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Organosulfates in aerosols downwind of an urban region in central Amazon†

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Organosulfates are formed in the atmosphere from reactions between reactive organic compounds (such as oxidation products of isoprene) and acidic sulfate aerosol. Here we investigated speciated organosulfates in an area typically downwind of the city of Manaus situated in the Amazon forest in Brazil during "GoAmazon2014/5" in both the wet season (February–March) and dry season (August–October). We observe products consistent with the reaction of isoprene photooxidation products and sulfate aerosols, leading to formation of several types of isoprene-derived organosulfates, which contribute 3% up to 42% of total sulfate aerosol measured by aerosol mass spectrometry. During the wet season the average contribution of summed organic sulfate concentrations to total sulfate was 19 ± 10% and similarly during the dry season the contribution was 19 ± 8%. This is the highest fraction of speciated organic sulfate to total sulfate observed at any reported site. Organosulfates appeared to be dominantly formed from isoprene epoxydiols (IEPOX), averaging 104 ± 73 ng m^{-3} (range 15–328 ng m^{-3}) during the wet season, with much higher abundance 610 ± 400 ng m^{-3} (range 86–1962 ng m^{-3}) during the dry season. The concentration of isoprene-derived organic sulfate correlated with total inorganic sulfate ($R^2 = 0.35$ and 0.51 during the wet and dry seasons, respectively), implying the significant influence of inorganic sulfate aerosol for the heterogeneous reactive uptake of IEPOX. Organosulfates also contributed to organic matter in aerosols (3.5 ± 1.9% during the wet season and 5.1 ± 2.5% during the dry season). The present study shows that an important fraction of sulfate in aerosols in the Amazon downwind of Manaus consists of multifunctional organic chemicals formed in the atmosphere, and that increased SO_2 emissions would substantially increase SOA formation from isoprene.

Environmental significance

Aerosols in the atmosphere affect climate and human health, but there are still major gaps in our understanding of fundamental processes including the interaction of natural and man-made emissions. Tropical vegetation emits large amounts of isoprene which undergo photochemical oxidation in the atmosphere. Reactions between oxidation products of isoprene can react with acidic sulfate aerosols, typically of anthropogenic origin, to form organosulfates. Here we find that these organosulfates make up a surprisingly high fraction of total sulfate in aerosols downwind of the city of Manaus situated in the Amazon forest. Increasing anthropogenic emissions of SO_2, forming sulfate aerosols, is thus also expected to increase formation of secondary organic aerosols from biogenic isoprene in other tropical regions with high isoprene emissions.

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1. Introduction

Isoprene (2-methyl-1,3-butadiene), emitted from vegetation, is the most important non-methane hydrocarbon emitted to the atmosphere (about 500 Tg per year),[1] where it undergoes photooxidation, forming a wide range of gaseous and particulate products.[2–5] Tropical forests, such as the Amazonian rainforest, emit particularly high amounts of isoprene and other terpenoids.[1,6] A substantial fraction of sub-micron organic aerosol mass in tropical regions originates from photochemical oxidation of isoprene[7–11] affecting *e.g.* aerosol hygroscopicity and formation of cloud condensation nuclei.[12–14]

Heterogeneous acid-catalyzed uptake of reactive isoprene oxidation products such as isoprene epoxydiols (IEPOX) and hydroxyhydroperoxides onto acidic sulfate aerosol particles leads to formation of organosulfates, in addition to other products such as methyl tetrols and their oligomers[3,15–19] and thus contributes to the mass concentration of secondary organic aerosol (SOA). This uptake is most efficient for sulfate aerosol particles not coated by other organics,[20,21] and can contribute to anthropogenic enhancement of biogenic SOA formation,[22–24] as previously observed *e.g.* in the southeastern US.[22,25] Analysis of specific molecular tracers in aerosols can provide information on sources and atmospheric processes.[26,27]

The region of Manaus was identified as a unique site for studying interactions of anthropogenic and biogenic emissions, since this city of about 2 million inhabitants is situated in the central region of the Amazon basin, which extends for more than 1000 km in every direction.[28,29] Power generation from combustion of fuel oil and diesel, as well as oil refinery operations, emit about 72 kton SO_2 per year in the region.[30] Additional sources of SO_2 and sulfuric acid in the Amazon include photochemical oxidation of dimethylsulfide (DMS) emitted from marine or terrestrial sources.[8,31,32] Tropical rainforests have been identified as a source of DMS, which may constitute an important regional source, though small on a global scale (about 6%),[33] and affect aerosol formation and the hydrological cycle.[34]

Recently de Sá *et al.*[35] reported that urban pollution from Manaus affected the formation of isoprene-derived SOA. In particular, they observed that sulfate enhanced formation of IEPOX-SOA, while NO suppressed it, consistent with expectations based on known isoprene oxidation chemistry.[35,36] Using ultra-high-resolution mass spectrometry, Kourtchev *et al.*[37] detected more than 2000 elemental formulae in aerosol samples collected downwind of Manaus. Up to 60% of the organic species were nitrogen- and/or sulfur-containing, and the dominant ion in most samples had the elemental formula of the isoprene-derived IEPOX organosulfate.[38]

In the present work, we investigate the contribution of organosulfates to the observed PM in the region using analysis of molecular tracers of aerosol sources and processes. Specifically, aerosol samples collected during both the wet season and the dry season were analyzed for organosulfates. Of particular interest is the contribution of organosulfates to total sulfate. In a previous study the average contribution of organic sulfate to total sulfate was estimated as about 5% (0–16%) for 12 sites distributed across USA, showing higher organic sulfate contributions to total sulfate in regions of lower sulfate concentrations.[39] In comparison, airborne measurements of IEPOX OS and acetic acid sulfate (also known as glycolic acid sulfate) in the tropospheric boundary layer in the eastern and western US showed ratios of organic sulfate to total sulfate of 3.5% and 2.4%, respectively.[40] Studies in other regions with very low isoprene emissions typically find lower average contributions of organic sulfate to total sulfate, such as a study in Northern Europe during winter (1.4 ± 0.9%) where organosulfate precursors were identified as monoterpenes and alkanes.[41]

Additional information on the biogenic sources of SOA was obtained in the present study from analysis of carboxylic acids from photochemical oxidation of monoterpenes. This methodology has previously been applied to study sources of SOA in Europe.[42,43] In this study we investigated molecular tracers of monoterpene SOA include pinic acid, pinonic acid and terpenylic acid from photochemical oxidation of α- and β-pinene,[44–47] in order to quantify SOA contributions from these potential sources. In addition we measured 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), which is formed through gasphase oxidation of pinonic acid, and is thus a tracer of photochemical processing of α- and β-pinene.[48,49]

2. Experimental

2.1 Sampling

Samples were collected as part of the Green Ocean Amazon (GoAmazon2014/5) field campaign[28,29] during intensive operating periods in February–March (IOP1 during the wet season) and August–October (IOP2 during the dry season) of 2014. Here we focus on measurements at site "T3" (3.21°S, −60.60°W), approximately 70 km downwind of Manaus (Fig. 1), situated on a cleared, pasture site about 500 m from any trees, 2 km north of the nearest paved road and about 2.5 km from the closest surrounding forest.

The prevailing wind direction was from the north-east in the wet season and from east during the dry season, transporting air masses over the Amazon forest to be mixed with the outflow from Manaus (to the east) before reaching the T3 site (Fig. 1). Transport time from city to T3 was typically 4–5 h.[36] Backward trajectories were simulated using HYSPLIT4 model.[50] Forcing meteorological conditions were taken from GDAS 3-hourly, global, 0.5° fields provided by NOAA's Air Resources Laboratory. Trajectories started from 10 m over T3 site, at every hour, for the period of our analysis.

Submicron aerosol samples (PM_1) were collected on quartz fiber filters (101.6 mm diameter, QM-A Quartz, Whatman) using a custom-built sequential filter sampler (Aerosol Dynamics, Inc.). Air was sampled 4 m above ground level, passed through tubing kept at temperatures below the dew point for trapping excess water, and then through a greaseless cyclone (with 1 μm aerodynamic diameter cut-point), before collection of particles. This sampling system is also expected to remove water-soluble reactive gas-phase species and thus reduce potential sampling artefacts.[51] Standard conditions were defined as 21.1 °C and

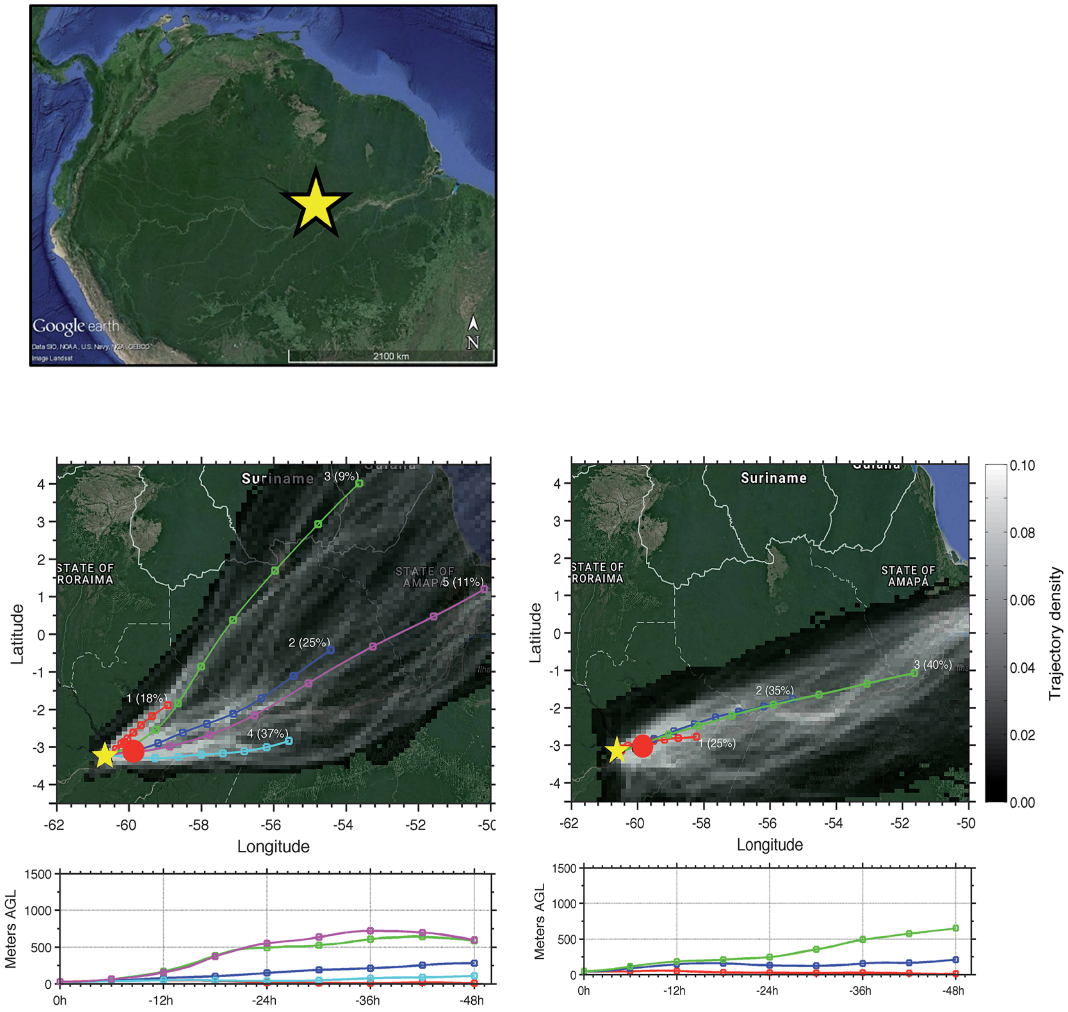

Fig. 1 Location of sampling site (yellow star), downwind of Manaus (red circle), in the central Amazon region in Brazil, and trajectory analysis for samples collected during the wet season (left) and dry season (right). Samples were selected to represent periods when airmasses arrived at the site after passing over the urbanized region of Manaus. Percentages denote the fraction of trajectories following each route.

101.3 kPa for the TSI flowmeter used to check sampling flow rate. Filters were pre-treated by baking them at 550 °C for 12 hours.

During IOP1 (wet season), sample collection occurred with 12 hour time resolution, from 06:15–18:00 and 18:30–06:15, local time (UTC-4). During IOP2 (dry season), sample collection occurred with 4 hour time resolution, from 06:00–09:55, 09:55–13:50, 13:50–17:45, 18:15–22:10, 22:10–02:05, and 02:05–06:00, local time. Field blanks were collected each week. Particle filters were kept frozen (−18 °C) and always transported on ice.

2.2 Analyses

Filter aliquots (47 mm diameter punches) were extracted in 1 : 1 mix of methanol and acetonitrile (AcN), aided by sonication for twenty minutes. The extract was filtered using a polytetrafluoroethylene syringe filter (Q-Max, Frisenette) and evaporated under a flow of dry, high-purity nitrogen gas. The residue was re-dissolved in 200 μL of 10% AcN with 0.1% acetic acid in MilliQ-water and analyzed using an ultrahigh performance liquid chromatograph coupled through an electrospray ionization source to a quadrupole time-of-flight mass spectrometer (UHPLC/ESI-qTOF-MS, Bruker Daltonics) operated in negative ionization mode. The extraction and analytical method, as well as identification and quantification of organosulfates, are described in detail elsewhere.[42,51,52]

Compounds were identified based on comparison of mass spectra and retention times with authentic standards when available or according to mass spectra and comparison with data from previous studies. An authentic standard of an organosulfate with molecular weight 216 (OS 216), derived from IEPOX,[53] was kindly obtained from Prof. J. Surratt and Prof. A. Gold (University of North Carolina – Chapel Hill) and used for quantification of all isoprene-derived organosulfates. Standards for carboxylic acids and monoterpene organosulfates have previously been listed.[41,54] Six-point calibration curves generally showed $R^2 > 0.99$. All concentrations were corrected according to recovery (59 ± 15%) except OS 216 which was only corrected according to ionization efficiency. Average blank concentrations, which were <0.3 ng m^{-3} for all organosulfates except OS 200 (0.8 ng m^{-3}), 0.5 ng m^{-3} for pinonic acid, and 0.02 ng m^{-3}

for other acids. The overall analytical uncertainty was estimated as 30%.

Mass concentrations of particle sulfate, organic mass, ammonium and nitrate species were measured using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer from Aerodyne, Inc., USA (HR-ToF-AMS, hereafter denoted AMS).[55,56] Details of the specific deployment were previously described.[35] The AMS measures aerosol composition after vaporization, typically at 600 °C, followed by electron ionization at 70 eV, which is thought to lead to fragmentation of organosulfates into separate sulfate and organic fragments.[57] In the current version, the instrument can thus detect the total sulfate concentration, *i.e.* organic plus inorganic, but cannot separate these two components.

3. Results and discussion

3.1 Overview

Organosulfates detected in atmospheric aerosols are typically reported based on their suggested precursor molecule. In this work we instead use a more stringent nomenclature in which organosulfates are identified by the structure of the molecule containing a sulfate group bonded to one carbon, *e.g.* acetone sulfate, instead of a suggested precursor molecule, *i.e.* hydroxyacetone sulfate. This nomenclature in accordance with standard IUPAC nomenclature will make it easier to recognize the molecular structures of organosulfates and avoid confusion as there can be several or unknown precursors to a specific organosulfate. For simplicity we will here use the abbreviation OS for organosulfate, followed by its molecular weight (*i.e.* OS 184) and IEPOX OS for 1,2,4-hydroxy-2-methyl-butyl-3-sulfate.

Table 1 lists average concentrations, as well as ranges, of major detected compounds and sulfate and organic aerosol (OA) measured by AMS during the aerosol sampling periods. Additional information on suggested molecular structures and precursors of organosulfates is provided in ESI Table S1.† The main observed organosulfates were derived from isoprene (namely OS 184, OS 200, OS 212, OS 214 and IEPOX OS[15,58,59]) and its oxidation products hydroxyacetone and hydroxyacetic acid (acetone sulfate and acetic acid sulfate).[59–61] Concentrations of organosulfates were dominated in both the wet and the dry season seasons by IEPOX OS (87 ± 4% and 61 ± 15%, respectively), in line with previous results from the same site.[37]

Summed concentrations of all detected organosulfates were observed at average concentrations of 104 ± 73 ng m^{-3} during the wet season (IOP1), and 612 ± 397 ng m^{-3} during the dry season (IOP2).

3.2 Results from the wet season

The organosulfate derived from IEPOX, OS 216, constituted about 80% of the organosulfate mass in the samples (Table 1 and Fig. 2). The variation in organosulfate levels between samples showed some relation with air pollution parameters such as ozone and sulfate (Fig. S1†). High correlations across different samples ($R^2 > 0.8$) were found between IEPOX OS and acetone sulfate (from hydroxyacetone),[60] hydroxy-butanone-sulfate (from methyl vinyl ketone),[59,62] and OS 214 (also derived from isoprene),[58] as listed in Table S2.† Acetic acid sulfate, OS 168, OS 170 and OS 182 from the isoprene oxidation products hydroxyacetic acid, methacrolein, 2-hydroxy propanoic acid and 2-methylglyceric acid were not observed at levels above the detection limit, in contrast to other studies in non-tropical regions and laboratory studies.[59–63] During the wet season, OS 200 was only observed at very low levels and was not correlated with other measured OS. Previous studies found that OS 200 can have several precursors, including the isoprene high-NO_x oxidation products 2-methylglyceric acid and methacrylic acid epoxide (MAE),[60,64] and also 2-methyl-3-buten-2-ol (typically emitted from vegetation in temperate climates).[65]

In some laboratory studies, OS 200 and OS 184 were both formed from ozonolysis of isoprene, rather than photooxidation.[59,66] A study at a forested site in the south-western US found much lower formation of OS 200 compared to IEPOX-OS, especially at higher temperatures, due to differences in production of their respective precursors (MAE *vs.* IEPOX).[67]

Of organosulfates derived from monoterpenes, only OS 250 from α-pinene[68] was observed at concentrations above the detection limit. The highest concentration of OS 250 (3.6 ng m^{-3}) was measured on March 10 (Fig. 2), when other oxidation products of α-pinene and β-pinene also showed slightly elevated concentrations (Fig. S2†), including first-generation products pinic acid and terpenylic acid. In general, carboxylic acids from oxidation of α-pinene and β-pinene were observed at low levels in the particle phase (Table 1 and Fig. S2†). For some compounds such as pinonic acid this is partly due to their relatively high vapor pressure and the high temperatures at this site, as previously seen.[69]

Organosulfate species from other sources were not observed above the detection limit or only at very low concentrations, including those formed from green-leaf volatiles, alkanes and polycyclic aromatic hydrocarbons.[70–72]

3.3 Results from the dry season

Concentrations of organosulfates were about four times higher on average during the dry season than during the wet season (Table 1). The main organosulfate compounds are IEPOX OS and OS 214 (also from isoprene), while the remaining organosulfates never make up more than 20% of the total organosulfate concentration.

The largest difference was observed for OS 200, with dry season average concentration (30 ± 13 ng m^{-3}) about 40 times the wet season average concentration (0.7 ± 0.8 ng m^{-3}). Additional OS species were detected in the dry season, namely acetic acid sulfate (OS 156) from glycolic acid and OS 170 from methyl glycolic acid or green-leaf volatiles.[59,61,70] Other types of organosulfates, either derived from green-leaf volatiles, alkanes and polycyclic aromatic hydrocarbons, were not observed above the detection limit or only at very low concentrations during the dry season.

Furthermore, while concentrations of some first-generation oxidation products of α-pinene and β-pinene (pinonic acid and terpenylic acid) were not observed above the detection

Table 1 Concentrations of molecular tracers, together with sulfate and organic aerosol concentrations measured by AMS. All concentrations are ng m^{-3}. Note that n.d. means that the compound was "not detected" above the detection limit (see Experimental section)

	Wet season		Dry season	
Compound	Average ± 1SD (n = 28)	Range	Average ± 1SD (n = 70)	Range
Acetone sulfate (OS 154)	4.6 ± 3.2	0.9–14.1	30 ± 15	n.d. to 70
Acetic acid sulfate (OS 156)	n.d	n.d.	25 ± 11	n.d. to 48
Propanoic acid 2-sulfate (OS 170)	n.d.	n.d.	8.8 ± 3.5	n.d. to 19.7
Hydroxy-butanone-sulfate (OS 184)	2.5 ± 1.6	0.7–6.3	19.0 ± 9.0	n.d. to 45.6
OS 200	0.7 ± 0.8	n.d. to 3.0	30 ± 13	n.d. to 71
OS 212	1.3 ± 1.5	n.d. to 5.1	n.d.	n.d.
OS 214	11.5 ± 9.3	1.5–41.3	101 ± 61	n.d. to 283
IEPOX OS (1,2,4-hydroxy-2-methyl-butyl-3-sulfate, OS 216)	83 ± 59	11–260	399 ± 308	39–1450
Total OS	**104 ± 73**	**15–328**	**612 ± 397**	**86–1962**
Pinonic acid	2.0 ± 1.5	0.3–5.4	n.d.	n.d.
MBTCA	4.4 ± 3.0	0.9–10.8	14.1 ± 6.2	n.d. to 32.0
Terpenylic acid	1.8 ± 3.1	0.4–16.8	n.d.	n.d.
Total sulfate	268 ± 136	59–550	1600 ± 917	595–4616
Organic aerosol (OA)	1671 ± 579	625–2680	8783 ± 2642	4539–16 064

limit, the second-generation oxidation product MBTCA showed an average concentration of 14.1 ± 6.2 ng m^{-3}, which was higher than during the wet season. This is in line with a longer photochemical aging time during the dry season, while rain-out during the wet season results in a larger influence of early oxidation products compared to more oxidized compounds. It should be noted that only a small fraction of pinonic acid (about 0–30%) is expected to be in the particle phase at this site, while MBTCA is primarily found in the particle phase.[69]

Fig. 3 shows concentrations of organosulfates in aerosol samples collected during the dry season. The higher time-resolution during the dry season allowed us to study the diurnal variation of molecular tracers. Levels of organosulfates were on some days higher during daytime than nighttime (*e.g.* 28 August, 22 September, 26 September, 27 September), while the picture was less clear on *e.g.* 19 September and 10 October.

Isoprene-derived OS peaked during daytime (10:00–18:00) and had minimum concentrations during night (22:00–06:00), similar to sulfate concentrations (Fig. 4) and the typical diurnal variation of isoprene emissions.[36,73] For comparison, full time-series of pollutants such as ozone and sulfate are shown in Fig. S1.† This is also in line with previous results from the same

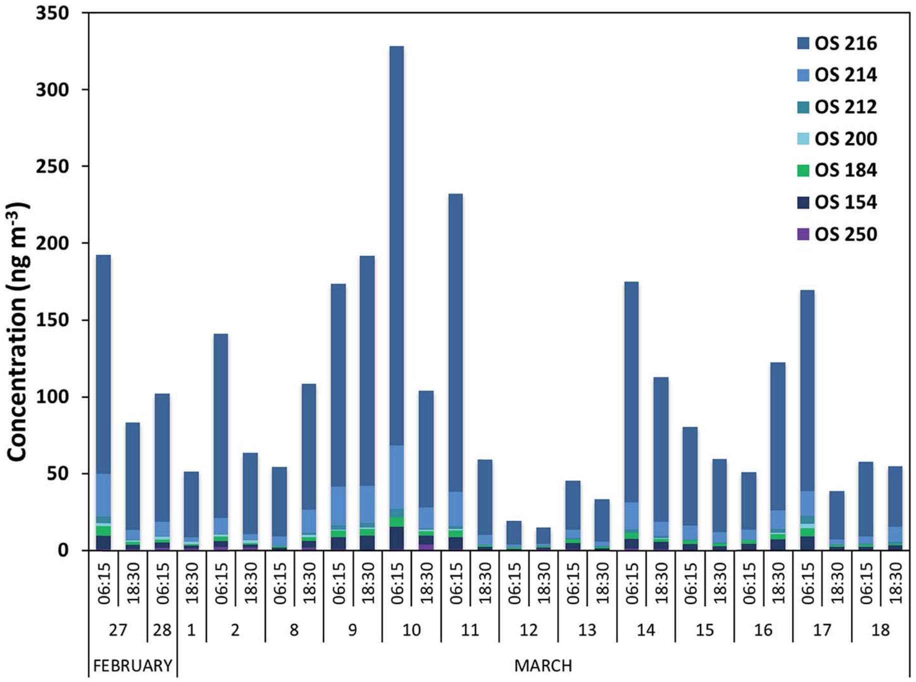

Fig. 2 Concentrations of OS in aerosol samples collected during the wet season (plotted according to local time). Note that the timeline is not continuous.

site during the wet season, where peak concentrations of isoprene oxidation products (2-methyl tetrols and methyl butene triols) were observed during afternoon hours, probably caused by the diurnal variation in isoprene emission and oxidation.[69] Isoprene-derived OS are formed locally or regionally during daytime, while during night-time there is less production and only loss processes (such as chemical reactions and particle deposition).

Fig. 4 also shows the average diurnal variation in the dry season of environmental parameters (relative humidity, RH, and temperature) and selected gases (ozone and nitric oxide + nitrogen dioxide, NO_x), as well as sulfate and OA measured by AMS. It is clear that sulfate, temperature and ozone all peak during daytime, while NO_x, and OA show lower concentrations in the morning and peak during night, probably due to a combination of boundary layer dynamics and dynamics of pollutant emission and advection from Manaus. In the dry season, OA concentrations are strongly affected by emissions from biomass burning,[28] while the effect on organosulfate concentrations is expected to be minimal, as biomass burning aerosols are typically less acidic.[74]

During the dry season the correlations between IEPOX OS and other OS were not as high as observed in the wet season. Only the coefficient of determination (R^2) between IEPOX OS and OS 214 (also from isoprene) was larger than 0.5, while R^2 for correlations of IEPOX OS with acetone sulfate, acetic acid sulfate, OS 184 and OS 200 were in the range 0.3–0.45 (see Table S2†). The correlation between IEPOX OS and sulfate is high during both the wet season ($R^2 = 0.50$) and the dry season ($R^2 = 0.69$), while the correlations between sulfate and other OS are lower (R^2 in the range 0.1–0.4). The correlation between OA and all OS species is also lower during the dry season (R^2 below 0.25).

There is a notable change regarding OS 200, which showed no correlation with IEPOX OS in the wet season but had $R^2 = 0.6$ in the dry season. Interestingly, OS 200 actually shows better correlation with all other OS and MBTCA than IEPOX OS does. Since OS 200 can also be formed from isoprene ozonolysis (in addition to being a product of 2-methylglyceric acid), this is in line with a somewhat larger influence of isoprene ozonolysis during the sampling period in the dry season (18 ± 14 ppbv ozone) than in the wet season (10.4 ± 6.6 ppbv ozone).

3.4 Contribution of organic sulfate to total sulfate

The observed contributions of organic sulfate to total sulfate are generally much higher than in most previous studies showing 0–16%.[39–41,53] Organic sulfate constituted on average 19 ± 10% of total sulfate concentration measured by AMS during the wet season (range 7–37%) and 19 ± 8% of total sulfate (3–42%) during the dry season. The average contributions and ranges were thus similar during the two periods.

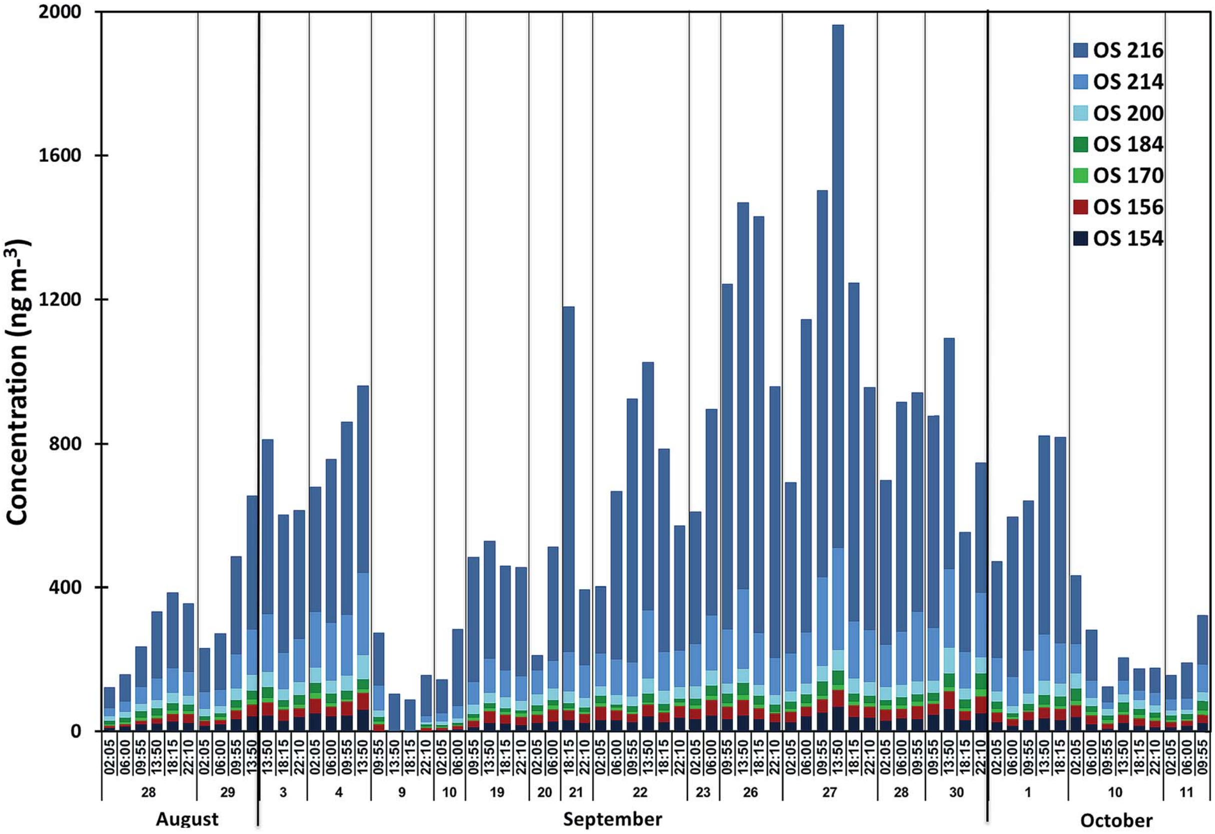

Fig. 3 Concentrations of OS in samples collected during the dry season (plotted according to local time). Note that the timeline is not continuous.

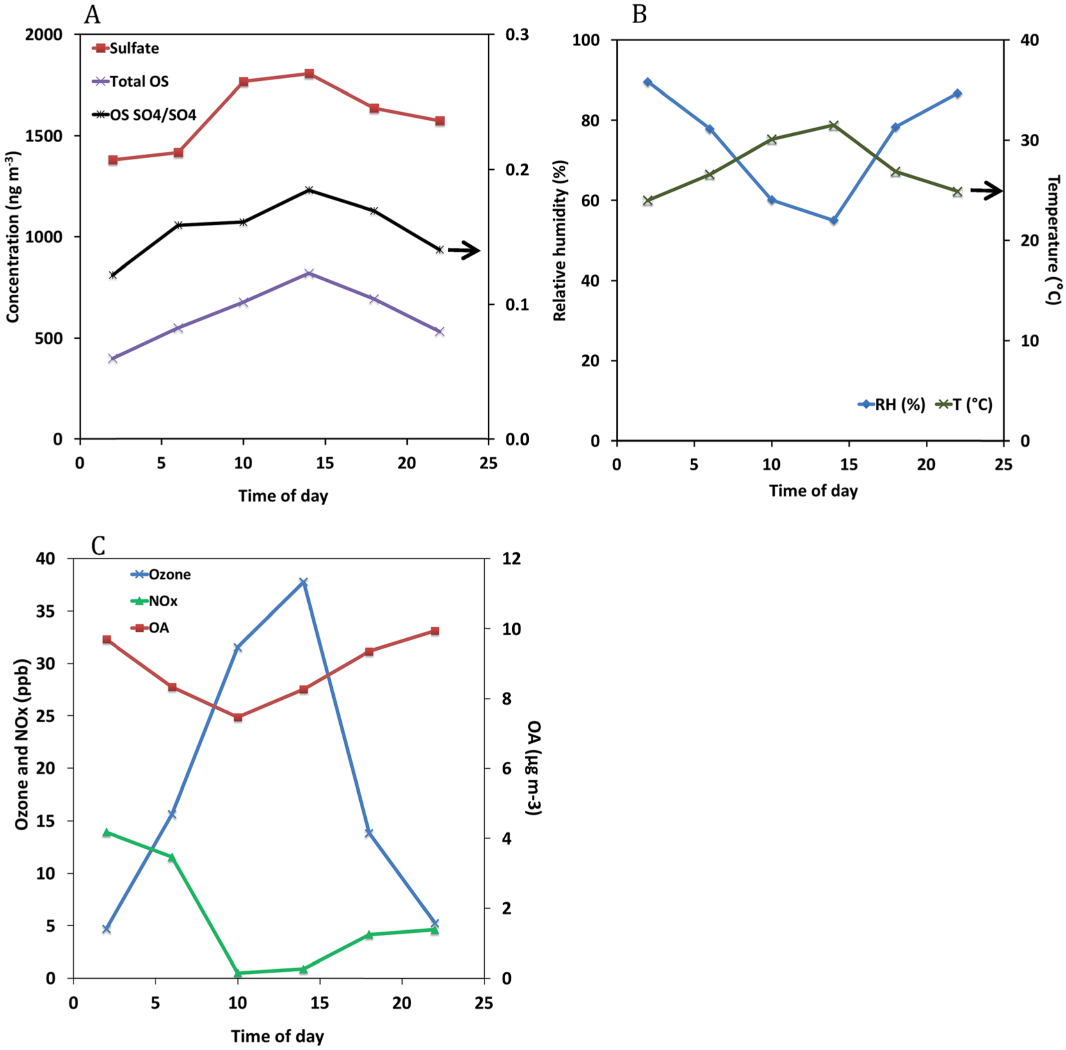

Fig. 4 Average diurnal variations during dry season of (A) total sulfate, total organosulfates (total OS), and the ratio of OS sulfate to total sulfate, and (B) relative humidity (RH) and temperature (*T*), as well as (C) ozone, NO_x, and OA. Note that the data only includes time periods where samples in the current study were collected.

In the southeastern US, another region with high isoprene emissions, isoprene-derived OS sulfate constituted only about 4.4% of total sulfate during summer.[53] During the wet season in the present study sulfate was much lower (0.27 ± 0.14 μg m^{-3}) compared to the southeastern US study (1.9 ± 1.2 μg m^{-3}), while levels of isoprene-derived OS were more similar (average concentration of 104 ng m^{-3} during the wet season compared to 181 ng m^{-3} in the southeastern US). On the other hand, during the dry season the concentration of total sulfate (1.6 ± 0.9 μg m^{-3}) was similar to the previous study in the US, but higher concentrations of isoprene-derived OS (610 ± 400 ng m^{-3}) were observed in the Amazon, indicating a factor of ~4 higher contribution of organic sulfate to total sulfate in our samples during the dry season.

A study in Northern Europe (during winter) found OS from monoterpenes and alkanes at higher levels than in the present study, while sulfate levels were in the same range (0.2–6 μg m^{-3}, average 1.9 ± 1.6 μg m^{-3}) yielding an overall OS to total sulfate ratio of only 1.4 ± 0.9%.[41] This shows that besides sulfate concentration, other variables such as precursor reactivity, particle pH and coating, as well as RH, influence formation of organosulfates. Furthermore, low NO_x levels means that HO_2 reaction pathways and peroxide chemistry are relatively more important in the Amazon region compared to previously investigated areas. This difference in photochemical oxidation pathways may also have implications for organosulfate formation.

Sulfate from isoprene-derived OS showed a clear association with inorganic sulfate during both the wet and the dry season (Fig. 5). The slope of the least squares regression line (not shown) is 0.17 ± 0.05 for IOP1 and 0.17 ± 0.02 for IOP2. The correlation of OS sulfate with inorganic sulfate was notable with $R^2 = 0.35$ during the wet season and $R^2 = 0.51$ in the dry season (both statistically significant with p-values < 0.01). During the wet season high OS concentrations often occur coincident with high OA levels (Fig. 5 and S3†), while the correlation between total OS and OA ($R^2 = 0.30$) is lower than for OS and inorganic sulfate (yet still significant with $p < 0.01$). The correlations indicate that both sulfate and OA may influence the formation of organosulfates during the wet season, when the atmospheric trace composition is more pristine. An association between OS and OA is not observed during the dry season (Fig. 5 and S3†), possibly due to the influence of additional OA from other sources. Correlation analyses did not identify other significant parameters affecting the formation of organosulfates. This included NO_x, ozone, temperature and RH.

The organic moiety of organosulfates contributed on average more than 3% to OA during both seasons. The average contribution was 3.5 ± 1.9% (range 0.8–7.3%) during the wet season, and 5.1 ± 2.5% (range 0.8–10.7%) during the dry season. This is also influenced by meteorological factors, as Fig. 1 shows that the sampling site was more often directly in the plume of Manaus during the dry season. The highest contributions of organosulfates to OA were observed during daytime, when organosulfate concentrations typically peaked.

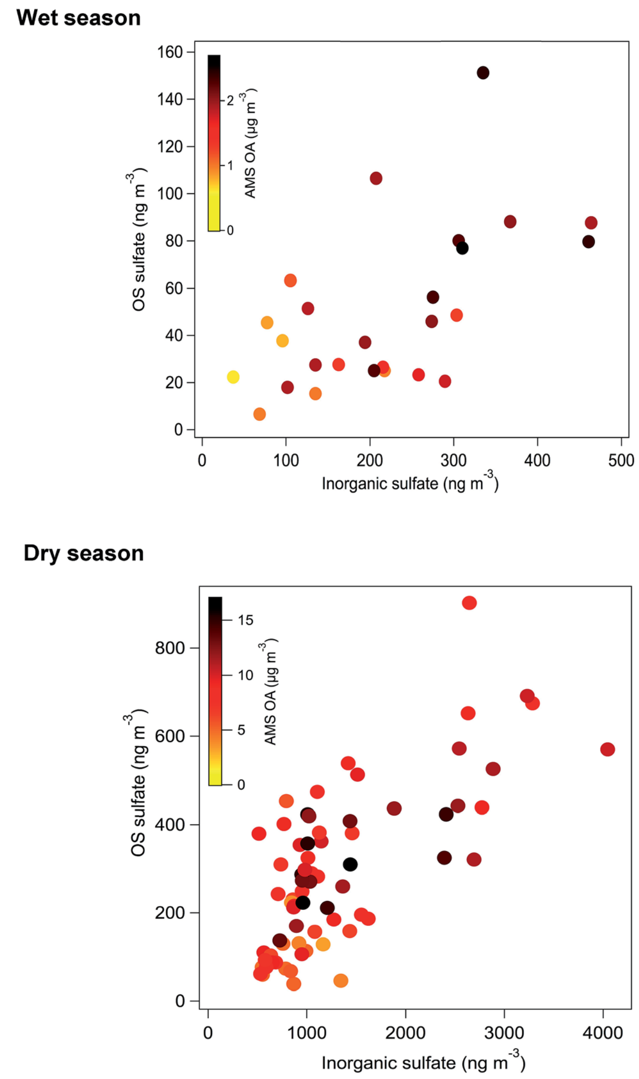

Fig. 5 Concentration of sulfate from isoprene-derived OS plotted against inorganic sulfate and colored according to concentration of organic PM_1 (AMS OA). Note the different scales for the two seasons.

Formation of organosulfates through heterogeneous reactions has been shown in laboratory studies to depend on availability of acidic sulfate aerosols and their coating with SOA.[20,21] At low RH (15%) the reactive uptake of IEPOX onto ammonium bisulfate particles is suppressed by coating with a-pinene SOA, while the influence of SOA coating is minimal at 50% RH.[21] Reactive uptake of IEPOX is thus expected to be less sensitive to SOA coating of sulfate aerosols in tropical regions where high relative humidity (>50% RH) is often observed. In the current study, air humidity was 74 ± 15% RH during the dry season and 81 ± 5% RH during the wet season.

The acidity of sulfate aerosols is a key factor for reactive uptake of IEPOX.[75] Measurements during the dry season showed that ammonium contained in aerosol particles was not sufficient to neutralize the particulate sulfate and nitrate.[76] A recent modeling study also suggests that the aerosol was highly acidic during the wet season of GoAmazon2014/5.[77]

Furthermore, uptake of IEPOX increases with increasing particle surface area.[75,78] The influence of particle liquid water content (LWC) is complex, since higher LWC can increase aqueous phase processes and surface area, but also dilutes aerosol acidity and nucleophile (sulphate ion) concentration, reducing heterogeneous reactive uptake.[79–81] Another yet uninvestigated factor is the possibility of aqueous phase oxidation of HSO_3^- by peroxides of isoprene, analogous to the mechanism suggested for peroxides from monoterpenes, which also was observed to form organosulfates.[82]

The very high organic sulfate to total sulfate ratio observed in the Amazon compared to other investigated sites globally can thus be explained by availability of reactive organic precursors (such as IEPOX) and presence of acidic sulfate aerosols at high relative humidity.

Overall, the results of the present study are relevant for understanding SOA formation in other regions in the tropics where highly urbanized settings coincide with high emissions of biogenic volatile organic compounds (VOC). It is especially important to further investigate the effect of sulfate aerosols, typically from combustion of fossil fuels but also from oxidation of naturally occurring DMS, for SOA formation in these regions, including effects on human health and regional climate. A better understanding of aerosol sources and formation processes will also lead to development of the most efficient mitigation measures.

4. Conclusion

In the present work we have investigated formation of organosulfate aerosol downwind of an urbanized region in the Amazon forest. The results show a high level of organosulfates derived from isoprene, which correlates well with concentration of total sulfate measured by AMS. On average, organic sulfate makes up 19 ± 10% of total sulfate during the wet season and 19 ± 8% during the dry season. Organosulfates also contribute to 3.5 ± 1.9% of organic matter in aerosols during the wet season and 5.1 ± 2.5% during the dry season. Additional analyses of molecular tracers and modeling studies are needed to improve our understanding of the formation of isoprene SOA and other sources of organic aerosols in general in the region. The findings of the present work show that acidic sulfate aerosols can critically affect SOA processes in tropical and sub-tropical areas with high emissions of isoprene. Increasing SO_2 emissions may thus lead to a substantial increase in SOA formation from biogenic isoprene in tropical forested regions.

Conflicts of interest

5

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