Trace metal analysis in cloud water during HCCT2010

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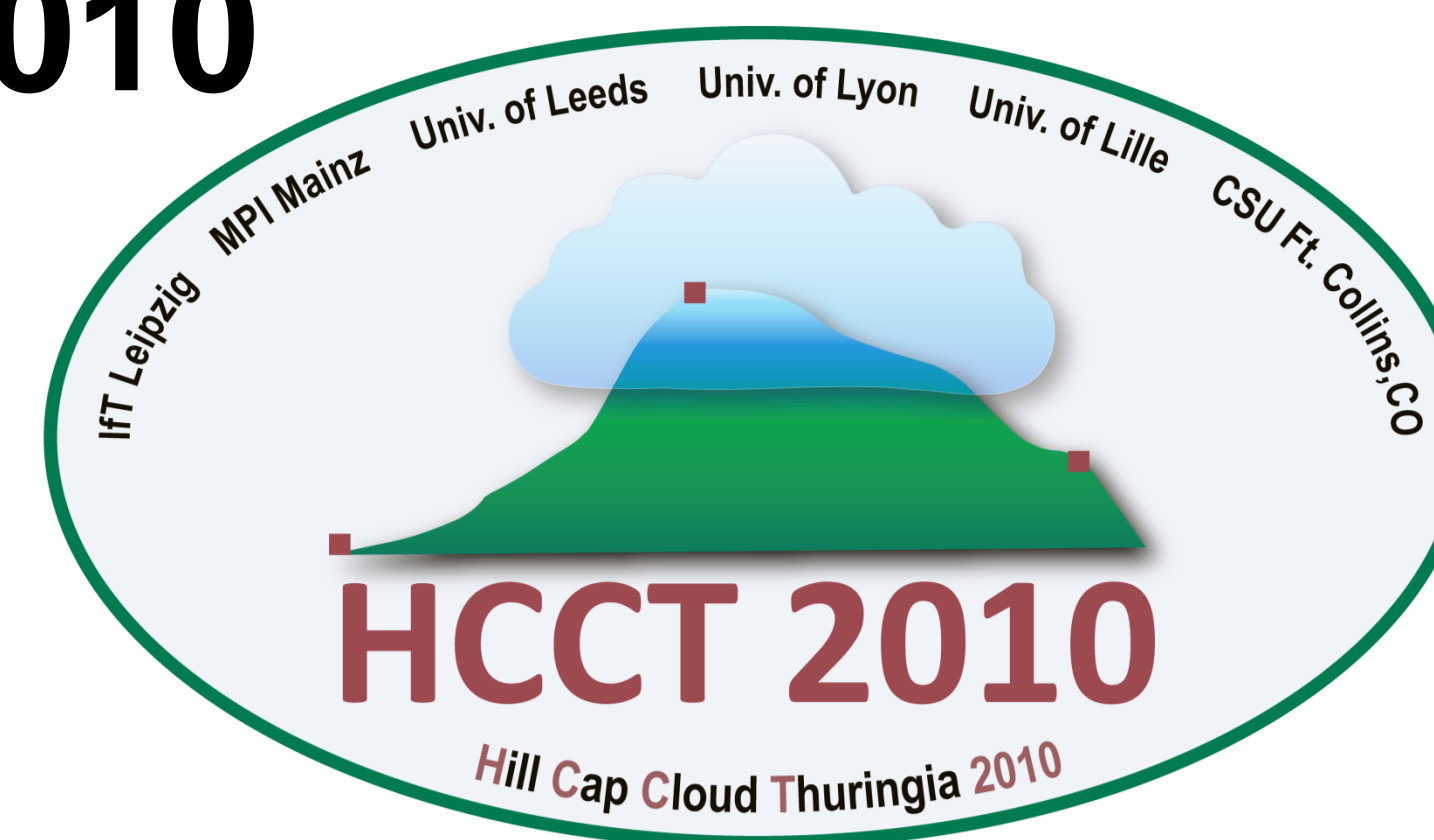
Introduction

Trace metals are known to play important roles in cloud chemistry. Trace metals serve as catalyst in the oxidation processes of S(IV) to S(VI) and contribute significantly to the radical budget (such as OH radical) important for aqueous phase reactions. Organic compounds such as oxalate can also complex with transition metal ions (TMI), thereby influencing their catalytic efficiency. Thus, trace metals as well as soluble TMIs analysis in cloud water were performed during the Hill Cap Cloud Thuringia (HCCT) 2010 campaign in Thüringer Wald (Germany). The aim was to find out the role TMIs and trace metals play in the cloud chemistry especially during orographic cloud formation. In addition to soluble TMI measurements done at the top of the hill with cloud water, aerosol particles were also analyzed for trace metal content at the valley stations to further investigate the particle chemical composition. The elements investigated were K, Fe, Ti, Cr, Ni, Co, Mn, V, Zn, Cu, Pb, Se, Rb, Sr, As. Here results of some full cloud events (FCE) during the campaign are presented.

Sampling Site

Fig. 1. Cloud water measurement tower during HCCT 2010 with collectors mounted at the sides at the top of the tower.

Experiment and Sampling

Cloud water sampling was done using a stainless steel Caltech active strand collector in an hourly routine. (Fig. 2). 1 ml of cloud water was filtered through a 0.45 µm filter, and 0.5 ml of the filtrate was used for TMI determination via an ion chromatograph (IC, Dionex ICS 900) using a post-column derivatization technique. The following TMIs were detected simultaneously at 530 nm using a variable wavelength UV/VIS detector: Fe (III), Cu (II), Ni (II), Zn (II), Cd (II), Co (II), Mn (II), and Fe (II). The ions were identified from their respective retention times on the chromatogram and quantification was done via external calibration. At the valley station particles were collected on aluminum and Nuclepore® foils using a Five-stage BERNER impactor with a PM_{10} cutoff (0.05 - 10 µm size range). The Nuclepore® foils were used for total metal analysis via total reflection x-ray fluorescence spectroscopy (TXRF).

Fig. 2. Stainless steel Caltech Active Strand cloud water collectors on the tower platform during a cloud event

Results

The concentrations obtained for the TMIs especially iron (0.1 to 3.8 µM) were within expected range for cloud water. Zn was found to be the most abundant element in the cloud water with days of high zinc concentration correlated with days of westerly air masses that have traveled through regions of high industrial activities. Fe (III) was the most observed soluble iron form in comparison to iron (II) except for some days where high UV radiation were observed during the passage of a thin cloud that led to a higher Fe (II) concentration compared to Fe (III).
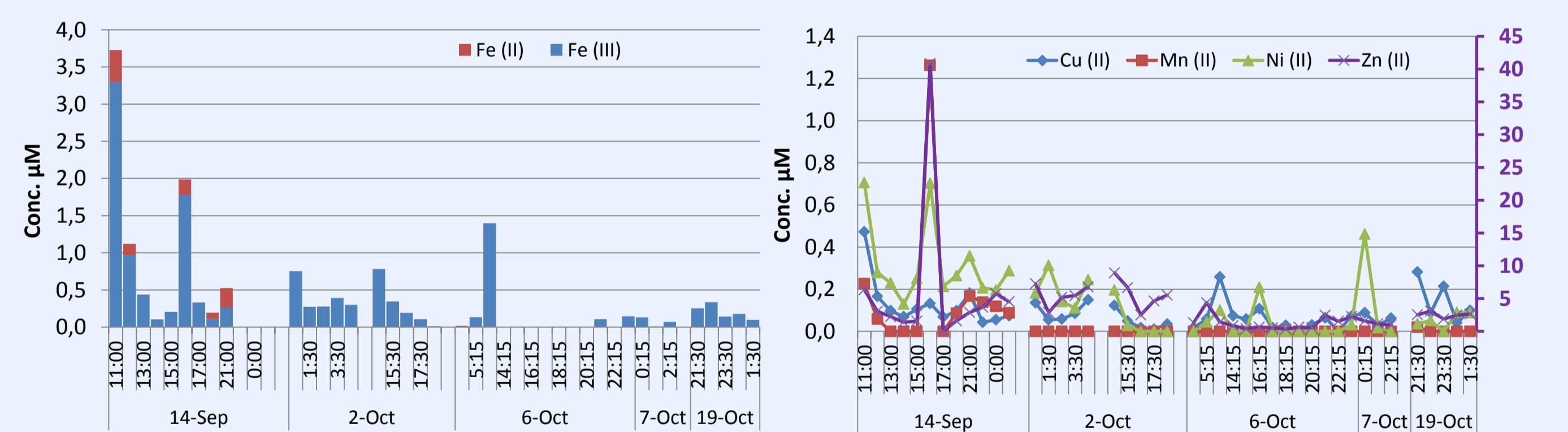
Size – resolved analysis of trace metals showed higher metal concentrations on stages 3 and 4 (1.2 - 3.5 µm) as shown on Fig 5. Fe and Zn were the most abundant elements followed by Pb and Cr. Pb was mostly present in the stages 2 and 3 indicating its anthropogenic origin. The decrease in mass concentration observed between Goldlauter (GL) and Gehlberg (GB) is likely due to particle deposition along their trajectory.

Fig. 3. Time series of soluble TMI ions. a) Fe(III) and Fe(II) with a dorminant Fe(III) presence and b) Cu(II), Mn(II), Ni(II) and Zn(II) with the Zn(II) axis (plotted on the right in purple) revealing the high concentrations of Zn observed during HCCT2010.

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. 4a). No significant correlation could be found between TMI solubility and cloud water pH except for Cu as shown on Fig 4b, 4c) for FCE 1.1 and FCE 13.3, respectively.
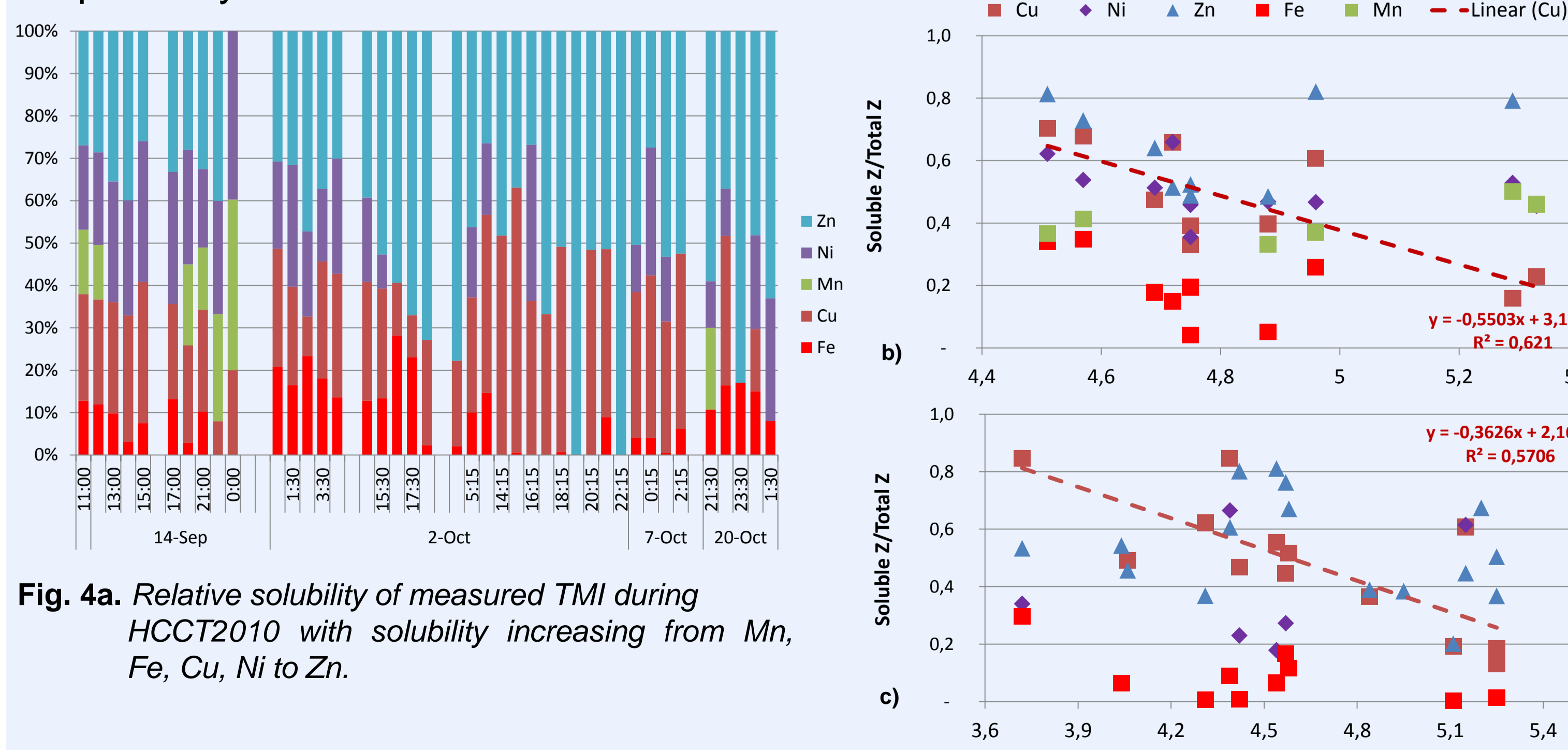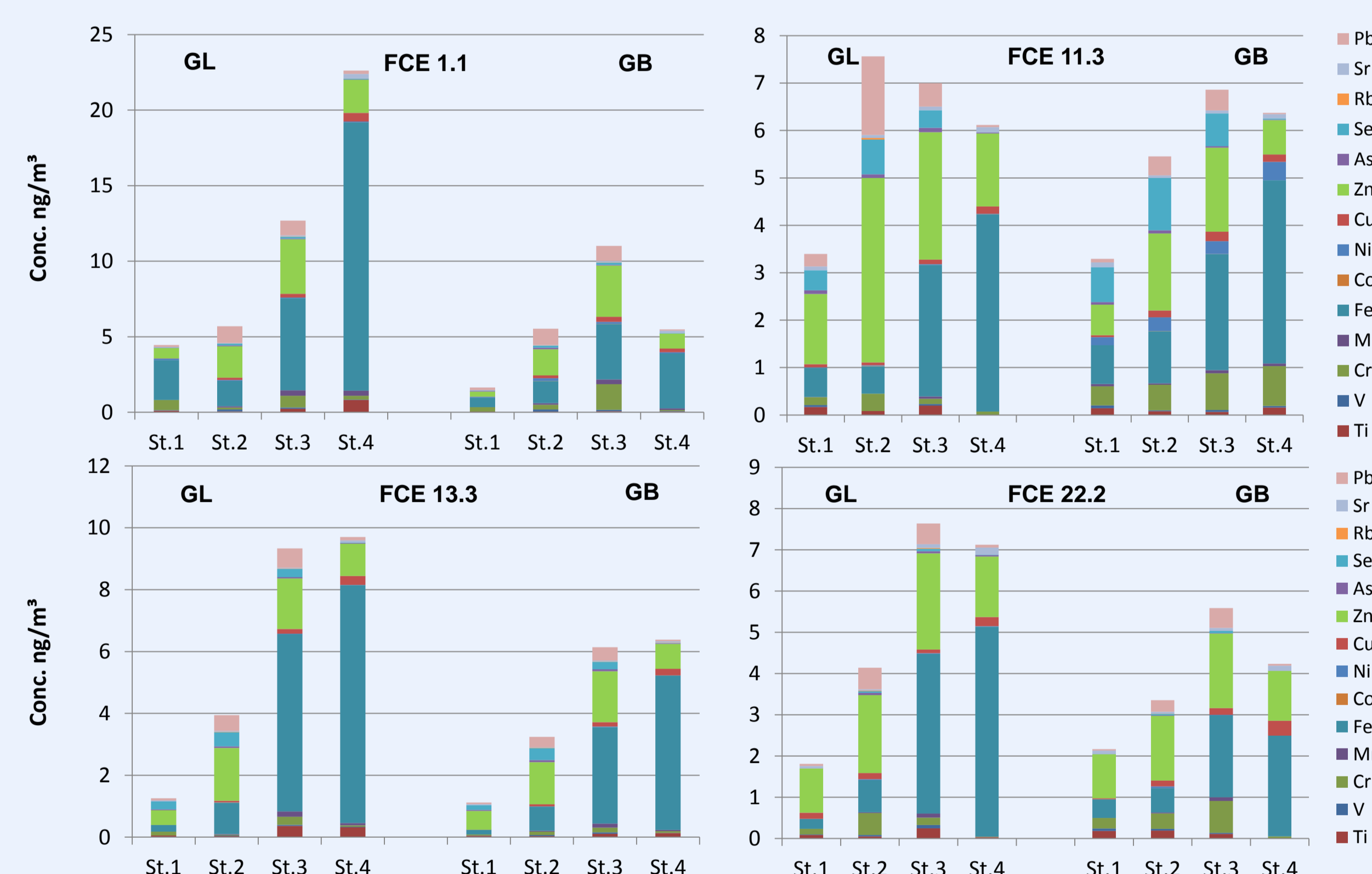

Fig. 4a. Relative solubility of measured TMI during HCCT2010 with solubility increasing from Mn, Fe, Cu, Ni to Zn.

Fig. 4b and 4c. Solubility dependency on pH during two full cloud events FCE 1.1 and FCE 13.3, respectively. Apart from Cu the solubility of the other TMIs show no good correlation with pH.

Fig. 5. 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.

The observed trace metals were found to be strongly correlated with levoglucosan, oxalic acid, OC/EC and also with inorganic ions such as NO_3^- and SO_4^{2-}. Table 1 shows the correlation coefficient (R^2) between some of these species. The good correlation observed between Fe and OC/EC, oxalate and levoglucosan shows that the metals especially iron was of diverse origin.

Table 1. Correlation coefficient between some trace metals and biomass, soot tracers and oxalate.

		Fe	Pb	Mn	Ti	Zn	K	As	Se
Levoglucosane	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							

Summary

TMI and trace metals were analyzed during HCCT2010. The results show that the metals were of diverse origin including biomass burning, anthropogenic activities as well as from soot. The solubility of the TMIs except for Cu did not show any strong correlation with the cloud water pH.