# Hydrospheric Trace Elements and Their Application in Tracing Water Pollutants

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# Final Report

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#### I. INTRODUCTION

In recent years, there has been renewed interest in attempts to develop tracer technologies that will be attractive alternatives to conventional radiotracer, chemical tracer and fluorescent dye technologies. In this report I summarize the principal findings of a project to develop certain rare earth elements with shortlived activation products as stable activable tracers for fluidbound pollutants in fresh waters.

A stable activable tracer is a stable material that is injected into a system under study and whose concentration in the system is measured by post-sampling activation analysis. One may initially inquire as to the advantages of such "artificial" tracers as compared to the "naturally occurring" trace elements in various systems which act as "natural" tracers. The artificial tracer has the advantages of having a controlled emission rate (either pulse or continuous injection as well as controlling the amount injected which is valuable in model validation studies. Artificial tracers can be injected in amounts sufficient to insure easy detection in the system under study and lend themselves better to simultaneous tracing of several similar pollutant sources.

What advantages do stable activable tracers possess in general or when compared, in specific situations to fluorescent dyes, radiotracers or conventional chemical tracers such as KHSO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, etc.? The advantages are:

 The tracers are non-toxic at concentrations encountered in environmental studies<sup>1</sup> in contrast to the real (or imagined) problems with radionuclide release in the environment. The use of radiotracers in long term environmental studies is especially objectionable because of the radiological hazards involved. There are no aesthetically objectionable modifications of water color during tracing with stable activable tracers.

- (2) The detection sensitivity of these tracers is very good. For example, for Dy, one can readily detect amounts of  $10^{-12}$ g. This allows pollutant tracing over very long distances not usually possible with fluorescent dyes or radioactive tracers. Stable activable tracers can be chosen such that their naturally occuring concentrations are very small. Conventional chemical tracers, such as  $K_2CO_3$  etc., usually have to be added in high concentration in order to remain detectable after dilution and to alleviate the "blank" problem. In such cases, the density of the tagged materials will exceed that of the water and they are no longer hydrologically equivalent.
- (3) The tracers can be bound as EDTA or DTPA complexes when used as tracers for fluid-bound materials and thus not suffer any adsorption by sediments, etc., as sometimes plagues the use of most dyes.
- (4) The detection of these tracers is not affected by the presence of water color or the occurrence of photochemical or radioactive decay of the tracer. Thus the highly colored effluent of some paper mills will not interfere with the tracing process.
- (5) According to our estimates (see Table II), the rare earth stable activable tracer is cost competitive with the use of radiotracers and fluorescent dyes.

(6) Effluents from specific pollutant sources can be marked with a given "finger-print" (fixed ratio of tracer elements) and the effluent from several sources traced simultaneously. By the careful selection of the elements and their ratio used in any one "fingerprint", results can be obtained that can be analyzed in one day or less in the laboratory. This avoids the traditional problem of activation analysis-based methods, i.e., one of long analysis times.

What elements should one choose as stable activable tracers? 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<sup>2</sup>. In a series of experiments at the Pennsylvania State University, Jester and co-workers<sup>3,4</sup> used Br and I (along with some studies of  $V^{++}$  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 study, Channell and Kruger<sup>5</sup> 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 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. 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. In unpublished work, Hansen<sup>6</sup> actually compared the behavior of long lived Eu, Tb and In activable tracers with the fluorescent dye Rhodamine B in a 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 or their use in large scale experiments. In a preliminary study Schmitt et al.<sup>7</sup> showed that the dispersal of La and Sm could be followed in rivers but made no attempts to systematically study the use of these elements as tracers. Indium and scandium were used as stable activable tracers for monitoring in-plant movements of water in wastewater treatment plants by Craft and Eicholz<sup>8</sup>. Dahl and co-workers<sup>9</sup> 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 <u>rare earth</u> <u>elements</u> with <u>short-lived activation products</u> 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. The tracers are injected into the water as DTPA anionic complexes thus insuring that the tracers remain fluid-bound. The

rationale behind the choice of tracer and its chemical form is discussed in Section II. In Section III of this report we describe the experimental methods employed in this study while the results of field and laboratory tests of the tracer are presented in Section IV. A brief summary of the work is made in Section V.

#### II. CHOICE OF TRACER

Table I shows the nuclear and economic properties of the tracer tested in this study, Dy, along with the frequently used In tracer which was also studied for comparison purposes. Also shown in this table are other possible stable rare earth tracers with shortlived activation products. Dy can be seen to be a "best case" rare earth tracer, thus leading to its choice as a prototype for the rare earth tracers.

According to the estimates of Channell and Kruger<sup>2</sup>, 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  $1.23 \times 10^{13}$  liters of water or greater) and is a factor of 2-5 times cheaper than the use of fluorescent dyes. Our estimate for a smaller scale study ( $\sim 5 \times 10^{10}$  liters) using dysprosium instead of the lanthanum employed by Channell and Kruger shows that the stable activable tracer technique is cheaper by a factor of  $\sim 3$  to 4 times when compared to tracers and yet comparable to the use of fluorescent dyes. Table II is a compilation of our cost estimates involving rare earth tracers with short lived activation products. 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.

Table I: Properties of Some Rare Earth Stable Activable Tracers with Short Lived (t1/2 ~1 Day) Activation Products.

Elenent	Cost(\$/kg) <sup>a</sup>	Target Nuclide <sup>b</sup>	$\mathrm{E}_{\gamma}$ (%Abundance) $^{\mathrm{b}}$	t <sub>1/2</sub>	g/10 <sup>4</sup> cts	Cost(\$/10 <sup>4</sup> cts)
e)	45	Ce-136	446.0(2.3%)	- (- 4 0.6	0.085	3.8x10
Pr	236	Pr-141	1575.5(3.7%)	19.2 h	0.018	$4.27 \times 10^{-3}$
PN	176	Nd-148	211.3(27%)	1.8 h	5.93x10 <sup>-4</sup>	1.04x10 <sup>-4</sup>
Sm	320	Sm-154	104.3(73%)	22.997 m	3.3IX10-5	1.05x10 <sup>-5</sup>
Eu	3960	Eu-151	121.8(37%)	9.30 h	1.32x10 <sup>-7</sup>	5.24x10
Gđ	3720	Gd-158	363.6(9%)	18.706 m	1.11×10 <sup>-4</sup>	4.13x10 <sup>-4</sup>
P	920	DV-164	94.7(4%)	2.334 h	1.56×10 <sup>-6</sup>	1.44x10 <sup>-0</sup>
Ho	1100	Ho-165	80.6(54%)	66.78 m	2.42×10 <sup>-6</sup>	2.67x10 <sup>-0</sup>
ਮ ਸ਼	420	Er-170	112.0(25%)	7.519 m	3.61x10 <sup>-4</sup>	1.51x10 <sup>4</sup>
q7	860	Yb-176	151.0(16%)	1.900 h	1.77x10 <sup>-4</sup>	$1.52 \times 10^{-4}$
Γn	18000	Lu-175	88.4(10%)	3.679 h	2.04x10 <sup>-5</sup>	3.67×10_6
In d	1760	IN-115	1097.2(30%)	54 m	6.80×10 <sup>-7</sup>	1.21x10

- Alfa Catalog, Ventron Corp., Danvers, MA,1977-1978. (Large quantities can be purchased at significantly lower cost. å
- I.Binder, R.Kraus, R, Xlein, D.Lee and M.M.Fowler, "A Chemist's Gamma Ray Table", Lawerence Berkeley C.M.Lederer, J.M. Hollander, I. Perlman, Table of Isotope, 6th edition (Wiley, N.Y., 1967) Laboratory Report, LBL-6515, June, 1977. ġ
- c. Assume 1 minute irradiation at a flux of  $10^{13}$  n/cm<sup>2</sup>/sec. Delay of 5 m, count 3 m. Sample positioned one cm away from a 40 cm<sup>3</sup> 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 purposes.

#### Table II: Cost Analysis of Tracer Method

Volume of Water tagged	5 x 10 <sup>10</sup> liters
Duration of Experiment	l day
Number of Samples taken	100 samples
Rhodamine WT	
Weight needed	110 lb
Tracer Cost	\$ 457
Analysis Cost	\$ 200

Tritiumb

Activity needed	81 Ci
Tracer Cost	\$ 243
Analysis Cost <sup>d</sup>	\$3000

Total \$3243

Total \$ 657

Dyprosium<sup>C</sup>

Weight needed	10 lb
Tracer Cost	\$ 250
Analysis Cost	\$ 600

Total \$ 850

- A. Tracer cost based upon an average minimum concentration of 1.3 x  $10^{-5}$  g/m<sup>3</sup> and a tracer cost of 4.15 dollars/lb.
- b. Tracer cost based upon an average concentration of 1.622 nCi/l and a cost of \$3/Ci for Tritium.
- c. Tracer cost based upon an average concentration of 100 ng/l 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.

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

As far as hazardous nature of the tracer is concerned, the use of rare-earth tracers pose no detrimental effects because the tracers are non-toxic at the concentration encountered in environmental studies<sup>15-17</sup>. Because of the good detection sensitivities for these elements, the levels used in tracer experiments were  $\sim 10^{-10}$  of the levels at which serious health hazards are expected to occur.

A key component of any tracer method for tracing fluid-bound substances is that tracer does not decompose or is not adsorbed/ absorbed significantly during the course of the experiment. To alleviate such problems of tracer loss, one method has been the employment of aminocarboxylic acid chelates of the tracers. These complexes form some of the most stable water soluble complexes 18,19 and should constitute a group of potentially useful water tracers. This is especially true with the DTPA (diethylenetriamine pentaacetic acid) complexes of the rare earths which are more stable than EDTA or NTA complexes by factors of greater than 10<sup>5</sup> (see Table V). In addition, the DTPA anionic complexes tend to be more conservative than cationic complexes<sup>20,21,22</sup>. We have thus chosen to inject our rare earth tracers as DTPA anionic complexes to trace the movement of fluid-bound pollutants in fresh water.

Element**	Median	Range	
Ag	0.00013	0.00001 - 0.0035	5
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	
Cđ	0.08	April Sam Anno Sam Sam	
Cl	7.8	5 - 35	
Co	0.00090	0.0001 - 0.006	
Cr	0.00018	0.0001 - 0.08	
Cs	0.0002	0.00005 - 0.0003	5
Cu	0.01	0.006 - 0.4	
Fe	0.67	0.01 - 1.4	
Ga	0.001		
Hg	0.00008	the design and the set	
ĸ	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	$3.9 \times 10^{-10}$	state term and term street	
Rb	0.0015	0.001 - 0.008	
Se	0.02		
Sn	0.00004		
Sr	0.08	0.003 - 0.8	
Th	0.00002	and the second second	
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	0.00009		
La	0.00033		
Sm	0.00012		
Dy	<0.000017		
In	<0.000001		

Table III: Elemental Composition of River Water 10,11,12,13,14

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

		EDTA	DTPA	NTA
M	etal	log K <sub>S</sub>	log K <sub>S</sub>	log K <sub>s</sub>
Ba	(II)	7.8	8.6	6.41
Sr	(11)	8.6	9.7	
Mg	(II)	8.7	9.0	7.00
Ca	(11)	10.7	10.7	8.17
Sc	(III)	23.1		
Ti	(III)	21.3		
v	(II)	12.7	15.1	
v	(III)	25.9		
Cr	(III)	24.0		·
Mn	(II)	14.0	15.1	7.44
Fe	(II)	14.3	16.5	8.84
Fe	(III)	25.1	28.6	15.87
Co	(II)	16.3	18.4	10.6
Co	(III)	∿36		100 Aug 100
Ni	(II)	18.6	19.6	11.26
Cu	(II)	18.8	21.1	12.68
Zn	(II)	16.5	18.3	10.45
cd	(II)	16.5	18.9	
Hg	(II)	21.8	26.7	
AL	(111)	16.1	D	Box part 2010
Ga	(III)	20.3	-	
In	(III)	25.0		~ ~ ~
Sn	(II)	13.5		
Pb	(II)	18.0	18,8	11.80
Y	(III)	18.0	22.4	11.48
La	(III)	15.5	19.9	10.36
Ce	(III)	15.9	20.4	10.43
Pr	(III)	16.4	21.8	10.30
Nđ	(III)	16.6	22.2	10.49
Sm	(III)	17.1	22,8	11.13
Eu	(III)	17.3	22.9	10.79
Gđ	(III)	17.3	23.0	11.17
Tb	(III)	17.9	23.2	11.31
Dy	(III)	18.3	23.4	11.74
Er	(III)	18.8	23.1	11.90
Tm	(III)	19.3	22.9	11.79
Yb	(III)	19.5	23.0	11.98
Lu	(111)	19.8	22.4	12.10

Table V Stability constants for various metals with EDTA, DTPA, and NTA<sup>18</sup>,19

#### III. 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<sup>23,24</sup>). 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 Related to Tracer Methodology

Prior to field tests of the tracers, certain preliminary laboratory experiments were performed to answer crucial questions in the development of a proper experimental methodology. A brief description of these experiments, the protocol used and their results is given below:

### 1. Development of Preconcentration Procedures for Tracers and Other Dissolved Species

Because of the expected low tracer concentrations encountered in real field experiments and the need to measure background levels of other dissolved species in fresh waters, we needed to develop a quick, effective method of preconcentrating dissolved species in

water samples. We chose to use filtration through an assembly of anionic and cationic ion-exchange filter papers (Gelman Acropore SB-6407 and SA-6404, respectively, containing Dowex 1-X18 and Dowex 50W-X8 resins). The following experiments were done as a part of developing this preconcentration methodology.

#### a. Trace Element Content of the Collection Media

The applicability of ion-exchange filter papers as a preconcentration media for dissolved species in natural waters depends on, among other things, the presence of a low trace element content of these media. Low trace element content of these filters can alleviate the problem of "blank" corrections which may introduce and cause erroneous results especially in quantitative work. To evaluate the trace element content 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 VI and show an acceptably low trace element content of these papers.

# b. Number of Filtrations Necessary to Achieve Quantitative Recovery of the Tracer

To establish the number of times a solution containing dissolved tracer species must be filtered to achieve quantitative recovery of the tracer, solutions containing radioactive Sm and La chelates (at pH  $\sim$ 7.2) were filtered 1, 3, 5, 7, 10 and 20 times through single layers each of the cationic and anionic ion-exchange filters. The results showed >99% recovery of the tracer in a single pass through the filters.

Trace Element Content of Nuclepore Membrane Filter, Cationic and Anionic Ion-Exchange Filter Papers. (ng/cm<sup>2</sup>) Filter Papers. Table VI: v

	Nuclepore M	embrane Filter	Ion-Exchange	Filter Paper	
Element	This Work	Literature* (c)	Cationic <sup>(a)</sup>	Anionic <sup>(b)</sup>	
Na	10	8-47	82	478	
Вг	1.49	0.37-2.80	24.75	12.10	
' uM	0.44	0.07-0.31	28.04	32.85	
Sn	0.005	0.001-0.002	1.15	0.29	
םמ'	0.0004	0.000016	0.0024		
8	0.29	8	0.40	0.03	
Zn	Ч		342	335	
К	6	8	32	131	
La	0.104	1		F T L	
Я		[]	31.7	29.4	
ът В			Let	267.4	
W.				0.5	
SG	I		menter	0.052	

- Gelman Instrument Company, Ann Arbor, Michigan. Gelman Acropore SA-6404. (a)
- Jones, R.A., MS Thesis, Department of Chemistry, Oregon State University, 1977. Gelman Instriment Company, Ann Arbor, Michigan Gelman Acropore SB-7407. (c) (q)
  - 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. Due to the large variation in the reported values, the ranges rather than average values are reported here. \*

c. Effect of pH on Efficiency of Tracer Collection The tracers Sm and Ce were shown to be quantitatively picked up (>99% pickup) over a pH range from 2.5-7.

#### d. Effect of Tracer Species on Tracer Collection

DTPA complexes of La, Ce, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu and In (adjusted to pH 7.2) were filtered through anion exchange filters and found to be picked up to an extent of >99% in a single filtration.

#### e. Efficiency of Ion Exchange Papers for Any Dissolved Species in Willamette River Water

One important aspect of this work is the determination of the naturally occurring levels of the tracer elements present as dissolved species in the fresh water systems under study. As a by product of such investigations, one measures the abundances of several other elements in these samples. In order to render such data meaningful, one needs to establish the efficiency of the preconcentration measures used in this work for <u>any</u> dissolved species, not just the tracer species. Radiotracers of several elements were added to fresh Willamette River Water, diluted to natural concentrations and allowed to equilibrate. The usual preconcentration steps were then applied to this sample and the results shown in Table VII were obtained. Examination of the data in Table VII shows that quantitiative recovery of most dissolved species is achieved by the use of cationic filters. The inclusion of anionic filters boosts the overall recovery to over 90% in most cases.

# Table VII: Pickup Efficiency of Various Types of Filters for Naturally Occurring Trace Elements in Willamette River Water

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
Уb	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	
Та	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		

The Nuclepore and Whatman filter results represent the fraction of the tracer species found as suspended particulate.

#### 2. Testing of Sample Preservation Procedures

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<sup>25</sup>. 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<sup>26,27</sup> that rapid freezing of the samples provide a better alternative to chemical preservation.

To confirm the effectiveness of freezing as an acceptable sample preservation procedure, two approaches were employed; (i) Clean neutron activated polyvials were placed into one liter sample container filled 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 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 convincing evidence of such happenings, i.e., trace elements being leached out, adsorbed or desorbed during this freezing

process, suggesting that freezing is a good if not perfect way of preserving the samples.

# C. Procedure for Sample Preparation and Analysis

Based upon the experiments described in Section B above, a procedure was established for the preservation and analysis of any water sample containing dissolved species or suspended particulate matter. The procedure is shown in Figure I. Each water sample collected was thus broken into three components: (a) suspended particulate, (b) dissolved anions, (c) dissolved cations.

In studies of the natural "background" of tracer elements in the water systems under study, sediment samples were collected at the same points as the water samples. In general, these samples 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 then sieved through a 48 mesh or279 micron sieve.

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

The elemental contents of all samples were measured using instrumental neutron activation analysis (INAA). The suspended particulates from the water samples were collected on tared Nuclepore filters, desssicated to constant weight and then reweighed to obtain a gravimetric analysis. The weighed filters were then pelletized and then encapsulated in plastic irradiation vials



Figure: I A schematic diagram of the sample collection and analysis procedures.

for neutron activation together with appropriate elemental standards of interest. Similar sample preparation procedure was applied to the ion-exchange filters. Approximately 100-150 mg of sediment per sample was encapsulated in precleaned polyvials and then neutron activated. The sequential activation procedure employed to measure the elemental contents of the various samples is summarized in Table VIII. 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 appropriate cooling period of 3-5 minutes. Using such short irradiation procedure, approximately 10 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 additional delay of 2-3 weeks. Such sequential counting provide half-life checks for most radionuclides and all the half-lives measured agreed with ±10% of the accepted values<sup>28</sup> 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<sup>29</sup>, NBS-SRM 1632 Coal<sup>30</sup>, NBS-SRM 1633 Coal Fly Ash<sup>31</sup> were irradiated and counted under identical conditions as the samples being analyzed. Use of these NBS standards can provide checks on the

	Product					Eymeas	sured
Element	Radionuclides	Halt-	life*	Delay Time	Count Time	(kev)	*
נמ	A1-28	2.241	mins	3 - 5 mins	300 secs	1778.9	
V	V-52	3.77	mins			1434	
Ti	Ti-51	5.80	mins			319.8	
Ca	Ca-49	8.80 .	mins			3084.4	
Mg	Mg-27	9.46	mins			1014	
CI	C1-38	37.094	mins	1 - 2 hrs	900 secs	1642.4	
In	In-116m	54.101	mins			1097	(417)
Ba	Ba-139	1.42	hrs			165.8	
Dy	Dv-165	2.334	hrs	5 - 6 hrs		94.7	
Mn	Mn-56	2.58	hrs			846.6	(1810)
Sr	Sr-87m	2.81	hrs			388.4	
Lu	Lu-176m	3.69	hrs			88.4	
Eu	Eu-152m'	9.30	hrs			121.8	(344.3)
ĸ	K-42	12.401	hrs	1 - 2 days	1 - 2 hrs	1524.7	
Zn	Zn-69m	13.80	hrs			438.7	
Ga	Ga-72	14.10	hrs			629.9	(834)
Na	Na-24	15.00	hrs	2		1368.5	
¥7	W-187	23.899	hrs'			685.7	
As	As-76	1.096	hrys			657.2	(559,1)
Br	Br-82	1.479	days			776.5	
La	La-140	1.675	days			1586.4	
Sm	Sm-153	1.933	days			103.2	
υ	Np-239	2.350	days			228.2	
Sb	Sb-122	2.72	days			563.9	
Lu	Lu-177	6.710	days			208.4	
Rb	Rb-86	18.60	days	2 - 3 week	s 10-20 hrs	1078.8	
Th	Pa-233	27.00	days			311.9	
Cr	Cr-51	27.7	days			320	
Yb	Yb-169	32.00	days			197	(177)
Ce	Ce-141	32.50	days			145	
Hf	Hf-131	42.50	days			482	
Fe	Fe-59	44.60	days			1099	(1292)
Ni	Co-58	71.30	days			810.8	
Sc	Sc-46	83.80	ddays			889	
Ta	Ta-182	115.00	days			1221	
Se	Se-75	120.00	days			264.6	
Zn	Zn-65	244.00	days			1115.5	
Cs	Cs-134	2.06	yrs			605	(796)
Co	Co-60	5.26	yrs			1173.2	(1332.5)
Eu	Eu-152	13.20	yrs			121.8	(1408)

Table VIII Summary of Neutron Activation Analysis Procedure:

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

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 values. Our results and the NBS or literature values are summarized in Tables IX, X and XI.

#### Laboratory and Field Studies of Tracer Stability

Perhaps the most important characteristic of any tracer of fluid-bound materials is whether the tracer is conservative, i.e., are there losses of tracer due to physical, chemical, etc. processes. The following experiments were performed to test this aspect of the behavior of our stable activable tracers.

# D. Laboratory Studies of the 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 behavior and stability of the chelated tracer under simulated river conditions. Briefly, the experiments consist of placing known quantities of Dy and In-DTPA chelates ( $\sim 10^{-6}_{-6}$ M) in Erlenmeyer flasks agitated continuously in a thermostatically controlled shaker baths at a temperature of 10°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 purpose of these experiments is to evaluate the effect of the actions of (i) sediments and suspended particulates, (ii) suspended

Table IX Elemental Abundances in NBS Standard Reference Materials

Element	This Work	NBS & Literature <sup>a</sup>	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	85 + 1	82 + 6	1.04 + 0.10
K(%)	1.46 + 0.01	1.47 + 0.03	0.99 + 0.02
Mn	91 <del>+</del> 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	1.08 + 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	$2.9 \pm 0.03$	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	00.086 + 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

#### NBS-SRM 1571-Orchard Leaves

Grand Average =  $1.07 \pm 0.13$ 

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 X:

# Elemental Abundances in NBS Standard Reference Materials

Element	This Work	NBS & Literature <sup>a</sup>	This Work/NBS
Al (%)	1.73 <u>+</u> 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	0.48 + 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*	$0.97 \pm 0.12$
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	$1.05 \div 0.11$
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		And the second second
Cs	1.68 + 0.10	1.40 + 0.10	1.20 + 0.11
U	1.45 + 0.21	1.40 + 0.10	$1.04 \pm 0.17$
Sb	3.9 + 0.8	3.9 + 1.3	1.00 + 0.39
Та	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	Final Action of the second second	
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	$0.99 \pm 0.26$

#### NBS-SRM 1632-COAL

Grand Average = 1.02 + 0.07

- a. NBS Certificate of Analysis, SRM 1632-Coal, March,1977. Cordon,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 XI: Elemental Abundances in NBS Standard Reference Materials

Element	This Work	NBS & Literature <sup>a</sup>	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
HÍ	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	Course of the same	and a second
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

#### NBS-SRM 1633-Coal Fly Ash

Grand Average =  $0.98 \pm 0.07$ 

a. NBS Certificate of Analysis, SRM 1633-Coal Fly Ash, Oct., 1974. Gordon, G.E., et al., "Elemental Concentrations in the NBS Environmental 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.

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 dissolved 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.

# E. Field Studies

A series of field experiments were carried out to measure the "background" levels of the tracer elements in a typical fresh water system, the Willamette River of western Oregon, and to test the conservative nature of the tracers in the field.

# 1. Natural Trace Element Background Levels in the Willamette River

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 Willamette 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 involved 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. Sites chosen for this study include waste outfalls of paper and pulp mills, sewerage and metallurgical processor outfalls at various "urban" areas such as Eugene, Salem, Albany, and Corvallis as well as "rural" areas such as Harrisburg, Peoria, Newburg, Independence and Wilsonville. A complete list of the sampling sites involved is shown in Table XII. The Willamette River (See Map 1) is a relatively fast moving (~7 miles/hour) medium size (~100 ft. wide, 12 ft. 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 behavior.

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

#### Table XII: Sampling Sites:

- 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, Independence. 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 XII: 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, Harrisburg. 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.



ual Locations where Sediment and Water Samples were taken: see Table Sites on The Willamette River. ( Numbers on the Map Indicate the Act-Map II: Enlarged Map of The Willamette Valley Showing Various Sampling XVII for detailed Description of the Various Sampling Sites.)



was used for this purpose. The sediments obtained were immediately placed in precleaned polybottles and then transported to the laboratory where they were refrigerated prior to analysis.

#### 2. Field Tests of Tracer Conservation

To verify the conservative nature of the rare earth tracers in a field experiment, a solution of Dy DTPA tracer was continuously injected into the final effluent tank of the Albany, Oregon, municipal sewage treatment plant. The output of this effluent tank is then discharged directly into the Willamette River. Samples of the tracer were taken at various points downstream from the outfall.

In particular, a Dy DTPA tracer of known concentration  $(5.2 \times 10^{-2} \text{M Dy})$  was continuously injected at a constant rate  $(\sim 1 \text{ ml/sec})$  for a total period of 3 hours into the final effluent tank (discharge of about 4.5-5 million gallons per day) of the Albany municipal sewage treatment plant. Tracer injection was done using a home-made, battery-operated peristaltic pump with a constant injection rate and controlled by an automatic "on-off" timer (see Figure II).

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 (See Map 3), (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

FIGURE II; TRACER PUMP AND ACCESSORIES.



AUTOMATIC D.C.

TIMER

PERISTALTIC PUMP HEAD

D. C. Motor

BATTERY

TYGON TUBINGS.




from Western Kraft outfall and there is a sharp bend at this location causing very turbulent flow, (4) Station D is about two miles downstream 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 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 for the tracer concentration to reach a steady state.

## IV. RESULTS AND DISCUSSION

## A. Laboratory Experiments to Test the Time Dependence of the Tracer Stability Under Simulated River Conditions

Results of the laboratory experiments performed to test the stability of chelated and unchelated tracers under simulated river conditions are shown in Tables XIII-XVIand Figures III-VI.

Several general conclusions follow immediately from these experiments; (1) Chelation with DTPA greatly improves the solution stability of the tracers over the simple ionic form in all cases. Unchelated Dy and In suffer substantial losses after a period of eight days, with approximately 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/precipitation reactions, etc., and more than 95% of the original tracer remains in solution after a period of eight days. (2) Sorption of tracer to suspended particulates present in unfiltered river water was negligible compared to sorption to bottom sediments. This is, in all cases, probably due to the small quantity of particulates per unit volume of natural water compared to

# Table XIII: Time Dependence of Tracer Stability under Simulated River Conditions II (Filtered River Water)\*\*

	% of Original Tracer	Remaining in Solution
Time of Equilibration	DyDIPA Chelates	InDIPA Chelates
l hr	96.2 <u>+</u> 4.9	95.6 <u>+</u> 4.8
2	97.0 <u>+</u> 4.0	95.2 <u>+</u> 4.8
4	99.0 <u>+</u> 5.0	94.5 <u>+</u> 4.8
6	98.9 <u>+</u> 5.0	96.0 + 4.8
12	97.6 <u>+</u> 5.0	94.9 <u>+</u> 4.8
24	96.9 + 4.9	96.4 <u>+</u> 4.9
48	98.0 <u>+</u> 5.7	97.9 <u>+</u> 4.9
4 days	98.6 <u>+</u> 5.0	96.8 <u>+</u> 4.9
6	98.5 <u>+</u> 5.0	95.6 <u>+</u> 4.8
8	97.8 + 5.0	96.8 <u>+</u> 4.8

\*\*60 ml of fresh river water filtered through 0.45 micron Nuclepore filter.

# Table XIV: Time Dependence of Tracer Stability under Simulated River Conditions I (Unfiltered River Water)<sup>a</sup>

	Per cent of Original	Tracer Remaining
Time of Equilibration	DyDIPA Chelate	InDIPA Chelate
l hr	97.1 <u>+</u> 4.9	95.5 <u>+</u> <b>4</b> .8
2	95.8 <u>+</u> 4.8	95.5 <u>+</u> 4.8
4	94.6 + 4.8	95.5 + 4.8
6	97.3 <u>+</u> 4.9	97.3 + 4.6
12	95.6 + 4.8	100.9 + 5.8
24	97.1 <u>+</u> 4.8	98.0 <u>+</u> 5.2
48	97.0 <u>+</u> 4.9	98.7 <u>+</u> 5.1
4 days	98.3 <u>+</u> 4.9	96.7 <u>+</u> 5.2
6	98.3 <u>+</u> 4.9	97.4 + 4.9
8	96.2 <u>+</u> 5.0	97.4 + 4.9

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

Table XV: Time Dependence of Tracer Stability under Simulated River Conditions III (Sediment + Unfiltered River Water)\*

	% Original Tracer H	Remaining in Solution
Time of Equilbration	DyDIPA Chelate	InDIPA Chelate
l hr	100.8 + 5.2	$100.2 \pm 5.1$
2	99.3 <u>+</u> 5.1	$100.7 \pm 4.9$
4	100.0 + 5.2	100.9 + 5.0
6	100.8 + 5.2	97.1 + 5.1
12	99.4 <u>+</u> 5.1	94.8 ± 5.2
24	101.1 <u>+</u> 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 <u>+</u> 5.3	81.7 + 5.0
8	100.5 + 3.7	77.9 + 4.9

\*Mixture consists of 10 g of dried sediment plus 60 ml of unfiltered river water with pH adjusted to 7.2 and temperature maintained at 10°C.

Table XVI: Time Dependence of Tracer Stability under Simulated River Conditions IV (<u>Unchelated</u> Tracer + Sediment + River Water)\*

Time of	% Original Tracer Rer	maining in Solution
Equilibration	Dy Solution	In Solution
l hr	93.4 + 9.4	95.0 ± 10.7
2	88.5 + 8.9	91.8 <u>+</u> 10.4
4	87.3 + 8.8	90.6 <u>+</u> 10.3
6	86.8 + 9.8	84.4 + 9.8
12	85.6 + 8.6	69.5 <u>+</u> 8.5
24	84.8 + 8.6	64.5 + 7.4
48	81.8 + 8.6	63.3 <u>+</u> 7.6
4 days	77.5 <u>+</u> 7.8	57.1 + 7.6
6	66.4 <u>+</u> 7.8	50.9 + 6.3
8	65.2 <u>+</u> 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 under a temperature of 10<sup>0</sup>C and pH of 7.2









FIGURE V: TIME-DEPENDENCE OF TRACER STABILITY UNDER SIMULATED RIVER CONDITIONS III (SEDIMENT + UNFILTERED WATER)



the large amount of bottom sediments used in these tests. Finally, in comparing the solution behavior of the chelated tracers tested here, Dy DTPA holds the best tracer possibility since its solution stability is superior to the widely used In chelate.

## B. <u>Baseline Studies of Elemental Abundances in Willamette River</u> Water, Suspended Particulate and Sediments

This phase of work included the sampling of water and sediment from various parts of the Willamette River and constitutes 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. The average dissolved Dy concentration was found to be  $1.7 \times 10^{-5}$  ppm with a range of  $4 \times 10^{-6} - 4 \times 10^{-5}$  ppm. In concentrations were less than 10<sup>-6</sup> ppm. 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 Al-A23 in the Appendix). This data is plotted in Figures VII - XI and shows remarkable uniformity in sediment content from one sampling station to another. This suggests little or no detectable anthropogenic contribution to the trace element levels in these sediments. This conclusion is further reinforced by the data shown in Figure XII where the average trace element content of Willamette River sediment is compared to that of Oregon soils 32. The trace element content of the river sediment and Oregon soil is virtually identical again, indicating no significant anthropogenic trace element input to the sediments.



¢ (EI) (P) = (RB) 3 00 2 П SAMPLING STATION 4-00 ひ ÷ Ф ÷  $\infty$ 51 + 00 + FIGURE VIT ELEMENTAL ABUNDANCES IN WILLAMETTE SEDIMENTS 17 0  $\diamond$ + 0 0 D + ち  $\Diamond$ 0 + 0 0 П + \$ 1m ÷  $^{\circ}$ + **\$** 0 H ÷ 2 П + 0 П ອ +  $\Diamond$ a + 00 П 4. 0 D  $\diamond$ + 00-10 + 0 0 + 0 M D 0 + 00 MRG + \$0. 0 ł 20,0 10,0+ 30.01 50.0-40'05 47

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FIGURE X: ELEMENTAL ABUNDANCES IN WILLAMETTE SEDIMENTS





Relative Concentration

The average absolute and relative elemental concentrations in the suspended particulate matter are shown in Table XVI and Figure XIII. The results suggest that the suspended particulates are similar to the sediment in elemental composition and can be considered as primarily being "upswept" sediment.

The dissolved species concentrations show distince 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 and paper mill waste. One interesting byproduct 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 XIV, 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.

## C. Field Studies of Tracer Conservation

The results of the field studies of tracer conservation are shown in Tables XVII and XVIII. The detailed Dy concentration profiles shown in Table XVII indicate that it is not until the tracer arrives at Station E or D that it becomes well-mixed with the river water. (Samples 1-8 at each location were taken at

Element*	Absolute Concentration	Range *	Relative Concentration**
Fe(%)	2.82 <u>+</u> 0.01	0.56 - 10.46	1
Na	1721 <u>+</u> 2	560 - 8025	0.06
К	1477 <u>+</u> 13	585 - 6412	0.05
Mn	291 <u>+</u> 1	129 - 3070	0.01
Zn	108 <u>+</u> 3	45 - 3750	0.004
Cr	11.4 + 0.3	6.5 - 243	0.0004
Co	3.8 <u>+</u> 0.1	30 - 36.5	0.0001
Sc	1.8 <u>+</u> 0.1	1.17 - 17.4	0.00007
As	1.65 <u>+</u> 0.01	0.67 - 32.1	0.00006
Sm	1.20 <u>+</u> 0.01	0.34 - 6.26	0.00004
Br	5.46 <u>+</u> 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

Table XVI: Absolute and Relative Elemental Abundances in Suspended

otherwise.

\*\* Normalized to Fe = 1.0

Particulates



Figure XIV



Sample	Concentration	Sample	Concentration	Sample	Concentration	Sample	Concentration
Bl	118+4	ថ	143+2	đ		ГЗ	30 + 4
B2	76+4	g	84+2	D2	64+4	. E2	11 <del>-</del> 2
B3	22+3	ប	73+1	D3	18+2	· E4	9 + 1 2
B4	41+3	C4	27+2	54	Lost	王4	24 + 2
B5	18+3	ß	32+2	D5	16+3	ES	101+3
BG	50+3	CG	10+1	DG	43+3	EG	43+2
B7	11+2	C7	10+1	D7	41+4	E7	
, B8	23+3	C8	18+2	D8	42+2	<b>Е</b> 8	11+2
		හි	14+2	60	36+3	6 <b>프</b>	304 1
				•	+	I	
Wt.Averag	e 36+1 ppt		32+0.6 ppt		34+1 ppt		26 ± 0.8 ppt
River Dis	charge Rate = 78	20 Cfs	Tracer Discharge	Rate: 8.5	15 mg/sec		

Sampling Started: 13:00

Tracer Pump started at 12:30

	Distance from cion Injection Site	Time Sampling Started	% Original Tracer Remaining in Solution
B 35.9 <u>+</u> 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	89.28
* Concentrations are in	ppt (parts per trillion.		
Amount of Dy used = 1.	15.6219g River Disc	iharge Rate = 7820 Cf	s (Cubic feet/sec)

Concentration of Dy/ml of Tracer = 8,515 mg/ml

Tracer Purp Injection Rate = 1.0 ml/sec

roughly equally spaced locations normal to the direction of the river flow.) It can be seen that at Stations B and C the tracer concentrations tend to be higher along the bank of the river where the tracer was being injected.

At each sampling station, the Dy concentration profile was integrated and compared to the predicted amount of Dy in the river assuming no tracer loss and using known values of the river flow rate. The results, as shown in Table XVIII indicate that  $\sim 89\%$ of the tracer can be accounted for in our concentration profiles.

### V. CONCLUSIONS

The principal accomplishments of this research project may be summarized as follows:

1. A theory of how to best utilize stable, activable tracers to replace the use of fluorescent dye tracers and radio tracers in tracing fluid-bound materials in fresh waters was formulated, tested and verified.

 In a series of laboratory tests, the tracer was found to be stable in natural fresh water containing suspended sediment material.

3. The naturally occurring levels of the rare earth elements in the fresh water system under study, the Willamette River of western Oregon, were found to be quite low and in no way interferred with the use of these elements as tracers.

4. Effective means of injecting the tracer elements into effluent discharges were devised and tested along with suitable collection and analysis techniques to measure the tracer concentrations.

5. Background studies of the trace element content of the Willamette River water (dissolved species), suspended particulate matter and bottom sediments were made leading to many interesting results and conclusions.

- a. The trace element content of the sediments taken at each of the 23 sampling sites is relatively constant from site to site and agrees quite well with the trace element content of Oregon soil. There appears to be little, if any, anthrogenic contributions to the trace element levels in the sediments.
- b. The suspended particulate matter has a trace element content similar to that of the bottom sediments.
- c. The trace element content of the dissolved species shows statistically significant variations from one sampling site to another reflecting the entry of pollutant material into the Willamette River.
- d. The technique of fractionating the dissolved material into cationic and anionic fractions shows great promise as a method of developing more accurate "fingerprints" of pollutant sources.

6. A single tracer experiment in the Willamette River has demonstrated the conservative behavior of the tracers in the Willamette River.

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## APPENDIX

Element Abundances in the Willamette River System.

	Sampling Site: Eugene	River A	111e: 175		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( b/br )	( 5/61 )	( Tm/bu )	( Tm/Sn )	( Tm/gn )
Al	8.63 + 0.03%				
P.C	5.77 + 0.043	2.46 + 0.023	13 + 7	29 + 4	47 + 8
Ca Ca	3.97 + 0.97%	1			
Na	2,21 + 0.01%	2340 + 3	121 + 1		121 + 1
М	0.84 + 0.05%	1380 + 90	42 + 2	]	42 + 2
Ч.	0.75 + 0.01%	1	3		1
Nin	954 + 2	400 + 49	1.0 + 0.3		1.0 + 0.3
ដ ខ្ល	390 + 39	1			
Δ	133 + 3				
Zn		1608 + 232	3 + 1		3 + 7 9
Cr	91 + 3	10 + 1	12 + 0.1	0.96 + 0.06	13 + 0.1
N	40 + 24	49 + 21	I		1
2	33 + 11	I			
ő	31 + 1 31				
La	15 + 1				
00	23 + 0.3	11 + 2	0.0020 + 0.0005	0.086 + 0.008	0.088 + 0.008
сл С	20 + 0.1	8.8 + 0.3	0.0048 + 0.0002	0.0036 + 0.0003	0.0084 + 0.0004
54	6.2 + 0.3	1	I	I	
HC)	4.00 + 0.01	2.06 + 0.07	0.021 + 0.001		0.021 + 0.003
대	2.9 + 0.1	1	I		
ŢIJ	3.4 + 0.2				
χp	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	I	0.0003 + C.0001
3	1.5 + 0.1				
- SO	1.3 🕂 0.1	2.8 + 1.8	0.020 + 0.012		0.020 ± 0.01
כי	0.8 + 0.1				
Sb	1.0 + 0.0				
Ta	0.6 ± 0.1				
In	0.3 + 0.1				
d'L	7.0 + 9.0				

Table Al Elemental Abundances in Willamette River System

	Samoling Site: Harri	shirra 1 - River	Mile: 164		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element "	Sediment	Farticulates	Cations	Anions	ions
	(5/5d)	(5/5d) .	(Tu/bu)	(lm/gn)	(Tm/gn)
Al	8.96 + 0.04%				
0 F4	7.15 + 0.01%	2.21 + 0.01%	20 + 5	7 + 1	27 ± 5
Ca Ca	3.22 + 0.16%	l			
RA	1.63 + 0.01%	2150 + 37	160 ± 1		160 ± 1
М	0.73 + 0.01%	1321 + 111	27 + 2	·	27 ± 2
ŤÌ.	1.01 + 0.01%	1	1		Ĩ
uM .	1225 + 3	423 ± 17	1.0 + 0.3		1.0 ± 0.3
Ba	484 + 13	()			
Δ	178 + 3				
Zn	I	2231 + 1550	15 + 2		15  + 2
Сĸ	133 + 1	36 + 10	17.0 + 0.1	0.60 + 0.03	17.6 ± 0.1
Ni	53 + 23	< 30			
ধ্য	32 +1				
20	37 + 0.2				
La	20 + 1				
Ŀ9	31 + 0.1	11 + 2	0.45 + 0.002	0.052 + 0.006 0	).502·+ 0.006
S S	24 + 0.1	7.8 + 0.3	0.0022 + 0.0001	0.0056 + 0.00010.	0078 + 0.0001
As	5.6 + 0.2	1	[		
ES S	4.9 + 0.01	2.69 + 0.05	0.028 + 0.001	0	0.028 ± 0.001
Th	3.41 + 0.01				
Н£	4.53 + 0.01				
ах	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
2	1.5 + 0.1				
SS	2.1 + 0.1	2.8 + 0.2	0.037 + 0.014	0	0.037 <u>+</u> 0.014
1	1.2 + 0.1				
Sb	0.74 + 0.03				
d E	0.67 + 0.06				
Lu	0.35 + 0.01				
цр.	0.57 + 0.12				

Elemental Abundances in Willamette River System Table A2

	Sampling Site: Harn	risburg 2 River	Nile: 160 .		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( b/bn )	( 5/51 )	( Tm/bu )	( [m/bu )	( Tm/bu ).
71	8.25 + 0.04%				
0	6.22 + 0.01%	2.55 + 0.54	65 + 8	4 + 1	69 <del>+</del> 8
Ca	3.57 + 0.14%	I			
Na	2.18 + 0.01%	5814 + 185	134.0 + 0.3		134.0 + 0.3
X	0.89 + 0.04%	3518 + 296	36 + 2		36 + 2
Ti	0.74 + 0.05%	1	1		I
Ivin	944 + 2	682 + 85	1.2 + 0.3		
Ba	483 + 9	t			
Λ	157 + 2				
Zn	I	1356 + 41	13 + 2		13 + 2
CK	112.0'+ 0.5	243 + 4	35 + 0.01	0.36 + 0.03	35.36 + 0.03
Ni	52 + 15	255 + 107			ĺ
Rb	33 + 1	1			
0	30.0 + 0.1				
La	16.4 + 0.9				
	26.9 + 0.1	38 + 10	0.27 + 0.01	0.052 + 0.006	0.32 + 0.01
0 00	22.0 + 0.1	13 + 1	0.025 + 0.001	0.007 + 0.001	0.032 + 0.001
As	6.5 + 0.2	1	1	1	
E	3.99 + 0.01	2.85 + 1.01	0.021 + 0.005		0.021 + 0.005
rin	2.80 + 0.03	ſ.			
HE	4.16 + 0.06				
RP	2.58 + 0.01				
ងព	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		
NC	1.20 + 0.05				
SO	1.83 + 0.10		0.059 ± 0.012		0.059 ± 0.012
D	1.04 + 0.09				
Sb	0.73 + 0.01				
Ta	0.53 + 0.01				
Eu	0.29 + 0.01				
TD	0.51 + 0.11				

Table . A3 Elemental Abundances in Willamette River System

	Sampling Site: Peori	ia 1 River Mi	le: 144.9		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( 5/51 )	( 5/51 )	( Tu/Su )	( Tm/Gu )	( lm/gr )
IA	9.51 + 0.05%				
0 Li	5.28 + 0.02%	3.19 + 0.16%	15 <del> </del> 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
м	0.91 + 0.09%	2456 + 84	30 + 2		30 ± 2
÷E	0.74 + 0.048				
Nn	758 + 1	589 + 73			
Ва	540 + 15	I			
٨	136 + 4				
Zn	1	1852 + 661	12 + 2		12 ± 2
CK C	93.6 + 1.9	27 + 6	16.00 + 0.08	0.20 + 0.03	16.20 + 0.08
ĬN	57 + 20	<55	I		
Rh	32 + I				
، د د	34.8 + 0.3				
0 1	19.7 + 0.1				
0	23.6 + 0.1	14 + 1	0.038 + 0.02	0.018 ± 0.005	0.056 ± 0.02
	19.4 + 0.1	12.0 + 0.2	0.004 + 0.0001	0.00046 + 0.00012	0.004 + 0.0001
79	4.7 + 0.3	I			
ES	4.86 + 0.01	2.70 + 0.04	0.024 ± 0.001		0.024 + 0.001
HL HL	3.03 + 0.03				
ΗĒ	4.19 + 0.07				
47	2.60 + 0.04				100 COM 8 121 G 12
Br	3.56 + 0.20	26 + 2	2.08 ± 0.14	2.08 ++0.14	2.08 + 0.14
19	1.21 + 0.04	0.06 + 0.02			
t E	1.34 + 0.03	1		2	
	1.75 + 0.07		0.053 + 0.012	2	0.053 + 0.012
3:	1.06 + 0.06		I		
2, U C	0.67 + 0.02				
2 6	0.53 + 0.02				
1 2	0.35 ± 0.01				
.Q. Е	0.78 + 0.12				

Table A4 Elemental Abundances in Willamette River System

2		*			
	Sampling Site: Peoris	. 2 River Mile:	140.9	•	Sour Construction of the second se
		Suspended	Dissolved	Dissolved	TOTAL LUCATOR
Element	Sediment	Particulates	Cations	SHOTHA.	LUIS ,
	( 5/51 )	( b/bn )	( Tm/Bu )	( TW/BU )	1
AL	9.22 ± 0.05%				
ЪС Г	5.34 + 0.01%	3.76 ± 0.12%	22 + 5	-1 + 1- -1 -1	29 + 5
Ca	3.41 + 0.17%				
Na	2.18 + 0.01%	7143 + 30	90.0 + 0.3		90°0 + 0°3
X	0.94 + 0.10%	3950 + 115	18 + 2		18 ± 2
Τi	0.71 + 0.04%				
Nin	891 + 2	546 + 69	0.42 + 0.03		0.42 ± 0.03
Ba	508 + 15				
~ ~	153 + 3				91 25
22	1	689 + 89	16 + 2		16 + 2
l č	100.8 + 2.1	77 + 6	32.0 ± 0.1	0.17 + 0.033	32.2 ± 0.1
in in	58 + 30	<55			
1	35 + 1			- a	
2 8	30.5 + 0.2			-	
PI	17.8 + 0.1			54	
8	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
NG.	5.5 + 0.2	ſ	1	1	
ыs	4.2 + 0.01	•			
цц	2.76 + 0.09				
Н£	4.23 + 0.07				
र्वप्र	2.39 + 0.03				
пг	2.15 + 0.12	26 + 2		4.6 + 0.03	4.6 + 0.03
na	1.22 + 0.03	0.58 + 0.01		1	ſ
5	1.26 + 0.04	ł			
SS	1.76 + 0.07				
D	1.04 + 0.01 .				
Sb	0.73 + 0.02				
Та	0.53 + 0.02				
In	0.31 ± 0.11				
412	0.70 + 0.11				

Table AS Elemental Abundances in Willamette River System

	Sampling Si	te: Fischer Susp.Parti	. Island culates	River N Dissolved	Mile: 134 S Cations	Dissolveå	Anions	Total Diss	olved
Elemen	t ( ua/a )	Surface 0 ( uq.	.6xdepth /q )	Surface ( ng/	0.6xdepth /ml )	Surface ( ( ng/	0.5xdepth /ml )	Surface 0 ( ng/ml	.6xdepth )
Al	8.82+0.03\$	5.09+0.50							
Fe	5.81+0.01%	5.09+0.50		38+8	13+6	21+5	20+6	20+10	33+6
Ca	2.66++.12%	l			I				
Na	1.82+0.02%	8025+10	1869+30	160+1	156+1			T+09T	T+00T
×	0.74+0.01%	5446+1900	4667+1070	35+7	46+6			1+02	40+0
Τi	0.75+0.04%			and the second s					
M	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								•
Δ	187+6								
Zn	ľ -	1945+452	598+202	46+5				4040	
ч	127.2+0.4	150+33	I	29+1	26+1	1.50+0.1	0.53+0.04	30.5+1.0	26.5+1.0
Nİ	59+29								
Rb	33+1								
ല്	33.3+0.2								
La	20.0+0.1	20.4+3.9	7.2+1.6						
8	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
ຽ	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	I					
Sm	4.66 +0.01	4.78+0.30	2.69+0.76	30+4 *	30+4*	29+1 *		59+4*	30+4 *
나다	2.99+0.02	1							
lif	4.26+0.05	6.29+4.22	3.44+1.96						
qд	2.78+0.03								
Вг	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						
ሯ	1.46+0.04	I							
Cs	1.80+0.08								
þ	1,54+0.13								
qs	0.62+0.01			4.7+1.5		14+7		18.7+7	
Б	0.62+0.01								
Lu	0.25++.0.02								
d'L	0.65+0.10								
*	concentration a	re in parts	per trilli	.uo.					

Table A6 Elemental Abundances in Willamette River System
				13		
	Sampling S	ite: Alba Susp.Part	ny l ticulates	River Mile: 126. Dissolved Cations	2 Dissolved Anions	Total Dissolved
lement	Sediment	Surface (	0.6xdepth µg/g )	Surface 0.6xdepth ( ng/ml )	<pre>Nurface 0.6xdepth</pre>	Surrace U. bxdeptn ( ng/ml )
Al	8.51+0.04%					
0 F4	5.21+0.02%					
Ca	3.49+0.83%					
Na	2.02+0.03%	3990+20	5520+30	110+1 103+0.2		7.0+20T T+0TT
м	0.92+0.04%	3960+294	1722+134	40+6 38+3		40+0
1	0.65+0.02%					
MN	812+2	1660+29	552+30	0.37+0.09 0.70+0.01		0.3/+0.03 0. /+0.0T
Ba	544+33					•
Δ	142+3					
Zn	l	1416+283	644+107	10.4+0.3		10.4+0.3
5	85.2+1.4	86.7+28.3	3 72.5+11.7	1	1.39+0.13 0.32+0.06	1.39+0.13 0.32+0.06
ΝĻ	56+10	I	1		1	
쉆	42+6					
ව	29.1+0.4					
La	16.9+0.1		7.33+1.68			
8	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 AS	5.0+0.3	9.3+2.1	4.4+1.5	1	1	
Sm	3.99+0.01	1.69+0.92	1.14+0.11			
Th	3.06+0.07	1	I			
Ηf	3.33+0.11		1.96+0.67			
ЧY	2.42+0.10					
Вг	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
Ъu	1.05+0.07	0.39+0.12	0.39+0.02	0.44+0.01		0.44+0.01
2	1.17 +0.06		l			
Cs.	1.49+0.12		2.27+1.12			
D	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	1				
Γα	0.32+0.01					
цЪ,	0.43+0.14					

Table &7 Elemental Abundances in Willamette River System

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System	
River	
Willamette	
5	
Abundances	
Elemental	
A8	
Table	

	Sampling	Site: Alb	any 2	Ę	ver Mile:	125.2			
		Susp.Parti	culates	Dissolve	d Cations	Dissolved A	nions	Total Dis	solved
	Sediment	Surface 0	. 6xdepth	Surface	0.6xdepth	Surface 0.0	<b>6xdepth</b>	Surface C	.6xdepth
Element .	( 5/5r )	/6n )	G )	с ,	( Tm/5	.m/6u )	1)	/6u )	( TH
AL	9.13+0.03%								
о Щ	6.64+0.03%	0.82+0.11	0.96+0.10	0					
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
М	0.90+0.17%	1080+432	1228+22	33+6	14+4			33+6	14+4
ч.	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
Ва	483+ 8								
Δ	198+4								
Zn									000 0.010 0
ყ	96+1.6	23.9+4.5				0.52+0.05 0.0	113+0.002	cu.u=zc.u	0.013+0.00z
Nİ	59+31								
쉆	42+ 7								
ć	30.5+0.5								
e S		0 5040 9	4 5641 61						
La	1.010.04			+0-0	*0115	1 3454	21-42	1645*	40+04
00	28.8+0.2	2.0041.41	4.0.41.0.	2+2 2	11-70.		- 0 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	21	
SC.	21.7+0.1	2.4+0.1	2.2+0.1	1.5+0.5*	1.8+1.0*	23+1*	*1+8		
As	5.0+0.3	3.2+0.9	10.4+0.8			135+10* 1	74+20*	135+10*	T74+20×
Sm	4.14+0.01	0.75 +0.05	0.73+0.02	,					
년 년	2.99+0.08								
Hf	3.50+0.13								
qх	2.71+0.11					and a second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second sec			
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.(	33 2.2+0.	3*1.1+0.3*			2.2 + 0.3*	1.1+0.3*
6	1.31+0.06								
S	1.53+0.15		14						
D	1.09+0.12			•					
sb	0.71+0.04		1.90+0.(	52		0.007+0.001	0	.007+0.001	
Тa	0.90+0.05		l.						
Lu	0.33+0.01								
qL	0.60+0.16								
5	1								

\* Concentrations in parts per trillion.

	Sampling	Site: Alt Susp.Part:	any 3 iculates	Ri Dissolve	ver Mile: ] d Cations	122.70 Dissolved	Anions	Total D	issolved
	Sediment	Surface (	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth	Surface	0.6xdepth
Element	( 5/51 )	/6n )	( 5/	r >	( Tm/5	6u )	( Tm/)	ř ,	( TW/5
AL	9.08+0.04%								
Э £4	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%	I	Ì						
Na	1.67+0.03%	3545+7	8340+83	40+1	123+1		5	40+1	123+1
м	0.68+0.05%	2330+312	4465+175	25+7	15+6			25+7	15+6
ᆔ	0.74+0.02%	1	1						
Mn	739+5	1166+23	3070+37 1	.3.4+0.1	15.0+0.2	6.1+0.1	11.3±0.01	19.5+0.2	26.3+0.2
Ва	439+41		l						
Δ	180+3								
Zn	ł	3750+350	3710+358	6+2	19+5			6+2	19+5
ප ප	116.7+1.8 I	124.1+39.7	239.0+44.6	1	10+0.3 0	0.08+0.01	1.06+0.08	0.08+0.01	11. +0.3
ΪN	61+26		1		1	1	ł	l	I
Rb	39+12								
e S	38.4+0.6								
C F	20.7+0.1	7.9+2.8	2222+4.2						
	041.90	0 8 4 7 8 1	36 5+4 7 1	4.0+1.0*	156410*	*01+60L	75+9*	123+10*	231+11*
3	4 · O · I · O · O			+ u 0 - E	*	*10.14	*****	** 01-1-1	4 3 TU V*
, Sa	21.5+0.1	1, 8+0.4	14.3+0.5	T. /+0.5*	2.3+0.4*	3.4+0.4	4.0.0.0	0.1+0.0	0.010.0
As	5.7+0.3	20.2+5.8	32.1+3.7			6.4+17*	98 +T2*	64 +1.7*	* T+86
Sm	5.06+0.01	3.2+0.2	4.4+0.2 0	0.026+0.00	02 0.028+0.(	003	0	.026+0.02	2 0.028+0.003
Th	3.22+0.09	I							
Н£	3.32+0.12								
дX	2.79+0.12								
Вг	1.29+0.50	104+27	130+69			16.0+0.1	10.0+0.1	16.0+0.1	10.0+0.1
ng	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*
8	1.56+0.06	1	1						
i C	1.74+0.14								
3 =	T.266+0.12								
sb	0.66+0.11								
Та	0.63+0.05								
Γu	0.37+0.01								
дĽ	0.80+0.52								

Table A9 Elemental Abundances in Willamette River System

\* Concentrations in parts per trillion.

Table Alo Elemental Abundances in Willamette River System

Dissolved	0.6xdepth ng/ml )		32+9		138+1	48+6		1 2.8+0.1			123+22	55.4+2.0				* 0 1+0 6 *	*0+00	0100	9.3+1*	1 0.31+0.01	3.1+7*	i			1 5.40+0.01	*							
Total	Surface (		29+12		122+1	39+6		01 3.2+0.			21+4	18.6+0.1				48 0+8 0		0+ATT	47+1*	0.23+0.0	32+6*	l			4.40+0.0	3.50+0.3							
d Anions	0.6xdepth		17+5					0.03+0.0				1 7.4+0.3					+1-00	× C+77	4.6+0.8*	1.31+0.01	1				1 5.40+0.01								
119.45 Dissolve	Surface		13+9									0.64+0.					+0.00	· 2+59	43+1*	0.23+0.0	I				4.40+0.0								
ver Mile:	0.6xdepth		15+8		138+1	48+6		32.8+0.1			123+22	48.0+2.0				*U LTU O	0.410.0	44+6*	4.7+1.0*		32+7*	I				*							
Ri Dissolve	Surface		16+6		122+1	39+6		3.2+0.1			21+4	L8.0+0.1				*0.40V	+0-04	*8+cc	4 ° 0+0 • 9*		2 32+6*	i				3 3.5+0.3							
bany 4 culates	).6xdepth		0.96+0.11	1	1108+10	1228+22		165+8	ľ,		502+135	1				ש נדש ע	4.0T1.0		2.2+0.1	10.4+0.8	0.73+0.03	I			12.4+1.4	0.1810.0							
Site: Al Susp.Parti	Surface ( 1 ug/	0.82+0.11	0.82+0.11	1	1151+8	1080+432	1228+22	141+12	ſ		503+137						2.0 0.7	4.7+1.0	2.4+0.1	3.2+0.9	0.75+0.28	1			12.8+1.6	0.14+0.03							
Sampling	Sediment	8.83+0.01%	5.74+0.01%	2.85+0.10%	2.25+0.03%	1.21+0.07%	1.12+0.06%	948+2	562+12	119+3	r	83.3+0.6	58+22	49+2	36 740 2		ZT. 3+0. T	21.8+0.1	18.4+0.1	6.6 +0.5	4.76+0.01	3.98+0.03	5.80+0.10	2.96+0.04	1.49+0.18	1.33+0.03	1.62+0.06	1.81+0.08	1.87+0.08	0.61+0.02	0.61+0.05	0.40+0.01	0.48+0.01
	3]ement .	TR	Fig	Ca	Na	м	Ч.	Mn	Ba	Δ	Zn	CK	N;	- 4a	2 8	e Ce	Гa	8	, Sc	As	Sm	L'h	Η£	ЧX	В۲	Eu	ß	S	Þ	Sb	ца	Гu	дŢ

Table Ail Elemental Abundances in Willamette River System

	Sampling	Site: Western Kraf	t River Mile:	118.20	
		Susp. Particulates	Dissolved Cations	Dissolved Anions	Total Dissolved
	Sediment	Surface 0.6xdepth	Surface 0.6xdepth	Surface 0.6xdepth	Surface 0.6xdepth
Element	( 5/5H ) ·	( 5/54 )	( 1@/@U )	( ng/ml )	( Tm/pr )
A	8.64+0.04%	6.26+0.4			
ъ С	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+0.2 296+0.2
Х	0.91+0.12%	6412+1770	110 <u>+</u> 9 15 <u>+</u> 1.5		110+9 15+1.5
ŢŢ	0.78+0.02%				Woodd Friday and Dispersion was been as
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
Ва	522+4				
Δ	166+4.				
Zn	I	662+202	32+6 13+1		32 +6 13+ 1
ч	94.7+0.6	143.2+28.2	12.4±2.3	0.54+0.16 0.18+0.01	12.972.3 0.0840.01
11	60+20				
22	40+1				
e U	32.5+0.5	6.			
L'a	18.9+0.1	28.0+3.5			
8	24.3+0.3	24.1+4.4	1.6+0.4 1.7+0.4	38+7 3.3+0.6 3	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* 2	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 0.2/+0.01
Sm	4.25+0.01	6.26+0.2	0.05+0.01 0.02+0.01	0	0.05+0.01 0.02+0.01
ų	3.24+0.08				
Η£	4.89+0.07				•
Хb	2.48+0.03				
Br	3.85+0.22	124.6+7.4		10.0+0.1 4.6+0.1 1	0.0+0.] 4.6+0.1
Eu	1.17+0.06	1.49+0.01 0	.0014+0.0003	0.0	0004+0.0003
Å	1.37+0.01	Ľ			
S	1.74-0.10				
D	1.43+0.06				
Sb	0.54+0.01	5.8+2.8			
Та	0.60+0.05				
Lu	0.38+0.01				
ЧL	0.58+0.01				

System	
River	
Willamette	
.H	
Abundances	
Elemental	
Table Al2	

																													1		
ssolved 0.6xdepth /ml )	F+00	1.04	L. (+0, 53 f	71+8		8 7 80+0 08			35+6	114.1+12	I					* 10 64.0 0.4			× (+2,	,			41+0.2	10							
Total Di Surface ( ng	C FTC L	5	0 0 to 0 t	10-10-1					420+6	100.2+12	I				*01190				x 5+ 17				0440	7.01-00.1							
Anions .6xdepth ml )		Ø1107		2						1.11+0.08	ł					+ + + + + + + + + + + + + + + + + + +	4.0++.+	0.0110.03					41+0.2								
3.45 Dissolved Surface 0 ( ng/)		30+10					TO .0100 .0			0.18+0.01	1					+ + + + + + + + + + + + + + + + + + + +	6.8+0.6*	TO.01110.01				1000 C	68+0.1								
r Mile: 118 Cations .6xdepth ml )		101		1.1.0.02	21-17		1.80+0.00		2576	113+12	1					84+TO*	5.6+3.0*	5	27+4*												
 Rive Dissolved Surface 0 ( ng/)		20+1 20+1			0+1 0		5. /0+0.08		01000	01-100 L						*0T+64	3.1+1.0*		27+5*					1.00+0.4						~	
any 5 .culates ).6xdepth (g )																															
Site: Alb Susp.Parti Surface ( ( ug/		4.61+0.23%	9009+66	6155+318			1455+26		000.0000	20/8+328	+				19.8+2.9	17.5+2.3	14.0+0.3	8,9+2.4	4.48+0.88				143 ±53	.13+0.12				03+2.3			
Sampling Sediment ( uq/q )	9.44+0.03%	5.75+0.013	2.84+0.648	2.17+0.018	0.87+0.34%	0.92+0.038	764+5	077770	T anto	L C LTO CO		011-00	1+ 55	34.9+0.0	19.4±0.1	20.3+0.2	19.6+0.1	5.6+0.3	4.76+0.01	3.26+0.08	3.48+0.12	2.81+0.12	3.49+0.61	1.34+0.03 1	1.58+0.07	1.53+0.14	1.11+0.11	0.69+0.04 8	0.63+0.04	0.37+0.01	0.64+0.16
Element.	R	0 4	Ca.	Na	×	т;	ų	Ba	Δ	Zn	5	TN	쉺	e	La	8	Sc.	As	Sm	Th	Н£	qX	Br	Eu	'n	S	þ	Sb	Ъа	цц	QL

\* Concentrations in parts per trillion.

	Sampling Site: Inde	pendence 1 River Mil	e: 99.0		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( b/bn )	( 5/5r )	( Tm/gn )	( Tm/Bu )	( Tw/bu )
Al	9.28"+ 0.05%				
ъe	5.21 + 0.02%	1.89 + 0.03%		8.74 ± 1.00	8.74 ± 1.00
Ga	3.12 + 0.10%	1			
Na	2.03 + 0.01%	733 + 5	171 + 1	4	171 ± 1
Х	1.21 + 0.11%	605 + 75	36 + 6		36 + 6
ŢŢ	0.66 + 0.04%				
uM	695 + 2	238 + 2	1.46+0.03	0.033 + 0.0003	$1.49 \pm 0.03$
Ba	557 + 16	I	I	l	
Δ	123 + 3				
27	ł	53.5 + 7.8			53.5 + 7.8
i L	68.3 + 1.6	6.47 + 0.48	66.10 + 5.10		66.10 + 5.10
12	35 + 10		1		
10	34 + 1				
2 2	33.1 + 0.3				
U,	19.2 + 0.1	2.28 + 0.20	0.016 + 0.001		0.016 + 0.001
е 1		3.06 + 0.16		0.48 + 0.03	0.48 + 0.03
ვ				0 0034 + 0.0019	0.0034 + 0.0019
SC		4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4			
As	5.9 + 0.2	T-06 + 0.7		0.001 + 0.000	0.002 + 0.000
E S	4.55 + 0.01	0.44 + 0.01	0.026 + 0.001		0.026 + 0.001
L, L	3.78 + 0.09				
: 4 : 13	4.49 + 0.07				
1 2	2.59 + 0.04				
	2.15 + 0.16	3.28 + 0.20		$4.1 \pm 0.2$	4.1 + 0.2
41	1.13 + 0.05	0.13 + 0.03			
1 2	1.33 + 0.04				
7	1.97 + 0.06				
3:	1.30 + 0.03				
	0.71 + 0.03	0.19 + 0.13		0.009 + 0.003	0.009 + 0.003
	0.59 + 0.02				
T II	0.36 + 0.01				
3 .i 7 E	0.73 + 0.06				
21					

Table A13 Elemental Abundances in Willamette River System

	Samplin	g Site: Salem 1 Susp.Particulates	River Mile: Dissolved Cations	86.9 Dissolved Anions	Total Dissolved
	Sediment	Surface 0.6xdepth	Surface 0.6xdepth	Surface 0.6xdepth	Surface 0.6xdepth
Element .	( 5/51 )	( 5/51 )	( 1m/bu )	( lm/gl )	( TH/BL )
TY	9.39+0.11%	0.			
Pe	5.90+0.01%	0.56+0.12%		5.54+0.76 15.8+1.3	5.54+0.76 15.8+1.3
са Са	2.79+0.24%	1		1	1
Na	1.86+0.01%	1040+6 560+4	223 <u>+</u> 1 115+1		
X	0.77+0.05%	742+85 429+67	55+7 32+5		
τi	0.84+0.05%	1	1		
NIN	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
Ва	401+8	1	1		1
Λ	163+4				
Zn	1	61+6 45+6		0.59+0.12 1.48+0.15	0.59+0.12 1.48+0.15
გ	82.0+0.7	10.9+0.55 12.8+4.2	0.08+0.02	62+2* 276+60*	.62+2* 356+63*
ŢN	42 +13	4.53+1.48	1	1	1
<b>9</b> 2	35+2	1			
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			
g	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*
шS	4.55+0.06	0.45+0.09 0.34+0.01	23+1* 21+1*	1	28+1* 21+1*
цТ	3.48+0.04	0.46+0.06 0.29+0.05			1
Hf	4.93+0.10	0.87+0.27 0.30+0.10			
дX	2.59+0.03	0.42+0.09 0.23+0.08			
Вг	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
Бu	1.30+0.06	0.12+0.03	21	1	
6	1.43+0.05				
S	1.74+0.12				
n	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				
ДЪ	0.73+0.02				

\* Concentrations in parts per trillion.

Table A15 Elemental Abundances in Willamette River System

	Sampling Site: Sale	m 2 River Mil	e: 84.9		
		Suspended	Dissolved	Dissolved	Total Dissolved
lement	Sediment	Particulates	Cations	Anions	ions
	( 5/51 )	( 5/5n )	( Tm/bu )	( Tm/6n )	( Tm/gn )
Alz	9.01 + 0.07%				
щe	5.80 + 0.01%	$3.67 \pm 0.01$ %		48 + 3	48 + 3
Ca	2.86 + 0.14%				
Na	1.94 + 0.01%	4500 + 30	25 + 1		
К	0.86 + 0.06%	2974 + 36	19 + 2		
Ť	0.69 + 0.01	1	l		
Min	666 + 2	704 + 6	1 + 0.01	70 + 0.05	71 + 0.05
Ba	390 + 10	ſ	l		
2	160 + 4				
Zn	ł	631 + 41		3.41 + 0.23	3.41 + 0.23
CK	83.8 + 0.7	115.7 + 25.7	0.57 + 0.07	0.66 + 0.16	0.66 + 0.16
ĻΝ	42 + 10	I	I	1	I
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
00	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
막다	4.72 + 0.04	1.80 + 0.50	1		
НÉ	5.38 + 0.11	3.86 + 0.60			
д	2.72 + 0.04	I			
Вґ	6.88 + 0.34	80 + 19	•	48.56 + 2.73	48.56 + 2.73
Бu	1.45 + 0.06	0.99 + 0.17			1
6	1.69 + 0.06	3.08 + 0.61			
Cs	1.69 + 0.04	1			
D	1.74 + 0.01				
Sb	1.56 + 0.03	2.50 + 0.80.		0.044 + 0.004	0.044 + 0.004
e E	0.71 ± 0.05	ŀ		1	1
Lu	0.32 + 0.01				
άŢ,	0.96 + 0.02				

Table A16 Elemental Abundances in Willamette River System

	Samoling Site: Sale	im 3 River Mi	le: 84.9		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	. Sediment	Particulates	Cations	Anions	ions
	(5/51)	( 5/51 )	( Tm/54 )	( Tm/gn )	( Tm/gn )
Al	10.21 + 0.08%				
G Li	5.80 + 0.01%	3.56 + 0.16%	60 + 8	50 + 5	110 +9
Ca	2.00 + 0.19%	1	1	1	
Na	1.54 + 0.02%	3341 + 17	442++ 0.2		42 ± 0.2
м	0.80 + 0.05%	3039 + 162	19.5 + 2.3		19.5 + 2.3
Ti	0.89 + 0.01%	1			1
M	719 + 2	1127 + 7	24.0 + 0.1	0.50 + 0.005	24.5 + 0.1
Ba	391 + 10	l		l	1
Δ	188 <u>+</u> 1				
Zn	1	573 + 86	I0 + 1		
С С	01.0 + 1.0	I	l,	0.24 + 0.06	0.24 + 0.06
Ņİ	36 + 15			1	1
QN	46 + 3				
00	39.8 + 0.9	16.0 + 5.9			
ų L	$24.3 \pm 1.4$	$14.7 \pm 1.5$	0.025 + 0.003		0.025 + 0.003
Q, I	27.3 + 0.3		0.016+ 0.002	0.0040 + 0.0007	0.020 + 0.002
00	22.9 + 0.1	9.2 + 0.3	1000.0 +6000.0	0.0076 + 0.0007	0.0085 + 0.0007
0 0	7.0 + 0.3	8.3 + 1.4	I	1	1
E U	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			1
Нf	6.22 + 0.11	3.14 + 1.27			
dX A	3.02 + 0.04	ſ			
Br	7.05 + 0.25	62 + 3		3.12 + 0.05	3.12 + 0.05
En E	1.48 + 0.06	0.73 + 0.03			1
Ë	1.30 + 0.08	I			
a č	2.19 + 0.06	2.15 + 1.20			
3 =	1.81 + 0.06	1			
sb	0.94 + 0.02	0.68 ± 0.20		0.04 + 0.004	0.04 + 0.004
Та	1.13 + 0.08				
Гц	0.37 + 0.06				
Д,	1.04 + 0.02				

Table A17 Elemental Abundances in Willamette River System

	sampling site: si	alem 4 River N	Mile: 82.0 Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( 5/51 )	( b/br )	( lm/ml )	( Tm/bu )	( Tm/En )
Al	8.91 + 0.11%				
ъe	5.68 + 0.01%	5.02 + 0.12%		19.1 + 1.7	19.1 ± 1.7
Ca	2.62 + 0.13%	ł		l	
Na	1.76 + 0.02%	813 + 5	89.0 + 0.5		89.0 + 0.5
м	0.90 + 0.05%	585 + 72	33.0 + 4.8		38.0 + 4.8
Tİ	0.88 + 0.06%	1	1		I
uM	1146 + 2	130 + 1	7.4 + 0.1	0.035 + 0.001	7.4 + 0.1
Ba	489 + 17	I	I	1	
Δ	180 + 5				
Zn		148 + 4		1.70 ± 0.30	1.70 ± 0.30
ყ	94 + 1	119 + 4	0.88 + 0.12	0.26 + 0.06	. 1.14 + 0.18
Nİ	36 + 12	I	1	ľ	
ch A	39 + 2				
Ce	40.0 + 0.3	1.65 + 0.39			
La	25.8 + 0.1	1.92 + 0.15			
о С	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
ыS	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			
Η£	5.64 + 0.11	0.38 + 0.11			
КЪ	2.59 + 0.03	1			
Br	3.58 + 0.26	4.20 + 0.24		4.48 +0.21	4.48 ± 0.21
пд	1.21 + 0.07	0.10 + 0.03			
A	1.53 + 0.03				
Cs	2.21 ± 0.11				
D	2.22 ± 0.11				
Sb	0.45 + 0.02	0.10 + 0.05		0.012 + 0.003	0.012 + 0.003
Та	0.80 + 0.03	1			
Гu	0.43 + 0.01				
TD	0.46 + 0.01				

Table A18 Elemental Abundances in Willamette River System

	sampling Site: Ne	wburg 1 River M	ile: 52.50		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	. Anions	ions
	( 5/54 )	( b/bd )	( lm/gr )	( lm/pn )	( Tu/bu )
Al	8.91 + 0.11	+			
P.C	5.68 + 0.01	10.54 + 0.35		14 + 2	14 ± 2
Ca Ca	2.62 + 0.13	1		I	
RN R	$1.76 \pm 0.02$	3.32 + 0.02	1.0 + 0.1		110 + 0.1
Y.	0.90 + 0.05	2.18 + 0.07	-   -   -		
i.	0.88 + 0.06				
1:n	1146 + 2	2500 + 32	0 76 + 0.03	0 15 + 0.001	0.91 + 0.03
និង	489 + 17				
Δ	180 + 5				
Zn	I				
ы С	04 + 1	292 + 20		0.36 + 0.09	0.36 + 0.09
N.	36 + 12	-1		I	
1 1 1	39 + 2				
i O	40.0 + 0.3				
1 L	25.8 + 0.1	47.9 + 2.1			
	24.3 + 0.1			0.015 + 0.003	0.015 + 0.003
	20.3 + 0.1	38.0 + 0.6		0.0030 + 0.0002	0.0030 + 0.0002
	6.8 + 0.4	28 O + 0		0.097 + 0.007	0.097 + 0.007
2	5.47 + 0.01				0.003 + 0.0005
100	4.61 + 0.09	-1 -1			I
1 1	5.64 + 0.11				
цы Кр	2.59 ± 0.03				
i fa	3.58 + 0.26	170.02 + 4.13		7.5 + 0.01	7.5 ± 0.01
n E	1.21 + 0.07	1.96 + 0.46	0.001 + 0.0007		0.001 + 0.0007
8	1.53 + 0.03	1.80 ± 0.30			
1 80	2.21 ± 0.11				
	2.22 + 0.11				
יי כ ט כי	0.45 + 0.02			0.015 + 0.002	0.015 + 0.002
	0.80 ± 0.03				
, a	0.43 + 0.01				
19	0.46 + 0.01				

Table A19 Elemental Noundances in Willamette River System

	Sampling Site: Ne	ewburg 2 River Mile:	50.50		
		Suspended	Dissolved	Dissolved	Total Dissolved
Element	Sediment	Particulates	Cations	Anions	ions
	( 5/5r )	( 5/5t )	( lm/pn )	( Tm/2n )	( lm/sn )
Al (%)	8.94 ± 0.10				
Fe (%)	5.86 + 0.02	4.03 + 0.01	13 + 4	17 17 17	19 + 4
C3 (%)	2.85 + 0.24		I		
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
14 (%) 14	0.82 + 0.01	1	1		1
ų	961 + 2	0.24 + 0.001	1.1 + 0.1	0.05 + 0.001	1.1 + 0.1
52	553 + 9	I	1		I
2	168 + 6				
цZ					
Cr	90 + 1	101 + 6	26 + 0.1	0 30 + 0 01	26.4.4.0.1
Ņ	40 + 10		-1	-1	H
2	51 + 13				
00 CO	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
SG	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
с Ц С	4.82 + 0.04	4.37++ 0.07	0.024 + 0.004		0 024 + 0.004
T'T	4.38 + 0.03	1	-		
44	4.88 + 0.11				
ďΣ	2.27 + 0.29				
Вг	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
2	1.98 + 0.08	4.60 + 0.93	1		1
SO	2.35 + 0.70	1			
D	2.05 + 0.13				
Sb	0.63 + 0.02	4.17 + 0.59		0.032 + 0.002	0.032 + 0.002
ы Б	0.83 + 0.04	I		I	
Lt	0.53 + 0.01				
QH	0.81 + 0.06				

Table A20 Elementul Noundances in Willamette River System

	Sampling Site:	Newburg 3 Suspended	Fiver Mile: 48.00 Dissolved Cations	Dissolved Anions	Total Dissolved
	Sediment	Particulates	Surface 0.6xdepth	Surface 0.6xdepth	Surface 0.6xdepth
Element	( 5/511 )	( 5/5r )	( Tu:/bu )	( Im/gn )	( Tw/5u )
Al	9.28 + 0.12 %				
C C	5.83 + 0.01 %		4 + 0.5	5.6 + 1.4	9.6 + 1.5
g	3.25 + 0.27 %		1	1	1
na	2.06 + 0.02 %	0.310 + 0.02 %	118 + 0.1		118+ 0.1
х	0.98 + 0.02 %	0.53 + 0.02 %	1		1
Ч.	0.86 + 0.05	1			
N.N.	812 + 2	2020 + 12	2.67 + 0.03	0.08 + 0.002	2.75 + 0.03
Ba	559 + 9	1	1	I	, I
Δ	161 + 4				
Zn					
CK	94 + 1	37 + 11		0.019 + 0.005	0.019 + 0.005
Ni.	38 + 11	I		1	1
52	46 + 13				
S	43.7 + 0.2	18.0 + 8.2			
ца Та	23.6 + 0.1	10.9 + 0.7			
8	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 + 0.002
As	6.6 + 0.2	$6.0 \pm 1.1$		0.022 + 0.006	0.022 + 0.006
Sm	4.68 + 0.01	2.50 + 0.08	0.026 + 0.0004	1.	ł
L'L	4.40 + 0.03	1	-		
4	4.50 + 0.11				
C'Y	2.06 + 0.29				
ы М	2.21 + 0.12	50.76 + 1.41		5.0 + 0.05	5.0 + 0.05
ц Ш	1.52 + 0.06	0.84 + 0.28	0.0015 + 0.0004	I	0.0015 + 0.0004
2	2.14 + 0.04				l
Cs.	$2.41 \pm 0.08$				
þ	1.54 + 0.11				
S.5	0.56 + 0.01	3.56 ± 0.63		0.085 + 0.001	0.085 + 0.001
ស [-1	0.80 + 0.03				
11	0.47 + 0.01				
Ω L+	0.72 ± 0.01				

Table A21 Elemental Abundances in Willamette River System

TODIC 22					
	Sampling Site:	Wilsonville l Suspended	River Mile: 43.50 Dissolved Cations	Dissolved Anions	Total Dissolved
	Sediment	Particulates	Surface 0.6xdepth	Surface 0.6xdepth	Surface U. CMGepti
Element	( 5/5:1 )	( 5/51 )	( Tu/bu )	( THI/BU )	
AL AL	8.999 <u>+</u> 0.11%				
С Гщ	5.19 + 0.04%	$2.80 \pm 0.11$		3.6 ± 1.2	3.6 ± 1.2
Ca	3.56 + 0.54%				
aN Na	1.84 + 0.01%	$1.02 \pm 0.01$	102 ± 0.1		102 + 0.1
×	1.00 + 0.24	0.37 + 0.01%	l		Ĩ
i L	0.72 + 0.05%				
MM	643 + 1	$1450 \pm 9$			
190 L	492 + 66				
D	$164 \pm 5$				
Zn					
СK	93 + 4	146 + 10		0.290 + 0.007	0.290 + 0.007
- Z	32 + 19	1		1	1
22	30 + 12				
පී	39.4 + 1.0	12.0 + 5.8			
La	22.4 + 0.2	11.1 + 0.8			
8	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
Sil	5.25 + 0.02	3.16 + 0.08	0.029 + 0.00043	I	0.029 + 0.0004
с Н	3.85 + 0.22	I	I		ſ
44	3.77 ± 0.68				
d'Y	1.79 ± 0.31				
ы m	1.69 + 0.49	57.39 + 1.45		5.42 + 0.05	5.42 + 0.05
ក ជ	1.37 + 0.05	1.00 + 0.23	0.00130 + 0.00038	1	0.00130 + 0.00038
8	$1.51 \pm 0.05$	1.20 + 0.60	1		I
Cs	1.74 + 0.15				
p	1.41 + 0.21				
C2 S	0.62 ± 0.10	$1.25 \pm 0.60$		0.016 + 0.0016	0.016 + 0.0016
ପ E-1	0.74 ± 0.08				1
n Lu	0.38 ± 0.03				
цр,	0.66 + 0.17				

n Willamette River System

System	
River	
Willamette	
ц.	
Abundances	
23AElemental	
Table	

10 D	0 0
, (	) (
0.2	0.2
0.02	0.02
0.0004	0.000
0.0003	0.000