EQUILIBRIUM COMPOSITION OF AEROSOLS GENERATED FROM
SULPHURIC AND NITRIC ACIDS, WATER, AND AMMONIA

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18 Sammanfattning av projektet/rapporten (ange gärna målsättning, metod, teknik resultat m m)

The water-soluble part of airborne fine white (graphite poor) particles
is usually with reference to its ionic composition in equilibrium with
air. This has been checked by means of the phase diagram for the system
$(NH_4)_2SO_4 - H_2SO_4 - H_2O$ which is now available.

In the same way it has been shown that the ionic concentration in preci-
pitation probably represents equilibrium condition near the cloud base
and not at the ground level.

Finally the disagreement between the composition of the water-soluble
part of black (graphite rich) particles and the air according to the
phase diagram may be due to an analytical bias caused by a sorbed
alkaline layer on the graphite particles.

19 Sammanfattningen skriven av

Förf.

20 Förslag till nyckelord

Y. sulphuric acid, nitric acid, water, ammonia, phase diagram,
black and white particles, precipitation

21 Klassifikationssystem och klass

22 Indexterm

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EQUILIBRIUM COMPOSITION OF AEROSOLS GENERATED FROM SULPHURIC AND NITRIC ACIDS, WATER, AND AMMONIA

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A large number of investigations have shown that the ion composition of the water-soluble part of fine airborne particles consists predominantly of the ions NH_4^+, H^+, HSO_4^- and SO_4^{2-}.

The reason for this predominance is probably that the fine particles often appear initially in the form of sulphuric acid droplets. These then react in the air with water vapour and ammonia.

It has previously been stated (Brosset, 1978) that the concentration ratio $\left[NH_4^+\right]/\left[H^+\right]$ (more correctly, activity ratio) in the water solution constituting the whole or a part of airborne particles is dependent on the partial pressure of ammonia (pNH_3) in the air. Thus the ammonia concentration of the air will also affect the composition of the solid phases which, under certain conditions, may crystallise from the solution in question. However, this latter process is also dependent on the relative humidity (r.h.) of the air.

Furthermore, it is known that particles, when not too acid, contain nitrate. As the final oxidation step of nitrogen oxides is HNO_3, which exists in the atmosphere primarily in the gaseous phase, the nitrate concentration in question is likely to arise from the interaction of gaseous HNO_3 with the liquid phase of the particles.

In other words, the equilibrium concentration of particles originating from H_2SO_4 is determined by the phase diagram in the system

$$H_2SO_4 - H_2O - NH_3 - HNO_3$$
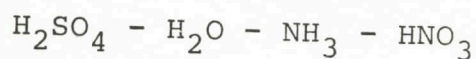
At present, only a few points in this diagram have been calculated (Lee and Brosset, 1979). More comprehensive data are available, however, for the acid part of the system

$$H_2SO_4 - H_2O - NH_3$$
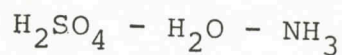
with the choice of components corresponding to

$$(NH_4)_2SO_4 - H_2SO_4 - H_2O.$$
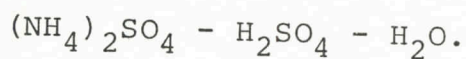
A phase diagram was evaluated for the latter system. It is based on solubility measurements by d'Ans (1913), water activity measurements by Tang et al. (1978), and calculations of the partial pressure of NH_3 (Lee and Brosset, 1979). The data from Tang et al. are given for 30°C but with good approximations they are valid for 25°C. All other data are valid for 25°C.

The diagram is presented in Fig. 1. It makes it possible to determine the phase composition and, for the liquid phase, the ionic composition of a particle originating from H_2SO_4, provided measurement data on ammonia concentration (pNH_3) and r.h. in the air are available.

However, such evaluation of the phase composition is easier if the diagram is drawn up in the form presented in Fig. 2.

Here, the axes represent r.h. in % and log pNH_3. The line L_1-L_2-L_3 is the solubility curve.

The area to the left of the solubility curve represents the liquid phase. If pNH_3 and r.h. are determined and give the values of point 1, the aerosol, if it is in equilibrium, consists of droplets.

The area $L_1L_2M_1$ represents the solid phase $(NH_4)_2SO_4$. If the corresponding analysis results in point 2, the particles, in equilibrium, are crystals of this compound.

Similarly, the area $L_2L_3M_3$ represents the solid phase $(NH_4)_3H(SO_4)_2$ and the area $M_1M_2M_3L_2$ represents a mixture of the solid phases $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$.

Unfortunately, those parts of the total diagram which correspond to temperature conditions normally prevailing in Sweden (0-10°C) are not yet available. Nevertheless, we have tried through approximations to produce a diagram for 10°C. It is represented in Fig. 3 together with a number of experimental results.

The experiments here consisted of two series of measurement of r.h. (every 6 h) and daily mean values of pNH_3 at a remote sampling station (40 km S Gothenburg). They also included the collection of daily samples of particles which were analysed for NH_4^+ and H^+.

According to the diagram, the particles during the tests in October 1978 should consist mainly of $(NH_4)_2SO_4$ and solution thereof. The analytical result showed very high values (~ 10 and more for $[NH_4^+]/[H^+]$. For the measurements during March 1979, the diagram predicts at least some formation of the phase $(NH_4)_3H(SO_4)_2$. The analytical result for $[NH_4^+]/[H^+]$ corresponded to values ranging from 2.8 to 1.7, showing that, in this case, the particles really were acid.

These results seem to indicate that observed particle compositions were in acceptable agreement with the phase diagram. However, with other observations this was not always the case.

As discussed above, strong acid is introduced into a liquid phase (water) in the form of H_2SO_4 and HNO_3. Part of these will be neutralised by NH_3. However, this neutralisation is a reversible process, depending on pNH_3 in the air. Hence, it seems reasonable to define a potential strong acid as the sum of the concentrations

$$2\left[SO_4^{2-}\right] + \left[NO_3^-\right]$$

The part of this potential acid represented by HNO_3 (q) is, consequently

$$q = \frac{\left[NO_3^-\right]}{\left[2\left(SO_4^{2-}\right)\right] + \left[NO_3^-\right]}$$

In connection with certain investigations, it was interesting to determine q in precipitation samples. In 1978-79, such measurements were performed both at the west and east coasts of Sweden. The result is shown in Fig. 4.

Somewhat unexpectedly, the result shows peak concentrations of q in the winter season, when pNH_3 is very low (Fig. 5). However, low pNH_3 at equilibrium corresponds to a low value of $\left[NH_4^+\right]/\left[H^+\right]$ which implies that the liquid phase is acid. But acid solution cannot contain a high concentration of NO_3^-, which is obvious from Table 1.

The conclusion which may be drawn from these results is that the precipitation samples were not in equilibrium with the air at ground level. Instead, they may have represented conditions prevailing near the clouds.

Another interesting point in the failure of the phase diagram is the composition of black particles.

During the winter half of the year such particles are transported episodically into the air over Scandinavia from central Europe (Brosset, 1976). As shown by Rosen et al. (1978), the black component in these particles (usually called soot) is in fact graphite. This means that a least the core of black particles may have the properties of charcoal.

Table 1

Chemical composition of solid phases

Composition of the liquid phase in terms of ratios of total concentration of $[NH_4^+]$ and $[SO_4^-]$. Relative humidity, partial pressures of NH_3, HNO_3 and HCl. Concentration of nitrate and chloride in solution amounts to 0.1 and 0.05, respectively of total sulphate.

No.	Solid phase	$\dfrac{2C_{(NH_4)_2SO_4}}{C_{H_2SO_4}+C_{(NH_4)_2SO_4}}$	r.h. %	p_{NH_3}	p_{HNO_3}	p_{HCl}
					ppb	
	$(NH_4)_2SO_4$	2.00	80	$1.3 \cdot 10^4$	$6.9 \cdot 10^{-5}$	$3.0 \cdot 10^{-4}$
	$(NH_4)_2SO_4$	1.86	79	$3.9 \cdot 10^{-1}$	2.7	$1.1 \cdot 10^1$
3	$(NH_4)_2SO_4$	1.74	77	$1.4 \cdot 10^{-1}$	8.1	$3.9 \cdot 10^1$
4	$(NH_4)_2SO_4$	1.53	72	$3.2 \cdot 10^{-2}$	$4.0 \cdot 10^1$	$2.0 \cdot 10^2$
	$\begin{cases} (NH_4)_2SO_4 + \\ +(NH_4)_3H(SO_4)_2 \end{cases}$	1.42	69	$2.0 \cdot 10^{-2}$	$9.7 \cdot 10^1$	$3.7 \cdot 10^2$
6	$(NH_4)_3H(SO_4)_2$	1.05	55	$1.7 \cdot 10^{-3}$	$2.5 \cdot 10^3$	$2.2 \cdot 10^4$
$7^{x)}$	$\begin{cases} (NH_4)_3H(SO_4)_2 + \\ +NH_4HSO_4 \end{cases}$	0.98	40	$1.3 \cdot 10^{-4}$	$1.3 \cdot 10^4$	$6.8 \cdot 10^5$
1'	none	2.00	88	$8.0 \cdot 10^3$	$9.0 \cdot 10^{-3}$	$2.4 \cdot 10^{-4}$
5'	none	1.42	81	$2.8 \cdot 10^{-2}$	$3.5 \cdot 10^{-1}$	$1.2 \cdot 10^2$
7'	none	0.98	60	$1.8 \cdot 10^{-3}$	$2.2 \cdot 10^3$	$1.3 \cdot 10^4$
7''	none	0.98	78	$5.5 \cdot 10^{-3}$	$1.9 \cdot 10^2$	$4.6 \cdot 10^2$

$^{x)}$ uncertain values

The interesting feature of these particles in this context is their low acidity. In Table 2, particle composition is compared for particles containing graphite (black) and particles almost without graphite (white). As will be seen, in the presence of graphite, $[NH_4^+]/[H^+]$ is much greater.

This indicates a clear disagreement with the phase diagram as wintertime, when black particles are observed, the ammonia concentrations prevailing are low (Fig. 5). Thus, at equilibrium conditions the particles should, according to the diagram, be acid.

The answer to this problem is probably given by Chang and Novakov (1975). They showed that soot, i.e. graphite, in the presence of nitrogen oxide at elevated temperatures (stack conditions) obtains a layer of reduced nitrogen groups. By means of vigorous water treatment, these can be leached out in the form of ammonia.

From these observations, the following hypothetical picture emerges:

Black particles contain a graphite core covered with an (alkaline) layer of adsorbed reduced nitrogen groups. This layer probably binds some acidic compounds. Outside of the sorbed phase, there is the usual solution (or crystals) containing NH_4^+, H^+, SO_4^{2-} and NO_3^-. This outer layer may be nearly in equilibrium with the atmosphere and at low pNH_3 it is consequently acid.

Table 2

Comparison of particle composition during white and black episodes.   1975 (Onsala)

Episode type	n equiv./m^3						NH_4^+/H^+	$Soot$ $\mu g/m^3$
	SO_4^{2-}	NO_3^-	$SO_4^{2-}+NO_3^-$	NH_4^+	H^+	$NH_4^++H^+$		
Black	308	33	341	342	7	349	51	23
White	317	<3	∿320	233	75	309	3.1	2.3

When leaching the particles for subsequent analysis of
the outer layer, part of the sorbed layer may also be dis-
solved, which will bias the result in the sense of reduced
acidity.

To summarise, the phase diagram is a rather useful tool
which until now has not been applied to any great extent
in atmospheric chemistry. First, it gives the information
whether obtained measurement results correspond to equilibrium
or not. In both cases, such information is valuable. Second,
the diagram makes it possible to calculate concentrations
which, for practical reasons, cannot be measured.

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Chang, S.G. and Novakov, T. 1975. Formation of pollution particulate nitrogen compounds by no-soot and NH_3-soot gas-particle surface reactions. Atm.Environ. Vol. 9, 495-504.
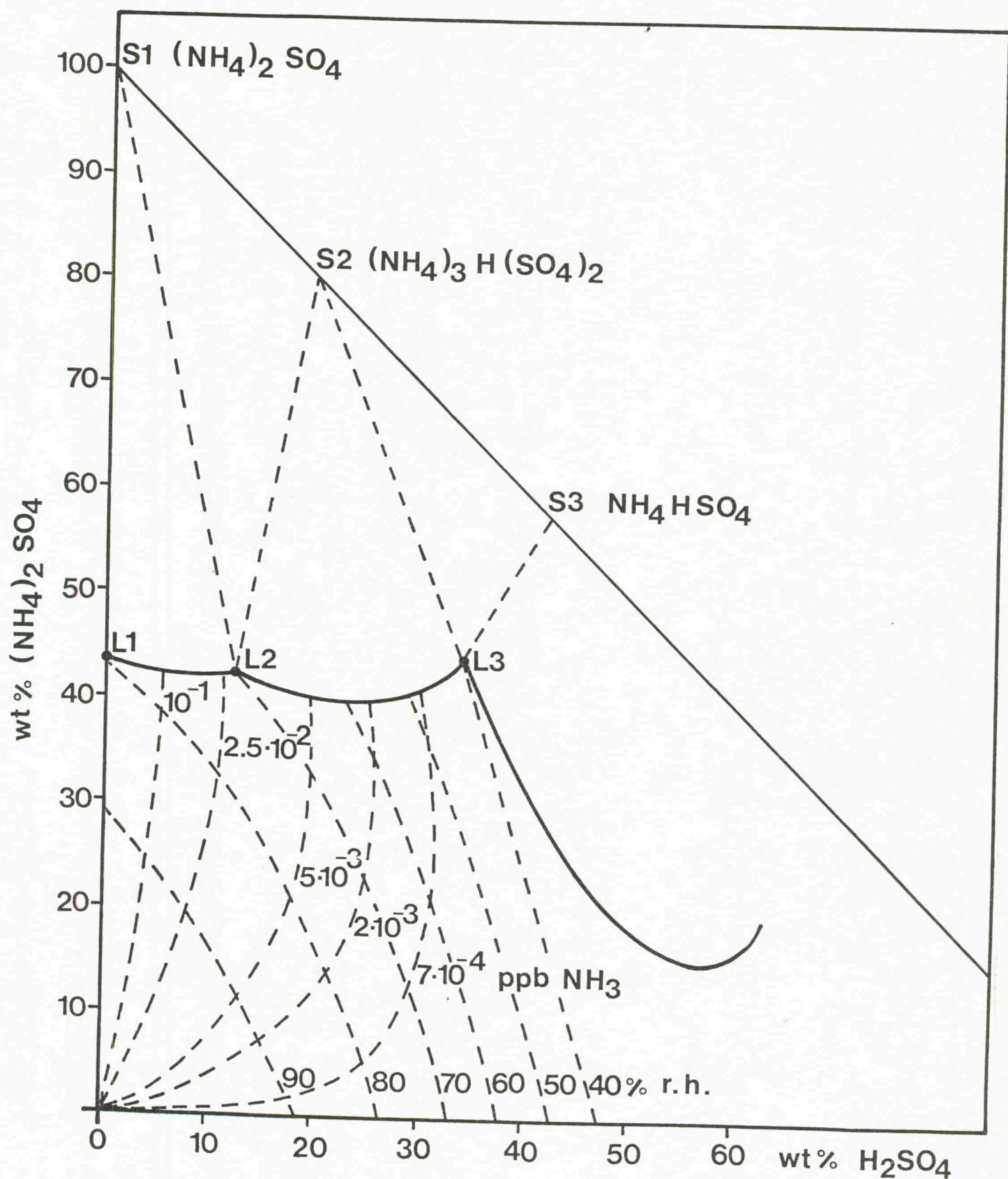
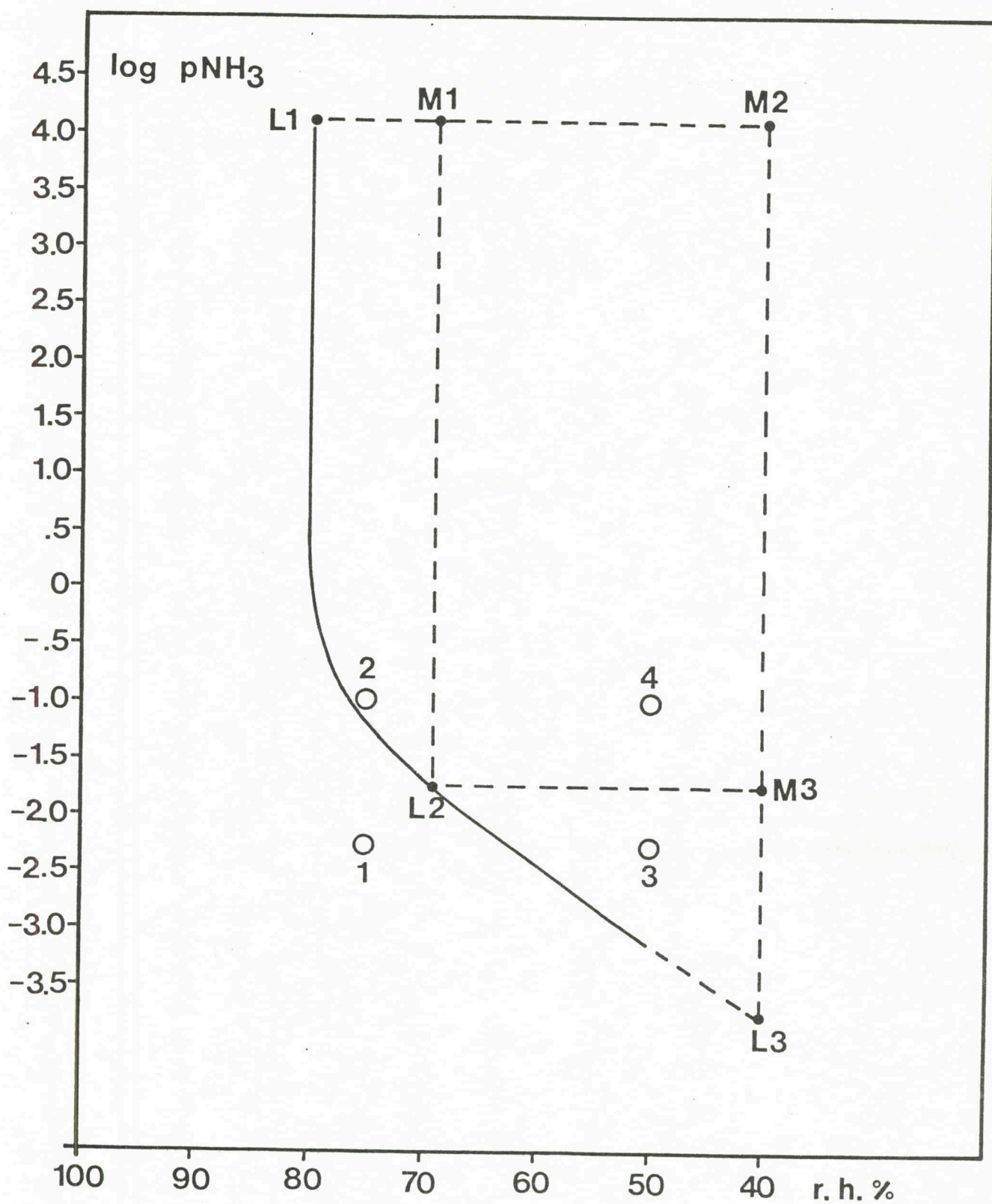Figure 1. Phase diagram for the system $(NH_4)_2SO_4$ – H_2SO_4 – H_2O at 25 °C.

Figure 2.   r.h. − log pNH₃ diagram at 25 °C.
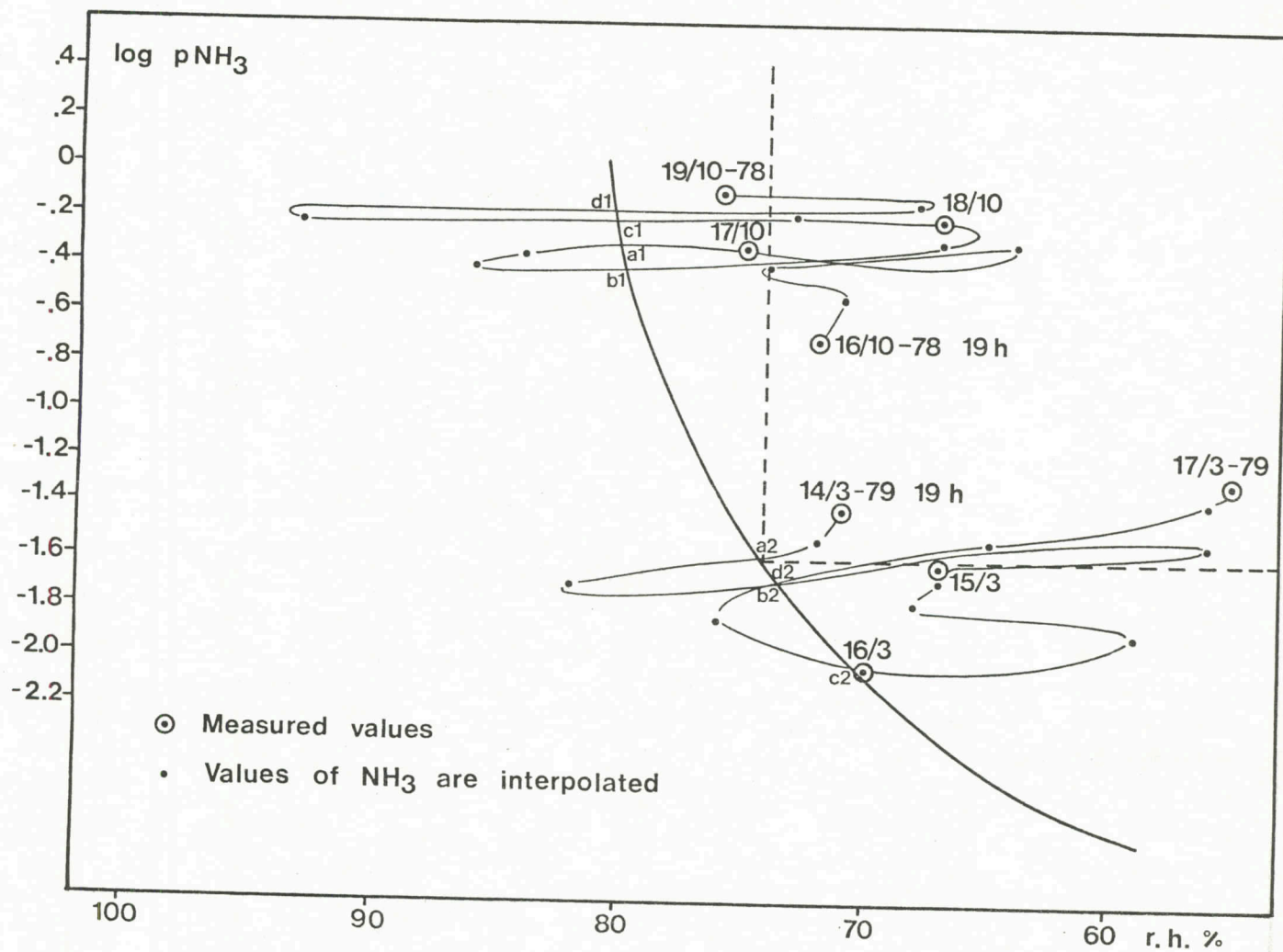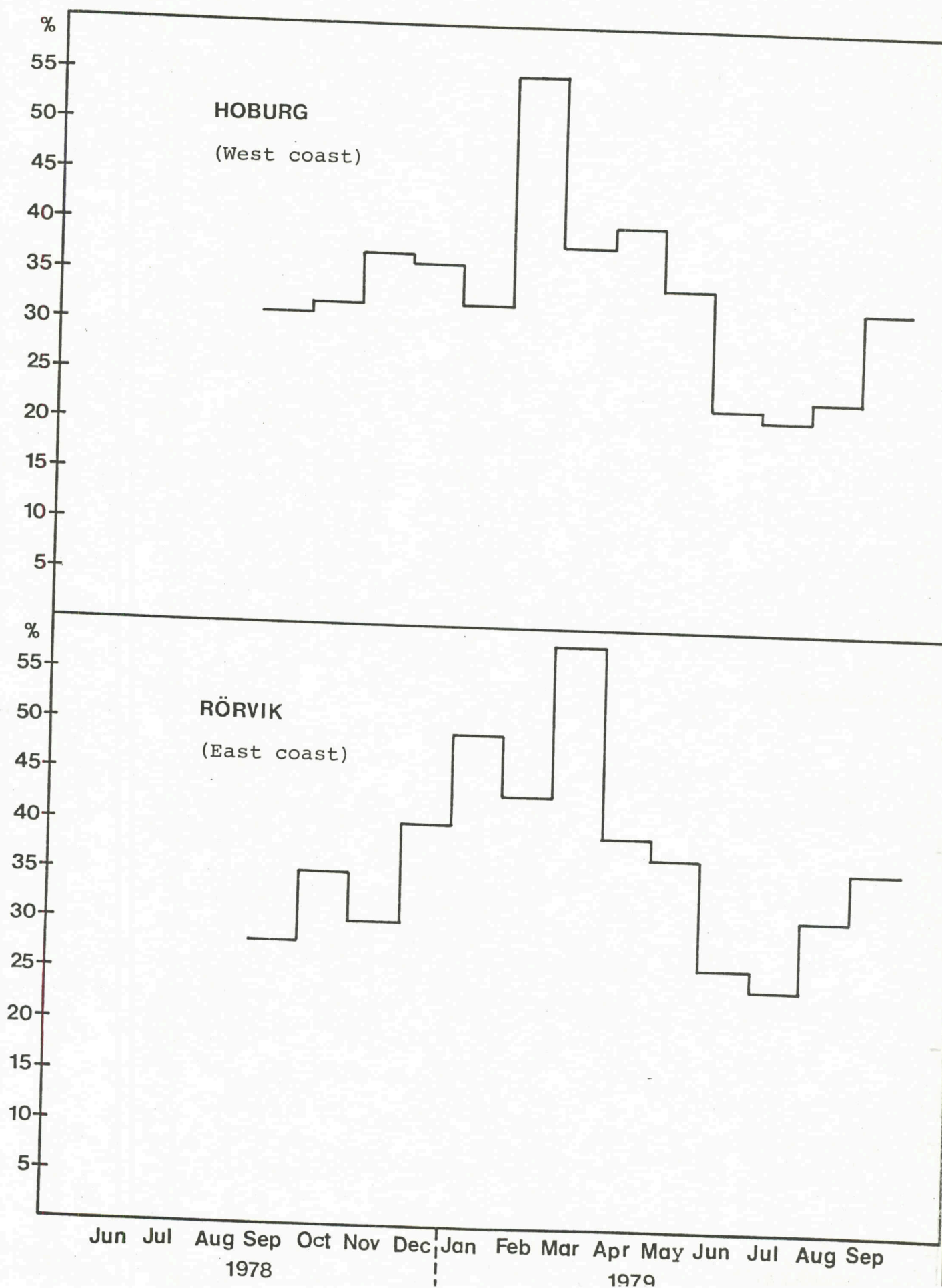
Figure 3.   Values of r.h. and pNH₃ at Rörvik during two
three-day periods.

Figure 4.   Monthly means of

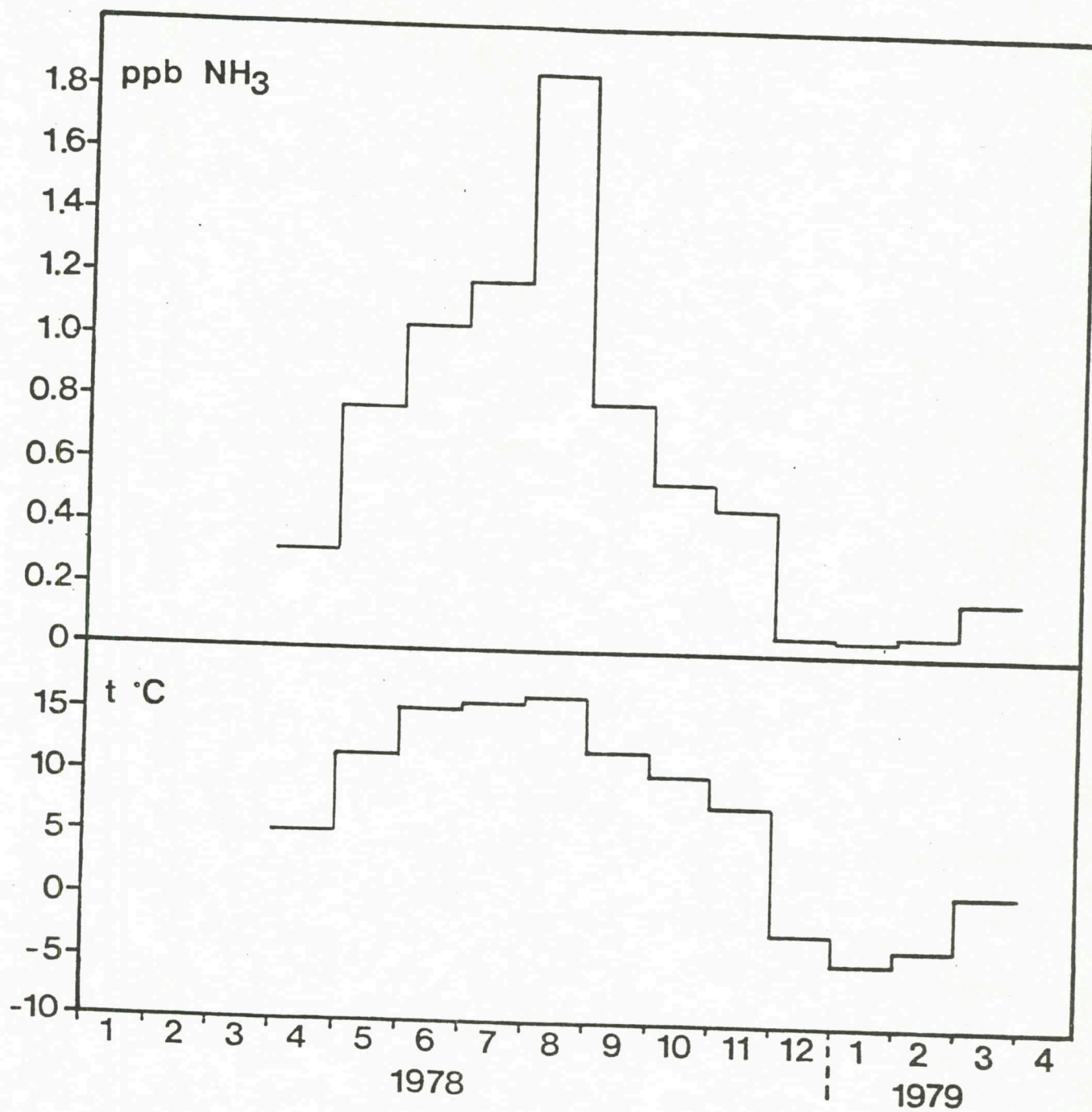$$q = \frac{[NO_3^-]_t \cdot 100}{2[SO_4^{2-}]_t + [NO_3^-]_t} \,\%$$

14.

Figure 5. Monthly means of ammonia concentration and temperature at Rörvik.