Chemical composition of isoprene SOA under acidic and non-acidic conditions: Effect of relative humidity

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Abstract. The effect of acidity and relative humidity on bulk isoprene aerosol parameters has been investigated in several studies, however few measurements have been conducted on individual aerosol compounds. While the focus of this study has been the examination of the effect of acidity and RH on secondary organic aerosol (SOA) chemical composition from isoprene photooxidation in the presence of NOx, a detailed characterization of SOA at the molecular level have been also conducted. Experiments were conducted in a 14.5 m^3 smog chamber operated in flow mode. Based on a detailed analysis of mass spectra obtained from GCMS of silylated derivatives in EI and CI modes, and UPLC/ESI/QTOF HRMS, and collision-induced dissociation in the positive and negative ionization modes, we characterized not only typical isoprene products, but also new oxygenated compounds. The analysis showed the presence of methylthreonic acids (mTr) and methyltartaric acids (mTA), proposed recently by our groups as isoprene aging SOA markers. Furthermore, a series of organosulfates (OSs) were tentatively identified including 2mTr-OS, 2mTA-OS and 2mTA nitroxy-OS. Under acidic conditions, the major identified compounds include 2-methyltetrols (2mT), 2-methylglyceric acid (2mGA) and 2mT-OS. Other products identified include epoxydiols, mono- and dicarboxylic acids, OSs, and nitroxy- and nitrosoxy-OSs. The contribution of SOA products from isoprene oxidation to $PM_{2.5}$ was investigated by analyzing ambient aerosol collected at rural sites in Poland. mTs, mGA and several organosulfates and nitroxy-OS were detected in both the field and laboratory samples. The influence of RH on SOA formation was modest in non-acidic seed experiments. Total SOC decreased with increasing RH. The yields of most compounds decreased, but the concentrations of 2mTA, IEPOX-OS, 2mGA-OS and 2mTr-OS increased with increasing RH. Some components followed this pattern while other were more abundant in non-acidic experiments or behaved in a mixed way, depending on RH.

Keywords: Isoprene, relative humidity, acidity, SOA, organosulfates

1 Introduction

Secondary organic aerosol (SOA), which is formed through complex physico-chemical reactions of volatile organic compounds (VOCs) emitted into the atmosphere from biogenic and anthropogenic sources, constitutes a great part of the continental aerosol mass (Guenther et al., 1995; Goldstein and Galbally, 2007). Isoprene (ISO) is the most abundant non-

5   methane hydrocarbon emitted to the atmosphere. Although its SOA formation yield is low, its high emission can contribute substantially to high organic aerosol loading. As a result, it is one of the most studied compounds emitted into the atmosphere (Guenther et al., 1995; Henze and Seinfeld, 2006; Fu et al., 2008; Carlton et al., 2009; Hallquist et al., 2009). The primary removal of ISO in the atmosphere is through the gas-phase reactions with hydroxyl radicals (OH), nitrate radicals (NO_3) and ozone (O_3) which result in the formation of numerous oxidized SOA components, including 2-

10   methyltetrols, 2-methylglyceric acid, C_5-alkene triols and C_4/C_5 organosulfates (OSs). These compounds were identified in ambient $PM_{2.5}$ (particulate matter with diameter < 2.5 μm) in several places around the world while SOA generated from isoprene was reported to account for up to 20 – 50% of the overall SOA budget (Clayes et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).

Over the last 15 years, intensive research has been conducted to study the contribution of isoprene oxidation to SOA

15   formation in the ambient atmosphere. The formation of isoprene SOA was controlled by various factors, mainly the aerosol acidity (Edney et al., 2005; Kleindienst et al., 2006; Surratt et al., 2007a, 2010; Jaoui et al., 2010; Szmigielski et al., 2010; Lewandowski et al., 2015; Wong et al., 2015), air humidity (RH) (Nguyen et al., 2011; Zhang et al., 2011; Lewandowski et al., 2015) and NO_x concentration (Kroll et al., 2006; Chan et al., 2010). In addition, a number of smog chamber experiments revealed that the yield of isoprene SOA increased under acidic conditions in part due to the enhanced formation of isoprene-

20   derived oxygenates, including organosulfates, through acid-catalyzed reactions (Surratt et al., 2007b, 2008, 2010; Gomez-Gonzalez et al., 2008; Offenberg et al., 2009). Chemical mechanisms have been proposed to rationalize these transformations (Hallquist et al., 2009). Key formation pathways included the ISO photooxidation in the presence of OH radicals under low-NO_x or high-NO_x conditions that produced oxygenated compounds, mostly epoxydiols (IEPOX), followed by their uptake into the particle phase and acid-catalyzed reactions therein. Recent laboratory results show that the

25   latter reactive uptake significantly depends on the acidity of the particle phase (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Gaston et al., 2014; Riedel et al., 2015). In addition, early smog chamber studies on isoprene ozonolysis by Jang et al. (2002) and Czoschke et al. (2003) showed enhanced SOA yields in the presence of acidified aerosol seeds.

Atmospheric organosulfates formed from various precursors are significant components of fine particulate matter (Surratt et al., 2008; Froyd et al. 2010; Stone et al., 2012; Tolocka and Turpin, 2012). The most common in the atmosphere

30   and investigated were organosulfates derived from the oxidation of ISO that were identified both in smog chamber experiments and in field studies. For many of these polar oxygenated compounds, chemical structures, MS fragmentation patterns and formation mechanisms have been tentatively proposed. The commonly detected components of ISO SOA attributed to processing of isoprene oxidation products such as IEPOX, methacrolein (MACR) and methyl vinyl ketone

(MVK), have the following MWs: 154, 156, 184, 198, 200, 212, 214, 216, 260, 334 (Surratt et al., 2007b, 2008, 2010; Gomez-Gonzalez et al., 2008; Kristensen et al., 2011; Zhang et al., 2011; Shalamzari et al., 2013; Schindelka et al., 2013; Nguyen et al., 2014; Hettiyadura et al., 2015; Riva et al., 2016). The mechanisms of organosulfate formation were proposed for the conditions of either acidified or non-acidified sulfate aerosol seeds (e.g. 2-methyltetrol OSs proposed respectively by

5   Kleindienst et al. (2007) and Riva et al. (2016)). Whereas Kleindienst et al. (2006) reported the formation of highly oxygenated products through OH radical oxidation, Riva et al. (2016) proposed an alternative route through acid-catalyzed oxidation by organic peroxides. Isoprene organosulfates were also reported to occur in the aqueous-phase through the photooxidation or dark reactions of isoprene in aqueous solutions containing sulfate and sulfite moieties (Rudzinski et al., 2004, 2009; Noziere et al., 2010). A detailed mechanism of this transformation has been tentatively proposed based on chain

10   reactions propagated by sulfate and sulfite radical anions (Rudzinski et al., 2009) and confirmed by mass spectrometric studies (Szmigielski, 2016). The acid-catalyzed formation of 2-methyltetrols was also suggested in aqueous phase oxidation of ISO with H_2O_2 (Claeys et al., 2004b).

      To date, only a few studies involving smog chamber experiments have examined the effect of relative humidity on the formation of isoprene SOA (Dommen et al., 2006; Nguyen et al., 2011; Zhang et al., 2011; Lewandowski et al., 2015).

15   However, the impact of RH may be important as it may affect the mechanism of SOA formation and hence the chemical composition, physical properties and yield of SOA (de P. Vasconcelos et al., 1994; Poulain et al., 2010; Guo et al., 2014). The chamber studies conducted by Dommen et al. (2006) and Nguyen et al. (2011) showed no effect of RH on the SOA formation in photooxidation of isoprene in the absence of sulfate aerosol seeds. However, subsequent studies revealed that isoprene SOA formation under high-NO_x conditions in the presence of acidified and non-acidified sulfate aerosol seeds

20   decreased as the RH increased, while the formation of organosulfates was enhanced (Zhang et al., 2011; Lewandowski et al., 2015). The latter observation can be explained by transformation of ISO propagated by sulfate/sulfite radical-anions in the aqueous particle phase or on the aqueous surface of aerosol particles (Zhang et al., 2011; Rudzinski et al., 2016; Szmigielski, 2016). The results obtained in the smog chamber experiments are not compatible with modelling predictions that ISO SOA yield would increase under humid conditions (Couvidat et al., 2011).

25   A recent study conducted in our laboratory focused on the effects of relative humidity on bulk SOA formation (e.g. SOC) from ISO photooxidation in the presence of NO_x (Lewandowski et al., 2015). These authors showed that humidity can have a profound effect on the acid-derived enhancement of isoprene SOC, while high content of aerosol water suppresses enhanced SOC formation by ISO photochemistry. In the present study, the main focus is to investigate at the molecular level the role of relative humidity on the chemical composition of isoprene SOA obtained under conditions of

30   acidic and non-acidic seed aerosol. Two techniques developed in our laboratories were used: (1) analysis of organosulfate compounds based on LC/MS (Szmigielski, 2016, Rudzinski et al., 2009) and (2) analysis of non-sulfate compounds based on derivatization techniques followed by GC-MS analysis (Jaoui et al., 2004). In this study, we have explored the RH effect of a wide range on isoprene polar oxygenated products, including, 2-methyltetrols, 2-methylglyceric acid, IEPOX, organosulfates (OSs), nitroxy-organosulfates (NOSs) and other oxygenates in the presence of acidified and non-acidified sulfate aerosol

seeds. In addition, a similar chemical analysis of PM$_{2.5}$ field samples was carried out to assess the possible link between this laboratory study and ambient SOA formation.

2 Experimental

ISO and the derivatizing agent BSTFA (*N,O*-bis(trimethylsilyl) trifluoroacetamide) with 1% trimethylchlorosilane
5   as catalyst were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) at the highest purity available and were used without further purification. Solvents with GC^2 quality were purchased from Burdick and Jackson (Muskegon, MI, USA).

2.1 Smog chamber experiments

Smog chamber experiments were conducted in a stainless-steel, fixed 14.5 m^3 volume chamber with interior walls fused with a 40-µm PTFE Teflon coating. Details of chamber operation, sample collection, derivatization procedure, and gas
10   chromatography–mass spectrometry (GC-MS) analysis method are described in more detail in Lewandowski et al. (2015). A combination of UV-fluorescent bulbs was used in the chamber as source of radiation from 300-400 nm with a distribution similar to that of solar radiation (Kleindienst et al., 2006). The reaction chamber was operated as a flow reactor with a residence time of 4 h, to produce a steady-state, constant aerosol distribution which could be repeatedly sampled at different seed aerosol acidities.

15   Two sets of experiments were conducted (Table 1) to explore the effect of humidity and acidity on isoprene SOA products. The ER667 experiment was conducted at 4 different humidity levels in the presence of ISO, NO$_x$ and ammonium sulfate as seed aerosol (1 µg m^{-3}). It provided as a base case for exploring the changes and nature of SOA products in the absence of significant aerosol acidity. The second experiment (ER662) was similar but run in the presence of a moderately acidic sulfate aerosol at constant concentration. They included 5 and 4 stages differing in humidity levels for ER667 (9%;
20   19%; 30%; 39%; and 49%) and ER662 (8%; 18%; 28%; and 44%) respectively. ISO was produced in a high pressure cylinder diluted with nitrogen (N$_2$). ISO and NO were added to the chamber through flow controllers. Temperature for all stages in the experiments was set to about 27 °C. Dilute aqueous solutions of ammonium sulfate and sulfuric acid as inorganic seed aerosol were nebulized to the chamber with total sulfate concentration of the combined solution held constant in order to maintain stable inorganic concentrations in the chamber (Lewandowski et al., 2015). NO and total NO$_x$ were
25   measured with a ThermoElectron (Model 8840, Thermo Environmental, Inc., Franklin, MA) oxides of nitrogen chemiluminescence analyzer. Temperature and relative humidity were measured with an Omega Digital Thermo-Hydrometer (Model RH411, Omega Engineering, Inc., Stamford, CT). Chamber ISO concentrations were measured using a gas chromatograph with flame ionization detection (Hewlett-Packard, Model 5890 GC). Chamber O$_3$ was measured with a Bendix ozone monitor (Model 8002, Lewisburg, WV, USA).

30   Chamber filter samples were collected for SOA products analysis at 16.7 L min^{-1} using 47-mm glass fiber filters (Pall Gelman Laboratory, Ann Arbor, MI, USA). After sample collection, filters were sonicated for 1 hour with methanol.

Prior to extraction, 20 µg each of *cis*-ketopinic acid and d_{50}-tetracosane were added as an internal standard (IS). The filter extracts were then dried and derivatized with 200 µL BSTFA and 100 µL pyridine, after which samples were heated at 70 °C to complete the reaction (Jaoui et al., 2004). Smog chamber filters as derivatized extracts were analyzed by GC-MS using a ThermoQuest (Austin, TX, USA) GC coupled with an ion trap mass spectrometer. The injector, heated to 270 °C, was

5   operated in splitless mode. Compounds were separated on a 60-m-long, 0.25-mm-i.d. RTx-5MS column (Restek, Inc., Bellefonte, PA, USA) with a 0.25-µm film thickness. The GC oven temperature program for the analysis started isothermally at 84 °C for 1 min followed by a temperature ramp of 8 °C min^{-1} to 200 °C, followed by a 2 min hold, then 10 °C min^{-1} to 300 °C and a 15-min hold. The ion source, ion trap, and interface temperatures were 200, 200, and 300 °C, respectively. Mass spectra were collected in both the chemical ionization (CI) and electron ionization (EI) modes (Jaoui et al., 2004). A

10   semi-continuous organic carbon/elemental carbon (OC/EC) instrument developed by Sunset Laboratories was used to measure organic carbon of the aerosol. The aerosol sample is collected onto a quartz filter positioned within the oven housing. Prior to the quartz filter, a carbon-strip denuder was placed in line to remove gas-phase organic compounds in the air stream which could interfere with the measurement. Analysis of the aerosol was made using a thermal optical technique, and a description of this instrument have previously been discussed by Kleindienst et al. (2006).

2.2 Ambient aerosol samples

Ambient fine aerosol samples ($PM_{2.5}$) were collected onto pre-baked quartz-fiber filters using a high-volume aerosol samplers (DH-80, Digitel) at the regional background monitoring station in Zielonka, located in the Kuyavian-Pomeranian Province in the northern Poland (53°39'N, 17°55'E) during the 2016 summer campaign, and at the regional

20   background monitoring station in Godow, located in the Silesian Province in southern Poland (49°55'N 18°28'E) in summer 2014. At both sites, strong emission of isoprene occurred. The Zielonka station is located in the forested rural area while the Godow station is located near a coal-fired power station in Detmarovice (Czech Republic) and close to big industrial cities of the Silesian agglomeration (Poland). Therefore, SOA collected in Godow can be influenced by anthropogenic aerosol precursors. The relative humidity level during sampling in Zielonka was 86%, SO_2 emission was estimated at 0.6 µg/m^3 and

25   OC value was 1.68 µg/m^3. The relative humidity level during sampling in Godow was 94%, SO_2 emission was estimated at 3.0 µg/m^3 (approximate value from the nearest sampling station - Zory) and OC value was 5.43 µg/m^3. Both locations were influenced by NO_x emission – slightly in Zielonka at 1.3 µg/m^3 and 30.0 µg/m^3 in Godow (approximate value from the nearest sampling station - Zywiec).

2.3 Sample preparation and LC-MS analysis

30   High-purity water (resistivity 18.2 MΩ·cm^{-1}) from a Milli-Q Advantage water purification system (Merck, Poland) was used for the reconstitution of aerosol extracts and preparation of the LC mobile phases. High purity methanol (LC-MS

ChromaSolv-Grade) used for extraction of SOA filters, reconstitution of aerosol extracts and preparation of the LC mobile phase was purchased from Sigma-Aldrich, Poland.

From each filter, two 1 cm^2 punches were taken and extracted twice with 15 mL aliquots of methanol using a Multi-Orbital Shaker (PSU-20i, BioSan). Each extraction lasted 30 minutes. Two extracts were combined and concentrated using a rotary evaporator (Rotavapor® R215, Buchi) to approx. 1 mL volume, then filtered with disposable 0.2 µm PTFE syringe filters and taken to dryness under a gentle stream of nitrogen at ambient temperature. The residues were reconstituted with 180 µL of 1:1 high purity methanol / water mixture (v / v), shaken for 1 minute and analyzed with UPLC / ESI (-) QTOF HRMS equipment consisting of a Waters Acquity UPLC I-Class chromatograph coupled with a Waters Synapt G2-S high resolution mass spectrometer. The chromatographic separations were performed using a Acquity HSS T3 column (2.1×100 mm, 1.8 µm particle size) at ambient temperature. The mobile phases were 10 mM ammonium acetate (eluent A) and methanol (eluent B). To obtain appropriate chromatographic separations and responses, a gradient elution program 13 minutes long was applied. The concentration of eluent B was 0 % for the first 3 min, increased to 100 % from 3 to 8 min, was held at 100 % from 8 to 10 min, and then decreased back to 0 % from 10 to 13 min. The initial and final flow rate was 0.35 mL/min and from 3 to 10 min was 0.25 mL/min. The sample injection volume was 0.5 µL. The Synapt G2-S spectrometer was equipped with an ESI source, which was operated in the negative ion mode. Optimal ESI source conditions were 3 kV capillary voltage, 20 V sampling cone and 20000 FWHM mass resolving power. The high resolution mass spectra were recorded from 50 to 600 *m/z* in MS or MS/MS modes. All data were recorded and analyzed with a Waters MassLynx V4.1 software package. During the analyses, the mass spectrometer was continuously calibrated by injecting leucine enkephalin (a reference compound) directly into the ESI source.

3 Results and discussion

3.1 Chemical characterization

Table 1 shows the steady state conditions for all stages of the smog chamber experiments, including the values determined for carbon yield, Secondary Organic Carbon (SOC) and organic mass to carbon mass ratio (OM/OC). The data indicate that with increasing RH, the formation of SOC and carbon yield was reduced, both under acidic and non-acidic conditions. The results obtained are consistent with those of Zhang et al. (2011). Secondary organic aerosol formed under non-acidic conditions was additionally analyzed for OM/OC and SOA yield. The average OM/OC ratio was 1.92 ± 0.13 and the average laboratory SOA yield measured in this experiment was 0.0032 ± 0.0004. The values of SOA yields agree with previous smog chamber studies (Edney et al., 2005; Kroll et al., 2006; Dommen et al., 2006; Surratt et al., 2007; Zhang et al., 2011).

Table 1. Initial and steady state conditions, yields and OM/OC data for smog chamber experiments on isoprene photooxidation in the presence of acidic and non-acidic seed aerosol.

Experiment ER662: Acidic seed aerosol (½ ammonium sulfate, ½ sulfuric acid by sulfate mass in precursor solution)

	Stage 1	Stage 2	Stage 3	Stage 4
RH (%)	8	28	44	18
Temperature (C)	27.0	27.3	26.9	27.5
Initial Isoprene (ppmC)	6.82	6.92	7.01	7.03
Initial NO (ppm)	0.296	0.296	0.296	0.296
Steady state conditions				
O_3 (ppm)	0.303	0.292	0.245	0.339
NO_x (ppm)	0.220	0.213	0.205	0.234
ΔHC ($\mu g\ m^{-3}$)	3266	3318	3357	3472
Carbon Yield	0.011	0.003	0.001	0.005
SOC ($\mu gC\ m^{-3}$)	32.3	7.9	3.8	15.7

Experiment ER667: Non-acidic seed aerosol (ammonium sulfate)

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
RH (%)	9	19	30	39	49
Temperature (C)	28.2	28.5	27.9	27.8	27.6
Initial Isoprene (ppmC)	8.11	8.29	8.25	8.25	8.19
Initial NO (ppm)	0.347	0.347	0.347	0.347	0.347
Steady state conditions					
O_3 (ppm)	0.331	0.305	0.329	0.393	0.281
NO_x (ppm)	0.260	0.247	0.241	0.229	0.226
ΔHC ($\mu g\ m^{-3}$)	3518	3556	3558	3515	3484
SOA yield	0.007	0.004	0.002	0.002	0.001
Carbon Yield	0.004	0.002	0.001	0.001	0.001
SOC ($\mu gC\ m^{-3}$)	13.3	7.7	4.6	3.2	3.5
OM/OC	1.96	2.00	2.02	2.03	1.59

The analysis of isoprene SOA from smog chamber experiments and field samples was based on the interpretation of
5   mass spectra of the derivatized (as silylated derivatives) and the underivatized ISO SOA products using GCMS (in EI and
CI) and LC-MS (in negative ion mode with electrospray ionization (ESI)), respectively. BSTFA react with each -COOH and
-OH groups of the compounds to produce a [-Si(CH$_3$)$_3$] moiety for each reactive hydrogen atom. The common characteristic
ions for all BSTFA derivatives are m/z 73, 75, 147, and 149. The adduct ions from the derivatives included m/z: $M^{+\bullet} + 73$,
$M^{+\bullet} + 41$, $M^{+\bullet} + 29$, and $M^{+\bullet} + 1$ while the fragment ions included m/z: $M^{+\bullet} - 15$, $M^{+\bullet} - 73$, $M^{+\bullet} - 89$, $M^{+\bullet} - 117$, $M^{+\bullet} - 105$,

$M^{+\bullet} - 133$, and/or $M^{+\bullet} - 207$ (Jaoui et al., 2004). The LC-MS analyses were used to identify organosulfates, nitroxy- and nitrosoxy-organosulfates. The compounds were recognized by deprotonated ions $[M - H]^-$ and the corresponding fragmentation pathways evaluated by MS/MS analyses. Organosulfates were recognized by the loss of characteristic ions of m/z: 80 (SO_3^-), 96 (SO_4^-) and 97 (HSO_4^-). The nitroxy-organosulfates and nitrosoxy-organosulfates were recognized based

5   on additional neutral losses of m/z 63 (HNO_3) and m/z 47 (HNO_2), respectively. Table 2 presents the list of compounds tentatively identified in the present study along with proposed structures, molecular weights (MWs) and main fragmentation ions (m/z). 2-Methylerythronic acid, 2-methylthreonic acid, and 2-methyltartaric acid are reported by our group to be markers for ISO aging process recently (Jaoui et al., 2018). To our knowledge, organosulfate (MW 230), 2-methyltartaric acid organosulfate (MW 244) and 2-methyltartaric acid nitroxy-organosulfate (MW 275) were identified for the first time.

Table 2. Products detected in SOA samples from smog chamber experiments using GC-MS and LC-MS.

GC-MS				
Chemical Formula	*m/z* BSTFA Derivative (methane-CI)	MW MW_BSTFA (g mol⁻¹)	Tentative Structure *	Nomenclature
$C_5H_{10}O_2$	247, 231, 157, 147, 73	102 246		3-methyl-3-butene-1,2-diol (C₅-diol-1)
$C_5H_{10}O_3$	263, 247, 173, 83, 73,	118 262		2-methyl-2,3-epoxy-but-1,4-diol (IEPOX-1)
$C_5H_{10}O_3$	263, 247, 173, 83, 73	118 262		2-methyl-3,4-epoxy-but-1,2-diol (IEPOX-2)
$C_4H_8O_4$	337, 321, 293, 219, 203	120 336		2-methylglyceric acid
$C_5H_{12}O_4$	409, 319, 293, 219, 203	136 424		2-methylthreitol
$C_5H_{12}O_4$	409, 319, 293, 219, 203	136 424		2-methylerythritol

Chemical Formula	m/z Main Ions	MW	Tentative Structure	Nomenclature
$C_5H_{10}O_5$	423, 393, 259, 191, 73	150 438		2-methylthreonic acid
$C_5H_8O_6$	481, 437, 335, 319, 73	164 452		2-methyltartaric acid
$C_8H_{14}O_7$	495, 321, 219, 203, 73	222 510		2-methylglyceric acid dimer

LC-MS

Chemical Formula	*m/z* Main Ions	MW (g mol⁻¹)	Tentative Structure *	Nomenclature
$C_5H_{10}O_6S$	197, 167, 97, 81	198		IEPOX-derived organosulfate
$C_4H_8O_7S$	199, 119, 97, 73	200		2-methylglyceric acid organosulfate
$C_5H_8O_7S$	211, 193, 113, 97	212		2(3*H*)-furanone, dihydro-3,4-dihydroxy-3-methyl-organosulfate
$C_5H_{10}O_7S$	213, 183, 153, 97	214		2,3,4-furantriol, tetrahydro-3-methyl-organosulfate
$C_5H_{12}O_7S$	215, 97	216		2-methyltetrol organosulfate
$C_5H_{10}O_8S$	229, 149, 97, 75	230		2-methylthreonic acid organosulfate

$C_5H_9O_9S$	243, 163, 145, 101	244		2-methyltartaric acid organosulfate
$C_5H_{11}NO_8S$	244, 226, 197, 183, 153, 97	245		2-methyltetrol nitrosoxy-organosulfate
$C_5H_{11}NO_9S$	260, 197, 183, 153, 97	261		2-methyltetrol nitroxy-organosulfate
$C_5H_9NO_{10}S$	274, 211, 193, 153, 97	275		2-methylthreonic acid nitroxy-organosulfate

* In the table only one possible isomer is shown.

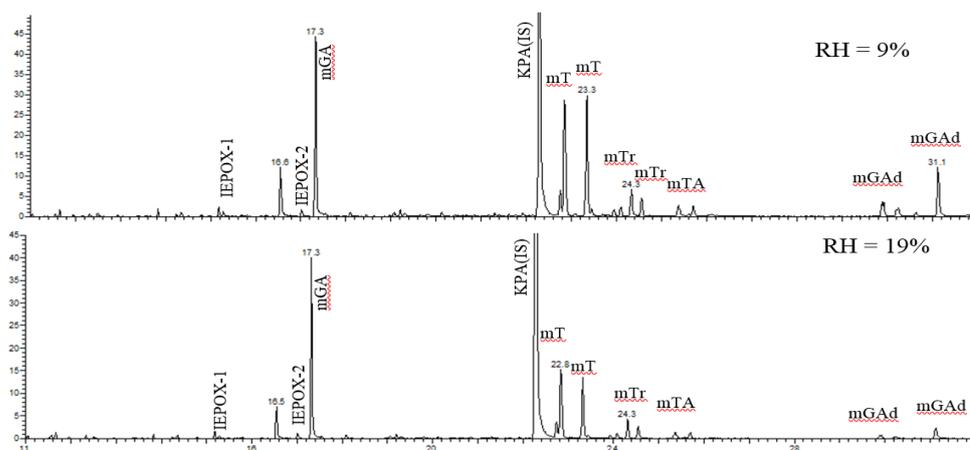
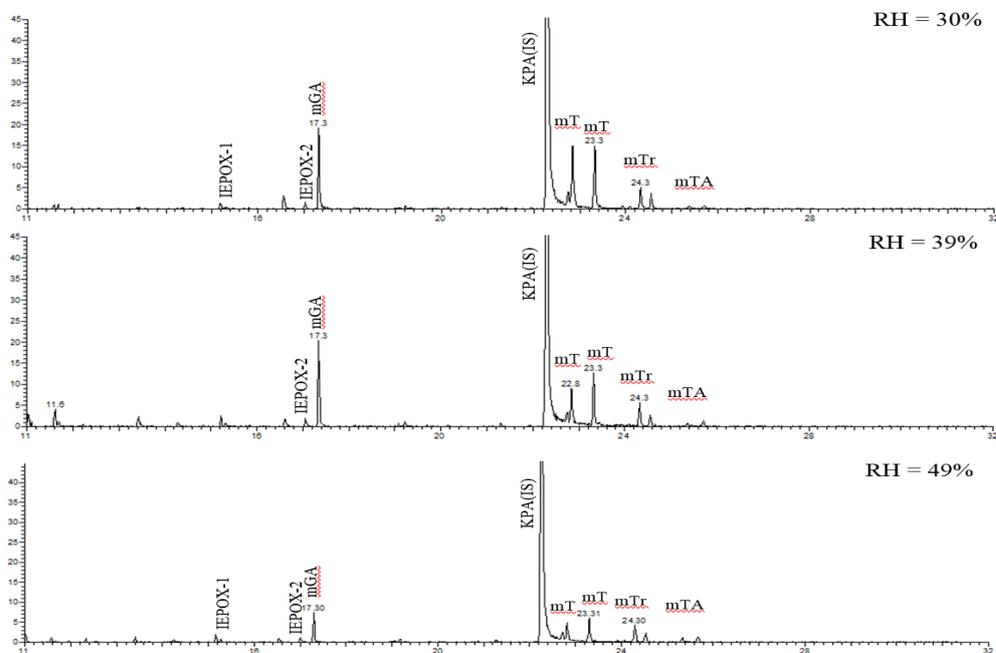



Figure 1. Extracted Ion Chromatograms (KPA: *m/z* 165; ketopinic acid (IS)); (IEPOX: *m/z* 173, 2 isomers), (mGA: 321; 2-methylglyceric acid), (mT: *m/z* 409; 2-methyltetrols, 4 isomers), (mTr: *m/z* 423; methylthreonic acids, 6 isomers), (mGA: *m/z* 495; 2-methylglyceric acid dimer, 3 isomers), (mTA: *m/z* 437; 2-methyltartaric acid, 2 isomers) for isoprene/NOx photooxidation experiments ER667 as a function of RH. Compounds detected as silylated derivatives. For clarity of the figure, not all isomers are shown.

Figure 1 presents GC-MS Extracted Ion Chromatograms (EIC) obtained for ER667 ISO non-acidic seed aerosol from photooxidation experiments at a wide range of relative humidities. According to attained chromatographic separations a number of isomers of analyzed compounds were distinguished, i.e. IEPOX-1 and IEPOX-2 or 4 isomers of 2-methyltetrols, however, only some of them are marked on the figure.

The formation of second generation compounds of ISO SOA such as 2-methyltetrols (mT) and 2-methylglyceric acid (2-mGA) is well documented in the literature. These compounds are isoprene SOA markers and were reported in many field measurements and smog chamber studies under low- and high-NOₓ conditions (Claeys et al., 2004a; Edney et al., 2005; Kroll et al., 2006; Surratt et al., 2006, 2010). The formation mechanism under low-NOₓ conditions has been explained by the reactive uptake of isoprene epoxydiols (IEPOX) onto acidic aerosol seeds (Paulot et al., 2009; Surratt et al., 2010) and under high-NOₓ conditions by the further oxidation of methacryloyl peroxynitrate (MPAN) (Chan et al., 2010; Surratt et al., 2010; Nguyen et al., 2015). Chemical mechanisms responsible for production of newly identified 2-methylerythronic acid, 2-methylthreonic acid and 2-methyltartaric acid are reported by Jaoui et al. 2018.

LC-MS analysis were focused mostly on the formation of the variety of organosulfates, nitroxy- and nitrosoxy-organosulfates, although compounds identified by GC-MS analysis (e.g. 2-methylglyceric acid, 2-methylglyceric acid dimer, 2-methyltetrols, 2-methyltartaric acid and 2-methyltreonic acid) were also observed in LC-MS measurement (data not presented in this manuscript). Mass spectra and proposed fragmentation pathways of newly identified components are

5   presented in section 3.4.

3.2 Effect of relative humidity and acidity on products formation

3.2.1 Non-acidic aerosol

Table 3 and Figures 2 – 3 present the estimated amounts of polar oxygenated products detected with GC-MS and LC-MS techniques in samples from ER667 photooxidation experiments with non-acidic aerosol seeds under various RH conditions. Eight products were quantified (as sums of respective isomers) based on the response factor of ketopinic acid using GS-MS. Nine other compounds were detected qualitatively using LC-MS, with chromatographic responses

15   representing the amounts of respective analytes. Therefore, the results should be understood as a tendency of product occurrence in the smog chamber experiments rather than the real amounts formed. Table 3 does not contain data on 2-methyltartaric acid organosulfate (MW 244) because it occurred in the samples merely in trace amounts.

Table 3. Estimated concentrations of reaction products (ng m^{-3}) from ER667 photooxidation experiments (neutral seed [H$^+$] = 54 nmol m^{-3}

20   air: Lewandowski et al., 2015).

	RH 9	RH 19	RH 30	RH 39	RH 49
GC-MS data *					
2-methylglyceric acid	379	255	155	171	70
2-methyltetrols	811	384	371	257	157
2-methylglyceric acid dimer	308	68	0	0	0
IEPOX-1	5	3	2	0	3
IEPOX-2	37	21	23	12	19
C$_5$-diol-1	9	6	3	0	0
2-methylthreonic acid	90	49	48	42	42
2-methyltartaric acid	31	15	9	5	21
LC-MS data **					
m/z [M – H]$^-$					
197	0.28	0.22	0.19	0.37	0.33
199	3.22	2.46	3.60	4.66	4.01
211	0.44	0.20	0.06	0.09	0

213	2.21	1.87	1.52	1.48	0.83
215	17.80	12.30	10.20	9.83	7.24
229	0.70	0.78	1.11	1.29	0.83
244	0.35	0.14	0	0	0.08
260	0.49	0.35	0.32	0.28	0.18
274	0.08	0.10	0.08	0.08	0.07

* MW as BSTFA derivative

** chromatographic responses of organosulfates [10^4]

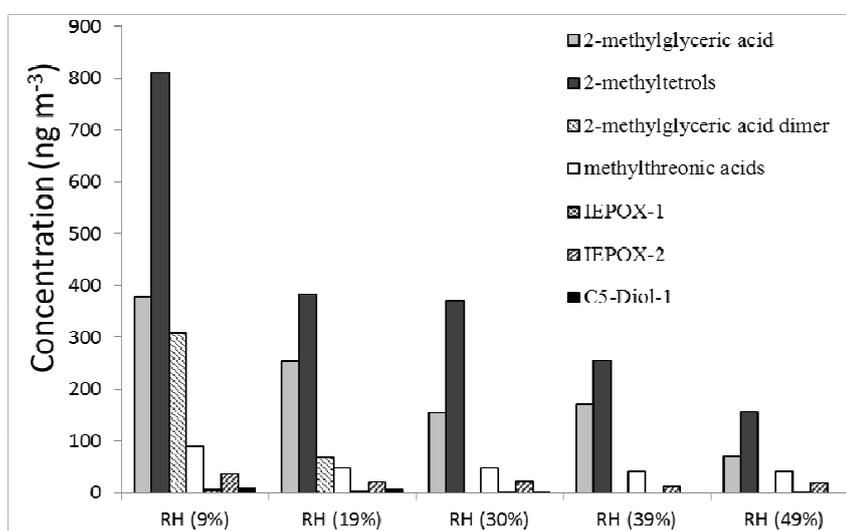



Figure 2. Concentrations of particle phase products from the non-acidic seed experiments (ER667) estimated with GC-MS.

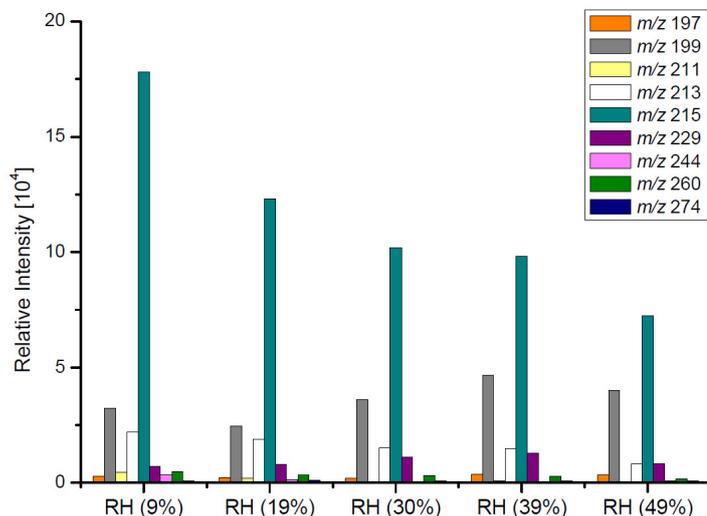



Figure 3. LC-MS chromatographic responses of OSs and NOSs from the non-acidic seed experiments (ER667).

The major SOA components detected were 2-methyltetrols, 2-methylgliceric acid and its dimer, whose maximal
5 concentrations exceeded 800, 350 and 300 ng/m³ respectively under low-humid conditions of RH 9% (Fig. 2). Among
compounds detected with LC-MS (Fig. 3), the most abundant were organosulfates derived from 2-methyltetrols (MW 216)
and 2-methylglyceric acid (MW 200). Other components were significantly less abundant. In most cases, increasing the RH
resulted in decreased yields of the products detected. Only a few compounds (2-methyltartaric acid, IEPOX-2, IEPOX-OS,
2-methylglyceric acid OS and 2-methylthreonic acid OS), deviated from the trend with the yields increased at medium and
10 high RH. Consequently, total SOC decreased with RH (Table 1). Generally, the influence of RH on the product yields was
mild, with the exception of 2-methyltetrols, 2-methylglyceric acid dimer and 2-methylthreonic acid which were produced in
significantly larger amounts at RH 9%. This is generally consistent with Dommen et al. (2006) and Nguyen et al. (2011),
who saw a negligible effect of relative humidity on SOA formation in photooxidation of isoprene in the absence of sulfate
seeds aerosol.

15 Usually, organosulfates derived from isoprene photooxidation, 2-methyltetrols and SOA yield were enhanced under
acidic conditions (Surratt et al., 2007a, 2007b, 2010; Gomez-Gonzalez et al., 2008; Jaoui et al., 2010; Zhang et al., 2011).
However, organosulfates were also formed in non-acidic experiments, probably through radical-initiated reactions in wet
aerosol particles containing sulfate moieties (Noziere et al., 2010; Perri et al., 2010). The NOS and OS compounds we
detected could also occur *via* this mechanism.

3.2.2 Acidic seed aerosol

Table 4 and Figures 4 - 5 present the estimated amounts of polar oxygenated products detected using GC-MS and
5   LC-MS techniques in samples from ER662 photooxidation experiments with acidic aerosol seeds under various RH
conditions. We detected the same compounds as in the non-acidic seed experiments, with the same analytical limitations of
the quantitation.

Table 4. Estimated concentrations of reaction products (ng m^{-3}) from ER662 photooxidation experiments (acidic seed [H$^+$] = 275 nmol m^{-3}
10   air: Lewandowski et al., 2015).

	RH 8	RH 18	RH 28	RH 44
GC-MS data *				
2-methylglyceric acid	3070	2136	982	473
2-methyltetrols	5357	4767	1029	341
2-methylglyceric acid dimer	90	144	102	43
IEPOX-1	1	133	6	0
IEPOX-2	10	3	0	0
C$_5$-diol-1	53	0	0	0
2-methylthreonic acid	42	28	6	4
2-methyltartaric acid	41	61	16	12
LC-MS data **				
m/z [M – H]$^-$				
197	0.88	0.30	0.21	0.10
199	3.44	1.49	2.62	1.12
211	1.78	0.50	0.76	0.48
213	5.41	1.94	3.40	1.96
215	59.00	18.40	12.30	3.23
229	0.41	0.31	0.39	0.27
244	4.50	1.16	0.72	0.42
260	0.92	0.88	0.45	0.29
274	0.60	0.58	0.36	0.12

* MW as BSTFA derivative

** chromatographic responses of selected main organosulfates [10^4]

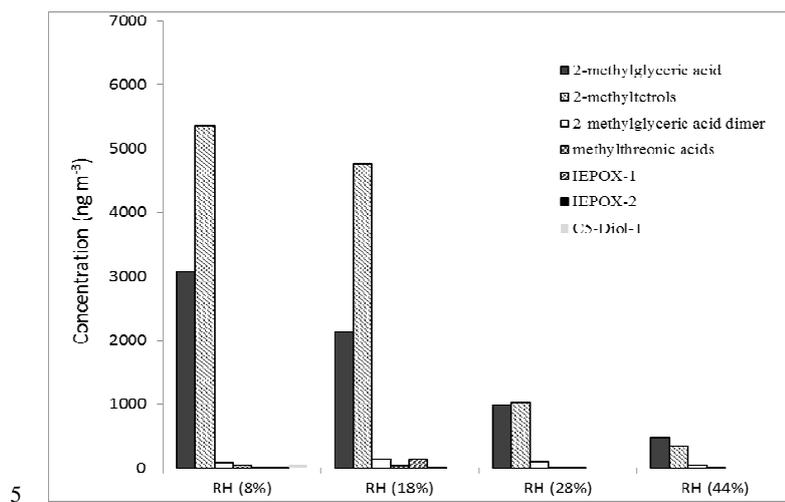
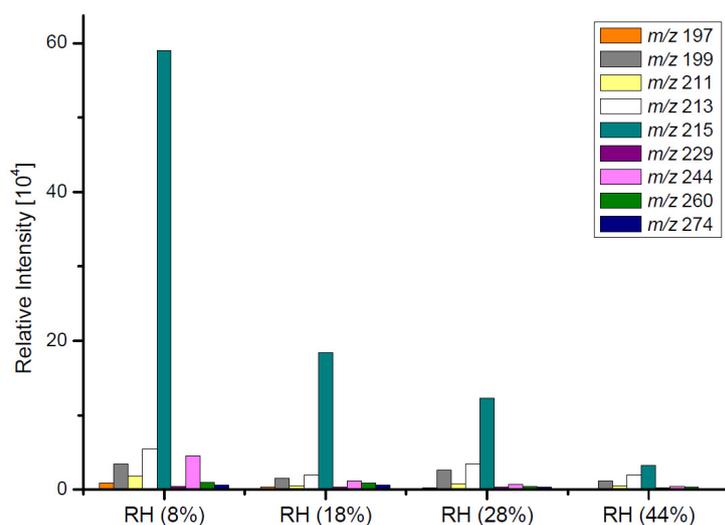



Figure 4. Concentrations of particle phase products from the acidic seed experiments (ER662) estimated with GC-MS.

10 **Figure 5**. LC-MS chromatographic responses of OS and NOS products from the acidic seed experiments (ER662).

Early smog chamber studies on isoprene ozonolysis by Jang et al. (2002) and Czoschke et al. (2003) showed enhanced SOA yields in the presence of acidified aerosol seeds. Recent laboratory results showed that the acidity of aerosol seeds plays a major role in the reactive uptake of isoprene oxidation products by particle phases (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Gaston et al., 2014; Riedel et al., 2015). In our study, secondary organic carbon (SOC) produced in acidic-seed experiments was always higher than in nonacidic-seed ones under corresponding RH conditions, while the difference diminished with increasing RH to a negligible value of 0.3 µgC m^{-3} at RH 44 – 49 (Table 1 and Fig. S1 (supplementary information)). However, formation of the individual organic compounds detected did not follow the same pattern. Figure 6 compares the results for 2-methylglyceric acid – combined effect of RH and H$_2$SO$_4$ was stronger than that of RH alone. Some of the compounds were produced in higher quantities in the acidic seed experiments (2-methylglyceric acid, 2-methyltetrols, furanetriol OS, 2-methyltetrol NOS, 2-methylthreonic acid NOS, furanone OS) while some other in the non-acidic seed experiments (IEPOX-2, methylthreonic acid, 2-methylglyceric acid OS, 2-methylthreonic acid OS). Yields of the remaining compounds followed a mixed pattern (supplementary information: see Figs S1, and S2, and Table S1).

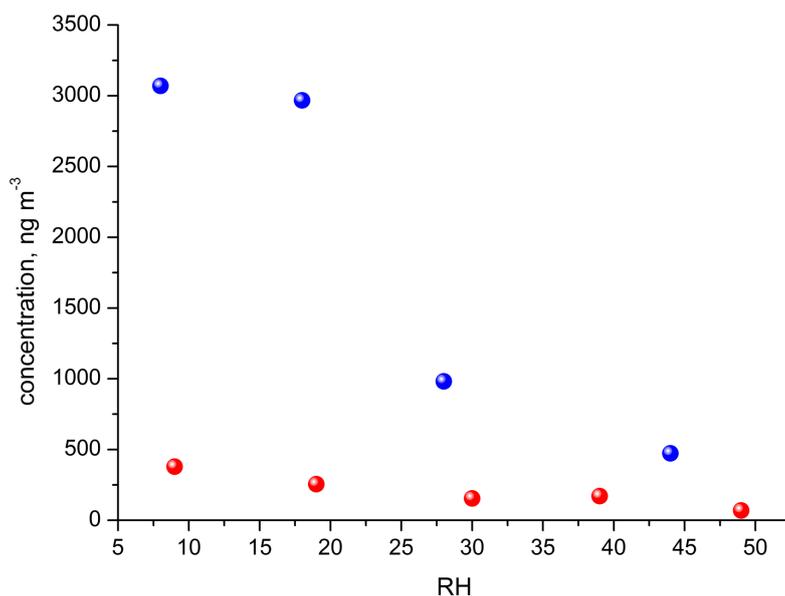



Figure 6. Influence of RH and seed acidity on the yield of 2-methylglyceric acid produced in chamber experiments with non-acidic seeds (red) and with acidic seeds (blue) (see similar figures for others compounds in Fig. S3: supporting information).

3.3 Chromatographic comparison of smog chamber experiments and field samples

We compared the results of smog chamber experiments with authentic samples of ambient fine aerosol collected at two rural sites in Poland, Zielonka and Godow. To keep the experimental and ambient conditions as similar as possible, we selected the experiments carried under the highest RHs: ER662 RH 44% (acidic seeds) and ER667 RH 49% (non-acidic seeds). Figures 7–14 show Extracted Ion Chromatograms (EIC) of selected components detected in respective filter extracts. Several compounds occurred both in the smog chamber SOA and in the ambient samples: 2-methylglyceric acid OS (MW 200), furanetriol OS (MW 214), 2-methyltetrol OS (MW 216), 2-methylthreonic acid OS (MW 230), 2-methylthreonic acid NOS (MW 275). Tartaric acid OS (MW 244) was found in ambient samples and only traces in acidic seed aerosol (Fig. 11) while 2-methyltetrol nitrosoxy-organosulfate (MW 245) – only in smog chamber SOA (Fig. 12). The EICs of 2-methyltetrol nitroxy-organosulfate (MW 261) were inadequate to provide reasonable fragmentations (Fig. 13). The comparison proves that the smog chamber studies on the formation of isoprene SOA in the presence of aerosol seeds and NO_x provided reasonable approximation of respective ambient processes even though only the Godow site could be influenced by nitrogen oxides. Having only the intensity-based data, we refrain from further quantitative speculations on the product occurrence.

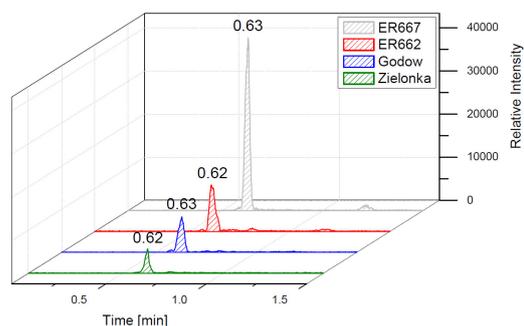



Figure 7. Extracted Ion Chromatograms (EIC) of organosulfate with MW 200 from field studies and smog chamber experiments.

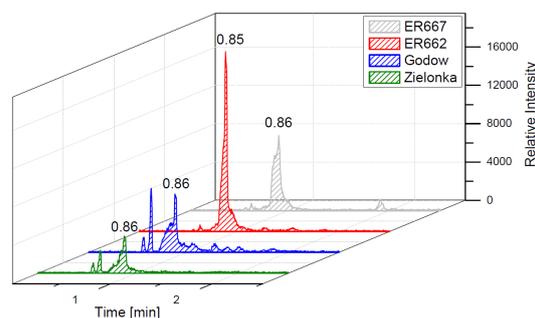



Figure 8. Extracted Ion Chromatograms (EIC) of organosulfate with MW 214 from field studies and smog chamber experiments.

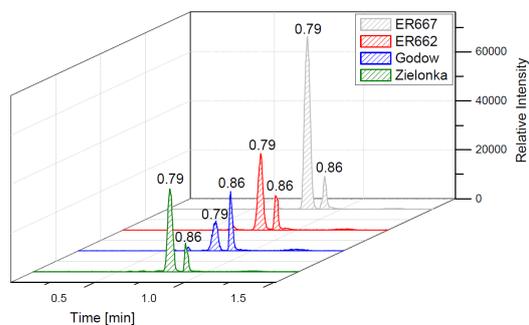
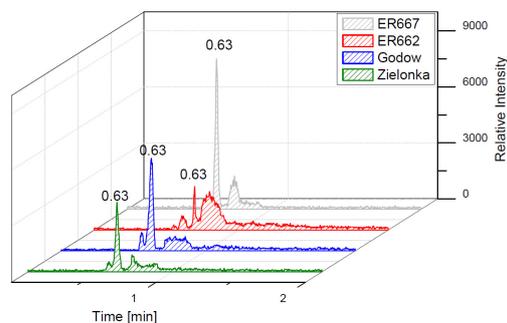



Figure 9. Extracted Ion Chromatograms (EIC) of organosulfate with MW 216 from field studies and smog chamber experiments.

5 **Figure 10**. Extracted Ion Chromatograms (EIC) of organosulfate with MW 230 from field studies and smog chamber experiments.

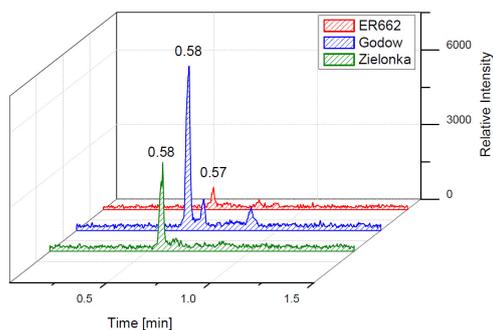



Figure 11. Extracted Ion Chromatograms (EIC) of
10 organosulfate with MW 244 from field studies and smog chamber experiments (not detected in ER667 sample).

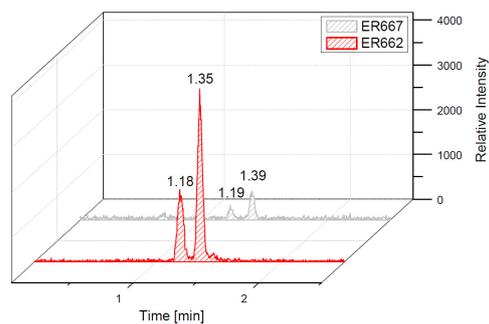



Figure 12. Extracted Ion Chromatograms (EIC) of nitrosoxy-organosulfate with MW 245 from smog chamber experiments (not detected in field samples).

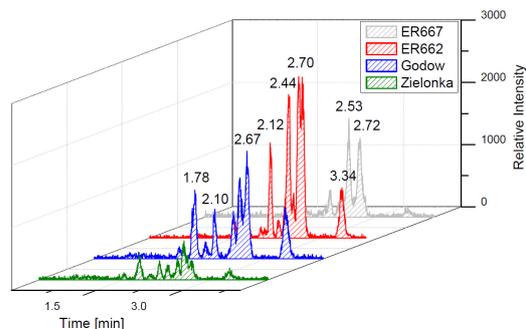



Figure 13. Extracted Ion Chromatograms (EIC) of nitroxy-organosulfate with MW 261 from field studies and smog chamber experiments.

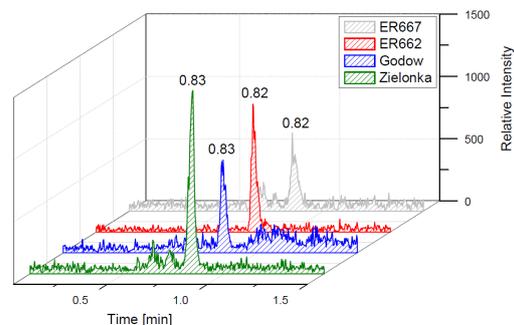



Figure 14. Extracted Ion Chromatograms (EIC) of nitroxy-organosulfate with MW 275 from field studies and smog chamber experiments.

3.4 Mass spectra and proposed fragmentation pathways of newly identified organosulfates, nitroxy- and nitrosoxy-organosulfates

All structures proposed below are tentative. Solely on the basis of high resolution mass data and fragmentation spectra recorded for HPLC-resolved peaks, it is not possible to distinguish between some isomers. It has to be also considered that some HPLC peaks, even plotted for the selected *m/z* value (extracted ion chromatograms), may correspond to more than one compound with the same molecular weight. This will result in the fragmentation spectra composed with the fragment ions coming from different precursor ions with the same *m/z*.

Our proposals for the structures of newly identified organosulfates, nitroxy- and nitrosoxy-organosulfates is based on the accurate mass measurements and the following assumptions:

    a)   all studied compounds have the same carbon backbone of 2-methylbutane;

    b)   the presence of the abundant *m/z* 97 peak corresponding to the HSO_4^- ion indicates that the hydrogen atom is present at the carbon atom next to one bearing $HO-SO_2-O-$ group (Attygalle et al., 2001). There can be, however, some exceptions as shown in Fig. 16 and 18;

    c)   when the condition given in b) is not fulfilled, elimination of sulfur trioxide molecule from the precursor ion can be observed (Szmigielski, 2013);

d) elimination of the HNO_2 and HNO_3 molecules from the precursor ion is diagnostic for the presence of the nitrous (-ONO) and nitric (-ONO$_2$) esters, respectively. Similarly to assumption a) β-hydrogen must be present to enable β-elimination.

The 2-methyltetrol nitroxy-organosulfate detected at *m/z* 260 corresponds to the major early eluting compounds both for the smog chamber and ambient fine aerosol (Fig. 13). The minor shifts in retention times of eluting compounds could be rationalized by matrix effect. Two partially resolved peaks of identical mass spectrometric profiles can be noted indicating diastereoisomeric forms. It is consistent with earlier studies (Gomez-Gonzalez et al., 2008; Surratt et al., 2007). A detailed interpretation of negative ion electrospray mass spectra led us to propose the structure for 2-methyltetrol nitroxy-organosulfates bearing a nitroxy moiety at the primary hydroxyl group of 2-methyltetrol skeleton and sulfate group at the secondary hydroxyl group (Fig 15), which is, however, in a stark contrast to earlier proposals by Gomez-Gonzalez et al. and Surratt et al. The main fragmentation pathways correspond to a neutral loss of 63 u (HNO_3) resulting in *m/z* 197 as a base peak and to bisulfate ion at *m/z* 97. Another diagnostic ion at *m/z* 184 could be attributed to a combined loss of NO_2 and CH_2O, pointing to the presence of hydroxymethyl group in the molecule. The presence of *m/z* 213 and 183 ions supports the rationale mentioned above due to a characteristic neutral loss of a CH_2O fragment. A revised structure for the MW 261 SOA component along with the proposed fragmentation scheme is given in Fig. 15 (the mass spectrum of another diastereoisomer is not shown).

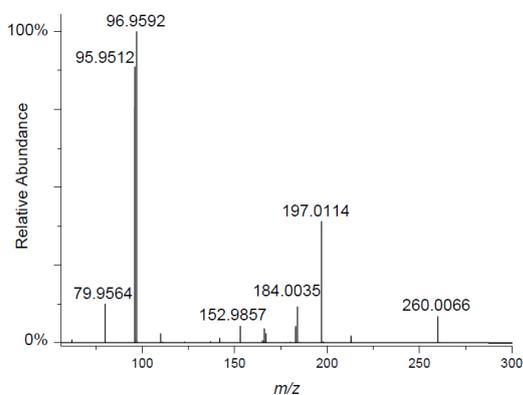
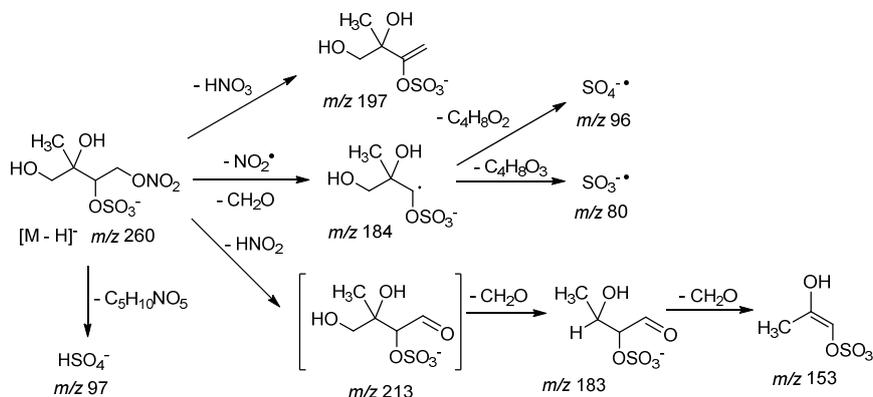



Figure 15. (-)Electrospray product ion mass spectrum of 2-methyltetrol nitroxy-organosulfate (MW 261) eluting at RT = 2.44 min. (Fig. 13) registered for the ER662 acidic seed aerosol along with proposed fragmentation pathway.

Another abundant smog chamber-generated SOA component was detected at m/z 244. However, in contrast to 2-methyltetrol nitroxy-organosulfate, we failed to detect the MW 245 unknown in ambient fine aerosol that would suggest it could play a relevant role as a reactive reaction intermediate in route to particle formation through isoprene photooxidation chains. Two base line-resolved peaks of identical electrospray product ion mass spectra could be attributed to diastereoisomers with an isoprene-retained backbone (Fig. 12 and 16). Surratt and co-workers observed the formation of the species in the isoprene photooxidation experiment under high-NO_x conditions and proposed the structure to 2-methylglyceric acid nitroxy-organosulfate (Surratt et al., 2007). However, in the light of our mass spectral data we evidence the MW 245 unknown is the C_5 organosulfate, namely 2-methyltetrol nitrosoxy-organosulfates. The m/z 244 → m/z 226 transition in the product ion mass spectrum (Fig. 16) points to the intact secondary hydroxyl moiety of the 2-metthyltetrol skeleton. The lack of HNO_3 elimination from [M – H]⁻ (m/z 244) precursor ion clearly excludes the presence of nitroxy group. However, an abundant m/z 197 ion, which forms through the HNO_2 loss, could be associated with the existence of the -O-NO residue. The structure assigned to the abundant MW 245 component of the ER662 acidic seed aerosol along with its proposed fragmentation scheme is presented in Fig. 16. The mass spectrum of another diastereoisomer is not given.

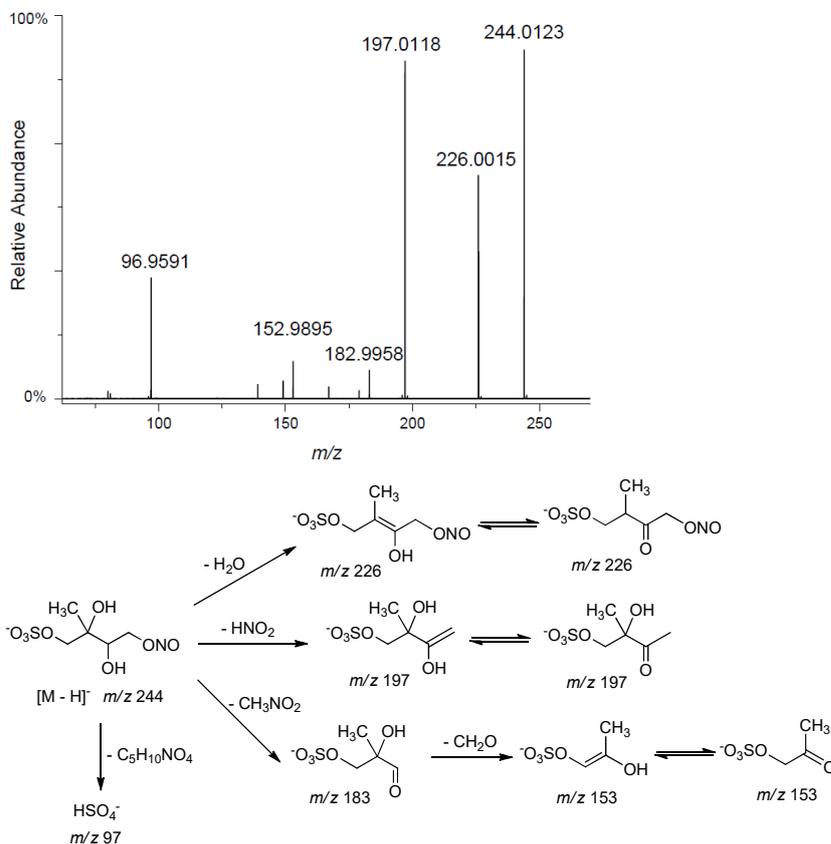



Figure 16. (-)Electrospray product ion mass spectrum of 2-methyltetrol nitrosoxy-organosulfate (MW 245) of the RT = 1.35 min peak (Fig. 11) acquired for the ER662 acidic seed aerosol along with the proposed fragmentation pathway.

The two other abundant SOA organosulfates were determined at *m/z* 243 and 229 for the smog chamber and ambient fine aerosol (Fig. 10 and 11), to our knowledge for the first time. The accurate mass data recorded for Godow fine aerosol (RT = 0.58 min. in Fig. 11, $C_5H_7O_9S$: 242.9813, error +0.2 mDa and RT = 0.63 min. in Fig. 10, $C_5H_9NO_8S$: 229.0020, error +0.2 mDa) suggested a greater oxidation stage of these unknown organosulfates compared to the composition of sulfated 2-

10   methyltetrols. Two partially resolved peaks of identical mass spectrometric signatures can be noted for these organosulfates indicating the presence of two chiral centres in their molecules (Fig. 10 and 11). In either case, first eluting diastereoisomers give rise to abundant peaks, while the second one is of minor intensity suggesting the preference of the formation of less hindered compounds both in the troposphere and smog chamber experiments. A detailed interpretation of product ion mass spectra allowed to assign structures of the MW 244 and MW 230 unknowns to 2-methyltartaric acid organosulfate and 2-

methylthreonic acid organosulfate, respectively (Fig 17 and 18; the mass spectrum of the minor diastereoisomer is not shown). Either spectrum displays abundant fragment ions at *m/z* 163 and 149, respectively, which could be explained by the SO₃ elimination from their precursor ions. Further fragmentations of *m/z* 163 ions, i.e., a neutral loss of water followed by decarboxylation reveals the simultaneous presence of -O-SO₃H and –CO₂H residues in the MW 230 diastereoisomeric organosulfates. However, the absence of the bisulfate ion in the spectrum of the MW 244 organosulfate clearly indicate a lack of a proton adjacent to the sulfated group, and thus allows to propose the sulfation of a secondary hydroxyl group. It is not the case of the MW 230 organosulfate and the presence of the bisulfate ion the MS/MS spectrum unambiguously reveals the sulfation at a primary hydroxyl group in the molecule. The proposed fragmentation schemes for the MW 244 and 230 novel organosulfates are depicted in Fig. 17 and 18. Mass spectra of related diastereoisomeric organosulfates are not presented.

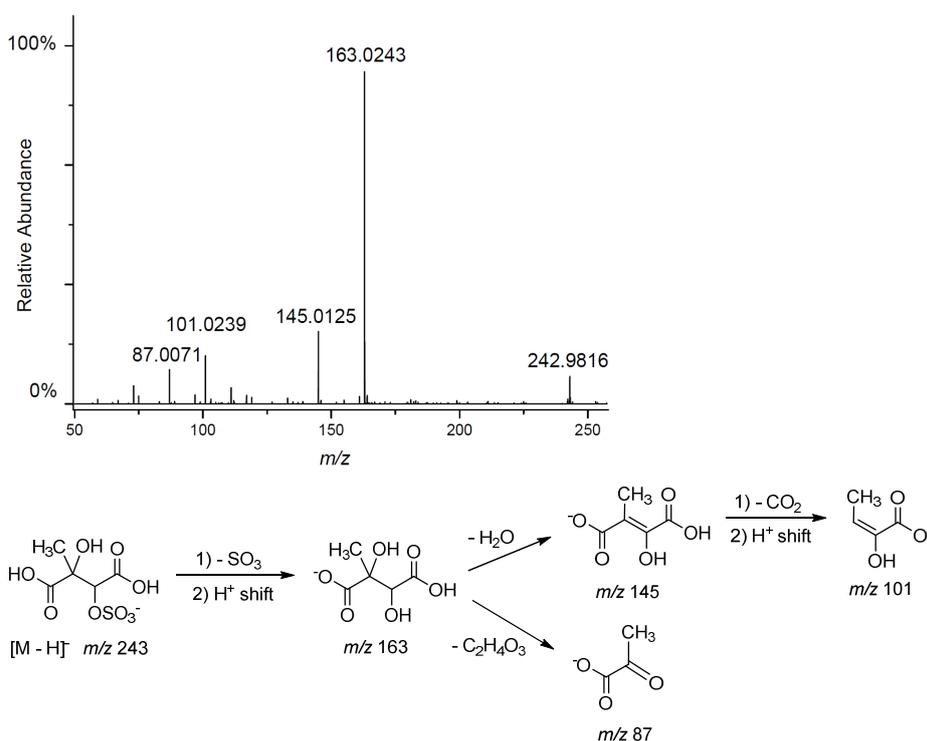



Figure 17. (-)Electrospray product ion mass spectrum of 2-methyltartaric acid organosulfate (MW 244) recorded for the RT = 0.58 min peak (Fig. 11) from Godow fine aerosol along with the proposed fragmentation pathway.

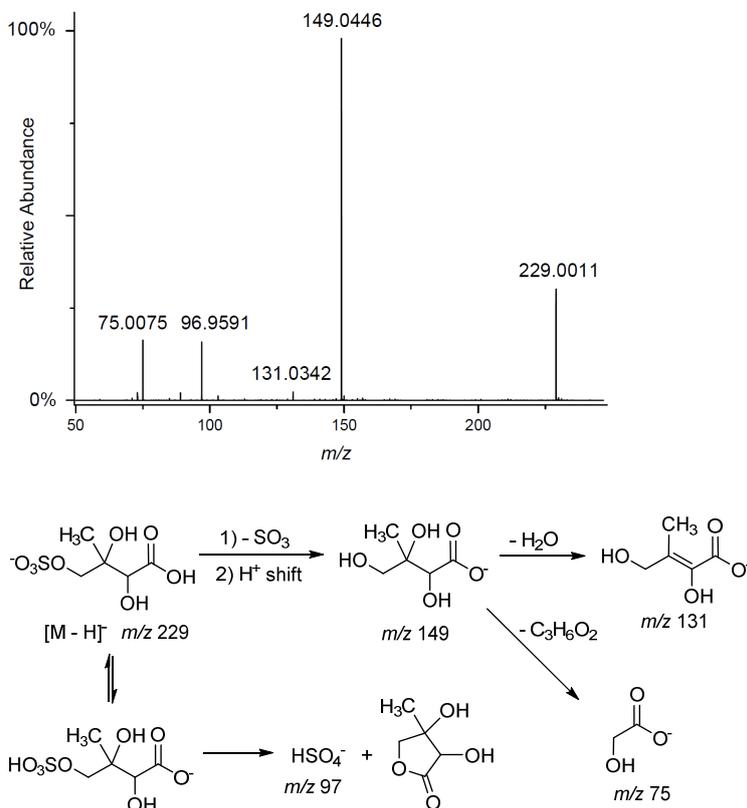



Figure 18. (-)Electrospray product ion mass spectrum of 2-methylthreonic acid organosulfate (MW 230) at RT = 0.63 min. (Fig. 10) acquired for Zielonka PM$_{2.}$ aerosol along with the proposed fragmentation pathway.

Another related organosulfate was detected at m/z 274 at abundant quantities in smog chamber-generated isoprene SOA and rural PM$_{2.5}$ aerosol (Fig. 14), to our knowledge for the first time. Transitions m/z 274 → m/z 211 (a loss of HNO$_3$) and m/z 274 → m/z 97 (a loss of C$_5$H$_7$NO$_6$) provided by product ion mass spectrum for Zielonka fine aerosol (Fig. 19) along with the high resolution data (RT = 0.83 min., C$_5$H$_7$NO$_{10}$S: 273.9873, error +0.4 mDa) clearly points to isoprene-related nitroxy-organosulfate. A detailed explanation of other diagnostic ions led to propose the structure of 2-methylthreonic acid nitroxy-organosulfate (Fig 19). It could be assumed that due to a high oxidation stage (C/O = 0.5) the MW 275 organosulfate could be marker of isoprene aged aerosol. However, the further study is warrant to rationalize the formation mechanism and reactivity in the atmosphere.

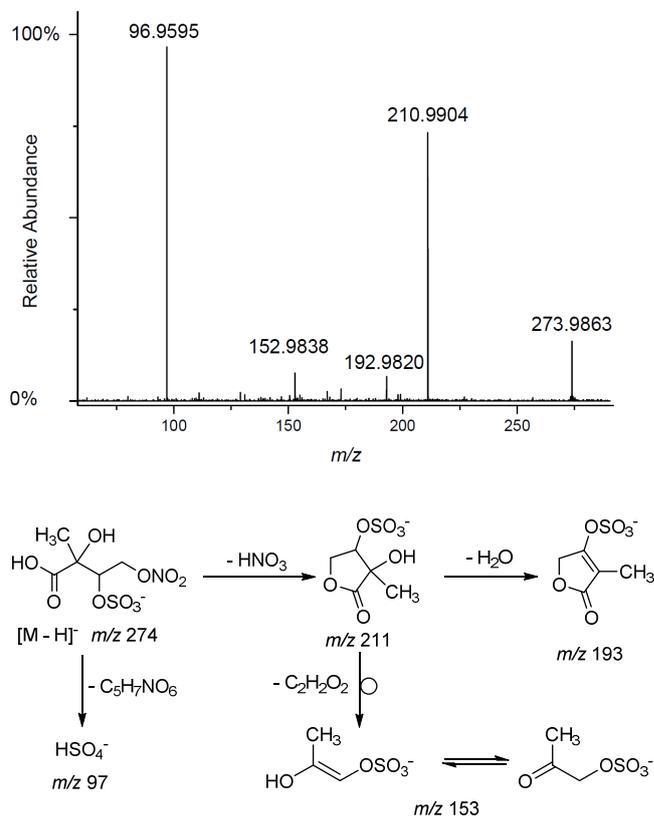



Figure 19. (-)Electrospray product ion mass spectrum of 2-methylthreonic acid nitroxy-organosulfate (MW 275) of the RT = 0.83 min
5   peak (Fig. 14) recorded for Zielonka PM$_{2.5}$ aerosol along with the proposed fragmentation pathway.

4 Summary

We characterized several organic components of isoprene SOA particles some of which have been reported in the
literature. Methylthreonic acids (MW 150) and methyltartaric acid (MW 164), a highly oxygenate molecules, proposed
recently as ISO aging SOA markers were also present in this study. However, several compounds were identified for the first
10   time, including: 2-methylthreonic acid (MW 150), 2-methyltartaric acid (MW 164), 2-methylthreonic acid organosulfate
(MW 230), 2-methyltartaric acid organosulfate (MW 244) and 2-methyltartaric acid nitroxy-organosulfate (MW 275).
Further research is warranted to rationalize the mechanisms of their formation in the atmosphere. The quantitation data
revealed 2-methyltetrols, 2-methylglyceric acid and 2-methyltetrol organosulfates as the most abundant components of
isoprene SOA. Other molecular components contributing to SOA mass were epoxydiols, mono- and dicarboxylic acids,
15   organosulfates as well as nitroxy- and nitrosoxy-organosulfates.

In addition, we showed that several organosulfates and nitroxy-organosulfates identified in smog chamber samples were also detected in samples of ambient aerosol collected at rural sites in Poland. Such consistency reinforces the relevance of the smog chamber findings even though 2-methyltetrol nitrosoxy-organosulfate (MW 245) was found only in chamber experiments.

5   The effect of relative humidity on SOA formation was mild in the non-acidic seed experiments. Total SOC decreased with increasing relative humidity (RH) but the individual components were influenced diversely. The yields of most compounds decreased, but more 2-methyltartaric acid, IEPOX OS, 2-methylglyceric acid OS and 2-methylthreonic acid OS were produced at medium and high humidity.

      The acidic seed experiments produced more SOC than the non-acidic ones, under all RH conditions. However, at
10   high humidity (44–49%), the difference was rather small. Some individual SOA components followed the same pattern while other were more abundant in non-acidic experiments or behaved in a mixed way, depending on RH.   Further experimental work on chemical mechanism and kinetics of reactions involved in formation of individual SOA components is required to explain the influence of acidity and liquid water content.

15   **Disclaimer.** The views expressed in this journal article are those of the author(s) and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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