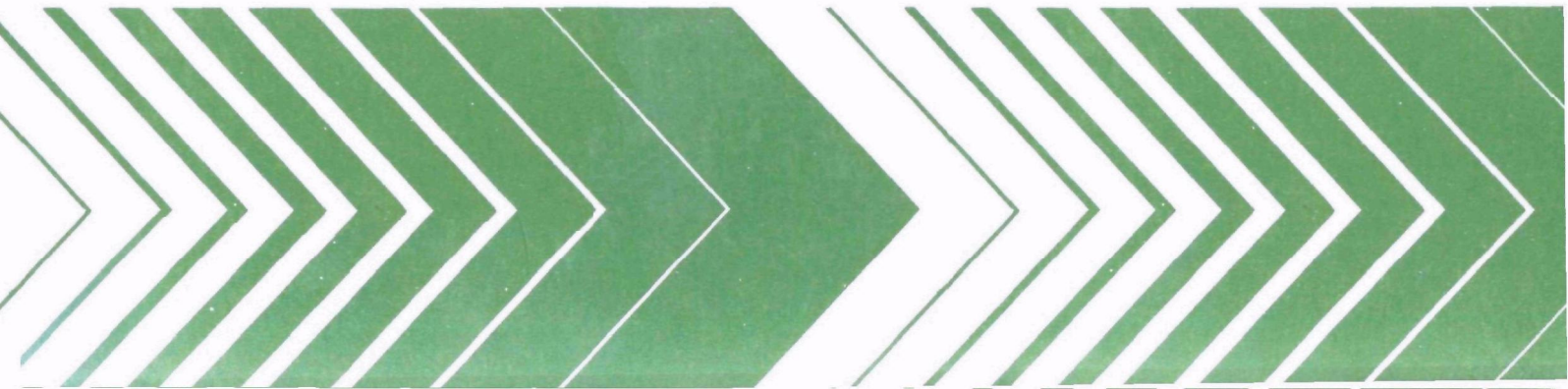


Research and Development



Great Smoky Mountain Preliminary Study for Biosphere Reserve Pollutant Monitoring



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GREAT SMOKY MOUNTAINS PRELIMINARY STUDY FOR
BIOSPHERE RESERVE POLLUTANT MONITORING

by

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FOREWORD

Protection of the environment requires effective regulatory actions based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of exposure to specific pollutants in the environment requires a total systems approach that transcends the media of air, water, and land. The Environmental Monitoring Systems Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This report presents the results of the field sampling program carried out in the fall of 1977. This was a multi-media, integrated sampling effort. Data collected gave estimates of detection limits, variability and levels of certain pollutants. Problems of logistics and access were dealt with. This study provides a basis for an expanded sampling program in the Great Smoky Mountain Biosphere Reserve which will help achieve the ultimate goal to develop a responsive and cost effective pollutant monitoring system for biosphere reserves in general.



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SUMMARY

A preliminary sampling program was initiated in the Great Smoky Mountains National Park, Tennessee, and North Carolina. This national park of 209,000 hectares was selected to be a part of the Southern Appalachian Biosphere Reserve cluster. It serves as a permanent reservoir of genetic material and a site where natural ecosystems can be sampled, studied, and preserved.

An interest in the state of the environment as indicated in the framework of the Man and Biosphere Program (MAB) necessitates the assaying and documenting of the environmental quality in these preserves. For this reason, a monitoring program was initiated. This initial program, a mutual effort by the U.S. Environmental Protection Agency and the U.S. National Park Service, had two objectives. The first objective was to determine the levels of trace elements and organic contaminants in physical and biological media. The second objective, following data analysis and evaluation, was to design an effective and cost-efficient pollutant monitoring system.

Physical and biological media sampled included air, water, soils, litter, and various plant species. Analytical results of these samples showed a variety of elemental contamination. The concentration of lead in litter at four sampling sites was of particular importance. The concentration ranged from 246 to 469 parts per million. These data, similar to those reported by other researchers, showed that lead levels increase with altitude.

A field sampling error of plus or minus 10 percent at the 95 percent confidence level was desired. The number of samples required to satisfy this condition for a permanent monitoring system, based upon the sample/element combination, was determined and used in subsequent studies.

Environmental monitoring, as defined by the U.S. Environmental Protection Agency, is the systematic collection of physical, chemical, biological, and related data pertaining to environmental quality, pollution sources, and other factors that influence or are influenced by environmental quality. Environmental quality data are essential for determining the exposure of critical populations at risk. Such data are obtained by establishing monitoring systems to identify and measure pollutants and their concentrations in air, water, vegetation, soil, and food. The identification and measurement of pollutants in preserved areas, such as the biosphere reserves, may permit the monitoring of subtle deleterious processes that may be masked in areas of high impact. In identifying and measuring the exposure of receptor communities to chemical or physical agents, monitoring data provide the basis for quantitating the contributions of environmental pathways for each chemical or physical form of the pollutant.

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INTRODUCTION

Man's impact on the environment is far-reaching and at times catastrophic. Gone are the days when the pollution emitted by man was assumed to impact only his immediate surroundings. Today, pollution problems are recognized as truly global in nature; they transcend geographic and political boundaries.

Elgmork et al. (1973) reported that snow in Norway contained several pollutants. They found levels of lead in the snow up to 98 micrograms per liter ($\mu\text{g/l}$), sulphur levels of 8.5 milligrams per liter (mg/l), and pH values as low as 3.25. The remoteness of these sampling areas from Norway's limited automobile and industrial areas precluded pollutant deposition from local sources. The researchers concluded that these pollutant levels resulted from contaminated air masses being brought in by low-pressure systems from the great industrial and urban areas of western and central Europe. Another study by Johnson et al. (1972) showed that streams in New England were acidified primarily through the washout of sulphur compounds during local rains. Most of this sulphur originated from the combustion of fossil fuels from large industrial centers of the eastern and central United States. Schlesinger et al. (1974) also reported that lead, cadmium, and mercury were present in precipitation on Mount Moosilauke in New Hampshire. They determined that low pressure-system tracks in North America coming from the large population and industrial areas of the central and mid-Atlantic regions of the United States converged on the northern New England States.

Lazarus et al. (1970) reported that increased levels of lead, zinc, copper, iron, nickel, and manganese were found in rainwater collected by a nationwide precipitation network. They concluded that man's industrial activities were the primary source of these pollutants in the rainwater. The highest overall concentrations occurred in the northeastern portion of the United States. Also, a significant statistical correlation existed between the lead concentrations at each precipitation sampling station and the quantity of gasoline sold in the vicinity of each of the collection points.

Chow and Earl (1970), studying lead aerosols in the vicinity of San Diego, California, reported that only a small fraction of the lead aerosols are deposited near the source of emission. They hypothesized that the majority of lead particulates are transported by major air currents and deposited throughout the world. Hirao and Patterson (1974) studied lead levels in Thompson Canyon, a remote site on the High Sierra Crest. According to their data, the 14-square-kilometer (km^2) watershed received 16 kilograms

(kg) of deposited lead per year. It was further determined that 97 percent of this lead was from anthropogenic sources. They stated:

"These findings show that a widespread assumption, that lead pollution is mainly confined to urban complexes and is essentially absent in open country, is improbable. . . ."

In addition to lead, other elements have been shown to be transported on a global basis. Weiss et al. (1971) sampled the Greenland icecap and presented data showing mercury levels that indicated a possible buildup of mercury in the ice sheet. For example, in samples representing deposition prior to 1952, the mean mercury concentration was 60 ± 17 nanograms per kilogram (ng/kg) of water. Samples representing deposition from 1952 to 1965 had a mean concentration of 125 ± 52 ng/kg of water.

Zoller et al. (1974) analyzed atmospheric particulate material at the South Pole for 22 elements. Antimony, lead, selenium, and bromine were all highly enriched over what could be expected from earth crustal values. They postulated that the source of these compounds was from high-temperature combustion of volcanic activity or from manmade fossil-fuel burning.

Global transport has also been confirmed for other pollutants such as DDT. For example, Anas and Wilson (1970) reported that northern fur seals collected on the Pribilof Islands, Alaska, in 1969 contained DDT and its isomers in both the nursing pup's fat tissue and in the mother's milk.

Concern over the widespread global contamination from man's activities has been one of the driving forces behind the attempt to establish a global network of biosphere reserve sites. The Study of Critical Environmental Problems Report (Massachusetts Institute of Technology, 1970) stated:

"Over the past few years, the concept of the earth as a 'spaceship' has provided many people with an awareness of the finite resources and the complex natural relationships on which man depends for his survival. These realizations have been accompanied by concerns about the impacts that man's activities are having on the global environment. Some concerned individuals, including well-known scientists have warned of both imminent and potential global environmental catastrophes."

A variety of organizations and committees--including the International Task Force of the Global Network for Environmental Monitoring; the Global Monitoring Task Force of SCOPE (Scientific Committee on Problems of the Environment); the Man and Biosphere Expert Panel on Pollution; the Study of Critical Environmental Problems (SCEP); Task Force II, Committee on International Environmental Affairs; and the SCOPE Commission on Environmental Monitoring Assessment--have called for the formation of a global monitoring network.

The United Nations Conference on the Human Environment (Man and Biosphere, 1974) held in Stockholm in June 1972 recommended the establishment

of the United Nations Environment Program. It also recommended the establishment of EARTHWATCH, which has a four-pronged program including monitoring, research, evaluation, and information exchange. The ultimate objective of EARTHWATCH was the establishment of a Global Environmental Monitoring System (GEMS). As part of this Global Environmental Monitoring System, it was recommended that biosphere reserves be established. The UN Conference on the Human Environment in 1972 also recommended that biological reserves be established within the framework of the Man and Biosphere Program. In addition, a report entitled "Man's Impact on the Global Environment," published by the Massachusetts Institute of Technology in 1970, recommended similar entities, calling them ecological baseline stations in remote areas or biosphere reserves.

Biosphere reserves may be defined as undisturbed and protected natural background areas of the Earth where life processes occur with minimal human interference. The requirements for, and the value of, biosphere reserves have previously been described in the report of the Ad Hoc Task Force on GNEM (Global Network for Environmental Monitoring) (1970) and the SCOPE Report No. 3 (Munn, 1973).

Specifically, the biosphere reserves were established to:

1. provide a permanent record of the state of the environment;
2. ensure the availability of undisturbed areas from which background data on pollutant levels could be obtained;
3. give indication of increasing levels of global pollution; and
4. serve as repositories for natural sources of genetic pools of animal and plant species.

Franklin (1976, 1977) identified the research and monitoring activities for which the reserves could be used. These included:

1. long-term baseline studies of environmental and biologic features;
2. research to help develop management policies for the reserves;
3. experimental or manipulative research;
4. environmental monitoring; and
5. study sites for selected MAB research projects.

A detailed concept paper has been published on the general approach to a pollutant monitoring system for biosphere reserves (Wiersma et al., 1978). In addition results from preliminary studies on the Great Smoky Mountains were presented at the Fourth Joint Conference on Sensing of Environmental Pollutants (Wiersma et al., 1977).

This report is the compilation and analysis of data generated from a monitoring study conducted in the Great Smoky Mountains National Park in cooperation with the U.S. Environmental Protection Agency (EPA) and the U.S. National Park Service. The objectives were to determine minimum pollutant levels, to identify the variability of collected samples, and to evaluate sampling techniques. Media sampled included air, water, unincorporated litter, soils, and vegetation.

CONCLUSIONS

The results and techniques identified indicate that sampling problems such as logistics and access into relatively remote areas are not limiting factors in the establishment of a pollutant monitoring system. Analytical detection limits employing techniques as described in this report for vegetation, soils, and litter were adequate for the completion of the stated objectives. Detection limits for selected trace elements in air will have to be improved either by analytical techniques or in sampling equipment design. Field sampling error, which was relatively high, can be adjusted by sampling design.

The collection of physical and biological data from natural areas within the Great Smoky Mountains National Park will establish the necessary criteria to develop a comprehensive pollutant monitoring program. Sampling techniques used, combined with long-term monitoring data, will serve to identify baseline conditions, identify pollutant concentrations, determine trends, and define physical and biological responses to man-induced contaminants.

FIELD SAMPLING METHODS

SOIL AND VEGETATION SAMPLING AND SITE DESCRIPTION

Four sampling sites within the national park were chosen for investigation. Vegetation, water, and unincorporated litter, defined as organic debris and its underlying fermentation layer, were collected at each site. Two of the sites were located on the north slope of the Great Smoky Mountains, a third on top of a ridge, and the fourth on the south-facing side of the park. The site locations are shown on Figure 1, labeled as 11, 12, 13, and 14.

Site 11 was located on the north side of the park at an elevation of about 1,100 m; this site was in a mature hardwood/hemlock forest. Species common in the overstory included hemlock, sugar maple, black cherry, tulip poplar, and magnolia. The understory was made up primarily of rhododendron.

Nine sampling points were originally planned per site using a 3 x 3 grid system. The distance between each grid point was to be 200 m. However, the thick understory and steep slopes at site 11 prevented this sampling scheme. The nine sampling points were laid out along a trail at 200-m intervals. Each sampling point was 40 m up slope from the trail.

Unincorporated litter was sampled at 10 locations evenly spaced around a 10-m diameter circle at each of the 9 sampling points at site 11. A 1-liter sample was collected at each location around the circle. The ten 1-liter samples were placed in a clean plastic bag and thoroughly mixed. After mixing, a 0.5-liter aliquot was collected and placed in a polyethylene container. At each of these 10 locations, a 5-centimeter (cm) deep soil sample was collected after the unincorporated litter layer was removed. In a manner similar to the unincorporated litter mixing and sampling techniques, the 10 soil samples were placed in a clean plastic bag, thoroughly mixed, and then subsampled. At each of the 10 sample points, 2 species of plants were sampled. The plant tissues collected were new leaf growth. For site 11, a 1-liter water sample was collected from a tributary stream near Roaring Fork Creek. Table 1 shows the kinds and number of samples collected at each site.

Sampling site 12 was located on Porters Flat at an elevation of 800 m. This site was composed primarily of 40-year-old second-growth hardwood. Hardwoods common in the overstory included hemlock, sugar maple, tulip poplar, and beech. The method of sampling was identical to that used at site 11. A 1-liter water sample was also collected at the footbridge on Porters Creek. A summary of the samples collected is presented in Table 1.

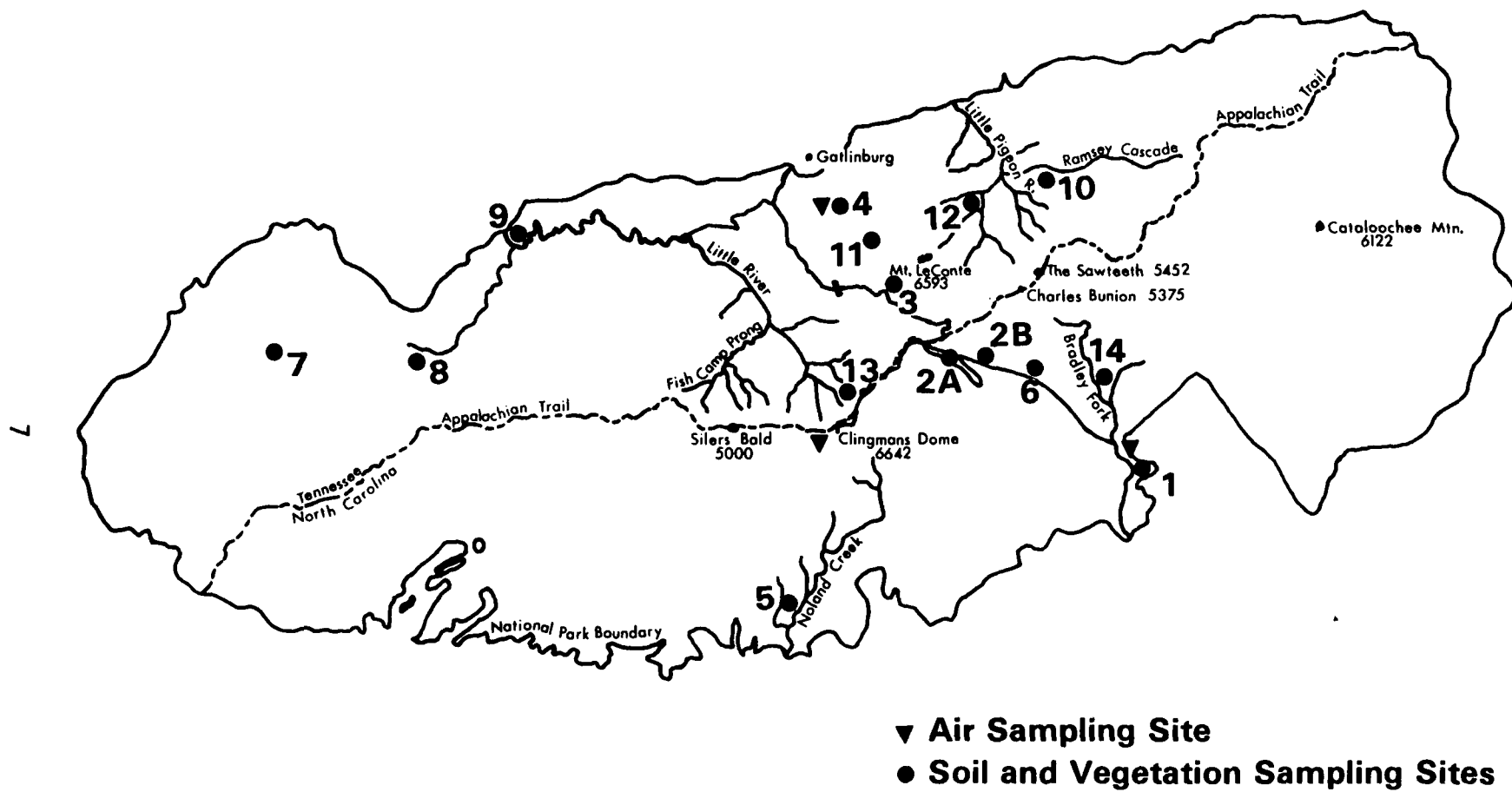


Figure 1. Sampling site locations in the Great Smoky Mountains National Park.

8

| Sample Type | Air Sampling Sites | | | Soil, Vegetation, and Water Sampling Sites | | | | | | | | | | | | | | Total Samples Collected | |
|----------------|--------------------|---|---|--|----|----|---|---|---|---|---|---|---|----|----|----|----|-------------------------|----|
| | 1 | 2 | 3 | 1 | 2A | 2B | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | | 14 |
| Air | | | | | | | | | | | | | | | | | | | |
| Trace metals | 4 | 4 | 4 | | | | | | | | | | | | | | | | 12 |
| Mercury traps | 4 | 4 | 4 | | | | | | | | | | | | | | | | 12 |
| Trace organics | 4 | 4 | 4 | | | | | | | | | | | | | | | | 12 |
| Water | | | | | | | | | | | | | | | | | | | |
| Trace metals | | | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 15 |
| Trace organics | | | | 1 | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | | | | | 10 |
| Soil | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | 9 | 9 | 9 | 9 | | 36 |
| Litter | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | 9 | 9 | 9 | 9 | | 36 |
| Vegetation | | | | | | | | | | | | | | | | | | | |
| Rhododendron | | | | | | | | | | | | | | 9 | 9 | | 9 | | 27 |
| Nettle | | | | | | | | | | | | | | 9 | | | | | 9 |
| Christmas fern | | | | | | | | | | | | | | | 9 | | | | 9 |
| Witch hobble | | | | | | | | | | | | | | | | | 9 | | 9 |
| Wood fern | | | | | | | | | | | | | | | | | 9 | | 9 |
| Yellow birch | | | | | | | | | | | | | | | | | | 9 | 9 |

Sampling site 13 was located on Mount Collins, about 3.3 km east of Clingmans Dome at an elevation of 1,800 meters (m). The topography at this site was relatively flat. The understory vegetation was dense, composed primarily of witch hobble, while the overstory was made up of mature red spruce and Fraser fir. A 3 x 3 grid design with 200 m between sampling points was used. A 1-liter water sample was collected from a spring 50 m below the site. Samples collected at this site are shown in Table 1.

Sampling site 14, located on the south side of the park, was 2.5 km north of the trail head at Smokemount Campground. The elevation at this site was 800 m. Sampling was conducted along Bradley Fork. The techniques used were identical to those used at sites 11 and 12. The water sample was collected from a tributary stream of Bradley Fork. The vegetation on this site was second-growth hardwood, about 40 years old and similar in composition to vegetation at site 12.

WATER SAMPLING

In addition to the four 1-liter water samples collected at sites 11, 12, 13, and 14, a variety of streams draining both the north and south slopes of the park were sampled. These sites, chosen with the aid of park personnel, were representative of the area's main drainage systems.

At each of these sampling sites a 1-liter sample was collected. The sample was placed in a Teflon bottle and immediately acidified with nitric acid. In addition, a 19.2-liter glass carboy was filled with water. The glass carboy had been previously cleaned to remove possible contamination by trace organics. Each of the 1-liter samples was analyzed for trace elements. The carboy samples collected for trace organic analyses were composited with the entire amount extracted.

The water sampling sites identified below are also shown on Figure 1.

- 1 - Oconaluftee River, at the bridge on Tow String Road
- 2A - Beechflat Creek, above the road cut on Highway 441 (trace element sample only)
- 2B - Beechflat Creek, directly below the road cut on Highway 441
- 3 - Walker Prong, 30 m east of Highway 441
- 4 - Twin Creeks, approximately 60 m from the Uplands Field Research Station
- 5 - Nolan Creek, about 1.7 km north of Fontana Lake Highway
- 6 - Beechflat Creek, 1.7 km below the cut on the east side of Highway 441
- 7 - Abrams Creek, near Cades Cove
- 8 - Abrams Creek, about 0.4 km east of the Cades Cove area
- 9 - Little River, about 90 m below the confluence of the Little River and the Middle Prong of the Little River
- 10 - Ramsey Cascade Creek, about 2.5 km from the bridge

AIR SAMPLES

Air samples were collected at three sites in the park (see Figure 1). One site was located at the Uplands Field Research Station near Gatlinburg, Tennessee (air site 3). A second (air site 2) was located at Clingmans Dome, the highest point in the park. The third was located at the Wranglers Corral near the intersection of Tow String Road and the Oconaluftee River on the south side of the park (air site 1).

At each station, three air samples were collected. One was analyzed for mercury, the second for trace elements, and the third for trace organics.

The mercury collection system, previously identified by Long et al. (1973), was composed of a 20-cm long, 5-millimeter (mm) diameter glass tube filled with silver wool. Air was pumped through the glass tube-silver wool trap at a flow rate of approximately 50 milliliters per minute (ml/min). After sampling, the trap was sealed, transported to the laboratory, and analyzed by a direct current plasma emission analytical system.

The second type of air monitoring device, for trace elements, consisted of a 0.8-micrometer (μm), type AA Millipore filter. After collection, the Millipore membrane filters were analyzed by photon-induced X-ray fluorescence as described by Jaklevic et al. (1976), Jaklevic et al. (1973), and Dzubay and Stevens (1975).

The third type of air sampler was a TEMPEST high-volume instrument utilizing a Bureau of Mines 3B-06 charcoal cartridge and a Whatman prefilter. Sampling was conducted at a flow rate of 13 cubic meters per hour (m^3/h). The charcoal cartridge and the prefilter were sent to the University of Iowa and analyzed for organic compounds by standard extraction and gas chromatograph techniques.

ANALYTICAL TECHNIQUES AND RESULTS

WATER

Organic Analyses

Analysis of Purgeable Volatile Organics--

The Environmental Protection Agency's Surveillance and Analysis Division of Region IV in Athens, Georgia, analyzed this group of samples by the purge-and-trap method. The results of these analyses using a gas chromatograph-mass spectrometer (GC-MS) detection system with a minimum detectable limit of 0.5 mg/liter showed that only methylene chloride, chloroform, acetone, *n*-hexane, and isooctane were found in the samples. However, the concentrations of these compounds were less than the calibration blanks: therefore, no purgeable organic compounds will be reported as being present in the biosphere samples.

Analysis of Non-Purgeable Volatile Organics--

Eight 19.2-liter wide-mouth bottles were washed with detergent and then rinsed three separate times with tapwater, distilled water, and acetone. After drying in an oven, each bottle was rinsed with a separate solution of 100 ml of methylene chloride. The washings were combined and then evaporated to 1 ml with a Kuderna-Danish (K-D) evaporator and micro-K-D. The washings were analyzed for impurities by gas chromatography using a 6-m x 2-mm i.d. glass column packed with 1 percent SP-2250 on 100/120 Supelcoport. The carrier gas used was 27 to 29 ml/min of helium. The injector temperature was 275°C and the FID detector temperature was 300°C. The temperature program called for 4 min at 50°C, rising 8°C/min to 260°C, with a final hold of 20 min. The injection size was 2 ml, and the attenuation was set so that 40 ng injected gave 10 to 90 percent deflection. The washings did not show any contaminants.

After the mouths were sealed with aluminum foil, the sample bottles were transported to the Great Smoky Mountains. As previously mentioned, the samples were collected throughout the national park (see Figure 1 for exact locations). One of the samples was lost during shipment because of container breakage.

The resins chosen for the accumulator columns were XAD-8, XAD-4/8, and 35/60 mesh Tenax. The XAD-4/8 is an equal dry-weight mixture of XAD-4 and XAD-8. All had been precleaned and stored for several months under methanol. About 50 ml of each resin were placed in separate chromatography tubes and washed with solvent. The XAD resins were washed with acetone and methylene chloride, and the Tenax was washed with acetone. The last 100-ml portion of effluent was collected, evaporated, and gas chromatographed as previously

described. Solvent impurities were also checked by gas chromatography. If peaks were present in the chromatograms, the washing process was repeated until either the chromatograms were free of peaks or the peaks had been reduced to an insignificant level.

The resins were placed in three separate columns connected in series. After the sample had passed through, they were stripped of accumulated organics and examined separately. The first column was XAD-8 because it was believed to reversibly sorb humic acids. It also served as a protector column for the XAD-4/8 column, protecting the XAD-4 resin from contamination by irreversibly sorbed humic material. The third column, Tenax, was used mainly to accumulate other compounds passing through the two previous columns.

This sampling train met the requirements of the project but was not ideal. Water passed from the sample bottle through a 60-mm i.d. Teflon tube to a glass connector on top of the first column. It went through the column, out a U-tube, up through the second column, through an inverted U-tube, and down through the third column. The water was forced through the train by a peristaltic pump attached to the bottom of the third column. A number of problems occurred with this system. First, a planned flow rate of 100 ml/min could not be maintained. Also, because of the short lengths of resin packing relative to the entire length of the column, several void areas within the system occurred. In addition, the columns would not hold the desired 50 ml of resin.

Because of these problems, the final dimensions and configuration of the accumulator columns were 14.6 ml of XAD-8 in a 13-cm x 1.2-cm i.d. column (ratio of length to diameter of 10.8), 26.6 ml of XAD-4/8 in a 13.3-cm x 1.6-cm column (length: diameter 8.3), and 45.5 ml of Tenax in a 14.5-cm x 2.0-cm column (length: diameter 7.2). The flow rate averaged about 40 ml/min.

The analytical techniques were designed to detect organics in water at 0.1 parts per billion (ppb). To test the analytical system, deuterated anthracene and 1,2-diphenyl hydrazine were selected as internal standards. Both of these compounds as well as azobenzene, a degradation product of 1,2-diphenyl hydrazine, are unlikely to be found in water.

Two separate standards were prepared for each of these two compounds in methylene chloride. One hundred microliters (μ l) of each solution was then dissolved in a liter of water. The liter of standard solution contained 16 μ g of the deuterated anthracene and 200 μ g of 1,2-diphenyl hydrazine, which represented approximately 0.1 ppb and 1.0 ppb concentrations, respectively. The first set was extracted with methylene chloride, concentrated, and gas chromatographed as described previously for the sample-bottle washings. The hydrazine (azobenzene) peak was about 60 percent of full scale while the deuterated anthracene was only about 4 percent of full scale as shown in Figure 2. The experiment did indicate that a detection limit of 0.1 ppb would be attainable.

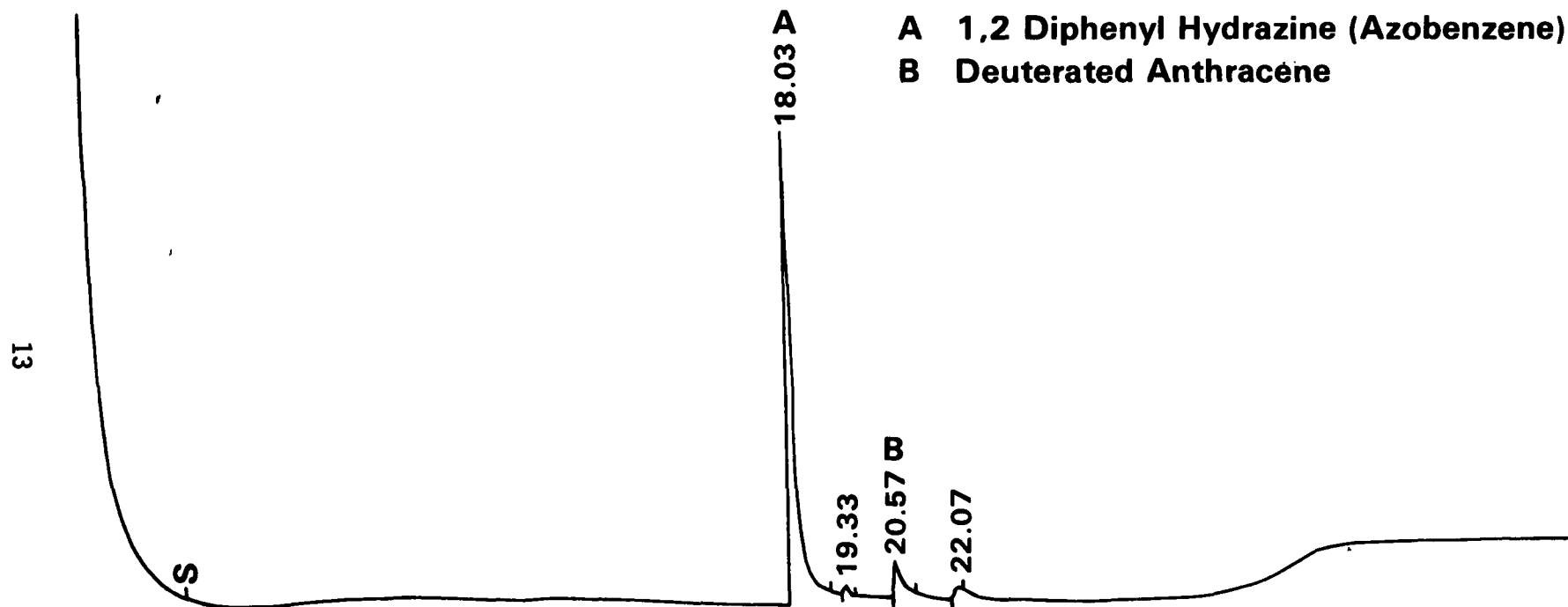


Figure 2. Gas chromatogram (FID) of internal standards, deuterated anthracene, and 1,2-diphenyl hydrazine.

The second liter of standard solution was used to spike the collected water samples. A 100-ml portion of the standard solution was added to each of the seven 19.2-liter samples, and a 200-ml portion to the eighth and ninth sample as they were being extracted. The final concentration of the anthracene and the 1,2-diphenyl hydrazine standards added to the water samples was 0.094 $\mu\text{g/l}$, representing 0.09 ppb and 1.19 ppb, respectively.

The water samples were not refrigerated or preserved in any way, and they remained sealed with aluminum foil and tape until sampled. A slight deposit of black sediment was observed on the bottom of each sampled container. This deposit, however, was not disturbed during the extraction of water from the bottles.

Sampling was conducted over a 5-day period in 16-hour increments. The sample train was constantly under a mild vacuum, and traces of air, probably from the ground-glass joints, could occasionally be seen passing through the system. After all of the water had passed through the columns, they were removed from the system. The excess water was drained off, and a stopcock adapter attached to the bottom of each column. Thirty ml of acetone was then added to the XAD-8 column, followed by 120 ml of methylene chloride. The combined collected effluents were mixed in a separatory funnel, with the small top layer of water separated from the organic layer. The organic extract was evaporated to 0.5 ml.

The XAD-4/8 column was treated similarly except that 50 ml of acetone and 200 ml of methylene chloride were used. The extract was evaporated to 0.87 ml. A small amount of white precipitate was observed in the extract following evaporation.

The Tenax column was eluted in two stages. First, 100 ml of acetone was added. It was dewatered by adding 200 ml of methylene chloride. After removing the water layer, the organic portion was evaporated to 10 ml. An additional 250 ml of acetone was added to the Tenax column. After collecting, it was added to the original 10 ml concentrate and evaporated to 1 ml. In addition, solvent blanks were prepared using the same amounts of solvents plus 10 ml of water.

The samples and the blanks were all examined by GC/FID using the GC conditions and procedures described previously. Most of the eluted compounds were found in the XAD-8 (Figure 3). No peaks having different retention times from those found in the XAD-8 extract were observed in the XAD-4/8 and Tenax extracts. The XAD-8 extract had nine peaks of 10 percent or more of full scale. Two of these were the spiked standards. XAD-4/8 had four peaks, and Tenax had two. The solvent blanks were all acceptable with essentially no discernible peaks.

After the three individual extracts had been examined by gas chromatography-mass spectrometry (GC-MS), they were combined and concentrated to 0.4 ml with a micro-K-D. The gas chromatogram (GC-FID) of this extract showed only four peaks as large or larger than the deuterated anthracene standard (Figure 4).

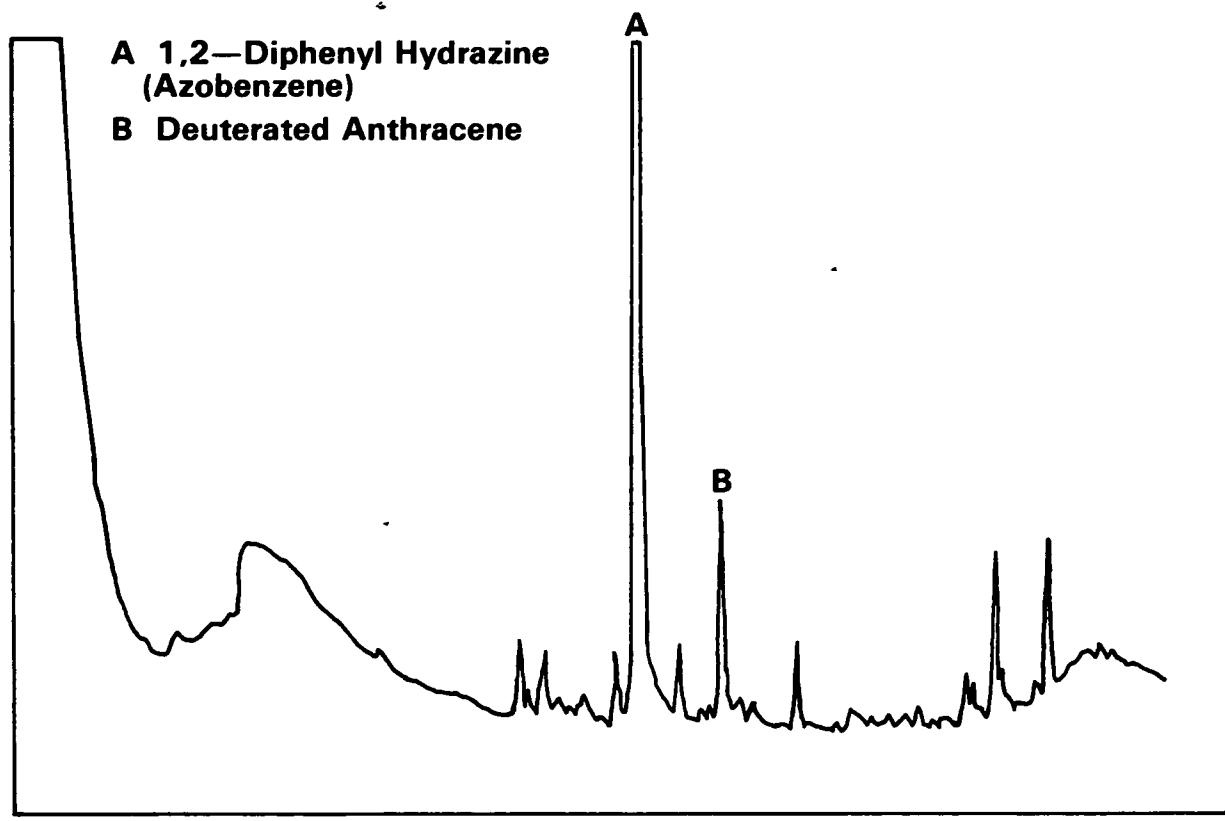


Figure 3. Gas chromatogram (FID) of biosphere reserve XAD-8 extract.

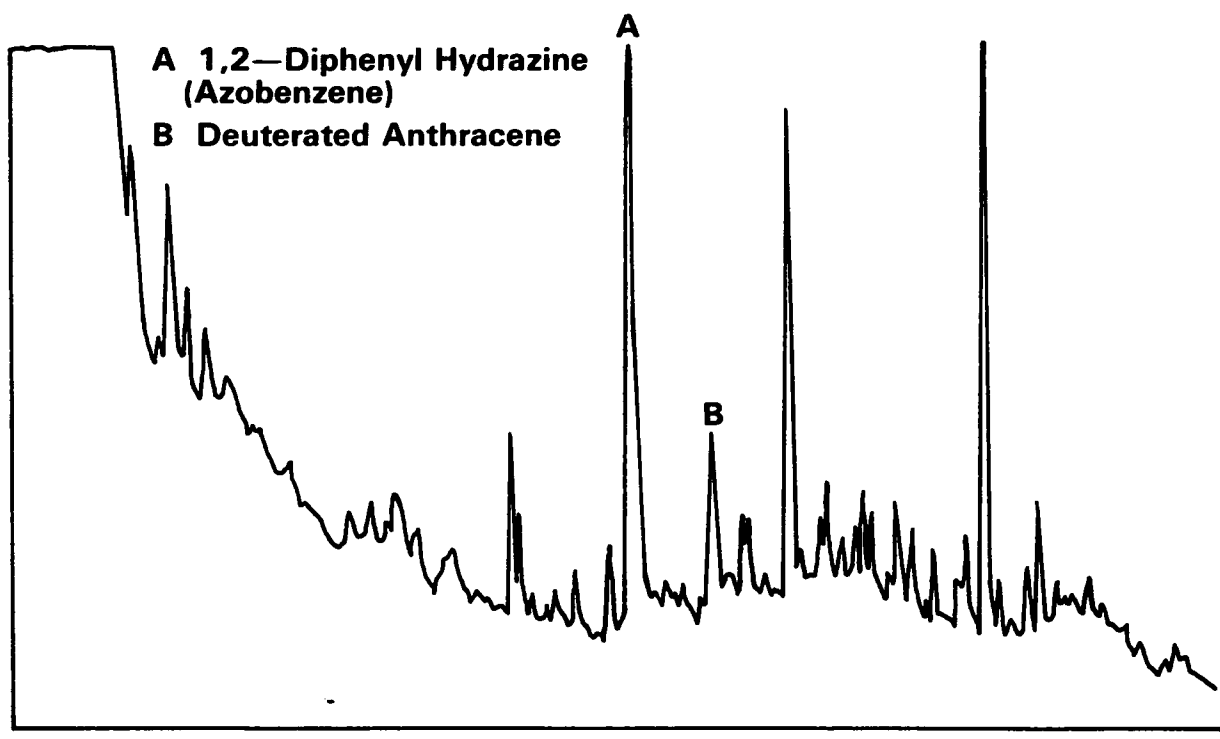


Figure 4. Gas chromatogram (FID) of biosphere reserve combined extracts.

The extracts were examined by GC-MS under the following techniques and conditions. A glass column (3 m x 3 mm) packed with 4 percent SP-2100 (equivalent to SE-30) on 80/100 Supelco was used. The temperature program was an initial hold at 50°C for 4 minutes, followed by heating to 240°C at 8°C/min. The GC was interfaced to the mass spectrometer by a two-stage glass frit-type separator. The mass spectrometer was a Varian CH5-DF that operated at the standard 70 eV and scanned once every 5 seconds. Two-μliter injections of samples were made. After the source pressure gauge indicated that most of the methylene chloride solvent had passed through the source, the filament was turned on and the scans started.

The data were processed on a Varian SS 166 data system equipped with a dual platter disc and nine-track magnetic tape. The spectra were computer-matched with a large mass spectral library by the Mass Spectral Search System at Cyphernetics Corporation in Ann Arbor, Michigan. Personnel interpretations of the individual spectra were also made.

The XAD-8 extract shown in Figure 5 was the most concentrated and complex. All contaminants found in the XAD-4/8 and Tenax extracts were also found in the XAD-8 extract. The two internal standards were only found in the XAD-8 extract.

The composited extract, similar to the individually examined extracts, showed peaks in the first and third portions of the chromatograms. The sensitivity and resolution of the GC-MS system used in this study were less than the FID gas chromatograph.

The only compound that was definitely identified in the water samples was toluene (Figure 6). There also was strong evidence for the presence of dimethyl hexene or methyl heptene, nonane or an isomer, trimethyl benzene or isomers, ethyl benzene, ethyl toluene, and three phthalate esters. The computer match also indicated that 2,4-di-t-butyl anisole, 2,5-di-t-amyl quinone, and 1,2,4-tri-t-butyl anisole may be present; these compounds are rarely, if ever, found in water.

Only toluene and nonane gave total ion currents stronger than that of the 0.09-ppb deuterated anthracene. It was concluded that no other compounds were present at greater concentrations than 0.09 ppb. It was believed that the recoveries of deuterated anthracene and 1,2-diphenyl hydrazine (azobenzene) from the dosed biosphere reserve sample were 100 percent. The concentration of nonane was approximately 1 ppb, and the toluene near 2 ppb.

Multielement Analysis

The one-liter water samples that had been preserved with 1 ml of ultrex nitric acid were analyzed for trace element constituents by two standard

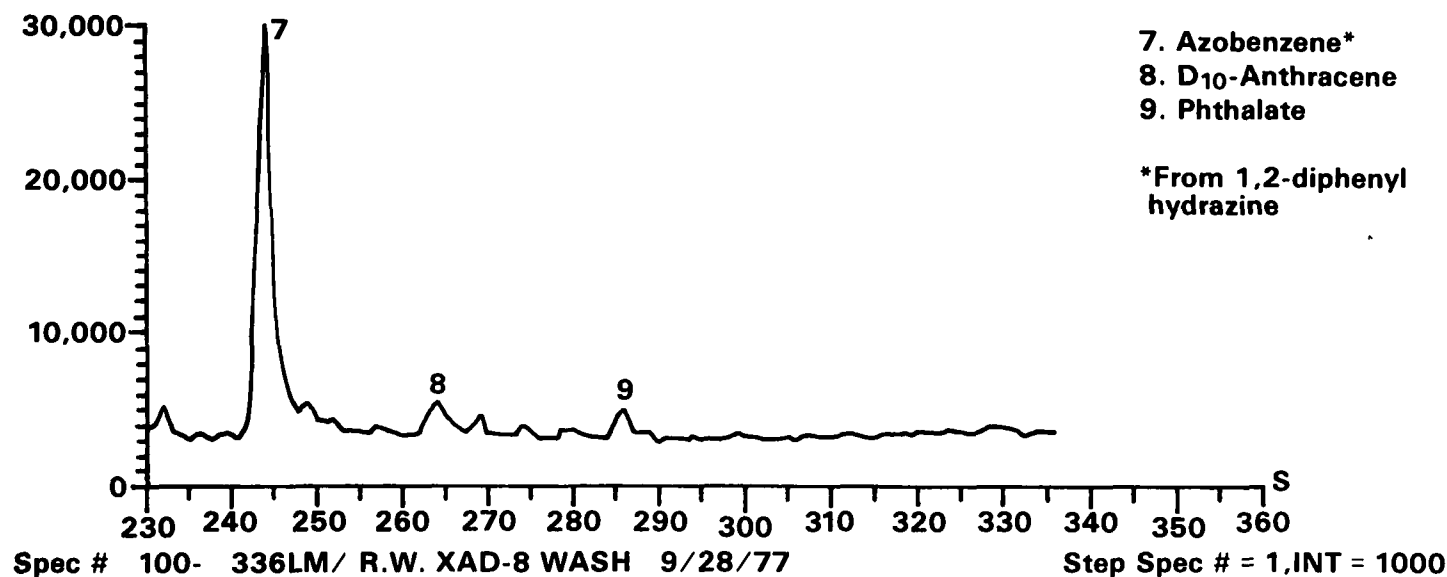
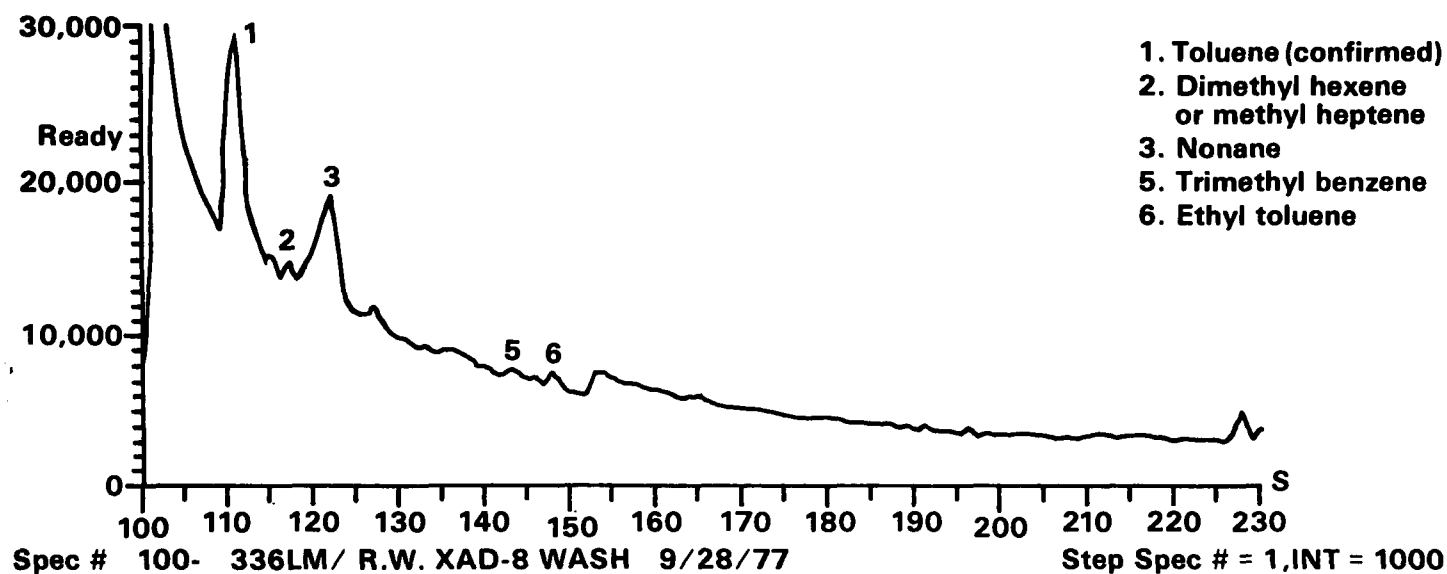


Figure 5. Computer-reconstructed gas chromatogram of biosphere reserve XAD-8 extract.

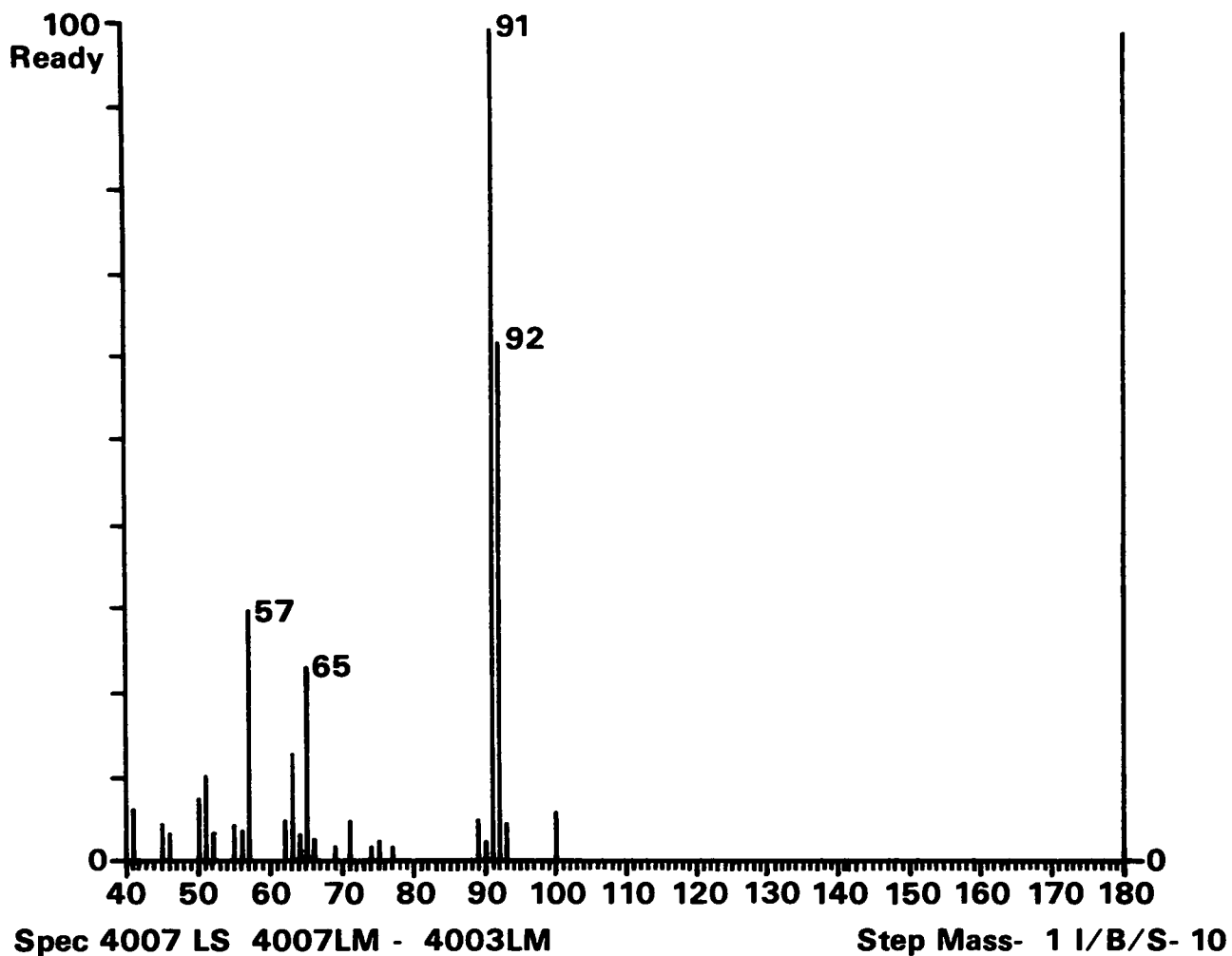


Figure 6. Computer-reconstructed gas chromatogram confirming presence of toluene.

multi-element techniques--inductively coupled plasma emission spectrometry (ICPES), and spark source mass spectrometry (SSMS). The ICPES was used because it is capable of giving rapid and accurate determinations of a specific group of 26 elements. The SSMS was used to provide a survey analysis of the entire spectrum of elements, except for the gases.

The procedures and techniques used for the multi-element analysis have been previously described by Elgmork et al. (1973) and Johnson et al. (1972).

The results, which are summarized in Tables 2 and 3, show the concentration range, average concentration, and frequency of occurrence for each element. Two samples, one from site 2B and the other from site 7, were not in the data shown in Tables 2 and 3. The reason for their omission was that the water from site 2B was collected below a construction area and the water from site 7 was collected at a point just below a cattle-grazing area.

Table 4 summarizes the results of all elements analyzed jointly by ICPES and SSMS analyses. The limit of detection for the SSMS for all elements was 0.001 mg/liter. The detection limits of ICPES are indicated by less than values shown on Table 4. The samples for SSMS were prepared in glass containers and were possibly contaminated with boron and silicon. For this reason, no analyses for these elements were reported.

As shown on Table 4, these samples all contained very low levels of most elements. Of the consent-decree elements, only zinc was found.

The zinc in the water sample collected at site 6 is of special interest because it was collected from an area that occasionally displays a white deposit on the stream rocks. U.S. National Park Service personnel suspected this deposit to be an aluminum salt; however, the aluminum concentration, 0.078 $\mu\text{g/liter}$, is below the average concentration shown on Table 2. This sample was also higher than the average in manganese content.

AIR

The results from the Millipore filters indicated no detectable levels of trace elements. Based on the maximum flow rates used and the detection limits, a "less than" level can be determined. For lead (Pb) it was estimated that, using a filter with 10.75-cm² area with a detection limit of 70 ng Pb/cm² of filter area and a maximum air volume sampled of 14.6 m³, the minimum detectable limit would be approximately 50 ng of Pb/m³ of air. It is not unreasonable to expect that the air concentration of lead in the park would be low. Jaklevic et al. (1976) reported that lead levels in air collected from rural areas contained approximately 100 ng/m³. Chow and Earl (1970) reported an average lead concentration in air of 50 ng/m³ at Mount Laguna, 45 miles from San Diego. An increase in flow rate or sampling time would increase the sensitivity of this system. The air sampling system employed has, with modification, been used successfully in remote areas of the Great Smoky Mountains National Park. This system has been described by Brown et al. (1979).

TABLE 2. SUMMARY OF ANALYSES OF ELEMENTS DETERMINED BY ICPEs AND SSMS (mg/liter)

| Element | Range | Average | Frequency (in 13) samples | Element | Range | Average | Frequency (in 13) samples |
|---------|----------------|---------|---------------------------------|---------|----------------|---------|---------------------------------|
| Ag | ND* | <0.001† | 0 | Mg | (1.19-0.12) | 0.32 | 13 |
| Al | (0.380-0.030) | 0.111 | 13 | Mn | (0.12-0.002) | 0.021 | 13 |
| As | ND | <0.001 | 0 | Mo | (0.001-<0.001) | <0.001 | 2 |
| B | (0.007-0.005) | 0.0054 | 5 | Ni | (0.001-<0.001) | <0.001 | 3 |
| Ba | (0.020-0.005) | 0.010 | 13 | Pb | ND | <0.001 | 0 |
| Be | ND | 0.001 | 0 | Sb | ND | <0.001 | 0 |
| Ca | (13.5-0.53) | 2.09 | 13 | Se | ND | <0.001 | 0 |
| Cd | ND | <0.001 | 2 | Sn | ND | <0.001 | 0 |
| Co | (0.003-<0.001) | 0.001 | 7 | Sr | (0.054-0.006) | 0.014 | 13 |
| Cr | (0.005-<0.001) | 0.001 | 7 | Ti | (0.004-<0.001) | 0.002 | 6 |
| Cu | (0.007-<0.001) | 0.002 | 9 | V | ND | <0.001 | 1 |
| Fe | (0.17-0.05) | 0.036 | 12 | Y | ND | <0.002 | 0 |
| Hg | ND | <0.010 | 0 | Zn | 0.014 | 0.014 | 1 |

* ND signifies the element was Not Detected in any sample

† Values shown as "less than" (<) are detection limits

TABLE 3. SUMMARY OF ANALYSES OF ELEMENTS DETERMINED BY
SSMS ONLY (mg/liter)

| Element | Range | Average | Frequency (in 13 samples) |
|---------|--------------|---------|------------------------------|
| Ce | 0.001-<0.001 | <0.001 | 1 |
| Rb | 0.003-0.001 | 0.002 | 13 |
| Br | 0.04-<0.001 | 0.010 | 12 |
| Ga | 0.05-<0.001 | 0.001 | 10 |
| Sc | 0.002-<0.001 | 0.001 | 6 |
| K | 0.9-0.1 | 0.38 | 13 |
| S | 2-0.1 | 0.48 | 13 |
| P | 0.02-0.003 | 0.011 | 13 |
| Na | 6-0.2 | 1.2 | 13 |
| F | 0.01-0.001 | 0.003 | 12 |

The mercury air traps and the associated analytical methods used indicated that mercury levels were not above background.

The charcoal filters were operated for the purpose of detecting organics in air. Only two of the charcoal cartridges were analyzed for organics. These samples included:

| <u>I.D. No.</u> | <u>Location</u> | <u>Operating Time (hrs)</u> | <u>Volume</u> |
|-----------------|---|-----------------------------|----------------------|
| 3C-3 | Uplands Field Research Station (Gatlinburg, Tennessee) | 24 | 314 m ³ |
| 1C-4 | Ocanaluftee River (Cherokee, North Carolina) | 9.9 | 125.2 m ³ |

The samples were prepared and analyzed as follows. The charcoal was removed from the metal canisters, placed in a flask, and shaken vigorously with 100 ml of petroleum ether. The sample was filtered with the petroleum ether concentrated by nitrogen blown down to 5 ml. The granules were then placed in another flask and shaken vigorously with carbon disulfide. Again the sample was filtered and the extract concentrated to 5 ml. The samples were then analyzed by gas chromatography using a 63-Ni detector.

The results are shown in Table 5 and in Figures 7 and 8 for the petroleum ether extraction only. Compound identifications were not performed, but the

TABLE 4. RESULTS OF MULTIELEMENT ANALYSES USING ICPEs AND SSMS FOR
GREAT SMOKY MOUNTAINS WATER SAMPLES (mg/liter)

| Element | Sample Number | | | | | | | | | | | | | |
|------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 1 | | 2A | | 2B | | 3 | | 4 | | 5 | | 6 | |
| | ICPEs | SSMS | ICPEs | SSMS | ICPEs | SSMS | ICPEs | SSMS | ICPEs | SSMS | ICPEs | SSMS | ICPEs | SSMS |
| Silver | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 |
| Aluminum | .043 | .03 | .053 | .040 | 1.77 | 1.0 | .18 | .4 | .042 | .04 | .030 | .07 | .078 | .04 |
| Arsenic | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Boron | <.005 | * | .007 | * | .012 | * | .005 | * | <.005 | * | <.005 | * | <.005 | * |
| Barium | .005 | .004 | .008 | .004 | .016 | .007 | .006 | .002 | .013 | .02 | .006 | .002 | .016 | .01 |
| Beryllium | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 |
| Calcium | .93 | .5 | 1.77 | 2.5 | 3.76 | 2.5 | .92 | 1.2 | 1.36 | 1.0 | .56 | .2 | 2.85 | 2.0 |
| Cadmium | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |
| Cobalt | <.005 | .001 | <.005 | .003 | <.005 | .008 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | .002 |
| Chromium | <.005 | <.003 | <.005 | .001 | <.005 | .001 | <.005 | <.001 | <.005 | .005 | <.005 | <.001 | <.005 | .001 |
| Copper | <.005 | .001 | <.005 | .001 | <.005 | .004 | <.005 | .001 | <.005 | <.001 | <.005 | .004 | <.005 | <.001 |
| Iron | .014 | .01 | .009 | .02 | .018 | .02 | .034 | .02 | .005 | <.001 | .02 | .01 | .005 | .005 |
| Mercury | .01 | ** | .01 | ** | .01 | ** | .01 | ** | .01 | ** | <.01 | ** | <.01 | ** |
| Magnesium | .2 | .2 | .34 | .3 | 1.5 | 1.0 | .25 | .2 | .23 | .2 | .12 | .2 | .84 | 1.0 |
| Manganese | .002 | .006 | .003 | .003 | 1.36 | 2.0 | .038 | .05 | .004 | .002 | .003 | .009 | .12 | .1 |
| Molybdenum | <.01 | <.001 | <.01 | <.001 | .014 | .007 | <.01 | .009 | <.01 | <.001 | <.01 | <.001 | <.01 | .001 |
| Nickel | <.005 | .001 | <.005 | <.001 | .018 | .03 | <.005 | <.001 | <.005 | .001 | <.005 | <.001 | <.005 | <.001 |
| Lead | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Antimony | <.010 | <.001 | <.010 | <.001 | <.010 | <.001 | <.010 | <.001 | <.010 | <.001 | <.010 | <.001 | <.010 | <.001 |
| Selenium | <.05 | <.001 | <.050 | <.001 | <.05 | .003 | <.050 | <.001 | <.050 | <.001 | <.050 | <.001 | <.050 | <.001 |
| Tin | <.05 | <.001 | <.050 | <.001 | <.05 | <.001 | <.050 | <.001 | <.050 | <.001 | <.050 | <.001 | <.050 | <.001 |
| Strontium | .008 | .004 | .018 | .02 | .025 | .03 | .006 | .005 | .012 | .008 | .006 | .003 | .024 | .02 |
| Titanium | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | .003 | <.005 | .002 | <.005 | .004 |
| Vanadium | <.005 | .001 | <.005 | <.001 | <.005 | .001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |
| Ytterbium | <.002 | *** | <.002 | *** | .011 | *** | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** |
| Zinc | <.005 | .001 | <.005 | .001 | .075 | .04 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | .014 | .005 |

(continued)

* Samples prepared in glass
** Not reported by SSMS
*** Internal standard

TABLE 4. (Continued)

| Element | Sample Number | | | | | | | | | | | | | | | |
|------------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 7 | | 8 | | 9 | | 10 | | 11 | | 12 | | 13 | | 14 | |
| | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS | ICPES | SSMS |
| Silver | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 |
| Aluminum | .13 | .2 | .052 | .08 | .05 | .09 | .072 | .04 | .044 | .04 | .046 | .08 | .38 | .3 | .3 | .3 |
| Arsenic | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Boron | .005 | * | <.005 | * | .005 | * | <.005 | * | <.005 | * | <.005 | * | <.005 | * | <.005 | * |
| Barium | .014 | .01 | .007 | .005 | .007 | .007 | .010 | .01 | .01 | .02 | .006 | .002 | .002 | .008 | .02 | .05 |
| Beryllium | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 | <.002 | <.001 |
| Calcium | 13.5 | 17.0 | .80 | .60 | 1.15 | 1.0 | .94 | .5 | 1.07 | 1.0 | .82 | .7 | .53 | .4 | .72 | .5 |
| Cadmium | <.005 | <.001 | <.005 | .001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |
| Cobalt | <.005 | .003 | <.005 | <.001 | <.005 | <.001 | <.005 | .002 | <.005 | <.001 | <.005 | .001 | <.005 | .003 | <.005 | <.001 |
| Chromium | <.005 | .003 | <.005 | .003 | <.005 | <.001 | <.005 | .002 | <.005 | <.001 | <.005 | .002 | <.005 | <.001 | <.005 | <.001 |
| Copper | <.005 | .005 | <.005 | <.001 | <.005 | .004 | <.005 | .007 | <.005 | .001 | <.005 | .002 | <.005 | .004 | <.005 | <.001 |
| Iron | .11 | .3 | .023 | .03 | .025 | .02 | .008 | .01 | .031 | .07 | .005 | .002 | .005 | .001 | .17 | .1 |
| Mercury | <.010 | ** | <.010 | ** | <.01 | ** | <.010 | ** | <.01 | ** | <.01 | ** | <.01 | ** | <.01 | ** |
| Magnesium | 1.19 | 1.0 | .14 | .4 | .22 | .5 | .18 | .3 | .16 | .3 | .22 | .5 | .15 | .1 | .15 | .3 |
| Manganese | .015 | .02 | .006 | .01 | .003 | .007 | .003 | .002 | .002 | .002 | .002 | .002 | .031 | .05 | .05 | .05 |
| Molybdenum | <.010 | <.001 | <.010 | <.001 | <.01 | <.001 | <.010 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 |
| Nickel | <.005 | .001 | <.005 | <.001 | <.005 | .001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |
| Lead | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Antimony | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 | <.01 | <.001 |
| Selenium | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Tin | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 | <.05 | <.001 |
| Strontium | .054 | .09 | .008 | .007 | .009 | .003 | .008 | .01 | .01 | .008 | .006 | .009 | .005 | .002 | .01 | .02 |
| Titanium | <.005 | .001 | <.005 | <.001 | <.005 | .004 | <.005 | .002 | <.005 | <.001 | <.005 | .002 | <.005 | <.001 | <.005 | <.001 |
| Vanadium | <.005 | .004 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |
| Ytterbium | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** | <.002 | *** |
| Zinc | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 | <.005 | <.001 |

* Samples prepared in glass

** Not reported by SSMS

*** Internal standard

TABLE 5. SUMMARY OF RETENTION VOLUMES (cc) FOR ^{63}Ni GAS CHROMATOGRAPHIC ANALYSES OF CHARCOAL FILTER SAMPLES NO. 1C-4 AND 3C-3 (Petroleum Ether Extracts)

| Instrument Parameters | Peak No. | Retention Volume (cc) | |
|--|----------|-----------------------|----------------------|
| | | 3C-3 (North Side) | 1C-4 (South Side) |
| Column temperature = 55°C Detector temperature = 272°C | 1 | --- | 30 |
| | 2 | --- | 40 |
| | 3 | 50 | 50 |
| | 4 | 70 | --- |
| | 5 | 100 | --- |
| | 6 | 110 | --- |
| | 7 | --- | 120 |
| | 8 | 150 | 150 |
| | 9 | 160 | --- |
| | 10 | 300 | --- |
| | 11 | 370 | 370 |
| Column temperature = 104°C Detector temperature = 273°C | 1 | --- | 10 |
| | 2 | 20 | 20 |
| | 3 | 30 | 30 |
| | 4 | 40 | 40 |
| | 5 | 50 | --- |
| | 6 | --- | 60 |
| | 7 | 120 | 120 |
| | 8 | 160 | --- |
| | 9 | 220 | --- |
| | 10 | --- | 230 |
| Column temperature = 151°C Detector temperature = 273°C | 1 | 10 | 10 |
| | 2 | 20 | 20 |
| | 3 | 40 | 40 |
| | 4 | 60 | 60 |
| | 5 | 110 | --- |
| | 6 | --- | 150 |
| | 7 | 160 | --- |
| Column temperature = 190°C Detector temperature = 276°C | 1 | --- | 6 |
| | 2 | 20 | 20 |
| | 3 | 30 | 30 |
| | 4 | 70 | 70 |
| | 5 | --- | 100 |
| | 6 | --- | 130 |
| | 7 | --- | 150 |
| | 8 | --- | 210 |
| | 9 | --- | 320 |

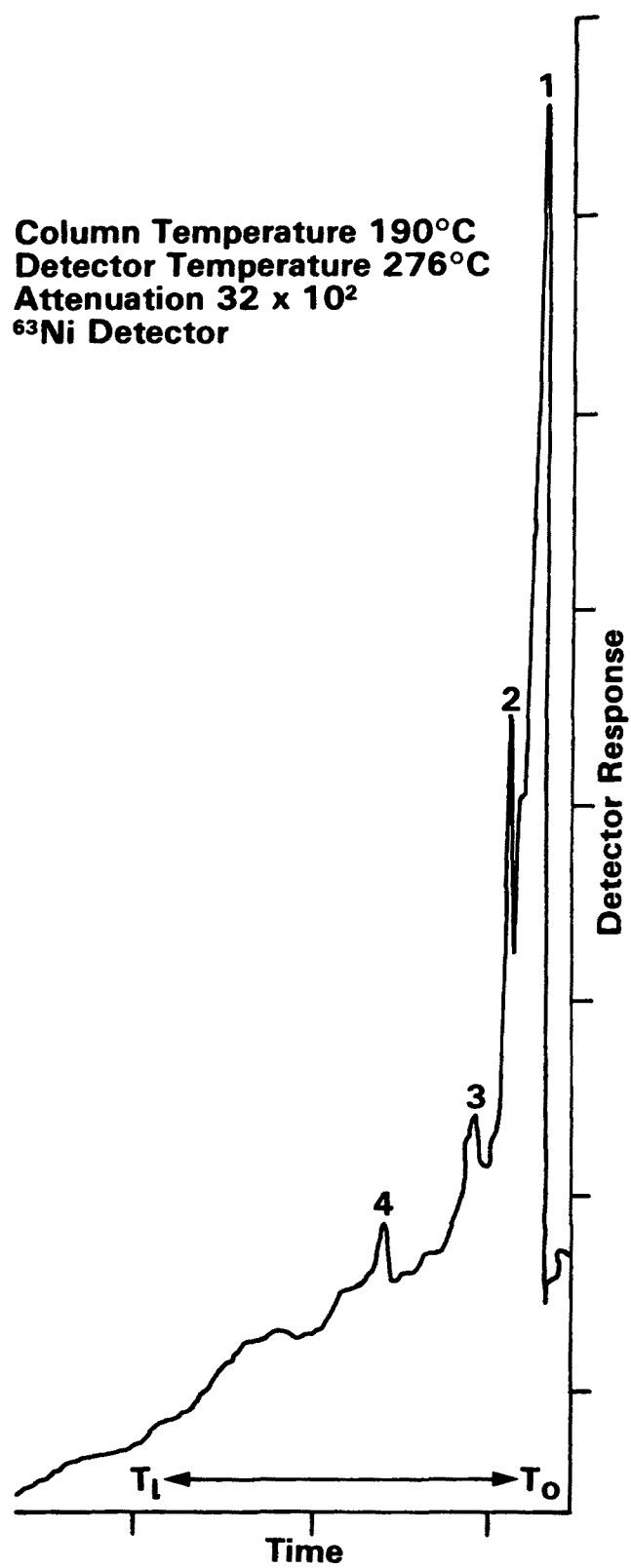


Figure 7. Chromatogram of petroleum ether extract of sample 3C-3.

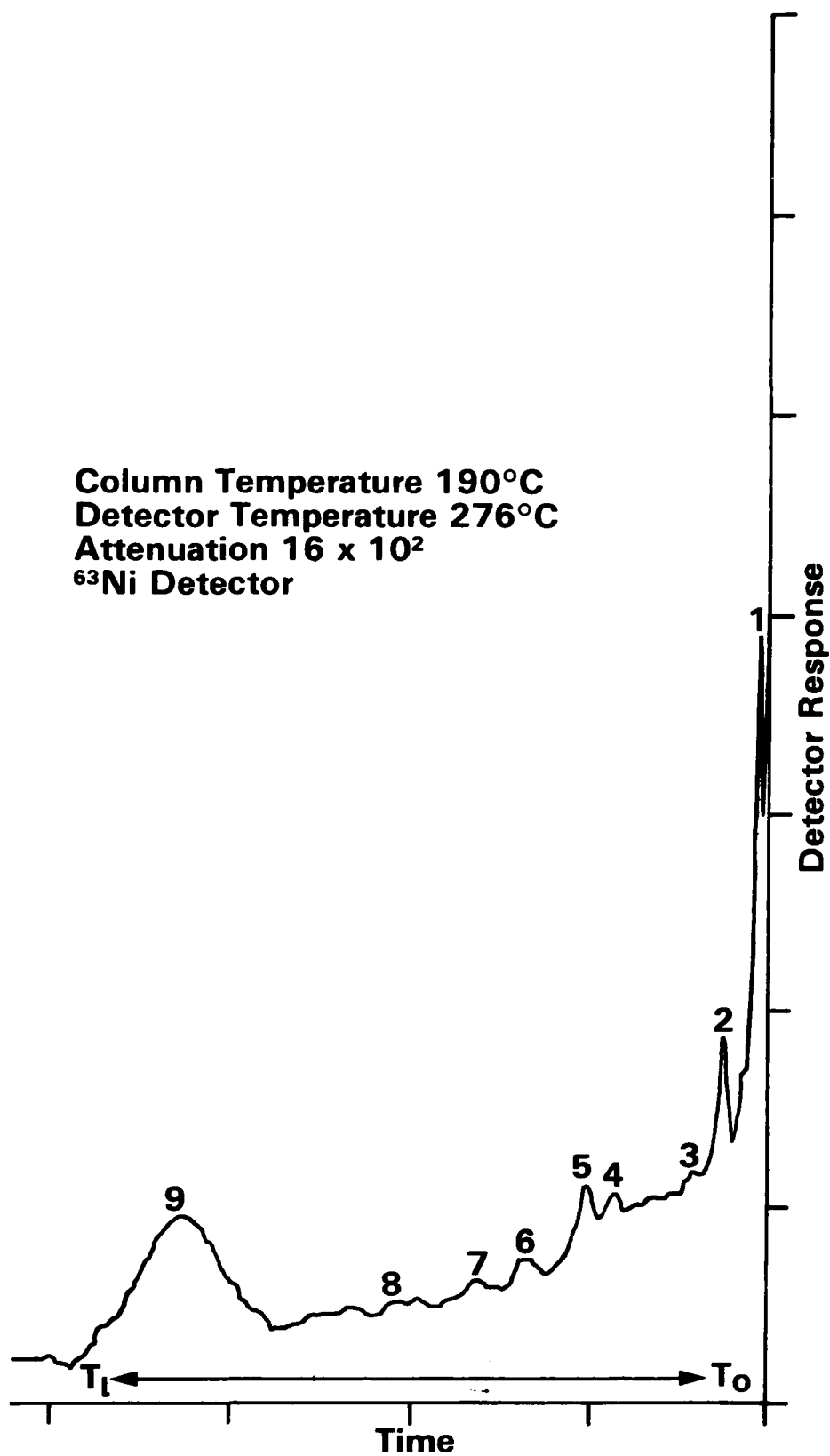


Figure 8. Chromatogram of petroleum ether extract of sample 1C-4.

comparisons of peaks between samples taken from the two sides of the park are of particular interest as shown in Table 5. All samples had a 2- μ l injection volume, chart speed was 2 min/cm, and carrier gas flow was 50 ml/min.

No attempt was made to identify the individual peaks. It is assumed most of the organics detected are of natural origin. Considerably more research and developmental effort is required before identification of airborne anthropogenic organics in background areas such as the Great Smoky Mountains can be accomplished.

In summary, the compounds detected at each site have either identical retention volumes or very similar retention volumes. Large differences in retention volumes occurred only when the column temperature was raised to 190°C.

VEGETATION AND LITTER

The vegetation was analyzed by the University of California's (UCLA) Laboratory of Nuclear Medicine and Radiation Biology. This analytical technique has been previously described by Alexander et al. (1975).

Vegetative standards obtained from the U.S. Bureau of Standards with certified trace element levels were submitted as quality assurance samples. Based upon the results of these standards, expected precision limits were calculated for this analytical technique. The precision limits are presented as follows:

| <u>Elements</u> | <u>Maximum Allowable % Deviation From a Known Value or COV of Replicates</u> |
|----------------------------------|--|
| K, Ca, Mg, Cu, Mn, B, Sr, Ba, Al | ±20% |
| P, Na, Zn, Fe, Cr, Ag, Ti, V | ±40% |
| Li, Pb | ±50% |

Minimum detection limits are:

| <u>Element</u> | <u>ppm</u> | <u>Element</u> | <u>ppm</u> | <u>Element</u> | <u>ppm</u> |
|----------------|------------|----------------|------------|----------------|------------|
| P | 50.0 | B | 0.2 | Sr | 0.2 |
| Na | 1.0 | Al | 0.1 | Ba | 0.2 |
| K | 150.0 | Si | 1.0 | Li | 0.3 |
| Ca | 1.0 | Ti | 0.5 | Ag | 0.1 |
| Mg | 50.0 | V | 1.0 | Sn | 0.3 |
| Zn | 5.0 | Co | 1.5 | Pb | 1.0 |
| Cu | 0.2 | Ni | 0.5 | Be | 0.2 |
| Fe | 0.6 | Mo | 0.2 | Cd | 3.0 |
| Mn | 0.1 | Cr | 0.2 | | |

These limits and precision values were accepted by the investigators.

The data for trace element values in vegetation and forest litter by site are summarized in Tables 6 through 17. The purpose in sampling vegetation was to obtain an estimate of field sampling error and to begin to define the possible use of certain types of vegetation for biological monitors.

Estimates of field sample error can be used to determine the number of samples required to reach a certain level of confidence. With the amount of data presented in Tables 6 through 17, it was not feasible to make this calculation for each sample type/element combination. The coefficients of variation are shown in Table 18 for certain elements found in vegetation. With the exception of manganese and aluminum most of the coefficients of variation range between 10 and 30 percent.

Arbitrarily, a desired sampling error of plus or minus 10 percent at the 95 percent confidence level was chosen. For example, if witch hobble, shown in Table 18 above, were chosen as a sample species and strontium as the element, it would be necessary to collect approximately 23 samples. Similar estimates can be made for all species and elements. During field sampling and analysis, the number of samples used would probably be controlled by the sample/element combination with the greatest variability tempered by the resources available.

For samples that exhibit a large coefficient of variation such as the manganese in rhododendron, the number of samples required to meet precision levels as stated would be approximately 100. A decrease in precision of only 2 percent would reduce the number of samples required to 71. Our conclusion concerning the required number of vegetation samples for a biosphere reserve monitoring system is that the number required for our desired confidence level is reasonable, and a cost-effective system can be designed.

Another consideration in determining the number of samples collected is the interaction of analytical error with field sampling error. All vegetation and litter samples in this study were analyzed in triplicate and replicated nine times on each sample site. With this type of design, analysis of variance techniques to determine the variability from the analytical error versus that from field sampling was accomplished (Snedecor, and Cochran 1967). The estimated variance of the sample mean per determination is given by the mean square between blocks (i.e., sites 11, 12, 13, and 14) divided by the total number of determinations. This in turn can be partitioned into the various components that contribute to this variance of the individual sample mean per determination. For example, for cobalt in forest litter, 2.2 percent of the variation per determination is due to analytical error, 11.1 percent is due to subsamples from within each site, and 86.7 percent is due to variation between the sites. For lead in forest litter, the estimated variance of the sample mean per determination is broken into the following relative contributions: 1.9 percent from analytical error, 7.4 percent from variability within a block, and 90.7 percent from variability between sites. In spite of the fact that the precision limits of acceptance for lead are plus or minus 50 percent, this is an example that, as large as the analytical error may be, the field error is much greater. Therefore, to reduce field study error and to increase the reliability of estimating trace element levels, more effort should be expended on collecting

TABLE 6. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 11

| Element | Concentration of Trace Element (ppm) in Subsamples* | | | | | | | | | |
|---------------|---|------|--------|-------|------|------|------|------|------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 5883 | 9587 | 8773 | 16433 | 8800 | 4857 | 9167 | 5590 | 4263 | 8150 |
| Barium | 188 | 309 | 196 | 208 | 325 | 140 | 281 | 168 | 181 | 222 |
| Beryllium | 0.6 | 0.6 | 0.5 | 1.2 | 0.4 | <0.2 | 0.8 | <0.2 | 0.5 | 0.5 |
| Boron | 32.2 | 14.6 | 17.0 | 13.5 | 9.6 | 13.3 | 11.5 | 10.2 | 10.1 | 14.6 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 680 | 1419 | 172 | 72 | 304 | 513 | 420 | 1290 | 1507 | 708 |
| Chromium | 14.9 | 35.4 | 11.1 | 27.7 | 18.2 | 5.1 | 15.3 | 7.7 | 5.6 | 15.6 |
| Cobalt | 1.5 | 2.1 | 1.0 | 2.6 | 1.5 | 1.5 | 1.5 | 1.9 | 1.5 | 1.7 |
| Copper | 18.4 | 38.8 | 25.6 | 40.1 | 25.2 | 24.7 | 23.5 | 24.7 | 26.1 | 27.1 |
| Iron | 5560 | 6653 | 7043 | 11367 | 6633 | 5893 | 7000 | 6123 | 5427 | 6855 |
| Lead | 217 | 191 | 279 | 314 | 266 | 181 | 323 | 212 | 231 | 246 |
| Lithium | 2.0 | 5.3 | 4.7 | 11.6 | 2.5 | 1.4 | 4.1 | 1.9 | 1.9 | 3.9 |
| Magnesium | 1397 | 2970 | 2190 | 5290 | 1787 | 1303 | 1987 | 1160 | 927 | 2119 |
| Manganese | 320 | 2220 | 1095 | 850 | 286 | 227 | 326 | 340 | 320 | 664 |
| Molybdenum | 1.4 | 2.7 | 2.2 | 5.1 | 2.2 | 0.8 | 2.3 | 1.1 | 0.9 | 2.1 |
| Nickel | 16.7 | 31.2 | 12.3 | 25.8 | 17.8 | 9.4 | 16.4 | 12.6 | 9.1 | 16.8 |
| Phosphorus | 1877 | 3323 | 1370 | <50 | 853 | <50 | 1910 | <50 | <50 | 1037 |
| Potassium (%) | 0.52 | 2.27 | 3.05 | 7.70 | 1.29 | 0.06 | 1.73 | 0.14 | 0.09 | 1.87 |
| Silicon (%) | 6.0 | 8.1 | 10.0** | 8.9 | 9.5 | 4.3 | 6.6 | 4.6 | 4.5 | 7.0 |
| Silver | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Sodium | 1290 | 2330 | 2050 | 3330 | 746 | 150 | 646 | 186 | 150 | 1210 |
| Strontium | 31.6 | 40.7 | 17.3 | 15.9 | 44.0 | 29.5 | 35.4 | 40.6 | 49.8 | 33.8 |
| Tin | <0.3 | 0.3 | <0.3 | 0.4 | 1.3 | <0.3 | 0.8 | 0.6 | 0.5 | 0.4 |
| Titanium | 786 | 1590 | 1707 | 2373 | 1513 | 508 | 1463 | 666 | 465 | 1230 |
| Vanadium | 11.4 | 17.3 | 17.9 | 27.6 | 16.7 | 5.9 | 15.6 | 8.0 | 6.0 | 14.0 |
| Zinc | 25.4 | 10.7 | 5.5 | <5.0 | 12.6 | 36.7 | 5.6 | 37.6 | 48.0 | 20.3 |

* except for potassium and silicon

** Upper limit of detection

ND = Not Detected

TABLE 7. SUMMARY OF TRACE ELEMENT VALUES IN NETTLE LEAVES FROM SITE 11

| Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 6090 | 806 | 1860 | 2960 | 3020 | 1601 | 1460 | 2140 | 572 | 2370 |
| Barium | 435 | 180 | 250 | 261 | 242 | 244 | 238 | 145 | 288 | 254 |
| Beryllium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Boron | 25.6 | 40.6 | 44.0 | 84.5 | 41.9 | 45.4 | 39.4 | 38.3 | 39.6 | 44.4 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 14800 | 25000 | 21900 | 18800 | 20100 | 25500 | 24200 | 17800 | 28700 | 21900 |
| Chromium | | | | | | | | | | |
| Cobalt | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Copper | 16.9 | 9.3 | 15.6 | 14.5 | 10.5 | 10.1 | 9.7 | 12.6 | 12.2 | 12.4 |
| Iron | 3890 | 309 | 848 | 1780 | 1800 | 911 | 657 | 1490 | 538 | 1360 |
| Lead | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Lithium | 5.5 | 5.5 | 2.9 | 3.3 | 3.4 | 3.0 | 2.7 | 3.0 | 3.6 | 3.7 |
| Magnesium | 8890 | 3916 | 5883 | 6480 | 6780 | 9440 | 8680 | 6150 | 7260 | 7050 |
| Manganese | 1060 | 228 | 342 | 808 | 493 | 374 | 554 | 437 | 267 | 507 |
| Molybdenum | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Nickel | 9.5 | 1.9 | 1.8 | 8.5 | 3.6 | 2.8 | 2.3 | 3.0 | 1.7 | 3.8 |
| Phosphorus | 5340 | 2220 | 2400 | 4240 | 3650 | 1650 | 1500 | 2180 | 2000 | 2800 |
| Potassium | 12800 | 41500 | 37100 | 43100 | 55000 | 48700 | 45800 | 65600 | 57500 | 45200 |
| Silicon | 78100 | 2780 | 6650 | 20500 | 21500 | 6670 | 4550 | 5770 | 3640 | 16700 |
| Silver | 0.2 | 0.4 | 0.4 | 0.5 | 0.3 | 0.3 | 0.4 | 0.4 | 0.3 | 0.3 |
| Sodium | 6190 | 90.8 | 117 | 414 | 334 | 103 | 84.4 | 128 | 86.3 | 839 |
| Strontium | 104 | 112 | 133 | 90.4 | 109 | 167 | 175 | 106 | 148 | 127.3 |
| Tin | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Titanium | 1630 | 48.9 | 216 | 613 | 642 | 146 | 99.5 | 313 | 91.4 | 421.8 |
| Vanadium | | | | | | | | | | |
| Zinc | 32.0 | 43.3 | 28.1 | 69.5 | 26.4 | 52.2 | 53.6 | 32.5 | 30.0 | 40.8 |

ND = Not Detected

TABLE 8. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 11

| Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 234 | 200 | 212 | 225 | 755* | 342 | 331 | 419 | 313 | 337 |
| Barium | 186 | 157 | 210 | 198 | 319 | 279 | 270 | 228 | 213 | 229 |
| Beryllium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Boron | 25.1 | 24.6 | 20.6 | 27.8 | 28.2 | 28.3 | 29.8 | 24.8 | 26.8 | 26.2 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 14700 | 14100 | 13300 | 14100 | 18000 | 18500 | 15600 | 12500 | 15100 | 15100 |
| Chromium | 0.2 | 0.2 | 0.2 | 0.3 | 1.0 | 0.7 | 0.8 | 0.8 | 0.8 | 0.6 |
| Cobalt | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Copper | 7.9 | 5.0 | 5.2 | 5.8 | 7.5 | 5.3 | 7.5 | 67 | 7.7 | 6.5 |
| Iron | 85.7 | 83.7 | 80.4 | 93.2 | 367 | 105 | 134 | 186 | 139 | 142 |
| Lead | <1.0 | <1.0 | <1.0 | 4.9 | <1.0 | 1.8 | <1.0 | 6.6 | <1.0 | 1.5 |
| Lithium | 0.4 | 0.4 | 0.6 | 0.5 | 1.0 | 0.9 | 0.9 | 0.5 | 1.0 | 0.7 |
| Magnesium | 2260 | 2410 | 2020 | 2330 | 3730 | 2930 | 3310 | 2230 | 3000 | 2690 |
| Manganese | 1390 | 1210 | 1840 | 1770 | 2470 | 2700 | 2460 | 1260 | 2350 | 1940 |
| Molybdenum | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Nickel | 1.1 | <0.5 | 0.8 | 2.6 | 0.7 | 0.6 | 1.4 | 2.3 | 1.5 | 1.3 |
| Phosphorus | 838 | 984 | 920 | 813 | 645 | 699 | 820 | 446 | 674 | 759 |
| Potassium | 14200 | 12200 | 9750 | 5740 | 10700 | 8550 | 11900 | 8180 | 13700 | 10500 |
| Silicon | 314 | 277 | 239 | 209 | 2473* | 497 | 378 | 576 | 452 | 601 |
| Silver | 0.7 | 0.6 | 0.8 | 0.9 | 1.1 | 1.0 | 1.0 | 0.9 | 1.1 | 0.9 |
| Sodium | 88.3 | 33.7 | 59.1 | 57.5 | 97.1 | 23.9 | 81.7 | 89.9 | 91.4 | 69.1 |
| Strontium | 48.2 | 24.7 | 30.3 | 51.7 | 73.4 | 64.7 | 66.2 | 59.9 | 56.6 | 52.8 |
| Tin | 0.3 | <0.3 | 0.5 | 1.1 | 0.6 | 0.9 | 1.1 | 1.4 | 1.1 | 0.8 |
| Titanium | 5.3 | 5.6 | 4.1 | 3.5 | 54.7* | 9.3 | 12.0 | 16.7 | 12.8 | 13.8 |
| Vanadium | 2.2 | 2.1 | 2.1 | 2.3 | 2.6 | 1.3 | 1.4 | 2.0 | 1.3 | 1.9 |
| Zinc | 18.1 | 16.1 | 13.9 | 13.0 | 12.6 | 12.3 | 12.0 | 10.9 | 8.4 | 13.0 |

* Possibly contaminated with soil
 ND = Not Detected

TABLE 9. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 12

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | |
|------------|--|------|-------|-------|-------|-------|-------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 9983 | 9057 | 9643 | 17167 | 9863 | 10336 | 12066 | 9740 | 10600 | 10940 |
| Barium | 277 | 341 | 213 | 285 | 222 | 224 | 229 | 241 | 133 | 241 |
| Beryllium | 0.6 | 1.0 | 0.7 | 0.8 | 0.2 | 0.4 | 0.3 | 1.0 | 1.2 | 0.7 |
| Boron | 7.6 | 13.7 | 8.7 | 17.4 | 17.9 | 16.5 | 7.3 | 10.4 | 12.6 | 12.5 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 358 | 1533 | 163 | 1.0 | 207 | 692 | 96.0 | 1054 | 335 | 493 |
| Chromium | 43.6 | 49.0 | 53.0 | 40.4 | 29.8 | 33.7 | 68.7 | 38.6 | 31.0 | 43.1 |
| Cobalt | 1.5 | 2.6 | 1.5 | 3.3 | 2.1 | 2.4 | 4.1 | 1.7 | 1.7 | 2.3 |
| Copper | 27.7 | 24.7 | 26.6 | 33.2 | 18.1 | 27.1 | 36.4 | 36.4 | 41.1 | 30.2 |
| Iron | 5997 | 6907 | 5710 | 10030 | 8127 | 8057 | 9473 | 4740 | 7977 | 7446 |
| Lead | 275 | 356 | 259 | 399 | 294 | 308 | 288 | 263 | 290 | 303 |
| Lithium | 6.0 | 5.8 | 8.9 | 17.4 | 9.0 | 10.4 | 12.3 | 6.9 | 9.4 | 9.6 |
| Magnesium | 1777 | 1640 | 2473 | 3600 | 1967 | 2417 | 2873 | 2187 | 2870 | 2423 |
| Manganese | 598 | 1180 | 769 | 1310 | 845 | 1129 | 1613 | 224 | 385 | 895 |
| Molybdenum | 2.6 | 2.5 | 2.9 | 5.4 | 2.5 | 2.5 | 4.2 | 2.5 | 3.7 | 3.2 |
| Nickel | 38.5 | 43.6 | 45.3 | 39.4 | 280 | 32.8 | 59.4 | 33.3 | 31.8 | 39.1 |
| Phosphorus | 466 | 3030 | 1620 | 560 | <50 | <50 | <50 | <50 | 11100 | 2036 |
| Potassium | 3.33 | 1.57 | 5.53 | 10.55 | 2.87 | 1.97 | 6.50 | 3.95 | 4.62 | 4.53 |
| Silicon | 9.8 | 7.6 | 10.0* | 10.0* | 10.0* | 9.1 | 9.8 | 10.0* | 10.0* | 9.6 |
| Silver | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Sodium | 3890 | 2140 | 4760 | 5390 | 3430 | 2640 | 3620 | 2180 | 2610 | 3410 |
| Strontium | 30.1 | 49.7 | 19.1 | 19.5 | 22.8 | 31.9 | 15.4 | 36.7 | 16.7 | 26.9 |
| Tin | 1.0 | 2.1 | 1.7 | 0.4 | 1.1 | 1.7 | 3.3 | 0.3 | 0.1 | 1.3 |
| Titanium | 2000 | 1281 | 2130 | 2453 | 1643 | 1467 | 2343 | 1199 | 1603 | 1791 |
| Vanadium | 13.3 | 13.6 | 15.4 | 39.0 | 18.8 | 17.1 | 29.0 | 8.8 | 16.8 | 19.0 |
| Zinc | <5.0 | 13.1 | <5.0 | <5.0 | 15.9 | 10.9 | <5.0 | 16.5 | 14.0 | 7.8 |

* Upper machine limit

ND = Not Detected

TABLE 10. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 12

| Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 251 | 305 | 429 | 196 | 283 | 277 | 447 | 383 | 320 | 321 |
| Barium | 336 | 319 | 343 | 359 | 213 | 202 | 317 | 340 | 318 | 305 |
| Beryllium | ND | | | | | | | | | |
| Boron | 17.8 | 14.6 | 12.5 | 25.6 | 18.8 | 19.1 | 21.0 | 24.7 | 21.0 | 19.4 |
| Cadmium | ND | | | | | | | | | |
| Calcium | 16700 | 16300 | 17200 | 16200 | 15000 | 17200 | 17500 | 17900 | 16900 | 16800 |
| Chromium | 0.4 | 0.4 | 0.7 | 0.2 | 0.4 | 0.6 | 0.6 | 2.3 | 0.4 | 0.7 |
| Cobalt | ND | | | | | | | | | |
| Copper | 4.5 | 5.9 | 5.8 | 5.8 | 5.9 | 6.2 | 6.0 | 11.9 | 5.0 | 6.3 |
| Iron | 75.9 | 119 | 188 | 69.1 | 80.5 | 75.2 | 150 | 118 | 92.8 | 107 |
| Lead | 4.5 | 2.8 | 2.0 | 1.8 | 1.4 | <1.0 | <1.0 | <1.0 | <1.0 | 1.5 |
| Lithium | 0.9 | 1.5 | 1.5 | 1.3 | 1.8 | 1.7 | 1.3 | 1.2 | 1.4 | 1.4 |
| Magnesium | 2320 | 2940 | 3130 | 2670 | 2040 | 2230 | 2750 | 2440 | 2600 | 2570 |
| Manganese | 1440 | 3230 | 2710 | 2060 | 634 | 1300 | 1820 | 2130 | 2010 | 1930 |
| Molybdenum | ND | ND | ND | | | | | | | |
| Nickel | 1.9 | 1.5 | 2.0 | <0.5 | <0.5 | <0.5 | <0.5 | 1.1 | <0.5 | 0.9 |
| Phosphorus | 498 | 720 | 216 | 1005 | 861 | 798 | 687 | 746 | 717 | 694 |
| Potassium | 5400 | 8910 | 7950 | 5160 | 7850 | 6170 | 8100 | 7660 | 6210 | 7050 |
| Silicon | 250 | 355 | 788 | 162 | 296 | 272 | 658 | 591 | 364 | 415 |
| Silver | 0.9 | 1.3 | 1.2 | 0.8 | 0.7 | 0.8 | 0.8 | 0.9 | 0.8 | 0.9 |
| Sodium | 48.2 | 28.9 | 50.9 | 84.0 | 91.8 | 79.1 | 72.1 | 71.0 | 52.4 | 64.3 |
| Strontium | 44.7 | 57.7 | 52.9 | 36.8 | 35.8 | 36.5 | 55.3 | 71.4 | 66.1 | 50.8 |
| Tin | 0.7 | 1.4 | 1.2 | 1.5 | 0.5 | 0.6 | 0.7 | 1.3 | 0.7 | 1.0 |
| Titanium | 8.4 | 10.2 | 17.7 | 8.4 | 6.8 | 6.3 | 22.1 | 14.2 | 8.9 | 11.4 |
| Vanadium | 1.5 | 1.2 | 1.6 | 1.2 | 2.7 | 2.3 | 1.8 | 2.1 | 1.8 | 1.8 |
| Zinc | 5.5 | 5.0 | <5.0 | 15.1 | 13.1 | 5.7 | 10.0 | 9.0 | 10.1 | 8.5 |

ND = Not Detected

TABLE 11. SUMMARY OF TRACE ELEMENT VALUES IN CHRISTMAS FERN FROM SITE 12

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | \bar{X} |
|------------|--|------|-------|-------|-------|-------|-------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| Aluminum | 786 | 451 | 694 | 683 | 617 | 509 | 784 | 820 | 471 | 646 |
| Barium | 86.8 | 60.9 | 111 | 152 | 117 | 101 | 129 | 88.7 | 85.8 | 103 |
| Beryllium | ND | | | | | | | | | |
| Boron | 10.4 | 8.8 | 12.7 | 17.6 | 12.0 | 9.6 | 12.4 | 14.1 | 6.1 | 11.5 |
| Cadmium | ND | | | | | | | | | |
| Calcium | 2850 | 1620 | 4960 | 8650 | 6450 | 3490 | 5290 | 3360 | 2070 | 4300 |
| Chromium | ND | | | | | | | | | |
| Cobalt | ND | | | | | | | | | |
| Copper | 4.1 | 3.3 | 7.4 | 7.2 | 5.4 | 4.9 | 4.9 | 4.6 | 4.1 | 5.1 |
| Iron | 174 | 45 | 100 | 126 | 84.8 | 57.0 | 121 | 79.6 | 31.2 | 91.1 |
| Lead | ND | | | | | | | | | |
| Lithium | 0.6 | 0.4 | 0.7 | 0.9 | 0.8 | 0.7 | 0.8 | 0.9 | 0.7 | 0.7 |
| Magnesium | 2430 | 2790 | 3050 | 3010 | 3380 | 3010 | 2580 | 2700 | 3230 | 2780 |
| Manganese | 149 | 172 | 173 | 191 | 169 | 165 | 185 | 199 | 142 | 172 |
| Molybdenum | ND | | | | | | | | | |
| Nickel | 3.4 | 3.4 | 3.2 | 2.9 | 3.0 | 3.2 | 4.2 | 3.7 | 3.6 | 3.1 |
| Phosphorus | 304 | 672 | 964 | 980 | 591 | 617 | 569 | 519 | 588 | 645 |
| Potassium | 13400 | 8730 | 20400 | 23900 | 19600 | 17300 | 14100 | 21200 | 14500 | 17000 |
| Silicon | 702 | 156 | 266 | 416 | 525 | 167 | 679 | 219 | 74.2 | 356 |
| Silver | 0.4 | 0.3 | 0.4 | 0.4 | 0.3 | 0.3 | 0.5 | 0.4 | 0.4 | 0.4 |
| Sodium | 28.3 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 25.9 | <1.0 | <1.0 | 6.0 |
| Strontium | 34.2 | 25.0 | 39.0 | 51.7 | 42.8 | 28.8 | 44.0 | 34.7 | 30.3 | 36.7 |
| Tin | ND | | | | | | | | | |
| Titanium | 6.8 | 0.9 | 4.5 | 2.8 | 9.7 | 6.1 | 2.0 | 8.2 | 3.7 | 4.7 |
| Vanadium | ND | | | | | | | | | |
| Zinc | 11.8 | 14.6 | 17.9 | 22.3 | 17.8 | 16.8 | 9.8 | 12.9 | 7.4 | 14.5 |

ND = Not Detected

TABLE 12. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 13

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | |
|------------|--|------|------|------|------|------|------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 7893 | 8527 | 7123 | 5553 | 7873 | 8703 | 8903 | 9713 | 12667 | 8461 |
| Barium | 180 | 222 | 208 | 199 | 189 | 262 | 229 | 254 | 332 | 230 |
| Beryllium | 0.8 | 0.6 | 0.4 | 0.3 | 0.3 | 0.2 | 0.2 | 3.9 | 5.3 | 1.3 |
| Boron | 15.5 | 21.0 | 13.7 | 31.7 | 15.9 | 13.6 | 5.6 | 8.9 | 28.0 | 17.1 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 851 | 92 | 200 | 232 | 371 | 132 | 151 | 28 | 7 | 229 |
| Chromium | 12.3 | 14.7 | 15.4 | 6.1 | 10.5 | 13.7 | 13.5 | 20.4 | 29.3 | 15.1 |
| Cobalt | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 2.4 | 2.0 | 1.0 | 0.5 | 1.5 |
| Copper | 30.8 | 19.0 | 18.1 | 15.9 | 20.8 | 22.7 | 22.3 | 26.6 | 25.0 | 22.3 |
| Iron | 6560 | 5486 | 4256 | 3847 | 6463 | 7847 | 5813 | 6373 | 8453 | 6122 |
| Lead | 424 | 459 | 479 | 378 | 453 | 477 | 397 | 610 | 879 | 506 |
| Lithium | 3.7 | 4.8 | 4.5 | 4.0 | 5.0 | 5.0 | 4.8 | 3.8 | 6.1 | 4.6 |
| Magnesium | 1150 | 1327 | 1143 | 934 | 1277 | 1647 | 1813 | 2130 | 3413 | 1648 |
| Manganese | 261 | 200 | 232 | 165 | 274 | 244 | 256 | 227 | 278 | 237 |
| Molybdenum | 2.0 | 1.9 | 1.5 | 1.1 | 1.7 | 2.2 | 1.8 | 2.8 | 3.8 | 2.1 |
| Nickel | 13.1 | 15.1 | 15.7 | 7.3 | 13.1 | 14.9 | 15.4 | 20.3 | 29.8 | 16.1 |
| Phosphorus | 1740 | 1033 | 226 | 250 | <50 | <50 | <50 | 11740 | 22433 | 4158 |
| Potassium | 0.64 | 1.18 | 0.96 | 0.56 | 0.55 | 1.12 | 1.17 | 2.45 | 5.37 | 1.55 |
| Silicon* | 7.3 | 7.9 | 7.7 | 4.4 | 7.1 | 6.8 | 7.5 | 8.7 | 10.0 | 7.5 |
| Silver | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Sodium | 696 | 1720 | 1830 | 622 | 1120 | 1940 | 2580 | 3000 | 5850 | 2150 |
| Strontium | 26.7 | 21.4 | 24.5 | 19.2 | 22.9 | 23.3 | 25.9 | 14.6 | 20.8 | 22.1 |
| Tin | 1.2 | 2.2 | 2.3 | 1.6 | 2.0 | 2.0 | 1.1 | <0.3 | <0.3 | 1.4 |
| Titanium | 857 | 1400 | 1073 | 869 | 961 | 1330 | 1196 | 1811 | 2780 | 1364 |
| Vanadium | 11.2 | 13.7 | 12.4 | 11.5 | 13.4 | 15.1 | 14.0 | 14.8 | 17.0 | 13.7 |
| Zinc | 52.6 | 12.4 | 12.4 | 17.3 | 17.9 | 6.3 | 9.3 | 8.2 | 14.4 | 16.8 |

* Upper machine limit
 ND = Not Detected

TABLE 13. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 13

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | \bar{X} |
|------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| Aluminum | 539 | 766 | 403 | 560 | 466 | 432 | 581 | 572 | 500 | 535 |
| Barium | 230 | 181 | 188 | 172 | 169 | 181 | 194 | 222 | 165 | 189 |
| Beryllium | ND | | | | | | | | | |
| Boron | 30.2 | 24.9 | 18.6 | 19.8 | 19.0 | 20.0 | 21.1 | 21.9 | 18.2 | 21.5 |
| Cadmium | ND | | | | | | | | | |
| Calcium | 14400 | 5370 | 5830 | 7770 | 5510 | 5880 | 4450 | 6400 | 6220 | 6870 |
| Chromium | ND | | | | | | | | | |
| Cobalt | ND | | | | | | | | | |
| Copper | 7.7 | 7.4 | 6.4 | 5.9 | 6.4 | 6.4 | 5.7 | 6.1 | 5.3 | 6.4 |
| Iron | 191 | 293 | 118 | 194 | 180 | 151 | 150 | 139 | 150 | 174 |
| Lead | ND | | | | | | | | | |
| Lithium | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| Magnesium | 2730 | 3520 | 3760 | 3550 | 3430 | 3320 | 3450 | 2770 | 3490 | 3340 |
| Manganese | 2540 | 1070 | 1240 | 592 | 1040 | 1030 | 312 | 613 | 611 | 1000 |
| Molybdenum | ND | | | | | | | | | |
| Nickel | 3.6 | 1.7 | 2.4 | 2.8 | 3.6 | 3.4 | 3.2 | 3.3 | 4.2 | 3.4 |
| Phosphorus | 1880 | 1450 | 978 | 802 | 853 | 945 | 536 | 805 | 563 | 978 |
| Potassium | 7600 | 27300 | 22700 | 26500 | 19600 | 26000 | 17300 | 19900 | 19900 | 20800 |
| Silicon | 708 | 1810 | 301 | 494 | 607 | 359 | 2780 | 1440 | 690 | 1020 |
| Silver | 0.9 | 0.3 | 0.7 | 0.6 | 0.7 | 0.6 | 0.5 | 0.6 | 0.6 | 0.6 |
| Sodium | 86.8 | 85.1 | 73.7 | 72.8 | 76.7 | 71.6 | 75.1 | 78.2 | 73.3 | 77.0 |
| Strontium | 56.9 | 29.5 | 22.9 | 27.4 | 26.1 | 28.6 | 31.3 | 31.0 | 30.5 | 31.6 |
| Tin | ND | | | | | | | | | |
| Titanium | 18.3 | 22.8 | 4.4 | 14.6 | 12.0 | 7.8 | 7.5 | 7.5 | 9.9 | 11.6 |
| Vanadium | ND | | | | | | | | | |
| Zinc | 46.5 | 73.8 | 47.3 | 44.2 | 56.3 | 31.0 | 39.5 | 48.8 | 49.2 | 48.5 |

ND = Not Detected

TABLE 14. SUMMARY OF TRACE ELEMENT VALUES IN WITCH HOBBLE FROM SITE 13

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | |
|------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 598 | 975 | 464 | 613 | 559 | 592 | 655 | 707 | 771 | 659 |
| Barium | 242 | 204 | 304 | 286 | 271 | 301 | 258 | 252 | 252 | 263 |
| Beryllium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Boron | 28.6 | 18.1 | 27.0 | 27.7 | 22.5 | 26.9 | 23.8 | 28.8 | 35.7 | 26.6 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 13300 | 5450 | 16100 | 15100 | 13800 | 14500 | 11700 | 12700 | 14300 | 13000 |
| Chromium | 0.2 | <0.2 | 0.4 | 0.4 | 0.5 | 0.5 | 0.3 | 0.2 | 0.5 | 0.3 |
| Cobalt | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Copper | 6.1 | 6.5 | 10.3 | 9.1 | 5.8 | 8.0 | 8.2 | 10.0 | 10.1 | 8.2 |
| Iron | 212 | 430 | 164 | 180 | 165 | 229 | 244 | 239 | 298 | 240 |
| Lead | 1.2 | <1.0 | 5.5 | 7.3 | 6.7 | <1.0 | 3.7 | <1.0 | <1.0 | 2.7 |
| Lithium | 1.8 | 0.7 | 2.0 | 1.7 | 1.3 | 1.7 | 1.8 | 1.9 | 2.0 | 1.6 |
| Magnesium | 4300 | 4160 | 3400 | 2600 | 3170 | 2780 | 2880 | 2510 | 2960 | 3200 |
| Manganese | 1760 | 635 | 2560 | 2490 | 2280 | 1710 | 1770 | 1910 | 1640 | 1860 |
| Molybdenum | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Nickel | <0.5 | 1.0 | <0.5 | 0.8 | <0.5 | 0.7 | 0.5 | 1.4 | 0.9 | 0.7 |
| Phosphorus | 1220 | 279 | 1297 | 1463 | 979 | 1042 | 878 | 1323 | 813 | 1033 |
| Potassium | 4140 | 24200 | 8470 | 10700 | 6460 | 3160 | 8310 | 12300 | 15400 | 10400 |
| Silicon | 1440 | 8110 | 565 | 589 | 596 | 1140 | 765 | 825 | 1490 | 1730 |
| Silver | 0.8 | 0.6 | 1.1 | 1.1 | 1.2 | 0.8 | 0.9 | 0.9 | 0.8 | 0.9 |
| Sodium | 67.1 | 59.3 | 86.7 | 76.5 | 56.3 | 76.6 | 96.5 | 88.9 | 81.1 | 76.5 |
| Strontium | 69.3 | 31.8 | 64.8 | 58.8 | 47.8 | 73.9 | 52.7 | 56.7 | 77.0 | 59.2 |
| Tin | 1.1 | 0.3 | 0.9 | 0.8 | 0.4 | 0.3 | 0.3 | 0.3 | <0.3 | 0.5 |
| Titanium | 24.3 | 29.3 | 16.1 | 19.5 | 17.0 | 20.4 | 27.6 | 22.7 | 34.3 | 23.5 |
| Vanadium | 2.3 | 2.2 | 2.3 | 2.4 | 2.4 | 2.5 | 1.9 | 2.6 | 2.2 | 2.3 |
| Zinc | 66.1 | 56.4 | 61.2 | 41.3 | 33.5 | 25.9 | 49.1 | 31.0 | 35.0 | 44.4 |

ND = Not Detected

TABLE 15. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 14

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | |
|------------|--|-------|------|------|-------|------|------|-------|------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 8310 | 15267 | 5707 | 5267 | 10363 | 8480 | 6510 | 11700 | 4887 | 8499 |
| Barium | 258 | 272 | 351 | 335 | 211 | 334 | 299 | 282 | 191 | 282 |
| Beryllium | 2.0 | 2.0 | 0.3 | <0.2 | 1.2 | 0.8 | 0.2 | 0.5 | 0.9 | 0.9 |
| Boron | 12.3 | 19.2 | 8.3 | 6.6 | 5.4 | 8.8 | 5.6 | 13.7 | 9.0 | 9.9 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 750 | 908 | 6080 | 1240 | 137 | 515 | 753 | 634 | 3690 | 1634 |
| Chromium | 22.5 | 16.3 | 18.8 | 12.1 | 20.4 | 11.5 | 13.9 | 31.2 | 7.9 | 17.2 |
| Cobalt | 3.2 | 8.2 | 2.5 | 4.2 | 2.2 | 3.4 | 3.6 | 5.1 | 1.5 | 3.8 |
| Copper | 31.4 | 54.1 | 20.1 | 20.8 | 29.7 | 19.2 | 16.4 | 40.8 | 21.7 | 28.3 |
| Iron | 10710 | 11560 | 4966 | 7426 | 7700 | 7370 | 5600 | 10140 | 5230 | 7856 |
| Lead | 463 | 466 | 106 | 183 | 320 | 353 | 195 | 225 | 119 | 270 |
| Lithium | 10.4 | 15.3 | 3.7 | 3.4 | 8.2 | 5.5 | 3.9 | 13.1 | 3.5 | 7.4 |
| Magnesium | 2717 | 6497 | 2070 | 1733 | 2507 | 1640 | 1513 | 4673 | 1723 | 2793 |
| Manganese | 1727 | 4207 | 1250 | 1239 | 1197 | 932 | 755 | 2527 | 719 | 1616 |
| Molybdenum | 3.2 | 6.2 | 1.0 | 1.1 | 2.6 | 1.8 | 1.4 | 3.5 | 0.9 | 2.4 |
| Nickel | 25.6 | 23.3 | 20.8 | 18.5 | 24.3 | 17.1 | 18.6 | 33.3 | 17.1 | 22.1 |
| Phosphorus | 1834 | 1650 | 1250 | <50 | 1757 | 953 | <50 | <50 | 715 | 907 |
| Potassium | 1.47 | 3.44 | 0.34 | 0.16 | 2.02 | 0.85 | 0.62 | 2.81 | 0.27 | 1.33 |
| Silicon | 8.7 | 9.8 | 4.9 | 5.0 | 10.0* | 7.1 | 4.8 | 9.7 | 4.4 | 7.2 |
| Silver | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Sodium | 830 | 5070 | 307 | 421 | 648 | 295 | 216 | 3450 | 378 | 1290 |
| Strontium | 21.7 | 42.5 | 76.5 | 57.0 | 18.1 | 47.8 | 41.8 | 33.5 | 68.4 | 45.3 |
| Tin | 0.8 | <0.3 | <0.3 | 0.8 | 0.6 | 1.4 | 1.4 | 1.8 | <0.3 | 0.8 |
| Titanium | 2457 | 1263 | 548 | 567 | 1873 | 1360 | 850 | 2017 | 708 | 1294 |
| Vanadium | 22.1 | 14.1 | 6.5 | 7.6 | 14.6 | 12.2 | 9.1 | 13.7 | 4.7 | 11.6 |
| Zinc | 60.8 | 19.0 | 17.4 | 19.0 | 3.3 | 29.6 | 6.5 | 6.7 | 42.0 | 22.7 |

* Upper machine limit
 ND = Not Detected

TABLE 16. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 14

| Element | Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | \bar{X} |
|------------|--|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| Aluminum | 262 | 284 | 429 | 274 | 334 | 337 | 454 | 464 | 322 | 351 |
| Barium | 270 | 243 | 237 | 377 | 260 | 260 | 315 | 272 | 213 | 271 |
| Beryllium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Boron | 14.4 | 19.0 | 16.1 | 12.7 | 16.8 | 20.7 | 24.5 | 16.6 | 15.8 | 17.4 |
| Cadmium | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Calcium | 15200 | 15800 | 15600 | 14800 | 13500 | 12100 | 12900 | 14700 | 15200 | 14400 |
| Chromium | 0.3 | 0.2 | 0.5 | 0.4 | 0.2 | 0.2 | <0.2 | 0.3 | 0.2 | 0.3 |
| Cobalt | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Copper | 5.6 | 5.2 | 5.5 | 6.1 | 6.5 | 10.9 | 8.2 | 5.0 | 5.9 | 6.5 |
| Iron | 79.3 | 73.6 | 131 | 86.6 | 116 | 118 | 185 | 154 | 111 | 117 |
| Lead | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| Lithium | 1.4 | 1.7 | 1.5 | 1.6 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | 0.7 |
| Magnesium | 1890 | 2120 | 2150 | 3190 | 2270 | 2510 | 2310 | 2460 | 2360 | 2360 |
| Manganese | 963 | 596 | 954 | 1460 | 1520 | 2290 | 2110 | 707 | 658 | 1250 |
| Molybdenum | ND | | | | | | | | | |
| Nickel | <0.5 | <0.5 | <0.5 | <0.5 | 2.1 | 2.0 | 2.2 | 2.3 | 2.8 | 1.4 |
| Phosphorus | 945 | 824 | 883 | 934 | 1203 | 1587 | 1510 | 832 | 965 | 1075 |
| Potassium | 5430 | 3440 | 6560 | 7570 | 8280 | 13300 | 12300 | 10100 | 10500 | 8610 |
| Silicon | 300 | 408 | 882 | 384 | 501 | 462 | 711 | 912 | 428 | 554 |
| Silver | 0.5 | 0.5 | 0.5 | 0.7 | 0.6 | 0.7 | 0.7 | 0.5 | 0.5 | 0.6 |
| Sodium | 22.1 | 79.0 | 74.0 | 23.9 | <1.0 | <1.0 | <1.0 | 42.8 | <1.0 | 26.9 |
| Strontium | 51.8 | 49.9 | 78.7 | 117 | 93.7 | 117 | 141 | 66.9 | 61.0 | 86.4 |
| Tin | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| Titanium | 7.9 | 8.8 | 15.2 | 9.1 | 10.1 | 7.2 | 13.7 | 12.1 | 5.6 | 10.0 |
| Vanadium | 1.4 | 2.0 | 2.2 | 2.0 | 1.3 | 1.6 | 1.3 | 1.2 | <1.0 | 1.5 |
| Zinc | 7.0 | 11.7 | 11.2 | 14.4 | 15.2 | 22.0 | 17.4 | 13.5 | 15.5 | 14.2 |

ND = Not Detected

TABLE 17. SUMMARY OF TRACE ELEMENT VALUES IN YELLOW BIRCH FROM SITE 14

| Concentration of Trace Element (ppm) in Subsamples | | | | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | \bar{X} |
| Aluminum | 568 | 274 | 254 | 229 | 178 | 341 | 284 | 203 | 267 | 277 |
| Barium | 281 | 422 | 348 | 440 | 295 | 418 | 215 | 207 | 318 | 327 |
| Beryllium | ND | | | | | | | | | |
| Boron | 17.5 | 19.4 | 19.0 | 18.0 | 24.1 | 26.5 | 16.2 | 17.1 | 19.0 | 19.7 |
| Cadmium | ND | | | | | | | | | |
| Calcium | 16300 | 17100 | 15800 | 16000 | 14100 | 25800 | 16800 | 10700 | 17100 | 16600 |
| Chromium | ND | | | | | | | | | |
| Cobalt | ND | | | | | | | | | |
| Copper | 6.1 | 8.1 | 5.2 | 6.0 | 6.4 | 8.2 | 4.7 | 6.0 | 7.4 | 6.4 |
| Iron | 133 | 115 | 117 | 116 | 101 | 144 | 111 | 117 | 128 | 120 |
| Lead | ND | | | | | | | | | |
| Lithium | 0.7 | 1.0 | 0.8 | 1.4 | 1.1 | 1.8 | 1.1 | 0.8 | 1.7 | 1.1 |
| Magnesium | 2510 | 2290 | 2170 | 3760 | 3170 | 5670 | 2960 | 25000 | 3500 | 3170 |
| Manganese | 1220 | 1220 | 404 | 1990 | 1780 | 2400 | 808 | 1750 | 974 | 1390 |
| Molybdenum | ND | | | | | | | | | |
| Nickel | 3.9 | 4.8 | 4.1 | 2.6 | 3.2 | 2.5 | 2.7 | 4.0 | 6.4 | 3.9 |
| Phosphorus | 1390 | 1510 | 1200 | 2490 | 2220 | 2580 | 1500 | 1520 | 1150 | 1730 |
| Potassium | 12800 | 41500 | 37100 | 43100 | 55000 | 48700 | 13400 | 9710 | 20200 | 18900 |
| Silicon | 738 | 576 | 637 | 827 | 531 | 2100 | 833 | 1660 | 910 | 979 |
| Silver | 0.9 | 0.9 | 0.8 | 0.9 | 0.9 | 1.1 | 0.5 | 0.8 | 0.6 | 0.8 |
| Sodium | 71.1 | 73.6 | 71.2 | 79.2 | 71.8 | 751 | 74.4 | 75.0 | 72.8 | 73.8 |
| Strontium | 67.4 | 93.8 | 76.5 | 123 | 83.9 | 88.5 | 55.7 | 61.8 | 99.2 | 83.3 |
| Tin | ND | | | | | | | | | |
| Titanium | 13.2 | 13.1 | 13.7 | 10.1 | 7.7 | 13.1 | 12.7 | 7.2 | 13.0 | 11.5 |
| Vanadium | ND | | | | | | | | | |
| Zinc | 32.9 | 35.7 | 17.8 | 105.9 | 56.7 | 58.3 | 65.7 | 69.3 | 86.1 | 58.7 |

ND = Not Detected

TABLE 18. COEFFICIENTS OF VARIATION FOR ELEMENTAL LEVELS IN
VEGETATION SAMPLES COLLECTED IN THE GREAT SMOKY
MOUNTAINS BIOSPHERE RESERVE (%)

| Sample | Mn | Mg | Elements | Sr | Ba |
|--------------------------|------|------|----------|------|------|
| | | | Al | | |
| Rhododendron - site 11 | 21.4 | 38.5 | 51.4 | 30.4 | 22.3 |
| Rhododendron - site 12 | 13.5 | 39.8 | 25.9 | 26.0 | 22.1 |
| Rhododendron - site 14 | 15.3 | 50.4 | 22.3 | 37.8 | 17.3 |
| Witch Hobble - site 13 | 20.5 | 30.9 | 22.6 | 23.9 | 11.9 |
| Nettle - site 11 | 27.2 | 54.2 | 66.8 | 28.7 | 31.1 |
| Christmas Fern - site 12 | 18.5 | 10.8 | 21.9 | 23.2 | 26.1 |
| Wood Fern - site 13 | 10.6 | 64.6 | 20.0 | 34.6 | 12.1 |
| Yellow Birch - site 14 | 34.2 | 45.4 | 30.9 | 24.9 | 26.6 |

samples in the field and less on reducing or improving analytical precision. Similar types of calculations were made for all elements in the forest litter; however, no deviations from the above pattern were noted.

While this presampling of Great Smoky Mountains National Park was originally designed as a pilot study for a larger project, the results for lead in litter are of particular interest. Levels of lead in soil around power plants range from 5 to 100 ppm (Lindberg et al., 1975; Wiersma and Crockett, 1978). Linzon et al. (1976) reported an overall lead level in soil of 292 ppm in urban areas near a secondary lead smelter. Gill et al. (1974) reported lead levels ranging from 89.3 ppm to 1,403 ppm in soil collected in five U.S. cities. The soil lead levels found in this study were relatively low--15 to 20 ppm--while the lead levels in litter are comparable to lead concentrations found in soil in urban areas.

Sites 11, 12, and 14 are located at relatively low altitudes--near 1,000 m--while site 13 is located at a high altitude--approximately 2,000 m. The lead levels in litter for sites 11, 12, and 14 range between 246 to 303 ppm, whereas the average lead level at the high altitude site, site 13, was 506 ppm. An analysis of variance indicated a significant difference among the four sites at the 99 percent confidence level. An orthogonal comparison confirmed that the lead contamination at site 13 was significantly higher than at sites 11, 12, and 14.

These data are very similar to data reported by Reiners et al. (1975) for the White Mountains of New Hampshire. They reported that lead levels in the litter layer increased with altitude until the Krumholz Forest was reached, where a slight decrease in concentration occurred. The lead levels in the

White Mountains ranged from 35 to 336 ppm, with the fir forest sites having the highest concentrations.

The lead found in the Great Smoky Mountains appears to be from nonnatural sources. Lead levels in soils collected beneath the litter layer are not excessively high. Translocation of lead in vegetation is minimal, and only small amounts of lead were detected in the vegetation sampled. The vegetation samples were collected from the understory. The majority of the litter comes from the overstory canopy (Lutz and Chandler, 1961), which could be an effective filter for airborne lead particles. The air samples did not collect lead; however, the limit of analytical detection was fairly high--50 ng/m³. Also rain could wash considerable quantities of lead from the air (Schlesinger et al., 1974). Therefore, it is unlikely that the high levels of lead detected in the litter are part of natural lead sources, but rather reflect deposition of lead from outside sources. Similar conclusions were made by Reiners and his research associates (Reiners et al. 1975).

There is some indication that certain plants may be better pollutant accumulators than others. For example, witch hobble is the only understory plant that shows lead residue. Also its average content of elements that may be associated with entrapped dust, such as aluminum and silica, are at least twice as high as those values for rhododendron. This could be related to leaf morphology. Witch hobble has a large broad leaf with a rough surface. Rhododendron leaves are elongated, with a fairly large surface area but a shiny, smooth surface. The results are too preliminary to draw more than an indication of the possible selection of witch hobble as a biological monitor. Other parameters need addressing, such as uptake and translocation, before definite conclusions can be made.

SOIL ANALYSES

Sample preparation included adding 25 ml of concentrated nitric acid to a 10-g aliquot of oven-dried soil. After digestion for a 24-hour period, the soil was separated from the supernatant by centrifugation and filtration and washed three times with distilled deionized water. The supernatant and washes were combined in a volumetric flask and diluted to 100 ml. In addition to the soil extracts, distilled water blanks, acid blanks, standards, and spiked standards were analyzed in duplicate for zinc, lead, copper, cadmium, manganese, and lithium. The analyses were accomplished by standard techniques using a Perkin-Elmer 603 Atomic Absorption Spectrophotometer.

The results are summarized in Table 19. A slight increase in soil lead is present at site 13. The high cadmium level for site 13 is the result of two samples that, when analyzed, gave a high value for cadmium. The quality assurance samples, analyzed simultaneously with the field samples, gave no reason to reject the two high cadmium samples.

TABLE 19. RESULTS OF SOIL ANALYSES FOR GREAT SMOKY MOUNTAINS ($\mu\text{g/g}$)

| | Site 11 | Site 12 | Site 13 | Site 14 |
|-----------|---------|---------|---------|---------|
| Cadmium | 1.0 | 0.9 | 3.0* | 0.8 |
| Copper | 5.7** | 4.3** | 4.3 | 11.9 |
| Lead | 18.0 | 15.0 | 20.0 | 15.0 |
| Lithium | 9.8 | 8.9 | 4.3 | 17.7 |
| Manganese | 190.2 | 223.7 | 39.9 | 486.9 |
| Zinc | 36.0 | 34.0 | 21.0 | 63.0 |

* Two very high values were detected (14.1 and 9.2 $\mu\text{g/g}$). When not included, mean cadmium levels for site 13 are 0.5 $\mu\text{g/g}$.

** Single analysis

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APPENDIX
SCIENTIFIC NAMES OF PLANTS USED IN THIS REPORT

| | |
|----------------|----------------------------------|
| Beech | <i>Fagus grandifolia</i> |
| Black cherry | <i>Prunus serotina</i> |
| Christmas fern | <i>Polystichum acrosticoides</i> |
| Fraser fir | <i>Abies fraseri</i> |
| Hemlock | <i>Tsuga canadensis</i> |
| Magnolia | <i>Magnolia fraseris</i> |
| Nettle | <i>Laportea canadensis</i> |
| Red spruce | <i>Picea rubens</i> |
| Rhododendron | <i>Rhododendron spp.</i> |
| Sugar maple | <i>Acer saccharum</i> |
| Tulip poplar | <i>Liriodendron tulipifera</i> |
| Witch hobble | <i>Viburnum alnifolium</i> |
| Wood fern | <i>Dryopteris campyloptera</i> |
| Yellow birch | <i>Betula allegheniensis</i> |

| TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i> | | |
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| | 15. SUPPLEMENTARY NOTES | |
| 16. ABSTRACT <p>A presampling of physical and biological media at preselected locations on the Great Smoky Mountains Biosphere Reserve was completed. The media collected, which included air, water, soils, litter, and various plant species, were used to determine elemental concentrations and to help in the design of an efficient and cost-effective monitoring system.</p> <p>The results showed that air concentrations of trace elements were below detectable limits. Indications of organic air contaminants were evident.</p> <p>A number of compounds such as zinc, toluene, and methylene chloride were found in water. In addition, dimethyl hexene, ethyl benzene, and phthalate esters are suspected water contaminants.</p> <p>Analytical results of the vegetation, soils, and litter showed a variety of elemental contamination. The concentration of lead in the litter layer at four sampling sites ranged from 246 to 469 ppm. These data, similar to those reported by other researchers showed that lead levels increased with altitude.</p> <p>Based upon a field sampling error of plus or minus 10 percent at the 95 percent confidence level, the number of samples required to satisfy this condition, based upon the samples/element combination, was calculated.</p> | | |
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