

METHODS FOR COLLECTION AND ANALYSIS OF PRECIPITATION: TRACE METALS

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TRACE METALS

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GLOSSARY

Term	Abbreviation	Definition
Accuracy		The difference between the mean value and the true value when the latter is known or assumed. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value, due to the experimental method. In practice, it is expressed as the difference between the mean value obtained from repetitive testing of a homogenous sample and the accepted true value: Bias = measured value - true value
Black Body Emission		A wide spectrum of electromagnetic radiation emitted from a black body. Graphite is close to being a black body and will emit at high wavelengths and temperatures. The emission is reflected from the window of the hollow cathode lamp.
Control Limits	CL	Statistically derived values that limit the range of acceptable random error in a measurement process. They consist of an upper and lower range of acceptable values that are defined as $\pm 3s$ from the mean.
Field Blank	FB	An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a collection vessel, holding time, preservatives, and all other sample processing and analysis protocols.
Fluorohydrocarbon Plastics		Plastics formed from polymers made only with fluorine, hydrogen, and carbon.
Laboratory Spike		A known volume of analyte that is added to a sample. The concentration of analyte spiked into the sample usually approximates the expected concentration

of that analyte in the unspiked sample or the mid-point of the calibration curve. The difference in concentration between the spiked and the unspiked sample is used to calculate a method percent recovery.

Mean Bias
$$\frac{\sum \text{bias for each sample}}{\text{total number of replicates (n)}}$$

Mean Percent Recovery
$$\frac{\sum \text{percent recovery for each sample}}{\text{total number of replicates (n)}}$$

Method Detection Limit MDL The minimum concentration of an analyte that can be reported with 99% confidence that the value is above zero. The MDL is operationally defined as:

$$MDL = s t_{(n-1, 1-\alpha=0.99)} \quad (1)$$

where:

s = standard deviation of repetitive measurements (7) of a solution containing the analyte at a concentration near the MDL.

$t_{(n-1, 1-\alpha= 0.99)}$ = student's t value for a one-tailed test appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Percent Bias The difference between the mean value obtained by repeated testing of a homogenous sample and the accepted true value expressed as a percentage of the true value:

$$\% \text{ Bias} = 100 \times [(V_m - V_t)/V]$$

where: V_m = measured value
 V_t = true value

(1) Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde. "Trace Analyses for Wastewaters". Environmental Science and Technology, 1981, Vol. 15, No. 12. pp. 1426-1435.

Percent Recovery	An estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as:
	$\% \text{ Recovery} = 100 \times [(a - b)/c]$
	<p>where: a = measured concentration of spiked sample b = measured concentration of unspiked sample c = calculated spike concentration</p>
Polyethylene	A branched chain high molecular weight hydrocarbon, resulting from the polymerization of ethylene. High density polyethylene (HDPE) has minimal branching.
Polystyrene	A plastic formed from the polymerization of styrene (a synthetic resin made from vinyl benzene).
Precision	The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the value obtained about the mean value. It is often reported as a sample standard deviation (s).
Pyrolytic Coating	A thin surface layer of carbon produced by heat in an atmosphere of methane gas.
Quality Control Check Sample	<p style="text-align: center;">QCS</p> A sample containing known concentrations of analytes prepared by the analyst or a laboratory other than the laboratory performing the analysis. The performing laboratory uses this sample to demonstrate that it can obtain acceptable results with procedures used to analyze wet deposition samples. Analyte true values are known by the analyst.
Refractory	Resistant to decomposition at high temperatures.
Relative Standard Deviation	<p style="text-align: center;">RSD</p> The standard deviation expressed as a percentage.
	$\text{RSD} = 100 \times (s/\bar{x})$
	<p>where: s = sample standard deviation x = mean value</p>

Sensitivity

The method signal response per unit of analyte. In atomic absorption spectrophotometry, sensitivity is defined as the concentration of analyte which produces a 1% absorption signal (0.0044 absorbance) under optimal conditions (2).

$$\text{sensitivity} = \frac{\text{concentration} \times 0.0044}{\text{measured absorbance}}$$

Standard Deviation

s

A number that represents the dispersion of values around their mean, calculated as:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

where: x_i = each individual value
 \bar{x} = average of all values
n = number of values

Statistical Control

The description of a measurement process that is characterized solely by random errors.

Warning Limits

WL

Limits used in quality control charts to indicate that the analytical procedure is close to being out of statistical control. They consist of an upper and lower range of values that are defined as $\pm 2s$ from the mean value.

Zero Standard

A calibration standard used to set the instrument response to zero. It contains all of the matrix components of the remaining calibrants except the method analyte.

(2) Varna, A. Handbook of Atomic Absorption Analysis, Vol. 1, CRC Press, Inc., Boca Raton, Florida, 1984, p. 29.

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INTRODUCTION

The initial focus of the research efforts covered by this contract was on the development of standardized methods for the collection and analysis of precipitation samples. The scope of these efforts, however, was limited to the major anionic and cationic components found in precipitation. These constituents included pH, SO₄, NO₃, Cl, F, PO₄, Ca, Mg, Na, K, NH₄, alkalinity, conductivity, and acidity.

Other elements are also found in atmospheric deposition at potentially harmful concentration levels. A special class of these elements includes trace and/or toxic metals. The concentrations of some of these metals are elevated above background levels in atmospheric deposition and there can be substantial biological effects of these metals on receiving systems.

An extensive five year cooperative study on lead in the environment conducted by the Universities of Illinois and Missouri and Colorado State University measured lead concentrations in dustfall and precipitation samples collected in a 225 square kilometer watershed in East Central Illinois (Rolfe and Haney, 1975; Boggess and Wixson, 1977). Results from this short duration monitoring effort indicated that the urban wet deposition of lead was twice that of the rural sector. This correlated well with the increased lead concentrations found in aerosol samples from the urban sampling area.

Specific information on what other metals are elevated, what the degree of enrichment is over scales of time and space, and finally the effects that these elevated concentrations have on terrestrial and aquatic ecosystems are not well known.

Information on nineteen metals in atmospheric deposition, potentially toxic to humans and other organisms, was accumulated by Galloway et al. (1980) to determine the state of knowledge that existed about metals in atmospheric deposition and if current concentrations threaten human or other organism health. Based on rates of emission, atmospheric concentrations, and known temporal trends in deposition, they concluded that the greatest increases in concentrations of metals in atmospheric deposition due to anthropogenic activity are expected for Ag, Cd, Cu, Pb, Sb, Se, Zn, with smaller increases expected for Cr and V and with little or no increase expected for Co, Mn, and Ni. There were insufficient data to rank Mo, As, Be, Sn, Te, and Tl.

The currently available data base on these metals in atmospheric deposition supported these expectations. The metals Zn, Pb, Cu, Mn, Ag, As, and V had measured concentrations 30 to 200 times higher in atmospheric concentration or deposition in rural continental areas than in remote areas such as the South Pole. Other metals such as Sb, Se, Cr, and Ni, had concentrations that were 10 to 30 times greater in rural areas than in remote areas. Only Pb and Hg are currently found in precipitation at some levels greater than the federal drinking water standard. Cd, Cu, Hg, Pb, and Zn approach the limits for other biological effects (Gough et al., 1979).

In addition to several recommendations on the need for more research in specific areas, Galloway et al. (1980) proposed:

"A national network to determine the temporal and spatial trends of metals in atmospheric deposition must be established."

The National Acid Precipitation Assessment Plan (NAPAP, 1981), prepared by the Interagency Task Force on Acid Precipitation, also addressed the importance of trace metal inputs to aquatic and terrestrial receiving systems by both wet and dry deposition processes. Elevated trace metal depositions to aquatic systems can have detrimental effects on both plant and animal life. An additional concern expressed in the NAPAP is the potential for adverse human health effects from the consumption of leafy vegetables subjected to elevated levels of heavy metals from both wet and dry deposition.

One of the information needs specified in the NAPAP concerning the deposition of trace metals related to the National Trends Network (NTN).

"The NTN will provide a long-term record of geographical and temporal variations of the major anions and cations in wet and dry deposition, and periodic measurements of toxic metal ions and selected organic substances."

Before routine measurements of trace metals in atmospheric deposition can be made, however, standardized procedures for the collection and analysis of samples need to be developed. Available data on trace metals in atmospheric deposition were gathered using a wide variety of collection devices, varying handling procedures, and different analytical techniques. An examination of the currently available data reveals a wide range of concentration values, in large part due to the variations in sampling and analysis protocols that were followed. Data interpretation, therefore, is a difficult, if not meaningless, task to undertake. Clearly a need exists to formalize collection and analysis procedures in order to collect representative data that will be of use to both biological effects researchers and to regulatory agencies. The research described in the following sections has been designed to increase the base of knowledge concerning the collection, processing, and analysis of wet deposition for trace metal content.

SAMPLE COLLECTION

COLLECTOR DESIGN

Most of the larger precipitation chemistry monitoring networks are currently using wet-only collection equipment for the analysis of major inorganic species in wet deposition. The collection of wet-only deposition is equally important for trace metal determinations, since the environmental effects of these elements are determined by their solubility which in turn influences their mobility and bioavailability.

As early as 1976, Galloway et al. demonstrated that the presence of dry deposition in precipitation samples can partially neutralize the free acidity and thereby affect metal solubility. This was further verified by the research of Gatz et al. (1984) who investigated metal solubilities in atmospheric deposition in a Chicago suburb over a period of fifteen months. They found solubility differences between sample types for Cd, Cu, Pb, and Zn, with higher soluble fractions in wet precipitation samples than in either bulk or dry deposition samples.

Metals such as Cd and Pb, which are associated with submicrometer particles, are removed primarily by wet deposition; metals bound on coarse particles, such as Mn and Fe, are removed mostly by dry deposition processes (Georgii et al., 1983). These studies emphasize the importance of the separate collection of wet and dry deposition to accurately assess both the sources and sinks of trace metal elements.

The collection of wet-only samples for this project was carried out using an Aerochem Metrics Model 301 wet/dry precipitation sampler. Part of the study involved the use of an in situ filtration collector. For this purpose, the Aerochem Metrics collector was modified as shown in Figure 1. The counterweight bar was cut and the middle portion removed, so that the tubing could be connected from the collection funnel to the receiving bottle. The bucket was shortened by one inch and a hole cut in the bottom for passage of the polypropylene cone and tubing.

The Aerochem Metrics collector is constructed from aluminum so there is a potential for contamination, especially if the winds are strong during a precipitation event. To minimize this potential source of contamination, a polycarbonate lid for the collector is recommended. Aerochem Metrics supplies these lids, which are easily interchangeable with the standard reciprocating aluminum lid.

COLLECTION VESSEL

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) currently collects atmospheric wet deposition in white high density polyethylene (HDPE) buckets. These buckets are suitable for the determination of major inorganic constituents (Stensland et al., 1980), but have not been thoroughly investigated for trace metal sampling. Evaluation of the buckets, as well as nylon-reinforced polyethylene bag bucket liners and a HDPE funnel and

bottle assembly, was a major focus of this project. Adsorption and/or desorption of the metals aluminum, cadmium, copper, iron, lead, manganese, vanadium, and zinc were studied as a part of this evaluation.

The buckets and lids were cleaned in a Forma-Fury laboratory glassware washer with water (references to water are understood to indicate water conforming to ASTM Specification D1193, Type II). The total wash time was 40 minutes. The buckets were stored in new polyethylene bags, and were rinsed with water again prior to use. Buckets and lids were not reused.

In order to investigate the desorption of metals from the HDPE collection buckets, one liter of either water (pH 5.7) or a 0.016N nitric acid (pH 1.8) solution was poured into each bucket. The sample was then swirled five times in the bucket and a 60 mL aliquot was immediately poured into an acid leached HDPE bottle (Table 1). This constituted the 0-day sample. The buckets were then covered with lids and subsequent samples were taken at 1, 3, and 7-day intervals. The deionized water samples were acidified to pH 1.8 with nitric acid immediately after being poured into the 60 mL bottles. For each of the two sample types, five buckets were evaluated.

Buckets lined with the nylon-reinforced polyethylene bags were also evaluated with the same two sample types. Four buckets for each sample type were investigated. The liners were inserted into the buckets and rinsed thoroughly with water before use. The sampling procedure was the same as for the unlined buckets.

Table 2 shows the bucket blank leachate results for the unlined buckets cleaned in the glassware washer and those lined with the nylon-reinforced polyethylene bags. Both bucket treatments resulted in zinc desorption to levels well above the method detection limit (MDL) of 0.5 ug/L. Iron desorption into the pH 1.8 solution from both HDPE bucket walls and bag liner walls was also apparent.

Acid cleaning of the buckets was then conducted to abate the desorption. Ten buckets were cleaned in the glassware washer as described before and then leached with 1.6N nitric acid (pH 0.2) for three days, followed by three days with water. They were further rinsed thoroughly with water before use. Five of these buckets were tested with one liter each of 0.016N nitric acid (pH 1.8) and five with 0.0004N nitric acid (pH 3.4). Again, 0, 1, 3, and 7-day samples were taken. The 0.0004N nitric acid samples were further acidified to pH 1.8 in their 60 mL bottles prior to analysis. Only zinc and iron concentrations were measured in the acid-cleaned bucket leachates.

The results, shown in Table 3, indicate decreased iron desorption, but significantly increased desorption of zinc. Tables 2 and 3 data for aluminum, iron, and zinc desorption are presented graphically in Figures 2-4. It is obvious from these plots that both bucket and liner desorption rates are variable.

To evaluate adsorption onto the collector surface, synthetic trace metal solutions were prepared. USEPA quality control check sample (QCS)

481, Trace Metals I, Concentration 2 at a 1:20 dilution was used to approximate the median rural concentrations reported by Galloway et al. (1982) and diagramed in Figure 5. The synthetic samples were formulated at pH 3.4. The results, presented in Figures 6 and 7, compare the concentration levels measured during the seven day exposure period. As with the previously described experiment, sample aliquots were withdrawn at 0, 1, 3, and 7-day intervals. Precision and bias data for the two bucket treatments, calculated as percent recoveries of the true values, are shown in Table 4. The lined bucket concentration values for vanadium (Fig. 7) are extremely variable. The vanadium analyses were conducted using an inductively coupled argon plasma spectrometer (ICP) by the Illinois Natural History Survey (INHS). Analyses of the other metals were conducted by graphite furnace atomic absorption spectroscopy (GFAA) at the Illinois State Water Survey.

Tramontano et al. (1986) also found increased concentrations of metals in blank leachates following extensive acid cleaning of the buckets. In water acidified to pH 2 with hydrochloric acid, they measured concentration increases from <1 ug/L to 16 ug/L copper, 11 ug/L lead, 10.5 ug/L manganese, and 27 ug/L zinc.

There is wide disagreement in the literature with regard to adsorption/desorption characteristics of polyethylene bags used as bucket liners. Our results differ from two recent studies, those of Chan et al. (1983) and Good and Schroder (1984). Both studies found no desorption of metals from polyethylene bag surfaces. Their MDL's were 4-40 times higher than the ones reported here, however. Both studies also found adsorption of iron and lead onto the bag walls after three days. Chan et al. (1983) also found that aluminum and zinc were adsorbed. This is in contrast to our findings of 124% recovery of aluminum and 100% recovery of zinc after seven days. Tramontano et al. (1985) have found polyethylene bags to be suitable for trace metal sample collection, if they are cleaned sequentially with soapy water, acetone, hydrochloric acid, nitric acid, and high-purity deionized water. The entire cleaning process they describe takes about one week.

The funnel and bottle modification to the Aerochem Metrics collector was evaluated as an in situ filtration device, as shown in Figure 8. The top opening of the funnel is the same diameter as the buckets (30 cm), so that the catch area is the same. The HDPE funnel and polypropylene cone were washed in the glassware washer, as the buckets were. The fluorinated ethylene propylene (FEP) tubing was cleaned by running two liters of water through it. The 2 liter low density polyethylene (LDPE) bottle was rinsed with water and then leached with water for one week. It was rinsed again prior to use.

Blank leachate values for the funnel and bottle collector are presented in Table 5. The procedure that was followed differed from the bucket procedure in that the samples were immediately acidified to pH 1.8, instead of remaining in the collector and being poured off at 0, 1, 3, and 7-day intervals.

The field blank analyses presented in Table 6 show a direct comparison of blank leachate values obtained from the funnel and bottle

in situ filtration collector and the bucket collector. Here, a 1 liter water sample acidified to pH 4.3 with nitric acid was poured into the collectors and left for 24 hours. It was then taken into the laboratory and processed as described previously. Each sample was left in the collection vessel and 0, 1, 3, and 7-day aliquots were removed and acidified to pH 1.8. The desorption of zinc from both the unlined and lined bucket collectors was five times higher than in the funnel and bottle collector. The other metals had values below the MDL's, indicating no desorption problems.

The funnel and bottle collector was further evaluated in the laboratory with the in situ filtration modification (Fig. 8). Here, samples were spiked with known amounts of trace metals prior to filtration. Spike recovery results are shown in Table 7. Although statistically significant biases were found for cadmium, iron, and manganese, the recoveries are within acceptable limits for GFAA analyses.

Table 8 compares the bias and precision obtained from synthetic quality control check (QCS) samples that were exposed in the three collector types. The single-operator analytical bias and standard deviation obtained from these synthetic samples are also included for comparative purposes (Table 9). All of the biases are within two standard deviations (95% confidence level) of the QCS sample, with the exception of aluminum in the buckets lined with nylon-reinforced polyethylene bags. It is unclear why the biases for zinc are so low (below MDL) when the blank leachate values were eight to fifteen times the MDL.

The unlined HDPE buckets were ruled out as recommended collection vessels because of iron and zinc contamination problems, which acid cleaning did not eliminate. Many researchers are now recommending the use of polyethylene bag liners for wet deposition collection. The theoretical advantages of the liners are: decreased expense, ease in handling and shipping, and elimination of bucket washing. However, the potential for contamination from increased handling is great. The liners are awkward to insert into the buckets and secure to them. They can be flattened against the walls of the bucket by either inserting a hand (covered with a disposable glove) into the bucket, or by using a vacuum pump to evacuate the air between the bucket and the liner.

Because of so much manipulation and the awkwardness in getting the liner to seat properly, it is very susceptible to contamination. The level of impurities found in these liners also appears to vary considerably depending on the supplier. This variability requires an extensive evaluation of any liner that is to be used for trace metal studies. Any type of rigorous acid cleaning also increases the supply and man-hour costs considerably. Because of these considerations and the results obtained from the blank leachate and spike recovery studies, we have recommended the use of a funnel and bottle collector for routine collection of samples for trace metal analyses.

COLLECTOR SITING

Collector siting considerations depend on the project objectives. Factors which must be evaluated before deciding on a site include emission sources, precipitation event types and frequencies, land use, etc. In their review and assessment of trace metals in atmospheric deposition, Galloway, et al. (1982) separated collection sites into three categories: urban, rural, and remote. Median trace metal concentrations of these three site types differ by orders of magnitude. Specific siting criteria used by the NADP/NTN program are explained in detail in Bigelow (1984). Many of the siting considerations that are important when measuring major ions in precipitation are also applicable to trace metal measurements. These criteria may be used as a guide in siting collectors for trace metals analyses.

SAMPLING FREQUENCY

Sampling frequencies vary due to study objectives and design. Collection frequencies may, therefore, range from subevent sampling to monthly sampling. Comparison of data obtained using different sampling frequencies is meaningless, since sample stability and soluble/insoluble metal distributions may be compromised by longer sampling periods. Peden and Skowron (1978) found that unfiltered samples could undergo dramatic chemical changes during the first week if no preservation procedures were employed. The pH values increased significantly after one day and concentrations of Ca²⁺, Mg²⁺, and Na⁺ increased during the first week. In addition, the possibilities of sample evaporation and/or contamination are also increased with longer sampling durations. For these reasons, collection periods of more than one day are not recommended. When sampling for trace metal determinations, sample collection frequency may vary from subevent to daily sampling periods.

SAMPLE HANDLING AND PROCESSING

PRESERVATION TECHNIQUES

Filtration

Filtration of wet deposition samples followed by acidification has been shown to be necessary to stabilize the sample so that the natural distribution of metals is preserved (Rattonetti, 1976). If precipitation samples are acidified prior to filtration, insoluble particulates that are present in the sample will be partially dissolved, releasing additional metals into solution. Similarly, if particulate matter is not removed from the sample, metals that were originally in solution may be adsorbed onto the insoluble matter and reduce the apparent soluble concentration. Since the environmental effects of trace metals are dependent on their solubility, it is important to maintain the natural partitioning of the soluble and insoluble species.

Laboratory filtration of samples was evaluated in order to develop a procedure that would reliably separate these fractions while ensuring that metals were neither lost from solution nor added from the filtration process. The use of polysulfone filter funnels was first evaluated for trace metal adsorption/desorption characteristics. Gelman 47 mm magnetic filter funnels were chosen because of their design features that facilitate cleaning and handling. All surface areas are polysulfone and there are no metal o-rings or clamps required for assembly. Acid cleaning of these funnels was also evaluated as a part of the filtration procedure. Leaching for two hours in 20% nitric acid caused the sealant to the magnet to break down; therefore, an alternative cleaning procedure was adopted:

1. Rinse well with ASTM Type II water.
2. Clean with Type II water for 5 minutes in an ultrasonic cleaner which has been lined with a plastic bag.
3. Rinse well.
4. Dry in a clean air workstation.
5. Store in a polyethylene bag.
6. Funnels cannot be stored in water. This will also cause a breakdown in the sealant to the magnet.

After cleaning, samples were poured through the funnel (without a filter) into an acid cleaned (Table 1) 60 mL HDPE bottle. Water (pH 5.7), 0.016N HNO_3 (pH 1.8), and a synthetic quality control sample (pH 3.4) were again used. The water and synthetic samples were acidified to pH 1.8 after sampling. Five samples of each matrix type were collected. The funnels were cleaned after each sample. The water and the 0.016N HNO_3 samples were below MDL's for all of the metals. Table 10 shows percent recovery values for the quality control sample. Both the funnel adsorption and desorption data indicate no significant contamination or adsorption of metals attributable to the cleaning procedures or the filtration apparatus.

Traditionally, 0.4 um pore size polycarbonate membrane filters and 0.45 um pore size cellulose ester filters have been used to separate operationally defined soluble and insoluble fractions of water samples. The differences in construction of these two filter types result in marked differences in filtration efficiencies as well in the metal blank levels characteristic of each filter type. The thin polycarbonate membranes (5-10 um) act as screen filters with individual pores of uniform diameter. The thicker cellulose filters (100-150 um) act more as depth filters with tortuous channels which trap particles smaller than the nominal pore size (Laxen and Chandler, 1982). While the depth filters may be more efficient at removing particles (e.g. they can remove particles smaller than the rated pore size), they are also hygroscopic making them difficult to use for gravimetric determinations of insoluble metals. The polycarbonate filters exhibit a better correlation between nominal pore size and effective pore size (Sheldon, 1972; Laxen and Chandler, 1982) as shown in Figure 9.

Nuclepore polycarbonate membrane filters were used to evaluate desorption/adsorption characteristics and a comparison was also made between 0.2 um and 0.4 um pore size filters (47 mm diameter). The filters were rinsed with deionized water before being placed in the filter funnel. Three hundred milliliters of deionized water were then passed through the filter by vacuum filtration in order to leach out any soluble impurities on the filter or from the filtration apparatus itself. Sixty milliliter aliquots of each sample were filtered directly into acid leached HDPE bottles, and acidified to 0.016N HNO₃. Unfiltered aliquots were also acidified in order to compare filtration efficiencies between the two different pore sizes. Five types of samples were analyzed:

- 1) Deionized water (pH 5.7)
- 2) USEPA QCS sample (pH 3.4)
- 3) 0.0004N HNO₃ (pH 3.4)
- 4) 0.0005N HNO₃ (pH 4.3)
- 5) Composite rain sample (pH 4.0)

For each sample type, ten aliquots were filtered (five through 0.4 um pore size filters and five through 0.2 um pore size filters). For the deionized water, 0.0004N HNO₃, and 0.0005N HNO₃ samples, all measured concentrations were at or below MDL's for all of the metals (Al, Cd, Cu, Fe, Mn, Pb, V, and Zn). Results for the USEPA QCS sample and the composite rain sample are presented in Table 11. There are no desorption or adsorption problems evident for the metals of interest. In addition, a paired t-test conducted on the data obtained from samples collected using 0.2 and 0.4 um pore size membranes revealed no significant differences in concentrations at the 95th confidence interval.

To further verify the suitability of the 0.4 um polycarbonate filters housed in the polysulfone filter funnels, spike recovery data were collected. Wet deposition samples were spiked with known amounts of trace metals prior to filtration. The spike recovery data summaries are shown in Table 12.

Filtration at the site would seem ideal to minimize changes in metal distributions between the soluble and insoluble phases. Because of the contamination problems caused by the lack of clean laboratory facilities at most collection sites, however, field filtration of samples is impractical. An enclosed in situ filtration device would achieve the quickest possible sample filtration and minimize the potential for sample contamination. The in situ gravity filtration device pictured in Figure 8 was evaluated in the laboratory by collecting spike recovery data. In this procedure, the samples were spiked and then poured into the receiving funnel. They were passed through the 0.4 μ m polycarbonate filter by gravity filtration. The filter was contained in a Teflon tetrafluoroethylene (TFE) in-line filter holder (Fig. 10). The filter had been previously leached with 300 mL of water using vacuum filtration. Blanks (pH 5.7, 4.3, and 3.4), synthetic QCS samples (pH 3.4), and composite precipitation samples were all processed in this manner. The samples were collected directly into acid leached HDPE bottles and acidified to pH 1.8 with HNO_3 . The spike recovery results were shown in Table 7.

Acidification

Many researchers have demonstrated that acidification of water samples to pH <2 minimizes container adsorption effects (Struempfer, 1973; Subramanian et al., 1978). Whenever possible, samples should be acidified immediately after collection to minimize the chances for metal adsorption onto container walls. Preacidified collection containers are impractical, however, since the acid concentrations would be nonuniform with varying precipitation amounts.

The ideal collection situation would seem to be an in situ filtration device with immediate acidification of the filtrate. We approached this ideal by conducting field investigations of the in situ gravity filtration collector. The collection bottle (2 liter conventional polyethylene CPE) was preweighed and leached for one week with water. When the sample was collected, the bottle was again weighed to determine the sample volume and the volume of HNO_3 required to lower the pH to 1.8 units (0.016N HNO_3).

The Aerochem Metrics Model 301 wet/dry precipitation sampler is currently in use in the NADP/NTN program to sample for major inorganic constituents. This standard sampler was compared to a similar sampler that had been modified for in situ filtration (Fig. 1) as described in the Sample Collection section. These samples were collected daily. The collection vessels were processed according to the handling protocols outlined in Figures 11 and 12. Five precipitation events were collected south of Champaign, Illinois during February, 1986. These results, which include a time series analysis, are presented in Figures 13-17.

The first two events (Figs. 13 and 14) were wet deposition resulting from storms at the Champaign collection site. The in situ filtration sample collected in the second event (Fig. 14) did not pass through the filter and still remained in the receiving funnel. It was collected from the funnel, filtered in the laboratory, and processed as

the others were. There was not sufficient sample to complete all of the desired 7-day analyses for this event.

Events three, four, and five (Figs. 15-17) consisted of wet deposition samples previously collected in conjunction with the weekly NADP/NTN sampling program. One liter of these samples was poured into the collection bucket in the unmodified sampler and one liter into the funnel of the in situ filtration sampler. They were then left for 24 hours in the sampler and collected as real samples. Event number three zinc concentrations again indicate zinc desorption from the bucket (Fig. 15a). Event four shows some unexplained pH differences between the bucket sample and the in situ filtration sample (Fig. 16b). The pH value of this sample upon arrival from the NADP/NTN site was 4.97. Field blanks were sampled in a similar manner. The blanks also remained in the collectors for 24 hours and were then collected and processed as event samples. The metal concentrations in the field blanks were below the method detection limits except for Zn. The pH and Zn results are shown in Figure 18.

The limited number of events involved in this comparison, coupled with problems of freezing within the filter holder and concerns about the filter clogging with some sample types prevent recommendation of the in situ filtration apparatus at this time. However, we are recommending collection with the funnel and bottle modification, without the in situ filter, because of greatly reduced Fe and Zn contamination problems. The in situ filtration collector definitely shows promise, but further research is needed to develop a system to: 1) prevent filter freeze-up through the use of heated electrical tape and/or better insulation and 2) eliminate the clogging of filters by employing serial gradient filters or a vacuum/pressure filtration mechanism.

SAMPLE PROCESSING CONSIDERATIONS

Wet deposition samples are characterized by very low trace metal concentrations (Fig. 5). Careful collection and processing of these samples is necessary to prevent contamination and/or loss of metals from solution. Potential contamination sources include collection apparatus and containers, laboratory water, filters and filtration device, the laboratory environment, acids used for sample preservation, and storage bottles.

In order to minimize metal contamination during sample collection, the Aerochem Metrics sampler may be modified by replacement of the aluminum lid with the alternate polycarbonate lid. Laboratory water conforming to ASTM Specification D1193, Type II must be delivered through entirely nonmetallic components. The recommended sampling and storage containers of either polyethylene or fluorohydrocarbon construction (Batley and Gardner, 1977; Struempfer, 1973) must be meticulously cleaned with continual monitoring of the cleaning procedure by the extensive use of blank solutions. Laxen and Harrison (1981) compared 13 cleaning methods for polyethylene containers and recommended a 48-hour soak with 10% HNO₃ as the best method. The step-by-step acid cleaning procedure used throughout this work is outlined in Table 1.

Laboratories should be free from external contamination sources, as outlined in Section 6.6 of the appended Method 200.6. Polycarbonate membrane filters housed in polysulfone filter holders and leached with 300 mL of Type II water (via vacuum filtration) were free of trace metal contamination in our research.

As a continual check on trace metal contamination from all of these sources, field and laboratory blanks must be included with the routine samples. Ideally, one of each type of blank is processed after every 20 samples. We have found Baker Instra-Analyzed Nitric Acid to be adequate for use as a preservative for trace metal samples and standards. The desired acid specifications are detailed in Section 7.4 of Method 200.6.

SAMPLE ANALYSIS

In selecting the recommended methods for trace metal analysis of wet deposition, the following factors were considered important:

1. method detection limits
2. applicable concentration ranges
3. spike recovery data
4. method precision and bias
5. interferences
6. availability of instrumentation
7. single vs. multi-element techniques
8. analytical throughput
9. required pre-concentration procedures

A literature study of various analytical methods and preconcentration techniques was conducted with these considerations in mind. The analytical methods that were reviewed included:

1. anodic stripping voltammetry (ASV)
2. instrumental neutron activation analysis (INAA)
3. graphite furnace atomic absorption spectrophotometry (GFAA)
4. inductively coupled plasma emission spectroscopy (ICP)

Of the methods listed, the two most frequently used techniques for precipitation chemistry analyses are GFAA and ICP. Laboratories involved in precipitation chemistry research routinely use atomic absorption or ICP instrumentation. While INAA combines low method detection limits with nondestructive analysis, the availability of reactor facilities severely limits the use of this technique for most analysts. Additionally, the need for very long activation times for some of the elements of interest in precipitation samples significantly increases the analytical costs associated with this technique.

Certain ASV techniques can achieve detection limits comparable to those obtained with GFAA. Lingerak, et al. (1985) employed active carbon impregnated filter paper to overcome organic interferences in the analysis of precipitation. With computerized flow-injection differential pulse anodic stripping voltammetry (FI-DPASV), analyses of 150 precipitation samples agreed well with atomic absorption analyses. Detection limits with ASV can be as low as 0.01 to 0.1 ug/L. Although ASV appears to be a reliable method for trace metal analyses, the analytical throughput is also limited by the relatively long exposure times required for high sensitivity determinations.

The solution concentration techniques that were investigated included:

1. electrolytic preconcentration
2. chelation/ion exchange
3. chelation/solvent extraction
4. coprecipitation/cocrystallation
5. evaporation

Electrolytic preconcentration is accomplished in the ASV method of analysis discussed above. It has also been used to concentrate samples on the graphite tubes used in GFAA (Bailey and Matousek, 1977). Electrodeposition requires few reagents and the instrumentation is simple. However, electrodeposition techniques are generally very slow, particularly with samples characterized by low concentrations of metals.

Chelation/ion exchange, chelation/solvent extraction, and coprecipitation/cocrystallation techniques involve numerous reagents and sample handling, with varying recoveries for different metals and a greater potential for contamination of low level samples.

Evaporation appears to be the simplest, most efficient method of concentration for wet deposition samples. Since wet deposition samples are characterized by low ionic strength, amplification of matrix effects is generally not a problem.

Based on these considerations, the following laboratory investigations were carried out to compare analysis techniques and concentration procedures.

1. GFAA (no preconcentration) vs. ICP (with preconcentration)
2. INAA vs. GFAA (no preconcentration)
3. preconcentration by evaporation vs. chelation/ion exchange

The GFAA determinations were conducted at the Illinois State Water Survey Laboratory. An Instrumentation Laboratory (IL) Model Video 22 atomic absorption spectrophotometer equipped with an IL Model 655 furnace atomizer was used to measure trace metal concentrations. Samples were delivered to the furnace by an IL Fastac 254 autosampler. Operating conditions are outlined in Table 13.

Personnel at the USEPA Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio performed the ICP analyses. Analyses were conducted using a Jarrel-Ash Model 1160 ICP. The method employed was USEPA Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes.

INAA analyses were conducted at the McMaster University Nuclear Reactor in Hamilton, Ontario, Canada. The methods used are described by Landsberger, et al. (1985). A comparison of the method detection limits for these three methods at the facilities listed is shown in Table 14.

INAA VERSUS GFAA ANALYSIS

Sheldon Landsberger of the McMaster University Nuclear Reactor evaluated INAA on a limited number of samples that were also used for the GFAA/ICP comparisons. Four filtered precipitation samples plus four with known amounts of analyte spikes were submitted for this cursory examination. In addition, two synthetic QCS samples (WP 1178 and WP 481) and two acid blanks were tested. Results are shown in Tables 15 and 16. Although the sample number is too small to generalize on the reliability

of this technique for precipitation analyses, Tables 17 and 18, with data extracted from the study of Jervis, et al. (1983), indicate that INAA has limitations in terms of sensitivity and precision when compared to GFAA or ICP techniques.

GFAA VERSUS ICP ANALYSIS

For comparison of GFAA and ICP methods of analysis, samples were sent to the USEPA-EMSL in Cincinnati, Ohio, where they were analyzed by ICP. These samples were first concentrated by a factor of ten at the ISWS laboratory, resulting in final acid concentrations of 1% HNO₃ and 5% HCl. The concentration procedure was carried out by evaporation in a laminar flow clean air workstation. Initially, 400-mL Teflon evaporating dishes were used. Because of contamination and highly variable spike recovery data, 400-mL Nalgene Type HP Beakers were substituted. Comparisons of reagent blank and synthetic QCS sample results for the two types of evaporation vessels are shown in Tables 19 and 20. Evaporation time decreased from 4 to 4 1/2 hours with the evaporating dishes to less than 3 hours with the Type HP beakers. Precision and bias results for wet deposition samples which were first spiked, concentrated by evaporation, and analyzed by ICP are shown in Table 21. A second set of samples concentrated in the same way by a factor of 20 was also analyzed. Results are shown in Table 22.

The National Bureau of Standards (NBS) routinely concentrates water samples by using chelation/ion exchange techniques (personal communication; Robert L. Watters, Jr., Analytical Chemistry Division, NBS). To evaluate this method of sample preconcentration for wet deposition, we utilized the method described by Sturgeon, et al. (1980). The initial sample volume was 100 mL, and the concentration factor for each sample was approximately 10 (individual sample concentration factors were calculated by sample weight). The samples were analyzed by ICP and results compared with those concentrated by evaporation. The comparison results are shown in Tables 23-25. The recoveries for Fe, Pb, Mn, and V improved with the evaporation method while the chelation/ion exchange method gave a better aluminum recovery (Table 24).

Evaporation was chosen as the more reliable method because of the obvious advantages for Fe and Pb recoveries as well as its relative simplicity. While chelation/ion exchange works well for samples with more complex matrices, the additional reagents, sample handling, and time required are unnecessary for wet deposition samples.

Table 26 compares GFAA and ICP as analysis methods for wet deposition samples. Data summarized in this table are extracted from Tables 7, 12, and 21. As indicated by the spike recovery data, preconcentration of samples by up to a factor of 20, followed by ICP analysis, provides comparable results to those obtained by direct GFAA. GFAA analysis is the generally preferred technique, however, because of the relative simplicity in sample handling (no preconcentration required), suggesting decreased potential for contamination.

The basic philosophy throughout this study has been to keep sample handling and the addition of reagents to a minimum, thus minimizing pathways for analyte loss or contamination. Vanadium was excluded from the GFAA methods because of the extreme difficulty involved in the routine determination of highly refractory elements by this technique. The time required to carry out these vanadium determinations would not be cost effective in a routine study.

The advantages of simultaneous determinations of all of these metals by ICP are obvious, and this method is viewed by the authors as an alternative method for trace metal determinations of wet deposition. The additional sample handling and analyst time required for the concentration step must be weighed against the time savings gained by the multielement capabilities of ICP techniques.

SUMMARY AND RECOMMENDATIONS

The focus of this research effort was on the development of sampling and analysis protocols that could be used for the routine determination of trace metals in atmospheric deposition. An additional objective was to utilize, wherever possible, existing precipitation collectors and analytical techniques so that the procedures developed would be practical for use by researchers investigating precipitation quality. The Aerochem Metrics Model 301 precipitation collector, which is the standard collector for the U.S. National Trends Network, was comprehensively evaluated for its suitability for trace metal studies. Although the design and construction of the sampler itself proved to be suitable for trace metal investigations, the HDPE collector vessel in current use leaches unacceptably high levels of zinc into the sample. This leaching of metal ions into solution was exacerbated when acidic solutions were tested. In addition to zinc, high levels of iron were measured when the sample acidity increased. The use of polyethylene liners in the collection buckets was investigated as a possible alternative but again high levels of zinc, aluminum, and iron were found. Acid rinsing of the HDPE buckets prior to use did not eliminate the leaching of iron and zinc.

The desorption problems encountered with these two collection substrates led to minor structural modifications to the Aerochem sampler in order to utilize a different collection vessel. At the same time, an in situ filtration device was added to remove insoluble particulates from the precipitation samples at the time of collection. The modified collector consists of a polyethylene funnel insert in place of the HDPE bucket. The funnel is connected to an in situ membrane filter holder and a two liter conventional polyethylene collection bottle. The use of a bottle in place of the bucket allows for sample collections in vessels that are free from contamination and can easily be removed and transferred to a laboratory for further processing and analysis. The in situ filtration device removes particulates that can adsorb metals from solution. Upon receipt in the laboratory, an appropriate volume of nitric acid can be added to stabilize the metals. The reported limitations of the in situ filtration device, including clogging of the membrane filter from samples with high particulate loadings and freezing of the sample delivery lines during winter collection periods, are problems that could be overcome with only minor modifications to the current design.

As an alternative approach to the in situ filtration device, laboratory filtration protocols were developed. The focus of this portion of the work was to provide for efficient removal of sample particulates while at the same time not altering the concentrations of any of the metals of interest by adsorption or desorption processes. A polysulfone filtration apparatus with polycarbonate membranes was found to be suitable for trace metal determinations. No significant adsorption or leaching of metal ions was apparent using this combination. For real precipitation samples, no differences were found when comparing 0.2 and 0.4 micrometer pore size membranes.

The selection of suitable analytical techniques for trace metal determinations is predicated on the low concentration levels characteristic of precipitation. In addition, speed of analysis, freedom from significant interferences, and availability of instrumentation are factors that are important when recommending one analytical procedure in preference to another. The instrumental techniques that were evaluated and shown to be applicable to trace metal determinations on a routine basis were graphite furnace atomic absorption spectrophotometry (GFAA) and inductively coupled plasma spectrometry (ICP). Instrumental neutron activation analysis did not provide comparable sensitivity and accuracy to the other two techniques.

Although GFAA provides detection limits that are generally an order of magnitude lower than ICP, the multielement capability of this technique is a cost effective alternative when coupled with a suitable preconcentration step. Both evaporation and ion exchange techniques were investigated as viable procedures for concentrating samples prior to ICP analysis. Data obtained from these comparisons revealed that evaporative concentration of samples up to twenty-fold was possible with no significant interferences from matrix components or sample contamination. The use of teflon beakers with solid graphite bottoms is recommended because much higher heating temperatures are possible than with traditionally constructed teflon beakers. An ion exchange procedure using Chelex resins provided similar results to those obtained by evaporation but the extra sample handling steps involved make contamination a greater possibility.

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Table 1. Acid Cleaning Procedure for Bottles
and Collection Vessels

1. Rinse thoroughly with water.
2. Fill with 3.2N nitric acid and leach for 48 hours.
3. Discard leachate and rinse thoroughly with water.
4. Refill with water and leach for 24 hours.
5. Discard leachate and rinse thoroughly with water.
6. Refill with water and store.
7. Rinse thoroughly before use.

NOTE: All references to water are understood to indicate water conforming to ASTM Specification D1193, Type II.

Table 2. Blank Leachate Analyses for HDPE Sampling Buckets
(percent frequency of method detection limit concentrations)

Metal	MDL, ug/L	Unlined Buckets n=20		Lined Buckets n=16	
		Deionized Water	0.016N HNO ₃	Deionized Water	0.016N HNO ₃
Al	3.5	100	100	69 (6.6) ^b	31 (8.5)
Cd	0.05	100	100	88 (0.07)	100
Cu	0.9	100	100	100	100
Fe	1.1	100	20 (16.6)	100	38 (3.2)
Pb	1.1	100	90 (2.8)	100	100
Mn	0.8	100	100	100	100
V ^c	12	90 (18)	95 (13)	100	88 (19)
Zn	0.5	35 (4.0)	0 (14.7)	0 (11.6)	19 (11.0)

a. Lined with nylon-reinforced polyethylene bags

b. Numbers in parentheses are maximum values (ug/L)

c. Vanadium was determined by ICP; All other metals were determined by GFAA

Table 3. Blank Leachate Analyses for HDPE Sampling
 Buckets Leached with 1.6N HNO₃
 (percent frequency of method detection limit)

Metal	MDL, ug/L	n ^a	0.0004N HNO ₃ Blank	0.016N HNO ₃ Blank
Fe	1.1	16	100	85 (1.8) ^b
Zn	0.5	16	25 (42.0)	5 (115)

a. Number of replicates

b. Numbers in parentheses are maximum values (ug/L)

Table 4. Precision and Bias for Trace Metal Recoveries from Unlined HDPE Buckets and Buckets Lined with Nylon-Reinforced Polyethylene Bags

Metal	Amount Added, ug/L	n ^a	Mean Percent Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L	Statistically Significant Bias? ^b
Al	36.5	20 ^c	105.2	1.9	2.8	Yes
		16 ^d	124.7	9.0	2.9	Yes
Cd	1.95	20 ^c	94.4	-0.11	0.08	Yes
		16 ^d	96.9	-0.06	0.05	Yes
Cu	17.0	20 ^c	102.4	0.4	0.8	No
		16 ^d	99.4	-0.1	0.4	No
Fe	39.8	20 ^c	99.7	-0.1	1.5	No
		16 ^d	108.3	3.3	2.0	Yes
Pb	21.8	20 ^c	98.6	-0.3	0.8	No
		16 ^d	95.9	-0.9	0.6	Yes
Mn	17.4	20 ^c	100.0	0.0	0.6	No
		16 ^d	101.7	0.3	0.8	No
V	42	20 ^c	114.3	6	5	Yes
		16 ^d	114.3	6	10	Yes
Zn	20.9	20 ^c	100.5	0.1	1.6	No
		16 ^d	100.0	0.0	0.8	No

a. Number of replicates

b. 95% confidence level (ASTM Standard D2777-77, 1983) .

c. Unlined HDPE buckets

d. Lined buckets

Table 5. Blank Leachate Analyses for Funnel and Bottle Collector

Metal	n ^b	pH	Mean Concen., ug/L	Standard Deviation, ug/L	Maximum Concentration, ug/L
Al	3	3.4	<3.5	2.7	4.3
	5	4.3	<3.5	0.5	<3.5
	3	5.7	<3.5	2.1	4.3
Cd	3	3.4	<0.05	0.02	<0.05
	5	4.3	<0.05	0.02	<0.05
	3	5.7	<0.05	0.03	0.07
Cu	3	3.4	<0.9	0.3	<0.9
	5	4.3	<0.9	0.2	<0.9
	3	5.7	<0.9	0.2	<0.9
Fe	3	3.4	<1.1	0.4	1.2
	5	4.3	<1.1	0.1	<1.1
	3	5.7	<1.1	0.1	<1.1
Pb	3	3.4	<1.1	0.3	<1.1
	5	4.3	<1.1	0.6	<1.1
	3	5.7	<1.1	0.4	<1.1
Mn	3	3.4	<0.8	0.2	<0.8
	5	4.3	<0.8	0.2	<0.8
	3	5.7	<0.8	0.3	<0.8
V	3	3.4	<11.6	1.4	<11.6
	1	4.3	<11.6	---	
	3	5.7	<11.6	3.0	<11.6
Zn	3	3.4	1.8	1.0	2.9
	5	4.3	<0.5	0.3	0.6
	3	5.7	<0.5	0.1	<0.5

a. Determined by GFAA

b. Number of samples

Table 6. Field Blank Analyses
(0.0005N HNO)

Metal	In Situ Filtration (n=4)			HDPE Bucket (n=4)		Bucket, Filtered (n=4) ^{a,b}	
	MDL, ug/L	Frequency of MDL, %	Maximum Value, ug/L	Frequency of MDL, %	Maximum Value, ug/L	Frequency of MDL, %	Maximum Value, ug/L
Al	3.5	100	<MDL	100	<MDL	100	<MDL
Cd	0.05	100	<MDL	100	<MDL	100	<MDL
Cu	0.9	100	<MDL	100	<MDL	100	<MDL
Fe	1.1	100	<MDL	100	<MDL	100	<MDL
Pb	1.1	100	<MDL	100	<MDL	100	<MDL
Mn	0.8	100	<MDL	100	<MDL	100	<MDL
Zn	0.5	75	0.6	0	2.6	0	2.5

- a. 0.4 um polycarbonate filter
b. Filtered in the laboratory

Table 7. Single-Operator Precision and Bias for Trace Metals Determined from Analyte Spikes of Samples (6 Blanks, 2 Synthetic, 5 Wet Deposition)

Metal	Amount Added, ug/L	n ^b	Mean Percent Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L	Statistically Significant Bias?
Al	18.5	12	95.7	-0.8	2.1	No
Cd	6.11	13	109.2	0.56	0.73	Yes
Cu	11.0	13	100.0	0.0	0.6	No
Fe	11.1	12	89.2	-1.2	0.9	Yes
Mn	10.1	13	107.9	0.8	0.5	Yes
V	19.5	12	101.5	0.3	1.6	No
Pb	20.8	13	101.9	0.4	1.5	No
Zn	21.9	13	107.8	1.7	4.7	No

- a. Samples were spiked prior to filtration in the in situ filtration collector
b. Number of replicates
c. 95% confidence interval (ASIM Standard D2777-77, 1983)

Table 8. Precision and Bias of Synthetic QCS Solutions (pH 3.4)

Metal	True Value	Analytical (Table 9)		Unlined Buckets (n=20)		Lined Buckets (n=16)		In Situ Filtration Collector (n=2)	
		Bias, s ^a , ug/L	s, ug/L	Bias, s, ug/L	s, ug/L	Bias, s, ug/L	s, ug/L	Bias, s, ug/L	s, ug/L
Al	36.5	-0.7	3.4	1.9	2.8	9.0	2.9	-4.0	0.7
Cd	1.95	-0.01	0.09	-0.11	0.08	-0.06	0.05	-0.03	0.01
Cu	17.0	0.2	0.8	0.4	0.8	-0.1	0.4	1.0	1.5
Fe	39.8	-0.4	2.3	-0.1	1.5	3.3	2.0	2.0	1.6
Pb	21.8	-0.8	1.0	-0.3	0.8	-0.9	0.6	0.2	0.6
Mn	17.4	0.5	0.8	0.0	0.6	0.3	0.8	0.0	0.2
Zn	20.9	-0.8	1.1	0.1	1.6	0.0	0.8	-1.2	0.9

a. Sample standard deviation

Table 9. Single-Operator Precision and Bias for Trace Metals Determined by GFAA from USEPA Quality Control Check Samples

Metal	Theoretical Concentration, ug/L	Measured Concentration, ug/L	n ^a	Bias, ug/L	Bias, %	Precision, s, ug/L	Precision, RSD, %
Aluminum	36.5	35.8	34	-0.7	-1.9	3.4	9.6
Cadmium	1.56	1.55	49	-0.01	-0.6	0.09	6.0
Copper	17.0	17.2	65	0.2	1.2	0.8	4.6
Iron	39.8	39.4	52	-0.4	-1.0	2.3	5.9
Lead	21.8	20.9	51	-0.8	-3.7	1.0	5.0
Manganese	17.4	17.9	32	0.5	2.9	0.8	4.2
Vanadium	42.3	45.0	20	2.7	6.4	5.6	12.4
Zinc	20.9	20.1	71	-0.8	-3.8	1.1	5.3

a. Number of replicates

Table 10. Precision and Bias for Trace Metal Spike Recoveries from Polysulfone Filter Funnels (without filters)

Metal	Amount Added, ug/L	n	Mean Percent Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L
Al	36.5	5	104.1	1.5	3.6
Cd	2.06	5	99.5	-0.01	0.03
Cu	16.8	5	97.6	-0.4	0.4
Fe	36.9	5	99.7	-0.1	0.8
Pb	21.2	5	103.8	0.8	0.5
Mn	18.3	5	97.8	-0.4	0.6
V	40	5	107.5	3	5
Zn	19.7	5	101.5	0.3	0.8

a. Number of replicates

Table 11. Laboratory Filtered Samples
 (0.2 um vs 0.4 um pore size Nuclepore
 polycarbonate filters)

Metal	Unfiltered, ug/L	Filtered			
		0.4 um		0.2 um	
		Mean	s ^a	Mean	s ^a
Al	34.4 ^b	33.5	1.8	33.6	1.3
	5.7 ^c	4.3	0.5	4.4	0.5
Cd	1.80 ^b	1.80	0.03	1.80	0.05
	<0.06 ^c	0.06	0.03	0.06	0.04
Cu	16.3 ^b	16.2	0.5	16.2	0.5
	3.8 ^c	4.6	0.5	4.1	0.4
Fe	36.0 ^b	35.0	1.0	35.3	0.4
	10.0 ^c	9.6	0.2	9.4	0.3
Mn	17.2 ^b	17.7	0.5	17.6	0.8
	1.5 ^c	1.3	0.7	1.3	0.7
Pb	19.8 ^b	19.3	0.8	19.7	0.6
	2.4 ^c	2.5	0.3	2.2	0.1
V	46 ^b	42	3	42	2
	<10 ^c	<10		<10	
Zn	20.1 ^b	18.8	0.7	18.9	0.2
	31.0 ^c	31.6	1.0	31.4	1.3

- a. Sample standard deviation
 b. Synthetic QCS solution (pH 3.4)
 c. Composite wet deposition (pH 4.0)

Table 12. Precision and Bias for Trace Metals Determined from Analyte Spikes of Wet Deposition Samples (Filtered in Lab)

Metal	Amount Added, ug/L	n	Mean Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L	Significant Bias?
Al	30.9	12	102.4	0.7	4.1	No
Cd	1.99	12	95.7	-0.08	0.26	No
Cu	16.5	12	101.4	0.2	0.5	No
Fe	38.2	12	90.6	-3.7	1.3	Yes
Pb	20.5	12	89.6	-2.1	2.1	Yes
Mn	17.0	12	98.9	-0.2	0.4	No
V	49.5	12	95.8	-2.1	6.1	No
Zn	20.2	12	115.8	3.2	1.4	Yes

- a. Samples were spiked prior to filtration
- b. Number of samples
- c. 95% confidence level (ASTM Standard D2777-77, 1983)

Table 13. Operating Conditions for GFAA Determination of Trace Metals in Wet Deposition Samples

Metal	Wavelength Setting, nm	Spectral Bandwidth, nm	Integration Mode	Graphite Tube Coating	Deposition Time, sec	Furnace Settings,					
						Dry	Temp, C	Time, sec	Pyrolyze	Atomize	Temp, C
Al	309.3	1.0	peak area	pyrolytic	20	0/0	150/5	900/20	1100/35	2700/0	2700/5
Cd	228.8	1.0	peak height	uncoated	15	0/0	150/5	225/10	300/10	1900/0	1900/10
Cu	324.7	1.0	peak height	uncoated	30	0/0	150/5	550/15	750/15	2600/0	2600/5
Fe	248.3	0.3	peak height	pyrolytic	6	0/0	150/5	650/15	900/15	2300/0	2300/5
Pb	283.3	1.0	peak height	uncoated	15	0/0	150/5	350/15	550/15	2000/0	2000/5
Mn	279.5	0.3	peak height	uncoated	10	0/0	150/5	400/20	600/20	2500/0	2500/5
V	318.5	0.3	peak height	pyrolytic	30	0/0	150/5	500/15	750/15	2700/0	2700/10
Zn	213.9	1.0	peak area	pyrolytic	3	0/0	150/5	325/15	425/15	1900/10	1900/0

- a. Instrumentation Laboratory (IL) Model 254 Fastac Autosampler
b. IL Model 655 Furnace Atomizer

Table 14. Method Detection Limits

Metal	Method		
	GFAA ^b	ICP ^c	INAA ^d
Al	3.5	28	0.6
Cd	0.05	1	
Cu	0.9	3	5
Fe	1.1	6	400 (concentrated x100)
Pb	1.1	16	
Mn	0.8	0.3	0.3
V	11.6	3	0.05
Zn	0.5	2	15 (concentrated x100)

a. Glaser et al., 1981

b. Analyzed at the Illinois State Water Survey

c. Analyzed at the USEPA-EMSL, Cincinnati, Ohio

d. Analyzed at McMaster University, Hamilton, Ontario

Table 15. Precision and Bias for Trace Metals Determined from Analyte Spikes of Wet Deposition Samples

Metal	Amount Added, ug/L	n ^c	INAA ^a		GFAA ^b	
			Mean Bias, ug/L	Standard Deviation, ug/L	Mean Bias, ug/L	Standard Deviation, ug/L
Al	18.5	4	-12.0	23.3	-0.8	1.5
		3 ^d	-0.8	7.6	-0.6	1.5
Cu	11.0	4	4.0	6.0	0.2	0.4
Mn	10.1	4	-0.1	0.4	1.3	0.7
V	19.5	4	-55.6	119.5	1.3	1.3
		3 ^d	4.1	0.2	1.7	1.3

a. Analyzed at McMaster University, Hamilton, Ontario

b. Analyzed at the Illinois State Water Survey

c. Number of replicates

d. Outlier removed. For both of these metals, one spike gave a negative recovery. This was removed and the comparison shown.

Table 16. Trace Metal Analyses of USEPA Quality Control Check Samples

Metal	Theoretical Concentration, ug/L	INAA ^a Measured Concentration, ug/L	ICP ^b Measured Concentration, ug/L
Al	106 ^c 146 ^d	204 137	222
Cu	8.9 ^c 67.8 ^d	<33 80	1
Mn	13.0 ^c 69.6 ^d	134 62.5	12
V	130 ^c 169 ^d	155 181	121

- a. Analyzed at McMaster University, Hamilton, Ontario
- b. Analyzed at the USEPA-EMSL Laboratory, Cincinnati, Ohio
- c. USEPA Water Pollutant 1178 quality control samples (WP1178)
- d. USEPA Water Pollutant 481 quality control samples diluted by five (WP481)

Table 17. Comparison of INAA and GFAA for Analysis of Trace Metals in NBS-SRM 1643a, Trace Elements in Water (Jervis et al., 1983)

Metal	True Value, ug/L	Measured Value, ug/L	
		INAA	GFAA
Cd	10±1	ND ^a	12.5±1.3.
Cu	18±2	ND	17±2
Fe	88±4	ND	80±8
Pb	27±1	ND	28±3
Mn	31±2	24±2.5	32.5±3.3
V	53±3	53±1	NA ^b
Zn	72±4	ND	70±7

a. Not detected

b. No data available

Table 18. Comparison of INAA and GFAA for the Analysis of Trace Metals in the Soluble Portion of Snow (Jervis et al., 1983)

Metal	INAA		GFAA	
	Error, ^a %	Sensitivity, ^b ug/L	Error, ^c %	Sensitivity, ^d ug/L
Al	±7%	4	±10%	1
Cd	---	60	±10%	1
Cu	±20%	15	±10%	1
Fe	---	<1550	±10%	22
Pb	---	---	±10%	1
V	±6%	0.2	---	---

- a. Sum of the standard deviation of the activation constants (5%) and the standard deviation of reproducibility
- b. Determination limit ±10% at 95% confidence level
- c. Sum of the standard deviation of reproducibility (3%-5%), pipetting errors (2%) and deviations from the standard working curves
- d. Determined by the slope of the standard calibration curve

Table 19. Reagent Blank Analyses for Samples Concentrated by a Factor of 10 and Analyzed by ICP^a

Metal	Nalge HP Beakers		Teflon Evaporating Dishes	
	Mean Concentration, ug/L ^b	Standard Deviation, ug/L	Mean Concentration, ug/L	Standard Deviation, ug/L
Al	<2.8	1.0	<2.8	3.0
Cd	0.1	0.1	<0.1	0.1
Cu	<0.3	0.1	<0.3	0.4
Fe	0.6	0.1	5.5	4.0
Pb	<1.6	1.3	1.7	1.4
Mn	<0.03	0.05	0.2	0.2
V	<0.3	0.05	<0.3	0.1
Zn	<0.2	0.2	5.1	5.5

a. Sample volume = 250 mL evaporated to 25 mL

b. Adjusted for ten-fold concentration factor

Table 2Q. Analyses for Synthetic Samples
 Concentrated by a Factor of 10
 and Analyzed by ICP^a

Metal	Nalge HP Beakers				Teflon Evaporating Dishes			
	Original Concen., ug/L	n	Mean Recovery, %	RSD	Original Concen. Range, ug/L	n	Mean Recovery, %	RSD
Al	44.4	8	98.9	2.1	10-106	12	109.1	9.8
	33.4	9	100.0	1.9				
Cd	1.8	19	96.1	5.8	0.33-9.1	12	77.4	22.2
Cu	1.8	20	94.4	9.4	1.5-60	12	77.5	29.6
Fe	4.4	20	100.0	8.0	50-39.8	12	112.0	10.4
Mn	2.6	20	96.2	3.8	5.0-17.4	10	98.6	1.7
Pb	8.6	20	94.0	12.4	5.0-43.0	10	94.0	11.0
V	26.0	20	98.3	2.7	1.0-130	12	96.4	3.4
Zn	2.0	18	102.0	11.5	3.0-74	12	108.8	11.2

a. Sample volume = 250 mL evaporated to 25 mL

b. Number of replicates

Table 21. Precision and Bias for Trace Metals Determined from Analyte Spikes of Wet Deposition

Metal	Amount Added, ug/L	n	Mean Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L	Statistically Significant Bias?
Al	44.4	7	98.9	-0.5	1.0	No
Cd	1.8	10	94.4	-0.1	0.1	Yes
Cu	1.8	10	94.4	-0.1	0.1	Yes
Fe	4.4	10	111.4	0.5	1.2	No
Pb	8.6	10	98.8	-0.1	1.1	No
Mn	2.6	10	96.2	-0.1	0.1	Yes
V	26.0	10	99.6	-0.1	0.7	No
Zn	2.0	8	100.0	0.0	0.3	No

- a. Samples were concentrated by a factor of 10 (evaporation) and analyzed by ICP
- b. Number of analyses
- c. 95% confidence level (ASTM Standards D2777-77, 1983)

Table 22. Trace Metal Spike Recoveries from Samples Analyzed by ICP^a

Metal	Blanks (n=3)	Synthetic Samples		Wet Deposition
	Mean Concen., ug/L ^b	Mean Concen., ug/L	Mean Recovery, %	Mean Concentration, ug/L
Al	1.0±0.2	40.0±3.4 ^c 19.5±0.4 ^d	109.6 107.1	3.2±0.4 ^d 2.6±1.2 ^e
Cd	0.03±0.06	1.91±0.12 ^c 0.98±0.06 ^d	97.9 100.5	0.02±0.06 ^d 0.05±0.00 ^s
Cu	0.1±0.0	17.2±0.8 ^c 9.0±0.0 ^d	101.2 105.9	3.8±0.4 ^d 1.4±0.2 ^e
Fe	0.3±0.2	39.8±1.8 ^c 18.5±1.0 ^d	100.0 93.0	3.0±0.0 ^d 1.0±0.0 ^e
Pb	0.2±0.4	23.1±3.0 ^c 10.7±0.6 ^d	106.0 98.2	2.1±0.6 ^d 0.8±0.4 ^e
Mn	0.2±0.4	17.9±0.6 ^c 8.8±0.2 ^d	102.9 101.1	0.5±0.4 ^d 0.6±0.2 ^e
V	0.1±0.2	42.3±1.8 ^c 20.2±0.4 ^d	100.0 95.3	0.3±0.0 ^d 0.2±0.0 ^e
Zn	0.03±0.06	21.4±0.8 ^c 11.3±0.6 ^d	102.4 108.6	45.5±1.6 ^d 11.6±0.2 ^e

a. Samples were concentrated by a factor of 20 (by evaporation) and analyzed by ICP

b. ± values are twice the sample standard deviation

c. n = 5

d. n = 3

e. n = 2

Table 23. Trace Metal Concentrations in
Blanks, Analyzed by ICP

Metal	Evaporation (n=4)		Chelex (n=6)	
	Mean Value, ug/L	Standard Deviation, ug/L	Mean Value, ug/L	Standard Deviation, ug/L
Al	2.0	1.02	2.2	1.15
Cd	0.05	0.06	0.08	0.00
Cu	0.2	0.50	0.4	0.22
Fe	0.6	0.13	0.5	0.20
Pb	0.8	1.32	0.6	0.67
Mn	<0.02	0.05	0.1	0.1
V	0.05	0.1	0.1	0.10
Zn	0.1	0.18	0.3	0.22

Table 24. Trace Metals in Synthetic Samples, Analyzed by ICP

Metal	True Value, ug/L	Evaporation ^a		Chelex ^b	
		Concen., ug/L	Recovery, %	Concen., ug/L	Recovery, %
Al	36.5	39.5	108.2	38.5	105.5
Cd	1.95	1.75	89.7	1.74	89.2
Cu	17.0	15.9	93.5	15.9	93.5
Fe	39.8	39.0	98.0	34.9	87.7
Pb	21.8	21.3	97.7	20.1	92.2
Mn	17.4	17.0	97.7	16.8	96.6
V	42.3	41.0	96.9	39.6	93.6
Zn	20.9	22.1	105.7	19.6	93.8

a. Number of replicates = 4

b. Number of replicates = 6

Table 25. Trace Metals in Wet Deposition Samples Analyzed by ICP Versus GFAA

Metal	GFAA Analysis, ug/L	ICP Analyses		
		Evaporation (x10), ug/L	Evaporation (x20), ug/L	Chelex, ug/L
Al	<3.5	4.6	3.2	3.0
	<3.5	2.7	2.6	2.7
Cd	<0.05	0.01	<0.05	0.04
	<0.05	0.01	0.05	0.04
Cu		3.5	3.8	3.0
		1.2	1.4	1.4
Fe	1.9	2.6	3.0	2.2
	<1.1	1.0	1.0	0.8
Pb		2.3	2.0	1.4
		0.4	0.8	0.5
Mn	<0.8	0.2	0.5	0.5
	<0.8	0.2	0.5	0.4
V		0.4	0.3	0.2
		0.1	0.2	0.1
Zn	38.0	43.8	45.6	35.2
	12.2	11.0	11.6	10.4

Table 26. GFAA vs ICP Analysis of Analyte Spikes of Wet Deposition

Metal	GFAA			ICP ^a		
	Amount Added, ug/L	Mean Recovery, %	Significant Bias?	Amount Added, ug/L	Mean Recovery, %	Significant Bias?
Al	18.5	95.7	No	44.4	98.9	No
	30.9	102.4	No			
Cd	6.11	109.2	Yes	1.8	94.4	Yes
	1.99	95.7	NO			
Cu	11.0	100.0	No	1.8	94.4	Yes
	16.5	101.4	No			
Fe	11.1	89.2	Yes	4.4	111.4	No
	38.2	90.6	Yes			
Pb	20.8	101.9	No	8.6	98.8	No
	20.5	89.6	Yes			
Mn	10.1	107.9	Yes	2.6	96.2	Yes
	17.0	98.9	No			
V				26.0	99.6	No
Zn	21.9	107.8	No	2.0	100.0	No
	20.2	115.8	Yes			

a. Samples concentrated by a factor of 10 (evaporation)

b. 95% confidence level (ASTM Standards D2777-77, 1983)

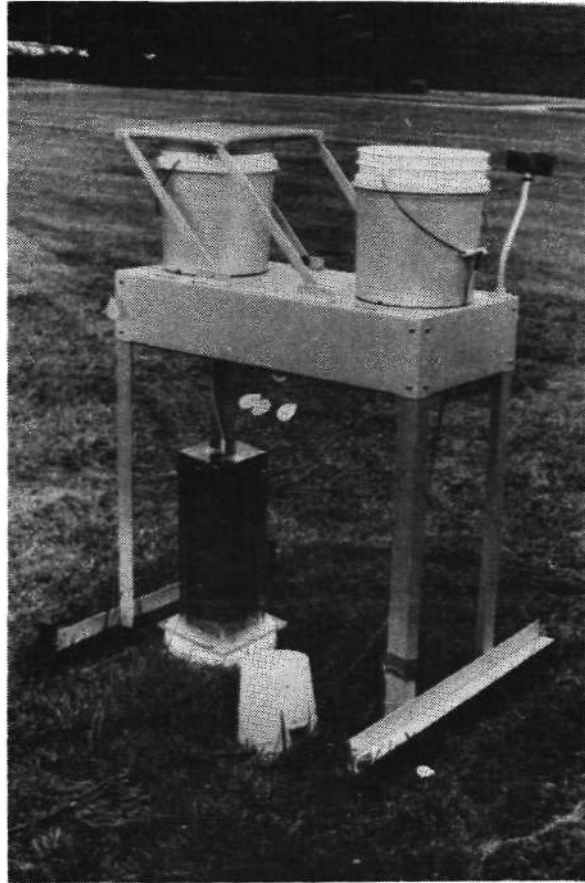


Figure 1. Aerochem Metrics Model 301 wet/dry precipitation sampler modified as an in-situ filtration collector

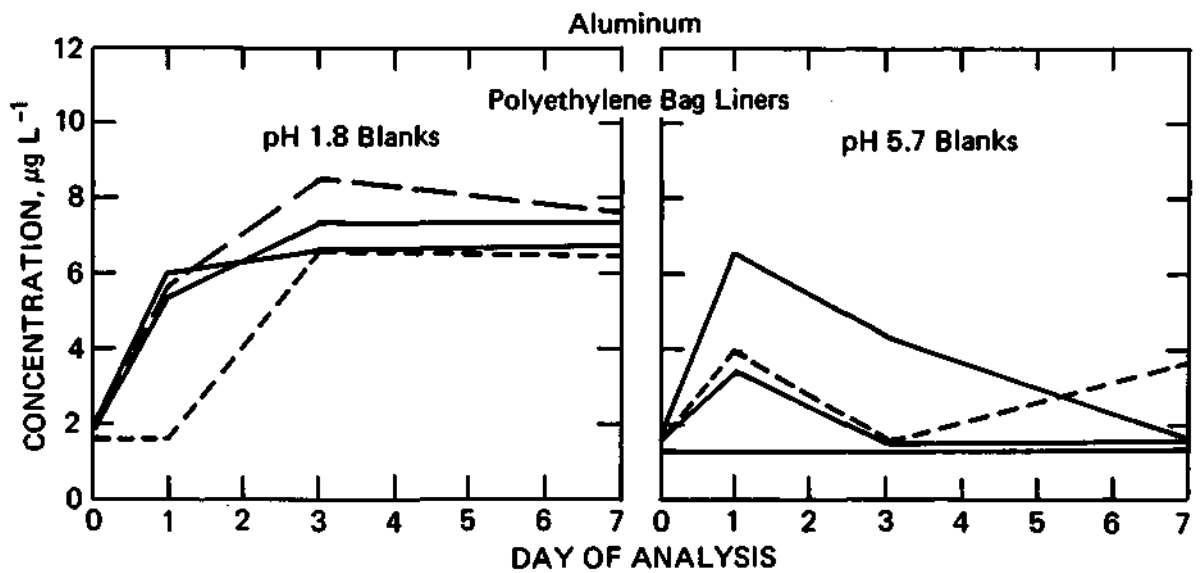


Figure 2. Aluminum concentrations in blank leachate analyses of collection vessels

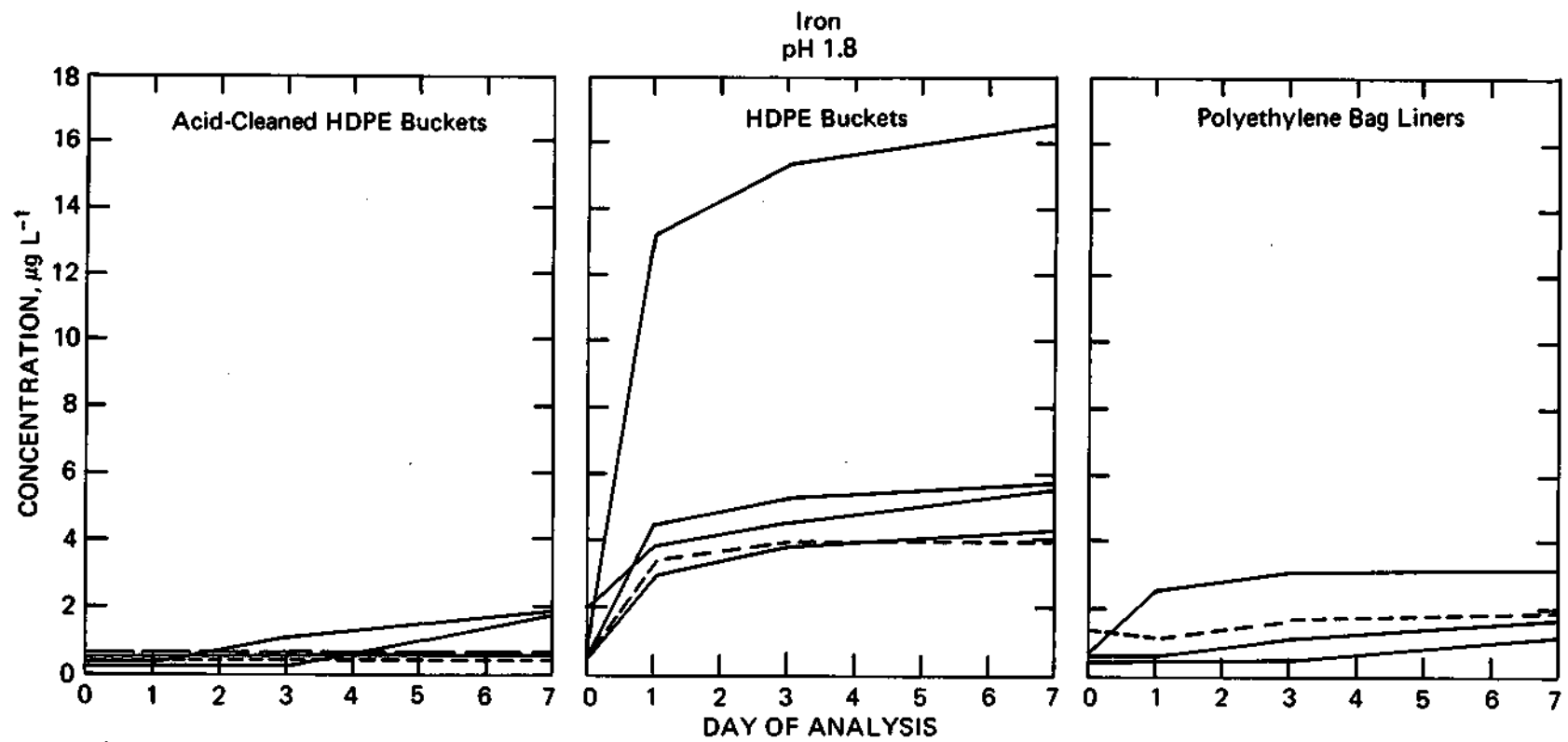


Figure 3. Iron concentrations in blank leachate analyses of collection vessels

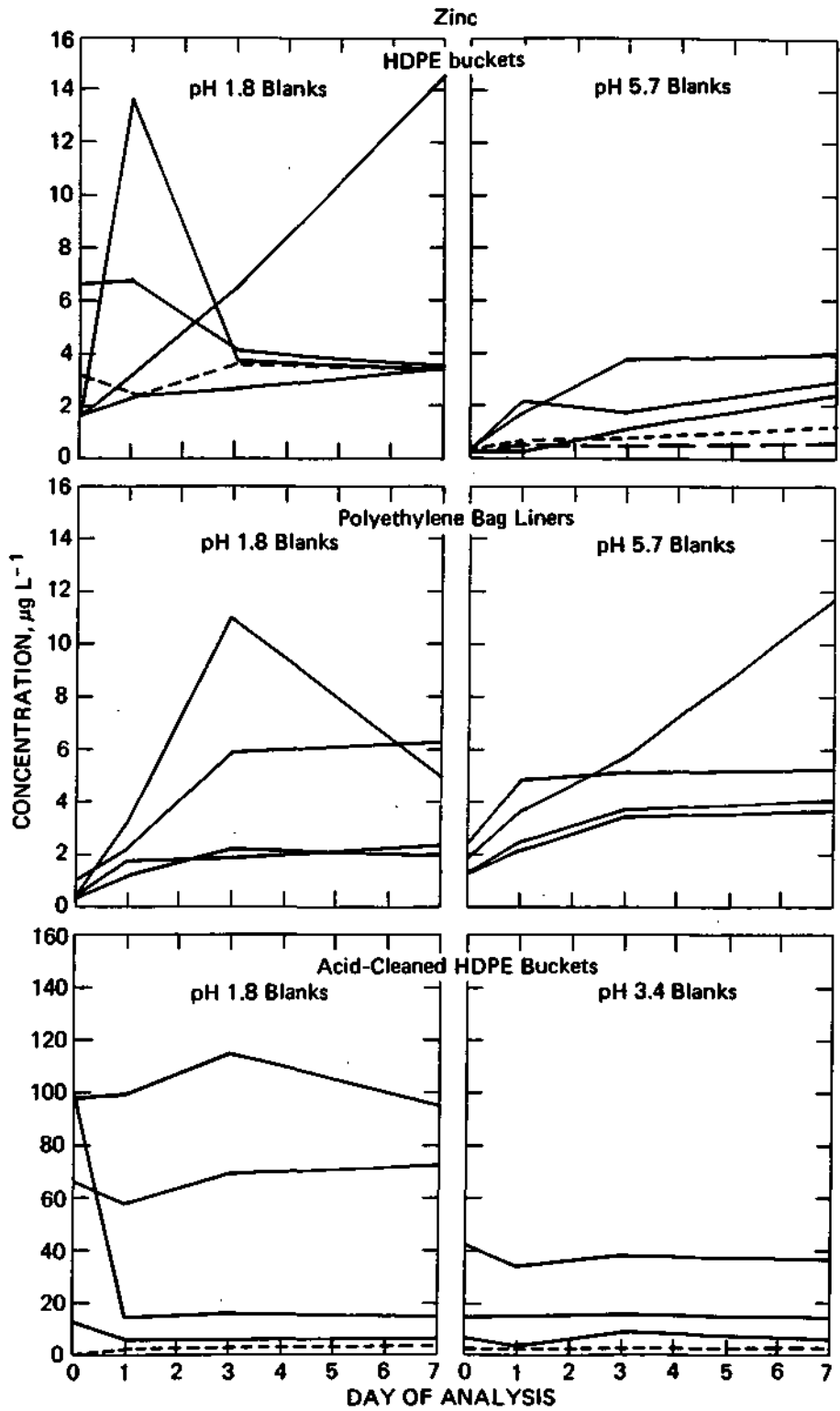


Figure 4. Zinc concentrations in blank leachate analyses of collection vessels

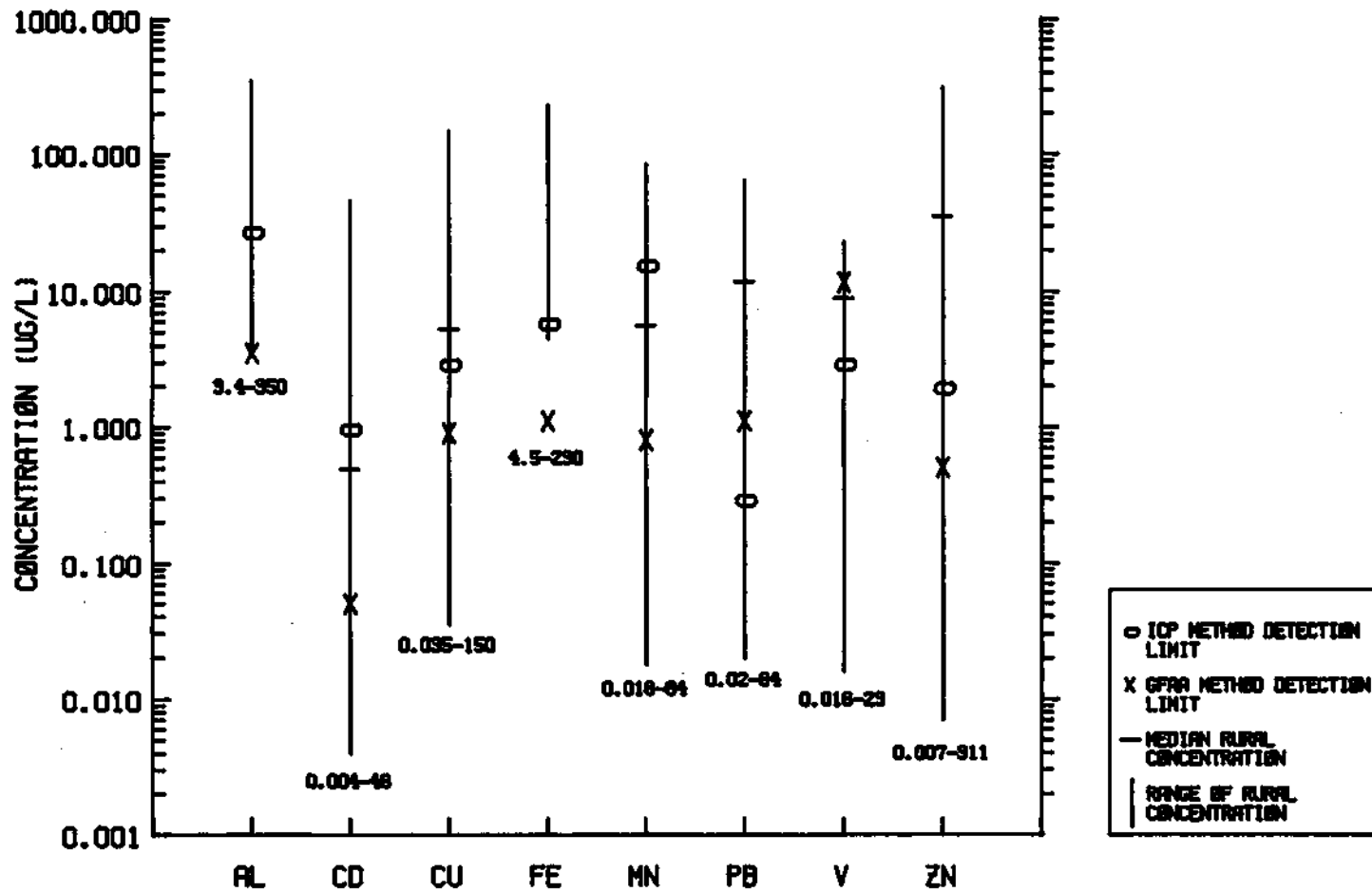


Figure 5. Ranges of metal concentrations in wet deposition from rural and remote areas (from Galloway, et al., 1982; Jeffries and Snyder, 1981; Tyree, 1981)

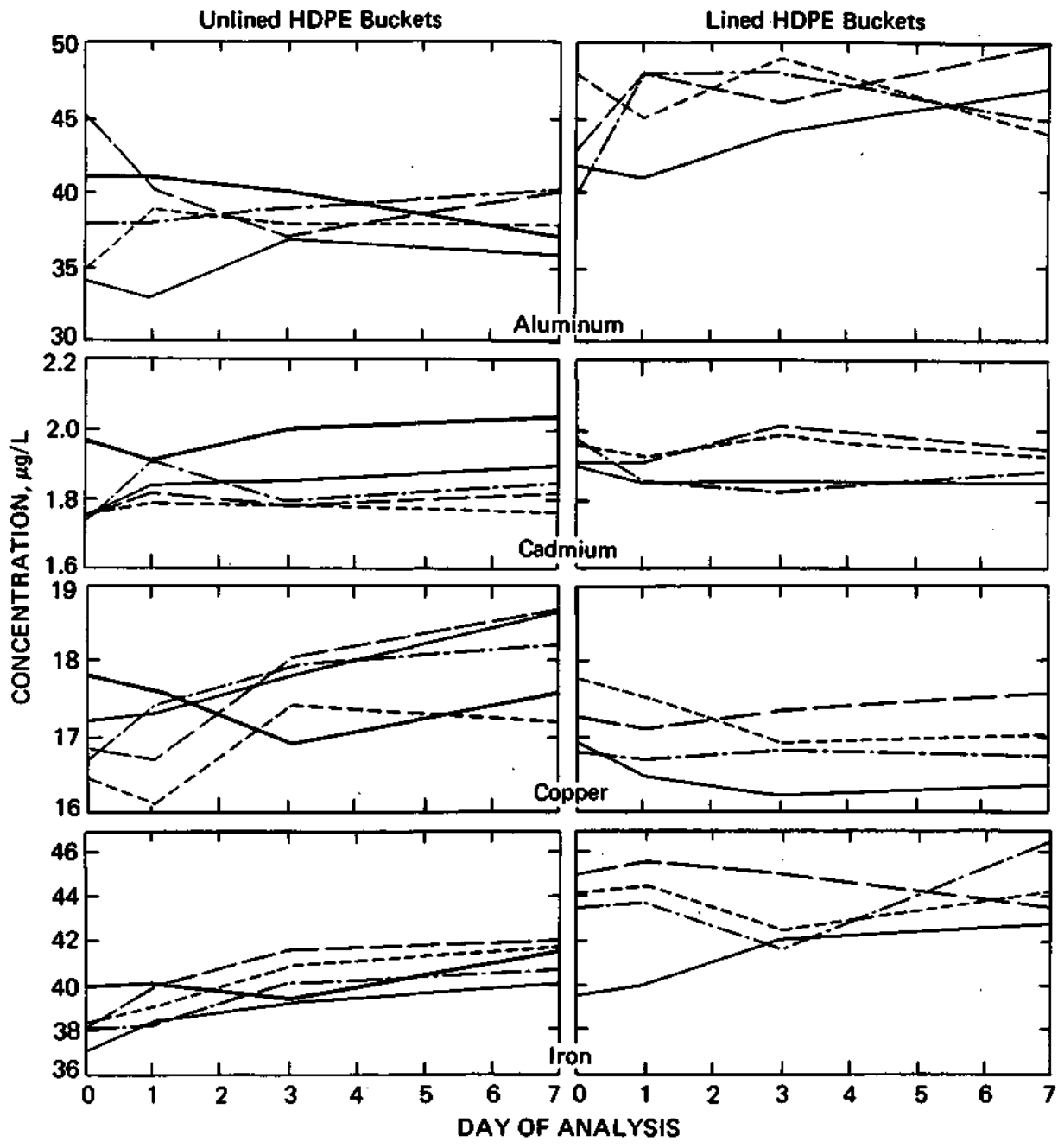


Figure 6. Trace metal recoveries in water-washed HDPE collection buckets and buckets lined with nylon reinforced polyethylene bags (Al, Cd, Cu, and Fe)

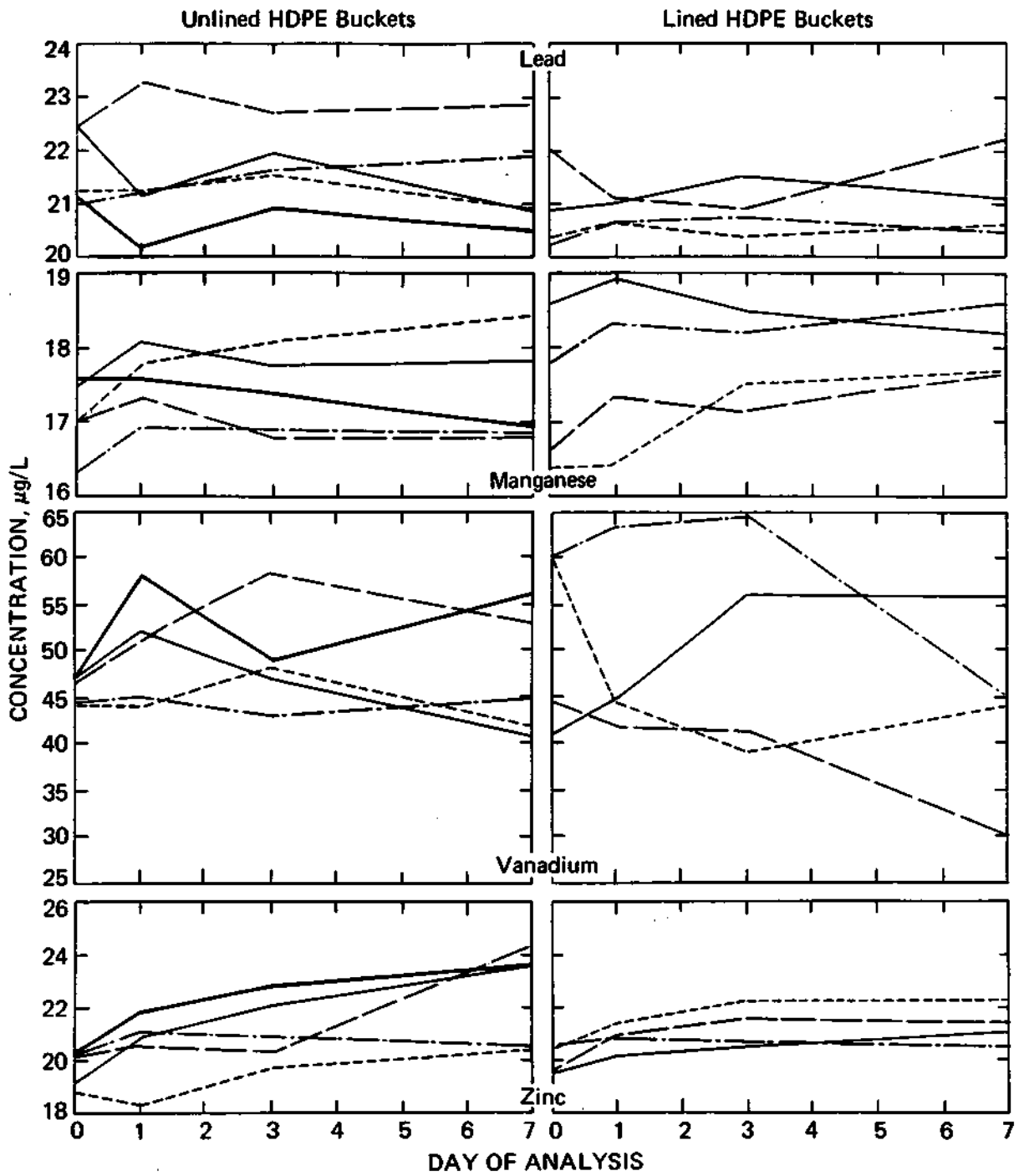


Figure 7. Trace metal recoveries in water-washed HDPE collection buckets and buckets lined with nylon reinforced polyethylene bags (Pb, Mn, V, Zn)

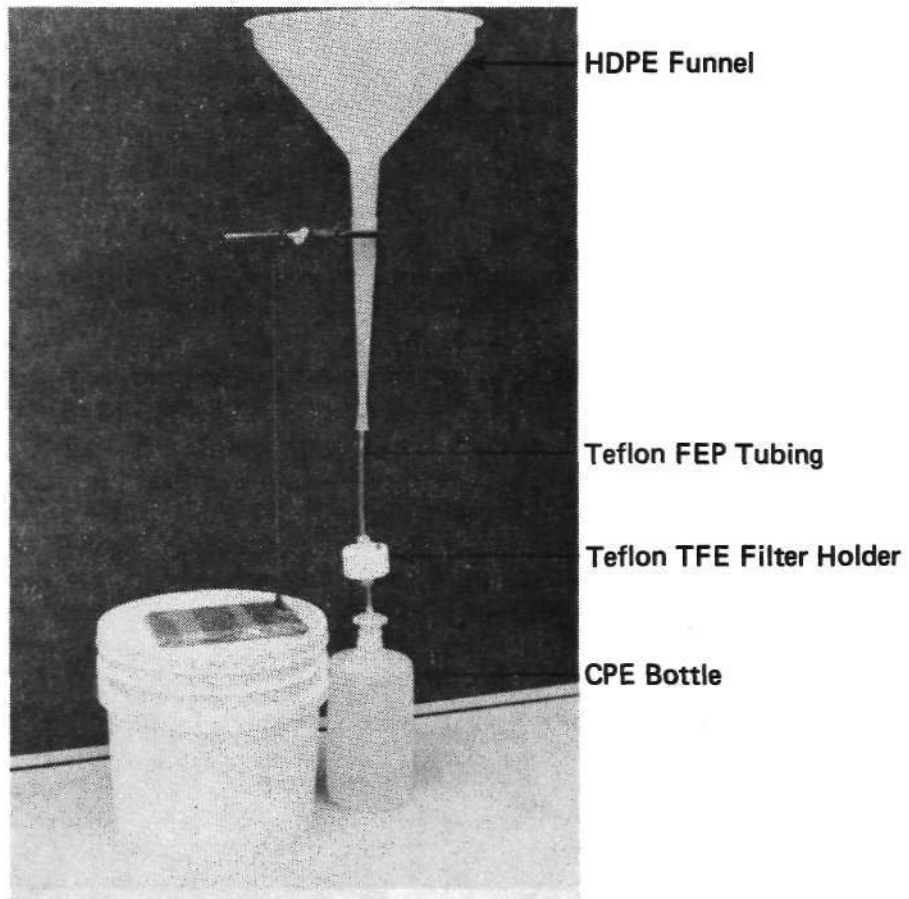


Figure 8. Funnel and bottle in situ filtration collector

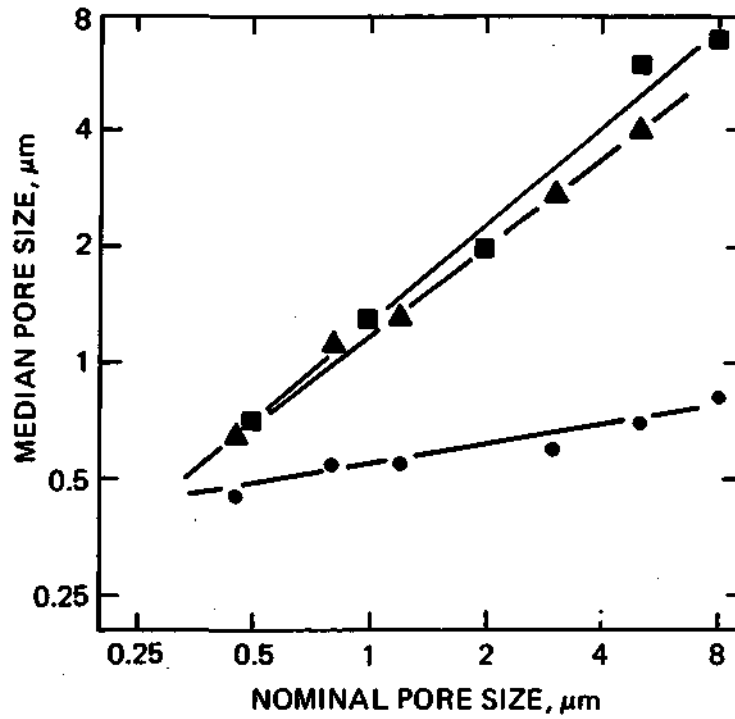


Figure 9. Relationship between nominal pore size and effective pore size of filters (from Sheldon, 1972) - metal membrane, - polycarbonate membrane, • - cellulose ester membrane.

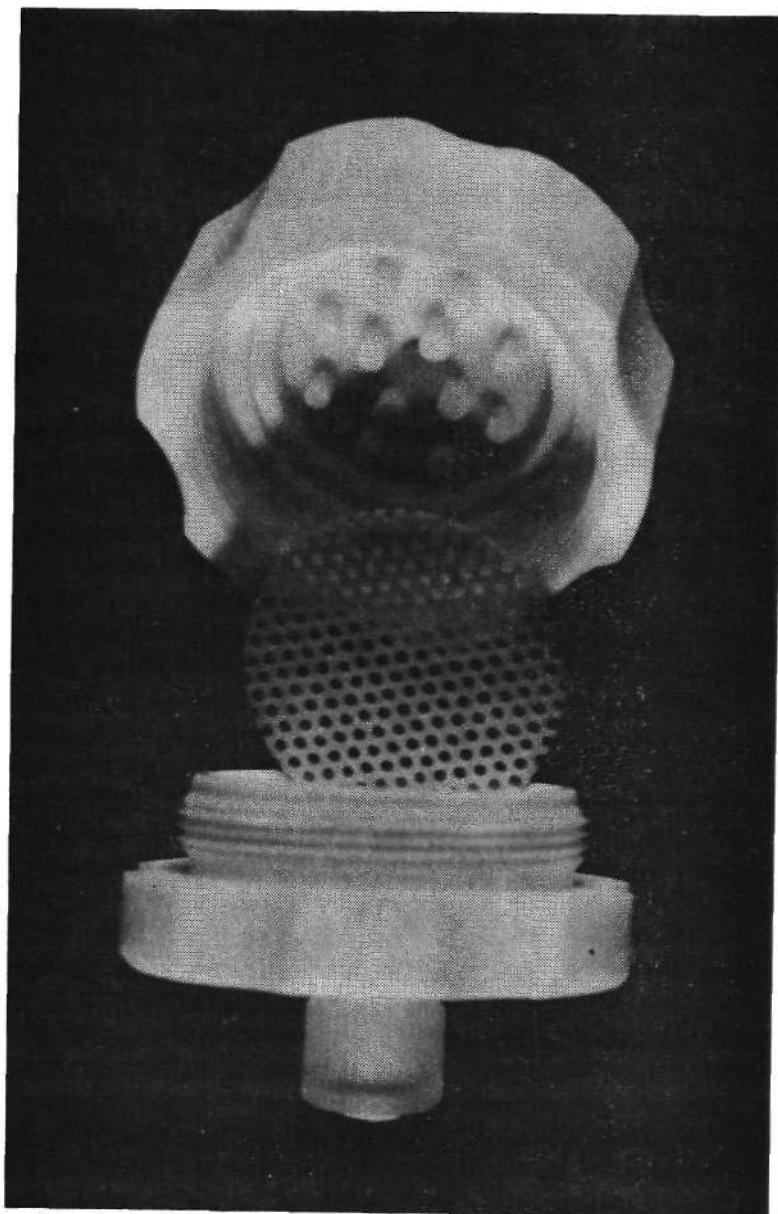


Figure 10. Teflon (tetrafluoroethylene, TFE) in-line filter holder

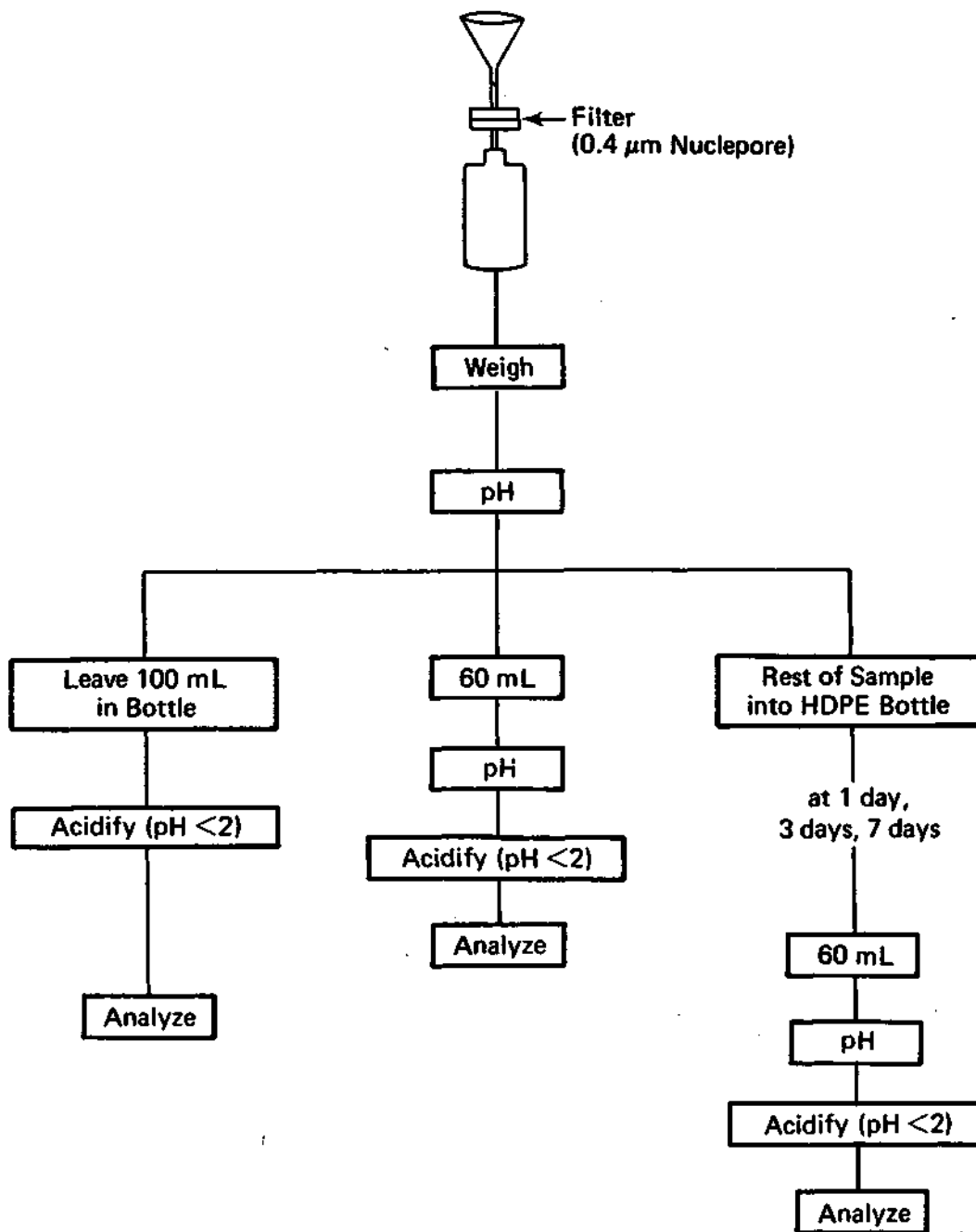


Figure 11. Sampling protocol for in situ filtration collection of wet deposition

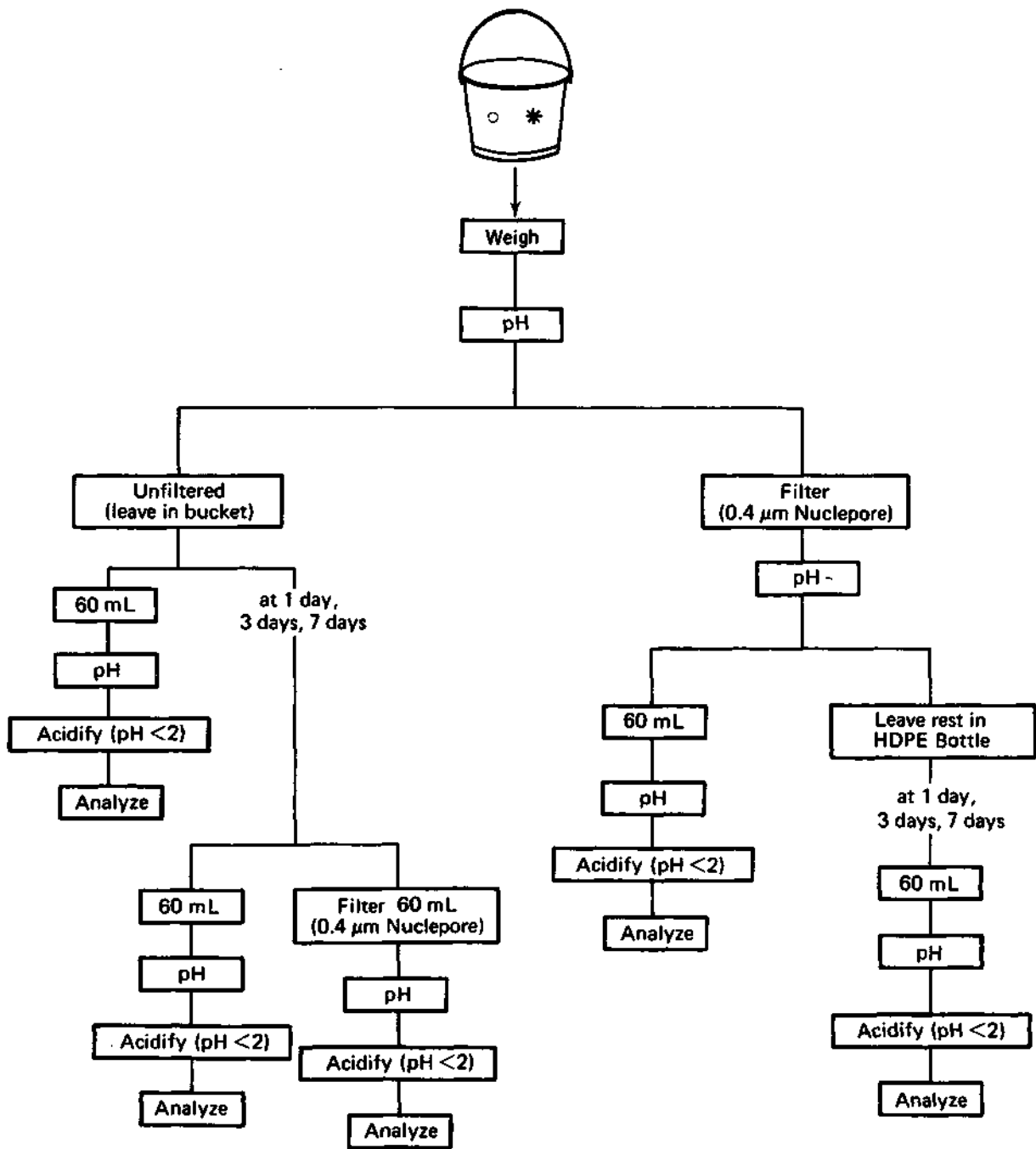


Figure 12. Sampling protocol for bucket collection of wet deposition

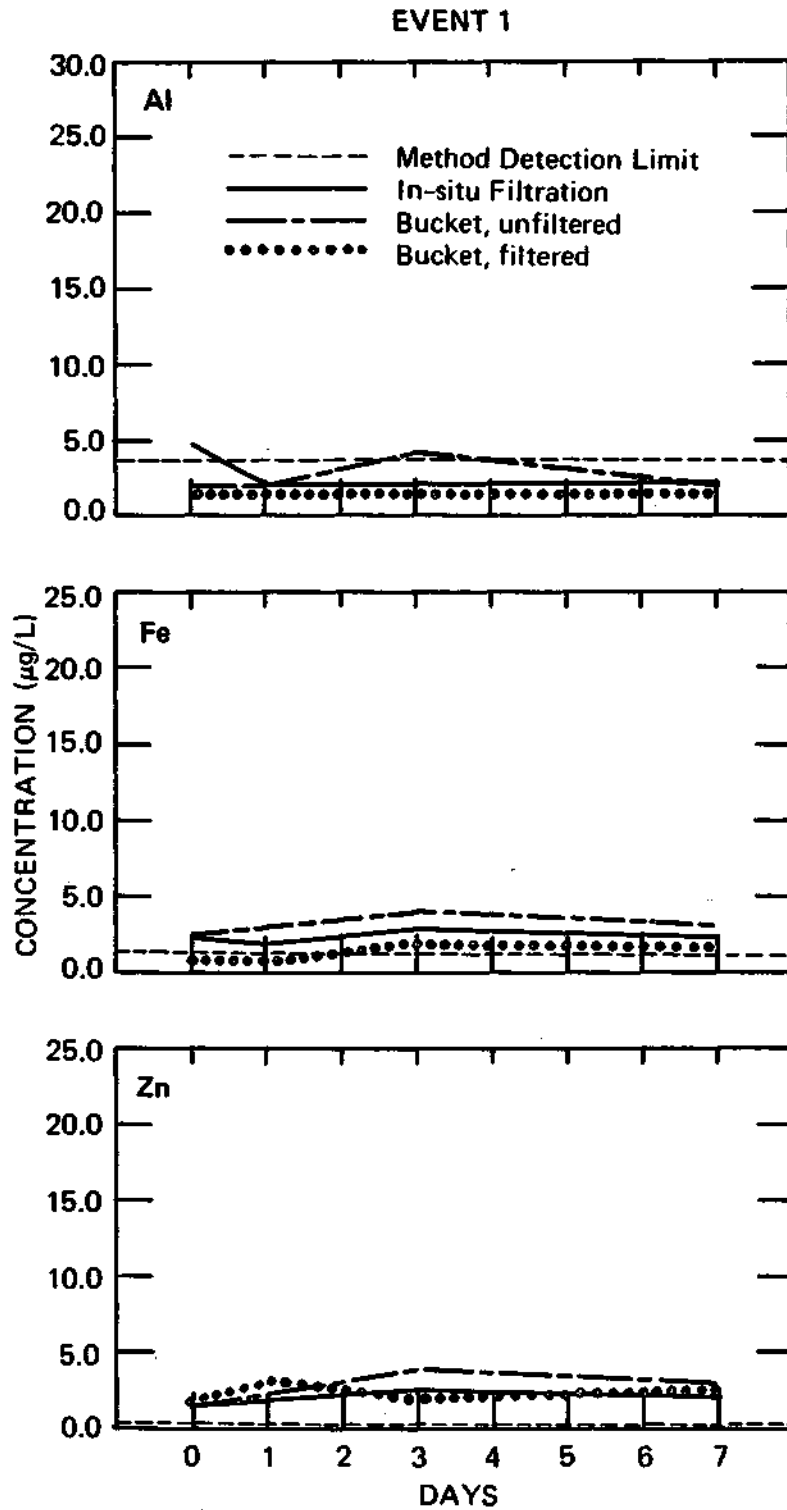


Figure 13a. Rainfall of 1.07 inches, Champaign, IL, February 4, 1986 (Al, Fe, and Zn)

EVENT 1

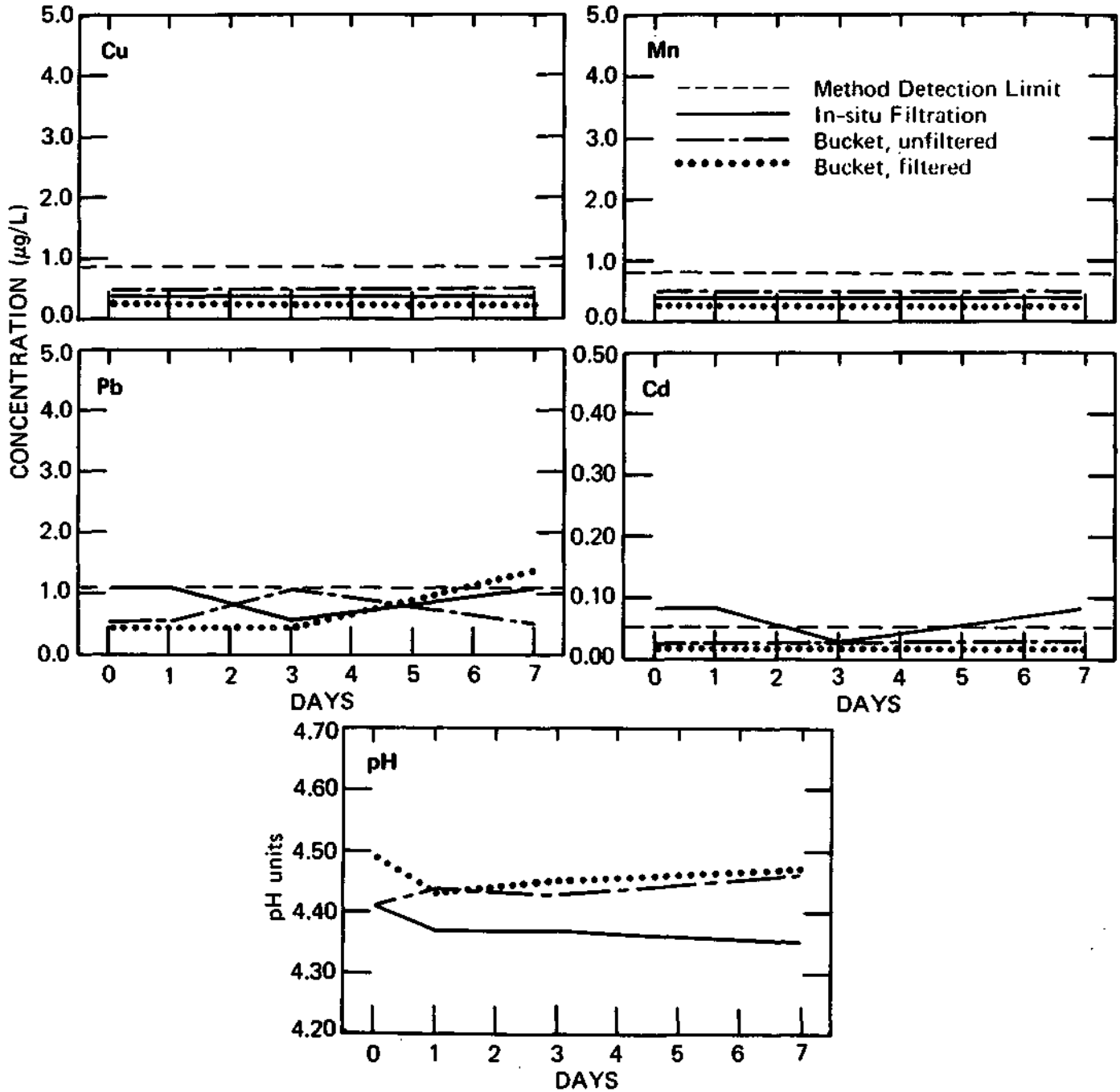


Figure 13b. Rainfall of 1.07 inches, Champaign, IL, February 4, 1986 (Cu, Mn, Pb, Cd, and pH)

EVENT 2

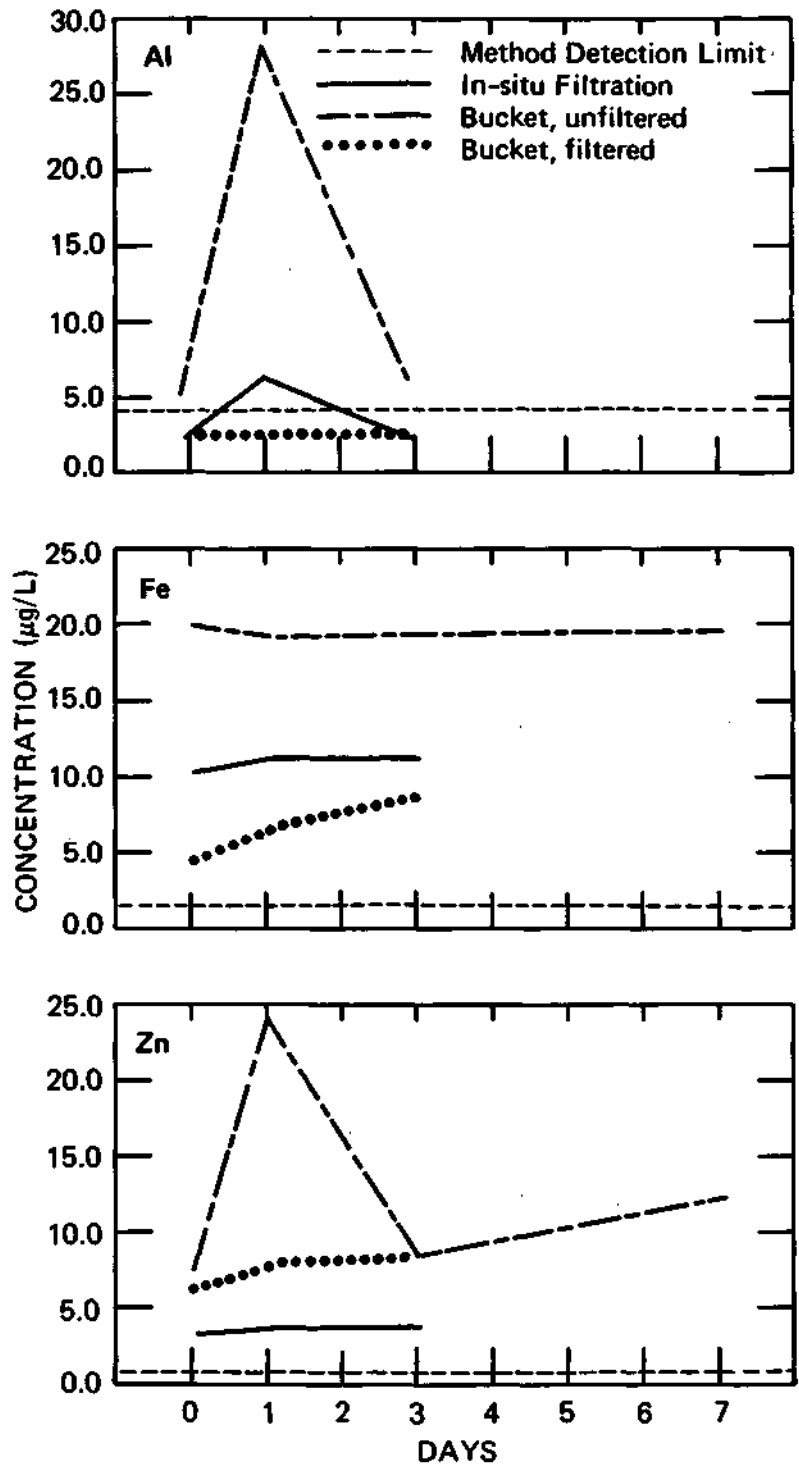


Figure 14a. Rainfall of 0.35 inches, Champaign, IL, February 5, 1986 (Al, Fe, and Zn)

EVENT 2

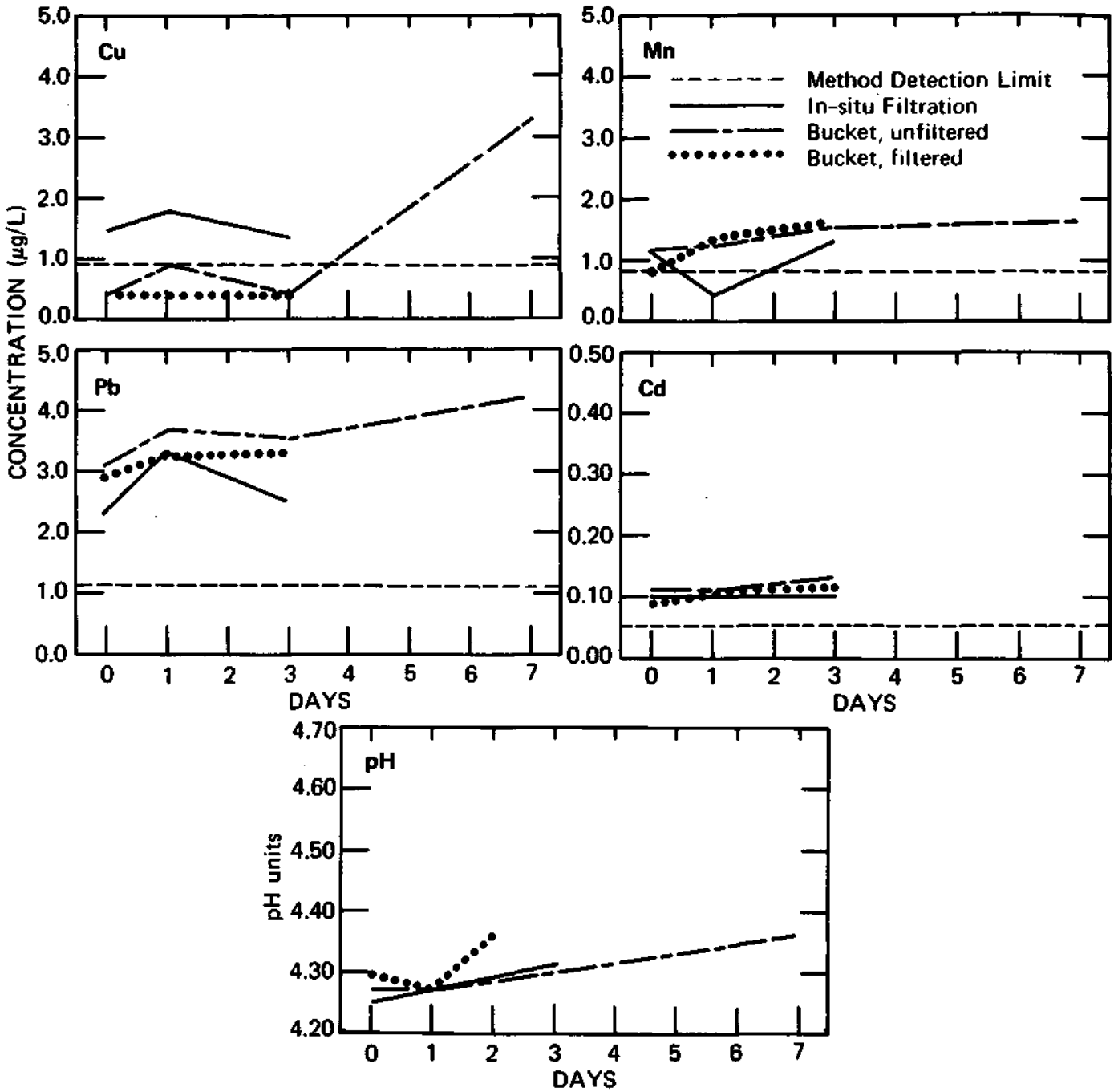


Figure 14b. Rainfall of 0.35 inches, Champaign, IL, February 5, 1986 (Cu, Mn, Pb, Cd, pH)

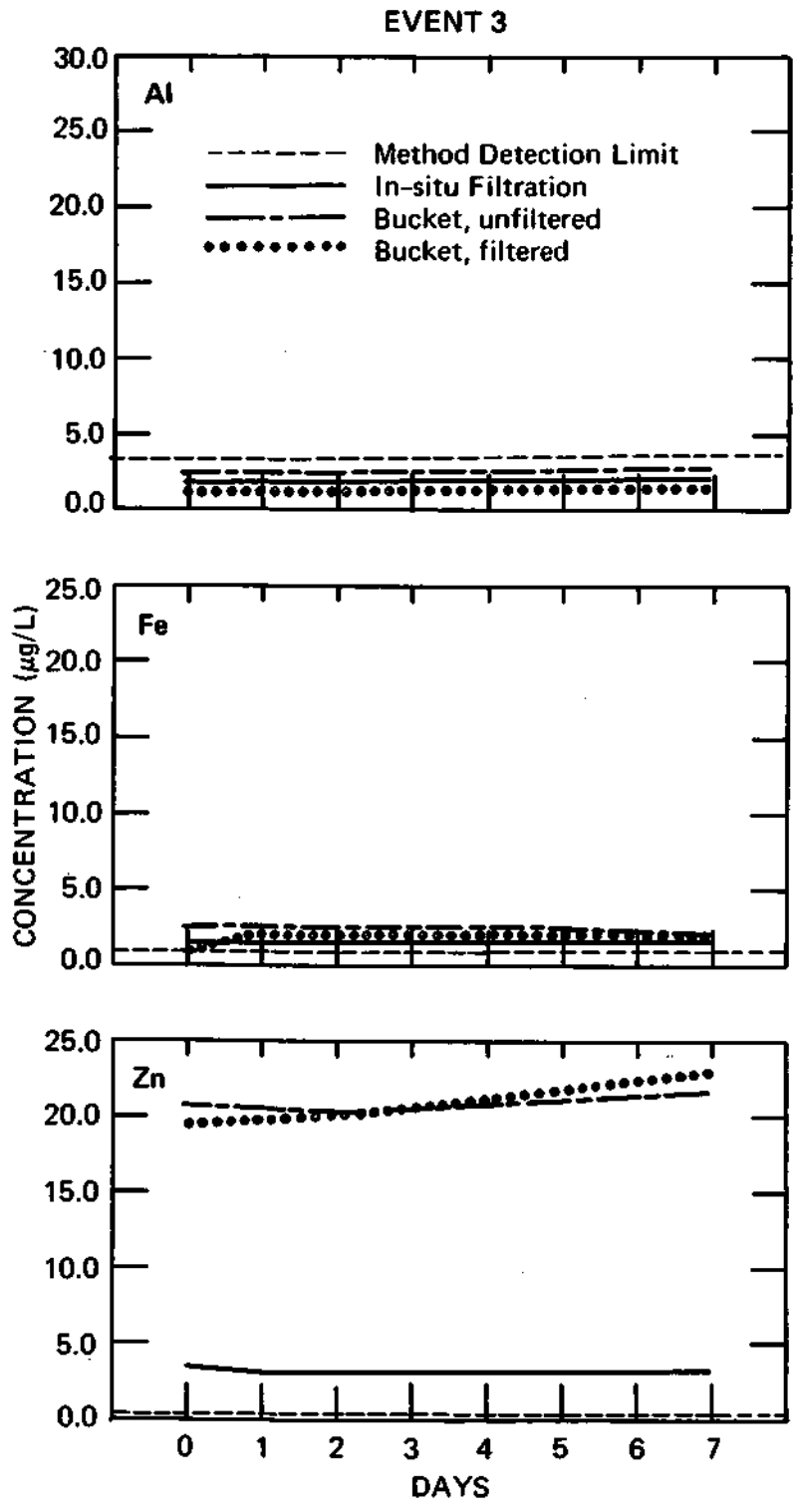


Figure 15a. NADP/NTN wet deposition sample E01940W (collected at Illinois site 47 on February 4, 1986) (Al, Fe, and Zn)

EVENT 3

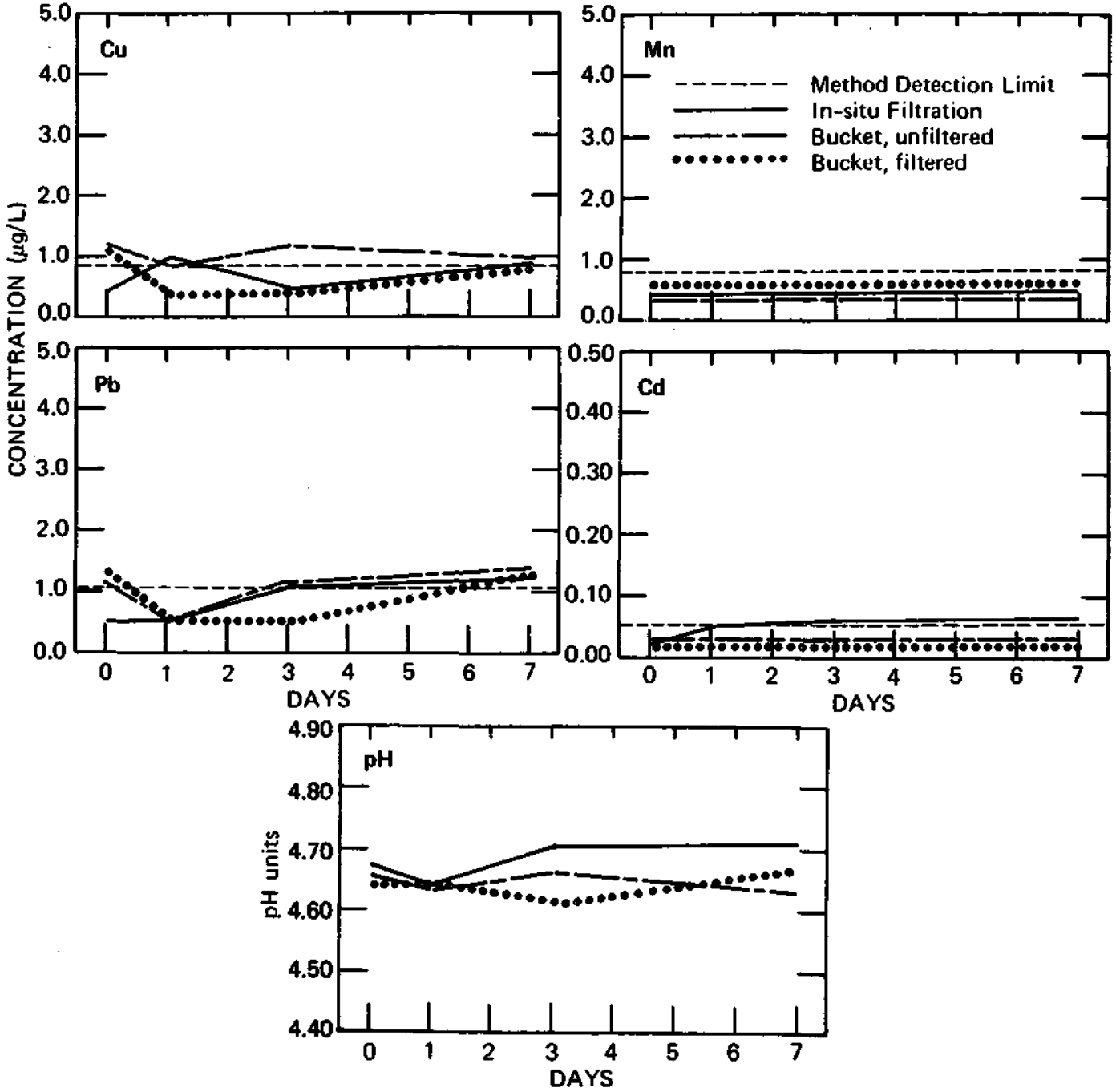


Figure 15b. NADP/NTN wet deposition sample E01940W (Cu, Mn, Pb, Cd, pH)

EVENT 4

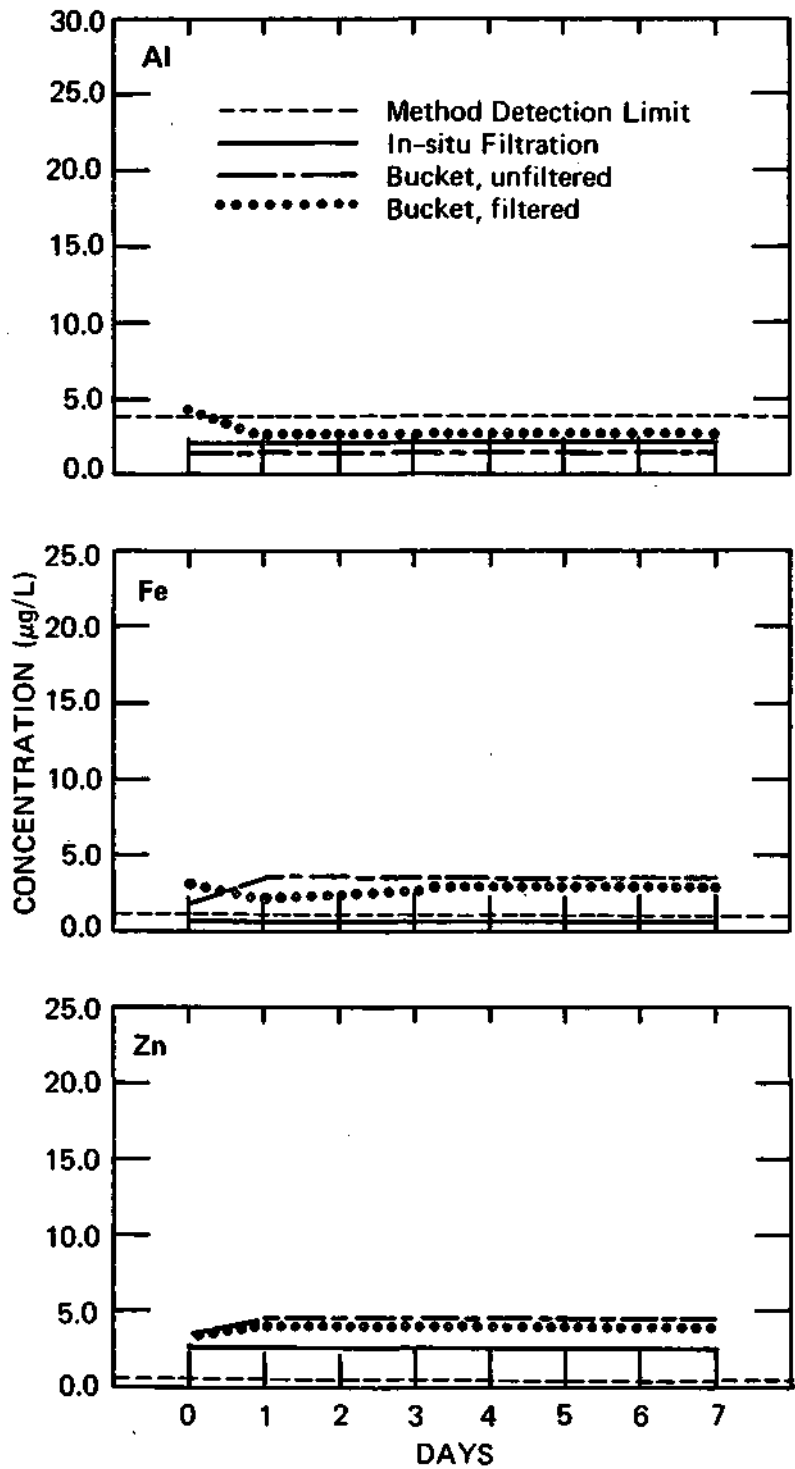


Figure 16a. NADP/NTN wet deposition sample E01950W (collected at Oklahoma site 25 on February 4, 1986) (Al, Fe, and Zn)

EVENT 4

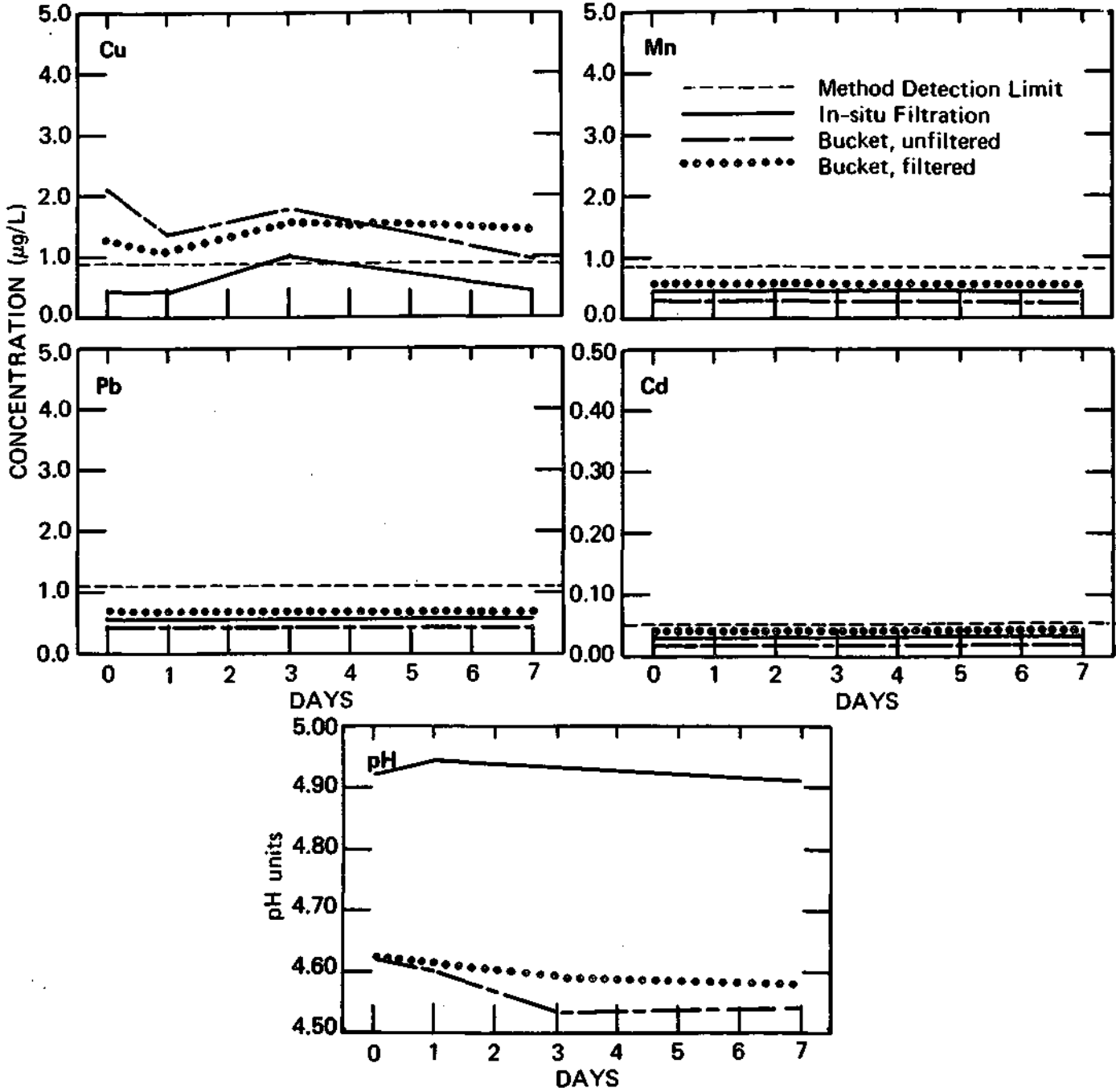


Figure 16b. NADP/NTN wet deposition sample E01950W (Cu, Mn, Pb, Cd, pH)

EVENT 5

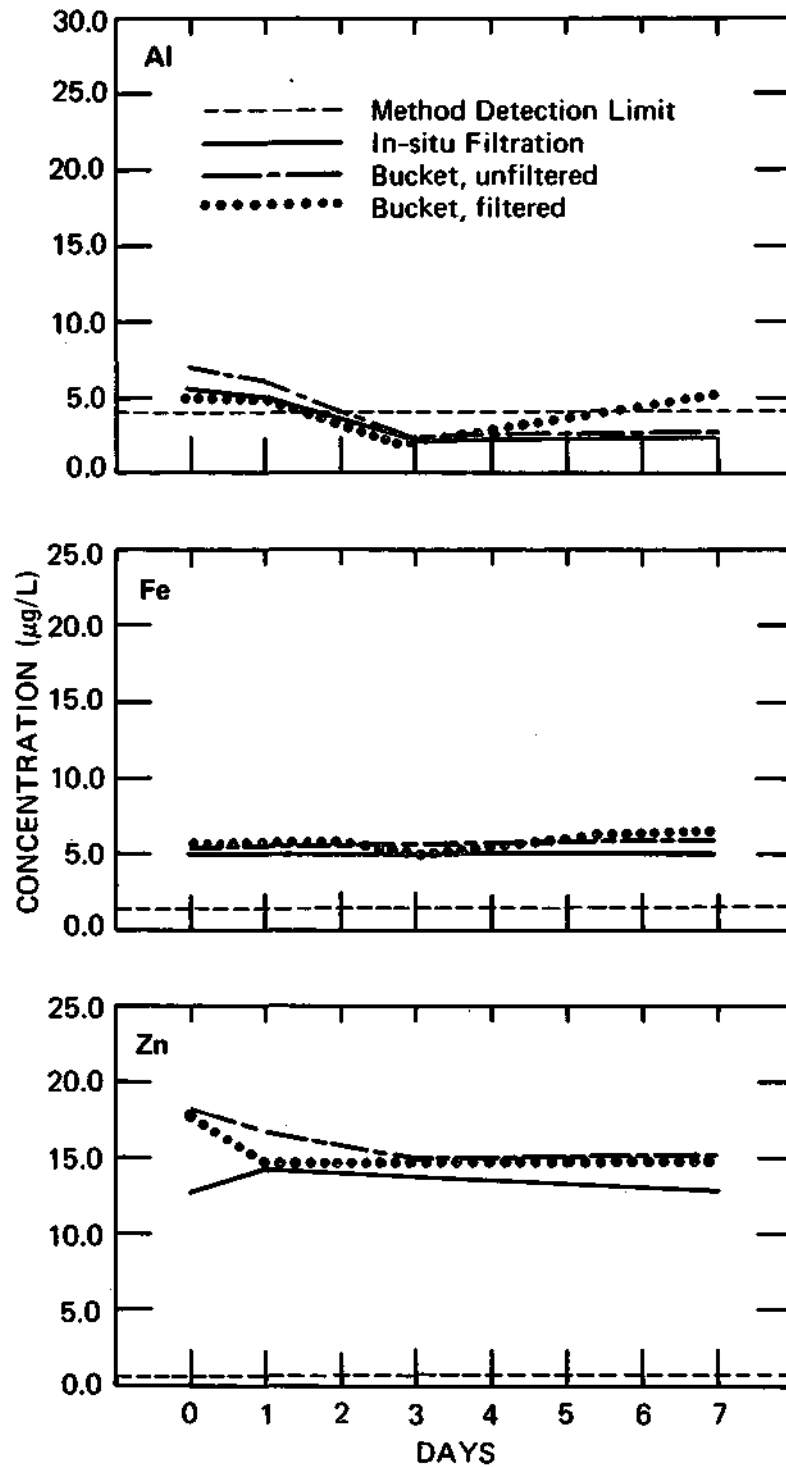


Figure 17a. NADP/NTN wet deposition sample E01890W (collected at Illinois site 63 on February 4, 1986) (Al, Fe, and Zn)

EVENT 5

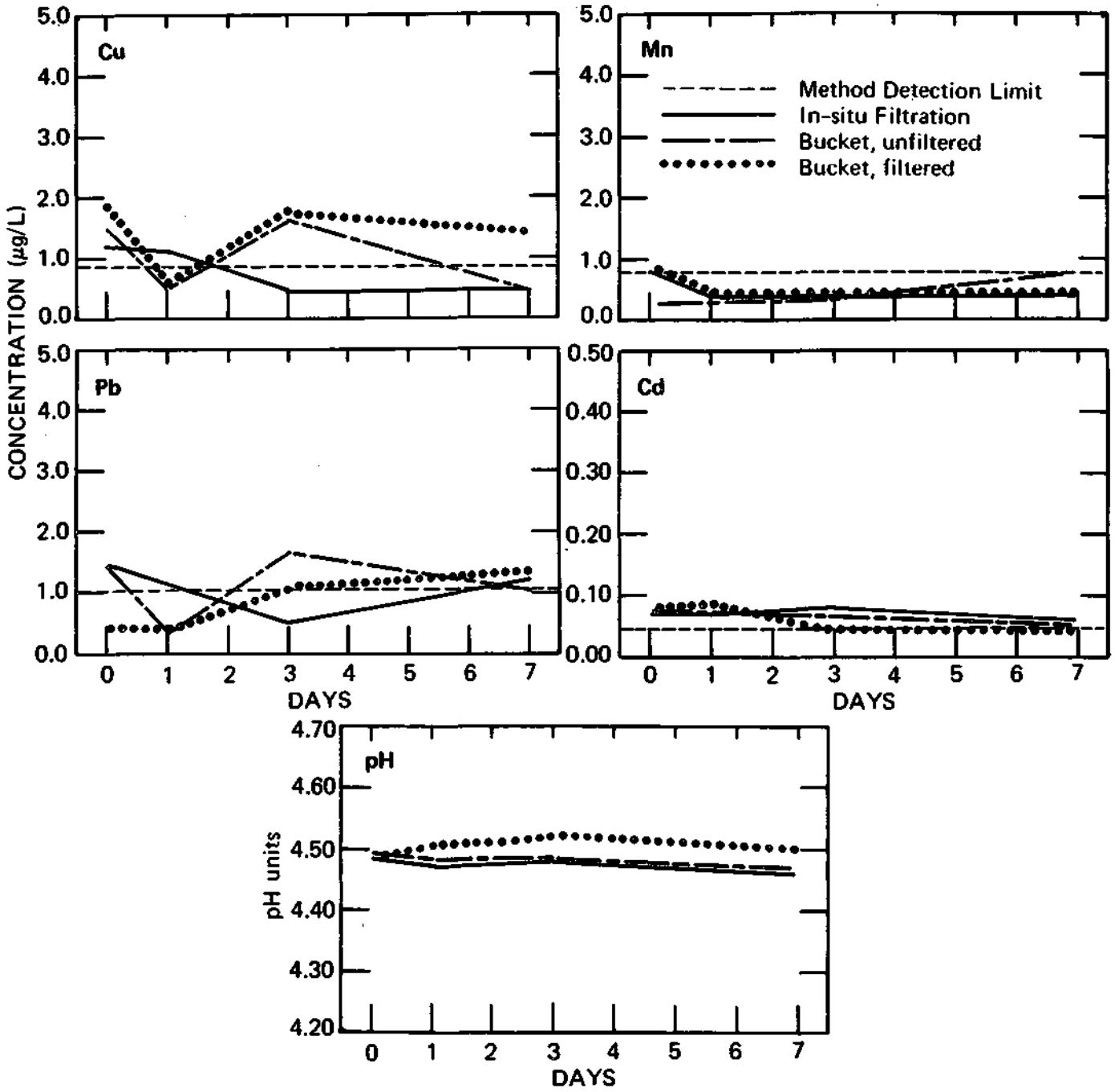


Figure 17b. NADP/NTN wet deposition sample E01890W (Cu, Mn, Pb, Cd, pH)

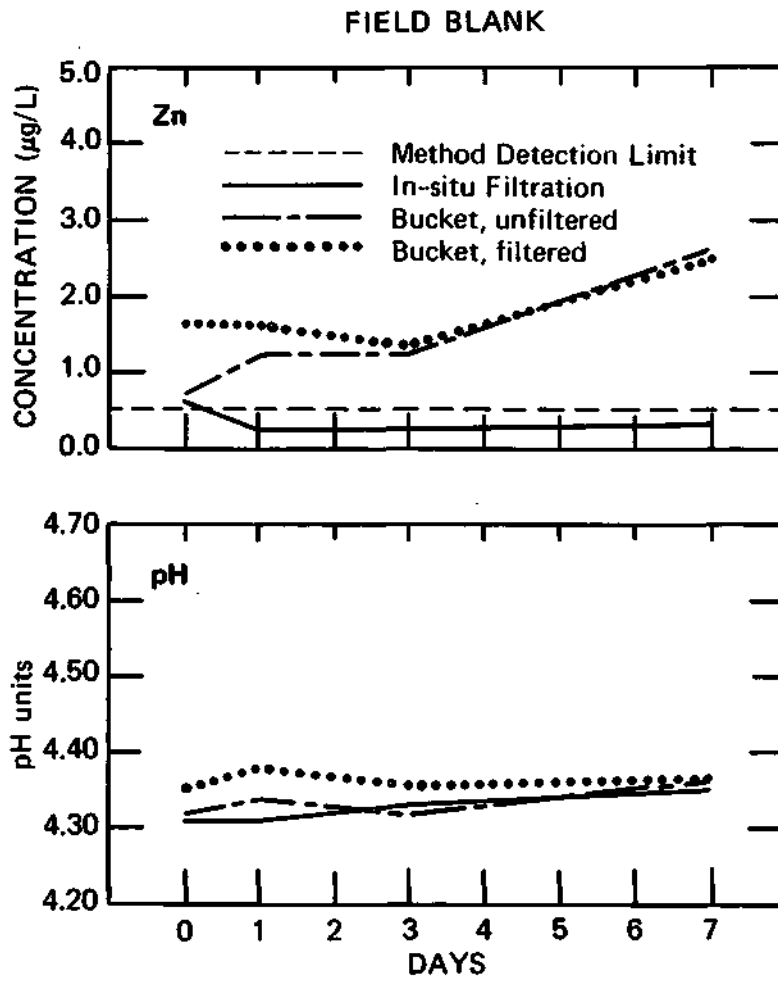


Figure 18. Field blank results (0.0005N HNO)

Method 200.6 – Dissolved Aluminum, Cadmium, Copper,
Iron, Lead, Manganese, and Zinc in
Wet Deposition by Graphite Furnace
Atomic Absorption Spectrophotometry

January 1988

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TABLES

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1. SCOPE AND APPLICATION

- 1.1 This method is applicable to the determination of dissolved aluminum, cadmium, copper, iron, lead, manganese, and zinc in wet deposition by graphite furnace atomic absorption spectrophotometry (GFAAS).
- 1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.
- 1.3 The method detection limits (MDL) (see Glossary) for the above analytes were determined from replicate analyses of calibration standards containing 10 ug/L Al, 0.25 ug/L Cd, 5.0 ug/L Cu, 5.0 ug/L Fe, 2.5 ug/L Pb, 5.0 ug/L Mn, and 2.5 ug/L Zn. The MDL's and concentration ranges of this method are presented in Table 1.
- 1.4 GFAAS is recommended when minimal MDLs are needed or when sample size is limited.

2. SUMMARY OF METHOD

- 2.1 A discrete volume of solution containing the metal(s) of interest is deposited into a graphite furnace where it is electrothermally dried, pyrolyzed, and atomized. The dense population of ground state atoms is confined in the graphite tube. Conversion of nearly all the analyte into atoms and increased atom residence times in the light path improve method detection limits up to three orders of magnitude over flame atomic absorption spectrophotometry (FAAS) methods. These ground state atoms absorb electromagnetic radiation over a series of narrow, sharply defined wavelengths. A spectrally pure line source of light, usually a hollow cathode lamp specific to the metal of interest, is used to pass a beam through the tubular graphite furnace. Light from the source beam, less whatever intensity was absorbed by the ground-state atoms of the analyte, is isolated by the monochromator and measured by the photodetector. The amount of light absorbed by the atoms is proportional to the concentration of the metal in solution. The relationship between absorption and concentration is expressed by Beer's Law:

$$\log (I / I_0) = abc = A$$

where: I = incident radiant power
I₀ = transmitted radiant power
a = absorptivity (constant for a given system)
b = sample path length
c = concentration of absorbing species (ug/L)
A = absorbance

The atomic absorption spectrophotometer is calibrated with standard solutions containing known concentrations of the element(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

3. DEFINITIONS

- 3.1 ABSORBANCE (A) – the logarithm to the base ten of the reciprocal of the transmittance, (T):

$$A = \log (1/T)$$

0.0044 A = the absorption of 1% of
the transmitted light.

The absorbance is related to the analyte concentration by Beer's Law (Sect. 2.1) where $1/T = 1 / I$.

- 3.2 ATOMIC ABSORPTION – the absorption of electromagnetic radiation by an atom resulting in the elevation of electrons from their ground states to excited states. Atomic absorption spectrophotometry involves the measurement of light absorbed by atoms of interest as a function of the concentration of those atoms in a solution.
- 3.3 SPECTRAL BANDWIDTH – the wavelength or frequency interval of radiation leaving the exit slit of a monochromator between limits set at a radiant power level halfway between the continuous background and the peak of an emission line or an absorption band of negligible intrinsic width (14.1).
- 3.4 SPECTROPHOTOMETER – an instrument that provides the ratio, or a function of the ratio, of the radiant power of two beams as a function of spectral wavelength. These two beams may be separated in time and/or space.
- 3.5 GRAPHITE TUBE FURNACE – an electrothermal atomizer consisting of a tubular graphite furnace connected to a power unit. The furnace is contained in a water-cooled housing and is purged with inert gas. Voltage is passed directly through the graphite tube via electrodes, producing furnace temperatures over 3000 C.
- 3.6 PLATFORM – a thin graphite plate which is inserted into the graphite tube. The sample is deposited directly onto the platform, which heats more slowly than the surrounding tube. Atomization is delayed, and occurs in a higher temperature environment.
- 3.7 HEATING CYCLES
- 3.7.1 Dry – the sample is heated to evaporate the solvent.
- 3.7.2 Pyrolyze (Char/Ash) – the residue is heated to a temperature selected for decomposition and volatilization of the matrix components. The temperature must be controlled to prevent vaporization of the analyte.
- 3.7.3 Atomize – the furnace temperature is increased to completely convert the analyte into ground state atoms.

3.8 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Matrix effects are common in GFAAS, causing enhancement or suppression of the formation of ground state atoms.

4.1.1 Chemical Interferences – If the sample contains a compound that does not dissociate in the pyrolyzation stage of the furnace program it may alter atomization rates, allow molecular analyte loss, or cause the analyte to remain nonvolatile.

4.1.1.1 Aluminum has a tendency to form highly refractory carbides on the furnace surface. The carbide is difficult to dissociate completely. The use of pyrolytically coated graphite and a platform will reduce this interference. Since the platform heats primarily by radiation, its temperature increase is slower than that of the tube walls. Sample deposition onto the platform allows the sample to be atomized into a higher temperature environment, reducing the effect of the sample matrix. The pyrolytic coating minimizes sample penetration into the graphite, reducing carbide formation.

4.1.1.2 Aluminum forms stable nitrides at high temperatures in the presence of nitrogen. To avoid this interference, use argon as the purge gas (14.3).

4.1.1.3 Acidifying standards and samples to 0.5% (v/v) **nitric acid (0.08N HNO₃) will prevent hydrolysis of aluminum ($Al^{+3} + H_2O \rightleftharpoons H^+ + AlOH^{+2}$).**

4.1.1.4 Volatile halide interferences can be prevented by avoiding the use of halide acids as preservatives. Nitric acid is recommended.

4.1.1.5 Nitric acid concentrations in samples and standards must be closely matched. Different concentrations result in changes in the decomposition and volatilization of the acid and other matrix components in the pyrolyzation stage of the furnace program. This difference will also affect vaporization of the analyte.

- 4.1.2 Physical interferences may occur due to nonuniform distribution of samples on the tube surface, resulting in varied atomization rates and/or crystal formation. This problem can be abated by an automatic sample injection system that uses a nebulizer to deposit the sample in aerosol form (14.4).
- 4.1.3 Nonspecific background absorption is due to light scattering and/or molecular absorption by the matrix components. Highly volatile elements tend to vaporize before the matrix components can be completely decomposed and volatilized. Various background correction systems are available.
 - 4.1.3.1 Zeeman – An external magnetic field splits the atomic spectral line into polarized components. When the magnetic field is applied, only background absorbance is measured. When the magnetic field is off, the absorbance of the sample and background are both measured. The difference between the two measurements is the background corrected value.
 - 4.1.3.2 Continuum Source – Light from a continuum (broad-band) source and from the analyte spectral source are monitored separately. The light from the analyte source is absorbed by the analyte and the background, while light from the continuum source is absorbed only by the background. Their difference is the background corrected value.
 - 4.1.3.3 Smith-Hieftje – The line source is cycled at low and high currents. At low current, light is absorbed by both the analyte and the background. A brief pulse of high current is passed through the hollow cathode lamp. This causes non-excited atoms of the source element to undergo self-reversal, emitting light at wavelengths other than that of the analyte. At the high current pulses, the light is absorbed mainly by the background. The difference between the measurements at low and high currents is the background corrected value (14.5).
- 4.1.4 Although wet deposition samples are characterized by low ionic strength, the use of background correction is recommended.
 - 4.1.4.1 The nitric acid matrix of the samples may be a source of nonspecific background absorption.
 - 4.1.4.2 The salts present in coastal wet deposition samples may cause chemical interferences (e.g. halides).
 - 4.1.4.3 Wet deposition samples from urban areas will have a more complex matrix. These samples may require the use of the standard addition technique (14.6).

4.1.4.4 Cadmium, lead, and zinc are highly volatile. They tend to vaporize before the matrix components can be completely decomposed and volatilized.

4.2 Memory effects can occur when an analyte from a previous sample is not completely atomized. These effects will result in elevated concentration readings. To check for this interference, analyze a zero standard immediately after a high concentration sample. If an atomization peak is observed, refer to Appendix A.

5. SAFETY

5.1 Use a fume hood, protective clothing, and safety glasses when handling concentrated acids and metallic cadmium, lead, and manganese (Sect. 7).

5.2 The operator should wear eye protection (welder's goggles) to avoid eye damage from the ultraviolet light emitted by the furnace during atomization.

5.3 To avoid severe skin burns, do not touch the furnace until it has returned to ambient temperature.

5.4 The GFAA instrumentation operates at high voltages. Check furnace and electrode alignment and connections before applying power.

5.5 Metallic cadmium, lead, manganese, their stock standard solutions, and spent hollow cathode lamps are hazardous wastes. Dispose of them appropriately (14.7).

5.6 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.8).

6. APPARATUS AND EQUIPMENT

6.1 ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS) – Select a single-beam or double-beam instrument with adjustable spectral bandwidth, wavelength range of 190-400 nm, background correction capabilities, zero and calibration controls.

6.1.1 Spectral Line Source – Use single element lamps. Hollow cathode lamps or electrodeless discharge lamps (EDL) may be used.

6.1.2 Photomultiplier Tube – Select a photomultiplier tube with optimal quantum efficiency in the wavelength range of 190-400 nm.

6.2 GRAPHITE FURNACE – Select a furnace with precise temperature control to 2800 C, variable gas flow rates, and a cooling system.

6.3 SAMPLE INTRODUCTION SYSTEM

6.3.1 Pipette – For manual introduction of the sample into the furnace, select a microliter pipette with disposable polypropylene tips. Precision requirements are 1.0% relative standard deviation (RSD) at volumes less than 10 uL and <0.7% RSD at volumes greater than 10 uL.

6.3.2 Autosampler – An autosampler, although not required, is recommended for improved precision. It should be equipped with a dust cover to prevent airborne contamination.

NOTE: An autosampler that uses a nebulizer to deposit the sample as an aerosol will abate some interferences (Sect. 4.1.2).

6.4 DATA AQUISITION SYSTEM

6.4.1 Strip Chart Recorder – Select a recorder with a full scale response of 0.25 seconds or better and a variable chart speed.

6.4.2 Printer – A printer may be used to document data. Either a graphics option or a strip chart recorder in tandem with the printer is required to establish furnace parameters. (Sect. 11.3).

6.5 Maintain a set of Class A (14.9) volumetric flasks to be used only when making dilute working standards for the analysis of wet deposition samples. New glassware should be cleaned according to Sect. 7.11 before use. Store filled with water (Sect. 7.2) and covered.

6.6 LABORATORY FACILITIES – Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air work stations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. If a clean air work station is unavailable, samples must be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room. Point of use 0.2 um filters are recommended for all faucets supplying water (Sect. 7.2) to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions. The circulation and delivery systems for water (Sect. 7.2) must be constructed entirely of non-metal components.

6.7 PRECIPITATION SAMPLER – The use of a wet-only sampler is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability.

6.8 FILTRATION APPARATUS – A polysulfone filtration apparatus is recommended. Do not use glass.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS – Use chemicals of reagent grade or better for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER – Use water conforming to ASTM Specification D 1193, Type II (14.10).

7.3 ARGON – Use standard, welder's grade compressed argon. A line filter or trap is recommended to ensure particle and moisture free gas. Nitrogen is not recommended because of its tendency to form stable nitrides with aluminum at high temperatures.

7.4 HYDROCHLORIC ACID – Use concentrated hydrochloric acid (HCl, sp gr 1.19) that meets the following specifications for trace metal analysis: <0.05 mg/L Al, <0.02 mg/L Fe, and <0.005 mg/L Cd, Cu, Pb, Mn, and Zn.

7.5 HYDROCHLORIC ACID (6.0 N) – Add 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) to an equal volume of water (Sect. 7.2).

7.6 NITRIC ACID – Use concentrated nitric acid (HNO₃, sp gr 1.43) that meets the specifications for trace metal analysis (Sect. 7.4).

7.7 NITRIC ACID (8.0 N) – Add 1 volume of concentrated nitric acid (HNO₃, sp gr 1.43) to an equal volume of water (Sect. 7.2).

7.8 NITRIC ACID (3.2 N) – Add 1 volume of concentrated nitric acid (HNO₃, sp gr 1.43) to 4 volumes of water (Sect. 7.2).

7.9 STOCK STANDARD SOLUTIONS – Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as detailed below. Store the solutions at room temperature in polyethylene containers.

7.9.1 Aluminum Solution, Stock (1.0 mL = 1.0 mg Al) – Dissolve 1.000 g of pure aluminum wire in 50 mL of concentrated HCl (Sect. 7.4) over low heat. Cool and dilute to 1 L with water (Sect. 7.2).

7.9.2 Cadmium Solution, Stock (1.0 mL = 1.0 mg Cd) – Dissolve 1.000 g of pure metallic cadmium in 50 mL of 6.0 N HCl (Sect. 7.5) and dilute to 1 L with water (Sect. 7.2).

- 7.9.3 Copper Solution, Stock (1.0 mL = 1.0 mg Cu) – Dissolve 1.000 g of electrolytic copper in 50 mL of 8.0 N HNO₃ (Sect. 7.7) and dilute to 1 L with water (Sect. 7.2).
- 7.9.4 Iron Solution, stock (1.0 mL = 1.0 mg Fe) – Dissolve 1.000 g of pure metallic iron in 50 mL of 6.0 N HCl (Sect. 7.5) and dilute to 1 L with water (Sect. 7.2).
- 7.9.5 Lead Solution, Stock (1.0 mL = 1.0 mg Pb) – Dissolve 1.000 g of pure metallic lead or 1.598 g of lead nitrite (Pb(NO₃)₂) in 50 mL of 8.0 N HNO₃ (Sect. 7.7) and dilute to 1 L with water (Sect. 7.2) .
- 7.9.6 Manganese Solution, Stock (1.0 mL = 1.0 mg Mn) – Dissolve 1.000 g of pure metallic manganese in 50 mL of 8.0 N HNO₃ (Sect. 7.7) and dilute to 1 L with water (Sect. 7.2).
- 7.9.7 Zinc Solution, Stock (1.0 mL = 1.0 mg Zn) – Dissolve 1.000 g of pure metallic zinc in 50 mL of 6.0 N HCl (Sect. 7.5) and dilute to 1 L with water (Sect. 7.2).
- 7.10 GRAPHITE FURNACE TUBES
- 7.10.1 Pyrolytically coated graphite tubes will improve sensitivity, reduce memory effects, and decrease carbide formation by reducing sample penetration into the tube wall.
- Note: The samples are acidic (Sect. 8.4) and will degrade the coating resulting in a decrease in the signal to noise ratio.
- 7.10.2 Platforms or graphite tubes with walls thicker in the center are recommended as a method of decreasing interferences (Sect. 4.1.1.1) (14.4).
- 7.11 BOTTLES FOR SAMPLES AND STANDARDS – Use polyethylene or fluorohydrocarbon plastic containers (14.11).
- 7.11.1 Rinse thoroughly with water (Sect. 7.2).
- 7.11.2 Fill with 3.2 N HNO₃ (Sect. 7.8) and leach for 48 hours.
- 7.11.3 Discard leachate and rinse thoroughly with water (Sect. 7.2).
- 7.11.4 Refill with water (Sect. 7.2) and leach for 24 hours.
- 7.11.5 Discard leachate and rinse thoroughly with water (Sect. 7.2).
- 7.11.6 Refill with water (Sect. 7.2) and store.
- 7.11.7 Rinse thoroughly with water (Sect. 7.2) before use (14.12).

- 7.12 SAMPLE CONTAINERS – Use disposable polystyrene sample cups that have been thoroughly rinsed with water (Sect. 7.2). Do not reuse.
 - 7.12.1. Check sample cups for contamination. If contamination is a problem, clean the sample cups as directed for bottles (Sect. 7.11) .
 - 7.13 FUNNEL ~ Select a funnel constructed of polyethylene or fluorohydrocarbon plastic.
 - 7.14 TUBING AND CONNECTORS – Connections from the funnel to the sample collection bottle must be constructed of polyethylene or fluorohydrocarbon plastic.
 - 7.15 FILTERS – Use 0.4 μm polycarbonate membrane filters which have been leached with 300 mL of water (Sect. 7.2).
 - 7.16 BAGS – Store clean funnels and tubing in new polyethylene bags.
8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE
- 8.1 Collect samples in a funnel connected to a preweighed sample bottle. All components should be constructed of polyethylene (14.11) or fluorohydrocarbon plastic. Clean according to Section 7.11 (14.12) . Cap collection bottles after cleaning. Air dry funnels and tubing in a laminar flow clean air work station and store in new polyethylene bags.
 - 8.1.1. Evaluate the cleaning procedure according to Section 10.3. and check for desorption and/or adsorption of trace metals (14.11).
 - 8.2 The use of wet-only samplers is recommended (Sect. 6.7). Sample collection frequency may vary from subevent to event sampling periods. Collection periods of more than one day are not recommended since sample integrity may be compromised by longer exposure periods.
 - 8.3 Immediately after collection, weigh the sample bottle to determine the sample volume. Filter the sample through a 0.4 μm polycarbonate membrane (Sect. 7.15). Monitoring of the filtration procedure is necessary to ensure that metals are neither adsorbed nor desorbed on the membrane or filtration apparatus.
 - 8.4 Immediately after filtration, acidify the filtrate to pH 1.8 (0.016N HNO_3 [Sect. 7.6]). This will stabilize and preserve the metals in solution. Filtered and acidified samples are stable for up to three months.

9. CALIBRATION AND STANDARDIZATION

9.1 CALIBRATION SOLUTIONS

- 9.1.1 Five calibration standards and one zero standard are required. The lowest calibration standard should contain the metal of interest at a concentration of one to five times the method detection limit. The highest standard concentration is determined by curve linearity, sensitivity, and expected analyte concentrations. The remaining standards are uniformly distributed between the low and high standards. Suggested calibration standard concentrations are listed in Table 2.
- 9.1.2 Calibration standards may be prepared as single or mixed element standards. Prepare calibration standards by diluting stock standards with water (Sect. 7.2). Acidify the solution to pH 1.8 (0.016N HNO₃ [Sect. 7.6]) for Cd, Cu, Fe, Pb, Mn, and Zn. Acidify aluminum standards to pH 1.1 (0.08N HNO₃ [Sect. 7.6]). Use plastic tipped pipettes that are within the precision tolerances specified in Sect. 6.3.1.
- 9.1.3 The calibration standards for Al, Cd, Cu, Fe, Mn, Pb, and Zn are stable for three months if stored at room temperature in nitric acid leached (Sect. 7.11) high density polyethylene (HDPE) or fluorohydrocarbon bottles.

NOTE: If bottles are used that are made of a plastic other than HDPE, the cleaning procedure must be evaluated according to Sect. 10.3.

9.2 CALIBRATION

- 9.2.1 A calibration curve must be constructed every day and with each replacement of the graphite tube. If the instrument is turned off or if there is an interruption in the heating cycle, verify the calibration curve by analyzing a mid-scale standard.
- 9.2.2 Clean any residue from the graphite tube by heating to atomization temperature until there is no absorbance signal. Analyze the zero standard and check for peaks in the atomization stage. If a peak is apparent, analyze another zero standard. An atomization peak indicates a memory effect (Sect. 4.2), zero standard contamination, or contamination in the furnace components. Refer to Appendix A for corrective action. When atomization of the zero standard results in no absorbance peaks, continue.

9.2.3 Analyze the calibration standards and record their absorbances. Duplicates of each midpoint standard should agree within < 5% RSD for Cd, Cu, Fe, Mn, and Zn and 10% RSD for Al and Pb.

9.2.4 Construct calibration curves for each metal.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for precipitation measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.13). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS – Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Method Variability – After a calibration curve has been constructed, reanalyze additional aliquots of all the standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value (\bar{x}) for determining the control limits. A warning limit of $\bar{x} + 2s$ and a control limit of $\bar{x} + 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) – Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified concentration as the mean (target) value.

Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as described in Sect. 10.5 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 3. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

- 10.2.3 Laboratory Spike Solutions – A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.13), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.
- 10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability. Typical single operator precisions are presented in Table 3.
- 10.3 Monitor the cleaning procedure by pouring a measured volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentration of the metals of interest. If any of the measured concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.
- 10.4 Keep daily records of calibration data and the instrument operating parameters. Use these historical data as general performance indicators. Gross changes in sensitivity, curve linearity, or photomultiplier tube voltage are indicative of a

problem. Possibilities include instrument malfunction, defective graphite tube, arcing in the furnace, improper optimization, faulty hollow cathode lamp, contamination, and/or inaccurate standard solutions.

- 10.5 Analyze a quality control check sample (QCS) after a calibration curve has been established. This sample may be formulated in the laboratory or obtained from the U.S. Environmental Protection Agency (USEPA), Environmental Monitoring and Support Laboratory in Cincinnati, Ohio. The check sample selected must be within the range of the calibration standards, and it must be prepared at the same acid concentration. If the measured value for the QCS falls outside of the $\pm 3s$ limits (Sect. 10.2.1), or if two successive QCS checks are outside of the $\pm 2s$ limits, a problem is indicated with the spectrophotometer or calibration curve. Reestablish the baseline with the zero standard and/or recalibrate. If the QCS analysis is still beyond control limits, inaccurate working standards might be the problem. Prepare new standards. Plot the data obtained from the QCS checks on a control chart for routine assessment of bias and precision.
- 10.6 Reestablish the baseline with the zero standard after every ten samples. Verify the calibration curve after a maximum of twenty samples and at the end of each day's analyses by analyzing calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.2.1, recalibrate the system and reanalyze all samples from the last time the system was in control.
- 10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.
- 10.8 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.13). Compare the results obtained from the spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.
- 10.9 Participation in performance evaluation studies is recommended for precipitation chemistry laboratories. The samples used for these performance audits should contain the metals of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for precipitation chemistry laboratories are conducted

semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

- 10.10 INSTRUMENT MAINTENANCE – Strictly adhere to manufacturer's maintenance schedule.
 - 10.10.1 Exposed optical mirrors should be replaced yearly to maintain optimal sensitivity and precision.
 - 10.10.2 Clean all exposed lenses weekly. Use methanol and lint-free laboratory wipes.
 - 10.10.3 Each time the graphite tube is changed, thoroughly clean the furnace parts and electrodes with methanol. Check all parts for wear and replace when necessary.

11. PROCEDURE

11.1 SET AAS PARAMETERS

- 11.1.1 Lamp Current – Refer to manufacturer's guidelines for optimization of this parameter. The use of excessively high currents will shorten lamp life. High currents also cause line broadening, resulting in a reduction in sensitivity and calibration curve linearity. The use of currents that are too low will cause lamp instability and insufficient throughput of energy through the instrument's optical system. The result is increased signal noise due to excess electrical gain applied to the photodetector.
 - 11.1.2 Light Beam – Focus the light beam in the center of the graphite tube according to the manufacturer's guidelines. Rotate the lamp within its holder for maximum energy output readings.
 - 11.1.3 Furnace Alignment – Position the atomizer cell so that the light beam passes through the center of the graphite furnace allowing optimum light transmission.
 - 11.1.4 Wavelength – Set the wavelength according to Table 4 following manufacturer's guidelines.
 - 11.1.5 Spectral Bandwidth – Select the appropriate bandwidth according to Table 4.
- 11.2 When a new graphite tube is installed, condition and clean the tube by the following procedure:
- 11.2.1 Dry stage – 500 C for 15 sec.
 - 11.2.2 Pyrolyze stage – 1500 C for 10 sec.

11.2.3 Atomize stage — 2500 C for 10 sec.

Repeat Sections 11.2.1-11.2.3 after injecting an acid blank.

11.3 SET FURNACE PARAMETERS

11.3.1 Gas Settings — Follow manufacturer's guidelines.

11.3.2 Cooling Water — Follow manufacturer's guidelines for water flow. Tap water may be used if filtered to remove particulates.

11.3.3 Set furnace parameters according to manufacturer's guidelines or those presented in Table 4.

11.3.4 Adjustments to the settings in Sect. 11.3.3 will be necessary in order to establish optimal furnace settings specific to the instrument in use. Use a strip chart recorder or video graphics to monitor the drying, pyrolyzation, and atomization cycles.

11.3.4.1 Inject the highest concentration calibration standard into the furnace and initiate the dry cycle. Refer to Table 4 for guidelines in selecting appropriate sample volume. The sample will block the light path (shown with an absorbance increase). The solvent should evaporate slowly and evenly with no sputtering, so that the signal decreases steadily to the baseline before entering the pyrolyzation stage (Fig. 1).

11.3.4.2 Adjust the pyrolyzation stage temperature so that it is high enough and long enough to decompose and volatilize the matrix components without losing any of the analyte. The non-atomic absorption signals should return to the baseline before the atomization stage begins (Fig. 2).

NOTE: The nitric acid in the matrix (Sect 8.4) may cause nonatomic absorption signals in the pyrolyze stage.

11.3.4.3 Adjust the atomization stage temperature so that it is high enough to volatilize all of the analyte. The use of too high a temperature will result in premature deterioration of the graphite tube, black body emission, and/or poor precision. The absorbance signal should be returning to baseline before the end of the atomization stage (Fig. 2).

NOTE: To determine whether all of the analyte has been atomized, analyze a zero standard. If there is an atomic absorption signal during atomization, the atomization temperature is too low (Fig. 3). Adjust accordingly.

- 11.3.4.4 Analyze the standard at the final settings.
 - 11.3.4.5 Repeat the steps in Sect. 11.3.4.1-4, if necessary, making temperature and time adjustments to achieve optimal atomization.
 - 11.3.4.6 Turn on the background corrector, and adjust according to manufacturer's guidelines. Analyze the same calibration standard at the settings determined in Sect. 11.3.4.1-5.
 - 11.3.4.7 Compare the traces of Sect. 11.3.4.5 and 11.3.4.6. The background correction trace should have no peaks in the pyrolyzation stage. The peaks in the atomization stage should be similar on the two traces. If the settings are correct, almost all of the nonatomic absorption will be in the pyrolyzation stage and all of the atomic absorption will be in the atomization stage (Fig. 4).
 - 11.3.4.8 If premature analyte vaporization is apparent on the background corrected trace, readjust the temperature settings. If any adjustments are made, repeat steps 11.3.4.1-7. Continue until the conditions in Sect. 11.3.4.7 are met.
 - 11.3.4.9 Record the final settings for each metal. Once the settings are established, they can be used routinely.
 - 11.3.4.10 Typical atomization profiles for each metal are shown in Fig. 5. Typical absorbances for the sample volumes recommended are listed in Table 5.
- 11.4 Calibrate according to Section 9.2.
 - 11.5 Verify the calibration curve according to Section 10.5.
 - 11.6 For aluminum determinations, increase the nitric acid concentration of the sample (Sect. 4.1.1.3). Pour the sample into the sample cup containing the acid.
 - 11.7 Analyze duplicates of all samples. The duplicates must agree within 10% RSD. The reported value is the mean of the duplicates.. If precision is poor, refer to Appendix A.

11.8 If the absorbance (or concentration) for a given sample exceeds the calibration range, dilute a separate sample with the zero standard.

11.9 When analysis is complete, follow the manufacture's instructions for instrument shut-down.

12. CALCULATIONS

12.1 For each metal of interest, calculate a linear least squares fit of the standard concentration as a function of the measured absorbance. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in ug/L

x = absorbance measured

B_0 = y-intercept calculated from: $y - B x$

B_1 = slope calculated from:

$$\frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2}$$

where: \bar{x} = mean of absorbances measured

\bar{y} = mean of standard concentrations

n = number of samples

The correlation coefficient should be 0.999 or greater. Determine the concentration of the metal of interest from the calibration curve.

12.2 If the relationship between concentration and absorbance is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation 0.999. The second degree polynomial equation is expressed as follows:

$$y = B_2 x^2 + B_1 x + B_0$$

Determine the concentration of metal of interest from the calibration curve.

12.3 An integration system or internal calibration software may be used to provide a direct readout of the concentration of the metal of interest.

12.4 Report concentrations in ug/L. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

- 13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.15). The results are summarized in Table 6.
- 13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 3.

14. REFERENCES

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- 14.15 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1)
"Estimating Analytical Procedure Variability by Using Spike
Recoveries", Standard D 4210, Annex A4, 1983, p. 7.

Table 1. Method Detection Limits and Concentration Ranges for Graphite Furnace Atomic Absorption (GFAA) Trace Metal Analysis of Wet Deposition.

Analyte	Method Detection Limit, ug/L	Concentration Range, ug/L
Aluminum	3.5	3.5 - 60.0
Cadmium	0.05	0.05 - 2.00
Copper	0.9	0.9 - 40.0
Iron	1.1	1.1 - 50.0
Lead	1.1	1.1 - 50.0
Manganese	0.8	0.8 - 20.0
Zinc	0.5	0.5 - 30.0

Table 2. Suggested Calibration Standard Concentrations for
GFAA Determination of Trace Metals in Wet Deposition.

Al ug/L	Cd ug/L	Cu ug/L	Fe ug/L	Mn ug/L	Pb ug/L	Zn ug/L
zero	zero	zero	zero	zero	zero	zero
3.5	0.05	0.9	1.1	1.1	0.8	0.5
15.0	0.50	10.0	12.5	5.0	12.5	7.5
30.0	1.00	20.0	25.0	10.0	25.0	15.0
45.0	1.50	30.0	37.5	15.0	37.5	22.5
60.0	2.00	40.0	50.0	20.0	50.0	30.0

Table 3. Single-Operator Precision and Bias for Trace Metals
Determined from USEPA Quality Control Check Samples.

Metal	Theoretical	Measured	n ^a	Bias,		Precision,	
	Concentration, ug/L	Concentration ug/L		ug/L	%	s, ug/L	RSD, %
Aluminum	36.5	35.8	34	-0.7	-1.9	3.4	9.5
Cadmium	1.56	1.55	49	-0.01	-0.6	0.09	5.8
Copper	17.0	17.2	65	0.2	1.2	0.8	4.6
Iron	39.8	39.4	52	-0.4	-1.0	2.3	5.8
Manganese	13.0	13.4	32	0.4	3.1	0.6	4.5
Lead	21.8	20.9	51	-0.8	-3.7	1.0	4.8
Zinc	20.9	20.1	71	-0.8	-3.8	1.1	5.5

a. Number of replicates

Table 4. Operating Conditions for GFAA Determination of Trace Metals in Wet Deposition Samples.

Metal	Wavelength Setting, nm	Spectral Bandwidth, nm	Integration Mode	Graphite Tube Coating	Sample Size, uL	Furnace Settings, ' Temp, C / Time, sec					
						Dry		Pyrolyze		Atomize	
Al	309.3	1.0	Peak Area	pyrolytic	25	70/5	110/45	900/20	1100/35	2700/0	2700/5
Cd	228.8	1.0	Peak Height	uncoated	25	70/5	110/45	225/10	300/10	1900/0	1900/10
Cu	324.7	1.0	Peak Height	uncoated	100	80/15	110/45	550/15	750/15	2600/0	2600/5
Fe	248.3	0.3	Peak Height	pyrolytic	25	70/5	110/35	650/15	900/15	2300/0	2300/5
Pb	283.3	1.0	Peak Height	uncoated	25	70/5	110/45	350/15	550/15	2000/0	2000/5
Mn	279.5	0.3	Peak Height	uncoated	25	70/5	110/45	400/20	600/20	2500/0	2500/S
Zn	213.9	1.0	Peak Area	pyrolytic	5	70/5	110/20	325/15	425/15	1900/10	1900/0

- a. These settings are specific for the Instrumentation Laboratory Model 655 Furnace Atomizer. They are to be used as guidelines.
- b. All dry and pyrolyze settings and the Zn atomization setting are ramp settings. The Al, Cd, Cu, Fe, Pb, and Mn atomize settings are step settings.

Table 5. Typical Absorbance Values for Trace Metal GFAA Analyses.

Metal	Concentration ug/L	Sample Volume uL	Absorbance
Aluminum	60.0	25	0.150 - 0.250
Cadmium	2.00	25	0.250 - 0.300
Copper	40.0	100	0.250 - 0.300
Iron	50.0	25	0.400 - 0.500
Lead	50.0	25	0.250 - 0.500
Manganese	20.0	25	0.400 - 0.500
Zinc	20.0	5	0.500 - 0.700

a. Absorbance values vary with instrumentation. These values are guidelines only.

Table 6. Single-Operator Precision and Bias for Trace Metals Determined from Analyte Spikes of Wet Deposition Samples.

Metal	Amount Added, ug/L	n ^b	Mean Percent Recovery, %	Mean Bias, ug/L	Standard Deviation, ug/L	Statistically Significant Bias?
Al	18.5 ^d	12	95.7	-0.8	2.1	no
	30.9 ^e	12	102.4	0.7	4.1	no
Cd	6.11 ^d	13	109.2	0.56	0.73	yes
	1.99 ^e	12	95.7	-0.08	0.26	no
Cu	11.0 ^d	13	100.0	0.0	0.6	no
	16.5 ^e	12	101.4	0.2	0.5	no
Fe	11.1 ^d	12	89.2	-1.2	0.9	yes
	38.2 ^e	12	90.6	-3.7	1.3	yes
Pb	20.8 ^d	13	101.9	0.4	1.5	no
	20.5 ^e	12	89.6	-2.1	2.1	yes
Mn	10.1	13	107.9	0.8	0.5	yes
	17.0 ^s	12	98.9	-0.2	0.4	no
Zn	21.9 ^d	13	107.8	1.7	4.7	no
	20.2 ^e	12	115.8	3.2	1.4	yes

- a. Samples were spiked prior to filtration.
- b. Number of replicates (each replicate is the mean of two readings)
- c. 95% confidence level (14.14).
- d. In situ filtration collector (funnel and bottle)
- e. Filtered in lab

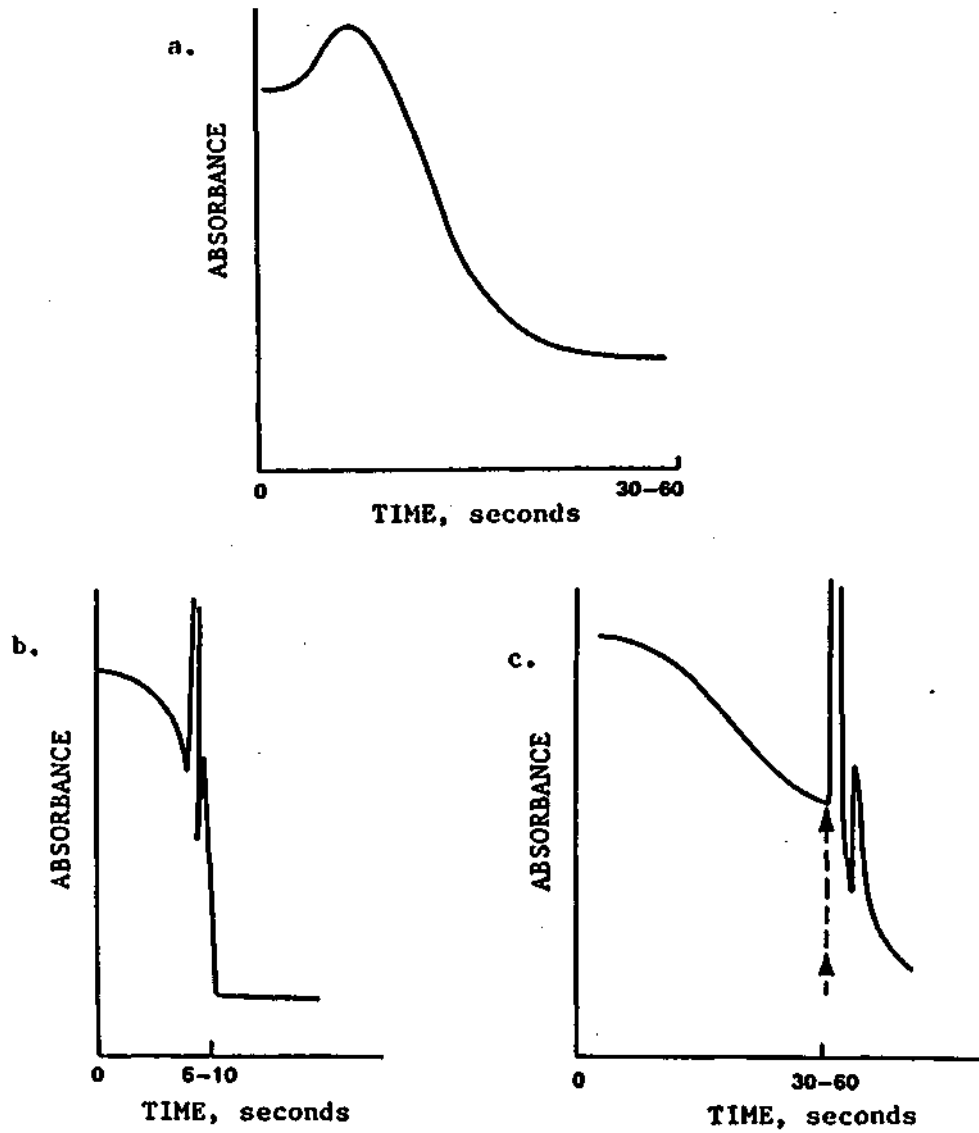


Figure 1. Recorder Traces for Drying Cycles in GFAA Analyses.

- a. Correct Drying Cycle.
- b. Drying Too Fast (analyte loss in dry cycle).
- c. Drying Too Slow (analyte loss in pyrolyze cycle).

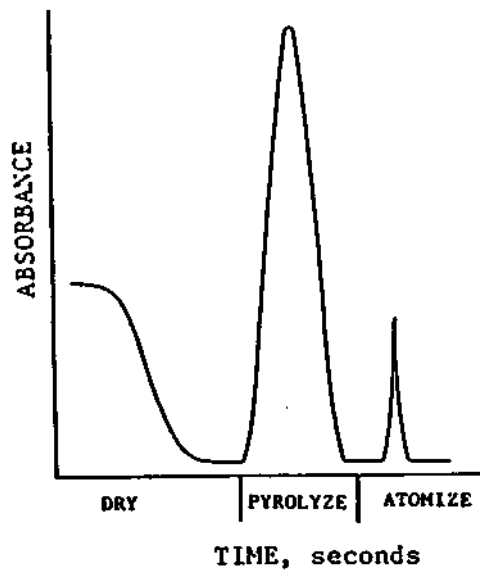


Figure 2. Ideal GFAA Recorder Trace Without Background Correction.

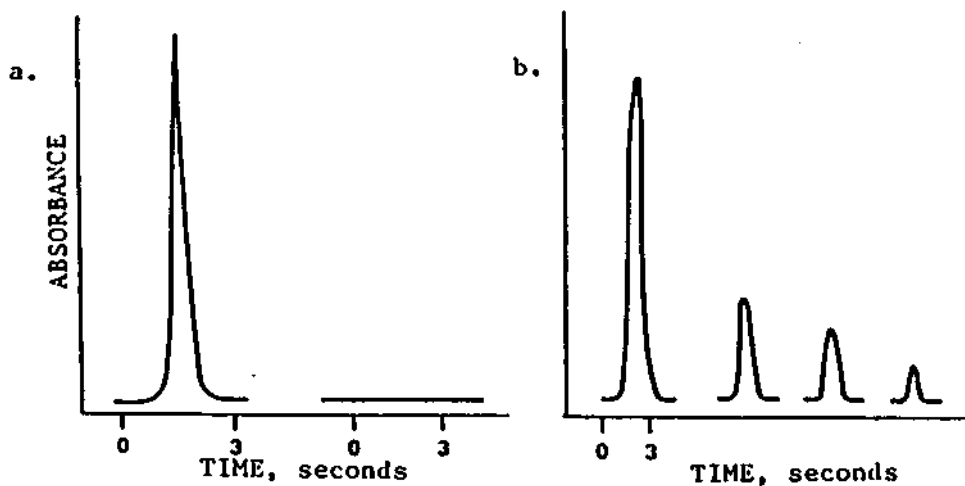


Figure 3. GFAA Atomization Cycle.

- a. Ideal Atomize (zero signal on subsequent zero standard analysis).
- b. Poor Atomize (sample carry-over on subsequent zero standard analysis).

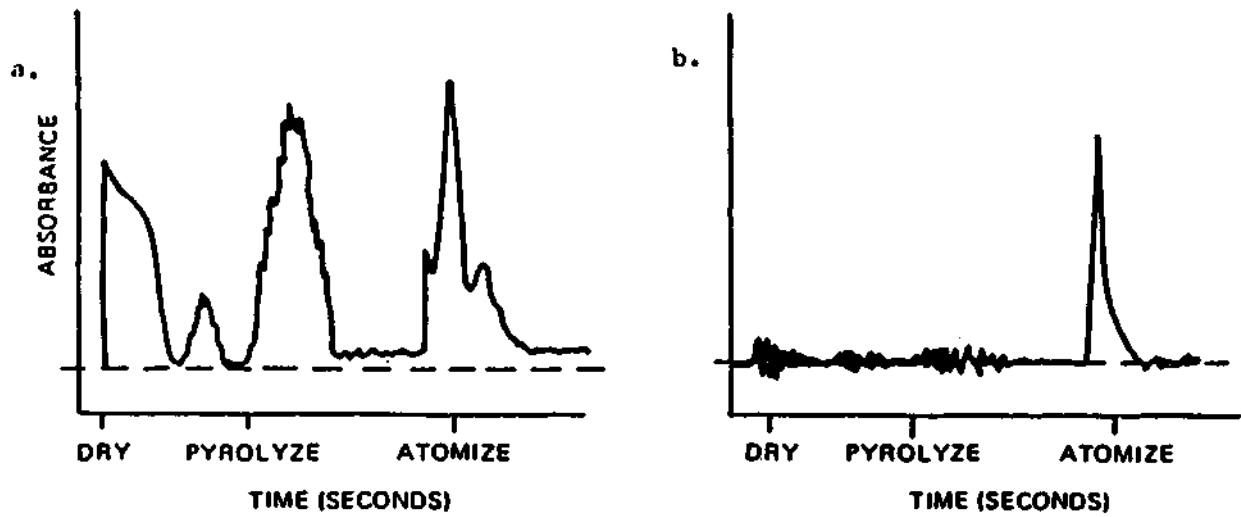


Figure 4. Typical GFAA Recorder Tracings (14.3).

- a. Signal Plus Background.
- b. Background Corrected Signal.

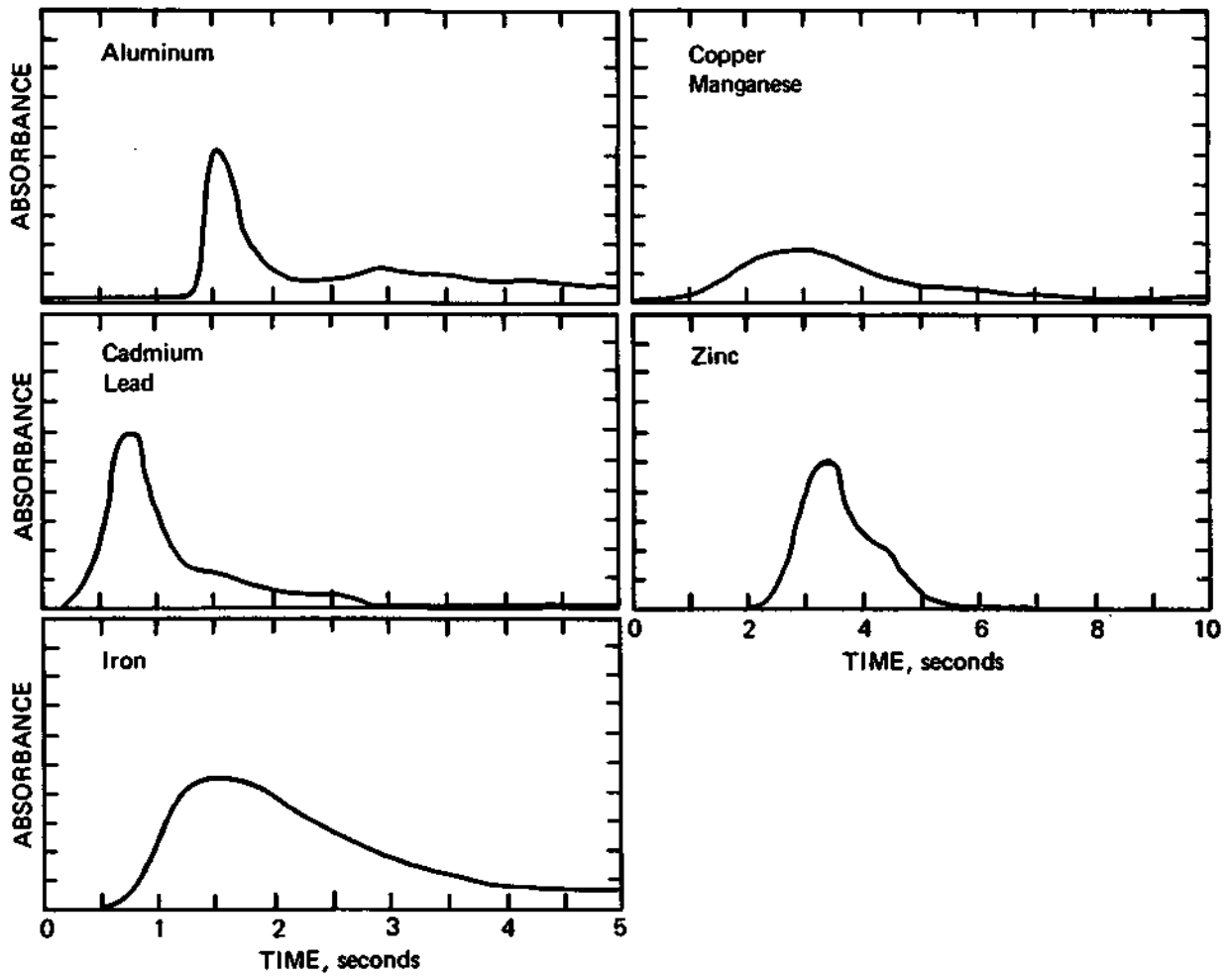


Figure 5. Trace Metal Atomization Profiles in GFAA Analyses.

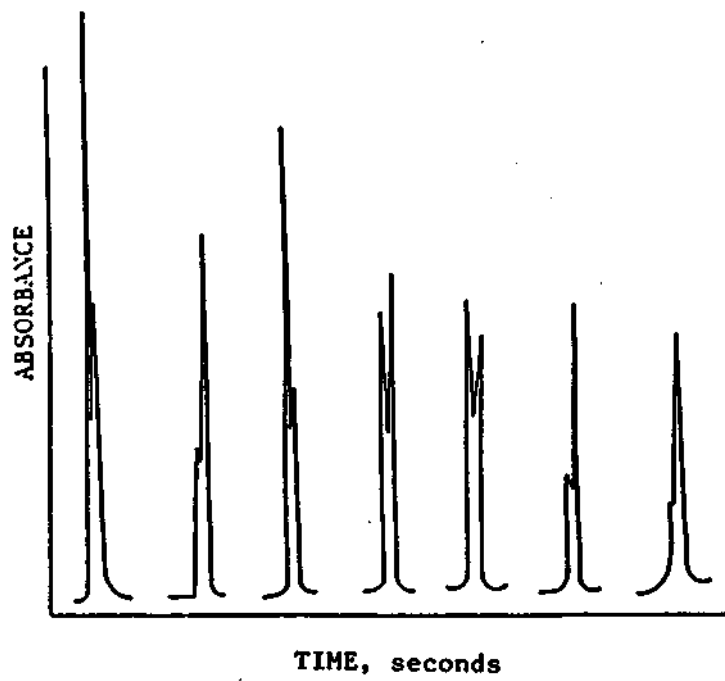


Figure 6, Multiple Atomization Peaks in GFAA Analyses (14.3).

APPENDIX A. Troubleshooting in GFAA Analysis
of Wet Deposition.

<u>Problem</u>	<u>Possible Cause</u>	<u>Possible Solution</u>
Decrease in Sensitivity	Analyte loss in dry cycle (Fig. 1b)	Reduce dry temperature.
	Analyte loss in pyrolyze cycle (Fig. 1c)	Increase dry temperature or time. Lower pyrolyze temperature
	Degraded graphite	Change graphite tube.
	Dirty optical lenses	Clean exposed lenses with methanol.
	Incomplete atomization of analyte	Increase atomization temperature.
	Calibration standard changes	Make new calibration standards.
	Lamp deterioration	Replace lamp.
	Gas flow too high	Reduce gas flow.
Poor Precision	Arcing in furnace	Change graphite tube.
		Clean electrodes with methanol.
		Tighten contacts between graphite and electrodes.
	Changes in line voltage	Put furnace on an isolated circuit. Install a line surge supressor.
	Cooling water flow rate too slow	Increase flow rate. Clean water-cooling system.

APPENDIX A. (cont.)

Problem	Possible Cause	Possible Solution
Poor Precision (continued)	Dirty pipette tip	Replace pipette tip
	Improper temperature settings	Reset furnace parameters (Sect. 11.3)
Multiple Atomization Peaks (Fig. 6)	Degraded graphite	Install new graphite tube.
	Spattering of sample within tube	Reduce dry temperature.
	Analyte in multiple valence states	Increase pyrolysis time and/or temperature.
	Blackbody emission from graphite tube	Realign furnace. Reduce slit height. Increase lamp current and decrease photomultiplier voltage. Decrease atomization temperature.
Memory Effects	Sample carry over (Fig. 3b)	Cycle a series of zero standards until there are no atomization peaks. Increase atomization temperature and time.
	Contamination	Change graphite tube. Clean furnace with methanol. Check zero standard for contamination. Check sample cups for contamination (Sect. 7.12.1).