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Atmospheric long range transport of lead to Denmark

By M. F. HOVMAND*, *Institute of Plant Ecology, University of Copenhagen, Øster Farimagsgade 2 D, DK-1353 Copenhagen, Denmark*

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ABSTRACT

Lead in bulk precipitation (rain water + dustfall) was measured in 42 randomly taken 24-hour samples from Keldsnor, Langeland, Denmark. Trajectories were computed to find the origin of the rain-bearing air masses. It is shown that the mean lead concentrations of bulk precipitation in cases with air trajectories from Central Europe, England and the Atlantic, respectively, were significantly different at the 0.1% level. From the amount of precipitation and the frequency of transport events, it is estimated that ~2/3 of the lead deposition in the rural environment of Denmark more than 100 m from roads is transported from long range.

1. Introduction

Natural lead emission comes into the atmosphere mainly from soil dust, fire in wood and peat, and volcanic activity. These contributions are less than 1% of the anthropogenic lead emission (Patterson, 1965). Ninety-five per cent of the anthropogenic lead emission comes from the use of antiknock additives in gasoline for automobiles (Snyder, 1971). The lead emission to the atmosphere in Denmark is calculated to be 900 metric tons/year (Miljøministeriet, 1976).

Lead aerosols emitted to the atmosphere are partly deposited locally within 100 m from roads and partly deposited at greater distances up to several hundred km from the sources. The very local lead deposition gives an exponential decline in the lead concentration in air and vegetation with distance from roads (Snyder, 1971; Rühling and Tyler, 1968). Kainz (1973) showed that 10% of the emitted lead was deposited within 100 m of the road. Little and Wiffen (1977) found that less than 10% was deposited within 30 m of a motorway. The local deposition within 100 m of roads is estimated to be around 10% of the lead emitted in Denmark. This deposition which has local origin is not included in the following computations.

Lead aerosols and sulphur compounds are transported over great distances (Prahm et al., 1976; Odén, 1968; Førland, 1973). This leads to fairly uniform deposition over large areas, as also indicated in lead analyses of mosses showing a fairly even distribution over Scandinavia with a decreasing level from south to north (Rühling and Tyler, 1971). Analyses in our laboratory of lead in bulk precipitation from 15 stations in Denmark and southern Sweden also showed a remarkably uniform distribution.

The aim of this investigation was to estimate the national contribution to lead measured in bulk precipitation in the rural areas of Denmark, more than 100 m from roads. Bulk precipitation is defined as the material sampled in a funnel during wet and dry periods. The total atmospheric deposition on land surfaces is probably greater than bulk precipitation due to the aerosol capturing capacity of the vegetation.

2. Materials and methods

2.1. *Sampling procedure*

The location of the sampling station is Keldsnor Lighthouse, 10°.73 E, 54°.73 N, 9 m above sea level on the south of Langeland island (see Fig. 1). There is no polluting activity in the vicinity of the station. The distance to the nearest country road is

* Present affiliation: Dept. of Sanitary Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark.

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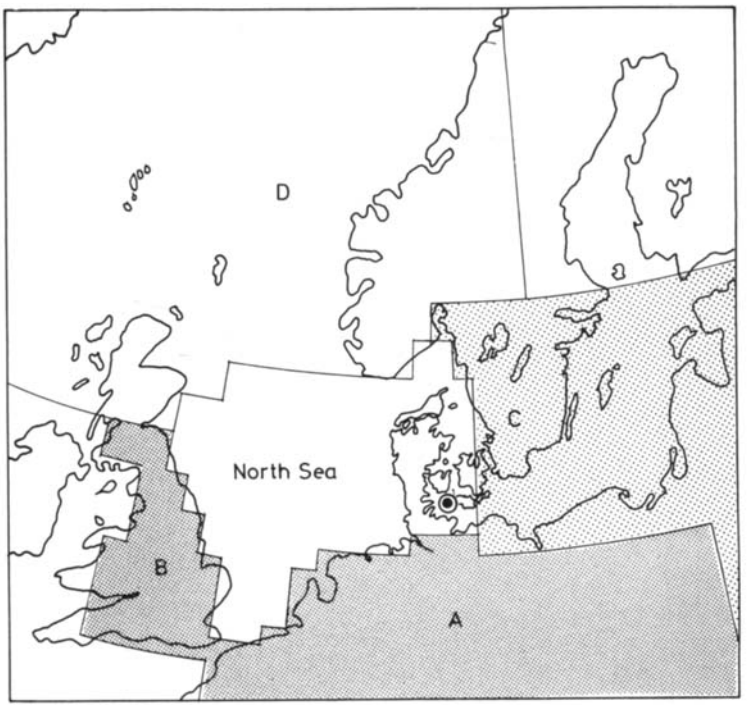

Fig. 1. Estimated mean anthropogenic SO_2-emission in areas A and B (20 metric tons $km^{-2} \cdot yr^{-1}$), area C (2 metric tons $km^{-2} \cdot yr^{-1}$) and area D (0.1 metric tons $km^{-2} \cdot yr^{-1}$). The sampling station is indicated with an encircled dot.

4 km, and the nearest town with more than 5000 inhabitants is 30 km away. The sampling equipment is a NILU funnel-bottle system (Norwegian Institute for Air Research). The upper part of the funnel is a cylinder 200 mm in diameter and 200 mm high. The upper edge of the funnel is 2500 mm above ground level. Collections were taken at 0700 GMT, 0800 local time; the bottle was replaced once daily. Precipitation recordings are from the meteorological station at Keldsnor.

2.2. *Chemical analysis*

The samples were stored in polyethylene bottles in a refrigerator. An aliquot of each sample was taken for chemical analysis according to the OECD programme LRTAP (Ottar, 1973). The remaining sample was sent to our laboratory and analysed within 4 months of collection. The samples were not acidified. Ten samples were analysed before and after acidification with 1 ml concentrated HNO_3. No significant difference was found.

Lead was analysed by flameless atomic absorption, Perkin–Elmer 303/HGA-70. Twenty μl were injected into the cuvette, a standard curve was established with lead standards in 0.1 N HNO_3 to keep lead in solution. The method was controlled by measuring lead in solvent extracts (DDDC/Xylene). The interfering effects of NaCl in the samples were measured by adding NaCl to the lead standards. Coefficient of variation on pooled data of the three methods was less than 15%.

2.3. *Trajectory analysis*

The rain bearing air masses and the corresponding precipitation samples were classified according to which of the areas A, B, C or D the air masses had passed through during the previous 48 hours. The sulphur dioxide emission from the areas is given in Fig. 1.

Areas with high sulphur emission are expected to exhibit a high lead emission. Therefore the lead emission from areas adjacent to Denmark was classified based on sulphur emission data by Ottar (1976). The proportion between SO_2- and Pb-emission in Denmark is approximately 570 000 metric tons/900 metric tons $\simeq$ 600 SO_2/Pb (Prahm and Torp, 1973; Miljøministeriet, 1976).

The air masses passing the sampling station during the 24-hour sampling period are described by geostrophic air trajectories computed at the 1000 mb level using the method proposed by Petterssen (1956). For every 24-hour sampling period two trajectories were computed from data collected at 0700 GMT and 1900 GMT. In all 128 trajectories were computed by the Danish Meteorological Institute, Air Pollution Section, Copenhagen. This kind of air trajectories has shown to be useful in tracing pollutants over great distances in Europe (Prahm et al., 1976).

Fifty-four samples were collected at random during the period 16 December 1974 to 1 April 1976. For two samples no trajectories could be computed. Three samples were so small that no representative aliquot could be taken. Seven samples had received precipitation from air masses which had passed more than one of the areas defined in Fig. 1. Forty-two samples were used for the computations; these samples were classified into four groups, A, B, C and D of trajectory events according to the origin of the air masses, Fig. 1. In only two precipitation events had the rain bearing air masses passed area C. No statistics were performed for this group.

3. Results

The concentration of metal in 24-hour concentration samples might be influenced by the amount of precipitation. Ångström (1952) has demonstrated a logarithmetic correlation between the amount of precipitation and wet deposition of NH_4^+ and NO_3^-. In this work several relations between deposition of lead and the amount of precipitation within groups A, B and D have been investigated. The curve giving the best fit was of the form $M(x) = a \cdot x^b$, $M(x)$ is the lead deposition (μg Pb/m^2) per 24 hours, and x is the measured precipitation (mm) in the same period, a and b are constants. The b values for the three groups of trajectory events were, however, not significantly

Table 1. *The lead concentration in bulk precipitation classified according to trajectories. The concentrations were found significantly different. $F = 19.4$ with (2, 37) degrees of freedom, $P < 0.001$*

Source area	Number of samples	Weighted mean $\hat{K}$ (μg/l)	Standard deviation of $\hat{K}$ (μg/l)
A	13	18.3	6.0
B	11	10.9	1.6
C	2	7.2	
D	16	3.7	0.5

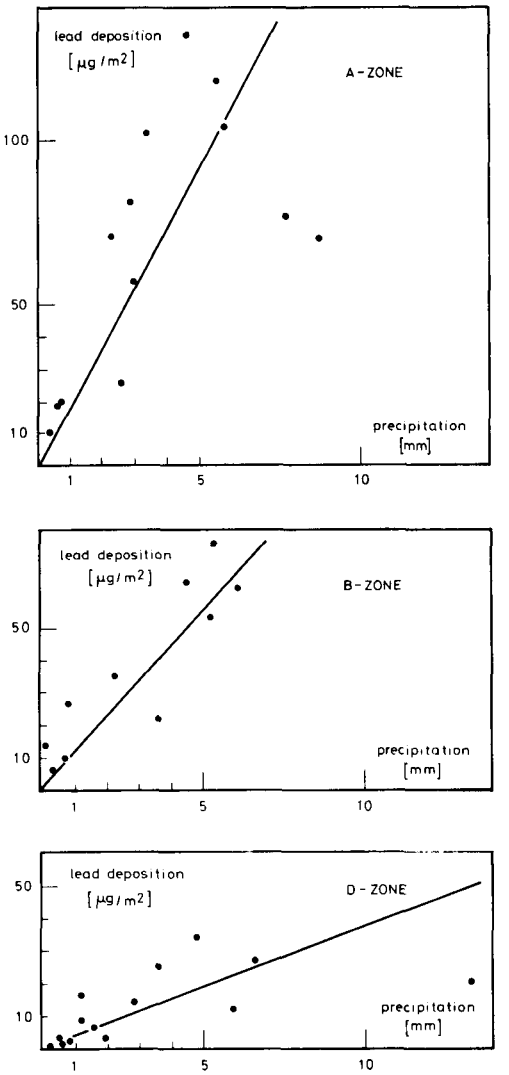

Fig. 2. The relation between amount of precipitation and deposition of lead in 24-hour bulk precipitation samples. A-, B- and D-zones refer to the area the air trajectory passed through during the previous 48 hours (see Fig. 1). The lines are determined from the weighted mean concentration.

different from 1. Consequently, in the following computations a linear equation of the form $M(x) = K \cdot x$ is used. The coefficient of correlation r is for A-trajectory events 0.63, for B- and D-trajectory events it is 0.77. This means that the coefficients of correlations differ significantly from zero at a 5% level. The estimate $\hat{K}$ in the above relation is determined for each group by a weighted linear regression analysis, assuming that the variance of $M(x)$ is proportional to the rainfall x, the estimated mean concentration

$$\hat{K}_v = \frac{\Sigma M(x_i)}{\Sigma(x_i)}$$

is a weighted mean value of the measured concentrations in trajectory group v (v = A, B, D). The estimated mean concentrations for the three groups are found mutually significantly different at the 0.1% level, Table 1.

To determine the part of the lead deposition transported long range the estimated lead deposition values $\hat{K}_v \cdot x_v$ from A, B, and C trajectories are subtracted an estimated lead deposition value ($\hat{K}_D \cdot x_v$) which could be expected from D-trajectory events with precipitation x_v, (Fig. 2) and (Table 2). $\hat{K}_v$ and x_v being the estimated mean concentration and the total amount of precipitation sampled from group v (v = A, B, D). The difference $(\hat{K}_v - \hat{K}_D)x_v$ is thus the estimated long range transported lead deposition originating from area v.

Since the estimated concentration is calculated as the weighted average of the observed concentrations, it follows that the estimated total lead deposition $\hat{K}_v \cdot x_v$ equals the actually measured lead deposition.

Table 2. *Sum of lead deposition classified according to trajectories from source areas*

Source area	Sum rain mm	Actual sum Pb $\mu g/m^2$	Estimated Danish origin $\mu g/m^2$	Estimated long range transported $\mu g/m^2$
A	48.4	887	178	709
B	38.7	422	142	208
C	3.6	25	12	13
D	47.3	174	174	—
Sum	138.0	1508	506	1002
%		100	34	66

4. Discussion

The concentration of lead in bulk precipitation is highly dependent upon which of the source areas A, B, C or D the rain bearing air masses have passed during the 48 hours before sampling.

As shown in Fig. 2 there is a considerable variation in the lead concentration of rain originating from air masses coming from the same area. This may be due to several factors such as wind speed, dispersion in the troposphere and washout efficiency. These parameters are not included in this investigation. The emissions within the areas A, B, C and D are not uniform and the discrete divisions of the areas contribute to the deviation, especially when air masses pass close to the borderlines.

It is known that air masses from the Atlantic have very low lead concentrations <1 ng/m^3 (Prahm et al., 1976). Therefore it is postulated that all the lead deposition from D-trajectory events originates from Denmark.

The variance on the longe range transported lead deposition ($V(T)$) from area A and B is of the form:

$$V(T) = V(\hat{K}_A) \cdot (x_A)^2 + V(\hat{K}_B) \cdot (x_B)^2 + V(\hat{K}_D)(x_A + x_B)^2 = 20{,}031\ (\mu g/m^2)^2$$

x_A and x_B are the total amount of precipitation from A-respectivity B-trajectories. The standard deviation is 142 $\mu g/m^2$ or 9% of the total lead deposition.

The computations show that 66% $\pm$ 9% of the lead deposition has foreign origin, probably a minimum value. If the D-trajectory air masses do, after all, contain some lead before they pass over Denmark, the national contribution is overestimated. As the A-trajectory air masses often do not pass Denmark before they arrive at Keldsnor sampling station, the foreign contribution is underestimated. Whether the computed ratio between long range transported lead and lead emitted within the country is general for the whole country or not, depends on several factors such as (1) the lead concentration in bulk precipitation sampled in Keldsnor in comparison with samples from other parts of the country, and (2) the lead deposition in the analysed period in proportion to a period of several years. Table 3 gives a comparison between 24-hour samples from this investigation and

Table 3. *Comparison between 24-hour samples from this investigation and monthly samples from Keldsnor and average for Denmark*

	Rain (mm)	Pb-concentration (μg/l)	Pb-deposition (mg/m^2 · yr)
24 hour samples Keldsnor 42 events	138	11	—
Monthly samples* Keldsnor	344	17	5.8
Monthly samples* 13 station average Denmark 1975	504	14	7.1

* 10 ml concentrated HNO_3 is added to each monthly sample.

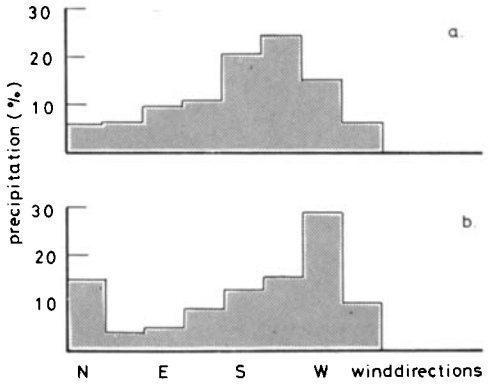

Fig. 3. Distribution of amount of precipitation in percent for 8 wind directions. a, Kastrup 12°.40E, 55°.38N average for the period 1952–1973. b, Keldsnor distribution for this investigation, 42 events.

monthly samples from Keldsnor and the rest of the country. The lead concentration in monthly samples from Keldsnor for 1975 was not significantly different from samples from the rest of the country. A higher lead concentration in monthly samples than in 24-hour samples was expected, as monthly samples contain more dry fallout than 24-hour samples, and as concentrated HNO_3 was added to the monthly samples to dissolve lead on particles.

Fig. 3 shows the distribution of the amount of precipitation for eight wind directions measured over a period of 20 years. The figure also shows the distribution of precipitation in this investigation. A secondary maximum in North is caused by one event with 13 mm precipitation.

5. Conclusion

Air masses from the Atlantic gave precipitation with a significantly lower lead concentration than air masses from Central Europe and England. Lead in bulk precipitation where the rain bearing air masses have moved from the Atlantic directly to Denmark is postulated to have Danish origin. It is estimated that about 2/3 of the lead deposition in the background area of Denmark is long range transported.

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ПЕРЕНОС СВИНЦА АТМОСФЕРОЙ С БОЛЬШИХ РАССТОЯНИЙ В ДАНИЮ

В Келдсноре, Лангеланд, Дания, измерялось содержание свинца в суммарных осадках (дождевая вода + осаждение пыли) в 42 24-часовых пробах, случайно распределенных во времени. Для нахож дения мест происхождения воздушных дождевых масс вычислялись их траектории. Показано, что средние концентрации свинца в суммарных осадках в случаях траекторий из Центральной Европы, Англии и Атлантики были существенно разными на уровне 0,1%. Из количества осадков и частоты событий переноса оценено, что около 2/3 осаждений свинца в сельской местности Дании, удаленной более, чем на 100 м от дорог, переносится с больших расстояний.