TLW 6075

LEAD TRACER STUDIES OF SOILS

Final Report

by

M. W. Nathans

to:

Haskell Laboratory
E. I. DuPont de Nemours and Company
Elkton Road
Newark, Delaware 19711

REF: P.O. No. J-7141

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ABSTRACT

Lead concentration and isotopic composition data obtained from soil cores from four regions throughout the world were analyzed. An effect caused by the injection of lead into the atmosphere by human activities could not be demonstrated. Approximate calculations of the transport and deposition of lead showed that any expected effect on a global basis, is of the same order of magnitude or lower than the natural variability of the concentration and isotopic composition of lead in the earth's crust.

I. INTRODUCTION

During the past year, data have been obtained by Trapelo/West and by Isotopes Inc. on the content and isotopic composition of lead in soils at the surface and at a depth of about 30 inches in order to determine if sources other than the matrix itself had contributed to the total lead in the soil surface. The soils had been obtained in the form of cores from a number locations throughout the world. In addition, two air filter samples taken at two of the locations had also been analyzed. This report provides "interpretations of the lead data" and includes "an analysis of the data, interpretation in light of pertinent information available in literature and elsewhere, and writing of a brief report summarizing findings and making recommendations concerning the program"[1]

II. DESCRIPTION OF SAMPLES

Samples were analyzed from Norway, Peru, India, and Africa.

The Norwegian samples (series 345) were taken from three locations and in the general area east of the Nordfjord. Samples A1 and A2 were from a farm inland near the village of Skjåk. The land was used as grazing land, had never been turned, but was occasionally sprayed with chemical fertilizers. Yearly precipitation at the closest meteorological station is 400 $\pm$ 70 millimeters.

Samples B1 and B2 came from a farm near Oppstryn on the western side of the hills with respect to Skjåk. This land also was used for grazing, had never been turned, nor fertilized. Annual rainfall is about 1000 millimeters.

Samples C1 and C2 came from a field near Maurstad, near the Nordfjord isthmus, that is used for grazing. Use of fertilizers is unknown. The nearest meteorological station had recorded a mean annual precipitation of about 1800 millimeters.

The soil of the Skjåk samples was mould, that of the Oppstryn and Maurstad samples was peat.

The Peruvian samples (series 346) all originated from the Eastern slopes of the Andes near the border with Brazil. All six samples were obtained within a few yards of each other.

The Indian samples originated from three areas in the Western Ghats mountains, away from human activities. Samples 1A and 1B were from the Thirtahalli range, samples 2A and 2B from the Hongere (Hosanagara) range, samples 3 A and 3 B from the Shanker range. The samples were taken about 30 to 50 miles west of the town of Shimoga (Shivamagga), southwest of Goa, where the annual rainfall is about millimeters.

The African samples are from the Kalahari Desert, in Bechuanaland. The air particulate samples are from the same region.

III. REVIEW OF EXPERIMENTAL METHODS

The experimental methods used by Trapelo/West have been described in detail in attachments to a previous data report.[3] About 2 inches of soil were removed from the top and from the bottom of the cores and dried at 110° C. Samples of about 1 to 2 grams were removed by means of a riffle sampler. These samples were close to being representative. They were completely dissolved in nitric, hydrofluoric, and perchloric acids, after which a known amount of ^{212}Pb was added. The lead was extracted and purified by ion exchange techniques and yielded by counting the radioactive tracer. Total lead was determined by atomic absorption spectrophotometry. For mass spectrometry the lead was further purified by lead sulfide precipitation. The instrument used was a single-focusing mass spectrometer with a thermal ionization source calibrated by means of the National Bureau of Standards common lead standard No. 981.

The method used by Isotopes, Inc. is described briefly in a recent paper by Ault, Senechal, and Erlebach [4] where further reference is made to a report by the same authors to the American Petroleum Institute and the International Zinc Research Organization.[5] According to this method also, the samples were completely dissolved in mineral acids, and the lead was extracted and purified by standard ion exchange techniques. No yield tracer was used apparently. Mass spectrometric analyses were done on a CEC 21-703 B solid source, 12 inch radius, 60° sector mass spectrometer. Abundance measurements were made by isotopic dilution with a calibrated ^{204}Pb solution.

Both laboratories obtained the isotopic ratios by averaging about 20 scans across the isotopic peaks during the period of best emission stability. The errors reported on single samples represent the standard deviations calculated from the scans.

IV. SUMMARY OF DATA

The data subjected to analysis in this report are shown in Table I. They have been reported previously [1,6,7]. The errors shown for the isotopic ratio data from Trapelo/West are lower than those shown in References 1 and 6, because an error was discovered in the original calculations.

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TABLE I TOTAL LEAD CONTENT AND ISOTOPIC COMPOSITION OF SOIL CORE SAMPLES OF DIFFERENT ORIGIN

Sample	Total Pb (μg/g) 110° Dried	450° Ashed	206/204	206/207
Norway				
345 - A1T	13.8	23.9	18.71 ± .03	1.188 ± .001
A1B	15.3	15.6	19.20 ± .06	1.226 ± .003
A2T	11.8	23.9	18.47 ± .04	1.189 ± .001
A2B	15.9	16.2	18.95 ± .02	1.219 ± .002
B1T	13.5	42.3	17.82 ± .02	1.155 ± .001
B1B	1.2	18.2	18.34 ± .04	1.172 ± .002
B2T	38.4	118.8	17.87 ± .04	1.172 ± .002
B2B	0.8	11.0	18.20 ± .03	1.169 ± .001
C1T	32.6	121.6	18.17 ± .05	1.181 ± .002
C1B	2.2	15.9	18.84 ± .05	1.208 ± .002
C2T	38.6	95.4	18.38 ± .06	1.167 ± .002
C2B	15.9	16.3	17.74 ± .14	1.150 ± .009
Peru				
346 - 1T	16.5	17.9	18.72 ± .03	1.198 ± .0004
1B	22.3	23.3	18.72 ± .03	1.199 ± .002
2T	18.2	19.3	18.47 ± .03	1.211 ± .001
2B	28.8	30.4	18.72 ± .04	1.198 ± .002
3T	18.0	23.8	18.84 ± .03	1.195 ± .003
3B	23.7	24.5	18.68 ± .05	1.199 ± .003
4T	21.8	24.3	18.63 ± .04	1.196 ± .003
4B	23.3	24.3	18.99 ± .07	1.186 ± .003
5T	19.5	21.9	18.90 ± .04	1.197 ± .002
5B	26.9	28.7	18.65 ± .04	1.198 ± .002
6T	21.8	25.3	18.16 ± .06	1.208 ± .002
6B	25.2	26.7	18.80 ± .03	1.204 ± .004
India				
1AT	14.5		17.43 ± .08	1.150 ± .002
1AB	53.3		16.44 ± .15	1.078 ± .013
1BT	16.0		17.83 ± .13	1.124 ± .003
1BB	23.2		16.86 ± .05	1.118 ± .002
2AT	17.2		17.08 ± .05	1.141 ± .002
2AB	14.7		16.87 ± .08	1.110 ± .002
2BT	20.7		18.09 ± .28	1.122 ± .006
2BB	19.1		- -	1.068 ± .005
3AT	16.9		18.35 ± .05	1.164 ± .002
3AB	18.8		19.48 ± .44	1.15 ± .02
3BT	17.7		18.51 ± .11	1.142 ± .002
3BB	15.6		17.59 ± .23	1.155 ± .004

TABLE I Continued

Sample	Total Pb (μg/g) 110° Dried	450° Ashed	206/204	206/207
Africa				
RCK -64T	1.8_7		19.45 ± .05	1.241 ± .001
RCK -64B	2.3_8		19.57 ± .06	1.245 ± .001
RCK -68T	3.6_7		19.25 ± .08	1.213 ± .004
RCK -68B	3.0_0		19.46 ± .07	1.229 ± .004
ATM -26 *	41.5**		17.49 ± .04	1.131 ± .005
ATM -28*	40.7**		17.45 ± .06	1.131 ± .003

* Ground filter units

** The total filter paper blank was 41.3 μg Pb/g. It is not known if the concentrations presented here have been corrected for the blank. It must be assumed, however, that this has been done.

V. GENERAL DISCUSSION OF THE DATA

It must be recognized that soils and rocks are not necessarily homogeneous. Consequently, small samples may not be as representative as is desired. For example, the presence or absence of pieces of rock or gravel may affect the results of measurements of the total lead content. Also, small local variations in the mineralogical composition of the rock or soil may have an effect. Thus, differences between the lead contents of corresponding portions of cores from proximate locations are to be expected.

Details are as follows:

Norway, 345 A: The average for the core tops, 23.9 ± 0.3 μg/g. The difference appears to be significant.

Norway, 345 B: The variability is obviously quite large. Significant differences exist between the lead content of the top and the bottom of the cores. Of particular interest is the low ash content of the bottom as compared to that of the top of the core -- about 7 percent compared to about 30%. In samples A1 and 2, and C2, the ash residue of the core bottoms comprise in excess of 98 percent of the dry weight (14 percent in the bottom of core C2) showing large horizontal as well as vertical variations in the organic matter content.

Norway, 345 C: As in the previous sample, the tops of the cores contain considerably more lead than the bottoms.

Peru, 346-1 through 6: The average lead content of the core tops is 22.1 ± 2.8 μg/g, of the bottoms 26.3 ± 2.8 μg/g. Although in terms of the standard deviations the difference is not significant, the fact that consistently the bottoms show a higher lead content than the tops suggests that there indeed may be a real difference.

India: Here, the lead content of the soil at the surface is less than that 3 feet down in cores 1A and 1B. By contrast, no significant difference appears to exist between the tops and bottoms of cores 2A and 2B and cores 3A and 3B.

Africa: Although only one core each from the two locations was analyzed, so that no real estimate of the variability of the lead concentrations can be made, the experience with the other samples discussed in this report suggests that the differences between the tops and the bottoms of the cores are not significant.

Differences in the lead concentrations of surface soil and soil three feet or so below the surface may result from one or more causes. One obvious cause is a difference in the mineralogy of the area at different depths. Such differences may not only result from weathering of the bedrock, but may be inherent in the geologic formation that comprises the first few feet of soil (or rock). It should be noted that the terms "mineralogy" and "geology" are used in a very broad sense, to include any detritus and organic material originating from plant and animal sources, mineral sediments, etc. A much less likely cause for topsoil having a lower lead concentration than subsurface soil is preferential leaching of lead to lower depths.

Only in the Norwegian samples is the top concentration significantly larger than the bottom concentration, particularly in samples B and C. In sample A, this conclusion is somewhat masked by the low weight loss on ashing of the bottoms compared to the tops. It is probable that these differences are caused by human activity. However, it is suggested that industrial activity rather than automobile traffic (leaded gasoline additives) is the cause. Analyses of soils in the U.S. in close proximity to densely traveled highways have revealed the following:[4,8,9]

1. A sample of topsoil 7.6 meters east of the Baltimore.-Washington Parkway at Bladensburg, Maryland (traffic density greater than 56,000 vehicles per day) contained 122 parts per million of lead, a similar sample taken 7.6 meters west of the highway contained 99 parts per million of lead. By contrast, samples taken from 10 - 15 centimeters below the surface at a distance of 30 meters from the highway contained 12 parts per million of lead.[8]
2. Similarly samples taken near U.S. Highway 1 near the U.S. Department of Agriculture Plant Industry Station at Beltsville, Maryland (traffic density 24,000 vehicles per day) showed a lead concentration in the top soil of 239 parts per million west of the highway, and of 403 parts per million east of the highway at equal distances of 7.6 meters. At 30 meters from the highway and 10 - 15 centimeters below the surface, the concentration was about 60 parts per million.[8]

3. A profile of two soil cores taken from an area very close to and downwind from an unspecified highway with a vehicle count of 58,000 vehicles per day showed the lead concentration to decrease from about 70 to 80 parts per million at the surface to less than 0.005 parts per million at 20 inches below the surface. However, these data only show that portion of the lead that is soluble in 10 percent nitric acid during a three-day contact time [9].

4. A profile of a soil core from the Camp Gaw Reservation in the New Jersey Highlands between Westwood, New Jersey and Ringwood, New Jersey, near U.S. Highway 202 and a few miles south of the New York Thruway shows the lead concentration to decrease from about 47 parts per million at the surface to about 12 parts per million at a depth of 16 inches. [4]

In comparison to the numbers shown from sites in the United States close to well traveled highways, the contrast in the lead concentrations at the surface and 36 inches below the surface in the Norwegian cores B and C is as great. Yet the population density and hence the traffic density is much less in Norway than in the United States, particularly in the region sampled. However, in our brief investigation we were not able to find any other activities, such as mining or manufacturing that might account for the high lead concentrations in the top soil. The lack of contrast in the Norwegian sample A may be explained by the presence of an intervening mountain range, if one assumes that there is an external source of lead for location B and C.

The interpretation of the isotopic ratio data poses some difficulty as a result of the wide variation in isotopic ratios found in nature. Table II lists isotopic ratios in ore leads and Table III lists such ratios in rocks, all from global locations. The data have been taken from a tabulation by Rankama [10]. The numbers in Table II are unweighted averages of the ratios obtained from individual sites in the various countries as listed by Rankama. Such an averaging procedure is somewhat questionable, but the results are valid in terms of our subsequent arguments. The data are plotted in Figure 1 as the 206/204 ratio versus the 206/207 ratio. The correlation lines have been drawn in by visual estimation rather than by a least squares or other statistical method. It is of interest that the correlation line for the rock lead lies somewhat below that for the ore lead, although there is some overlap of the compositions between the two types of lead.

TABLE II ISOTOPIC COMPOSITION OF ORE LEAD

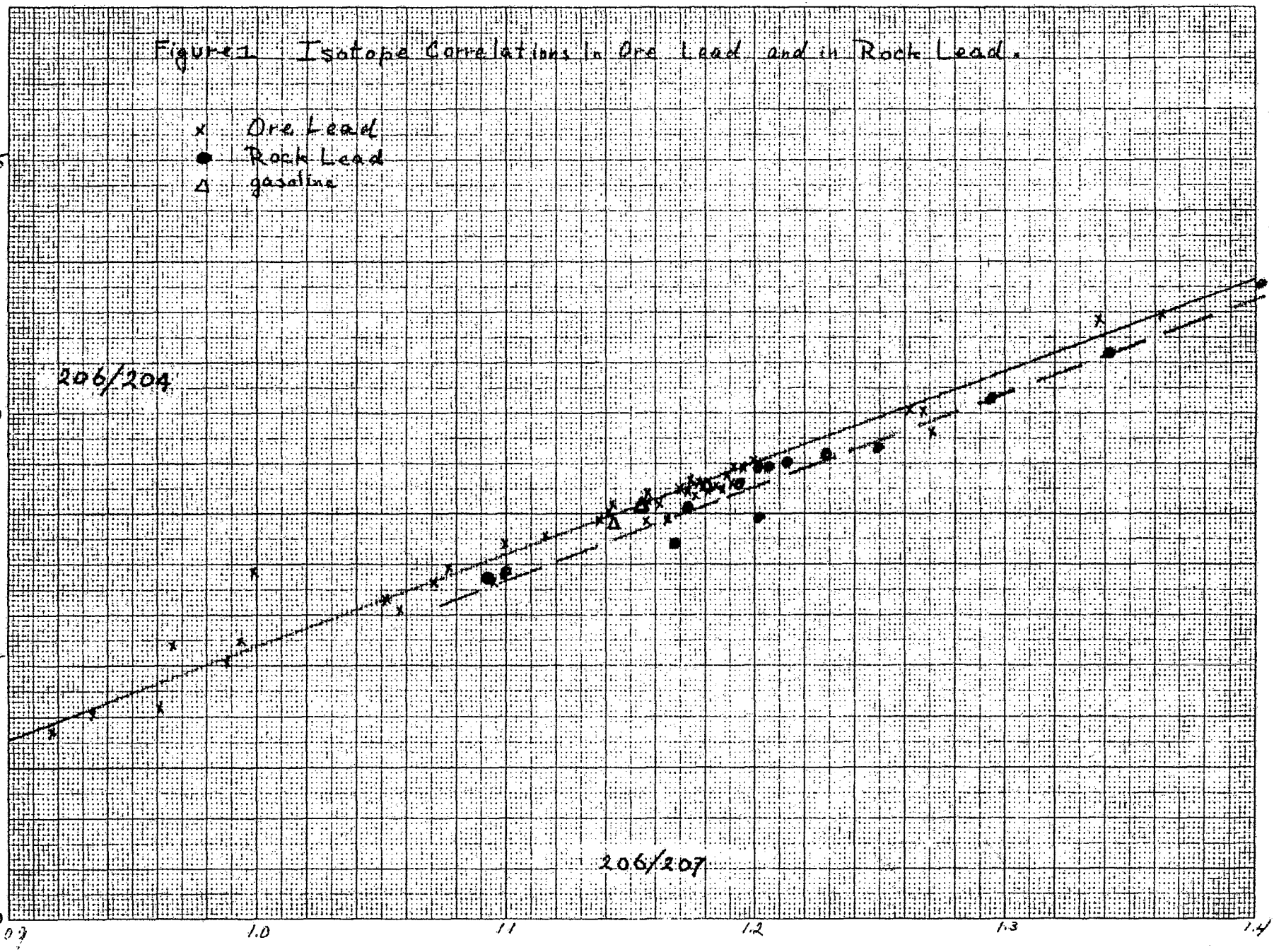
Region of Origin	206/204	206/207
Austria	18.45	1.170
Czechoslovakia	17.85	1.158
Finland	16.81	0.999
France	18.60	1.191
Germany	18.32	1.176
Great Britain	18.71	1.174
Italy	18.60	1.178
Poland	18.60	1.178
Romania	19.04	1.200
Spain	18.40	1.157
Sweden	15.40	0.966
Switerzerland	18.76	1.189
Armenia	18.43	1.181
Caucasia	18.19	1.162
Karelo-Finnish SSR	19.58	1.271
Ukraine	17.55	1.116
India	14.17	0.961
Japan	18.47	1.187
Kirgiz SSR	18.16	1.143
Siberia	17.87	1.165
Algeria	18.87	1.192
Cameroon	17.86	1.138
Congo	18.15	1.144
Equatorical Africa	18.00	1.141
Guinea	15.38	0.994
Ivory Coast	15.02	0.988
Kenya	14.05	0.934
Malagasy Republic	16.92	1.077
Morocco	18.40	1.173
Nigeria	18.89	1.196

TABLE II ISOTOPIC COMPOSITION OF ORE LEAD
(Continued)

Region of Origin	206/204	206/207
Sierra Leone	13.69	0.918
Southern Rhodesia	16.63	1.095
Southwest Africa	18.32	1.157
Union of South Africa	16.30	1.052
(Main Reef, Sub Nigel Mine)	~ 54.3	~ 2.35
California	16.07	1.058
Colorado	18.52	1.185
Connecticut	18.82	1.192
Idaho	16.63	1.071
Illinois	21.92	1.363
Massachusetts	20.01	1.268
Missouri	21.85	1.338
South Dakota	17.41	1.100
Utah	20.05	1.262
Boliva	18.35	1.182

TABLE III ISOTOPIC COMPOSITION OF ROCK LEAD

Material	Isotopic Ratio 206/204	206/207
dunite (less spinel) Twin Sisters, Wash. U.S.A.	19.17	1.228
basalt (less spinel) quarternary, 1800 flow, Hualalai Volcano, Hawaii, U.S.A.	18.62	1.193
olivine bomb in basalt, Hualalai Volcano	19.29	1.249
plateau basalt, quarternary, Columbia River, Snake River Plains, Idaho, U.S.A.	18.12	1.173
basalt, recent, Kamchatka, USSR	17.40	1.168
granodiorite, Parygino, Altar Mountains, USSR	17.90	1.201
granite, precambrian, Essonville, Monmouth Twp, Haliburton Co., Ontario, Canada (whole rock)	20.25	1.294
perthite from granite pigmatite, near Tory Hill, Monmouth Twp.	16.81	1.100
microcline, from granite pegmatite, precambrian, Brown Derby Mine, near Gunnison, Colo., U.S.A.	16.72	1.093
copper minerals, oxidized, in granite pegmatite, Kheto-Lambina, northern Karelia	39.56	2.337
copper minerals, oxidized, in granite pegmatite, Alakurtti	25.60	1.552
manganese nodule, quaternary, Pacific Ocean (acid soluble)	18.91	1.205
red clay, quarternary, Pacific Ocean	18.95	1.202
limestone, Leadville, Colo. USA	21.23	1.341
dolomite, hydrothermal, edge of alteration zone, Leadville	22.65	1.424
Lead, recent, Pacific Ocean	19.04	1.213



In Figure 2, isotope correlations are shown for gasoline, gasoline additives, snow from Lassen National Park in California and from Greenland, as well as for Pacific and Atlantic Ocean sediments. The data, provided by Chow [11] all lie on or very closely above the correlation line for ore lead, as was expected.

In Figure 3, we have plotted the isotopic composition of lead in the Norwegian soil cores. All compositions appear generally to be more characteristic of rock lead, with the possible exception of the top surface of cores A1 and C2. However, if the results from "duplicate" cores are averaged (Table IV, Figure 5), the compositions all are more characteristic of those of rock lead than of ore lead. It is of interest to note that the closest ore bodies, namely in Sweden and in Finland, have 206/204 ratios much lower than other European ores (Table II). However, the average ore lead composition indicated was calculated without the ores from Sweden and Finland, but also without those from Czechoslovakia and from Romania; the former omission to provide a comparison, the latter because these ores are assumed to be less likely in use in Norway.

In any event, the isotopic data show significant differences between the lead near Skjåk, inland, and the lead on the western slopes of the mountains. However, the suggestion that the lead from the western slopes contains contributions caused by human activity as indicated by the concentration data cannot be confirmed on the basis of the isotopic composition alone.

The data from the cores from Peru, India, and Africa are plotted in Figure 4. The Peruvian data are close together, but the results from samples 2T, 4B, and 6T may have to be confirmed. When the data are averaged, however (Table IV), the results show no differences between the surface and the subsurface lead compositions.

The African cores show small differences between locations. There is no indication of the presence of contributions by non-indigenous lead. In particular, the isotopic composition of the air samples show no relation to that of the soil. The 206/204 ratio is higher than that in all other samples (except India 3 A-B, see below) and in this connection, it is of interest to note the existence of a galena (PbS) near Witwatersrand in the Union of South Africa with 206/204 ratios between 40 and 60.

An examination of the data from the Indian cores shows the Thirtahalli lead (1 A, B) to be typical of rock lead. There is no special indication that the Hongere

lead, is any different -- the variation between the A and B samples is rather large, and we question the validity of the 206/204 ratio for sample 2 B. The Shanker sample, although showing some large variations in the data, is clearly different, corresponding to ore lead. Yet, the lead is most likely indigenous, since the concentration in the soil corresponds to that found in the other Indian samples, and no effect of depth on the concentration is apparent.

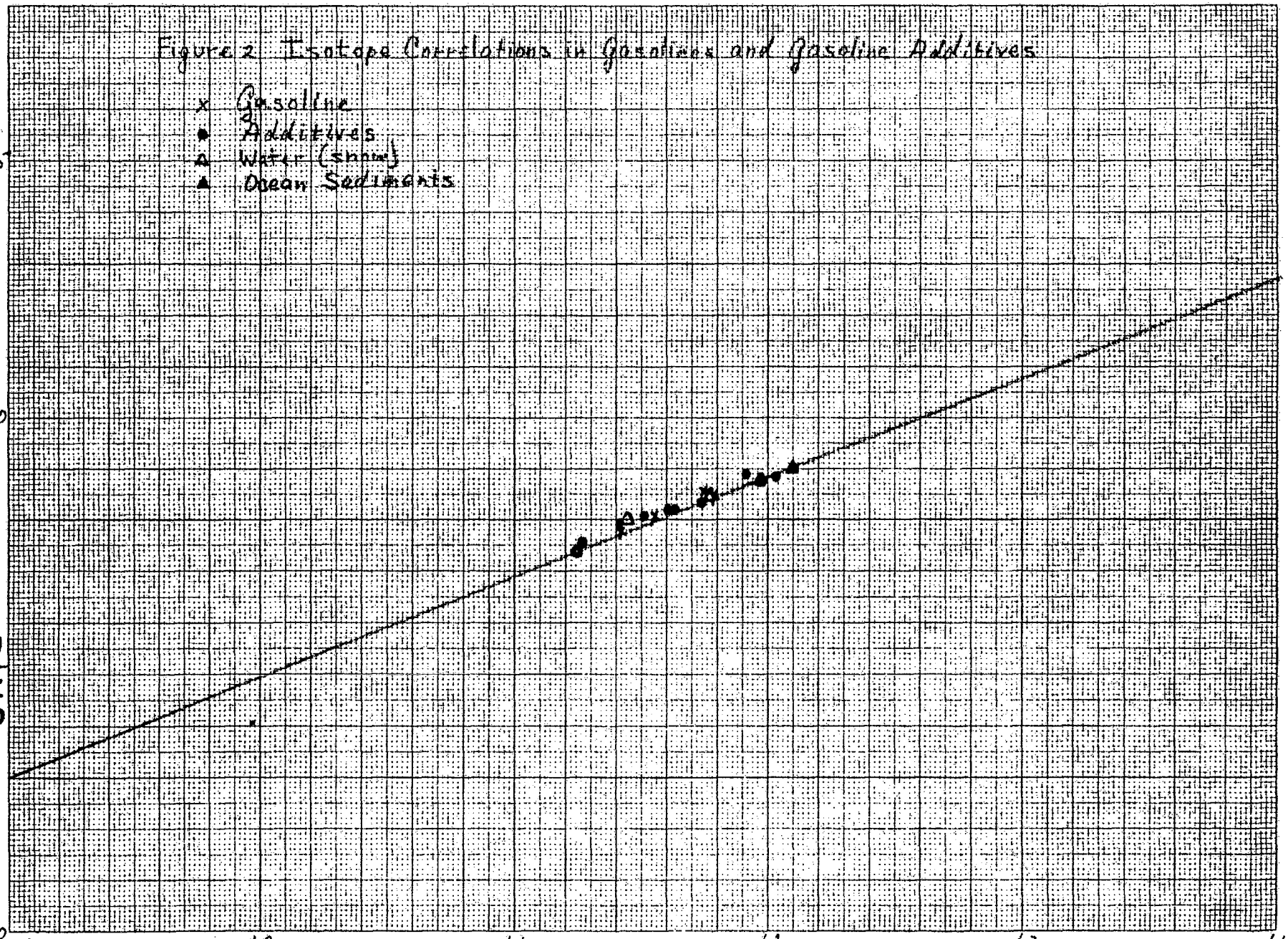
TABLE IV LEAD ISOTOPIC COMPOSITION AVERAGED OVER REPLICATE SAMPLES AND COMPARED TO ORE LEAD FROM PROXIMATE REGIONS

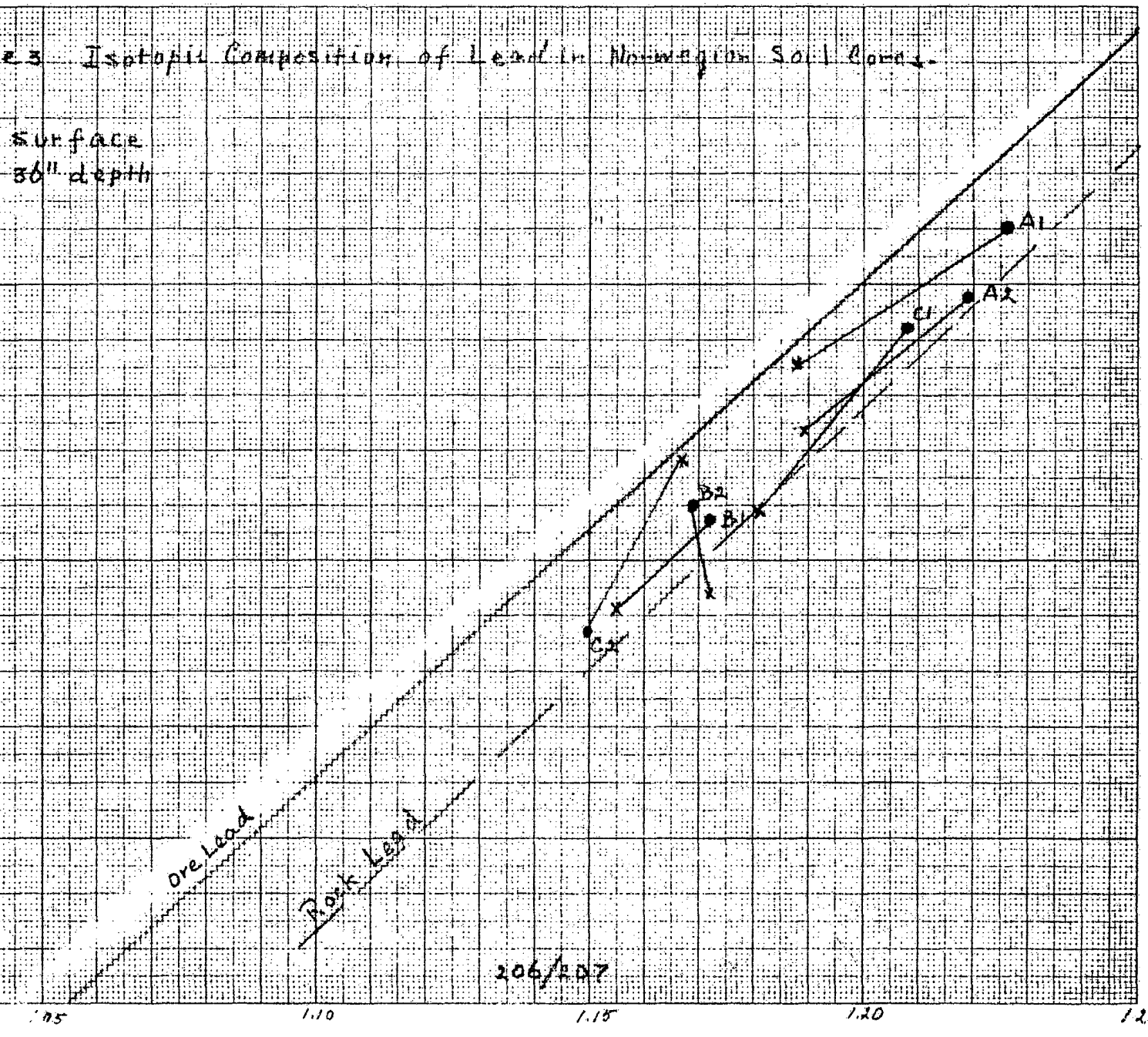
Sample		206/204	206/207	μg Pb/g
Norway	AT	18.59	1.188	23.9
	AB	19.08	1.223	15.9
	BT	17.85	1.164	80
	BB	18.27	1.171	14.6
	CT	18.28	1.174	109
	CB	18.19	1.179	16.1
Ave. Europe*		18.48	1.175	
Ave. Finland & Sweden		~ 16.1	~ 0.98	
Peru	T	18.62	1.201	19.3
	B	18.76	1.197	25.0
Boliva		18.35	1.182	
India	1T	17.41	1.137	15.2
	1B	16.65	1.098	38
	2T	17.58	1.131	19.0
	2B	(16.87)	1.089	16.9
	3T	18.43	1.153	17.3
	3B	18.58	1.15	16.2
India		14.17	0.961	
Africa	T	19.35	1.227	2.8
	B	19.51	1.237	2.6
S.W.Africa		18.32	1.157	
Main Reef Mine		~ 54.3	~ 2.35	

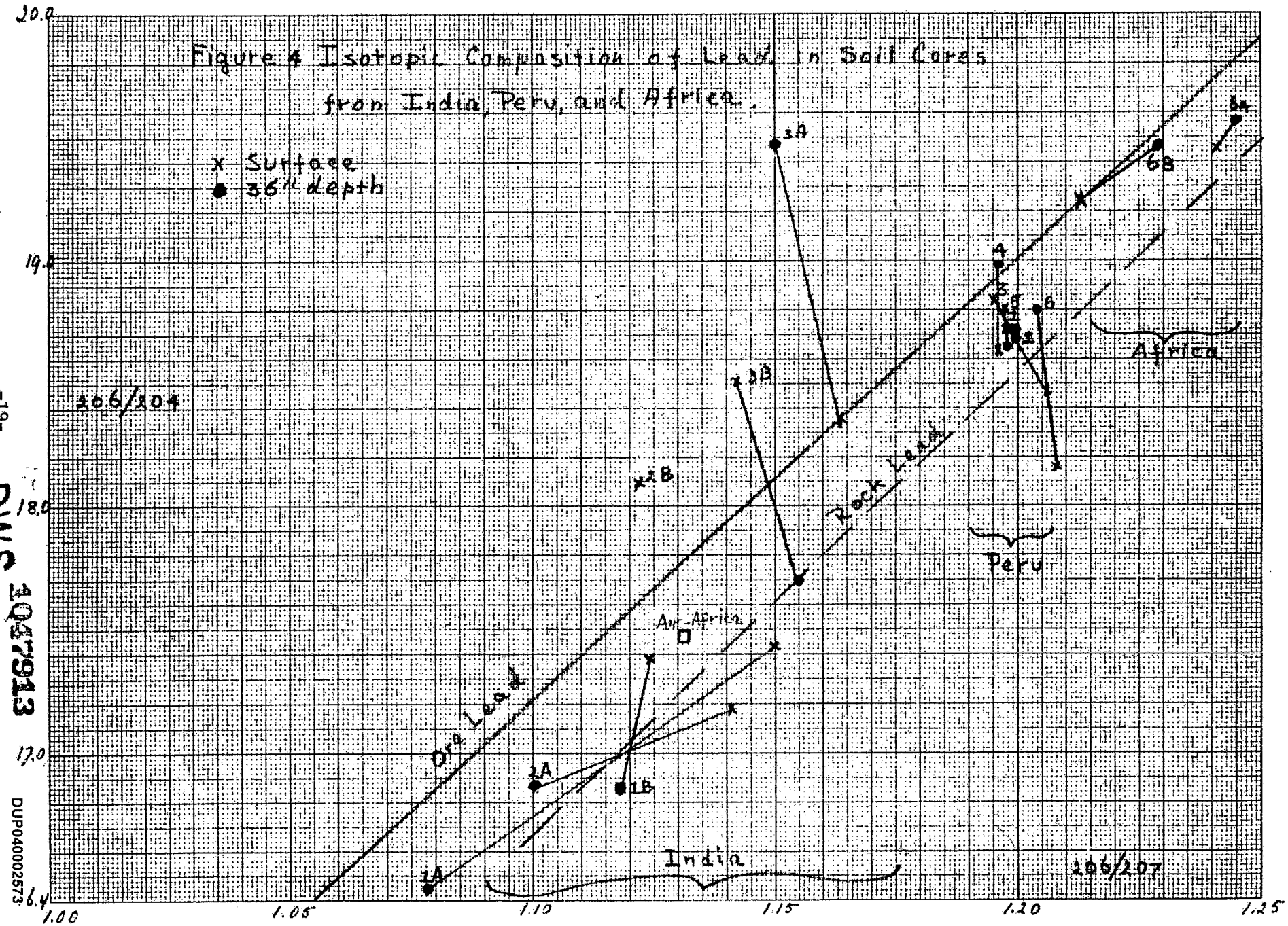
* Ore data from Finland, Sweden, Czechoslovakia, and Rumania omitted - see te t.

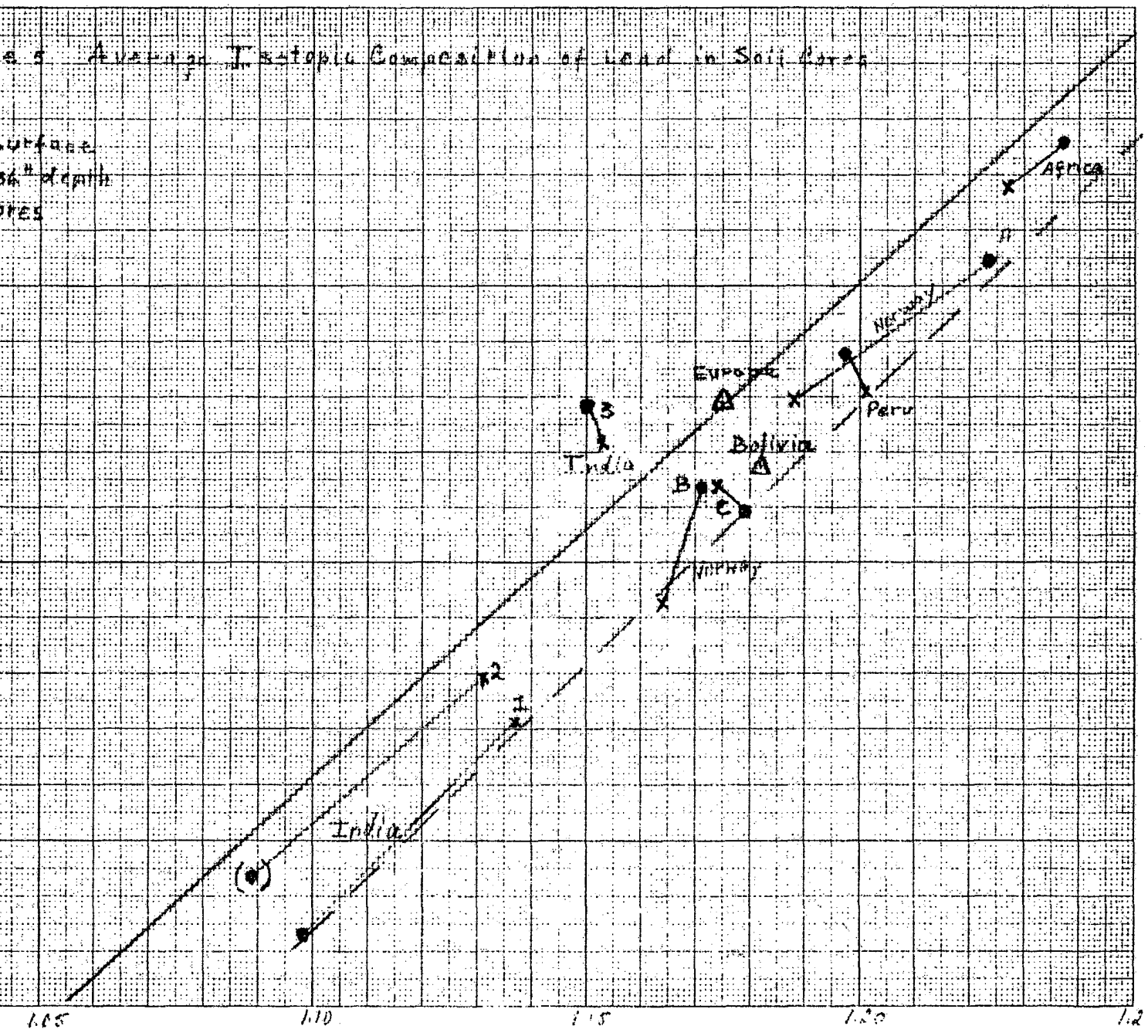
Figure 2 Isotope Correlations in Gasolines and Gasoline Additives

x Gasoline
● Additives
▲ Water (snow)
▲ Ocean Sediments









VI. THE RELATION BETWEEN AIRBORNE LEAD AND LEAD IN SOIL

A sufficient number of studies have been made to show that the lead concentrations in soil and in air close to the source of the lead are considerably enhanced [8,9,12,13,14]. Chow has shown that such atmospheric lead is introduced primarily by the burning of leaded gasolines by isotopic analysis of aerosols and gasolines and gasoline additives [11]. However, the problem that is being investigated is the extent of lead contamination in the general environment and on a global basis. It would appear from the data generated by us that lead contamination of soil on a global basis is as yet unmeasurable. Thus a question is raised concerning the rates of transport, dispersion, and deposition of lead at long distances from its principal sources, and the contribution of lead-containing natural aerosol to the total atmospheric lead levels.

A major problem in the determination of the contamination by lead (and other pollutants) is our lack of knowledge of "background" levels. In particular, it is quite probable that the background is some complicated function of geography, geology, and climate, not only of the local area, but over distances of many thousands of miles. Delany et al [15], for example, have found sand from the Sahara in air-particulate collections from the Bahamas. Chow, Earl, and Bennett [16] have made a limited number of measurements of lead in the atmosphere above the eastern and central Pacific Ocean, and concluded the lead content of the marine atmosphere to be about 0.0010 micrograms per cubic meter. Yet, even this low lead level is considered by the authors to be evidence of lead pollution, by the following argument: According to Prospero et al [17] the continental dust loading over the eastern equatorial Pacific ranged, in 1967, from 0.06 to 2 micrograms per cubic meter. If the natural lead content of continental dust is 15 parts per million (approximate crustal abundance) the maximum lead concentration in the Pacific air should be between 1×10^{-6} and 30×10^{-6} micrograms per cubic meter. These values are several orders of magnitude smaller than those found by Chow in the marine aerosol. Yet one must be very careful in accepting such conclusions: Chow made his collections on Millipore filters with 0.45 micron mean pore size, whereas Prospero and Bonatti used nylon mesh panels that are efficient only particles down to 2 microns diameter.[15] Particle size distribution measurements of the marine aerosol have, to my knowledge, not been made, so that the weight fraction in particles smaller than 2 microns in diameter is not known. My own experience and deductions from the literature on

size distributions over continents suggest that between about 0.1 micron and 10 microns (approaching the largest size present at higher altitudes) the mass distribution varies approximately as (diameter)$^{-1}$. Hence a significant fraction of the mass is present in particles below 2 microns, although not enough to change Prospero and Bonatti's numbers by an order of magnitude.

Additional collections of the marine aerosol, also by the mesh technique, were made by Parkin, Phillips, and Sullivan over the North Atlantic between Ireland and New Foundland, in the Bay of Maine, and off Cape Cod.[18] The dust concentration varied with the season. In January 1969, it was roughly constant between Ireland and New Foundland at 0.003 micrograms per cubic meter, yielding an estimated 15×10^{-6} (abundance) $\times 3 \times 10^{-3} = 45 \times 10^{-9}$ micrograms of lead per cubic meter of air. In August 1969, when the snows had melted, the dust concentration varied between 0.003 at Ireland, and 0.01 to 0.03 micrograms per cubic meter near New Foundland. Thus, more than 90 percent of the dust originates from the North American continent. The increase in dust loading increases sharply in the Bay of Maine and near Cape Cod, and streams of polluted air were recognizable. The spreading of one such stream was followed across the Atlantic by using fly ash spherules as tracers. The width of the stream increased five-fold between New Foundland and Ireland. Although this measurement was very approximate, it shows that horizontal diffusion is relatively slow and that world-wide deposition may very well occur primarily in overlapping bands emanating from specific points or areas of origin and following the prevailing wind directions. Consequently, if such contamination would be noticeable in soil longitudinal profile of soil coring far from inhabited areas would be needed to prove it. Generally, the presence of pollutants in surface air far from their source has been noticed by mineralogical examinations of the dust. Specifically, talc, a carrier for DDT, has been found in atmospheric dust over the Coral Sea[19], for example.

Rancitelli and Perkins have measured the concentrations of seven elements in the atmosphere, namely, silver, cobalt, chromium, iron, antimony, scandium, and zinc at altitudes between 3 and 15 kilometers between Albuquerque, New Mexico, Spokane, Washington. Table V lists the average concentrations taken from their data, as well as some elemental concentration ratios. A comparison with natural abundance ratios shows that antimony, silver, chromium and zinc are all enriched, by one or more orders of magnitude, with respect to iron, whereas cobalt and

TABLE V ATMOSPHERIC CONCENTRATIONS OF SOME TRACE ELEMENTS*

Altitude (km)	Concentrations (nanograms/m^3)						
	Fe	Sb	Co	Ag	Cr	Sc	Zn
3.1	500	0.22	0.16	0.02	6	0.16	142
4.6	60	0.10	0.04	0.06	4	0.036	14
6.1	195	0.075	0.085	0.018	5.5	0.030	9
8.8	71	0.29	0.022	22	2.7	0.008	8.7
11.4	45	0.005	0.059	0.03	4	0.003	1.4
15.2	21	0.008	0.014	0.04	0.4	0.0009	2.1
Relative Natural Abundance	50,000	1	23	0.10	200	5	132

	Concentration Ratios					
	Sb/Fe	Co/Fe	Ag/Fe	Cr/Fe	Sc/Fe	Zn/Fe
3.1	0.00044	0.00032	0.00004	0.012	0.00032	0.28
4.6	0.0017	0.00067	0.0010	0.067	0.00060	0.23
6.1	0.00038	0.00044	0.000092	0.028	0.00015	0.046
8.8	0.0041	0.00031	0.31	0.038	0.00011	0.12
11.4	0.00011	0.0013	0.00067	0.089	0.000067	0.031
15.2	0.00038	0.00067	0.0019	0.019	0.000043	0.10
Natural	0.000020	0.00046	0.000002	0.0040	0.0001	0.0026

* From Reference 20

possibly scandium are not. Is this evidence of pollution, noticeable as high as 15 kilometers above the surface of the earth? Silver enrichment may have resulted from cloud seeding experiments -- yielding a clue to the fate of such silver. Chromium may have been introduced with iron, zinc is widely used and discarded, and may have been introduced by burning. The contribution to iron by pollutant sources may be too small to affect the abundance ratios of cobalt and scandium significantly.

If lead is present in its natural abundance ratio to iron, namely 15/50,000, the lead concentration would be between 6×10^{-6} and 150×10^{-6} micrograms per cubic meter, about the same estimate made by Chow from Prospero's data for the Pacific Ocean atmosphere. However, the total natural dust loading is probably much less at higher altitudes than near the surface, maybe by a factor of ten or more, so that Chow's data are approached. Yet it must be kept in mind that Chow's data were obtained over the ocean, whereas those of Rancitelli and Perkins were obtained over land. Clearly, the combined rates of horizontal and vertical transport are important in the interpretation of these and similar data.

Measurements at land stations have been, and still are being made by the National Air Pollution Control Administration (National Air Sampling Network, NASN) and the Health and Safety Laboratory (HASL) of the U.S. Atomic Energy Commission. In addition, we have two air particulate samples from the Kalahari Desert, the origin of two of the soil cores analyzed. High altitude measurements of elements other than lead have been made, for example, by Rancitelli and Perkins.[20]

Surface air dust loadings and lead concentrations in the United States have been measured primarily with the NASN. Table VI shows some of the data for the year 1957 by region[21]. Of interest are the comparatively low levels over the Great Plains and the Rocky Mountains where the population density is reduced, and the fact that the lead content of the aerosol is between two and three orders of magnitude greater than the natural abundance of lead.

HASL operates an international network (80th meridian") for radioactivity measurements. The stations from which lead data have been extracted are listed in Table VII[21]. The data are plotted in Figures 6a, b and c. No special precautions have been made to prevent lead contamination of the samples during handling and analysis. Most samples were obtained from areas of considerable human activity, but of particular interest are the samples from Chacaltaya (5250 meters elevation), Punta Arenas, and Thule. Average lead concentrations at these three locations are about 0.02, 0.06 and 0.01 micrograms per cubic meter.

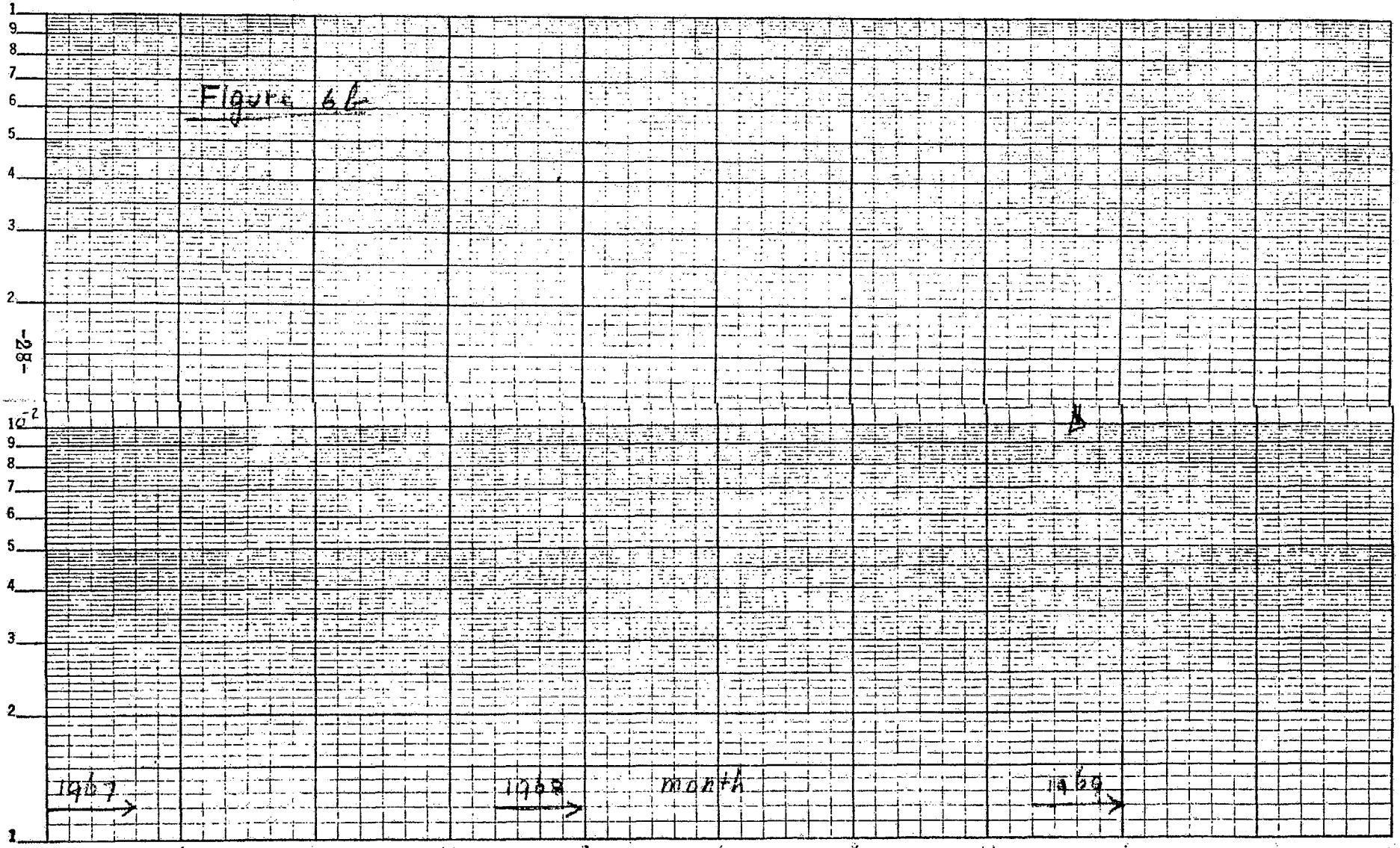
TABLE VI DUST AND LEAD LOADING OF SURFACE AIR OVER THE UNITED STATES IN 1957

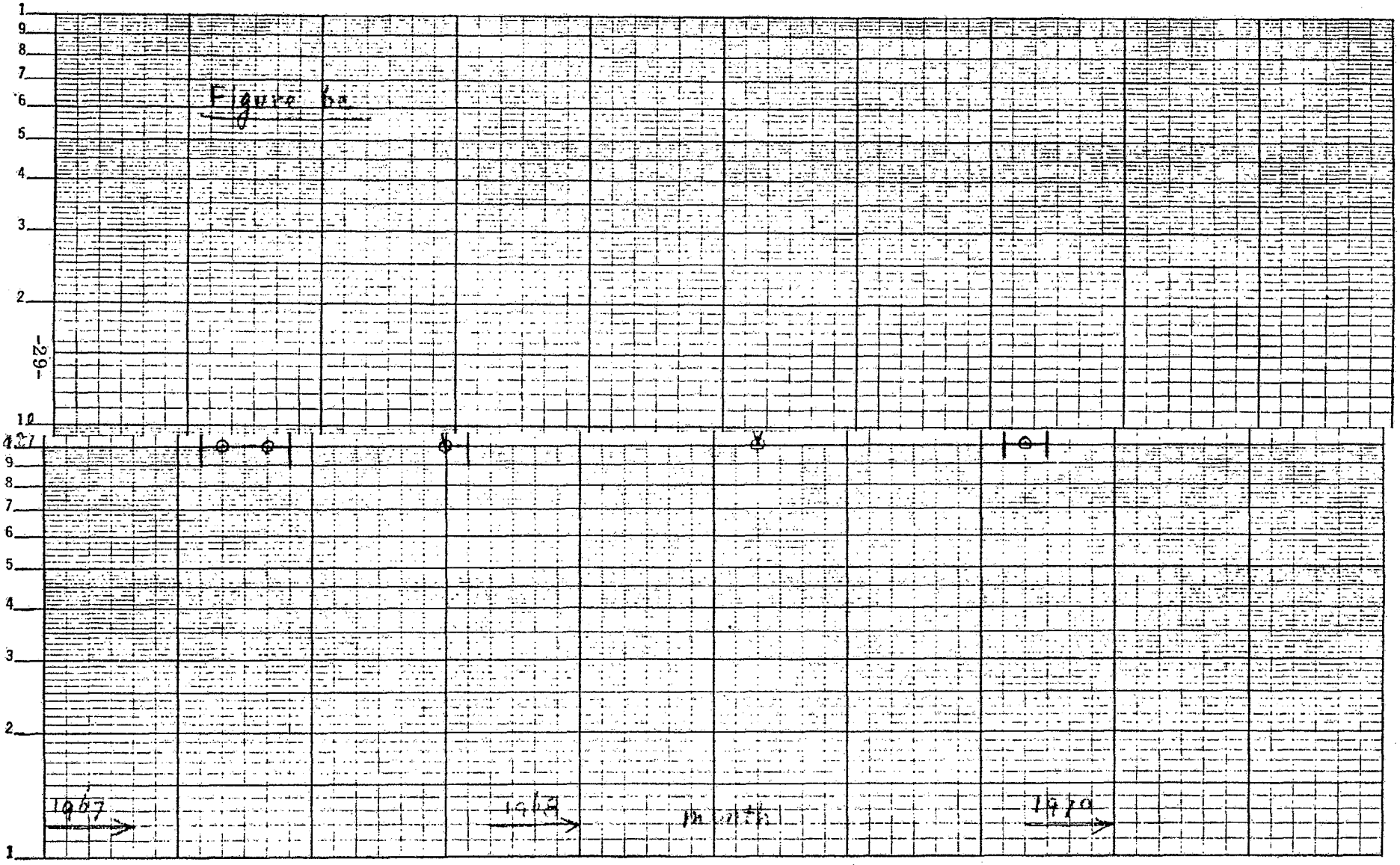
Region	Total Particulate $\mu g/m^3$	Lead $\mu g/m^3$	Percent Lead
National	118	0.5	0.4
New England	98	0.7	0.7
Mid Atlantic	130	0.6	0.5
Mid East	121	0.6	0.5
South East	121	0.5	0.4
Mid West	145	0.5	0.3
Great Plains	137	0.2	0.1$_5$
Gulf South	108	0.4	0.4
Rocky Mountains	90	0.2	0.2
Pacific Coast	136	0.7	0.5

TABLE VII HASL STATIONS FROM WHICH LEAD DATA ARE AVAILABLE

Station	Latitude	Longitude	Elevation (m)
Thale, Greenland	76° 36' N	68° 35' W	259
New York, New York	40° 48' N	73° 58' W	38
Sterling, Virginia	38° 58' N	77° 25' W	76
Miami, Florida	25° 49' N	80° 17' W	4
Bimini, Bahamas	25° 46' N	79° 22' W	3
San Juan, Puerto Rico	18° 26' N	66° 00' W	10
Balboa, Panama Cancal Zone	8° 58' N	79° 34' W	23
Guayaquil, Ecuador	2° 10' S	79° 52' W	7
Lima, Peru	12° 01' S	77° 08' W	13
Chacaltaya, Bolivia	16° 21' S	68° 07' W	5220
Antofagasta, Chile	23° 37' S	70° 16' W	31
Santiago, Chile	33° 27' S	70° 42' W	520
Punta Arenas	53° 08' S	70° 53' W	35

Figure 6a. Monthly Load Comparisons at Selected Sites in the HASL Network





These values are all higher than those found or inferred to be in marine and high altitude tropospheric atmospheres. Thus, the data do suggest global effects of air pollution. Yet the environmental levels drop off rather rapidly laterally with wind direction as shown also by the levels at Antofagasta relative to those at Santiago, for example. Finally, the data do not show an increasing trend over the two year period that data are available.

We shall now try to make some estimates of the effect of global lead on lead concentrations in the upper layers of the soil.

The annual consumption of lead in the United States in 1963 was estimated by McCaldin to be 1,163,00 short tons [22] or 1.06×10^{12} grams, of which 1.75×10^{11} grams was in the form of gasoline antiknock additives. He also estimated that 60 percent of the lead from gasoline additives remains airborne, i.e., 1.05×10^{11} grams. There will be some contribution to the airborne lead from sources other than gasoline, so that we estimate about 1.5×10^{11} grams of airborne lead originating in the United States. We further estimate that one-third of the total lead consumption in the Northern hemisphere occurs in the United States, so that a total of 4.5×10^{11} grams of airborne lead was generated in 1963, almost all above 30° N latitude. The average residence time of particulate pollutants in the atmosphere has been estimated to be about 8 days, [24] so that there is no significant holdup. We further assume that the lead eventually deposited on soil and water is equivalent to thirty years consumption at the 1963 level, i.e., 1.35×10^{13} grams. Let us now deposit this lead in a band around the globe of the width of the United States, i.e., 1500 miles wide and about 20,000 miles long. The area of this band is 7.8×10^{17} square centimeters, so that $(1.35 \times 10^{13})/(7.8 \times 10^{17}) = 1.73 \times 10^{-5}$ grams of lead is deposited per square centimeter. Since between 1 and 2 inches of soil (average 4 centimeters) is analyzed, the contribution from pollutant lead to indiginous lead is about 4.3 micrograms per cubic centimeter, or about 2.0 micrograms per gram of surface soil analyzed, if one assumes an average density of the surface soil of about 2.2 grams per cubic centimeter. Deposition will be affected by rainfall, proximity to the source, geographic peculiarities, and so on, so that regions may exist where the deposition is much less, or much higher than indicated. It would appear, however, that the average value of the deposition will be difficult to recognize without a large body of data, as it is hidden in the natural variations of the measured lead concentrations in soils.

Average airborne lead concentrations may also be calculated. We shall assume the lead to be dispersed within the same band, but to an altitude of 1000 meters and we shall further assume a residence time of 10 days. Thus 1.2×10^{10} grams of lead is dispersed in $7.8 \times 10^{13} = 7.8 \times 10^{16}$ cubic meters, yielding a concentration of about 0.15 micrograms per cubic meter, a little lower than has been observed in highly polluted areas, but much higher than has been observed or inferred in marine atmospheres. An increase in the height of the air in which the lead is dispersed makes, at most, one order of magnitude difference. Consequently, we are led to the conclusion that only a small fraction of the total lead injected into the atmosphere is transported over large distances before being deposited.

The consequences for the United States are as follows: The area is about one-seventh that of the band considered before, the lead release about one-third. Hence, the smoothed-out concentration in the top 4 centimeters of soil is $(1/3)/(1/7) \times 2 = 5$ micrograms per gram. The average air concentration is calculated as follows: The average wind speed is 15 miles per hour, from west to east. Hence, an air change occurs every 3000/15 = 200 hours. During this period of about 8.3 days, a total of $(4.5 \times 10^{11}$ grams/year) x (8.3 days)/(365 days per year) = 1×10^{10} grams is generated. This is dispersed in an air volume of $(1/7) \times (7.8 \times 10^{16}) = 1.1 \times 10^{16}$ cubic meters. The result is a concentration of 0.9 micrograms per cubic meter, in good agreement with the data in Table V. This calculation, therefore, confirms our previous conclusion that most of the lead is not transported over very large distances, even the 60 percent that is not deposited in the immediate vicinity of the source. We must further conclude that the deposition in regions far removed from sources will probably yield much lower concentrations than the 2 micrograms of grams per soil calculated.

VII. CONCLUSIONS

1. Differences in the concentrations and isotopic compositions of lead between the top few centimeters of soil and the soil 30 to 40 inches below the surface in cores obtained from a number of global locations are within the natural variability of the concentration and isotopic composition indigenous lead.

2. Order of magnitude calculations of global deposition of lead from pollutant sources have shown that such deposition, on the average, would lead to concentration changes in the top soil that are of the same order of magnitude or less than the measured natural variations of the lead content.

VIII. RECOMMENDATIONS

1. More precise calculations of the transport of lead from its sources should be done. Sufficient experimental data are available for such calculations (e.g., in "Meteorology and Atomic Energy", David H. Slade, ed., published by the Technical Information Division of the U.S. Atomic Energy Commission, July, 1968). The results should then be used to calculate deposition rates and changes in soil concentration as a function of distance from the source. Multiple sources should be taken into account.

2. A sampling program should be conducted over distances intermediate from the source, not exceeding several hundred kilometers. Ideally, the source should be chosen such that the "deposition field" is unique, i.e., that the lead deposited originates from that source only. A possible example is Denver. The program should be tied in with the calculations.

3. An investigation should be made of the possible use of a natural trace element as a background tracer. This tracer should not be a significant component of the particulate matter released by the source together with the lead. The concentration ratio of lead to this tracer should then be followed. Scandium is a candidate tracer, but another, less ubiquitous element may be a better candidate.

4. A modest sampling and analysis program in a river above the first industrial injection of lead should be considered. The river should pass through one or more regions with high lead concentrations in the air. Both water samples and riverbed samples should be obtained. It may be assumed that most of the lead contributed by the atmosphere will appear in the sediments.

Analysis of available marshland cores from the Delaware basin are included in this recommendation.

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TLW 6075

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Final Report

by

M. W. Nathans

to

Haskell Laboratory
E. I. DuPont de Nemours and Company
Elkton Road
Newark, Delaware 19711

June 22, 1970