Quantification of imidazoles in ambient aerosol particles from different environments in Europe and China

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Motivation

Imidazoles are potential:

- Brown carbon constituents: They were found in numerous laboratory studies, as a secondary product of the reaction of glyoxal or methylglyoxal with nitrogen-containing compounds like ammonia, amines and amino acids (De Haan et al., 2009; Kampf et al., 2012; Powelson et al., 2014)
- Photosensitizers: They can convert volatile organic compounds to less volatile compounds leading to particle growth, a modified particle composition and thus modified physical properties as well as gas-phase HO_2 production (Aregahegn et al., 2013; González Palacios et al., 2016)
- Hazardous components of aerosol particles: Imidazoles, such as 4-methylimidazole, are known for their carcinogenic potential (National Toxicology, 2007)

However only few studies yielded qualitative evidence of imidazoles in ambient aerosol particles. Therefore, the **aim** was to detect and for the first time quantify imidazoles in ambient aerosol particles.

Methods

- Atmospheric particles (PM1 or PM10) collected with a Digitel DHA-80 high volume filter during 12 or 24 h
- Enrichment from aqueous particle extracts by solid phase extraction (mixed mode, strong cation exchange)
- Analysis by capillary elctrophoresis - elctrospray ionization - time-of-flight - mass spectrometry (CE-ESI-TOF-MS)

Table 1. Overview of sampling sites, terminology, sampling period, sampling duration and according atmospheric conditions during the sampling period.

Sampling site	Designation	Geographic coordinates	Sampling period (sampling duration per filter)	Comments
Roof of the Leibniz Institute for Tropospheric Research, Leipzig, Germany	TROPOS	51.35 °N, 12.43 °E	January 2014 (12 h, day and night)	Urban background, strong influence of biomass burning aerosol during measurement period, TROPOS and Melpitz are influenced by similar regional air masses, due to proximity
Melpitz, Germany	Melpitz Wi Melpitz Su	51.53 °N, 12.93 °E	January to February 2013 (24 h) June to July 2013 (24 h)	Rural background
San Pietro Capofiume, Italy	SPC	44.65 °N, 11.62 °E	June 2012 (12 h, day and night)	PEGASOS campaign, rural site
Xianghe, China	Xianghe	39.75 °N, 116.96 °E	July 2013 (12 h, day and night)	CAREBeijing–NCP 2013 campaign, rural background, urban outflow
Wuqing, China	Wuqing	39.39 °N, 117.02 °E	March 2006 (24 h)	HACHI campaign, rural background, urban outflow

Qualitative identification of imidazoles

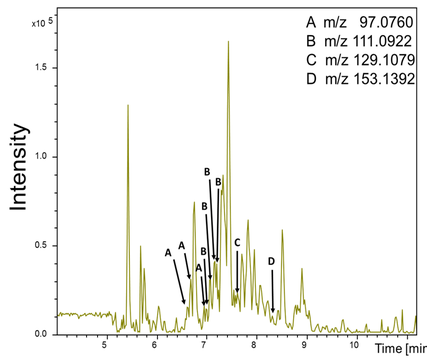

Figure 1. Base peak electropherogram obtained from the Melpitz sample of 16 July 2013. Base peaks referring to possible imidazole compounds are indicated with capital letters.

Identification of five imidazoles:

- 4-Methylimidazole (4MI)
- 1-Ethylimidazole (1EIM)
- 2-Ethylimidazole (2EIM)
- 1-Butylimidazole (BIM)
- Imidazole-2-carboxaldehyde (IC) in its hydrated form (HIC)

Evidences for the presence of a homologues series of alkyl-substituted imidazoles

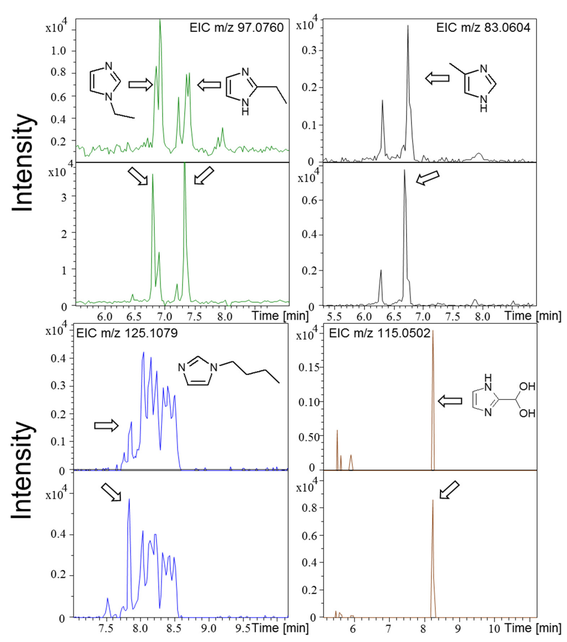

Figure 2. Selected extracted ion electropherograms of identified imidazoles after sample preparation of an ambient filter sample. Top: pure extract. Bottom: extract spiked with 5 µM standard solution. Arrows mark the peak of the identified compound.

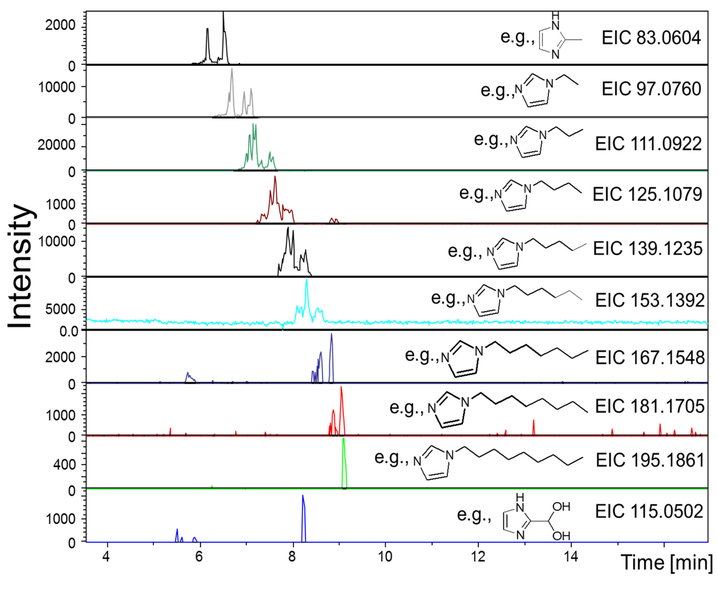

Figure 3. Extracted ion electropherograms of m/z values found in the literature and present study that are tentatively assigned to imidazoles, based on their exact mass. For each electropherogram an example for a possible structure is given.

Quantification of imidazoles

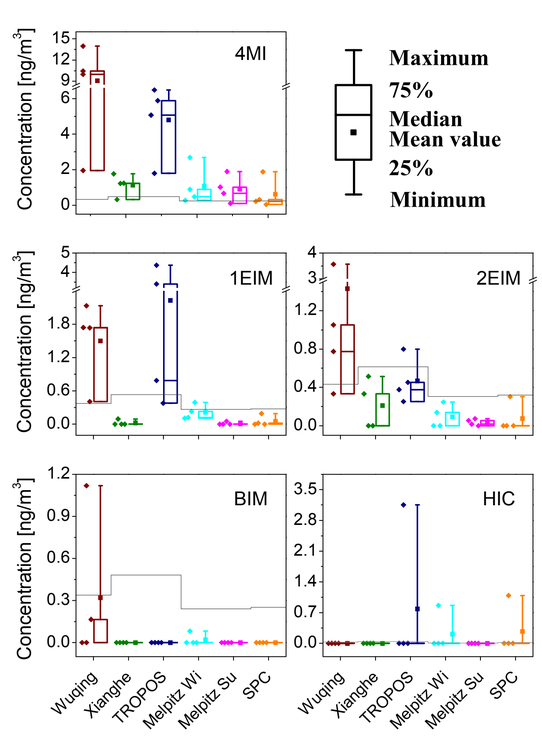

Figure 4. Concentrations of identified imidazoles at the sampling sites plotted as box plots and single data points. The gray solid line represents the mean method detection limit.

Screening study:

- Four samples of each campaign (Table 1)
- Concentrations range between 0.2 and 14 ng/m³
- 4MI was found to be the most abundant imidazole
- Occurrence of imidazoles seems to be favored at sites with strong biomass burning influence or connected to more polluted air masses
- No connection was found between aerosol particle pH and imidazole concentration
- Concentrations are generally higher at night time than at daytime

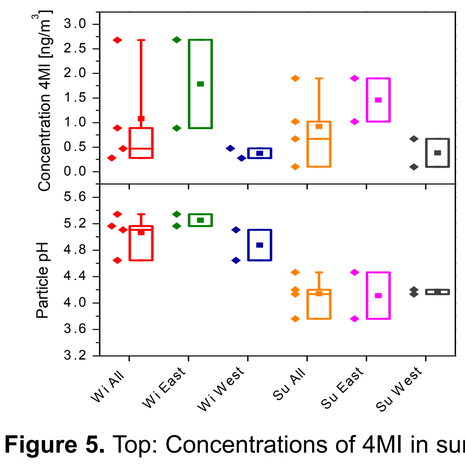

Figure 5. Top: Concentrations of 4MI in summer (Su) and winter (Wi) at Melpitz. Air mass origin is indicated as East and West. Bottom: Aerosol particle pH values at Melpitz.

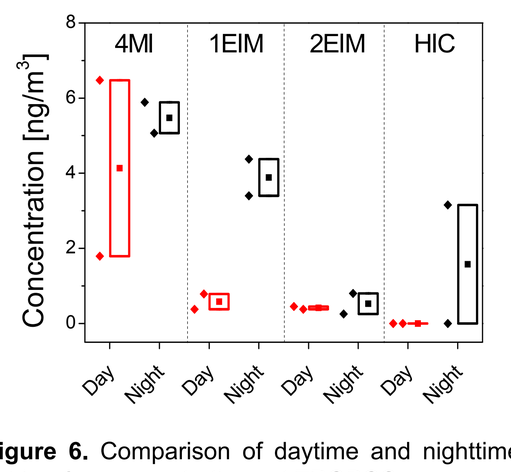

Figure 6. Comparison of daytime and nighttime imidazoles concentrations at TROPOS.

Conclusions

- First quantification of imidazoles in ambient aerosol particles
- Signals corresponding to a homologous series of alkylated imidazoles were found

This work:

- Corroborates laboratory studies by showing that imidazoles are present in ambient aerosol samples in measurable amounts.
- Further motivates to explore the potential photosensitizing properties of small alkyl-substituted imidazoles.

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