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Publication Date

2014-09-01

DOI

10.1016/j.atmosenv.2014.05.049

Peer reviewed



Published in final edited form as:

Atmos Environ (1994). 2014 September 1; 94: 366–373. doi:10.1016/j.atmosenv.2014.05.049.

Aromatic organosulfates in atmospheric aerosols: synthesis, characterization, and abundance

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Abstract

Aromatic organosulfates are identified and quantified in fine particulate matter (PM_{2.5}) from Lahore, Pakistan, Godavari, Nepal, and Pasadena, California. To support detection and quantification, authentic standards of phenyl sulfate, benzyl sulfate, 3- and 4-methylphenyl sulfate and 2-, 3-, and 4-methylbenzyl sulfate were synthesized. Authentic standards and aerosol samples were analyzed by ultra-performance liquid chromatography (UPLC) coupled to negative electrospray ionization (ESI) quadrupole time-of-flight (ToF) mass spectrometry. Benzyl sulfate was present in all three locations at concentrations ranging from 4 – 90 pg m⁻³. Phenyl sulfate, methylphenyl sulfates and methylbenzyl sulfates were observed intermittently with abundances of 4 pg m⁻³, 2–31 pg m⁻³, 109 pg m⁻³, respectively. Characteristic fragment ions of aromatic organosulfates include the sulfite radical (*SO₃⁻, *m/z* 80) and the sulfate radical (*SO₄⁻, *m/z* 96). Instrumental response factors of phenyl and benzyl sulfates varied by a factor of 4.3, indicating that structurally-similar organosulfates may have significantly different instrumental responses and highlighting the need to develop authentic standards for absolute quantitation organosulfates. In an effort to better understand the sources of aromatic organosulfates to the atmosphere, chamber experiments with the precursor toluene were conducted under conditions that form biogenic organosulfates. Aromatic organosulfates were not detected in the chamber samples,

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suggesting that they form through different pathways, have different precursors (e.g. naphthalene or methyl-naphthalene), or are emitted from primary sources.

Keywords

sulfate ester synthesis; atmospheric aerosol; mass spectrometry; toluene

1. Introduction

Sulfate esters (a.k.a. organosulfates) are ubiquitous in atmospheric aerosols, having been detected in remote, urban, forested, marine, and arctic locations worldwide (Romero et al. 2005; Surratt et al. 2007; Frossard et al. 2011; Kristensen et al. 2011; Mazzoleni et al. 2012; Stone et al. 2012). Monosulfate esters are strong acids with pK_a values estimated below -3 (Guthrie 1978), so they are deprotonated ($R-O-SO_3^-$) in environmental systems. These negatively charged molecules are highly water-soluble and non-volatile, such that they remain in the particle phase in the atmosphere. Organosulfates may play a role in climate forcing, by direct light absorption (Nguyen et al. 2012) and/or by affecting aerosol hygroscopicity due to their acidic and amphiphilic nature. They also help to reconcile the under-predictions of particle-phase organic carbon in atmospheric models by providing a means to account for acid-catalyzed secondary organic aerosol (SOA) formation (Iinuma et al. 2013; Pye et al. 2013).

The total atmospheric abundance of organosulfates has been estimated to range from 4-30% of fine particle organic mass (Surratt et al. 2008; Frossard et al. 2011; Stone et al. 2012). These estimates remain highly uncertain due to the lack of quantitation standards and direct measurement techniques. Tolocka and Turpin (2012) calculate the upper limit of organosulfate contributions to fine particle ($PM_{2.5}$) organic mass at 5-10% for background locations in the United States. Meanwhile, individual organosulfate species account for less than 1% of organic mass (Iinuma et al. 2009; Olson et al. 2011; Kundu et al. 2013), indicating that organosulfate concentrations are not dominated by a few highly abundant species and, instead, are present in a wide range of chemical forms.

The chemical structures of organosulfates range from small molecules to high-molecular weight organic matter (Stone et al. 2009), with a high oxygen-to-carbon ratio (Mazzoleni et al. 2012; Stone et al. 2012). Qualitative surveys of organosulfates have revealed that they are largely aliphatic in structure and also contain hydroxy, carboxylic acid, and nitrooxy functional groups (Lin et al. 2012). Among the most abundant and ubiquitous organosulfates are those derived from isoprene and isoprene oxidation products (Zhang et al. 2012; Lin et al. 2013b); these small, multi-functional organosulfates have been widely observed in ambient aerosol (Surratt et al. 2007; Kristensen et al. 2011; Stone et al. 2012), and used as markers of isoprene-derived SOA in field experiments (Zhang et al. 2012; Lin et al. 2013b).

Aromatic organosulfates, containing an intact aromatic ring, have recently been observed in ambient aerosol in Lahore, Pakistan (Stone et al. 2012; Kundu et al. 2013) and in urban sites in East Asia in low abundance (Lin et al. 2012). Kundu et al. (2013) unequivocally

identified benzyl sulfate against a synthesized authentic standard, quantified its monthly-average concentration in PM_{2.5} (0.05 – 0.50 ng m⁻³).

The current study builds on the tentative identification of homologous series of phenyl and benzyl sulfates with methyl substituents by Kundu et al. (2013). Series of phenyl and benzyl sulfates were synthesized and confirmed as constituents of fine particulate matter. These standards were used to study their mass spectra and response factors under negative ESI, and to evaluate their abundance in atmospheric aerosols from three distinct urban locations: Lahore, Pakistan, Godavari, Nepal, and Pasadena, California, USA. The potential for secondary formation of aromatic organosulfates from toluene was also examined (Zhang et al. 2012).

2. Materials and Methods

2.1. Synthesized product characterization

Aromatic organosulfates standards were characterized by high resolution mass spectrometry (HRMS, Micromass Q-ToF Premier, Waters) with negative ESI and ¹H nuclear magnetic resonance (NMR, Bruker DRX, 400 MHz). Phenyl sulfates were also characterized by ¹³C NMR. Standardization of the aromatic organosulfates was performed in D₂O using ¹²C NMR (Varian 300 MHz). For quantification purposes, dichloroacetic acid (DCA) was used as an internal standard, following Olson et al. (2011). Phenols and benzyl alcohols were obtained from Acros Organics or Sigma Aldrich and were used without further purification.

2.2. General procedure for the synthesis of phenyl sulfates

The reagent 2,2,2-trichloroethyl chlorosulfate (TCE) was prepared from trichloroethanol and sulfonyl chloride following Hedayatu et al. (1971). A solution of TCE in dry tetrahydrofuran (THF, 10 mL) was added dropwise to phenols (1.0 equiv), triethylamine (1.2 equiv), 4-dimethylaminopyridine (DMAP, 1.2 equiv), in dry THF (40 mL) and was stirred for 2 h (Liu et al. 2004; Li et al. 2010). The reaction mixture was then extracted with ethyl acetate and washed with H₂O, 1.0 N HCl, and saturated brine. The organic layer was then dried with Na₂SO₄ and solvent removed under vacuum. The resulting white residue was purified by silica gel column chromatography with hexane and ethyl acetate (10:1, v/v) as mobile phase. The TCE-sulfate ester was then dissolved in methanol and excess ammonium formate and zinc powder were added to generate the free sulfate ester. Reaction progress was monitored with thin-layer chromatography. The product was purified with column chromatography on silica gel with dichloromethane, methanol, and ammonium hydroxide (30:6:1, v/v/v) as mobile phase. Following vacuum filtration, excess solvent was removed under reduced pressure and the product dried with light heating.

2.2.1. Phenyl sulfate, ammonium salt—Yield: 31 %; purity: 93 %; white solid; ¹H NMR (400 MHz, CD₃OD): δ/ppm 4.60 (s, 4H), 7.12-7.38 (m, 5H); ¹³C-NMR (400 MHz, CD₃OD): δ/ppm 122.2, 125.5, 129.8, 153.7; HR-MS (ESI, negative) *m/z* (relative intensity, %): 172.9903 (17, C₆H₅O₄S⁻), 93.0328 (100), 79.9559 (10).

2.2.2. 3-Methylphenyl sulfate, ammonium salt: Yield: 64 %; purity 85 %; white solid; ^1H NMR (400 MHz, CD_3OD): δ/ppm 2.32 (s, 3H), 6.97-7.21 (m, 4H); ^{13}C -NMR (400 MHz, CD_3OD): δ/ppm 21.3, 119.3, 122.9, 126.8, 129.9, 140.4, 153.6; HR-MS (ESI, negative) m/z (relative intensity, %): 187.0061 (17, $\text{C}_7\text{H}_7\text{O}_4\text{S}^-$), 107.0484 (100), 79.9561 (10).

2.2.3. 4-Methylphenyl sulfate, ammonium salt: Yield: 39 %; purity: 85%; white solid; ^1H NMR (400 MHz, CD_3OD): δ/ppm 2.24 (s, 3H), 7.05-7.10 (m, 4H); ^{13}C -NMR (400 MHz, CD_3OD): δ/ppm 20.9, 122.5, 130.7, 135.7, 151.8; HR-MS (ESI, negative) m/z (relative intensity, %): 187.0061 (19, $\text{C}_7\text{H}_7\text{O}_4\text{S}^-$), 107.0486 (100), 79.9560 (17).

2.3. General procedure for the synthesis of benzyl sulfates

Benzyl and methylbenzyl sulfates were synthesized following Olson et al. (2011), wherein benzyl alcohol, 2-, 3-, and 4-methylbenzyl alcohols were dissolved in acetonitrile with N,N -diisopropylethylamine (DIEA). The solution was cooled to 0 °C before slow addition of chlorosulfonic acid. The reaction was allowed to proceed in an ice bath for 3 hours, prior to removal of acetonitrile under reduced pressure. The resulting product mixture was liquid and was not subjected to further purification.

2.3.1. Benzyl sulfate—Purity: 44 %; ^1H NMR (400 MHz, D_2O): δ/ppm 5.03 (s, 2H), 7.37-7.44 (m, 4H); HR-MS (ESI, negative) m/z (relative intensity, %): 187.0049 (58, $\text{C}_7\text{H}_7\text{O}_4\text{S}$), 107.0483 (4), 95.9507 (100), 80.9639 (21), 79.9553 (11).

2.3.1. 2-Methylbenzyl sulfate: Purity: 42 %; ^1H NMR (400 MHz, D_2O): δ/ppm 2.33 (s, 3H), 5.05 (s, 2H), 7.18-7.38 (m, 4H); HR-MS (ESI, negative) m/z (relative intensity, %): 201.0210 (25, $\text{C}_8\text{H}_9\text{O}_4\text{S}^-$), 96.9575 (56), 95.9499 (100), 91.0527 (4), 80.9628 (6), 79.9549 (6).

2.3.1. 3-Methylbenzyl sulfate: Purity: 33 %; ^1H NMR (400 MHz, D_2O): δ/ppm 2.30 (s, 3H), 4.98 (s, 2H), 7.13-7.32 (m, 4H); HR-MS (ESI, negative) m/z (relative intensity, %): 201.0210 (25, $\text{C}_8\text{H}_9\text{O}_4\text{S}^-$), 96.9575 (55), 95.9499 (100), 91.0525 (4), 80.9627 (6), 79.9550 (6).

2.3.1. 4-Methylbenzyl sulfate: Purity: 32 %; ^1H NMR (400 MHz, D_2O): δ/ppm 2.21 (s, 3H), 4.98 (s, 2H), 7.12-7.25 (m, 4H); HR-MS (ESI, negative) m/z (relative intensity, %): 201.0208 (25, $\text{C}_8\text{H}_9\text{O}_4\text{S}^-$), 96.9559 (4), 95.9498 (100), 80.9627 (9), 79.9550 (7).

2.4 Aerosol Sample Collection

2.4.2. Lahore, Pakistan— $\text{PM}_{2.5}$ samples in Lahore were collected onto prebaked quartz fiber filters (QFF, Pall Life Sciences, Tissuquartz, 47mm diameter) using a medium-volume sampling apparatus (URG-3000, Chapel Hill, NC, USA). The sampler was located on the rooftop of the Institute for Environmental Engineering on University of Engineering and Technology campus (Stone et al. 2010a). Samples were collected from January 2007 – January 2008 following the one-in-six sampling schedule. A sample collected on December 26, 2007 was used for qualitative identification of aromatic organosulfates and a composite of sub-samples from March 2007 was used for quantitation.

2.4.2. Godavari, Nepal—PM_{2.5} samples were collected onto prebaked 47mm QFF using a medium-volume sampling apparatus (URG-3000, Chapel Hill, NC, USA) as part of the Atmospheric Brown Cloud monitoring network. The sampler was located at the International Center for Integrated Mountain Development (ICIMOD) Training and Demonstration site in the southeastern foothills of the Kathmandu Valley. Samples were collected daily during 2007; sub-samples from twenty-eight filter samples from February were composited and analyzed.

2.4.3 Pasadena, California, USA—PM_{2.5} samples were collected onto prebaked QFF (Pall Life Sciences, Tissuquartz filters, 20.3cm × 25.4 cm) using high-volume PM_{2.5} samplers (Tisch Environmental) at the Pasadena ground site during the 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) field study Ryerson et al. (2013). PM_{2.5} filter samples collected on 5 June and 6 June were analyzed in this study. PM_{2.5} mass was estimated as the sum of measured PM₁ components and the product of the PM_{2.5-1} volume concentration and an assumed aerosol density of 1.49 (Hayes et al. 2013).

2.5 Elemental and Organic Carbon Analysis

PM_{2.5} organic and elemental carbon (OC and EC) measurements were made from QFF using a Sunset Laboratories OCEC analyzer (Model 3F, Forest Grove, OR). Pasadena filter samples were analyzed following the NIOSH thermal-optical transmittance protocol (Hayes et al. 2013), whereas the Lahore and Godavari samples were analyzed by the ACE-Asia protocol (Schauer et al. 2003).

2.6 Organosulfate Extraction

Sub-samples of QFF were combined in pre-baked and solvent-rinsed jars and were extracted into high-purity methanol (99.9%, Fisher Scientific) by 40 minutes of sonication (Branson 5510). Extracts were then filtered with a pre-rinsed polytetrafluoroethylene (PTFE) syringe filter (13 mm, 0.2 μm pore size, Whatman) and reduced in volume under high-purity nitrogen (5 psi) and gentle 50 °C heating. Once dry, samples were reconstituted in 2:1 water-methanol (v/v) to 200 μL. This extraction procedure gave average recoveries of 84% for benzyl sulfate, 76% for phenyl sulfate, and 92% for 3-methylphenyl sulfate.

2.7 Instrumental Analysis of Aromatic Organosulfates

Synthesized standards and aerosol samples were analyzed by UPLC-HRMS following the method described by Kundu et al. (2013). Briefly, UPLC separation occurred on a high-strength silica (HSS) reversed-phase octadecyl (C18) column (ACQUITY UPLC® HSS T3, 2.1 mm ID × 75 mm length, 1.8 μm particle size). Aqueous (high-purity water with resistivity > 18.2 Ω cm) and methanol mobile phases each contained 0.1% glacial acetic acid and followed the gradient elution program described by Surratt et al. (2008), with re-equilibration prior to the next injection. The column temperature was maintained at 45 °C, mobile phase flow rate at 0.3 mL min⁻¹, and injection volume at 5.0 μL.

UPLC eluent was directed to the Q-ToF HRMS operating in negative ESI mode. Mass spectra were collected from *m/z* 40 to 400 in reflectron mode with V geometry. Val-Tyr-Val (Sigma-Aldrich, *m/z* 379.2029) was used for lock mass correction. Tandem mass

spectrometry (MS^2) utilized 15 V collision energy. All sample and standard spectra were background subtracted. Calibration standards of phenyl sulfate, 3-methylphenyl sulfate, benzyl sulfate, 2-methylbenzyl sulfate, and 3-methylbenzyl sulfate with concentrations ranging from approximately 0.5 to 25 $ng\ mL^{-1}$ were analyzed to construct six-point linear calibration curves ($R^2 > 0.995$) based on peak area molecular ion chromatograms. The method detection limit was 0.35 $ng\ mL^{-1}$. Aromatic organosulfates were not detected in laboratory or field blank samples.

2.8 Smog Chamber Experiments

Toluene photooxidation experiments were conducted to determine if aromatic organosulfates form under the same conditions as biogenic organosulfates and if aerosol acidity affects this formation. Toluene-derived SOA was generated in the University of North Carolina 274 m^3 dual outdoor smog chamber facility located in Pittsboro, NC, under clear natural sunlight (Kamens et al. 2011; Zhang et al. 2011). Chambers were vented with rural North Carolina background air (with $< 8-10\ \mu g\ m^{-3}$ aerosol mass) for at least 12 hours before each experiment.

Experimental conditions used to generate toluene-derived SOA are summarized in Table 1. Prior to the start of each experiment, neutral or acidic seed aerosol was introduced into each side of the chamber by atomizing a 0.06 M ammonium sulfate (aq) or 0.06 M magnesium sulfate plus 0.06 M sulfuric acid (aq), respectively, to mass concentrations of 35–38 $\mu g\ m^{-3}$. Seed aerosol volume concentrations and size distributions were measured by a scanning mobility particle sizer (TSI 3080, Shoreview, MN) with a condensation particle counter (TSI 3022A, Shoreview, MN) as described in Zhang et al. (2011). Background aerosol filter samples of seed aerosol only (totaling $\sim 2.6\ m^3$), were collected on Teflo® substrates (Pall Life Sciences, 47-mm, 1- μm pore size). Nitric oxide (NO) was injected into the chamber from a high-pressure gas cylinder. Ozone and nitrogen oxides ($NO_x = NO + NO_2$) were measured by UV photometric (Thermo-Environmental 49P) and chemiluminescent (Bendix Model 8101B) analyzers. High-purity liquid toluene (99.8%, Sigma-Aldrich) was heated in a U-tube and flushed into the chamber with high-purity N_2 . Toluene was measured by gas chromatograph/flame ionization detector. Filter samples of the toluene-derived SOA (totaling $\sim 10.9\ m^3$) were collected after the aerosol volume concentration peaked. Backup Teflon filters were also collected to evaluate evaporative losses. Figure S1 (supporting information) shows that the experimental profile for gases and aerosol mass concentrations were similar between the neutral and acidic experiments.

3. Results and Discussion

3.1 Mass Spectral Fragmentation of Aromatic Organosulfate Standards

Aromatic organosulfate standards were analyzed by high-resolution MS^2 ; resulting production mass spectra; Figure 2 shows the corresponding mass fragmentation patterns. The molecular ion for phenyl sulfate (Figure 2A) was observed at m/z 172.9903 (with molecular formula of $C_6H_5O_4S^-$ and error of -3.5 ppm); major fragments included the sulfite radical at m/z 79.9559 (SO_3^- , -11.3 ppm) and the phenolate anion at m/z 93.0328 ($C_6H_5O^-$, -12.9 ppm) formed by the neutral loss of SO_3 . The errors in observed m/z relative to their

theoretical m/z are expressed in parts per million and consequently errors increase as m/z decreases. The observed phenyl sulfate spectrum was consistent with prior studies (Attygalle et al. 2001). 3-Methylphenyl sulfate (Figure 2B) produced a molecular ion at m/z 187.0061 ($C_7H_7O_4S^-$, -2.1 ppm) and major fragments included the sulfite radical at m/z 79.9561 ($^*SO_3^-$, -8.8 ppm) and the 3-methylphenolate anion at m/z 107.0484 ($C_7H_7O^-$, -12.1 ppm) formed by the neutral loss of SO_3 . The product ion mass spectrum for 4-methylphenyl sulfate was not different from 3-methylphenyl sulfate, and is not shown.

The characteristic mass spectral features of phenyl sulfate and methylphenyl sulfates are the sulfite radical (m/z 80) and neutral loss of SO_3 (also 80). The sulfite radical at m/z 80 has previously been observed for organosulfates with aliphatic, aromatic, and allylic structures (Attygalle et al. 2001; Surratt et al. 2007). To form the sulfite radical the organosulfate S-O bond undergoes homolytic cleavage as described by Attygalle et al. (2001). The neutral loss of SO_3 (m/z) by heterolytic cleavage from phenyl and methylphenyl sulfates gives rise to even-electron phenolate and methylphenolate anions. These anions are resonance stabilized and have the greatest intensity in product ion spectra. The spectra shown in Figure 2A and 2B are notably void of the bisulfate anion at m/z 97, which is commonly observed for organosulfates of aliphatic structure (Attygalle et al. 2001; Romero et al. 2005; Surratt et al. 2007; Stone et al. 2009). The bisulfate anion (HSO_4^-) at m/z 97 forms by concerted syn-elimination of a hydrogen atom from a carbon atom in the C2 position from the sulfate moiety; such elimination is not observed in aryl or vinyl sulfate esters (Attygalle et al. 2001) such as these.

The MS fragmentation of benzyl sulfate are consistent with prior work by Kundu et al. (2013) and Attygalle et al. (2001). Notably, benzyl sulfate is a conformational isomer of methylphenyl sulfates and its molecular ion was detected at m/z 187.0049 ($C_7H_7O_4S^-$, -8.6 ppm). Major fragments of benzyl sulfate include the sulfite radical 79.9553 ($^*SO_3^-$, -18.8 ppm) and sulfate radical 95.9507 ($^*SO_4^-$, -10.4 ppm). The formation of the sulfate radical occurs by homolytic fission of the C-O bond and is characteristic of allylic and aryl organosulfates, which can resonance-stabilize the simultaneously forming allylic and benzyl radicals (Attygalle et al. 2001).

Product ion spectra for 2-methylbenzyl sulfate and the 3-methylbenzyl sulfate are shown in Figure 2C and 2D, respectively. The molecular ion for 2-methylbenzyl sulfate was observed at m/z 201.0210 ($C_8H_9O_4S^-$, -6.0 ppm) with major fragments including the sulfite radical at m/z 79.9549 ($^*SO_3^-$, -23.8 ppm), the bisulfite anion at m/z 80.9628 (HSO_3^- , 22.2 ppm), the 2-methylbenzenide anion at m/z 91.0527 ($C_7H_7^-$, -23.7 ppm), the sulfate radical at m/z 95.9499 ($^*SO_4^-$, -18.8 ppm), and the bisulfate anion at m/z 96.9575 (HSO_4^- , -20.6 ppm). The molecular ion for 3-methylbenzyl sulfate was observed at m/z 201.0210 ($C_8H_9O_4S^-$, -6.0 ppm) with major fragments including the sulfite radical at m/z 79.9550 ($^*SO_3^-$, -22.5 ppm), the bisulfite anion at m/z 80.9627 (HSO_3^- , -23.5 ppm), and the sulfate radical 95.9499 ($^*SO_4^-$, -18.8 ppm). The mass spectra for 3-methylbenzyl sulfate and 4-methylbenzyl sulfate were sufficiently similar that the latter is not shown.

The characteristic fragments benzyl sulfate and methylbenzyl sulfates are the sulfite radical ($^*SO_3^-$, m/z 80) and the sulfate radical ($^*SO_4^-$, m/z 96). The bisulfite anion (HSO_3^- , m/z 81)

was detected only for the three methylbenzyl sulfate isomers. The bisulfate anion (HSO_4^- , m/z 97) was detected for 2-methylbenzyl sulfate only, because of the proximity of the methyl group to the sulfate moiety. In the case of 2-methylbenzyl sulfate, the bisulfate anion is not formed by syn elimination, as described previously, but by proton transfer from the nearby methyl group (Attygalle et al. 2001). The identification of characteristic fragment ions of aromatic organosulfates will facilitate their identification and quantification in atmospheric aerosol samples.

3.3 Identification and Quantification of Aromatic Organosulfates in Ambient Aerosol

Aromatic organosulfate standards were analyzed by UPLC-ToF MS; extracted ion chromatograms (EIC) for the molecular ions 172.99 ± 0.01 ($\text{C}_6\text{H}_5\text{SO}_4^-$, phenyl sulfate), 187.00 ± 0.01 ($\text{C}_7\text{H}_7\text{SO}_4^-$, benzyl sulfate and methylphenyl sulfates), and 201.02 ± 0.01 ($\text{C}_8\text{H}_9\text{SO}_4^-$, methylbenzyl sulfates) are shown in Figure 3A. Retention times of aromatic organosulfate standards on the reversed-phase UPLC column were 4.9 minutes for phenyl sulfate, 5.8 minutes for benzyl sulfate, 6.3 for 3- and 4-methylphenyl sulfates, which coeluted, 6.8 minutes for 2-methylbenzyl sulfate, and 7.0 minutes for 3- and 4-methylbenzyl sulfates, which also co-eluted. For the homologous series of phenyl and benzyl sulfates, retention on the UPLC column increased with increasing methyl substitution. In reversed-phase LC solute retention is caused by hydrophobic interactions between the nonpolar portion of the molecule and the octadecyl stationary phase. Analytes with increasingly hydrophobic characteristics (i.e. additional methyl groups) have stronger interactions with the stationary phase and longer retention times.

Ambient $\text{PM}_{2.5}$ samples, extracted into methanol, from Lahore, Pakistan, Godavari, Nepal, and Pasadena, CA, USA were analyzed by the same analytical method as the standard solutions and resulting EIC are shown in Figure 3B-D. Aromatic organosulfates were identified using high-resolution MS data (described in Section 3.1) and UPLC retention times. The aerosol sample from Lahore (Figure 3B) contained phenyl sulfate, benzyl sulfate, methylphenyl, and methylbenzyl sulfates. Of the aromatic organosulfates, only benzyl sulfate was detected in the Godavari, Nepal sample and benzyl sulfate and methylphenyl sulfates were detected in the Pasadena, CA samples.

Ambient concentrations of aromatic organosulfates are summarized in Table 2 with ambient OC, EC, and $\text{PM}_{2.5}$ mass concentrations. Concentrations of aromatic organosulfates were greatest in Lahore; the sum of three methylbenzyl sulfate isomers had the greatest abundance with 109 pg m^{-3} followed by benzyl sulfate at 90 pg m^{-3} , the three methylphenyl sulfate isomers at 31 pg m^{-3} , and phenyl sulfate with 4.4 pg m^{-3} . With sub-nanogram per cubic meter concentrations, aromatic organosulfates are significant contributors neither to $\text{PM}_{2.5}$ mass nor OC nor total organosulfates.

The ambient concentrations of aromatic organosulfates were approximately an order of magnitude lower at Godavari and Pasadena, which also had substantially lower OC and EC concentrations. Prior studies have documented the contributions of motor vehicles, fossil fuel use, and biomass burning to these three study sites (Stone et al. 2010a; Stone et al. 2010b; Hayes et al. 2013). In addition to having OC loadings 6-9 times greater than Godavari and Pasadena, the coal combustion impact at Lahore was an order of magnitude

greater than the other sites. Coal burning serves as a source of atmospheric sulfur and acidity, which may promote aromatic organosulfate formation. Biomass burning was suggested to be a source of aromatic organosulfates in Lahore by Kundu et al. (2013) following the correlation of benzyl sulfate with levoglucosan ($R^2 = 0.82$), suggesting aromatic organosulfates may derive from cresols or lignin-breakdown products emitted by biomass burning (Schauer et al. 2001). Likewise, fossil fuel use is a source of aromatic VOC to the atmosphere and may be a potential precursor to organosulfates.

3.4 Mass Spectral Response of Aromatic Organosulfate Standards

Due to the lack of authentic standards for atmospherically-relevant organosulfates, researchers have used surrogate standards for semi-quantitation. For organosulfate quantification in chamber experiments and ambient aerosols, camphor-10- sulfonic acid (Iinuma et al. 2007), sodium propylsulfate (Lin et al. 2013a), sodium 2-ethylhexyl sulfate (Stone et al. 2009), sodium galactose sulfate (Stone et al. 2012), sodium octyl sulfate and sodium decyl sulfate (Kahnt et al. 2013) have been used, which have different organic and ionic functional groups. Surrogates provide only a rough approximation of organosulfate concentrations, because they cannot represent the behavior of the analytes in the MS detector.

The homologous series of phenyl and benzyl sulfates synthesized in this study were used to investigate how organosulfates of similar molecular structure respond under ESI-MS conditions. Calibration curves for aromatic organosulfate standards based on peak area of molecular ions were developed over the concentration range of 1.0 – 25.0 ng mL⁻¹ and are shown in Figure 4. The response factors (i.e. slope of the calibration curves with units of counts per ng mL⁻¹) ranged from a low of 0.32 ± 0.03 for phenyl sulfate to 1.39 ± 0.06 for 3-methylphenyl sulfate, which differ by a factor of 4.3. Statistical analysis of least-squares linear regression parameters indicated significant differences ($p = 0.01$) in the response of phenyl sulfate from the four other standards. Benzyl sulfate and the structural isomers, 2- and 3-methyl benzyl sulfate did not have significantly different responses at the 95% confidence interval. These results demonstrate that significant biases may be introduced in to absolute quantitation of organosulfates when using a surrogate standard. Even when surrogate standards are structurally similar (i.e. phenyl sulfate and 3-methylphenyl sulfate), response factors may differ by more than a factor of four. Thus, future developments in detection and quantification of organosulfates should proceed in parallel with authentic standard development.

3.5 Toluene Chamber Samples

The photooxidation of toluene under conditions that form biogenic organosulfates (Zhang et al. 2012) did not produce detectable amounts of aromatic organosulfates. From this result, we conclude that aromatic organosulfates form under conditions and perhaps chemical pathways that are different from biogenic organosulfates. Primary combustion of biomass burning or fuels with high sulfur content are also suggested sources (Kundu et al. 2013).

Other volatile organic compound (VOC) precursors, such as styrene or polycyclic aromatic hydrocarbons (PAH), form aromatic ring-retaining SOA products (Shakya et al. 2010).

Notably, in the study of SOA produced from the photooxidation of naphthalene in the presence of ammonium sulfate seed aerosol using ESI-HRMS, Kautzman et al. (2010) observed the molecular ion at m/z 172.9903 ($C_6H_5O_4S^-$) at 4.1 minutes which accounted for 0.5% of the signal. This peak was tentatively assigned as an isomer of hydroxybenzene sulfonic acid due to the similar MS^2 spectra of an authentic standard; however the observed retention times did not match the standard (0.95 min). Instead, there is a closer match to the phenyl sulfate retention time reported in this study (at 4.9 minutes). These data support that phenyl sulfate could be produced from the photooxidation of naphthalene in the presence of sulfate aerosol. Likewise, methylphenyl sulfates could be produced from the photooxidation of methyl naphthalene. Future work should examine the chemical composition of SOA produced from naphthalene and methyl naphthalene in the presence of sulfate aerosol in order to evaluate the extent to which they contribute to aromatic organosulfates in the atmosphere.

4. Conclusions

Aromatic organosulfates are ubiquitous components of atmospheric aerosol, though observed at low atmospheric abundance ($< 0.1 \text{ ng m}^{-3}$). These molecules are unique from other organosulfates reported in the literature, in that they contain intact aromatic rings and sulfate moieties in the phenyl and benzyl positions. Through authentic standard development, we have identified the characteristic fragment ions of aromatic organosulfates, which include the sulfite radical ($^*SO_3^-$, m/z 80) and the sulfate radical ($^*SO_4^-$, m/z 96), but largely exclude the bisulfite anion (HSO_3^- , m/z 81) and bisulfate anion (HSO_4^- , m/z 97), which are characteristic of aliphatic organosulfates. The importance of using authentic standards for absolute quantitation has been demonstrated, while the use of surrogate standards may significantly bias quantitative results. While the sources of aromatic organosulfates in the atmosphere have not yet been fully elucidated, the toluene photooxidation experiments described herein show that they form under conditions different from biogenic organosulfates or have other VOC precursors. This work increases the breadth of understanding the composition and abundance of organosulfates in the atmosphere, and highlights the important role of authentic standard development in organosulfate identification and quantitation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Frank Keutsch, Ge Yu, and Jean C. Rivera at the University of Wisconsin-Madison for synthesizing benzyl and methylbenzyl sulfates, Lynn Teesch and Vic Parcell at the University of Iowa High Resolution Mass Spectrometry Facility for assistance with instrumental analysis, Patrick Hayes and Jose Jimenez for useful discussions on the estimation of $PM_{2.5}$ mass during CalNex, Bidya Banmali Pradhan and Pradeep Dangol at ICIMOD for collection of samples at Godavari, Tauseef Quraishi (retired) from the University of Engineering and Technology for collection of samples in Lahore, Pakistan, and Haofei Zhang for useful discussions, and James Schauer at the University of Wisconsin-Madison for access to filter samples. Research at the University of Iowa was funded by the Office of the Vice President for Research Mathematical and Physical Sciences Program. The synthesis of the phenol sulfate standards was in part supported by NIH grants ES05605 and ES013661 from the National Institute of Environmental Health Sciences. The University of North Carolina researchers thank Alion Science and Technology (subcontract EP-D-05-065) for supporting filter collection efforts during the 2010 CalNex field campaign.

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Highlights

- Homologous series of benzyl and phenyl sulfates were synthesized.
- Aromatic organosulfates were identified and quantified in ambient aerosol.
- Major ESI fragments of aromatic organosulfates include the sulfite and sulfate radicals.
- Toluene chamber experiments did not generate aromatic organosulfates.

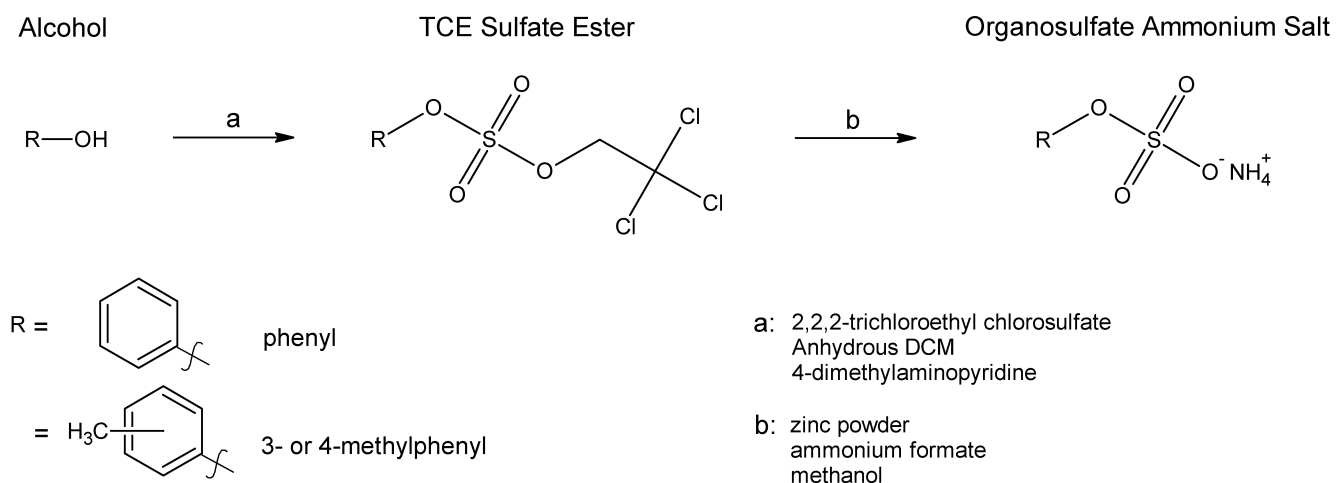


Figure 1.
The reaction scheme used in the synthesis of phenyl sulfate ammonium salts, via a trichloroethylester sulfate intermediate.

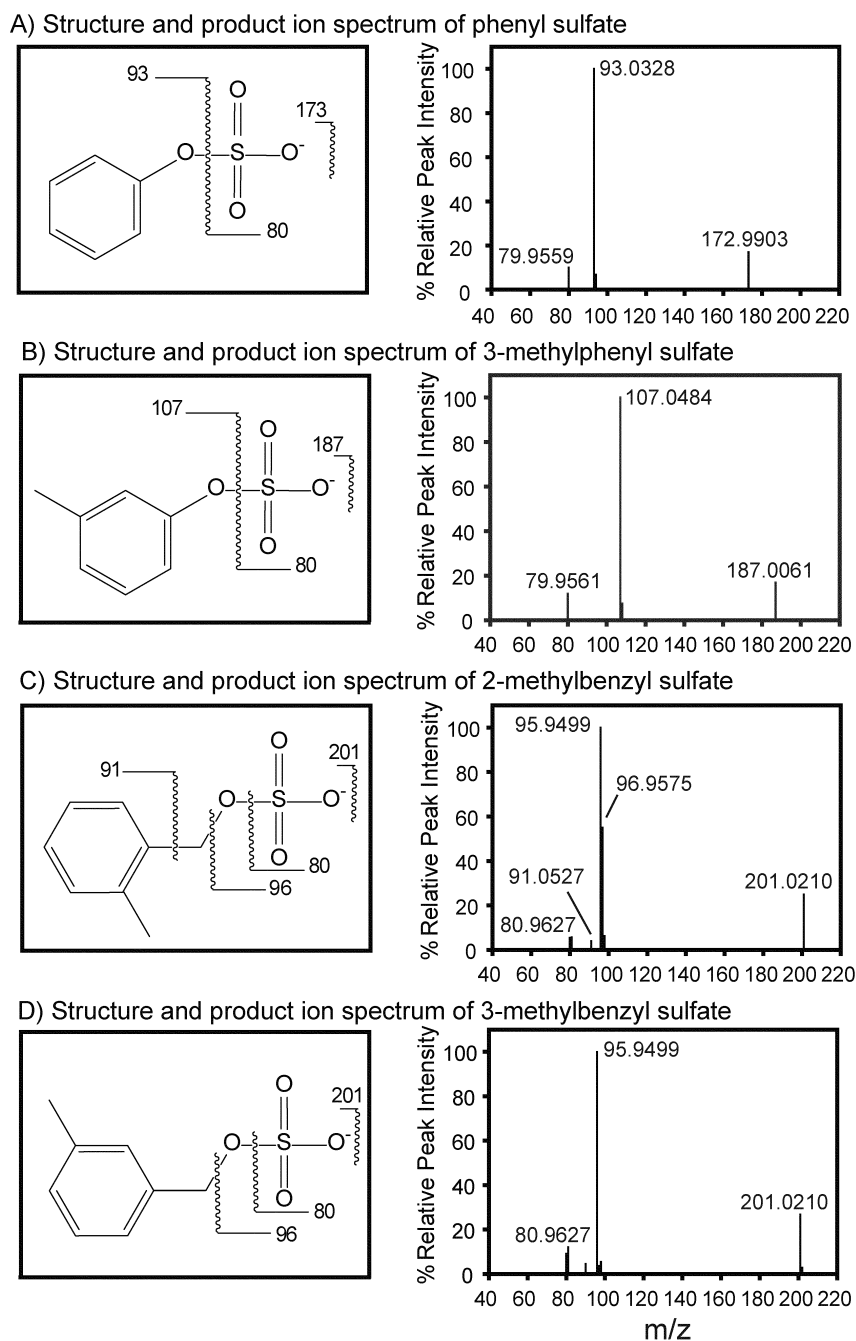


Figure 2. Molecular structures, fragmentation patterns, and MS² spectra of A) phenyl sulfate, B) 3-methylphenyl sulfate, C) 2-methylbenzyl sulfate and D) 3-methylbenzyl sulfate.

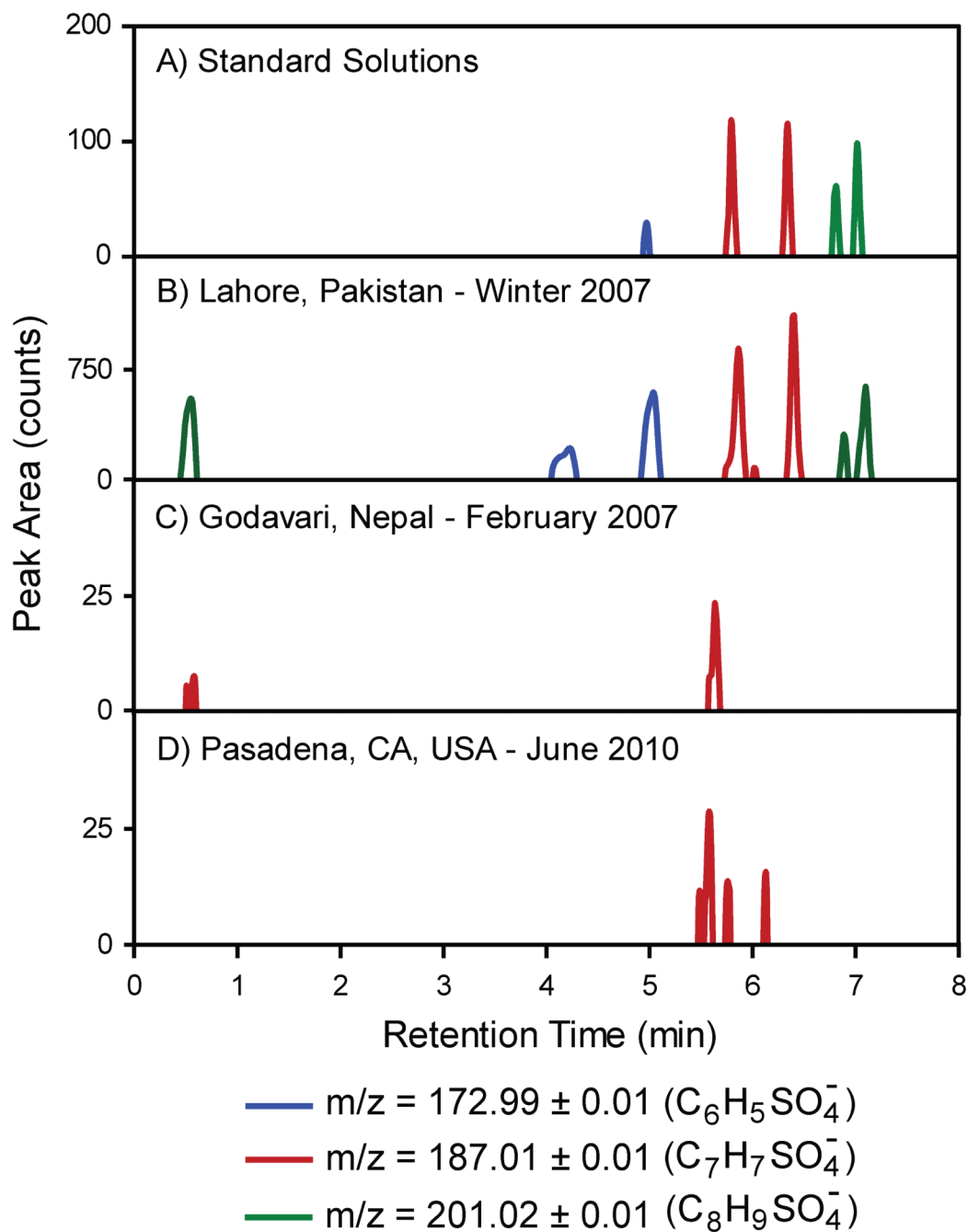


Figure 3.

Overlaid extracted ion chromatograms for aromatic organosulfate molecular ions. A) Standard solutions at 5 ng mL^{-1} , and $PM_{2.5}$ samples from B) Lahore, Pakistan, C) Godavari, Nepal, and D) Pasadena, California.

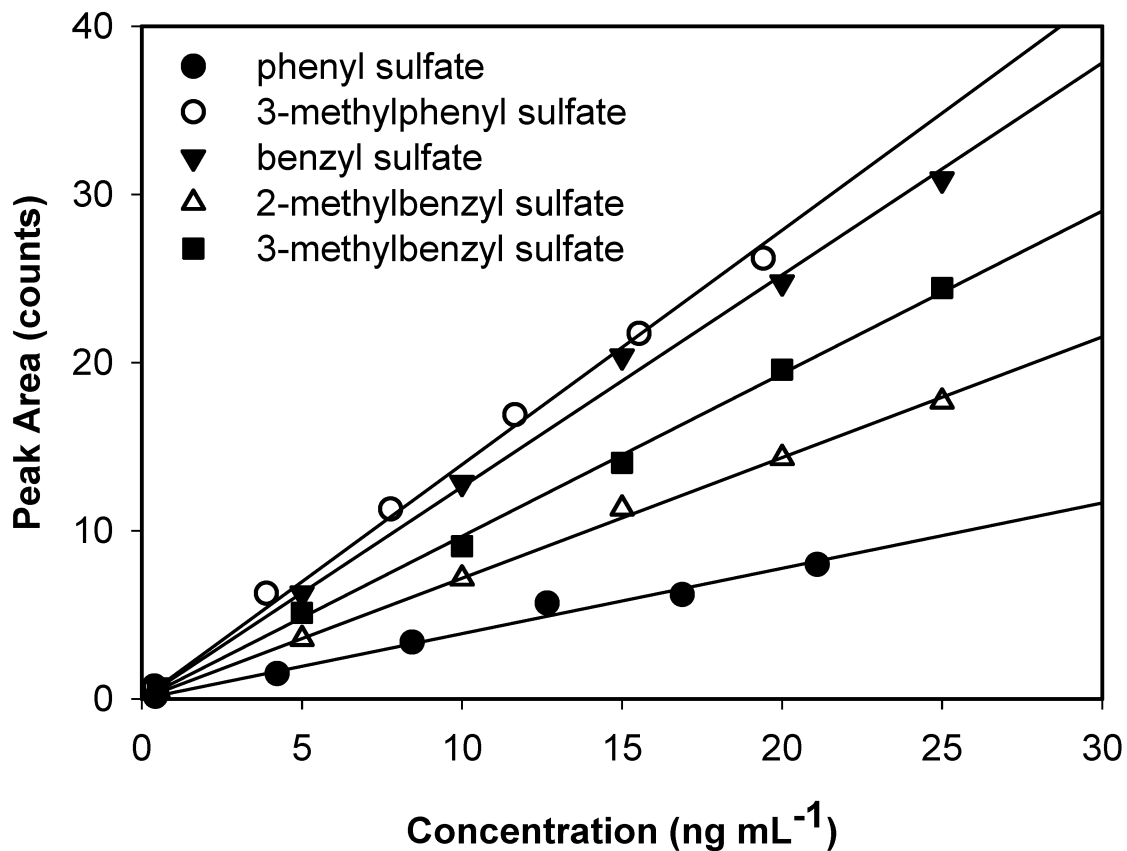


Figure 4. Comparison of response factors of synthesized aromatic organosulfates measured by UPLC-ToF.

Table 1

Experimental conditions and results for toluene/NO_x experiments conducted in UNC dual outdoor smog chamber.

Experimenta ID ^a	Initial [toluene] (ppb)	Initial [NO ₂] (ppb)	Initial [NO ₂] (ppb)	Initial O ₃ (ppb) ^b	Initial toluene/ NO _x	RH (%) ^c	Max O ₃ (ppb)	Max SOA concentration (μg m ⁻³)
Acidic	189	99	4	b.d.l.	1.8	63	161	15.9
Neutral	189	99	3	b.d.l.	1.9	63	151	19.4

^a Acidic seed aerosol was generated from atomizing 0.06 M MgSO₄ + 0.06 M H₂SO₄ (aq) solution into north chamber; neutral seed aerosol was generated from atomizing 0.06 M (NH₄)₂SO₄ (aq) solution into south chamber.

^b b.d.l. = below detection limits.

^c These are average values from the experiments.

Table 2

Concentrations of PM_{2.5}, organic carbon, elemental carbon, and aromatic organosulfates at the study sites.

Site Name	Date	Sampling Rate (n)	PM _{2.5} 3 (µg m ⁻³)	Organic Carbon (µgC m ⁻³)	Elemental Carbon (µgC m ⁻³)	Aromatic Sulfate Concentration (pg m ⁻³)			
						Phenyl Sulfate	Benzyl Sulfate	Methylphenyl Sulfates ^a	Methylbenzyl Sulfates ^b
Lahore, Pakistan	March, 2007	1-in-6 day (6)	177.1	44.6	11.1	4.4	90	31	109
Godavari, Nepal	February, 2007	Daily (28)	42.0	4.7	1.3	ND	3.9	ND	ND
Pasadena, USA	5 June, 2010	23-hour (1)	44.1	7.3	0.6	ND	6.3	2.3	ND
Pasadena, USA	6 June, 2010	23-hour (1)	41.8	7.6	0.5	ND	6.8	2.3	ND

ND - not detected

^a sum of 2-, 3-, and 4- methyl phenyl sulfate.

^b sum of 2-, 3-, and 4- methyl benzyl sulfate.