An Abstract of The Thesis of

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IN   Chemistry   PRESENTED ON   June 12, 1978.
{ Major)   (Date)

Title: The Use of Stable Activable Tracers in Hydrology.

A tracer method utilizing stable activable tracers (involving rare earth nuclides with short-lived { $t_{1/2} < 1$ day} activation products) for tracing fluid bound substances in fresh water is explored. Simulated laboratory studies showed these tracers (Dy and In) when chelated with diethylenetriaminepentaacetic acid (DTPA) to be stable (<20%) in natural waters for periods up to 8 days. Background studies showed the Dy and In content of natural waters and sediments to be low enough as not to interfere with these tracers. Also such tracers can be analyzed rapidly and are cost-competitive with radiotracers or fluorescent dyes. Field studies demonstrate the conservative nature of the tracers and point to the usefulness of simple anion/cation fractionation in dissolved species pollutant identification.

The Use of Stable Activable Tracer in Hydrology

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of

the requirements for the

degree of

MASTER OF SCIENCE

June, 1979

APPROVED:

Redacted for Privacy

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Date thesis is presented June 12, 1978.

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INTRODUCTION

The water which man uses is primarily fresh water from rivers and lakes because of its availability and accessibility. Unfortunately, rivers have long bee used as a means for disposal of wastes. It is common practice to discharge sewage into streams and even when wastes materials are buried, ground water may carry some of these materials in solution and discharge it into streams.

Increasing human activities have resulted in an exponential increase in the amount of sewage and waste being discharged directly into rivers. Such large outpour of pollutants inevitably upsets the natural self-purification capability and balance of the aqueous environment. With ever increasing demands being placed on surface water for disposal of man's waste products combined with the dwindling quantity and quality of "pure" water available for human consumption makes it imperative that the capacity of these waters for assimilating wastes be known for the protection of their many beneficial uses. Thence one can establish a meaningful discharge standard and/or devise optimum strategies for improvement of water quality. It is equally important to be able to "trace" or track down the "natural" or man-made pollution sources, which may be unknown or unseen, as well as their ultimate fate in the receiving water in order to achieve the objectives mentioned above.

The use of tracers of one type or another, to investigate phenomena in hydrology that have not previously been easily amenable to investigation, has been an active field of study within environmental

science and engineering. Among the many phenomena studied are (1) Flow rates (2) Dispersion coefficients (3) Ground water characterization (4) Sediment transport (5) Soil erosion (6) "Tracing" and "characterization" of pollution sources.

Numerous types of tracers are available and employed in various hydrologic studies but generally they fall into three main categories (1) Chemical tracers, e.g. NaCl, $KHSO_4$, K_2CO_3 etc., (2) Radioactive Tracers such as Rb-86, Tritium, P-32, I-131, Br-82 etc. (3) Dyes such as fluorescein, Rhodamine-B etc.

Chemical tracers have been used successfully on a multitude of occasions but usually such tracers have to be added in high concentrations in order to remain detectable after subsequent dilution and to alleviate the "blank" problem. Also when tracers of such high concentrations are used, the density of the tagged materials will exceed that of the natural water and they are no longer hydrologically equivalent.

Radioactive isotopes[1,2,3,4,5,6] are commonly used tracers in studying various hydrologic phenomena. Unfortunately, there are situations where the use of radioisotopes is inadvisable because of safety or public health considerations. The use of long-lived radioisotopes are usually avoided because of their long residence time could cause long term health hazard but if short lived isotopes are used, then rigid time table must be followed. Also the use of long or short-lived radiotracers in the environment is becoming politically unfeasible; typical lead times to do radiotracer experiments in open streams are fast becoming a year or more due to regulatory problems.

Numerous fluorescent dyes [7,8,9] such as Rhodamine B, Fluo-
rescein etc., are also frequently encountered in water resources research
but suffer several drawbacks; among them are (1) they present aesthe-
tically objectionable modifications of water color; (2) occurence of
photochemical decay of many fluorescent dyes limit their uses to short
term studies; (3) dyes applicable to water of high quality only. Heavily
polluted water with high turbidity and color interferes with the use of
dye tracers.

In brief, all the aforementioned tracers suffer one or more
shortcomings and none are ideal. Also, a persistent phenomenon in using
tracers of one kind or another is the loss of tracers with time. The
limited data now available indicate that the added material may upset a
previously stable chemical regimen with the result that some of the
tracer material is removed by the biota and sediments in the rivers. With
the above considerations in mind, it is obvious that there is need to
develop a conservative fluid-bound tracer of high solution stability
which is safe, readily available, reasonably priced, with high detection
limit/sensitivity, low natural background concentration, that will cha-
racterize the flow of the water mass being traced without retardation
due to chemical or physical reactions and without modifications of the
intrinsic transmission characteristic of the water body. This develop-
ment would bring significant progress to water resources and hydrolo-
gical studies.

The choice of a specific tracer hinges on its meeting cer-
tain basic criteria. It is probably naive to assume that a single
tracer would be applicable to all natural waters. To the extent that

the chemical, physical and biological properties of natural water sys-
tems vary, the choice of tracers may also vary. Some of the basic cri-
teria that must be met are:

(1) Tracer should possess a high detection sensitivity for
the particular mode of analysis.

(2) Tracer should be reasonable in cost in terms of both time
and materials.

(3) Tracer should have a low natural concentration in water
mass into which it will be introduced.

(4) Tracer should not be hazardous at the concentrations or
total amount necessary for its use.

(5) Tracer should remain in solution, resisting precipitation,
sorption etc.

At this point, it would be appropiate to define the term
Stable Activable Tracer. A stable activable tracer is essentially a
chemical element or stable non-radioactive nuclide that one injects into
the system under study, followed by sampling and measurement of the tra-
cer concentration by activation analysis.

Not unlike other tracer technique, in order to choose the
appropiate stable activable tracer, the aforementioned criteria should
be met to an appreciable degree. In addition, it should possess favour-
able nuclear properties and that include:

(1) The thermal neutron capture cross section of the isotope
should be appreciable.

(2) The product from the (n, γ) activation of the stable

isotope should have a half-life of days or less and should emit readily detected gamma rays.

Probably no universal tracer exists that is suitable for all problems. A number of excellent studies have been carried out and some of these are summarized by Kruger[10]. In a series of experiments at the Pennsylvania State University. Jester and co-workers[11,12] used Br$^-$ and I$^-$ (along with some studies of V^{3+} and Co^{++} ions in natural waters) to mimic the movement of soluble species in natural waters. These studies were incomplete in that no attempts were made to quantitatively measure the stability of the tracer in the systems under study and because of the higher concentrations of these elements in natural waters, it was not possible to do large scale pollutant tracing. In a pioneering survey, Channell and Kruger[13] studied the possible use of rare earth tracers to follow pollutant dispersion in San Francisco Bay. They were able to demonstrate the general feasibility of this approach, but again the lack of detailed field studies of the tracer stability , the conservative nature of the tracer, as well as not utilizing the capability of simultaneous multiple source tracing leaves many unanswered questions.

In unpublished work, Hansen[14] actually compared the behaviour of long lived Eu,Tb and In activable tracers with fluorescent dye Rhodamine B in small (0.5 mile long) stream. Over this distance, Hansen showed the conservative nature of the tracers but did not demonstrate the economic viability of these tracers of their use in large scale experiments. In a preliminary study Schmitt et al.[15] showed that the dispersal of La and Sm could be followed in rivers but made no attempts

to study systematically the use of these elements as tracers. Indium and scandium were used as stable activable tracers for in-plant movements of water in wastewater treatment plants by Craft and Eicholz[16]. Dahl and co-workers[17] have shown that $In(NO_3)_3$ could be used to trace water stream patterns and pollutant dispersal in and around the harbor of a Norwegian town.

In this work, we explore the feasibility of using rare earth elements with short-lived activation products such as Dy or Lu as stable activable tracers. The rare earths are easily detected by instrumental neutron activation analysis allowing long range pollutant tracing and the use of environmentally insignificant tracer levels while the use of short-lived activation products allows rapid sample analysis and thus makes the tracers more cost competitive. Also the proposed use in our work of rare earth nuclides with short-lived activation products compared to the longer lived activation products proposed by Channell and Kruger should greatly improve the economic viability of the activable tracer technique, a stumbling block in the Channell and Kruger studies.

How does the stable activable tracer we propose to develop meet all the aforementioned criteria? First of all, let us examine Table I which includes some representative figures comparing some rare earth elements, which, when subjected to neutron activation analysis, produced the greatest amount of activity per dollar of tracer cost. This is of course, equivalent to asking which tracer is simultaneously cheap and easy to detect. Again, in compiling such a table, the nuclear properties (i.e. cross sections, half-lives, gamma ray

Table I: Properties of Some Rare Earth Stable Activable Tracers with Short Lived ($t_{1/2} < 1$ Day) Activation Products.

Element	Cost($/kg)[a]	Target Nuclide[b]	E_γ(%Abundance)[b]	$t_{1/2}$[b]	g/10^4cts	Cost($/10^4$cts)
Ce	45	Ce-136	446.0(2.3%)	9.0 h	0.085	3.8×10^{-3}
Pr	236	Pr-141	1575.5(3.7%)	19.2 h	0.018	4.27×10^{-3}
Nd	176	Nd-148	211.3(27%)	1.8 h	5.93×10^{-4}	1.04×10^{-4}
Sm	320	Sm-154	104.3(73%)	22.997 m	3.31×10^{-5}	1.05×10^{-5}
Eu	3960	Eu-151	121.8(37%)	9.30 h	1.32×10^{-7}	5.24×10^{-7}
Gd	3720	Gd-158	363.6(9%)	18.706 m	1.11×10^{-4}	4.13×10^{-4}
Dy	920	Dy-164	94.7(4%)	2.334 h	1.56×10^{-6}	1.44×10^{-6}
Ho	1100	Ho-165	80.6(54%)	66.78 m	2.42×10^{-6}	2.67×10^{-6}
Er	420	Er-170	112.0(25%)	7.519 m	3.61×10^{-4}	1.51×10^{-4}
Yb	860	Yb-176	151.0(16%)	1.900 h	1.77×10^{-4}	1.52×10^{-4}
Lu	18000	Lu-175	88.4(10%)	3.679 h	2.04×10^{-5}	3.67×10^{-4}
In d	1760	In-115	1097.2(80%)	54 m	6.80×10^{-7}	1.21×10^{-6}

a. Alfa Catalog, Ventron Corp., Danvers, MA,1977-1978.(Large quantities can be purchased at significantly lower cost.

b. C.M.Lederer,J.M.Hollander,I.Perlman,Table of Isotope, 6th edition (Wiley,N.Y.,1967) I.Binder,R.Kraus,R,Klein,D.Lee and M.M.Fowler,"A Chemist's Gamma Ray Table",Lawerence Berkeley Laboratory Report,LBL-6515,June,1977.

c. Assume 1 minute irradiation at a flux of 10^{13} n/cm^2/sec. Delay of 5 m, count 3 m. Sample positioned one cm away from a 40 cm^3 Ge(Li) detector.

d. In is not a member of the rare-earth family, it is a well known stable activable tracer and therefore included here for comparison purpose.

energy efficiencies etc.) chemical costs and amount of chemical required are all incorporated into the calculation. It should be fairly obvious by examining the table that Dy and In are by far, the most cost effective tracers using stable activable tracer technique. (Dy is a prototype for the rare earth tracers; In is a well known stable activable tracer. Dy is the thing under study whereas In is used for comparison purposes.) Furthermore their radioactivities are such that analyses can be performed in the laboratory in less than 15 min./sample, thus enabling low analysis cost and rapid availability of tracer experiment results.

According to the estimate of Channell and Kruger[10], the rare earth stable activable tracer technique has roughly the same cost as radiotracers for intermediate and large scale studies (10 million acre feet or 1.23×10^{13} liters of water or greater) and a factor of 2 - 5 times cheaper than the use of fluorescent dyes. Our estimate for a smaller scale study (~ 5×10^{10} liters) using dysprosium instead of the lanthannum employed by Channell and Kruger shows that the stable activable tracer technique is cheaper by a factor of ~ 3 to 4 times than radiotracers and yet comparable to the use of fluorescent dyes. Table II is a compilation of our estimate which compares the costs of using the three different tracer techniques. The cost estimates are to be taken as rough approximations and are intended merely to demonstrate that the costs associated with these technologies are similar.

Notwithstanding that cost is an important factor in selecting a tracer, it is also critical that the tracer one employs for a specific study has a low natural background concentration. Some representative

Table II: <u>Cost Analysis of Tracer Method</u>

Volume of Water tagged	5×10^{10} liters
Duration of Experiment	1 day
Number of Samples taken	100 samples
Rhodamine WT[a]	
Weight needed	110 lb
Tracer Cost	$ 457
Analysis Cost[d]	$ 200
Total	$ 657
Tritium[b]	
Activity needed	81 Ci
Tracer Cost	$ 243
Analysis Cost[d]	$3000
Total	$3243
Dyprosium[c]	
Weight needed	10 lb
Tracer Cost	$ 250
Analysis Cost[d]	$ 600
Total	$ 850

A. Tracer cost based upon an average minimum concentration of 1.3×10^{-5} g/m^3 and a tracer cost of 4.15 dollars/lb.

b. Tracer cost based upon an average concentration of 1.622 nCi/1 and a cost of $3/Ci for Tritium.

c. Tracer cost based upon an average concentration of 100 ng/1 and a cost of Dy of $ 25/lb

d. All samples analysis charges based upon current charges of Oregon State University in-house service analysis groups. The tritium analysis charge includes cost of preconcentration.

elemental abundances in river water are shown in Table III. Examination of Table III shows that the choice of Dy and In, due to their low natural abundance in natural water system, is warranted.

As far as hazardous nature of the tracer is concerned, the use of rare-earth tracers poses no detrimental effects because the tracers are non-toxic at the concentration encountered in environmental studies. Table IV shows the toxicity of some rare earth compounds in laboratory rats. Assume that the same LD_{50} applies to human beings, it would imply that a man who weighs 80 kg would have to inject the equivalent of 88 gm of Dy metal to achieve the LD_{50} concentration assuming all Dy ingested is retained. The typical Dy tracer concentration in the Willamette River experiments is about 50 ppb (parts per billion) including the natural background and that would mean he would have to drink approximately 10^{6} liters of Willamette River water in order to reach the LD_{50} concentration. This is equivalent to drinking the whole Willamette river and that is rather impossible.

As yet there is still the unresolved question of tracer loss which has plagued most experimenters. As indicated earlier, in tracing fluid bound substances, the tracers should remain water soluble, stable and conservative under "real" situations. To alleviate the problem of tracer loss, one approach has been the use of chelating agents that form complexes of high stability with the tracers and allow them to remain soluble in the presence of adsorbing materials as well as other chemical or biological species.

The metal chelates of aminocarboxylic acids of the rare

Table III: Elemental Composition of River Water[18,19,20,21,22]

Element**	Median	Range
Ag	0.00013	0.00001 - 0.0035
Al	0.34	0.01 - 2.5
As	0.0004	0.0004 - 0.23
Au	0.00006	-------
Ba	0.054	0.009 - 0.15
Br	0.021	0.005 - 140
Ca	15	4 - 120
Cd	0.08	------
Cl	7.8	5 - 35
Co	0.00090	0.0001 - 0.006
Cr	0.00018	0.0001 - 0.03
Cs	0.0002	0.00005 - 0.0002
Cu	0.01	0.006 - 0.4
Fe	0.67	0.01 - 1.4
Ga	0.001	------
Hg	0.00008	------
K	2.3	1.4 - 10
Mg	4.1	1.5 - 5
Mn	0.002	0.00002 - 0.13
Mo	0.000035	------
Na	6.3	3 - 25
Pb	0.005	0.0006 - 0.12
Ra	3.9 x 10^{-10}	------
Rb	0.0015	0.001 - 0.008
Se	0.02	------
Sn	0.00004	------
Sr	0.08	0.003 - 0.8
Th	0.00002	-----
Ti	0.0086	0.11
U	0.001	0.00002 - 0.05
V	0.001	0.007
Zn	0.01	0.0002 - 1
Zr	0.0026	0.00005 - 0.022
Eu	0.000009	-----
La	0.00033	-----
Sm	0.00012	-----
Dy		-----
In		-----

** All concentrations are in ppm (parts per million.)

Table IV: <u>Toxicity of Some Rare Earth Compounds</u>**

<u>Rare-Earth Chlorides</u>		$L.D._{50}$	<u>Rare-Earth Citrates</u>		$L.D._{50}$
Lanthanum	(La)	362.07	Lanthanum	(La)	82.66
Cerium	(Ce)	352.34	CCerium	(Ce)	149.52
Samarium	(Sm)	365.38	Samarium	(Sm)	164.25
Europium	(Eu)	387.80	Europium	(Eu)	186.67
Dysprosium	(Dy)	342.80	Dysprosium	(Dy)	113.12

<u>Rare-Earth EDTA</u>		$L.D._{50}$	<u>Rare-Earth Nitrates</u>		$L.D._{50}$
Lanthanum	(La)	37.26	Lanthanum	(La)	------
Cerium	(Ce)	37.57	Cerium	(Ce)	1355
Samarium	(Sm)	311.18	Samarium	(Sm)	981
Europium	(Eu)	240.09	Europium	(Eu)	1704
Dysprosium	(Dy)	-------	Dysprosium	(Dy)	1103

** All $L.D._{50}$ are in ppm of metal/Kg body weight of laboratory animal - oral dosage.

earths represent some of the most stable water soluble complexes. The stability constants of some of the rare earth chelates [27,28] are shown in Table V and Figure I. Examination of the table and figure shows that DTPA (Diethylenetriamine tetraacetic acid) complexes are more stable than other complexes, such as EDTA (Ethylenediamine tetraacetic acid), NTA (Nitrilotriacetic acid) and CDTA (Cyclohexanediamine tetraacetic acid) by factors of greater than ten and should constitute a group a potentially useful water tracers. Use of anionic chelates such as DTPA as tracers and the preconcentration of samples using anionic ion-exchange filter paper have the added advantage of lessening the sodium content of our samples which is inherently present in all environmental samples and interferes or masks the gamma-ray contribution of the activation products of interest. Also anionic tracer species tend to be more conservative than cationic species [29,30,31] in natural water. These observations result from the presence of surface active, electrically charged collodial particles and surface coatings. Common colloids in fresh water, such as hydrous iron and manganese oxides and clays, possess negative electrostatic charges. This explains the greater susceptibility of cationic species to undergo sorption.

In brief, what advantages do these techniques possess in general or when compared to fluorescent dyes or radiotracers? The advantages are:

(1) The tracers are non-toxic at concentrations encountered in environmental studies in contrast to the real (or imagined) problems with radionuclides release in the environment. There are no aesthetically objectionable modification of water color during tracing.

Table **V** Stability constants for various metals with EDTA, DTPA, CDTA and NTA[27,28].

Metal	EDTA log K_S	DTPA log K_S	CDTA log K_S	NTA log K_S
Ba (II)	7.8	8.6	8.0	6.41
Sr (II)	8.6	9.7	10.0	---
Mg (II)	8.7	9.0	10.3	7.00
Ca (II)	10.7	10.7	12.08	8.17
Sc (III)	23.1	--	---	---
Ti (III)	21.3	--	---	---
V (II)	12.7	15.1	---	---
V (III)	25.9	--	19.40	---
Cr (III)	24.0	--	---	---
Mn (II)	14.0	15.1	16.78	7.44
Fe (II)	14.3	16.5	---	8.84
Fe (III)	25.1	28.6	---	15.87
Co (II)	16.3	18.4	18.92	10.6
Co (III)	∿36	--	---	---
Ni (II)	18.6	19.6	19.4	11.26
Cu (II)	18.8	21.1	21.30	12.68
Zn (II)	16.5	18.3	18.67	10.45
Cd (II)	16.5	18.9	19.23	---
Hg (II)	21.8	26.7	24.4	---
Al (III)	16.1	--	17.6	---
Ga (III)	20.3	--	22.91	---
In (III)	25.0	--	---	---
Sn (II)	13.5	--	---	---
Pb (II)	18.0	18.8	19.68	11.80
Y (III)	18.0	22.4	19.15	11.48
La (III)	15.5	19.9	16.26	10.36
Ce (III)	15.9	20.4	16.76	10.43
Pr (III)	16.4	21.8	17.31	10.30
Nd (III)	16.6	22.2	17.63	10.49
Sm (III)	17.1	22.8	18.38	11.13
Eu (III)	17.3	22.9	18.62	10.79
Gd (III)	17.3	23.0	18.77	11.17
Tb (III)	17.9	23.2	19.50	11.31
Dy (III)	18.3	23.4	19.69	11.74
Er (III)	18.8	23.1	20.68	11.90
Tm (III)	19.3	22.9	---	11.79
Yb (III)	19.5	23.0	21.12	11.98
Lu (III)	19.8	22.4	---	12.10

FIGURE I: STABILITY CONSTANTS OF SOME RARE EARTH COMPLEXES.
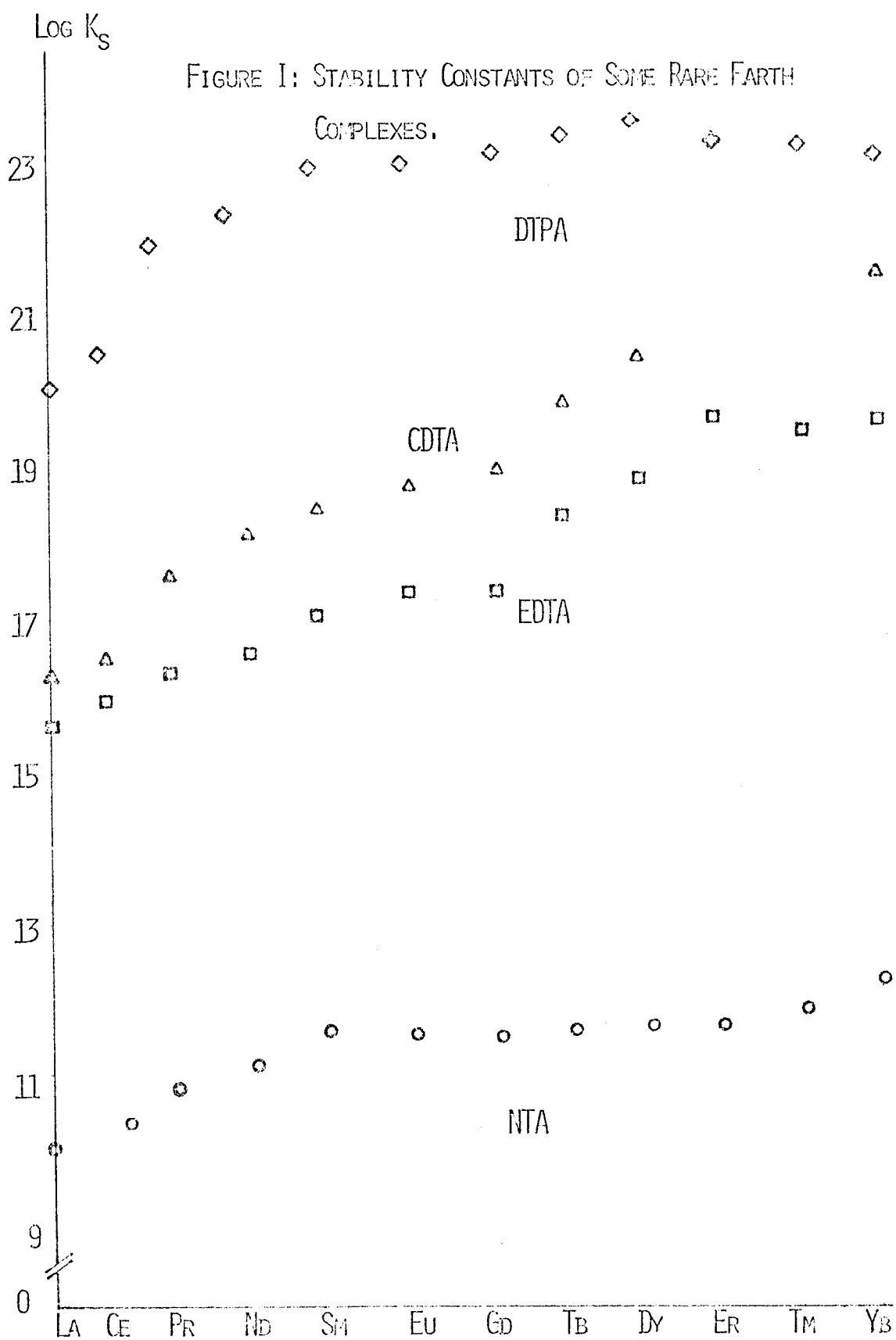
(2) The detection sensitivity of these tracers is very good. For example, for Dy, one can readily detect amounts of as low as 10^{-12}g. This allows pollutant tracing over very long distances not usually possible with fluorescent dyes or radioactive tracers.

(3) The tracers can be bound as EDTA or DTPA complexes and thus not suffer appreciable adsorption by sediments etc., as sometimes plaques the use of various dyes.

(4) The detection of these tracers is not affected by the presence of water color or the photochemical decay of the tracer.

(5) Their cost effectiveness is extremely competitive and attractive.

(6) Effluents from specific pollutant sources can be marked with a given "fingerprint" or "codon" and the effluent from several sources can be traced simultaneously.

In addition to all the above advantages, use of artificial tracers is superior to using "naturally-occurring" trace element in various hydrologic system as tracers. The "artificial" tracer has the advantages of:

(1) Controlled emission rates (either "pulse" or continuous injection as well as the magnitude of the tracer injected) which aid in model validation studies,

(2) Easy detection in that one can arrange that the tracer levels at all points in the system are well above detection limits.

(3) Cleaner multiple source tracing in that one can, by marking each of the several pollutant sources with a different tracer,

cleanly simultaneously trace the emissions from several sources in the area where the discharges mix.

In essence, the objectives of the study are as follows:

(1) To develop and laboratory test tracer techniques (involving the use of stable activable trace element, such as the rare earth elements and/or involving the use of "naturally occurring" trace elements) to trace the fate of fluid-bound pollutants in fresh water.

(2) To field test these tracer techniques. Extrapolation of laboratory results into the field is best done with questioning reservation. It is imperative to test the validity of these tracers developed in the "real" situations because there are variables that cannot be simulated in laboratory tests.

(3) To map the existing levels of trace elements present at various locations in the water and sediments in the Willamette River. This is an integral and essential part of the research because the practical sensitivity for quantitative tracer determination is limited by the residual or natural tracer concentration in water. Besides, mapping the existing trace element levels present for the discharge of various types of effluent sources, such as pulp and paper mills, sewerage outfall, metallurgical processors etc., can provide possible "fingerprints" of unique sets of trace element patterns from each of the aforementioned sources which can then be compared with the artificial tracer dispersal patterns.

EXPERIMENTAL

The overall plan for the research involved the laboratory development and testing of stable activable tracer (SAT) techniques to monitor pollutant transport in fresh waters followed by detailed field studies.

A. Tracer Preparation:

The stable activable tracers chosen for this work include indium (In) and the rare-earth element dysprosium (Dy). Oxides of the elements were dissolved in a minimum amount of hot concentrated nitric acid and a solution of diethylenetriamine pentaacetic acid (DTPA) was added to form a 1:1 complex of the rare earth chelate. (Complexometric titration using Erio-chrome Black T as indicator confirmed the 1:1 molar relationship[32,33]). The metal chelate solution was then diluted with fresh river water to the desired concentration prior to use in the field experiments.

B. Laboratory Studies:

Prior to field studies, certain preliminary laboratory experiments were performed to verify: (1) The effectiveness of the ion-exchange filter paper as a preconcentration medium for the chelated tracer as well as the natural elemental species present in the river water, (2) The extent of chelate formation, (3) The stability of the DTPA tracer complexes under simulated natural conditions, (4) The low intrinsic trace

element content of the ion-exchange filter papers, (5) The minimum number of filters and filtrations required to achieve optimum recovery, (6) Effectiveness of the freezing procedure as a sample preservation step.

(1) Effectiveness of Ion-Exchange Filter Papers as a Preconcentration Medium:

Many trace elements in natural water are present at sub-ppb levels and the quantity of tracer used in field experiments is usually kept to a minimum due to reasons of economics, public health considerations etc. The utilization of an efficient method of tracer and trace element recovery and concentration from the natural water would greatly enhance tracer utility and trace element determinations by reducing the in situ concentrations necessary for the quantitative determinations and increasing detection sensitivity.

To confirm that ion-exchange filter paper is an effective preconcentration medium for the tracer species as well trace elements present in natural water, two set of experiments were performed. The first experiment involved the preparation of radioactive ^{116m}In-DTPA, ^{165}Dy-DTPA as well as other rare-earth chelates at a concentration of $\sim 10^{-6}$M at a pH of 7.2 corresponding to the natural water pH and then filtering the solutions through an assembly of cationic and anionic ion-exchange filter papers (Gelman Acropore SB-6407 and SA-6404 containing Dowex 1-X18 and Dowex 50W-X8 resins respectively { See Appendix 1}). The second experiment involved the preparation of unchelated radioactive solutions of In, Dy, the rare-earths as well as some commonly

occurring elements such as Co,Fe,Zn,Cr etc.and then filtered these solutions through assembly of cationic and anionic ion-exchange filters. The results of such experiments are shown in Tables VI & VII.

(2) Extent of Chelate Formation:

The practical extent of the complex formation was verified by passing aliquots (~1 ml) of DTPA chelates of the radioactive ^{165}Dy ^{116m}In and other rare-earths, diluted with 500 ml of distilled water and pH adjusted to ~7.2, and filtered through two layers each of the cationic and anionic filters. Theoretically, the chelates which are in anionic form would be picked up by the anionic exchangers and any Dy,In or rare-earths that fail to form the anionic complexes will presumably be picked up by the cationic exchanger and thereby provide an indication of the extent of the chelate formation. The results of such an experiment are shown in Table VI.

(3) Time Dependence of Tracer Stability under Simulated River Conditions

One of the main criteria of a "good" tracer is that it should remain in solution and resist losses due to precipitation, sorption etc. Prior to the commencement of field studies, preliminary laboratory experiments were performed to investigate the behaviour and stability of the chelated tracer under simulated river conditions. Briefly, the experiments consist of placing known quantities of Dy and In-DTPA chelates ($\sim10^{-6}$M) in Erlenmeyer flasks agitated continuously in a thermostatical-

Table VI: Per Cent Formation and Pickup of Some Rare-Earth and Indium
DTPA Chelates at Natural pH.

| Compound | Anionic Ion-Exchange Filter | | Cationic Ion-Exchange |
	% Formation[a]	% Pickup[b]	% Compound that failed to form chelate[c]
LaDTPA	99.7	99.4	0.5
CeDTPA	99.5	95.4	0.6
SmDTPA	99.3	96.7	0.9
EuDTPA	99.2	95.5	0.7
GdDTPA	98.0	92.0	1.1
TbDTPA	98.6	92.5	1.0
DyDTPA	99.1	92.5	0.1
HoDTPA	99.0	92.0	0.9
YbDTPA	99.2	94.6	0.7
LuDTPA	99.3	95.4	0.7
InDTPA	99.7	94.1	0.2

a: Single filtration through two anionic ion-exchange filters, tracer solutions diluted with distilled water and pH adjusted to 7.2

b: Same as above except river water is used.

c. Single filtration through two layers of cationic ion-exchange filters, tracer solutions diluted with river water and pH adjusted to 7.2

Table VII; Pickup Efficiceny of Various Types of Filters**

Element	Cationic	Anionic	Nuclepore	Whatman #1
La	99.47	0.03		0.27
Ce	99.71			0.25
Sm	99.66	0.01		0.28
Eu	99.37			0.17
Tb	99.52			0.27
Dy	99.03			0.07
Yb	99.67	0.01		0.27
Lu	99.60	0.02		0.29
In	99.20			
Co	96.23	3.79	1.78	
Cs	93.36		0.60	
Ta	8.65	84.19	7.16	
Se	84.80	13.10	2.10	
Hg	1.94	91.58	2.35	
Cr	95.64		4.36	
Sc	67.90	32.04	0.06	
Ni	95.70		4.30	
Zn	98.60	0.11	0.79	0.50
Ba	100.00			
As		46.41	39.18	14.40
Sb		54.15		

** All radiotracers are diluted with fresh river water and pH adjusted
   to 7.2 prior to filtration through 2 layers of each filter.

ly controlled shaker baths at a temperature of $10^{O}C$ for a period of one hour to eight days with various combinations of river water and sediments: (i) 60 ml of unfiltered river water plus 10 g of river sediment (ii) 60 ml of unfiltered river water and (iii) 60 ml of filtered river water. The purposes of these experiments is to evaluate the effect of the actions of (i) sediments and suspended particulates (ii) suspended particulates and (iii) "pure" river water respectively on the stability of the tracer species.Unchelated Dy and In solutions were also tested and the results compared with the chelated solutions. Samples of each solution were withdrawn as a function of time. These were centrifuged to remove large suspended particulate matter and the remaining solution filtered through a series of Nuclepore, anionic and cationic filters. The Nuclepore membrane filter serves to remove any fine suspended particulates larger than 0.45 microns in size while the tracers and trace elements in the river water were collected onto the anionic and cationic filters respectively. The Dy and In content of the anionic filter and filtrate were measured using the technique of Instrumental Neutron Activation Analysis (INAA) to determine the percentage of the original tracer remaining in solution as a function of time. The results of these experiments are shown in Tables VIII - XI.

(4) <u>Trace Element Contents of Nuclepore Membrane Filter, Cationic and Anionic Ion-Exchange Filters:</u>

The applicability of the Nuclepore , cationic and anionic

Table VIII: Time Dependence of Tracer Stability under Simulated
River Conditions I (Unfiltered River Water)[a]

Time of Equilibration	Per Cent pf Original Tracer Remaining	
	DyDTPA Chelate	InDTPA Chelate
1 hr	97.1 ± 4.9	95.5 ± 4.8
2	95.8 ± 4.8	95.5 ± 4.8
4	94.6 ± 4.8	95.5 ± 4.8
6	97.3 ± 4.9	97.3 ± 4.6
12	95.6 ± 4.8	100.9 ± 5.8
24	97.1 ± 4.8	98.0 ± 5.2
48	97.0 ± 4.9	98.7 ± 5.1
4 days	98.3 ± 4.9	96.7 ± 5.2
6	98.3 ± 4.9	97.4 ± 4.9
8	96.2 ± 5.0	97.4 ± 4.9

a; 60 ml of unfiltered fresh river water maintained at a
constant temperature of 10°C

Table IX: Time Dependence of Tracer Stability under Simulated

River Conditions II (Filtered River Water)**

Time of Equilibration	% of Original Tracer Remaining in Solution	
	DyDTPA Chelates	InDTPA Chelates
1 hr	96.2 ± 4.9	95.6 ± 4.8
2	97.0 ± 4.0	95.2 ± 4.8
4	99.0 ± 5.0	94.5 ± 4.8
6	98.9 ± 5.0	96.0 ± 4.8
12	97.6 ± 5.0	94.9 ± 4.8
24	96.9 ± 4.9	96.4 ± 4.9
48	98.0 ± 5.7	97.9 ± 4.9
4 days	98.6 ± 5.0	96.8 ± 4.9
6	98.5 ± 5.0	95.6 ± 4.8
8	97.8 ± 5.0	96.8 ± 4.8

** 60 ml of fresh river water filtered through 0.45 micron

Nuclepore filter.

Table X: Time Dependence of Tracer Stability under Simulated
River Conditions II (Sediment + Unfiltered River
Water)*

Time of Equilbration	% Original Tracer Remaining in Solution	
	DyDTPA Chelate	InDTPA Chelate
1 hr	100.8 + 5.2	100.2 + 5.1
2	99.3 + 5.1	100.7 + 4.9
4	100.0 + 5.2	100.9 + 5.0
6	100.8 + 5.2	97.1 + 5.1
12	99.4 + 5.1	94.8 + 5.2
24	101.1 + 5.2	91.9 + 5.0
48	100.5 + 5.2	85.3 + 4.8
4 days	99.4 + 3.6	82.3 + 4.8
6	101.2 + 5.3	81.7 + 5.0
8	100.5 + 3.7	77.9 + 4.9

* Mixture consists of 10 grams of dried sediment plus 60 ml
of unfiltered river water with pH adjusted to 7.2 and temp-
erature maintained at 10°C.

Table XI: Time Dependence of Tracer Stability under Simulated
River Conditions IV (Unchelated Tracer + Sedinnet +
River Water)**

Time of Equilibration	% Original Tracer Remaining in Solution	
	Dy Solution	In Solution
1 hr	93.4 + 9.4	95.0 + 10.7
2	88.5 + 8.9	91.8 + 10.4
4	87.3 + 8.8	90.6 + 10.3
6	86.8 + 9.8	84.4 + 9.8
12	85.6 + 8.6	69.5 + 8.5
24	84.8 + 8.6	64.5 + 7.4
48	81.8 + 8.6	63.3 + 7.6
4 days	77.5 + 7.8	57.1 + 7.6
6	66.4 + 7.8	50.9 + 6.3
8	65.2 + 6.6	37.2 + 5.3

** Mixture consists of unchelated Dy and In solution in
60 ml of unfiltered river water and 10 g of sediments
equilibrated at a temperature of $10^{\circ}C$ and pH of 7.2

filters to remove suspended particulates and dissolved species in natural water samples hinges on, among other things, the low intrinsic trace element contents of these filters. Low trace element content of these filters can alleviate the problem of "blank" corrections which may introduce and cause erroneous results especially in quantitative works. To evaluate the trace element contents of these filters, samples were taken at random from the same batch, pelletized with a portable pellet press and then neutron activated. The pelletized samples provide identical irradiation and counting geometry for all the samples. Results of such determinations are shown in Table XII.

(5) The Minimum Number of Filters and Filtrations Required to Achieve Optimum Recovery:

Theoretically, the ion exchange capacity of a single ion exchange filter far exceeds the usual quantity of trace elements present in fresh water system (See Table III and Appendix I). However, in order to utilize these filters more efficiently and economically in terms of time and money, certain experiments were performed to determine (i) the minimum number of filters required to achieve maximum recovery (ii) the optimum number of filtrations required to achieve maximum retention of dissolved species of interest and (iii) effects of pH on the pickup efficiency of these filters.

In order to achieve maximum exchange, the filtration process must be repeated until equilibrium between the disks and the solution is established . The quantity of ions collected during a single paasage

Table XII: Trace Element Content of Nuclepore Membrane Filter, Cationic and Anionic Ion-Exchange Filter Papers. (ng/cm^2)

| Element | Nuclepore Membrane Filter | | Ion-Exchange Filter Paper | |
	This Work	Literature* [c]	Cationic[a]	Anionic[b]
Na	10	8-47	82	478
Br	1.49	0.37-2.80	24.8	12.1
Mn	0.44	0.07-0.31	28.0	32.9
Sm	0.005	0.001-0.002	1.15	0.29
Eu	0.0004	0.000016	0.0024	---
Co	0.29	---	0.40	0.03
Zn	1	---	342	335
K	9	---	32	131
La	0.104	---	---	---
Cr	---	---	31.7	29.4
Fe	---	---	---	267
W	---	---	---	0.5
Sc	---	---	---	0.052

(a) Gelman Acropore SA-6404. Gelman Instrument Company, Ann Arbor, Michigan.

(b) Gelman Acropore SB-7407. Gelman Instrument Company, Ann Arbor, Michigan.

* Due to the large variations of the reported values, the ranges rather than average values were reported here.

(c) Jones,R.A., MS Thesis, Department of Chemistry, Oregon State University, 1977.

Shum,Y.S.,Loveland,W.D., Atmos.Environment, 8,645 (1974)

Ricci,E., et al., "Nuclear Method in Environmental Research", USERDA Report Conf-740701,1974.

through the paper depends on the quantity of ions in solution, the number unfilled ion-exchange sites in the disk and the affinity of the ions for the resin in the disk. In order to establish the standard number of filtrations to be used in subsequent work, solutions containing radioactive Sm and La at a pH of ~7.2 were filtered 1,3,5,7,10 and 20 times through double layers each of the cationic and anionic ion-exchange filters. The results are shown in Table XIII.

To estimate the minimum number of filters required to achieve optimum quantitative recovery of tracer/trace elements, radioactive tracers of Sm and La were filtered through single/double layer(s) of cationic ion-exchange filter(s) 1,3,5,7,10 or 20 times. The experiment is important from the standpoint of economics and time. The less the number of filters required the less the time it will take for the filtration process and hence less expensive. The results of such experiments are shown in Table XIV.

In addition to the above series of experiments, tracer solutions of La and Ce adjusted to various pH (pH 1 to pH 7) were filtered through double layer of cationic filters and the radioactive on the top and bottom filter as well as filtrate were counted and the efficiency of the ion-exchanger at various pH determined. The results are shown in Table XV.

(6) Effectiveness of Freezing Procedure as a Sample Preservation Step:

It may be worthwhile to point out that there is no one technique of preservation that can maintain complete stability for every constituent after the sample is removed from the parent source[34]. Tradition-

Table XIII: Variation of Per Cent Pickup with the Number of Filtrations**

Number of Filtrations	Filter	La % Pickup	Sm % Pickup
1	Top	98.63	99.18
	Bottom	1.37	0.82
	Filtrate		
3	Top	99.87	99.38
	Bottom	0.13	0.62
	Filtrate		
5	Top	99.70	99.83
	Bottom	0.30	0.17
	Filtrate		
7	Top	99.74	99.87
	Bottom	0.26	0.13
	Filtrate		
10	Top	99.96	99.64
	Bottom	0.04	0.36
	Filtrate		
20	Top	99.96	99.89
	Bottom	0.04	0.11
	Filtrate		

** Result is the average of 3 determinations each.

Table XIV: Effect of Number of Filtrations and Number of Filters on the Pickup Efficiency of Ion-Exchange Filters.**

Number of Filtrations	La Tracer		Sm Tracer	
	Single Filter	Double Filter	Single Filter	Double Filter
1	98.2%	99.9	98.8	100.0
3	99.0%	100.0	99.1	100.0
5	99.4%	100.0	99.4	100.0
7	98.3%	99.9	99.4	100.0
10	97.9%	100.0	99.4	100.0
20	99.9%	100.0	98.66	100.0
				100.0

** The radioactive Sm and La are in distilled water matrix and pH adjusted to 7.2.

Table XV: Variation of Pickup Efficiency with Variations in pH*

pH	Filter	Sm %Pickup	Ce % Pickup
1	Top	92.2	96.4
	Bottom	7.3	3.6
	Filtrate		
1.5	Top	98.9	98.6
	Bottom	1.1	1.4
	Filtrate		
2	Top	96.1	98.9
	Bottom	3.9	1.1
	Filtrate		
2.5	Top	100.0	100.0
	Bottom		
	Filtrate		
3	Top	100.0	100.0
	Bottom		
	Filtrate		
3.5	Top	100.0	100.0
	Bottom		
	Filtrate		
4.5	Top	100.0	100.0
	Bottom		
	Filtrate		
5	Top	97.3	98.4
	Bottom	2.7	1.6
	Filtrate		
6	Top	100.0	N.D.**
	Bottom		
	Filtrate		
6.5	Top	98.7	98.8
	Bottom	1.3	1.2
	Filtrate		
7	Top	100.0	100.0
	Bottom		
	Filtrate		

* Distill Water Matrix   ** Not Determined

ally, the acidification of water samples is considered by many as "the" way of preserving metallic ions in solution[35]. However, acidification of the water samples will not be indicative of the true metal content of the water samples at its source, since most inorganic constituents will have been desorbed from the suspended particulates. It is also important to consider the adsorption and leaching of soluble materials upon and from the walls of the sample containers, and for this reason it is necessary to acidify[36]. This may seem paradoxical since one must acidify and yet cannot and the obvious solution is to filter and to a acidify or otherwise prevent container surface adsorption in the field. In addition, it is most unfortunate that a wide variety of solvents, reagents and other materials encountered in trace analysis contain ex-teemely high impurity levels of various elements[37]. Table XVI will il-lustrate the level of contamination from some common reagents an ana-lyst may use and encounter.

In our case, we elect to freeze the samples to eliminate the adsorption and leaching of soluble materials upon and from the walls of the containers as well as desorption of inorganic constituents from the suspended particulates. Indeed, it has been demonstrated by the Battelle Pacific Northwest Laboratories and National Bureau of Standards [38,39] that rapid freezing of the samples provide a better alternative to chemi-cal preservation.

To confirm the effectiveness of freezing as an acceptable sam-ple preservation procedure, two approaches were employed; (i) Clean neutron activated polyvials were placed into a one liter sample container

Table XVI: <u>Trace Element Contents of Some Common Laboratory Solvents, Reagents and Other Materials</u>[**]

	Zn	Fe	Sb	Co	Cr	Sc	Cs	Ag
Quartz distilled water	9.5	<0.2	∿0.10	∿0.20	<10	0.0025	0.12	<0.02
Double distilled water	∿1	<0.2	<0.01	<0.02	∿2	<0.0001	<0.01	<0.02
Triple distilled water	∿0.5	∿1	∿0.02	<0.02	12	∿0.0002	<0.01	<0.02
Nitric Acid	13	∿2	∿0.03	0.018	72	0.0007	<0.01	∿0.24
Double distilled nitric acid	∿2	∿1	∿0.04	∿0.03	13	∿0.008	<0.1	0.29
Hydrochloric Acid	22	∿1	0.20	∿0.09	1.1	0.002	<0.002	<0.1
Ammonium Hydroxide	2.3	<0.1	<0.006	0.009	<0.04	<0.0003	<0.002	<0.1
Quartz Tubing	20	N.M.	58	1.7	225	0.10	0.29	<0.1
Borosilicate glass	730	280,000	2900	81	N.M.	106	<100	<0.001
Kimwipe Tissue	48,800	1000	16	24	500	14	<0.1	∿0.8
White Plastic tape	2.94x10^{5}	N.M.	67,100	<4	U.M.	84	<50	U.M.
Scotch Magic Mending Tape	1410	5130	33	6.1	<10	0.48	<0.3	<10
Millipore Filter	2370	330	39	13	17,600	0.79	1.5	<0.05
Teflon	9.3	35	0.4	11.7	<30	<0.004	<0.01	<0.3
Plexiglas	<10	<140	<0.01	<0.05	<10	<0.002	<0.06	<0.03
Polyvinyl Chloride (PVC)	7120	270,000	2690	45	2	4.5	<1	<5

[**] All concentration are in parts per billion (ppb)

filled up with fresh river water and then frozen. (ii) Radioactive tracers were mixed with fresh river water and then placed in a sample container. The mixture was then frozen. The frozen solutions in (i) and (ii) were later thawed, the surface layers discarded and all the solution removed. The solution in (i) was filtered through double layers each of cationic and anionic ion-exchange filters to pick up any radioactive trace elements which may have been desorbed or leached out from the vials during the freezing process. The solution in (ii) was removed, and the sample container analyzed for any radioactivity it may have picked up during the freezing process. Both experiments show little or no

evidence of such happenings i.e., trace elements being leached out, absorbed or desorbed during this freezing process, suggesting that freezing is a good if not perfect way of preserving the samples. On the other hand, the trace element content of the container are very low and the quantity leached out or sorbed/desorbed may be beyond the detection limit and may contribute an insignificant amount to the "true" trace element content even if all the leaching and/or sorption or desorption reaction did take place.

In experiments performed to test the recovery of tracers/trace elements in natural water, there were several difficulties. Firstly, the filtration rate is extremely slow due to blockage of the ion-exchange filters and Nuclepore prefilters. It was decided to introduce a Whatman No.1 filter which has larger pore size to screen out the larger particulates and thus minimize the blockage of the Nuclepore and ion-exchange filter and thereby speed up the time needed for each filtration. However,

the introduction of such prefilters brought up additonal problems; (i)
How much of the dissolved species will be retained by these prefilters
and (ii) How much trace elements will be leached out from this filters
during the filtration process? To evaluate this, two experiments were
performed; (1) 500 ml of fresh river water was filtered through neutron
activated Nuclepore and Whatman filters and any radioactive trace elements
leached out from the filters picked up by cation and anionic ion-exchange
filters . (2) 500 ml of fresh river water was mixed with radioactive
solution of some common cationic and anionic species present in natural
water and filtered through layers of cationic and anionic ion-exchanger.
The experiments revealed that the retention of radionuclides by the
prefilters is very small usually less than 1% and the amount of trace
elements leached out is negligible. Results of the experiments are shown
in Table VII.

Additional laboratory study of the entire sampling and preser-
vation procedure carried out for the Dy and In chelates added in known
concentrations showed better than 95% recovery.

C. Field Studies

Basically, this phase of the research involves field studies of
the use of tracers to trace discharges from typical Willamette River
waste outfalls and to field test the conservative nature of the tracers
developed.

In order to employ the tracers chosen, it is necessary to
verify, first of all, the expected low levels of Dy and In in the Willa-

mette River water and sediments and obtain at the same time "background" information on other major or minor elements present.

Part of our "baseline" studies of the Willamette River involves the collection of both bottom sediments and water samples from selected sites along the river. The selection of the various sites is based on the following criteria: (i) Accessibility (ii) Proximity of location where substantial number of industries are located (iii) Locations far enough downstream from each effluent source to allow thorough mixing[40,41]. Sites chosen for this study include waste outfalls of paper and pulp mills, severage and metallurgical processor outfalls at various "urban" areas such as Eugene, Salem, Albany, and Corvallis as well as "rural" area such as Harrisburg, Peoria, Newburg Independence and Wilsonville. A complete list of the sampling sites involved is shown in Table XVII. The Willamette River (See Map 1) is a relatively fast moving (~7 miles/hour) medium size (~100 ft wide, 12 feet deep) river originating in the high Cascade mountains of Oregon and flowing north for about 150-200 miles through the fertile agricultural lands of the Willamette Valley (Map 2) to the Columbia River. Also shown in Map 2 are the locations of significant industrial outfalls along the river used in the tests of the tracer behaviour.

All sediment and water sampling was done from a boat. "Surface" water samples were obtained by dipping a one-liter "open-mouthed" polyethylene bottle into the stream. "Deep" samples were taken using a commercial messenger-operated Nansen type trace metal water sampling bottle[42]. The water temperature and pH were measured

Table XVII <u>Sampling Sites</u>

(1) Wilsonville 2: 2 miles downstream of Clark's Marina, Wilsonville,
River mile: 39.50

(2) Wilsonville 1: 2 miles upstream of Clark's Marina, Wilsonville.
River Mile: 43.50

(3) Newburg 3: 2 miles downstream of Newburg Boat Ramp, Newburg.
River Mile: 48.00

(4) Newburg 2: Newburg Boat Ramp - Paper Mill Otfall, Newburg.
River Mile: 50.50

(5) Newburg 1: 2 miles upstream from Newburg Boat Ramp, Newburg.
River Mile: 52.50

(6) Salem 4: 2 miles downstream of Wallace Park Boat Ramp, Salem.
River Mile: 82.00

(7) Salem 3: Lagoon approximately 50 yds from Boise-Cascade Outfall,
Salem. River Mile: 84.90

(8) Salem 2: Boise-Cascade Paper Mill Outfall, 500 yds from Wallace
Park Boat Ramp, Salem. River Mile: 84.90

(9) Salem 1: 2 miles upstream of Wallace Park, Salem.
River Mile: 86.90

(10) Independence 2: Half mile downstream of Independence Boat Landing
Independence. River Mile: 97.50

(11) Independence 1: One mile upstream of Independence Landing, Indepen-
dence. River Mile: 99.00

(12) Western Kraft Outfall: Western Kraft Paper Mill Outfall, 2 miles
downstream of Bryant Park Ramp, Albany. River Mile: 118.20

Table XVII Sampling Sites (continued)

(13) Albany 5: One and quarter miles downstream of Bryant Park, Albany.
River Mile: 118.45.

(14) Albany 4: 3/4 mile downstream of Bryant Park Ramp, Albany.
River Mile: 119.45

(15) Albany 3: 2.5 miles upstream of Bryant Park Ramp, Albany.
River Mile: 122.70

(16) Albany 2: 5 miles upstream of Bryant Park Boat Ramp, Albany.
River Mile: 125.20

(17) Albany 1: 6 miles upstream from Bryant Park Ramp, Albany.
River Mile: 126.20

(18) Fischer Island: Approximately 1.8 miles upstream of Mary's River
Landing, Corvallis. River Mile: 134.

(19) Peoria 2: 2 miles downstream from Peoria Park, Peoria.
River Mile: 140.90

(20) Peoria 1: 2 miles upstream of Peoria Park, Peoria.
River Mile; 144.90

(21) Harrisburg 2: 2 miles downstream of Harrisburg Boat Landing, Harr-
isburg. River Mile: 160.00

(22) Harrisburg 1: 2 miles upstream of Harrisburg Landing, Harrisburg.
River Mile: 164.00

(23) Eugene: Downstream of Armitage Park Boat Ramp, N.E. of Eugene.
River Mile: 175.00

Map I: Map of Oregon Showing the Locations of The Willamette River and

Major Population and Industrial Centers Along the River.

COLUMBIA RIVER

COLUMBIA
PLATEAU

Portland

Wilsonville

WALLOWA
MOUNTAIN

Newburg

RANGE

RIVER

OCEAN

Salem

RANGE

BLUE
MOUNTAIN

Independence

Albany

Corvallis

PACIFIC

WILLAMETTE

Peoria

CENTRAL OREGON
PLATEAU

Harrisburg

Eugene

CASCADE

COAST

KLAMATH
BASIN

HIGH
DESERT

ROGUE RIVER BASIN
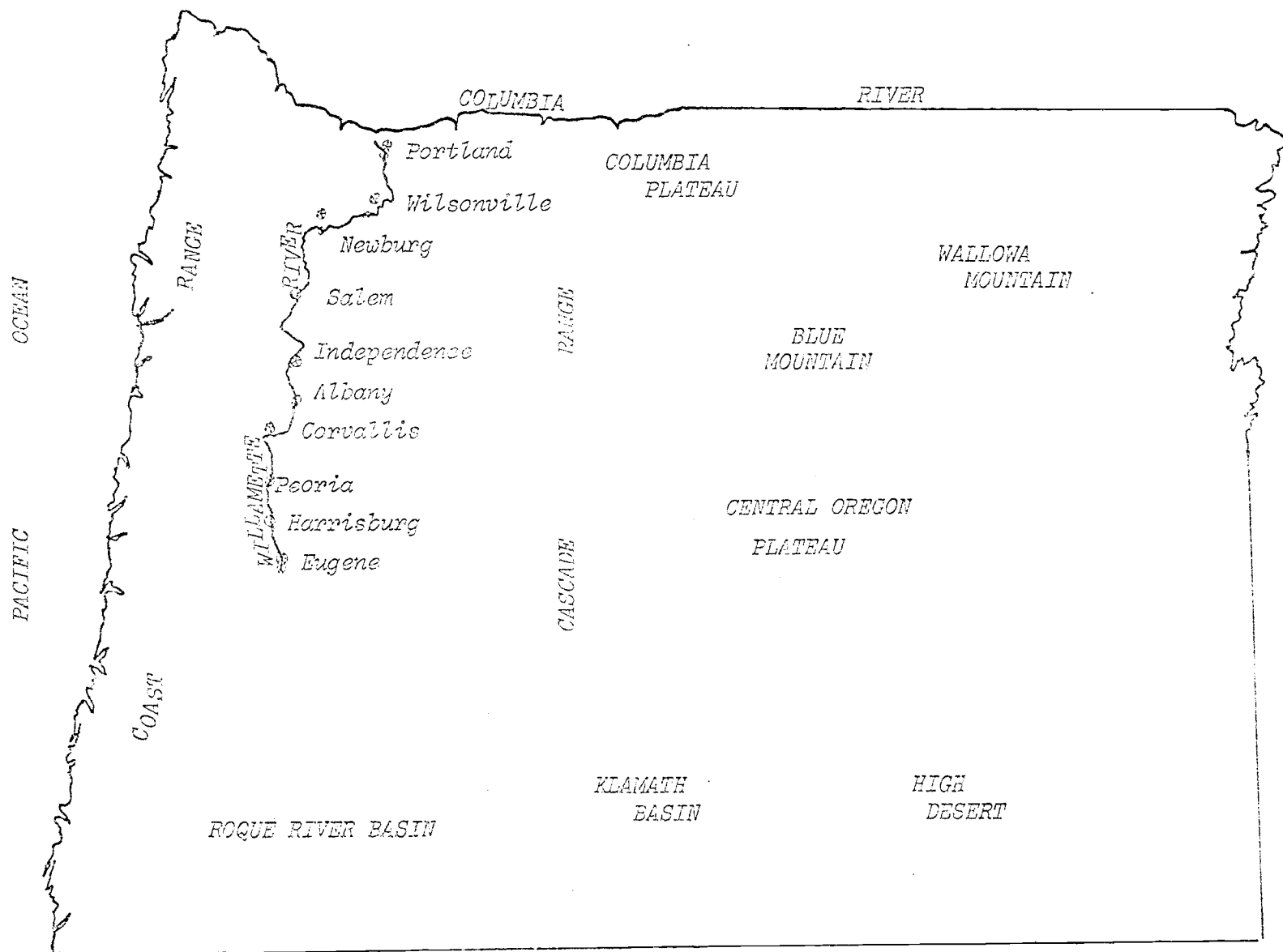
Map II: Enlarged Map of The Willamette Valley Showing Various Sampling

Sites on The Willamette River.(Numbers on the Map Indicate the Act-

ual Locations where Sediment and Water Samples were taken: see Table

XVII for detailed Description of the Various Sampling Sites.)

N
W — E
S

WASHINGTON

COLUMBIA RIVER

PORTLAND

North

WILSONVILLE
NEWBURG 21   23
20   22
19

Yamhill

South

Mollala

Yamhill

Butte

River

18 17
15 16 SALEM
Creek

INDEPENDENCE 14
13

North
Santiam

12
11
10
8 9
7 ALBANY South

Mary's
River CORVALLIS
6
Santiam

OREGON

5
PEORIA
4

Long
3 HARRISBURG
2

Tom
1
Mckenzie River

EUGENE
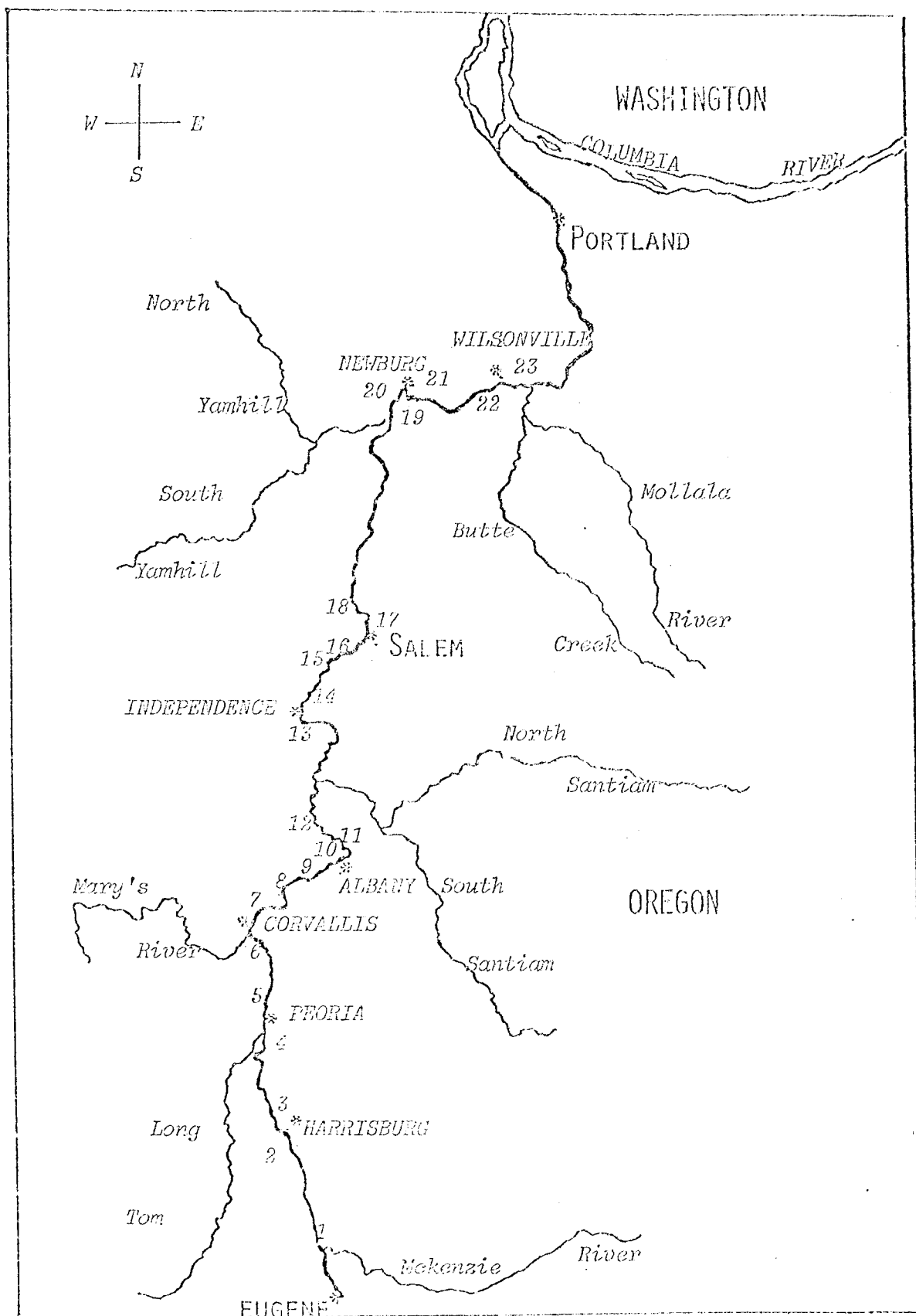
immediately after collection of samples . No chemical preservatives were added to the samples but the samples were kept in a dark, cool place and refrigerated upon arrival at the laboratory. Sediment samples were also collected at points where the water samples were taken. A simple messenger operated scoop dredge was used for this purpose. The sediments obtained were immediately placed in precleaned polybottle and then transported to the laboratory where they were refrigerated prior to analysis.

In actual tracer field studies, the tracer solution was injected continuously into the river via a home-made battery operated peristaltic pump with a constant injection rate (typically 1-2 ml/sec) and controlled by a built-in automatic on-off timer. (See Figure II) The tracer injection was typically performed at or near the river bank to simulate the dumping of sewage and/or pollutants into the river.

Three separate field tests were conducted:

(i) Freeway Lake Experiment (ii) Willamette River Experiment I and

(iii) Willamette River Experiment II.

(i) Freeway Lake Experiment: Freeway Lakes consists of three adjoining lakes connected to one another by narrow channels. They are located approximately two miles south of the City of Albany and right next to U.S. Interstate Highway No.5. The lakes are 7, 9.4, 21.5 acres in area and typically 10 - 12 feet deep. The lakes are all spring fed without any obvious outlet and constitute a quasi-dynamic system. Freshly prepared DyDTPA tracer was "spot" injected into the smaller lake (Lake I) and samples taken from the three lakes on the same day, one

FIGURE II: TRACER PUMP AND ACCESSORIES.

BATTERY

TYGON TUBINGS.

AUTOMATIC D.C. TIMER

D.C. MOTOR   PERISTALTIC PUMP HEAD
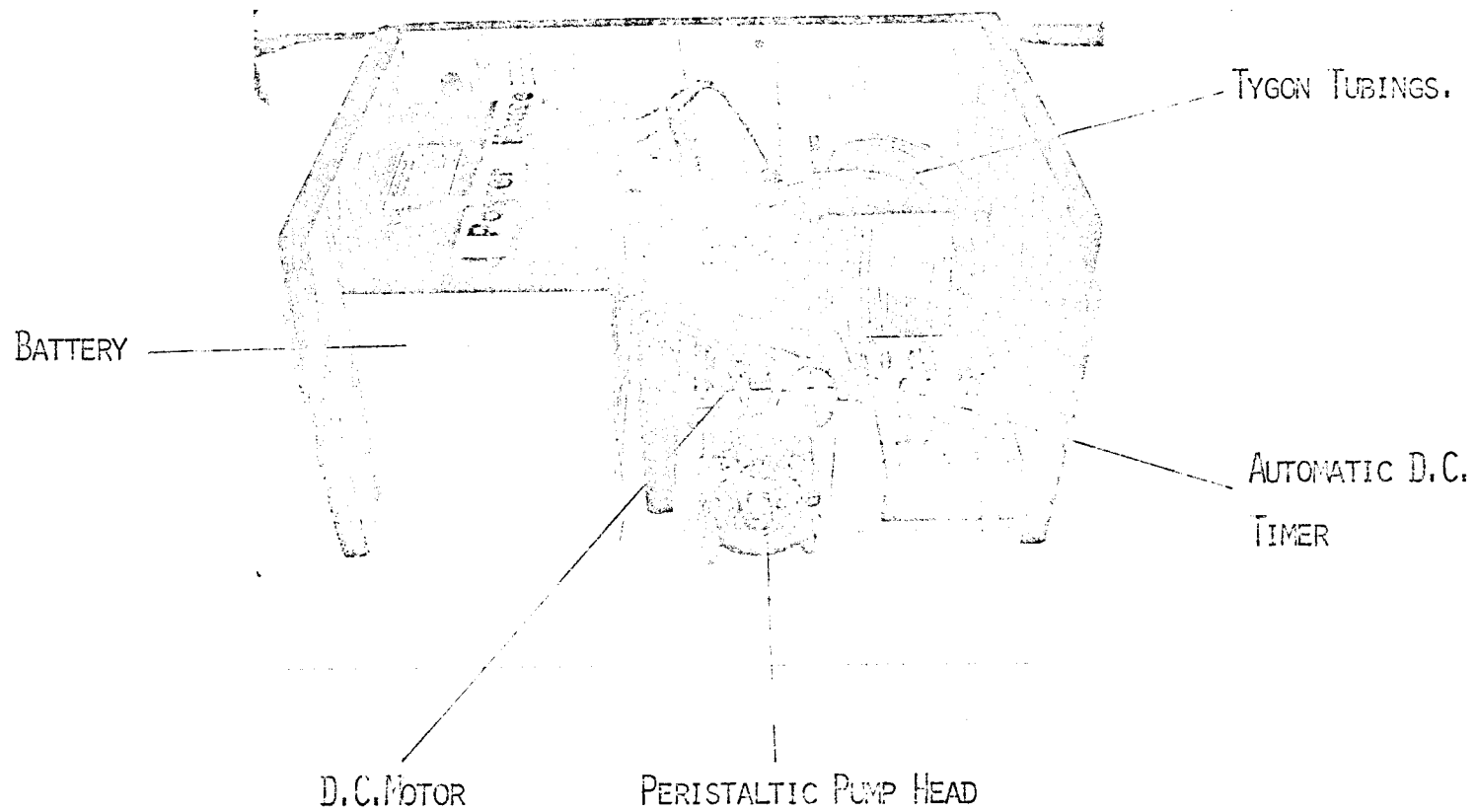
two, three and fifteen days from various representative points of the three lakes. Result of these experiments are shown in Figures III, IV and V and Table XVIII. The primary purpose of this experiment is to test the conservative nature of the tracers in actual field situation, because the laboratory experiments performed on the same tracer lack many of the natural "ingredients" present in the lake e.g. vegetation that may adversely affect the behaviour of the tracer.

(ii) Willamette River Experiment I: This experiment was carried out in an open, flowing river and was performed to test not only the tracer stability but also water sampling logistics, i.e. coordinating time between injection and sampling etc. The tracer was injected at a constant rate and known concentration for a period of 1 hour 20 min. using a peristaltic pump (See Figure II). The injection was performed at the bank of the Peoria City Boat Ramp and was intended to simulate the dumping of sewage/pollutants by diffuser into the open river. Samples were collected in Corvallis some ten miles downstream.

To establish the tracer arrival time at the sampling sites downstream, current river discharge data (obtained from N.W.Water Resources Data Center, USGS, Portland. OR. and U.S.Army Corps. of Engineers, Portland, OR.) coupled with information from the U.S.G.S. Hydrologic Investigation Atlas #HA-273 was used[43]. Prior to the predicted tracer arrival time, "blank" background water samples were taken from a small motor-driven boat at various horizontal and longitudinal positions along the river at two depths, a "surface" depth and a "deep" sample taken at 0.6 x the depth of the river. The river depth was measured by means of a"water ruler" (See Figure VI) and the sample

Table XVIII: Freeway Lakes Tracer Stability Experiment Concentration
            Profile *

Time (Day)		Lake I**	Lake II**	Lake III**	% Tracer Remaining
One	Mass of Tracer	16.32g	2.88g	Negligible	96%
	Average Concentration	189 ± 5 ppt	25 ± 7 ppt	Negligible	80%
Three	Mass of Tracer	3.27g	3.80g	8.93g	80%
	Average Concentration	38 ± 1 ppt	33 ± 1 ppt	31 ± 1 ppt	
Fifteen	Mass of Tracer	2.38g	4.23g	9.28g	79%
	Average Concentration	28 ± 1	38 ± 1 ppt	33 ± 1 ppt	

* Initial amount of Dy as DyDTPA added + 20.0 g

** Lake I,II,III represent lakes with area of 7, 9.4 and 21.5 acres
respectively

Mass of tracer in each lake is estimated by multipling the average
concentration by the area and estimated depth of each lake. All
concentrations are in ppt (parts per trillion)

Average concentrations reported are the weighted averages.

Figure III: Freeway Lakes Tracer Stability Field Tests Concentration Profile (First Day)
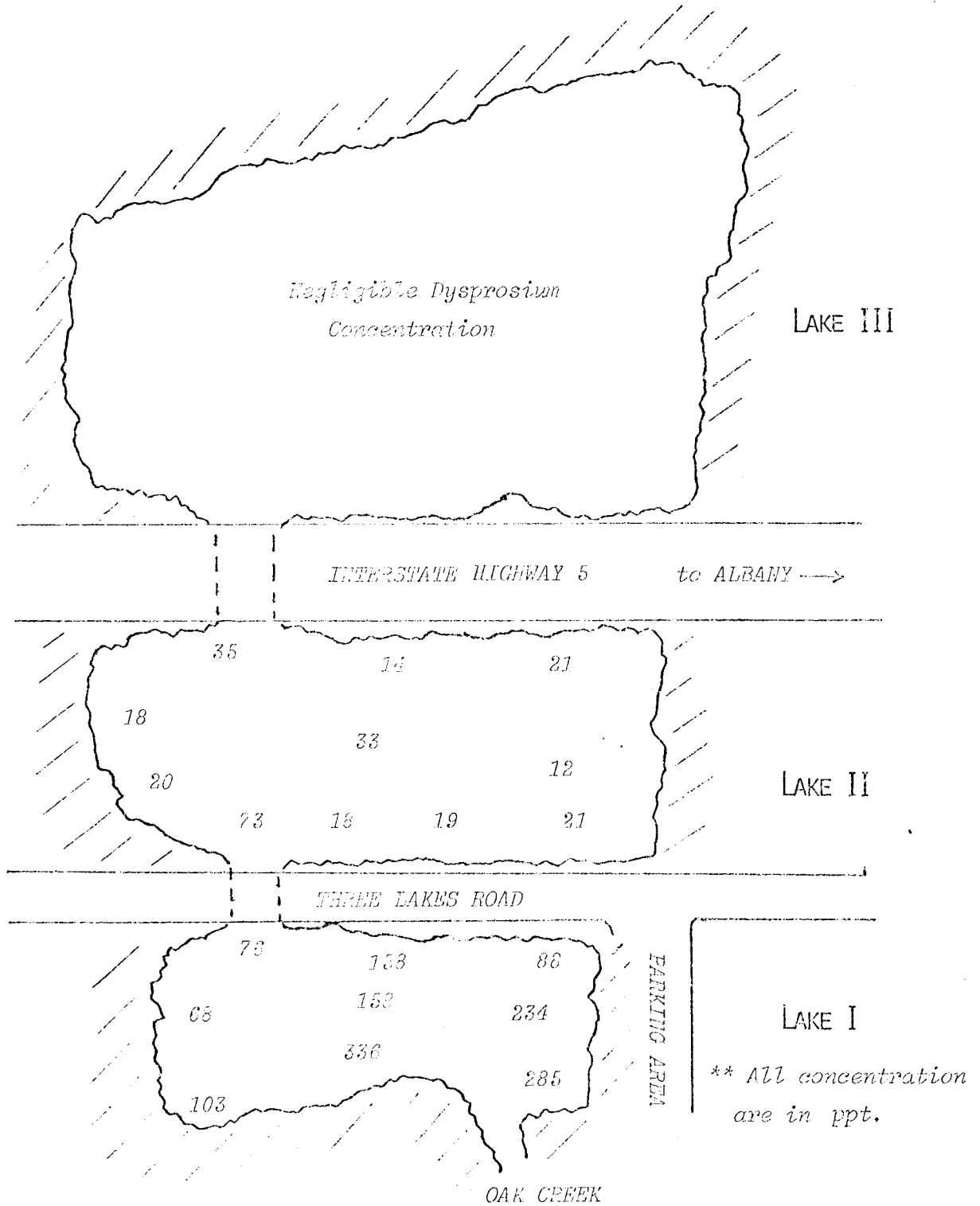
Figure IV: Freeway Lakes Tracer Stability Field Tests
Concentration Profile (Third Day)

LAKE III

25^{**}

45

26   30

23   35   29

INTERSTATE HIGHWAY 5   To ALBANY →

LAKE II

28   34^{**}

38

35   76

30

27   38

THREE LAKES ROAD

LAKE I

69   38 26^{**}

31   31

55   30

PARKING AREA

*** All Concentrations*
are in ppt.

OAK CREEK
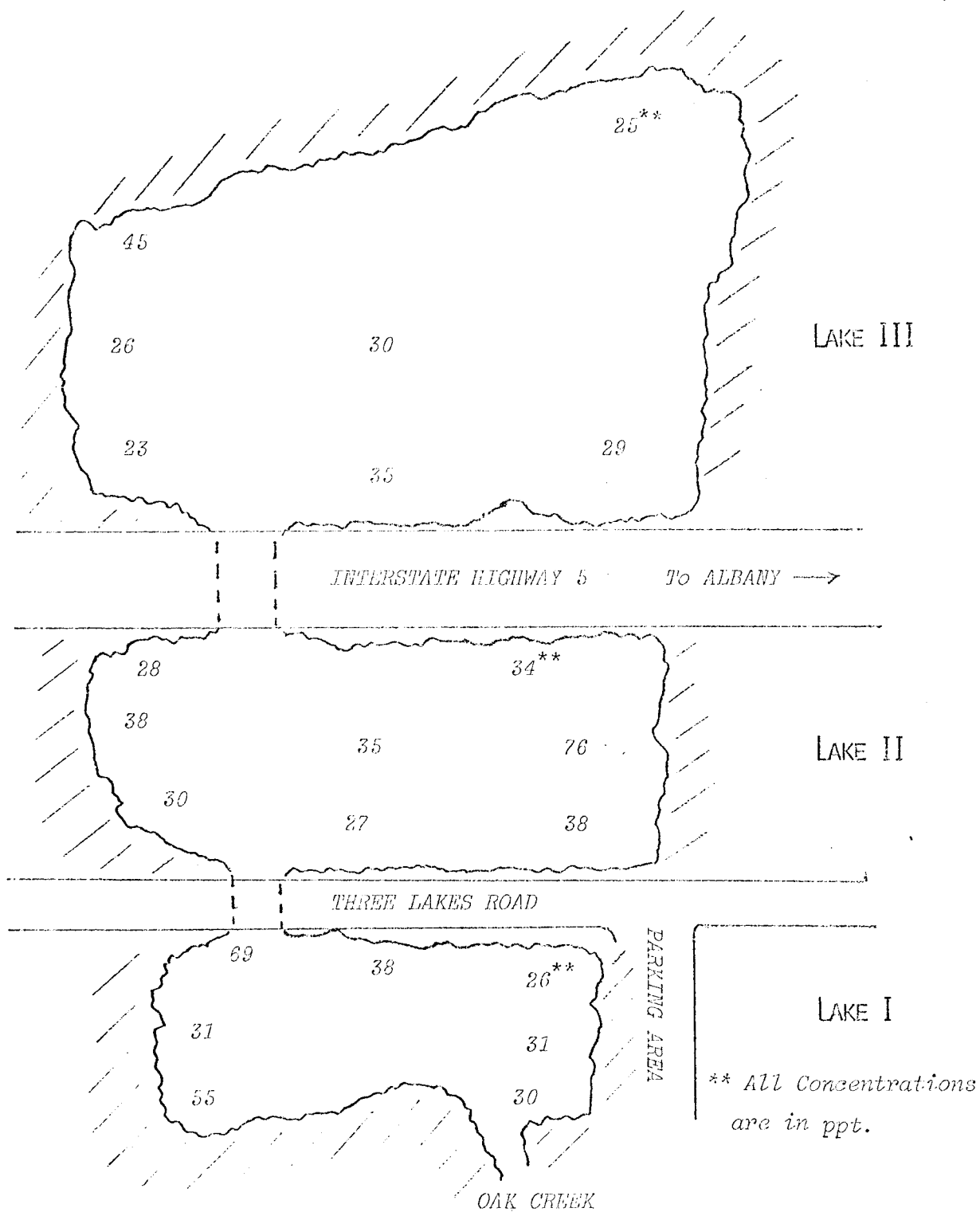
Figure: V   Freeway Lakes Tracer Stability Field Tests
Concentration Profile (Fifteenth Day)
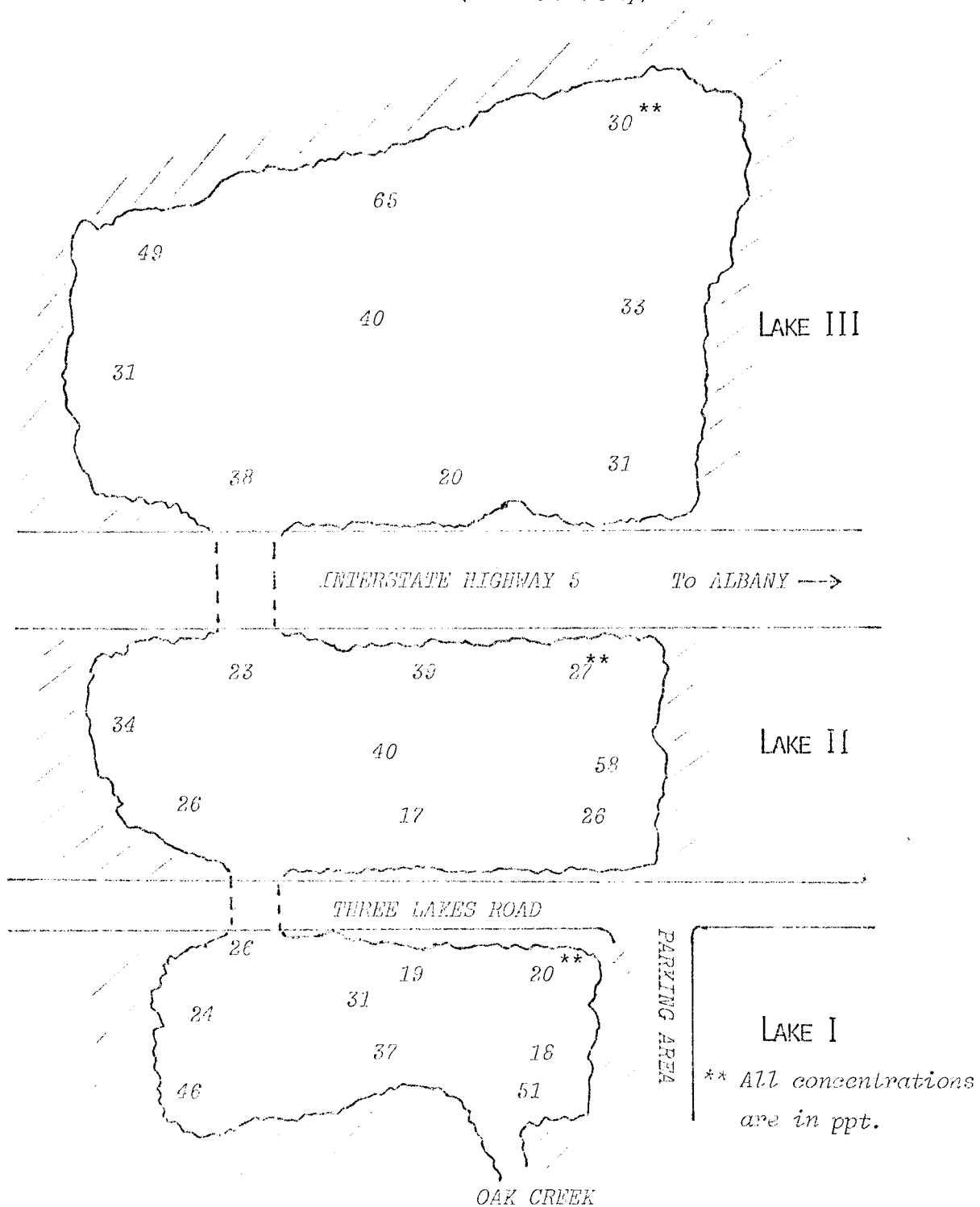
FIGURE VI: WATER SAMPLING EQUIPMENT
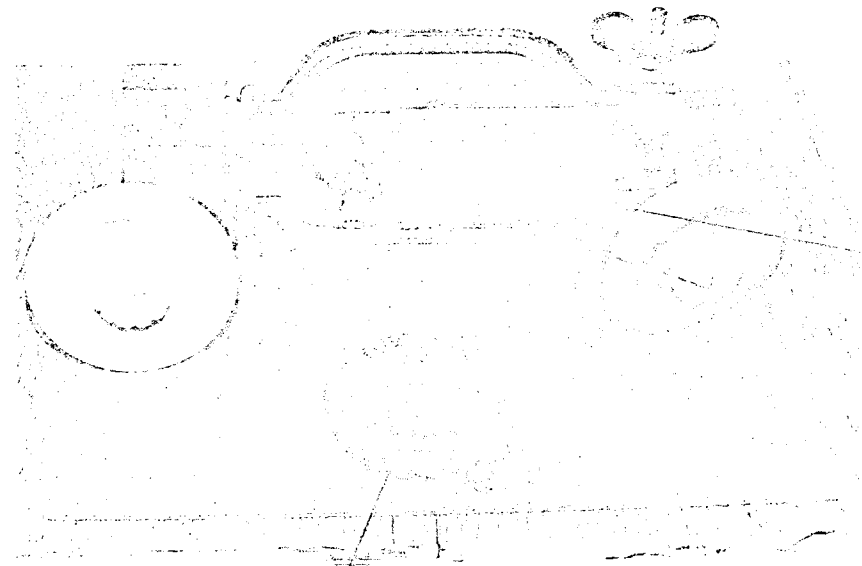
TRACE ELEMENT
WATER SAMPLING
BOTTLE.

WATER RULER

sizes were typically 500-1000 ml. Sampling commenced about an hour earlier than the predicted tracer arrival time and the samples were taken at an interval of five minutes each.

(iii) <u>Willamette River Experiment II</u>: This experiment involves the continuous injection of the tracer solution into the final effluent tank of the Albany municipal sewage treatment plant before being discharge into the Willamette River. The effluent tank is located about half a mile from the bank of the Willamette River. The purpose of the experiment is to compare the behaviour of the tracer and any significant trace elements emitted from the outfall. Samples were taken at various points at various times downstream from the outfall. Results of these experiments are shown in Tables XXXIV and XXXV.

D. <u>Sample Preparations</u>.

For water samples, prior to analysis, the surface layer was thawed and discarded to eliminate any surface contaminants that may leached out from the container. The sample was then melted and filtered through 0.45 micron Nuclepore filter to collect the suspended particulates. The filtrates were then filtered through anionic and cationic ion-exchange filters, thus separating the original water samples into three different components: (a) Suspended particulates (b) Dissolved anions and dissolved cations. The entire sampling and analysis procedure is summarised in Figure VII.

Sediment samples were also collected at points where the water samples were taken as pointed out earlier. In general, the sample

```
                    ┌──────────────────────────────┐
                    │   Collection of Samples      │
                    │   (measure pH & temp.)       │
                    └──────────────────────────────┘
                                  │
                       ┌──────────────────────┐
                       │   Freeze Samples.    │
                       └──────────────────────┘
                                  │
        ┌─────────────────────────────────────────────────────────────┐
        │ Arrive at Lab: (1) Remove frozen samples from container.     │
        │                (2) Etch surface of samples to remove         │
        │                    surface contaminants.                     │
        │                (3) Melt samples at room temperature.         │
        └─────────────────────────────────────────────────────────────┘
                                  │
        ┌─────────────────────────────────────────────────────────────┐
        │  Filter solution with 0.45 micron Nuclepore filters          │
        │            to remove particulate matters.                    │
        └─────────────────────────────────────────────────────────────┘
                                  │
                       ┌──────────────────────┐
                       │    Filter filtrates  │
                       └──────────────────────┘
                     ┌────────────┴────────────┐
        ┌──────────────────────┐      ┌──────────────────────┐
        │   Cationic Ion       │      │   Anionic Ion        │
        │  Exchange Filters    │      │  Exchange Filters    │
        └──────────────────────┘      └──────────────────────┘
                     │                            │
        ┌──────────────────────┐      ┌──────────────────────┐
        │ Pelletize and Encapsulate   │  Encapsulate filtrates │
        │ filters for irradiation.    │  for irradiation.      │
        └──────────────────────┘      └──────────────────────┘
                     │                            │
        ┌─────────────────────────────────────────────────────────────┐
        │ Irradiate filter & filtrates for appropaite time & flux in   │
        │                      OSU reactor.                            │
        └─────────────────────────────────────────────────────────────┘
                                  │
        ┌─────────────────────────────────────────────────────────────┐
        │  Analyse samples with ND 4420 multichannel analyzer          │
        │            and 40 c.c Ge(Li) detector.                       │
        └─────────────────────────────────────────────────────────────┘
                                  │
                       ┌──────────────────────┐
                       │    Data Analysis.    │
                       └──────────────────────┘
```
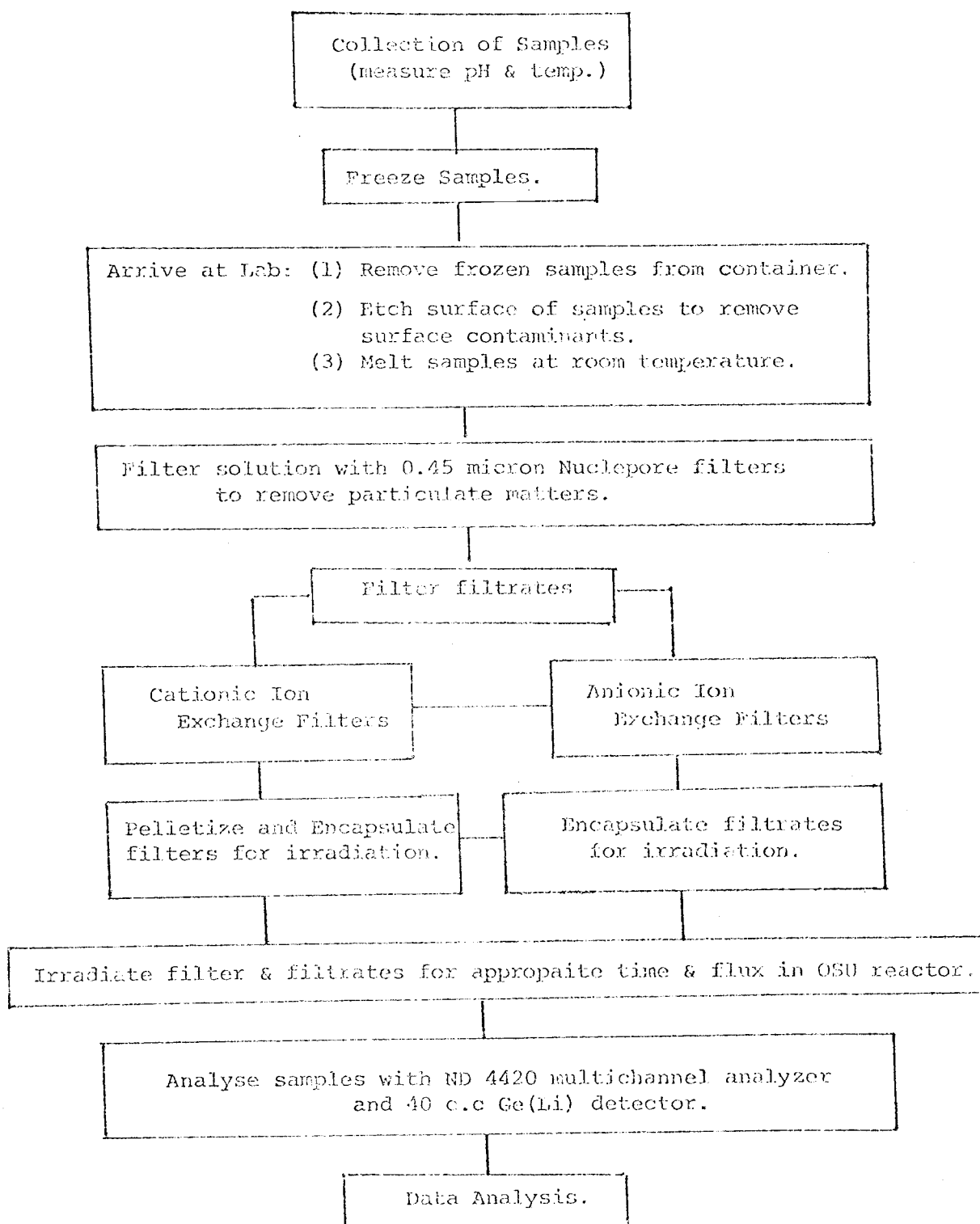
Figure: VII   A schematic diagram of the sample collection and analysis
procedures.

were treated as follows:

(1) Samples were dried at 75°C to roughly constant weight.

(2) Dried sediments then crushed into coarse grains using a "Jaw Crusher" and then into fine powders by using a semi-micro "Pulverizer".

(3) Pulverized sediments were sieved through a 48 mesh or 279 micron sieve.

(4) Sieved samples were dried at 105°C to constant weight and then cooled in dessicator before weighing.

E. Sample Analysis:

The requirement of accurate, precise and rapid analytical procedure for the examination, identification and measurement of pollutants in water and waste samples is a difficult and challenging problem in analytical chemistry because the pollutants are present in extremely low concentrations relative to the substrate. Table XIX provides an interesting comparison of some of the more commonly employed analytical techniques [45]. However, none of the techniques provide complete answer to the large variety of problems involved in trace analysis. The method that allows the determination of the largest number of elemental concentrations in the most complex matrices will be the most powerful.

In this work, instrumental neutron activation analysis (INAA) was used to determine the elemental abundances in sediments, suspended particulates, dissolved cationic and anionic species because of it superior sensitivity (See Table XX) freedom from contamination , non-destructive nature and applicable to a wide variety of matrices without any

Table XIX: Comparison of Analytical Techniques for Pollutants

Technique	Advantages	Limitations
Atomic absorption & fluorescence	Applicable to more than 60 elements Simple spectra and instrumentation Sensitive Rapid	Simultaneous multielement analysis difficult
Mass Spectrometry	Multielement technique Excellent sensitivity Plasma source promises rapid analysis	Specialised sample preparation techniques for spark source Plasma source still in development phase
Atomic Emission	Mutielement analysis feasible Sensitive Rapid Plasma source eliminates most chemical interferences	Flame sources have significant matrix effect
Neutron Activation Analysis	Freedom from contamination Excellent sensitivity for some elements Applicable to a wide variety of matrices	Total time for multielement analysis may be long
X-ray fluorescence	Direct examination often feasible May be nondestructive Multielement technique Rapid	Limited sensitivity Particle size effect must be carefully controlled.
Anodic stripping Voltammetry	Simple technique and equipment Excellent sensitivity for some elements	Not suitable for a wide range of elements

Table XX : Comparison of Sensitivity by Neutron Activation Analysis

and Spectrochemical Methods[45].

| Element | Neutron Activation | Spectrochemical Methods | | |
		Copper Spark	DC Arc	Flame Photometry
Na	0.00035	0.1	20	0.0002
Al	0.00005	0.1	0.2	20
Cl	0.0015			
K	0.004	0.1		0.01
Ca	0.19	0.1		0.03
Sc	0.0001	0.005		
Ti	0.1	0.1		2
V	0.00005	0.05		2
Cr	0.01	0.05	2	1
Mn	0.00003	0.02	0.2	0.1
Fe	0.45	0.5	0.2	2
Co	0.001	0.5		10
Ni	0.0015	0.1	4	10
Cu	0.00035		0.2	0.1
Zn		2	20	2000
Ga	0.00235	1		1
As	0.0001	5	10	
Se	0.0025			
Br	0.00015			
Rb	0.0015	0.2		0.1
Sr	0.03	0.5		0.1
In	0.000005	1	1	1
Sb	0.0002	5	4	
Cs	0.0015	0.5		1
Ba	0.0025	0.1		3
La	0.0001	0.05		5
Ce	0.005	0.5		20
Sn	0.00003	0.2		100
Eu	0.0000015	0.02		
Tb	0.0002			
Dy	0.0000015	0.5		10
Yb	0.0001	0.1		
Lu	0.000015	2		
Hf	0.001	0.5		
Ta	0.00035	1		
Hg	0.0065	5	2	100
Pb	0.1	0.05	0.2	20
U	0.0005	1		10

elaborate sample preparation.

The suspended particulates from the water samples were collect-
ed on tared Nuclepore filters, dessicated to constant weight and then
reweighed to obtain a gravimetric analysis. The weighed filters are then
pelletized and then encapsulated in plastic irradiation vials for neutron
activation together with appropiate elemental standards of interest. Simi-
lar sample preparation procedure was applied to the ion-exchange filters.

Approximately 100-150 mg of sediment per sample was used. The
samples were encapsulated in precleaned polyvials (See Appendix II) and
then neutron activated .

(1) Instrumentation: The gamma ray spectrometer used in this
work consist of a Nuclear Data 2200/4420 multichannel Analyzer coupled
with a 40/60 c.c. Ge(Li) detector. Prior to all sample analysis, the
spectrometer energy calibration was established using a point source stan-
dard such as the NBS-SRM 4216B Mixed Radionuclide Gamma-Ray Emission Rate
Point Source Standard with gamma ray energies spanning from the .088 Mev
γ-ray of Cd-109 to the 1.836 Mev γ-ray from the decay of Y-88.

(2) Neutron Activation Analysis: The sequential activation
procedure employed to meaure the elemental contents of the various samples
is summarised in Table XXI. Typically, the samples and standards were
irradiated for 4/5 minutes in the pneumatic terminal or "rabbit" system
of the OSU Triga Reactor for the determination of short-lived radionuclides
such as Al,V,Ti etc. After irradiation, the samples were transferred to
new clean counting vials and counted after an appropiate cooling period
of 3-5 minutes. Using such short irradiation procedure, approximately 10

Table XXI: Summary of Neutron Activation Analysis Procedure:

Element	Product Radionuclides	Half-Life*	Delay Time	Count Time	E_γ measured (kev)*
Al	Al-28	2.241 m	3 - 5 m	300 s	1778.9
V	V-52	3.77			1434
Ti	Ti-51	5.80			319.8
Ca	Ca-49	8.80			3084.4
Mg	Mg-27	9.46			1014
Cl	Cl-38	37.094	1 - 2 h	900 s	1642.4
In	In-116m	54.101			1097 (417)
Ba	Ba-139	1.42 h			165.8
Dy	Dy-165	2.334	5 - 6 h		94.7
Mn	Mn-56	2.58			846.6 ((1810)
Sr	Sr-87m	2.81			388.4
Lu	Lu-176m	3.69			88.4
Eu	Eu-152m	9.30			121.8 (344.3)
K	K-42	12.401	1 - 2 d	1 - 2 h	1524.7
Zn	Zn-69m	13.80			438.7
Ga	Ga-72	14.10			629.9 (834)
Na	Na-24	15.00			1368.5
W	W-187	23.899			685.7
As	As-76	1.096 d			657.2 (559.1)
Br	Br-82	1.479			776.5
La	La-140	1.675			1586.4
Sm	Sm-153	1.933			103.2
U	Np-239	2.350			228.2
Sb	Sb-122	2.72			563.9
Lu	Lu-177	6.710			208.4
Rb	Rb-86	18.60	2 - 3 w**	10-20 h	1078.8
Th	Pa-233	27.00			311.9
Cr	Cr-51	27.7			320
Yb	Yb-169	32.00			197 (177)
Ce	Ce-141	32.50			145
Hf	Hf-181	42.50			482
Fe	Fe-59	44.60			1099 (1292)
Ni	Co-58	71.30			810.8
Sc	Sc-46	83.80			889
Ta	Ta-182	115.00			1221
Se	Se-75	120.00			264.6
Zn	Zn-65	244.00			1115.5
Cs	Cs-134	2.06 y			605 (796)
Co	Co-60	5.26			1173.2 (1332.5)
Eu	Eu-152	13.20			121.8 (1408)

*Binder,L., et.al, "A Chemist's Gamma Ray Table", LBL-6516, UC-34C,1977.

**m = minute, s = seconds d = days, h = hours, w = week,y = year

to 13 elements can be determined. After a delay of about one week, the samples together with fresh elemental standards were reirradiated in the rotating rack of the OSU reactor for a period of 1-6 hours. After cooling for 1-2 days, the samples were counted for 1-2 hours and then recounted for 10-20 hours after an additonal delay of 2-3 weeks. Such sequential counting provide half-life checks for most radionuclides and all the half-lives measured agreed within ± 10% of the accepted values[46] and abundances calculated from successive counts usually agreed within statistical counting error.

In addition to the "home-made" composite elemental standards, standard reference materials such as NBS-SRM 1571 Orchard Leaves[47], NBS-SRM 1632 Coal[48], NBS-SRM 1633 Coal Fly Ash[49] were irradiated and counted under identical conditions as the samples being analyzed. Use of these NBS standards can provide checks on the accuracy and precision of this work. The elemental abundances of various standard reference materials measured in this work agreed well within experimental errors with the accepted NBS and literature[50] values. Our results and the NBS or literature values are summarized in Tables XXII, XXIII and XXIV.

A further ensurance was provided by the results of the "round-robin" intercomparison run for the determination of trace elements in soil samples sponsored by the International Atomic Energy Agency[51]. Again our results as shown in Table XV compared very favourably with the reported values and this provide us confidence in the reliability of the technique employed.

By irradiating and counting both the samples with a standard

Table XXII Elemental Abundances in NBS Standard Reference Materials

NBS-SRM 1571-Orchard Leaves

Element	This Work	NBS & Literature[a]	This Work/NBS
Al (%)	0.04 ± 0.01	0.043	0.93 ± 0.23
Fe (%)	316 ± 4	300 ± 20	1.05 ± 0.07
Ca (%)	2.17 ± 0.22	2.09 ± 0.03	1.04 ± 0.11
Na (ppm)	85 ± 1	82 ± 6	1.04 ± 0.10
K (%)	1.46 ± 0.01	1.47 ± 0.03	0.99 ± 0.02
Mn (ppm)	91 ± 3	91 ± 4	1.00 ± 0.05
Ba	46 ± 1	(44)	1.05 ± 0.02
Zn	27 ± 1	25 ± 3	1.08 ± 0.14
Cr	2.9 ± 0.3	2.6 ± 0.3	1.12 ± 0.17
Rb	13 ± 1	12 ± 1	1.03 ± 0.12
Ce	0.99 ± 0.03	0.90*	1.10 ± 0.03
La	1.27 ± 0.01	1.05*	1.21 ± 0.01
Co	0.20 ± 0.01	(0.20)	1.00 ± 0.01
Sc	0.076 ± 0.001	0.065*	1.17 ± 0.02
As	12 ± 2	10 ± 2	1.20 ± 0.20
Sm	0.13 ± 0.04	0.10*	1.30 ± 0.40
Th	0.064 ± 0.002	(0.065)	0.98 ± 0.05
Hf	0.036 ± 0.002	0.037*	0.97 ± 0.05
Yb	0.031 ± 0.013	0.025*	1.24 ± 0.52
Br	9.15 ± 0.04	(10)	0.92 ± 0.01
Cs	0.050 ± 0.001	(0.040)	1.25 ± 0.03
U	0.033 ± 0.009	0.029 ± 0.005	1.14 ± 0.37
Sb	3.6 ± 0.2	2.9 ± 0.03	1.24 ± 0.15
Ta	0.007 ± 0.001	0.010*	0.70 ± 0.10
Lu	0.0038 ± 0.0010	0.0033*	1.15 ± 0.30
Tb	0.011 ± 0.005	0.013*	0.85 ± 0.38
Eu	0.023 ± 0.008	0.023 ± 0.021*	1.09 ± 0.38
Se	0.086 ± 0.005	0.08 ± 0.01	1.08 ± 0.15
Sr	38 ± 5	33*	1.15 ± 0.15
Cl	717 ± 65	(690)	1.04 ± 0.09

Grand Average = 1.07 ± 0.13

a. NBS Certificate of Analysis, SRM 1571-Orchard Leaves, August,1976.
   Morrison G.H.,Nadkarni,R.,"Multielement Instrumental Neutron
   Activation Analysis of Biological Materials", Anal.Chem., Vol.45,
   No.11, 1973.
   Goldberg,E.D., "Strategies for Marine Water Pollution Monitoring",
   Wiley Interscience,N.Y. 1976.
* Certified NBS values are indicated by asteriks,values in parentheses
  are uncertified NBS values. Unmarked values are literature values.
  All concentrations are in ppm (microgram/g dry weight of sample)
  unless otherwise specified.

Table XXIII: Elemental Abundances in NBS Standard Reference Materials

NBS-SRM 1632-COAL

Element	This Work	NBS & Literature[a]	This Work/NBS
Al(%)	1.73 + 0.05	1.85 + 0.13	0.94 + 0.07
Fe(%)	0.93 + 0.04	0.87 + 0.03*	1.03 + 0.06
Ca(%)	0.45 + 0.06	0.43 + 0.05	0.94 + 0.16
Na	383 + 12	414 + 20	0.93 + 0.05
K(%)	0.28 + 0.02	0.28 + 0.03	1.00 + 0.13
Ti	986 + 238	1100 + 100	0.90 + 0.23
Mn	42 + 1	40 + 3	1.05 + 0.08
Ba	356 + 33	352 + 30	1.01 + 0.13
V	34 + 3	35 + 3*	0.97 + 0.12
Zn	37 + 4	37 + 4*	1.00 + 0.15
Cr	21.0 + 0.8	20.2 + 0.5*	1.04 + 0.05
Ni	14 + 3	15 + 1*	0.93 + 0.21
Rb	22 + 1	21 + 2	1.05 + 0.11
Ce	19.9 + 1.5	19.5 + 1.0	1.02 + 0.09
La	11.2 + 0.6	10.7 + 1.2	1.05 + 0.13
Co	6.3 + 0.4	(6)	1.05 + 0.07
Sc	4.0 + 0.2	3.7 + 0.3	1.08 + 0.10
As	6.0 + 0.7	5.9 + 0.6*	1.02 + 0.16
Sm	1.75 + 0.04	1.7 + 0.2	1.03 + 0.12
Th	3.3 + 0.2	3.2 + 0.2	1.03 + 0.09
Hf	1.00 + 0.06	0.96 + 0.05	1.04 + 0.08
Yb	0.82 + 0.01	0.70 + 0.10	1.17 + 0.17
Br	18.0 + 3.1	19.3 + 1.9	0.93 + 0.19
Dy	1.27 + 0.04	-------	-------
Cs	1.68 + 0.10	1.40 + 0.10	1.20 + 0.11
U	1.45 + 0.21	1.40 + 0.10	1.04 + 0.17
Sb	3.9 + 0.8	3.9 + 1.3	1.00 + 0.39
Ta	0.25 + 0.02	0.24 + 0.04	1.04 + 0.19
Lu	0.14 + 0.01	0.14 + 0.01	1.00 + 0.10
Tb	0.27 + 0.03	0.23 + 0.05	1.17 + 0.29
Eu	0.34 + 0.08	0.32 + 0.04	1.06 + 0.28
Se	2.8 + 0.5	2.9 + 0.3*	0.97 + 0.20
Zr	35 + 11	-------	-------
Sr	150 + 30	161 + 16	0.93 + 0.21
Hg	0.13 + 0.04	0.12 + 0.02	1.08 + 0.38
Cl	885 + 200	890 + 125	0.99 + 0.26

Grand Average = 1.02 + 0.07

a. NBS Certificate of Analysis, SRM 1632-Coal, March,1977.
   Gordon,G.E.,et al "Elemental Concentrations in NBS Environmental
   Coal and Fly Ash Standard Reference Materials",Anal.Chem.,Vol.47,
   No.7, June 1975.

* Values in asteriks are certified NBS values. Values in parentheses
   are noncertified NBS values.
   All values are in ppm (microgram/g dry weight of sample) unless
   indicated otherwise.

Table XXIV :Elemental Abundances in NBS Standard Reference Materials

NBS-SRM 1633-Coal Fly Ash

Element	This Work	NBS & Literature[a]	This Work/NBS
Al(%)	13.2 ± 0.1	12.7 ± 0.5	1.04 ± 0.04
Fe(%)	6.0 ± 0.1	6.2 ± 0.3	0.97 ± 0.05
Ca(%)	4.2 ± 0.5	4.7 ± 0.6	0.89 ± 0.16
Na	3395 ± 84	3200 ± 400	1.06 ± 0.14
K (%)	1.57 ± 0.06	(1.72)	0.91 ± 0.03
Ti	8750 ± 1400	7400 ± 300	1.18 ± 0.20
Mn	437 ± 8	493 ± 7*	0.89 ± 0.02
Ba	2760 ± 126	2700 ± 200	1.02 ± 0.09
V	196 ± 14	214 ± 8*	0.92 ± 0.07
Zn	189 ± 22	210 ± 20*	0.90 ± 0.14
Cr	126 ± 1	131 ± 2*	0.96 ± 0.02
Ni	114 ± 5	98 ± 3*	1.16 ± 0.06
Rb	118 ± 16	(112)	1.05 ± 0.14
Ce	140 ± 1	146 ± 15	0.96 ± 0.10
La	82 ± 1	82 ± 2	1.00 ± 0.03
Co	39.2 ± 0.8	(38)	1.03 ± 0.02
Sc'	25 ± 1	27 ± 1	0.93 ± 0.05
As	59 ± 2	61 ± 6*	0.97 ± 0.09
Sm	11.8 ± 0.1	12.4 ± 0.9	0.95 ± 0.07
Th	24.5 ± 0.4	(24)	1.02 ± 0.02
Hf	7.6 ± 0.5	7.9 ± 0.4	0.96 ± 0.08
Yb	6.4 ± 0.3	7 ± 3	0.91 ± 0.39
Br	10 ± 1	12 ± 4	0.83 ± 0.29
Dy	10.25 ± 0.17	----	---
Cs	8.6 ± 0.3	8.6 ± 1.1	1.00 ± 0.13
U	11.1 ± 0.7	11.6 ± 0.2*	0.96 ± 0.06
Sb	7.0 ± 0.1	6.9 ± 0.6	1.01 ± 0.09
Ta	1.8 ± 0.3	1.8 ± 0.3	1.00 ± 0.20
Lu	1.0 ± 0.1	1.0 ± 0.1	1.00 ± 0.10
Tb	1.8 ± 0.3	1.9 ± 0.3	0.95 ± 0.22
Eu	2.4 ± 0.1	2.5 ± 0.4	0.95 ± 0.16
Se	9.7 ± 0.5	9.4 ± 0.5*	1.03 ± 0.08
Zr	300 ± 18	301 ± 20	1.00 ± 0.09
Cl	40 ± 8	42 ± 10	0.95 ± 0.30

Grand Average = 0.98 ± 0.07

a. NBS Certificate of Analysis,SRM 1633-Coal Fly Ash, Oct.,1974.
   Gordon,G.E., et al., "Elemental Concentrations in the NBS Environ-
   mental Coal and Fly Ash Standard Reference Materials", Anal.Chem.,
   Vol.47, No.7, June,1975.

* Numbers in asteriks are certified NBS values, values in parentheses
   are noncertified NBS values.

Table XXV Elemental Abundances in IAEA Soil-5** Materials:

Element*	This Work	IAEA Values	This Work/IAEA
Al(%)	8.42 + 0.04	8.19 + 0.28	1.03 + 0.04
Fe(%)	4.85 + 0.02	4.45 + 0.19	1.09 + 0.05
Na(%)	1.91 + 0.06	1.92 + 0.11	0.99 + 0.06
K (%)	1.86 + 0.20	1.86 + 0.15	1.00 + 0.11
Ti(%)	0.48 + 0.01	(0.47)	1.02 + 0.02
Mn	935 + 13	852 + 37	1.09 + 0.05
Ba	596 + 66	561 + 53	1.06 + 0.15
Cr	30.9 + 2.9	28.9 + 2.8	1.07 + 0.14
Rb	143 + 7	138 + 7	1.03 + 0.08
Ce	52.4 + 0.3	59.7 + 3.0	0.88 + 0.04
La	31.1 + 2.1	28.1 + 1.5	1.11 + 0.09
Co	15.7 + 0.66	14.8 + 0.76	1.06 + 0.07
Sc	15.8 + 0.10	14.8 + 0.66	1.06 + 0.05
As	118.9 + 4.0	93.9 + 7.5	1.26 + 0.11
Sm	4.83 + 0.01	5.42 + 0.39	0.89 + 0.06
Th	12.4 + 1.4	11.3 + 0.73	1.09 + 0.14
Hf	6.7 + 0.29	6.3 + 0.3	1.06 + 0.07
Yb	2.61 + 0.20	2.24 + 0.30	1.17 + 0.14
Br	7.51 + 1.10	5.4 + 1.0	1.39 + 0.33
Cs	56.8 + 1.4	56.7 + 3.3	0.99 + 0.06
U	5.20 + 0.40	3.04 + 0.51	1.71 + 0.32
Sb	15.9 + 0.6	14.3 + 2.2	1.11 + 0.18
Ta	0.768 + 0.068	0.764 + 0.056	1.01 + 0.18
Lu	0.405 + 0.010	0.336 + 0.044	1.20 + 0.16
Tb	0.546 + 0.098	0.665 + 0.075	0.82 + 0.17
Eu	1.13 + 0.01	1.18 + 0.08	0.96 + 0.06
Se	1.50 + 0.20	(1.4)	1.07 + 0.14
Sr	411 + 27	(330)	1.24 + 0.08

Grand Average = 1.09 + 0.17

* All concentrations are in ppm (micrograms/gram dry weight of sample) unless otherwise indicated.
** International Atomic Energy Agency intercomparison run Soil-5 for the determination of trace elements in soil, IAEA/RL/46, Jan.,1978. Values in brackets are information values only.

under identical conditions, it is possible to quantify the concentrations of any element present in the unknown samples. The basic equation for quantitative activation analysis is: [52,53,54]

$$W = (A M / \sigma f \phi \ 6.02 \times 10^{23} \{1 - e^{-\lambda t}\})$$

where W = weight of the element

A = induced activity at EOB (End of Bombardment)

ϕ = Neutron Flux in neitrons/cm^2/sec

σ = Thermal neutron capture cross-section in barns

f = Fractional abundance of the particular isotope of the element concerned.

λ = Decay constant of the induced radionuclides

t = Irradiation time

M = Atomic weight of the element

The weight of the element of interest can then be determined as follows:

$$\frac{\text{Weight of Element in Unknown}}{\text{Weight of Element in Standard}} = \frac{\text{Activity of Element in Unknown}}{\text{Activity of Element in Standard}}$$

It would of course necessary to make appropiate decay corrections, background corrections and other interferences.

In certain environmental samples, interferences from radionuclides of interest as well as that caused by the fast neutron flux of the Triga reactor occur and sometimes are quite important & significant Correction factors must be determined in order to produce accurate and unambiguous results. Examples of some of the more prominent and common interferences encountered in environmental analyses are shown in Table XXV.

Table XXVI : Common Gamma Ray Counting Interferences Encountered

in Environmental Analyses:

Radionuclides	E_γ (kev)	Interferences
^{152m}Eu	121.8	$^{152}Eu(121.8$ kev$)$
^{177}Zn	1115.5	$^{46}Sc(1120.5$ kev$)$
		$^{182}Ta(1121$ kev$)$
^{74}Se	264	$^{182}Ta(264$ kev$)$
^{64}Cu	511	All positron emitters
^{203}Hg	279	$^{75}Se(280$ kev$)$
^{27}Mg	1014	$^{27}Al(n,p)^{27}Mg$
		$^{30}Si(n\,\alpha)^{27}Mg$
^{24}Na	1368	$^{24}Mg(n,p)^{24}Na$
		$^{27}Al(n,\alpha)^{24}Na$
^{27}Al	1778.9	$^{28}Si(n,p)^{28}Al$
		$^{31}P(n,\ )^{28}Al$
^{56}Mn	846.9	$^{56}Fe(n,p)^{56}Mn$
	or 1810	$^{59}Co(n,\alpha)^{56}Mn$

RESULTS AND DISCUSSION

(1) Efficiency of Ion Exchange Filter Paper as a preconcentration medium for dissolved/tracer species in river water:

Results of laboratory experiments performed to evaluate and validate the effectiveness of ion-exchange filters as good and efficient preconcentration medium for dissolved and/or tracer species are shown in Tables VI and VII.

Examination of the data in Table VII show that quantitative recovery of most dissolved species is achieved in most instances by the use of cationic filters. The inclusion of anionic filters boosts the overall recovery to over 90% in most cases. This brings out an important aspect of the nature of chemical speciation of dissolved ions in the natural water system. It is presumptuous and erroneous to assume the dissolved ions exist in certain state (cationic/anionic/neutral) without detailed and intimate knowledge of the chemical/physical environment and parameters such as the pH, presence of dissolved organics etc., which heavily interact and influence and control the state of beings of the dissolved species.[55,56,57,58] It is therefore imperative in quantitative trace analysis to include both anionic and cationic exchangers. Extensive studies of the uses of ion exchange filters had been carried out by Campbell[59,60,61,62] et al. However, their studies were mostly carried out in distilled water and at pH (1-7) which do not reflect the "real" situation. For example, no consideration was given to the presence of alkali salts and/or chelating substances which may

adversely affect the collection efficiency of the desired ions as well as the state of the dissolved species.

Nelson et al.,[63] have shown that radionuclides of Zn,Sb,Sc and Mn in the Columbia River are distributed among particulate materials, cationic, anionic and uncharged in true solution as shown below:

Distribution of Chemical Forms of Zn,Sb,Sc & Mn in Columbia River

Per Cent Soluble Fraction In

Element	Cationic	Anionic	Uncharged
Zn	83	12	5
Sb	0	16	84
Sc	4	79	17
Mn	48	43	10

There is also considerable evidence that element such as Cu,As,Fe,Co,Cr etc., are present partially as stable organic complexes in water.[55,56,57,58]

In our study, the pickup efficiency of Sb by the cationic and anionic assembly is very poor and that suggests Sb may be in the neutral form and not affected or picked up by the ion exchanger. Zn, however,is found mostly in the cationic form, similiar to the findings of Nelson [63] et al., as shown above. Sc behaves directly opposite to that found by Nelson and exists mostly in the cationic form. It is difficult to compare the two sets of data which may reflect very different environmental history.

The pickup of the In and Rare-Earth DTPA chelates by the an-

ionic ion-exchange filter is very satisfactory and in most cases better than 92%. As shown by the data of Table VI, the degree of chelate recovery from natural waters is lower than that in distilled water. This may be due to (i) The presence of foreign ions which compete for the sites in the ion-exchangers. (ii) Chelates may be sorbed by the suspended particulates and thus retained by the Nuclepore prefilter. (iii) The chelates are decomposed and the metallic ions released are subsequently hydrolysed, precipitated and/or sorbed onto the surface of the suspended particulates in water. Despite the slightly lower recovery efficiency in the natural water matrix, the overall efficiency of these ion-exchangers are still very high (>90%) in most cases and thus warrant their being adopted as preconcentration media for the tracers.

(2) Extent of Chelate Formation:

Table VI also summarize the results of the experiments performed to test the extent of chelate formation. The data indicate that less than 1% of the Dy, In and REE failed to be chelated as anionic complexes and hence picked up by the cationic ion-exchanger. Filtration through anionic ion-exchange filters showed that >99% of the chelates are picked up and thereby reaffirms the results obtained earlier using cationic ion-exchange filters. The retention of the chelates on the anionic filters also provides an indication of the ability of the chelate to recover the chelates (However, such results may be misleading because the chelates were prepared in distilled water and hence the quantity of competing ions/species present is very small. These competing ions may compete for the ion-exchange sites and thus decreasing the quantity

may compete for the ion-exchange sites, thus decreasing the quantity
of chelate picked up by the ion-exchanger. Also presence of other
chelating species may cause the breakdown of the Dy and In chelate.)

(3) Time Dependence of the Tracer Stability under simulated
river conditions:

One of the main criteria of a "good" tracer is that it should
remain in solution and resist losses due to precipitation, sorption etc.
Results of preliminary laboratory experiments performed to test the
stability of chelated tracers under simulated river conditions are
shown in Tables VIII,IX,X and Figures VIII,IX and X. The experiment
was also repeated for unchelated Dy and In solutions and the results
are shown in Table XI and Figure XI.

Several general conclusions follow immediately from these
experiments; (1) Chelation with DTPA greatly improves the solution
stability over simple ionic form in all cases. Unchelated Dy and In
suffers substantial losses after a period of eight days, with approxi-
mately 70 and 38 per cent of the original tracer remaining in solution,
respectively. Chelated tracers, on the other hand, tend to be more
resistant to decomposition/sorption/hydrolysis/precipiatation reactions
etc., and more than 95% of the original tracer remain in solution aft-
ter a period of eight days. (2) Sorption of tracer to suspended par-
ticulates present on unfiltered river water was negligible compared
to sorption to bottom sediment. This is, in all cases, probably due
to the small quantity of particulates per unit volume of natural water

FIGURE VIII: TIME DEPENDENCE OF TRACER STABILITY UNDER SIMULATED
RIVER CONDITIONS I (UNFILTERED RIVER WATER)

% ORIGIBAL TRACER REMAINING
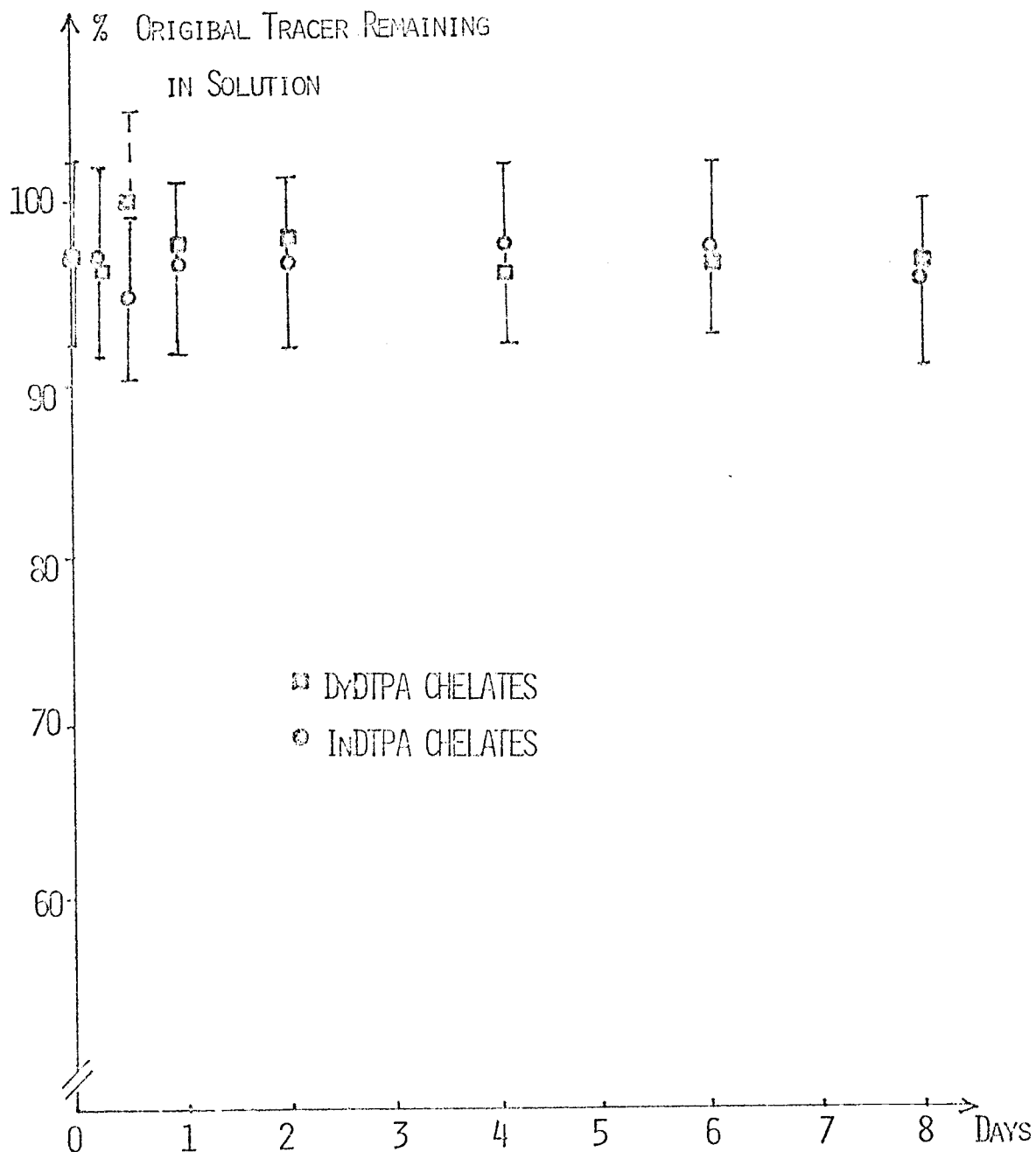IN SOLUTION

▫ DyDTPA CHELATES
○ InDTPA CHELATES

FIGURE IX: TIME DEPENDENCE OF TRACER STABILITY UNDER SIMULATED
RIVER CONDITIONS II (FILTERED RIVER WATER)

FIGURE X : TIME DEPENDENCE OF TRACER STABILITY UNDER SIMULATED
RIVER CONDITIONS III (SEDIMENT + UNFILTERED WATER)
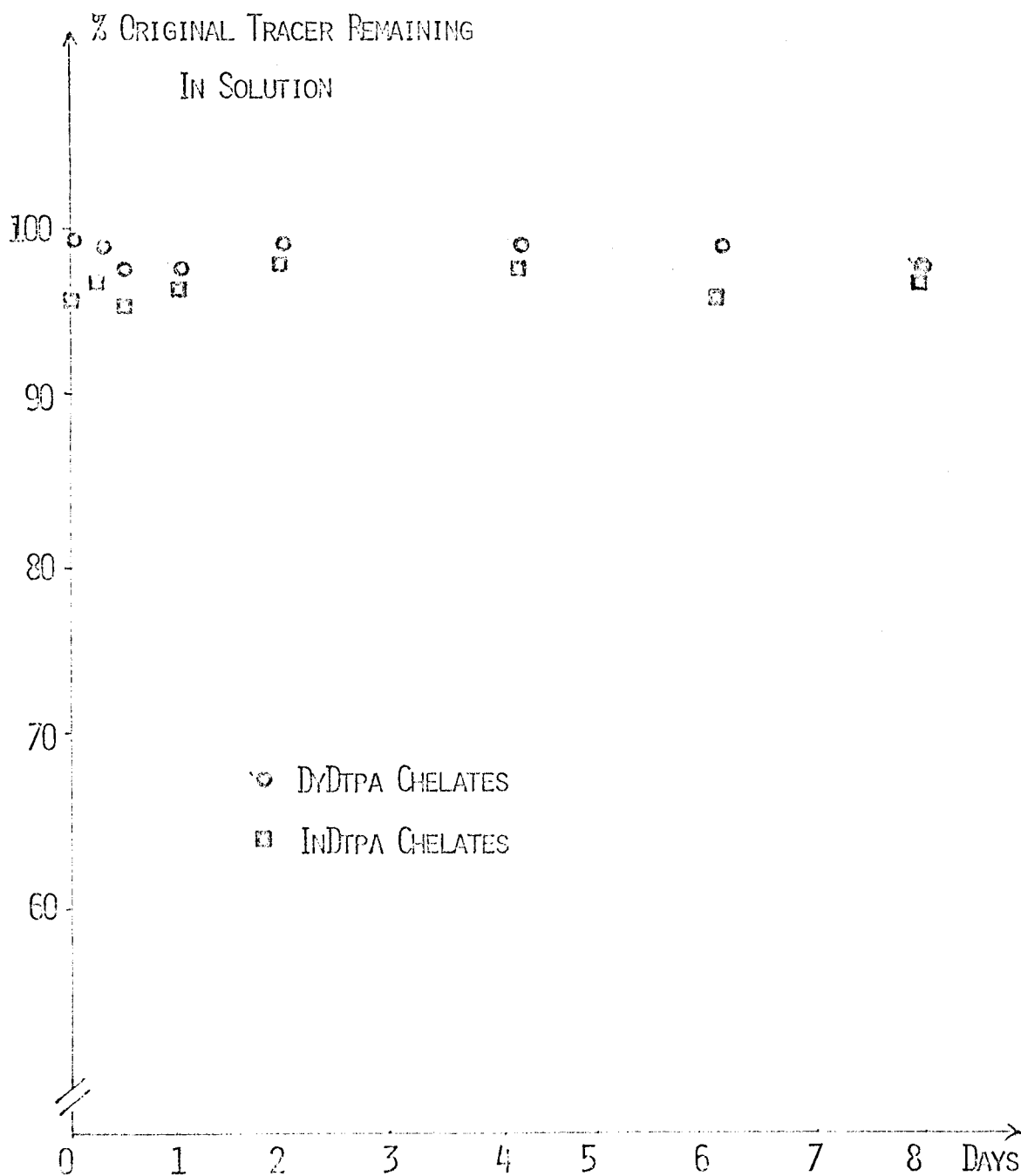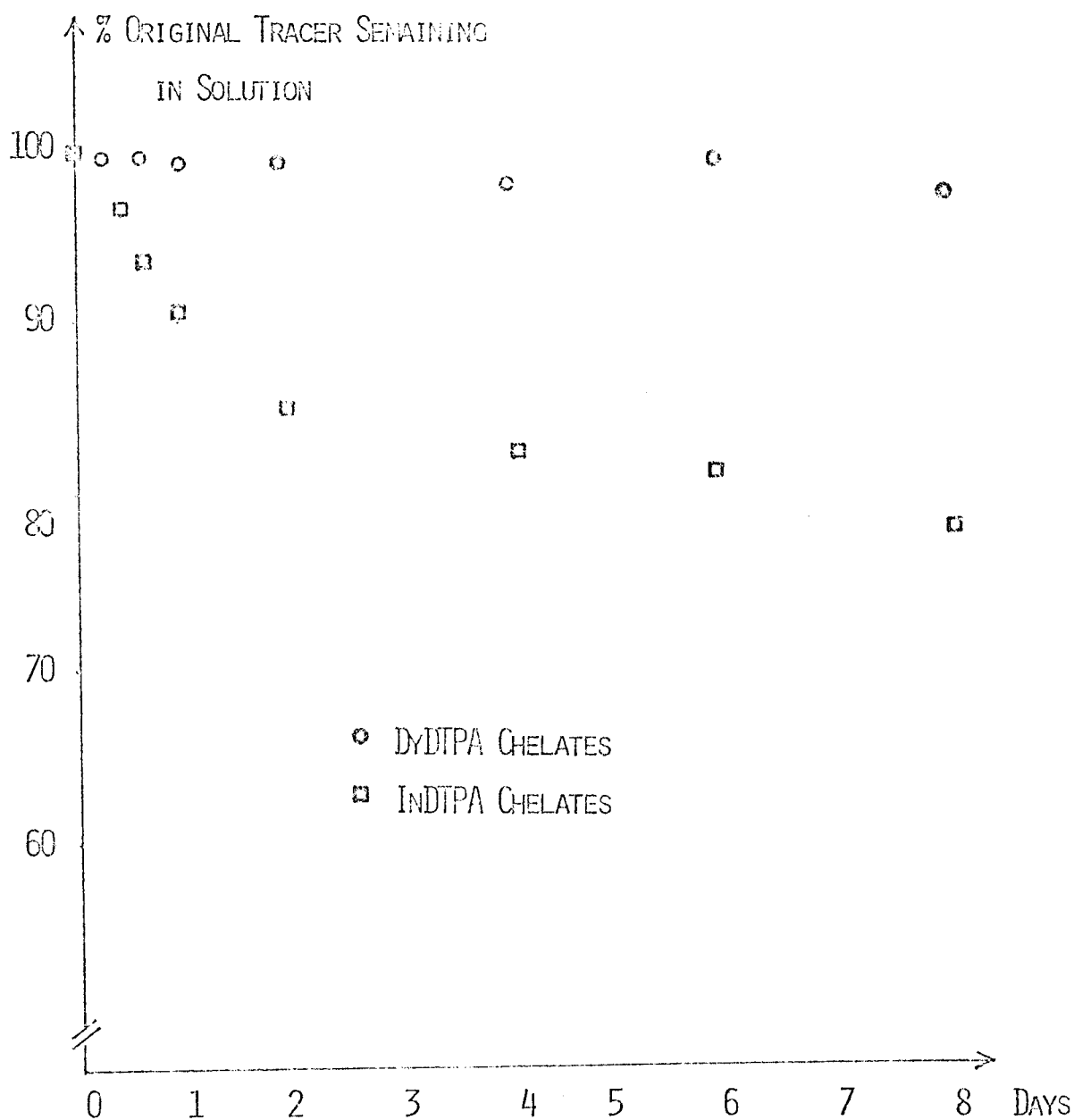
% ORIGINAL TRACER REMAINING
IN SOLUTION

FIGURE XI: TIME DEPENDENCE OF TRACER STABILITY
UNDER SIMULATED RIVER CONDITIONS

(DY)

(IN)

□ DY SOLUTION

IN SEDIMENT + UNFILTERED RIVERWATER

○ IN SOLUTION

100

90

80

70

60

50

40

30

1   2   3   4   5   6   7   8   DAYS

compared to the large amount of bottom sediments used in these tests. (3) Simple ionic forms of Dy and In are rapidly removed by sorption onto sediments and/or precipitation due to hydrolysis etc.

Our initial worry that some dissolved species such as Fe(III) and a few other trivalent ions which form DTPA chelates which are as stable or even more stable than the tracer complexes (See Table V), thus affecting the stability of the chelate proved to be unfounded. The afore-mentioned series of experiments suggests that Fe may not be present as Fe(III) or the quantity of Fe(III) and other trivalent ions is very low in the natural system.

Previous investigations[64,65,66] have indicated that the oxidation of Fe(II) is severely retarded in many natural water which contain humic substances. Indeed, it has been demonstrated that organic compounds which possess the structural features of humic substances and synthetic organic matter e.g. detergents, NTA, EDTA, are capable of significantly altering the rate of oxidation of ferrous iron. A model was developed by Singer et al[67] to explain the behaviour of iron in the presence of humic substances. A schematic of this model is as follows:

$$
\begin{array}{ccc}
& \text{Fe(II)-Org} \xrightarrow{\hspace{0.5em} O_2 \hspace{0.5em}} \text{Fe(III)-Org} \longrightarrow \text{Fe}^{2+} + \text{Oxidized Org} \\
\text{Org} \updownarrow & \updownarrow & \updownarrow \\
& \text{Fe}^{2+} \xrightarrow{\hspace{0.5em} O_2 \hspace{0.5em}} \text{Fe}^{3+} \\
& & \updownarrow \; \text{OH}^- \\
& & \text{Fe(OH)}_3
\end{array}
$$

In the absence of appreciable quantities of dissolved organic
matter, ferrous iron is oxidized rapidly upon the introduction of oxy-
gen to ferric iron which precipitates as $Fe(OH)_3$ and is removed from the
system . If significant concentrations of organic matter are present,
the complexation reactions with ferrous iron will compete with the oxy-
genation reaction. The fractions of ferrous iron complexed or oxidized
will depend on the pH and the quantity and types of organic matter present.
Aqueous iron behaves according to the model because of the relative ease
with which the ferrous-feric couple can undergo reversible oxidation and
reduction. However other metals, notably manganese and cobalt, also po-
ssess this property such that the potential pathways are not specific
for iron. In addition, the complexing ability of the organic matter
for other metals (regardless of their redox characteristics) plus the
adsorptive capacity of hydrous ferric oxide for other metals indicates
that such a model may have significant effect on the availability and
distribution of other trace elements in natural waters.

Finally, in comparing the solution behaviour of the chelated
tracers developed here, DyDTPA holds the best tracer possibility since
its solution stability is superior to the In chelate.

(4) Number of Filters and Filtrations Required to Achieve Optimum Recovery of Dissolved Species and Tracer in River Water:

Results of experiments performed to evaluate the minimum
number of filters and number of filtrations required to achieve quanti-
tative recovery are shown in Tables XIII and XIV. Auxiliary experiment

performed to determine the effect of pH on the pickup efficiency of the ion-exchanger and the results are shown in Table XV.

Several facts stand out from such experiments. (1) One to three filtrations seem to be quite adequate in removing the tracers quantitatively. An increased number of filtrations beyond three appears to have slight or negligible effect on increasing the pickup efficiency. This result are in accord with the findings reported by James[68] [69] and Van Grieken[70] who found satisfactory collection efficiencies after only one pass. Campbell et al., however recommend that solutions to be analyzed be filtered seven times to achieve high collection efficiencies. In addition to evidence provided by the above experiments, results obtained in other experiments performed previously (See Table VII) have shown that two filtrations provide pickup efficiency >90% in most cases. Therefore, filtering a solution twice should lead to satisfactory collection efficiency for many elements and was adopted for subsequent work.

In general, two filters are used in every experiment and the first or top ion exchange filter removed more than 90% of the dissolved species in a single filtration as evident in the results in Table XIV. In fact, results in Table XIII provide evidence that this finding is correct and furthermore the pH does not have drastic effects on the efficiency of these filters. This result is contrary to the findings of Campbell[59-62] who observed that all the cations tested are precipitated at pH ~7 and therefore removed from the solution. However, results by Van Grieken[70], Taylor[71] Holynska[72] and Underwood[73] all suggest quantitative recovery is achieved at neutral pH (~7.2). Nevertheless, it was

decided as a general and good practice in subsequent work to filter
the samples through two disks of ion-exchanger twice to ensure quanti-
tative recovery especially in the event of high trace element concen-
tration in the water samples which may exceed the ion-exchange capaci-
ty of the single disk.(The ion-exchange capacity of cationic filter
is approximately 5.1 meq*and that of the anionic filter is approximate-
ly 3.2 meq*; see also Appendix I & IV)

In experiments performed to test the recovery of tracers and
dissolved species in natural water, there were several initial diffi-
culties as discussed previously (See p.36) Firstly, the filtration rate
is extremely slow. Secondly, the possible retention/leaching of trace
elements by/from prefilters (Nuclepore/Whatman Number 1) included to
remove particulates and speed up the filtartion rate. Results of such
experiments are shown in Table VII. The percentage retention of the
rare earths are negligible in both kinds of filters. However, the com-
mon natural elements are retained more substantially by the Nuclepore
especially in the case of As and Ta. The higher retention by the Nucle-
pore is probably due to the fact that any dissolved ions sorbed onto
the suspended particulates may be retained by the filters. The Whatman
filters which have larger pore size (10 μm compared with the 0.45 μm
pore size of the Nuclepore) than Nuclepore and thus retain only lar-
ger particulates which in turn offer less surface area per unit weight
of particulates for any sorption reactions than those retained by the
Nuclepore. The retention of rare earths by the Whatman filter is pro-
bably due to their high affinity for the cellular materials which con-

stitute the bulk of the Whatman filter and such phenomenon is also observed by Chatter et al.[74] The high retention of As by Nuclepore is a mystery and beyond any logical explanation.

In general, it would seem that the Nuclepore filter should provide an excellent medium for separating particulate materials from the dissolved species. It has high tensile strength, is non-hydroscopic, has low intrinsic trace element content (Table XII) and high degree of uniformity of physical properties (See Appendix III), all of which are criteria of providing good quantitative recovery of particulate matter. Whatman filter, on the other hand, seems to be less efficient as a filter for quantitative determination, is more hydroscopic and has higher intrinsic trace element content.

(5) Baseline Studies of Elemental Abundances in Willamette River Water and Sediments:

This phase of work include the sampling of water and sediment from various parts of the Willamette River and constitute an integral part of the subsequent tracer work. One criteria for a good tracer is that its natural concentration in the water system should be low. As part of the measurements of the background levels of the tracer elements we measured the abundances of more than thirty elements in the sediment, suspended particulates, dissolved cationic and anionic species at each of the twenty three sampling locations. (See Table A1-A23 in Appendix V)

In addition to compiling "baseline" data, this study is also intended to investigate and pinpoint if there is any unique trace ele-

ment(s)characteristic of some of the pollution sources which may be used as "natural" tracer(s). Table XXVII summarizes and compares the average elemental composition of the Willamette River sediments with other terrestrial sources. The absolute elemental composition of the sediment from each site are shown in Tables A1-A23 (Appendix V) and Figures XII, XIII,XIV,XV and XVI.

Figures XVII,XVIII and Table XXVIII show the relative elemental abundances of the Willamette sediments using the elemental abundances of "Oregon Soils"[76] (Table XXIX) and basaltic rocks as representative crustal materials of the Willamette Valley. The results suggest little anthropogenic contribution.(The high elemental content of the sediment may obscure the contribution of any anthropogenic source.)

The absolute and relative elemental abundances of the suspended particulates are shown in Table XXX and Figure XIX. The results suggest that the suspended particulates are similar to the sediment in elemental concentrations and can be considered as "upswept" sediment. The depletion of certain elements compared to the sediment suggest that other materials such as suspended organic particulates, biota which may include zooplankton etc are also part of the particulate measured. Despite of the uncertainiy in what constitutes the suspended particulate, the basic composition is similar to the sediment.

The dissolved species concentrations show distinct anthropogenic contributions and characteristic "fingerprints" can be developed for pulp and paper mill effluent, sewage outfalls etc. For example, it appears that Zn and Br represent useful tracers for sewage outfalls along the Willamette River while Cr and As act as tracers for pulp

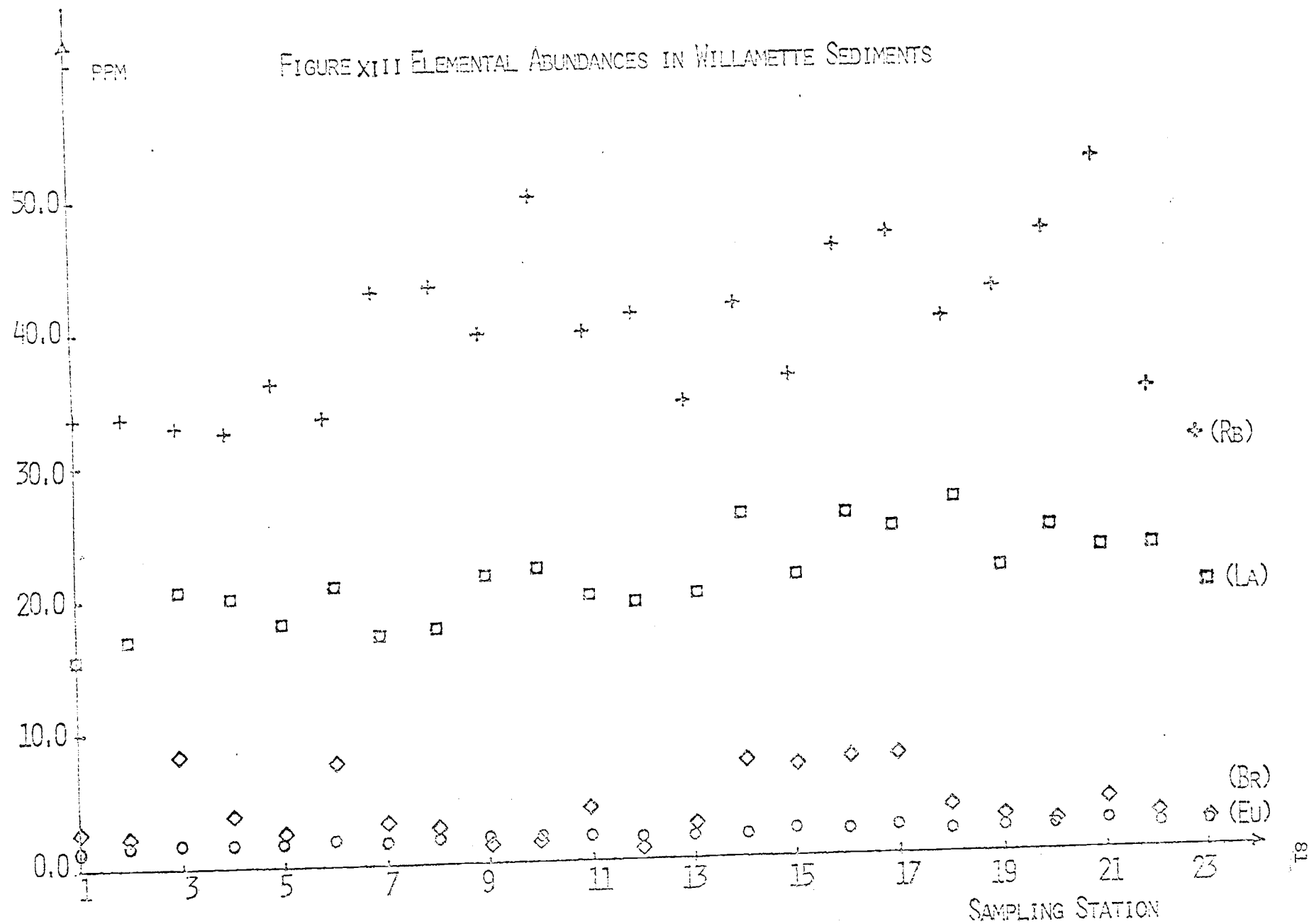FIGURE XII ELEMENTAL ABUNDANCES OF WILLAMETTE SEDIMENTS
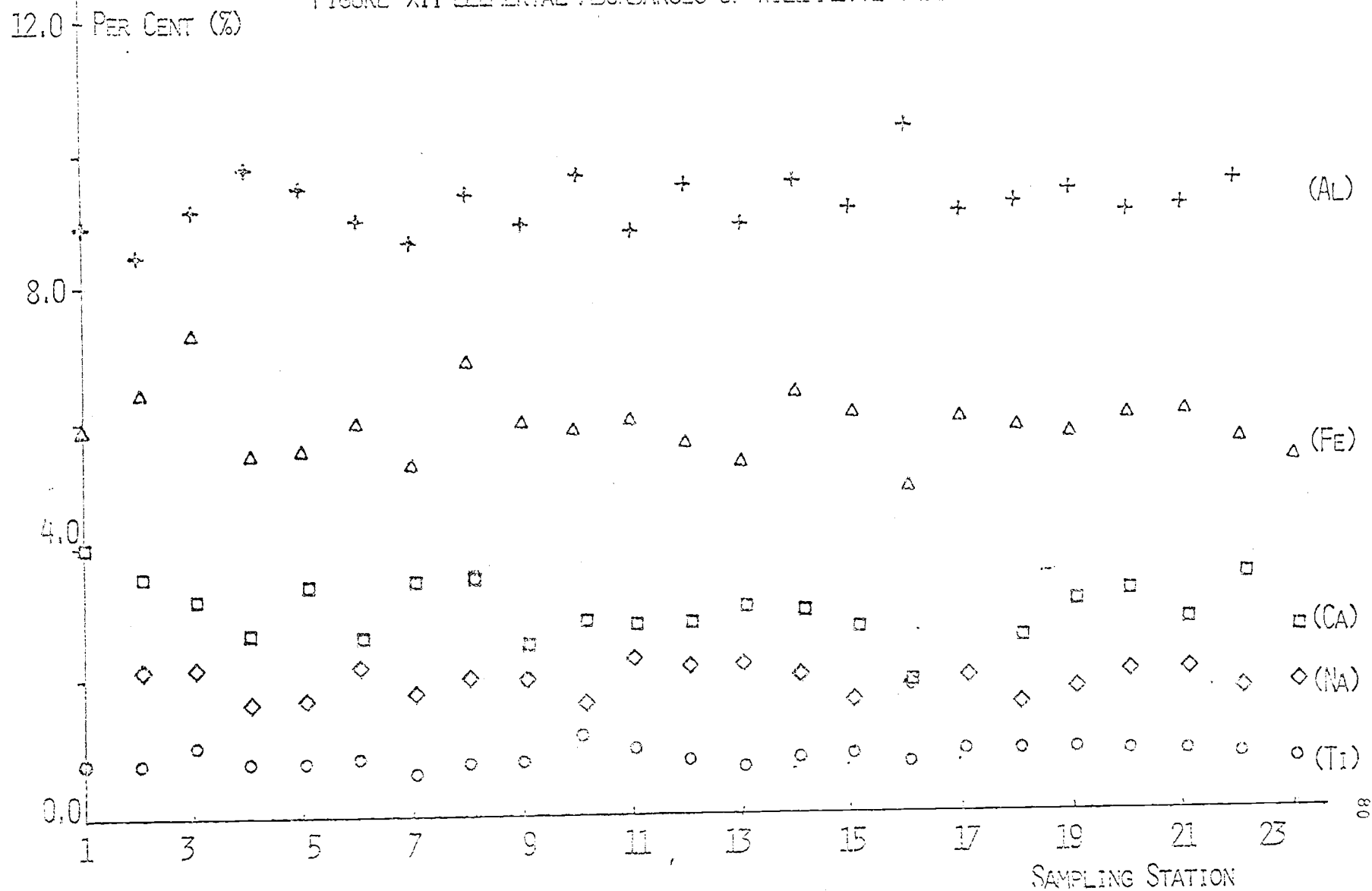
Table XXVII Elemental Abundances in Willamette River Sediments as Compared to Other Terrestrial Sources

Element	Willamette River Average	Range	Basaltic Rocks Averages	Sedimentary Rocks Averages	Crustal Abundances Averages
Al(%)	8.4 ± 0.1	7.8-9.5	8.76	10.45	8.23
Fe(%)	5.8 ± 0.1	4.8-7.2	8.56	3.33	5.63
Ca(%)	2.8 ± 0.03	1.9-7.2	6.72	2.53	4.15
Na(%)	1.9 ± 0.03	1.5-2.3	1.94	0.66	2.36
K(%)	0.83 ± 0.01	0.7-1.2	0.83	2.28	2.09
Ti(%)	0.81 ± 0.11	0.7-1.1	0.90	0.48	0.57
Mn(ppm)	818 ± 1	666-1255	2200	670	950
Ba	486 ± 2	390-562	270	800	425
V	166 ± 1	123-188	200	130	135
Cr	99 ± 0.1	68-133	300	160	100
Ni	44 ± 5	32-61	160	95	75
Rb	36 ± 0.4	30-51	45	400	90
Ce	36 ± 5	29-46	10	30	60
La	22 ± 0.1	16-26	27.0	40	30
Co	27 ± 0.1	20-31	45.0	23	25
Sc	20 ± 0.1	18-24	24.0	10	22
As	5.8 ± 0.1	4.4-7.0	2.0	6.6	1.8
Sm	4.7 ± 0.5	4.0-5.6	1.5	5.0	6.0
Th	3.5 ± 0.01	2.8-4.7	3.0	1.1	9.6
Hf	4.6 ± 0.01	3.3-6.2	2.0	4.0	3.0
Yb	2.8 ± 0.01	1.8-3.3	1.0	2.2	3.0
Br	3.6 ± 0.04	0.5-8.4	3.00	6.0	2.5
Eu	11.3 ± 0.1	1.1-1.5	--	1.0	1.2
Dy	1.5 ± 0.27	1.2-2.2	1.5	4.0	3.0
Cs	1.9 ± 0.02	1.3-4.1	--	1.2	3
U	1.4 ± 0.01	0.8-2.6	0.8	3.2	2.7
Sb	0.74 ± 0.04	0.5-1.6	0.15	1.0	0.2
Ta	0.62 ± 0.01	0.2-1.1	1.0	3.5	2
Lu	0.38 ± 0.01	0.3-0.5	--	0.2	0.5
Tb	0.52 ± 0.01	0.4-0.8	--	0.9	0.9

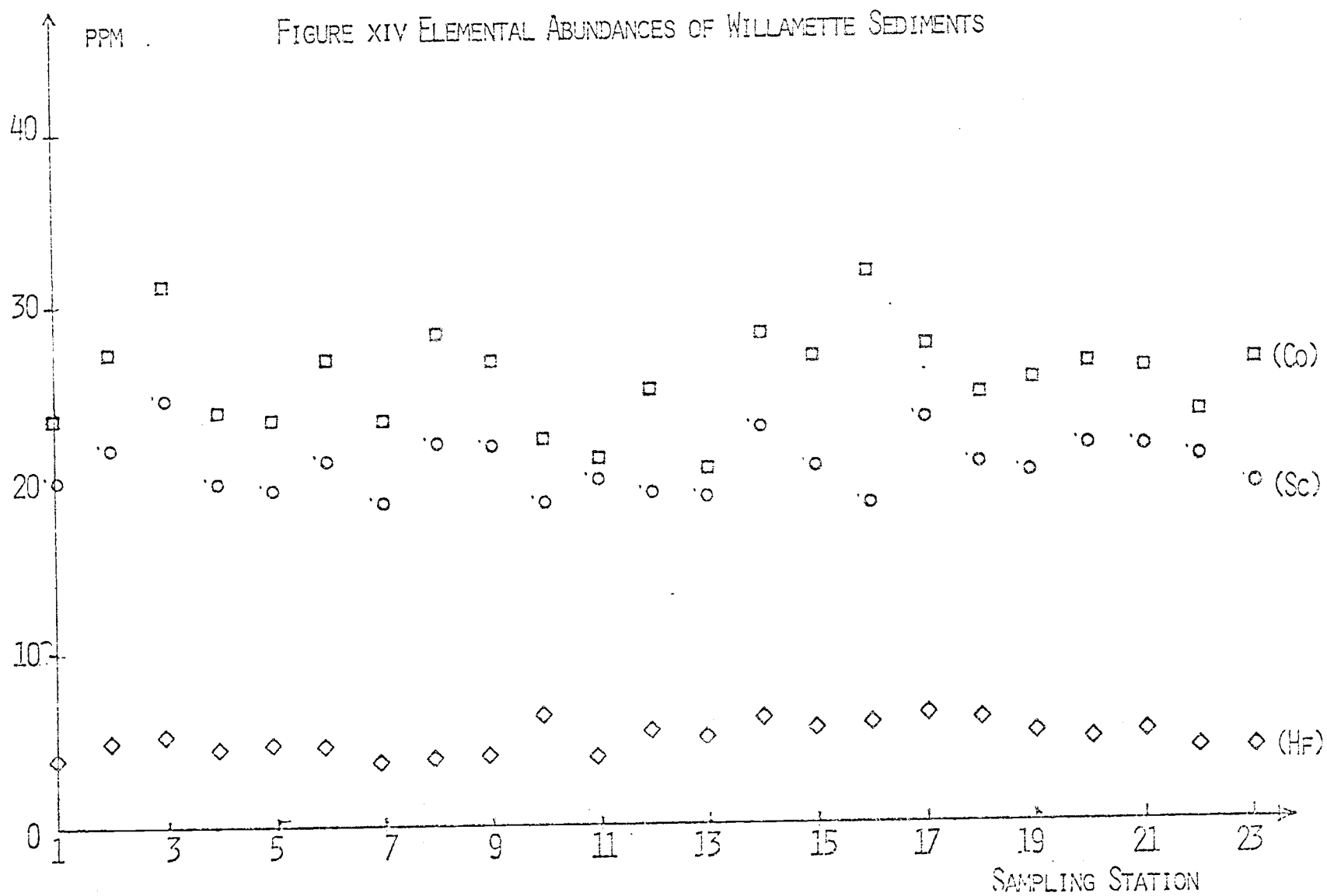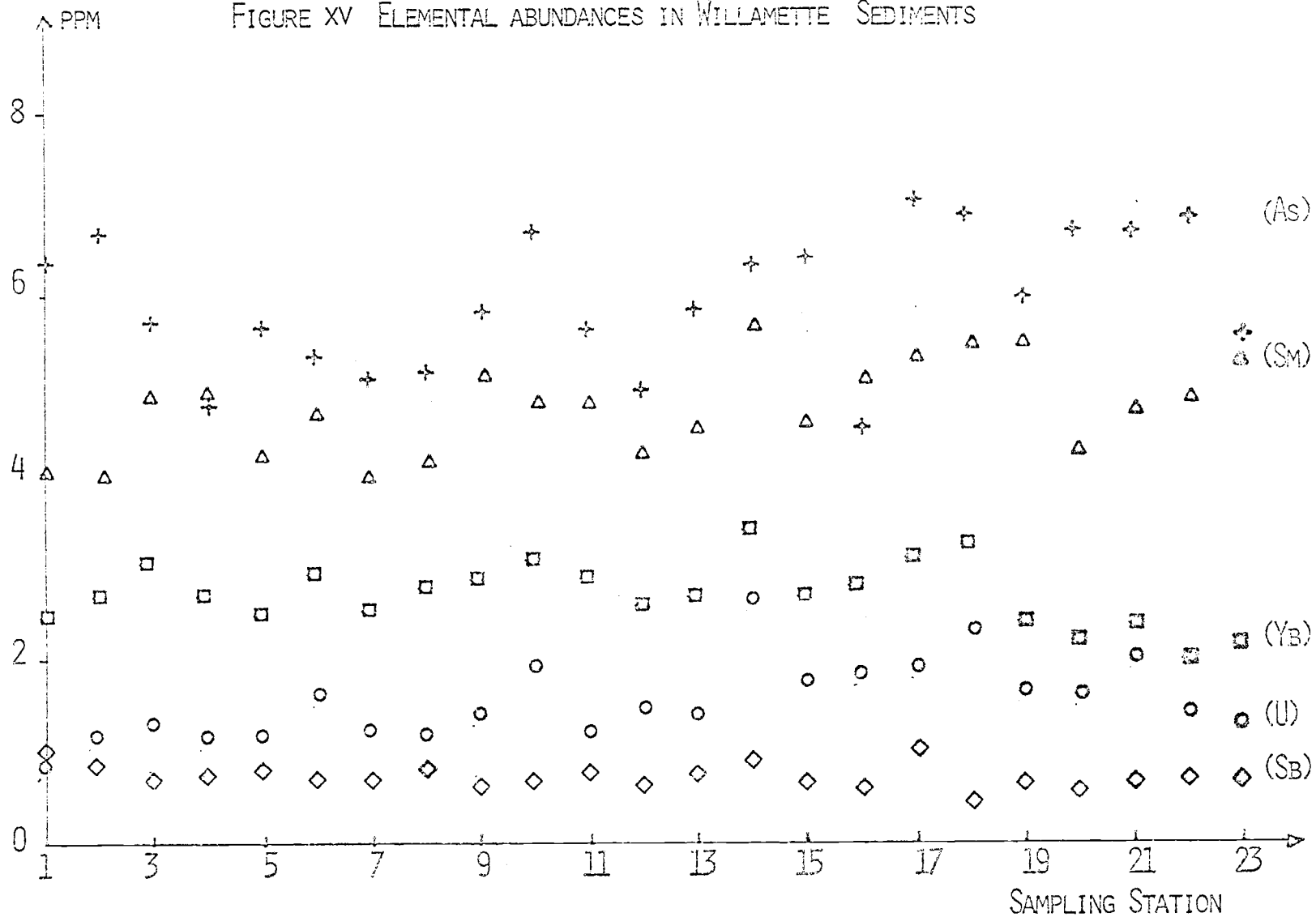FIGURE XIII ELEMENTAL ABUNDANCES IN WILLAMETTE SEDIMENTS

Figure XIV Elemental Abundances of Willamette Sediments

FIGURE XV ELEMENTAL ABUNDANCES IN WILLAMETTE SEDIMENTS

SAMPLING STATION

83

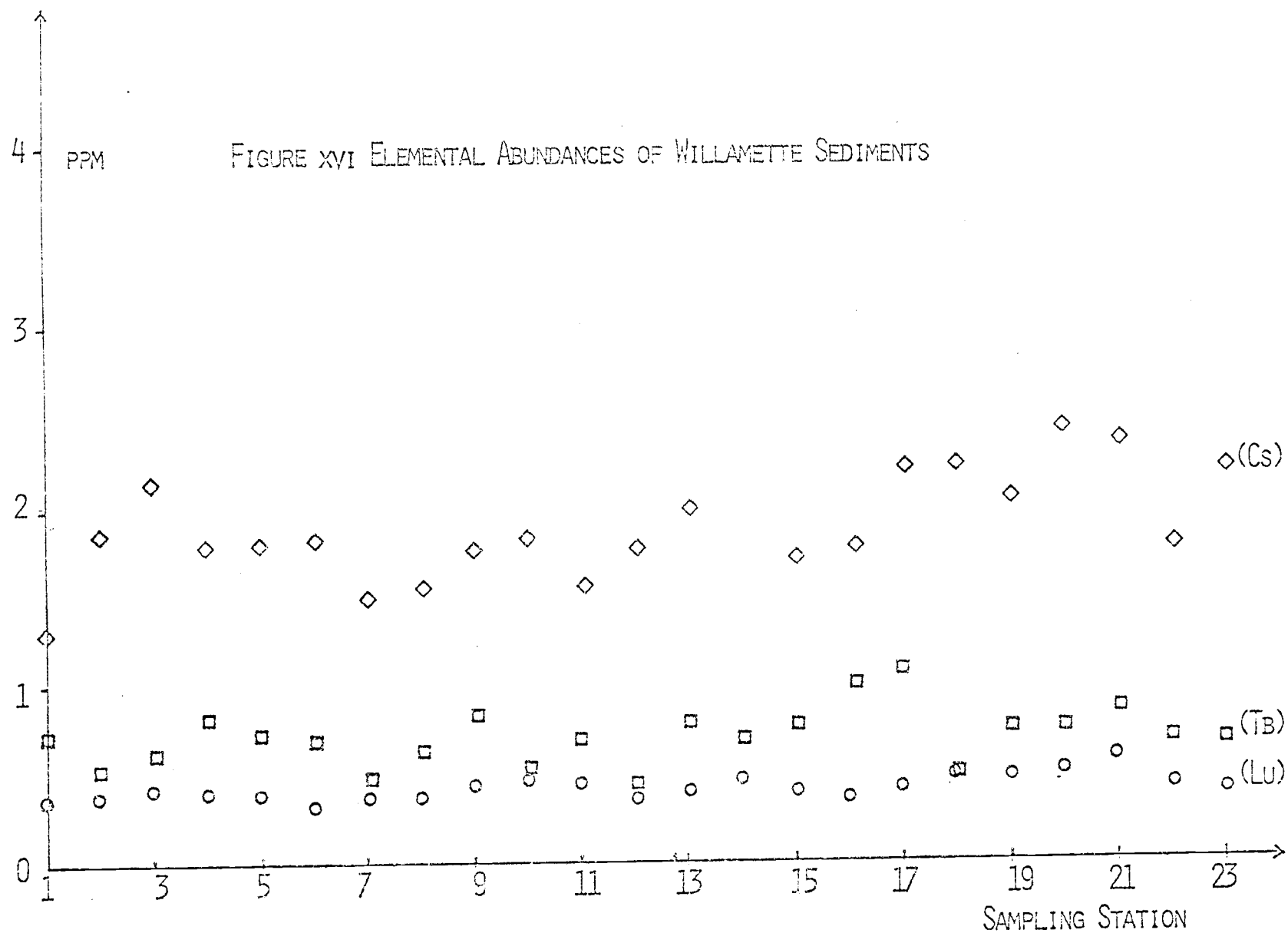FIGURE XVI ELEMENTAL ABUNDANCES OF WILLAMETTE SEDIMENTS

PPM

SAMPLING STATION

84

Table XXVIII: Relative Elemental Concentration in Willamette Sediments I

Element*	Absolute Concentration	Relative Concentration **
Al (%)	8.4	1
Fe (%)	5.8	0.7
Ca (%)	2.8	0.3
Na (%)	1.9	0.2
K (%)	0.83	0.1
Ti (%)	0.81	0.1
Mn	818	0.01
Ba	486	0.006
V	166	0.002
Cr	99	0.001
Ni	44	0.0005
Pb	36	0.0004
Ce	36	0.0004
La	22	0.0003
Co	27	0.0003
Sc	20	0.0002
As	5.8	0.00007
Sm	4.7	0.00006
Th	3.5	0.00004
Hf	4.6	0.00005
Yb	2.8	0.00003
Br	3.6	0.00004
Eu	1.3	0.00002
Dy	1.5	0.00002
Cs	1.9	0.00002
U	1.4	0.00002
Sb	0.74	0.000009
Ta	0.62	0.000007
Lu	0.38	0.000005
Tb	0.52	0.000006

* All numbers are in micrograms per gram of dry sediment unless indicated otherwise.

** Normalized to Al = 1.0

Table XXX: Elemental Concentrations in Oregon Soil[76]

Element	Absolute Concentration	Range
Al (%)	9.95 + 1.05	9.32 – 11.27
Fe (%)	5.68 + 2.09	3.25 – 9.80
Ca (%)		
Na (%)	0.54 + 0.13	0.43 – 0.61
K (%)	0.68 + 0.01	0.23 – 1.55
Ti (%)	0.73 + 0.02	0.43 – 1.28
Mn	667 + 5	211 – 2505
Ba	468 + 2	284 – 823
V	178 + 3	93 – 365
Zn	172 + 1	112 – 329
Cr	136 + 3	55 – 321
Ni	54 + 3	22 – 150
Ce	41 + 2	17 – 77
La	22 + 2	9.5 – 44.7
Co	23 + 5	7.3 – 70.4
Sc	23 + 2	11.8 – 48.1
As	3.0 + 1.2	2.2 – 5.6
Sm	4.77 + 1.38	3.6 – 6.3
Th	4.99 + 3.76	1.49 – 12.7
Hf	4.56 + 1.56	3.11 – 6.40
Yb	2.14 + 1.01	2.00 – 2.26
Br	6.69 + 1.70	3.89 – 11.4
Eu	1.53 + 1.04	1.4 – 1.6
Cs	1.53 + 3.86	0.34 – 4.19
Sb	0.54 + 2.02	0.31 – 1.17
Ta	0.83 + 1.57	0.48 – 1.21

* All concentrations are in ppm unless indicated otherwise.

Figure XVII: Relative Concentration of Elements in Willamette Sediment (Normalised to Al = 1.0)

Basaltic

Rocks
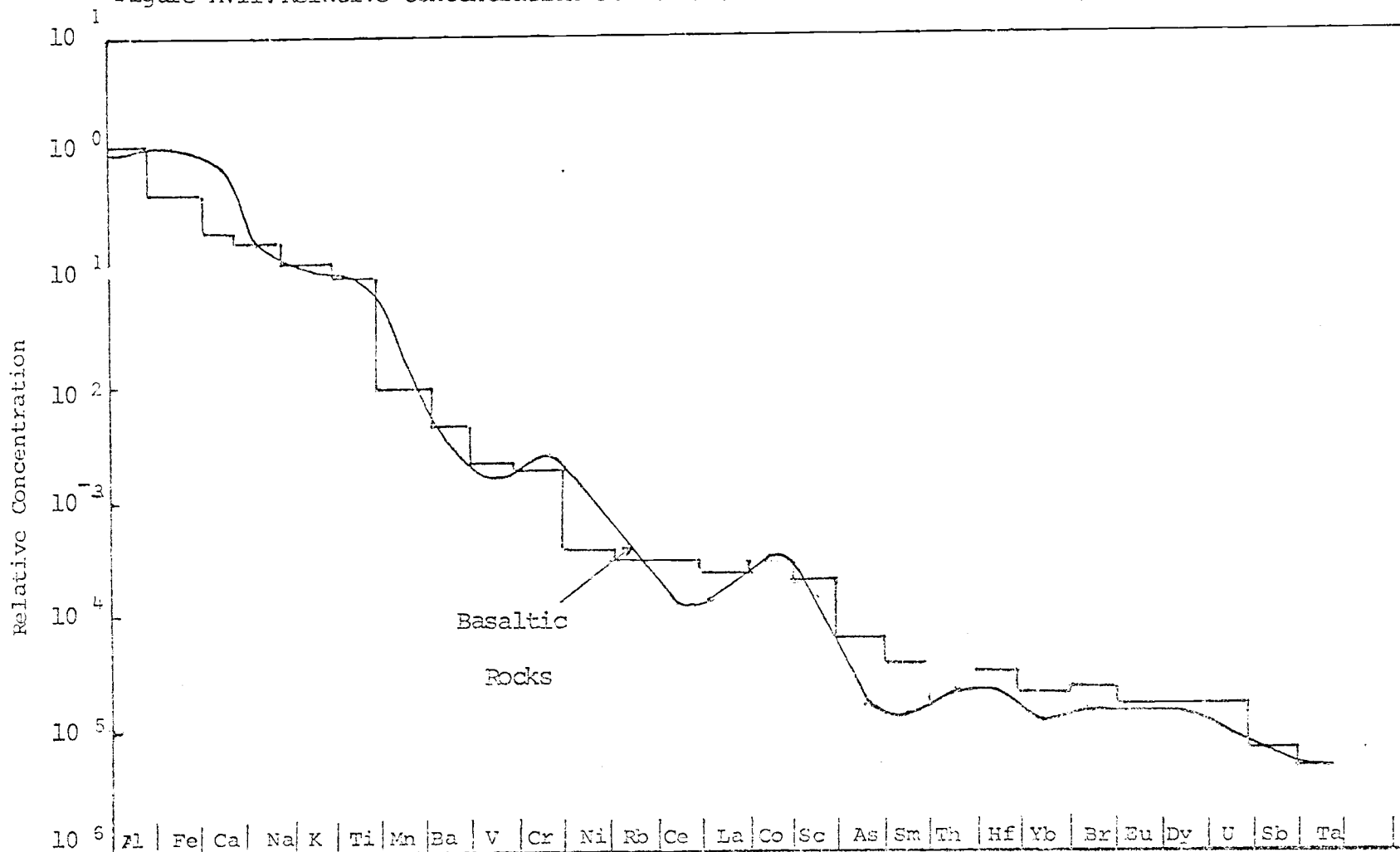
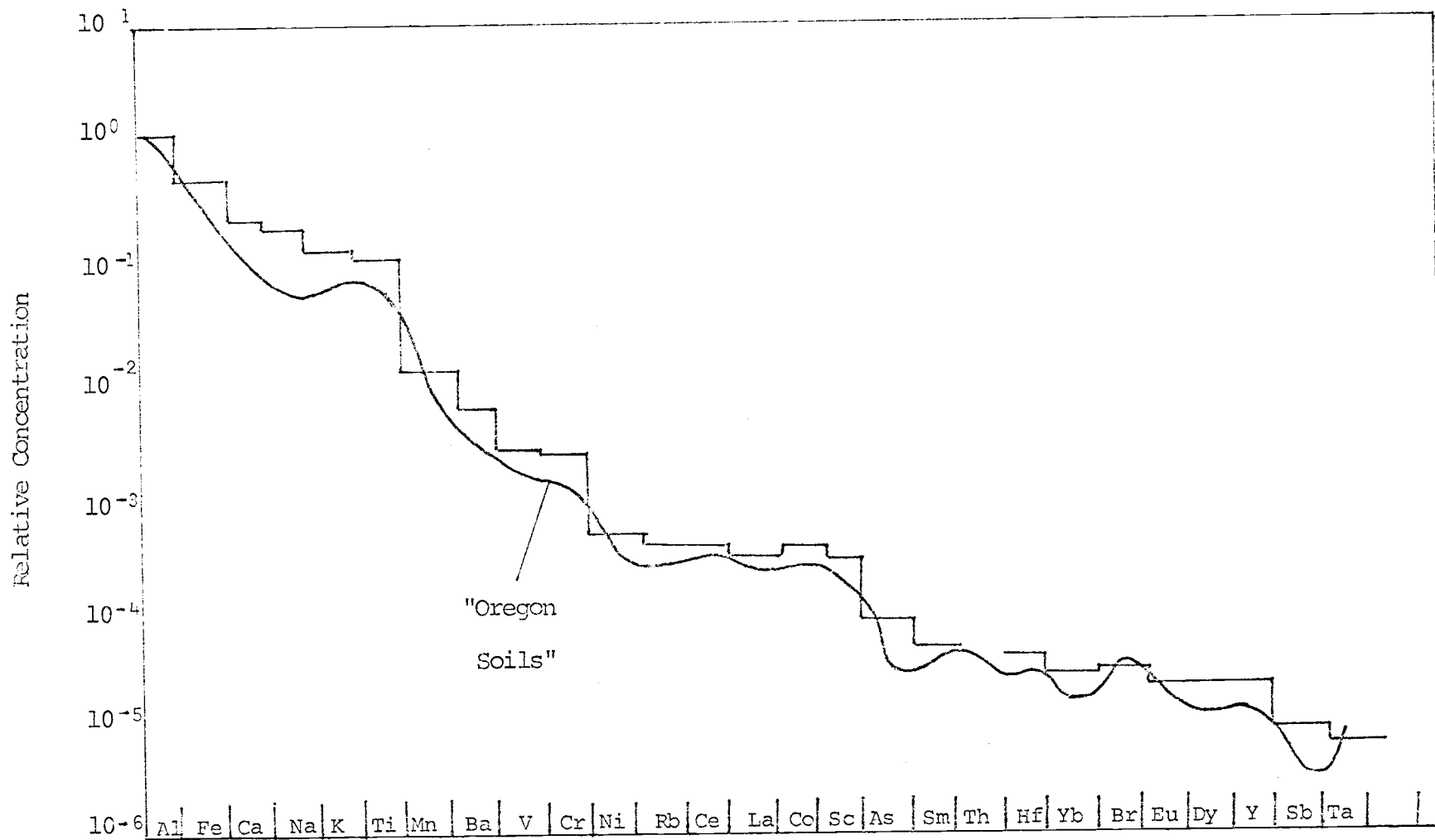Figure XVIII: Relative Concentration of Elements in Willamette Sediments (Normalized to Al=1.0)

"Oregon

Soils"

Relative Concentration

10⁻¹

10⁰

10⁻¹

10⁻²

10⁻³

10⁻⁴

10⁻⁵

10⁻⁶

Al Fe Ca Na K Ti Mn Ba V Cr Ni Rb Ce La Co Sc As Sm Th Hf Yb Br Eu Dy Y Sb Ta

88

Table XXX Absolute and Relative Elemental Abundances in Suspended

Particulates

Element*	Absolute Concentration	Range*	Relative Concentration**
Fe (%)	2.82 ± 0.01	0.56 – 10.46	1
Na	1721 ± 2	560 – 8025	0.06
K	1477 ± 13	585 – 6412	0.05
Mn	291 ± 1	129 – 3070	0.01
Zn	108 ± 3	45 – 3750	0.004
Cr	11.4 ± 0.3	6.5 – 243	0.0004
Co	3.8 ± 0.1	30 – 36.5	0.0001
Sc	1.8 ± 0.1	1.17 – 17.4	0.00007
As	1.65 ± 0.01	0.67 – 32.1	0.00006
Sm	1.20 ± 0.01	0.34 – 6.26	0.00004
Br	5.46 ± 0.11	3.28 – 143	0.0002
Eu	0.014 ± 0.001	.0014 – 1.19	0.0000005

* All concentrations are in ppm (parts per million) unless indicated otherwise.

** Normalized to Fe = 1.0

Figure XIX : Relative Elemental Abundances in Suspended Particulates (Normalized to Fe = 1.0)
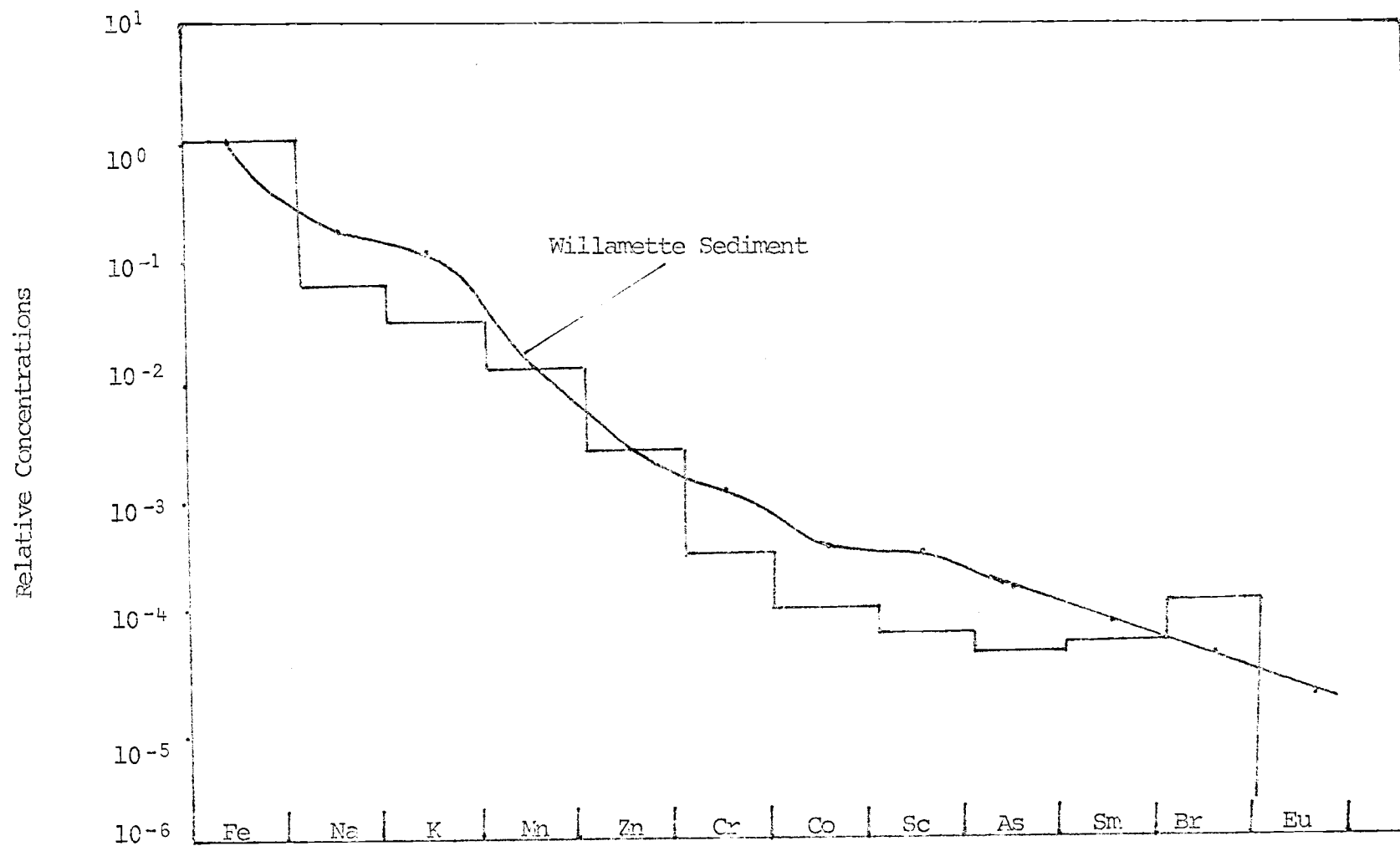
Table XXXI: Hydrospheric Trace Element Abundances in Various American Locations (ng/ml)

Element	This Work		Pacific N.W.		Willamette at Portland		United States	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Br	4.52±0.01	2.1-48						
Co	0.03±0.001	0.02-0.5	8	1-17			17	1-48
Cr	0.14±0.001	0.01-66	6	1-36	1		9.7	1-112
Fe	20±6	5-10	2	2-256	59	15-138	52	1-4600
K	26±1	-110						
Mn	2.38±0.01	4-71	2.8	0.4-28	1.4	0.4-3.2	58	0.3-3230
Na	112±1	40-440						
Zn	20±2	0.6-123	40	2-330	28	12-70	64	22-1183
Eu*	1.23±0.03	0.3-440*						
Sm*	18.6±0.3	20-59						
Sc*	7.7±0.1	2.0-24.4						

a: Kopp,J.F.,Kroner,R.C., "Trace Elements in Water of U.S.",U.S.Dept.ofIInterior,F.W.P.C.A., Division

of Pollution Surveillance, Cincinnati, OHIO.

* Concentration in parts per trillion (pg/ml)

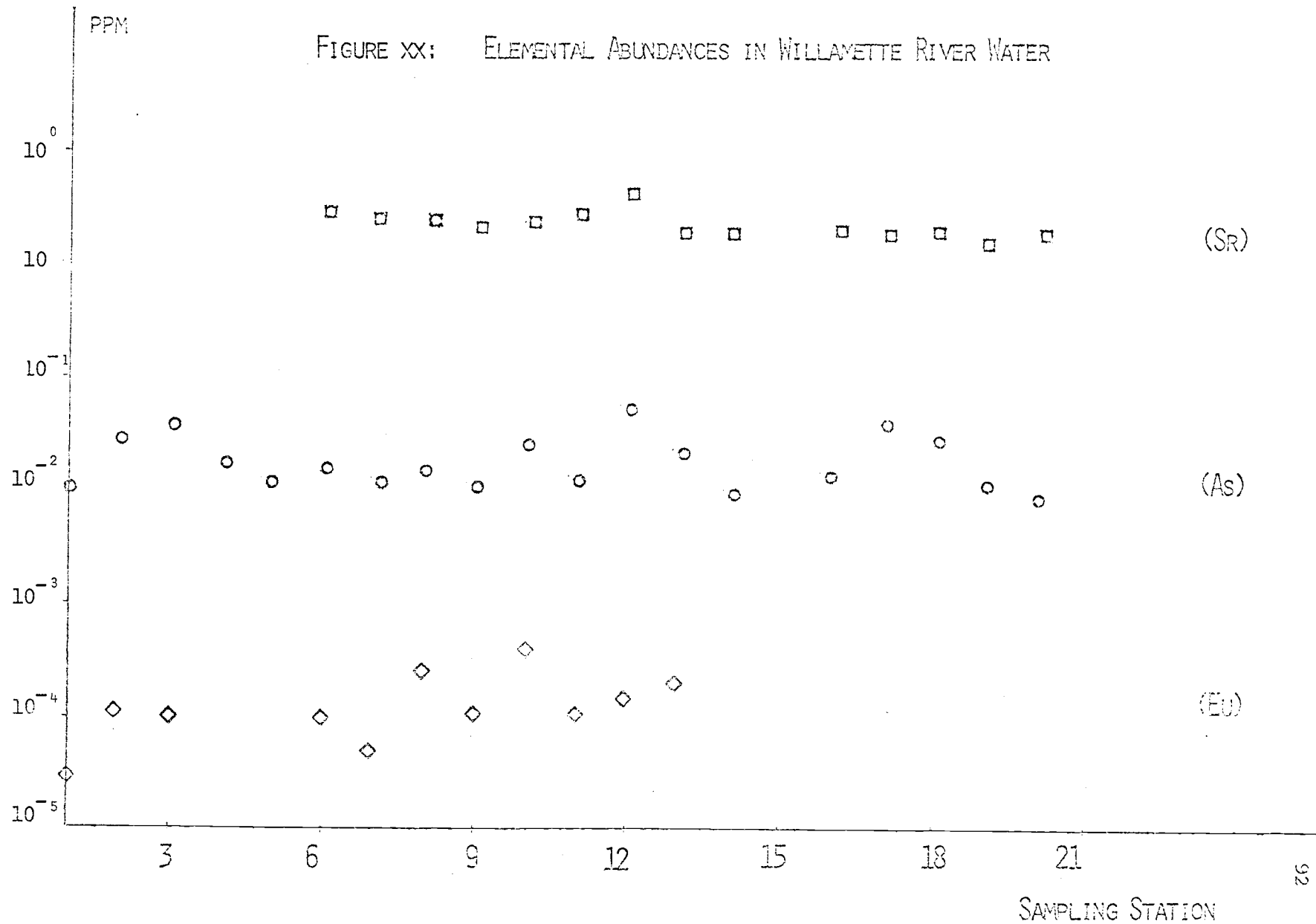FIGURE XX: ELEMENTAL ABUNDANCES IN WILLAMETTE RIVER WATER

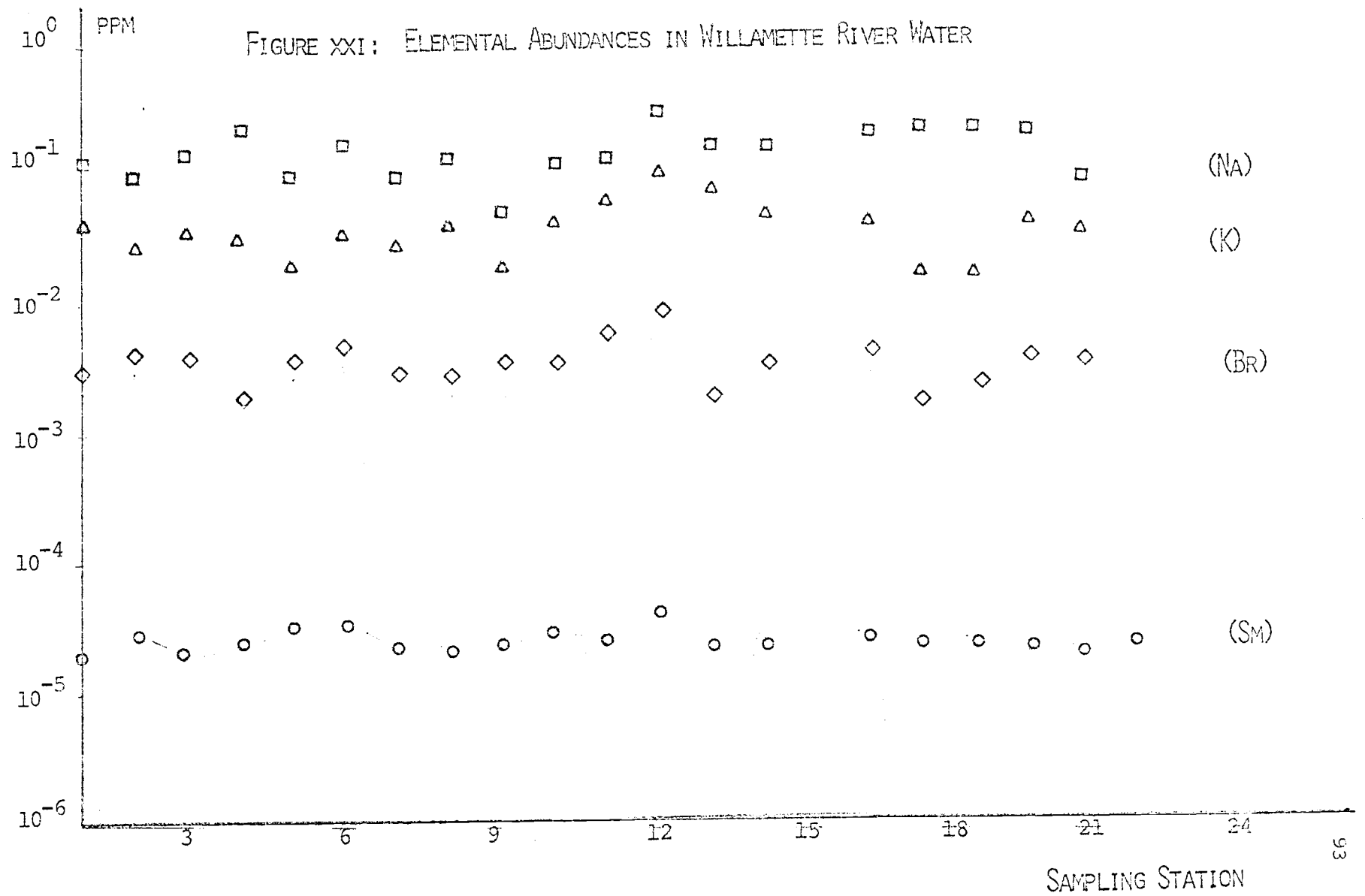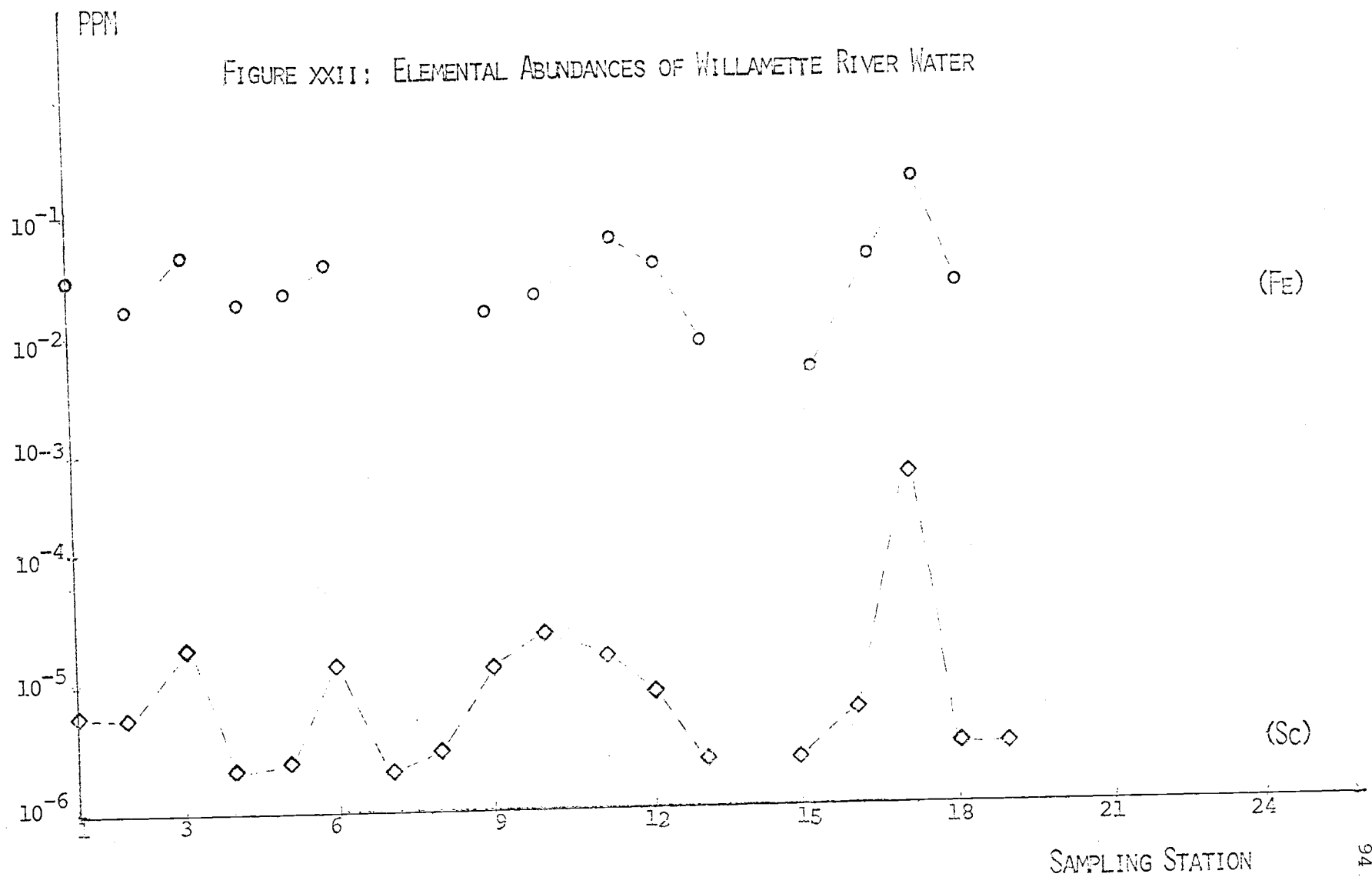FIGURE XXI: ELEMENTAL ABUNDANCES IN WILLAMETTE RIVER WATER

FIGURE XXII: ELEMENTAL ABUNDANCES OF WILLAMETTE RIVER WATER

and paper mill waste. One interesting by-product of this investigation is the finding that the simple fractionation of the dissolved species into cationic and anionic fractions is a powerful tool in pollutant source identification. In Figure XXII, we show the total dissolved Co concentration, the anionic Co concentration and cationic Co concentration as a function of position along a section of the Willamette River. The resolution of the middle peak in the total dissolved Co concentration into its anionic and cationic components has revealed that two separate sources, a cationic source (a sewage outfall) and an anionic source (a paper mill), are contributing to this peak. Also an inspection of Figure XXI shows the main "region" of more polluted water in general; this include the Harrisburg area, Albany area and the Salem area. This is especially true in the case of Albany and Salem which consitute the two larger municipality contributing wastes along the Willamette River.

It is important to reiterate that in quantitative and quali-tative trace analysis of dissolved species in water to take into con-sideration the chemical speciation that may have occured. It is pre-sumptuous and erroneous to assume the dissolved ions exist in a cer-tain state without intimate knowledge of the parameters which heavily influence the state of beings of these dissolved species.

(6) Freeway Lake Experiments:

The primary purpose of this experiment as described earlier is to test the conservative nature of the tracer in actual field situ-ation and in the presence of "natural ingredients" such as dissolved

Figure XXIII: Total Dissolved, Cationic and Anionic Co Concentration

along Willamette River.

96
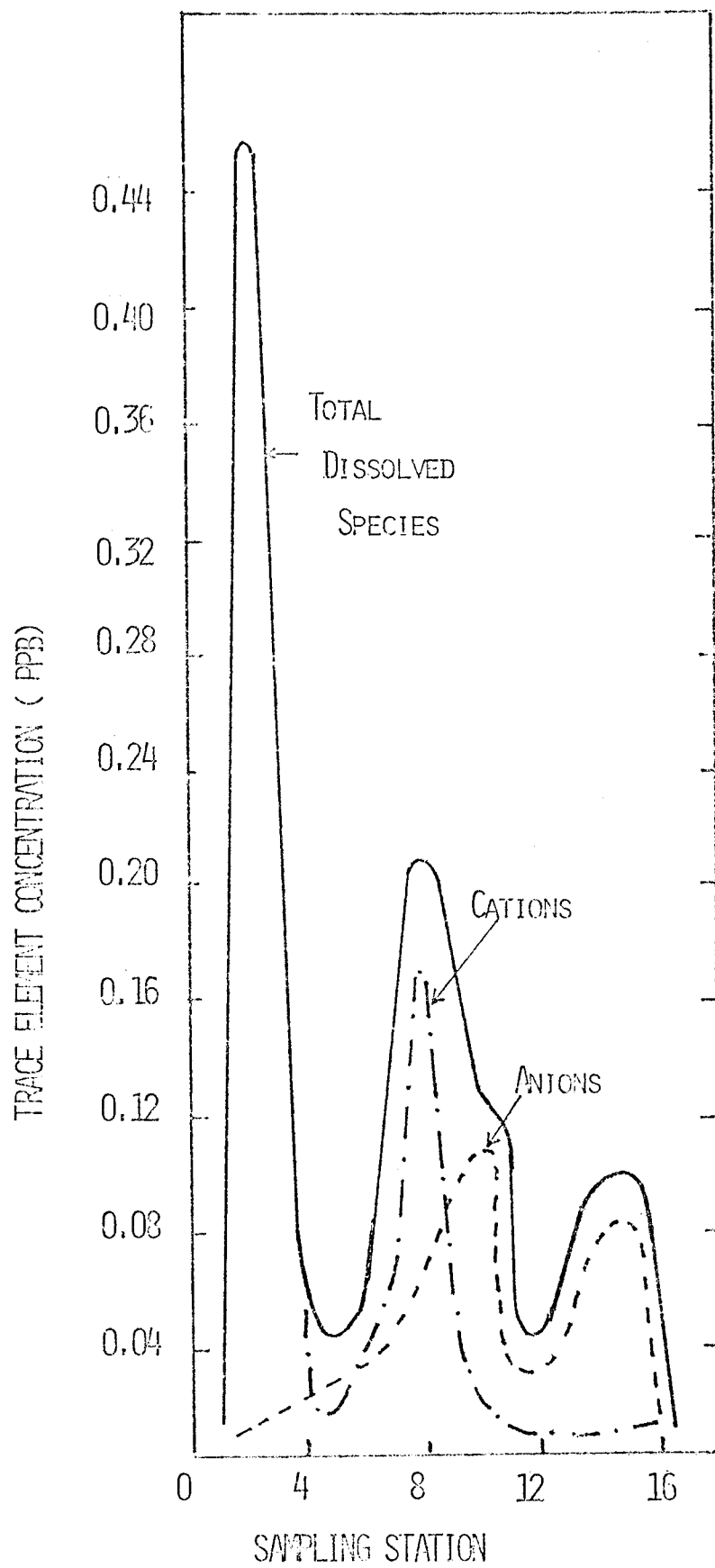
organics etc. The water in the lakes are heavily turbid, muddy yellow in color and contain large amount of suspended particulate. This should provide an ideal situation where the application of fluorescent dye may be unsatisfactory and the use of activable tracer becomes the only alternative.

Results of these experiments are shown in Figures III,IV and V and Table XVIII. The behaviour of the tracer can best be summarized in the plot of tracer concentration versus time as shown in Figure XXIV. A mass balance calculation of the quantity of the tracer remaining in solution is calculated by multiplying the average concentration of each tracer in each lake (See Figures III,IV and V) by the volume of water present in each lake. The volume of each lake is estimated by multiplying the area by its average depth. Several assumptions were made in such calculations: (1) The mass of water in each lake remains fairly constant during the sampling period. This was based on the observation that the water depth gauge under the bridge which connects Lake I and Lake II remained paractically constant during this period of time. (2) The average depth calculated by taking the mean of the depths at various points of the lakes represent the "true" depth. Again, it must be stressed at the outset that the largest source of error in our mass balance calculation stems from the inability to know the volume of water present. The calculated percentage of tracer left after 1,3 and 15 days is shown in Table XVIII. The results indicate that at least 96,80 and 78 per cent of the tracer initially added still remain in solution after a period of 1,3 & 15 days respectively. The results indicate the lower limit of the

tracer stability because no consideration is given to the amount of tracer carried away by the outflow/efflux of the lakes. From the concentration versus time plot in Figure XXIV., it can be seen that after a period of one day, no appreciable quantity of tracer migrated to the larger lake which is more than 100 yards away from the point of injection. Oak Creek which flows into Lake I probably provides the "pushing" power in addition to the wind in causing the turbulence necessary for complete mixing in the lakes. The concentration profiles of the three lakes show that during the 15 day experiment, the concentration of the two larger lakes increased while the concentration in the smaller lake decreased, indicating continuous migration/diffusion of the tracer towards the larger lakes. Further examination of the concentration profiles of the tracers indicate that the tracer concentrations are highest at "dead" spots or points where the water is stagnant.

(7) Willamette River Experiment I:

The main objective of this experiment is to test the conservative nature of the tracer in addition to providing a good test of sampling logistics and validity of the U.S.G.S.Hydrologic Investigation Atlas in predicting tracer arrival time .
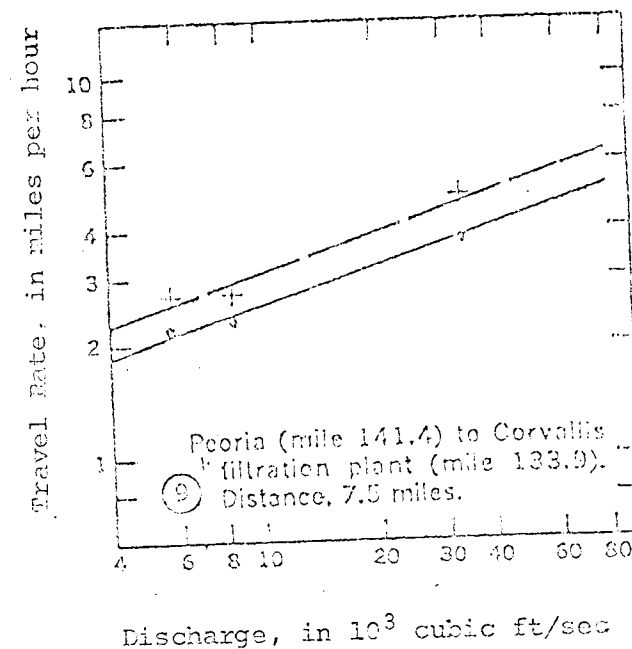
At this point, it may be useful to explain briefly how to derive tracer arrival time using discharge data and the U.S.G.S.Hydrologic Investigation Atlas such as the "The Travel Rates of Water for Selected Streams in the Willamette River Basin" (See Table XXXII) The table on the top provides daily discharge record at various gauging stations.

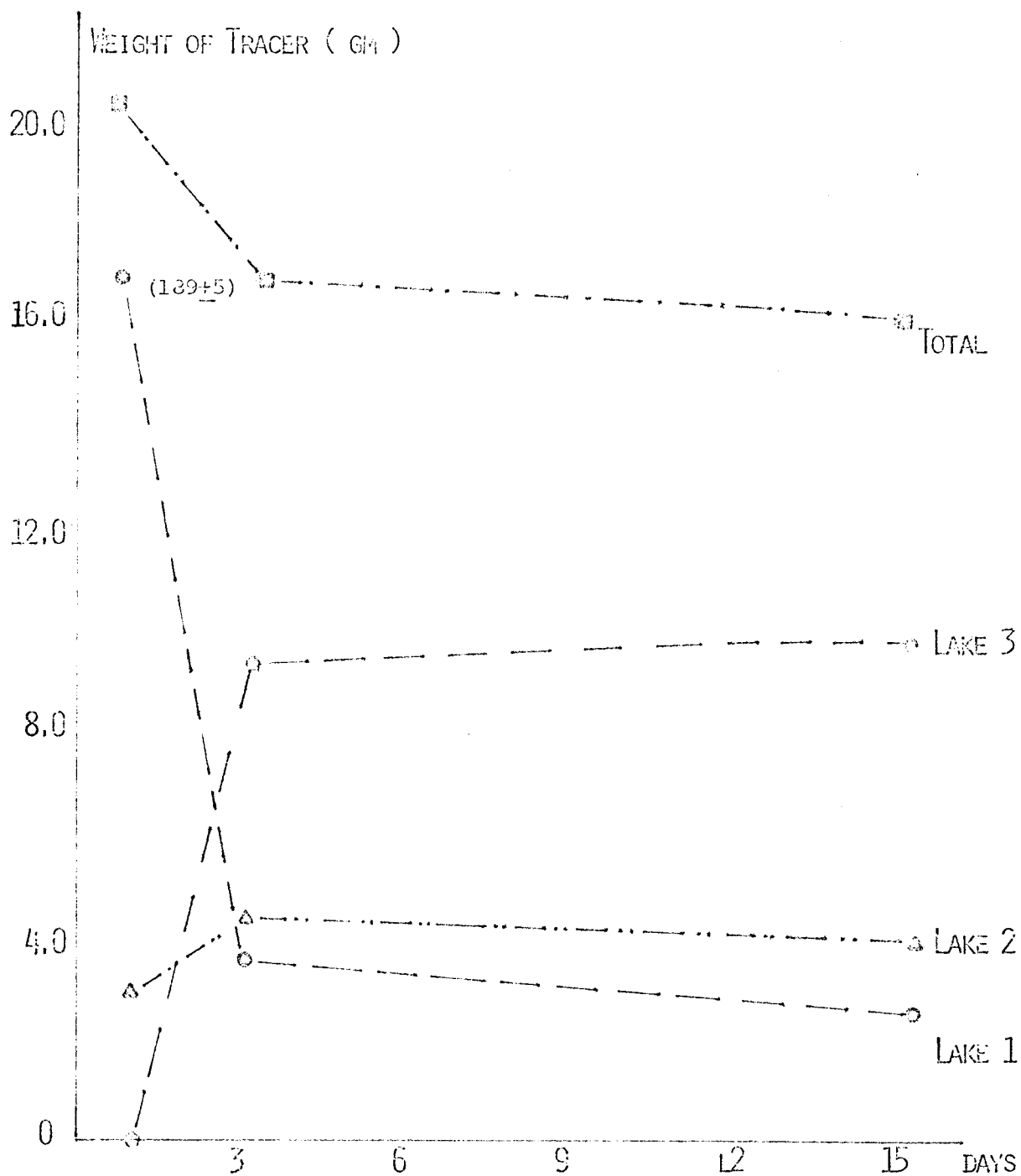Table XXXII: Daily Stream Data and Travel Rates of Water

DAILY STREAM DATA

U. S. ARMY ENGINEER DISTRICT, PORTLAND								DATE 15 OCT 1975			
STATION	STREAM	BASIC DATA			OBSERVED DATA			NATIONAL WEATHER SERVICE STAGE FORECAST			
		DRAINAGE AREA SQ.MI.	TEMP. OF BASE W.S.EL.	STAGE, FEET MAJOR FLOOD / BANK FULL	STAGE, FEET		DISCHARGE C.F.S.				
					OBSERVED	STAGE CHANGE					
MAIN STEM WILLAMETTE RIVER											
EUGENE	WILLAMETTE	2,000	330.6	23.0 17.2	10.8	+ 0.3	3,860				
HARRISBURG	WILLAMETTE	3,410	293.13	17.0 12.3	9.19	+ 0.13	6,690				
CORVALLIS	WILLAMETTE	4,300	191.97	26.0 19.0	4.9	- 0.5	6,440				
ALBANY	WILLAMETTE	4,840	151.18	12.0 11.3	9.19	- 0.59	7,700				
SALEM	WILLAMETTE	7,280	104.18	32.3 23.7	6.41	- 0.44	13,420				
WILL. FALLS UPR	WILLAMETTE	10,100	32.14	17.0 13.0	4.2	- 0.1					
WILL. FALLS LWR	WILLAMETTE	10,170	0.43	42.0 33.0	4.6	0					
PORTLAND	WILLAMETTE	11,200	1.11	23.0 12.3	5.2	+ 0.1	54,700				
MAIN TRIBUTARIES WILLAMETTE RIVER											
JASPER	M.F. WILL.	1,310	212.45	15.0 11.3	11.17	+ 0.72	3,840				
GOSHEN	C.F. WILL.	412	423.12	18.0 11.7	5.1	+ 0.7	470				
VIDA	MCKENZIE	730	391.71	14.0 9.3	4.6	+ 0.1	2,240				
MONROE	LONG TOM	391	229.31	9.0 3.4	5.66	- 0.27	1,050				
JEFFERSON	N. SANTIAM	663	422.45	11.0 9.3	2.43	- 0.22	2,270				
MEHAMA	N. SANTIAM	642		11.0 10.0	2.34	- 0.01	1,330				
JEFFERSON	SANTIAM	1,790	109.63	23.0 12.1	2.44	- 0.06	3,230				
DEVER	LUCKIAMUTE	243	121.17	727.0 29.0	1.85	- 0.01	56				
MONMOUTH	S. YAMHILL	305	42.11	42.0 30.0	1.59	- 0.05	50				
DILLEY	TUALATIN	123	147.31	16.3 11.0	9.1	0	220				
FARMINGTON	TUALATIN	341	109.40	24.0 17.0	7.63	- 0.24	120				
SCHOLLS	TUALATIN	11.7	178.47	11.0 9.0	11	—					

** Dashed curve defines the travel rate of the leading edge

Solid curve defines the travel rate of the maximum concentration.

Peoria (mile 141.4) to Corvallis filtration plant (mile 133.9). Distance, 7.5 miles.

Travel Rate, in miles per hour

Discharge, in 10^3 cubic ft/sec

FIGURE XXLI: FREEWAY LAKES TRACER STABILITY EXPERIMENT CONCENTRATION - TIME PROFILE

while the diagrams are travel-rate graphs determined by dye-tracer studies. In each diagram there are two curves, the dashed curve represents the leading edge of the tracer, whereas the solid curve represents the peak concentration of the tracer. The travel rate for a particular subreach is obtained from the graph by entering the discharge figure for the particular subreach and finding the coincident travel rate from the appropiate curve. Travel time can be derived for each subreach by dividing the distance along the subreach shown under each graph, by the travel time. Likewise, time of travel can be calculated for the peak concentration of the tracer by using the peak concentration-discharge relation. For example, the tracer was injected at Peoria Boat Ramp and samples collected at Corvallis near the Oregon State Crew Dock. The tracer travel time can be calculated as follows:

Subreach	Discharge	Leading Edge Travel Rate	Distance	Travel Time
9	4170 cfs	2.3 mph	7.5 miles	3.26 hrs

since the OSU crew dock is approximately one mile down stream from the Corvallis filtration plant, an additonal 0.43 hour should be added. This provide a rough indication that the tracer will arrive the sampling site 3.69 hours after commencement of tracer injection. However, sampling was begun an hour earlier than the predicted tracer arrival time and samples were taken at an interval of five minutes. In using the continuous injection method [77], it is necessary to remove samples over a finite period of time when the tracer concentration is constant but unless some indicator is used, the presence of a region of uniform concentration at the sampling point is not evident. In such circumstances, a large

number of samples is taken to guarantee coverage of the transit period. Since we have yet to prove the prediction of the tracer arrival time using the Hydrologic Atlas #HA-273 is accurate, we decided therefore to take samples every five minutes to ensure our sampling covers the tracer transit period.

The total quantity of tracer used was 39.1015 grams of Dy, chelated with DTPA and diluted to 8.3 liters with distilled water and then pumped continuously for a period of 1 hour and 20 minutes at a rate of 1.0 ml/sec. The river discharge rate at the day of the experiment was 4170 cfs (cubic feet per sec) or 118 cms (cubic meters per sec).

By using the following relationship:

$$Q \int (C_q - C_b) \, dt \quad \text{or} \quad Q \, \Sigma (C_q - C_b) \Delta t \quad\quad (1)$$

where dt or Δt is the time span between samples

    Q is the river discharge rate

    C_q is the concentration of downstream samples

    C_b is the background concentration

the amount of tracer present in the river during the sampling period can be calculated. The total amount of tracer injected into the river is represented by the following relationship:

$$qC_Q T \quad\quad\quad\quad (2)$$

where C_Q = tracer concentration.

    q = tracer injection rate.

    T = total tracer injection time.

Since the C_q, T, q, Q terms are known, C_q and C_b can be measured and Δt is also known, the extent of the tracer approaches ideality with

regard to solution stability can be obtained from the ratio of equation (1) and (2):

$$\{ \, Q \, \Sigma(C_q - C_b) \Delta t \, \} \, / \{ \, qC_Q T \, \}$$

In the estimate of $Q \Sigma(C_q - C_b) \Delta t$ one assumes that the cross sectional concentration of the tracer is uniform, that is to say, the tracer is well mixed at the sampling point. There are several criteria that will determine the where and when sampling should be done: (1) Sampling should be performed at point(s) far enough downstream for complete mixing to have occured. The correct choice of this point is important. If the sampling point is too close to the injection point, errors may result from incomplete mixing but if the measuring point is too distant, excess dispersion occur and the tracer is over diluted. The lower limit of the working distance is determined by the mixing of the tracer with the river water. The mixing is fast if the injection is performed in a region where velocity of the current is higher than mean velocity (bottlenecks, sharp bends, rapids etc.) or in zones of eddy currents. In these places, the injected substances mixes with the water after travel a short distance and the concentration quickly becomes uniform. In plain winding rivers, portions (lateral zones) of the tracer cloud can enter stagnent waters and are later carried again by the current at a low velocity, this effect lead to a significant broadening of the tracer cloud and therefore, to an increase of mixing length. Several empirical equations have been proposed for determining the minimum required distance for adequate mixing; e.g. (i) $L_{mix} = kQ^{1/3}$ [80] where k is a constant equal to 200 for side injection and

50 for center injection, Q = river discharge rate. (ii) I_{mix} = 0.13 x

(b^2/H) (C/g) $(0.7C + 6)$ [81] where b = mean width of the stream, H =mean

depth of the stream and C = Chezy's Coefficient (15<C<50) which depends

on the nature of the river bed and g is the acceleration of gravity.

Using the two empirical equations, one finds I_{mix} is between 0.6 mile

and 15.8 miles. Unfortunately, the first relationship grossly underes-

timates the mixing length while the second equation overestimates it.

Since Corvallis is about 10 miles downstream from Peoria, we felt the

tracer would be well mixed at the sampling point. The results of the

experiment are shown in Table XXXIII and Figure XXV and they show at

least 82% of the tracer species remain in solution during the experiment.

The number shown above (82%) is estimated as follows:

From Table XXXIII $\Sigma C_q \Delta t$ = 166746

$Q \Sigma C_q \Delta t$ = 166746 x 4170 x 28.316 x 10^3 x 10^{-12} = 19.69 g Dy

Weight of Dy used = 39.1015 g

Total volume of tracer solution = 8.3 liter

Concentration of tracer solution = 4.71 g/l

Tracer injection rate = 1 ml/sec Total time of injection =

1 hr & 25 mins. Total quantity of tracer injected = qC_QT =

1 x 4.71 x 10^{-3} x 85 x 60 = 24.03 g

Ratio of Equation (1)/Equation (2)

= (19.69/24.03)x 100% = 81.9%

A plot of the concentration versus time curve is shown in

Figure XXV. One can see immediately that the curve represents the

latter portion of the finite period of time when the tracer concentra-

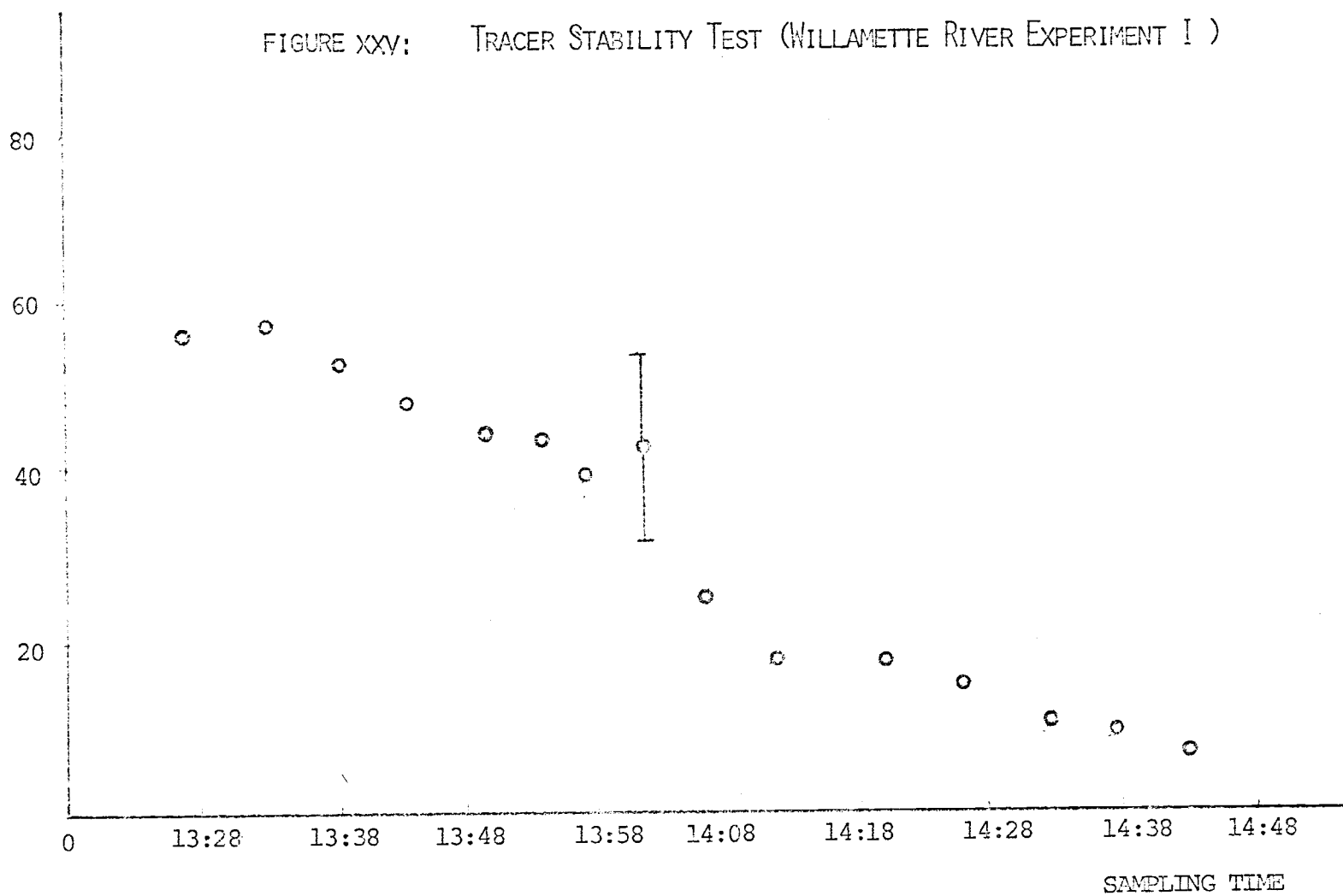FIGURE XXV: TRACER STABILITY TEST (WILLAMETTE RIVER EXPERIMENT I)

Table XXXIII: Data Log of Tracer Stability Field Test I (Willanette River)

Sample	Time	Δt (Minutes)	Concentration C_q^*
m2s1	1323		
		5	56.6 ± 10.3
m2s2	1328		
		5	55.6 ± 12.6
m2s3	1333		
		5	52.3 ± 8.1
m2s4	1338		
		5	49.0 ± 9.0
m2s5	1343		
		5	49.9 ± 9.8
m2s6	1348;30		
		5:30	43.4 ± 8.0
m2s7	1353		
		5	40.0 ± 11.4
m2s8	1359		
		5	43.8 ± 10.5
m2s9	1403		
		5	23.8 ± 2.6
m2s10	1408		
		5	20.1 ± 7.0
m2s11	1413		
		5	19.4 ± 3.4
m2s12	1418		
		5	15.4 ± 2.7
m2s13	1423:30		
		5:30	14.4 ± 3.0
m2s14	1428:30		
		5:30	15.4 ± 3.2
m2s15	1433		
		5	18.7 ± 2.1
m2s1	1438		
		5	16.5 ± 2.6
m2s1	1443		
		5	8.7 ± 3.6
m2s18	1448		

* Concentration are in ppt (parts per trillion)

tion is constant. In fact, the portion of the curve which represents the gradual build up of the tracer concentration is absent signifying a misjudgment in the timing of the sample collection. According to the USGS Atlas, at a discharge of 4170 cfs or 118 cms, it would take between 3 to 4 hours for the tracer to arrive at the sampling point. Since the injection is performed at the river bank, it would take a considerably longer time to arrive at Corvallis as explained previously. However, a glimpse at Figure xxv suggests otherwise. The explanation can be due to the tremendous change in hydraulics of the river which may have taken place since the Atlas was published (The Atlas was published in 1968). Factors such as bank irregularity, vegetation, channel alignment, river bed configuration, channel obstruction, converging or diverging streams drastically affect the flow in the river. The discharge rate used in estimating the travel time is for Harrisburg between there is no gauging station between Peoria and Corvallis and the discharge rate was adopted without taken into consideration of the discharge into the Willamette from the Long Tom and Mary's Rivers which may increase the discharge rate between Peoria and Corvallis and hence decrease the time needed to arrive at the sampling point.

If the plateau of the curve extends far backward, it would be immediately obvious that the time-concentration integration of the "tail" portion will be smaller than that obtained from the plateau. This means the amount of tracer remaining in solution as calculated by the above technique underestimates the tracer stability.

(8) Willamette River Experiment II:

This experiment involes the continuous injection of DyDTPA tracer of known concentration (145.62 g of Dy, dissolved in nitric acid and diluted to 17.1 liters with distilled water) at a constant rate (1 ml/sec) for a total period of 3 hours into the final effluent tank (Discharge about 4.5 to 5 million gallons per day)of the Albany Municipal Sewage Treatment Plant located about half a mile from the bank of the Willamette River.

The main objective of this experiment is to test again the conservative nature of the tracer and in addition try to find out if there is any unique trace element present in the effluent that may serve as a "natural" tracer. Results of such experiments are shown in Tables XXXIV and XXXV. A sketch of the sampling locations is shown in Figure XXVI.

Sampling of background began approximately an hour prior to the commencement of tracer injection and samples were taken above the sewage outfall, at and below the outfall to obtain a complete profile of the "blank" trace element distribution.

Four sampling stations were established (1) Approximately 150 yards from the outfall (Station B) (2) Station C is located right above Western Kraft and about a mile downstream from the outfall. (3) Station E is located about one mile downstream from Western Kraft outfall and there is a sharp bend at this location thus causing very turbulent flow. (4) Station D is about two miles down stream from the Western Kraft outfall and was in a region where the flow was rather sluggish and not turbulent. All these stations were chosen to represent

Table XXXV   Results of Tracer Field Experiment II (Willamette River)

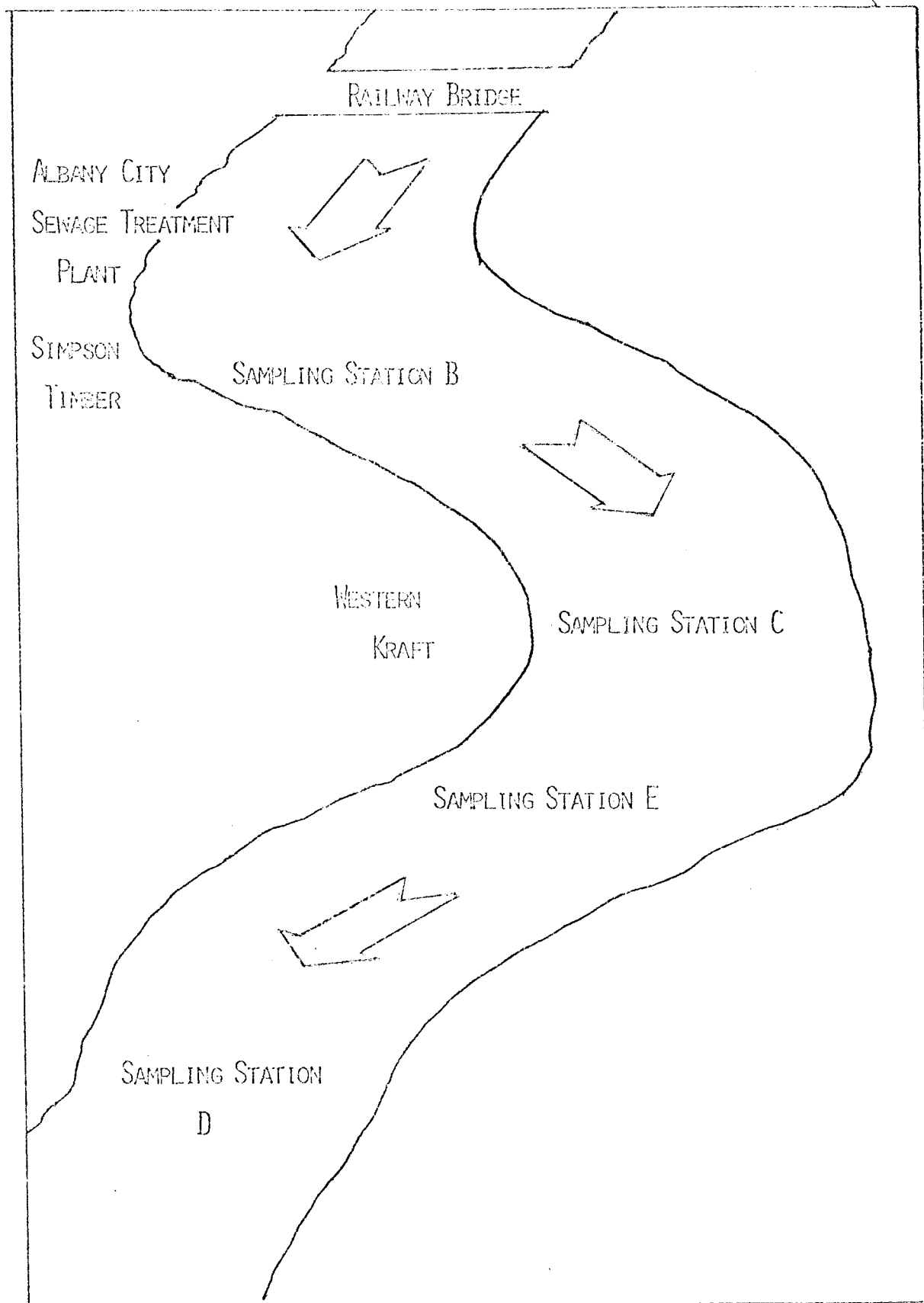| Sampling Station	Average Concentration	Distance from Injection Site	Time Sampling Started	% Original Tracer Remaining in Solution.
B	35.9 ± 1.1	150 yds	13:00	93.4%
C	32.5 ± 6.2	1 mile	13:30	84.5%
D	34.4 ± 1.1	2 mile	14:00	89.5%
E	34.3 ± 0.8	3 mile	14:30	89.2%

* Concentrations are in ppt (parts per trillion.

Amount of Dy used = 145.6219g   River Discharge Rate = 7820 Cfs (Cubic foot/sec)

Concentration of Dy/ml of Tracer = 8.515 mg/ml

Tracer Pump Injection Rate = 1.0 ml/sec

RAILWAY BRIDGE

ALBANY CITY
SEWAGE TREATMENT
PLANT

SIMPSON
TIMBER

SAMPLING STATION B

WESTERN
KRAFT

SAMPLING STATION C

SAMPLING STATION E

SAMPLING STATION
D

different parts of the river showing distinct hydraulic characteristics.

The actual sampling started about an hour after the tracer pump was turned on to allow ample time such that the tracer concentration will reach a steady state. After taking cross-sectional samples from Station B, the sampling station was then moved to the next point downstream as shown in Figure XXVI. The results of the experiments are shown in Tables XXXIV and XXXV and a glimpse at the results indicate that the shorter distance involved shows that the tracer is not well mixed resulting in a rather non-uniform tracer distribution at various sampling sections. In general the tracer concentrations tend to be higher along the bank of the river where injection of the tracer is carried out. The per cent of tracer remaining in solution can then be calculated using the hydrologic information and results in Table XXXIV and XXXV as follows:

The first assumption made in the calculation is that the weighted average of the tracer concentration at a particular sampling site represents the "True" concentration.

Weight of Dy = 145.6219 g

Total volume of Tracer Solution = 17.1 liters

Concentration of Tracer solution = 8.5 mg/ml

Tracer Injection Rate = 1 ml/sec

Quantity of Tracer injected = 8.5 mg/sec

River Discharge Rate = 7820 cfs

Concentration of Tracer in River = $8.5 \times 10^{-3}/7820 \times 28.32 \times 10^3$

$= 38.4$ pg/ml (ppt) assuming no loss etc.

Concentration of tracer at Station B = 35.9 ppt

Hence % remaining in solution = $35.8/38.4 \times 100\% = 93.4\%$ etc

Finally, ratios between concentrations of dissolved Zn and Br and the DyDTPA tracer at various sampling lovations were calculated and the results are shown in the following table:

Table XXXVI: Ratio of (Zn/Dy) and (Br/Dy) at various sampling locations:

Sampling Station	Dy*	Zn*	Br*	Zn/Dy	Br/Dy
B	35.9 ± 1.1	19 ± 5	10 ± 0.1	0.5 ± 0.1	0.3 ± 0.01
C	32.5 ± 6.2	432 ± 6	68 ± 0.1	13.3 ± 0.5	2.1 ± 0.4
D	34.4 ± 1.1	32 ± 6	10 ± 0.1	0.9 ± 0.2	0.3 ± 0.01
E	34.3 ± 0.8	21 ± 4	6 ± 0.1	0.6 ± 0.1	0.2 ± 0.01

* Concentrations in ppt

The large increase in the ratios at station C which is located about 150 yd from the sewage outfall indicate that the source of Zn and Br is not from the sewage plant. However, the ratios decrease at point D but more drastically for the Zn indicating that Zn is probably removed more rapidly than Br. The Br/Dy ratio behaves fairly constant at various points except at point C which can be due to the influx from some source between the sewage outfall and the Western Kraft Outfall.

CONCLUSION

The laboratory and field experiments performed in this work indicate that chelated tracers possess significantly greater solution stability than unchelated tracers. Nevertheless, loss of tracer is observed in all cases and that may be attributed to (1) exchange reactions with metal species present in the river water during storage prior to analysis, (2) sorption reaction with solid phases including sediment and sample container, and/or (3) biodegradation of the chelate.

By freezing the water samples, we found little or no evidence of metallic species being sorbed onto or leached out from sample container and contamination from chemical reagents/solvents is thus reduced to a minimum.

Results of field experiments performed demonstrate that stable activable tracers involving the use of REE with short-lived activation products which can be analyzed rapidly are cost competitive with radio-tracers and fluorescent dyes and should be given a place along with other tools of environmental scientists in studying pollutant dispersal and other phenomena in the fresh water system.

We also made a reasonably detailed survey of the elemental contents of sediments and water at some of the more highly populated and industrialized "hot" spot along the Willamette River. This "baseline" study is intended primarily to verify the expected low levels of Dy,In and REE in the Willamette River water and sediment and to obtain information on the trace element distribution in the river to see if any characteristic "trace element fingerprint" can be determined for the various

industrial or waste discharge along the river. Water quality is measured directly by the analysis of the water, however, the results are subjected to much variations depending on the season, recent rains, river level, local temperature etc. It is therefore presumptuous to say that the "grab" samples we analyzed are truly indicative of the elemental concentrations in the river water without taking into consideration the factors mentioned above. Nevertheless, the information can serve as new analytical data on Willamette River water quality and can help in assessing new pollutant release into the Willamette River. The background concentration of Dy, In and REE in the Willamette River are extremely low and this makes the use of anionic DTPA chelates of Dy,In and/or other REE very attractive water tracers. The Dy,In and REE concentration in sediment are much higher than that present in the river water. However, no metals were present at levels that might present an ecological threat.

The application of ion-exchange filter in our routine water sample preconcentration and fractionation, because of its low selectivity, has the advantage of recovering quantitatively most of the elements of interest. Also the anion exchange filter possesses several intrinsic qualities which make it uniquely suited to recovery of the DTPA metal chelates from fresh water. By recovering only anionic species, contamination from activable cations is drastically reduced and the bulk of the anion exchanger consists of elements (C, N, H and O) with low thermal neutron capture cross-section, it provides an irradiation matrix with low background. In addition, the use of cationic and anionic ion-exchanger can cause a simple fractionation of the dissolved species and provide a rough indication of the chemical speciation of the natural water.

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APPENDIX

Appendix I: Physical Characteristics of Ion-Exchange Membrane[a]

Ion-Exchange Acropor	SA-6404	SB-6407
Ion-Exchange Resin	Dowex 50W-X8	Dowex 1-X-8
Exchange Type	Strong Acid Cation Exchange	Strong Base Anion Exchange
Cross-Linkage & Ionic Form	8% DVB (H+)	8% DVB (Cl^-)
Ion-Resin Type	Sulphonic Acid cross-linked to polystyrene	· Quaternary Ammonium cross linked to polystyrene
Filter Size	47 mm	47 mm

mg per 47 mm filters		
Total	115	100
Fabric	64	64
Ion-Exchange Resin	32.5	27
Binder Resin	18.5	7
Ion-Exchange Resin Capacity meq/g [b]	5.1	3.2

a: Gelman Instrument Company, Ann Arbor, MI 48106.

b. Ion exchange capacity in milliequivalent per gram of ion exchange resin.

APPENDIX II

POLYVIALS CLEANING PROCEDURE

(1) WASH POLYVIALS WITH 2N NITRIC ACID FOR 10 MINUTES USING "ULTRASONIC" CLEANER*

(2) RINSE POLYVIALS WITH DISTILLED WATER FOR SEVERAL TIMES.

(3) WASH POLYVIALS WITH ABSOLUTE (95%) ETHANOL IN "ULTRASONIC" FOR ABOUT 10 MINUTES.

(4) DRAIN THE ALCOHOL AND WASH WITH ACETONE FOR 10 MINUTES.

(5) AIR DRY POLYVIALS ON A CLEAN SHEET IN "CLEAN" ROOM EQUIPPED WITH LAMINAR FLOW FILTER.

* Manufactured by Branson Cleaning Equipment Co., Shelton, Connecticut, U.S.A.

Appendix III: Physical Properties of Nuclepore Membrane [a]

Property	Specification
Tare Weight	0.5 to 1.0 $\pm$ 5% mg/cm^2 depending on pore size

Trace Element Content

Aluminum	50	ng/cm^2
Calcium	0.1	ng/cm^2
Chronium	12.0	ng/cm^2
Copper	3.0	ng/cm^2
Iron	90.0	ng/cm^2
Magnesium	6.0	ng/cm^2
Molydenum	7.0	ng/cm^2
Nickel	7.0	ng/cm^2
Potassium	17.0	ng/cm^2
Sodium	66.0	ng/cm^2
Tin	3.0	g/cm^2
Titanium	12.0	g/cm^2
Zince	6.0	g/cm^2

Property	Specification
Hydroscopicity	Non-hydroscopic. Only 0.24% weight gain after immersion in water for 24 hours.
Tensile Strength	3000 psi minimum
Pore Geometry and Distribution	Near perfectly cylindrical pores normal to surface with evenly random dispersion. Pore size deviation is +0 to -20%

a; Nuclepore Filtration Products for the Laboratory, Catalog Lab 30, Nuclepore Corporation, Pleasanton, CA 94566.

Appendix IV: Ion-Exchange Capacity of Ion Exchange Filters

	Cation Exchange	Anion Exchange
Filter Size	47 mm	47 mm
Effective Filter Area	35 mm	35 mm
Effective Wt. of Ion-Exchange Resin	24.2 mg	20.11 mg
Total Effective Ion-Exchange Capacity per Filter	0.123 meq*	0.064 meq*
Theoretical Quantity of Exchnaged Ions		
Fe^{3+}	2275 µg	
Ba^{2+}	8446 µg	
Ca^{2+}	2465 µg	
Na^{+}	2828 µg	
Br^{-}		5114 µg
Cl^{-}		2269 µg

* meq = milliequivalent.

Appendix V

Table Al   Elemental Abundances in Willamette River System

Sampling Site: Eugene   River Mile: 175

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.68 + 0.03%				
Fe	5.77 + 0.04%	2.46 + 0.02%	18 + 7	29 + 4	47 + 8
Ca	3.97 + 0.97%				
Na	2.21 + 0.01%	2340 + 3	121 + 1	---	121 + 1
K	0.84 + 0.05%	1380 + 90	42 + 2	---	42 + 2
Ti	0.75 + 0.01%				
Mn	954 + 2	400 + 49	1.0 + 0.3		1.0 + 0.3
Ba	390 + 39				
V	133 + 3				
Zn	---	1608 + 232	3 + 1		3 + 1
Cr	91 + 3	10 + 1	12 + 0.1	0.96 + 0.06	13 + 0.1
Ni	40 + 24	49 + 21			
Rb	33 + 11				
Ce	31 + 1				
La	15 + 1				
Co	23 + 0.3	11 + 2	0.0020 + 0.0005	0.086 + 0.008	0.038 + 0.008
Sc	20 + 0.1	8.8 + 0.3	0.0048 + 0.0002	0.0036 + 0.0003	0.0084 + 0.0004
As	6.2 + 0.3				
Sm	4.00 + 0.01	2.06 + 0.07	0.021 + 0.001		0.021 + 0.003
Th	2.9 + 0.1				
Hf	3.4 + 0.2				
Yb	2.4 + 0.1				
Br	2.0 + 0.1	32 + 2		3.20 + 0.01	3.20 + 0.01
Eu	1.1 + 0.1	0.45 + 0.002	0.0003 + 0.0001		0.0003 + 0.0001
Dy	1.5 + 0.1				
Cs	1.3 + 0.1	2.8 + 1.8	0.020 + 0.012		0.020 + 0.01
U	0.8 + 0.1				
Sb	0.9 + 0.1				
Ta	0.6 + 0.1				
Lu	0.3 + 0.1				
Tb	0.6 + 0.1				

Table A2   Elemental Abundances in Willamette River System

Sampling Site: Harrisburg 1   River Mile: 164

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.96 ± 0.04%				
Fe	7.15 ± 0.01%	2.21 ± 0.01%	20 ± 5	7 ± 1	27 ± 5
Ca	3.22 ± 0.16%				
Na	1.68 ± 0.01%	2150 ± 37	160 ± 1		160 ± 1
K	0.73 ± 0.01%	1321 ± 111	27 ± 2		27 ± 2
Ti	1.01 ± 0.01%				
Mn	1225 ± 3	423 ± 17	1.0 ± 0.3		1.0 ± 0.3
Ba	484 ± 13				
V	178 ± 3				
Zn		2231 ± 1550	15 ± 2		15 ± 2
Cr	133 ± 1	36 ± 10	17.0 ± 0.1	0.60 ± 0.03	17.6 ± 0.1
Ni	53 ± 23	<30			
Rb	32 ± 2				
Ce	37 ± 0.2				
La	20 ± 1				
Co	31 ± 0.1	11 ± 2	0.45 ± 0.002	0.052 ± 0.006	0.502 ± 0.006
Sc	24 ± 0.1	7.8 ± 0.3	0.0022 ± 0.0001	0.0056 ± 0.0001	0.0078 ± 0.0001
As	5.6 ± 0.2				
Sm	4.9 ± 0.01	2.69 ± 0.05	0.028 ± 0.001		0.028 ± 0.001
Th	3.41 ± 0.01				
Hf	4.53 ± 0.01				
Yb	2.9 ± 0.1				
Br	8.4 ± 0.2	44.4 ± 3.8		4.30 ± 0.04	4.30 ± 0.04
Eu	1.3 ± 0.1	0.28 ± 0.01	0.0003 ± 0.0001		0.0003 ± 0.0001
Dy	1.5 ± 0.1				
Cs	2.1 ± 0.1	2.8 ± 0.2	0.037 ± 0.014		0.037 ± 0.014
U	1.2 ± 0.1				
Sb	0.74 ± 0.03				
Ta	0.67 ± 0.06				
Lu	0.35 ± 0.01				
Tb	0.57 ± 0.12				

Table A3 Elemental Abundances in Willamette River System

Sampling Site: Harrisburg 2   River Mile: 160

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.25 ± 0.04%				
Fe	6.22 ± 0.01%	2.55 ± 0.54	65 ± 8	4 ± 1	69 ± 8
Ca	3.57 ± 0.14%				
Na	2.18 ± 0.01%	5814 ± 185	134.0 ± 0.3		134.0 ± 0.3
K	0.89 ± 0.04%	3518 ± 296	36 ± 2		36 ± 2
Ti	0.74 ± 0.05%				
Mn	944 ± 2	682 ± 85	1.2 ± 0.3		
Ba	483 ± 9				
V	157 ± 2				
Zn		1356 ± 41	13 ± 2		13 ± 2
Cr	112.0 ± 0.5	243 ± 4	35 ± 0.01	0.36 ± 0.03	35.36 ± 0.03
Ni	52 ± 15	255 ± 107			
Rb	33 ± 1				
Ce	30.0 ± 0.1				
La	16.4 ± 0.9				
Co	26.9 ± 0.1	38 ± 10	0.27 ± 0.01	0.052 ± 0.006	0.32 ± 0.01
Sc	22.0 ± 0.1	13 ± 1	0.025 ± 0.001	0.007 ± 0.001	0.032 ± 0.001
As	6.5 ± 0.2				
Sm	3.99 ± 0.01	2.85 ± 1.01	0.021 ± 0.005		0.021 ± 0.005
Th	2.80 ± 0.03				
Hf	4.16 ± 0.06				
Yb	2.58 ± 0.01				
Br	1.84 ± 0.14	18 ± 1		4.10 ± 0.04	4.10 ± 0.04
Eu	1.15 ± 0.06	0.054 ± 0.012	0.0014 ± 0.0003		
Dy	1.20 ± 0.05				
Cs	1.83 ± 0.10		0.059 ± 0.012		0.059 ± 0.012
U	1.04 ± 0.09				
Sb	0.73 ± 0.01				
Ta	0.53 ± 0.01				
Lu	0.29 ± 0.01				
Tb	0.51 ± 0.11				

Table A4   Elemental Abundances in Willamette River System

Sampling Site: Peoria 1   River Mile: 144.9

Element	Sediment (μg/g)	Suspended Particulates (μg/g)	Dissolved Cations (ηg/ml)	Dissolved Anions (ηg/ml)	Total Dissolved ions (ηg/ml)
Al	9.51 + 0.05%				
Fe	5.28 + 0.02%	3.19 + 0.16%	15 + 5	7 + 2	22 + 5
Ca	2.68 + 0.15%	2200 + 12			
Na	1.71 + 0.01%	2219 + 12	210.0 + 0.5		210.0 + 0.5
K	0.91 + 0.09%	2456 + 84	30 + 2		30 + 2
Ti	0.74 + 0.04%				
Mn	758 + 1	589 + 73			
Ba	540 + 15				
V	136 + 4				
Zn		1852 + 661	12 + 2		12 + 2
Cr	93.6 + 1.9	27 + 6	16.00 + 0.08	0.20 + 0.03	16.20 + 0.08
Ni	57 + 20	<55			
Rb	32 + 1				
Ce	34.8 + 0.3				
La	19.7 + 0.1				
Co	23.6 + 0.1	14 + 1	0.038 + 0.02	0.018 + 0.005	0.056 + 0.02
Sc	19.4 + 0.1	12.0 + 0.2	0.004 + 0.0001	0.00046 + 0.00012	0.004 + 0.0001
As	4.7 + 0.3				
Sm	4.86 + 0.01	2.70 + 0.04	0.024 + 0.001		0.024 + 0.001
Th	3.03 + 0.08				
Hf	4.19 + 0.07				
Yb	2.60 + 0.04				
Br	3.56 + 0.20	26 + 2	2.08 + 0.14	2.08 ++0.14	2.08 + 0.14
Eu	1.21 + 0.04	0.06 + 0.02			
Dy	1.34 + 0.03				
Cs	1.75 + 0.07		0.053 + 0.012		0.053 + 0.012
U	1.06 + 0.06				
Sb	0.67 + 0.02				
Ta	0.53 + 0.02				
Lu	0.35 + 0.01				
Tb	0.78 + 0.12				

Table A5. Elemental Abundances in Willamette River System

Sampling Site: Peoria 2   River Mile: 140.9

Element	Sediment (μg/g)	Suspended Particulates (μg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	9.22 ± 0.05%				
Fe	5.34 ± 0.01%	3.76 ± 0.12%	22 ± 5	7 ± 1	29 ± 5
Ca	3.41 ± 0.17%				
Na	2.18 ± 0.01%	7143 ± 30	90.0 ± 0.3		90.0 ± 0.3
K	0.94 ± 0.10%	3950 ± 115	18 ± 2		18 ± 2
Ti	0.71 ± 0.04%				
Mn	891 ± 2	546 ± 69	0.42 ± 0.03		0.42 ± 0.03
Ba	508 ± 15				
V	153 ± 3				
Zn		689 ± 89	16 ± 2		16 ± 2
Cr	100.8 ± 2.1	77 ± 6	32.0 ± 0.1	0.17 ± 0.033	32.2 ± 0.1
Ni	58 ± 30	<55			
Rb	35 ± 1				
Ce	30.5 ± 0.2				
La	17.8 ± 0.1				
Co	23.0 ± 0.1	17.8 ± 0.7	0.0036 ± 0.0016	0.031 ± 0.005	0.035 ± 0.005
Sc	19.2 ± 0.1	13.9 ± 0.2	0.0041 ± 0.0002	0.00046± 0.00001	0.00456 ± 0.0002
As	5.5 ± 0.2				
Sm	4.2 ± 0.01				
Th	2.76 ± 0.09				
Hf	4.23 ± 0.07				
Yb	2.39 ± 0.03				
Br	2.15 ± 0.12	26 ± 2		4.6 ± 0.03	4.6 ± 0.03
Eu	1.22 ± 0.03	0.58 ± 0.01			
Dy	1.26 ± 0.04				
Cs	1.76 ± 0.07				
U	1.04 ± 0.01				
Sb	0.73 ± 0.02				
Ta	0.53 ± 0.02				
Lu	0.31 ± 0.11				
Tb	0.70 ± 0.11				

Table A6 Elemental Abundances in Willamette River System

Element	Sediment (μg/g)	Susp.Particulates Surface (μg/g)	Susp.Particulates 0.6xdepth (μg/g)	Dissolved Cations Surface (ng/ml)	Dissolved Cations 0.6xdepth (ng/ml)	Dissolved Anions Surface (ng/ml)	Dissolved Anions 0.6xdepth (ng/ml)	Total Dissolved Surface (ng/ml)	Total Dissolved 0.6xdepth (ng/ml)
		Sampling Site: Fischer Island		River Mile: 134					
Al	8.82±0.03%								
Fe	5.81±0.01%	5.09±0.50		38±8	13±6	21±5	20±6	59±10	33±6
Ca	2.66±±.12%							160±1	156±1
Na	1.82±0.02%	8025±10	1869±30	160±1	156±1			35±7	46±6
K	0.74±0.01%	5446±1900	4667±1070	35±7	46±6				
Ti	0.75±0.04%								
Mn	948±2	1848±7	1199±2	1.7±0.1	1.2±0.1			1.7±0.1	1.2±0.1
Ba	468±6								
V	187±6								
Zn		1945±452	598±202	46±5				46±5	
Cr	127.2±0.4	150±33		29±1	26±1	1.50±0.1	0.53±0.04	30.5±1.0	26.5±1.0
Ni	59±29								
Rb	33±1								
Ce	33.3±0.2								
La	20.0±0.1	20.4±3.9	7.2±1.6						
Co	26.7±0.1	15.6±4.4	14.7±2.8	36±7*	11±4*	12±4*	3.6±0.3*	48±8*	14.6±4.0*
Sc	20.8±0.1	17.4±0.7	6.7±0.4	15±1*	3.4±0.7*	9.4±2.0*		24.4±2.2*	3.4±0.7*
As	5.3±0.1	9.6±3.7	18.4±1.7						
Sm	4.66±0.01	4.78±0.30	2.69±0.76	30±4*	30±4*	29±1*		59±4*	30±4*
Th	2.99±0.02								
Hf	4.26±0.05	6.29±4.22	3.44±1.96						
Yb	2.78±0.03								
Br	7.62±0.21	180.9±9.1	39.0±3.7			7.7±0.1	7.7±0.1	7.7±0.1	7.7±0.1
Eu	1.24±0.03	1.10±0.10	0.44±0.05						
Dy	1.46±0.04								
Cs	1.80±0.08								
U	1.54±0.13								
Sb	0.62±0.01			4.7±1.5		14±7		18.7±7	
Ta	0.62±0.01								
Lu	0.25±±.0.02								
Tb	0.65±0.10								

* concentration are in parts per trillion.

Table A7 Elemental Abundances in Willamette River System

		Sampling Site: Albany 1	River Mile: 126.2						
		Susp.Particulates		Dissolved Cations		Dissolved Anions		Total Dissolved	
	Sediment	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth
Element	(μg/g)	(μg/g)		(ng/ml)		(ng/ml)		(ng/ml)	
Al	8.51+0.04%								
Fe	5.21+0.02%								
Ca	3.49+0.83%								
Na	2.02+0.03%	3990+20	5520+30	110+1	103+0.2			110+1	103+0.2
K	0.92+0.04%	3960+294	1722+134	40+6	38+3			40+6	38+3
Ti	0.65+0.02%								
Mn	812+2	1660+29	552+30	0.37+0.09	0.70+0.01			0.37+0.09	0.7+0.01
Ba	544+33								
V	142+3								
Zn		1416+283	644+107	10.4+0.3				10.4+0.3	
Cr	85.2+1.4	86.7+28.3	72.5+11.7			1.39+0.13	0.32+0.06	1.39+0.13	0.32+0.06
Ni	56+10								
Rb	42+6								
Ce	29.1+0.4								
La	16.9+0.1		7.33+1.68						
Co	22.8+0.1	20.2 +2.8	8.5+0.2	3+2*	1.+0.1*	28 +7.0*	3+1*	31+7*	4+1*
Sc	18.3+0.1	9.4+0.3	7.4+0.3	0.44+0.01*	1.99+0.5*	2.4+0.3*	7.0+0.7	2.8+0.3*	9.0+0.7*
As	5.0+0.3	9.3+2.1	4.4+1.5						
Sm	3.99+0.01	1.69+0.92	1.14+0.11						
Th	3.06+0.07								
Hf	3.33+0.11		1.96+0.67						
Yb	2.42+0.10								
Br	1.88+0.34	14.5+4.6	47.9+3.0			3.40+0.04	4.00+0.05	3.40+0.04	4.0+0.05
Eu	1.05+0.07	0.39+0.12	0.39+0.02	0.44+0.01				0.44+0.01	
Dy	1.17 +0.06								
Cs	1.49+0.12		2.27+1.12						
U	1.15+0.10								
Sb	0.67+0.11	2.37+1.7	1.30+0.6			0.11+0.01	9.5+5*	0.11+0.01	9.5+5*
Ta	0.67+0.04								
Lu	0.32+0.01								
Tb	0.43+0.14								

Table A8   Elemental Abundances in Willamette River System

	Sampling Site: Albany 2		River Mile: 125.2					
		Susp.Particulates	Dissolved Cations		Dissolved Anions		Total Dissolved	
	Sediment	Surface 0.6xdepth	Surface 0.6xdepth		Surface 0.6xdepth		Surface 0.6xdepth	
Element	(µg/g)	(µg/g)	(ηg/ml)		(ηg/ml)		(ηg/ml)	
Al	9.13±0.03%							
Fe	6.64±0.03%	0.82±0.11 0.96±0.10						
Ca	3.43±0.80%							
Na	2.02±0.01%	1249±18 1108±10	125±0.4	32±0.1			125±0.4	32.0±0.1
K	0.90±0.17%	1080±432 1228±22	33±6	14±4			33±6	14±4
Ti	0.74±0.09							
Mn	1040±3	129±3 165±1	1.8±0.1	2.3±0.1	1.25±0.02 0.42±0.01		3.05±0.10	2.72±0.10
Ba	483±8							
V	198±4							
Zn					0.52±0.05 0.013±0.002		0.52±0.05	0.013±0.002
Cr	96±1.6	23.9±4.5						
Ni	59±31							
Rb	42±7							
Ce	30.5±0.5							
La	17.0±0.1	2.52±0.9 4.56±1.61						
Co	28.8±0.2	2.55±1.47 4.67±1.02	3±2*	11±8*	13±5* 31±8*		16±5*	42±8*
Sc	21.7±0.1	2.4±0.1 2.2±0.1	1.5±0.5*	1.8±1.0*	23±1* 8±1*		24.5±1*	9.8±1.0*
As	5.0±0.3	3.2±0.9 10.4±0.8			135±10* 174±20*		135±10*	174±20*
Sm	4.14±0.01	0.75 ±0.05 0.73±0.02						
Th	2.99±0.08							
Hf	3.50±0.13							
Yb	2.71±0.11							
Br	2.33±0.49	12.8±1.6 12.4±1.4			3.00±0.04 4.80±0.04		3.00±0.04	4.00±0.05
Eu	1.24±0.03	0.14±0.02 0.18±0.03	2.2±0.3*	1.1±0.3*			2.2 ± 0.3*	1.1±0.3*
Dy	1.31±0.06							
Cs	1.53±0.15							
U	1.09±0.12							
Sb	0.71±0.04	1.90±0.62			0.007±0.001		0.007±0.001	
Ta	0.90±0.05							
Lu	0.33±0.01							
Tb	0.60±0.16							

* Concentrations in parts per trillion.

Table A9   Elemental Abundances in Willamette River System

Sampling Site: Albany 3   River Mile: 122.70

Element	Sediment (μg/g)	Susp.Particulates Surface (μg/g)	Susp.Particulates 0.6xdepth (μg/g)	Dissolved Cations Surface (ng/ml)	Dissolved Cations 0.6xdepth (ng/ml)	Dissolved Anions Surface (ng/ml)	Dissolved Anions 0.6xdepth (ng/ml)	Total Dissolved Surface (ng/ml)	Total Dissolved 0.6xdepth (ng/ml)
Al	9.08±0.04%								
Fe	5.82±0.03%	5.69±0.38	10.46±0.48		40±7	16±5	40±6	16±5	80±9
Ca	2.53±0.88%								
Na	1.67±0.03%	3545±7	8340±83	40±1	123±1			40±1	123±1
K	0.68±0.05%	2330±312	4465±175	25±7	15±6			25±7	15±6
Ti	0.74±0.02%								
Mn	739±5	1166±23	3070±37	13.4±0.1	15.0±0.2	6.1±0.1	11.3±0.01	19.5±0.2	26.3±0.2
Ba	439±41								
V	180±3								
Zn		3750±350	3710±358	6±2	19±5			6±2	19±5
Cr	116.7±1.8	124.1±39.7	239.0±44.6		10±0.3	0.08±0.01	1.06±0.08	0.08±0.01	11. ±0.3
Ni	61±26								
Rb	39±12								
Ce	38.4±0.6								
La	20.7±0.1	7.9±2.8	2222±4.2						
Co	26.1±0.2	13.4±3.9	36.5±4.7	14.0±1.0*	156±10*	109±10*	75±9*	123±10*	231±11*
Sc	21.5±0.1	7.8±0.4	14.3±0.5	1.7±0.5*	2.3±0.4*	3.4±0.4*	4.0±0.5*	5.1±0.6*	6.3±0.6*
As	5.7±0.3	20.2±5.8	32.1±3.7			6.4±17*	98 ±15*	64 ±17*	98±1 *
Sm	5.06±0.01	3.2±0.2	4.4±0.2	0.026±0.002	0.028±0.003			0.026±0.022	0.028±0.003
Th	3.22±0.09								
Hf	3.32±0.12								
Yb	2.79±0.12								
Br	1.29±0.50	104±27	130±69			16.0±0.1	10.0±0.1	16.0±0.1	10.0±0.1
Eu	1.36±0.03	0.45±0.05	1.19±0.15	1.0±0.1*	0.5±0.3*			1.0±0.1*	0.5±0.3*
Dy	1.56±0.06								
Cs	1.74±0.14								
U	1.266±0.12								
Sb	0.66±0.11								
Ta	0.63±0.05								
Lu	0.37±0.01								
Tb	0.80±0.52								

* Concentrations in parts per trillion.

Table A10   Elemental Abundances in Willamette River System

Sampling Site: Albany 4   River Mile: 119.45

Element	Sediment (µg/g)	Susp.Particulates (µg/g)		Dissolved Cations (ng/ml)		Dissolved Anions (ng/ml)		Total Dissolved (ng/ml)	
		Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth
Al	8.83+0.01%	0.82+0.11							
Fe	5.74+0.01%	0.82+0.11	0.96+0.11	16+6	15+8	13+9	17+5	29+12	32+9
Ca	2.85+0.10%								
Na	2.25+0.03%	1151+8	1108+10	122+1	138+1			122+1	138+1
K	1.21+0.07%	1080+432	1228+22	39+6	48+6			39+6	48+6
Ti	1.12+0.06%	1228+22							
Mn	948+2	141+12	165+8	3.2+0.1	32.8+0.1		0.03+0.01	3.2+0.1	32.8+0.1
Ba	562+12								
V	119+3								
Zn		503+137	502+135	21+4	123+22			21+4	123+22
Cr	83.3+0.6			18.0+0.1	48.0+2.0	0.64+0.1	7.4+0.3	18.6+0.1	55.4+2.0
Ni	58+22								
Rb	49+2								
Ce	36.7+0.2								
La	21.3+0.1	2.5+0.9	4.6+1.6	48+8*	9.0+1.0*			48.0+8.0*	9.0+1.0*
Co	21.8+0.1	4.7+1.0		55+8*	44+6*	64+8*	22+5*	119+8*	66+8*
Sc	18.4+0.1	2.4+0.1	2.2+0.1	4.0+0.9*	4.7+1.0*	43+1*	4.6+0.8*	47+1*	9.3+1*
As	6.6 +0.5	3.2+0.9	10.4+0.8			0.23+0.01	.31+0.01	0.23+0.01	0.31+0.01
Sm	4.76+0.01	0.75+0.28	0.73+0.02	32+6*	32+7*			32+6*	31+7*
Th	3.98+0.03								
Hf	5.80+0.10								
Yb	2.96+0.04								
Br	1.49+0.19	12.8+1.6	12.4+1.4			4.40+0.01	5.40+0.01	4.40+0.01	5.40+0.01
Eu	1.33+0.03	0.14+0.03	0.18+0.03	3.5+0.3*				3.50+0.3*	
Dy	1.62+0.06								
Cs	1.81+0.08								
U	1.87+0.08								
Sb	0.61+0.02								
Ta	0.61+0.05								
Lu	0.40+0.01								
Tb	0.48+0.01								

* Concentration in parts per trillion (ppt)

Table A11 Elemental Abundances in Willamette River System

Sampling Site: Western Kraft   River Mile: 118.20

Element	Sediment (µg/g)	Susp.Particulates Surface (µg/g)	Susp.Particulates 0.6xdepth (µg/g)	Dissolved Cations Surface (ng/ml)	Dissolved Cations 0.6xdepth (ng/ml)	Dissolved Anions Surface (ng/ml)	Dissolved Anions 0.6xdepth (ng/ml)	Total Dissolved Surface (ng/ml)	Total Dissolved 0.6xdepth (ng/ml)
Al	8.64±0.04%								
Fe	5.44±0.01%	6.26±0.41		35±8		25±5	31±4	70±9	31±4
Ca	2.85±0.08%								
Na	2.17±0.08%	7732±72		300.0±0.2	296±0.2			300.0±0.2	296±0.2
K	0.91±0.12%	6412±1770		110±9	15±2			110±9	15±1.5
Ti	0.78±0.02%								
Mn	817±2	2099±9		2.96±0.10	2.73±0.02	1.02±0.01	1.05±0.01	3.98±0.10	3.78±0.02
Ba	522±4								
V	166±4								
Zn		662±202		32±6	13±1			32 ±6	13± 1
Cr	94.7±0.6	143.2±28.2		12.4±2.3		0.54±0.16	0.18±0.01	12.9±2.3	0.08±0.01
Ni	60±20								
Rb	40±1								
Ce	32.5±0.5								
La	18.9±0.1	28.0±3.5							
Co	24.3±0.3	24.1±4.4		1.6±0.4	1.7±0.4	38±7	3.3±0.6	39.6±7	5.0±0.7
Sc	18.8±0.1			11.0±0.7*	1.8±0.6*	15.0±1.5*	10.0±1.0*	26.0±1.7*	11.8±1.2*
As	4.9±0.4	17.1±3.2				0.44±0.02	0.27±0.01	0.44±0.02	0.27±0.01
Sm	4.25±0.01	6.26±0.2		0.05±0.01	0.02±0.01			0.05±0.01	0.02±0.01
Th	3.24±0.08								
Hf	4.89±0.07								
Yb	2.48±0.03								
Br	3.85±0.22	124.6±7.4				10.0±0.1	4.6±0.1	10.0±0.1	4.6±0.1
Eu	1.17±0.06	1.49±0.01		0.0014±0.0003				0.0004±0.0003	
Dy	1.37±0.01								
Cs	1.74±0.10								
U	1.43±0.06								
Sb	0.54±0.01	5.8±2.8							
Ta	0.60±0.05								
Lu	0.38±0.01								
Tb	0.58±0.01								

* Concentrations in ppt (parts per trillion)

Table A12   Elemental Abundances in Willamette River System

		Sampling Site: Albany 5		River Mile: 118.45					
		Susp.Particulates		Dissolved Cations		Dissolved Anions		Total Dissolved	
	Sediment	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth
Element	(µg/g)	(µg/g)		(ng/ml)		(ng/ml)		(ng/ml)	
Al	9.44+0.03%								
Fe	5.75±0.01%	4.61±0.23%		20±1	10±1	30±10	10±6	50±10	20±7
Ca	2.84±0.64%	9009±66							
Na	2.17±0.01%	6155±318		130.0±0.4	186.0±1.1			130.0±0.4	186.0±1.1
K	0.87±0.34%			57±6	71±8			57±6	71±8
Ti	0.92±0.03%								
Mn	764±5	1455±26		5.70±0.08	7.80±0.08	6.80±0.01		12.50±0.08	7.80±0.08
Ba	512±45								
V	185±3								
Zn		2078±328		420±6	35±6			420±6	35±6
Cr	82.9±1.2	110.8±24.1		100±12	113±12	0.18±0.01	1.11±0.08	100.2±12	114.1±12
Ni	59 +18								
Rb	39 +7								
Ce	34.9±0.5								
La	19.4±0.1	19.8±2.9							
Co	20.3±0.2	17.5±2.3		79±10*	84±10*	17±1*	4 ±1	96±10*	88±10*
Sc	19.6±0.1	14.0±0.3		3.1±1.0*	5.6±3.0*	6.8±0.6*	4.9±1.1*	9.9±1.2*	10.5±3.2*
As	5.6±0.3	8.9±2.4				0.11±0.01	0.07±0.03	0.07±0.01	0.07±0.03
Sm	4.76±0.01	4.48±0.88		27±5*	27±4*			27 ±4*	27±5*
Th	3.26±0.08								
Hf	3.48±0.12								
Yb	2.81±0.12								
Br	3.49±0.61	143 +53				68±0.1	41±0.2	68±0.1	41±0.2
Eu	1.34±0.03	1.13±0.12		1.00±0.4				1.00±0.40	
Dy	1.58±0.07								
Cs	1.53±0.14								
U	1.11±0.11								
Sb	0.69±0.04	8.03±2.3							
Ta	0.63±0.04								
Lu	0.37±0.01								
Tb	0.64±0.16								

* Concentrations in parts per trillion.

Table A13 Elemental Abundances in Willamette River System

Sampling Site: Independence 1   River Mile: 99.0

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	9.28 + 0.05%				
Fe	5.21 + 0.02%	1.89 + 0.03%		8.74 + 1.00	8.74 + 1.00
Ca	3.12 + 0.10%				
Na	2.03 + 0.01%	733 + 5	171 + 1		171 + 1
K	1.21 + 0.11%	605 + 75	36 + 6		36 + 6
Ti	0.66 + 0.04%				
Mn	695 + 2	238 + 2	1.46+0.03	0.033 + 0.0003	1.49 + 0.03
Ba	557 + 16				
V	123 + 3				
Zn		53.5 + 7.8			53.5 + 7.8
Cr	68.3 + 1.6	6.47 + 0.48	66.10 + 5.10		66.10 + 5.10
Ni	35 + 10				
Rb	34 + 1				
Ce	33.1 + 0.3				
La	19.2 + 0.1	2.28 + 0.20	0.016 + 0.001		0.016 + 0.001
Co	20.3 + 0.1	3.06 + 0.16		0.48 + 0.03	0.48 + 0.03
Sc	18.6 + 0.1	1.62 + 0.21		0.0034 + 0.0019	0.0034 + 0.0019
As	5.9 + 0.2	1.06 + 0.2		0.082 + 0.006	0.082 + 0.006
Sm	4.55 + 0.01	0.44 + 0.01	0.026 + 0.001		0.026 + 0.001
Th	3.78 + 0.09				
Hf	4.49 + 0.07				
Yb	2.59 + 0.04				
Br	2.15 + 0.16	3.28 + 0.20		4.1 + 0.2	4.1 + 0.2
Eu	1.13 + 0.05	0.13 + 0.03			
Dy	1.33 + 0.04				
Cs	1.97 + 0.06				
U	1.30 + 0.03				
Sb	0.71 + 0.03	0.19 + 0.13		0.009 + 0.003	0.009 + 0.003
Ta	0.59 + 0.02				
Lu	0.36 + 0.01				
Tb	0.73 + 0.06				

Table A14 Elemental Abundances in Willamette River System

Sampling Site: Independence 2   River Mile: 97.50

Element	Sediment (μg/g)	Suspended Particulates (μg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.71 + 0.11				
Fe	6,23 + 0.06	2.87 + 0.01		6.74 + 1.59	6.74 + 1.59
Ca	3.02 + 0.16				
Na	1.65 + 0.01	0.65 + 0.03	127 + 11		127++ 11
K	0.77 + 0.29	0.36 + 0.01	40 + 5		40 + 5
Ti	0.76 + 0.05				
Mn	877 + 2	1514 + 9	9.8 + 0.4	0.033 + 0.0003	9.8 + 0.0
Ba	544 + 11				
V	149 + 4				
Zn					
Cr	112 + 1	6.50 + 2.00	66 + 5		66 + 5
Ni	35 + 11				
Rb	41 + 2				
Ce	45.8 + 0.2				
La	24.9 + 1.3	13.34 + 0.50	0.014 + 0.001		0.014 + 0.001
Co	28.2 + 0.1	13.21 + 1.01		0.012 + 0.002	0.012 + 0.002
Sc	22.4 + 0.1	16.70 + 4.00		0.0044 + 0.0002	0.0044 + 0.0002
As	6.3 + 0.2	6.97 + 1.00		0.098 + 0.007	0.098 + 0.007
Sm	5.64 + 0.01	3.24 + 0.05	0.032 + 0.005		0.032 + 0.005
Th	4.29 + 0.04				
Hf	5.49 + 0.08				
Yb	3.29 + 0.06				
Br	7.09 + 0.18	18.94 + 0.78		4.9 + 0.04	4.9 + 0.04
Eu	1.29 + 0.05	0.77 + 0.10	0.0009 + 0.0004		0.0009 + 0.0004
Dy	1.64 + 0.06	3.35 + 0.56			
Cs	4.14 + 0.15				
U	2.60 + 0.11				
Sb	0.82 + 0.02				
Ta	0.71 + 0.03				
Lu	0.42 + 0.01				
Tb	0.66 + 0.07				

Table A15a Elemental Abundances in Willamette River System

Sampling Site: Independence 3   River Mile: 99.0

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	9.28 + 0.05%				
Fe	5.21 + 0.02%	1.89 + 0.03%		8.74 + 1.00	8.74 + 1.00
Ca	3.12 + 0.10%				
Na	2.03 + 0.01%	733 + 5	171 + 1		171 + 1
K	1.21 + 0.11%	605 + 75	36 + 6		36 + 6
Ti	0.66 + 0.04%				
Mn	695 + 2	238 + 2	1.46+0.03	0.033 + 0.0003	1.49 + 0.03
Ba	557 + 16				
V	123 + 3				
Zn		53.5 + 7.8			53.5 + 7.8
Cr	68.3 + 1.6	6.47 + 0.48	66.10 + 5.10		66.10 + 5.10
Ni	35 + 10				
Rb	34 + 1				
Ce	33.1 + 0.3				
La	19.2 + 0.1	2.28 + 0.20	0.016 + 0.001		0.016 + 0.001
Co	20.3 + 0.1	3.06 + 0.16		0.48 + 0.03	0.48 + 0.03
Sc	18.6 + 0.1	1.62 + 0.21		0.0034 + 0.0019	0.0034 + 0.0019
As	5.9 + 0.2	1.06 + 0.2		0.082 + 0.006	0.082 + 0.006
Sm	4.55 + 0.01	0.44 + 0.01	0.026 + 0.001		0.026 + 0.001
Th	3.78 + 0.09				
Hf	4.49 + 0.07				
Yb	2.59 + 0.04				
Br	2.15 + 0.16	3.28 + 0.20		4.1 + 0.2	4.1 + 0.2
Eu	1.13 + 0.05	0.13 + 0.03			
Dy	1.33 + 0.04				
Cs	1.97 + 0.06				
U	1.30 + 0.03				
Sb	0.71 + 0.03	0.19 + 0.13		0.009 + 0.003	0.009 + 0.003
Ta	0.59 + 0.02				
Lu	0.36 + 0.01				
Tb	0.73 + 0.06				

Table A15   Elemental Abundances in Willamette River System

Sampling Site: Salem 1 — River Mile: 86.9

Element	Sediment (µg/g)	Susp.Particulates Surface (µg/g)	Susp.Particulates 0.6xdepth (µg/g)	Dissolved Cations Surface (ng/ml)	Dissolved Cations 0.6xdepth (ng/ml)	Dissolved Anions Surface (ng/ml)	Dissolved Anions 0.6xdepth (ng/ml)	Total Dissolved Surface (ng/ml)	Total Dissolved 0.6xdepth (ng/ml)
Al	9.39±0.11%								
Fe	5.90±0.01%	0.56±0.12%				5.54±0.76	15.8±1.3	5.54±0.76	15.8±1.3
Ca	2.79±0.24%								
Na	1.86±0.01%	1040±6	560±4	223±1	115±1			223±1	115±1
K	0.77±0.05%	742±85	429±67	55±7	32±5			55±7	32±5
Ti	0.84±0.05%								
Mn	1045±2	227±2	163±2	1.10±0.03	0.46±0.01		0.35±0.01	1.10±0.03	0.81±0.01
Ba	401±8								
V	163±4								
Zn		61±6	45±6			0.59±0.12	1.48±0.15	0.59±0.12	1.48±0.15
Cr	82.0±0.7	10.9±0.55	12.8±4.2		0.08±0.02	62±2*	276±60*	62±2*	356±63*
Ni	42 ±13		4.53±1.48						
Rb	35±2								
Ce	29.7±0.8	4.48±0.37	4.53±1.48						
La	20.8±0.8	2.20±0.20	1.86±0.08						
Co	26.6±0.3	2.22±0.10	1.56±0.13			54±3*	53±3*	54±3*	53±3*
Sc	20.1±0.1	1.89±0.02	1.17±0.02			4.1±0.2*	4.8 ±0.2*	4.1±0.2*	4.8±0.2*
As	6.3±0.2	1.24±0.02	0.67±0.14			128±20*	153±4*	128±20	153±4*
Sm	4.55±0.06	0.45±0.09	0.34±0.01	28±1*	21±1*			28±1*	21±1*
Th	3.48±0.04	0.46±0.06	0.29±0.05						
Hf	4.93±0.10	0.87±0.27	0.30±0.10						
Yb	2.59±0.03	0.42±0.09	0.23±0.08						
Br	6.52±0.14	2.97±0.24	5.37±0.22			4.15±0.05	4.25±0.05	4.15±0.05	4.25±0.05
Eu	1.30±0.06	0.12±0.03							
Dy	1.43±0.05								
Cs	1.74±0.12								
U	1.68±0.04								
Sb	0.65±0.02	0.26±0.16	0.26±0.13			4.6±0.1*	6.4±1.1*	4.6±0.1*	6.4±1.1*
Ta	0.65±0.08								
Lu	0.34±0.06								
Tb	0.73±0.02								

* Concentrations in parts per trillion.

Table Al6 Elemental Abundances in Willamette River System

Sampling Site: Salem 2   River Mile: 84.9

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ŋg/ml)	Dissolved Anions (ŋg/ml)	Total Dissolved ions (ŋg/ml)
Al z	9.01 + 0.07%				
Fe	5.80 + 0.01%	3.67 + 0.01%		48 + 3	48 + 3
Ca	2.86 + 0.14%				
Na	1.94 + 0.01%	4500 + 30	25 + 1		25 + 1
K	0.86 + 0.06%	2974 + 36	19 + 2		19 + 2
Ti	0.69 + 0.01%				
Mn	666 + 2	704 + 6	1 + 0.01	70 + 0.05	71 + 0.05
Ba	390 + 10				
V	160 + 4				
Zn		631 + 41		3.41 + 0.23	3.41 + 0.23
Cr	83.8 + 0.7	115.7 + 25.7	0.57 + 0.07	0.66 + 0.16	1.23 + 0.17
Ni	42 + 10				
Rb	45 + 4				
Ce	39.5 + 0.9	16.1 + 4.1			
La	21.9 + 2.3	11.3 + 0.9	0.018 + 0.005		0.018 + 0.005
Co	31.3 + 0.4	12.9 + 0.7		0.083 + 0.005	0.083 + 0.005
Sc	18.0 + 0.1	8.61 + 0.2		0.72 + 0.004	0.72 + 0.004
As	7.0 + 0.3	12.3 + 4.1		0.070 + 0.005	0.070 + 0.005
Sm	5.05 + 0.01	3.59 + 0.52	0.027 + 0.001		0.027 + 0.001
Th	4.72 + 0.04	1.80 + 0.50			
Hf	5.38 + 0.11	3.86 + 0.60			
Yb	2.72 + 0.04				
Br	6.88 + 0.34	80 + 19		48.56 + 2.73	48.56 + 2.73
Eu	1.45 + 0.06	0.99 + 0.17			
Dy	1.69 + 0.06	3.08 + 0.61			
Cs	1.69 + 0.04				
U	1.74 + 0.01				
Sb	1.56 + 0.03	2.50 + 0.80		0.044 + 0.004	0.044 + 0.004
Ta	0.71 + 0.05				
Lu	0.32 + 0.01				
Tb	0.96 + 0.02				

Table A17 Elemental Abundances in Willamette River System

Sampling Site: Salem 3   River Mile: 84.9

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	10.21 ± 0.08%				
Fe	5.80 ± 0.01%	3.56 ± 0.16%	60 ± 8	50 ± 5	110 ±9
Ca	2.00 ± 0.19%				
Na	1.54 ± 0.02%	3341 ± 17	442++ 0.2		42 ± 0.2
K	0.80 ± 0.05%	3039 ± 162	19.5 ± 2.3		19.5 ± 2.3
Ti	0.89 ± 0.01%				
Mn	719 ± 2	1127 ± 7	24.0 ± 0.1	0.50 ± 0.005	24.5 ± 0.1
Ba	391 ± 10				
V	188 ± 1				
Zn		573 ± 86	10 ± 1		
Cr	91.0 ± 1.0			0.24 ± 0.06	0.24 ± 0.06
Ni	36 ± 15				
Rb	46 ± 3				
Ce	39.8 ± 0.9	16.0 ± 5.9			
La	24.3 ± 1.4	14.7 ± 1.5	0.025 ± 0.003		0.025 ± 0.003
Co	27.3 ± 0.3		0.016± 0.002	0.0040 ± 0.0007	0.020 ± 0.002
Sc	22.9 ± 0.1	9.2 ± 0.3	0.0009± 0.0001	0.0076 ± 0.0007	0.0085 ± 0.0007
As	7.0 ± 0.3	8.3 ± 1.4			
Sm	5.43 ± 0.01	2.96 ± 0.10	0.026 ± 0.001		0.026 ± 0.001
Th	4.64 ± 0.04	2.39 ± 0.90			
Hf	6.22 ± 0.11	3.14 ± 1.27			
Yb	3.02 ± 0.04				
Br	7.05 ± 0.25	62 ± 3		3.12 ± 0.05	3.12 ± 0.05
Eu	1.48 ± 0.06	0.73 ± 0.03			
Dy	1.80 ± 0.08				
Cs	2.19 ± 0.06	2.15 ± 1.20			
U	1.81 ± 0.06				
Sb	0.94 ± 0.02	0.68 ± 0.20		0.04 ± 0.004	0.04 ± 0.004
Ta	1.13 ± 0.08				
Lu	0.37 ± 0.06				
Tb	1.04 ± 0.02				

Table A18 Elemental Abundances in Willamette River System

Sampling Site: Salem 4   River Mile: 82.0

Element	Sediment (μg/g)	Suspended Particulates (μg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.91 + 0.11%				
Fe	5.68 + 0.01%	5.02 + 0.12%		19.1 + 1.7	19.1 + 1.7
Ca	2.62 + 0.13%				
Na	1.76 + 0.02%	813 + 5	89.0 + 0.5		89.0 + 0.5
K	0.90 + 0.05%	585 + 72	38.0 + 4.8		38.0 + 4.8
Ti	0.88 + 0.06%				
Mn	1146 + 2	130 + 1	7.4 + 0.1	0.035 + 0.001	7.4 + 0.1
Ba	499 + 17				
V	180 + 5				
Zn		148 + 4		1.70 + 0.30	1.70 + 0.30
Cr	94 + 1	119 + 4	0.88 + 0.12	0.26 + 0.06	1.14 + 0.18
Ni	36 + 12				
Rb	39 + 2				
Ce	40.0 + 0.3	1.65 + 0.39			
La	25.8 + 0.1	1.92 + 0.15			
Co	24.3 + 0.1	3.54 + 0.20		0.045 + 0.004	0.045 + 0.004
Sc	20.3 + 0.1	1.57 + 0.46		0.005 + 0.001	0.005 + 0.001
As	6.8 + 0.4	1.22 + 0.16		00.11 + 0.02	0.11 + 0.02
Sm	5.47 + 0.01	4.20 + 0.10	0.023 + 0.001		0.023 + 0.001
Th	4.61 + 0.09	0.40 + 0.06			
Hf	5.64 + 0.11	0.38 + 0.11			
Yb	2.59 + 0.03				
Br	3.58 + 0.26	4.20 + 0.24		4.48 +0.21	4.48 + 0.21
Eu	1.21 + 0.07	0.10 + 0.03			
Dy	1.53 + 0.03				
Cs	2.21 + 0.11				
U	2.22 + 0.11				
Sb	0.45 + 0.02	0.10 + 0.05		0.012 + 0.003	0.012 + 0.003
Ta	0.80 + 0.03				
Lu	0.43 + 0.01				
Tb	0.46 + 0.01				

Table A19   Elemental Abundances in Willamette River System

Sampling Site: Newburg 1   River Mile: 52.50

Element	Sediment (µg/g)	Suspended Particulates (µg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al	8.91 ± 0.11	±			
Fe	5.68 ± 0.01	10.54 ± 0.35		14 ± 2	14 ± 2
Ca	2.62 ± 0.13				
Na	1.76 ± 0.02	3.32 ± 0.02	110 ± 0.1		110 ± 0.1
K	0.90 ± 0.05	2.18 ± 0.07			
Ti	0.88 ± 0.06				
Mn	1146 ± 2	2500 ± 32	0.76 ± 0.03	0.15 ± 0.001	0.91 ± 0.03
Ba	489 ± 17				
V	180 ± 5				
Zn					
Cr	94 ± 1	292 ± 20		0.36 ± 0.09	0.36 ± 0.09
Ni	36 ± 12				
Rb	39 ± 2				
Ce	40.0 ± 0.3				
La	25.8 ± 0.1	47.9 ± 2.1			
Co	24.3 ± 0.1	51.2 ± 4.3		0.015 ± 0.003	0.015 ± 0.003
Sc	20.3 ± 0.1	38.0 ± 0.4		0.0030 ± 0.0002	0.0030 ± 0.0002
As	6.8 ± 0.4	28.0 ± 3.4		0.097 ± 0.007	0.097 ± 0.007
Sm	5.47 ± 0.01	11.54 ± 0.20	0.003 ± 0.0005		0.003 ± 0.0005
Th	4.61 ± 0.09				
Hf	5.64 ± 0.11				
Yb	2.59 ± 0.03				
Br	3.58 ± 0.26	170.02 ± 4.13		7.5 ± 0.01	7.5 ± 0.01
Eu	1.21 ± 0.07	1.96 ± 0.46	0.001 ± 0.0007		0.001 ± 0.0007
Dy	1.53 ± 0.03	1.80 ± 0.30			
Cs	2.21 ± 0.11				
U	2.22 ± 0.11			0.015 ± 0.002	0.015 ± 0.002
Sb	0.45 ± 0.02				
Ta	0.80 ± 0.03				
Lu	0.43 ± 0.01				
Tb	0.46 ± 0.01				

Table A20 Elemental Abundances in Willamette River System

Sampling Site: Newburg 2   River Mile: 50.50

Element	Sediment (μg/g)	Suspended Particulates (μg/g)	Dissolved Cations (ng/ml)	Dissolved Anions (ng/ml)	Total Dissolved ions (ng/ml)
Al (%)	8.94 + 0.10				
Fe (%)	5.86 + 0.02	4.03 + 0.01	13 + 4	6 + 2	19 + 4
Ca (%)	2.85 + 0.24				
Na (%)	1.76 + 0.01	0.95 + 0.002	165 + 0.4		165 + 0.4
K (%)	0.96 + 0.01	0.65 + 0.02	125 + 0.1		125 + 0.1
Ti (%)	0.82 + 0.01				
Mn	961 + 2	0.24 + 0.001	1.1 + 0.1	0.05 + 0.001	1.1 + 0.1
Ba	553 + 9				
V	168 + 6				
Zn					
Cr	90 + 1	101 + 6	26 + 0.1	0.39 + 0.01	26.4 + 0.1
Ni	40 + 10				
Rb	51 + 13				
Ce	44.0 + 0.3	30.4 + 4.8			
La	22.1 + 0.1	16.8 + 0.7			
Co	26.1 + 0.1	21.2 + 2.0		0.122 + 0.004	0.122 + 0.004
Sc	21.3 + 0.6	14.5 + 0.3		0.005 + 0.0002	0.005 + 0.0002
As	6.6 + 0.2	7.9 + 1.1		0.10 + 0.006	0.10 + 0.006
Sm	4.82 + 0.04	4.37+ + 0.07	0.024 + 0.004		0.024 + 0.004
Th	4.38 + 0.03				
Hf	4.88 + 0.11				
Yb	2.27 + 0.29				
Br	3.83 + 0.13	38.55 + 1.27		4.86 + 0.05	4.86 + 0.05
Eu	1.28 + 0.06	1.16 + 0.16	0.0005 + 0.0001		0.0005 + 0.0001
Dy	1.98 + 0.08	4.60 + 0.93			
Cs	2.35 + 0.70				
U	2.05 + 0.13				
Sb	0.63 + 0.02	4.17 + 0.59		0.032 + 0.002	0.032 + 0.002
Ta	0.83 + 0.04				
Lu	0.53 + 0.01				
Tb	0.81 + 0.06				

Table A21 Elemental Abundances in Willamette River System

	Sampling Site: Newburg 3	River Mile: 48.00			
	Sediment	Suspended Particulates	Dissolved Cations Surface 0.6xdepth	Dissolved Anions Surface 0.6xdepth	Total Dissolved Surface 0.6xdepth
Element	(μg/g)	(μg/g)	(ng/ml)	(ng/ml)	(ng/ml)
Al	9.28 ± 0.12 %				
Fe	5.83 ± 0.01 %		4 ± 0.5	5.6 ± 1.4	9.6 ± 1.5
Ca	3.25 ± 0.27 %				
Na	2.08 ± 0.02 %	0.310 ± 0.02 %	118 ± 0.1		118 ± 0.1
K	0.98 ± 0.02 %	0.53 ± 0.02 %			
Ti	0.86 ± 0.05				
Mn	812 ± 2	2020 ± 12	2.67 ± 0.03	0.08 ± 0.002	2.75 ± 0.03
Ba	559 ± 9				
V	161 ± 4				
Zn					
Cr	94 ± 1	87 ± 11		0.019 ± 0.005	0.019 ± 0.005
Ni	38 ± 11				
Rb	46 ± 13				
Ce	43.7 ± 0.2	18.0 ± 8.2			
La	23.6 ± 0.1	10.9 ± 0.7			
Co	26.1 ± 0.1	76.7 ± 4.0		0.013 ± 0.003	0.013 ± 0.003
Sc	21.3 ± 0.1	7.64 ± 0.2		0.0047 ± 0.0002	0.0047 ± 0.0002
As	6.6 ± 0.2	6.0 ± 1.1		0.022 ± 0.006	0.022 ± 0.006
Sm	4.68 ± 0.01	2.50 ± 0.08	0.026 ± 0.0004		
Th	4.40 ± 0.03				
Hf	4.50 ± 0.11				
Yb	2.06 ± 0.29				
Br	2.21 ± 0.12	50.76 ± 1.41		5.0 ± 0.05	5.0 ± 0.05
Eu	1.52 ± 0.06	0.84 ± 0.28	0.0015 ± 0.0004		0.0015 ± 0.0004
Dy	2.14 ± 0.04				
Cs	2.41 ± 0.08				
U	1.54 ± 0.11				
Sb	0.56 ± 0.01	3.56 ± 0.63		0.085 ± 0.001	0.085 ± 0.001
Ta	0.80 ± 0.03				
Lu	0.47 ± 0.01				
Tb	0.72 ± 0.01				

Table 22AElemental Abundances in Willamette River System

Element	Sampling Site: Wilsonville 1 Sediment (µg/g)	Suspended Particulates (µg/g)	River Mile: 43.50 Dissolved Cations Surface 0.6xdepth (ng/ml)	Dissolved Anions Surface 0.6xdepth (ng/ml)	Total Dissolved Surface 0.6xdepth (ng/ml)
Al	8.999+ 0.11%				
Fe	5.19 ± 0.04%	2.80 ± 0.11%		3.6 ± 1.2	3.6 ± 1.2
Ca	3.56 ± 0.54%				
Na	1.84 ± 0.01%	1.02 ± 0.01%	102 ± 0.1		102 ± 0.1
K	1.00 ± 0.24%	0.37 ± 0.01%			
Ti	0.72 ± 0.05%				
Mn	643 ± 1	1450 ± 9			
Ba	492 ± 66				
V	164 ± 5				
Zn					
Cr	93 ± 4	146 ± 10		0.290 ± 0.007	0.290 ± 0.007
Ni	32 ± 19				
Rb	30 ± 12				
Ce	39.4 ± 1.0	12.0 ± 5.8			
La	22.4 ± 0.2	11.1 ± 0.8			
Co	23.3 ± 0.3	13.1 ± 2.5		0.0018 ± 0.0003	0.0018 ± 0.0003
Sc	20.5 ± 0.5	10.64 ± 0.23		0.0030 ± 0.0002	0.0030 ± 0.0002
As	6.8 ± 0.6	4.69 ± 1.4		0.064 ± 0.007	0.064 ± 0.007
Sm	5.25 ± 0.02	3.16 ± 0.08	0.029 ± 0.00043		0.029 ± 0.0004
Th	3.85 ± 0.22				
Hf	3.77 ± 0.68				
Yb	1.79 ± 0.31				
Br	1.69 ± 0.49	57.39 ± 1.45		5.42 ± 0.05	5.42 ± 0.05
Eu	1.37 ± 0.05	1.00 ± 0.23	0.00130 ± 0.00038		0.00130 ± 0.00038
Dy	1.51 ± 0.05	1.20 ± 0.60			
Cs	1.74 ± 0.15				
U	1.41 ± 0.21				
Sb	0.62 ± 0.10	1.25 ± 0.60		0.016 ± 0.0016	0.016 ± 0.0016
Ta	0.74 ± 0.08				
Lu	0.38 ± 0.03				
Tb	0.66 ± 0.17				

Table 23A Elemental Abundances in Willamette River System

Element	Sampling Site: Wilsonville 2 Sediment (μg/g)	Suspended Particulates (μg/g)	River Mile: 39.50 Dissolved Cations Surface 0.6xdepth (ng/ml)	Dissolved Anions Surface 0.6xdepth (ng/ml)	Total Dissolved Surface 0.6xdepth (ng/ml)
Al	9.33 $\pm$ 0.11%				
Fe	5.50 $\pm$ 0.02%	2.32 $\pm$ 0.10%	3.0 $\pm$ 1.1	22.8 $\pm$ 2.3	25.8 $\pm$ 2.7
Ca	2.74 $\pm$ 0.77%				
Na	1.90 $\pm$ 0.25%	0.61 $\pm$ 0.01%	90 $\pm$ 0.2		90 $\pm$ 0.2
K	0.77 $\pm$ 0.25%	0.29 $\pm$ 0.01%			
Ti	0.79 $\pm$ 0.05				
Mn	693 $\pm$ 3	1812 $\pm$ 12	2.16 $\pm$ 0.02	1.61 $\pm$ 0.01	3.77 $\pm$ 0.03
Ba	493 $\pm$ 51				
V	161 $\pm$ 5				
Zn					
Cr	79 $\pm$ 3	68 $\pm$ 8		0.33 $\pm$ 0.01	0.33 $\pm$ 0.01
Ni	37 $\pm$ 23				
Rb	34 $\pm$ 13				
Ce	35.7 $\pm$ 1.0	14.5 $\pm$ 5.4			
La	19.6n $\pm$ 0.2	11.9 $\pm$ 0.7			
Co	26.5 $\pm$ 0.4	13.9 $\pm$ 2.01		0.025 $\pm$ 0.003	0.025 $\pm$ 0.003
Sc	19.1 $\pm$ 0.4	10.6 $\pm$ 0.2		0.0065 $\pm$ 0.0002	0.0065 $\pm$ 0.0002
As	5.5 $\pm$ 0.5	6.1 $\pm$ 1.2		0.118 $\pm$ 0.0074	0.118 $\pm$ 0.0074
Sm	4.36 $\pm$ 0.01	1.41 $\pm$ 0.03	0.027 $\pm$ 0.0004		0.027 $\pm$ 0.0004
Th	3.77 $\pm$ 0.20				
Hf	3.69 $\pm$ 0.23				
Yb	2.02 $\pm$ 0.24				
Br	1.85 $\pm$ 0.43	18.30 $\pm$ 0.96		4.50 $\pm$ 0.04	4.50+ $\pm$ 0.04
Eu	1.29 $\pm$ 0.07	0.62 $\pm$ 0.21	0.00096 $\pm$ 0.00037		0.00096 $\pm$ 0.00037
Dy	1.48 $\pm$ 0.03	1.69 $\pm$ 1.10			
Cs	2.13 $\pm$ 0.15				
U	1.27 $\pm$ 0.19				
Sb	0.59 $\pm$ 0.23	1.73 $\pm$ 0.46		0.0333 $\pm$ 0.0021	0.033 $\pm$ 0.0021
Ta	0.67 $\pm$ 0.07				
Lu	0.34 $\pm$ 0.02				
Tb	0.64 $\pm$ 0.16				