Complexation of transition metal ions by organic and inorganic ligands in size-segregated atmospheric aerosol particles in Melpitz, Germany

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KLIMZUG climate change in regions

MOTIVATION

Complexation of trace metal ions (TMI) influences

- **Physical properties:**
  - Absorption wavelength λ
  - Absorption coefficient ε
- **Chemical behavior:**
  - Photochemistry: $[Fe^{III}L]^{3+} + h\nu \rightarrow Fe^{2+} + \cdot L^{+}$
    - Nature of L, e.g. oxalate
    - Nature of ·L, e.g. ·OH, $\cdot SO_4^-$, …
    - Quantum yield (QY) of photochemical reactions: L= OH: QY = 0.126; L = $(Oxalate)_2$: QY = 1.23 (based on Fe^{2+})
  - RedOx chemistry:
    - Oxidation of Fe(II):

$[Fe^{II}(H_2O)_6]^{2+}$	$+ O_2/O_3/\cdot OH$	$\rightarrow Fe^{3+}$	$k_{relative} = 1$
$[Fe^{II}(SO_4)_1]$ (aq)	$+ O_2/O_3/\cdot OH$	$\rightarrow Fe^{3+}$	$k_{relative} = 0.4$
$[Fe^{II}(OH)_1]^{+}$	$+ O_2/O_3/\cdot OH$	$\rightarrow Fe^{3+}$	$k_{relative}$ = several 1,000

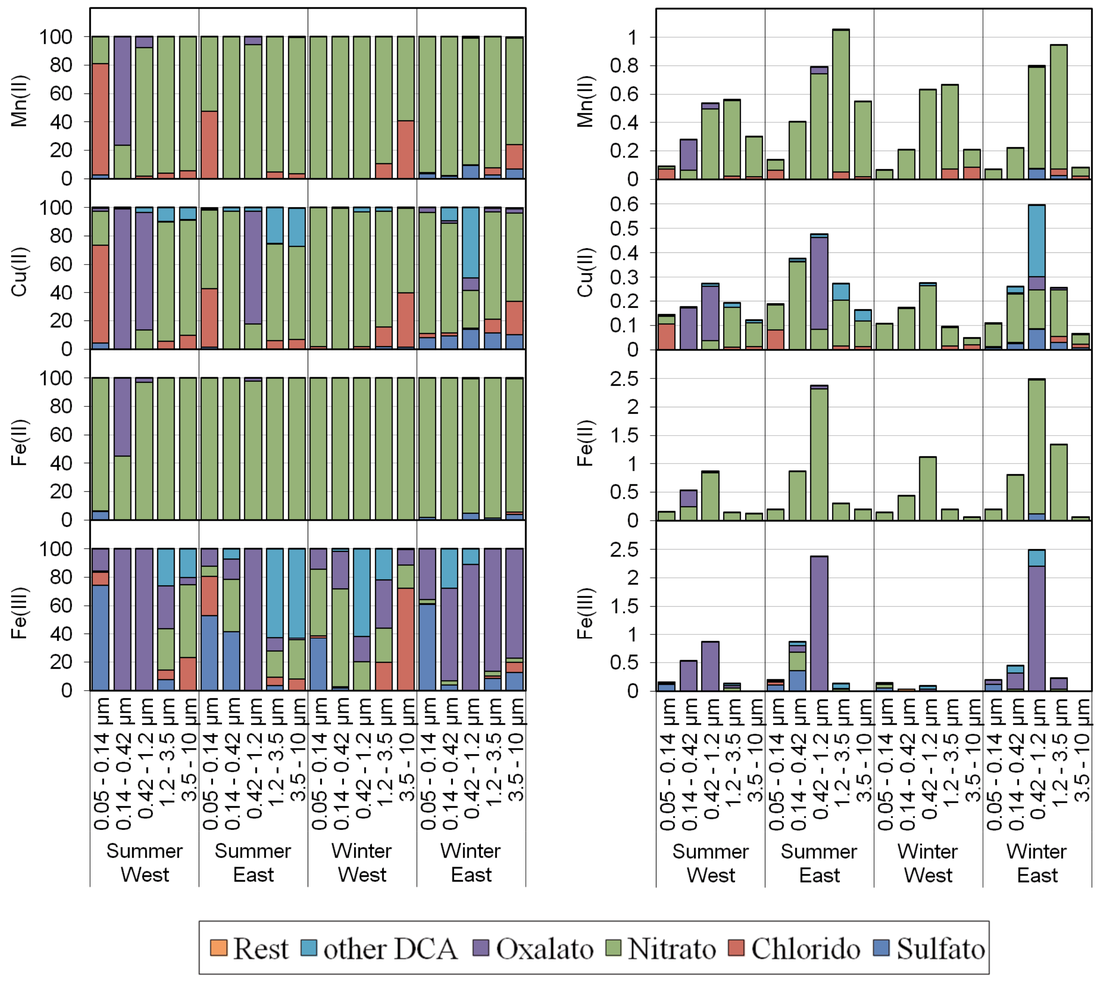
→ **knowing the complexation of TMI is important!**

RESULTS

Aerosol aqueous phase concentrations

Aerosol aqueous phase pH is between 0.6 and 2.1 (average: 1.3; summer: 1.1; winter: 1.6).
Aerosol aqueous phase ionic strength is between 4.3 M and 12.9 M (average: 8.6 M; summer: 10.0 M; winter: 7.2 M).
Aerosol aqueous phase concentrations are not as variable as aerosol mass concentrations and show only minor differences between the categories.

Complexation



Mn(II): mainly nitrate (summer, small particles: also chloride, oxalate)
Cu(II): mainly nitrate (summer, small particles: also chloride, oxalate; eastern categories: also DCA, oxalate)
Fe(II): mainly nitrate (summer, small particles: also oxalate)
Fe(III): mainly oxalate (small particles: also sulfate, coarse particles: inorganic complexes)

Season: more nitrate in winter than in summer; in summer more oxalate
Air mass origin: small influence; East: more sulfate, West: more chloride

Organic complexation is important, especially in summer and for aged particles (Winter East, 0.42 – 1.2 µm)!

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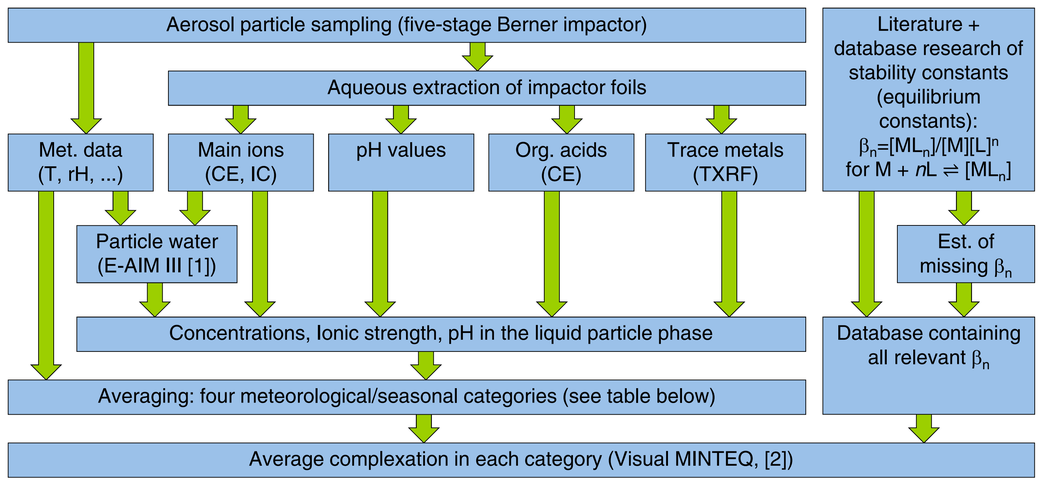
APPROACH

General



Sampling and Averaging

– Berner impactor cutoff diameters: 0.05 / 0.14 / 0.42 / 1.2 / 3.5 / 10 µm (→ five size fractions)
– Impactor runtime: 24 h (0:00 CET – 24:00 CET); sampled air volume: 108m³
– Determination of the air mass origin of each sampling day using backward trajectories (NOAA HYSPLIT [3])
– In total, 20 size-segregated samples were taken

Category	Season	Air mass origin	Number of sampling days
Summer West	May-October	West	6
Summer East	May-October	East	4
Winter West	November-April	West	5
Winter East	November-April	East	5

Modelling: Visual MINTEQ [2]

- Formation of solids is possible
- Ionic strength correction of β_n: Davies equation: $\lg \beta_n = \lg \beta_n^0 + A \cdot \Delta z^2 \cdot \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.31 \cdot I \right)$
  with: β^0_n = stability constant (at $I = 0$); $A = 0.511$ (water, 25° C); $\Delta z^2 = \Sigma z^2_{products} - \Sigma z^2_{reactants}$; z = charge; I = ionic strength)
- Consideration of:
  - SO_4^{2-}, HSO_4^-, Cl^-, NO_3^-, OH^-, NH_3, Oxalate, H-Oxalate, Tartronate, H-Tartronate, Malonate, H-Malonate, Malate, H-Malate, Succinate, H-Succinate.
  - Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, H^+.
- Oxidation state of iron: Fe(II) = Fe(III) = 0.5 $Fe_{total, measured by TXRF}$
- Calculation at 25° C
- Consideration of complexes up to ML_2

CONCLUSION

Comparison to published data

Study	Matrix	Mn(II)	Cu(II)	Fe(II)	Fe(III)
[4]	Atm. droplets	not complexed	not complexed	*not studied*	OH, Sulfite
[5]	Rain	not complexed	not complexed	not complexed	OH
[6]	Atm. water	*not studied*	*not studied*	not complexed	Oxalate
[7]	Cloud, fog	not complexed	not complexed	not complexed	OH, Oxalate
[8]	Rain	*not studied*	*not studied*	not complexed	OH, Oxalate
This study	**Aerosol particles**	**Nitrate**	**Nitrate, Oxalate**	**Nitrate**	**Oxalate**

Summary

– Compared to dilute samples (rain/fog/cloud waters), complexation in aerosol particles seems to be more important.
– Organic complexation is important, especially in summer.
– Oxalate often precipitates (calcium oxalate, magnesium oxalate) and thus not always forms complexes.

Outlook

– Combination of E-AIM and Visual MINTEQ would be preferable (one model instead of two).
– Better description of stability constants' ionic strength dependence (for highly concentrated aqueous phases)?
– Better time resolution (e.g. MARGA, PILS samples: ~ 1 h resolution)?

ACKNOWLEDGEMENTS

Financial support:
• German Federal Ministry of Education & Research (grant 01LR0802, REGKLAM; REGKLAM is part of KLIMZUG funding)
• German Federal Environment Ministry (grant F&E 370343200, GUAN)
Technical staff: A. Dietze, S. Fuchs, A. Grüner, E. Neumann, R. Rabe, A. Rödger, A. Thomas
Undergraduate students & interns: E. Charlesworth, A. Rau