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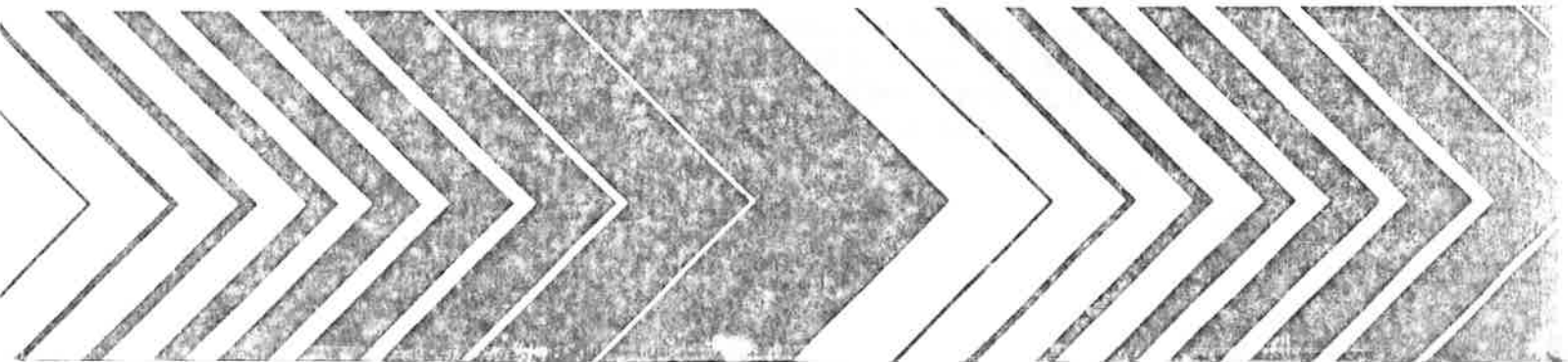
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INSTRUMENTS
EPA-600/4-80-002
January 1980 DSC III 3

Research and Development



Lead Particles in the Great Smoky Mountains Biosphere Reserve



EPA-600/4-80-002
January 1980

LEAD PARTICLES IN
THE GREAT SMOKY MOUNTAINS BIOSPHERE RESERVE

by

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FOREWORD

Protection of the environment requires effective regulatory actions based on sound technical and scientific data. The data 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 at 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 study was conducted to determine the concentrations and physical characteristics of lead particulates in remote areas in the Great Smoky Mountains National Park. The study is part of the development of a pollutant monitoring system for biosphere reserves. The information should be useful to EPA scientists, land management persons and international agencies concerned with global pollution. For further information contact the Exposure Assessment Research Division of this Laboratory.



George B. Morgan
Director

Environmental Monitoring Systems Laboratory
Las Vegas

ABSTRACT

Air monitoring using 0.45-micrometer Millipore® filters at eight remote sites in the Great Smoky Mountains National Park has shown that lead particulates are contributing to the contamination of this designated biosphere reserve. Analytical results of these filters by atomic absorption spectrophotometry, x-ray fluorescence, and scanning electron microscopy showed that lead air concentrations varied from a high of 140 ng/m³ to a low of 19 ng/m³.

The lead particles were primarily spherical in shape, measuring less than one micrometer in diameter. The chemical composition of these submicrometer-sized particles was predominately lead associated with small amounts of sulfur. The lead particulates that were greater than 1.0 micrometer in diameter were not spherical in shape and contained other elements such as iron, calcium, magnesium, and silicon.

The spherical shape of the lead particulates indicates that the moieties were formed by high temperature processes, such as by internal combustion engines. Also, the small particulate size may indicate long range transport and subsequent deposition from urban and/or industrialized areas.

INTRODUCTION

In September 1977, a pilot study was initiated in the Smoky Mountains National Park to begin the development of a pollutant-monitoring system for biosphere reserves. Smoky Mountains National Park is a designated biosphere reserve and this program has been described in detail by Franklin (1977). The project was a cooperative study between the U.S. Environmental Protection Agency and the U.S. Park Service.

This study discovered high lead concentrations in forest litter (Wiersma, Brown and Crockett, 1977). Concentrations of lead ranged from about 250 $\mu\text{g/g}$ at lower elevational sites to over 450 $\mu\text{g/g}$ at the high altitude site. These levels matched the data reported by Reiners, Marks and Vitousek (1975) for the White Mountains of New Hampshire. They found lead levels in the hundreds of parts per million range in forest litter. They also found an increase of lead residues in litter with altitude up to the Krummholz, where there was a slight decrease in lead concentration. They concluded that the increased lead concentration probably was the result of long-range transport processes.

The source of the lead in the Smoky Mountains study was unknown. Vehicular traffic in the Park is heavy and could be a local source. However, long-range transport and lead sources remote from the Park could also contribute to the lead burden.

That lead could be transported over long distances is widely reported in the literature. Hirao and Patterson (1974) report that lead had contaminated a remote site, Thompson Canyon, in the High Sierra of California. Zoller, Gladney and Duce (1974) reported lead atmospheric particulates collected at the South Pole were highly enriched compared to what could be expected from normal crustal weathering. Murozumi, Chow and Patterson (1969) present evidence of increasing residues of lead in Greenland snow and attributed this increase to advent of leaded automobile fuels. Finally, Elgmork, Hagen and Langeland (1973) found levels of lead in snow in Norway of up to 98 $\mu\text{g/l}$. They also found high sulphur levels in the form of sulphate of up to 19 mg/g. They concluded that these pollutants had been transported to Norway and deposited via precipitation. The sources were thought to be the large industrial and urban complexes of central and western Europe.

A second study was undertaken in May of 1978 to determine lead concentration in the atmosphere over remote areas of the Park and to characterize lead particulates by size and chemical composition. We also hoped to determine, if possible, the source of lead in the Smoky Mountains.

METHODOLOGY

A comprehensive sampling program was carried out in the Smoky Mountains National Park in May 1978. As part of the program, special efforts were made to collect air particulate samples in remote areas of the Park. The filters would then be analyzed by three independent techniques: atomic absorption (AA) spectroscopy; x-ray fluorescence techniques; scanning electron microscopy (SEM) techniques for particle size, shape, and surface composition.

Two remote sites were established in the Park. These were the Silers Bald site (site 12) and Sawteeth site (site 11) (Figure 1). Criteria for the selection of these sites were:

1. At least 8 kilometers from the nearest road that had any automobile traffic
2. located at as high an elevation as possible
3. located in a cleared area whose diameter was at least five times the height of the surrounding forest.

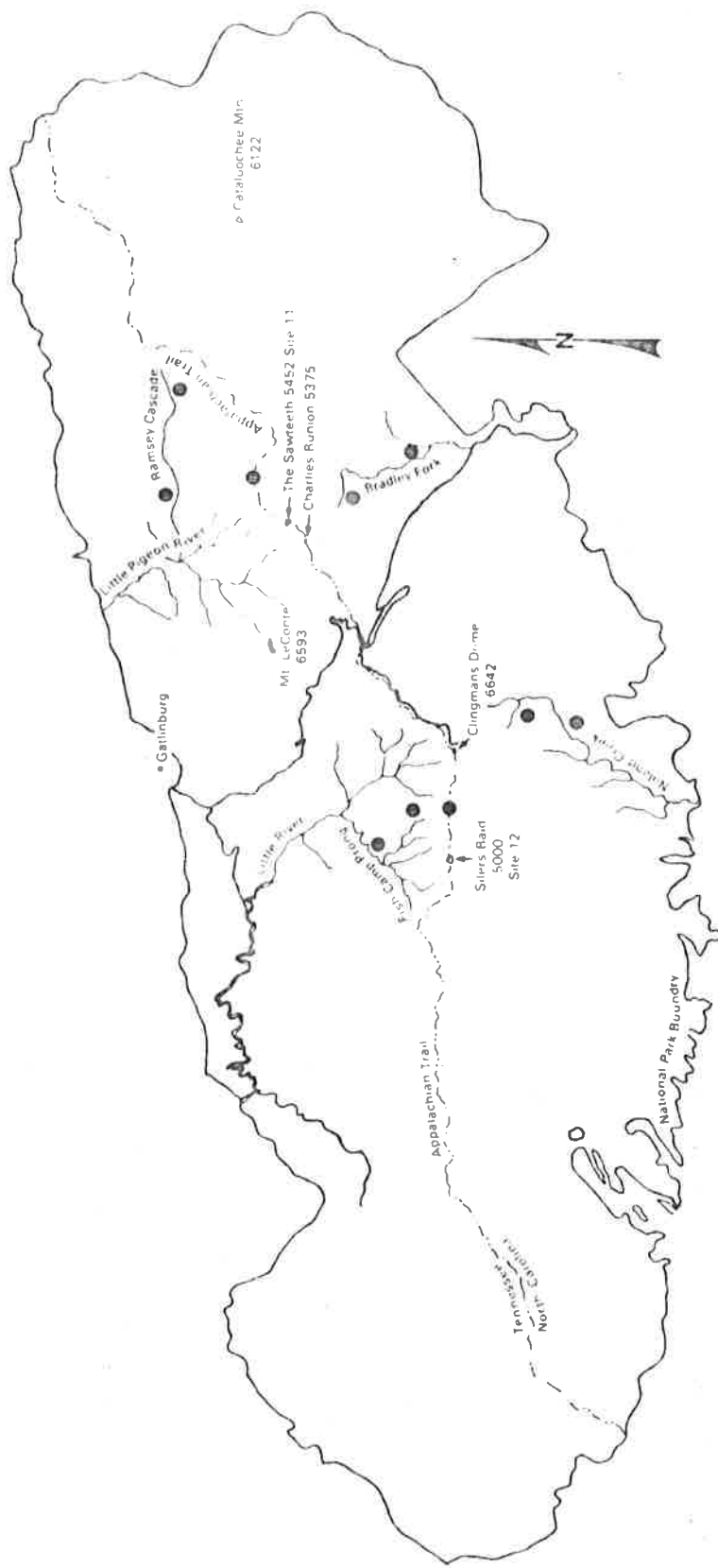
The two sites chosen met these criteria.

In addition, eight other air monitoring sites were established. However, these were coordinated with vegetation and soil sampling and did not meet the requirements mentioned above. All were located under forest canopy. Only those for which filters were analyzed for lead are shown on Figure 1. All the sites that were located under the forest canopy were a minimum of 3 kilometers from a road where automobile traffic was permitted, most were considerably further away, up to 10 kilometers.

Millipore® filters (0.45 μ m), were purchased already mounted and sealed in plastic holders. The plastic filter holders were not opened until the air monitoring system was ready to be turned on in the field. Millipore filters were set up in groups of four at each site. In general this allowed one filter for x-ray analysis, another filter for SEM analysis, a third filter for AA analysis and the fourth to be archived. Unopened filters, that went into the field, were submitted for analysis along with the opened filters.

Table 1 is a summary of the sites, sampler flow rates, length of time sampled, volume of air sampled, type of analyses, and site description.

An air sampling system was specifically designed to meet the needs of this project. Local power sources were not available where the air samplers were to be operated. The use of gasoline-powered generators was ruled out because



● Sampled Spring, 1978

Figure 1. Location of air sampling sites in the Great Smoky Mountains National Park, May/June 1978.

TABLE 1. SUMMARY OF AIR SAMPLING SITES IN THE GREAT SMOKY MOUNTAINS NATIONAL PARK*

Site No.	Name	Site Description	Number of hours Operated	Average flow rate (lpm)	Total air sampled (m ³)	Types of Analyses x-ray SEM AA
12	Silers Bald	Open, remote site 8 kilo-meters from nearest road	188.5	1.0	11.3	X X
11	Sawteeth	Open, remote site 8 kilo-meters from nearest road	168.0	1.0	10.1	X X
1	Fish Camp Prong	Logged hardwood forest-- North slope	69.5	1.0	4.2	X X
3	Low altitude Ramsey Cascade	Unlogged hardwood forest-- North slope	167.0	1.0	10.0	X X
4	High altitude Ramsey Cascade	Unlogged hardwood forest-- North slope	162.5	0.9	8.8	X X
5	Low altitude Noland Creek	Logged hardwood forest-- South slope	142.5	1.0	8.6	X X
6	High altitude Noland Creek	Unlogged hardwood forest-- South slope	144.5	1.0	8.7	X X
8	High altitude Richland Mt.	Unlogged hardwood forest-- South slope	142.0	1.0	8.5	X X
--	Las Vegas, NV	Urban environment	120.0	1.0	7.2	X X

* samples were collected at all stations in the Park between May 21 and 31, 1978.

of contamination problems and propane gas generators were not used because of logistics. Therefore, a portable, battery-operated system was needed. This system has been described in detail by Brown et al. 1979. Basically it is a DuPont air pump (Model P-4000A) operated by a specially designed battery pack using Gates rechargeable sealed acid batteries. Air flow was controlled by Dwyer adjustable rotameters connected to the Millipore filters and DuPont pump by amber latex laboratory tubing. As can be seen from Table 1, these pumps operated continuously for up to 188 hours. Except for one site, flow rates held constant throughout the entire sampling time. Of the 10 stations established, only 2 failed during the sampling period. One site appeared to have been tampered with, either by a human or wild animal, and the other site showed no obvious reasons for the failure to operate. It is suspected that the problems were in the power supply since both pumps operated normally when attached to a different battery pack.

Filters were collected, resealed and submitted for analysis. The x-ray fluorescence technique used was as described by Jaklevic et al. (1973) and Jaklevic, Loo and Goulding (1976). Scanning electron microscope analyses were used to determine particle size and composition. Atomic absorption spectrometric analyses were done at Carnegie-Mellon University.

RESULTS AND DISCUSSION

Tables 2 and 3 show results of the x-ray fluorescence and atomic absorption spectrometric analyses, respectively. Atomic absorption analyses are for two different filters exposed simultaneously at each site. Results for lead show reasonable agreement between the two methods. The value of lead in the blanks was divided by the total lead in each filter as a measure of reliability of the handling and processing of the samples.

TABLE 2. SUMMARY OF RESULTS OF X-RAY FLUORESCENCE ANALYSES*

Element	Site Number (Results in ng/m ³)						Las Vegas
	1	3	4	5	6	8	
Titanium	ND**	12	19	14	ND	18	128
Manganese	ND	28	ND	39	46	36	ND
Iron	ND	80	112	182	134	179	1690
Lead	ND	ND	68	88	103	89	530

* cross check samples indicate precision of reported data to be:

Ti = $\pm 30\%$; Mn = $\pm 25\%$; Fe = $\pm 50\%$; Pb = $\pm 15\%$.

** none detected.

TABLE 3. ATOMIC ABSORPTION ANALYSES FOR LEAD (ng/m³)

Site	Average* $\pm$ Average deviation (ng/m ³)	(%)	Blank $\div$ Total Sample
1	19	23	0.74
3	40	12	0.36
4	42	13	0.37
5	140	20	0.16
6	120	26	0.19
8	94	23	0.22
11	58	55	0.32
12	51	13	0.28

* Blank values already subtracted

The absence of detectable levels for site 1 by x-ray fluorescence may be explained by the low total volume of air sampled at that site. Apparently the residue levels for lead at site 3 were below or at the detection limits for the x-ray fluorescence technique.

It is interesting to note that sites 5, 6, and 8, located on the south slopes of the Park, all have a higher lead concentration than sites 1, 3, and 4, located on the north slopes of the Park. Wind data were obtained from the National Climatic Center in Asheville, North Carolina. The data were from a mountain top site 96 kilometers due east of the Great Smoky Mountains National Park. The winds during the sampling period were always out of the south or west. If pollutants were moving into the park from distant sources, then the wind data along with the data for elevated lead levels on the southern slopes of the Park would tend to be mutually supportive.

Zoller, Gladney and Duce (1974) reported lead concentration in air at the South Pole as 0.63 ng/m^3 . They also reported that lead had a very high enrichment factor for air when compared to expected levels based on normal crustal weathering. Adams et al. 1977, measured lead concentration in air near the top of Chacaltaya Mountain in Bolivia. The station is located approximately 25 km north of LaPaz at an altitude of 5220 m. Lead concentrations measured by x-ray emission on $0.4 \mu\text{m}$ Nucleopore® filters showed lead levels ranging from 4.0 to 7.1 ng/m^3 . Chow and Earl report lead levels in air at the Mount Laguna station at the San Diego State College Astronomical Observatory about 45 miles east of San Diego averaged approximately 50 ng/m^3 . Moyers et al., 1977, reported lead levels at a desert site about 60 miles southeast of Tucson to be 67 ng/m^3 .

Urban levels are much higher. Dzubay and Stevens (1975) report lead levels for St. Louis to be about 460 ng/m^3 . Davidson (1977) reports atmospheric lead concentrations for the Los Angeles area of 1160 ng/m^3 to 1254 ng/m^3 . Liroy, Wolff and Kneip (1978) reported average lead concentrations in air for New York City of 1388 ng/m^3 .

The levels from the Smoky Mountain samples varied from 40 ng/m^3 , typical of a site 40 to 60 miles from a large urban area, to 140 ng/m^3 , which is high for a supposedly pristine background area.

Three Millipore filter pads taken from different locations in the Park were analyzed by SEM. Of the 669 particles characterized, 19 were found to contain lead as the predominant element on the particle surface. This is about 3 percent of the total number of particles characterized. As a crude analogy, Chow and Earl (1970) reported that lead aerosols made up 3 to 4 percent of the total suspended particulate matter in downtown San Diego. A summary of the physical and chemical properties is presented in Table 4.

In general most lead particles were spherical, were less than 1 micrometer in diameter, and contained lead as the major surface constituent with small amounts of sulfur. The majority of the lead-containing particles larger than $1 \mu\text{m}$ were not spherical and contained other elements (Fe, Ca, Mg, Si) in addition to lead and sulfur.

TABLE 4. SUMMARY OF LEAD PARTICLES CHARACTERIZED BY SCANNING ELECTRON MICROSCOPY

Site Name	Particle Size/Shape (μm)	Elemental Makeup
Silers Bald (Site 12, Total particles examined = 270)	5, Rectangle	Pb, S (Mg, Ca, Fe)*
	1.5, Sphere	Pb, S (Mg, Ca, Fe)*
	1.0, Sphere	Pb, S
	0.8, Sphere	Pb, S
	1.0, Sphere	Pb, S
	1.0 x 1.5, Oval	Pb, S
	0.8, Sphere	Pb, S
	1.0, Sphere	Pb, S
	1.5, Sphere	Pb, S, Ba (Ca, S)*
	0.5, Sphere	Pb, S
	1.0, Sphere	Pb, S
Sawteeth Site (Site 11, Total particles examined = 135)	0.5, Sphere	Pb, S (Ca, K, Si)*
	0.6 x 1.0 Oblong Sphere	Pb, S
	0.5 x 0.8, Oval	Pb, S
Ramsey Cascade (Site 3, Total particles examined = 264)	1.5, Sphere	Pb, S** (K, Ca, Si, Fe)*
	1.0, Sphere	Pb, S
	0.8, Sphere	Pb, S
	0.6 to 0.7, Sphere	Pb, S
	1.5 to 2.5,	Pb, S

* trace constituents

** Sulphur questionable

The spherical nature of the lead particulate indicates that the moieties were formed via some high temperature process. Although other lead sources are possible, we presume that the most probable source of the lead is automotive exhaust. This agrees with previous observations using light microscopy to analyze particulate from air samples collected by 4-stage differential samplers (Mammerorella, 1973).

In addition it has been observed that two types of lead-containing particulate are emitted from automotive exhaust (Keyser, Natusch, Evans, and

Linton, 1978). The first is described as being irregular in shape, greater than 10 μm in cross section and containing Fe, Pb, S, Br, and Cl with varying amounts of Ca and Si. The second type is represented by spherical particles of less than 1 μm in diameter and contains Pb, Br, and Cl. Although the halogens were not found in any of the particulates studied in the present work, the two types of particles are represented with the majority being less than 1 μm . Evidence exists in the literature that the halogens (Br) decrease as the transport distance and exposure time increases. In a study in Europe Rentschler, (1977) found Br/Pb ratios in larch needles that ranged from 1.3 (221 $\mu\text{gNo/g}$: -289 $\mu\text{gBr/g}$) for highly traveled areas to 0.4 (-11.4 $\mu\text{gNo/g}$: 4.3 $\mu\text{gBr/g}$) for reasonably remote areas.

No bromine was detected by the SEM method in the samples collected in the Smoky Mountains. The SEM analyses of particle size indicated that most of the lead particles were one micron or less in diameter. The absence of bromine and a small particle size would indicate that the particles had moved over long distances. However, not enough lead particles were examined to allow a statistically meaningful frequency distribution to be constructed. Also, no climatological data were collected. Therefore, the question of whether lead contamination is coming from within the Park (heavy automobile traffic) or from outside the Park (upwind urban/industrial centers) remains unanswered.

It should be mentioned that Elias et al., (1978), using cascade impactors, examined size distributions of airborne lead and other species in a remote area of the Sierra Nevada mountains. They found only 11% of the airborne lead particles were larger than 4 μm aerodynamic diameter.

Another feature of these particles of Table 4 is the constant association of sulphur with lead. The exact makeup of the lead/sulphur chemical compound (the x-ray backscatter pictures indicate a uniform distribution of lead and sulphur in lead particles) is unknown. However, there is some evidence in the literature that lead particles act as a surface for the conversion of SO_2 to sulfate. Moyers et al. (1977) calculated the correlation coefficient for lead and sulphate (SO_4^{2-}) for urban areas of 0.49. This same pairing had a correlation coefficient of 0.78 for samples collected at a site 60 miles southeast of the urban area. However, we are not suggesting that the compound is lead sulphate. At this time there is not enough information to make this statement.

All the data collected so far indicate lead in concentrations relatively high for a background area, having a high temperature combustion process as their source and a size distribution favoring long-term transport.

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-80-002	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE LEAD PARTICLES IN THE GREAT SMOKY MOUNTAINS BIOSPHERE RESERVE		5. REPORT DATE January 1980
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G. B. Wiersma, C. W. Frank, C. I. Davidson and K. W. Brown		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Las Vegas, Nevada 89114		10. PROGRAM ELEMENT NO. XH1627J
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency-Las Vegas, NV Office of Research and Development Environmental Monitoring Systems Laboratory Las Vegas, Nevada 89114		13. TYPE OF REPORT AND PERIOD COVERED Interim FY-79
		14. SPONSORING AGENCY CODE EPA/600/07
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS		
DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Environmental biology Site survey Pollution Chemistry	Biosphere reserves Great Smoky Mountains National Park	06F 08G 08H 07B 07C 07D
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 16
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE