (D) can be compared by

$$W = (^{51}\text{Cr}/^{124}\text{Sb})_U / (^{51}\text{Cr}/^{124}\text{Sb})_D \quad (1)$$

If the ratio at station D is less than the ratio at station U, and the decrease is due primarily to radioactive decay, then the activities of the two stations are related by

$$({}^{51}\text{Cr})_{\text{D}} = ({}^{51}\text{Cr})_{\text{U}} e^{-\lambda_{\text{Cr}} t}$$

and

$$({}^{124}\text{Sb})_{\text{D}} = ({}^{124}\text{Sb})_{\text{U}} e^{-\lambda_{\text{Sb}} t}$$

where  $\lambda_{\text{Cr}}$  = radioactive decay constant of  ${}^{51}\text{Cr} = 0.0249 \text{ days}^{-1}$   
 $\lambda_{\text{Sb}}$  = radioactive decay constant of  ${}^{124}\text{Sb} = 0.0116 \text{ days}^{-1}$ .

If these equations are substituted into equation (1), the activities at the two stations are eliminated:

$$W = ({}^{51}\text{Cr}/{}^{124}\text{Sb})_{\text{U}} / ({}^{51}\text{Cr})_{\text{U}} e^{-\lambda_{\text{Cr}} t} / ({}^{124}\text{Sb})_{\text{U}} e^{-\lambda_{\text{Sb}} t}$$

or 
$$W = e^{-\lambda_{\text{Sb}} t} / e^{-\lambda_{\text{Cr}} t} = e^{-(\lambda_{\text{Sb}} - \lambda_{\text{Cr}}) t}; \quad (2)$$

$t$  in the equation is the decay time of the two radionuclides, i. e., the time of flow from the upstream station to the downstream station. If equation (2) is solved for  $t$ , the result is

$$t = \ln W / -(\lambda_{\text{Sb}} - \lambda_{\text{Cr}}) \quad (3)$$

In the following discussion, one standard deviation of the  ${}^{51}\text{Cr}/{}^{124}\text{Sb}$  ratio determined the uncertainty of the flow time. One standard deviation was subtracted from the initial value of the ratio to obtain a downstream value. Three samples were selected randomly and the  ${}^{51}\text{Cr}/{}^{124}\text{Sb}$  ratio and the standard deviation was calculated. The results are summarized in Table 5.

The uncertainty related to flow was greatly reduced by coincidence counting. The mean experimental standard deviations from Table 2 were used to estimate an average decrease in uncertainty. If the

Table 5. Uncertainty of the  $^{51}\text{Cr}/^{124}\text{Sb}$  ratio.

Station	Date	Count Method	$R_1 = x \pm 1\sigma$	$R_2 = x - 1\sigma$	$W = R_1/R_2$	$\ln W$	$t$ (days)
4	7 March	Coinc.	$62.7 \pm 5.9$	56.8	1.104	0.099	7.4
		Well	$126 \pm 36$	90.0	1.400	0.336	25.2
3U	3 April	Coinc.	$114 \pm 16$	98.0	1.162	0.150	11.3
		Well	$121 \pm 30$	91.0	1.330	0.285	21.4
Point Adams	10 April	Coinc.	$208 \pm 40$	168.0	1.238	0.214	16.1
		Well	$157 \pm 49$	108.0	1.452	0.373	28.0

experimental standard deviations were 9% and 17%, respectively for  $^{51}\text{Cr}$  and coincidence counted  $^{124}\text{Sb}$ , then the average error of the ratio would be

$$\sqrt{(17\%)^2 + (9\%)^2} = 19\%$$

and the uncertainty in days is

$$t = \ln(x/0.81x) / (\lambda_{\text{Sb}} - \lambda_{\text{Cr}}) = 16 \text{ days,}$$

where the upstream station is  $x$  and the downstream station is  $x - 0.19x = 0.81x$ . For well counted  $^{124}\text{Sb}$ , the average would be

$$\sqrt{(49\%)^2 + (9\%)^2} = 50\%$$

and the uncertainty from this determination is

$$t = \ln(x/0.5x) / (\lambda_{\text{Sb}} - \lambda_{\text{Cr}}) = 52 \text{ days.}$$

If the counting error of about 20% of the coincidence system is also considered (see page 46), the total error of the ratio with  $^{124}\text{Sb}$  from coincidence counting would be

$$\sqrt{(17\%)^2 + (9\%)^2 + (20\%)^2} = 28\%$$

and the total uncertainty would be

$$t = \ln(x/0.72x) / (\lambda_{\text{Sb}} - \lambda_{\text{Cr}}) = 25 \text{ days.}$$

Thus the total uncertainty of the coincidence system is much less than that of the well detecting system.

Flow times in the Columbia River have been previously determined using radioactive tracers (Table 6). Determination of flow times of less than 25 days for the Columbia River from Hanford to Point Adams would not be reliable during the summer freshet.

Flow between these locations could possibly be measured during the seasons of low river discharge (about  $3 \times 10^6$  l/sec), because the flow time of about 19 days approaches the lower limit of uncertainty of 25 days.

Table 6. Flow times of the Columbia River.

From	To	Discharge (l/sec)	Flow time (days)
<u>Nelson et al., 1966</u>			
Pasco, Wn.	Vancouver, Wn.	$3.1 \times 10^6$	13.6
		$5.4 \times 10^6$	6.5
<u>Hanson, 1966</u>			
Hanford, Wn.	Astoria, Ore.	$3.7 \times 10^6$	19
		$8.2 \times 10^6$	12

Velocity measurements of the Columbia River plume in the ocean using the  $^{51}\text{Cr}/^{124}\text{Sb}$  ratio might be possible although the southern extent of the plume in the summer (about 420 km) is shorter than the distance from Pasco to Astoria (about 530 km). The flow rate of the plume was calculated by Osterberg, Cutshall and Cronin (1965) to be about 11.4 km/day. In 25 days, a particle in the plume would travel about 290 km. Thus, flow rate could be determined within the length of the plume, excluding decrease in activity due to uptake by biota and sediments. However, dilution and dispersion of  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  could afford an increasing uncertainty in the ratio away from the mouth of the Columbia River.

The uncertainty could be reduced by taking the mean of a large number of samples and considering the sample standard deviation as the uncertainty. The "t" distribution test could be used to test whether the means are significantly different. Coincidence counting is not more precise than well counting and would not be necessary for river data. However, the lower minimum detection level of coincidence counting would be necessary for the diluted concentrations of  $^{124}\text{Sb}$  in the ocean.

The transport rate of a radionuclide at a location in the river is the product of its activity per unit volume multiplied by the river discharge at that location. The transport rate of radionuclides into the ocean has been calculated from the discharge at Vancouver, Washington, rather than at the mouth of the river, to avoid chemical effects of estuarine water on their physical distribution. Transport rate at Vancouver is considered an index of discharge of radionuclides into the ocean. The average annual transport rate of  $^{51}\text{Cr}$  and  $^{65}\text{Zn}$  in 1962 was 650 and 29 curies per day (Ci/d), respectively (Wilson, 1963). Average transport rates in this research were calculated with the average discharge of the Columbia River for March and April at Vancouver and the average total activity of  $^{51}\text{Cr}$ ,  $^{46}\text{Sc}$ , and  $^{65}\text{Zn}$ , and the average soluble activity of  $^{124}\text{Sb}$  of all the samples. The transport rates were 1.5 Ci/d for  $^{124}\text{Sb}$ , 200 Ci/d for  $^{51}\text{Cr}$ , 11 Ci/d for  $^{46}\text{Sc}$  and 10 Ci/d for  $^{65}\text{Zn}$ . At some point in time, there should be an



equilibrium between supply of activity to the ocean and decay. This equilibrium can be denoted as

$$dA_s/dt = A_e \lambda$$

where  $dA_s/dt$  = supply (transport rate) of activity

and  $A_e$  = the equilibrium amount of activity.

By substituting the transport rate past Vancouver into the equation, the equilibrium activities are approximately 140 Ci of  $^{124}\text{Sb}$ , 8000 Ci of  $^{51}\text{Cr}$ , 1300 Ci of  $^{46}\text{Sc}$ , and 3500 Ci of  $^{65}\text{Zn}$ . The corresponding values from Wilson (1963) in 1962 were 25,000 Ci of  $^{51}\text{Cr}$  and 9000 Ci of  $^{65}\text{Zn}$ . Different river discharge volumes and dubious comparison between an annual and a seasonal average may be sources of the different transport rates and radioactivity levels, but the main reason is probably that more reactors were operating in 1962.

Depletion is removal of activity from the river. Perkins et al. (1966) estimated the percent depletion between Pasco and Vancouver, Washington, for February, March, and April of 1964 to be about 25% for  $^{124}\text{Sb}$ , 30% for  $^{51}\text{Cr}$ , 75% for  $^{46}\text{Sc}$ , and 75% for  $^{65}\text{Zn}$ . Percent depletion was calculated by subtracting the Vancouver transport rate from the Pasco transport rate and dividing by the Pasco transport rate. Depletion was not successfully estimated in this research due to lack of discharge data between two stations and because the stations were sampled only once each month. An attempt was made to estimate depletion between Bonneville and Camas by using monthly

discharge at Bonneville and Vancouver. Depletion between Vancouver and Point Adams was estimated with average monthly discharge at Vancouver and at the mouth of the Columbia River. Of the 16 values calculated, ten were negative, ranging from -1% to -370%. Negative depletion indicates the addition of activity to the river. The stations on 3 April were the only ones that had positive results. Using the activity at Vancouver (station 3U) and an average of Point Adams and station 4 activities, the results were +35% for  $^{124}\text{Sb}$ , +16% for  $^{51}\text{Cr}$ , +33% for  $^{46}\text{Sc}$ , and +45% for  $^{65}\text{Zn}$ . Effects of the estuarine environment and possible scouring during the high discharge cast doubt upon the credibility of these values. Sampling the Columbia River several times in one month at Bonneville Dam and three days later at station 4 on the Washington side of the river would have given a better estimate of depletion between these two stations. The average monthly discharge at Bonneville Dam and the mouth of the river could be used.

The units of particulate activity were pCi/l, but these units should be revised. The amount of particulate activity is a function of the amount of matter suspended in the river; the latter, in turn, is a function of the river discharge. During periods of high discharge, bottom sediments may be resuspended and contribute more particulate activity to the water. Particulate activity units should reflect the amount of matter in the water, such as pCi/gram of matter or pCi/

turbidity. The denominators could then be related to the volume of water. Other areas of further investigation that are indicated by this research are:

1. Physical and chemical distribution of radionuclides behind a dam;
2. Mechanism of particulate  $^{65}\text{Zn}$  decrease in a sulfite liquor outfall and measurement of its persistence in the river;
3. Depletion of activity from the water and estimation of total inventory of radionuclides in the sediments between Bonneville Dam and the estuary; and,
4. Horizontal comparison study of flushing times of the ship channel and of an adjacent shallow channel.

## METHODS EVALUATION

The results of the collected data indicated several disadvantages in the experimental technique used. The drawbacks arose in sample collection, filtration procedure, and imprecision of coincidence counted  $^{124}\text{Sb}$ .

As more samples are taken, it becomes easier statistically to detect small differences in sample populations. This is due to the increased degrees of freedom. Only one particulate and two soluble values were obtained for each station on two dates, so detection of small variations was not possible in this study. Thus, possible variations in the physical distribution of radionuclides induced by conditions at Camas, Washington, Bonneville Dam, and the Willamette River could not be tested by meaningful statistical techniques. Several replicate samples should have been taken on a single day and processed at each location to observe changes in the amount and distribution of activity due to environmental conditions. A single water mass should have been sampled as it moved downstream from Bonneville Dam to the estuary.

In an attempt to retain more particulate  $^{124}\text{Sb}$ , soluble duplicates from a station were filtered with the same filter. This technique prevented replicate values for particulate  $^{51}\text{Cr}$ ,  $^{46}\text{Sc}$ , and  $^{65}\text{Zn}$  from being obtained and still yielded only small activities of particulate  $^{124}\text{Sb}$ . In situ filtering of large volumes of water with different

filters would have eliminated this problem. In addition, the apparatus for filtering probably contaminated the filtrate so that stable trace element analysis could not be run.

Ferric hydroxide is a fast method for initial separation of the radionuclides from the water sample. Samples for coincidence counting were thus reduced from 16 l to about 4 ml, a factor of about 4000. Extraction efficiency was tested by spiking tap water with a known amount of radioactivity and then by carrying the concentration procedure through the drying step. Four replicates were prepared and compared by radioanalysis to the initial volume of the spike. Recovery was ( $86 \pm 2\%$ ) for  $^{124}\text{Sb}$ , ( $87 \pm 3\%$ ) for  $^{46}\text{Sc}$ , and ( $95 \pm 3\%$ ) for  $^{65}\text{Zn}$ . Pipetting error, sample and background counting errors, standard deviation of the mean of the four spiked samples and the standard deviation of the ratio of prepared to initial spikes were included in the standard deviation. Hanson (1967) reported 98% recovery for soluble  $^{51}\text{Cr}$ .

The radioactive spikes were cations of Sb, Sc, and Zn whereas in the river, soluble Sb and Sc exist primarily as uncharged or anionic species (Nelson et al., 1966). This difference in chemical forms could afford a discrepancy between laboratory recovery experiments and actual recovery from the river.

The reagents and carriers used in the ferric hydroxide scavenging method precludes stable trace elements from being determined. In

addition, the amount of Sb in some of the reagents as an impurity is larger than the estimated concentration of Sb in the Columbia River. Silker (1964) reported the concentration of As in the Columbia River to be about two parts-per-billion (ppb). If the Sb to As ratio in the earth's crust is assumed to be about 0.5 at most (Onishi and Sandell, 1955), then the estimated concentration of Sb in the Columbia River is one ppb. The amount of Sb in the FeIII reagent was about one ppb and more Sb was probably added from the SnII reagent. Evaporation of the filtered sample would be a better method of concentration if determination of trace elements is desired.

The precision of coincidence counting was determined by counting the soluble fraction of a river sample for 400 minutes 17 times. After the background was subtracted and the counts corrected for decay, the net counts ranged from 65 to 119. The mean and the standard deviation were 87 and 17, respectively. Twelve of the counts were within one standard deviation, while all of the counts were within two standard deviations of one another. The lack of precision is basically due to the low level of  $^{124}\text{Sb}$ . A background count rate of 0.05 counts per minute was almost 20% of a sample net count rate. The background rate may vary up to 30%. If the background counts varied widely between each counting period, the  $^{124}\text{Sb}$  levels could be appreciably affected.

There are several possibilities for improving counting precision.

The number of  $^{124}\text{Sb}$  counts could be increased by increasing the sample size and by lengthening the counting time. This would reduce the statistical error of counting. The background level could be reduced further by increasing the lead shielding around the crystals or by adding a scintillation shielding that electronically reduces the background.

## CONCLUSIONS

The essential inferences from this thesis are:

1. Antimony-124 in the Columbia River exists primarily in the soluble phase of the aqueous environment.
2. Because an insufficient number of samples was taken, significant differences in sample populations could not be determined between the upstream and downstream stations at Bonneville Dam, Camas, Washington, and around the mouth of the Willamette River. The data show similar levels of radioactivity in the Columbia River during the sampling period.
3. The coincidence counting system that was developed had a lower minimum detection level than the well detection system, but the 20% relative standard deviation of coincidence counting which was due to small sample activity reduced this advantage of greater sensitivity.
4. The soluble  $^{51}\text{Cr}/^{124}\text{Sb}$  ratio did not vary significantly downstream in the Columbia River from Bonneville Dam to Point Adams, Oregon. Thus, they both appear to be conservative in the river.
5. Flow rates determined for the Columbia River from Hanford, Washington to Point Adams, Oregon would be unreliable during the summer freshet because of uncertainty due to the standard deviation of the ratio of soluble  $^{51}\text{Cr}$  to coincidence counted  $^{124}\text{Sb}$ . Flow rate determinations of the Columbia River plume in the



ocean would be possible in the summer, although dilution and dispersion of activity would probably increase the uncertainty.

## SUMMARY

1. Antimony-124 in the Columbia River originates at the Hanford reactors. Although its concentration in the river is low, it appears to be conservative during transport downstream to the ocean.
2. Water samples were collected with a plastic bucket at eight stations in the Columbia River in February, March, and April. They were transported back to the laboratory for filtration through a 0.45 micron filter and a prefilter and concentrated by ferric hydroxide scavenging.
3. Antimony-124 in the soluble and particulate samples was counted by coincidence and well detection.
4. The coincidence system yielded a lower minimum detection level for  $^{124}\text{Sb}$ , but it had a relative standard deviation of 20% due to the low levels of  $^{124}\text{Sb}$ .
5. The increase of soluble  $^{65}\text{Zn}$  downstream at station 3D on 7 March was probably due to release of particulate  $^{65}\text{Zn}$  induced by pulp mill outfall at St. Helens.
6. The soluble activities of  $^{124}\text{Sb}$ ,  $^{51}\text{Cr}$ ,  $^{46}\text{Sc}$ , and  $^{65}\text{Zn}$  generally did not vary largely on any one date. Percent particulate  $^{51}\text{Cr}$  and  $^{124}\text{Sb}$  varied more than did percent particulate  $^{46}\text{Sc}$  and  $^{65}\text{Zn}$ .
7. The ratio of soluble  $^{51}\text{Cr}$  to soluble  $^{124}\text{Sb}$  did not vary significantly in the region studied.

8. Flow time in the Columbia River using the ratio of soluble  $^{51}\text{Cr}$  to soluble coincidence counted  $^{124}\text{Sb}$  would not be reliable during the summer freshet because the uncertainty related to the standard deviation of the ratio would be greater than the flow time.
9. The average transport rate (activity per unit volume multiplied by river discharge) of radionuclides into the ocean was computed to be 1.5 Ci/d for  $^{124}\text{Sb}$ , 200 Ci/d for  $^{51}\text{Cr}$ , 11 Ci/d for  $^{46}\text{Sc}$ , and 10 Ci/d for  $^{65}\text{Zn}$ . The equilibrium activity of the radionuclides in the ocean was calculated to be 140 Ci of  $^{124}\text{Sb}$ , 8000 Ci of  $^{51}\text{Cr}$ , 1300 Ci of  $^{46}\text{Sc}$ , and 3500 Ci of  $^{65}\text{Zn}$ .

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## APPENDICES

Appendix A. Soluble activities with one experimental standard deviation (pCi/l).

Date	Station	Distance from river mouth	$^{124}\text{Sb}$ (coincidence)	$^{124}\text{Sb}$ (well)	$^{51}\text{Cr}$	$^{46}\text{Sc}$	$^{65}\text{Zn}$
27 February	1U	235 km	$4.1 \pm 0.4$	$3.7 \pm 1.0$	$411 \pm 26$	$5.3 \pm 1.4$	$2.5 \pm 0.4$
			$4.8 \pm 0.5$	$3.7 \pm 1.2$	$422 \pm 24$	$9.1 \pm 2.0$	$2.6 \pm 0.8$
	1D	234 km	$3.9 \pm 0.4$	$3.8 \pm 1.8$	$463 \pm 44$	$7.1 \pm 2.9$	$7.5 \pm 0.5$
			$4.6 \pm 0.5$	$3.5 \pm 1.3$	$477 \pm 33$	$11.2 \pm 2.4$	$4.5 \pm 1.4$
	2U	195 km	$3.9 \pm 0.4$	$3.5 \pm 1.9$	$459 \pm 44$	$11.0 \pm 3.5$	$5.1 \pm 1.7$
			$3.9 \pm 0.4$	$3.9 \pm 1.2$	$461 \pm 31$	$8.3 \pm 1.9$	$3.3 \pm 0.6$
2D	193 km	$3.8 \pm 0.4$	$3.9 \pm 1.1$	$432 \pm 27$	$9.0 \pm 1.8$	$3.2 \pm 0.4$	
		$4.4 \pm 0.4$	$3.7 \pm 1.1$	$428 \pm 27$	$7.8 \pm 1.7$	$3.1 \pm 0.4$	
7 March	3U	171 km	$1.2 \pm 0.2$	$1.3 \pm 0.6$	$280 \pm 16$	$5.8 \pm 1.0$	$1.6 \pm 0.2$
			$1.2 \pm 0.2$	$1.5 \pm 0.6$	$296 \pm 18$	$5.6 \pm 1.0$	$1.7 \pm 0.2$
	3D	139 km	$1.4 \pm 0.2$	$1.4 \pm 0.2$	$89 \pm 5$	$1.7 \pm 0.3$	$4.9 \pm 0.5$
			$0.4 \pm 0.1$	$0.6 \pm 0.2$	$89 \pm 5$	$1.4 \pm 0.3$	$4.5 \pm 0.5$
		50 km	$5.2 \pm 0.4$	$2.6 \pm 0.7$	$324 \pm 20$	$4.8 \pm 1.1$	$9.0 \pm 1.7$
			$2.5 \pm 0.2$	$2.7 \pm 0.7$	$333 \pm 20$	$5.2 \pm 1.0$	$9.9 \pm 1.6$
13 March	1U	235 km	$2.1 \pm 0.2$	$2.2 \pm 0.6$	$183 \pm 12$	$5.7 \pm 0.9$	$14.1 \pm 1.6$
			$3.0 \pm 0.2$	$1.6 \pm 0.5$	$81 \pm 7$	$4.3 \pm 0.9$	$12.8 \pm 1.8$
	1D	234 km	$2.2 \pm 0.2$	$2.3 \pm 0.6$	$185 \pm 13$	$5.4 \pm 1.0$	$15.2 \pm 1.6$
			$1.6 \pm 0.5$	$2.4 \pm 0.5$	$178 \pm 11$	$5.8 \pm 0.8$	$18.8 \pm 1.5$
	2U	195 km	$2.3 \pm 0.2$	$2.0 \pm 0.6$	$180 \pm 12$	$5.3 \pm 0.9$	$14.9 \pm 1.5$
			$3.2 \pm 0.3$	$2.5 \pm 0.6$	$194 \pm 13$	$6.2 \pm 0.9$	$13.2 \pm 1.4$
2D	193 km	$2.2 \pm 0.2$	$2.7 \pm 0.5$	$184 \pm 11$	$6.0 \pm 0.8$	$14.7 \pm 1.3$	
		$2.4 \pm 0.3$	$2.5 \pm 0.6$	$180 \pm 13$	$6.4 \pm 1.0$	$13.4 \pm 1.5$	



Appendix A. (Continued).

Date	Station	Distance from river mouth	$^{124}\text{Sb}$ (coincidence)	$^{124}\text{Sb}$ (well)	$^{51}\text{Cr}$	$^{46}\text{Sc}$	$^{65}\text{Zn}$
3 April	3U	171 km	$2.6 \pm 0.2$	$2.2 \pm 0.5$	$226 \pm 12$	$5.9 \pm 0.9$	$6.6 \pm 1.2$
			$2.1 \pm 0.2$	$1.8 \pm 0.6$	$230 \pm 13$	$12.0 \pm 1.3$	$11.3 \pm 1.8$
	3D	135 km	$1.5 \pm 0.2$	$1.5 \pm 0.3$	$152 \pm 7$	$4.4 \pm 0.5$	$5.7 \pm 0.7$
			$1.4 \pm 0.2$	$1.3 \pm 0.3$	$154 \pm 8$	$3.7 \pm 0.6$	$5.0 \pm 0.8$
	4	55 km	$1.9 \pm 0.2$	$1.6 \pm 0.4$	$183 \pm 9$	$3.9 \pm 0.6$	$3.5 \pm 0.8$
$1.8 \pm 0.2$			$1.3 \pm 0.4$	$190 \pm 10$	$5.1 \pm 0.8$	$3.3 \pm 1.0$	
10 April	Pt. Adams	11 km	$0.9 \pm 0.2$	$1.1 \pm 0.4$	$179 \pm 10$	$3.9 \pm 0.7$	$3.7 \pm 0.9$
			$1.3 \pm 0.2$	$0.9 \pm 1.1$	$154 \pm 21$	$6.4 \pm 2.1$	$3.5 \pm 3.1$
			$1.1 \pm 0.2$	$1.4 \pm 0.2$	$170 \pm 9$	$3.3 \pm 0.4$	$2.8 \pm 0.6$
			$1.4 \pm 0.2$	$1.3 \pm 0.7$	$157 \pm 14$	$2.9 \pm 1.1$	$4.0 \pm 1.7$
			$1.4 \pm 0.2$	$1.5 \pm 0.2$	$150 \pm 6$	$2.9 \pm 0.3$	$2.9 \pm 0.4$
			$1.0 \pm 0.2$	$1.3 \pm 0.4$	$149 \pm 9$	$2.8 \pm 0.6$	$3.4 \pm 1.0$
			$1.2 \pm 0.2$	$1.4 \pm 0.4$	$146 \pm 9$	$2.6 \pm 0.6$	$2.9 \pm 0.9$
			$1.0 \pm 0.2$	$1.2 \pm 0.5$	$145 \pm 10$	$3.3 \pm 0.8$	$4.3 \pm 1.2$

Appendix B. Particulate activities with one experimental standard deviation (pCi/l).

Date	Station	Distance from river mouth	$^{124}\text{Sb}$ (coincidence)	$^{124}\text{Sb}$ (well)	$^{51}\text{Cr}$	$^{46}\text{Sc}$	$^{65}\text{Zn}$
27 February	1U	235 km	$0.29 \pm 0.04$	–	$20.2 \pm 1.2$	$10.5 \pm 0.4$	$7.1 \pm 0.5$
	1D	234 km	–	$0.01 \pm 0.14$	$10.0 \pm 1.2$	$10.2 \pm 0.4$	$9.9 \pm 0.6$
	2U	195 km	$0.14 \pm 0.04$	$0.05 \pm 0.14$	$10.7 \pm 1.2$	$10.4 \pm 0.4$	$7.5 \pm 0.6$
	2D	193 km	$0.42 \pm 0.05$	$0.19 \pm 0.10$	$17.9 \pm 1.2$	$10.2 \pm 0.4$	$6.0 \pm 0.4$
7 March	3U	171 km	–	–	$7.2 \pm 0.9$	$6.7 \pm 0.3$	$5.8 \pm 0.4$
	3D	139 km	$0.45 \pm 0.08$	–	$2.9 \pm 0.4$	$1.5 \pm 0.1$	$1.2 \pm 0.1$
	4	50 km	$0.35 \pm 0.06$	$0.03 \pm 0.10$	$17.8 \pm 1.3$	$7.3 \pm 0.3$	$5.7 \pm 0.3$
13 March	1U	235 km	$0.21 \pm 0.04$	$0.01 \pm 0.13$	$5.8 \pm 1.0$	$10.4 \pm 0.4$	$7.8 \pm 0.5$
	1D	234 km	$0.46 \pm 0.08$	$0.06 \pm 0.12$	$5.0 \pm 1.0$	$9.9 \pm 0.4$	$8.3 \pm 0.4$
	2U	195 km	–	$0.06 \pm 0.22$	$2.0 \pm 1.7$	$12.8 \pm 0.6$	$9.1 \pm 0.8$
	2D	193 km	$0.01 \pm 0.04$	$0.09 \pm 0.62$	$5.4 \pm 4.5$	$10.9 \pm 1.1$	$7.6 \pm 1.8$
3 April	3U	171 km	$0.30 \pm 0.06$	$0.15 \pm 0.14$	$8.5 \pm 1.0$	$10.8 \pm 0.4$	$7.6 \pm 0.5$
	3D	135 km	$0.02 \pm 0.03$	$0.03 \pm 0.09$	$7.3 \pm 0.8$	$8.5 \pm 0.3$	$5.0 \pm 0.4$
	4	55 km	$0.06 \pm 0.04$	$0.01 \pm 0.13$	$6.8 \pm 0.9$	$7.3 \pm 0.4$	$3.9 \pm 0.5$
10 April	Pt. Adams	11 km	–	$0.04 \pm 0.10$	$13.3 \pm 1.1$	$7.5 \pm 0.3$	$3.3 \pm 0.5$
			$0.06 \pm 0.04$	$0.13 \pm 0.10$	$10.2 \pm 0.9$	$6.8 \pm 0.3$	$4.1 \pm 0.4$
			$0.02 \pm 0.03$	$0.04 \pm 0.08$	$20.3 \pm 1.0$	$8.8 \pm 0.3$	$4.6 \pm 0.3$
			$0.05 \pm 0.06$	$0.07 \pm 0.13$	$22.4 \pm 1.6$	$8.6 \pm 0.4$	$4.6 \pm 0.6$