Title

Ubiquitous Production of Organosulfates during Treatment of Organic Contaminants with Sulfate Radicals

Journal

Environmental Science & Technology Letters, 8(7)

ISSN

2328-8930

Authors

Van Buren, Jean
Cuthbertson, Amy A
Ocasio, Daniel
et al.

Publication Date

2021-07-13

DOI

10.1021/acs.estlett.1c00316

Peer reviewed

HHS Public Access

Author manuscript

Environ Sci Technol Lett. Author manuscript; available in PMC 2022 January 13.

Published in final edited form as:

Environ Sci Technol Lett. 2021 July 13; 8(7): 574–580. doi:10.1021/acs.estlett.1c00316.

Ubiquitous Production of Organosulfates During Treatment of Organic Contaminants with Sulfate Radicals

Jean Van Buren[†], **Amy A. Cuthbertson**[‡], **Daniel Ocasio**[‡], **David L. Sedlak**[*,‡]

[†] Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720, USA

[‡] Department of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

Abstract

Oxidation of organic contaminants by sulfate radical ($SO_4^{\bullet-}$) is becoming more popular for the treatment of hazardous waste sites by *in situ* chemical oxidation (ISCO) and industrial wastewater by advanced oxidation processes (AOPs). It is well documented that $SO_4^{\bullet-}$ can produce similar oxygen-containing transformation products as hydroxyl radical–based treatment processes, but $SO_4^{\bullet-}$ also has the potential to produce organosulfates by radical addition. Experiments conducted with a suite of 23 aromatic and 5 aliphatic compounds, including several contaminants typically detected at hazardous waste sites, demonstrated the formation of at least one stable sulfate-containing product for 25 of the compounds. These compounds likely exhibit higher mobility in the subsurface due to a lower affinity for surfaces (e.g., aquifer solids, activated carbon) than most other transformation products. Although the health risks associated with organosulfates are still uncertain, some aromatic organosulfates produced in this study (i.e. phenyl sulfate and p-cresyl sulfate) are known to be harmful uremic toxins. Further study of organosulfate formation, fate, and toxicity is needed before $SO_4^{\bullet-}$–based treatment processes are more widely employed.

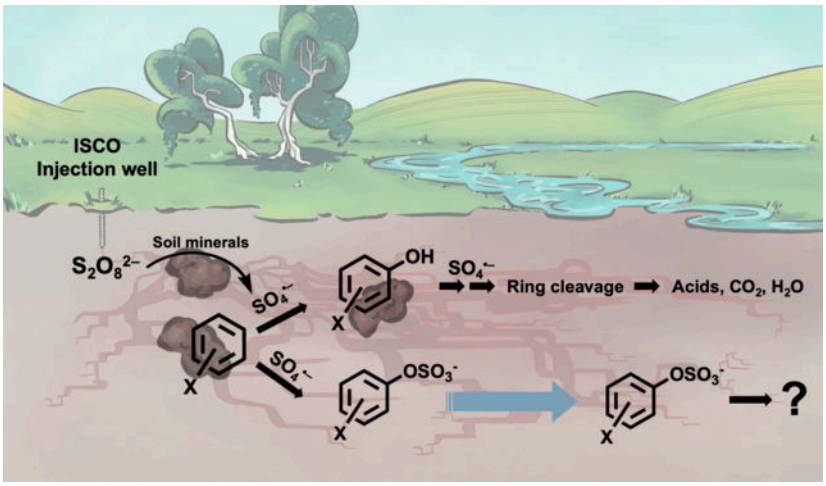
Graphical Abstract

[*]Corresponding author, sedlak@berkeley.edu.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.1c00316.

Details on chemicals used in experiments, exact mass values for sulfate-containing products, aqueous solubilities of organic compounds studied, HR-MS and LC-MS/MS spectra from oxidation experiments, LC-MS precursor ion scans and HR-MS spectra for organosulfate products.



Introduction

Over the past decade, the use of $SO_4^{\bullet-}$ as an oxidant of organic contaminants has received considerable attention. Specifically, injection of high concentrations of persulfate salts followed by thermal or base activation has become an important tool for ISCO at sites contaminated with petroleum hydrocarbons and recalcitrant organic contaminants.[1–3] Activation of peroxymonosulfate or peroxydisulfate salts by heat or ultraviolet light also has been proposed as an alternative to ozone or hydrogen peroxide–based advanced oxidation processes for the treatment of hazardous waste and industrial wastewater.[1,2,4,5] $SO_4^{\bullet-}$–based treatment technologies are attractive because $SO_4^{\bullet-}$ is a strong, moderately selective oxidant that can be produced easily from inexpensive reagents.[6]

Most research on the mechanisms of $SO_4^{\bullet-}$ reactions with organic compounds has focused on electron transfer and hydrogen abstraction because they are usually the dominant mechanisms through which $SO_4^{\bullet-}$ reacts.[7,8] Direct addition by $SO_4^{\bullet-}$ is known to occur, but it is usually considered a minor pathway.[7–11] Consistent with this view, researchers studying the treatment of contaminants with $SO_4^{\bullet-}$ have rarely considered the formation of stable organosulfate intermediates. As part of our recent effort to close the carbon mass balance during treatment of benzene and alkylated aromatic compounds with $SO_4^{\bullet-}$, we reported yields of organosulfate products from the oxidation of toluene in air-saturated solutions over 10%. Under anaerobic conditions, organosulfate yields increased by at least a factor of three.[12] Huang et al.[13] found that aromatic organosulfates were produced through a radical addition mechanism by the aqueous phase reactions of $SO_4^{\bullet-}$ with benzoic acid, phenol, and salicylic acid.

Recent research on atmospheric aerosols also indicates the formation of organosulfates in secondary organic aerosols.[14,15] Sulfate-containing organic compounds have been detected during the oxidation of aromatic hydrocarbons and biogenic volatile organic compounds.[13,16–21] Although Fe^{2+} and Mn^{2+} are believed to play a role in the process, particularly on dust particles, the role of $SO_4^{\bullet-}$ is uncertain and a radical addition mechanism has been recently proposed.[13,18,19,22,23] Researchers studying secondary organic

aerosols have estimated that organosulfates account for 5–10% of the organic mass in samples collected throughout the United States[24] and 7–16% in samples from the Southeastern United States.[25] Aromatic organosulfates in particular have been found in aerosols collected throughout the world.[20,26,27]

The formation of organosulfates during ISCO or industrial wastewater treatment is a concern for two reasons. First, addition of sulfate to an organic compound could increase its mobility by decreasing its partitioning to surfaces (e.g., aquifer solids, activated carbon). Second, some organosulfates also may be more toxic than their parent compounds due to some mode of action other than baseline toxicity. For example, *in vivo* metabolism of certain amino acids produces organosulfates associated with renal stress.[28,29] Metabolites such as p-cresyl sulfate and indoxyl sulfate are considered uremic toxins but their contribution to kidney disease was unclear[30] until recent studies directly linked exposure to phenyl sulfate and p-cresyl sulfate to kidney damage and renal cancer.[31–33] The toxicity of organosulfates is also a concern for inhalation of aerosol particles,[34] especially if compounds like p-cresyl sulfate and indoxyl sulfate are produced.

To extend our understanding of the formation of stable organosulfate products during treatment of organic contaminants with $SO_4^{\bullet-}$, we used LC-MS/MS fragmentation and high-resolution mass spectrometry to detect the formation of organosulfates from a suite of 28 organic contaminants. By comparing peak areas with those observed for p-cresyl sulfate —the only organosulfate compound for which an analytical standard was readily available— we assessed the approximate yield of organosulfates during degradation of these compounds in water treatment systems.

Materials and Methods

Organic reagents were used without further purification as detailed in the Supplementary Information section (Table S1). Inorganic compounds were obtained from Sigma-Aldrich. Solutions were prepared with 18.2 MΩ Milli-Q water from a Millipore System.

Reaction Conditions

Experiments were conducted in 8-mL quartz test tubes containing 10 mM $K_2S_2O_8$, buffered at pH 8 with a 50 mM borate buffer, prepared with boric acid and sodium borate. Liquid organic compounds were added into the borate buffer with an automatic micropipette. For compounds that were solids at room temperature, 10 to 20 mg of the pure material (i.e., enough to yield a final concentration of 1 mM) was added directly to the borate-buffered persulfate solutions. The solutions were initially air-saturated and on the basis of our previous research comparing air-saturated samples to deoxygenated samples,[12] we presume that O_2 was not depleted during the experiments. The quartz test tubes were thoroughly shaken and vortexed prior to initiating the experiment. Most of the organic compounds had solubilities above 1 mM and were assumed to reach equilibrium (Table S3). For several of the more hydrophobic compounds, visual observation indicated incomplete dissolution. Nonetheless, transformation products were still detected for these compounds.

Persulfate was converted into $SO_4^{\bullet-}$ by exposure to UV light produced by a 450-W medium pressure mercury lamp sleeved in a quartz immersion well (Ace Glass). Through the use of a cooling jacket around the lamp, the temperature in the reactor was maintained at 27 °C. After 10 minutes of UV exposure, samples were placed in the dark and submerged in an ice bath to slow further reactions. A control sample consisting of the borate-buffered persulfate solution without any added organic compound was analyzed along with each set of samples. In our previous study,[12] controls conducted in borate-buffered solutions of benzene, toluene, ethylbenzene, or xylene (BTEX) indicated losses due to direct photolysis without organosulfate production. The presence of 10 mM $S_2O_8^{2-}$ ($\epsilon_{254\ nm} \sim 200\ M^{-1}\ cm^{-1}$)[35] at the start of the process and about 5 mM after 10 min of UV irradiation screened most of the UV light, resulting in negligible loss through direct photolysis as discussed in Van Buren et al.[12] Solutions were stored at 4 °C until analysis, which occurred within 1–24 hours. Repeat analysis of samples indicated little loss of the organosulfates products after 1 to 3 months for storage at 4 °C. Each experiment was repeated on two or three separate occasions, depending on the contaminant group, with replicates on different days yielding similar results.

Product Analysis

Prior to conducting high-resolution mass spectrometry, 15 compounds were screened for organosulfate products using an Agilent 1200 series HPLC system coupled to a 6460C triple quadrupole mass spectrometer (LC-MS/MS) operating in negative mode with electrospray ionization (ESI). Chromatographic separation was achieved on a Phenomenex Synergi Hydro-RP column with a gradient program of 0.1% acetic acid in water and methanol at a flow rate of 0.4 mL/min with 25 μL injection volumes. The percentage of methanol in the gradient program was varied during the run: 0 min, 0%; 2 min, 0%; 11 min, 95%; 14 min, 95%; 14.1 min, 0%; 20 min, 0%. Full scans, precursor scans, and MS/MS spectra were obtained with a fragmentor voltage of 80 V. Precursor ion scans targeted m/z (−) 80, 81 ($SO_3^{\bullet-}$, HSO_3^-) and 96, 97 ($SO_4^{\bullet-}$, HSO_4^-), at a collision energy of 20%. MS/MS fragmentation was conducted with collision energies of 20% and 40%.

A total of 25 samples were analyzed with a Thermo Scientific LTQ Orbitrap XL coupled to an Agilent 1260 HPLC system to obtain accurate masses. The chromatographic method is detailed above and the Orbitrap was operated in negative mode using ESI.

Results and Discussion

On the basis of previous experiments,[12] conditions were chosen such that 50 to 75% of the parent compound would be transformed by $SO_4^{\bullet-}$, assuming that the reactivity of the compounds with $SO_4^{\bullet-}$ was similar to that of benzene (i.e., $k_{SO4\bullet-} \sim 3 \times 10^9\ M^{-1}\ s^{-1}$).[7] The exception to this assumption was nitrobenzene ($k_{SO4\bullet-} \leq 10^6\ M^{-1}\ s^{-1}$),[7] which still yielded detectable levels of sulfate-containing products under these conditions despite its lower reported rate constant.[36] Other substituents are likely to have smaller effects on the rate constants.[7,37] For example, $k_{SO4\bullet-}$ for benzene, phenol, and anisole ranged from 4.9×10^9 to $6.2 \times 10^9\ M^{-1}\ s^{-1}$.[38,39] Although these conditions assumed the highest possible concentration of sulfate-containing transformation products, some products of a second

attack by $SO_4^{\bullet-}$ were expected (i.e., the initial transformation products were approximately as reactive with $SO_4^{\bullet-}$ as the parent compounds).

Sulfate-containing products were detected after $SO_4^{\bullet-}$ treatment for 25 of the 28 organic compounds studied (Table 1). The only compounds for which no organosulfates were detected were benzenesulfonic acid and the two alkanes (i.e., heptane and iso-octane), however, this may be due to the low solubilities of heptane and iso-octane (Table S3). Negative mode ESI LC-MS full scans of these samples along with MS/MS fragmentation spectra for products provided evidence for formation of organosulfates (Figure S1). Fragmentation patterns were consistent with sulfate esters, which exhibit characteristic losses of $SO_3^{\bullet-}$ and/or HSO_4^-.[40,41] Multiple isomers with different retention times and identical fragmentation spectra were formed for over half of the detected organosulfates.

Organosulfate products were verified through exact masses obtained by Orbitrap high-resolution MS (HR-MS). Errors between the measured mass and those expected for the sulfate-containing product were less than 3 ppm, confirming the assigned formulas (Table S2). Because analytical standards were not available, insight into the yields of organosulfates can be compared with p-cresyl sulfate, a compound for which yields from toluene were approximately 10%. Assuming that the response factors were equivalent to that of p-cresyl sulfate for all sulfate esters, peak areas provide a qualitative understanding of the relative yields of organosulfates. However, it is possible that some of the differences among compounds were due to the incomplete dissolution of the parent compound or variability in instrument response. Under these conditions, peak areas suggested yields ranging from 0.06% for pyridine to about 50% for 1-octanol. Although m-xylene and ethylbenzene exhibited the lowest solubility (Table S3) out of the compounds for which organosulfate products were detected, organosulfate peak areas fell in the middle of this range for m-xylene and at the low end for ethylbenzene (Figure S3).

Chlorobenzene (Figure 1) serves as a representative example of the chromatograms and spectra for compounds included in the Supplementary Information. In the HR-MS analysis, two isomers with molecular ions of m/z 206.9522 were assigned the formula $C_6H_4O_4ClS$. For chlorobenzene, $SO_4^{\bullet-}$ is presumed to add onto the aromatic ring at both the *ortho* and *para* positions to the electron-withdrawing –Cl group to form both 2-chlorophenyl sulfate and 4-chlorophenyl sulfate. Peaks with this mass were detected at retention times of 10.2 and 11.2 minutes (Figure 1A, red chromatogram). Two additional sulfate-containing masses (m/z 223 and m/z 189) were identified by the precursor scan (Figure S2) and observed by HR-MS and MS/MS (Figure 1). Three peaks with a m/z of 222.9470 (Figure 1A, blue chromatogram) were assigned as $C_6H_4O_5ClS$, (4-chloro-3-hydroxyphenyl sulfate, 2-chloro-5-hydroxyphenyl sulfate, and 5-chloro-2-hydroxyphenyl sulfate). The isomers with m/z of 188.9861 (Figure 1A, green chromatogram), were assigned as $C_6H_5O_5S$, 2-hydroxyphenyl sulfate (pyrocatechol sulfate) and 4-hydroxyphenyl sulfate. MS^2 spectra were identical among isomers with a major fragment for all organosulfate products associated with the loss of sulfite ion radical ($SO_3^{\bullet-}$, m/z 80) from the molecular ion, consistent with the fragmentation pattern of organosulfates (Figure 1).[40,41] Fragmentation patterns for the remaining compounds analyzed by MS/MS were observed for the 11

aromatic compounds, while the three aliphatic compounds exhibited a fragment with a m/z 80 and/or 97 (HSO_4^-), presumably due to lack of additional ionizable groups (Figure S1).

A series of other hydroxysulfates ($HO–R–OSO_3^-$) were detected, usually with lower peak areas than $R–OSO_3^-$, for 21 of the 28 compounds (Table 1). One possible pathway for the formation of these compounds involves the reaction of $SO_4^{\bullet-}$ with a hydroxylated product formed by the initial radical attack on the parent compound. This result is evident by comparision of the sulfate products of o, m, and p-cresol with the hydroxysulfate products of the reaction of toluene with $SO_4^{\bullet-}$ (Figure 2). For p-cresol, a total of three compounds with sulfate groups were observed, likely corresponding to sulfate addition in the ortho and meta positions as well as on the methyl group (Figure S1D). At least four out of a total of five possible products were observed for o- and m-cresol while toluene exhibited at least six out of thirteen possible products.

Products containing a sulfate and an additional hydroxyl group were not detected for catechol, hydroquinone, 4-chlorophenol, and 4-nitrophenol. It is possible that catechol hydroxysulfate could not be detected due to the effect of the substituents on its retention time, as catechol sulfate eluted at 5.3 minutes and adding a hydroxyl group to phenol sulfate reduced its HPLC retention time by 2.9 minutes (Figure S1). If catechol or hydroquinine had undergone hydroxylation to form a trihydroxybenzene, it is possible that these products would undergo subsequent ring cleavage or direct thermal reaction with the remaining persulfate; our efforts to study the products of phenol oxidation by persulfate indicated that persulfate reacts quickly with dehydroxylated aromatics, especially at elevated temperatures (Sedlak et al. unpublished data).

No sulfate product was observed for oxidation of benzenesulfonic acid, and no products containing two sulfate groups were observed for any compound. It is possible that such compounds formed but eluted too early in the chromatography to be detected. A deactivating sulfate group may decrease the reactivity of an aromatic compound with $SO_4^{\bullet-}$ and inhibit further reaction,[7,42] however, phenyl sulfate and cresyl sulfate degraded after extended exposure to $SO_4^{\bullet-}$.[12]

Environmental Implications

After their formation, organosulfates can undergo further transformation through different mechanisms. Under ISCO conditions, organosulfates are stable with respect to hydrolysis,[42] and are probably less reactive with $S_2O_8^{2-}$ than their parent compound, but continued oxidation is possible through further reactions with $SO_4^{\bullet-}$.[12] Reaction with the $HO^{\bullet}$ produced during persulfate decomposition also may result in further transformation and eventually mineralization.[43–45]

Organosulfates could also undergo biotransformation. In addition to microbial attack on other parts of the molecules,[46,47] microbial sulfatase enzymes could cleave the sulfate ester at the C–OS bond to liberate the parent compound, or at the CO–S bond to form an alcohol.[48,49] The former reaction might make it seem as if an additional source of the compound was present after ISCO. However, deconjugation is unlikely to be a major

removal mechanism, because some sulfate-containing metabolites persist in the environment despite the widespread presence of sulfatase enzymes.[50,51]

Relative to the neutral aromatic or aliphatic parent compounds, hydroxylated products tend to partition to a lesser degree into the organic fraction of soils and aquifer solids through hydrophobic interactions. After they undergo sulfate addition, most of the compounds will exhibit a negative charge due to the acidic nature of the sulfate group. These transformation products exhibit an even lower affinity for soils or aquifer solids. Thus, partitioning of organosulfates through hydrophobic interactions will be replaced by electrostatic interactions (e.g., anion exchange, surface complexation). Although it is difficult to make predictions about the effect of sulfate addition on the transport of contaminants under all possible conditions, there is strong evidence that organosulfate compounds are more mobile than neutral, moderately hydrophobic contaminants in groundwater.

Steroidal estrogen contaminants in groundwater offer an instructive example of the way in which sulfate addition affects contaminant fate and transport.[52] During *in vivo* metabolism, steroids often undergo sulfate addition prior to elimination. As a result, a significant fraction of the steroidal estrogens occur in sewage as a mixture of estrogen sulfate conjugates (i.e., the parent estrogen with a sulfate group replacing the phenolic group) and in neutral forms (i.e., their pK_a values typically range from 10.3 to 10.8). The neutral steroids are moderately hydrophobic (i.e., the logarithms of their octanol-water partition coefficients typically range from 2.6 to 4.0).[53] Although research is limited, sorption of sulfate conjugates to soil appears to be insignificant compared to free estrogens.[54–57] Upon release to the subsurface (e.g., the discharge of septic tanks or during aquifer recharge) the mobility of the steroidal estrogens is modest, with retardation factors ranging from 16 to 20 in shallow aquifers.[58] Addition of a sulfate group yields a negatively charged conjugate that exhibits a much lower affinity for aquifer solids[53] and is relatively resistant to deconjugation.[59,60] By analogy to the aromatic and aliphatic compounds studied here, we expect that organosulfates like those listed in Table 1 will exhibit significant mobility in the subsurface or in soils relative to their uncharged precursors. Sulfate moieties also may be added to natural organic matter when $SO_4^{\bullet-}$ is used for treatment, altering the structure of the polymer as well as its solubility and charge.

To the best of our knowledge, toxicity data are only available for the benzene and toluene sulfates, and recent findings have raised concerns about the toxicity of these compounds.[31–33]

Hydroxyl radical–based treatment systems have been studied for several decades. Although the ability of $SO_4^{\bullet-}$ to oxidize organic compounds has been understood for almost as long, additional efforts need to be made to understand the formation, fate, and health effects of organosulfates produced in $SO_4^{\bullet-}$–based water treatment processes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This research was supported by the US National Institute for Environmental Health Sciences Superfund Research Program (Grant P42 ES004705) at the University of California, Berkeley. The authors thank Dr. Martyn Smith for his insight and guidance as well as Dr. Anthony Iavarone for his assistance with high resolution mass spectrometry.

References

(1). Tsitonaki A; Petri BG; Crimi M; Mosbk H; Siegrist RL; Bjerg PLIn Situ Chemical Oxidation of Contaminated Soil and Groundwater Using Persulfate: A Review. Crit. Rev. Environ. Sci. Technol. 2010, 40 (1), 55–91. 10.1080/10643380802039303.

(2). Wacławek S; Lutze HV; Grübel K; Padil VVT; Černík M; Dionysiou DDChemistry of Persulfates in Water and Wastewater Treatment: A Review. Chem. Eng. J. 2017, 330, 44–62. 10.1016/j.cej.2017.07.132.

(3). Krembs FJ; Siegrist RL; Crimi M; Furrer RF; Petri BGISCO for Groundwater Remediation: Analysis of Field Applications and Performance. Ground Water Monit. Remediat. 2010, 30 (4), 42–53. 10.1111/j.1745-6592.2010.01312.x.

(4). Wang J; Wang SActivation of Persulfate (PS) and Peroxymonosulfate (PMS) and Application for the Degradation of Emerging Contaminants. Chem. Eng. J. 2018, 334 (7 2017), 1502–1517. 10.1016/j.cej.2017.11.059.

(5). Ghauch A; Tuqan AMOxidation of Bisoprolol in Heated Persulfate/H_2O Systems: Kinetics and Products. Chem. Eng. J. 2012, 183 (2012), 162–171. 10.1016/j.cej.2011.12.048.

(6). Ike IA; Linden KG; Orbell JD; Duke MCritical Review of the Science and Sustainability of Persulphate Advanced Oxidation Processes. Chem. Eng. J. 2018, 338, 651–669. 10.1016/j.cej.2018.01.034.

(7). Neta P; Madhavan V; Zemel H; Fessenden RWRate Constants and Mechanism of Reaction of $SO_4^{\bullet-}$ with Aromatic Compounds. J. Am. Chem. Soc. 1977, 99 (1), 163–164. 10.1021/ja00443a030.

(8). Merga G; Aravindakumar CT; Rao BSM; Mohan H; Mittal JPPulse Radiolysis Study of the Reactions of $SO_4^{\bullet-}$ with Some Substituted Benzenes in Aqueous Solution. J. Chem. Soc., Faraday Trans. 1994, 90 (4), 597–604. 10.1039/FT9949000597.

(9). Norman ROC; Storey PM; West PRElectron Spin Resonance Studies. Part XXV. Reactions of the Sulphate Radical Anion with Organic Compounds. J. Chem. Soc. B1970, 1087–1095. 10.1039/J29700001087.

(10). Steenken SOne-Electron Redox Reactions between Radicals and Organic Molecules. An Addition/Elimination (Inner-Sphere) Path [1]. In Electron Transfer II. Topics in Current Chemistry; Mattay J, Ed.; Springer, Berlin, Heidelberg, 1996; Vol. 177, pp 125–145. 10.1007/3-540-60110-4_4.

(11). Luo S; Wei Z; Spinney R; Villamena FA; Dionysiou DD; Chen D; Tang CJ; Chai L; Xiao RQuantitative Structure–Activity Relationships for Reactivities of Sulfate and Hydroxyl Radicals with Aromatic Contaminants through Single–Electron Transfer Pathway. J. Hazard. Mater. 2018, 344, 1165–1173. 10.1016/j.jhazmat.2017.09.024. [PubMed: 28964582]

(12). Van Buren J; Prasse C; L. Marron E; Skeel B; L. Sedlak DRing-Cleavage Products Produced during the Initial Phase of Oxidative Treatment of Alkyl-Substituted Aromatic Compounds. Environ. Sci. Technol. 2020, 54 (13), 8352–8361. 10.1021/acs.est.0c00432. [PubMed: 32519538]

(13). Huang L; Liu T; Grassian VHRadical-Initiated Formation of Aromatic Organosulfates and Sulfonates in the Aqueous Phase. Environ. Sci. Technol. 2020, 54 (19), 11857–11864. 10.1021/acs.est.0c05644. [PubMed: 32969227]

(14). Herrmann H; Schaefer T; Tilgner A; Styler SA; Weller C; Teich M; Otto TTropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase. Chem. Rev. 2015, 115 (10), 4259–4334. 10.1021/cr500447k. [PubMed: 25950643]

(15). Surratt JD; Kroll JH; Kleindienst TE; Edney EO; Claeys M; Sorooshian A; Ng NL; Offenberg JH; Lewandowski M; Jaoui M; Flagan RC; Seinfeld JHEvidence for Organosulfates in Secondary Organic Aerosol. Environ. Sci. Technol. 2007, 41 (2), 517–527. 10.1021/es062081q. [PubMed: 17310716]

(16). Nozière B; Ekström S; Alsberg T; Holmström SRadical-Initiated Formation of Organosulfates and Surfactants in Atmospheric Aerosols. Geophys. Res. Lett. 2010, 37 (5), 1–6. 10.1029/2009GL041683.

(17). Schindelka J; Iinuma Y; Hoffmann D; Herrmann HSulfate Radical-Initiated Formation of Isoprene-Derived Organosulfates in Atmospheric Aerosols. Faraday Discuss. 2013, 165, 237–259. 10.1039/c3fd00042g. [PubMed: 24601005]

(18). Huang L; Coddens EM; Grassian VHFormation of Organosulfur Compounds from Aqueous Phase Reactions of S(IV) with Methacrolein and Methyl Vinyl Ketone in the Presence of Transition Metal Ions. ACS Earth Sp. Chem. 2019, 3 (9), 1749–1755. 10.1021/acsearthspacechem.9b00173.

(19). Huang L; Cochran RE; Coddens EM; Grassian VHFormation of Organosulfur Compounds through Transition Metal Ion-Catalyzed Aqueous Phase Reactions. Environ. Sci. Technol. Lett. 2018, 5 (6), 315–321. 10.1021/acs.estlett.8b00225.

(20). Riva M; Tomaz S; Cui T; Lin YH; Perraudin E; Gold A; Stone EA; Villenave E; Surratt JDEvidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol. Environ. Sci. Technol. 2015, 49 (11), 6654–6664. 10.1021/acs.est.5b00836. [PubMed: 25879928]

(21). Surratt JD; Gómez-González Y; Chan AWH; Vermeylen R; Shahgholi M; Kleindienst TE; Edney EO; Offenberg JH; Lewandowski M; Jaoui M; Maenhaut W; Claeys M; Flagan RC; Seinfeld JHOrganosulfate Formation in Biogenic Secondary Organic Aerosol. J. Phys. Chem. A2008, 112 (36), 8345–8378. 10.1021/jp802310p. [PubMed: 18710205]

(22). Schmidt M; Jansen Van Beek SM; Abou-Ghanem M; Oliynyk AO; Locock AJ; Styler SAProduction of Atmospheric Organosulfates via Mineral-Mediated Photochemistry. ACS Earth Sp. Chem. 2019, 3 (3), 424–431. 10.1021/acsearthspacechem.8b00178.

(23). Ren H; Sedlak JA; Elrod MJGeneral Mechanism for Sulfate Radical Addition to Olefinic Volatile Organic Compounds in Secondary Organic Aerosol. Environ. Sci. Technol. 2021, 55 (3), 1456–1465. 10.1021/acs.est.0c05256. [PubMed: 33475357]

(24). Tolocka MP; Turpin BContribution of Organosulfur Compounds to Organic Aerosol Mass. Environ. Sci. Technol. 2012, 46 (15), 7978–7983. 10.1021/es300651v. [PubMed: 22731120]

(25). Hettiyadura APS; Al-Naiema IM; Hughes DD; Fang T; Stone EAOrganosulfates in Atlanta, Georgia: Anthropogenic Influences on Biogenic Secondary Organic Aerosol Formation. Atmos. Chem. Phys. 2019, 19 (5), 3191–3206. 10.5194/acp-19-3191-2019.

(26). Staudt S; Kundu S; Lehmler HJ; He X; Cui T; Lin YH; Kristensen K; Glasius M; Zhang X; Weber RJ; Surratt JD; Stone EAAromatic Organosulfates in Atmospheric Aerosols: Synthesis, Characterization, and Abundance. Atmos. Environ. 2014, 94, 366–373. 10.1016/j.atmosenv.2014.05.049.

(27). Kundu S; Quraishi TA; Yu G; Suarez C; Keutsch FN; Stone EAEvidence and Quantitation of Aromatic Organosulfates in Ambient Aerosols in Lahore, Pakistan. Atmos. Chem. Phys. 2013, 13 (9), 4865–4875. 10.5194/acp-13-4865-2013.

(28). Gryp T; Vanholder R; Vaneechoutte M; Glorieux GP-Cresyl Sulfate. Toxins (Basel). 2017, 9 (2), 1–24. 10.3390/toxins9020052.

(29). Evenepoel P; Meijers BKI; Bammens BRM; Verbeke KUremic Toxins Originating from Colonic Microbial Metabolism. Kidney Int. 2009, 76 (SUPPL. 114). 10.1038/ki.2009.402.

(30). Vanholder R; Schepers E; Pletinck A; Nagler EV; Glorieux GThe Uremic Toxicity of Indoxyl Sulfate and P-Cresyl Sulfate: A Systematic Review. J. Am. Soc. Nephrol. 2014, 25 (9), 1897–1907. 10.1681/ASN.2013101062. [PubMed: 24812165]

(31). Kikuchi K; Saigusa D; Kanemitsu Y; Matsumoto Y; Thanai P; Suzuki N; Mise K; Yamaguchi H; Nakamura T; Asaji K; Mukawa C; Tsukamoto H; Sato T; Oikawa Y; Iwasaki T; Oe Y; Tsukimi T; Fukuda NN; Ho H-Jet al.Gut Microbiome-Derived Phenyl Sulfate Contributes to Albuminuria in Diabetic Kidney Disease. Nat. Commun. 2019, 10 (1), 1835. 10.1038/s41467-019-09735-4. [PubMed: 31015435]

(32). Wu TK; Wei CW; Pan YR; Hsu RJ; Wu CY; Yu YLThe Uremic Toxin P-Cresyl Sulfate Induces Proliferation and Migration of Clear Cell Renal Cell Carcinoma via MicroRNA-21/ HIF-1α Axis Signals. Sci. Rep. 2019, 9 (1), 1–10. 10.1038/s41598-019-39646-9. [PubMed: 30626917]

(33). Peng Y. Sen; Syu JP; Wang S. De; Pan PC; Kung HNBSA-Bounded p-Cresyl Sulfate Potentiates the Malignancy of Bladder Carcinoma by Triggering Cell Migration and EMT through the ROS/Src/FAK Signaling Pathway. Cell Biol. Toxicol. 2019. 10.1007/s10565-019-09509-0.

(34). Kramer AJ; Rattanavaraha W; Zhang Z; Gold A; Surratt JD; Lin YHAssessing the Oxidative Potential of Isoprene-Derived Epoxides and Secondary Organic Aerosol. Atmos. Environ. 2016, 130, 211–218. 10.1016/j.atmosenv.2015.10.018.

(35). Anipsitakis GP; Dionysiou DDTransition Metal/UV-Based Advanced Oxidation Technologies for Water Decontamination. Appl. Catal. B Environ. 2004, 54 (3), 155–163. 10.1016/j.apcatb.2004.05.025.

(36). Ji Y; Shi Y; Wang L; Lu JDenitration and Renitration Processes in Sulfate Radical-Mediated Degradation of Nitrobenzene. Chem. Eng. J. 2017, 315, 591–597. 10.1016/j.cej.2017.01.071.

(37). Ye T; Wei Z; Spinney R; Tang CJ; Luo S; Xiao R; Dionysiou DDChemical Structure-Based Predictive Model for the Oxidation of Trace Organic Contaminants by Sulfate Radical. Water Res. 2017, 116, 106–115. 10.1016/j.watres.2017.03.015. [PubMed: 28324707]

(38). Wojnárovits L; Takács ERate Constants of Sulfate Radical Anion Reactions with Organic Molecules: A Review. Chemosphere2019, 220, 1014–1032. 10.1016/j.chemosphere.2018.12.156. [PubMed: 33395788]

(39). Neta P; Huie RE; Ross ABRate Constants for Reactions of Inorganic Radicals in Aqueous Solution. J. Phys. Chem. Ref. Data1988, 17 (3), 1027–1284. 10.1063/1.555808.

(40). Metzger K; Erben G; Lehmann WD; Rehberger PAIdentification and Quantification of Lipid Sulfate Esters by Electrospray Ionization MS/MS Techniques: Cholesterol Sulfate. Anal. Chem. 1995, 67 (22), 4178–4183. 10.1021/ac00118a022.

(41). Hettiyadura APS; Stone EA; Kundu S; Baker Z; Geddes E; Richards K; Humphry TDetermination of Atmospheric Organosulfates Using HILIC Chromatography with MS Detection. Atmos. Meas. Tech. 2015, 8 (6), 2347–2358. 10.5194/amt-8-2347-2015.

(42). Hu KS; Darer AI; Elrod MJThermodynamics and Kinetics of the Hydrolysis of Atmospherically Relevant Organonitrates and Organosulfates. Atmos. Chem. Phys. 2011, 11 (16), 8307–8320. 10.5194/acp-11-8307-2011.

(43). Waldemer RH; Tratnyek PG; Johnson RL; Nurmi JTOxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products. Environ. Sci. Technol. 2007, 41 (3), 1010–1015. 10.1021/es062237m. [PubMed: 17328217]

(44). Zhou Y; Xiang Y; He Y; Yang Y; Zhang J; Luo L; Peng H; Dai C; Zhu F; Tang LApplications and Factors Influencing of the Persulfate-Based Advanced Oxidation Processes for the Remediation of Groundwater and Soil Contaminated with Organic Compounds. J. Hazard. Mater. 2018, 359 (April), 396–407. 10.1016/j.jhazmat.2018.07.083. [PubMed: 30055429]

(45). Lutze HV; Kerlin N; Schmidt TCSulfate Radical-Based Water Treatment in Presence of Chloride: Formation of Chlorate, Inter-Conversion of Sulfate Radicals into Hydroxyl Radicals and Influence of Bicarbonate. Water Res. 2015, 72, 349–360. 10.1016/j.watres.2014.10.006. [PubMed: 25455043]

(46). Cunningham JA; Rahme H; Hopkins GD; Lebron C; Reinhard MEnhanced in Situ Bioremediation of BTEX-Contaminated Groundwater by Combined Injection of Nitrate and Sulfate. Environ. Sci. Technol. 2001, 35 (8), 1663–1670. 10.1021/es001722t. [PubMed: 11329718]

(47). Deeb RA; Alvarez-Cohen LTemperature Effects and Substrate Interactions during the Aerobic Biotransformation of BTEX Mixtures by Toluene-Enriched Consortia and Rhodococcus Rhodochrous. Biotechnol. Bioeng. 1999, 62 (5), 526–536. 10.1002/(SICI)1097-0290(19990305)62:5<526::AID-BIT4>3.0.CO;2-8. [PubMed: 10099561]

(48). Kertesz MARiding the Sulfur Cycle - Metabolism of Sulfonates and Sulfate Esters in Gram-Negative Bacteria. FEMS Microbiol. Rev. 2000, 24 (2), 135–175. 10.1016/S0168-6445(99)00033-9. [PubMed: 10717312]

(49). Hanson SR; Best MD; Wong CHSulfatases: Structure, Mechanism, Biological Activity, Inhibition, and Synthetic Utility. Angew. Chemie - Int. Ed. 2004, 43 (43), 5736–5763. 10.1002/anie.200300632.

(50). Marco-Urrea E; García-Romera I; Aranda EPotential of Non-Ligninolytic Fungi in Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbons. N. Biotechnol. 2015, 32 (6), 620–628. 10.1016/j.nbt.2015.01.005. [PubMed: 25681797]

(51). Yu W; Du B; Yang L; Zhang Z; Yang C; Yuan S; Zhang MOccurrence, Sorption, and Transformation of Free and Conjugated Natural Steroid Estrogens in the Environment. Environ. Sci. Pollut. Res. 2019, 26 (10), 9443–9468. 10.1007/s11356-019-04402-z.

(52). Swartz CH; Reddy S; Benotti MJ; Yin H; Barber LB; Brownawell BJ; Rudel RASteroid Estrogens, Nonylphenol Ethoxylate Metabolites, and Other Wastewater Contaminants in Groundwater Affected by a Residential Septic System on Cape Cod, MA. Environ. Sci. Technol. 2006, 40 (16), 4894–4902. 10.1021/es052595+. [PubMed: 16955883]

(53). Hanselman TA; Graetz DA; Wilkie ACManure-Borne Estrogens as Potential Environmental Contaminants: A Review. Environ. Sci. Technol. 2003, 37 (24), 5471–5478. 10.1021/es034410+. [PubMed: 14717153]

(54). Scherr FF; Sarmah AK; Di HJ; Cameron KCSorption of Estrone and Estrone-3-Sulfate from CaCl2 Solution and Artificial Urine in Pastoral Soils of New Zealand. Environ. Toxicol. Chem. 2009, 28 (12), 2564–2571. 10.1897/08-534.1. [PubMed: 19656001]

(55). Bai X; Shrestha SL; Casey FXM; Hakk H; Fan ZModeling Coupled Sorption and Transformation of 17β-Estradiol-17-Sulfate in Soil-Water Systems. J. Contam. Hydrol. 2014, 168, 17–24. 10.1016/j.jconhyd.2014.09.001. [PubMed: 25247675]

(56). Bai X; Casey FXM; Hakk H; DeSutter TM; Oduor PG; Khan ESorption and Degradation of 17β-Estradiol-17-Sulfate in Sterilized Soil-Water Systems. Chemosphere2015, 119, 1322–1328. 10.1016/j.chemosphere.2014.02.016. [PubMed: 24630461]

(57). Goeppert N; Dror I; Berkowitz BSpatial and Temporal Distribution of Free and Conjugated Estrogens During Soil Column Transport. Clean - Soil, Air, Water2017, 45 (2). 10.1002/clen.201600048.

(58). Ying GG; Kookana RS; Dillon PSorption and Degradation of Selected Five Endocrine Disrupting Chemicals in Aquifer Material. Water Res. 2003, 37 (15), 3785–3791. 10.1016/S0043-1354(03)00261-6. [PubMed: 12867347]

(59). Ben W; Zhu B; Yuan X; Zhang Y; Yang M; Qiang ZTransformation and Fate of Natural Estrogens and Their Conjugates in Wastewater Treatment Plants: Influence of Operational Parameters and Removal Pathways. Water Res. 2017, 124, 244–250. 10.1016/j.watres.2017.07.065. [PubMed: 28763640]

(60). Kumar V; Johnson AC; Nakada N; Yamashita N; Tanaka HDe-Conjugation Behavior of Conjugated Estrogens in the Raw Sewage, Activated Sludge and River Water. J. Hazard. Mater. 2012, 227–228, 49–54. 10.1016/j.jhazmat.2012.04.078.

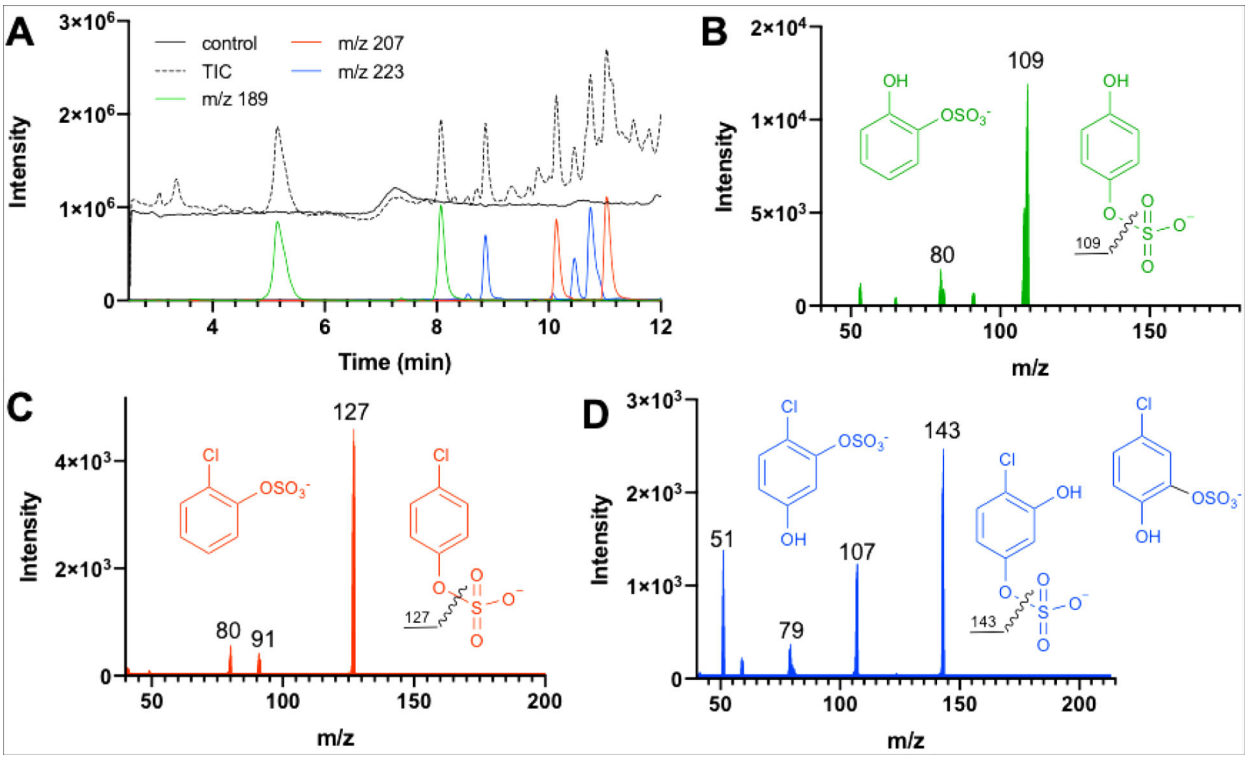


Figure 1.

Organosulfates produced by chlorobenzene and $SO_4^{\bullet-}$. A) LC-MS total ion chromatogram (TIC) and extracted ion chromatograms (EIC) of m/z 189, 207, and 223, compared to the TIC of a control experiment performed in the absence of chlorobenzene. The MS^2 spectra at the largest peak for b) m/z 189, c) m/z 207, and d) m/z 223 also depict the assigned structures and a representative fragmentation.

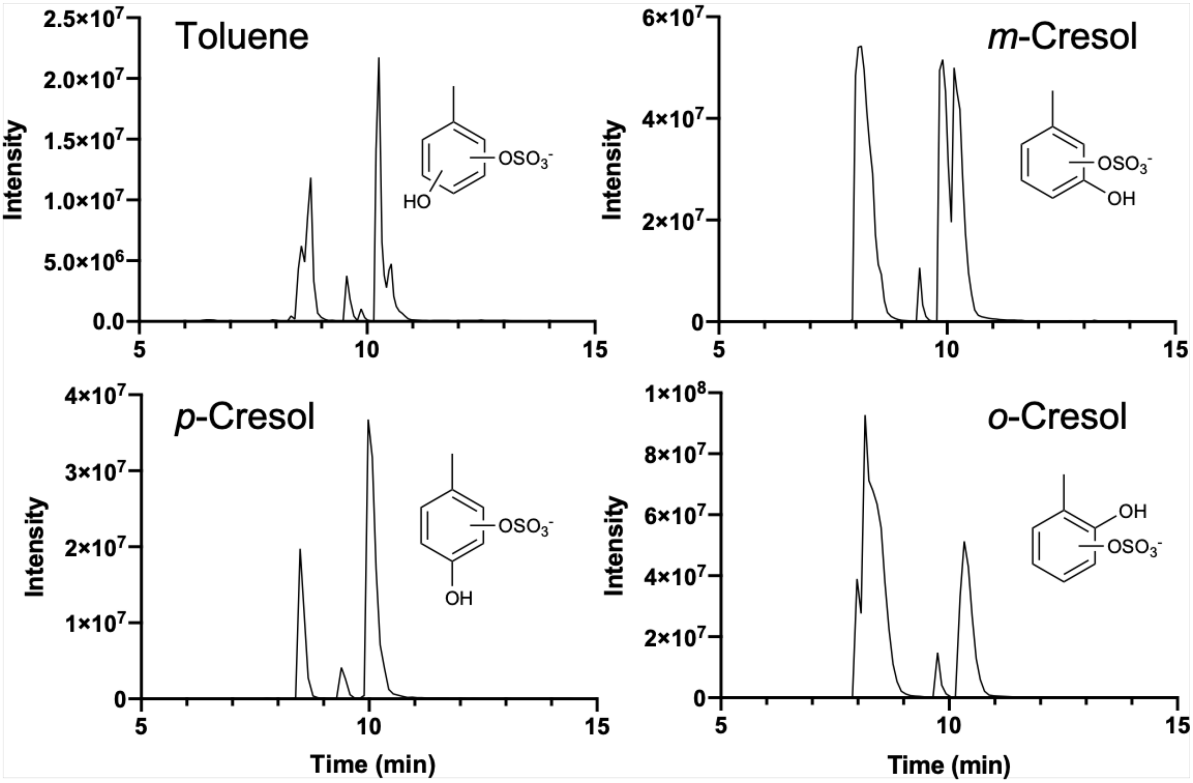


Figure 2.

High resolution LC-MS EIC of m/z 203.0017 ($C_7H_7O_5S$) for toluene and o-, m-, and p-cresol.

Table 1.

Orbitrap HR-MS–obtained organosulfate products of organic contaminants treated with UV/$S_2O_8^{2-}$.

Compounds	$R–OSO_3^-$	$HO–R–OSO_3^-$	Compounds	$R–OSO_3^-$	$HO–R–OSO_3^-$
Alkylbenzenes			**Phenols and quinones**		
Benzene	✓	✓	Phenol	✓	✓
Toluene	✓	✓	*o,m,p*-Cresol	✓	✓
Ethylbenzene	✓	✓	Benzoquinone	✓	✓
m-Xylene	✓	✓	Hydroquinone	✓	X
			Catechol	✓	X
Other substituents			4-Ethylphenol	✓	✓
Pyridine	✓	✓	2,3-Dimethylphenol	✓	✓
Benzaldehyde	✓	✓	4-Chlorophenol	✓	X
Chlorobenzene	✓	✓	4-Nitrophenol	✓	X
Benzoic acid	✓	✓	1-Naphthol	✓	✓
Nitrobenzene	✓	✓			
4-Methylanisole	✓	✓	**Aliphatics**		
Benzenesulfonic acid	X	X	Cyclohexane	✓	✓
			Piperidine	✓	✓
			Heptane	X	X
			Iso-octane	X	X
			1-Octanol	✓	✓

Sulfate esters are referred to as $R–OSO_3^-$ and hydroxysulfate esters are referred to as $HO–R–OSO_3^-$, with the R–group symbolizing the parent contaminant.

Green checks indicate that the compound was detected.

Red symbols indicate that the compound was not observed.

Exact masses and mass errors are included in Table S2.