

WET AND DRY SULPHUR DEPOSITION PATTERNS  
OVER EUROPE FOR THE PERIOD  
13.12.73 to 29.3.74

BY

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SUMMARY

On days with precipitation, a relation is established between mean  $SO_4$ -concentrations measured in precipitation at some LRTAP-stations and mean  $SO_2$ -concentrations, calculated with an one-layer Lagrangian dispersion model. The time period on which this relation is based is 107 days, 13th December, 1973 to 29th March, 1974. Using this relation, together with model calculations and the amount of precipitation analysed as fields every 12 hours, we have estimated the wet deposition field of  $SO_4$  over Europe for the period. Estimating the dry deposition field of  $SO_2$  by the same method as in ref. (1), and assuming the dry deposition of sulphate particles to be small, we have added dry deposition of  $SO_2$  and wet deposition of  $SO_4$  to give the calculated total deposition of sulphur. We have compared these estimates with the emissions.

WET DEPOSITION OF  $SO_4$

Our aim is to estimate the deposition of sulphur over Europe for the time period T, 13th December 1973 to 29th March, 1974. As for the wet deposition, the following method will be applied: First, we want to establish for the time period T a relation between the mean  $SO_4$ -concentrations measured in precipitation at some of the LRTAP-stations and the mean  $SO_2$ -concentrations for the days with precipitation, calculated with an one-layer Lagrangian dispersion model at the same stations (see ref. (1)). This model takes no account of the effects of precipitation on the  $SO_2$ -concentrations. Knowing the gridpoint values of precipitation and the model calculations of  $SO_2$ -concentrations every 12 hours, we can estimate for every gridpoint in T the following quantities:

- (a) the mean computed  $SO_2$ -concentration when there is precipitation,
- (b) the mean amount of precipitation when there is precipitation and
- (c) the number of 12 hours periods with precipitation

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By means of the relation mentioned above, which transforms mean computed  $SO_2$ -concentrations for days with precipitation to mean  $SO_4$ -concentrations in precipitation, and the quantities (a), (b) and (c), we can estimate the wet deposition of  $SO_4$  as a field over Europe in T.

### THE LRTAP MEASUREMENTS

The following symbols are used:-

T - the period of time, 13.12.73 to 29.3.74 (107 days)

N - the number of days in T (107)

$N_k$  - the number of days when precipitation is observed at the station k in T

k - index for station

i - index for day in T

$M_{ki}$  - the amount of precipitation measured at station k for day i

$C_{ki}$  - the  $SO_4$ -concentration measured in the precipitation at station k for day i

$$\bar{M}_k \equiv \frac{1}{N_k} \sum_{i=1}^N M_{ki} \quad (1)$$

$\bar{M}_k$  - the mean amount of precipitation on days when precipitation is observed at station k in T

$$\hat{C}_k \equiv \frac{1}{\bar{M}_k} \frac{1}{N_k} \sum_{i=1}^N C_{ki} M_{ki} \quad (2)$$

$\hat{C}_k$  - the "mean"  $SO_4$ -concentration (weighted with the amount of precipitation) measured in the precipitation that has fallen at station k in T.

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For the period T, we have calculated the quantities  $N_k$ ,  $\bar{M}_k$ ,  $\hat{C}_k$  and  $N_k \bar{M}_k \hat{C}_k$  for 64 stations scattered over Western Europe. The location of the stations are plotted on Fig. 1. The results are tabulated in Table 1. The quantity  $N_k \bar{M}_k \hat{C}_k$  is the wet deposition of  $SO_4$  at station k in T, plotted on Fig. 2. (The numbers on Fig. 2 are those from Table 1, transformed to  $[g SO_2/m^2]$ ). This estimate of the wet deposition of  $SO_4$  will later be referred to as estimate I.

Concentrations computed with a dispersion model:

The following symbols are used:

$q_{ki}$  - the  $SO_2$ -concentration computed with a dispersion model at station k for day i

$$\bar{q}_k \equiv \frac{1}{N_k} \sum_{i=1}^N q_{ki} \Delta_{ki} \quad (3)$$

$$\Delta_{ki} \begin{cases} = 1 & \text{for days with precipitation on station k} \\ = 0 & \text{for days with no precipitation on station k} \end{cases} \quad (4)$$

$\bar{q}_k$  - the mean computed  $SO_2$ -concentration for days with precipitation at station k in T. The same days contribute to  $\bar{q}_k$  in (3) as to  $\hat{C}_k$  in (2).

A relation between  $\hat{C}$  and  $\bar{q}$

For 27 stations, we have computed the quantities  $\bar{M}_k$ ,  $\hat{C}_k$  and  $\bar{q}_k$  in the way described above for the period T, tabulated in Table II. On Fig. 3, the values of  $\hat{C}_k$  for these stations are plotted against  $\bar{q}_k$ . We want to establish a relation between  $\hat{C}$  and  $\bar{q}$ . Simple linear regression gives the following line:

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$$\hat{C} = a_1 \bar{q} + b_1 \quad (5)$$

$$a_1 = 0.159 \frac{[\text{mg SO}_4/\text{l}]}{[\mu\text{g SO}_2/\text{m}^3]}$$

$$b_1 = 1.652 [\text{mg SO}_4/\text{l}]$$

$$R = 0.769 \quad (\text{correlation coefficient})$$

For the low values of  $\bar{q}$ , this straight regression line overestimates  $\hat{C}$ , (see Fig. 3).

We have chosen the following curve as an alternative:

$$\begin{aligned} \hat{C} &= a_2 \bar{q} \quad , \text{ for } \bar{q} < 12 \mu\text{g SO}_2/\text{m}^3 \\ \hat{C} &= a_3 \bar{q}^{\frac{1}{2}} - b_3, \text{ for } \bar{q} \geq 12 \mu\text{g SO}_2/\text{m}^3 \end{aligned} \quad (6)$$

$$a_2 = 0.306 \frac{[\text{mg SO}_4/\text{l}]}{[\mu\text{g SO}_2/\text{m}^3]}$$

$$a_3 = 1.375 \frac{[\text{mg SO}_4/\text{l}]}{[\mu\text{g SO}_2/\text{m}^3]^{\frac{1}{2}}}$$

$$b_3 = 1.087 [\text{mg SO}_4/\text{l}]$$

From Fig. 3, we can see that (6) gives a better estimate of  $\hat{C}$  than does the linear regression line (5).

#### Precipitation fields

Precipitation fields have been prepared manually every 12 hours for the period T. Precipitation data have been collected from various sources available at the Norwegian Meteorological Institute. Where no information on the amount of precipitation was available, an interpolation procedure

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has been applied, taking into account the weather situation. Analysed surface weather maps have been used in this connection.

Wet deposition of  $SO_4$  as a field (estimate II)

All the information we need in order to estimate the wet deposition field of  $SO_4$ , is now available. Knowing gridpoint values of precipitation and model calculations of  $SO_2$ -concentrations every 12 hours in T, we are able to estimate, for every gridpoint, the quantities:

- (a) the mean computed  $SO_2$ -concentration when precipitation is falling (using formulas similar to (3) and (4), and 12 hours time resolution).
- (b) the mean amount of precipitation when precipitation is falling (similar to (1) and 12 hours time resolution),
- (c) the number of 12 hours periods with precipitation

We use relation (6) to transform the quantity (a) to (d): mean  $SO_4$ -concentration in precipitation for every gridpoint.

The product of the quantities (d), (b) and (c) gives us the wet deposition of  $SO_4$  as a field in the region of calculation for the period T (estimate II). The results are shown on Fig. 4. All numbers have been transformed to  $[g SO_2/m^2]$ .

At the LRTAP-stations, we now have two different estimates of the wet deposition of  $SO_4$ .

- Estimate I: from the measurements at the LRTAP-stations, see page (4), Fig. 2 and Table I.
- Estimate II: (the method is explained above), as a field in the region of calculation, Fig. 4.

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To make comparison and check of the field estimate II against the station estimate I easier, we have placed Fig. 2 and Fig. 4 together, as Fig. 5.

As a total, the two estimates fit quite well, in some regions better than elsewhere. In the region to the east, south and over the sea, we have no check points. The precipitation data are here quite scattered, and the reliability of estimate II is less than in the central regions.

An interesting region is the north-western part of southern Norway. Here, the estimates of the wet deposition field of  $\text{SO}_4$  drop by a factor of ten over a distance of one grid-length (127 km), going from south to north (Fig. 4). The "clean" region to the north results from a negative correlation between precipitation and large computed  $\text{SO}_2$ -concentrations. More to the south, this correlation becomes positive, and together with large amounts of precipitation for south-westerly winds because of topography, the result is a large wet deposition of  $\text{SO}_4$ , as seen on Fig. 4.

In south-eastern Norway, wind directions from south to south-east also give orographic effects. With a positive correlation between precipitation and large computed  $\text{SO}_2$ -concentrations in this region, the result must be large values on the estimates presented on Fig. 5. As estimate I (from measurements at the LRTAP-stations) shows, this region has the greatest wet deposition of  $\text{SO}_4$  (see Fig. 2).

In other areas, there are some systematic deviations between the two estimates. In France for example, estimate I gives  $\text{SO}_4$ -depositions twice as great as estimate II. In Switzerland, the situation is reverse.

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Total deposition of sulphur

Under dry conditions, various authors (Heard and Wiffen, 1969; Georgii et al., 1970), have found the diameters of atmospheric sulphate particles typically in the (0.1 - 1)  $\mu\text{m}$  range. Particles of this size are found to have velocities of deposition about an order of magnitude smaller than the corresponding values established for  $\text{SO}_2$  (Chamberlain, 1966). The measurements show that the  $\text{SO}_2$ -concentrations are usually larger than the  $\text{SO}_4$ -concentrations. This indicates that dry deposition of sulphate particles is of the order of 10 % of the dry deposition of  $\text{SO}_2$ . We have ignored this contribution to the total sulphur deposition.

We have added wet deposition of  $\text{SO}_4$  to dry deposition of  $\text{SO}_2$ , to give the total deposition of sulphur, all numbers being transformed to  $[\text{g SO}_2/\text{m}^2]$ . The resulting pattern is shown on Fig. 7. As can be seen from Fig. 4 and Fig. 6, the similarity between Fig. 7 and Fig. 6 is striking. This shows that the estimated dry deposition of  $\text{SO}_2$  in most regions dominate, compared to the estimated wet deposition of  $\text{SO}_4$ . There are three regions where the reverse situation is the case, see Fig. 4 and Fig. 6: southern part of Norway, northern part of Italy, and in north England and Scotland. In all these regions, there are strong orographic effects.

If we subtract the amount of  $\text{SO}_2$  emitted in T from the estimated total deposition on Fig. 7, we get the numbers on Fig. 8. The emission field of  $\text{SO}_2$  used in all model calculations and comparisons is shown on Fig. 9, which also shows the extent of the region of calculation. The minus-regions on Fig. 8 are emitting more sulphur than they are receiving in the period T, thus exporting sulphur. The plus-regions are import regions. The unit on Fig. 8 is  $[0.1 \text{ g SO}_2/\text{m}^2]$ . Integrated over the whole region of calculation, we get the following numbers for the period T:



Dry deposition	:	6,7 . 10 <sup>6</sup>	tones SO <sub>2</sub>
Wet deposition	:	1,9 . 10 <sup>6</sup>	"
Total deposition	:	8,6 . 10 <sup>6</sup>	"
Total amount emitted	:	15,4 . 10 <sup>6</sup>	"
Total deposition minus total amount emitted:		- 6,8 . 10 <sup>6</sup>	"

The last number can be interpreted as flux out of the region of calculation.

It can be added that the available information on the amount of precipitation covering eastern Europe and Soviet Union are not as complete as elsewhere, and the total amount of precipitation in these regions is probably an underestimate. The consequence of this is that the wet deposition may also be underestimated. As a budget, the numbers presented above must be applied with care.

As regards the uncertainties in the estimate of wet and dry deposition fields of sulphur, based on model calculations, we can make the following list:

The model takes no account of the effects of precipitation on the SO<sub>2</sub>-concentrations. Certain parameters in the model ought to have been changed. The emission field of SO<sub>2</sub> ought to have been modified in some regions. The emissions are not dependent on time.

In the model calculations, we have used winds observed in the 850 mb surface for the transportation of the pollutants. This will as a mean, give too fast a transportation, and the direction will go too much to the right.

Further, it can be remarked that the time period T covers a winter period. We know that there can be a considerable

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difference between summer and winter situations as regard the transport of air pollution.

Changed frequency and amount of precipitation, change in the strength of the mean westerly wind and cyclonic activity will affect the deposition pattern of sulphur. Extrapolation in time from the estimates presented here, will add quite a lot to the uncertainties involved.

REFERENCES

- (1) Eliassen, Anton and Saltbones, Jørgen, 1975, A Simple Lagrangian Dispersion Model Applied to Sulphur Pollution over Europe.
- (2) Heard M.J. and Wiffen R.D. (1969), Atmospheric Environment 3, 337-340.
- (3) Georgii H.W., Jost D. and Vitze W. (1970), Berichte des Institutes für Meteorologie und Geophysik der Universität Frankfurt am Main, Nr. 23.
- (4) Chamberlain A.C. (1966), Proc. R. Soc. A. 296, 45-70.

Table I: Wet deposition of SO<sub>4</sub> at the LRTAP-stations in the time period T, 13.12.73 to 29.3.74

STATIONS	N <sub>k</sub>	$\bar{M}_k$ (mm)	$\hat{C}_k$ (mg SO <sub>4</sub> /l)	N <sub>k</sub> $\bar{M}_k$ $\hat{C}_k$ (mg SO <sub>4</sub> /m <sup>2</sup> )
A02	18	4.70	6.60	559.
CH1	45	5.07	0.96	219.
CH2	7	4.14	4.50	131.
CH3	9	4.57	8.27	340.
CH4	12	2.18	5.95	155.
CH5	17	6.48	3.10	342.
CH6	13	10.30	6.67	893.
D01	6	7.32	11.07	486.
D03	14	5.04	4.38	309.
DK1	71	13.94	1.01	998.
DK2	34	3.55	4.16	503.
DK3	30	4.71	4.15	586.
DK4	24	5.58	5.17	692.
DK5	29	3.86	5.05	565.
DK6	29	3.86	5.44	609.
F01	34	5.02	5.77	984.
F02	20	12.13	4.30	1043.
F03	35	7.82	2.60	711.
F04	8	15.66	2.44	306.
F05	31	6.88	6.34	1352.
F06	27	10.90	3.29	968.
IC1	44	6.71	1.74	513.
N01	46	11.53	4.06	2151.
N03	67	8.24	3.50	1931.
N05	52	7.22	4.44	1668.
N06	65	5.37	3.74	1304.
N07	65	7.16	4.90	2281.
N08	65	12.15	1.78	1404.
N09	60	12.20	1.87	1365.
N10	64	5.58	4.24	1516.
N14	44	8.73	2.20	844.
N15	59	5.66	0.46	154.
N16	42	3.30	1.97	273.
N18	33	6.44	3.58	761.
N19	22	5.38	4.61	546.
N20	39	5.64	3.30	727.
N22	36	4.20	5.11	772.
N23	42	6.11	5.47	1404.
N24	60	7.80	1.78	834.
N26	38	7.79	3.64	1077.
N27	62	3.61	1.23	274.
N28	34	2.65	0.92	83.
NL1	42	4.02	7.85	1326.
NL2	48	4.38	4.80	1010.
NL3	44	3.59	9.09	1437.
NL4	31	5.59	6.21	1075.
S01	37	4.93	5.38	982.
S02	49	2.47	2.61	315.
S03	18	6.48	4.08	476.
S04	27	4.60	4.14	515.
S05	32	5.82	1.41	263.
S06	5	2.36	5.72	67.
S07	29	4.63	4.91	659.
S08	20	5.71	7.09	809.
S09	27	5.23	4.54	642.
S10	30	5.59	1.05	177.
SF1	38	4.21	2.65	425.
SF2	50	2.21	2.95	327.
SF3	64	2.49	3.47	553.
SF4	54	3.06	1.57	259.
SF5	49	2.20	0.93	99.
UK1	48	3.56	3.51	599.
UK2	71	7.00	1.74	865.
UK12	60	5.46	2.34	765.

Table I:

- $N_k$  - number of days when precipitation is observed at station k.
- $\bar{M}_k$  - mean amount of precipitation in (mm), see eq. (1).
- $\hat{C}_k$  - "mean"  $SO_4$ -concentration in the precipitation in (mg  $SO_4/\ell$ ), see eq. (2).
- $N_k \bar{M}_k \hat{C}_k$  - wet deposition of  $SO_4$  at station k in (mg  $SO_4/m^2$ ).

All numbers refer to the period T: 13/12-73 to 27/3-74, (107 days). As for the geographic position of the stations, see Figure 1.

Table II: Calculated mean SO<sub>2</sub>-concentrations for days with precipitation, and "mean SO<sub>4</sub>-concentration in precipitation in the time period T at some of the LRTAP-stations.

STATION	Measured mean SO <sub>2</sub> for the total period (µg SO <sub>2</sub> /m <sup>3</sup> )	Measured mean SO <sub>2</sub> for days with precipit. (µg SO <sub>2</sub> /m <sup>3</sup> )	$\bar{q}_k$ (see eq (3)) (µg SO <sub>2</sub> /m <sup>3</sup> )	$\hat{C}_k$ (see eq (2)) (mg SO <sub>4</sub> /ℓ)
DK2	5.7	4.2	10.3	4.16
DK3	5.5	5.0	13.2	4.15
DK4	10.3	10.4	19.8	5.17
DK5	8.9	8.3	17.2	5.05
DK6	8.4	8.6	18.6	5.44
SF1	7.0	7.4	10.6	2.65
SF2	8.6	10.1	9.8	2.95
SF3	15.6	14.8	9.2	3.47
SF4	8.6	9.0	6.8	1.57
SF5	7.0	8.1	2.6	0.93
UK1	28.5	27.3	27.7	3.51
UK2	10.2	8.4	11.9	1.74
A02	16.1	14.0	30.6	6.60
D02	37.8	37.6	-	-
D03	17.8	15.1	16.6	4.38
NL1	29.0	29.0	35.9	7.85
NL2	23.0	23.0	32.3	4.80
NL3	19.2	19.2	26.4	9.09
NL4	36.2	36.4	36.6	6.21
N01	8.6	10.2	12.8	4.06
N03	7.3	7.9	11.7	3.50
N09	7.4	5.9	6.1	1.87
N22	13.5	11.6	12.6	5.11
N23	9.6	10.9	14.5	5.47
N25	4.3	-	-	-
S03	7.3	8.4	14.3	4.08
S04	5.6	6.7	12.4	4.14
S05	3.7	4.6	5.1	1.41
F01	23.4	19.1	17.0	5.77

The period T: 107 days; 13/12-73 to 29/3-74.



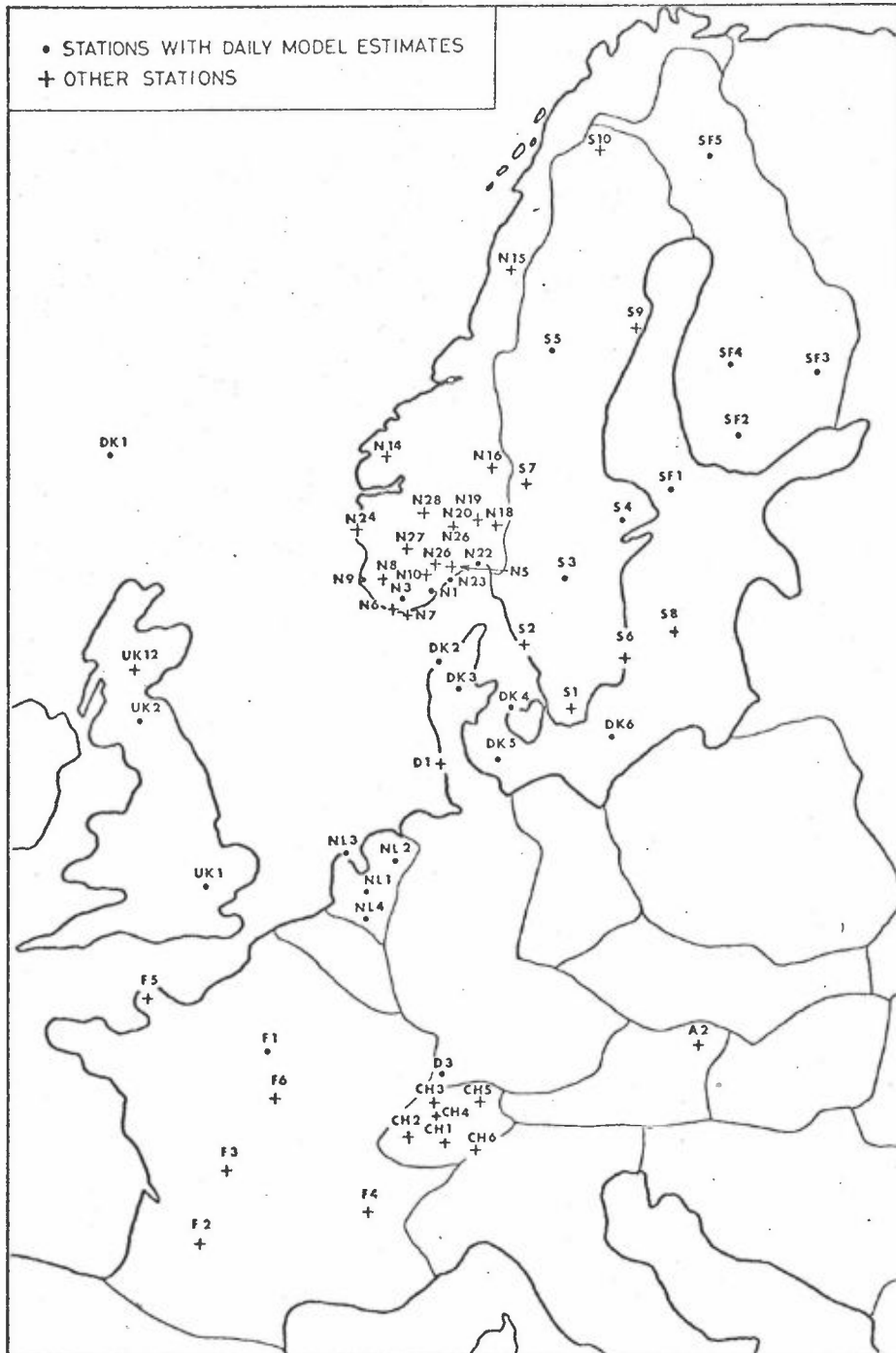


Figure 1: The LRTAP stations  
(one station is missing: IC 1 (Rjupnahød))



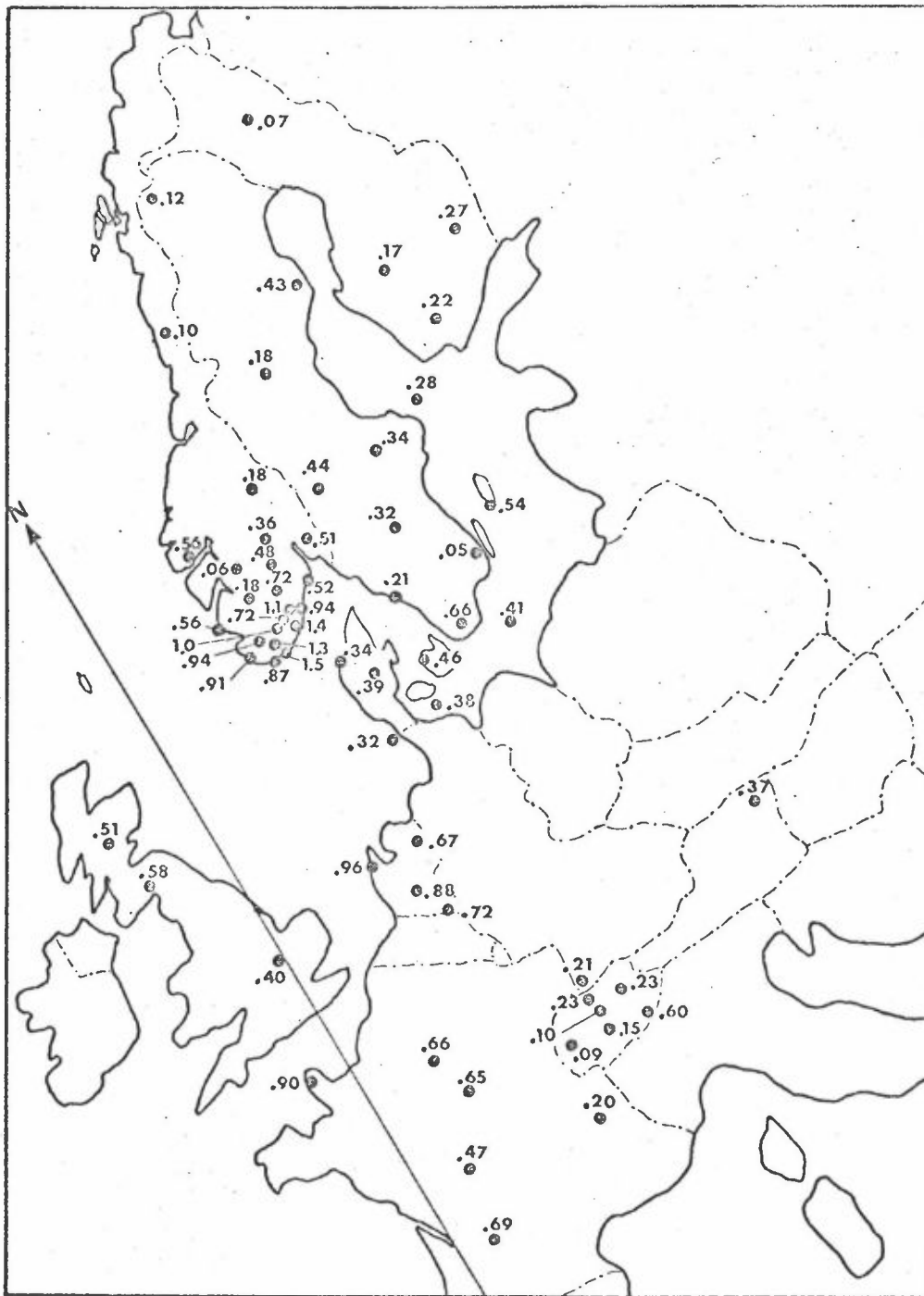


Figure 2: Estimated wet deposition of  $SO_4$  in T at 63 LRTAP stations (Estimate I).

T: (107 days) 13.12.73 → 29.03.74

Unit:  $[gSO_2/m^2]$

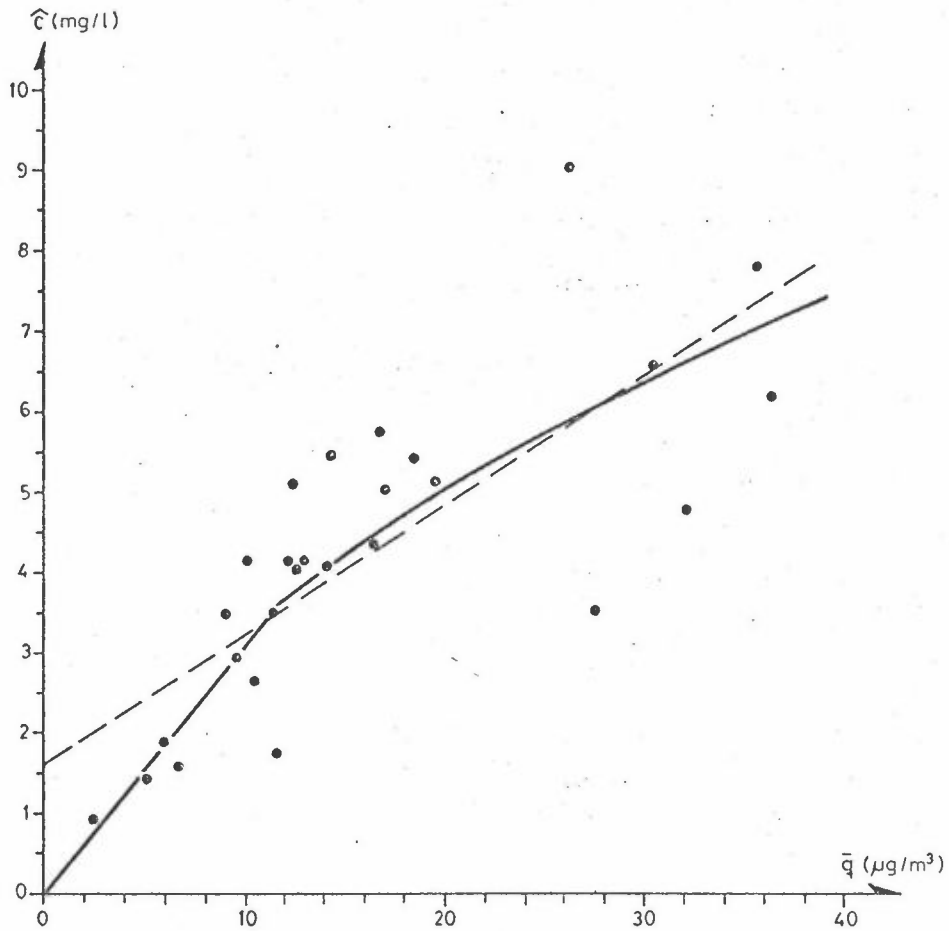


Figure 3:  $\hat{C}_k$  plotted against  $\bar{q}_k$  for 27 LRTAP stations.

$\hat{C}_k$  defined by eq. (2), [mg  $\text{SO}_4/\text{l}$ ]  
 $\bar{q}_k$  " " " (3), [ $\mu\text{g SO}_2/\text{m}^3$ ]

----- simple linear regression line, eq. (4)

———— the relation we have used, eq. (5)

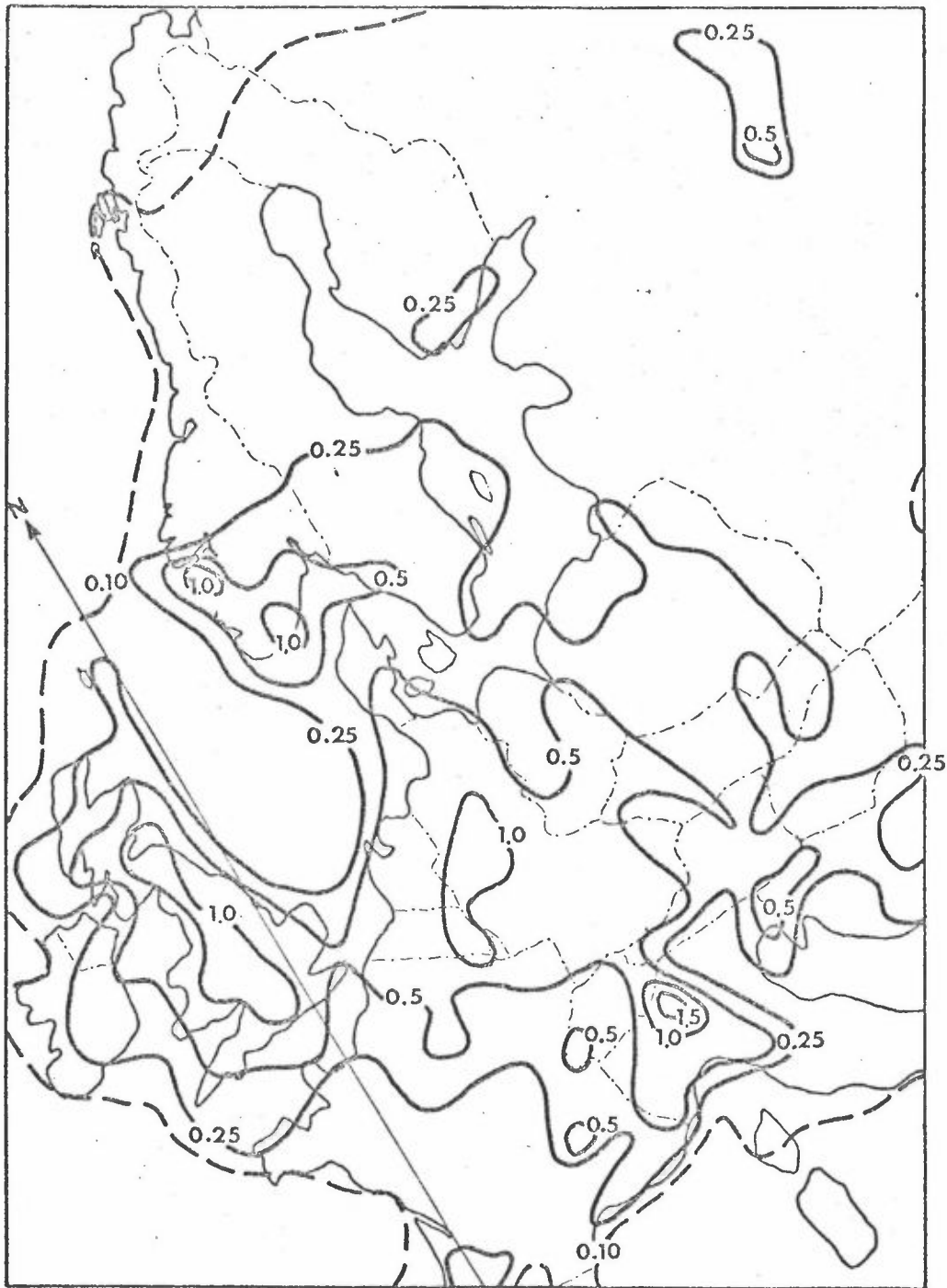


Figure 4: Estimated wet deposition of SO<sub>4</sub> in T as a field over Europe (Estimate II).

T - as on Fig. 2

Unit: [g SO<sub>2</sub>/m<sup>2</sup>]

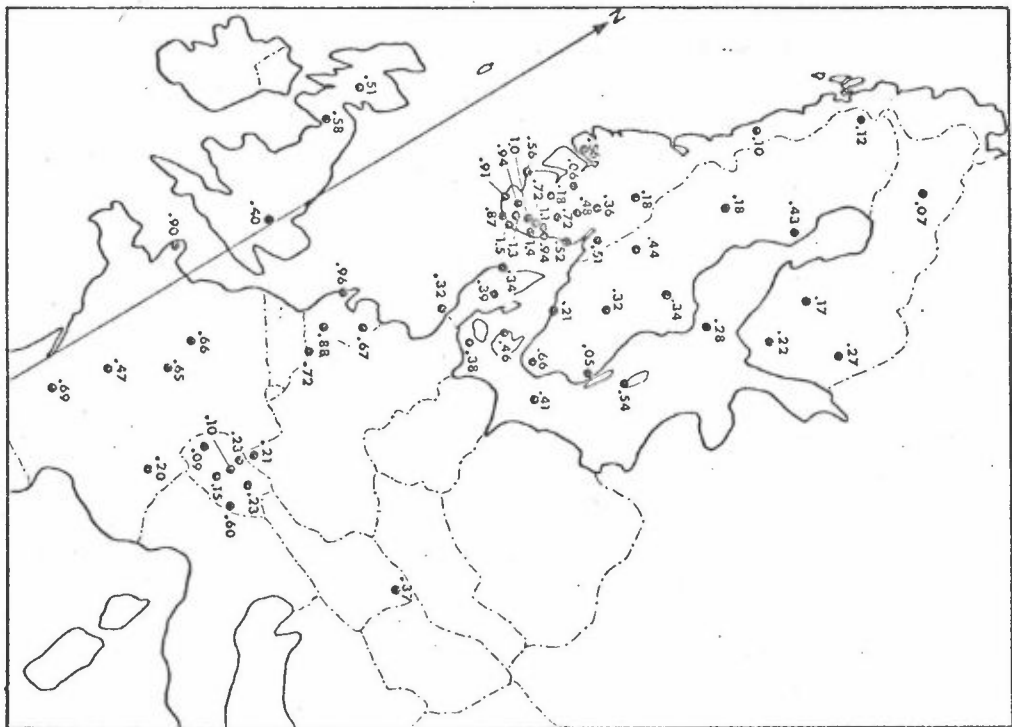
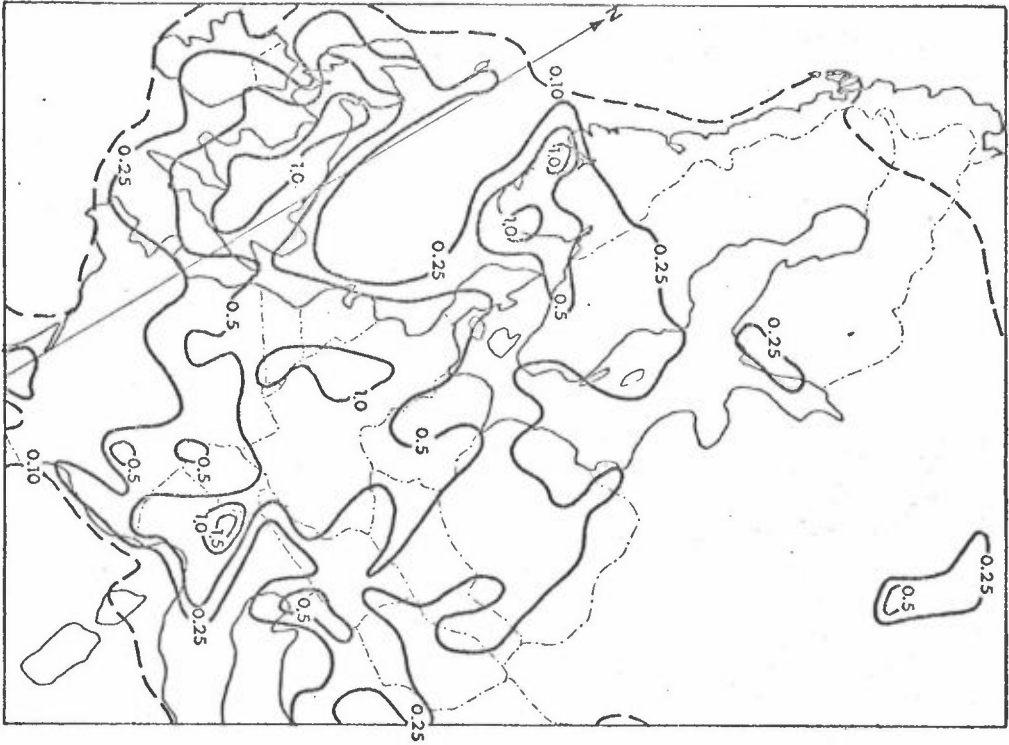


Figure 5 : Fig. 2 and Fig. 4 placed together to make comparison easier.  
Units:  $[g SO_2/m^2]$

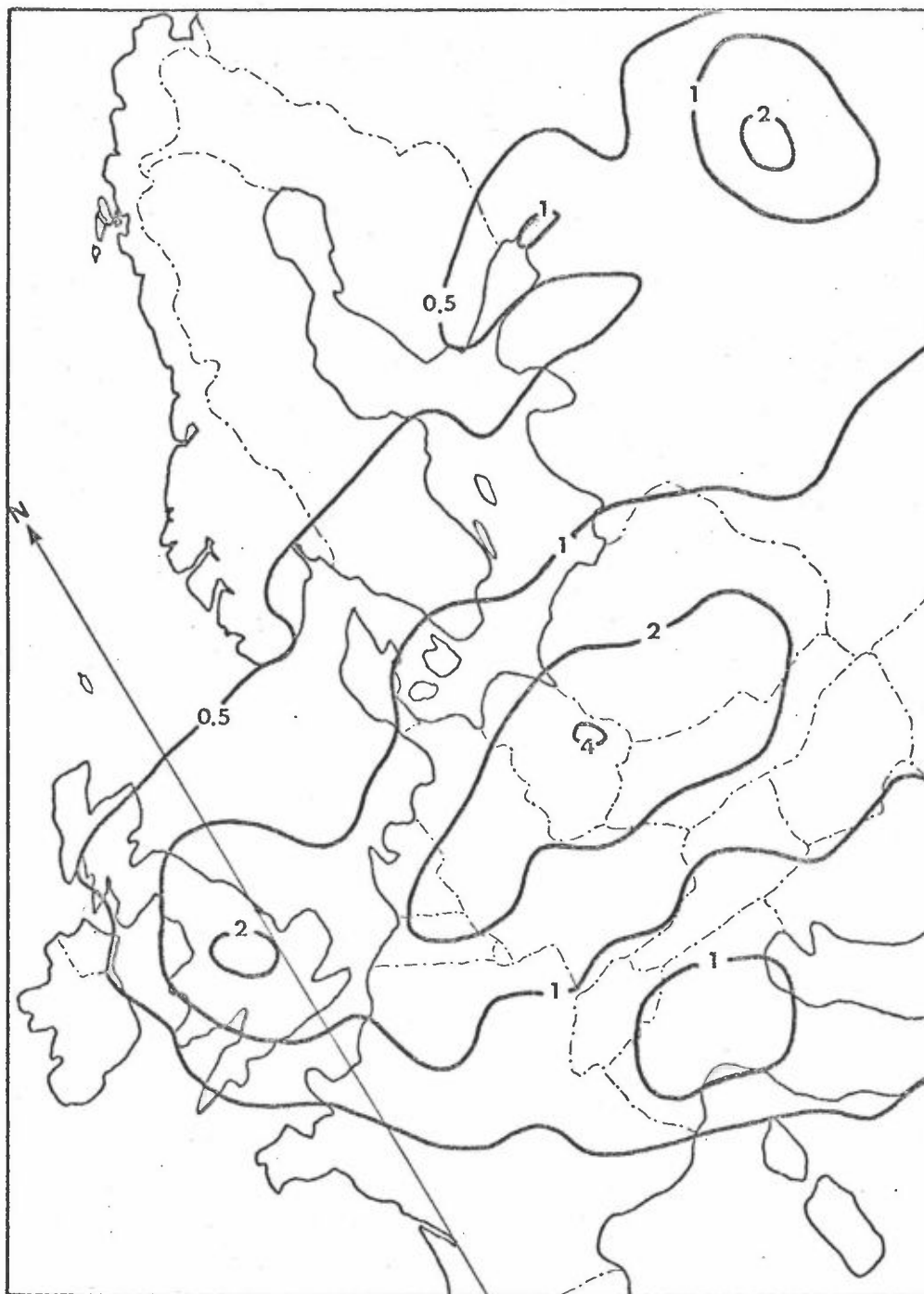


Figure 6 : Estimated dry deposition of  $\text{SO}_2$  in T as a field over Europe.

T - as on Fig. 2

Deposition velocity:  $v_g = 8 \cdot 10^{-3} \text{ ms}^{-1}$

Unit:  $[\text{g SO}_2/\text{m}^2]$

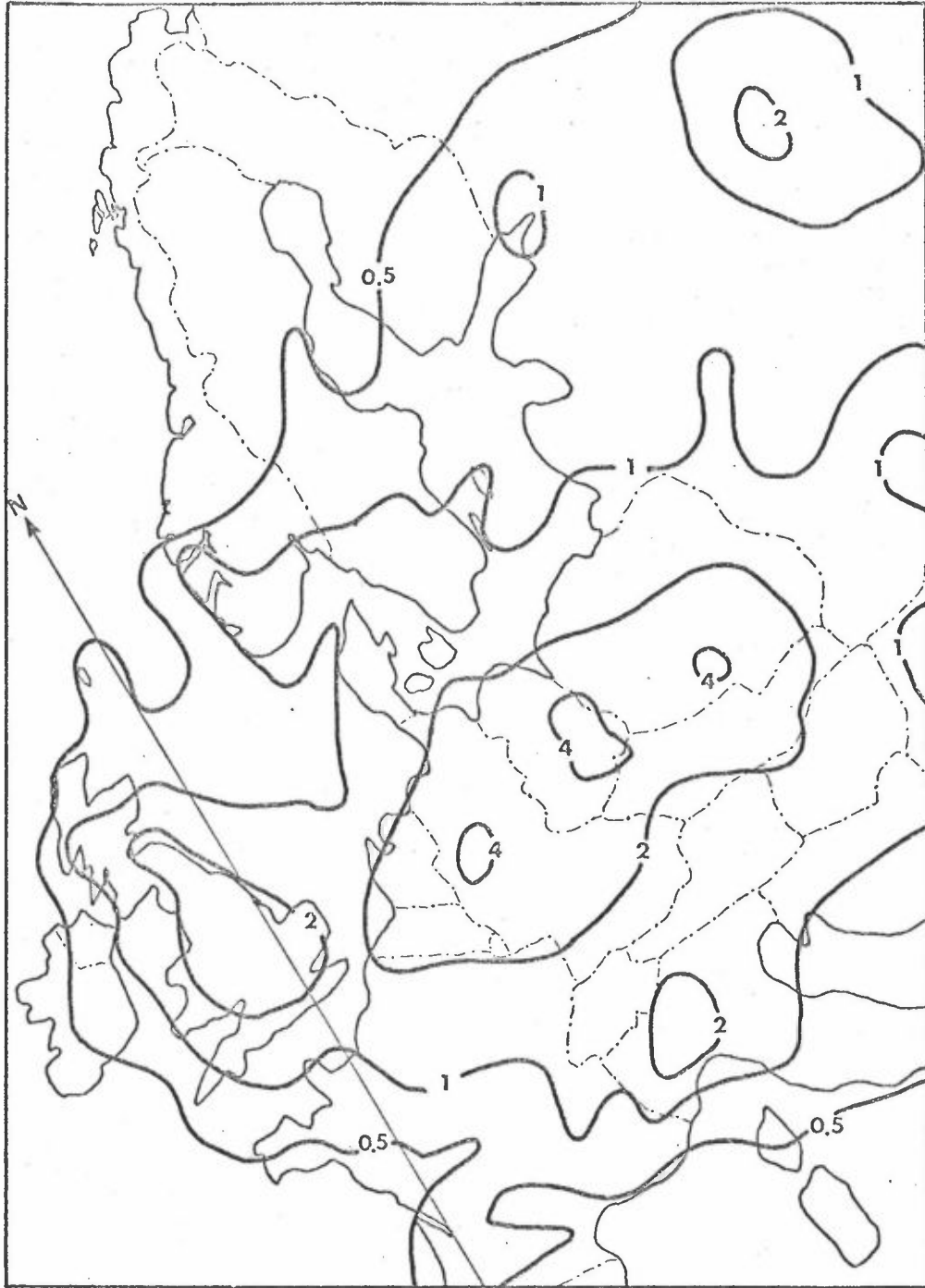


Figure 7: Estimated total deposition of sulphur in T  
Unit:  $[g SO_2/m^2]$

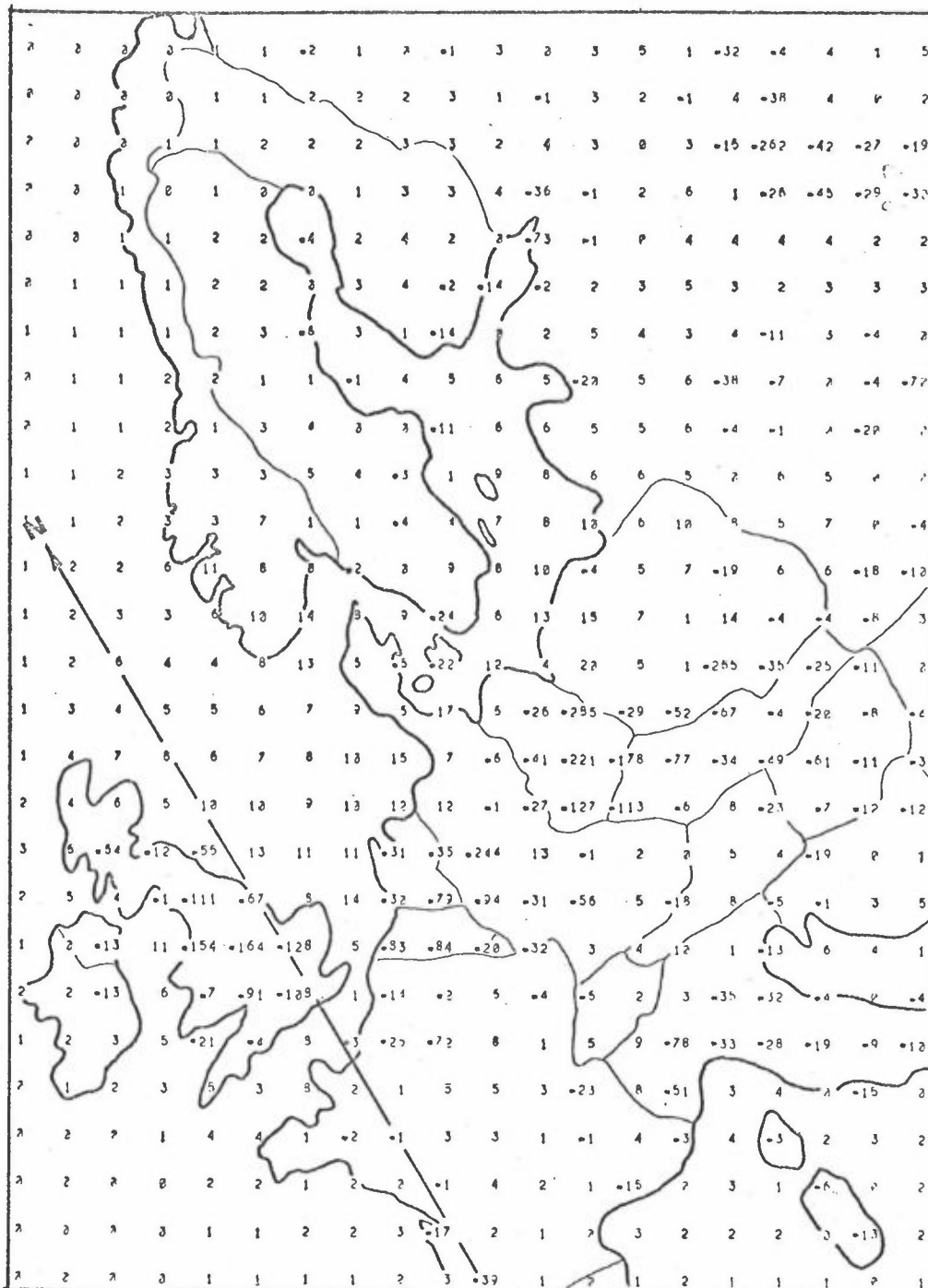


Figure 8: Total amount of SO<sub>2</sub> emitted, subtracted from estimated total deposition of SO<sub>2</sub> in T.  
 Unit: [0.1 g SO<sub>2</sub>/m<sup>2</sup>]

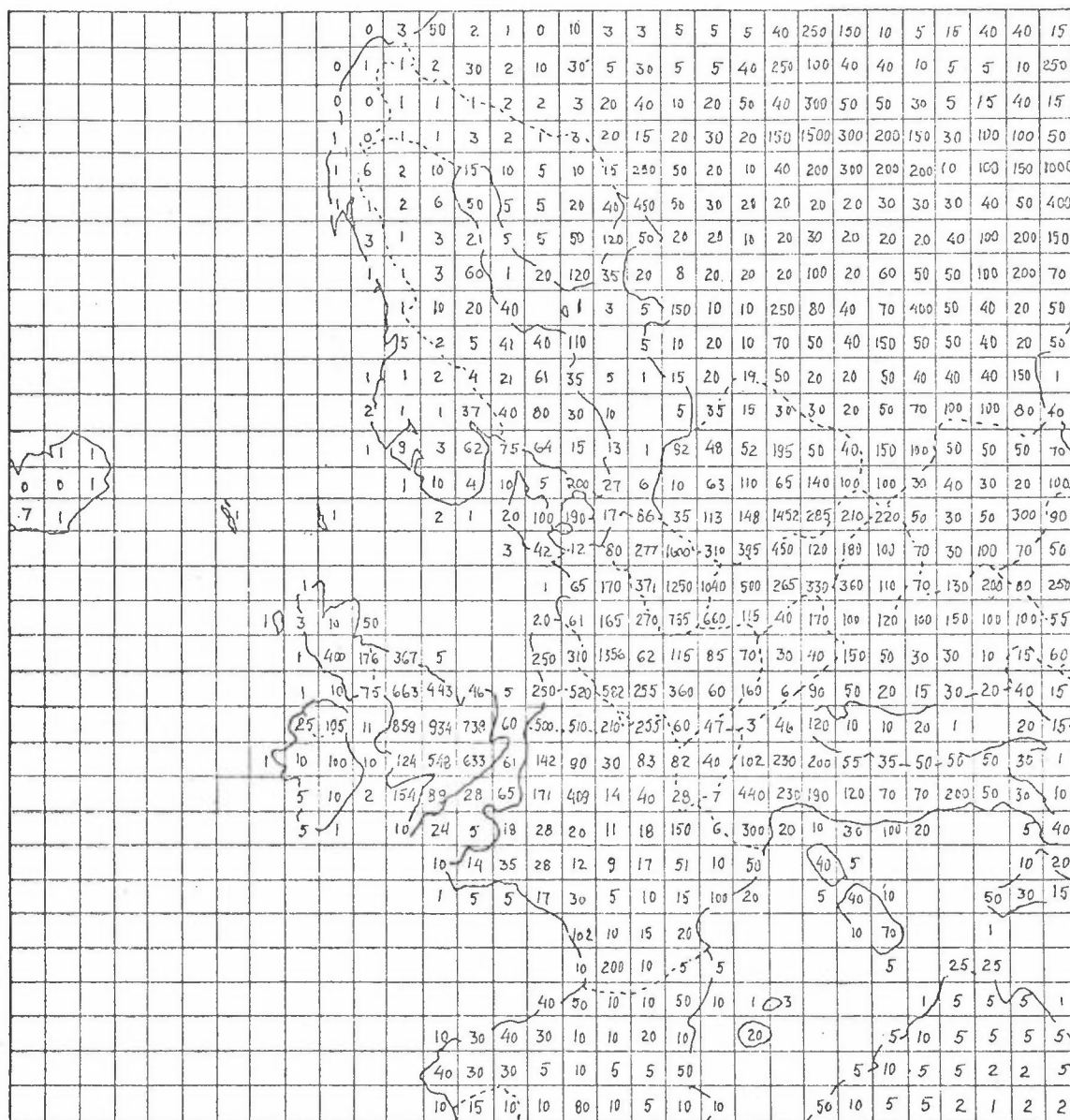


Figure 9 : The emission of  $SO_2$  in 1972/3

Unit: [10<sup>3</sup> tonnes  $SO_2$ /year]

Grid: 32 x 32 squares

$$d = 1.27 \cdot 10^5 \text{ m at } 60^\circ \text{ N}$$

The figure also shows the region of calculation.