Chris O'Hara

INTERNATIONAL LEAD ZINC RESEARCH ORGANIZATION, INC.

292 MADISON AVENUE, NEW YORK, N.Y. 10017
TELEPHONE 679-0080 (AREA CODE 212)
CABLE ADDRESS: INTLEAD NEW YORK

February 3, 1967

To: All Members of the Lead Environmental Health Committee

Re: Project LH-119 The Use of Lead Isotopic Composition as an Environmental Tracer

Attached is your copy of the six month progress report, also a ballot on which you will indicate your wishes as to the continuation of this project during the remainder of the year. The ballot should be returned to us by February 20.

You will remember that the first six months of this project was planned to develop the physical capabilities for microchemical isotopic analysis of lead from environmental samples. Since no other laboratory available to us has developed this capability, a good deal of groundwork was necessary on the part of Isotopes, Inc. A new laboratory has been built and set aside exclusively for our project. A number of environmental samples including air, water, and soil have been analyzed and the feasibility of doing this work has been established to our satisfaction.

In reading the results obtained in the progress report I wish to caution you that these results are included merely as demonstrations of the contractor's ability to make these analyses and are not to be construed as representative of anything in the environment. Because these results are not representative, I wish to caution you that they are CONFIDENTIAL and must not be distributed to unauthorized personnel. As you know, this project, together with many of our other environmental health projects, are very sensitive in their implications and premature disclosure of results could be most unfortunate.

The American Petroleum Institute has already given their approval to the one-year extension of this contract. The ILZRO Board of Directors has allocated the funds necessary to complete the project. It remains only for our Environmental Health Committee to express its approval before we can authorize the work to go on. Because the 1967 operation of this project has been planned as a one-year activity and because a complete year's work has already been planned, we are asking that you vote on this one-year extension as a package, rather than considering Phase II and Phase III separately, as originally outlined to you last year.

Very truly yours,

Don G. Fowler

Don G. Fowler
Project Manager

DGF:sv
2 encls.

Date _____

Re: LH-119 The Use of Lead Isotopic Composition
as an Environmental Tracer

To: Don G. Fowler, Project Manager
International Lead Zinc Research Organization, Inc.
292 Madison Avenue
New York, N. Y. 10017

I approve the commitment of $37,000 of ILZRO funds, plus an equal amount from the contribution of the anti-knock manufacturers in support of Phase II and Phase III of Project LH-119. My approval is made with the understanding that the American Petroleum Institute contributes an amount of money equal to that contributed by the lead industry, or $74,000.

[ ]

I do not approve.

[ ]

_____
Signature

Please return ballot by February 20, 1967.

Report on Project No. L-11 and LH-119
The Use of Lead Isotopic Composition as an Environmental Tracer

by

Dr. Eric H. Willis, Proj. Dir.
Dr. Wayne U. Ault
Dr. Ron G. Senechal
Mr. James Buckley

Prepared for
The Environmental Health Committee
The American Petroleum Institute

and

The Lead Health and Safety Committee
The International Lead Zinc Research Organization
The Lead Industries Association, Inc.

20 January 1967

Isotopes, Incorporated
123 Woodland Avenue
Westwood, N. J. 07675

Isotopes, Inc.

DISTRIBUTION

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Lead Industries Association, Inc.
292 Madison Avenue
New York, New York 10017

Attention: Mr. Don G. Fowler

The American Petroleum Institute — 100 copies
1271 Avenue of the Americas
New York, New York 10020

Attention: Dr. John C. Keller

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Westwood, New Jersey 07675

Isotopes, Inc.

INTRODUCTION - Project Orientation

The main purpose of the Project is to demonstrate that lead isotopic ratios can be used to characterize the various primary sources and reservoirs of lead in man's environment and thereby make available a useful tool to obtain information on the origin of particular environmental leads. Essential to this aim is the establishment of a clean "lead free" laboratory and micro-chemical techniques that will permit handling both micro- and macro-samples without contamination.

The analytical program planned consists of the measurements of 1) lead isotopic ratios, 2) very low lead abundances by isotope dilution techniques, and 3) low levels of Pb^{210}. The above activities and the development and evaluation of suitable analytical techniques essentially comprise Phase I of the Project which is the subject of this report.

Phase II involves conducting a feasibility study of the isotopic characterization of lead in primary sources, environmental media, and in man. Phase II has been actively anticipated by initiating a library of samples from pertinent locations so that the Project maintains its continuity. A third phase of extended environmental studies can then be undertaken profitably with the essential parameters established.

Specialized Laboratory Facilities

Clean Laboratory

To facilitate working with very low level lead abundances with a minimum of contamination a clean laboratory was constructed. Special attention was given to sources of background contamination of lead. This 600 $ft.^2$ clean laboratory with "lead free" paint, plumbing, and special hoods is now in full operation. Make up air is provided through an extended surface filter. Two exhaust hoods and one clean air hood are used for preparation of all reagents and samples, and cleaning of all labware.

Labware

In the analysis of microgram and submicrogram quantities of lead, the use of borosilicate glassware can be a serious source of contamination. Consequently, relatively simple procedures have been developed for chemical separation of lead, which require almost exclusively laboratory equipment of teflon or fused quartz glass. These materials have been selected because of their inertness and low lead content. Polyethylene or polypropolene labware are used, primarily for the storage of solutions, in circumstances when it is not subject to chemical or thermal degradation. Small 1 ml teflon beakers having conical bottoms and 10 ml beakers having tight-fitting, vented caps were fabricated. Transfer pipettes and simple ion exchange columns are made of fused quartz. Specially cut polyethylene bottles serve as dust-free containers for rinse water, isothermal stills, and dust covers for storage bottles.

Labware used respectively for micro-samples, macro-samples, and isotope-dilution are kept separate from each other and are cleaned in separate nitric-acid baths and rinse waters.

Lead Free Reagents and Laboratory Blanks

Lead in chemical reagents is the most important source of contamination in chemical separation of lead. The procedures developed for separation of lead in this work are simple ones requiring a relatively small number of reagents. The reagents which are used in largest quantity have been prepared using as a base the highly pure water from a fused quartz glass bi-distillation unit. The lead content of this water is ≤ 0.02 parts per billion.

Some reagents are commercially available with sufficiently low levels of lead. Specially pure HF, HCl, HNO_3, and NH_4OH reagents have been made by vapor distillation and isothermal distillation as indicated in Table 1. The most important of these have been analyzed for lead content which is also given in Table 1.

TABLE 1. Lead Content of Chemical Reagents

Reagent	Concentration	Preparation Procedure	Lead Content ppb.
H_2O	-	Distilled, Quartz Still	≤ 0.02
HF	20 N	Vapor Distillation	0.17
HCl	8.8 N	Vapor Distillation	0.19
	1 N	Dilute 8.8 N with quartz distilled water	n.d.
NH_4OH	~ 3 N	Isothermal Distillation	
	1 N	Dilute ~ 3 N with quartz distilled water	in process
$HClO_4$	conc.	Purchased, G. F. Smith	≤ 2.
HNO_3	conc.	Purchased, G. F. Smith	2.01
	1 N	Dilute conc. acid with quartz distilled water	n.d.
	conc.	Redistilled	0.02
H_3BO_3	crystals	Recrystallized using quartz distilled water	in process
$CuCl_2$	0.5 M	Dissolve commercial $CuCl_2$ in 1 N HCl; pass over column to remove lead	in process
Anion Exchange Resin AG 1 x 8		Purchased from Bio-Rad Laboratories; cleared with vapor-distilled HCl and with quartz distilled water	in process

NOTE: Reagents for which no determination of lead (n.d.) has been made or are in process are used only in small quantities. Estimated lead contents suggest that their contribution to the overall lead blank should be negligible. The validity of such estimates is established by blank runs on the entire lead separation procedure.

To evaluate the problem of airborne lead contamination teflon evaporating dishes (400 ml capacity) containing an acid solution are exposed to laboratory air. These results are given in Table 2.

The exposure in these tests were more than 100 times that of any sample preparation time; furthermore, in practice the samples remain covered at all times.

Sample blanks are also processed periodically through the complete chemistry as a test on the total procedure.

Analytical Standards and Intercalibration

The analytical standards consist of a gravimetric lead standard for calibrating the spike solutions, calibrated spike solution standards for abundance measurements by isotope dilution, and isotopic reference samples for inter-laboratory calibration on isotope ratio measurements.

Gravimetric Lead Standard: Carefully prepare standard solutions of lead have been prepared from spec-pure lead metal at concentrations very close to 1 mg/ml and 10 µg/ml. The isotopic composition of the spec-pure lead has been determined.

Spikes: A solution of Pb-204 was prepared from 99.8 percent enriched Pb-204 and contains approximately 3.1 µg Pb/ml for use in lead blank measurements and other abundance measurements by isotope dilution techniques.

A double spike containing 100 mg of 73 percent enriched Pb-204 and 500 mg of 92.4 percent enriched Pb-207 are on hand for evaluating any mass discrimination correction factors in the mass spectrometry.

Isotopic Reference Samples: Two isotopic reference samples are used for inter-laboratory comparisons. NBS-200 is the National Bureau of Standards lead isotopic reference standard and T-1003 is that prepared by a prominent Canadian (Toronto) research group. The initial project ratio work is compared with NBS-200.

TABLE 2. Airborne Lead in Laboratory Air

Location	Time exposed	Pb Content µg	Rate µg/hr
1. Work bench*	15 days (31 Aug - 15 Sep 66)	1.1	0.0031
2. Fume hood*	15 days (31 Aug - 15 Sep 66)	0.9	0.0025
3. Work bench	16 days (28 Oct - 14 Nov 66)	2.178	0.0053 ± .0002
4. Work bench**	7 days (1 Dec - 8 Dec 66)	1.871	0.0111 ± .0001

*Samples collected in laboratory room adjacent to one used for preparation of all project samples during period when Clean Laboratory was being readied. Others collected in Project Clean Laboratory.

**During collection of this bench blank although some maintenance work on the Clean Lab became necessary and the bench blank accordingly increased slightly, it is still at a level which would not be significant even if the sample were not covered during preparation.

Mass Spectrometry

Lead isotope ratios and low lead abundances by isotope dilution are measured on a Consolidated 21-703 solid source mass spectrometer. The multiple filament ion source has been evaluated in a series of experiments. The ionization efficiency, stability, and background signal intensity were most satisfactory with a technique using a single filament with boric oxide. Evaluation of tantalum and tungsten filaments showed that the lowest possible backgrounds in the mass regions of interest for the lead work could be obtained using tantalum.

Preliminary experiments suggested that lead might be stable in a silicate melt at higher temperatures than in a boric oxide melt, and hence might be ionized with higher efficiency. Experiments were made with filaments loaded with mixtures of calcium oxide, boric oxide, and silica. Complete reaction to form a homogeneous melt was difficult to achieve in vaccuo. Lead ion signals from such melts were subject to unsatisfactory instability. A more complete approach to homogeneity (complete reaction of silica) was achieved by heating the mixture in a nitrogen atmosphere rather than in vaccuo, and in this case the resultant lead ion signals were much more stable. More experiments are needed to establish that an improved sensitivity can be achieved with this type of matrix on the filament. Because preparation of such borosilicate melts is not a simple procedure, their use is not recommended for ordinary work. For extensive work with sub-microgram quantities of lead, further study of borosilicate melts could prove worthwhile.

Improved transmission in the ion source has been achieved by removing (the central part of) the defocus plate and the discriminator plate. The transmission efficiency of the ion source is improved by at least a factor of ten, an improvement essential for satisfactory lead isotopic analysis with samples of the order of 20 micrograms. These changes also reduce the intensity of the background spectrum in the lead mass region. This spectrum consists of aggregates of light elements and apparently originates from the parts of the ion source which are heated by the filament, rather than from the filament itself.

In order to reduce the effects of certain systematic errors on the precision of lead isotopic analysis, a well-defined procedure for mass spectrometry of lead has been developed. The criteria established in this procedure require a strong lead ion beam (close to 10^{-11} amperes), and so is applicable only to samples of more than 10 micrograms lead. A lower level of precision must be accepted for samples of less than 10 micrograms, because an electron multiplier detector must be used with such samples.

Because for this project it is necessary to work at sample levels of about 2 µg of lead and consequently an ion beam in the range of 10^{-12} to 10^{-13} amperes, and in order to achieve the level of precision necessary, a new system for measurements of the output of the ion detector (vibrating reed electrometer) has been considered. The new system would employ an integrating digital voltmeter, an instrument with both a wider useful range and much better linearity than a strip chart recorder. The use of such equipment would also eliminate the usual systematic errors introduced by scale factors and chart reading.

Pb-210 Analysis in Environmental Samples

The procedure for a very sensitive method of Pb-210 measurement involves several steps: separation of Pb-210 from its daughter products, allowing Bi-210 and Po-210 to grow back in for several months, a further separation of the daughter products, and counting of Po-210 α-activity as a measure of the Pb-210 present.

Nearly complete recovery of lead and polonium is possible. Variation in polonium recovery is minimized since it is always deposited from an identical matrix. Table 3 illustrates the recovery using Po-208 as a tracer. In the test results the temperature was allowed to vary between 85°C and 92°C resulting in a 91% yield. Yields of about 99% are attainable at constant solution temperature of 97°C. Percent recoveries were gravimetrically determined.

TABLE 3. Separation of Lead, Bismuth, and Polonium

Type	Pb Recovery	Bi Recovery	Po Recovery
Wash effluent	0	0	-
Strip effluent	9N HCl - 98%	Con HCl - 97%	Plated - 91%
Dpm added/found	208 ± 6/201 ± 6	208 ± 6/--	208 ± 6/210 ± 6

Lead Isotopic Ratio Measurements

Range, Precision and Limits of Detection. The isotopic ratios 206/204, 206/207, and 208/207 are used in order to show the maximum natural Pb-isotopic variation with the best analytical precision. These ratios have a range in nature from 8 to 20, 0.5 to 2, and 2 to 4 respectively, with twice this variation possible for so-called anamolous leads from certain primary sources. The precision presently attainable is 0.6, 0.3 and 0.3 percent respectively on samples which yield 2 µg of lead. The lower limit of detection of lead abundance with these techniques is a few tenths of a part per billion or better.

Preliminary Results

The lead isotope ratios shown in this report are only preliminary ratios on certain primary sources and environmental media which were spot-checked to give guidance early in the progress. The range of 206/204, 206/207 and 208/207 ratios found are plotted in Figures 1-3. A few preliminary observations can be made.

The sample results shown in Figures 1-3 consist of 1) three air particulate samples from Newark and Matuchen, N. J. and from Nanuet, N. Y., 2) eight TEL samples extracted from gasoline, 3) five lead metal samples used in TEL manufacture, 4) five grass samples and seven soil samples from a profile across the N. J. Turnpike 5) a surface and bottom (14-1/2 inch depth) soil sample from the top of a ridge in Ringwood State Park, N. J. (Rock outcrop of the area is dated at 1 b.y.) 6) a sample of leaves associated with

the grass samples, and 7) a coal and resulting fly-ash sample from a power generating station.

The lead isotopic ratios obtained to date show very promising possibilities. The wide range ratios in soil is to be expected since it represents the wide natural variations in primary source leads. Seven soil samples taken in a transverse profile (Figure 5) across the N. J. Turnpike give a limited range of ratios. A soil core taken from the top of a ridge in Ringwood State Park in the N. J. Highlands shows a greater range. Although the ratios do not overlap those from the N. J. Turnpike soils the top inch of the core was only slightly removed to the right in 206/204 and 208/207 ratios whereas the bottom of the core at 16 in depth was distinctly different. It appears that striking compositional differences are preserved over short vertical distances in the soil.

A number of sample types in figures 1-3 gave similar, rather limited ranges of isotopic ratio. These include air particulate, TEL, lead metal, leaves, grass and the turnpike soil profile. Lead in coal and the resulting fly ash samples collected at a power generating station gave the same isotopic ratios and appears significantly different from the above group.

Conclusions

The progress of Phase I of the project has been in accordance with the schedule outlined in the original proposal. The lead free laboratory has been completed and is functioning, lead free reagents have been prepared and tested, and standards have been obtained and prepared. The limits of detection are satisfactorily defined intercalibration, and precision and accuracy monitoring have been started and will continue throughout the project. Procedures for Pb-210 have been established and evaluated.

Analyses of typical environmental samples have verified that there is considerable variation in the lead isotopic ratios and indicate differences between some environmental media. A rather extensive sampling program is underway with a library of over 100 samples including series of vegetation,

soils, tree-rings, air filter samples, gasoline, coal and fly ash. This effort is continuing in a systematic manner.

Phase II Program Defined

The pilot studies to be conducted in Phase II are represented graphically in Figures 4 and 5 and Table 4. Figure 4 traces the path of lead from primary sources into the environmental media and man. It moves from the primary bedrock sources including mineral deposits through the radon gas phase and through mining and smelting into the environment as industrial products or as effluents.

The effort will be directed toward testing the feasibility of using isotopic characterization as a means of distinguishing various sources of environmental lead. An attempt will be made to identify and characterize primary sources such as bedrock, mineral deposits and special types of soil, industrial products and effluents like coal, fly-ash, and lead alkyls in gasoline, lead in fuel oil, paint, galvanizing and solder. Background information on the samples analyzed will be studied to understand the origin of the isotopic composition.

Through environmental media lead becomes available to man. Air particulate matter will be sampled at representative spots throughout the New York metropolitan area. Lead isotopic ratio measurements will be made on exchange samples from former and current studies where possible and which represent extremes of lead abundance and/or other known pollutants. Lead in water from public water systems will be compared to lead in hot water systems having soldered joints. The latter are known to be characterized by substantially higher lead. Vegetation adjacent to heavy turnpike traffic will be compared with soil and air particulate in the same or similar setting. Typical foods, tobacco and other plant types will be analyzed for Pb-210, lead abundance and isotopic composition.

Preliminary data on man, viz., blood, urine and feces in addition to air, water and food will be obtained. However, an extensive study of man in general from representative age groups, environments and occupations,

including cadavers of terminal patients with known histories, must await Phase III because of the magnitude of the problem. Sampling for this phase of the study will be done concurrent with Phase II. The guidance and cooperation of experts in lead biochemistry will be sought.

Being an industructable trace element, lead is recycled in the environment and biosphere, increasing in abundance in the main repository, soil. To evaluate this factor and to place the results of the environmental sampling program into historical perspective the feasibility of using tree ring sequences will be established.

Figure 5 shows the type of samples collected in an east-west profile across the N. J. Turnpike about midway between Philadelphia and N.Y.C. and some distance from any towns or factories. These will test and compare the lead abundances and isotopic ratios between grass and leaves and between vegetation and soil with distance from a heavily used traffic artery. Table 4 is an outline of Phase II samples. The categories in which certain select samples will be analyzed for lead abundances and lead-210 are also indicated.

Throughout Phase II we will continue efforts to develop cooperative research with other groups such as the Rutgers University group (Project L-5) and Public Health Service.

FIGURE 1. Lead 206/204 Ratios in Environmental Media

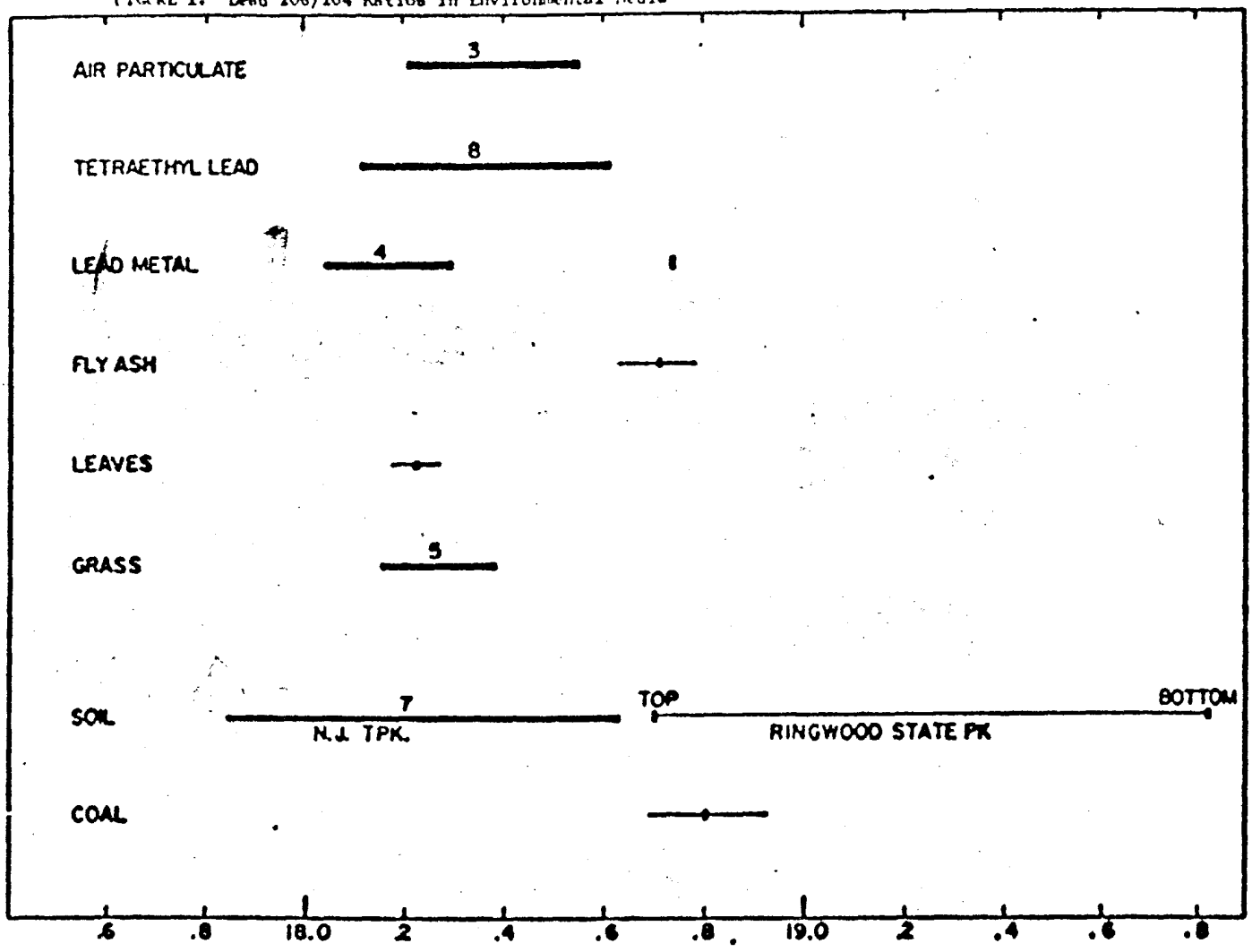


FIGURE 2. Lead 206/207 Ratios in Environmental Media

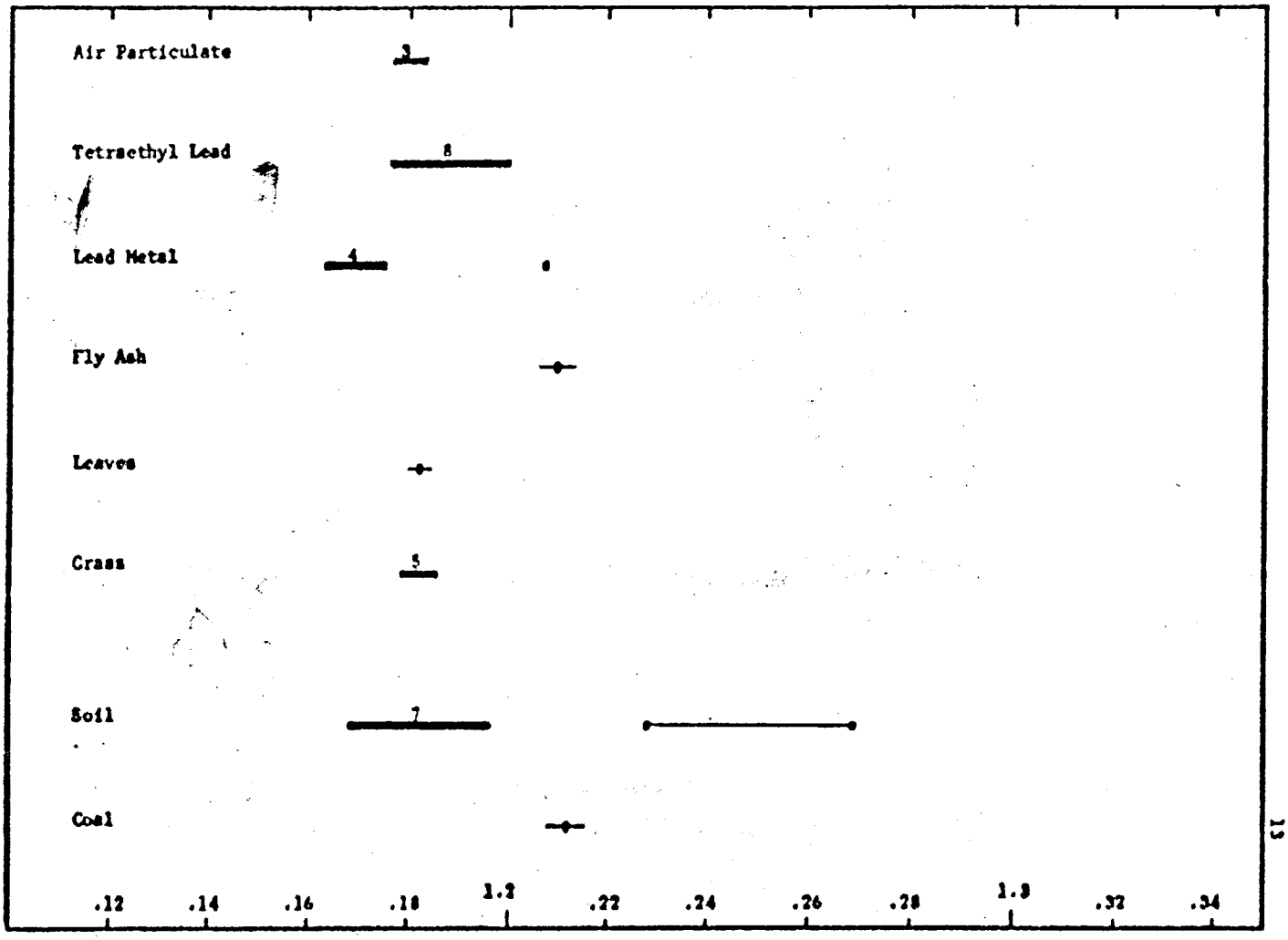
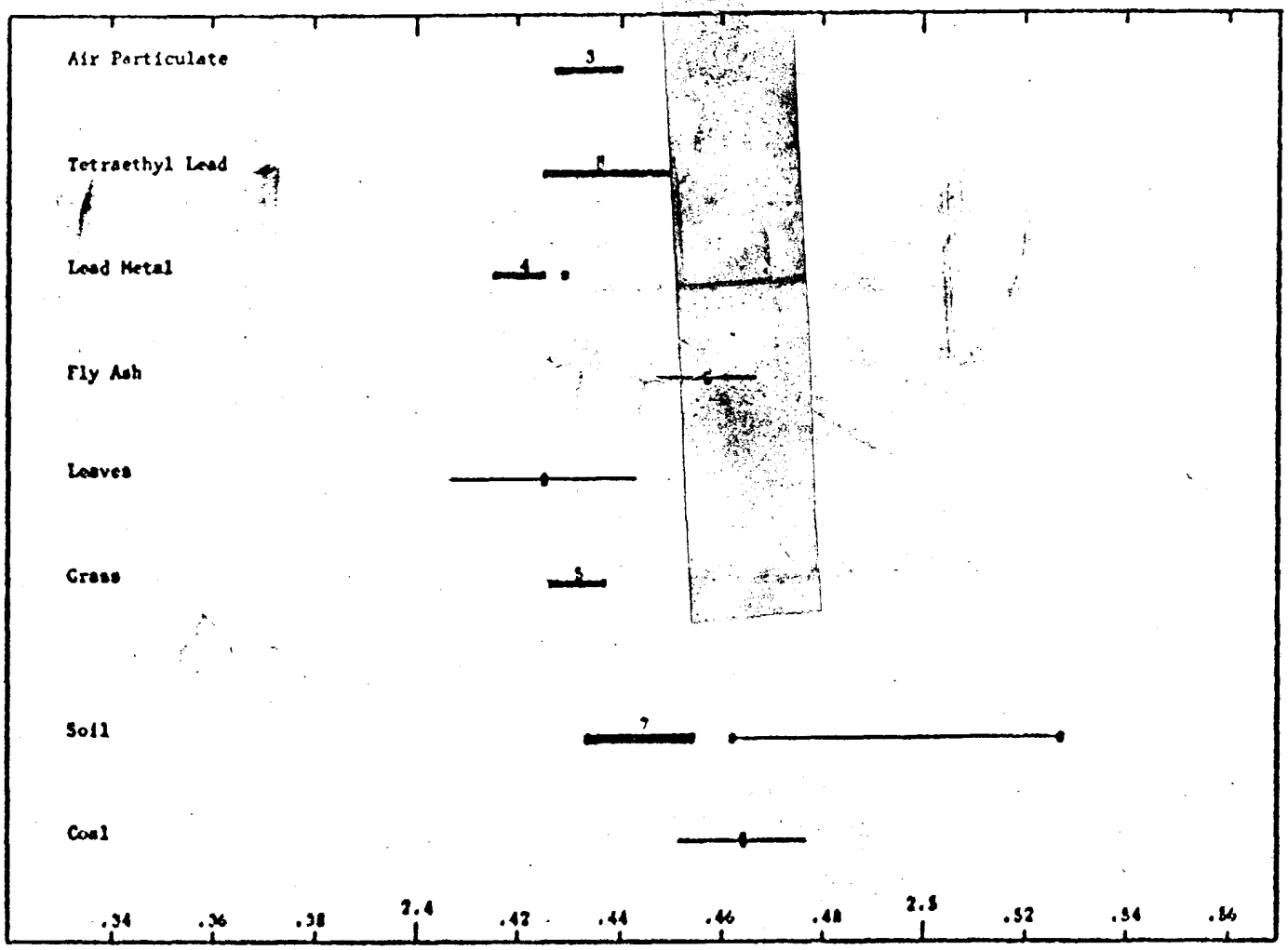


FIGURE 3. Lead 208/207 Ratios in Environmental Media



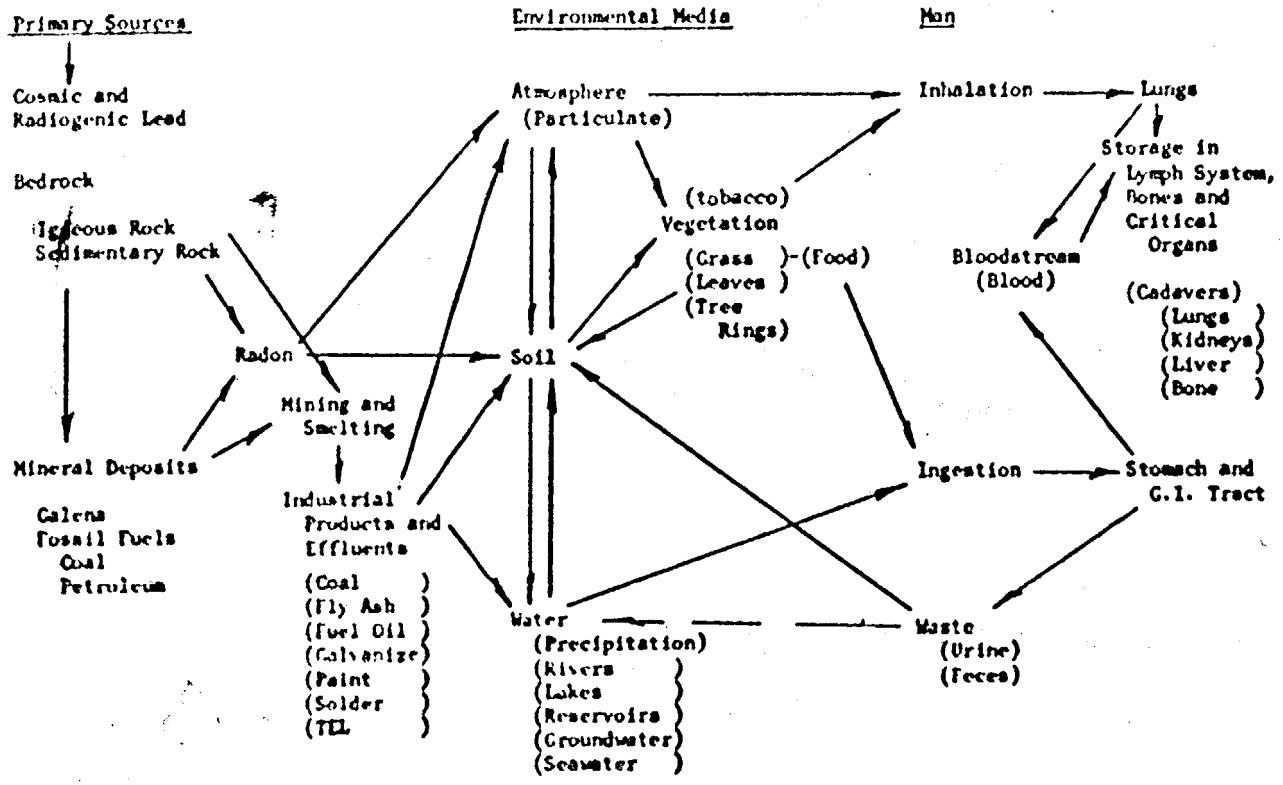


FIGURE 4. Geochemical-Biochemical Flow Diagram of Lead in Primary Sources, Environmental Media and Man.

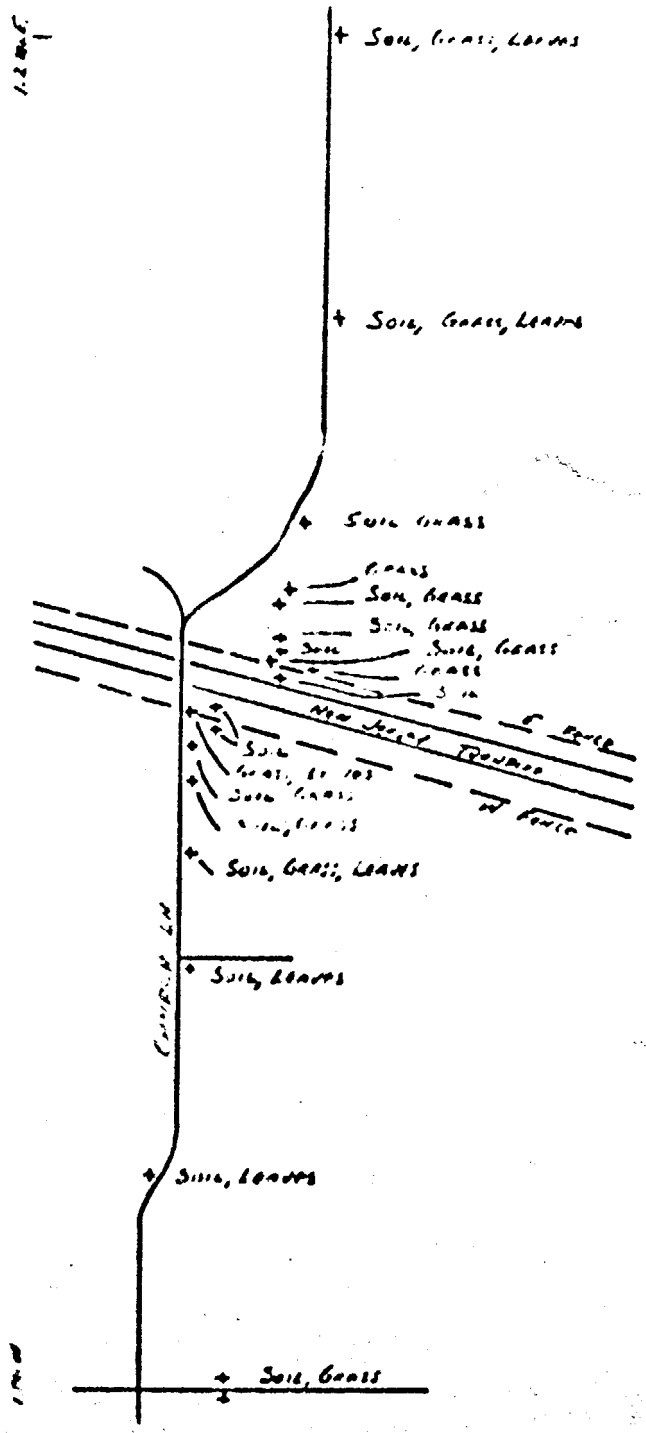


FIGURE 5. Profile Sampling across N. J. Turnpike midway between Philadelphia and New York City in vicinity of Helmetta, N. J. (sketch, not to scale)

TABLE 4. Outline of Sample Types

PHASE II		PHASE III
Primary & Industrial	Environmental Media	Man
Primary Bedrock Soils Mineral-Galena	Air*• Newark Paterson Westwood Nanuet PHS samples	A. General Population Hospital Patients Terminal Short Stay
Industrial TEL, Sludge Metal Paint Scrapings Solder Coal Fuel Oil Fly Ash from Coal Fuel Oil Incinerators	Water*• Cold Tap Hot Tap Vegetation Food Canned Frozen Fresh Cereal Meat Milk Tobacco* FDA samples	1. Blood Representative Age Groups Occupations Residential types Seasonal variation 2. Cadavers Lungs & Glands Bones Liver & Kidneys

TABLE 4. Outline of Sample Types (continued)

Primary & Industrial	Environmental Media	Man
	Grass*,**	B. A Man (or 2)
	Tpk profile	
	unwashed	1. Blood)Sampling
	washed	6-12 mos.
		2. Excrement)Bimonthly
		3. Food (extension of Phase II
	Trees	4. Air Assoc. with
	Leaves	subjects
	Rings	(Sampled Quarterly)
	(Hist)	
	Soil*	C. General Environment
	Tpk profile	1. Air
		Particle Size
		Geographic Locality
		2. Water
		Precipitation*
		Rivers
		Lakes
		Reservoirs
		Groundwater
		3. Vegetation
		Tree varieties
		4. Soil

*Some samples to be analyzed for Pb-210

**Some samples to be analyzed for Pb abundance

Samples of Phase II include
- Pb isotope ratios
- Pb abundance
- Pb-210