



**SELENIUM AND OTHER TRACE ELEMENTS IN AIR SAMPLES
COLLECTED NEAR THE WOOLEY VALLEY PHOSPHATE MINE WASTE
PILE,
Angus Creek and Little Long Valley, Caribou County, Idaho**

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TABLE OF CONTENTS

ABSTRACT	3
INTRODUCTION.....	4
Background	4
Environmental Concerns—Se and other trace elements.....	5
LOCATION	5
STUDY DESIGN AND SAMPLE COLLECTION	6
RESULTS.....	7
ACKNOWLEDGMENTS.....	9
REFERENCES CITED	10

FIGURES

Figure 1. Location map of study area showing air sampling sites.

Figure 2. Air sampling train used to collect volatile Se species.

TABLES

Table 1. Concentration of Se collected from air samples taken at two locations in Little Long Valley, Idaho. Site 6-20 is at the base of the Unit 4 dump of Wooley Valley Mine, and site 6-21 is approximately 1.5 km northwest of the dump.

ABSTRACT

This report presents analytical results of determinations of selenium and selected other trace elements for air samples taken near the Unit 4 waste rock dump of the Wooley Valley phosphate mine in southeastern Idaho. The purpose of the study was to determine if selenium and other geoenvironmentally-significant volatile trace elements that are present in the waste rock of the dump are also present in the nearby atmosphere. The dump is approximately 4 million m³ in volume. Twenty-four hour air samples were taken in June 2000 at two locations along Angus Creek in Little Long Valley, Idaho. The sampling site was located in a wetland at the toe of the waste dump through which drainage from the waste dump travels. The wetland is a candidate source for the release of volatile trace elements including selenium from the soil and/or plants. The wetland site was compared to a nearby background site. The results indicate that small but measurable elevations of selenium concentration, 40 – 50 ng/m³, occur in the near-ground atmosphere at the wetland compared with the background location. No other trace elements had detectable elevated concentrations at the wetland site.

INTRODUCTION

Background

U.S. Geological Survey (USGS) geologists have studied the Permian Phosphoria Formation in southeastern Idaho and the Western U.S. Phosphate Field throughout much of the twentieth century. In response to a request by the U.S. Bureau of Land Management (BLM), a new series of resource and geoenvironmental studies was initiated by the USGS in 1998. Present studies involve many scientific disciplines within the USGS and consist of (1) integrated, multidisciplinary research directed toward resource and reserve estimations of phosphate in selected 7.5-minute quadrangles; (2) elemental phase associations and mineralogical and petrochemical characteristics; (3) mobilization and reaction pathways, transport, and disposition of potentially toxic trace elements associated with the occurrence, development, and use of phosphate rock; (4) geophysical signatures; and, (5) improving the understanding of depositional origin.

To carry out these studies, the USGS has formed cooperative research relationships with: two Federal agencies, the Bureau of Land Management (BLM) and the U.S. Forest Service (USFS), which are responsible for land management and resource conservation on public lands and with five private companies currently leasing or developing phosphate resources in southeastern Idaho, including Agrium U.S. Inc. (Rasmussen Ridge mine), Astaris LLC (Dry Valley mine), Rhodia Inc. (Wooley Valley mine-inactive), J.R. Simplot Company (Smoky Canyon mine), and Monsanto Co. (Enoch Valley mine). Because raw data acquired during the project will require time to interpret, the data are released in USGS open-file reports for prompt availability to other workers. The USGS open-file reports associated with this series of resource and geoenvironmental studies are submitted to each of the Federal and industry collaborators for technical comment; however, the USGS is solely responsible for the data contained in the reports.

Approximately 12 percent of the nation's annual demand for phosphate is satisfied by the mining of the Permian Phosphoria Formation in the northwest United States. This formation is a marine sedimentary phosphorite deposit that extends over a 5-state region (McKelvey and others, 1959). Service (1966) provided an evaluation of the western phosphate industry in Idaho and a brief description of the mining history, ore occurrence, and geology. More detailed discussion of the Phosphoria Formation in the Western Phosphate Field is given by McKelvey and others (1959). Cressman and Swanson (1964) discussed detailed stratigraphy and petrology of these same rock units in nearby southwestern Montana. Gulbrandsen and Krier (1980) discussed general aspects of the large and rich phosphorus resources in the Phosphoria Formation in the vicinity of Soda Springs, Idaho. Gulbrandsen (1966, 1975, and 1979) summarized bulk chemical compositional data for various lithologies of the phosphatic intervals in the Phosphoria Formation.

In the Little Long Valley study area in southeastern Idaho, the Meade Peak Member—the phosphatic unit of the Phosphoria—occurs as a folded, often steeply-dipping unit with elongate surface exposures or near surface occurrence with north to northwest strike. Depending on the dip of the strata, a typical phosphate mine will be several hundred meters deep and several km long. Over the 15 to 20 year life of a typical

mine, 20 to 40 million tonnes of ore will be extracted and an amount of waste shale and chert of 2 to 5 times this amount will be generated and require disposal.

The Meade Peak is approximately 50 to 55 m thick. It has two phosphate ore zones, a lower and upper one of approximately 10 and 5 m thickness, respectively. The two ore zones are separated by a middle waste unit of shale that is approximately 18 to 20 m thick. Stratigraphy and description of measured sections at each of the four working mines in southeastern Idaho are summarized in reports by Tysdal and others (1999, 2000a, 2000b, and 2000c). When the formation is mined, the two ore zones are removed and the middle waste shale is removed and backfilled into the mine pit or placed in a cross-valley fill waste pile.

Environmental Concerns—Se and other trace elements

Elevated concentrations of Se and other geoenvironmentally-significant trace elements (e.g. As, Cd, Tl, U) within the middle waste shale of the Phosphoria have raised concerns about the introduction of these trace elements into the ecosystem as a result of mining and disposal of the waste shale. The purpose of the present study is to determine if any detectable amount of the Se or any other volatile trace elements in the vicinity of the Unit 4 dump of the Wooley Valley Mine is being released to the atmosphere as a gaseous species. A table in Piper and others (2000) summarizes enrichments of Se that occur in this area in various components of the ecosystem, with the exception of the atmosphere.

LOCATION

Figure 1 shows the wetland and background locations, labeled 6-20 and 6-21 respectively, where the air samples were taken. The air samples were collected in June 2000 from within Little Long Valley, which lies approximately 32 km northeast of Soda Springs, Idaho. This is within a region of southeastern Idaho that has had extensive phosphate mining over the past several decades and currently has four active phosphate mines. The main sample site is proximal to the headwaters of Angus Creek. It was chosen because these headwaters drain a wetland at the toe of the Unit 4 waste pile of the Wooley Valley phosphate mine. The dump is approximately 4 million m³ in volume (W. Johnson, BLM, 1999, oral communication; waste dump tonnage is estimated at 6 to 8 megatons and assumed density is about 1.5 ton/yd³). Furthermore, extensive geochemical sampling and analyses have been performed on solid, aqueous, and plant samples from this locale (Herring and others, 1999, 2000a, 2000b, 2000c; Stillings and others, 2000). Notable enrichments of Se and other trace elements occur in some samples of all three types of substrates at this locale.

STUDY DESIGN AND SAMPLE COLLECTION

It has been well established (Herring and others, 1999, 2000a, 2000b, 2000c) that Se is highly enriched in rocks of the Meade Peak in southeast Idaho. Furthermore, Se is present in components that are labile under weathering and/or other alteration processes. The primary purpose of this study is to gather information regarding the extent to which gas phase Se compounds and other volatile trace elements might enter the atmosphere at a reclaimed phosphate mine waste dump that contains middle waste shale from the Meade Peak. Note that this study was not designed to be an extensive air monitoring effort covering a large geographic area over an extended period of time. Rather, this work focuses on obtaining a snapshot of the magnitude of total airborne Se species through one diurnal cycle at a site where geological, biological, and hydrological conditions likely favor the formation of vapor phase compounds of Se and other volatile trace elements.

The wetland site, 6-20 on figure 1, is located in a marshy area containing grass, forbs, and willow at the toe of the Unit 4 dump, which drains as seeps and as sheet flow through the wetland. Seeps in this area drain from the base of the mine waste dump and ephemerally flow throughout the wetland. The wetland site has abundant vegetation and anoxic mud (Stillings and others, 2000)—ecosystem components that may favor the formation of volatile Se compounds due to the interaction of soil, water, and plants (Hansen and others, 1998). The background site, 6-21 on figure 1, is located 1.5 km northwest of the mine waste dump and downstream Angus Creek from the wetland site. The background site was chosen because it is in the same drainage as the wetland site, but at a distance sufficiently far and generally upwind of the wetland site such that presence of any airborne Se species from the wetland should be minimized and the Se concentration at this site should approximate background levels in this geographical area.

Airborne volatile Se compounds were collected using a conventional air sampling train as shown in figure 2. The pre-filter was a 47 mm diameter, 0.45 μm pore size TELFON® membrane filter. Its purpose was to exclude any solid phase Se species from entering the sampling train. An identical filter was placed in the sample train directly behind the second bubbling tower to prevent droplets of the reagent liquids from entering the pump. Ambient air was drawn continuously through the sampling train at a flow rate of 0.12 m^3/hr (2 L/min) over a period of 24 hours at each sampling site. A constant flow rate was maintained using a flow-limiting orifice in the sampling train just ahead of the pump. This orifice limits flow to the above number as long as a pressure differential of at least 50 kPa (approximately 1/2 atmosphere) is maintained across the orifice.

Samples were taken on consecutive days. Weather conditions during sample collections were fair, partly cloudy, with a high temperature of 18° C during the day, and a low of 7° C during the night. The reagents used in each of the gas scrubbing flasks are the same that have been used by previous workers (Zieve and Peterson, 1984; Weres and others, 1989) to collect all volatile Se compounds without regard to specific species. The first gas scrubbing flask in the sampling train contained 100 mL of 6M Ultrex nitric acid plus 25 mL of 30% Ultrex H_2O_2 ; and the second flask contained 100 mL of 0.05M NaOH plus 25 mL of 30% H_2O_2 . The inlet of the sampling train was 30 cm above the ground. Field blanks of each solution were bottled on site and were returned, along with the samples, to the laboratory for chemical analysis. As the complex chemical and/or

biochemical interactions within anoxic mud and those of plant uptake and transpiration could produce a host of different volatile selenium-containing compounds—e.g., from elemental to methylated—our experimental design was intended to include all likely compounds of volatile Se without separation of the various individual species. The combination of strongly oxidizing reagents used here permits total recovery of all vaporous selenium compounds (Hansen and others, 1998) likely to be present.

RESULTS

All sample solutions and their corresponding blanks were analyzed for Se and other trace elements using an inductively coupled plasma mass-spectrometry (ICP-MS) technique that has been previously described (Lamothe and others, 1999). The results obtained are shown in table 1. The decrease in the Se acid blank concentration on the second day of sampling is an indication that the walls of the sampling train are being leached by the vigorous agitation of the acidic solution during sampling. The concentration of Se in the air of the wetland at the base of the waste dump is elevated 7-fold compared to the background site further down valley. These data indicate that small but measurable amounts of Se are entering the atmosphere due to biological and environmental conditions that exist in the vicinity of the Wooley Valley Unit 4 waste dump site.

Table 1. Concentration of Se collected from air samples taken at two locations in Little Long Valley, Idaho. Site 6-20 is at the base of the Unit 4 dump of Wooley Valley Mine, and site 6-21 is approximately 1.5 km northwest of the dump.

	Concentration	Final volume	Volume of	Concentration
	in solution	of solution	air sampled	in air
Sample ID	Se ($\mu\text{g/L}$)	(L)	(m^3)	Se ($\mu\text{g/m}^3$)
6-20 acid blank	0.257			
6-21 acid blank	0.097			
6-20 acid trap	1.380			
6-21 acid trap	0.256			
6-20 acid trap, blank corr'd*	1.12	0.134	2.88	0.052
6-21 acid trap, blank corr'd	0.16	0.129	2.88	0.007
6-20 base blank	< 0.05			
6-21 base blank	< 0.05			
6-20 base trap	< 0.05			
6-21 base trap	< 0.05			
6-20 base trap, blank corr'd	< 0.05	0.126	2.88	< 0.002
6-21 base trap, blank corr'd	< 0.05	0.120	2.88	< 0.002
QC Summary:				
NIST-1640** found	23.2			
NIST-1640 true	22			
% Recovery	105%			
NIST-1643d** found	11.0			
NIST-1643d true	11.4			
% Recovery	96%			

*blank corr'd = solution concentration after subtraction of blank concentration.

**NIST-1640 and NIST-1643d are aqueous Standard Reference Materials that have certified values for selenium concentrations in solution.

Other geoenvironmentally-sensitive trace elements that were looked for, but not detected, in the wetland sample at concentrations different from those of the blank are: Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Tl, V, and Zn

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The samples were collected on the site of the Wooley Valley phosphate mine (inactive), operated by Rhodia Inc., near the Rasmussen Ridge phosphate mine, operated by the Agrium U.S. Inc. We thank Rhodia Inc. and Agrium U.S. Inc. for providing access.

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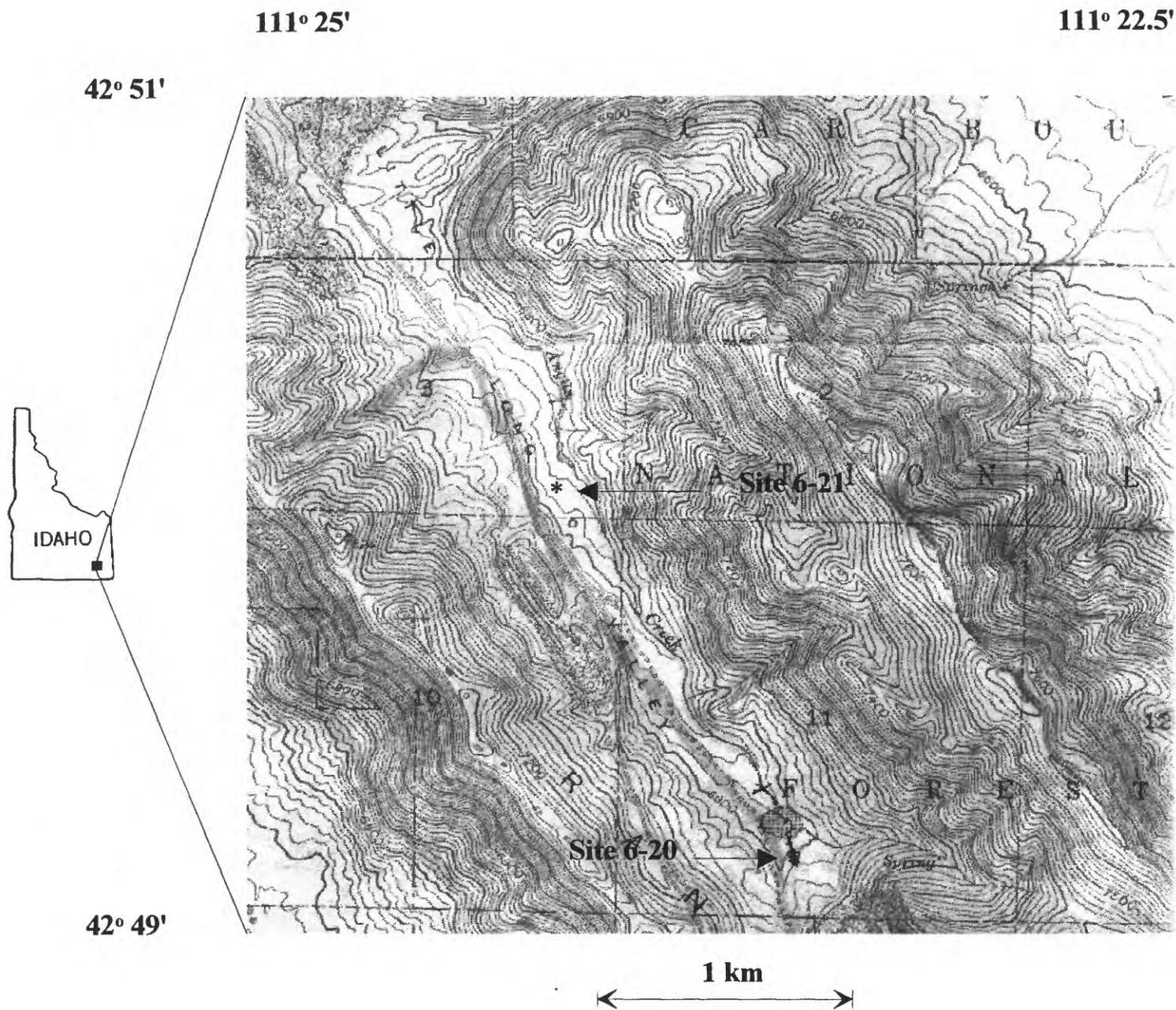


Figure 1. Location map of study area showing air sampling sites.

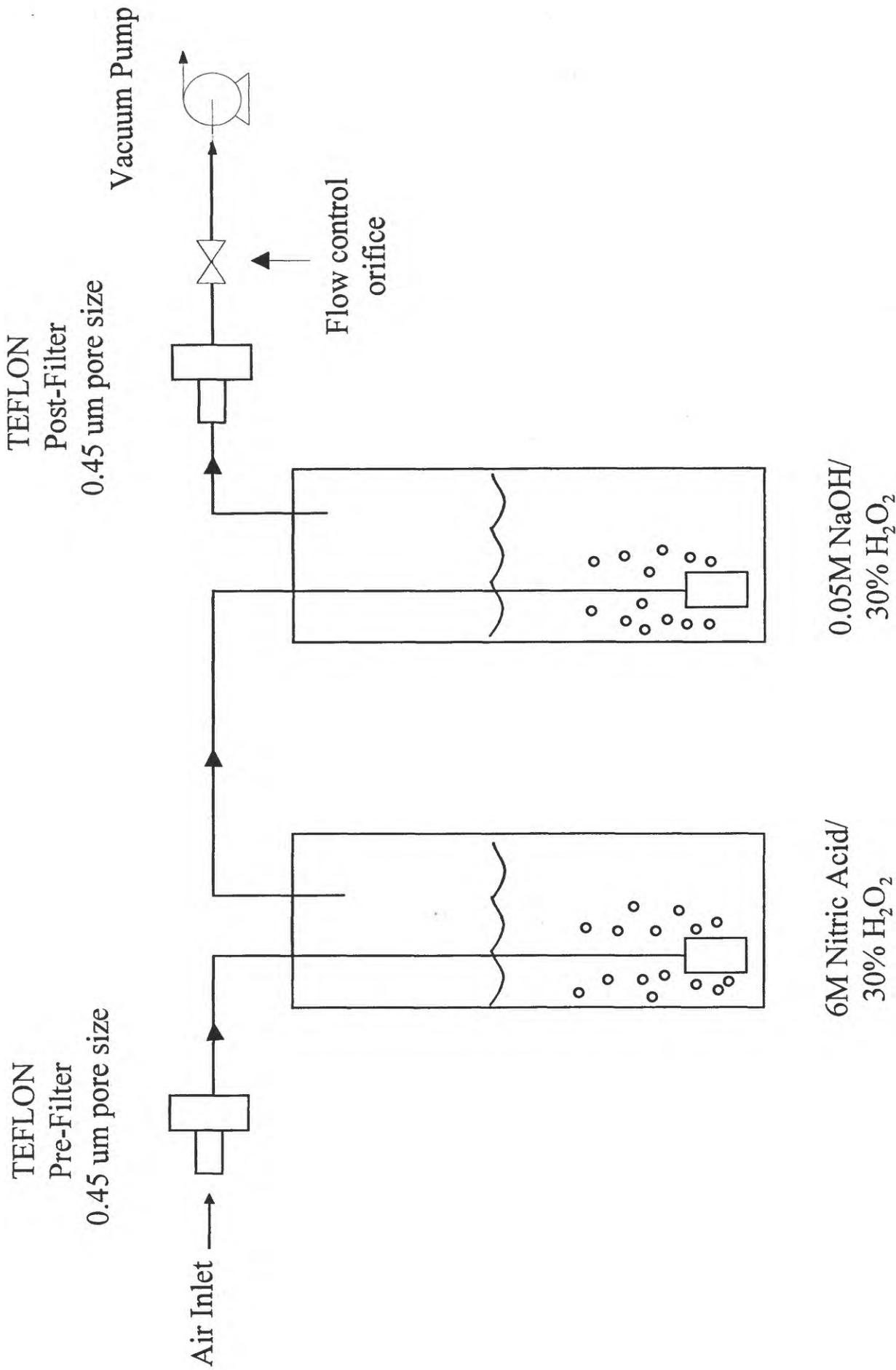


Figure 2. Air sampling train used to collect volatile Se species. Samples were collected for 24 hrs at a flow rate of 0.12 m³/hr.