

Editorial

Atmospheric Aqueous-Phase Chemistry

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The Atmosphere Special Issue “Atmospheric Aqueous-Phase Chemistry” comprises ten original articles dealing with different aspects of chemistry in atmospheric liquid water. Liquid water in cloud and fog droplets and in moist aerosol particles is ubiquitous in the atmosphere. Dissolved species from the soluble aerosol fraction as well as soluble trace gases undergo chemical reactions in the aqueous phase via different mechanisms, usually yielding different products from those in the gas phase. In addition to their different reactivity, the chemical species solubility determines their fate in the atmosphere, i.e., their involvement in gas-phase or aqueous-phase chemistry.

The articles of this Special Issue can be divided into three groups: (i) the first is mostly based on field measurements and/or combined field and modeling studies giving insights into the chemical characterization of different atmospheric liquid water samples from various environments [1–4]; (ii) the second group is focused on studies of aqueous-phase reactivity of some important atmospheric organic compounds [5–8]; (iii) and the final group comprises articles based on predictive modeling and/or combined modeling and laboratory studies providing insight into aqueous secondary organic aerosol (SOA) formation [9,10].

The lack of understanding of aerosol liquid water (ALW) and the extent to which this biases $PM_{2.5}$ (particulate matter) risk estimates as related to human exposure to water-soluble pollutants are key knowledge gaps. The associations among ALW, sulfate (as a surrogate for ALW), and changes to $PM_{2.5}$ mass based on filter equilibration were explored across the United States in 2004 by Babila et al. [1]. They found that during sampling and filter equilibration to standard laboratory conditions, ambient ALW mass was removed corresponding to up to 85% of the ambient water mass at most sampling sites. The removal of ALW can induce the evaporation of other semi-volatile compounds present in $PM_{2.5}$ and, thus produce an artifact in PM mass measurements, which is not uniform in space or time [1].

Renard et al. [2] performed statistical analyses (principal component analysis—PCA, agglomerative hierarchical clustering—AHC) of 295 cloud samples collected in the period 2001–2018 at the Puy de Dôme, France (PUY), which resulted in clustering of the cloud samples according to their chemical properties. Further, this classification was combined with a numerical analysis by CAT model (computing advection interpolation of atmospheric parameters and trajectory tool); and, finally, the influence of cloud microphysical properties (liquid water content—LWC and r_e) was investigated by PLS (partial least squares) analysis. The results suggested that cloud chemical composition at PUY was influenced by air mass history including several physicochemical processes (e.g., cloud condensation nuclei (CCN) physical and chemical processes, mass transfer of soluble species, multiphase reactivity), while the influence of cloud microphysics remained minor [2].

Chemical characteristics of organic matter and trace elements (TEs) in rainwater samples collected in an urban area of Zagreb, Croatia were investigated by Orlović-Leko et al. [3]. Their study included the magnitude and variability of TEs, dissolved (DOC)



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and particulate organic carbon (POC), and also some selected reactive classes of organic and sulfur species, which can have an important role in the processes of atmospheric and surface waters. Their results showed relatively low concentrations of DOC and TEs; in addition, the daily fluxes of Zn, Pb, Ni, AS and Cd were two to three times lower than those reported for urban sites in Europe.

The presence of reduced sulfur species (RSS) in the water-soluble fraction of fine marine aerosols from the Middle Adriatic area (Rogoznica Lake) was studied by Cvitešić Kušan et al. using voltammetric methods [4]. They confirmed two types of non-volatile RSS species: mercapto-type, which complexes Hg (RS-Hg) and sulfide/ S^0 -like compounds, which deposit HgS. Their study indicated the presence of mainly mercapto-type compounds in spring samples, which can be potentially associated with biological activity, while both types of compounds were identified in early autumn aerosols.

Intermediate-volatile organic compounds (IVOC) are recognized as important SOA precursors in the gas phase, while aqueous-phase SOA formation from IVOC is still unclear. Liu et al. [5] investigated aqueous oxidation of dibenzothiophene (DBT) as an example of IVOC. They demonstrated that both photo-oxidation by OH radicals and dark aging contribute to aqueous SOAs with yields of 32% and 15%, respectively. In addition, they found that during OH-initiated photochemical reactions of DBT, light-absorbing species are formed, which can significantly contribute to atmospheric brown carbon (BrC).

The study of Vidović et al. [6] demonstrated that aqueous-phase processing of 3-methylcatechol (3MC), as an important precursor to light-absorbing methylnitrocatechols (MNC), in the presence of HNO_2/NO_2^- , both under sunlight and in the dark, may significantly contribute to secondary BrC formation. Under illumination, the degradation of 3MC is faster than in the dark, but the yield of the main two products of the dark reaction (3-methyl-5-nitrocatechol, 3M5NC and 3-methyl-4-nitrocatechol, 3M4NC) is low, suggesting different degradation pathways of 3MC in the sunlight. Besides the primary reaction products (3M5NC and 3M4NC), second-generation products with absorption above 400 nm were also confirmed. The characteristic mass absorption coefficient (MAC) values were found to increase with increasing $NO_2^-/3MC$ concentration ratio and decrease with increasing wavelength.

In their work, Rudziński and Szmigielski [7] elucidated how quickly different nitrophenols, as common and hazardous environmental pollutants, are removed from the atmosphere via aqueous-phase reactions with sulfate radical anions ($SO_4^{\cdot -}$). Their rough estimations showed that the gas-phase reactions of 2-nitrophenol (2-NP) with OH or NO_3 radicals dominate over the aqueous-phase reaction with $SO_4^{\cdot -}$ in deliquescent aerosol and haze. In cloud, rain, and fog waters, aqueous-phase reactions of 2-NP with $SO_4^{\cdot -}$ radicals dominate if their concentrations are similar to those of OH or NO_3 radicals.

In the work of Schaefer et al. [8], the pH- and temperature-dependent oxidation reactions of dicarboxylic acids (succinic and pimelic acid), as important trace constituents in the troposphere present mostly in the particle phase, were investigated to determine the OH radical rate constants. They observed that the rate constant increases with increasing pH due to the deprotonation of the carboxylic group ($k(AH_2) < k(AH^-) < k(AH^{2-})$). The atmospheric lifetime of dicarboxylic acids was estimated to range from a few minutes under aerosol conditions to several hours under cloud conditions. The oxidation reaction by OH can act as a sink for dicarboxylic acids as well as a source of smaller dicarboxylic acids or multifunctional compounds.

The contribution of dark SOA formation from carbonyl-containing compounds (CVOCs) to overall aqueous aerosol optical properties is expected to be significant. The multiple pathways taking place in such systems and different chromophoricity of individual products make it complicated to reliably model the kinetics. In their work, Fan et al. [9] proposed an alternative method of representing UV–Vis absorbance spectra as a composite of Gaussian lineshape functions to infer kinetic information. Their data and model parameters were focused on the light-absorbing properties of glyoxal, methylglyoxal, and glycolaldehyde in

ammonium sulfate environments, selected due to their notable contributions to aqueous SOA mass.

Although it is recognized that SOAs are formed during chemical processing of organic material in aqueous aerosols and cloud water, it is not yet clear how much each of these processes contributes to total aerosol mass. In their work, Tsui et al. [10] used a photochemical box model (Gas-Aerosol Model for Mechanism Analysis—GAMMA 5.0) with coupled gas- and aqueous-phase chemistry to investigate the impact of aqueous reactions on isoprene epoxydiol (IEPOX) SOA formation in both aerosol and clouds, including cycling between the two phases upon the evaporation or condensation of water. Their results indicate that aqueous-phase chemistry in clouds (pH 4 or lower) may be a more substantial source of IEPOX SOA than formerly believed. This is primarily attributed to the relatively higher uptake of IEPOX to clouds compared with aerosol. Formation in clouds could account for the discrepancies between predicted IEPOX SOA mass from atmospheric models and measured ambient IEPOX SOA mass or observations of IEPOX SOA in locations where mass transfer limitations are expected in aerosols.

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Conflicts of Interest: The authors declare no conflict of interest.

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