

SONDERDRUCK AUS:

MODERN ECOLOGY

Basic and Applied Aspects

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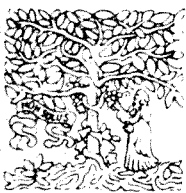
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Chapter 24

Transfer mechanisms and deposition rates of atmospheric pollutants

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24.1 Introduction

In light of the noticeable damage to different environmental elements in the marine and terrestrial ecosystems over the past few decades, the extent of man's influence on the natural and cultural environment is increasingly being brought into question. In this context man-made air pollution with its wide-spread interferences in natural cycles is of great importance.

The atmosphere is being burdened with a great volume and increasing number of airborne pollutants from various sources. Consequently it has become of far-reaching importance for the environment that the mechanisms of distribution of these pollutants, their residence time, the deposition, and in the final analysis, the effects of their deposition on the ground of totally different ecosystems are examined.

Although the causes and effects are well-known in most cases, objective data are often not available to obtain a balanced picture of the whole state of nature from the knowledge of the atmospheric deposition of pollutants and their distribution in

Table 24.1: Emissions of the pollutants nitrogen oxide (NO_x , calculated as NO_2), organic compounds (org.), sulphur dioxide (SO_2), carbon monoxide (CO), and dust, in the Federal Republic of Germany for the period 1966 to 1986 (data in million tons per year, after UBA 1989). The right column gives the change 1966–1986 in percent of the value of 1966.

	1966	1968	1970	1972	1974	1976	1978	1980	1982	1984	1986	%
NO_x	1.95	2.05	2.35	2.50	2.60	2.70	2.85	2.95	2.85	2.95	2.95	151
org.	2.20	2.35	2.60	2.65	2.55	2.55	2.55	2.50	2.40	2.40	2.45	111
SO_2	3.35	3.40	3.75	3.75	3.65	3.55	3.40	3.20	2.85	2.65	2.30	69
CO	12.40	12.90	14.00	14.00	13.70	13.00	12.40	11.70	9.80	9.20	8.90	72
dust	1.75	1.50	1.30	1.10	0.95	0.78	0.70	0.69	0.60	0.59	0.56	32

time and space.

Facts are needed to solve these problems, to find out about the kind of atmospheric transfers, their temporal variability as well as their spatial differences with regard to the different emission patterns.

Furthermore, it is important for any investigation of air purity and ecosystems to know about the physical and chemical changes of the pollutants which are occurring and how they are deposited over a long period of time. First, detailed statements about pollution in the Federal Republic of Germany and the various mechanisms of self-cleaning in the atmosphere will be discussed before the concluding results of typical examinations for single pollutants in different areas are dealt with.

24.2 The emissions of different pollutants in the Federal Republic of Germany

In this report about air pollution in the Federal Republic of Germany only those typical pollutants will be dealt with for which possible trends in the distributed amounts of emissions can be illustrated, because they have been measured over a sufficiently large area and over an adequate long period of time. These consist of the following: nitric oxides, organic compounds, sulphur dioxide, carbon monoxide and dust (Tab. 24.1).

Nitrogen compounds are found in the atmosphere as oxides, acids and in reduced form. The nitric oxides (NO_x), in particular, play an important role in the formation of photo-chemical smog and the acidification of fog and precipitation (FABIAN 1989). These pollutants which result from the reaction of atmospheric nitrogen with atmospheric oxygen are released into the air by nearly all kinds of combustion. Nitric oxides are emitted by traffic on a large scale. Additionally – but mainly in agricultural areas – nitrogen is released by nitrogenous fertilizers.

In 1986 2,950,000 tons of nitric oxides were emitted; compared to 1966 (= 100%) this means an increase to 151%. This can mainly be explained by the enormous increase in the number of automobiles, reaching 27,000,000 cars in 1986, twice the number of, for example, 1960. The largest shares of these emissions in 1986 were from traffic (52%) and power stations (24%).

The **organic** compounds are mainly substances which are derived from solvents (41%) or are released by combustion (45%). They are additionally released by transshipment and evaporation of petrol, e.g. during refuelling of automobiles. The emissions of organic compounds have hardly changed since 1966 having reached an amount of 2,450,000 tons in 1986.

95% of the **sulphur** released into the atmosphere by man-made processes is in the form of sulphur dioxide (KELLOG et al. 1972). Power stations produced the largest share of these emissions with 63%; industry had an 18% share. The remainder is made up of emissions from domestic households and, to a lesser extent, traffic. Since 1966 the SO₂ emissions have decreased from 3,350,000 tons to 2,300,000 tons (1986) thus falling to only 69% of the former amount. There are several reasons for this decrease. For example, the increasing consumption of low-sulphur fuels in power stations and the application of filters in smoke stacks.

The emissions of **carbon monoxide** – 80% of which are produced by incomplete combustion – have decreased from 12,400,000 tons (1966) to 8,900,000 tons (1986). This is due to the decreased combustion of solid fuels and the emission controls for automobiles.

The **dust** emissions have also been lowered in the same period from 1,750,000 tons (1966) to 560,000 tons (1986), dropping to less than a third of the former amount. This could be achieved by improved modern technology of dust filtration. However, industry still emits the greatest share of the dust, and traffic 10%. The remainder is caused by domestic households and low-consumption units.

All these emissions are bound up by transmission into long-range transport and are removed from the atmosphere by the different mechanisms of deposition.

24.3 Mechanisms of atmospheric self-cleaning

The atmospheric pollutants released by natural and man-made processes are removed from the atmosphere sooner or later. The important factors for the residence time are the height of the polluting sources, the speed of the chemical changes, the intensity of the ground-layer exchanges as well as the surface characteristics of the affected area and its affinity towards the pollutant on the ground (JACOBSEN et al. 1982).

We distinguish between three groups of gaseous pollutants because of their differing residence time in the atmosphere (Tab. 24.2).

While nitrogen and oxygen have residence times of some thousand, or even million, years gaseous pollutants of the second group (i.e. hydrogen, carbon dioxide, methane) have periods between two and eight years. In the third group we have

Table 24.2: Residence times of different gases in the atmosphere (from MESZAROS 1981)

<u>group 1</u>	
Helium	10 ⁷ yr
Nitrogen	~ 10 ⁶ yr
Oxygen	5 × 10 ³ yr
<u>group 2</u>	
Hydrogen	6–8 yr
Methane	4–7 yr
Carbon dioxide	5–6 yr
Ozone	2 yr
<u>group 3</u>	
Water vapor	10 d
Nitrogen dioxide	8–10 d
Ammonia	~ 5 d
Sulfur dioxide	~ 2 d
Carbon monoxide	5–12 d
Hydrogen sulfide	~ 12 d

the short-lived gases such as water vapour, sulphur dioxide and carbon monoxide with a duration of days or some hours.

The time that a substance remains in the atmosphere is expressed by JUNGE (1987) in the following equation:

$$\frac{dM}{dt} = Q - S \quad (24.1)$$

The term dM/dt describes the change in concentration of a substance in the atmosphere with respect to time; Q is the change in intensity at the source and S is the increase in intensity.

Ignoring the chemical changes, there are three mechanisms of pollutant reduction. These are dry, humid and wet deposition. A description of the theoretical fundamentals of dry and wet deposition is given by HERBERT (1987). JAESCHKE (1987) and SCHMITT (1987) discuss the mechanisms of humid deposition. While dry deposition occurs continually, humid and wet deposition are limited to the duration of fog and precipitation. For wet deposition to take place it is necessary that the rate of fall of raindrops or snowflakes be greater than any possible upwinds and that the drops do not evaporate on their way to the ground.

24.3.1 Dry deposition of pollutants

Dry deposition occurs at interfaces like the ground, vegetation or water surfaces. We distinguish between the following mechanisms of dry deposition:

- Sedimentation, especially with particles having radii of more than $0.5 \mu\text{m}$,
- Impaction, the deposition at obstacles in the stream of the air according to the law of inertia; this can also be the collection of particles by raindrops falling through a polluted atmosphere,
- Diffusio- and thermophoresis, pollutants are deposited because of prevailing water vapour in the atmosphere or temperature differences in the air,
- Turbulent and molecular diffusion, steering the process of deposition through Brownian motion and convective or turbulent motion.

The precise determination of dry deposition is still considerably difficult. The possibilities for the determination of dry deposition are listed in the following table; the capital letters show whether the quoted method is suitable for gases, G, or aerosols, A. The brackets indicate that the given method is less suitable for this form.

Profile method/Gradient method	G, (A)
Bowen-ratio method	G
Eddy correlation	G, (A)
Eddy accumulation	G, A
Variance method	G, (P)
Chamber method	G, (P)
Tracer method	(G), A
Mass-stream balance	G, A
Exposition of artificial surfaces	(G), A

It is impossible to describe all these individual methods within this report; instead the reader is referred to the survey of various works by HÖFKEN and BAUER (1985) from which the above information was also drawn.

The deposition rates of pollutants from the atmosphere onto exposed surfaces can be calculated with equation (24.2).

$$F = v_d \cdot C \quad (24.2)$$

Knowing the deposition velocity (v_d) and the concentration of pollutants (C) one can determine the rate of deposition (F).

For atmospheric gaseous pollutants, which are absorbed onto the ground relatively well, a mean value for the deposition velocity of $1 \text{ cm}\cdot\text{s}^{-1}$ (BEILKE 1975) is used. Examples for different deposition velocities have been summarized in Tab.

Table 24.3: Deposition velocities (v_d) of SO₂ over different surfaces (after MEYERS and BALDOCCHI 1988, FÄHNRICH and GEORGII 1989; from FÄHNRICH and GEORGII 1989 (No. 1-8), GEORGII 1989 (No. 9, 10))

No.	surface	method	v_d (cm·s ⁻¹)	author	year
1	water	Gradient	0.41	GARLAND	1977
2	calcareous-soil	Gradient	1.20	GARLAND	1977
3	grass	³⁵ SO ₂ -Tracer	0.80	OWERS	1974
4	wheat	Gradient	0.74	FOWLER	1976
5	pine	³⁵ SO ₂ -Tracer	0.10-0.60	GARLAND	1978
6	oak-hickory	Eddy-Correlation	0.21-1.14	MEYERS	1986
7	spruce	Filter sampling	0.11-0.86	FÄHNRICH	
8	beech	Filter sampling	0.25-0.70	FÄHNRICH	
9	snow	-	0.10	GEORGII	1989
10	forest (10 m tall)	-	0.10-2.00	GEORGII	1989

24.3. SO₂-deposition velocities of up to 8 cm·s⁻¹ were determined for urban areas (compare survey in SEHMEL 1980).

A mean value of $v_d = 0.8$ cm·s⁻¹ is often used for general calculations in Europe (OECD 1977), which together with the mean concentration of pollutants is taken to estimate deposition of SO₂ in areas with varying pollution patterns. As dry deposition is considerably influenced by vegetation we need precise facts for cause-and-effect research.

A calculation of the deposition rates of atmospheric sulphur e.g. areas of vegetation lead to errors in the estimates if a deposition velocity for SO₂ of $v_d = 0.8$ cm·s⁻¹ is used to the part of the dry deposition. It would be better to take the so called "critical loads" into consideration when calculating the total pollutant input in an ecosystem (NILSSON and GRENNFELT 1988). This will be dealt with again later.

24.3.2 Humid deposition of pollutants

Humid deposition is the process of pollutant decrease whereby droplets of fog and clouds act as "carriers" of the pollutants. This process ends with the settling of condensed vapour on the different surfaces - e.g. by the "sweep-out" of vegetation.

Pollutants can easily be absorbed during the formation of droplets in fog or cloud. We distinguish between three different forms of fog: radiation fog, upslope fog and frontal fog.

Radiation fog develops by radiation from the ground and tends to form in morphological depressions. It consists of small droplets, is not moist and contains

predominantly local pollutants which have mixed with the cold air in valleys or basins. Fog in valleys is mostly separated from a clear air mass above by a strong temperature inversion located at the height of the valley rim. This kind of fog is most prevalent in weather conditions with low wind velocities.

The formation of *upslope fog* is connected with expansive anticyclonic weather conditions. This fog is generated at inversions due to the presence of radiation together with sufficient air humidity. Since upslope fog usually covers relatively large areas, the pollutants in this fog are not only limited to those from local sources, but also consist of pollutants from other regions.

Frontal fog covers mountainous regions. As the occurrence of this fog is tied to the existence of frontal systems, the incorporated pollutants result from long distance transport. In the winter months, because of the lower level of the clouds larger areas are exposed to the humid deposition of pollutants than in the summer months. A considerable part of the annual precipitation on the luffslopes of highlands, in particular, is due to the "sweep-out" by vegetation. According to LINKE (1916) the additional moisture from dripwater is 66% in the Taunus region and 150% at the Rhön relative to precipitation in open spaces.

Previous works (e.g. HOUGHTON 1955) have already referred to the fact that the concentration of pollutants in fogdroplets was in some cases substantially higher than that in comparable samples of rainwater. Furthermore, there are considerable differences between the pollutants contained in the numerous droplets. The increased concentration of pollutants in fog is mainly caused by the favourable surface-to-volume ratio of fog, which consists of smaller droplets than rain, and by the higher concentration of pollutants near to the ground causing greater rates of absorption than at higher altitudes.

24.3.3 Wet deposition of pollutants

Wet deposition takes place through the precipitation of rain and snow. According to VDI RDL (1983) the mechanisms leading to the incorporation of gaseous pollutants and pollutant particles in clouddroplets or raindrops are :

- The formation of clouddroplets using sulphurous and nitrogenous aerosols as the nuclei of condensation; 80% of the sulphur and nitrogen compounds incorporated in raindrops are "embodied" in this way.
- The dissolution and oxidation of pollutants (SO_2 and NO_x) in raindrops. Because of the great surface-to-volume ratio and lower rate of fall small raindrops have a relatively high rate of absorption compared to large raindrops (LANDSBERG 1954, GEORGII 1965). This process is assumed to account for between 10% and 30% of the total absorption of pollutants.
- Diffusiophoresis, whereby smaller particles have a higher absorption rate than larger ones; on the whole this accounts for only about three per cent of the total absorption of pollutants.

- Brownian motion; this contributes only about one per cent to the absorption of pollutants.
- Impaction; this incorporation of pollutants by falling raindrops depends on the size of the falling drops and the intensity of precipitation, for smaller rain quantities (less than 2 mm per hour) this process contributes to about 30% of the total absorption of pollutants.

In wet deposition a distinction is made depending on where the pollutants have been absorbed by the raindrops. Incorporation into the falling raindrop which occurs below the cloud – that means between the base of the cloud and the ground – is called “washout” or “below cloud scavenging”. Should the absorption occur within the cloud, then the expressions “rainout” or “in cloud scavenging” are used.

Wet deposition can be calculated according to (24.3)

$$D_w = r_w \cdot C_{aq} \quad (24.3)$$

(D_w = wet deposition of pollutants, r_w = rate of precipitation, C_{aq} = Concentration of pollutants in the liquid phase).

In addition to this, the intensity of precipitation determines the washout rate: a high intensity provides a more efficient reduction of air-pollution; drizzle with a constant velocity is more efficient than rain with larger drops as it has a higher number of drops and, thus, a greater total surface area available for absorption (GEORGII and WÖTZEL 1970).

24.3.4 Filtration of pollutants by vegetation

Together with the settling of the atmospheric pollutants on the ground the filtration and ensuing absorption of pollutants by vegetation play an important role. If plants are seen as filtering elements in the environment it can be concluded that the total deposition of pollutants at forest locations below the canopy of treetops, either evergreen or deciduous, derives from humid, wet and dry depositions.

The humid and wet deposition by rain, snow or fog transfer the pollutants to the ground by way of an interdeposition on the plants.

A part of the pollutant particles or gaseous pollutants deposited by the mechanism of dry deposition are sedimented on to the different surfaces, another part is absorbed or adsorbed by the surfaces. This will be explained in detail later on. In addition, numerous pollutants are oxidized; this occurs either on the surface of the plant (e.g. by dew, interceptive or phytogenic water) or after the absorption by the plant into the cell.

The combined pollutants are gathered in the dripwater consist of according to their origin: the pollutants carried by rain (sum of “rainout” and “washout”), the pollutants deposited during dry periods which are washed off, thus excluding those particles remaining on the part of plants above the ground (according to HÖFKEN

et al. (1981), referring to HULL (1970), this is, with the exception of heavy metals and nitrogen components, only a negligible percentage) and those phytogenic substances derived from the washout of the plants ("leaching"). Leaching of these substances depends on the species of plant, the supply of nutrients, the pollutants involved as well as on the season (ULRICH et al. 1981). Furthermore, the leaching of Mg, Ca and K is intensified by the influence of various pollutants – such as SO₂ and/or O₃ (GUDERIAN et al. 1987). The leaching of sulphate–sulphur and nitrate–nitrogen could not be proved (HÖFKEN et al. 1981), and so the increase in these pollutants can only be due to the added dry deposition in the dripwater.

Dry deposition, which is interpreted by ULRICH et al. (1981) as the interception which is comprised of the adsorption of aerosols and fog and the absorption of gases at the plant surfaces, can be determined, for those pollutants which do not derive from leaching, from the difference between the concentrations in precipitation and the run-down from trunks (and stalks) as well as dripping.

The sum of all single depositions yields the total deposition in the region of the trunk and in the soil below. An admittedly smaller share of pollutants that sticks to the leaves of the trees can pass back into the atmosphere (re-suspension or re-insertion), by way of evaporation or dry mechanisms such as removal by the wind. Pollutants can also be taken up and integrated in the metabolism.

A certain portion of substances in the region of the tree trunk finds its way to the ground via the litter of needles and leaves. There they decompose and return to the natural soil and plant cycle.

However, when atmospheric pollutants are taken up by the plant two basic methods of uptake beside the rootsystem can be distinguished: cuticular and stomatic uptake. The cuticles do not put up the same resistance to diffusion at every point, possibly for species-specific reasons based on the different structures, but also because of differing sunshine conditions (leaves in the shadow or in the sun; ZIEGLER 1984). Age-dependent influences on the gas transport must also be considered. Gaseous pollutants are taken up by the stomata to a considerably higher degree than by the cuticles. The resistance which the gaseous pollutants have to overcome in the organs of assimilation consists of stomata resistance and resistance brought against the entering gases by the mesophyllic cells.

The influence open and closed stomata have on deposition velocity of SO₂ are described by the results of JACOBSEN et al. (1982). While the deposition velocities lie between 0.8 and 1.0 cm·s⁻¹ when the stomata are open, this value decreases below 0.4 cm·s⁻¹ at night, when the stomata are closed.

24.3.5 Methods of measurement of dry, wet and humid deposition

A distinction is made between two different collectors for rain-and-snow samples, the "bulk-collector" and the "wet-only collector" (dry-wet collector).

The bulk collectors are permanently exposed instruments consisting of funnels

which are connected to the collecting bottles by tubes. Since the funnels are permanently open they receive humid, wet and even dry depositions as a total integrated sample for the exposed period. A distinction between the three different deposition components cannot be made with this method. A separate collection of dry and wet depositions can be realized with a dry-and-wet collector. This apparatus basically consists of two collecting units with funnels and one lid, which closes the one or the other unit depending on the weather conditions. The samples are usually taken after each shower or, regardless of the number of rain or snowfalls, after one day.

The samples of dry depositions are collected over a period of some days or often one week in order to obtain a sufficient amount of collected pollutants for an analysis. In the last few years several different instruments have been used to collect dry and wet depositions in different projects. As the instruments were produced by different firms, they have different designs which can lead to changes in flow and, thus, cause diverging results. Comparing the different instruments in field studies it was found that obtaining similar results mainly depended on the shape of the funnel and the sensitivity of the precipitation sensor (WINKLER et al. 1989).

This is a potential source of error which has to be taken into consideration in the interpretation and comparison of measured values when different apparatuses are used.

Considerable difficulties in taking an exact and comprehensive sample of the range of droplet sizes still exist.

Fog collectors should be constructed in such way that the fog droplets can be sampled and sorted according to sizes ranging from $1\ \mu\text{m}$ to $50\ \mu\text{m}$ (PRUPPACHER and KLETT 1978). Furthermore for analytical reasons the sampling time should be kept as short as possible, in order to be able to analyze single fog occurrences.

The fog sampler should, therefore, have as large a collecting surface as possible to collect sufficient samples for chemical analysis in a very short time. There are different procedures to obtain fogwater samples:

- Passive (stationary) collectors using the Grunow method (GRUNOW 1953) and
- active rotating collectors and suction (impaction) collectors.

The advantage of active collectors is that the samples can be taken in relatively short time intervalls whereas this is only the case for passive collectors, if the wind velocity during the fog is great enough. This is usual for frontal fog.

Suction collectors are preferable in weather conditions with prevailing radiation fog (JAESCHKE 1987, SCHMITT 1987).

Due to the method of collection passive samplers probably represent the best approximation to the natural interception of vegetation.

24.4 Comparative analysis of pollution in an industrial agglomeration and a clean-air area

In the following the rates of deposition of pollutants will be discussed comparing two locations of measurement which differ with respect to their altitudes as well as their air quality. The first location is in the south of the City of "Bochum" (145 m a.s.l.) in the central Ruhr-District and is an urban location influenced by industry; the other location is far from industrial influence in the well-wooded "Sauerland" on the highest mountain, the "Kahler Asten", 845 m a.s.l., in the eastern Rhenish Slate Mountains. At both stations measurements were taken with automatic electrically driven dry-and-wet collectors.

24.4.1 Concentrations of pollutants

For a comparative analysis of the precipitation contents the diurnal concentrations of "wet-only samples" from both stations will be contrasted (Tab. 24.4).

The precipitation volume weighted mean values showed similar pH-values at both stations with a pH about 4.1. However, if the "Kahler Asten" values are used as a reference (= 100%) for the "Bochum" values to obtain an improved analysis then the values for the industrial location are:

152% for electrical conductivity,
130% for sulphate, 117% for nitrate,
178% for ammonium, 198% for chloride,
214% for calcium and 222% for lead.

This means an extraordinarily heterogeneous increase in the concentration of certain pollutants at the industrial location – quite low for nitrate (117%) and high for the heavy metal lead (222%) – with respect to the "Kahler Asten"-values.

24.4.2 Anion equivalents

In order to find out which of the examined ions contribute most to the acidity in precipitation the proportional shares of anion equivalents in precipitation were determined at both stations. While the amounts of SO_4 hardly showed any differences between both stations differences in anion equivalents of NO_3 were considerable (Tab. 24.5).

At the "Kahler Asten" the NO_3 value is higher than at the "Bochum" station, whereas the chloride value is lower. The higher NO_3 value at the less polluted location in the "Sauerland" could possibly arise from the higher degree of fertilization of agricultural acreage in the so-called "Soester Börde" and "Warburger Börde"; the higher chloride value in "Bochum" may be due to industry.

A seasonal pattern of the anion equivalents at both stations shows (Fig. 24.1) that the amount of SO_4 at the "Bochum" station increases in summer while at the

Table 24.4: Means of "wet-only" trace concentrations in rainfall samples ($\text{mg}\cdot\text{l}^{-1}$), pH-values, and electric conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) at "Bochum" station (Jan. 1983–Feb. 1984) and at "Kahler Asten" station (Nov. 1982–Nov. 1984, in italics). After KUTTLER (1986).

	weighted mean	arithm. mean	min.	max.	number of values
pH-value	4.16	4.23	3.45	5.50	124
	<i>4.09</i>	<i>4.22</i>	<i>3.30</i>	<i>6.65</i>	<i>276</i>
H^+ -ions	0.069	0.0588	0.00316	0.3548	124
	<i>0.080</i>	<i>0.0593</i>	<i>0.00022</i>	<i>0.5010</i>	<i>276</i>
electric conductivity	67.20	69.40	14.10	299.9	124
	<i>44.38</i>	<i>44.07</i>	<i>6.50</i>	<i>166.5</i>	<i>276</i>
SO_4^{2-} -S	2.09	2.73	0.41	10.99	124
	<i>1.61</i>	<i>1.82</i>	<i>0.27</i>	<i>6.31</i>	<i>276</i>
NO_3^- -N	0.62	0.79	0.15	4.04	114
	<i>0.53</i>	<i>0.61</i>	<i>0.06</i>	<i>3.28</i>	<i>263</i>
NH_4^+ -N	1.64	1.59	0.31	4.91	96
	<i>0.94</i>	<i>1.11</i>	<i>0.24</i>	<i>6.75</i>	<i>216</i>
Cl^-	2.18	3.07	0.21	22.76	84
	<i>1.10</i>	<i>1.28</i>	<i>0.15</i>	<i>12.25</i>	<i>158</i>
Ca^{2+}	1.33	1.75	0.20	11.30	102
	<i>0.62</i>	<i>0.73</i>	<i>0.09</i>	<i>6.64</i>	<i>218</i>
Pb^{2+}	0.040	0.036	0.001	0.283	62
	<i>0.018</i>	<i>0.019</i>	<i>0.001</i>	<i>0.117</i>	<i>89</i>

"Kahler Asten" station it is higher in spring and fall than in summer or winter. The clearest seasonal dependency was determined for chloride; at both stations considerably higher values were obtained in winter and fall than in summer and spring. It should also be mentioned that the seasonal differences are higher at the top of the "Kahler Asten" (winter 31.5%, spring 12.8%) than at the station

Table 24.5: Percentage of relative anion equivalents in rain water at "Bochum" station and "Kahler Asten" station (Jan. 1983–Feb. 1984). After KUTTLER (1986).

	SO_4^{2-}	NO_3^-	Cl^-
Bochum	55.5	18.5	26.0
Kahler Asten	57.6	23.1	19.3

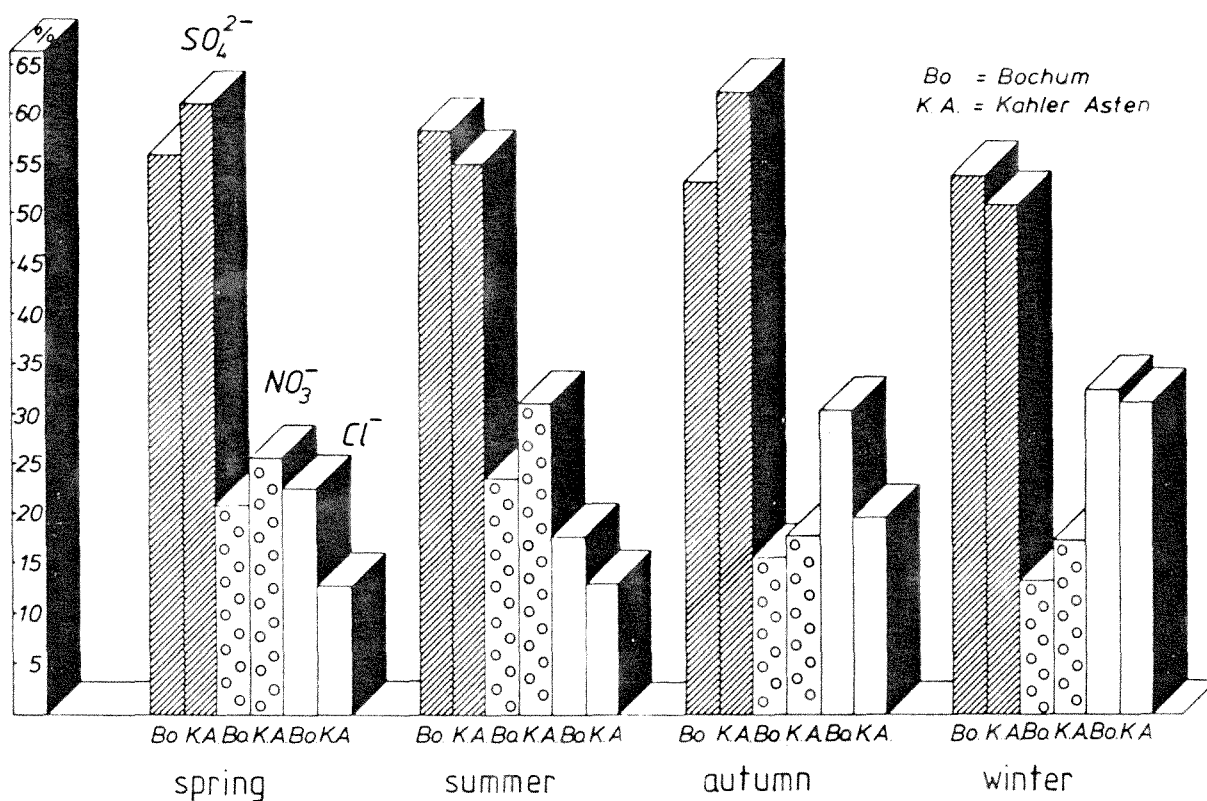


Figure 24.1: Percentage of anion equivalents in rain water samples at "Bochum" station and "Kahler Asten" station for different seasons (Jan. 1983–Feb. 1984). After KUTTLER (1986).

in "Bochum" (winter 32.7%, summer 17.8%). The more homogeneous pattern for chloride at the station in "Bochum" can be explained by the influence of industry. The consistently higher values at both stations in winter are caused by the predominance of advective weather conditions with more frequent intervals of "sea-spray" depositions than in other seasons.

Clear seasonal differences are also found in the case of NO_3^- : for summer and,

Table 24.6: Means of "wet-only" pollutant deposition at industrial area station (Bochum, 145 m a.s.l.; Jan. 1983–Feb. 1984) and of remote highland area station (Kahler Asten, 845 m a.s.l.; Nov. 1982–Nov. 1984). Values are in $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. After KUTTLER (1986).

	H^+	$\text{SO}_4^{2-}\text{-S}$	$\text{NO}_3^-\text{-N}$	$\text{NH}_4^+\text{-N}$	Cl^-	Ca^{2+}	Pb^{2+}
Bochum	0.165	4.47	1.32	3.23	5.04	2.98	0.067
Kahler Asten	0.322	6.28	1.94	3.71	4.78	2.50	0.071

to a lesser extent, for spring considerably higher values were calculated at both stations than for winter at both stations which may possibly be due to agricultural fertilization in the "Soester Börde" in these seasons. The seasonal differences are again greater at the "Kahler Asten" station than at the city station.

These results compare well with those determined by PERSEKE (1982) for the location "Deuselbach" (Hunsrück) and those by GEORGII et al. (1982) for precipitation samples on the "Kleiner Feldberg" in the Taunus Mountains.

24.4.3 Deposition of pollutants

The deposition rates at a particular location are determined from the concentration of a pollutant in precipitation and the amount of precipitation during the period of measurement. In order to obtain a better comparison the total amounts of precipitation were standardized to a period of one year: the total amount of precipitation for "Bochum" was 935 mm while the "Kahler Asten" received 1,724 mm, 1.8 times the amount of "Bochum". The mean values of "wet-only depositions" at both stations are arranged in Tab. 24.6. They show the following values for the "Kahler Asten" relative to "Bochum" (= 100%): H-ion = 195%, $\text{SO}_4\text{-S}$ = 140%, $\text{NO}_3\text{-N}$ = 147%, Cl = 95%, Ca = 84%, Pb = 106%. With the exception of chloride and calcium consistently higher rates of deposition were determined at the top of the "Kahler Asten" in spite of the lower concentration of pollutants (see Tab. 24.4).

The rates of dry deposition of the pollutants sulphate-sulphur, nitrate-nitrogen and chloride were also determined. Relative to total deposition (dry and wet) the values for dry deposition on the "Kahler Asten" were consistently lower.

The influx of aerosol depositions is therefore of less importance at the top of the "Kahler Asten" than in the industrial region. The standard deviations of the mean values of dry depositions at the mountain station shown in the third column of Tab. 24.7 are considerably lower than those in "Bochum". As these standard deviations are calculated from the values of each month they reflect the monthly fluctuations in the levels of dry deposition which are more homogeneously distributed on the "Kahler Asten" than in "Bochum".

Table 24.7: Total deposition (td), the percentage of dry deposition (dp), and its standard deviation (sd), of trace constituents at "Bochum" station and "Kahler Asten" station (Jan. 1983–Feb. 1984). After KUTTLER (1986).

			Bochum	Kahler Asten
SO ₄ ²⁻ -S	td	[mg·m ⁻² ·d ⁻¹]	6.60	7.26
	dp	%	34.1	21.8
	sd	%	16.1	9.4
NO ₃ ⁻ -N	td	[mg·m ⁻² ·d ⁻¹]	1.93	2.35
	dp	%	26.8	20.3
	sd	%	18.2	11.8
Cl ⁻	td	[mg·m ⁻² ·d ⁻¹]	5.14	6.18
	dp	%	29.2	15.5
	sd	%	15.5	12.9

This means that the lower amounts of dry deposition on the "Kahler Asten" show a more uniform distribution over the period of measurement than those at the station in the polluted area in "Bochum".

In this context the dependence of total deposition on the amounts of dry and wet deposition was also examined. It could be proved that high amounts of total deposition were caused, in general, by the predominating amounts of wet deposition at both stations. In order to show the dependence of the total deposition on the wet and dry depositions it was necessary to relate the total deposition to the percentage shares of dry and wet depositions at both stations. In the analysis shown for "Bochum" it can be seen that high depositions of the pollutants sulphate, nitrate and chloride occur when the ratio of wet deposition to dry deposition is much greater than 1. This relation is described shown by the regression line R 1 (Fig. 24.2).

For the three pollutants wet deposition amounts to between 80 and 95% when there are higher values of total deposition. In contrast, the course of regression line R 2, which describes the ratio of wet to dry deposition in July and August 1983, is completely contrary to that of regression line R 1. Although both months were extremely dry (July 25%, August 30% of the long-term mean values) relatively high amounts of total deposition, which were mainly caused by dry depositions – not by wet depositions which otherwise caused the main influx of these pollutants could be determined. This can be attributed to the extraordinarily high proportion of dry hours (98% of all hours in the month) causing an accumulation of the aerosols sulphate and nitrate in the layer of the air at ground level. The same analysis

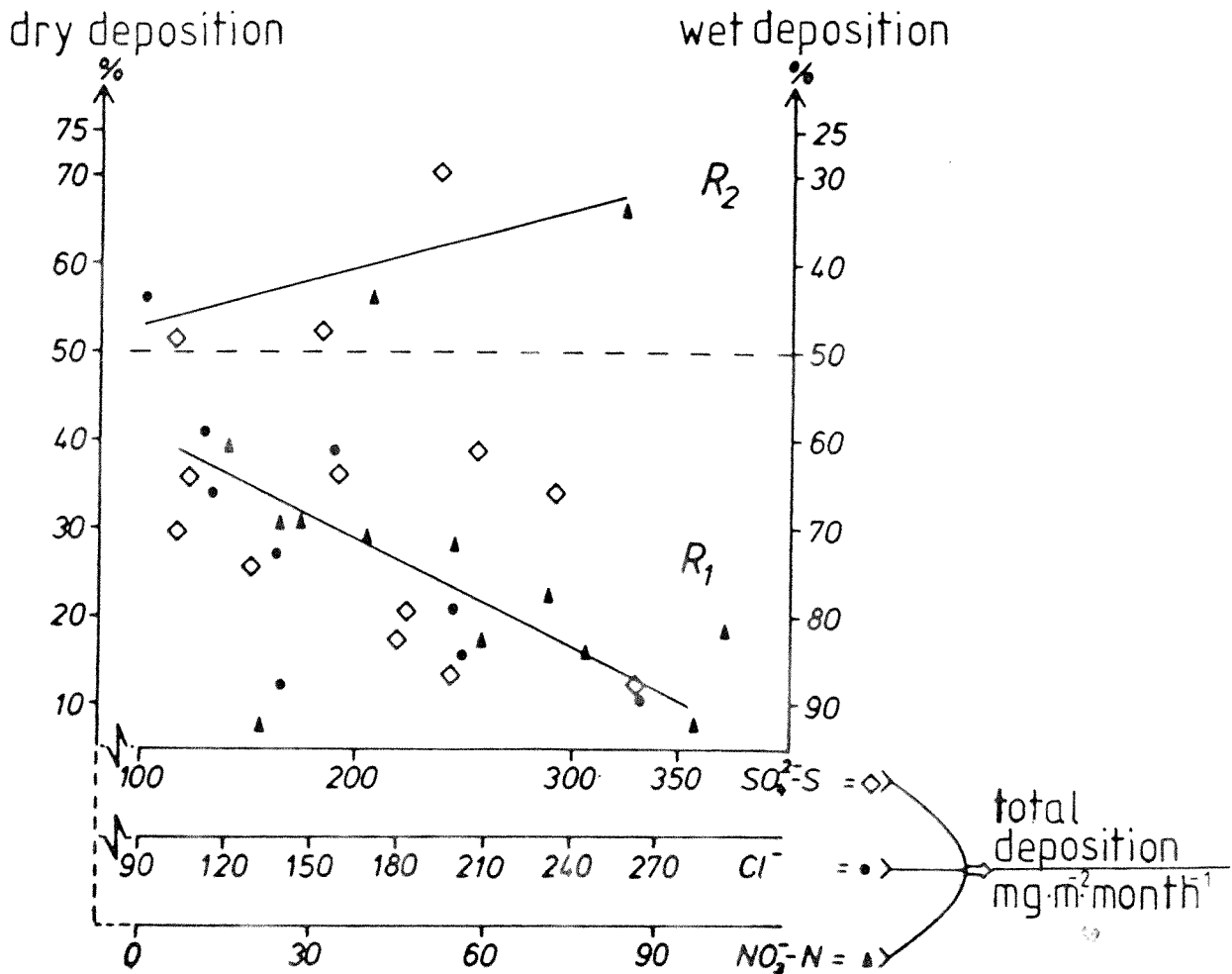


Figure 24.2: Dependence of total deposition on dry and wet deposition at "Bochum" station (Jan. 1983–Feb. 1984). After KUTTLER (1986).

shows a totally different situation at the "Kahler Asten" location (Fig. 24.3).

On the one hand there is no clear regression of the values of the pollutants to a straight line as was the case for "Bochum" – this is especially the case for chloride which shows the greatest deviations. On the other hand there is no dominance of dry deposition in relation to wet deposition in July and August although these months were also extremely dry in the mountain area.

Dry deposition is substantially less important at the top of the "Kahler Asten", even during dry months, than in the industrial region where the dry deposition of the aerosols sulphate and nitrate exceeds wet deposition when the amount of precipitation is low.

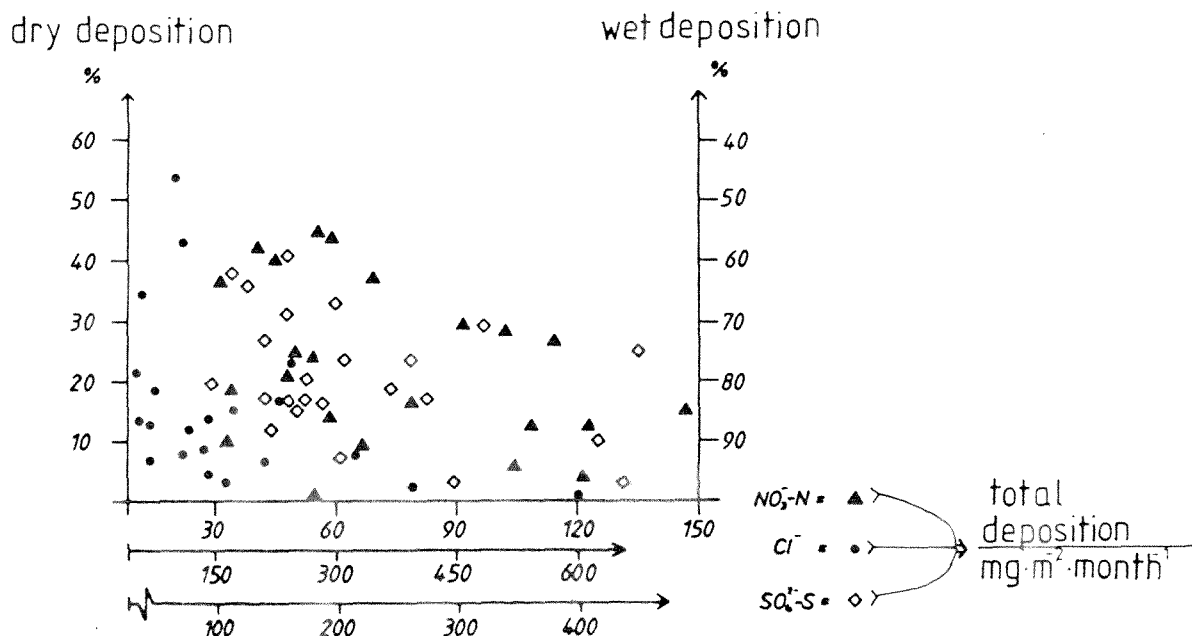


Figure 24.3: Dependence of total deposition on dry and wet deposition at "Kahler Asten" station (Nov. 1982–Nov. 1984). After KUTTLER (1986).

24.5 Results of investigations of pollutant transfer into individual tree stands

It is a significant aim of research to obtain information about the filtration of trees or forests in the analysis of ecological cycles in order to ascertain the effects of pollution on ecosystems covered with vegetation.

In this respect it is not only necessary to determine the concentration of pollutants in the air, but also the resulting influx in the soils and, consequently the amounts of pollutants per unit ground area.

In the following the extent of filtration of H-ion, $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ on the basis of the monthly mean values of pollutant concentrations in the dripwater from tree tops as well as pollutant deposition will be presented, with the aid of Tables 24.8 and 24.9, for different trees at a site in "Bochum" (the Botanical Gardens of the "Bochum" University).

The mean pH-value of precipitation was 4.1 during the measurement period of 13 months. Slightly increased values were found under a canopy of beech and holly. Under spruce and pine as well as oak, however, the values were lower. The sulphate-sulphur concentrations were generally higher in the dripwater; under spruce a value of 38 mg of $\text{SO}_4\text{-S}$ per litre, nearly 16 times the concentration outside the canopy, was obtained.

Considerably increased concentrations of nitrate - nitrogen were also found in dripwater and were again the highest under spruce (as was the case for sulphate-

Table 24.8: Monthly means of pH-values and trace concentrations [$\text{mg}\cdot\text{l}^{-1}$] of SO_4^{2-} -S and NO_3^- -N of open space rain samples and dripwater of different trees. The symbols in column 1 mean: S: SO_4^{2-} -S; N: NO_3^- -N. After KUTTLER (1986).

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	mean
Open space:													
pH	4.78	4.41	4.15	4.75	4.04	3.28	4.66	5.31	6.63	4.46	4.18	4.17	4.10
S	1.91	2.18	1.51	3.10	2.15	2.71	3.00	3.43	-	2.24	1.78	2.67	2.42
N	0.45	0.54	0.68	0.93	1.06	0.72	0.61	0.86	-	0.45	0.54	0.36	0.65
Beech (<i>Fagus sylvatica</i>):													
pH	4.56	6.29	4.05	4.43	4.92	4.32	4.62	5.01	6.38	4.21	3.78	4.08	4.33
S	3.17	4.13	3.63	4.06	5.38	2.61	5.61	4.32	16.50	4.88	4.12	5.14	5.30
N	0.18	0.61	1.67	1.31	1.76	1.69	2.08	1.63	6.64	0.88	1.51	1.04	1.80
Holly (<i>Ilex aquifolium</i>):													
pH	4.88	4.53	4.87	4.78	4.19	4.75	5.18	5.17	5.91	4.92	5.64	5.01	4.79
S	5.38	4.61	6.77	6.73	6.40	4.76	8.58	4.81	18.05	5.61	5.84	9.76	7.23
N	1.56	1.38	2.19	1.92	3.61	1.74	2.57	1.69	5.48	0.27	2.76	0.95	2.18
Spruce (<i>Picea abies</i>):													
pH	3.64	3.90	3.48	3.54	3.78	3.91	3.65	5.18	4.84	3.68	3.18	3.57	3.66
S	34.91	23.99	49.30	52.20	35.80	16.04	21.19	14.38	75.34	44.74	35.01	52.99	38.00
N	7.54	5.13	15.06	7.72	12.87	9.84	9.13	5.47	32.95	17.03	12.95	10.43	12.17
Black pine (<i>Pinus nigra</i>):													
pH	4.16	4.05	3.89	3.77	3.70	3.75	4.05	4.25	4.07	3.58	3.50	3.60	3.80
S	10.49	6.50	14.12	10.92	8.31	4.19	5.94	4.62	29.40	6.96	5.77	12.05	9.94
N	2.60	1.94	4.00	2.28	4.13	1.89	2.82	2.05	11.14	2.42	1.54	2.73	3.30
Scotch pine (<i>Pinus sylvestris</i>):													
pH	4.01	4.06	3.77	3.90	3.62	3.79	3.95	4.54	3.86	3.56	3.52	3.53	3.77
S	10.13	8.18	12.01	11.41	7.95	3.40	9.77	5.48	31.45	9.70	8.09	13.04	10.88
N	1.90	1.85	4.54	2.39	3.68	2.12	2.64	2.55	18.20	3.47	2.50	3.09	4.08
Oak (<i>Quercus robur</i>):													
pH	4.24	3.87	3.80	8.81	4.12	4.71	4.89	5.12	6.02	4.07	3.25	3.69	3.91
S	5.47	5.91	7.16	5.64	7.26	7.00	10.92	6.76	26.69	9.07	7.72	6.93	8.88
N	1.08	0.79	2.01	1.45	2.30	1.71	1.21	2.15	9.31	1.42	0.72	0.97	2.09

Table 24.9: Monthly sums of trace depositions of open space rain samples and drip water of different trees. The symbols in column 1 mean: S: SO_4^{2-} -S; N: NO_3^- -N. Values are in $[\text{mg}\cdot\text{m}^{-2}\cdot\text{month}^{-1}]$. After KUTTLER (1986).

	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	mean
Open space:													
H ⁺	2.00	2.32	4.94	0.74	6.14	66.30	1.51	0.77	0.005	3.90	3.85	0.55	7.75
S	232.00	130.30	103.90	129.70	144.60	271.30	208.00	358.10	-	252.80	103.30	218.50	195.70
N	53.10	32.20	46.70	38.20	72.20	92.40	41.90	134.40	-	51.10	31.60	29.20	56.60
Beech (<i>Fagus sylvatica</i>):													
H ⁺	2.50	0.025	3.90	1.28	0.48	3.58	0.91	1.13	0.004	3.36	5.55	4.72	2.90
S	296.30	202.60	158.50	139.50	213.90	194.90	212.50	501.10	171.70	266.10	212.00	292.40	230.90
N	75.30	30.10	73.70	35.50	70.70	126.10	78.60	184.80	69.00	47.90	50.50	58.80	75.40
Holly (<i>Ilex aquifolium</i>):													
H ⁺	0.96	0.95	0.58	0.41	3.35	1.43	0.29	0.93	0.017	1.50	0.066	0.44	0.91
S	393.90	134.50	289.50	164.60	322.70	384.40	374.00	665.40	254.90	700.40	168.00	261.90	343.70
N	113.00	45.40	93.90	47.40	188.30	140.80	112.40	232.90	70.40	33.80	79.40	42.90	100.60
Spruce (<i>Picea abies</i>):													
H ⁺	14.40	3.34	12.21	2.97	2.62	10.37	5.19	0.93	0.045	8.64	6.00	6.78	6.12
S	2196.70	636.20	1819.50	535.20	509.80	1352.80	491.60	2045.90	233.50	1852.70	318.50	1335.30	1110.60
N	474.90	135.90	555.60	158.20	203.30	830.80	211.70	777.30	102.20	705.60	117.20	263.30	378.00
Black pine (<i>Pinus nigra</i>):													
H ⁺	7.20	4.03	7.31	3.82	7.88	19.80	4.61	7.96	1.26	18.90	10.70	14.90	9.03
S	1096.00	297.40	810.60	246.20	332.60	470.60	311.60	658.90	439.30	503.90	197.40	719.80	507.00
N	269.10	87.60	227.10	102.30	163.20	210.80	146.40	290.90	164.80	172.90	66.90	161.90	172.00
Scotch pine (<i>Pinus sylvestris</i>):													
H ⁺	13.10	4.20	15.60	3.80	13.50	19.30	4.40	4.30	1.50	22.10	13.80	22.80	11.60
S	1374.70	397.20	1113.20	326.90	450.70	409.40	475.10	826.00	352.40	786.90	372.80	1016.70	658.50
N	340.30	108.50	417.80	143.80	206.30	253.60	127.60	382.30	202.10	280.30	114.80	238.60	234.70
Oak (<i>Quercus robur</i>):													
H ⁺	9.70	10.60	15.70	7.50	4.10	2.10	0.50	1.12	0.01	8.10	38.90	22.20	10.00
S	933.50	467.50	705.70	275.30	392.30	750.20	404.20	1007.60	355.60	874.10	540.50	836.80	628.60
N	183.20	61.70	198.20	70.00	123.10	181.50	44.70	318.50	122.50	134.90	49.40	104.40	132.70

sulphur). The highest concentrations occurred when there was rain after a dry period of several days. The characteristic months for these results were April and September for which the highest concentrations of pollutants in the dripwater were found.

It was generally evident that the variability of the monthly mean values of pollutant concentrations was relatively high during the year in open spaces as well as under vegetation canopy. In particular, the dripwater under spruce showed considerable monthly dependent deviations which lead to the intermittent influx of pollutants in soil-ecosystems.

The distribution and level of pollutant concentrations in Tab. 24.9 show that the influx rates of H-ions at sites with holly, beech and spruce were, in some cases, considerably lower than at sites without vegetation. For pine and oak, however,

higher values were obtained.

The influx rates for sulphate-sulphur and nitrate-nitrogen were generally higher under all the measured trees. Values for sulphate - sulphur from 1.2 (under beech) up to 5.7 (under spruce) times the value for open space was measured. For nitrate-nitrogen a range from 1.3 (beech) to 6.7 (spruce) times the value for open space was determined.

Very high monthly deposition rates for all sites were obtained during the rainy months January, March, August and December and mainly low values for the dry months April and September.

Referring to the accumulation of pollutants NO_3 and SO_4 one can basically say that spruce and scots pine have the greatest filtration capacity while the beech has the lowest (compared to open space).

Not only the absolute amount but also the temporal distribution of the depositions during the measuring period, as was the case with the concentrations in the dripwater are relevant when considering the ecological consequences of the pollutants.

As a comparison of the monthly totals within the measurement period for the different locations shows there are extraordinarily large fluctuations between the months (Tab. 24.9). These can be considered in terms of the proportional standard deviation calculated on the basis of the monthly total values with reference to the total mean value of the respective measurement station. These values, for the pollutants sulphate and nitrate (excluding the location under spruce), varied from 40% to 62%. Under spruce trees, however, they reached a higher standard deviation of between 66% and 73%. It can be concluded that tree stand are exposed to a high influx of pollutants over various periods of time resulting in the corresponding impact on the given ecosystem.

24.6 Conclusion and discussion

In this report results of measurements of wet and dry depositions of atmospheric pollutants have been presented for an air polluted industrial site and a location far from industrial influence in the Rhenish Slate Mountains ("Kahler Asten"). It is not only their geographical location which is of significance to their air quality, but also their orographic situation: "Bochum" at an altitude of 145 m a.s.l., the "Kahler Asten" 845 m a.s.l.

The evaluation of the dry and wet depositions clearly shows the different air qualities of both areas. Comparing these values to those found by other measuring networks (Tab. 24.10) the weighted wet-only concentrations of precipitation for the trace substances sulphate and lead show typical increases in the industrial areas, while there are considerably lower values at those sites far from industry which are mainly exposed to long-range transport.

However, there is not such a clear dependence on industry observable for the trace substance nitrate. This is probably due to the fact that this trace sub-

Table 24.10: Weighted means of "wet-only" trace concentrations in rainfall samples at different stations in the Federal Republic of Germany. After GEORGII et al. 1982 (No. 1-6), KUTTLER 1986 (No. 7, 8); from KUTTLER (1986).

No.	Location	SO ₄ ²⁻ -S	NO ₃ ⁻ -N (mg·l ⁻¹)	Cl ⁻	Pb ²⁺ (μg·l ⁻¹)
1	Schleswig	1.78	0.76	3.51	12.8
2	Braunschweig	1.96	0.87	1.30	23.2
3	Essen	2.19	0.88	2.03	47.2
4	Kl. Feldberg/Ts.	1.73	0.72	1.15	24.0
5	Frankfurt/M.	1.89	0.76	1.14	32.3
6	Hohenpeißenberg	1.35	0.72	3.64	11.6
7	Bochum	2.09	0.62	2.18	41.0
8	Kahler Asten	1.51	0.53	0.85	10.7

stance is released into the atmosphere by agricultural utilization nearly everywhere. Chloride shows increased values at coastal stations and in industrial regions. The comparatively high value measured in precipitation on the mountain "Hohenpeißenberg" may have been caused by a local source.

With regard to the proportions of the most important acidic anions in precipitation for both stations sulphate ions account for more than 50% followed by chloride ions (26%) at the "Bochum" station and nitrate ions (18.5%). On the mountain "Kahler Asten", however, nitrate accounts for a higher share than chloride. "Bochums" higher chloride level can be explained by its somewhat shorter distance from the sea and the industrial release of HCl. Results obtained by the UBA-network in the Federal Republic of Germany show that sulphate participates to 50-60%, nitrate to 23-27% and chloride to 4-10% in the process of acidification.

Increases in the values for chloride by up to 40% have been found in precipitation samples originating from industrial agglomerations and coastal stations (MÜLLER et al. 1982). The analysis of the annual distribution of the anion contents showed a high level of sulphate ions for both stations with a summer maximum in "Bochum" and highest values in fall and spring on the "Kahler Asten". The clearest seasonal dependence, however, was determined for chloride anions whose part in acidification was greater in winter and fall than in summer and spring. When rain coming from the north-western direction was collected at both stations it could indeed be determined that the levels of chloride ions were enhanced at both stations proving the unmistakable influence of the sea.

The different altitudes of "Bochum" and the "Kahler Asten" also allow statements about the absorption of the trace substances in the raindrops to be made. By being able to distinguish between the different kinds of rain the proportion of "rainout" ("in cloud scavenging") and "washout" ("below cloud scavenging") could

be calculated.

Comparative measurements (for "Bochum" and "Kahler Asten") showed that the total amount of precipitation at "Bochum" was 57% of the "Kahler Asten" level. However, in "Bochum" the trace substance levels were, for sulphate 77%, for nitrate 71% and for each of ammonium and chloride 91% of those levels found on the "Kahler Asten". Relative to the lower amount of precipitation a higher influx of pollutants was clearly observed in "Bochum". Assuming that the greatest share of wet deposition on the less polluted "Kahler Asten" originates from "rainout" and – among other things because of the increase of the duration of rainy periods – , it can be concluded that the higher levels in "Bochum" mainly result from the "washout" from the approximately 700 m high air-layer between the altitudes of "Kahler Asten" and "Bochum". On this basis the following levels of below cloud scavenging were calculated: for sulphate 40%, for nitrate 29% and for ammonium and chloride 65% – all relative to the determined total deposition for "Bochum".

These levels were confirmed not only by comparative measurements in an earlier investigation in Frankfurt/M. and on the nearby mountain "Kleiner Feldberg" (800 m a.s.l. in the Taunus Mountains) carried out by GEORGII (1965), but also by investigations into the "washout" phenomenon in the Soviet Union in which levels of 45–78% for below cloud scavenging were quoted (PETRENCHUK and SELEZNEVA 1970).

The measured values of depositions at both stations clearly showed that dry deposition makes up considerable share of total deposition in the industrial region while it is less important in the clean-air locations.

The results of our measurements are compatible with the data available for several regions in the FRG. If the sulphur deposition is taken (Tab. 24.11) the converted value of $1.6 \text{ g S}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ for the industrial city "Bochum" compares well with the values of other industrial cities. The annual "Kahler Asten" value of $2.0 \text{ g S}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ corresponds to those found at other hill stations. Furthermore, the proportional shares of dry deposition fit well to the distributional pattern of the FRG with high levels in urban and industrial regions and lower levels at clean-air locations.

Our data reveals that wet deposition reaches values of between 1 and 2 $\text{g S}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the FRG while dry deposition only makes up 0.2 to 0.8 $\text{g S}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$. When calculated over the total area of the FRG (250,000 km^2) annual dry and wet depositions of 300,000 to 700,000 tons of sulphur are obtained. If this is compared with the total SO_2 -S emissions in 1984 (see Tab. 24.1) proportions of at least 23% to a maximum of about 54% were deposited in this way. In these calculations of total sulphur deposition the deposition rates of gaseous sulphur (e.g. SO_2) have not been considered. In addition, the influx of trace substances by fog was not determined.

In the last few years more studies into the influx of pollutants by fog have been carried out at several different locations in the FRG (e.g. SCHMITT 1987, SCHELL and GEORGII 1989, MUNGER et al. 1983). They confirm earlier investigations

Table 24.11: Wet and dry sulphate-sulphur deposition in the Federal Republic of Germany (results of measurements No. 1 to 10 after GEORGI 1989; No. 11 and 12 after KUTTLER 1986).

No.	location	precipitation (mm·yr ⁻¹)	deposition		dry part of total deposition %
			wet (gS·m ⁻² ·yr ⁻¹)	dry (gS·m ⁻² ·yr ⁻¹)	
1	Frankfurt/M.	752	1.4	0.4	22
2	Essen	1,018	2.0	0.6	23
3	Jülich	735	1.4	0.5	26
4	Braunschweig	745	1.2	0.4	25
5	Hamburg	1,011	1.8	0.4	18
6	Hof	811	1.3	0.4	23
7	Schleswig	1,091	1.7	0.4	19
8	Deuselbach (Hunsrück)	914	1.1	0.2	15
9	Kl. Feldberg (Taunus)	1,192	2.0	0.5	25
10	Hohenpeißenberg	1,201	1.4	0.3	18
11	Bochum	863	1.6	0.8	34
12	Kahler Asten (Rhenish Slate Mnts.)	1,498	2.0	0.6	22

(e.g. MROSE 1966) showing that the concentrations of various trace substances were considerably higher in fog water than in rainwater.

KROLL and WINKLER (1989) recently published the results of their comparative measurements at several stations in clean-air areas (highlands), including mountain "Kahler Asten". In Tab. 24.12 the measured concentrations and calculated depositions from KROLL and WINKLERS fog study are compared with the results of examinations of the rainwater at the same location. The values from the fog water analysis have been converted to mg·m⁻²·d⁻¹ for the sake of comparison. The results show considerably higher concentrations in fog water than in rainwater, especially for nitrate, ammonium and lead. With respect to depositions via fog and rain the deposition of sulphate and chloride is higher in rain, whereas nitrate is deposited to a greater extent by dripwater in the tree stands due to fog.

The deposition values for ammonium via fog and rain are in the same order of magnitude. There is no doubt that the depositions by fog, especially in the foggy highlands, for example there are up to 100 foggy days in the Rhenish Slate Mountains annually (SCHIRMER 1976), play an important part in pollution analysis of any ecosystem which have to be considered in examinations of ecological balances. This is true on the one hand because of the higher influx into forest-soil ecosystems,

Table 24.12: Mean values of trace substance concentrations in fog water and pollutant deposition rates via fog interception (after KROLL and WINKLER 1989) compared with trace substance concentrations in rain water and wet-only deposition rates via rain (after KUTTLER 1986) at the remote highland area station "Kahler Asten" (845 m a.s.l.; Rhenish Slate Mountains).

	SO ₄ ²⁻ -S	NO ₃ ⁻ -N	Cl ⁻	NH ₄ ⁺ -N	Pb ²⁺	reference
Concentrations:						
		(mg·l ⁻¹)			(μg·l ⁻¹)	
fog	3.5	4.7	2.1	4.5	86	KROLL & WINKLER (1989)
rain	4.1	1.6	1.1	0.9	18	KUTTLER (1986)
Deposition:						
		(mg·m ⁻² ·d ⁻¹)				
fog	3.5	4.8	2.2	4.5	-	KROLL & WINKLER (1989)
rain	6.3	1.9	4.8	3.7	-	KUTTLER (1986)

on the other hand because of the fact that increases in acidity of up to a factor of 1,000 have been found, due to the reduction in volume by evaporation of the fog droplets which settled onto the leaves of the trees (FREVERT and KLEMM 1984). Of course, this can cause lethal damage to the epidermal cuticles.

The dominating filtration of atmospheric pollutants by trees could be clearly demonstrated. However, the values under spruce were considerably higher in "Bochum" than at other locations in Northrhine-Westphalia (see Tab. 24.13). This can be explained by the industrial influence in "Bochum", but also by the measurements under single trees. HÖFKEN et al. (1981) mentioned the same fact concerning their investigations. They calculated a factor of increase of 1.3 for nitrate compared to measurements under forest canopies.

In recent discussions about the specification of emission limits for the protection of vegetation and ecosystems the emphasis on the concentration of pollutant in the air is no longer seen as a sufficient mean of control. The so-called "critical loads" which indicate those limits under which no damage to the ecosystem will occur have increasingly become the point of discussion. Hitherto, "critical loads" were only published for sulphur and nitrogen compounds (NO_x and NH₄⁺) (NILSSON and GRENNFELT 1988). The critical loads for forest soils for sulphur range from 3 to 32 kg·ha⁻¹·yr⁻¹. The relatively large range is due to the number of different soils with various buffer capacities. If the measured values for "Bochum" are converted, a sulphate-sulphur influx of 24 kg·ha⁻¹·yr⁻¹ is obtained; under spruce the influx rate reached as much as 135 kg·ha⁻¹·yr⁻¹ - exceeding the critical load many times.

For the influx of nitrogen an exceeding of the critical load by up to a factor of 20 can be assumed from the results of this investigation and other surveys in Northrhine-Westphalia (e.g. BARTELS and GEHRMANN 1990).

Table 24.13: Total Deposition of SO_4^{2-} -S and NO_3^- -N at open space and in throughfall of beech and spruce at different locations in Northrhine-Westphalia (NRW), Federal Republic of Germany. Values are in $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

SO_4^{2-} -S	NO_3^- -N	location	period	reference
Open space:				
8.8-12.8	3.2-4.1	Burgholz/Solingen	5/83-10/83 5/84-10/84	KUTTLER (1987)
5.8	2.5	Paderborn	11/82-10/83	BLOCK & BARTELS (1985)
4.2	1.6	Monschau	11/82-10/83	BLOCK & BARTELS (1985)
6.5	1.9	Bochum	4/82-4/83	KUTTLER (1986)
-	1.6-2.8	10 stations at non-industrial sites of NRW	1982-1988	BARTELS & GEHRMANN (1990)
Beech:				
16.3-15.8	3.3-4.2	Burgholz/Solingen	5/83-10/83 5/84-10/84	KUTTLER (1987)
7.0	2.8	Paderborn	11/82-10/83	BLOCK & BARTELS (1985)
6.0	1.9	Monschau	11/82-10/83	BLOCK & BARTELS (1985)
7.7	2.5	Bochum	4/82-4/83	KUTTLER (1986)
-	2.7-4.1	10 stations at non-industrial sites of NRW	1982-1988	BARTELS & GEHRMANN (1990)
Spruce:				
15.4-23.7	3.3-6.2	Burgholz/Solingen	5/83-10/83 5/84-10/84	KUTTLER (1987)
9.1	2.6	Paderborn	11/82-10/83	BLOCK & BARTELS (1985)
7.4	2.2	Monschau	11/82-10/83	BLOCK & BARTELS (1985)
37.0	12.6	Bochum	4/82-4/83	KUTTLER (1986)
-	3.0-5.8	10 stations at non-industrial sites of NRW	1982-1988	BARTELS & GEHRMANN (1990)

As any exceeding of the critical load values leads to an extraordinarily severe destabilization of ecosystems in forests and lakes, these critical deposition values – together with the air-pollution limits – become more and more important in discussions about the protection of our environment.

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