

DRY DEPOSITION MEASUREMENTS USING WATER AS A RECEPTOR: A CHEMICAL APPROACH

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Abstract. The field measurement of dry deposition still represents a difficult task. In our approach, a 1 to 2 cm thick layer of water in a petri dish with a diameter of 22 cm, serves as a surrogate surface. The atmospheric constituents taken up by the water can be analyzed chemically by the same procedure as for the wet deposition samples. In contrast to solid surrogate surfaces, water exhibits the following advantageous properties: low and constant surface resistance, high sticking coefficient for aerosols, and predictable sorption behavior for gases. Consequently, the deposition rates measured to the wet surface are generally higher, by up to a factor of 4 for NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} , than those to a dry surface, but still smaller than the concurrent wet deposition rates. We observed the following average dry deposition rates in $\mu\text{mol m}^{-2} \text{d}^{-1}$: NH_4^+ 48.3, Ca^{2+} 40.7, Na^+ 15.8, Mg^{2+} 8.4, K^+ 4.2, H-Aci 36.4; SO_4^{2-} 57.2, Cl^- 39.2, NO_3^- 34.5, HSO_3^- 5.7, formate 4.0; acid soluble metals: Fe 2.8, Zn 0.60, Cu 0.11, Pb 0.073, Cd 0.0022. The soluble fraction of Zn, Cd, Cu, Pb and Fe in the dry deposition varied with the pH of the water phase corresponding to the adsorption tendency of these metals to oxide surfaces. The sampling method also allows tracing of regionally and locally emitted atmospheric pollutants. In our study the local pollution sources included road salting, construction work and a refuse incinerator. Finally, chemical reactions occurring in the atmosphere, such as the conversion of Cl^- to HCl by HNO_3 or the oxidation of SO_2 , can be identified by evaluating the data. The method proposed is relevant to measure reproducibly the dry deposition of a variety of compounds to water bodies and moist vegetation.

1. Introduction

Mass fluxes from the atmosphere to the earth's surface are commonly classified as dry or wet deposition. Dry deposition involves the transport and removal of aerosols and gases from the atmosphere onto surfaces in the absence of precipitation (see e.g. Lindberg *et al.*, 1986). Dry deposition contributes significantly to the total input from atmosphere and depends strongly on meteorological conditions and local anthropogenic emissions. Wet deposition is the flux of mass by precipitation of rain, hail, and snow.

Although considerable work has been done developing adequate field methods to quantify the atmospheric input to natural surfaces, its measurement still remains a difficult task, for a review see e.g. Davidson and Wu, 1990; Hicks, 1986. Dry deposition involves complex physical and chemical processes which can also be influenced by the measuring procedure.

The mass transfer of species from the atmosphere can be defined as the product of a species specific deposition velocity and the atmospheric concentration of the species. This transfer process can be separated into three consecutive steps: aero-

dynamic transport through the boundary layer, transport across the surface laminar sub-layer and finally interaction at the surface. Each step exhibits its corresponding resistance. As the depositing species differ widely in terms of size and adsorption characteristics, different dry deposition measurement methods will be better suited to determine the deposition of a particular class of species.

Micrometeorological approaches to the measurement of dry deposition concentrate on the aerodynamic transport processes and do not account directly for the chemical processes occurring at the surfaces or for the chemical properties of the depositing species. On the other hand, the methods measuring the accumulation on surrogate surfaces depend on the physical and chemical properties of the surface, however, with the exception of aerodynamically designed surrogate surface samplers (Davidson *et al.*, 1988) they do not directly take into account the air flow above the surface, that can influence the collection efficiency. So far, mainly solid surfaces such as teflon plates, various types of filters, and polyethylene buckets and petri dishes have been used as surrogate surfaces (Dolkse and Gatz, 1985; Davidson *et al.*, 1985; Davidson and Wu, 1990). In studying the transport of particles to surfaces (see e.g. Noll *et al.*, 1988), inert and flat surrogate surfaces are used preferentially. All these solid surfaces exhibit a low absorbance capacity for gases and a low sticking capacity for aerosols. When measuring during all seasons, wetting by dew or fog can cause the surface resistance to change during the exposure time.

In contrast to solid surrogate surfaces, water displays entirely different characteristics. Most gaseous pollutants are absorbed according to Henry's law and many deposited species will react irreversibly to form nonvolatile products. In the frame of the mass transfer model, water represents a surrogate surface with a low and constant surface resistance for many gases and a with a high sticking coefficient for aerosols.

Water is the major natural surface below the atmosphere. Consequently, dry deposition to natural surface waters (marine and freshwater) is one of the key processes for understanding the cycling of elements in the environment. In addition to natural water bodies wet surfaces are encountered in the respiratory organs of all living organisms (e.g., stoma in leaves) and in the pores of soils. Moreover, in humid regions the ground is frequently wetted by dew or fog.

Most of these natural surfaces have receptor properties different from standard dry or wet surfaces. However, one can argue that biological surfaces are closer in nature to a water surface than to a standard plastic, teflon or glass surface. In the light of all the advantages, and concerning its importance in natural systems, it is surprising that to date water has been scarcely used as a surrogate surface for measuring the dry deposition of all kinds of compounds (Dasch, 1985).

The purpose of this work was to measure and to evaluate dry deposition rates to a water surface for a great variety of airborne materials in a suburban area of Switzerland. In this article we (1) compare the results obtained by our sampling technique with other dry deposition measurements using solid surrogate surfaces performed in the same area. (2) We derive important relationships between com-

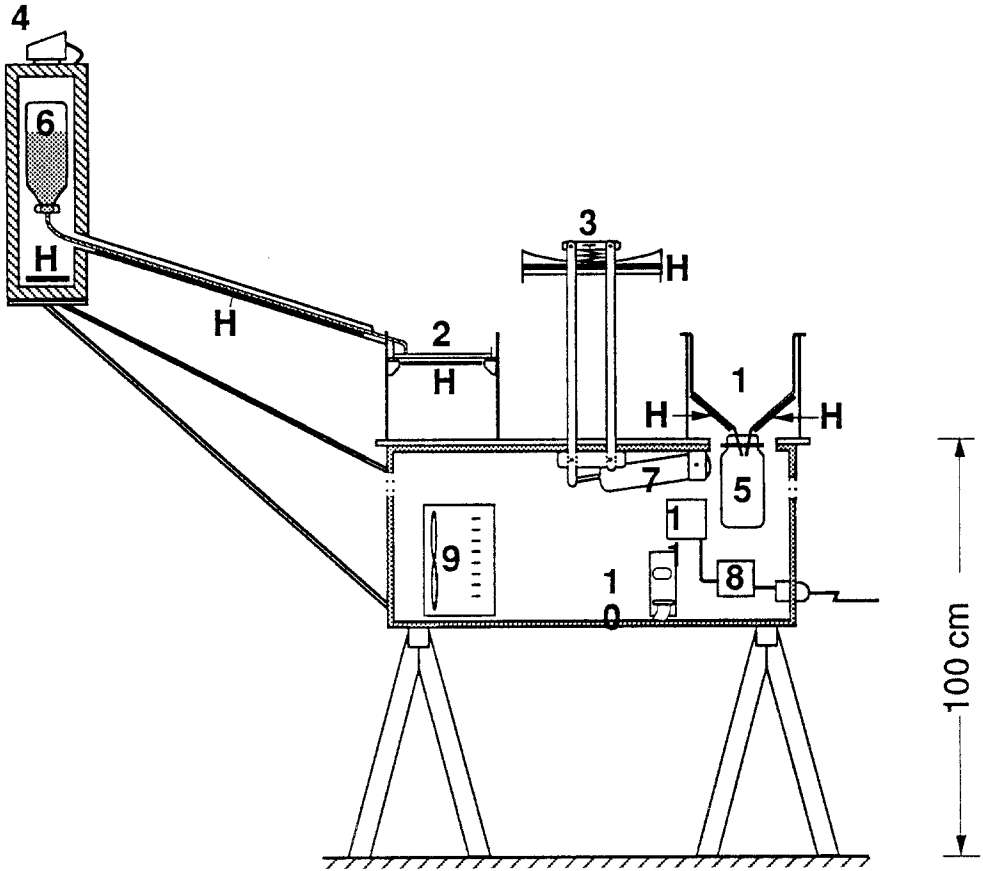


Fig. 1. Combined wet/dry sampler (modified EAWAG version of Georgii sampler developed at the University of Frankfurt) with water as a surrogate surface for measuring the dry deposition. (1) funnel for wet deposition, (2) petri dish, diameter 22 cm, containing the water, (3) movable cover, (4) rain and snow sensor, (5) collection bottle, (6) Mariotte's water reservoir, (7) motor, (8 and 11) electronic control interfaces, (9) heating fan, (10) event logger, (H) heating tape.

pounds in the atmosphere from the concentrations analyzed in the water and the corresponding deposition rates. This gives an insight into the composition of the dry deposited material, and in various cases this allows the unambiguous identification of the local sources of pollution. Finally (3), chemical interactions between the compounds in the aqueous medium, taking place both in the atmosphere (fog, rain) and/or in the surrogate surface water, can be evidenced by the presented treatment of the data.

2. Methods

From June 1985 to December 1987 biweekly composite samples of dry and wet deposition were taken with the aid of a combined wet/dry sampler. The sampling

site was on the roof, about 10 m above ground, of our Institute situated in a suburban area of Zürich, Switzerland.

SAMPLER

The sampler used, see Figure 1, was a modified and further developed version of a sampler constructed by Rohbock and Georgii, 1982. The dry deposition sampler consisted of a removable petri dish, diameter 22 cm, which was filled with double distilled water. The water level in the dish was regulated by the relative position of the bent end of the polyethylene tube connected to a 2 L Mariotte's bottle. Therefore the water depth in the dish varied between 1 and 2 cm. By this simple device the water which evaporated from the dish was replaced automatically with double distilled water. The petri dish was mounted in a polyethylene tube for protection, as high as the construction and the closing of the cover allowed. The Mariotte's bottle, sheltered in an insulated box, was placed at a distance of about 80 cm from the petri dish in order to minimize the disturbance of the air flow above the dish.

The wet deposition sampler, also housed in a protective polyethylene tube, consisted of a polyethylene cylinder, diameter 25 cm, height 13 cm, welded to a funnel. The base of the funnel passed through the cover of a polyethylene bottle to which it was welded. The 2 L polyethylene sampling bottle was screwed into the fixed cover. This device allowed a complete sampling of rain (splash loss and evaporation were minimized) and efficient protection against contamination by dust and gases. The wet deposition sampler fulfills all the requirements set by the German Standard for Rain Sampling (VDI 3870, 1988).

The movable cover was also constructed of polyethylene. It covered alternately the dry or wet sampler port. Its movement was regulated by the rain and snow sensor (made by Thies Germany, its characteristics are described by Winkler, 1990), fixed on the protective box of the Mariotte's bottle. The surface and the rim of the cover were constructed in such a way that rain water on the cover could not drip into the wet or dry sampler during movement. The underside of the cover was also made of polyethylene.

Heating coils placed on various surfaces enabled operation of the combined sampler until the air temperature fell below -5°C . Each heater element was regulated individually by a thermosensor.

All materials coming into contact with the samples, as well as the neighboring parts, were made of a polyethylene containing no color or light stabilizer in order to avoid contamination by metals, especially heavy metals. The purity of the polyethylene chosen was checked by leaching experiments.

All parts coming into contact with the samples were carefully cleaned. The procedure was as follows: immersion in dilute HCl for 1 day, rinsing, bathing in deionized water for 1 week, rinsing with double distilled water, and storing in double distilled water.

SAMPLING

Dry deposition: at the end of the 2 week sampling period the petri dish was removed and the water was transferred, without loss, into a precleaned polyethylene bag. Afterwards the dish was rinsed twice with 50 to 100 mL double distilled water, the rinsing water was also added to the sample. The dish was replaced by a clean one.

Wet deposition: at the end of the 2 week sampling period the sample bottle was replaced with a new one. The funnel was changed every second month or earlier if soot was visible in the funnel.

Before storing the samples at 4 °C, the water volume in both containers was determined by weighing. The samples were usually analyzed within 1 week.

ANALYTICAL METHODS

Since the concentrations found in the water of the dry deposition samples were in the same range as those in rain water, the same analytical procedures could be used for both.

The major anions and cations (except ammonium) in the filtered water samples were determined by ion chromatography and by flame atomic absorption, respectively. Ammonium was determined by flow injection analysis (Zürcher and Gisler, 1987), and the free Acidity or H-Acidity was determined by Gran titration (Johnson and Sigg, 1985). The heavy metals were analyzed in the acidified samples (pH ~2) by atomic absorption; Zn and Fe using the flame technique, and Cu, Cd and Pb using the graphite furnace.

In a separate series of experiments (from April to December 1987), metal concentrations in the filtrates and in the particles collected on filters were determined. 150 to 400 mL of the surrogate surface water was filtered through 0.45 µm filters and acidified to pH 2; the filters were digested with aqua regia.

The SO₂ and NO_x concentrations in the air were measured continuously at a nearby station (0.3 km E) of the Swiss National Air Pollution Monitoring Programm (NABEL). The air temperature was measured continuously at a meteorological station 7 km NW.

The following formula was used to calculate the deposition rates R [$\mu\text{M m}^{-2} \text{d}^{-1}$]:

$$R = \frac{c \times V}{A \times t}$$

c = concentration in the sample, rinsing water included [$\mu\text{M L}^{-1}$]

V = volume of the sample, rinsing water included [L]

A = surface area of the petri dish (dry deposition), or of the funnel (wet deposition) [m^2]

t = sampling period [d].

TABLE I

Arithmetic means and ranges of dry deposition rates in the biweekly samples and few air parameters from June 1985 to March 1987

Parameter	Unit	Arithmetic mean	10th percentile	90th percentile
<i>Major ions</i>				
	$\mu\text{M m}^{-2}\text{d}^{-1}$			
NH ₄ ⁺		48.3	12.6	104
Ca ²⁺		40.7	14.0	69
Na ⁺		15.8	3.4	37
Mg ²⁺		8.4	3.4	14.8
K ⁺		4.19	1.65	8.8
SO ₄ ²⁻		57.2	26.3	104
Cl ⁻		39.2	15.5	74
NO ₃ ⁻		34.5	14.3	60
HSO ₃ ⁻		6.0	0.09	21
formate ^a		4.0	1.1	8.3
H-Aci	$\mu\text{M m}^{-2}\text{d}^{-1}$	36.4	-33	125
pH (sample + rinsing water)		4.24	6.54	3.76
<i>Heavy metals</i>				
	$\mu\text{M m}^{-2}\text{d}^{-1}$			
Fe acid soluble		2.83	0.61	5.1
Fe total ^b		5.22	2.9	9.5
Zn acid soluble		0.60	0.29	1.4
Zn total ^b		0.59	0.40	0.81
Cu acid soluble		0.106	0.035	0.23
Cu total ^b		0.14	0.085	0.18
Pb acid soluble		0.073	0.017	0.135
Pb total ^b		0.075	0.045	0.12
Cd acid soluble		0.0022	0.0008	0.0038
Cd total ^b		0.0034	0.0019	0.0059
<i>Additional parameters measured in the air</i>				
Air temperature	°C	8.4	-2.7	19.7
SO ₂	ppb	9.8	1.9	24.2
NO _x	ppb	79.2	29.4	122

^a from April 1986 to November 1986.

^b from April to December 1987.

3. Results and Discussion

Table I summarizes the results obtained during the measurement period. The temporal (seasonal) variations of the biweekly deposition rates for Na⁺, Cl⁻, Ca²⁺, H-Aci, and some heavy metals (Zn, Cd and Cu) are illustrated in Figure 2.

The following evaluation of the data is based partly on the stoichiometry of the compounds that are deposited by dry deposition and partly on chemical processes which have been observed in the aqueous atmospheric phase, rain and fog, from our previous work (Johnson *et al.*, 1987; Sigg *et al.*, 1987; Behra *et al.*, 1989). We took as the starting point of our evaluation the correlations between the different constituents of the dry deposition. This procedure was chosen instead of factor

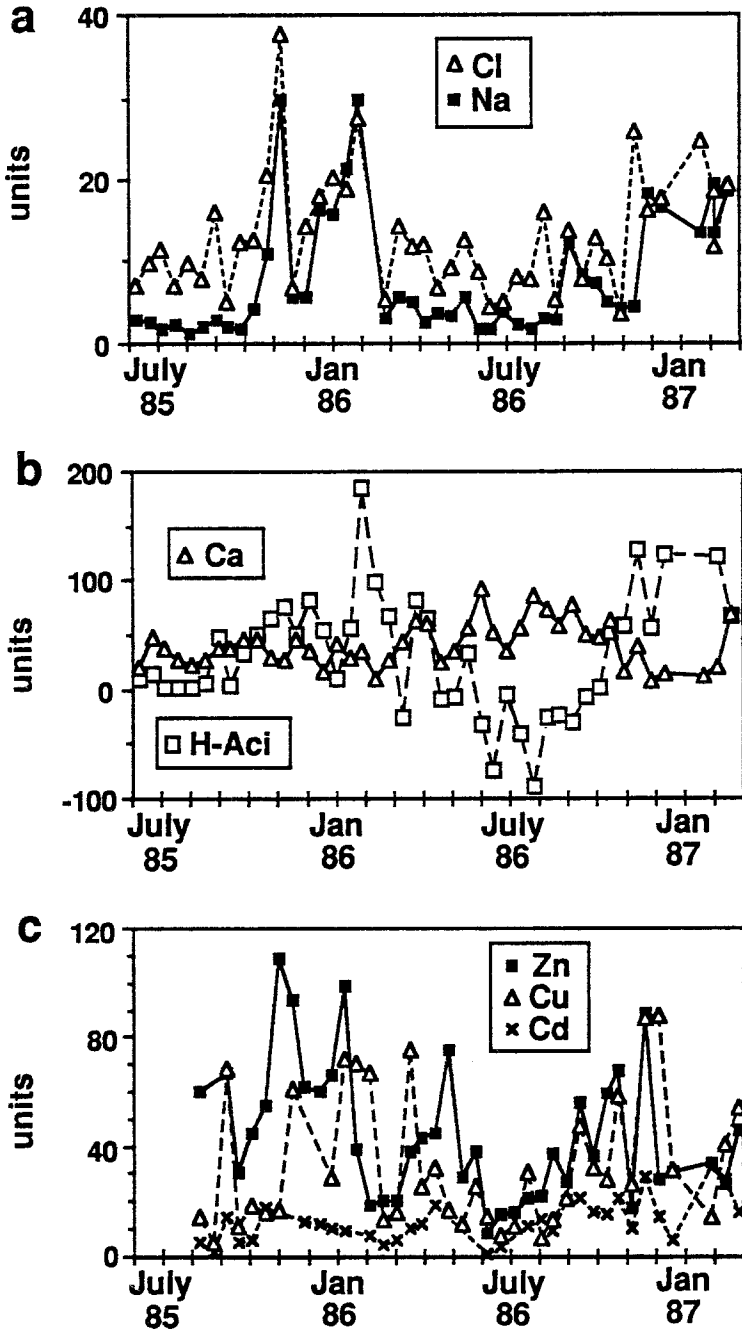


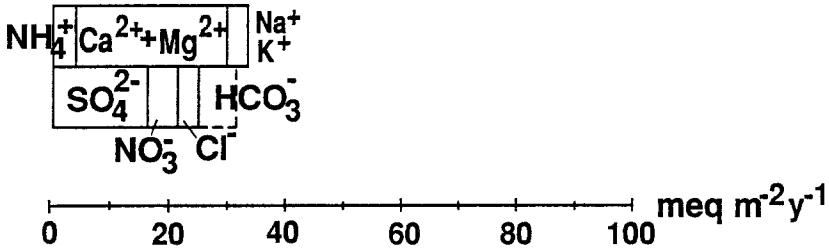
Fig. 2. Seasonal variation of dry deposition rates for some selected species during the measuring period June 1985 to March 1987. (a) Cl⁻: 1 unit = 3 μM m⁻² d⁻¹; Na⁺: 1 unit = 2 μM m⁻² d⁻¹. (b) Ca²⁺ and H-Aci: 1 unit = 1 μM m⁻² d⁻¹. (c) Heavy metals (acid soluble fractions). Zn: 1 unit = 1 μg m⁻² d⁻¹ (0.015 μM m⁻² d⁻¹); Cu: 1 unit = 0.2 μg m⁻² d⁻¹ (0.0031 μM m⁻² d⁻¹); Cd: 1 unit = 0.02 μg m⁻² d⁻¹ (0.00188 μM m⁻² d⁻¹).

DRY DEPOSITION RATE

wet surface (water)

NH_4^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Na^+ K^+	H^+
$\text{SO}_4^{2-} + \text{SO}_3^{2-}$	NO_3^-	Cl^-	HCO_2^-

dry surface (polyethylene balls)



WET DEPOSITION RATE

NH_4^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Na^+ K^+	H^+
$\text{SO}_4^{2-} + \text{SO}_3^{2-}$	NO_3^-	Cl^-	HCO_2^-

Fig. 3. Comparison of yearly deposition rates for the dry deposition measured to different surrogate surfaces, but using the same type of sampler. Note that significantly higher deposition rates are measured to a wet surface than to a dry one. Moreover, the acidity of the deposition is greatly increased due to the efficient collection of acidic gases by water. (HCO_2^- = formate anion)

analysis as special attention is drawn to the seasonal variations of atmospheric pollution, an important aspect which cannot be considered by the factor analysis procedure. Moreover, the procedure used permits the identification of local emission sources which often display strong seasonal variations.

3.1. COMPARISON BETWEEN DIFFERENT SURROGATE SURFACES

In Figure 3 the yearly averages of the deposition rates measured by a water surrogate surface and by a dry surface (polyethylene balls, diameter 1 cm, in the petri dish, diameter 15 cm) are compared. The latter was measured with the same type of sampler at a nearby station 1.3 km N, operated as a part of a short term deposition monitoring program in the State of Zurich (Hertz *et al.* 1988). This station is situated in the same valley and suburban area as our sampler. For both station a similar

pollution pattern can be assumed, since there exists only one major pollution source in the valley, namely a refuse incinerator plant 3.5 km WNW. As expected, the wet deposition rates are very similar at both station. However, the dry deposition rates, for all species measured on the wet surface always exceeded those measured on the dry surface. This relationship also holds when comparing our results with other stations of the cited monitoring program covering an area of 1700 km². In Figure 3, a significant difference of up to a factor of 4 is noted for the gases (SO₂, HCl, HNO₃, NH₃) and aerosols ((NH₄)₂SO₄, (NH₄)₂NO₃, CaCO₃, NaCl) which are more efficiently deposited to a water surface than to a dry surrogate surface. As a consequence of the increased affinity for gaseous acids, the water of the surrogate surface was slightly acidic on average, i.e. exhibits an H-Aci. In contrast, the dry deposition measured using a dry receptor or calculated as the difference between bulk (measured by a continuously open sampler) and wet deposition is slightly alkaline, i.e. exhibits an alkalinity (Zobrist, 1983).

A similar difference in the dry deposition rates for SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺ is noted at the station Dübendorf, when comparing the deposition measured in 1986 on the wet surface with those calculated from the difference between bulk and wet deposition in 1978/79 (Zobrist, 1983), i.e. on a dry surrogate surface. No significant changes in the regional pollution pattern has occurred over the years.

Thus it is clearly shown that different surrogate surfaces yield different dry deposition rates and therefore different ratios between dry and wet deposition and total deposition rates. In our case, the differences are especially pronounced for SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺. We think that the method using the wet surrogate surface yields a more appropriate value of the atmospheric mass flux deposited under dry conditions to natural waters and to vegetation.

3.2. ACID-BASE RELATIONSHIPS

The cation-anion balance of inorganic compounds reflects the internal consistency of the dry deposition data (Figure 4a). The slight excess of cations (slope = 0.96) indicates the presence of deprotonated organic acids. Inclusion of the formate anion data, see Table I, which was measured only during a restricted time period of 6 mo, into the charge balance yields a slope nearer to one. From the cation-anion balance the base neutralizing capacity or the free acidity, H-Aci, which is the H⁺ balance with respect to the reference level H₂CO₃, can be derived (Stumm and Morgan, 1981) where

$$\begin{aligned} \text{H-Aci} &= \sum \text{anions of strong acids} - \sum \text{base cations} \\ &= [\text{Cl}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{HSO}_3^-] + \sum[\text{HOrg}] \\ &\quad - [\text{Na}^+] - [\text{K}^+] - 2[\text{Ca}^{2+}] - 2[\text{Mg}^{2+}] - [\text{NH}_4^+] - \sum[\text{Org}^-]. \quad (1) \end{aligned}$$

In the acidic range (3.5 < pH < 5) the free acidity corresponds to the sum of the strong and weak acids, expressed as (Zobrist, 1987):

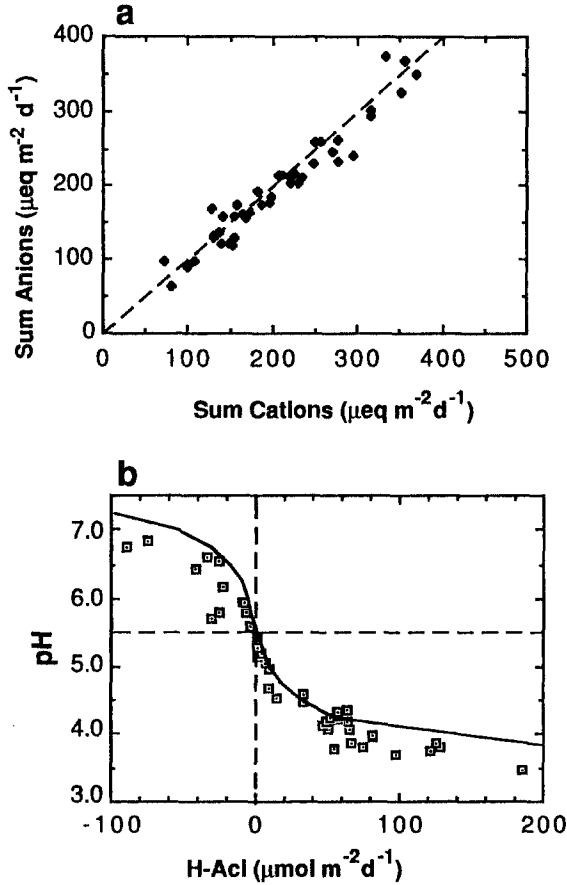


Fig. 4. (a) Relationship between the sum of anions ($\text{Cl}^- + \text{NO}_3^- + 2\text{SO}_4^{2-} + \text{HSO}_3^-$) and the sum of cations ($\text{H-Aci} + \text{Na}^+ + \text{K}^+ + 2\text{Ca}^{2+} + \text{NH}_4^+$) in the dry deposition with water as surrogate surface. Regression: sum anions = $1.88 + 0.955$ sum cations ($r^2 = 0.94$, $p < 0.1\%$). Dashed line: hypothetical balance (slope = 1). (b) pH versus H-Aci (determined by Gran titration). The curve is the acidimetric titration of pure water in equilibrium with atmospheric CO_2 . Deviation from this curve is due to the presence of organic acids and sulfite. The crossing point of dashed lines corresponds to the conditions of pure water in equilibrium with CO_2 without any excess of acid or base.

$$\text{H-Aci} \approx [\text{H}^+] + \sum[\text{HOrg}] + [\text{HSO}_4^-] + [\text{H}_2\text{SO}_3] + [\text{HNO}_2] + [\text{HF}]. \quad (2)$$

In the range of negative free acidity or positive alkalinity ($\text{Alk} = -\text{H-Aci}$), H-Aci is equal to:

$$\text{H-Aci} \approx -[\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] - \sum[\text{Org}^-] - [\text{NH}_3] - [\text{SO}_3^{2-}]. \quad (3)$$

The calculated H-Aci and the H-Aci determined by Gran titration agree to within 10%.

Figure 4b shows the dependence of pH on measured H-Aci. The data fall along a curve which corresponds to an acidimetric titration curve of fog or rain water in equilibrium with NH_3 , SO_2 , and CO_2 (Behra *et al.*, 1989). For comparison, the acidimetric titration curve of pure water saturated with atmospheric CO_2 is also

depicted. The data fall on this curve under neutral conditions with respect to CO_2 (i.e. no excess of acid or base) corresponding to a $\text{pH} \approx 5.6$ (Stumm and Morgan, 1981). However, at lower pH values the data display higher acidities than would be predicted from the strong acids alone. Scatter of the data is noted especially around $\text{pH} 4.3$. This again indicates a significant contribution from organic acids rather than the weak inorganic acids listed in Equation (2), the contribution of weak inorganic acids, according to calculation, is not significant. In the upper range of the curve, i.e. under neutral conditions, the data are characterized by higher buffering capacity compared to the pure carbonate system. In this pH range the only compounds that can cause this shift are organic compounds and the sum of HSO_3^- and SO_3^{2-} , the concentration of the other potential bases (Equation (3)) being too low to affect the acidity.

3.3. SOURCES FOR CHLORIDE

Cl^- deposition rates show distinct seasonal variation (Figure 2). Systematically higher rates are observed during the winter period. This is also true for Na^+ , which shows a good correlation with Cl^- during the winter period. The simultaneous increase of these ions is caused by systematic salting of the public roads during periods when the air temperature falls below 0°C . The impact of this salt application is illustrated in Figure 5a where the number of nights below 0°C during the sampling period show an excellent correlation with Na^+ . This dependence is not as clear-cut for Cl^- , the deposition rate of which is systematically higher than that of Na^+ . The excess of Cl^- over Na^+ indicates an additional input of Cl^- , such as HCl gas and NH_4Cl aerosols (Johnson *et al.*, 1987; Sigg *et al.*, 1987; Ruprecht and Sigg, 1990). $\text{HCl}(\text{g})$ is emitted from a near-by refuse incineration plant (3.5 km WNW) (Johnson *et al.*, 1987). The influence of these sources is shown by a plot of Cl^- vs pH (Figure 5b) which shows a increase of Cl^- at pH below 4.5 but no dependence at higher pH conditions.

During the warmer season deposition rates of Na^+ and Cl^- are comparatively low and no correlation between these compounds is noted as can be expected from the very minor influence of the distant sea. Thus the seasonal behavior observed here contrasts with coastal regions where the influence of seasalt is dominant and an excess of Na^+ over Cl^- is observed (Munger *et al.*, 1989). However, in the presence of NaCl aerosols in winter, similar processes as in coastal regions appear to influence Cl^- cycling in the atmosphere. This can be inferred from the correlation between Na^+ and NO_3^- (Waldman and Hoffmann, 1988) (Figure 5c) which arises from the generation of HCl gas and NaNO_3 from the interaction of NaCl with HNO_3 gas. Therefore, in addition to the generation of HCl by the local combustion of organochlorine compounds, a second source of HCl from NaCl is inferred.

3.4. SOURCES FOR CALCIUM

Ca^{2+} deposition rates were found to vary considerably, from 10 to $180 \mu\text{M m}^{-2}\text{d}^{-1}$, during the measured time period. Consistently high deposition rates were observed

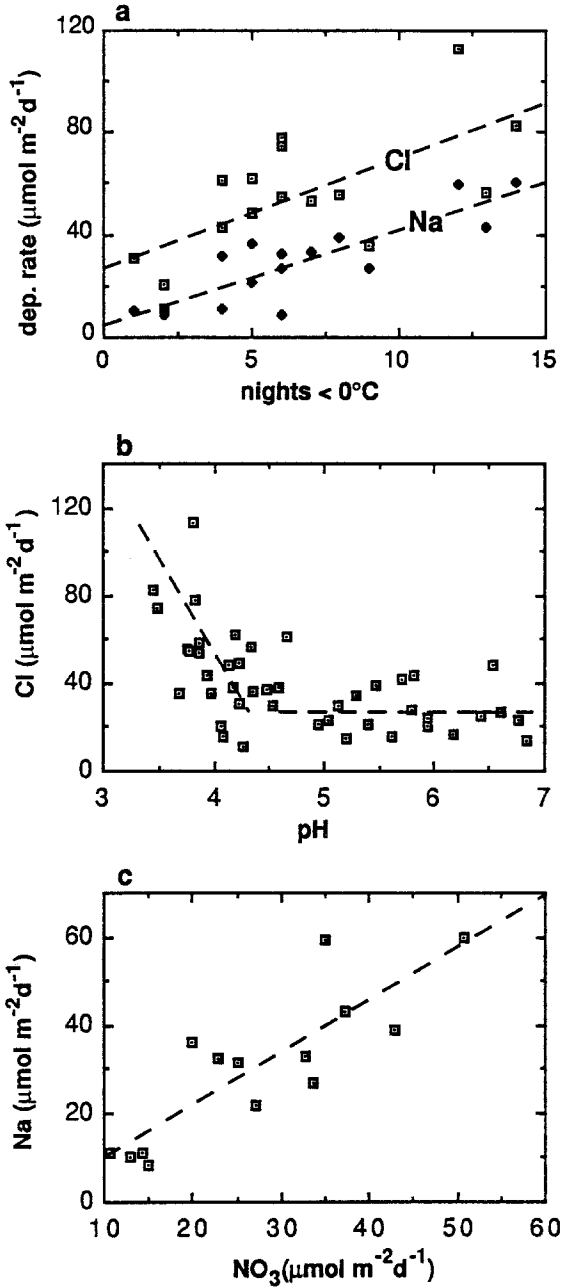


Fig. 5. Relationships between Cl⁻ and other parameters. (a) Dry deposition rate of Na⁺ and Cl⁻ during winter period as a function of number of nights when the temperature of air is below 0 °C. (It can be assumed that about the same quantity of road salt is applied every night for which the air temperature falls below 0 °C). Regression: Cl⁻ = 24.4 + 4.32 (days < 0 °C), $r^2 = 0.44$, $p < 1\%$; Na⁺ = 3.2 + 3.72 (days < 0 °C), $r^2 = 0.73$, $p < 0.1\%$. (b) The relationship between the dry deposition of Cl⁻ and pH in the sampling water indicates the importance of HCl as a source of Cl⁻. Lines represent best fit between pH 3 and 4.5 and between 5 and 7, respectively. (c) Relationship of Na⁺ vs NO₃⁻ in the dry deposition rates during the winters 1986 and 1987 indicating the interaction of NaCl with HNO₃. Regression: slope = 1.1, $r^2 = 0.71$, $p < 0.1\%$.

in the summer of 1986 when Ca^{2+} and H-Acidity are anticorrelated (Figure 2). During this period the measured free acidity is mainly negative i.e. the alkalinity is positive. This arises from the presence of HCO_3^- in the sampled water, which results from the dissolution of CaCO_3 . The mineral was present in significant amounts in soil dust released during the summer of 1986 due to the construction of a viaduct near-by the measuring station.

3.5. HEAVY METALS: pH-DEPENDENT DISTRIBUTION BETWEEN PARTICLES AND WATER

In comparison to the total concentrations measured as the sum of particles and filtrate, the samples measured directly at pH 2, see Table I, gave near to 100%

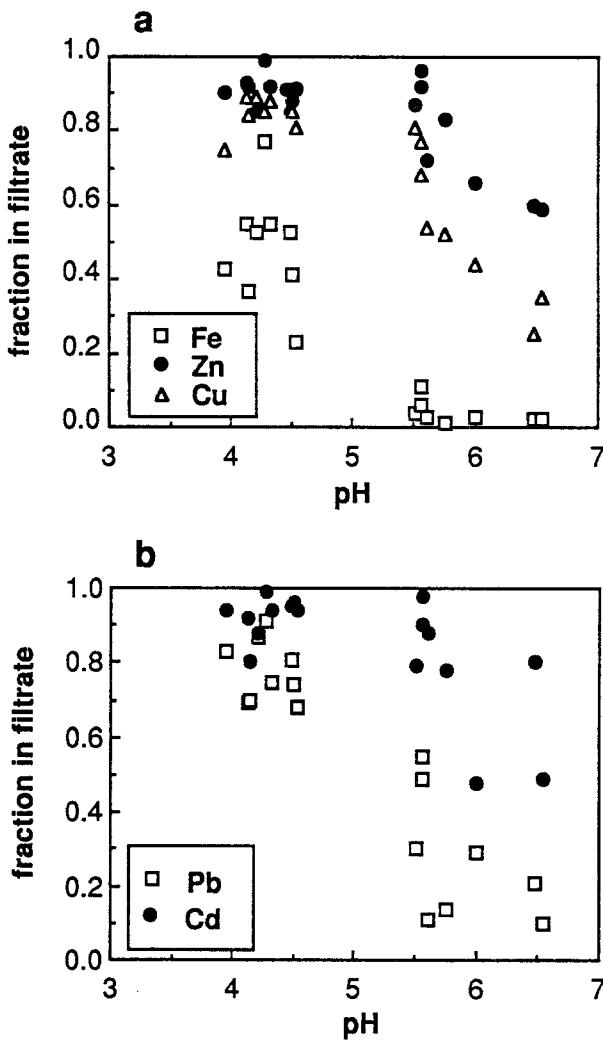


Fig. 6. Fraction of the total metal found in the filtrate of the sampling water in function of the pH measured in this water.

for Pb, Zn, but only 55% for Fe, indicating that significant amounts of Fe are in material soluble only in concentrated acids. The differences in the results for Cu and Cd may be due to seasonal fluctuations accounted differently in the means.

The percentage of metal ions in the filtered fraction is represented as a function of the pH value in the water sample in Figure 6. The measured distribution of metal ions between the particulate and the 'dissolved' fraction corresponds to their pH-dependent release from the collected particulate matter according to the pH value of the sample, which is established by the dry deposition of acidic and basic compounds. Differences in the solid/solution ratios can be neglected in this representation since visually they vary only slightly.

Although the filtrate may still contain some smaller particles and thus is not truly representative of the dissolved fraction, some characteristic differences of the pH-dependence are found for the 5 elements considered. Fe is found in significant concentrations in the filtrate only at pH values < 5 ; at higher pH it is found almost exclusively in the particulate phase. The fraction of Pb in the filtrate depends strongly on the pH in the pH-range 4 to 7. Cu is found mostly in the filtrate at pH values < 5.5 , but the filtered fraction decreases strongly in the pH-range 5.5–7. Cd and Zn are found mostly in the filtered fraction at pH values < 6 ; however, the filtered fraction decreases somewhat at pH values > 6 .

Different processes may contribute to the pH-dependence of the solubility of these metals:

- it is likely that Fe occurs in the particles as iron oxide or hydroxide and that Fe measured in the filtrate would correspond to the dissolution of these oxide particles. The concentration observed in the filtrate is, however, high compared to the solubility of an amorphous iron hydroxide (calculated with $\log K_{s0} = -38.7$). This effect may be caused by small particles passing through the filters, in addition complexation of Fe in the aqueous phase and occurrence of Fe (II) at low pH could also play a role.

- for Pb, Cd, Cu, Zn several different processes are possible; they may occur in the aerosols either as discrete phases (oxides or halides) or in association with more abundant solid phases such as aluminium oxides, silicates and carbonaceous particles. Upon the impaction of the particles on the water surface, a redistribution of the dissolved and particulate species may take place. Soluble phases such as halides may be dissolved, and the released metal ions may subsequently be adsorbed on the aluminium oxide, iron oxide or silicate particles present in the suspension. The observed differences in pH-dependence correspond qualitatively to the order of the binding strengths of these elements to oxide particles (Schindler and Stumm, 1987), i.e. $\text{Pb} \approx \text{Cu} > \text{Zn} > \text{Cd}$. This supports the idea of a control of the dissolved fraction by pH-dependent binding to oxide surfaces.

The role of iron oxides as an adsorbing phase is further indicated by the correlation between the Pb and Fe deposition rates (Figure 7a). The Pb emissions are certainly mostly from car exhausts; Pb may, however, be scavenged by dust particles containing iron oxides and transported in the atmosphere together with Fe. In a recent study

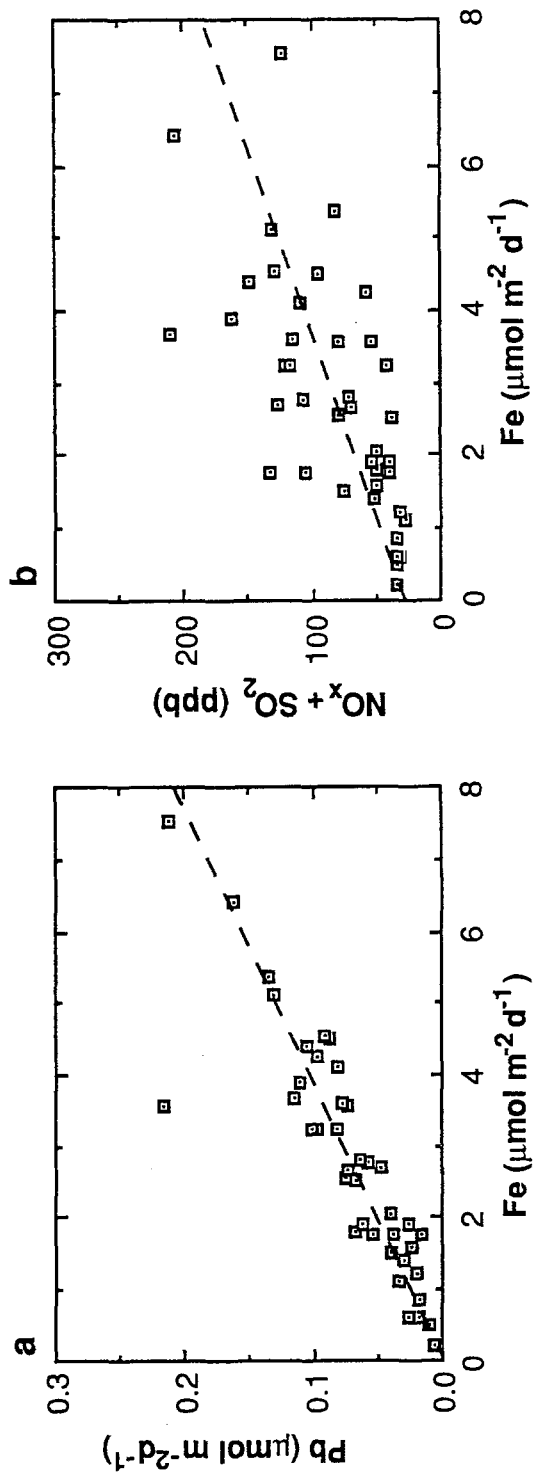


Fig. 7. Relationship between acid-soluble iron and other compounds. (a) Pb vs Fe deposition rate. Regression: slope = $2.7 \cdot 10^{-2}$, $r^2 = 0.76$, $p < 0.1\%$. (b) Fe vs sum of NO_x and SO_2 gas (ppb). Regression: $r^2 = 0.46$, $p < 0.1\%$.

of aerosol sources, road dust was found to contain a high percentage of iron oxide as well as a high Pb content (Hildemann *et al.*, 1991). On the other hand, the acid-soluble Cu, Cd, and Zn do not show any dependence on Fe. These three heavy metals appear to be emitted principally by the same source (Johnson *et al.*, 1987), as can be inferred from their tendency to follow a similar pattern with time, see Figure 2.

Observed deposition rates of acid-soluble Fe are generally higher during winter when more acidic conditions prevail due to higher emissions of SO₂ and NO_x. Fe shows a fairly good correlation with SO₂ + NO_x concentrations in the atmosphere (Figure 7b), which were measured independently. In the summer, however, Fe deposition rates show a tendency to increase with increasing Ca²⁺ and therefore also to increase with decreasing acidity (see section above). Thus, in this case Fe appears to be primarily emitted by the same source as calcium carbonate, i.e. soil dust, which presumably also contains iron oxide particles.

3.6. REACTIONS OF AMMONIA AND AMMONIUM

Fluxes of NH₄⁺ unlike many other compounds, do not show any distinct seasonal variations. Occasionally, extremely high deposition rates (> 100 μM m⁻²d⁻¹) were measured. Interestingly, these high NH₄⁺ deposition rates correspond in most cases to periods of frequent fog occurrence (data not shown). During fog episodes high concentrations of NH₄⁺, which have also been observed at the same location (Johnson *et al.*, 1987; Behra *et al.*, 1989), have been attributed mainly to the presence of NH₄⁺ aerosols ((NH₄)₂SO₄, NH₄HSO₄, NH₄NO₃, NH₄Cl). The production of (NH₄)₂SO₄ in the fog is increased at high concentrations of NH₄⁺ because higher NH₃ concentrations in the air accelerates the oxidation of SO₂ (Behra *et al.*, 1989). Therefore high NH₄⁺ concentrations induce high SO₄²⁻ concentrations. In addition, the deposition of fog contributes significantly to the NH₄⁺ and SO₄²⁻ concentrations in the dry deposition fraction (Zobrist *et al.*, 1987). Hence, during periods of high NH₄⁺ fluxes, the molar ratio of SO₄²⁻:NH₄⁺ is 1:2. This clearly indicates the deposition of ammonium sulfate aerosols.

In winter, generally, lower levels of NH₄⁺ in the dry fraction are observed, whereas Cl⁻ levels are comparatively high due to the input of NaCl from road salt (Figures 2 and 5a) and the release of HCl gas (see above section). It is interesting to note that the excess of Cl⁻ with respect to NaCl shows a linear correlation with NH₄⁺ deposition (figure not shown) during the cold season, i.e. under rather acidic conditions. Moreover, the ratio between the excess Cl⁻ and NH₄⁺ concentration is nearly 1:1. This indicates that during cold periods and periods of high HCl concentrations substantial amounts of NH₄Cl aerosols are formed in the atmosphere which are deposited by dry deposition. This is supported by the fact that the excess Cl⁻ with regard to NH₄⁺ correlates with Na⁺ and with NO₃⁻, again in both cases with a 1:1 ratio. Thus the above mentioned formation of HCl gas by reaction of NaCl aerosols with HNO₃ appears to be effectively coupled with the subsequent formation of NH₄Cl.

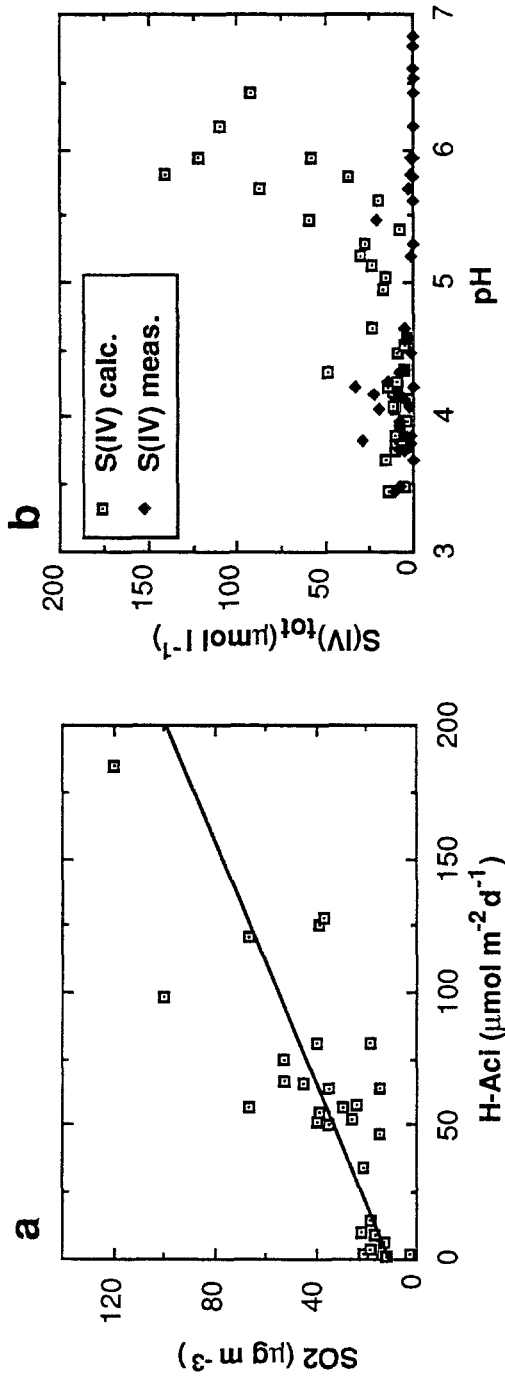


Fig. 8. Sulphur compounds. (a) SO₂ concentration in the air as a function of H-Aci in the sampling water, indicating the SO₂ sorbed is oxidized to H₂SO₄. Regression: $r^2 = 0.58$, $p < 0.1\%$. (b) Total S(IV) concentration in function of the pH. Calculated concentrations assuming equilibrium conditions with respect to SO₂(g).

3.7. OXIDATION OF SO₂(g)

Although SO₂ concentrations in the atmosphere (data from Luftbelastung 1985, 1986 and 1987) varied considerably during the sampling period, the average concentrations appear to reflect conditions within the water used as the surrogate surface. This is illustrated by the good correlation between SO₂ and H-Aci (Figure 8a). On the other hand the correlation between NO_x and H-Aci is weak, indicating that oxidation of SO₂ occurs rapidly and to a large extent in the sampling water contrary to NO_x which is oxidized in the gas phase. The oxidation of SO₂ in atmospheric waters (rain, fog) is strongly dependent on pH (Jacob and Hoffmann, 1983). Under the assumption, that the averaged SO₂ represents roughly atmospheric conditions during the sampling interval the amount of SO₂ oxidized can be estimated by comparing equilibrium and measured S(IV) concentrations. The equilibrium concentration of dissolved S(IV) (SO₂(aq), HSO₃⁻ and SO₃²⁻) is derived from the Henry's law constant and the first and second acidity constants, respectively (Behra *et al.*, 1989). The calculated total dissolved S(IV) as a function of pH is depicted in Figure 8b in which the measured average S(IV) concentration is also presented. At acidic conditions (pH values < 5) the calculated and measured S(IV) agree reasonably well, whereas at higher pH values the calculated values are much higher than the measured ones. This is due to oxidation of S(IV) to SO₄²⁻ in the water phase which is strongly favoured at pH values greater than 5 in the presence of O₃. At pH below 5, light induced oxidation of SO₂ may occur in the presence of H₂O₂, Behra *et al.* (1989). The correlation of SO₂ with acidity (Figure 8a) may be related either to the acidity produced by its oxidation in the water phase and/or to the deposition of acidic aerosols (H₂SO₄, NH₄HSO₄). This is also supported by the inability of the other possible strong acids (HCl, HNO₃) to account for more than half of the measured acidity. In addition, SO₄²⁻ shows much less dependence on pH, which indicates the importance of neutral NH₄⁺ aerosols as the principal source of SO₄²⁻.

4. Conclusions

The use of a water layer in a petri dish exposed to the atmosphere during dry periods yielded interesting and useful dry deposition data. Evaluation of the seasonal variation and of the correlations between different constituents demonstrates the effects of common atmospheric pollutants such as SO₂ and NH₄⁺ aerosols. In addition, other uncommon and unknown pollution sources could be identified by the help of the water layer exposed to the atmosphere. In our case, the pollutants and pollution sources were: NaCl aerosols from road-deicing during cold periods, soil dust from construction works and HCl gas from an incinerator.

Careful evaluation of the relationships between the measured ion concentrations in the water layer or the deposition rates also reveals that well-known, as well as unexpected chemical reactions are taking place either in the atmosphere and/

or in the sampling water. The behavior and oxidation of the absorbed SO_2 corresponds to the known aqueous oxidation in the atmosphere. The conversion of Cl^- to HCl by HNO_3 in the atmosphere has already been established. The correlation of Fe with Pb but not with Zn and Cd leads to the idea that iron oxide particles may be the carrier of the Pb emitted by automobiles. Trace metals carried with dry deposition are dissolved according to the composition of the water acting as a receptor; this would be the case for deposition either on a water surface or on a moist surface, for example on vegetation or soil.

The dry deposition rates measured on the water surface are remarkably higher than those on solid surrogate surface, measured with the same sampler design, and those calculated from the difference between bulk and wet deposition. This is due to the low and constant surface resistance and the high collection efficiency of the water layer for aerosols, especially for aqueous NH_4 aerosols, and the high absorbance of gaseous pollutants.

These results clearly show that a water layer in a petri dish is an expedient device in the category of surrogate surfaces. It enables the continuous measurement of the time integrated dry deposition of gases and aerosols. In addition, it represents a versatile tool enabling the detection and tracing of pollution sources and the identification of chemical processes occurring in the atmosphere.

Besides the advantageous features of the water surface, we are aware that this sampling method also shares the drawbacks of all measuring devices using a surrogate surface.

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