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A relationship between liquid water content and chemical composition in clouds

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Abstract

In this paper we present two-year results from the Cloud Chemistry Measurements Programme, carried out at Mt. Brocken/Harz (Germany) to assess the influence of cloud physical parameters on the chemical composition of clouds. There are large variations in the chemical composition of cloud water. We found that the liquid water content of clouds predominantly determines the ionic content. The relationship is best approximated by a power function, nearly identical for all chemical species. We identified deviations of data points from the general relationship accompanying events with different air pollution situations. An important conclusion is that cloud chemistry monitoring in the sense of air pollution studies is meaningless without measurement of cloud physical parameters. These are liquid water content, cloud base altitudes, and to some extent, droplet size distribution.

1. Introduction

Clouds play a immense role in transport and transformation of atmospheric trace species. They redistribute gas phase species, especially through vertical mixing and influence photochemical processes. Clouds transfer aerosols by nucleation and gaseous species by scavenging them into the liquid phase. Chemical processes in cloud water are often more effective than in the gas phase and therefore must be included in any atmospheric budget of trace species. Finally, precipitating clouds remove trace species via wet deposition from the atmosphere. Clouds have an important indirect effect on climate forcing. Moreover, there could be a feedback via aerosols and chemical processes that change the physical properties of clouds. The climate discussion leads to an increasing interest in aerosol–cloud processes and cloud chemistry.

Numerous investigators have reported data on cloud acidity and chemistry of cloud water collected at mountain sites (Okita, 1968; Falconer and Falconer, 1980; Möller et al., 1994b; Acker et al., 1995; Fuzzi, 1995; Weathers et al., 1995 and many others).

A Mountain Cloud Chemistry Program (MCCP) was created in eastern North America for assessment of atmospheric exposure and deposition to high elevation forests because ionic deposition may be 2 to 5 times the deposition received due to precipitation. Results of these studies (network of 6 stations) of atmospheric chemistry and physics are presented by Mohnen and Kadlec (1989), Saxena et al. (1989), Mohnen et al. (1990), DeFelice and Saxena (1991) and others. Within the MCCP were different mean liquid water contents (LWC) of clouds found at the measurement stations ($0.20\text{--}0.46\text{ g/m}^3$) and it was concluded that the observed LWC values at any site were mostly a function of site elevation relative to the cloud base height and synoptic meteorology (Mohnen et al., 1990). We started a mountain cloud chemistry program on Mt. Brocken (51.80°N , 10.67°E)/Harz Mountains in Germany (see also Fig. 1) in 1991 to study the role of clouds in the atmospheric budget of air pollutants. Mt. Brocken is the highest elevation in the northern part of Central Europe (1142 m a.s.l.). Because of the high occurrence of clouds (40–50% as yearly mean) the station is focused on a programme for long-term sampling of cloud water.

We adopted experiences from the MCCP in the eastern United States (Saxena and Lin, 1990; Mohnen and Vong, 1993) for this first continuously mountain site cloud monitoring in Europe.

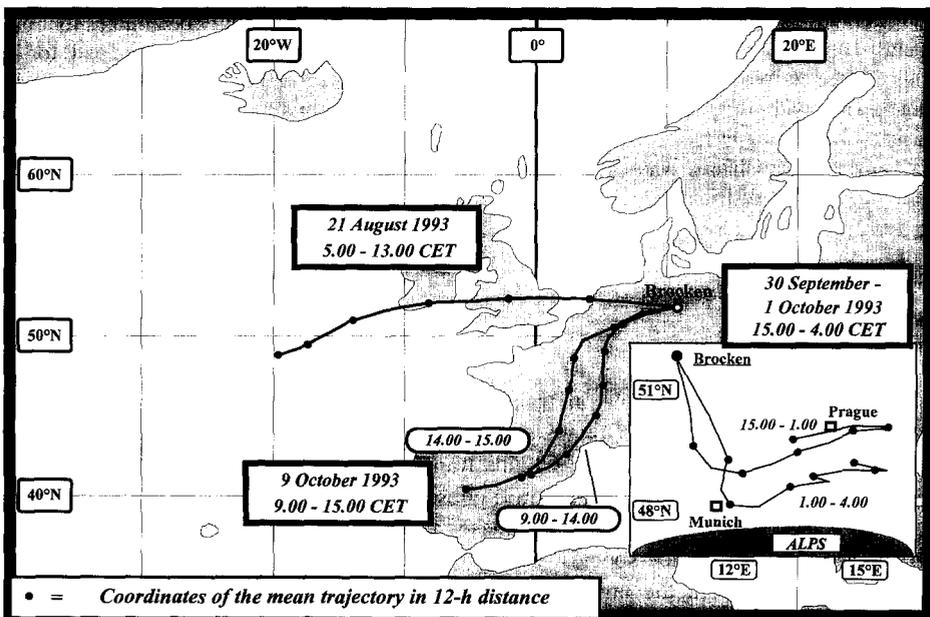


Fig. 1. Location of Mt. Brocken in Europe and mean 72-h back trajectories for selected events (see Fig. 6 and Tables 4 and 5).

The height of cloud water collection above cloud base is expected to be an important source of variability in both cloud water chemistry and LWC. Nucleation of pre-existing aerosol, condensation of diffusing water vapour, and droplet growth occur with vertical motion of clouds overrunning mountaintops. The Junge (1963) formulation for nucleation scavenging implies that the concentration of cloud water solute varies with the inverse of LWC.

The results of many LWC measurements for different low level cloud types and LWC profiles through clouds have been published in literature (Daum et al., 1984; Matveev, 1984; Nicholls, 1984; Mazin and Khrgian, 1989; Johnson et al., 1992). For some cloud types (cumulus, stratocumulus and stratus clouds) the LWC increases with height above the cloud base. The level of the maximum LWC is near the cloud top. The maximum LWC in a cloud is determined by the cloud depth and temperature at the cloud base (Mazin and Khrgian, 1989). Although the concentrations of trace substances in clouds are expected to vary with liquid water content, few analysis at Whiteface Mountain (Mohnen et al., 1990) and at Mt. Brocken (Möller et al., 1995) have shown a significant correlation between cloud water concentration and LWC and there was a significant altitudinal gradient found within clouds for the main ions, with higher concentrations at or near the cloud base (Wieprecht et al., 1995).

In our group Oestreich (1995) developed regional cloud climatology statistics from historical (1967–1990) and current (1991–1993) Mt. Brocken cloud observation data (observed by the German Weather Service at Mt. Brocken and at Braunlage, 8 km south of Mt. Brocken). During “station in cloud” the cloud types stratocumulus with 37.9% and stratocumulus and cumulus together (Sc/Cu) with 31.6% are strongly dominant. The cloud base is often between 900–1200 m a.s.l. for convective clouds (cumulus, cumulonimbus, Sc, Sc/Cu) and 700–800 m a.s.l. for stratiform clouds (stratus neb., stratus fractus).

The aim of this contribution is to present relationships between liquid water content and ionic content of collected cloud water for nonprecipitating clouds at Mt. Brocken. We found large differences in the chemical composition of cloud water from event to event, much more than it is known from precipitation chemistry studies, Table 1 (Rodhe and Granat, 1984; Marquardt and Ihle, 1988; Baron and Denning, 1993; Hansen et al., 1994).

Table 1

Mean chemical composition including minima and maxima of cloud water collected at Mt. Brocken (in $\mu\text{eq l}^{-1}$)

Year	<i>n</i> ^a	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	H ⁺
1992	37	331	387	127	391	156	147	40	39
		41	21	6	9	< 1	10	1	< 0.1
		1194	1071	579	1007	854	1311	212	339
1993	570	372	398	91	590	81	73	35	113
		24	18	2	2	2	3	5	< 0.02
		3667	5423	883	5409	980	2245	530	1500

^a Number of events (sampling time resolution in 1992) and 1-h samples in 1993 (131 events).

In principle, there are three different reasons for these variations: (a) differences in the air pollution situation, (b) large scale transport characteristics and (c) cloud dynamic and microphysical behaviour. Assessment and understanding of the role of clouds in atmospheric chemistry require a separation between the different causes that are responsible for the chemical composition of cloud water, e.g. droplet size distribution, (ten Brink et al., 1987; Noone, 1988; DeFelice and Saxena, 1991; Leitch et al., 1992; Collett et al., 1995).

2. Experimental

The investigations have been done at Mt. Brocken which is located in the Harz mountains at the former border between Eastern and Western Germany (Fig. 1). We built the station in 1990/91 and started the monitoring programme in 1992. Cloud water is collected in 1-h sampling periods (before 1993 on event basis) using a string collector (ASRC-type), installed within an automatic “wet-only” sampling unit (Mohnen and Kadlecek, 1989). To exclude dilution of cloud water ion content by precipitation during sampling (concentrations of the major ions NH_4^+ , H^+ , SO_4^{2-} , NO_3^- were substantially higher in cloud water than in precipitation (Mohnen et al., 1990)), we use only data of nonprecipitating clouds for any relationships. Duration of cloud events is between 15 min and 37 h (we defined a cloud event by LWC registration $\geq 25 \text{ mg m}^{-3}$ and ≥ 15 min). On the other hand, the cloud event is defined to be finished, when the monitored LWC signal is $< 25 \text{ mg m}^{-3}$ for more than 15 min. The cloud collector is always exposed 1 h, i.e., cloud water was sampled between 15 min (minimum sampling time to get reasonable amounts of water for chemical analysis) and 1 h. The number of cloud water samples, assigned to a cloud event is therefore between 1 and m ($m = 37$ in 1993). The 1-h samples are stored in a cooled collector unit and analyzed by ion chromatography within 10 days in our laboratory in Berlin. Samples with defined (well known) chemical content are used to check the whole procedure (sampling, storage, transport, analysis) for any kind of contamination. All analytical data are validated by check of the ion balance between cations and anions and by comparison of the measured with the theoretical calculated conductivity (the required accuracy is $< \pm 20\%$). Laboratory work is checked every year by participation at an international intercalibration with standard reference materials organized by U.S. EPA within the network of the World Meteorological Organization (Hunike, 1993).

Liquid water content (LWC) of clouds is measured continuously by a laser forward scattering technique using a Gerber Particulate Volume Monitor (Gerber, 1984). The registered on-line analogue signal from the measurement system is used to automatically calculate 10-min averages of LWC. Meteorological standard parameters (wind direction and velocity, temperature and humidity, global radiation) are measured by commercial instruments (Thies company). The cloud sampling and the meteorological equipment are placed on the top platform of our station which is at the mountain top (diameter about 500 m, heathland; timber line about 100–200 m below the top). Trace gases are monitored with instruments from Thermoenvironment (SO_2), Ecophysics (NO/NO_2), Dasibi (O_3) and Aerolaser (H_2O_2). All data are recorded by two independent systems:

(a) 30-s averages by a commercial data acquisition system (Labtech notebook) and (b) by x–y-recorders for on-line registration. The whole measurement and analytical programme are under QA/QC control within the SANA project (joint research project on recovery of the atmosphere in eastern Germany) based on an adopted quality assurance philosophy from the U.S. Environmental Protection Agency (Mohnen and Vong, 1993). Beside the monitoring programme we carried out different measurement campaigns in which we measured more species and parameters (e.g., H_2O_2 , NH_3 , aerosols, S(IV) and NO_2^- in aqueous phase, droplet size distribution, Möller et al., 1994a).

Backward trajectories on 3-d orientated isentropic surfaces (Fig. 1) are computed by a model using a mixed dynamic/kinematic procedure (Reimer and Scherer, 1991).

3. Results and discussion

The frequency distribution of LWC classes for every year since the beginning of the Mt. Brocken cloud chemistry program shows small variations in distribution and yearly average LWC (Fig. 2).

The variation of LWC with time during cloud events, however, could be significant (Fig. 3). We found three “types” of LWC behaviour:

(a) sharp decrease or increase of LWC within a time scale between a few minutes and 1 h (sample 2 in Fig. 3a) showing an ending or beginning of the cloud event;

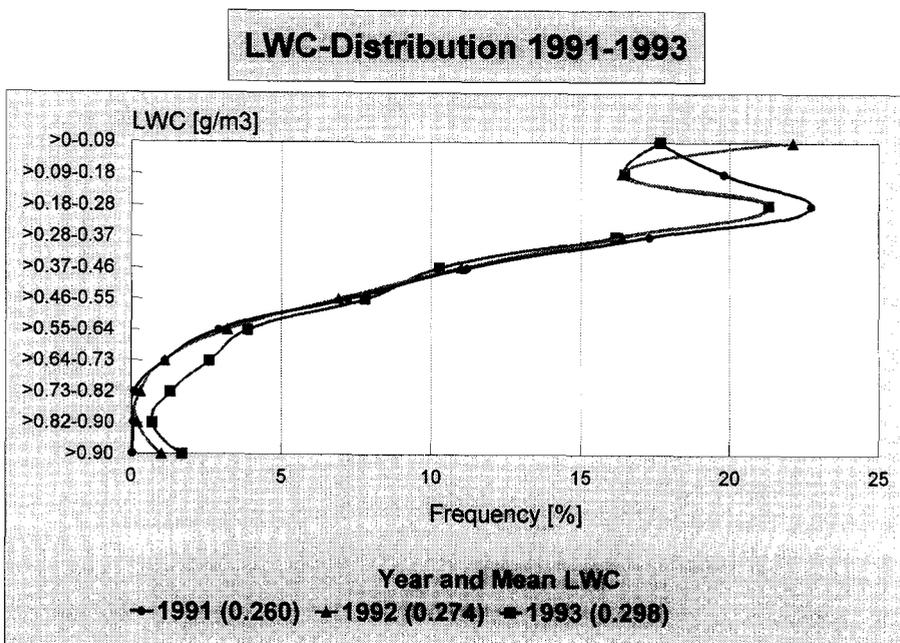


Fig. 2. Frequency distribution of cloud water LWC.

(b) small LWC variation within a cloud event (sample 1 in Fig. 3a), assuming a sampling inside the cloud (well above the cloud base) and

(c) high fluctuation of LWC with time (sample 3 in Fig. 3b), typical for sampling nearby the cloud base or while passing interrupted clouds, i.e., cloud events with short-time cloud-free periods (LWC tend to 0).

The chemical composition of samples, representing these “types” (Table 2), is quite different. Möller et al. (1994a,b) discussed these differences as an indication for a relationship between LWC and total ionic content (TIC) of cloud water. TIC represents the sum of liquid phase concentrations of SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ and K^+ . The increases in cloud water ionic content in sample 2 can be explained simply by droplet evaporation. Deviations of the chemical concentration between the species

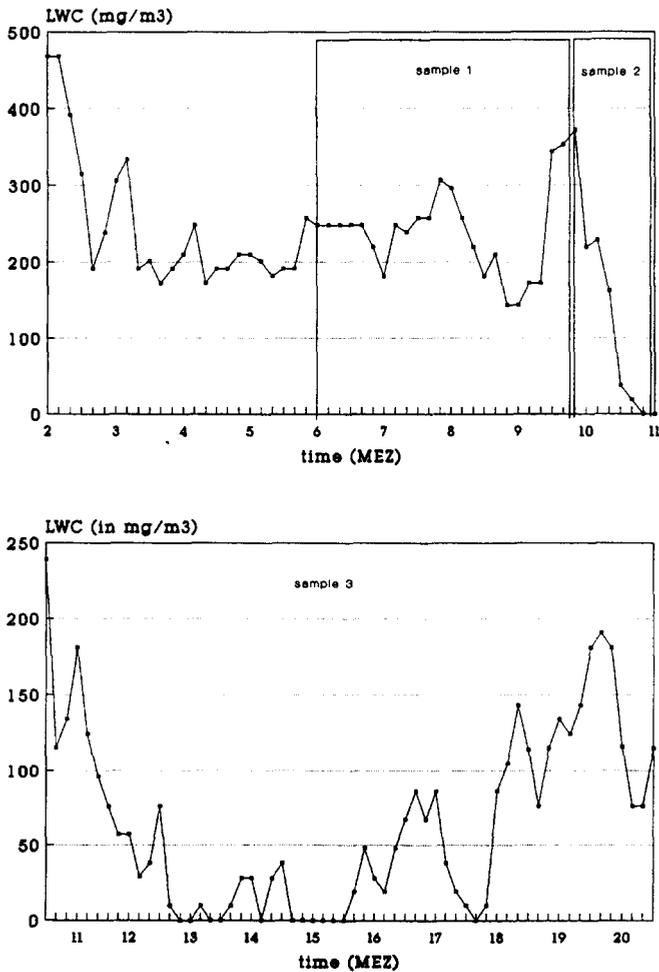


Fig. 3. Examples for time-dependency of LWC (mg m^{-3}) while cloud water sampling; (a) 18 June 1992; (b) 10 October 1992.

Table 2

Chemical composition of cloud water sampled during events of different LWC 'types' (see text for explanation and cf. Fig. 3); in $\mu\text{eq l}^{-1}$

Sample No.	Mean LWC (mg m^{-3})	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}
1	243 ± 60^a	62	296	327	48	9
2	134 ± 44	187	602	644	93	43
3	78 ± 55	579	462	519	373	98

^a Standard deviation σ of averaged LWC during sampling time.

can be explained by nonhomogeneous distribution of solute chemical species over the droplet spectrum and droplet-size depending evaporation. Principally, the same explanation is valid for sampling at cloudbase level and during interrupted clouds (sample 3). From this behaviour we adopt the LWC standard deviation σ as criterion for subdividing of cloud water samples into two classes:

Class A: $\sigma > 50\%$ for events according to "type" a and c
(mean $\sigma \geq 60\%$)

Class B: $\sigma < 50\%$ for events corresponding to "type" b
(mean $\sigma \leq 30\%$)

The relation between TIC and LWC, based on all 1-h samples of cloud water, collected in 1993 from nonprecipitating clouds, suggested basically a physical relationship (Fig. 4). The best approximation of this relationship ($r = 0.52$) is given by a power function:

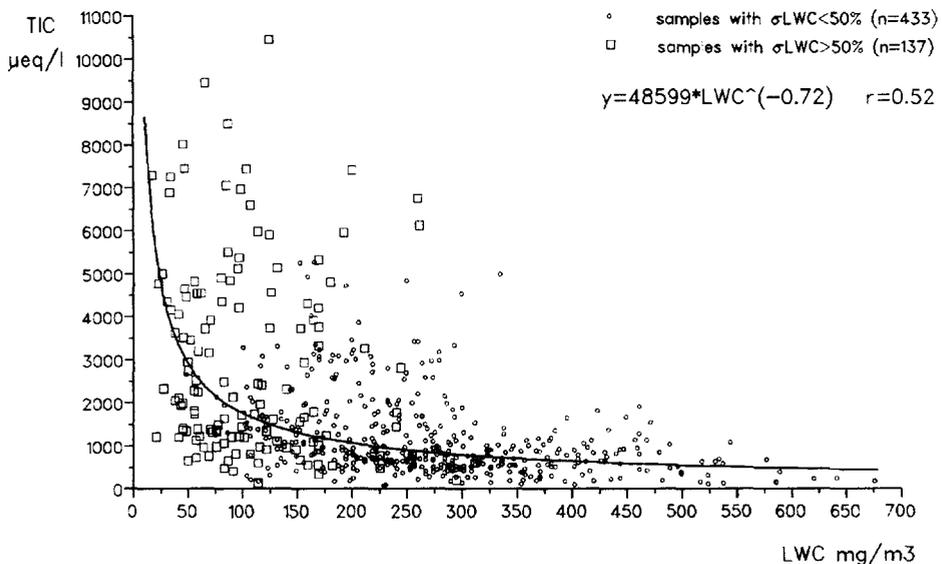


Fig. 4. Relationship between total ionic content (TIC) and LWC for all 1-h samples collected in 1993 from non-precipitating clouds ($n = 570$) subdivided into classes of different LWC standard deviation σ .

$$\text{TIC} = 48599 \cdot \text{LWC}^{-0.72}, \quad (1)$$

where TIC in $\mu\text{eq l}^{-1}$ and LWC in mg m^{-3} . It seems obvious that both areas of the function are represented either by samples from “class A” (high increase of TIC with small decrease of LWC) or “class B” (small decrease of TIC when LWC is greater than 150 mg m^{-3}). It follows from regression Eq. (1) that $Y = \text{TIC} \cdot \text{LWC}^{0.72}$ must be constant. The product TIC · LWC represents the total mass within an air parcel which is solute in cloud drops (see discussion below). We found the following relationships for class A and class B samples:

$$Y_1 = 5574 + 24 \cdot \text{TIC} \quad (\text{class A}; r = 0.82) \quad (2)$$

$$Y_2 = 9571 + 43 \cdot \text{TIC} \quad (\text{class B}; r = 0.91) \quad (3)$$

The only significant difference between Eq. (2) and Eq. (3) lies in the slope, suggesting different physical processes which are “responsible” for the relation between TIC and LWC. The TIC–LWC relationship within “class A” is a result of droplet evaporation due to entrainment of subsaturated air, i.e., LWC becomes smaller (large number and small diameter) while the solute mass is more fixed. Furthermore gas–liquid transfer is more efficient at smaller than at larger droplets. Highly soluble trace gases (like nitric acid and ammonia) can be transported by entrainment into the cloud. Thus the TIC increases also. We should remember that “class A” samples represent collected cloud water nearby the cloud base. The decrease of TIC with an increase of LWC for higher LWC (samples collected inside the cloud, “class B”) could be explained in contrast to “class A” as a dilution effect: The absolute amount of water increases more rapidly than the amount of other substances. Moreover, after quite a short time almost all molecules of trace gases have been already scavenged, and only water vapour remains for condensation. A very likely explanation for large TIC variation in cloud water samples consists in assuming a sampling at different heights above the cloud base and adopting the well-known increase of LWC with the altitude.

The functional relationship between ionic content (IC) and LWC is similar for single species; the parameters of the equation $\text{IC} = b \text{LWC}^{-a}$ are summarized in Table 3. The exponent lies between 0.72 and 0.79, with the exception of 1.02 for calcium. An exponent of 1 shows a relationship between IC and LWC simply given by dilution and concentration. However, counteracting other effects cannot be excluded. An exponent $a < 1$ means that the product $\text{IC} \cdot \text{LWC}$, representing the total solute mass per air volume, increases proportionally to $\text{LWC}^{(1-a)}$. This suggests that there is an interaction between LWC and the total mass of chemical species, acting as cloud condensation nuclei (CCN) or transferred into cloud droplets.

We feel that the physical meaning of TIC · LWC is closely connected with the reservoir distribution of trace species within the cloud. Therefore, we now discuss the

Table 3
Power law constants of the relationship between IC and LWC

Species	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	Ca^{2+}	Mg^{2+}
<i>b</i>	13792	11719	2450	22308	1525	6816	1309
<i>a</i>	0.77	0.73	0.75	0.78	0.72	1.02	0.79

mass budget of chemical species, distributed between aerosol, gas, and liquid phase. The total mass within an air parcel (M_{burden}) is given by the sum of mass solute ($\text{TIC} \cdot \text{LWC}$) and insoluble ($M_{\text{insoluble}}$) in cloud water and the interstitial mass (M_{interst}); $M_{\text{insoluble}}$ represents insoluble cores of CCN and surface adsorbed material (e.g., black carbon), suspended in cloud water samples:

$$M_{\text{burden}} = \text{TIC} \cdot \text{LWC} + M_{\text{insoluble}} + M_{\text{interst}}, \quad (4)$$

where M_{interst} is the sum of non-activated CCN, non-scavenged gases and particulate matter, not being CCN (e.g., biogenic and organic particles, black carbon, insoluble mineral particles)

$$M_{\text{interst}} = \text{CCN}_{\text{non-activ}} + \text{GAS}_{\text{non-scav}} + \text{non-CCN}. \quad (5)$$

In order to simplify the discussion, we do not consider non-CCN and $M_{\text{insoluble}}$ in the following which is realistic because any contribution from these parts of particulate matter to the mass budget of the components of our interest, listed in Table 3, is negligible. It should be mentioned, however, that TIC in Eq. (4) is not absolutely identically with the analytical estimated TIC_{anal} (which is the sum of analytically estimated ions in cloud water). No cloud water collector can collect with 100% efficiency. Only in the case of 100% sampling efficiency or a homogeneous distribution of chemical species over the cloud drops, we can assume $\text{TIC}_{\text{anal}} = \text{TIC}$. Unfortunately, there are a few indications from size fractional cloud water sampling (e.g., Ogren and Charlson, 1992) that the chemical composition in clouds is size-dependent. Therefore, a variable sampling efficiency (which is dependent on wind speed and collector design) could lead to differences between TIC_{anal} and TIC. This must be considered in the interpretation of analytical results from sampled cloud water.

Total cloud condensation nuclei (CCN) can be divided into activated CCN, forming cloud droplets via nucleation, and — under the given circumstances — non-activated CCN (Gillani et al., 1992):

$$\text{CCN}_{\text{total}} = \text{CCN}_{\text{activated}} + \text{CCN}_{\text{non-activ}}. \quad (6)$$

We will now try to answer the question what possible reasons are for an increase of $\text{TIC} \cdot \text{LWC}$ with raising LWC (Fig. 5). The function $\log(\text{TIC} \cdot \text{LWC}) = f(\text{LWC})$, presented in Fig. 5, is linear with a small positive slope. The relationship between “total mass, transferred into cloud water” ($\text{TIC} \cdot \text{LWC}$) and LWC is mutual: existence of CCN is a precondition for LWC and, on the other hand, existing LWC is a precondition for gas scavenging and subsequent chemical reactions. Sharing between activated and non-active CCN is not fixed. The percentage of activation also depends on supersaturation and chemical characteristics of CCN. Immediately after nucleation $\text{TIC} \cdot \text{LWC}$ is identical to $\text{CCN}_{\text{activated}}$. LWC increases with growing supersaturation while the initial CCN number distribution is constant. As a result, however, components of the interstitial mass could be activated and $\text{TIC} \cdot \text{LWC}$ enlarges. Greater LWC means higher dilution and, consequently (in first approach), larger pH and solubility of some “acid” gases, which are involved in protolytic equilibria (e.g., SO_2 , HNO_2 , CO_2). Liquid-phase chemistry in cloud droplets does not change the total mass but the reservoir distribution between solute species and its gaseous precursors due to pH and concentration depen-

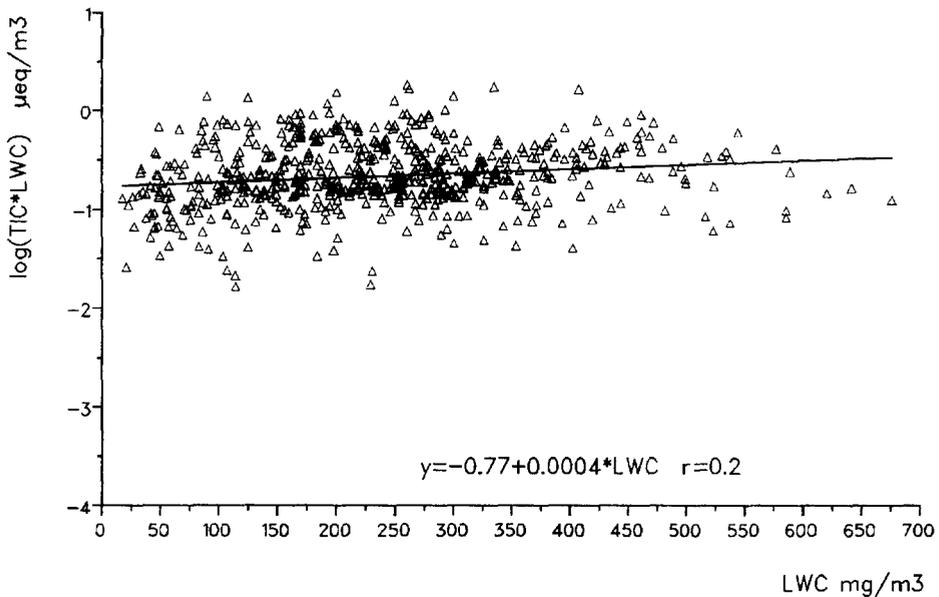


Fig. 5. Functional relationship between $\log(TIC \cdot LWC)$ and LWC.

dent equilibria. The initial chemistry of drops determines the “chemical fate” of individual droplets (Möller and Mauersberger, 1992). Coalescence changes the droplet size distribution and the internal mixing of solute species and, consequently, conditions for liquid phase chemistry and gas–liquid equilibria.

In coincidence with this theoretical conception are experimental results of a measurement campaign performed in 1994 at Mt. Brocken to study the cloud water composition and related gas phase, meteorological and cloud physical parameters at three different altitudes above cloud base in cooperation with six German cloud groups. We converted the liquid phase concentrations into air equivalents ($TIC \cdot LWC$) and we found higher amounts of total dissolved material at greater distances above the cloud base (Pahl, 1995). The change in aerosol reservoir distribution from interstitial to activated CCN can cause gradients in weighted concentrations. Entrainment also leads to a possible change of the total solute mass in a cloud. With increasing height above the cloud base, LWC increases due to adiabatic condensation. The growth of solute mass due to gas scavenging and liquid phase reactions, however, becomes smaller. It is reasonable that with increasing distance from the cloud base the mass transport of “fresh” gas species (SO_2 , HNO_3 , NH_3) and reactants (H_2O_2 , O_3 , OH) via entrainment into the inner cloud will be limited due to previous scavenging. On the other hand this means that the increase of TIC near the cloud base could not only be explained by droplet evaporation but also by scavenging of trace species with entrainment.

The logarithm pattern shows variations of $TIC \cdot LWC$ in the order of one magnitude below and above the line over the whole range of LWC (Fig. 5). We will discuss these variations now as influences other than LWC. The phenomenological behaviour between

Table 4

Mean chemical composition (in $\mu\text{eq l}^{-1}$) and LWC (in mg m^{-3}) for selected events with different air mass characteristics

	No. 1	No. 2	No. 3	No. 4	No. 5
<i>n</i>	13	9	6	11	10
Cl ⁻	52 ± 36	36 ± 33	281 ± 282	24 ± 34	27 ± 26
NO ₃ ⁻	1038 ± 381	561 ± 329	455 ± 224	110 ± 73	183 ± 146
SO ₄ ²⁻	1508 ± 564	468 ± 346	450 ± 242	96 ± 91	193 ± 190
NH ₄ ⁺	1596 ± 539	902 ± 771	858 ± 490	150 ± 165	217 ± 267
Na ⁺	37 ± 25	15 ± 14	324 ± 350	21 ± 29	11 ± 8
Ca ²⁺	423 ± 328	14 ± 17	55 ± 40	9 ± 7	60 ± 86
Mg ²⁺	86 ± 54	3 ± 5	76 ± 79	8 ± 9	11 ± 8
H ⁺	289 ± 286	236 ± 173	40 ± 78	50 ± 33	97 ± 40
TIC	5036 ± 1851	2477 ± 1417	2540 ± 1642	470 ± 389	858 ± 725
LWC	162 ± 70	274 ± 100	160 ± 147	350 ± 181	166 ± 128

ionic content of cloud water and liquid water content of the air parcel (LWC), discussed here, is one (microphysical) reason for fluctuations of chemical composition. Other reasons, already mentioned above, could be different air mass characteristics (large-scale transport processes and air pollution situation) and dynamic processes (cloud type characteristics).

To explain a major portion of the variance in the chemistry and meteorological data base 72-h back trajectory calculations are made for every event (Fig. 1). In the next section we show examples for the influence of the air pollution characteristics on TIC.

The TIC–LWC relationships for the selected cloud events (Tables 4 and 5) are fitted by power curves (Fig. 6), are similar to TIC–LWC variations between all 1-h samples collected in 1993 (as shown in Fig. 4). The time dependency of LWC is presented as an example for the cloud event of 30 September to 1 October 1993 (Fig. 7); the

Table 5

Characterization of selected cloud events in 1993

Event	Characteristics
No. 1: 30 September to 1 October	Extreme polluted cloud; the air parcel was first under extreme stagnant conditions over Bohemia, than shifted to southerly directions
No. 2: 21 August	Typical for the main wind direction (270°) crossing industrial areas
No. 3: 9 October	Inhomogeneous transport episode from south western directions, in the last part of the trajectory the wind shifted to westerly directions, the LWC during the last hour is very low (46 mg/m ³)
No. 4: 11 October	Event with air masses from southwestern directions crossing low polluted regions
No. 5: 5 October	End of a long cloud event (started 10.00 MEZ on October 3) with transport over northern France and northeastern Atlantic and with precipitation before October 5 MEZ = CET = Central European Time

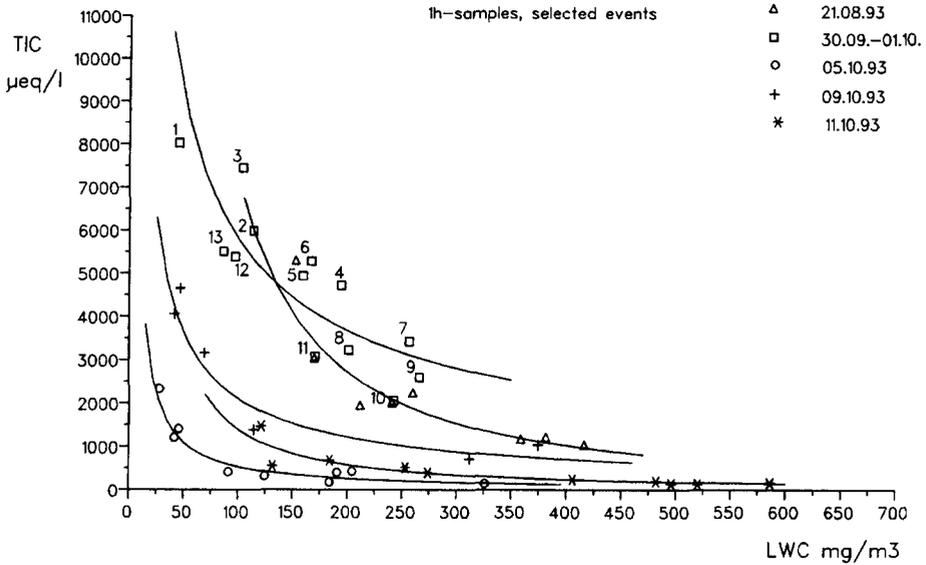


Fig. 6. Relationship between TIC and LWC for selected cloud events.

corresponding samples (points within Fig. 6) are marked. Samples from the beginning and ending of the cloud event lie in the TIC–LWC diagram at the upper left-hand side. Samples taken during the middle of the cloud event represent points in the lower part of the TIC–LWC diagram. The positions of the power curves in the diagram (Fig. 6),

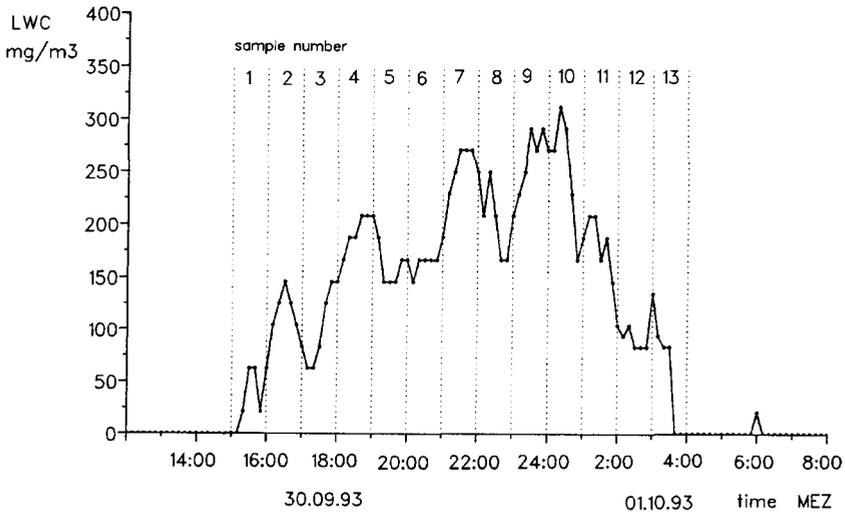


Fig. 7. Time dependent LWC for the cloud event from 30 September to 1 October 1993; sampling time and number of collected samples are marked.

representing selected events, however, are different. It is obvious that the TIC–LWC curves of selected events scatter around an “averaged” power function (cf. Fig. 4). Table 4 shows that the absolute figure of TIC for a given LWC is characterized by the cloud event. The events selected and presented in the TIC–LWC diagram (Fig. 6) can be distinguished by the air mass characteristics as given in Table 5. It is clearly shown that high polluted air masses lead to larger TIC for given LWC and vice versa for low polluted air.

4. Conclusions

Long-term sampling is necessary to separate different microphysical, dynamic and air pollution influences in the chemical composition of clouds. A chemical intercomparison of cloud water samples is impossible without information of cloud physical parameters. Our dataset of cloud water samples without precipitation allowed us to present a general relationship between LWC and the chemical composition of cloud water. This relationship is generally given by a power function, and valid for all main chemical species.

The main reason for this behaviour is a concentration effect resulting from evaporating droplets and a dilution effect due to water condensation on existing droplets. The normalisation of cloud water concentrations to the soluted mass per air volume give the possibility to explore influences like transport pattern, deposition or season on cloud water composition. Results from our dataset demonstrate that the soluted mass per air volume increases with increasing LWC or, in other words, with the altitude above cloud base. This was confirmed by the results of a measuring campaign on Brocken carried out in June 1994, where we analysed cloud water composition at different altitudes above cloud base. We propose that different types of CCN are activated at different values of supersaturation. Besides, pH and chemical composition of initial droplets after nucleation are important for the further grow of solute mass due to influences on gas scavenging and liquid phase chemistry. It appears to be necessary to classify any cloud chemical data into classes homogeneous in terms of precipitation, sampling height above cloud base, cloud type, droplet size distribution and air mass history.

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