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SWEDISH WATER AND AIR POLLUTION RESEARCH LABORATORY

INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING

DEPOSITION OF AIR-BORNE MERCURY AROUND SWEDISH CHLOR-ALKALI PLANTS SURVEYED BY ANALYSES OF SNOW AND MOSS

Thomas Wallin

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DROTTNING KRISTINAS VÄG 47 D
BOX 5607
S-114 86 STOCKHOLM 5 · SWEDEN
TEL. 08-22 25 40

TELEGRAMS WATERRESEARCH

DJURGÅRDSGATAN 26
BOX 4052
S-400 40 GOTHENBURG 4 · SWEDEN
TEL. 031-42 01 60

DEPOSITION OF AIR-BORNE MERCURY AROUND SWEDISH CHLOR-ALKALI PLANTS SURVEYED BY ANALYSES OF SNOW AND MOSS

Thomas Wallin

Swedish Water and Air Pollution Research Laboratory,
Box 5207, S-402 24 Gothenburg, Sweden.

Abstract

The local deposition of air-borne mercury around a number of chlor-alkali plants situated in the middle and the northern parts of Sweden was surveyed by means of two different methods: (1) analyses of mercury in snow samples collected within a circular area of radius about 5 km around the plant and (2) analyses of mercury accumulated in the carpet-forming moss Hypnum cupressiforme, collected within a circular area of radius about 15 km.

The sampling localities were distributed mainly along 5 transects and at different distances from the emission source.

The mercury content of snow and moss tissue was determined by neutron activation analysis. Several similarities in the fall-out patterns were observed around the investigated plants. The highest mercury concentrations in snow and moss were found close to the plants and decreased rapidly with increased distance from the emission source within the first kilometres. At an average distance of 3-6 and 9-15 km the mercury concentrations in snow and moss respectively were usually not significantly higher than the estimated background levels (~0.1 ng/g in snow and ~120 ng/g in moss). Annual fall-out was estimated by the two methods and indicated that only a minor part of emitted mercury $\lesssim$10% is deposited locally. The major part seems to spread over very large areas and contributes to the back-ground deposition and probably also to the global circulation.

Introduction

The knowledge of the circulation of mercury in the environment is still rather limited especially considering air-borne mercury. There are, however, strong reasons to suppose that also air-borne mercury as well as mercury discharges to water and ground may be introduced, sooner or later, into biological cycles. As a consequence, the emissions of mercury to the atmosphere and the further transport mechanisms have been given increased attention (Hammond 1971, Jenne 1970, Joensuu 1971 and Weiss et al. 1971).

One of the main sources of mercury emissions of industrial origin to the atmosphere is, in Sweden, the electro-chemical industry producing chlorine and alkali using mercury cells.

The local deposition of mercury around five Swedish chlor-alkali plants was studied in the late winter of 1971 by analyses of mercury in snow samples (Jernelöv and Wallin 1973). This study was followed by a similar investigation in the summer of 1972 when a different method was used (Wallin, to be published). The latter was based on analysis of mercury accumulated in the carpet-forming moss Hypnum cupressiforme. The investigation comprised six different plants, three of which were identical to those studied by the snow method. The purpose of this paper is to compare the results and summarize the main conclusions reached with the two methods used.

Emissions

The mercury loss from a chlor-alkali plant to the atmosphere originates mainly from a) the ventilation air outlets where elementary mercury appears in a highly diluted vapourous state, b) hydrogen gas outlets, where elementary mercury appears in concentrations of about saturation level. Usually, the hydrogen gas is cooled to between $\pm$ 0 and + 10°C before emission. At some of the plants all or part of the hydrogen produced was used for synthesis purposes. The level above the ground of the outlets was 5-15 m. Usually the major loss

of mercury to the atmosphere from chlor-alkali plants originates from the ventilation air. Estimated total emissions are given in the table.

Methods and materials

Snow sampling Three snow samples were collected from each of 14 localities in the surroundings of each plant. These localities were distributed at different distances and in different directions from the plant to cover as well as possible a circular area with a radius of about 5 km. The samples were taken vertically through the snow cover by means of a glass tube in order to measure the average deposition over a long period. The age of the snow cover was estimated by meteorological data and ranged from 1-2 months. (For further details see Jernelöv and Wallin 1973).

Moss sampling Similarly, three moss samples were collected from about 25 localities around each plant. The distribution of the "moss localities" was partly influenced by the results obtained by the snow study. They were distributed at the distance of about 0.5--2.5--5--9--15 km along 5 transects in different directions from each plant to cover a circular area with a radius of about 15 km.

The regional background levels of mercury in snow and moss were estimated from samples collected at a distance of about 20 and 70 km from each plant respectively. The mercury concentration in snow and dried moss was determined by neutron activation analysis. (For Further details see Wallin, to be published).

Analysis of moss samples has proved to be a very useful tool in surveying heavy metal deposition from the atmosphere, locally around emission sources as well as over larger areas (Tyler 1971, Goodman and Roberts 1972). Mercury deposition has earlier been studied by moss analyses by Huckabee 1973, Rühling and Tyler 1973 and Yeaple 1972.

Results and discussion

The fall-out patterns

The fall-out patterns around the plants, reflected by snow and moss samples showed many features in common when comparing the two methods as well as the individual plants were compared. Typical fall-out patterns obtained by the two methods are presented in Fig. 1 and 2. The mercury level estimated by analysis of the three separate samples is pointed out at the different localities. The joint effect of mercury deposition from two plants situated close together is illustrated in Fig. 3.

The highest mercury concentrations were found with very few exceptions in the vicinity of the emission source and could sometimes exceed the background level of the region by a factor of 10 or even more. A decline in mercury concentration was recorded with increased distance from the source. This was most pronounced within the first few kilometers after which the regional background level seemed to be reached asymptotically. At an average distance of 3-6 and 9-15 km the mercury concentrations in snow and moss respectively were usually not significantly higher than the estimated background level. These levels were about 0.1 ng/g in snow and about 120 ng/g in moss. Fall-out curves based on average mercury concentration in snow and moss plotted against the distance from the three plants where both kinds of study were carried out are shown in Figs. 4-6.

The slopes of the curves suggest an exponential relationship between fall-out and distance. The slightly steeper course of the snow curve may be explained by a smaller mercury emission during the winter period due to lower temperature and a consequently lower evaporation in the cell-rooms. The contact between mercury vapours and cold air may also facilitate condensation and thereby cause a relatively higher deposition in the close vicinity of the plant.

Effects of dominating winds and local topography on the spreading patterns were suggested in at least some of the areas studied by the moss method. For example, the transects NNE and ENE in Fig. 2 showed relatively higher concentrations in moss.

Estimation of local fall-out quantities

Estimates were made of the annual fall-out of mercury within the investigated areas (Table). These calculations were based on assumptions whose influences on the fall-out were difficult to judge. (Jernelöv and Wallin 1973, Wallin to be published) They can, however, serve as an indication of the order of magnitude of the fall-out. Calculations of the deposition originating from the plant (i.e. background fall-out subtracted) over a circular area of radius 5 km gave higher values when based on the moss study (Table). The order of magnitude was 5 and 10 kg respectively by the two methods. The same fall-out over an area of radius 15 km calculated from the moss study ranged from 10-50 kg at the different plants. It should be noted, however, that the innermost area (radius 0-500 m) was omitted from these calculations due to lack of samples. However, the slopes of the curves suggest a high deposition within this area.

Compared to the emission data (Table) only a minor part of emitted mercury, up to ~10 %, were recovered within the investigated areas. The comparatively low fall-out % at plant 1 (Table) was difficult to explain. Anyhow, the major part of mercury emitted from the chlor-alkali industries seems to spread over very large areas and probably contributes to the background deposition and maybe also to the global circulation. Though only a minor fraction was traced locally this contamination deserves further attention. Very little is still known about the further transport mechanisms of mercury in the ground. Accumulation in soil, drainage to adjacent water systems

or even reintroduction to the atmosphere by evaporation are mechanisms which must be taken into consideration.

Comparison of the methods

The two methods used have both proved to be suitable when studying the local fall-out of mercury around a distinct emission source. The main differences between the methods are that the results obtained from the snow study are based on measurements in a snow cover about 1-2 months of age and evidently during winter conditions. Such "short" periods of course make this method sensitive to accidental fluctuations of the emissions and to variations of climatic factors. The moss method, on the contrary, is supposed to reflect a deposition over a longer period - approximately four years (=assumed average age of H. cupressiforme). Rühling and Tyler (1973) support the hypothesis that the uptake of heavy metal ions by the moss from the melting snow cover is mainly the same as from rainwater. The duration of the snow cover should consequently be of minor importance for the annual uptake. If this mechanism is valid also for mercury, the use of mosses as indicator of mercury deposition is to be preferred. Improvments of the method are necessary, however, to make possible more accurate quantitative estimates of fall-out. Further studies will be carried out to better establish the relation between observed mercury levels in the moss and the actual supply from the atmosphere.

References

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Table Estimated mercury emissions to the atmosphere and fall-out of mercury over circular areas around 8 chlor-alkali plants.

Plant No.	Estimated emissions to the atmosphere[xx] kg/year	Estimated fall-out originating from the plant kg/year			The same fall-out in % of estimated emissions		
		snow study	moss study		snow study	moss study	
		0,5-5 km	0,5-5 km	0,5-15 km	0,5-5 km	0,5-5 km	0,5-15 km
1	950	6,5	10,5	12	0,7	1,1	1,3
2	100	4,5	6,5	10,5	4,5	6,5	10,5
3	30	0,5	-	-	2,0	-	-
4	290	5,5	17,5	31	1,9	6,0	10,7
5[x]	(20)[x]	4,5	-	-	(21,5)	-	-
6	180	-	8,5	13		4,7	7,2
7	470	-	16,5	47		3,5	10,0
8	280	-	11,0	34		3,9	12,1

[x] This plant was closed in the winter of 1972. Furthermore the emission to the atmosphere was probably underestimated.

[xx] The estimates of emissions from 1, 2 and 4 are improved compared to in Jernelöv and Wallin in 1973.

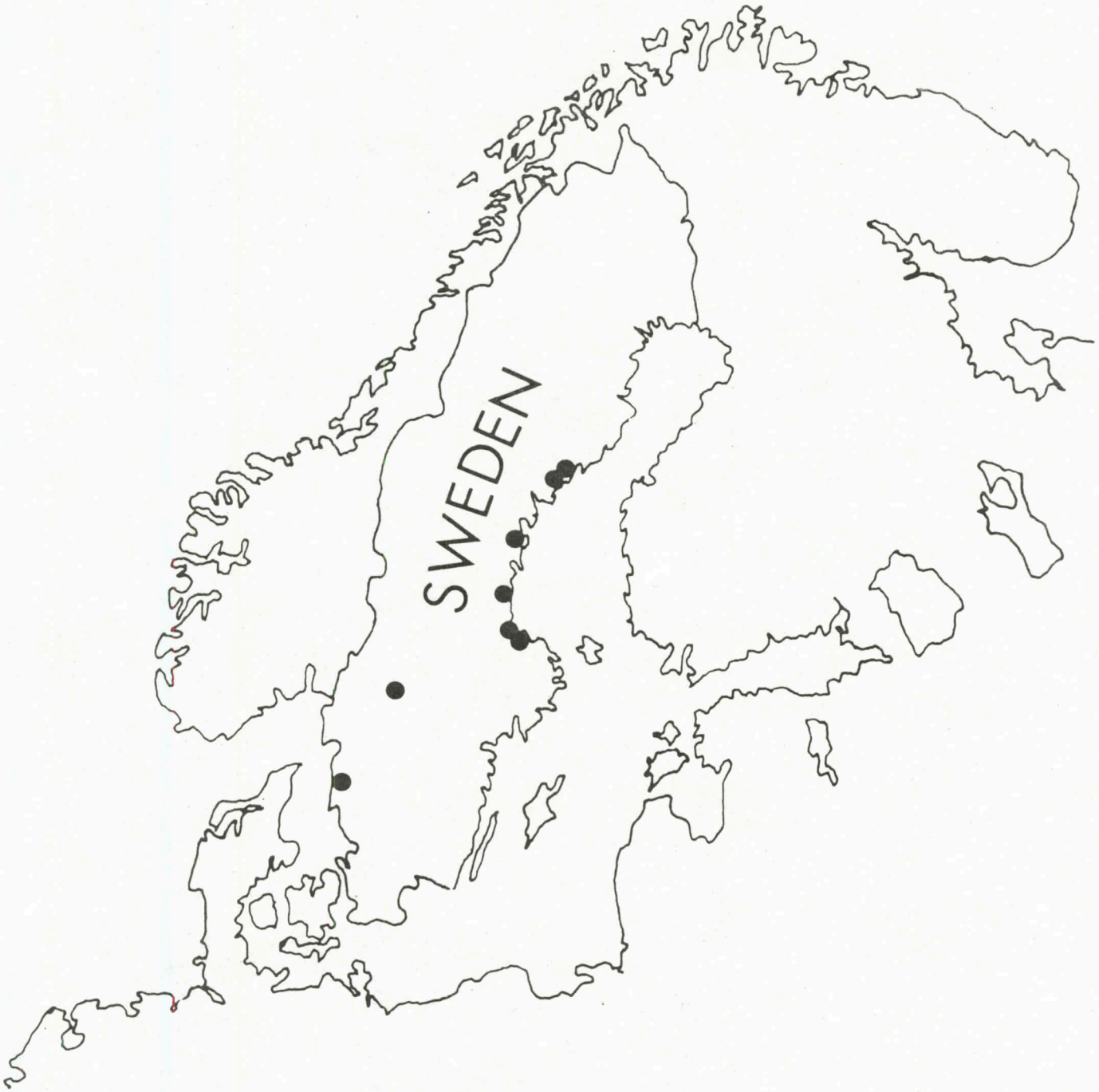
Text to the figures:

Fig. 1 Mercury in snow samples from the surroundings of a chlor-alkali plant.

Fig. 2 Mercury in moss samples from the surroundings of a chlor alkali plant.

Fig. 3 Mercury in moss samples from the surroundings of two nearby situated chlor-alkali plants at a reciprocal distance of 7 km.

Fig. 4-6 Concentration of mercury in snow and moss as a function of the distance from the emission source.



Geographical distribution of the investigated industries in Sweden

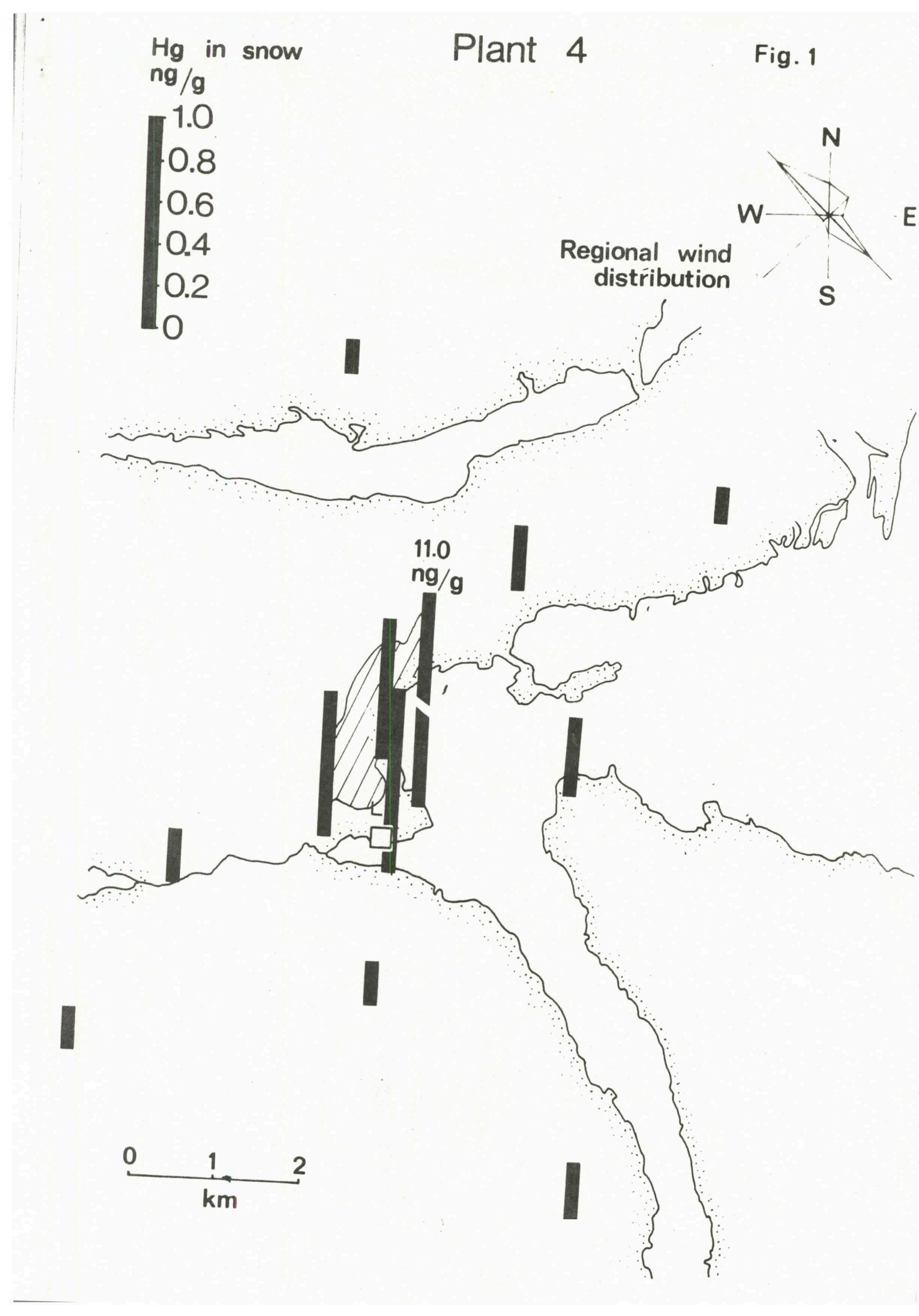

Hg in snow
ng/g
1.0
0.8
0.6
0.4
0.2
0
Plant 4
Fig. 1
N
W
E
S
Regional wind
distribution
11.0
ng/g
0
1
2
km

Fig. 2

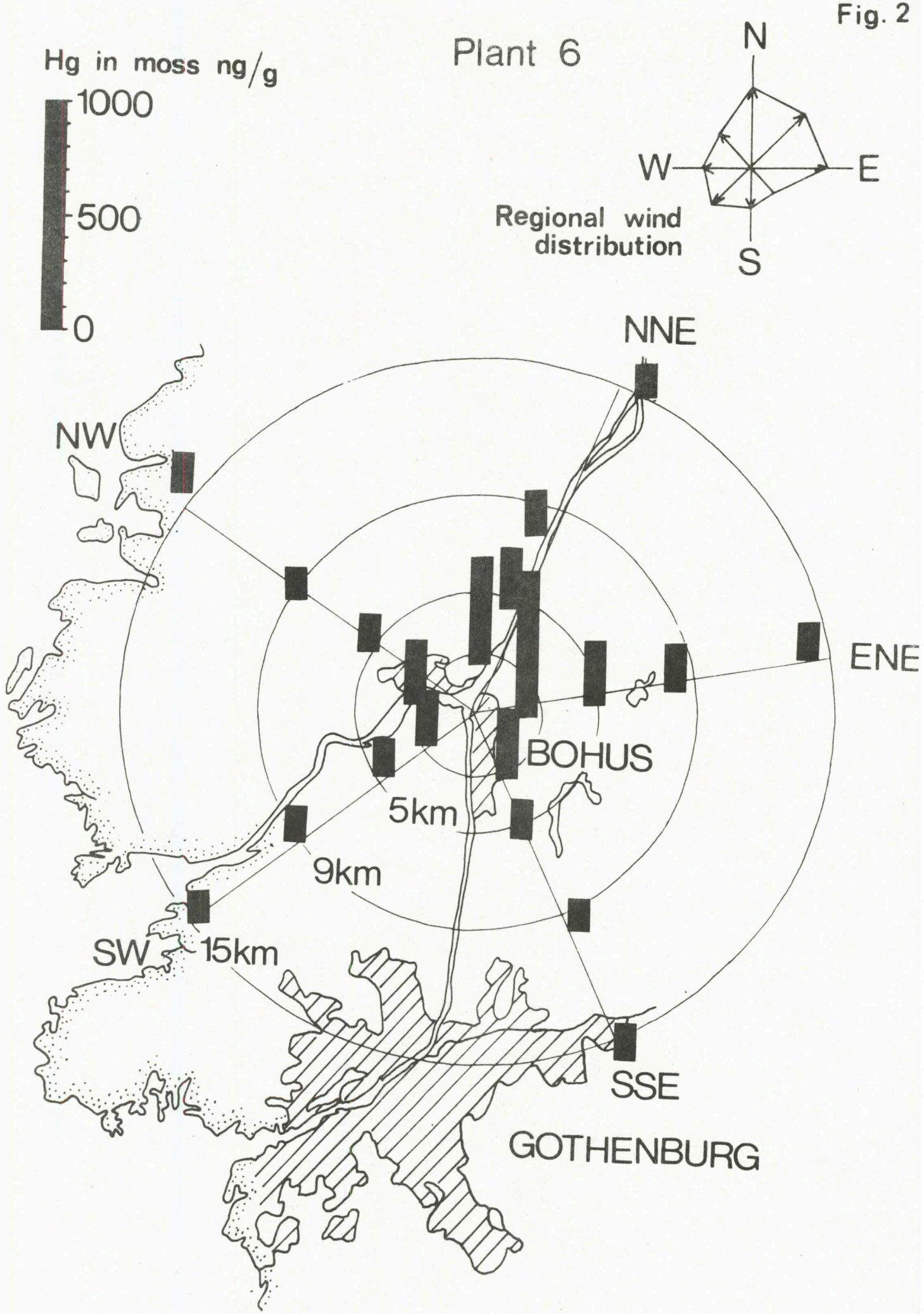

Plant 6
Hg in moss ng/g
1000
500
0
N
W
E
S
Regional wind distribution
NNE
NW
ENE
BOHUS
5km
9km
15km
SW
SSE
GOTHENBURG

Fig. 3

Plant 7 and 8

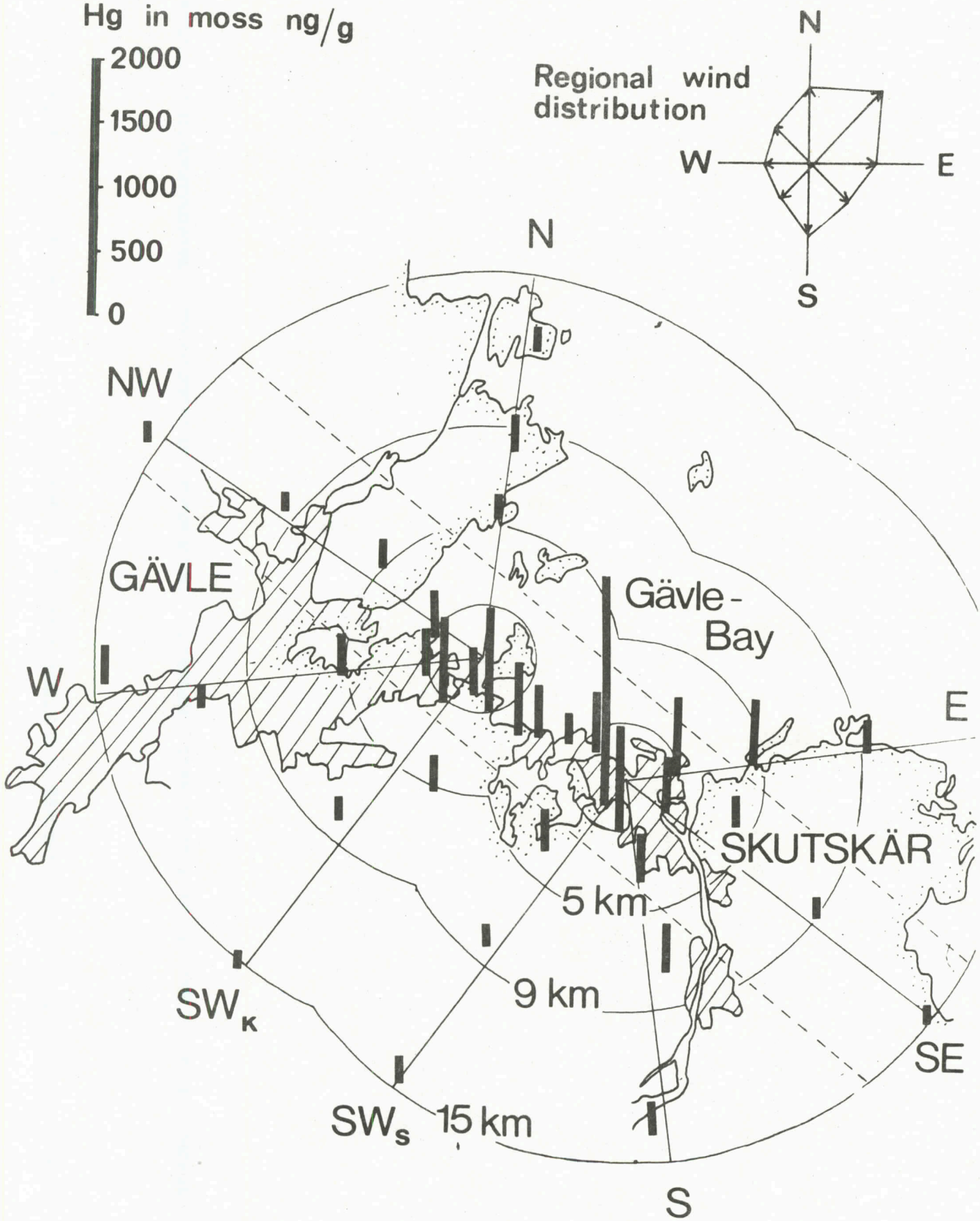


Fig. 4

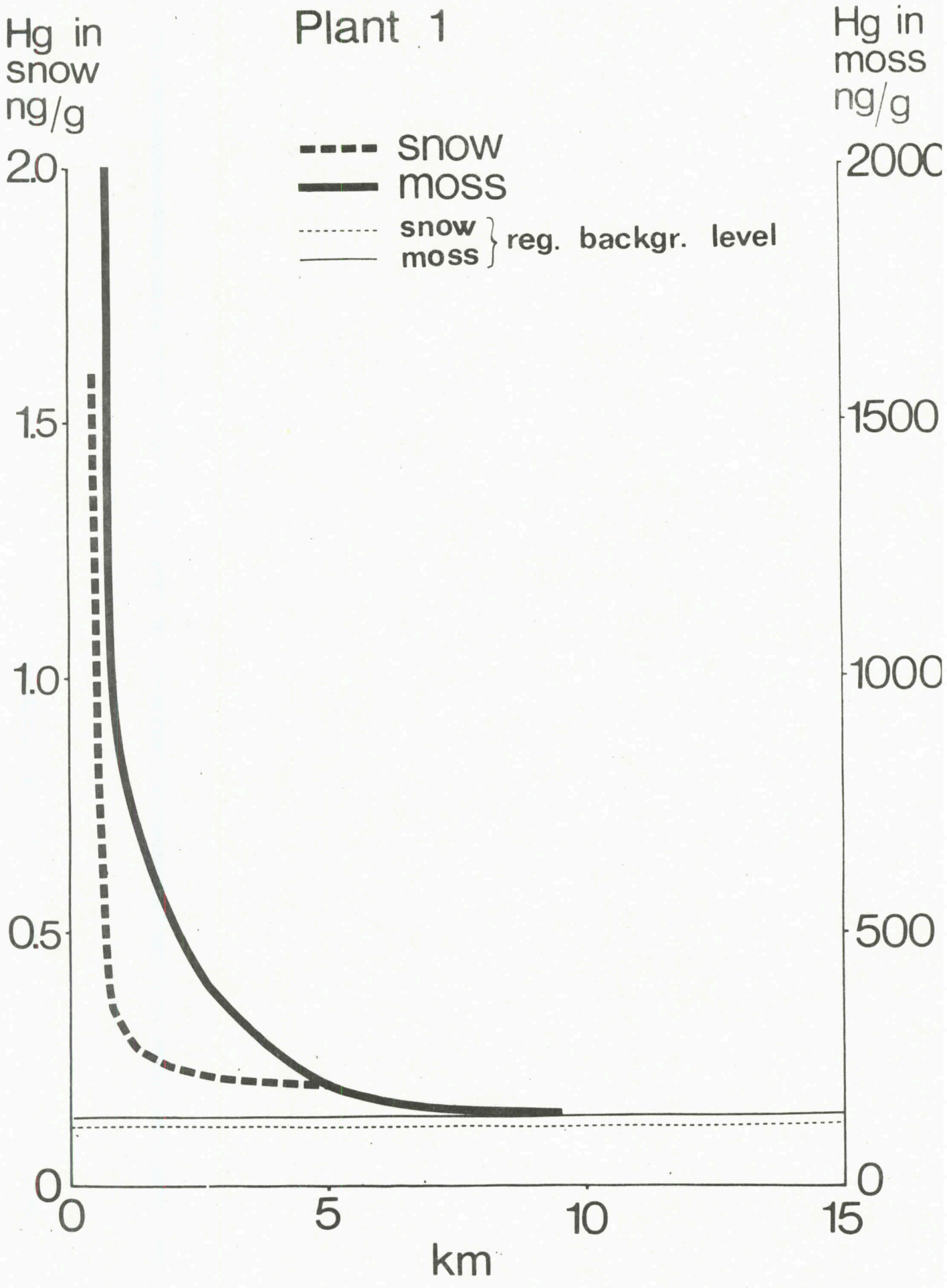

Plant 1
Hg in snow ng/g
Hg in moss ng/g
snow
moss
snow
moss
reg. backgr. level
2.0
1.5
1.0
0.5
0
2000
1500
1000
500
0
0
5
10
15
km

Fig. 5

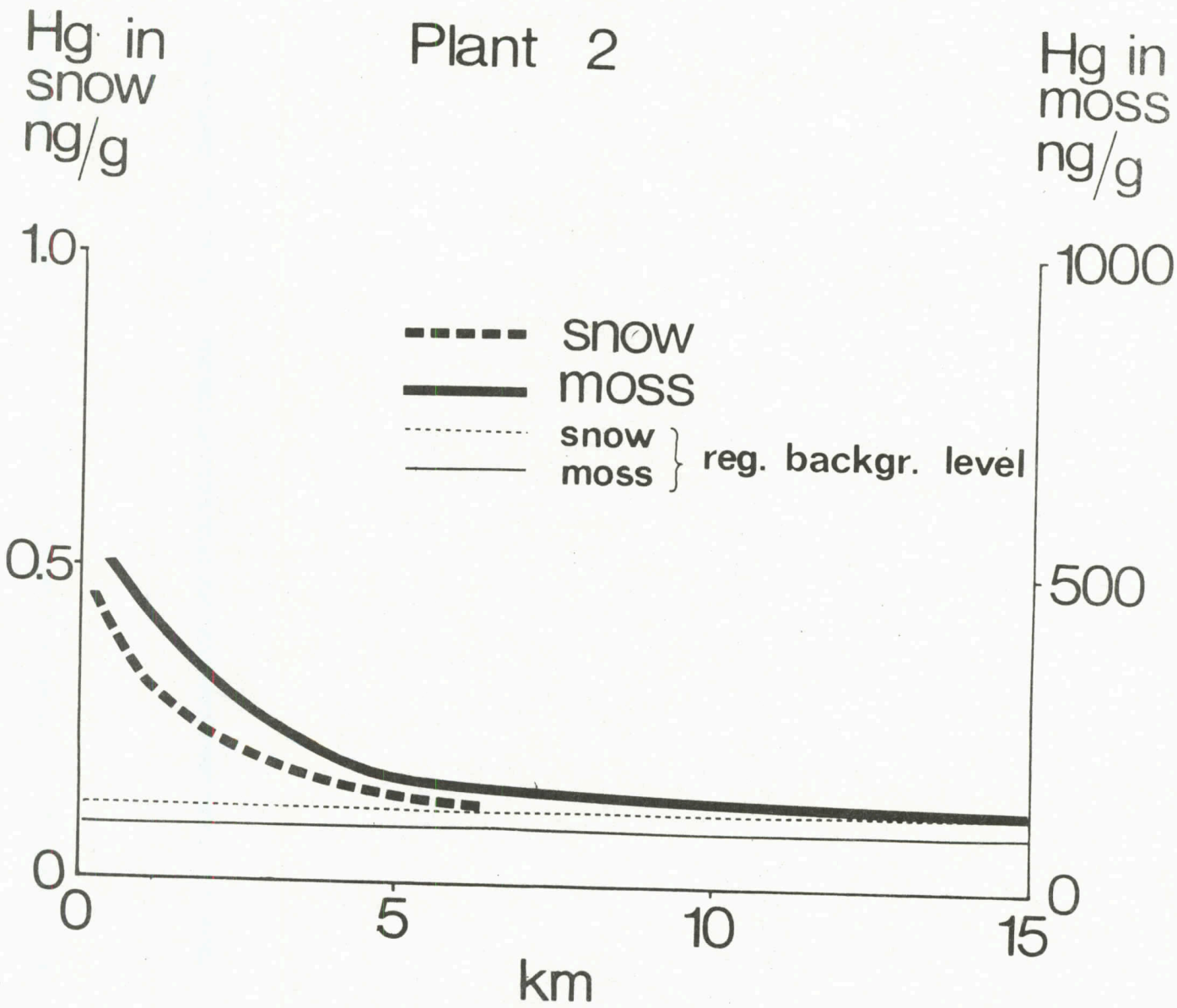
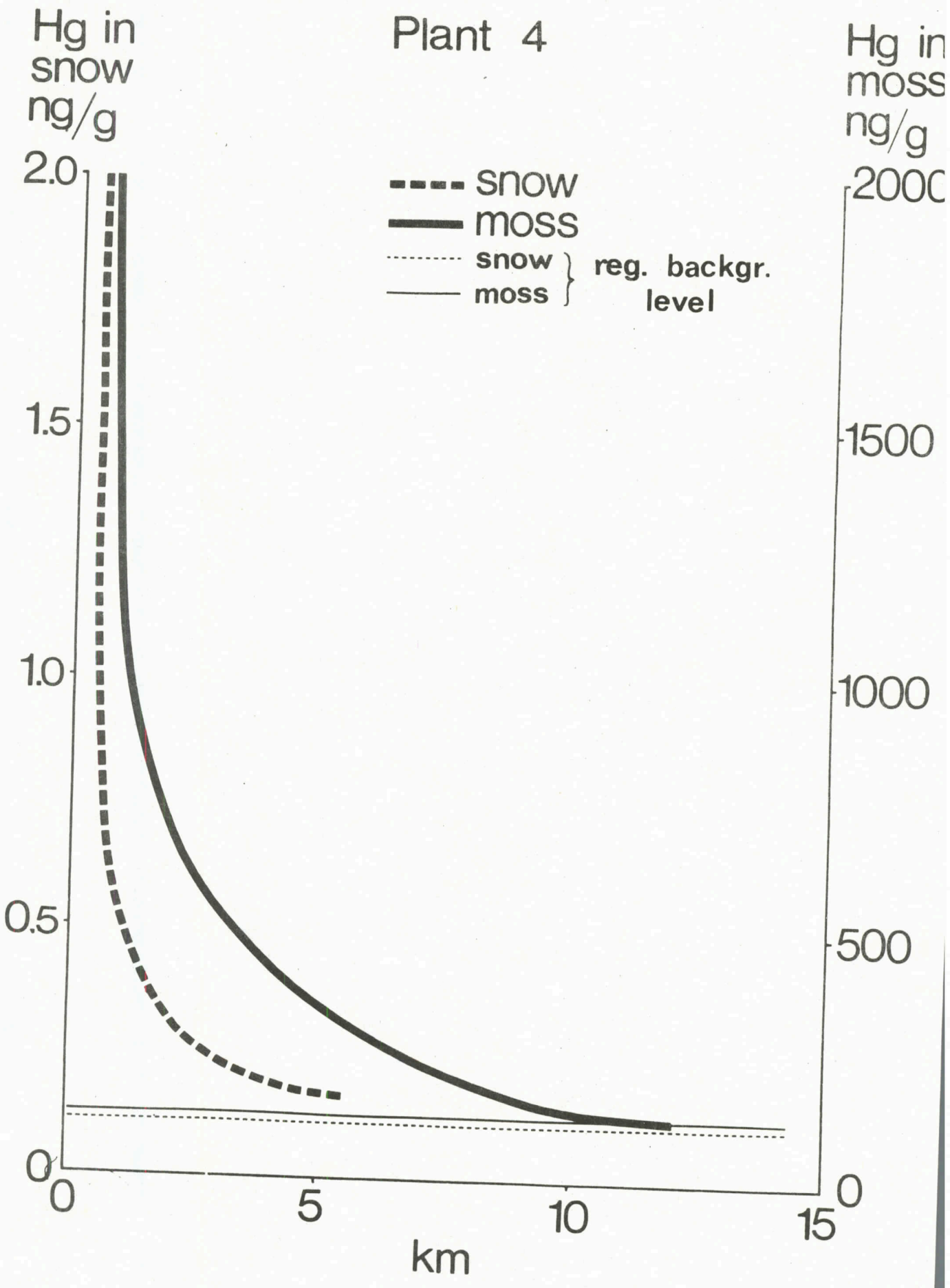

Hg in snow ng/g
Plant 2
Hg in moss ng/g
1.0
0.5
0
1000
500
0
snow
moss
snow
moss
reg. backgr. level
0
5
10
15
km

Fig. 6


Plant 4
Hg in snow ng/g
Hg in moss ng/g
snow
moss
snow
moss
reg. backgr. level
2.0
1.5
1.0
0.5
0
2000
1500
1000
500
0
0
5
10
15
km