LRTAP-3/74

ADVANCED STATIONS.

RESULTS FROM 45-DAY PERIOD OF EXTENDED CHEMICAL ANALYSIS PROGRAMME, FEBRUARY 15 - MARCH 31, 1974

A preliminary discussion

(Steering Committee, 26-27 September 1974)

Kjeller, 16th September 1974

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INTRODUCTION

At the last meeting of the Steering Committee, it was decided that a total of 100 samples from one sampling site in each country should be analyzed for strong acid, nitrate, ammonium, and other species in addition to sulphate in airborne particulate matter. Precipitation samples from the same site should be analyzed for the same components.

The samples were to be taken within 2 periods, the first 45-day period of 24-hourly samples from February 15th, and a second period later in 1974, subject to decision by the Steering Committee.

This is a preliminary report of the results from the first 45-day period. The discussion of the results is only meant to draw attention to conclusions which may be drawn at this stage.

RESULTS

6 countries have reported results from the first period (the United Kingdom, France, Denmark, Norway, Sweden and Finland). Copies of the results are enclosed. Table I lists the data available.

In addition, similar data from 1973 are also available from Sweden, Denmark, Finland and Norway in connection with the NORDFORSK 100-days programme. These data will be reported separately.

Chemical composition

Figure 1 shows the mean values of watersoluble aerosol constituents for the 6 stations. For easy comparison the values have been given in nanoequivalents per cubic metre. Because of errors and uncertainties in the chemical analysis, the sum of anionic and cationic charges is not always zero. It should also be recalled that the number of components analysed is not complete. Chloride, phosphate, zinc, and lead has not been determined. Iron and aluminium will have an effect on the H^+ titration results, depending on the titration procedure, and the filter medium will absorb protons to some extent (1). Nevertheless, the agreement is generally good, which indicates that the ionic ballance of the watersoluble aerosols is mainly determined by the concentration of the components: sulphate, ammonium and nitrate.

The chemical composition of aerosol and precipitation is rather variable from one station to another. Particularly interesting are the high concentrations of ammonium and nitrate ions observed at Cottered and Keldsnor. Because ammonium nitrate decomposes if the partial pressure of ammonia falls below a critical level corresponding to a few micrograms of ammonia per cubic metre, ammonium nitrate in the aerosol phase will not occur simultaneously with an acid aerosol containing sulphuric acid. In Norway at Birkenes (N 01), and at Råö (S 02) in Sweden, the concentration of nitrate in the aerosol therefore is generally very low.

Nitrate in precipitation, however, is not negligible. It is interesting to note that at N 01 nitrate and ammonium in precipitation are very well correlated, see Table II (correlations between concentrations in precipitation), and that they also are present in nearly equimolar amounts. This relationship has also been found in samples from the winter 1973-74 (2), but no explanation for this behaviour has so far been found.

From this brief discussion one may conclude that the emissions of nitrogen compounds and the chemical reactions of these compounds in the atmosphere are very important for the understanding of the behaviour of the sulphur oxides, particularly the formation of acid aerosols.

Comparison of air and precipitation data

The low frequency of rainfalls only to some extent permits a statistical comparison of air and precipitation data. In Figures 2 - 7 the units neq/m^3 and μeq/ℓ have been used to allow a visual comparison of the concentrations of aerosols in the air and the concentrations of watersoluble constituents in precipitation.

The ratio of these units correspond to a cloud water concentration of 1 g/m^3. This implies that if the precipitation is formed by coalescence of cloud droplets, and the cloud droplets take up all the aerosols in the form of condensation nuclei, the concentrations of ammonium (or any other ion) in μeq/ℓ of precipitation will be the same as the concentrations of particulate ammonium in the air expressed as nanoequivalents/m^3.

This of course represents a much too simplified picture of rainout and washout processes. Nevertheless, comparison of the left (air) and right (precipitation) coloumns in Figure 2 - 7 indicates that much of the concentration in the precipitation can be explained by aerosol scavenging, and that the efficiency of this process is fairly high ($\gtrsim$ 50%).

The ratio of ammonium to sulphate is generally higher in aerosols than in rainfall. This may be explained by assuming that part of the sulphate in precipitation originates from sulphur dioxide which has been taken up and oxidized in the cloud droplets.

As pointed out by Penkett (3), sufficient ozone is present in the atmosphere to give SO_2 oxidation rates in cloud droplets which are high enough to contribute significantly to the sulphate formation in rain.

In addition to this, it may also be that the composition of the aerosols at ground level is different from the composition at rainforming levels several hundred metres above the ground. In particular, the ammonia concentration shows a pronounced decay with height (4), more so than sulphur dioxide (5). This will be more pronounced near the sources and in continental regions with agricultural activity.

When the air masses have passed over the North Sea or the Skagerak and subsequently been broken up by the topography, these differences may not be so important.

Average washout factors are given in Table III. The definition of this factor is the ratio of the average air concentration, given in μg per kg of air, to the average concentration in precipitation, given in μg per kg water.

Following the discussion above, complete rainout and a cloud water concentration of 1 g/m^3 corresponds to a washout ratio of 7.7 x 10^2.

When the washout ratio is significantly higher, as for nitrate at Råö and Birkenes, the concentration level of this component in precipitation must be partly due to other effects. In this case the cause probably is rainout/washout of gaseous nitrogen components.

RELATIONSHIP BETWEEN MEASUREMENTS AND METEOROLOGICAL CONDITIONS

Trajectories have been calculated for the stations Birkenes, Cottered, Jokioinen, Keldsnor, Råö and Vert-le-Petit during the period. Since no data are available for the emission of nitrogen compounds, or for atmospheric conditions of importance for transformation processes etc. the use of the trajectories is limited to finding the trajectories for air samples of particular interest.

Trajectories for the 10 aerosol samples of highest sulphate air concentrations, and for the 10 samples of highest acid aerosol concentrations are shown in figures 8 to 23.

These figures give trajectories every 6 hour. For comparison the figures 24 to 35 give trajectories every 24 hour for the whole period. The trajectories are computed for 850 mb and are presented with 12 hours timestep.

The numbers in the figures indicate the starting point 48 hours before arrival and the positions of the stations

1. Birkenes
2. Råö
3. Jokioinen
4. Keldsnor
5. Cottered
6. Vert-le-Petit

La Crouzille's position is indicated by the number 7.

CONCLUSION

Continued measurements are needed in order to obtain a better data basis. It will be important that more countries find it possible to participate in this part of the programme.

The preliminary results given indicate that nitrogen compounds are of particular importance for the formation of acid precipitation. In continued measurements these should therefore be given priority and it should be considered to measure also nitrogen dioxide in the gaseous phase.

REFERENCES

(1) Askne, C., Brosset, C., Ferm, M. — Determination of the proton-donating property of air-borne particles. IVL Publication B 157. Swedish Water and Air Pollution Research Laboratory, Gothenburg - Aug. 1973.

(2) Nordø, J. — Sulphur pollution arising from distant emission sources. Lecture presented at the ELMIA A/B Conference, Jönköping, Sweden. September 2nd., 1974.

(3) Penkett, S.A. — Nature, 240, pp 105-106, 1972.

(4) Georgii, H.W., Müller, W.J. — Tellus, 26, pp 180-185, 1974.

(5) Jost, D. — Tellus, 26, pp 206-211, 1974.

FIGURES

TABLES

Air samples

Country	Strong acid	NO_3-N	NH_4-N	SO_4	Ca	K	Fe	Mg	Na	Cl	TPM
UK	-	x	x	x	x	-	-	x	-	-	-
France	x	x	-	x	x	x	x	x	x	-	x
Sweden	x	x	x	x	x	x	x	-	x	-	x
Denmark	x	x	x	x	x	-	x	-	x	-	x
Finland	x	x	x	x	x	-	x	-	x	-	-
Norway	x	x	x	x	x	x	x	x	x	x	-

Precipitation samples.

Country	Strong acid	NO_3-N	NH_4-N	SO_4	Ca	K	Fe	Mg	Na	Cl	N.S.
UK	-	x	x	x	x	-	-	x	-	-	14
France	x	x	-	x	x	x	-	x	x	-	12
Sweden	x	x	x	x	x	-	-	-	x	-	6
Denmark	x	x	x	x	x	-	-	-	x	-	12
Finland	x	x	x	x	x	-	x	x	x	-	29
Norway	x	x	x	x	x	x	-	x	-	-	21

Table I: 45-days period February 15 - March 31, 1974
Data available.

Sampling period:

United Kingdom	A 22/2 - 31/3	P 15/2 - 31/3
France	A 15/2 - 23/3	P 15/2 - 31/3
Sweden	A 15/2 - 1/4	P 15/2 - 31/3
Denmark	A 15/2 - 31/3	P 15/2 - 31/3
Finland	A 15/2 - 28/2; 16/3 - 24/4	P 15/1 - 31/5
Norway	A 15/2 - 31/3	P 1/2 - 31/3

	ml prec.	H^+	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+	NO_3^-	SO_4^{2-}	SO_4^{2-} corrected
ml prec.	1.00									
H^+	-.21	1.00								
Ca^{2+}	-.27	.36	1.00							
K^+	-.37	.16	.55	1.00						
Mg^{2+}	-.15	.02	.37	.66	1.00					
Na^+	-.28	.30	.21	.61	.91	1.00				
NH_4^+	-.08	.59	.55	.18	.06	.43	1.00			
NO_3^-	-.12	.83	.45	.25	.06	.38	.86	1.00		
SO_4^{2-}	-.13	.38	.19	.41	.31	.54	.50	.51	1.00	
SO_4^{2-} corrected	-.07	.27	.01	.06	-.02	.24	.42	.33	.82	1.00

Table II: Correlations between concentrations in precipitation. Birkenes March 25 - June 27, 1973.

Component \ Station	UK 1	F 03	DK 5	SF 2	S 02	N 01
H^+	108.		2.9	45.	92.	70.
SO_4^{2-}	5.4	17.	12.	9.6	7.1	16.
NH_4^+	4.0		6.2		5.4	17.
NO_3^-	7.9		9.6		33.	149.
Ca^{2+}	9.9	39.	10.		27.	35.
Mg^{2+}	12.	40.				34.
Na^+				12.	53.	
K^+						33.

Table III: Washout ratio in units $10^2 \frac{\text{kg air}}{\text{kg rain}}$.
Period February 15 - March 31

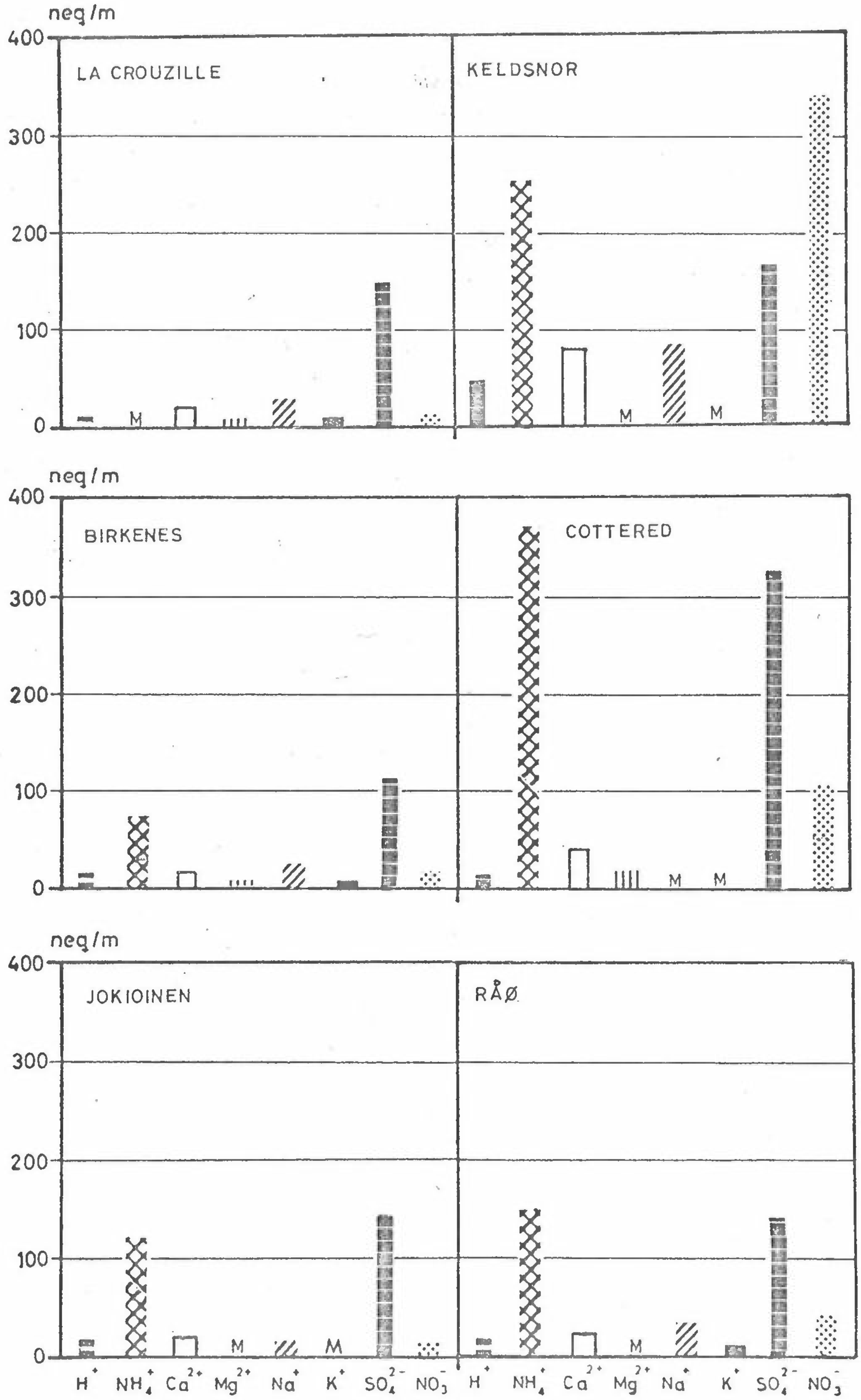


Figure 1: Air samples, February 15 - March 31, 1974.
Mean values in neq/m^3.

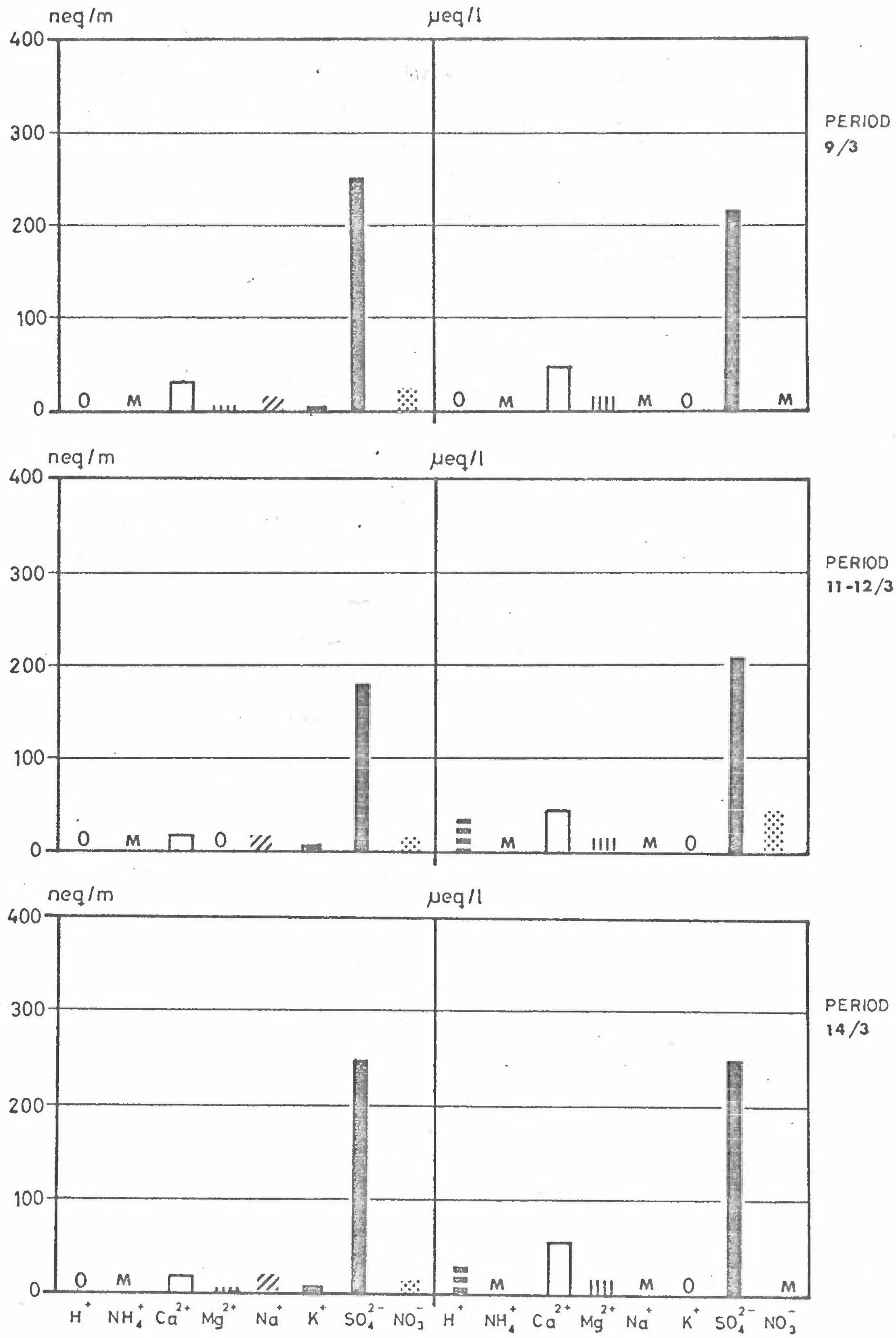


Figure 2: Station F 03. Short periods, mean concentrations in air and precipitation samples.

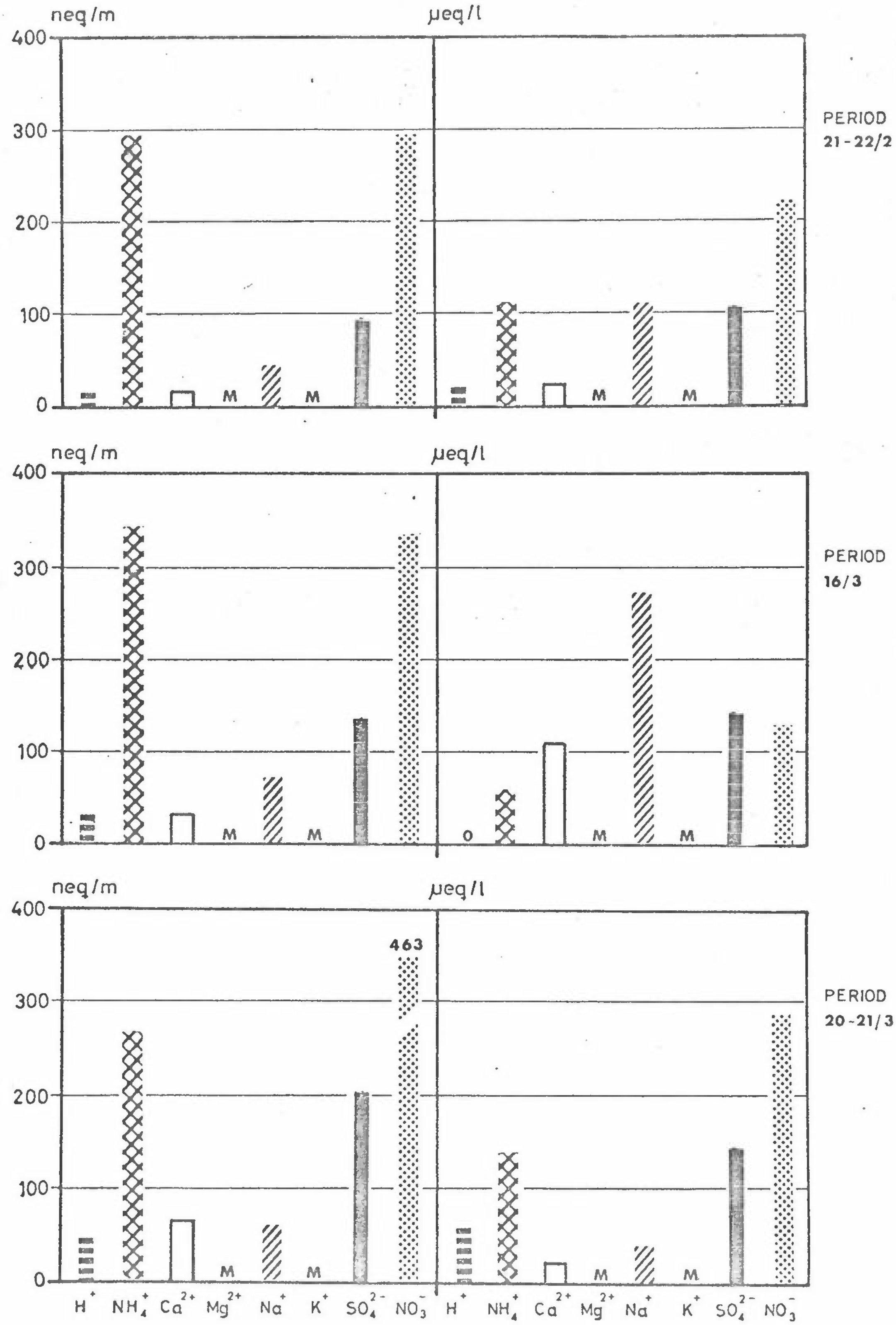


Figure 3: Station DK 5. Short periods, mean concentrations in air and precipitation samples.

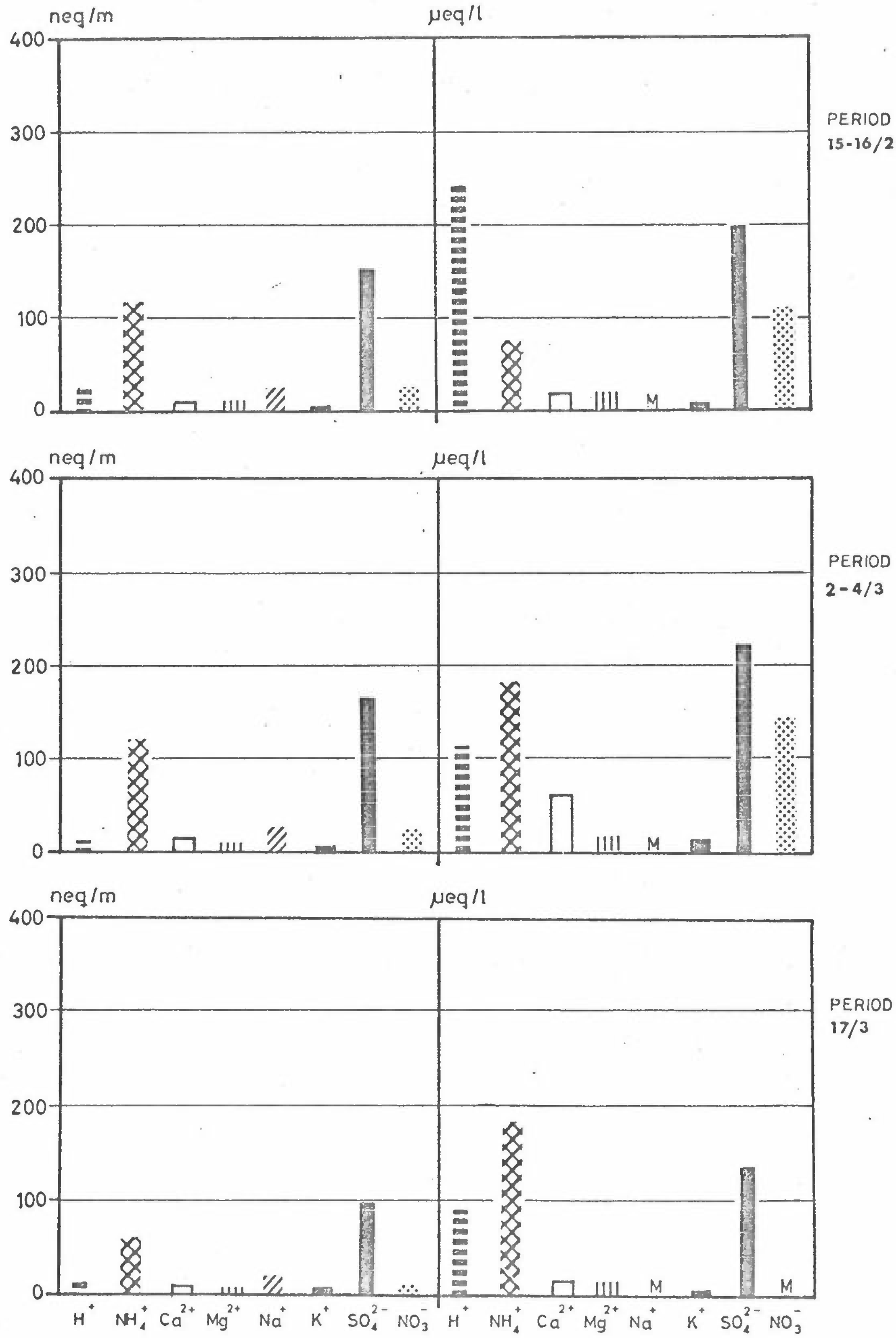


Figure 4: Station N 01. Short periods, mean concentrations in air and precipitation samples.

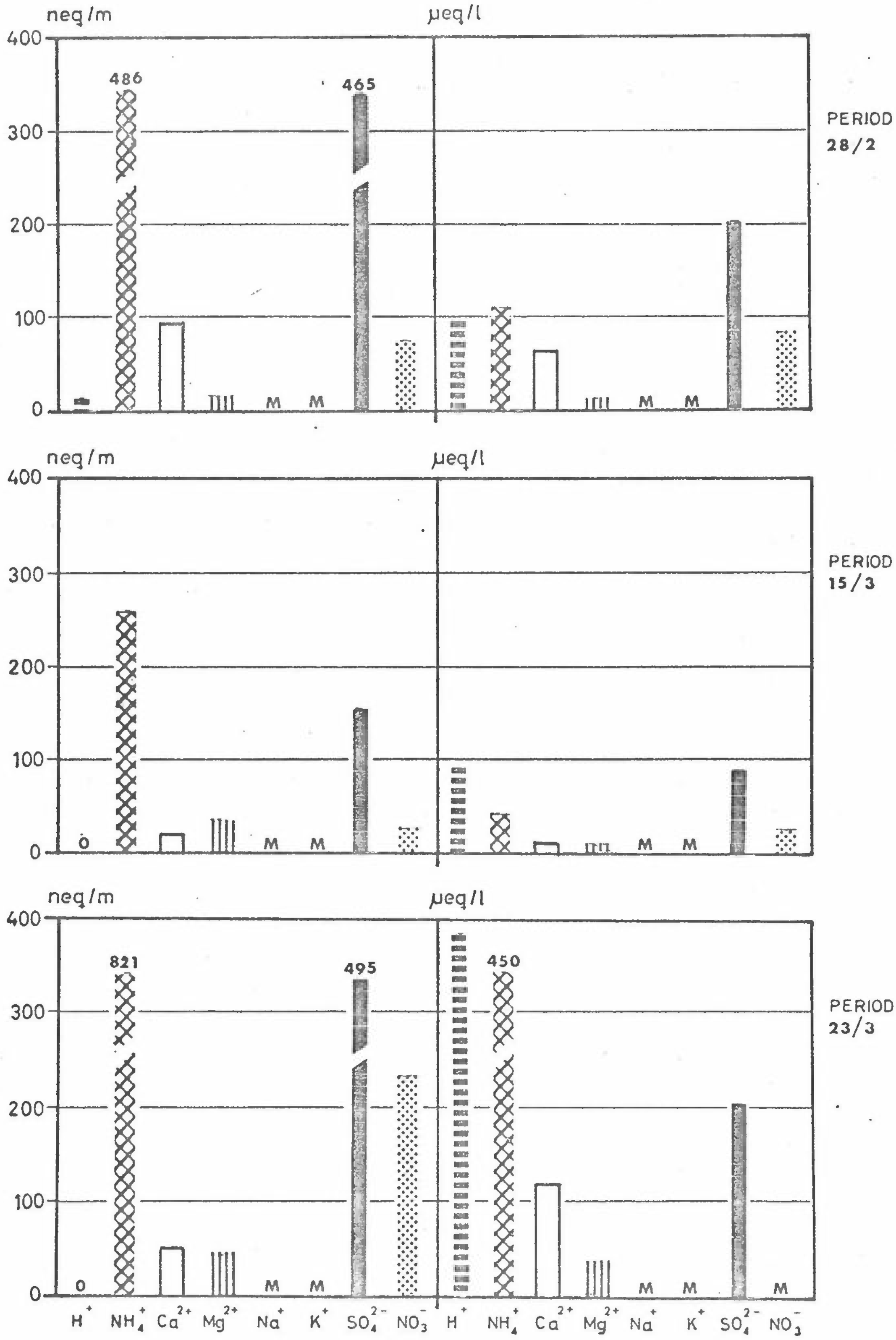


Figure 5: Station UK 1. Short periods, mean concentrations in air and precipitation samples.

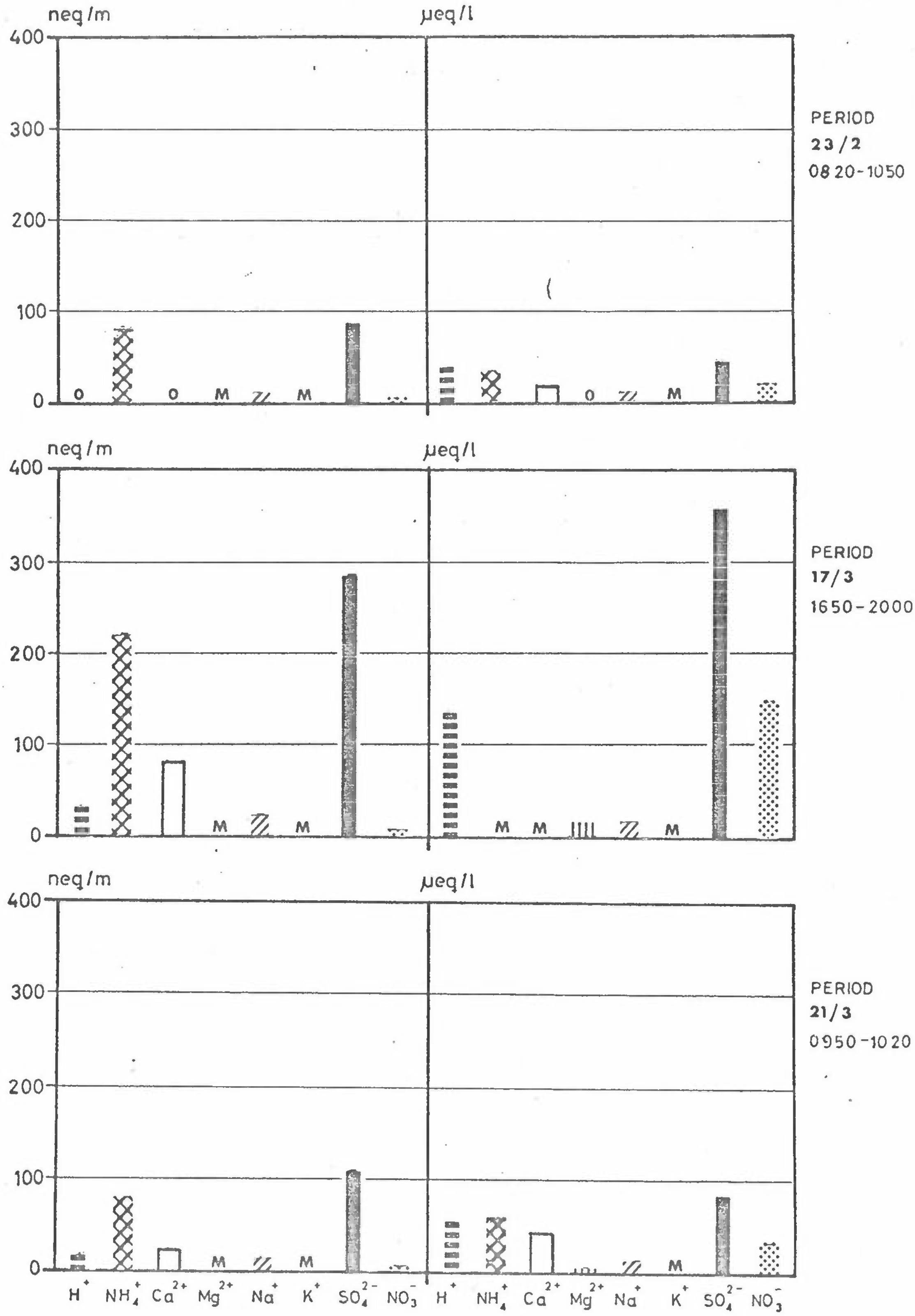


Figure 6: Station SF 2. Short periods, mean concentrations in air and precipitation samples.

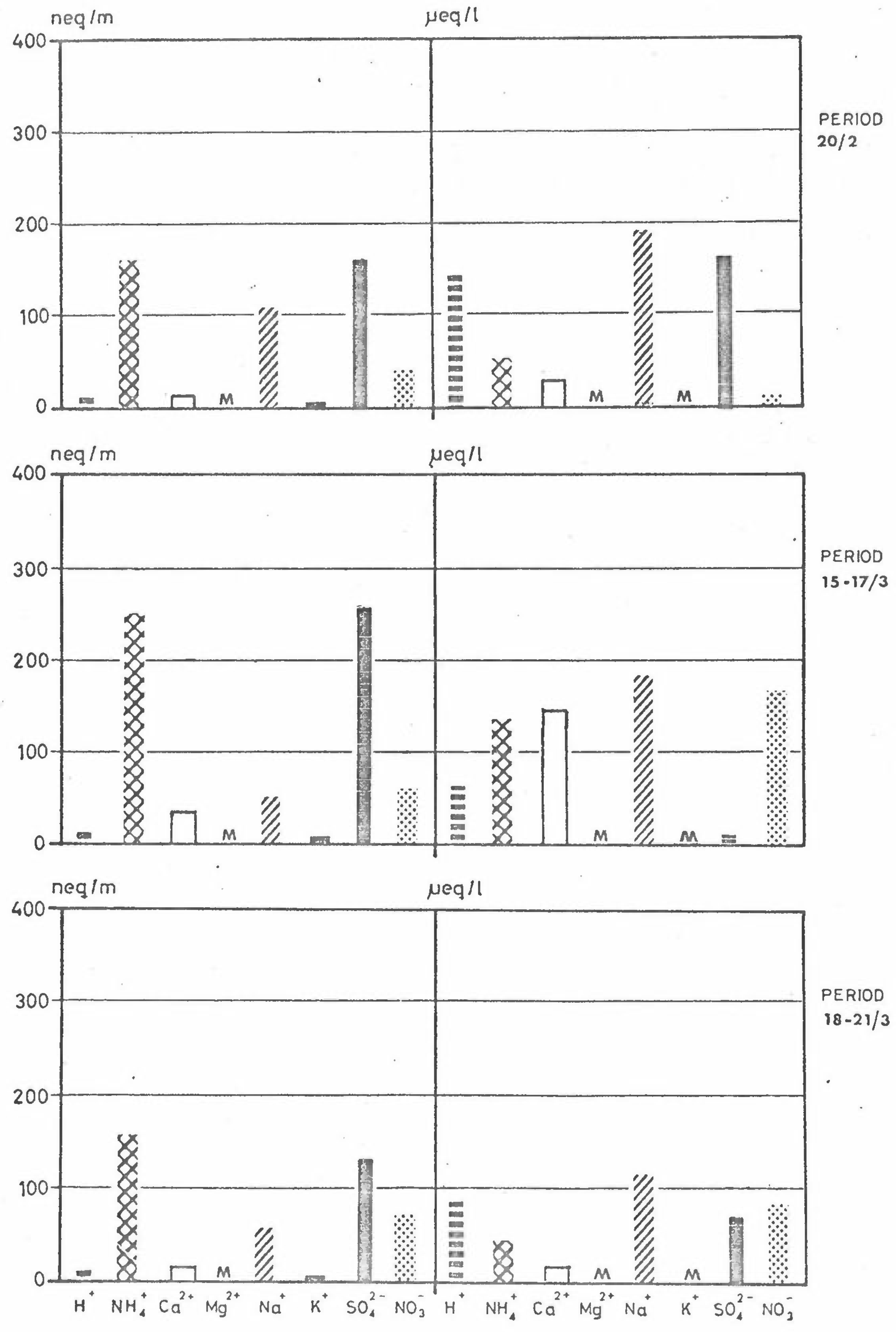
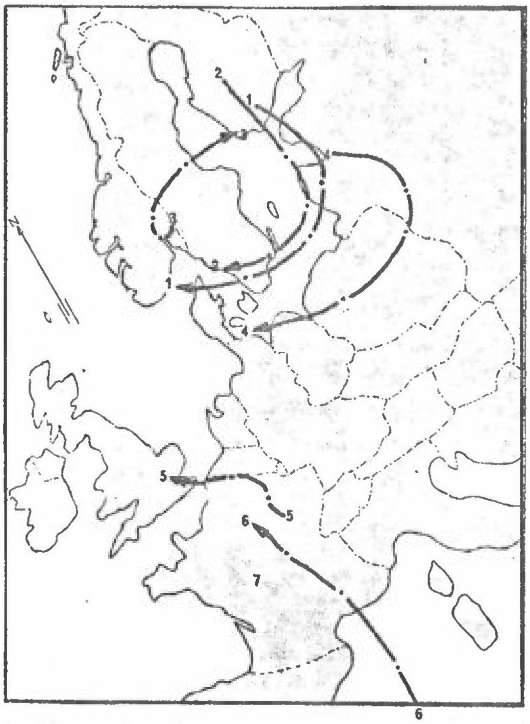


Figure 7: Station S 02. Short periods, mean concentrations in air and precipitation samples.



Trajectories arriving at
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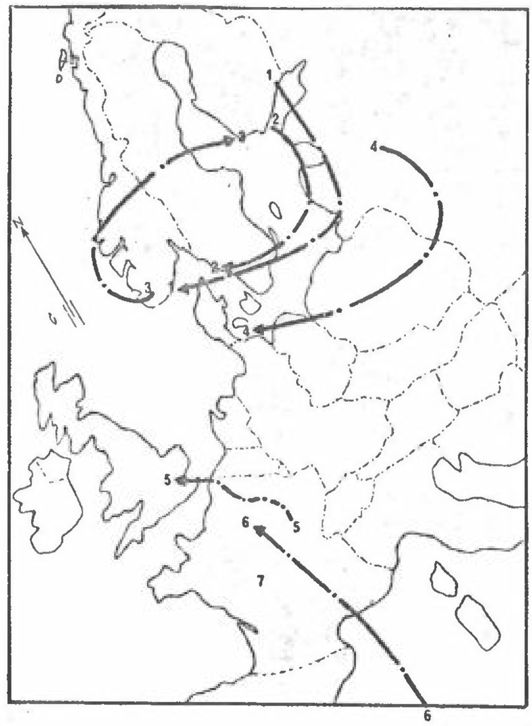

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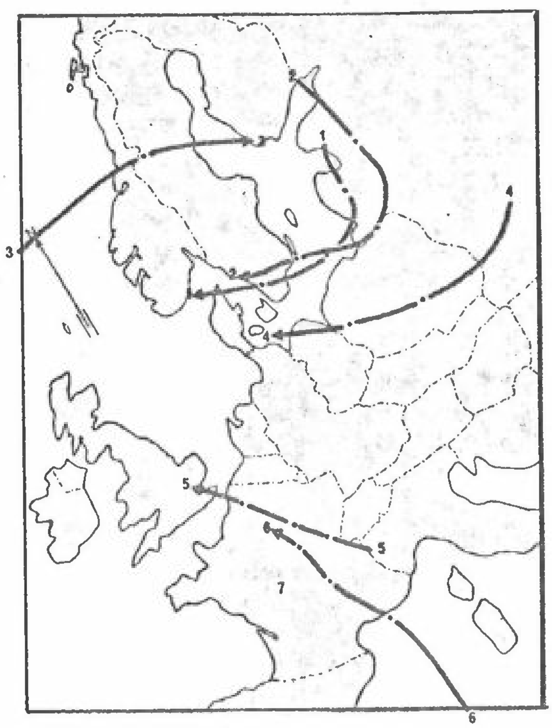

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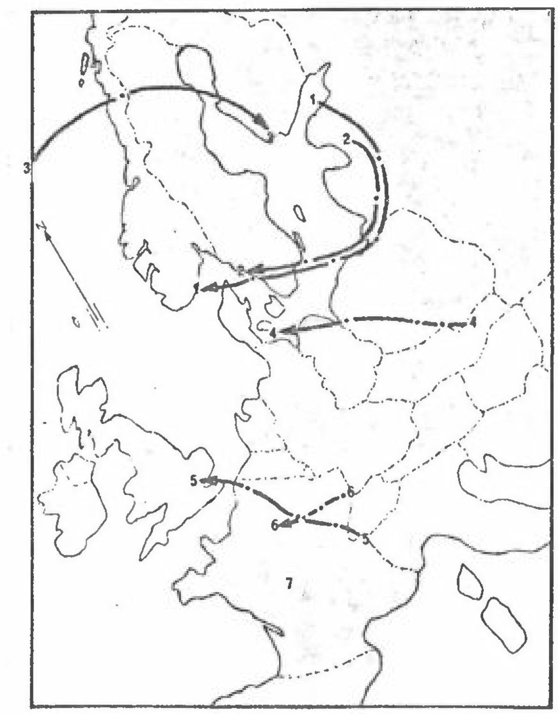

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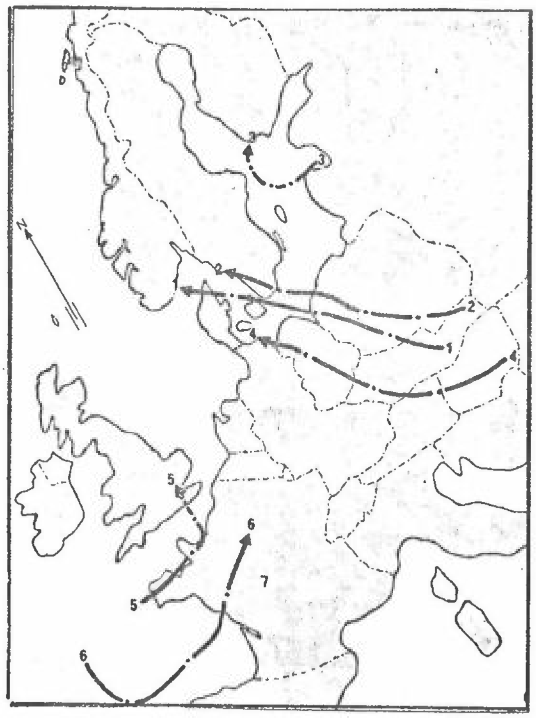
FIGURE 8

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	1.7
S 02	3.8
SF 2	3.1
DK 5	3.9
UK 1	<u>49.9</u>
F 01	-



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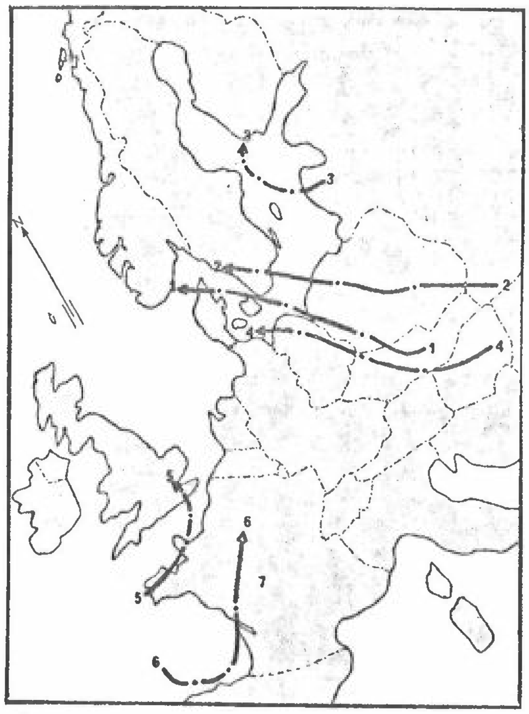

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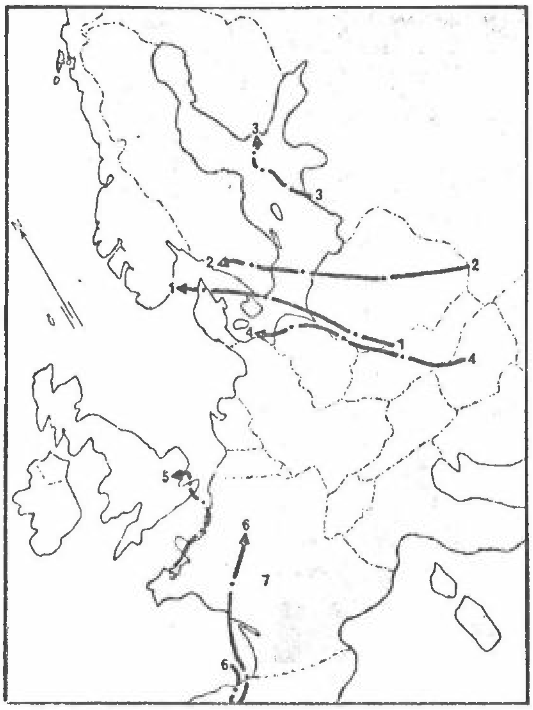

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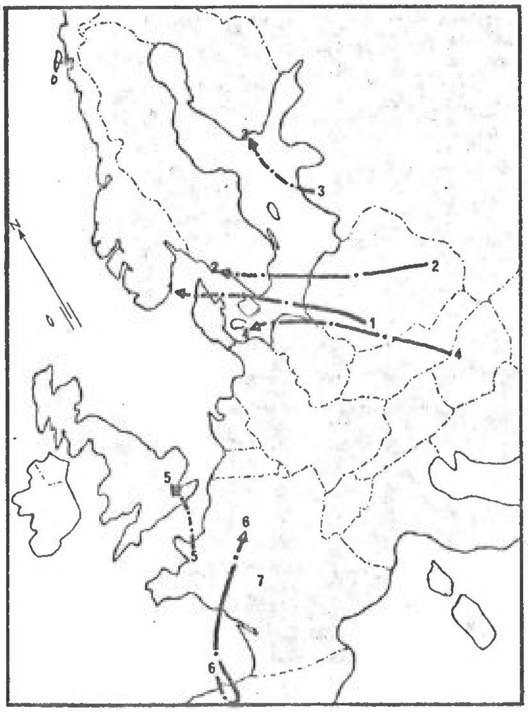

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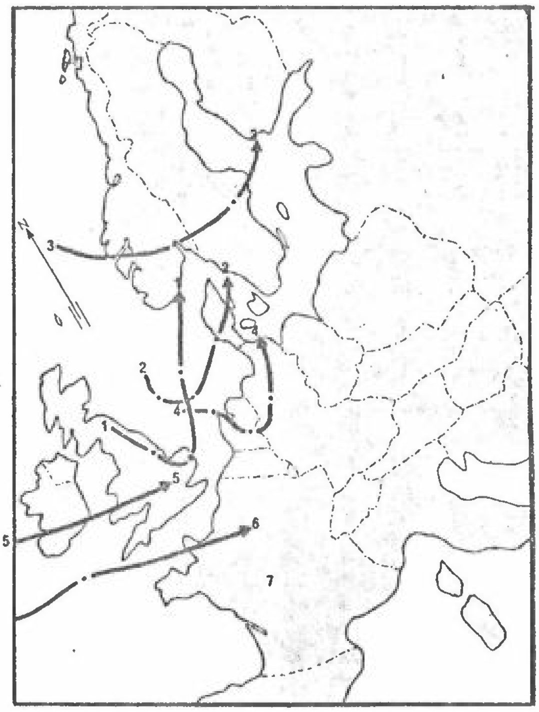
FIGURE 9

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	6.5
S 02	8.0
SF 2	-
DK 5	13.5
UK 1	29.5
F 03	1.8



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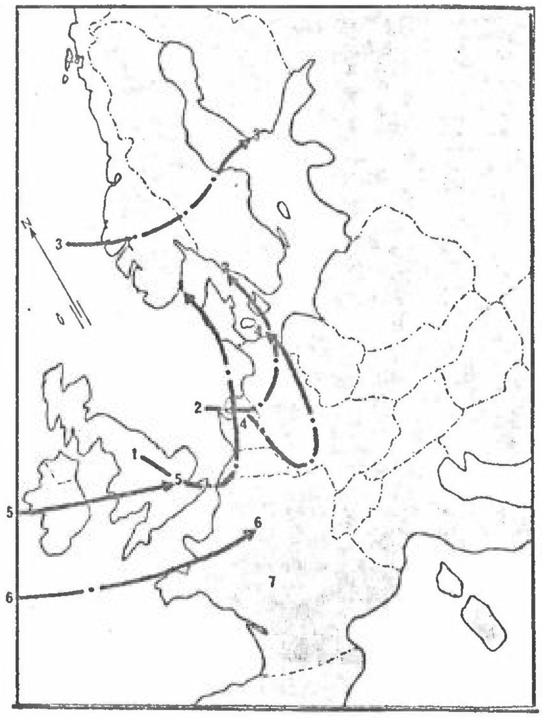

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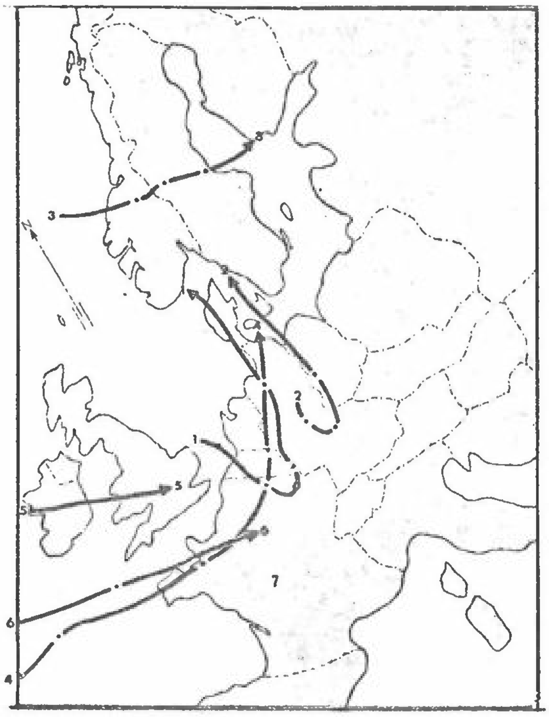

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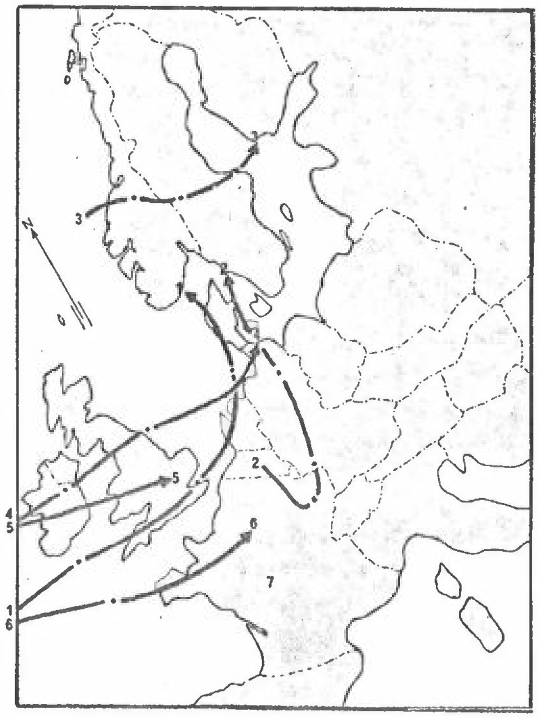

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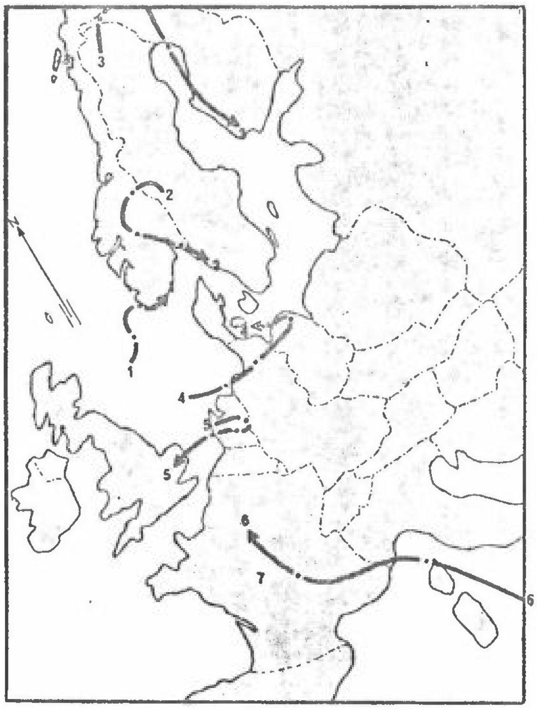
FIGURE 10

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	25.0
S 02	12.5
SF 2	4.2
DK 5	6.4
UK 1	-
F 03	0.9



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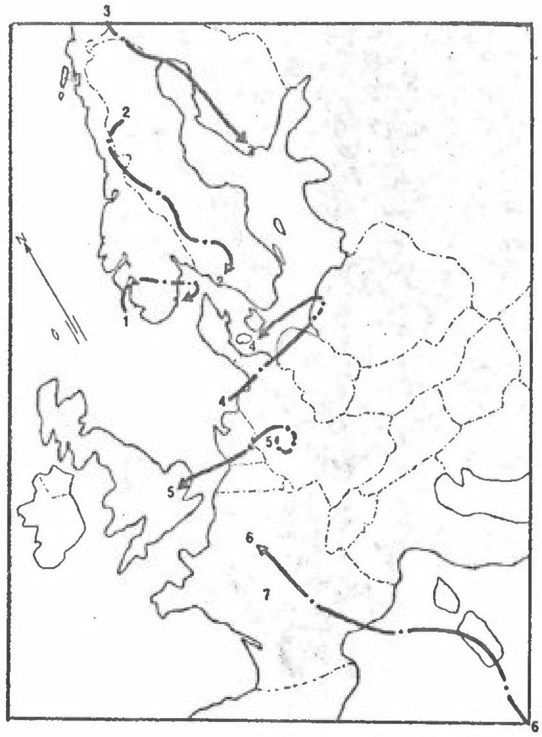

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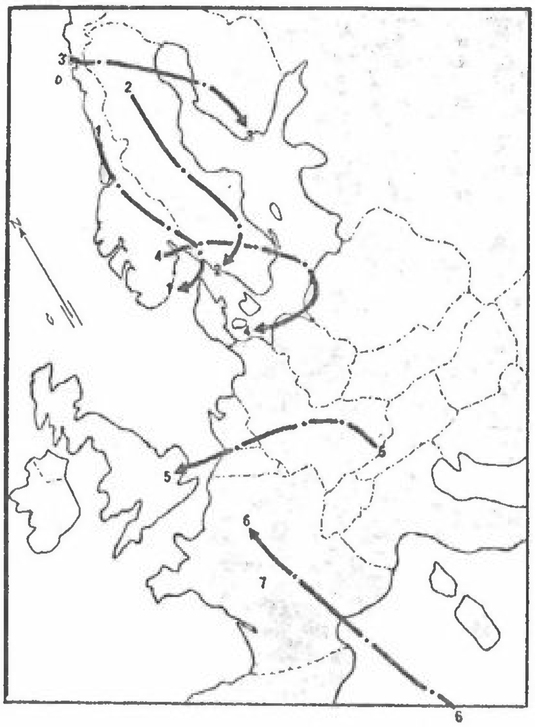

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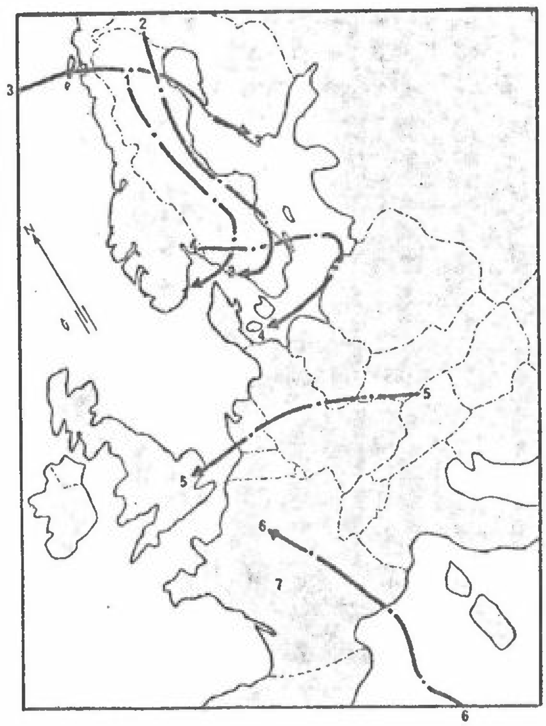

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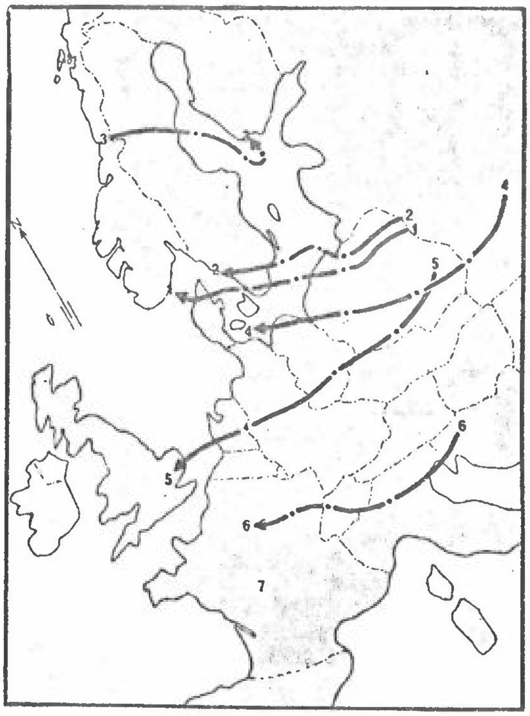
FIGURE 11

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	4.1
S 02	4.1
SF 2	1.7
DK 5	3.7
UK 1	23.9
F 03	2.2



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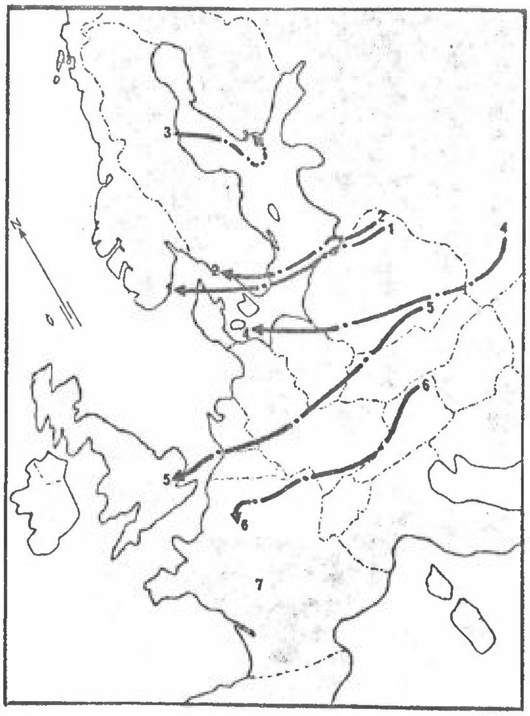

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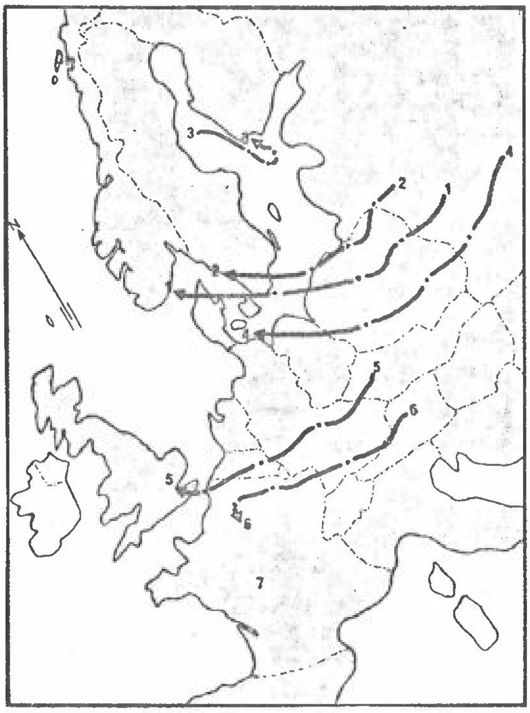

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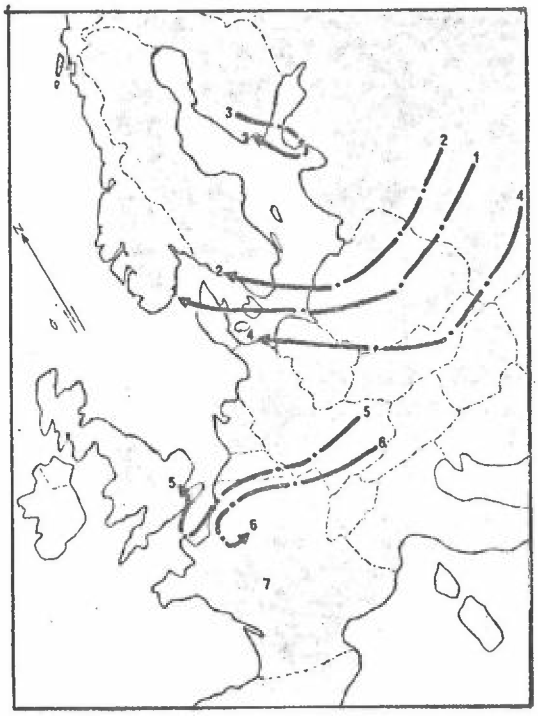

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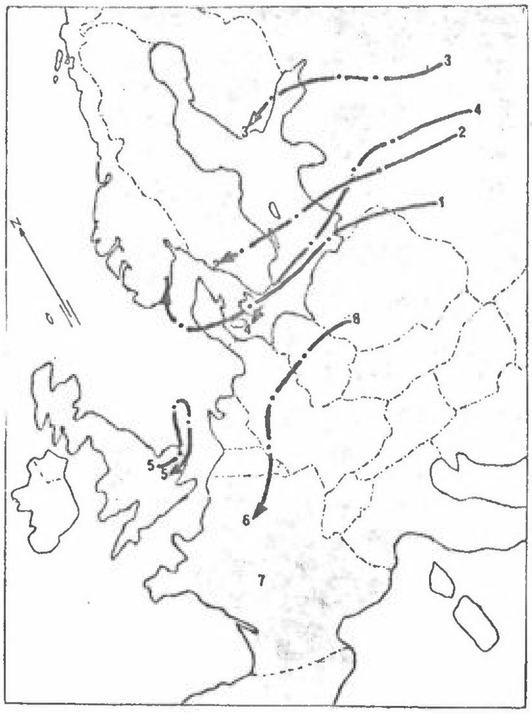
FIGURE 12

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	4.0
S 02	1.0
SF 2	5.4
DK 5	15.1
UK 1	22.3
F 03	18.2



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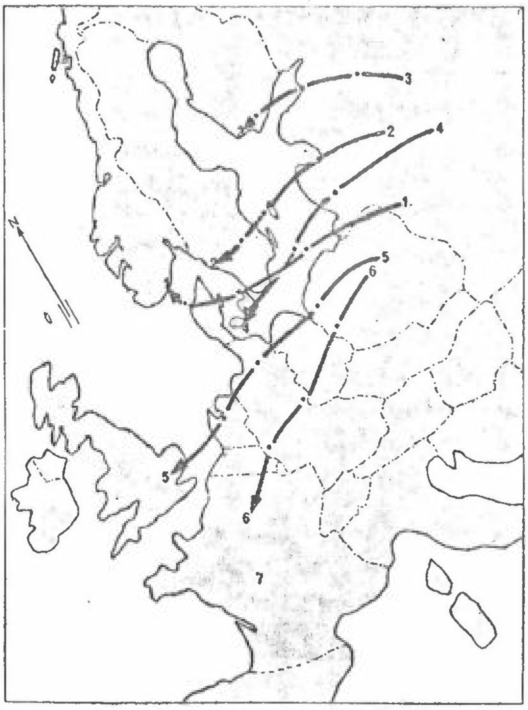

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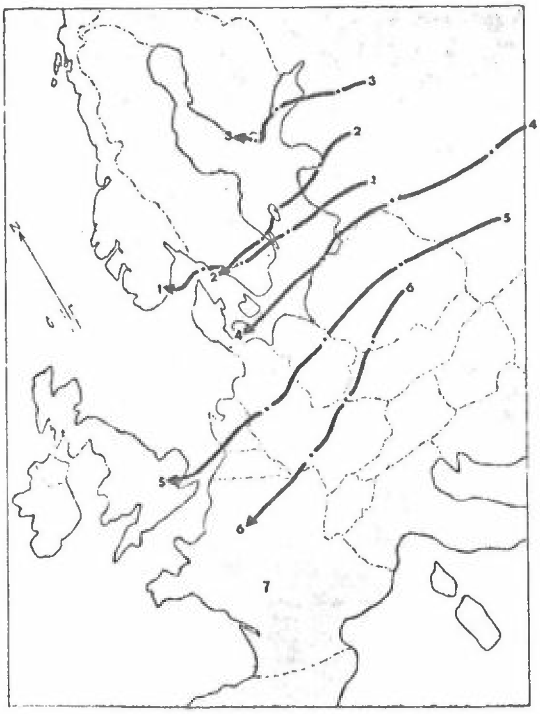

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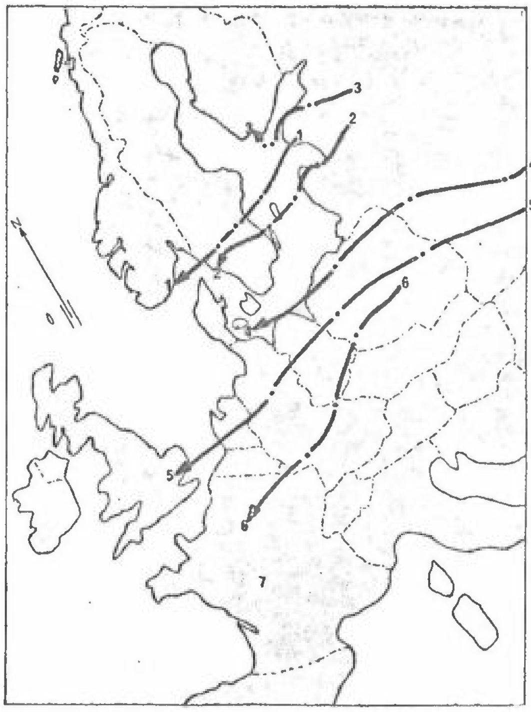

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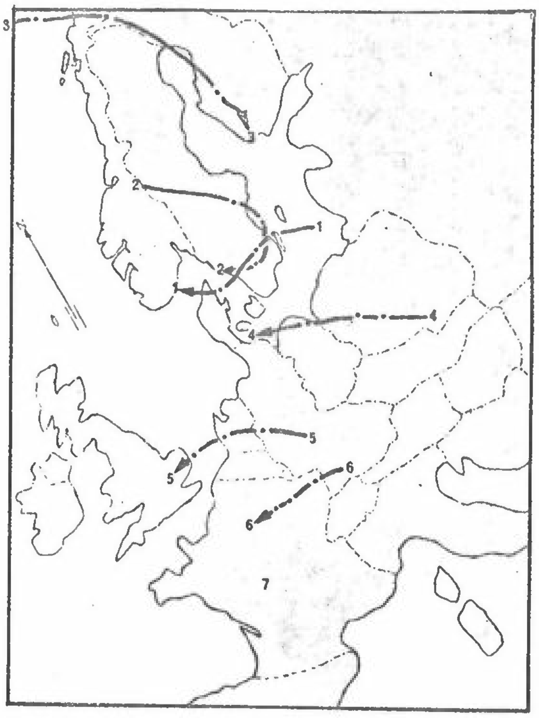
FIGURE 13

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	8.8
S 02	2.1
SF 2	-
DK 5	4.5
UK 1	-
F 03	22.3



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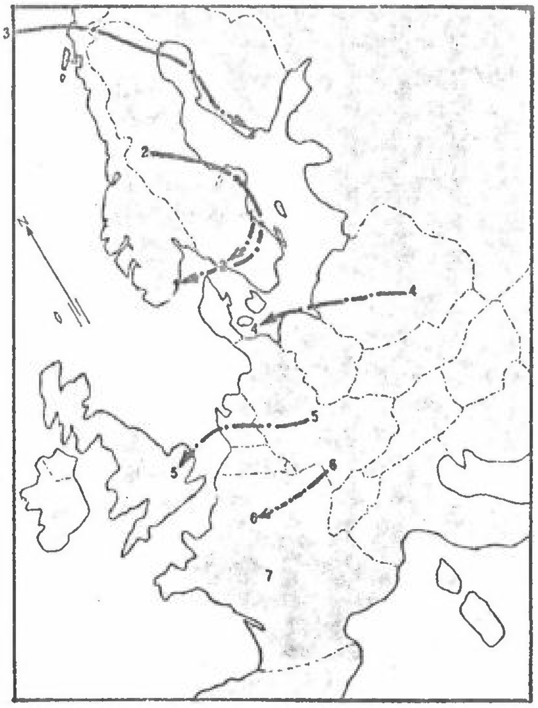

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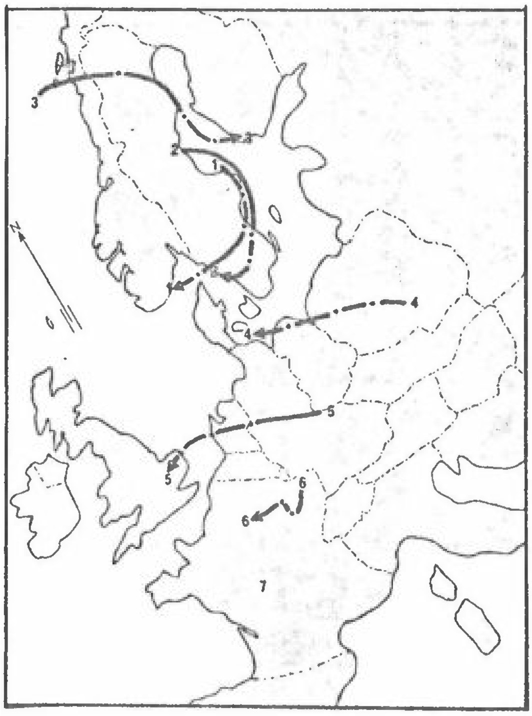

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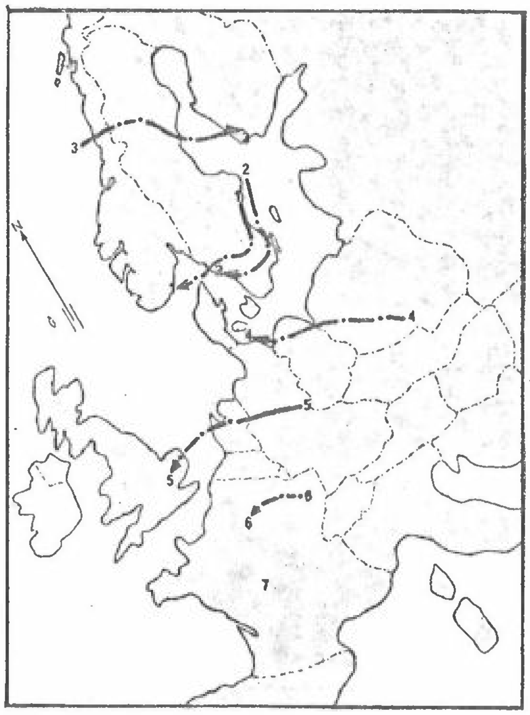

Trajectories arriving at
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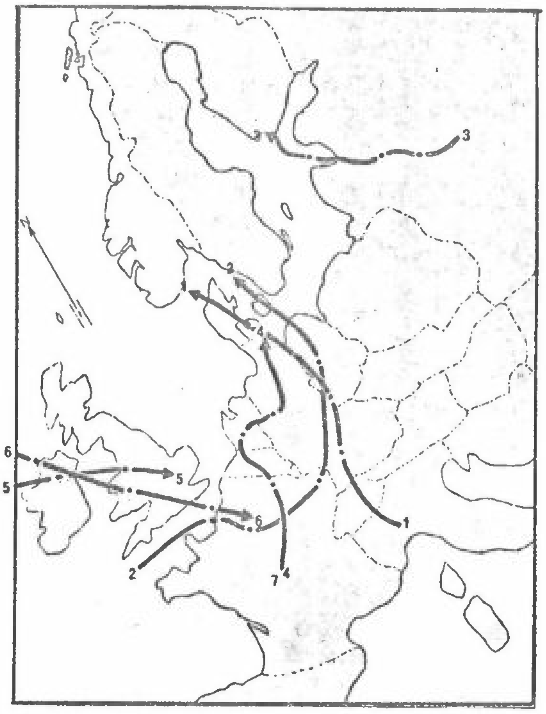
FIGURE 14

Day with high sulphate concentration.
Observed sulphate concentration:

N 01	3.1
S 02	2.7
SF 2	3.3
DK 5	1.4
UK 1	18.7
F 03	-



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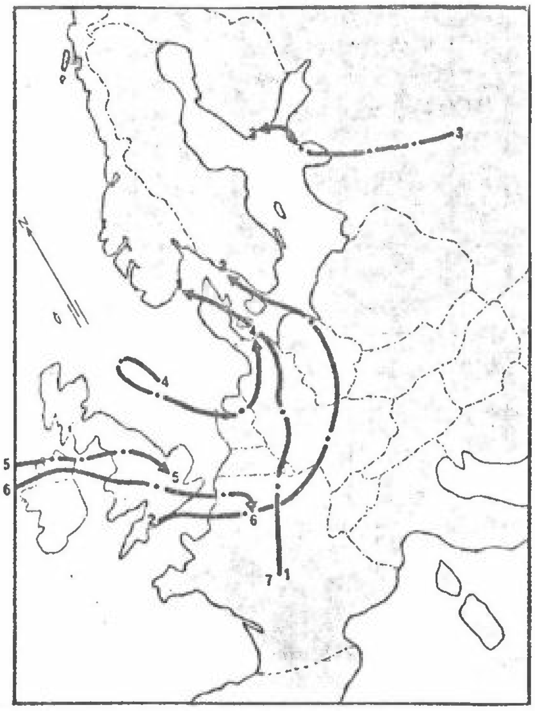

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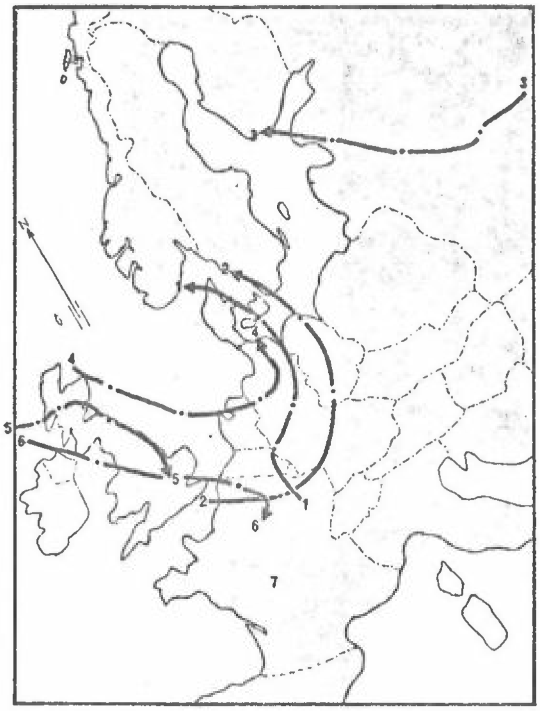
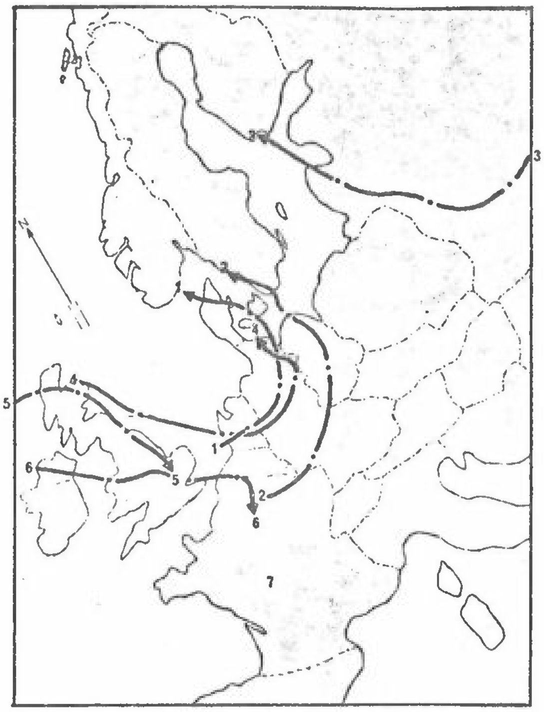


Trajectories arriving at
740303, 12 GMT.

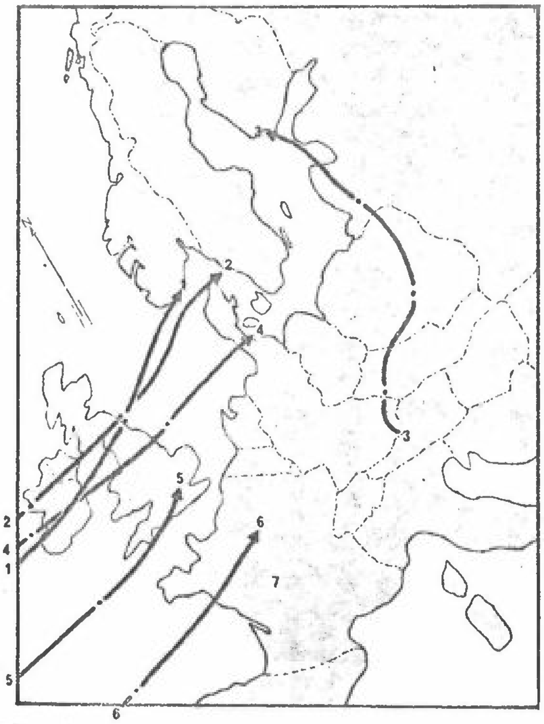


Trajectories arriving at
740303, 18 GMT.

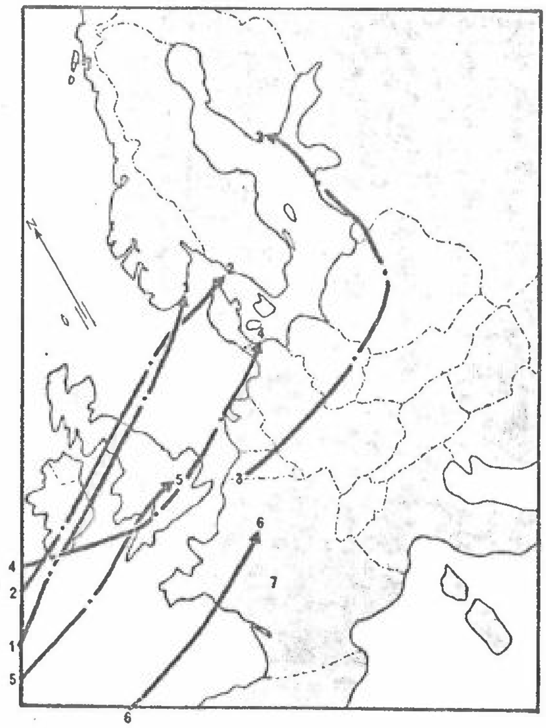
FIGURE 15

Day with high sulphate concentration.
Observed sulphate concentration:

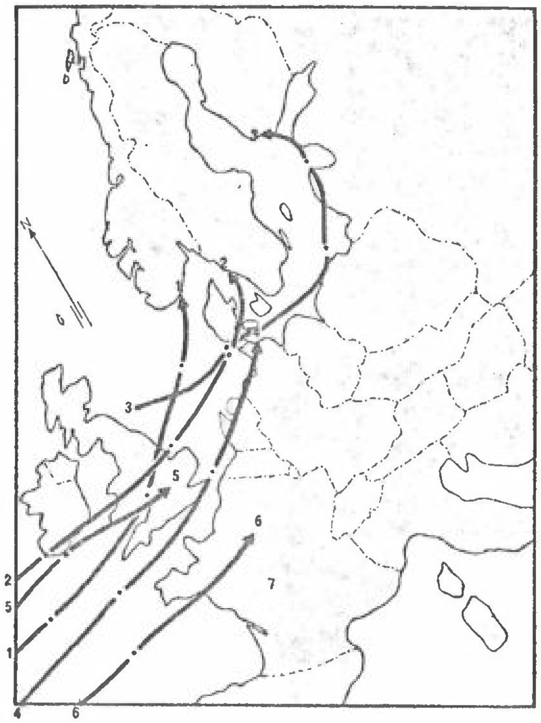
N 01	9.4
S 02	8.5
SF 2	-
DK 5	17.6
UK 1	-
F 03	4.9



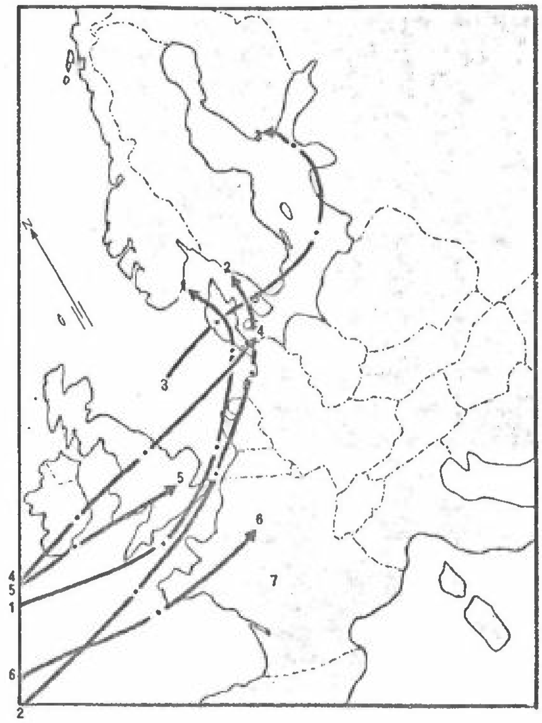
Trajectories arriving at 740318, 0 GMT.



Trajectories arriving at 740318, 6 GMT.



Trajectories arriving at 740318, 12 GMT.

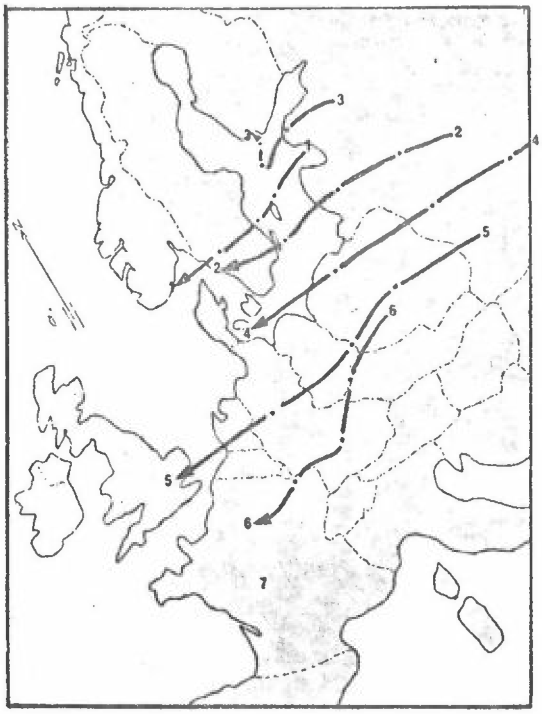


Trajectories arriving at 740318, 18 GMT.

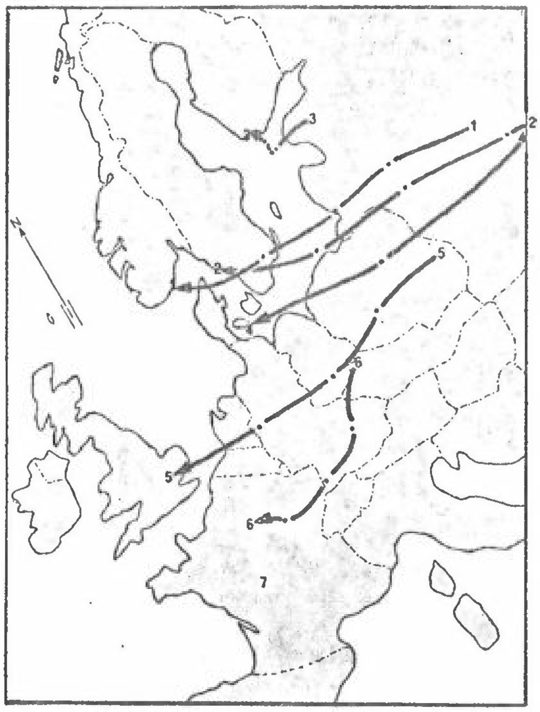
FIGURE 16

Day with high sulphate concentration.
Observed sulphate concentration:

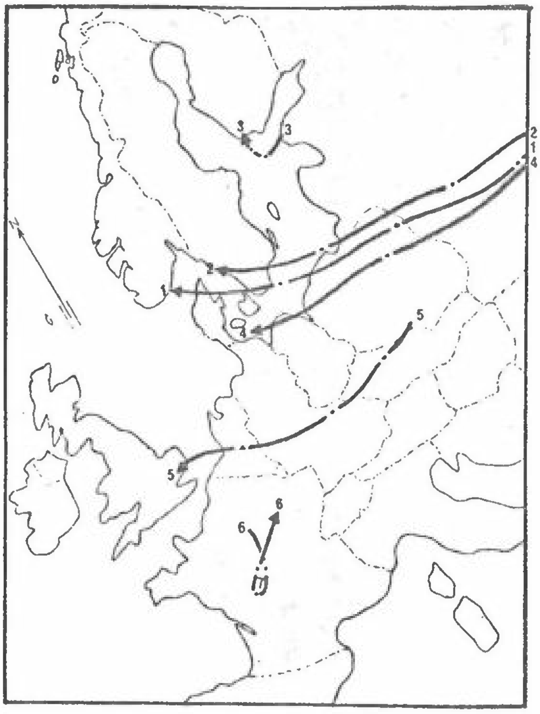
N 01	2.3
S 02	8.7
SF 2	17.0
DK 5	-
UK 1	-
F 03	1.5



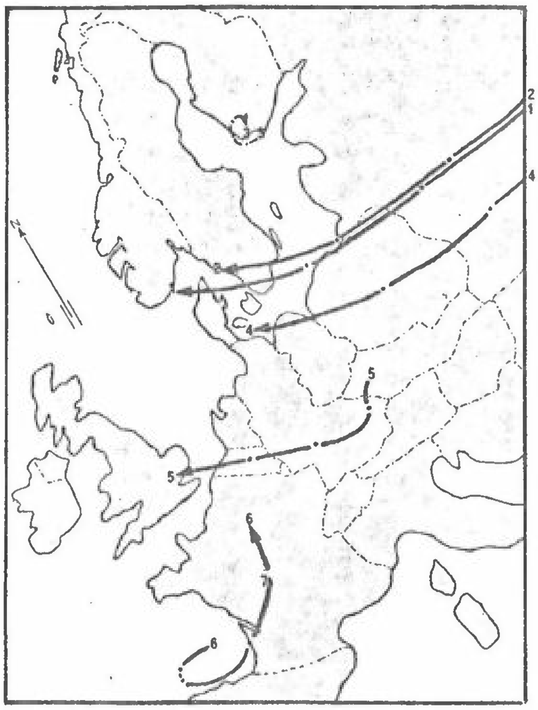
Trajectories arriving at
740309, 0 GMT.



Trajectories arriving at
740309, 6 GMT.



Trajectories arriving at
740309, 12 GMT.

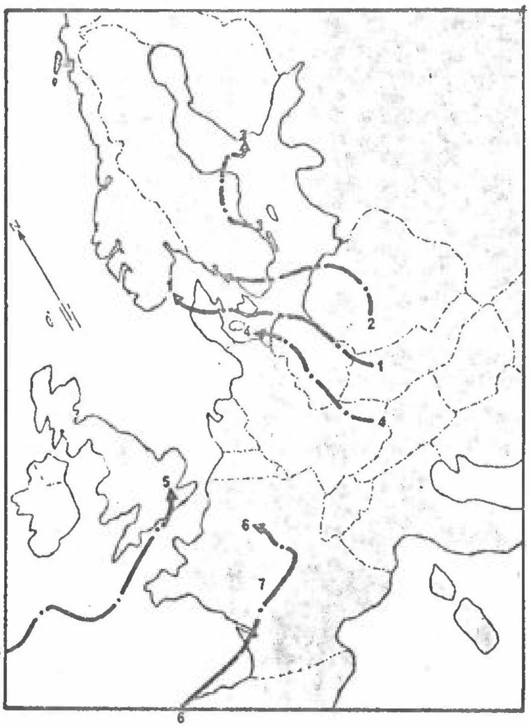


Trajectories arriving at
740309, 18 GMT.

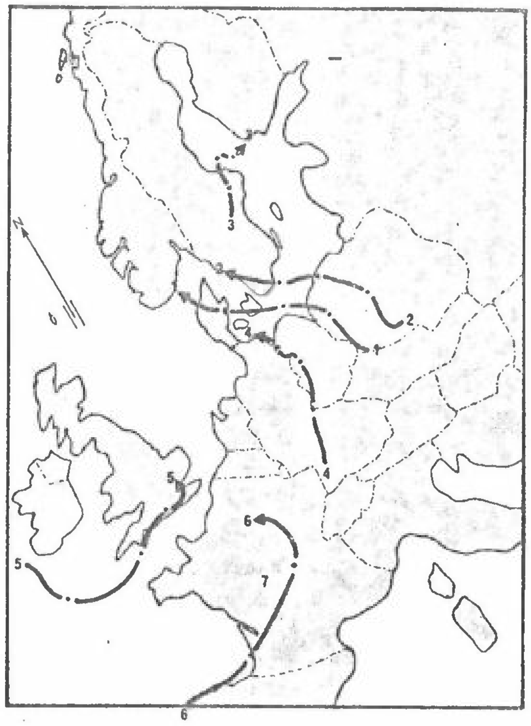
FIGURE 17

Day with high strong acid concentration.
Observed strong acid concentrations:

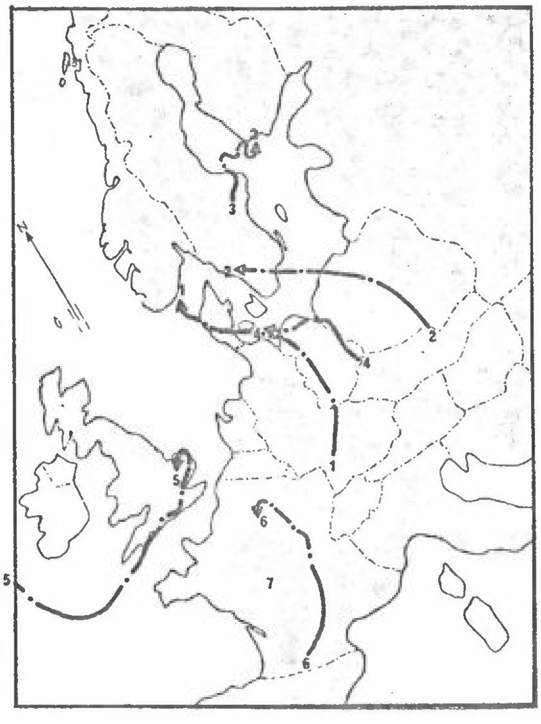
N 01	84
S 02	3
SF 2	-
DK 5	22
UK 1	-
F 03	0



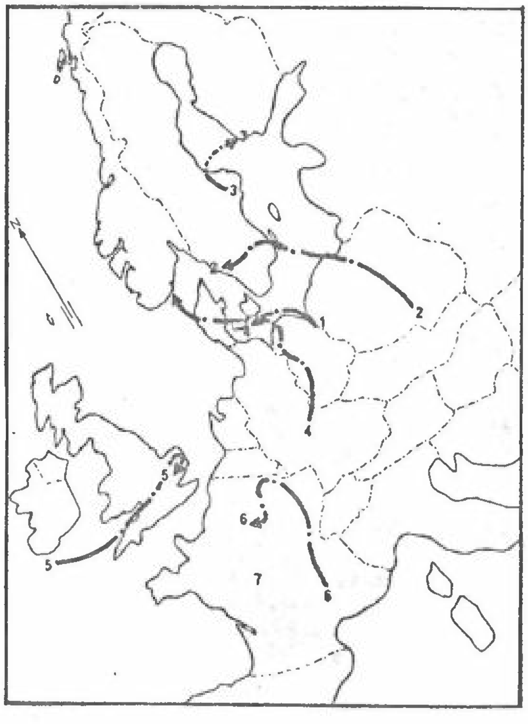
Trajectories arriving at
740217, 0 GMT.



Trajectories arriving at
740217, 6 GMT.



Trajectories arriving at
740217, 12 GMT.

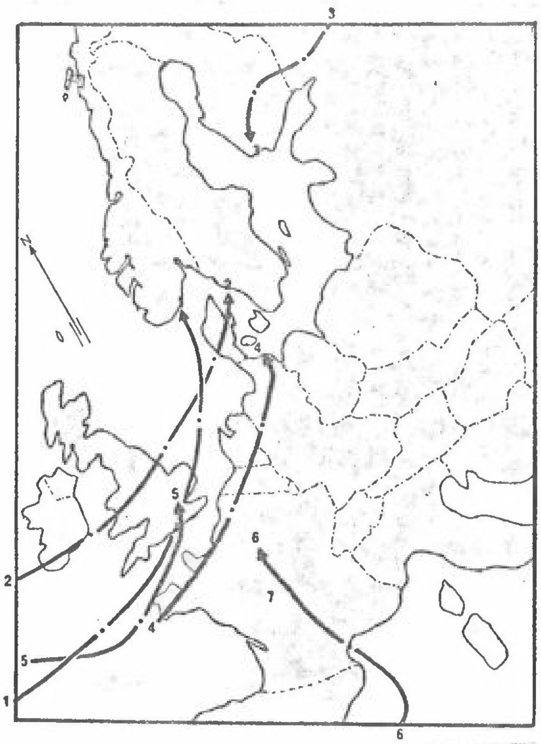


Trajectories arriving at
740217, 18 GMT.

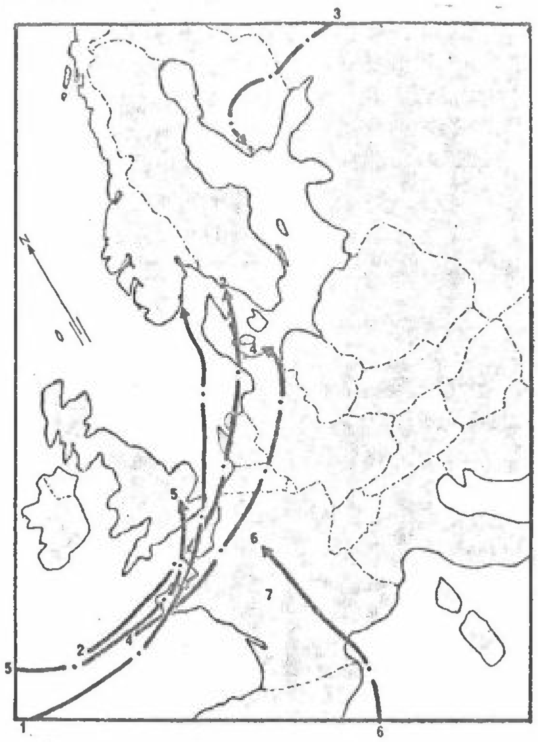
FIGURE 18

Day with high strong acid concentration.
Observed strong acid concentrations:

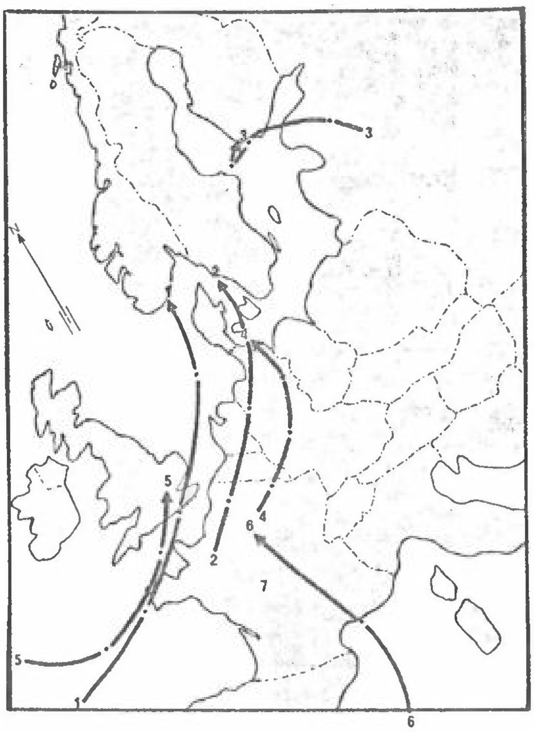
N 01	54
S 02	42
SF 2	48
DK 5	27
UK 1	-
F 03	0



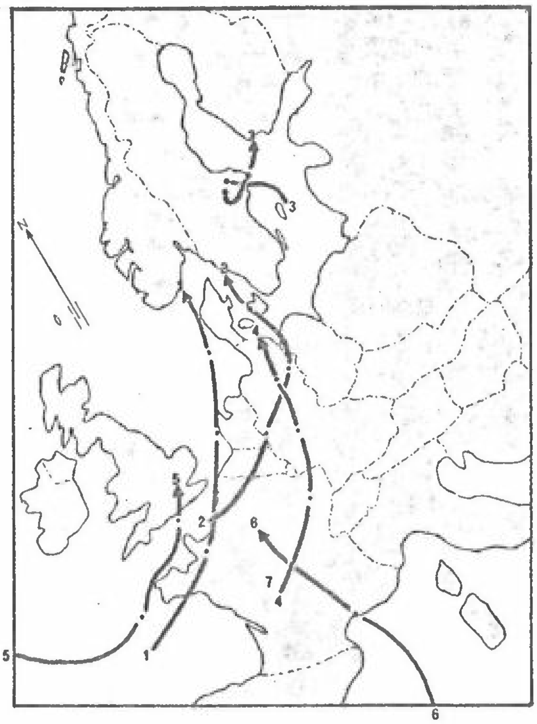
Trajectories arriving at
740320, 0 GMT.



Trajectories arriving at
740320, 6 GMT.



Trajectories arriving at
740320, 12 GMT.

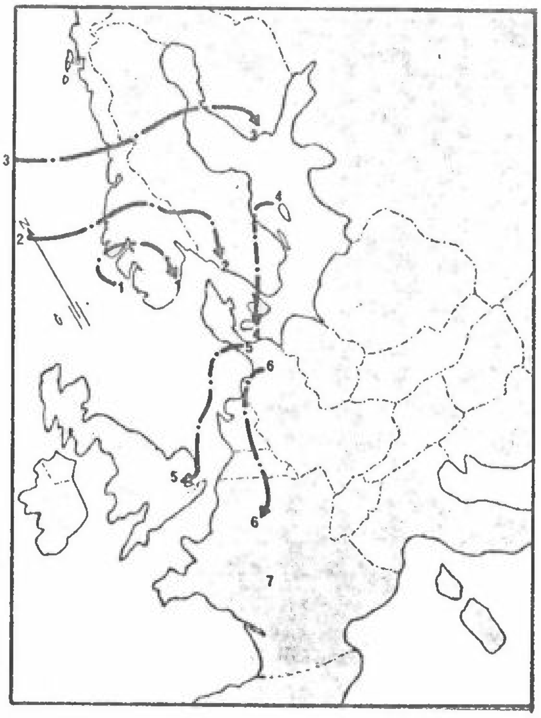


Trajectories arriving at
740320, 18 GMT.

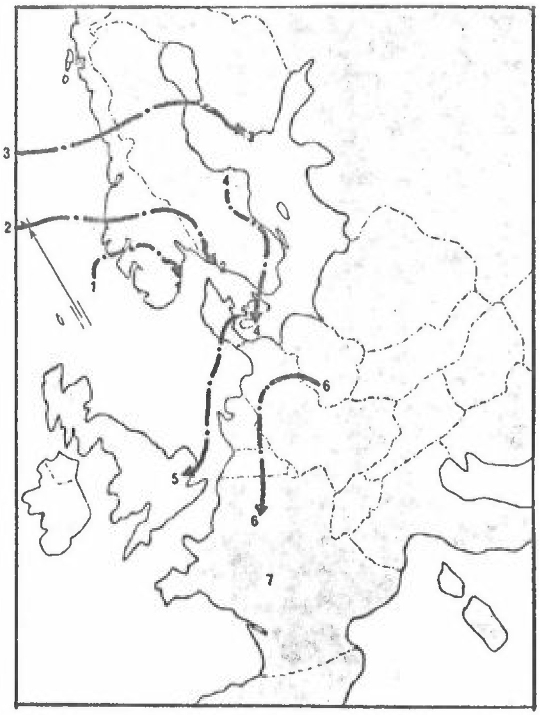
FIGURE 19

Day with high strong acid concentration.
Observed strong acid concentrations:

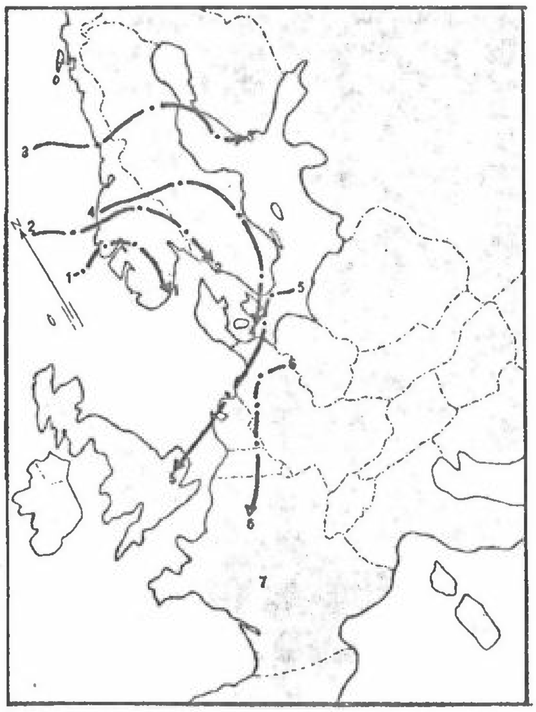
N 01	3
S 02	12
SF 2	40
DK 5	53
UK 1	-
F 03	-



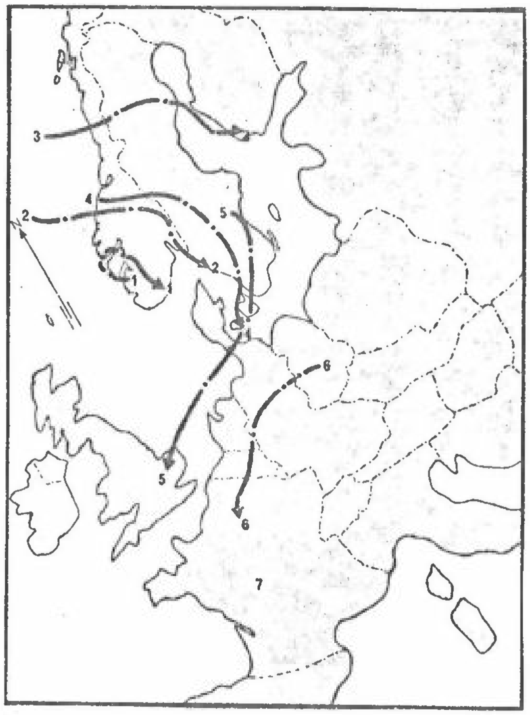
Trajectories arriving at
740219, 0 GMT.



Trajectories arriving at
740219, 6 GMT.



Trajectories arriving at
740219, 12 GMT.

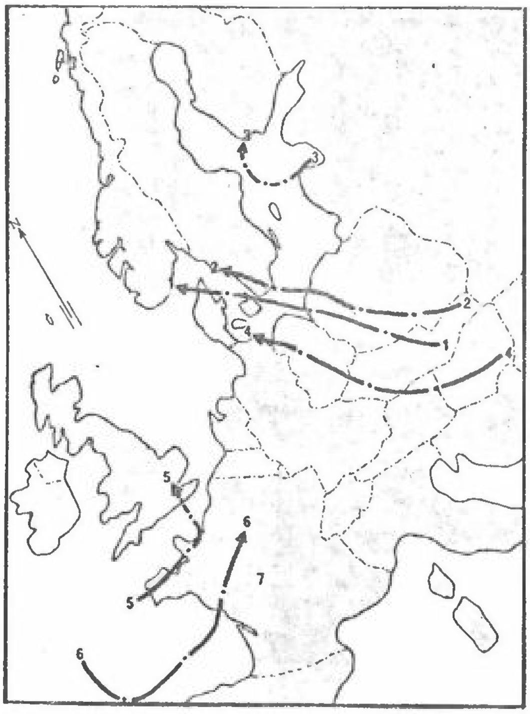


Trajectories arriving at
740219, 18 GMT.

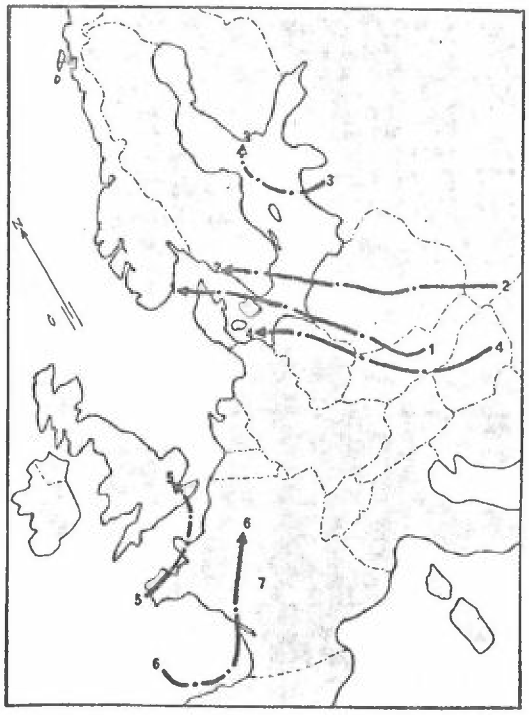
FIGURE 20

Day with high strong acid concentration.
Observed strong acid concentrations:

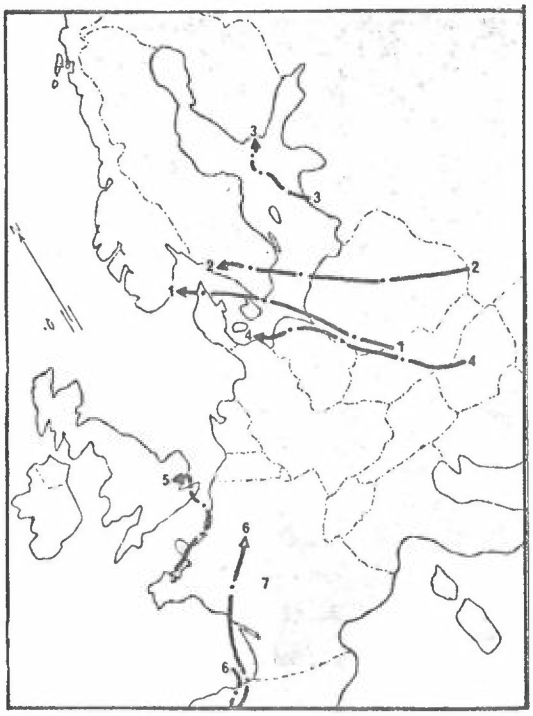
N 01	27
S 02	7
SF 2	52
DK 5	9
UK 1	-
F 03	0



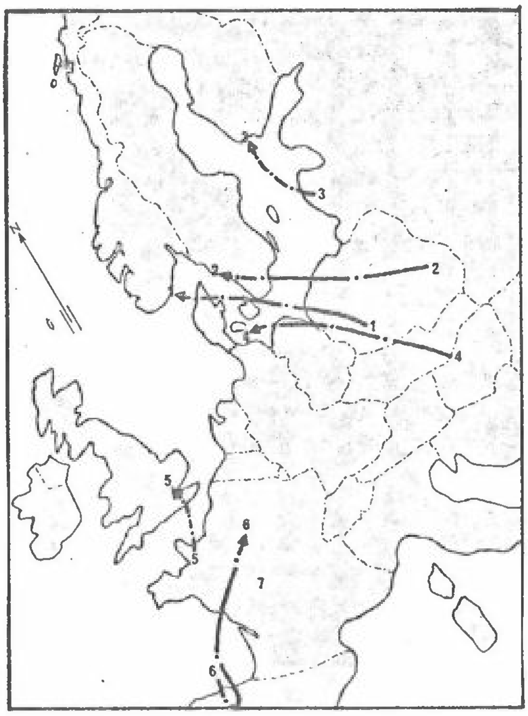
Trajectories arriving at 740313, 0 GMT.



Trajectories arriving at 740313, 6 GMT.



Trajectories arriving at 740313, 12 GMT.

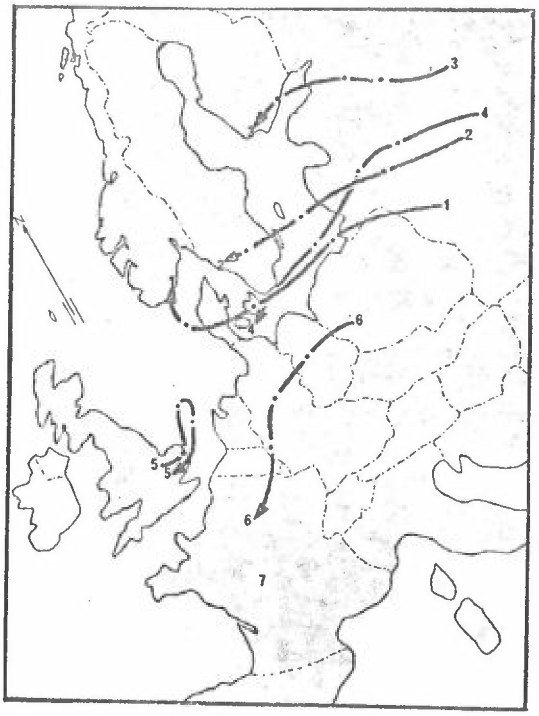


Trajectories arriving at 740313, 18 GMT.

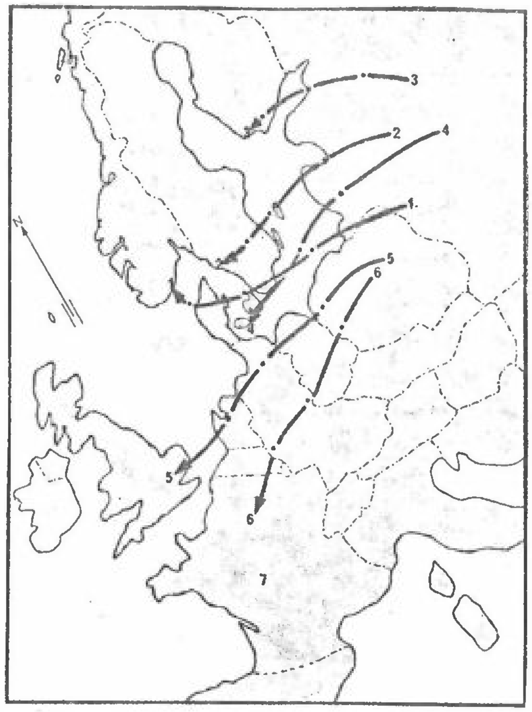
FIGURE 21

Day with high strong acid concentration.
Observed strong acid concentrations:

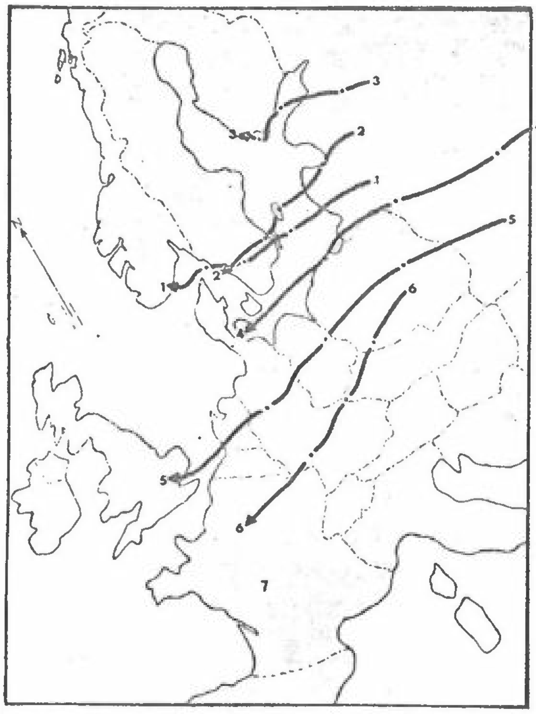
N 01	7
S 02	15
SF 2	-
DK 5	52
UK 1	50
F 03	0



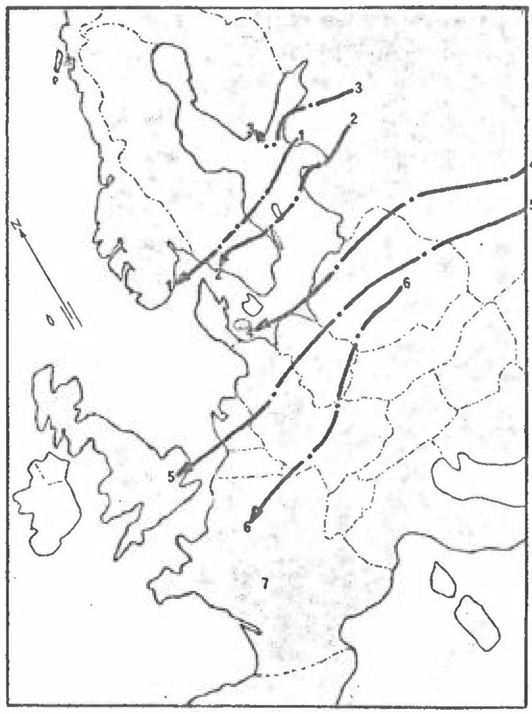
Trajectories arriving at
740308, 0 GMT.



Trajectories arriving at
740308, 6 GMT.



Trajectories arriving at
740308, 12 GMT.

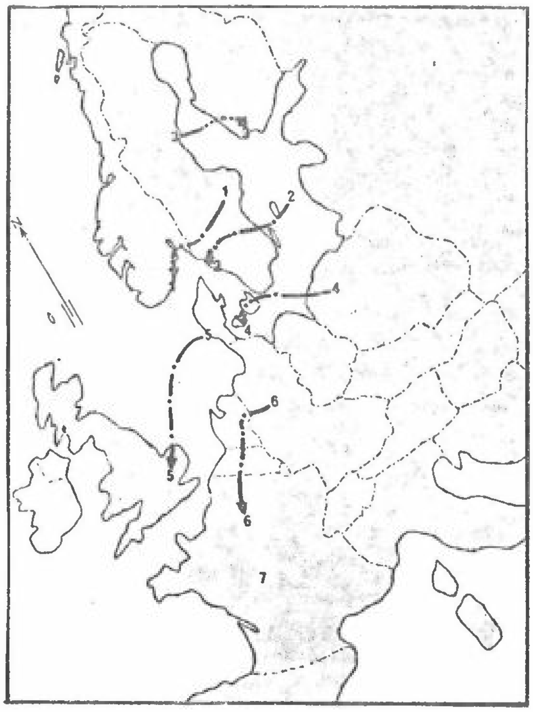


Trajectories arriving at
740308, 18 GMT.

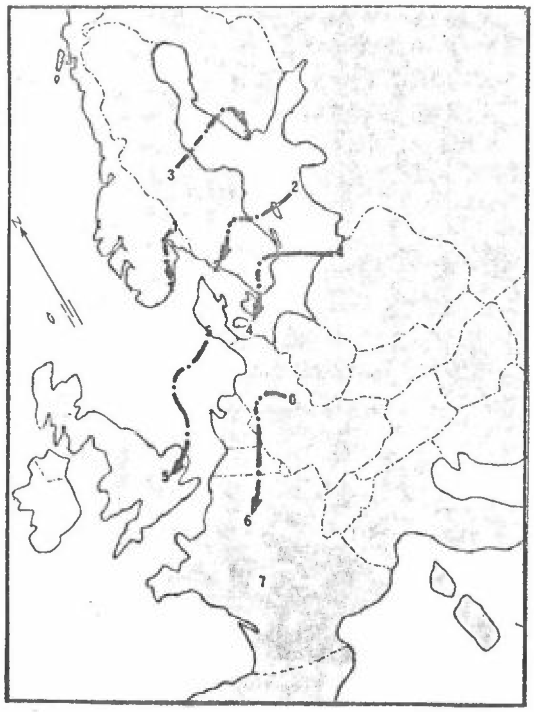
FIGURE 22

Day with high strong acid concentration.
Observed strong acid concentrations:

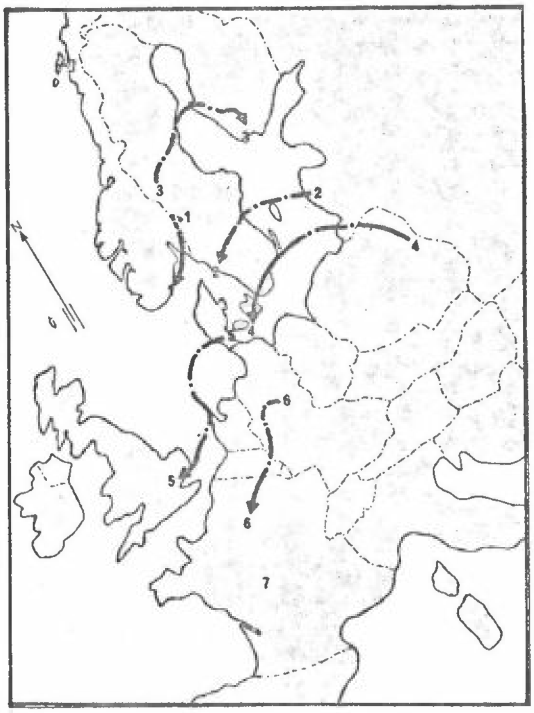
N 01	45
S 02	3
SF 2	-
DK 5	26
UK 1	-
F 03	0



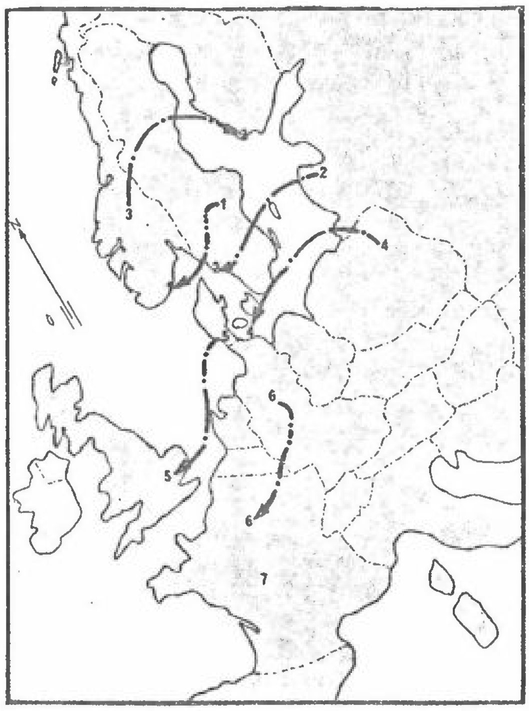
Trajectories arriving at
740331, 0 GMT.



Trajectories arriving at
740331, 6 GMT.



Trajectories arriving at
740331, 12 GMT.

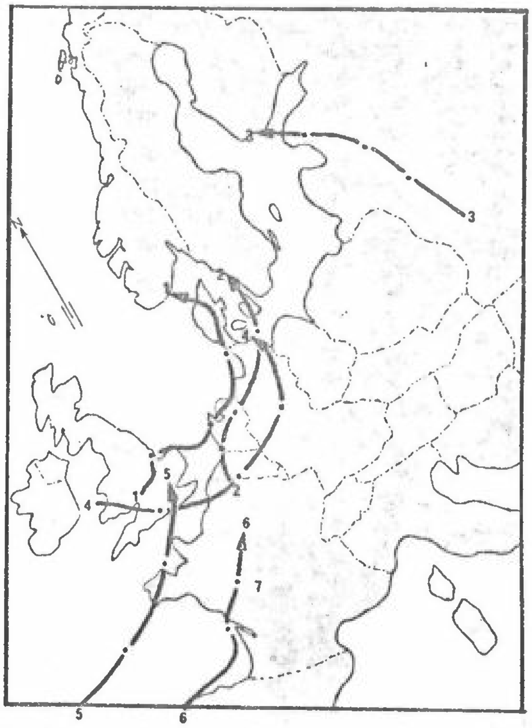


Trajectories arriving at
740331, 18 GMT.

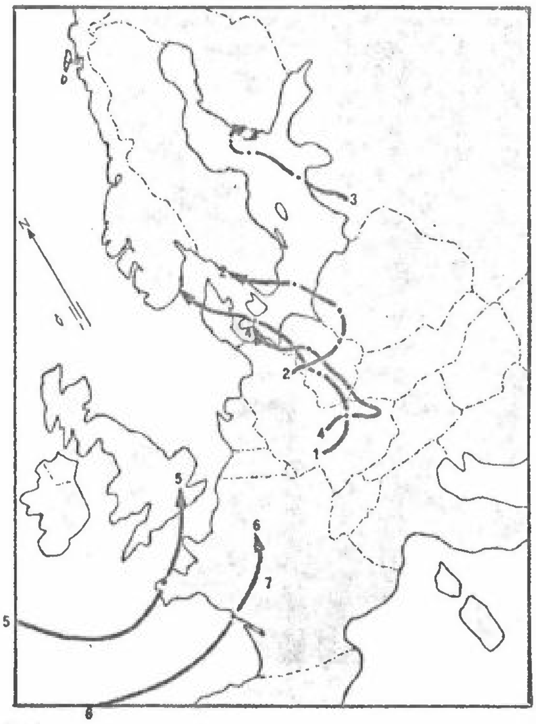
FIGURE 23

Day with high stronc acid concentration.
Observed strong acid concentrations:

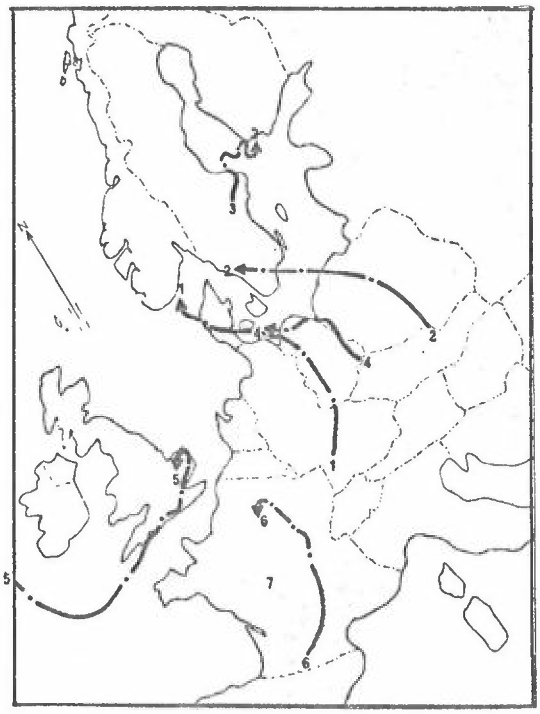
N 01	44
S 02	9
SF 2	5
DK 5	1
UK 1	0
F 03	-



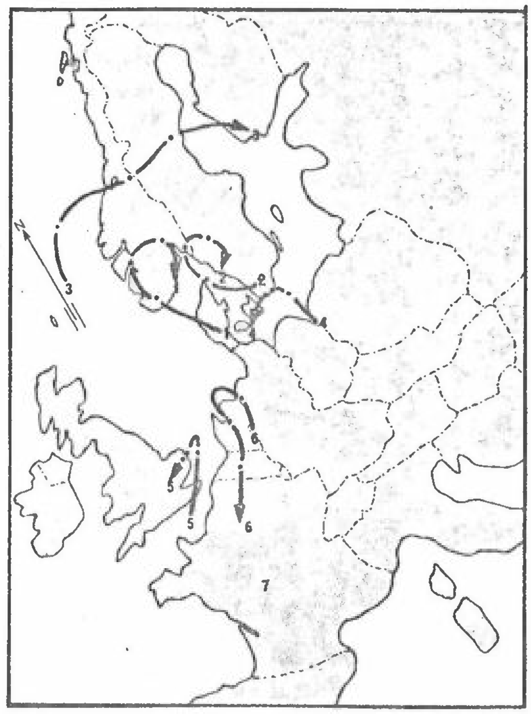
Trajectories arriving at
740215, 12 GMT.



Trajectories arriving at
740216, 12 GMT.

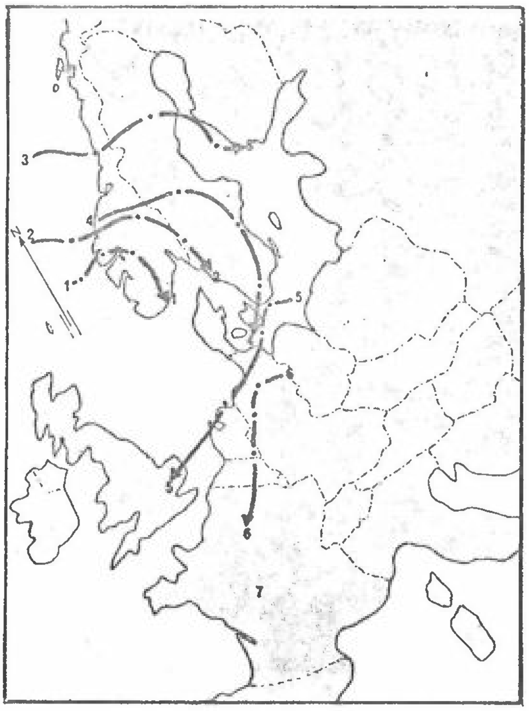


Trajectories arriving at
740217, 12 GMT.

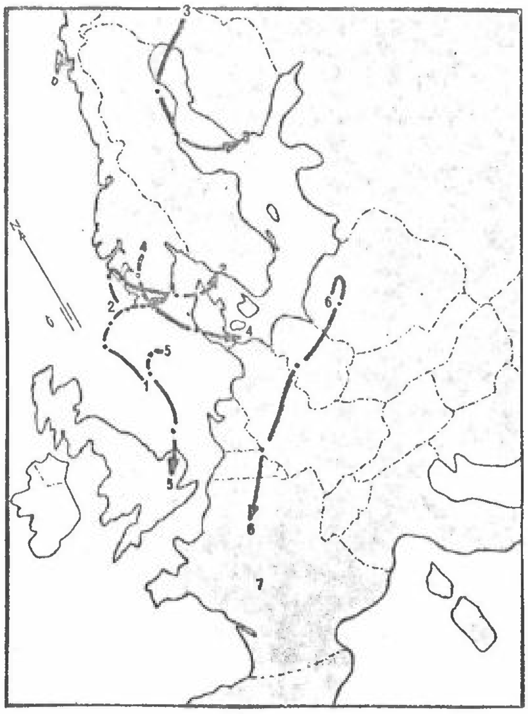


Trajectories arriving at
740218, 12 GMT.

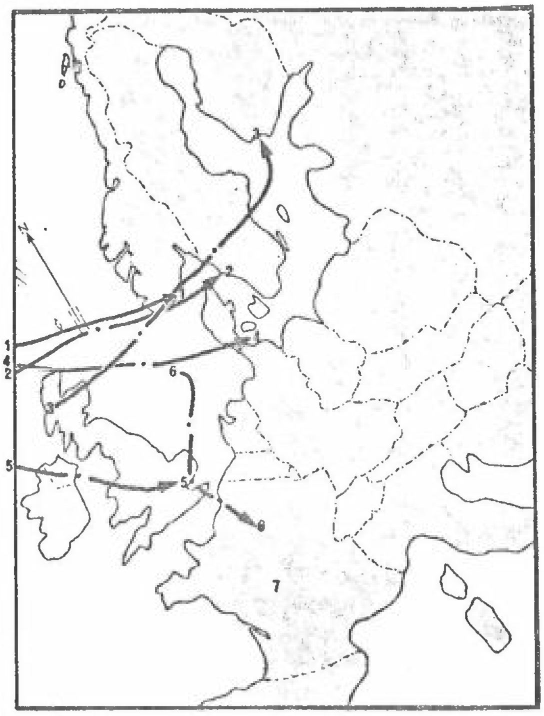
FIGURE 24



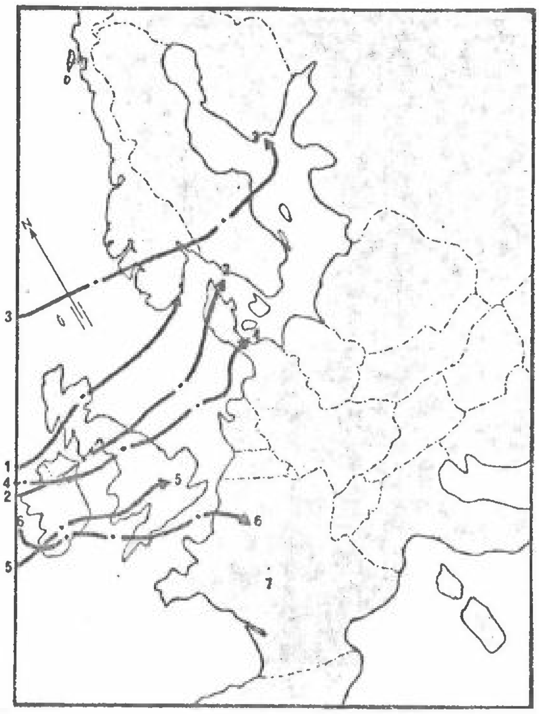
Trajectories arriving at
740219, 12 GMT.



Trajectories arriving at
740220, 12 GMT.

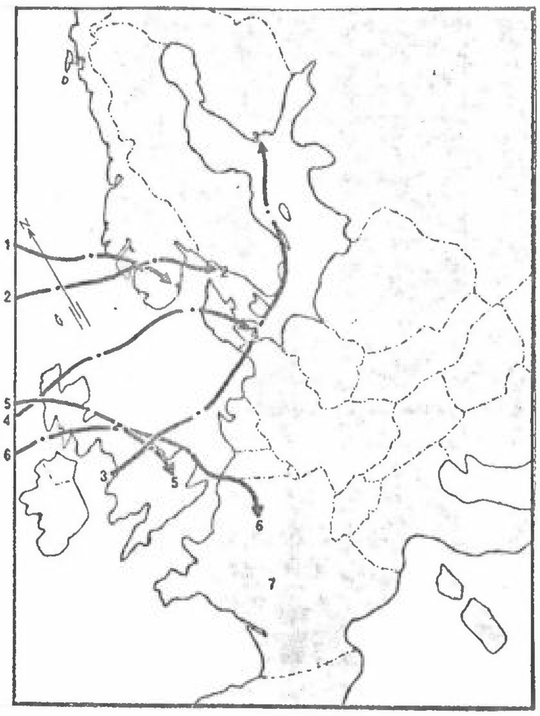


Trajectories arriving at
740221, 12 GMT.

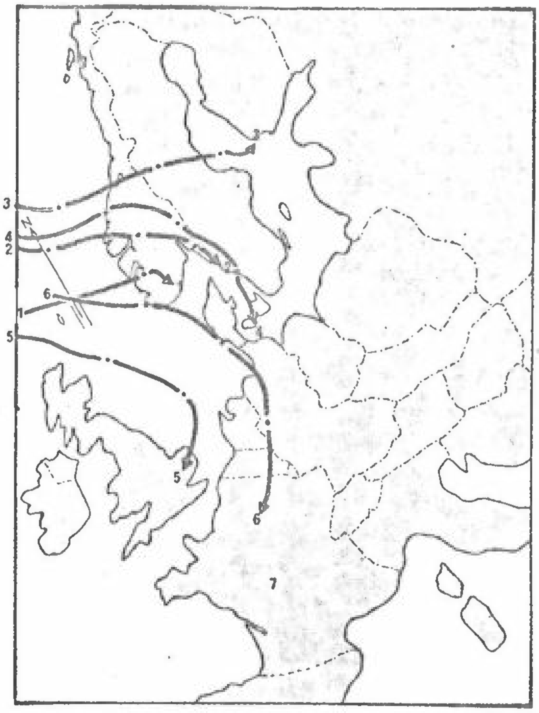


Trajectories arriving at
740222, 12 GMT.

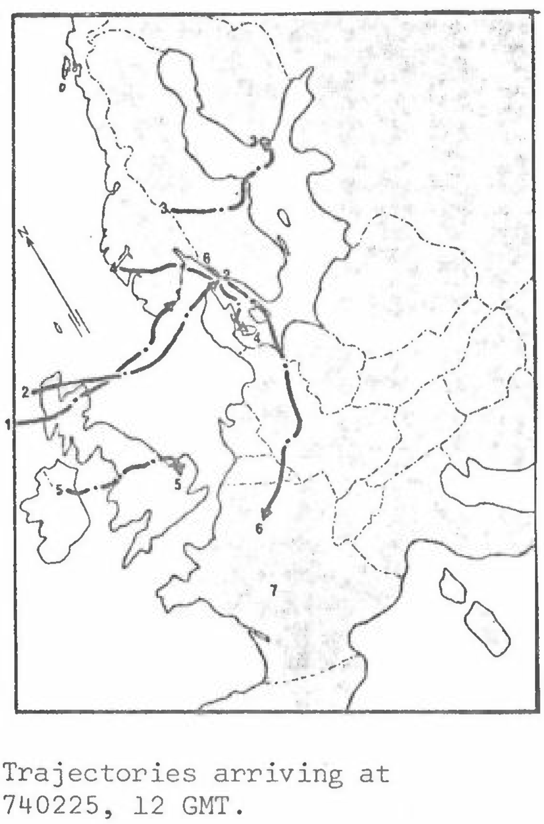
FIGURE 25



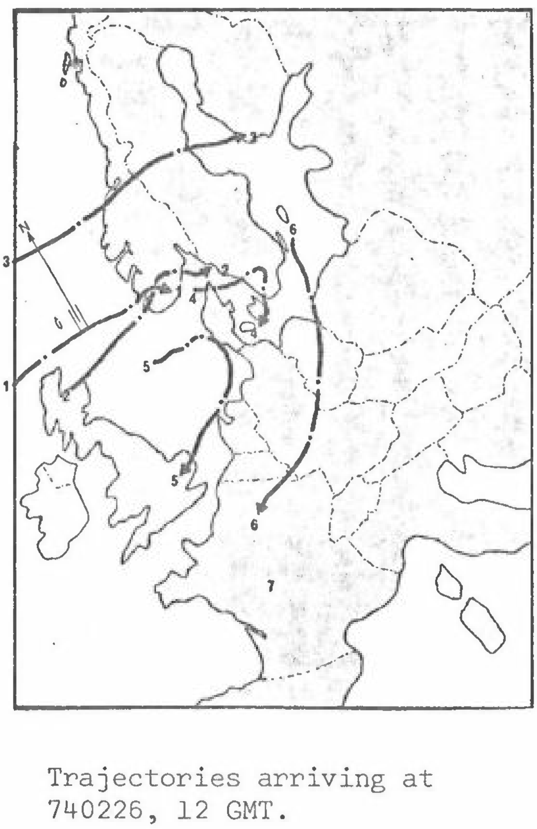
Trajectories arriving at
740223, 12 GMT.



Trajectories arriving at
740224, 12 GMT.

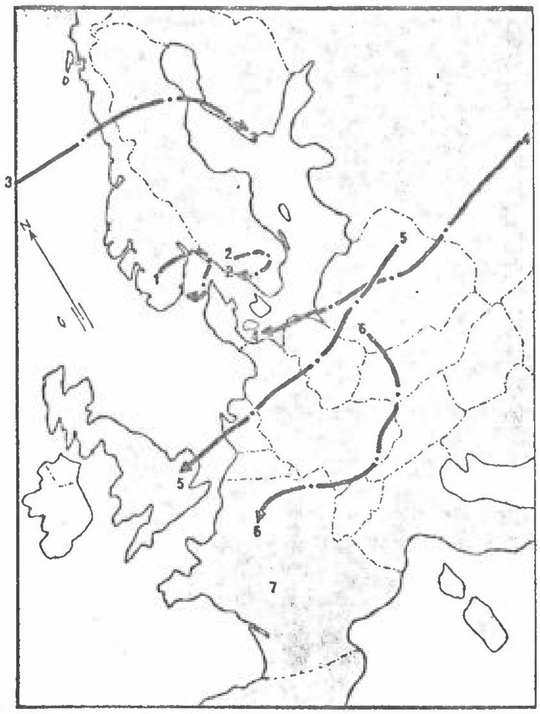


Trajectories arriving at
740225, 12 GMT.

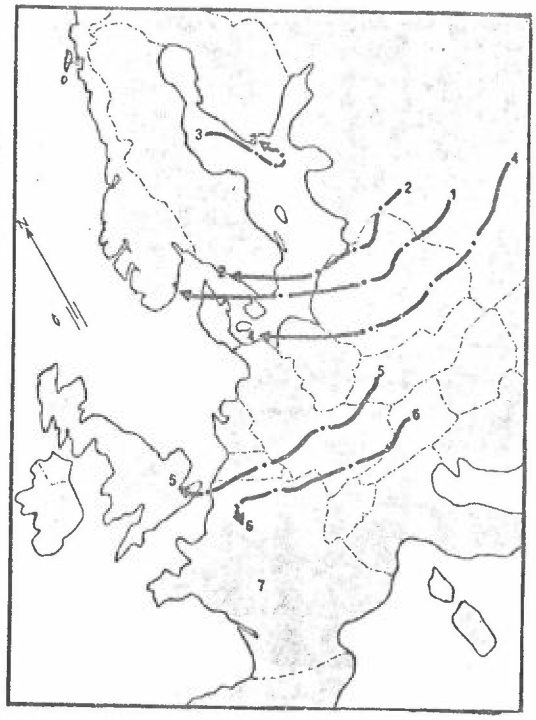


Trajectories arriving at
740226, 12 GMT.

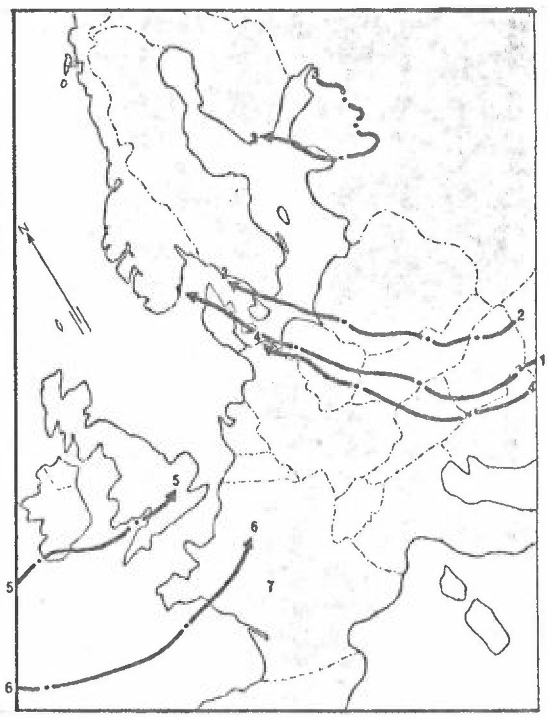
FIGURE 26



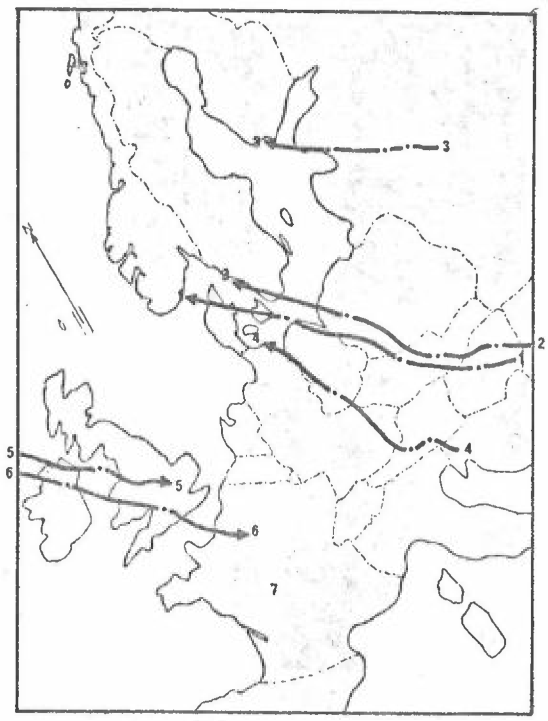
Trajectories arriving at
740227, 12 GMT.



Trajectories arriving at
740228, 12 GMT.

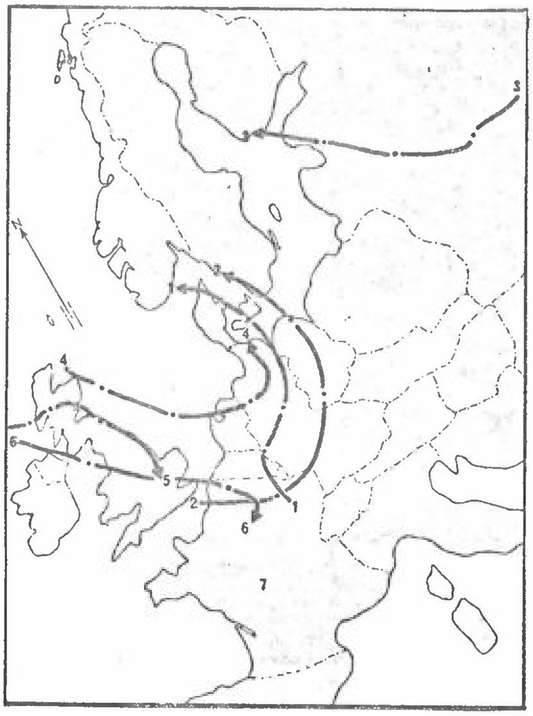


Trajectories arriving at
740301, 12 GMT.

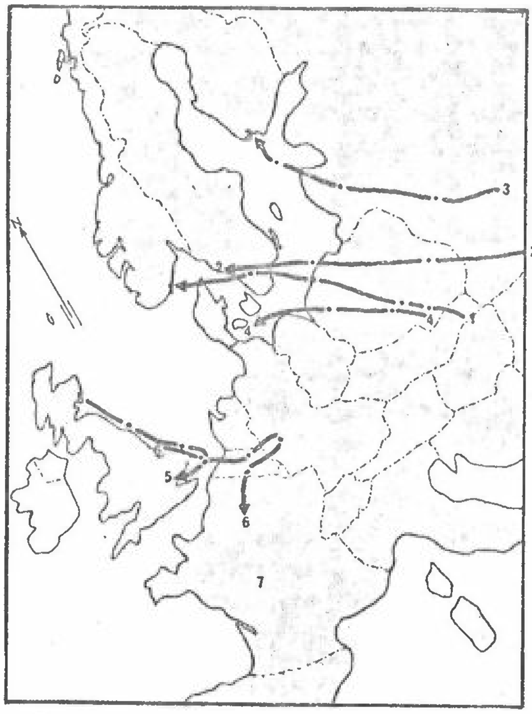


Trajectories arriving at
740302, 12 GMT.

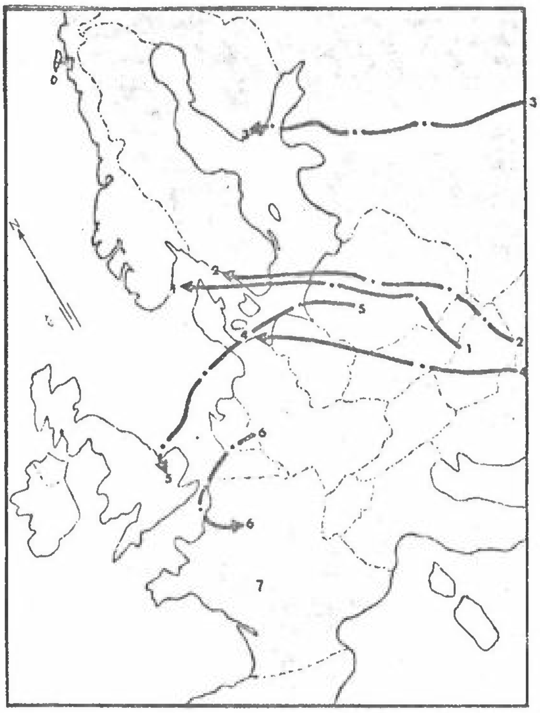
FIGURE 27



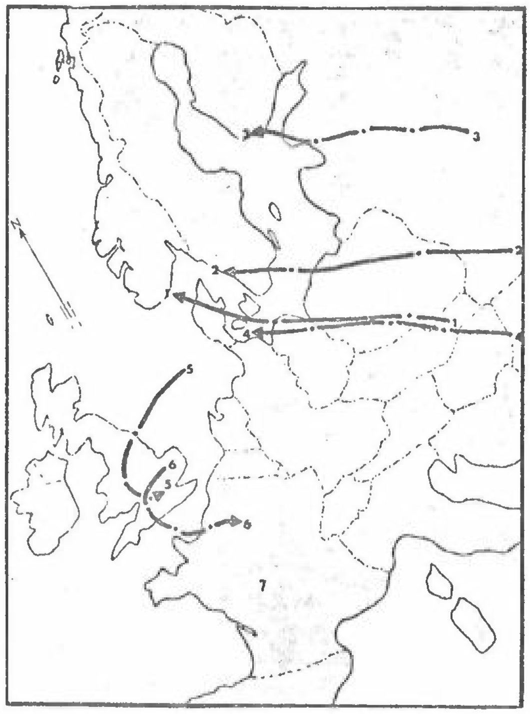
Trajectories arriving at
740303, 12 GMT.



Trajectories arriving at
740304, 12 GMT.

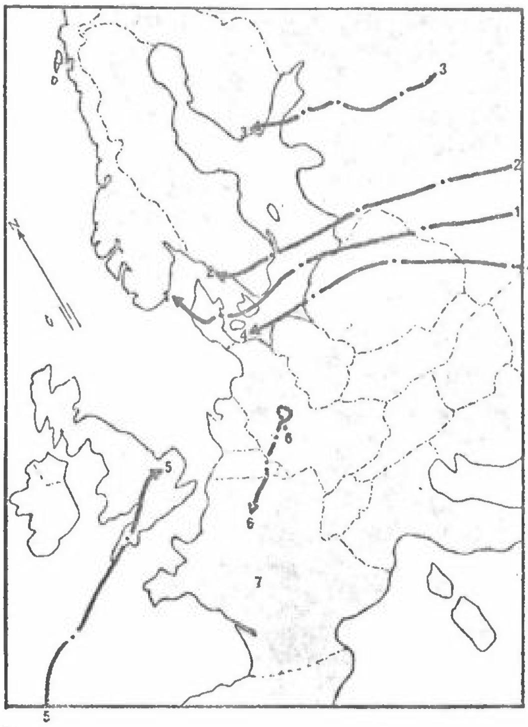


Trajectories arriving at
740305, 12 GMT.

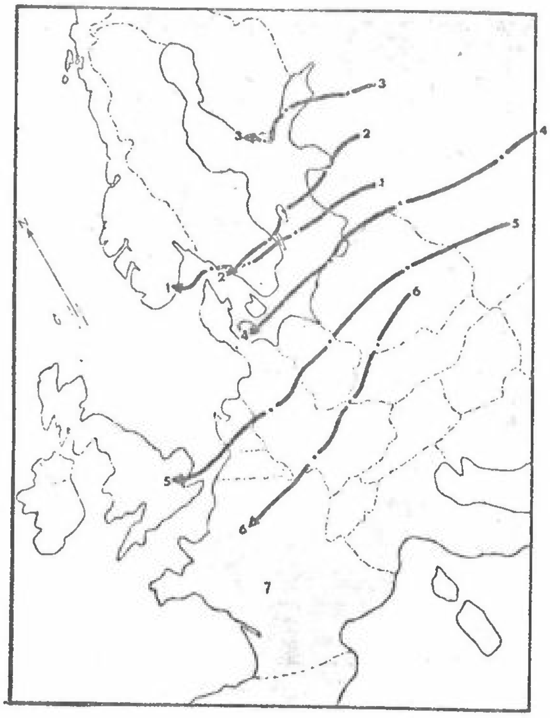


Trajectories arriving at
740306, 12 GMT.

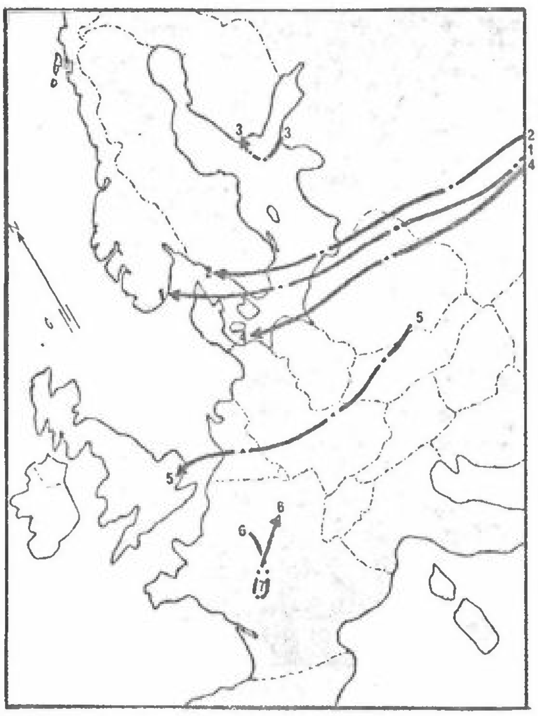
FIGURE 28



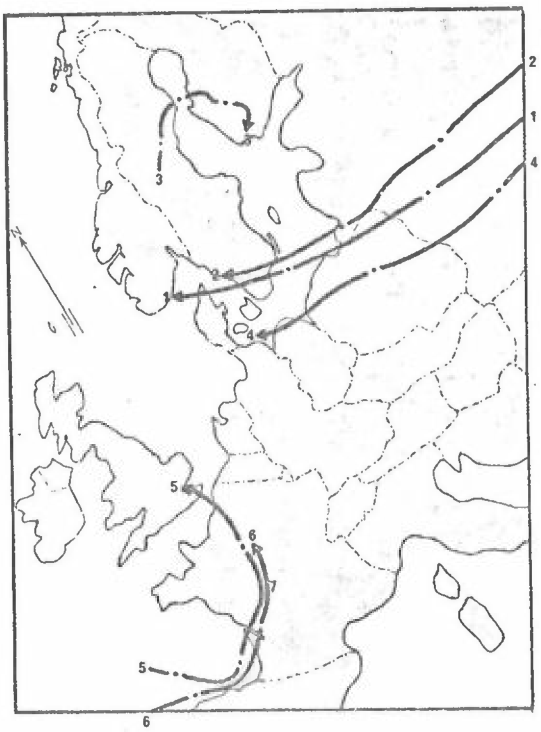
Trajectories arriving at
740307, 12 GMT.



Trajectories arriving at
740308, 12 GMT.

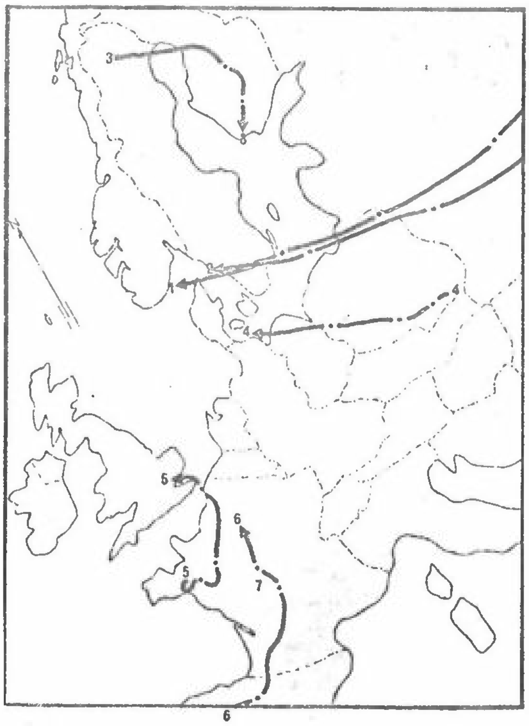


Trajectories arriving at
740309, 12 GMT.

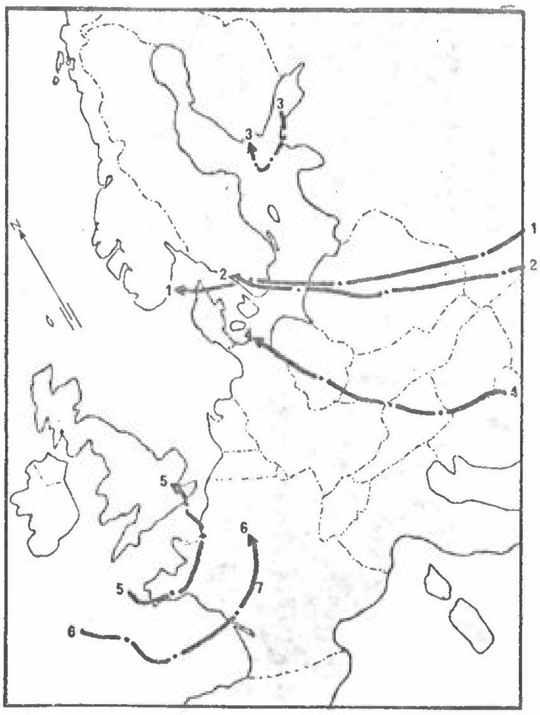


Trajectories arriving at
740310, 12 GMT.

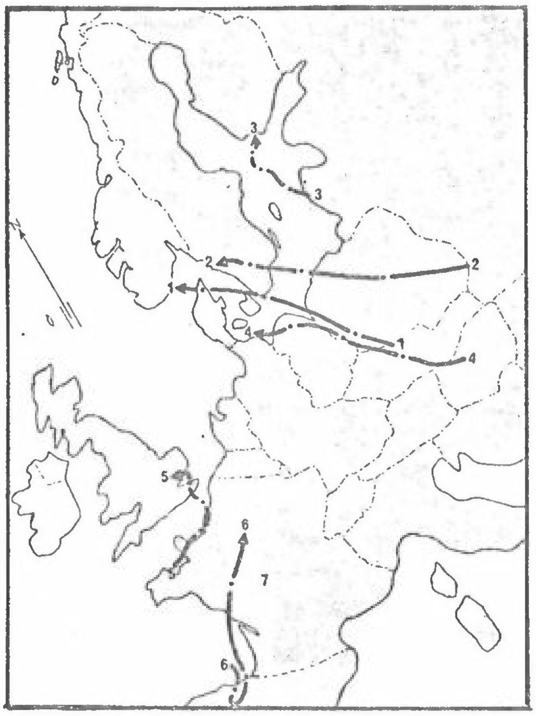
FIGURE 29



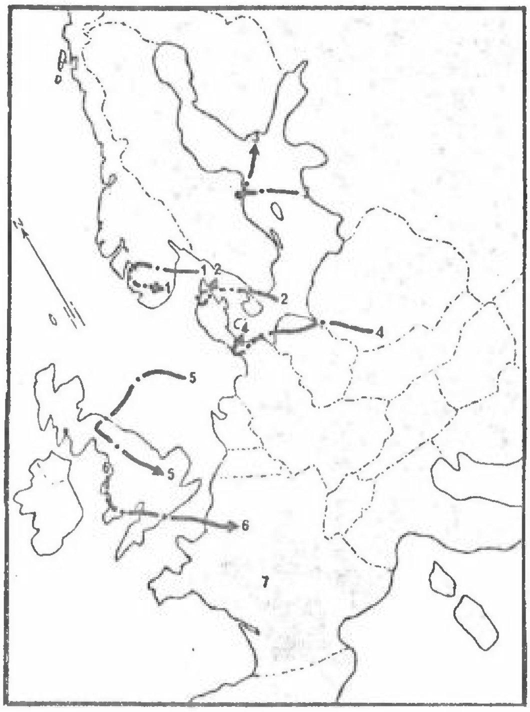
Trajectories arriving at
740311, 12 GMT.



Trajectories arriving at
740312, 12 GMT.

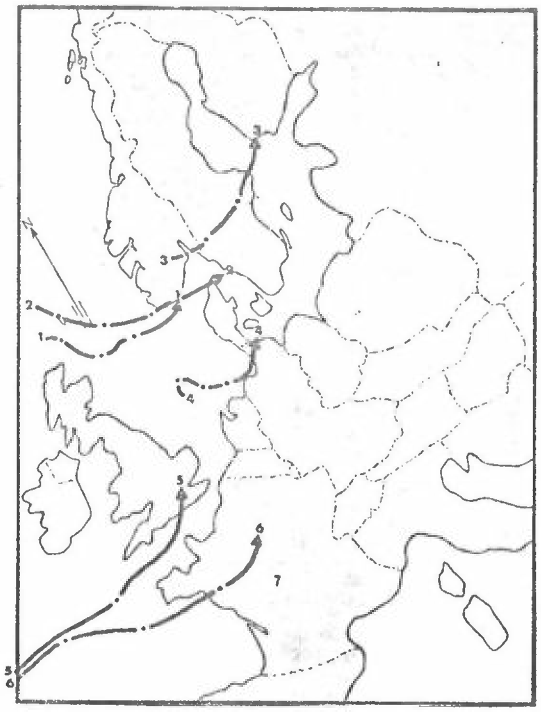


Trajectories arriving at
740313, 12 GMT.

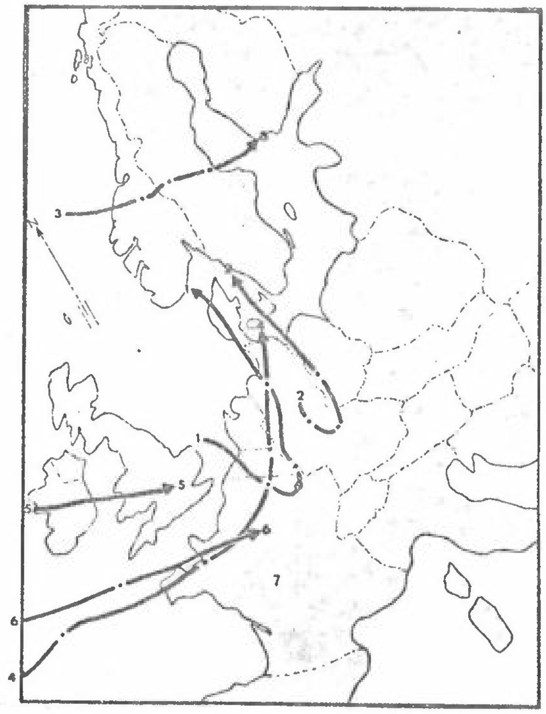


Trajectories arriving at
740314, 12 GMT.

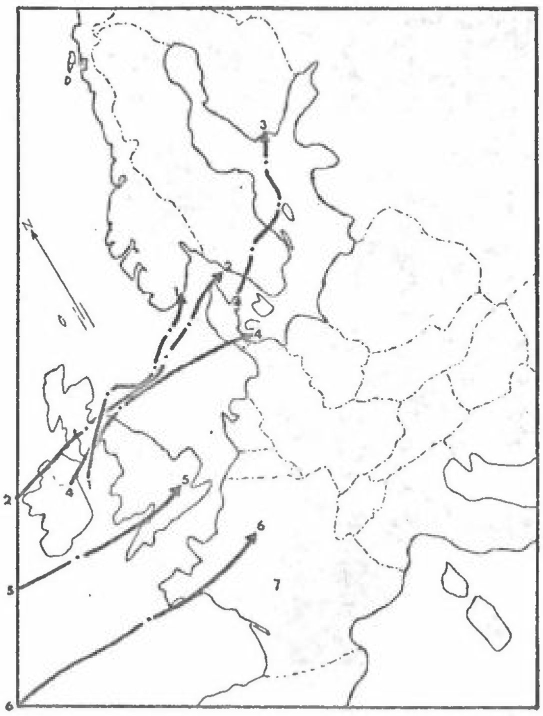
FIGURE 30



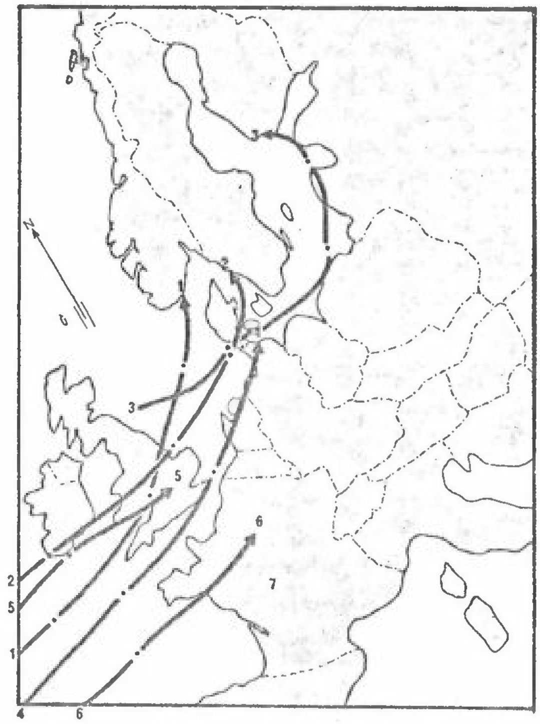
Trajectories arriving at
740315, 12 GMT.



Trajectories arriving at
740316, 12 GMT.

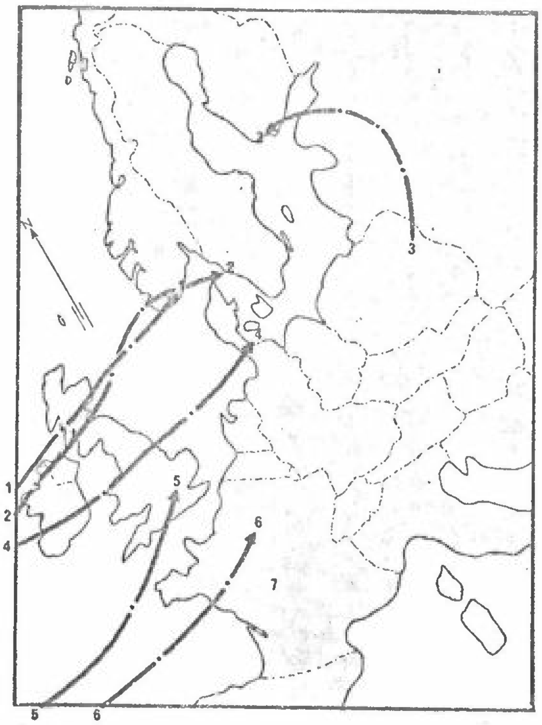


Trajectories arriving at
740317, 12 GMT.

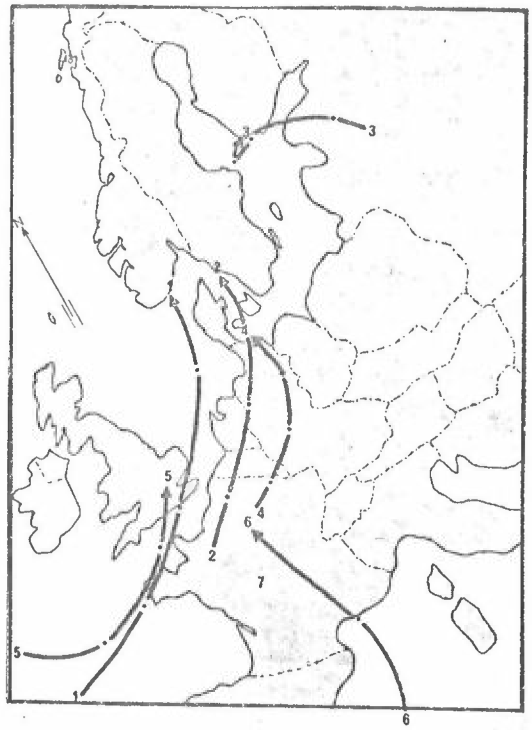


Trajectories arriving at
740318, 12 GMT.

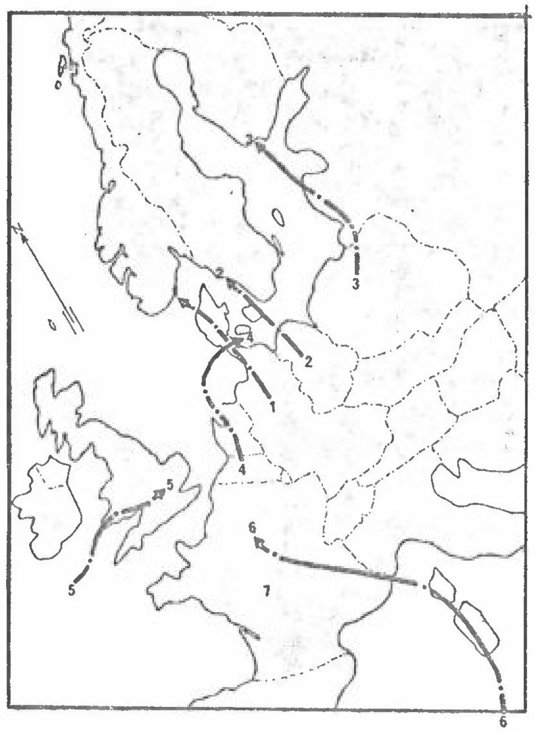
FIGURE 31



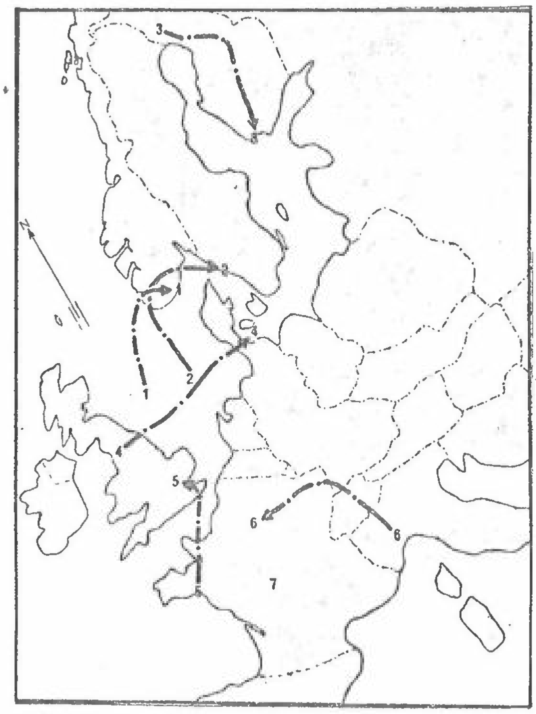
Trajectories arriving at
740319, 12 GMT.



Trajectories arriving at
740320, 12 GMT.

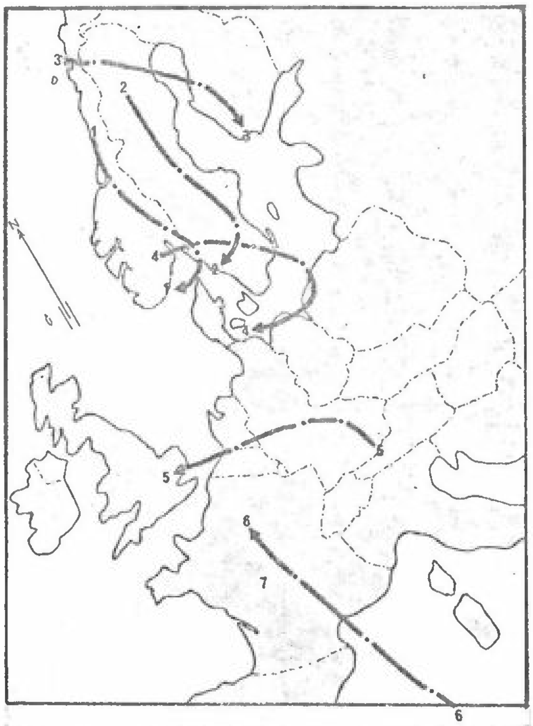


Trajectories arriving at
740321, 12 GMT.

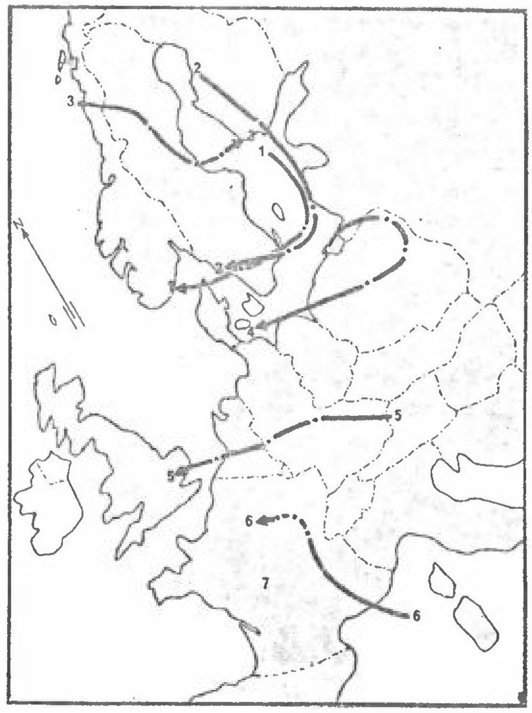


Trajectories arriving at
740322, 12 GMT.

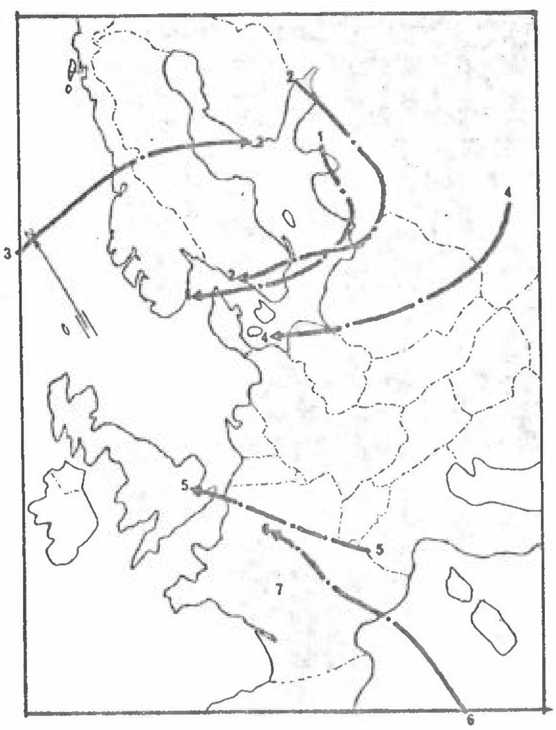
FIGURE 32



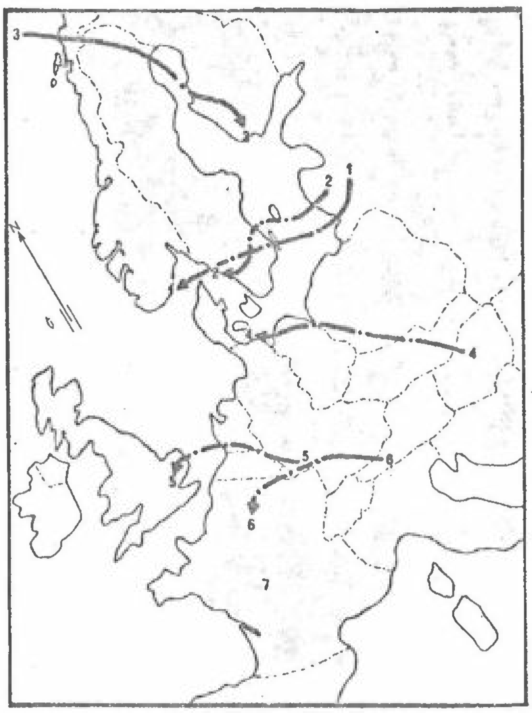
Trajectories arriving at 740323, 12 GMT.



Trajectories arriving at 740324, 12 GMT.

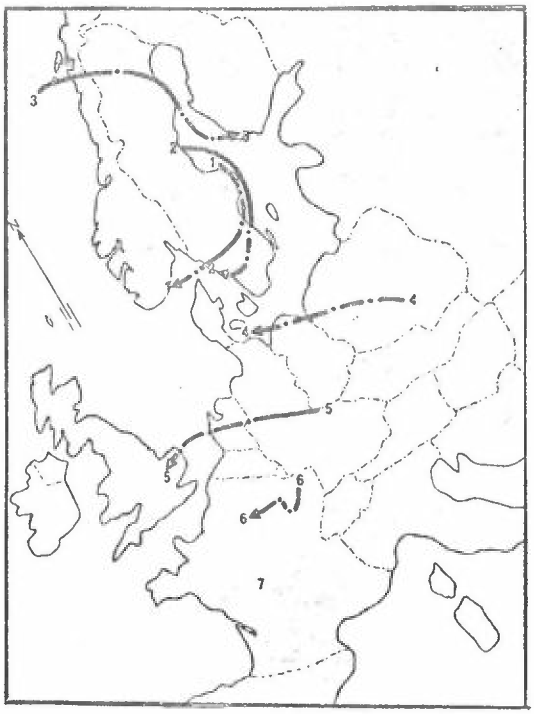


Trajectories arriving at 740325, 12 GMT.

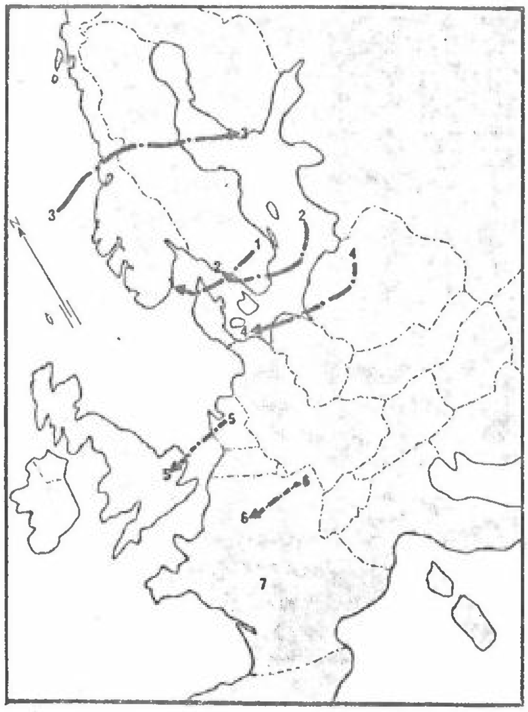


Trajectories arriving at 740326, 12 GMT.

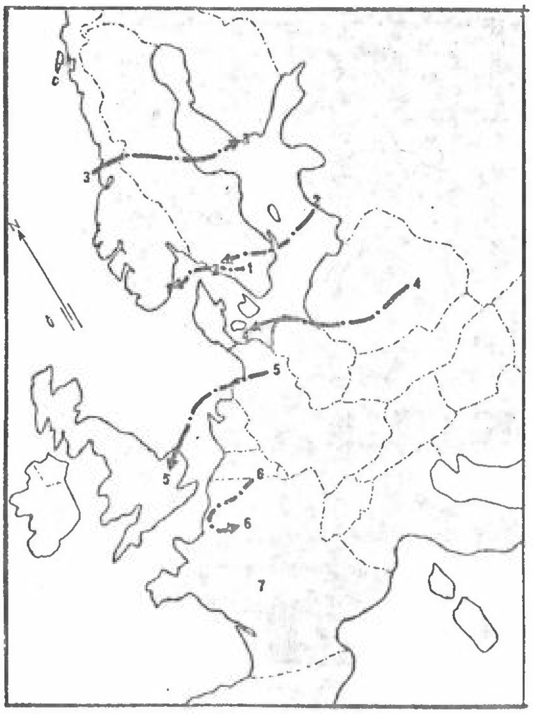
FIGURE 33



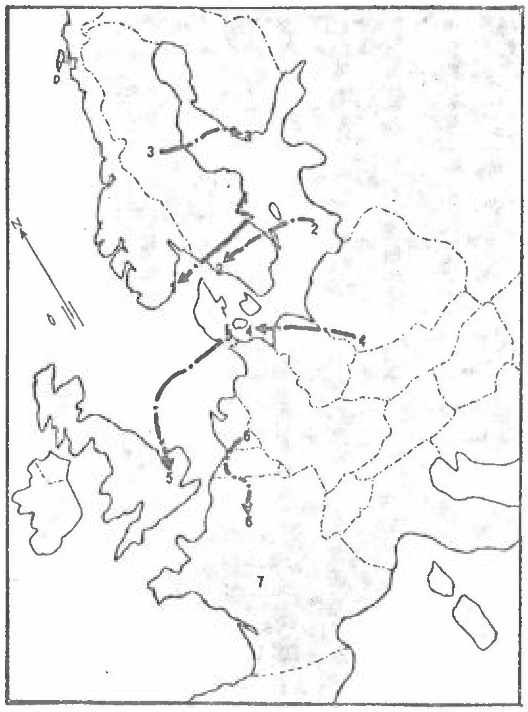
Trajectories arriving at 740327, 12 GMT.



Trajectories arriving at 740328, 12 GMT.

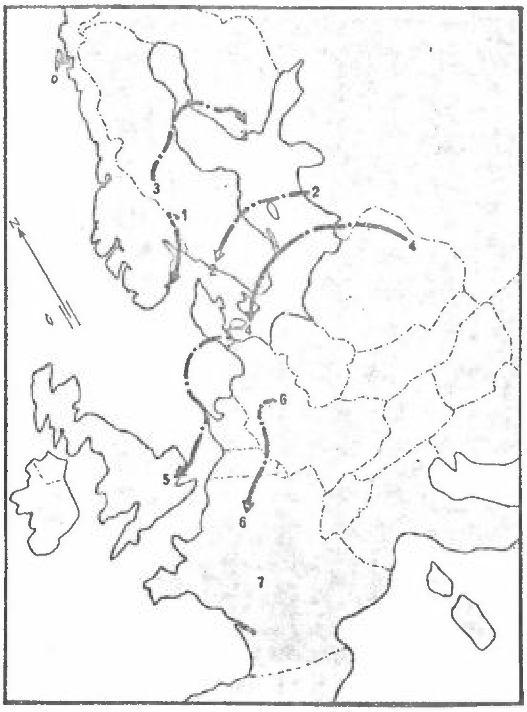


Trajectories arriving at 740329, 12 GMT.



Trajectories arriving at 740330, 12 GMT.

FIGURE 34



Trajectories arriving at
740331, 12 GMT.

FIGURE 35