



Multiphase studies in continental and marine atmospheres

Karin Acker, Wolfgang Wieprecht, Detlev Möller
Brandenburg Technical University, Dept. of Air Chemistry (ack@btu-lc.fta-berlin.de)

Abstract

The largest uncertainty in future climate predictions is caused by aerosols and clouds and their interaction with radiation. Hydrochloric acid (HCl) in the gas phase, chloride and sodium in the particle phase were measured first time with high time-resolution and simultaneously with a number of other atmospheric components (in gas, liquid and particulate phase) as well meteorological parameters during two intensive campaigns to study the phase partitioning of chlorine. To a significant extent, sea salt already is depleted in Cl in air masses reaching the west coastal site (Mace Head) of Ireland ($20 \pm 10\%$ in marine air; $46 \pm 19\%$ in continental influenced air) and to a much higher extent ($83 \pm 13\%$) in air masses reaching a continental station (Melpitz) in Germany caused by acid replacement by nitric and sulphuric acid

1. Introduction

Aerosol particles have multiple impacts on atmospheric properties: response to climate by optical properties, providing cloud condensation nuclei, being a heterogeneous surface for multiphase chemical reactions, e.g. oxidation of sulphur dioxide (SO_2), and a source for reactive chlorine [4], [6]. A loss of chlorine from the marine particulate sea salt phase into the gas phase was already observed 50 years ago, years later also from continental aerosol and was found to be connected with reactions of nitric acid (HNO_3) and SO_2 on the particle surface causing degassing of hydrochloric acid (HCl) [3]. Under the assumption that sea salt aerosol (SSA) is the exclusive source of sodium in the atmosphere where it is present only in the particle and hydrometeor phase the sodium to chlorine ratio is a relevant criteria to characterise the variation in chlorine phase partitioning. Only simultaneous measurements of gaseous HCl and of chlorine and sodium in the particle phase can clarify the question if the equivalent deficit in chlorine can be found as HCl in the gas phase. Therefore two intensive field campaigns were conducted in continental (2006) and marine (2008) atmospheres.

2. Experimental

Measurements were done at two of the European Supersites for Atmospheric Aerosol Research (EUSAAR) representative of a specific climate or ecosystem and equipped with a high level of instrumentation. The Irish station Mace Head ($53^\circ 19' \text{N}$, $9^\circ 54' \text{W}$; 5–12 m asl; Fig. 1a) is located ~88 km west of Galway city on the eastern seaboard of the North Atlantic Ocean and operated by NUI Galway [5]. The terrain is mostly low lying and undulating, the soil is predominantly peat covered in rough grasses with a significant amount of exposed granite rock. The German research station Melpitz ($51^\circ 32' \text{N}$, $12^\circ 54' \text{E}$; 87 m asl; Fig. 1b) operated by IfT Leipzig [7] is located ~40 km north east of the city Leipzig (~1 million inhabitants) and surrounded by grassland and mixed forests.



Fig. 1a and b: View to the stations Mace Head (left) and Melpitz

At both sites HCl, HNO_3 and other gaseous species were measured by a coupled wet denuder sampling / ion chromatography analysis technique. This diffusion based system separating the gaseous species from their corresponding particulate ions was extended by a steam chamber for simultaneous sampling of the soluble total suspended matter (TSP) fraction to determine components like sodium, chloride, nitrate, sulphate [1]. The whole system (beside a very short Teflon inlet) was operated in an air conditioned container at $\sim 20^\circ \text{C}$ (pre-concentration time: 30 min; sample air flow: 10 l min^{-1} ; limit of quantification: 10 ng m^{-3}). Sampling of particulate matter (PM) was also done using high-volume sampler (DIGITEL) with different inlets and 5-stage Berner impactors (IfT EMEP study). Precipitation amount and composition (Eigenbrodt wet-only

sampler) have been evaluated for the data interpretation. 96h back trajectories (NOAA Hysplit model) are used to determine the air mass origins.

3. Results

In our studies the (mass) Na to Cl ratio found in sea water ($R_{\text{sea}}=0.56$) is used for calculation of the degree in chlorine loss in particulate matter by the relation $Cl_{\text{loss}}=1-R_{\text{sea}}/R_{\text{sample}}$.

3.1 Melpitz

Figure 2 presents detailed data from the campaign in early summer 2006. The air masses reaching this site were on average medium polluted: in continental SW air masses (19th to 22th June; Fig. 3a) NO_2 8; SO_2 4; BC 2.5; PM_{10} 22; $PM_{2.5}$ 20 $\mu\text{g m}^{-3}$; in maritime influenced westerly air masses (23th June; Fig. 3b) NO_2 6; SO_2 2; BC 1.6; PM_{10} 20; $PM_{2.5}$ 16 $\mu\text{g m}^{-3}$.

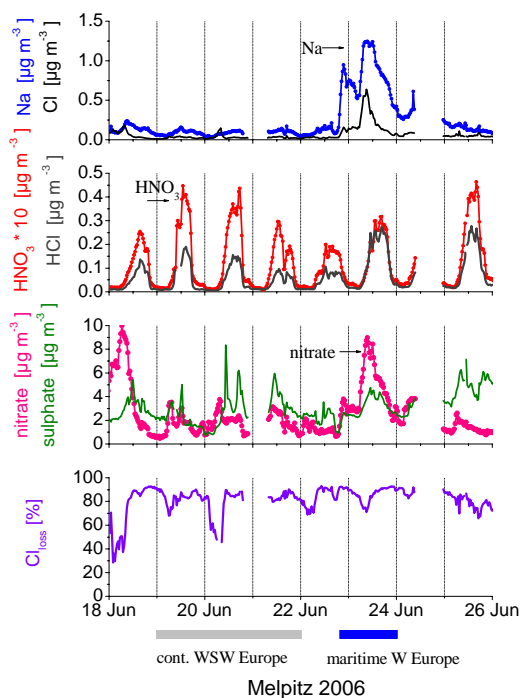


Fig. 2: Time series of particulate sodium, chloride, nitrate and sulphate, gaseous HNO_3 and HCl and the calculated loss in chlorine at Melpitz.

The mean mass Na to Cl ratio was found to be 3.6. No correlation between gaseous HCl and particulate Cl ($r^2=0.03$) was observed, due to faster removal of HCl during transport.

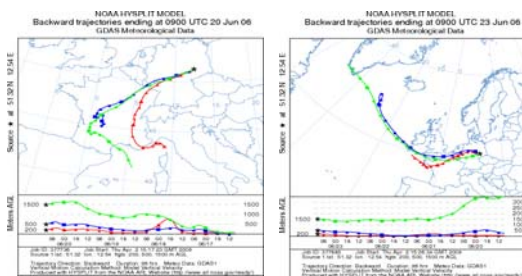


Fig. 3a and b: selected transport analysis Melpitz

A very high loss in chlorine in PM ($83\pm13\%$) has been calculated, not showing a significant dependency from the air mass sector and transport percentage (25-100%) above continent. A broad HCl maximum around noon/afternoon was measured. The correlation with HNO_3 is very high ($r^2=0.78$). The data support that HNO_3 is responsible for Cl depletion by reaction

$HNO_3(g) + NaCl(s,aq) \rightarrow NaNO_3(s,aq) + HCl(g)$, also because of drastically reduced SO_2 emissions in Europe compared to NO_2 .

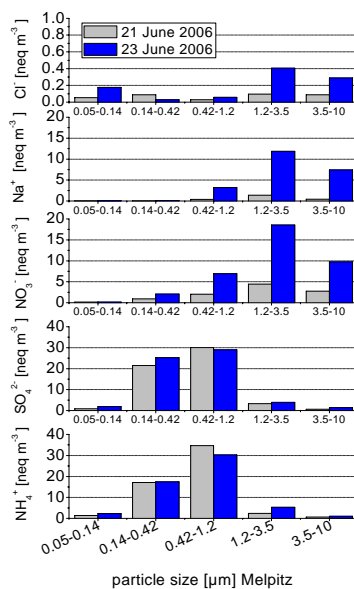


Fig. 4: Particle size aggregate sampling and chemical analysis of PM.

The data in Figure 4 confirm that HCl degassing apparently occurs on smaller particles ($< 1 \mu\text{m}$) due to sulphate formation and on larger particles due to sticking of HNO_3 (if available, what sufficient is the case only in continental air masses; in marine atmosphere exhaust plumes from ships are a source).

3.2 Mace Head

Figure 5 presents detailed data from the campaign in early summer 2008. The air masses reaching this site were very low polluted in North Atlantic Ocean clean marine air (25th to 29th June; Fig. 6a) NO_2 0.5; SO_2 0.1; BC 0.1; PM_{10} 28; $\text{PM}_{2.5}$ $8 \mu\text{g m}^{-3}$; partly differences are found in continental influenced air masses (4th to 6th June; Fig. 6b) NO_2 5; SO_2 0.5; BC 0.4; PM_{10} 13; $\text{PM}_{2.5}$ $7 \mu\text{g m}^{-3}$.

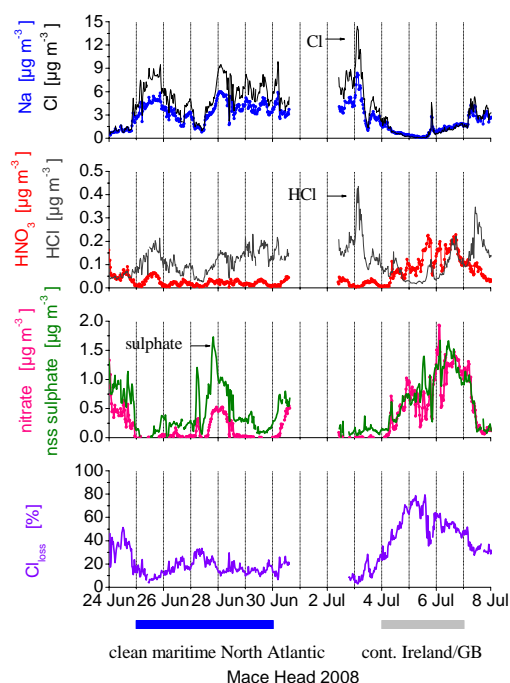


Fig. 5: Time series of particulate sodium, chloride, nitrate and sulphate, gaseous HNO_3 and HCl and the calculated loss in chlorine at Mace Head.

The mean mass Na to Cl ratio was found to be 0.74. Gaseous HCl is well correlated with particulate Cl ($r^2=0.46$), but to a significant extent ($20\pm 10\%$), sea salt already is depleted in Cl in air masses originate exclusive from the clean marine sector ($180\text{--}300^\circ$;

see also Figs. 6a, 8), mainly caused by HCl formation during heterogeneous sulphate formation.

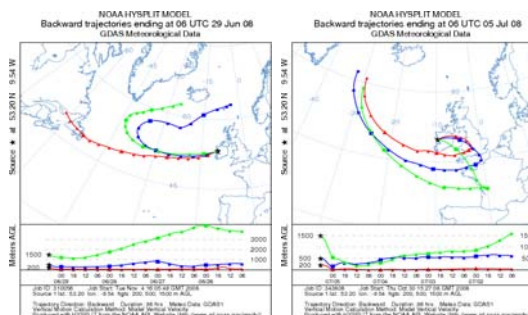


Fig. 6a and b: Selected transport analysis Mace Head

In continental influenced air masses ($45\text{--}135^\circ$, mainly Ireland and Great Britain; see also Figs. 6b, 8) a higher degree in Cl_{loss} ($46\pm 19\%$) was found due to additional acid replacement by nitric acid; the linear correlation between HCl and HNO_3 becomes significant and positive ($r^2=0.25$) compared to all data ($r^2=0.01$). The mean mass Na to Cl ratio in Mace Head wet only rain samples ($N=19$) was found to be 0.69. Gas and particle scavenging processes lead to an approximation to R_{sea} .

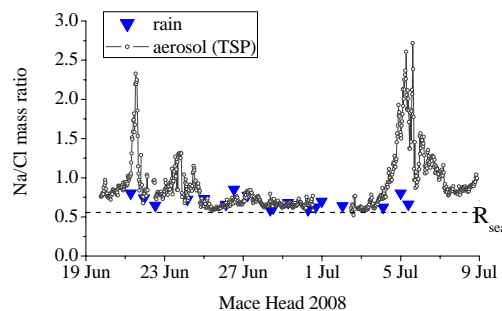


Fig. 7: Comparison of the Na to Cl ratio in Mace Head TSP and rain water

4. Conclusions

Figure 8 summarizes the wind direction dependence of the (mass) Na to Cl ratio of total suspended matter (time resolution 30 min) collected during two campaigns in a continental atmosphere as well on the border between ocean and continent.

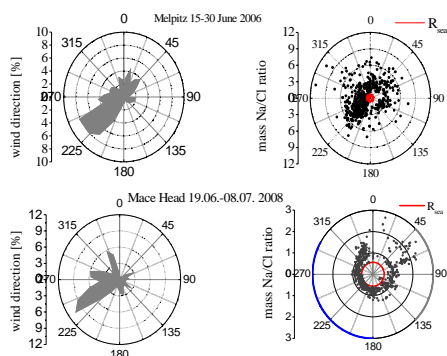


Fig. 8: Distribution of the wind direction during the field studies in Melpitz and Mace Head and comparison of the air mass history depended (mass) Na to Cl ratio.

The high loss of chlorine (as HCl) from sea salt will modify (a) the particles chemistry (mostly by nitrate enrichment) and (b) gas-phase chemistry (multiphase Cl partitioning) as well corrosive properties of the atmosphere. Possibly the global HCl formation from SSA is higher than the estimated value of 7.6 Tg a^{-1} found in the literature [2].

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft; the study in Mace Head was also an EUSAAR TNA activity within the EU FP6 program. The authors wish to thank the colleagues from IfT Leipzig and NUI Galway for valuable assistance.

References

- [1] Acker, K., Möller, D., Auel, R., Wieprecht, W., Kalaß, D.: Concentrations of nitrous acid, nitric acid, nitrite and nitrate in the gas and aerosol phase at a site in the emission zone during ESCOMPTE 2001 experiment. *Atmos. Res.* 74, pp. 507-524, 2005.
- [2] Erickson III, D. J., Seuzaret, C., Keene, W. C., Gong, S. L.: A general circulation model based calculation of HCl and ClNO₂ production from sea salt dechlorination: reactive chlorine emissions inventory. *J. Geophys. Res.*, 104, pp. 8347-8372, 1999.
- [3] Finlayson-Pitts, B.: The tropospheric chemistry of sea salt: A molecular-level view of the chemistry of NaCl and NaBr. *Chem. Rev.* 103, pp. 4801-4822, 2003.

[4] Möller, D.: The Na/Cl ratio in rain water and the sea salt chloride cycle. *Tellus* 42B, pp. 254-262, 1990.

[5] O'Connor, T.C., Jennings, S.G., O'Dowd, C.D.: Highlights of fifty years of atmospheric aerosol research at Mace Head. *Atmos. Res.* 90, pp. 338-355, 2008.

[6] O'Dowd, C. D., Smith, M. H., Consterdine, I. E., Lowe, J. A. Marine aerosol, sea-salt and the marine sulphur cycle: a short review. *Atmos. Environ.* 31, pp. 73-80, 1997.

[7] Spindler, G., Müller, K., Brüggemann, E., Gnauk, T., Herrmann, H.: Long-term size-segregated characterization of PM₁₀, P M_{2.5}, and PM₁ at the IfT research station Melpitz downwind of Leipzig (Germany) using high and low-volume filter samplers. *Atmos. Environ.* 38, pp. 5333-5347, 2004.