Characterization of trace metals during HCCT

K. Wadinga Fomba[1], K. Müller[1], T. Lee[2], J. Collett Jr.[2], and H. Herrmann[1]

1 Leibniz-Institute for Tropospheric Research, Permoserstr. 15, D-04318 Leipzig, Germany

2 Department of Atmospheric Science, Colorado State University, Ft. Collins, Co, 80523, USA

TROPOS
Leibniz Institute for Tropospheric Research

Member of the Leibniz Association

HCCT-2010

INTRODUCTION AND EXPERIMENT

- Trace metals play important roles in cloud chemistry. They serve as catalyst in the oxidation processes of S(IV) to S(VI) and contribute significantly to the radical budget such as OH radical which are important for aqueous phase reactions.
- During the Hill Cap Cloud Thuringia (HCCT) 2010 campaign in Thüringer Wald (Germany), aerosol trace metals as well as soluble TMI analysis in cloud water were performed to investigate their role in the cloud chemistry during orographic cloud formation.
- Soluble TMI measurements were done on cloud water samples collected at the top of the hill, while trace metal analysis were performed on size-resolved aerosol particles collected at the valley stations Gehlberg(GB) and Goldlauter (GL).
- Bulk cloud water was collected using a stainless steel Caltech active strand collector in an hourly routine (Fig. 1) while size-resolved cloud water was collected using a 3 stage collector.
- For TMI measurements, 0.5 ml filtrate from a 0.45 µm syringe filter was analyzed using an ion chromatograph (IC, Dionex ICS 900).
- The TMI's measured were Fe (III), Cu (II), Ni (II), Zn (II), Cd (II), Co (II), Mn (II), and Fe (II).
- At the valley stations, aerosol particles were collected on nucleopore filters using a five-stage Berner impactor with a PM_{10} cutoff (0.05 - 10 µm size range) for total metal analysis via total reflection x-ray fluorescence spectroscopy (TXRF). The elements investigated were Fe, Ti, Cr, Ni, Co, Mn, V, Zn, Cu, Pb, Se, Rb, Sr, As.

Fig. 1. *Stainless steel Caltech Active Strand cloud water collectors mounted parallel to each other on the tower platform.*

RESULTS

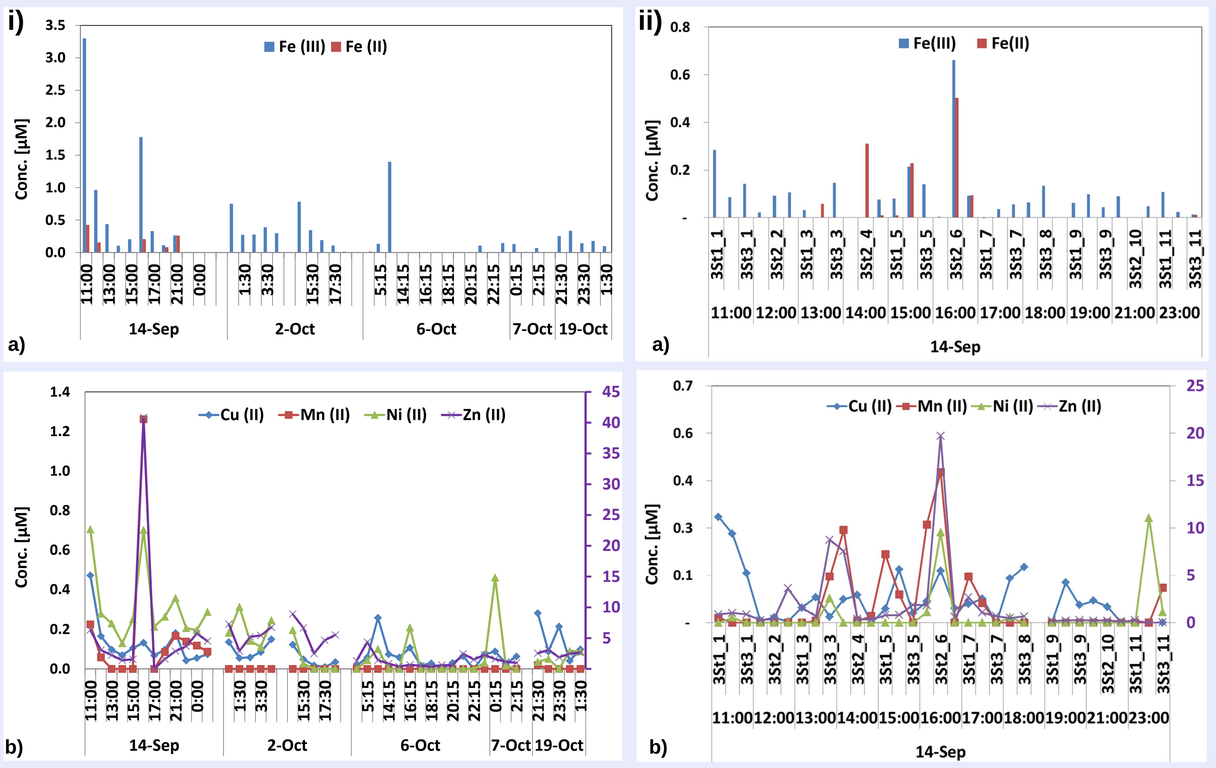

Fig. 2. *Temporal variability of **i)** size-resolved TMI from 3 stage cloud water collector during FCE 1.1 (14. sept.) and **ii)** bulk TMI concentrations from Caltech collectors for all FCE during campaign, showing a dorminant presence of **a)** Fe (III) over Fe(II) and **b)** Cu (II), Mn (II), Ni (II) and Zn (II) with the Zn (II) axis plotted on the right in purple revealing the highest TMI concentration in both bulk and size-resolved samples during HCCT2010.*

- TMI's concentrations (e.g. iron 0.1 to 3.8 µM) where within reported range for cloud water. Zn (2.2 to 39.8 µM) was the most abundant element in cloud water.
- Fe(II)/Fe (III) ratio were very low with a dominant presence of Fe (III) observed.
- As shown in FCE 1.1 below, Cu (II), Ni (II) and Mn (II) were mostly found in the coarse mode particles as compared to Zn (II) and Fe (III) which were found in all stages, indicating their different sources.
- No significant correlation was found between TMI solubility and cloud water pH except for Cu as shown on Fig 3a, and 3b), for FCE 1.1 and FCE 13.3, respectively.
- Averagely, TMI solubility increased from Mn, Fe, Cu, Ni to Zn. Iron solubility showed very little variations through out the campaign as shown on the relative solubility figure (Fig. 3b).

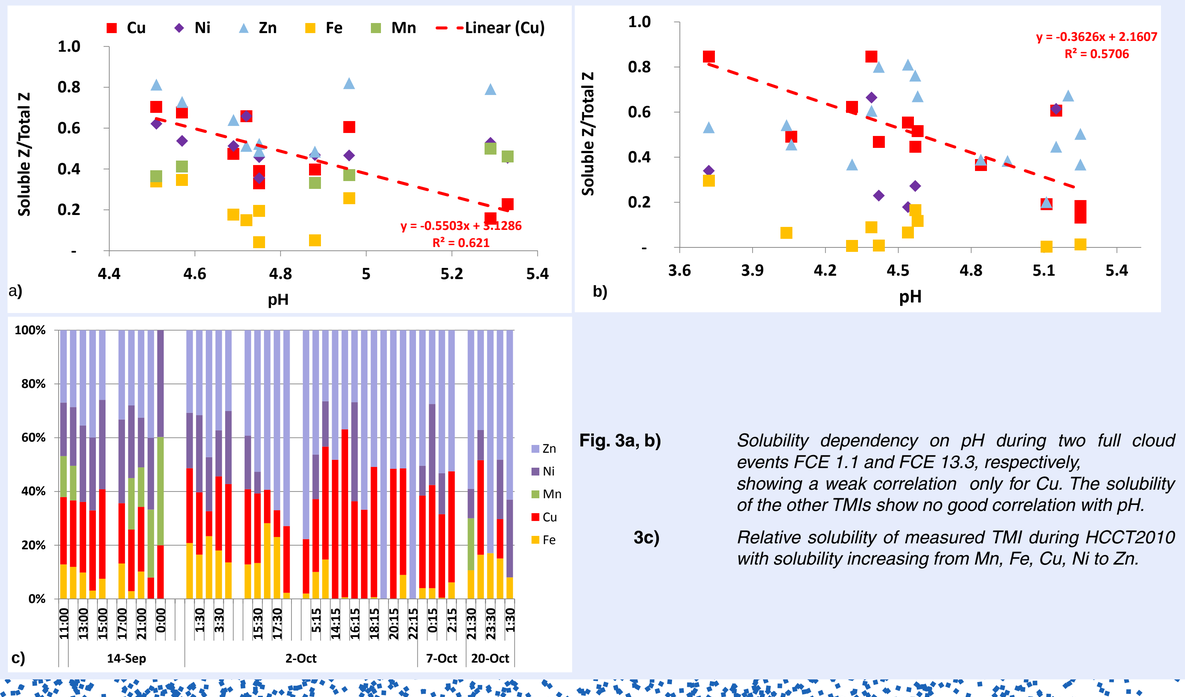

Fig. 3a, b) *Solubility dependency on pH during two full cloud events FCE 1.1 and FCE 13.3, respectively, showing a weak correlation only for Cu. The solubility of the other TMIs show no good correlation with pH.*

3c) *Relative solubility of measured TMI during HCCT2010 with solubility increasing from Mn, Fe, Cu, Ni to Zn.*

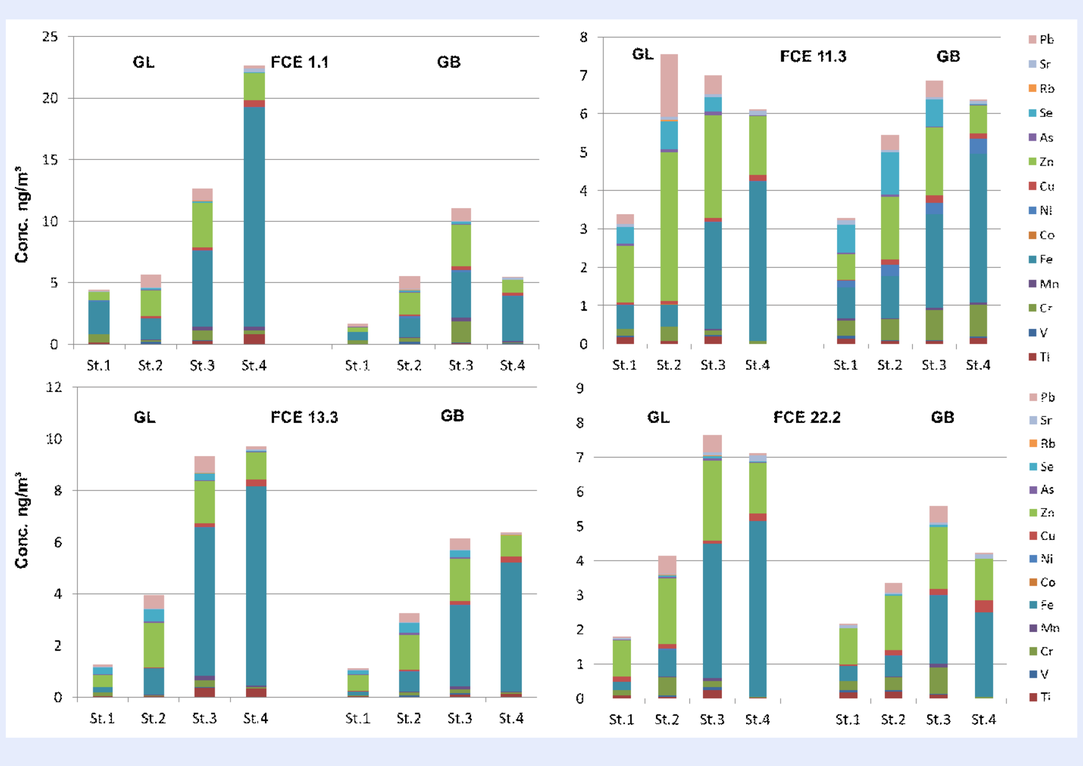

Fig. 4. *Size-resolved trace metal data during 4 full cloud events (FCE), FCE 1.1, 11.3, 13.3, and 22.2 during HCCT2010. Results show strong presence of Fe, Zn, Pb, Cr, V and As.*

- Size – resolved analysis of trace metals showed higher metal concetrations on stages 3 and 4 (1.2 - 3.5 µm) as shown on Fig 4.
- The decrease in mass concentration observed between Goldlauter (GL) and Gehlberg (GB) is likely due to particle deposition along the air mass trajectory.
- Similar to cloud water results, Fe and Zn were the most abundant elements followed by Pb and Cr.
- Good correlations were observed between some trace metals and levoglucosan, oxalic acid, OC/EC and also inorganic ions such as NO_3^- and SO_4^{2-}.
- The correlations observed between Fe and OC/EC, oxalate and levoglucosan (Table 1) shows that the metals (especially iron) were of diverse origin.

		Fe	Pb	Mn	Ti	Zn	K	As	Se
Levoglucosan	GL	0.82	0.71	0.68	0.76	0.7	0.69		
	GB	0.4	0.54	0.6	-0.9	0.2	0.06		
OC	GL	0.79	0.2	0.67	0.84				
	GB	0.85	0.38	0.27	0.36				
EC	GL	0.23	0.9					0.66	0.87
	GB	0.61	0.93					0.7	0.95
Oxalate	GL	0.97							
	GB	0.49							

Table 1. *Correlation coefficient (R^2) between some trace metals and biomass, soot tracers and oxalate.*

SUMMARY

TMI and trace metals were analyzed during HCCT2010. Trace metals were of diverse origin including, biomass burning, anthropogenic activities as well as from soot. Zn and Fe were the most abundant element in the cloud water and aerosol particles, respectively. The solubility of the TMIs except for Cu did not show any strong correlation with the cloud water pH. The solubility increased from Mn, Fe, Cu, Ni to Zn.