

Particulate Oxalate-to-Sulfate Ratio as an Aqueous Processing Marker: Similarity Across Field Campaigns and Limitations

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Abstract

Leveraging aerosol data from multiple airborne and surface-based field campaigns encompassing diverse environmental conditions, we identify a generally consistent oxalate-sulfate mass ratio, with a median of 0.0217 (95% confidence interval: 0.0154 – 0.0296; $r = 0.76$). Ground-based aerosol data show that the median oxalate-sulfate ratio is robust within both the mixed layer and the submicrometer particle size range, with higher values observed for supermicrometer particles. We demonstrate that dust and biomass burning emissions can separately bias this ratio towards higher values by at least one order of magnitude. Since sulfate is more readily measured, this ratio could be used to infer oxalate from sulfate in the absence of biomass burning and/or air masses rich with coarse aerosol types (especially dust). This ratio may also have implications for model estimates of secondary organic aerosol (SOA) formation, and particularly the aqueous processing route for oxalate production.

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Key Points:

- Oxalate-sulfate mass ratios show similarity across multiple environments (95% confidence interval: 0.0154 – 0.0296; $R = 0.76$; $N = 2948$)
- Oxalate-sulfate mass ratio is biased towards higher values in presence of coarse aerosol particles and/or biomass burning
- Ground-based, size-resolved measurements reveal that the ratio can be robust within the mixed layer for the submicrometer mode
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Abstract

Leveraging aerosol data from multiple airborne and surface-based field campaigns encompassing diverse environmental conditions, we calculate statistics of the oxalate-sulfate mass ratio (median: 0.0217; 95% confidence interval: 0.0154 – 0.0296; $R = 0.76$; $N = 2948$). Ground-based measurements of the oxalate-sulfate ratio fall within our 95% confidence interval, suggesting the range is robust within the mixed layer for the submicrometer particle size range. We demonstrate that dust and biomass burning emissions can separately bias this ratio towards higher values by at least one order of magnitude. In the absence of these confounding factors, the 95% confidence interval of the ratio may be used to estimate the relative extent of aqueous processing by comparing inferred oxalate concentrations between air masses, with the assumption that sulfate primarily originates from aqueous processing.

Plain Language Summary

The extent of atmospheric chemical processing remains an uncertain aspect of air mass characterization. Addressing this uncertainty is important because chemical reactions in the atmosphere in the presence of water (aqueous processing) produce a large fraction of global aerosol mass. The oxalate-to-sulfate ratio has been proposed as an indicator of aqueous processing, where higher values point to increased processing of an air mass. In this study, we quantify a range in the oxalate-to-sulfate mass ratio (0.0154 – 0.0296) using data from multiple field campaigns encompassing a diverse set of environments. This range is robust near the surface for particles below 1 micrometer in diameter. Larger particles, especially dust, and biomass burning particles significantly affect the oxalate-to-sulfate ratio and thus may confound the interpretation of a high oxalate-to-sulfate ratio as a signal of aqueous processing. In the absence of dust and biomass burning particles, the oxalate-to-sulfate ratio range may be used to compare the relative extent of aqueous processing between different air masses.

1 Introduction

Organic aerosol (OA) account for a major fraction of atmospheric aerosol particles (Hallquist et al., 2009; Kanakidou et al., 2005; Q. Zhang et al., 2007) comprising between 20 – 50% of fine aerosol mass in the continental mid-latitudes (Putaud et al., 2004; Saxena & Hildemann, 1996), 30–80% in the free troposphere (Murphy et al., 2006), and over 80% in tropical forests (Andreae & Crutzen, 1997; Roberts et al., 2001). Secondary organic aerosol (SOA) are derived from gas-to-particle conversion processes, including aqueous processing (Blando & Turpin, 2000; Ervens et al., 2011; Warneck, 2003), wherein oxidized volatile organic compounds (VOCs) partition into cloud droplets or wet aerosol particles and undergo chemical reactions to form low-volatility products that remain in the condensed phase (Ervens, 2015; Ervens et al., 2011; McNeill,

2015). The formation of SOA through aqueous processing has been estimated to serve as a global SOA source comparable to the gas-phase pathway, with 90% of aqueous-phase SOA formed in-cloud (Fu et al., 2008). Using the scheme from Fu et al. (2008), Heald et al. (2011) found contributions of SOA to total OA ranging between 20 – 80% across environments. Oxygenated organic species comprise 60 – 95% of total organic aerosol mass across urban and remote sites (Q. Zhang et al., 2007), while SOA from VOCs explains up to 70% of global organic carbon mass (Hallquist et al., 2009). However, despite improvements in modeling organic aerosol (Heald et al., 2005, 2011), atmospheric chemistry models still underestimate SOA (Schroder et al., 2018) due partly to an incomplete understanding and representation of aqueous processes, resulting in poor model parameterization (Hallquist et al., 2009; McNeill, 2015). The inclusion of SOA formation has been shown to decrease model bias (–64% to –15%) and increase model correlations with observations ($R = 0.5$ to 0.6) (Carlton et al., 2008); thus, improving SOA estimates is a key area of development for models to more accurately evaluate the impacts of atmospheric aerosol particles and reduce uncertainties regarding the net effect of aerosol particles on health and climate (IPCC, 2014).

Oxalic acid is the most abundant organic acid in tropospheric aerosol particles across different regions (Cruz et al., 2019; Yang et al., 2014; Ziemba et al., 2011). The dissociated ion oxalate (OXL) is a well-established tracer of aqueous processing, contributing 1 – 10 % of total particulate mass (Ervens, 2015; Myriokefalitakis et al., 2011) and 3 – 4% of total organic mass over marine/continental areas (Sorooshian et al., 2010). OXL is often used in combination with other secondary tracers such as SO_4^{2-} to assess the extent of aqueous processing in a region (Crahan et al., 2004; Hilario, Cruz, Banaga, et al., 2020; Sorooshian, Varutbangkul, et al., 2006; G. Wang et al., 2012; Yu et al., 2005). Direct sources are thought to be minor relative to production via aqueous processing (Ervens, 2015; Huang & Yu, 2007; Myriokefalitakis et al., 2011) and photochemistry (C. Zhang et al., 2020). Sources of gaseous OXL precursors include biomass burning (BB) (Narukawa et al., 1999; Yang et al., 2014) and biogenic emissions (Boone et al., 2015). Early model simulations overestimated OXL by an order of magnitude (Crahan et al., 2004) while global simulations by Myriokefalitakis et al. (2011) showed better agreement over marine/rural environments between observed and modeled OXL (modeled:observed slope = 1.16 ± 0.14 ; $R = 0.60$) but could not capture OXL over urban regions (weak correlation; $r \approx 0$). More recent work reports reduced discrepancy between models and observations for SOA concentrations (Hodzic et al., 2016; Pai et al., 2020; Zhu & Penner, 2019).

The OXL: SO_4^{2-} ratio has been suggested in past work to be an indicator of aqueous processing (Ervens et al., 2014; Wonaschuetz et al., 2012; Yu et al., 2005). The usage of the ratio as an aqueous processing marker implies that OXL and SO_4^{2-} are entirely sourced from aqueous-phase oxidation, whether it be in cloud droplets or wet aerosol particles, and does not account for gas-phase oxidation in cloud-free air (Ervens, 2015; D. D. Huang et al., 2020; Zhan et al., 2021). This is a good assumption for OXL as there is thought to be no gas-phase reaction that would produce OXL (i.e., an aqueous medium is required for OXL production) (Warneck, 2003); however, OXL is influenced by gas-particle partitioning equilibrium and can exist in the gas-phase as oxalic acid (Nah et al., 2018; Tao & Murphy, 2019). For SO_4^{2-} , gas-phase oxidation is an important source of uncertainty as it can dominate over aqueous processing at times (D. D. Huang et al., 2020). Though we also note that oxidation in the gas-phase is much slower than in the aqueous-phase (Cautenet & Lefeuvre, 1994) and aqueous-phase oxidation explains 60 – 90% of SO_4^{2-} in global models (Barth et al., 2000; Faloona, 2009; Fu et al., 2008).

The OXL: SO_4^{2-} ratio can serve as an aqueous processing marker because aqueous media (including clouds and wet aerosol particles) facilitate the production of both OXL and SO_4^{2-} at rates dependent on liquid water content for SO_4^{2-} formation and droplet surface area for OXL (Ervens et al., 2011). These two cloud parameters correlate within growing clouds (Kim et al., 2003), which connects in-cloud OXL and SO_4^{2-} production such that their ratio may lie within some range. The OXL: SO_4^{2-} ratio has been observed to correlate well with cloud fraction and fall within 0.01 – 0.03 between 0 – 4 km above ground level (AGL) when cloud fractions are high (Wonaschuetz et al., 2012). Therefore, identifying a range in the OXL: SO_4^{2-} ratio across different environments can be useful for comparing relative extents of aqueous processing with higher ratios suggesting more processed air. This comes with the assumptions outlined above that SO_4^{2-} is mainly sourced from aqueous processing, which may not hold for certain environments. However, this ratio

is expected to be particularly applicable near clouds. It is important to note that this ratio likely exhibits a seasonal cycle as observed in Tao & Murphy (2019). Work by Yao et al. (2004) also demonstrated seasonal shifts in the relative contributions of primary and secondary OXL.

Laboratory experiments are often relied on for mechanistic details of aerosol particles (e.g., Hennigan et al., 2010; Pang et al., 2019) but sometimes disagree with aircraft measurements (May et al., 2014). Thus, aircraft campaigns provide a valuable opportunity to study aerosol particles influenced by cloud processes in their most natural environment (Sorooshian et al., 2020). This study leverages composition data from multiple field campaigns, predominantly based on airborne measurements, to investigate the following questions: (1) Is there a generally consistent range of $\text{OXL}:\text{SO}_4^{2-}$ across different regions?; (2) does this ratio depend on particle size?; and (3) what conditions can significantly affect $\text{OXL}:\text{SO}_4^{2-}$ values?

2 Methods

This work relies mostly on airborne field datasets, with the focus predominantly being on particle-into-liquid sampler (PILS) data. The PILS converts sampled aerosol particles into droplets sufficiently large to be collected via inertial impaction, with the resultant liquid transported to vials on a rotating carousel for post-collection chemical analysis via ion chromatography (IC) (Sorooshian, Brechtel, et al., 2006; Weber et al., 2001).

Table 1 summarizes relevant details across campaigns, namely: the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT), the Marine Stratus/Stratocumulus Experiment (MASE-I), the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), the Marine Stratus/Stratocumulus Experiment II (MASE-II), the Nucleation in California Experiment (NiCE), the Atmospheric Tomography Mission (AToM), the Cloud, Aerosol, and Monsoon Processes-Philippines Experiment (CAMP²Ex), the ground-based CAMP²Ex weatHER and CompoSition Monitoring (CHECSM) study, and the Aerosol Cloud meTeorology Interactions oVer the western ATlantic Experiment (ACTIVATE). Note that species from AToM were collected by Soluble Acidic Gases and Aerosol (SAGA) filters (Dibb et al., 2002, 2003). We use ground-based data from Metro Manila, Philippines during CHECSM collected by a micro-orifice uniform deposit impactor (MOUDI) and analyzed via IC to assess how the $\text{OXL}:\text{SO}_4^{2-}$ ratio may vary within the mixed layer and across particle sizes. We examined a total of 53 MOUDI sets that were collected on a weekly basis with a sample duration of ~ 48 hours per set. Six of those sets were impacted by BB based on the criteria presented by Gonzalez et al. (2021) for the same dataset.

As we analyze a CAMP²Ex case study in Section 3.2, we summarize the campaign here with more details provided in Hilario et al. (2021). CAMP²Ex took place over the Western Pacific and aimed to study the influence of radiation, convection, and meteorology on aerosol and gas species. With 19 research flights between August to October 2019, CAMP²Ex provided a rich composition, radiation, and convection dataset spanning 0 – 9 km AGL. In this study, we analyze submicrometer non-refractory aerosol from the aerosol mass spectrometer (AMS; Aerodyne) (Canagaratna et al., 2007; DeCarlo et al., 2006) and size distributions collected by a laser aerosol spectrometer (LAS; TSI Model 3340) for particle diameters 50 – 3162 nm. A comparison of SO_4^{2-} from the PILS and AMS during CAMP²Ex shows good agreement (AMS:PILS slope = 0.81; $R = 0.88$), suggesting that SO_4^{2-} was predominantly in the submicrometer size range given the size ranges of the AMS (PM_{10}) and PILS ($\text{PM}_{2.5}$). Based on sea salt SO_4^{2-} calculations, less than 5% of SO_4^{2-} during CAMP²Ex originated from sea salt.

During AToM, CAMP²Ex, and ACTIVATE, the aerosol sampling inlet likely limited the upper size to approximately 4 μm (McNaughton et al., 2007) although there may have been additional impaction losses in the sampling lines internal to the aircraft that further smoothed the particle transmission curve near this upper bound. This higher cutoff size allowed for sampling of sea salt and dust.

To meaningfully compare $\text{OXL}:\text{SO}_4^{2-}$ ratios between campaigns, we separated out samples impacted by strong point sources (e.g., ship plumes, cattle feedlots, smoke) as identified using flight scientist notes and clear enhancements in particle concentration data. When calculating species ratios, we excluded instances when the denominator value was below its 5th percentile to reduce the uncertainty caused by low denominator

values. Ratios of species in this study refer to mass ratios unless otherwise indicated (e.g., molar ratios). To quantify an all-campaign statistic and uncertainty, median and 95% confidence intervals of the OXL:SO₄²⁻ ratio were derived via bootstrapping of all campaigns using different combinations of sample size and number of iterations, excluding samples with confounding influence (further details are provided in Table S1).

Table 1 . Details of aircraft campaigns analyzed. Statistics of oxalate (OXL) and sulfate (SO₄²⁻) collected by PILS from Figure 1 are listed (R = Pearson correlation, N = number of samples). Median absolute deviation (MAD) is provided as a measure of slope uncertainty (e.g., slope \pm MAD; r, N). Statistics are presented separately for biomass burning (BB) and non-biomass burning (non-BB) samples.

	Location	Location Characteristics	Years Analyzed	Maximum Altitude (km AGL)	Size Range	Slope (R; N) Non-BB	Slope (R; N) BB	Campaign Reference
ICARTT	Ohio River Valley, USA	Continental	August 2004	3	PM ₁	0.0259 \pm 0.0311 (0.85; 142)	-	Fehsenfeld et al. (2006) Sorooshian et al. (2006) Varutbangkul et al. (2006) Lu et al. (2007) Sorooshian et al. (2007) Lu, et al. (2007) Parrish et al. (2007) Sorooshian et al. (2007) Ng, et al. (2007) Lu et al. (2009) Sorooshian et al. (2009) Sorooshian et al. (2015)
MASE-I	Northeast Pacific Ocean	Coastal	July 2005	3.5	PM ₁	0.0233 \pm 0.0092 (0.51; 214)	-	
GoMACCS	Texas, USA	Continental	August – September 2006	5	PM ₁	0.0167 \pm 0.0253 (0.63; 867)	-	
MASE-II	Northeast Pacific Ocean	Coastal	July 2007	2.5	PM ₁	0.014 \pm 0.0085 (0.31; 438)	-	
NiCE	Northeast Pacific Ocean	Coastal	July – August 2013	3	PM ₁	0.0189 \pm 0.0039 (0.42; 67)	0.0244 \pm 0.0037 (0.25; 27)	
AToM	Pacific Ocean (50 °S to 50 °N; 155 °E to 235 °E) Atlantic Ocean (50 °S to 50 °N; 310 °E to 0 °E)	Marine	2016 – 2018	12	PM ₋₄	0.0265 \pm 0.0052 (0.72; 124)	-	Wofsy et al. (2016)

CHECSM	Metro Manila, Philippines	Coastal/Urban	2018 – 2019	Surface (85 m AGL)	PM ₁₈	0.0264 ± 0.0255 (0.73; 47)	0.1426 ± 0.0778 (0.82; 6)	Stahl et al. (2020a)
CAMP ² Ex	West Pacific Ocean	Marine/Coastal	August – October 2019	9	PM ₋₄	High-OXL: 0.3497 ± 0.063 (0.27; 109) High-SO ₄ ²⁻ : 0.0035 ± 0.0106 (0.43; 447)	0.048 ± 0.0462 (0.84; 94)	Hilario et al. (2020)
ACTIVATE	Northwest Atlantic Ocean	Coastal	August – September 2020	5	PM ₋₄	0.0167 ± 0.0132 (0.42; 273)	-	Sorooshian et al. (2019)

3 Results

3.1. Statistics of the OXL:SO₄²⁻ Ratio

Across multiple environments (Fig. 1), we observe similarities in the range of the OXL:SO₄²⁻ ratio (i.e., slope) across campaigns except for CAMP²Ex (discussed in Section 3.2). A combined plot of all campaigns suggests a common range of OXL:SO₄²⁻ across different environments (Fig. S1). Visually, the range in OXL:SO₄²⁻ (Fig. S1) decreases with increasing concentrations, perhaps from a clearer signal of aqueous processing at higher concentrations.

Bootstrapping across all campaigns reveals a stable median OXL:SO₄²⁻ of 0.0217 ($R = 0.76$; $N = 2948$) (details in Table S1) with 95% confidence interval bounds (0.0154 – 0.0296) indicating a relative uncertainty range of $\sim \pm 30\%$ about the median. The bootstrapped statistics are supported by averaging the OXL:SO₄²⁻ slopes between campaigns in Fig. 1 (mean: 0.0184, standard deviation: 0.007, median absolute deviation (MAD): 0.004), which, similar to our bootstrapping method, weights all campaigns equally and removes the statistical bias towards larger datasets. The bootstrapped 95% confidence interval of our observed OXL:SO₄²⁻ (0.0154 – 0.0296) is in excellent agreement with the ratio of yields between aqueous SOA (0.008 – 0.033; Ervens et al., 2011) and SO₄²⁻ (approximately unity), corroborating the hypothesis of a general range in OXL:SO₄²⁻. Numerous studies spanning a diverse set of environments have reported OXL:SO₄²⁻ values (Table S2) with several falling within our bootstrapped range.

Cumulative probability functions (CDFs) were plotted to more easily compare OXL:SO₄²⁻ between campaigns (Fig. S2). As point-by-point ratios are sensitive to background levels of OXL and SO₄²⁻, we plotted CDFs of their enhancement ratio ($\Delta\text{OXL}/\Delta\text{SO}_4$) where values were subtracted by their 10th percentile to approximate background levels per campaign. The resulting CDFs showed similar curves between multiple campaigns and revealed that approximately 20% of point-by-point OXL:SO₄²⁻ values fall within our bootstrapped 95% confidence interval (0.0154 – 0.0296) while $\sim 50\%$ of OXL:SO₄²⁻ values fall within 0.010 – 0.050. In comparison with the linear regression slope, point-to-point ratios are more susceptible to differences in background, resulting in differences in agreement with our 95% confidence interval (e.g., CHECSM). This is a consequence of the point-by-point calculation: although the dataset as a whole may have a mean slope within our confidence interval, there may still be variability in the OXL:SO₄²⁻ ratios of individual points. Thus, as the 10th percentile merely accounts for campaign backgrounds, the linear regression slopes (Fig. 1) may better handle different environments by implicitly accounting for individual background levels via non-zero intercepts.

Surface $\text{OXL}:\text{SO}_4^{2-}$ values from CHECSM agree with the bootstrapped 95% confidence interval for non-BB samples for PM_{18} (0.0264; Fig. 1g) and PM_1 (0.0196) modes ($R = 0.73$ for both). Size-resolved data show that this agreement is greatest between 0.32–1 μm (Fig. S3a), where OXL and SO_4^{2-} masses mostly reside (Cruz et al., 2019). An increase in supermicrometer $\text{OXL}:\text{SO}_4^{2-}$ (Fig. S3a) suggests the enhancement of OXL via gas-particle partitioning of OXL and/or its precursors onto coarse particles as documented for the CHECSM region (Stahl et al., 2020b; Stahl et al., 2021). These results suggest the ratio may be applicable to the mixed layer for submicrometer particles.

AToM provides insight into the $\text{OXL}:\text{SO}_4^{2-}$ ratio over remote marine environments in both hemispheres. The Pacific and Atlantic Oceans (< 3 km AGL) have a combined $\text{OXL}:\text{SO}_4^{2-}$ ratio of 0.0207 ($R = 0.51$) (Fig. 1f). Separately, the Pacific and Atlantic have ratios of 0.0180 ($R = 0.36$) and 0.0251 ($R = 0.72$), respectively, remarkably similar to other environments (Fig. 1). Across altitudes (Fig. S4), $\text{OXL}:\text{SO}_4^{2-}$ values for the Pacific between 0 – 7.5 km AGL are within our 95% confidence interval (Fig. S4a) but only near-surface Atlantic samples fall within our confidence interval (Fig. S4c), possibly due to OXL and/or its precursors undergoing gas-particle partitioning onto Saharan dust.

Variability in $\text{OXL}:\text{SO}_4^{2-}$ across campaigns was most evident in MASE-II (Fig. 1d) and CAMP²Ex (Fig. 1h), which had instances of very low $\text{OXL}:\text{SO}_4^{2-}$, attributable to (1) fresher plumes that have not had time to form OXL (Wonaschuetz et al., 2012), (2) the degradation of OXL into CO_2 (Zhou et al., 2020), (3) the formation of OXL-metal complexes (Sorooshian et al., 2013; Tao & Murphy, 2019), and (4) the presence of high SO_4^{2-} backgrounds. Correlation coefficients below 0.50 (Fig. 1) signify the presence of confounding sources, an expected result given the diversity of environments analyzed. Seasonal factors may also influence the ratio (Tao & Murphy, 2019). Variability between campaigns (Fig. 1) may be suggestive of SO_4^{2-} from cloud-free photochemistry and gas-phase oxidation (Ervens, 2015), which are important sources of uncertainty when using the $\text{OXL}:\text{SO}_4^{2-}$ ratio to assess aqueous processing, as our proposed range implies that SO_4^{2-} is mainly from aqueous processing.

The main utility of this ratio is to gauge relative rather than absolute extents of aqueous processing between air masses via a comparison of inferred OXL. Considering the differences between OXL and SO_4^{2-} in terms of their precursors, formation mechanisms, and sinks, the consistency of the $\text{OXL}:\text{SO}_4^{2-}$ ratio across multiple environments implies a convergence towards a fairly narrow range, which is assisted in part by the large sample sizes used in this study.

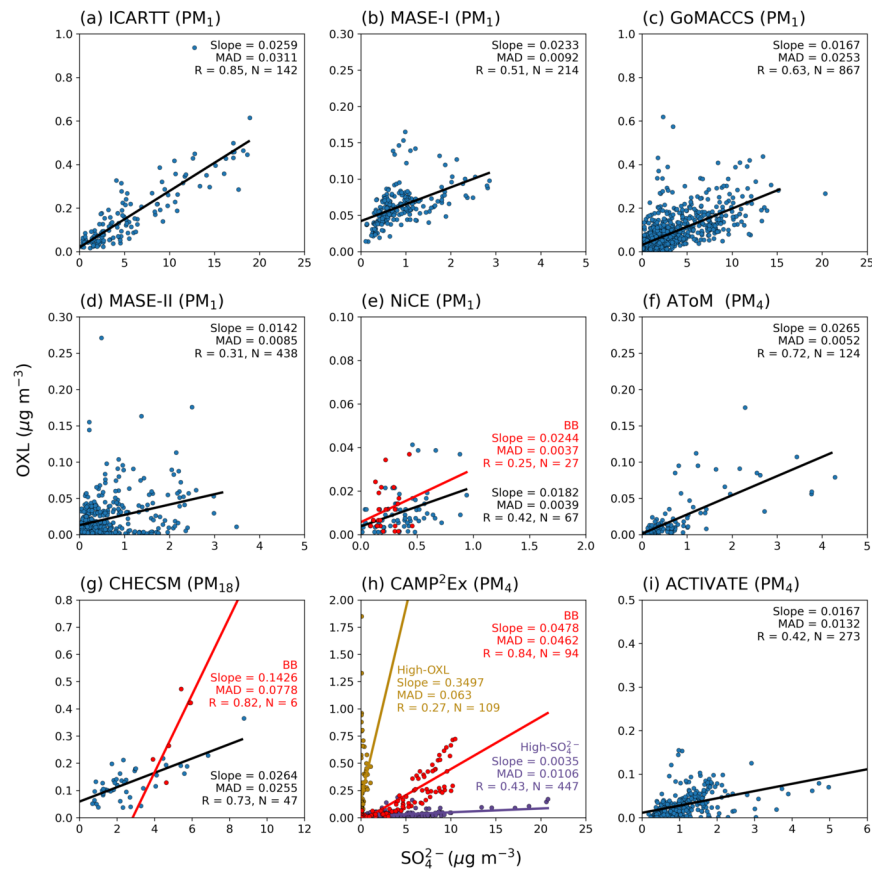


Figure 1 . Linear regressions of OX and SO_4^{2-} mass concentrations across different field campaigns sorted chronologically. All campaigns are aircraft-based except for CHECSM, which was ground-based. Statistics for BB-impacted samples are presented separately in red. CAMP²Ex high-OXL and high- SO_4^{2-} populations are colored in yellow and purple, respectively, in (h). Axes limits are not standardized across panels. In addition to Pearson’s R, the median absolute deviation (MAD) was used as a measure of slope goodness-of-fit.

3.2. Source of the CAMP²Ex high-OXL population

Oxalate and SO_4^{2-} from CAMP²Ex show three populations: high-OXL, high- SO_4^{2-} , and BB-impacted, each characterized by a distinct OX: SO_4^{2-} slope (Fig. 1h). BB-impacted samples are defined as data collected during RFs 9 and 10 (15 and 16 September 2019, respectively), which targeted smoke emissions. The high-OXL population was defined with $\text{OX}:\text{SO}_4^{2-} > 0.3$ and the high- SO_4^{2-} population with $\text{OX}:\text{SO}_4^{2-} < 0.06$; varying the high-OXL ratio lower threshold within 0.10 – 0.30 and high- SO_4^{2-} upper threshold within 0.06 – 0.10 does not impact results of the analyses presented below. Ensuing discussion about these three populations points to important influences on the OX: SO_4^{2-} ratio.

The high-OXL population during CAMP²Ex (Fig. 1h) was not observed in the other field campaigns. These high-OXL samples were mostly sampled within the free troposphere (> 5 km) (Fig. S5b), altitudes of which were rarely sampled in other field campaigns with ATOM being the exception. A few reasons can explain the high-altitude, high-OXL samples during CAMP²Ex: (1) OX’s lengthier chemical formation pathways compared to SO_4^{2-} (Ervens, 2015; Sorooshian, Lu, et al., 2007), (2) inefficient scavenging of gaseous precursors as air masses are transported upward (Heald et al., 2005), and (3) gas-phase OX and/or its precursors partitioning onto dust particles (Stahl et al., 2020b; Stahl et al., 2021; Sullivan & Prather, 2007). As the PILS sampled PM_4 during CAMP²Ex, we hypothesize that the enhanced OX is due to

gas-particle partitioning of OXL and/or its precursors onto coarse mode particles such as dust or sea salt (Mochida et al., 2003; Rinaldi et al., 2011; Sullivan & Prather, 2007; Turekian et al., 2003), evidenced by a prominent coarse mode peak ($D_p \sim 2.5 \mu\text{m}$) in the size distributions of high-OXL samples (Fig. S5). Among the two sources, dust is more likely based on the higher affinity of OXL and/or its precursors to partition onto dust particles compared to sea salt particles (Stahl et al., 2020b). Furthermore, efficient wet scavenging of sea salt reduces its free troposphere concentrations as compared to those of the marine boundary layer (Murphy et al., 2019; Schlosser et al., 2020).

Though both AToM and CAMP²Ex sampled a wide range of altitudes, no high-OXL population was observed during AToM. This is because CAMP²Ex operated near major dust sources such as the Maritime Continent (Hilario, Cruz, Cambaliza, et al., 2020) and continental Asia (Matsumoto et al., 2003) while data from AToM represent more remote marine environments (Table 1). Though the OXL:SO₄²⁻ ratio from AToM is indeed slightly enhanced aloft over the Atlantic (Fig. S4c), this is still a full order of magnitude lower than that of the high-OXL population from CAMP²Ex (Fig. 1h).

To more deeply characterize the high-OXL population, we compared several key variables between the CAMP²Ex high-OXL and high-SO₄²⁻ populations (Table S3), all of which showed statistically significant differences based on the Mann-Whitney U-test (99% confidence level; $p < 0.01$). The following characteristics hint to gas-particle partitioning of OXL and/or its precursors onto dust aloft as has been documented in other studies (e.g., Stahl et al., 2020b; Sullivan & Prather, 2007): (1) dust species such as Ca²⁺ (Kchih et al., 2015) had approximately double the mass concentration in high-OXL air as compared to high-SO₄²⁻ air (Table S3), (2) high-OXL air was mostly sampled in the free troposphere (Fig. S5), (3) ionic crustal ratios in the free troposphere ($> 5 \text{ km}$) were more similar to dust values than those for sea salt based on literature (Park et al., 2004; Švédová et al., 2019; Q. Wang et al., 2018) (Fig. 2), and (4) a prominent coarse mode peak is observed for high-OXL samples (Fig. S6). Among the other two campaigns sampling PM₄, elevated OXL:SO₄²⁻ values at higher altitudes were also observed during AToM (Fig. S4); during ACTIVATE, dust was not prevalent at the altitudes sampled ($< 5 \text{ km}$).

We next compared m/z 44_{AMS} and OXL (from PILS) to assess the possibility of gas-particle partitioning of OXL and/or its precursors onto coarse mode particles such as dust. m/z 44_{AMS} indicates the mass concentration of oxygenated/aged organic aerosol with the functional group CO₂⁺ (Q. Zhang et al., 2005), of which OXL is a subcomponent. As the AMS sampled PM₁ and the PILS sampled PM₄ in CAMP²Ex, their comparison lends insight into how coarse mode particles (i.e., 1–4 μm) may affect PILS observations. Furthermore, because OXL is one component of m/z 44_{AMS}, comparing PILS OXL (PM₄) to m/z 44_{AMS}(PM₁) can serve as an indicator of coarse mode OXL if OXL: m/z 44_{AMS} ≥ 1 as a highly conservative threshold. The high-OXL population has an OXL: m/z 44_{AMS} molar ratio of 2.84 ± 3.95 (Table S3), which provides strong evidence for coarse mode OXL (1–4 μm). This is supported by a high OXL:Org_{AMS} ratio in the high-OXL population (0.84 ± 0.98) compared to the high-SO₄²⁻ population (0.01 ± 0.01). Interestingly, Org_{AMS}:SO₄²⁻ is similar between the high-OXL (1.08 ± 1.34) and high-SO₄²⁻ populations (1.27 ± 1.02). Since the AMS samples PM₁, these findings offer more evidence that differences between populations lie in the coarse mode.

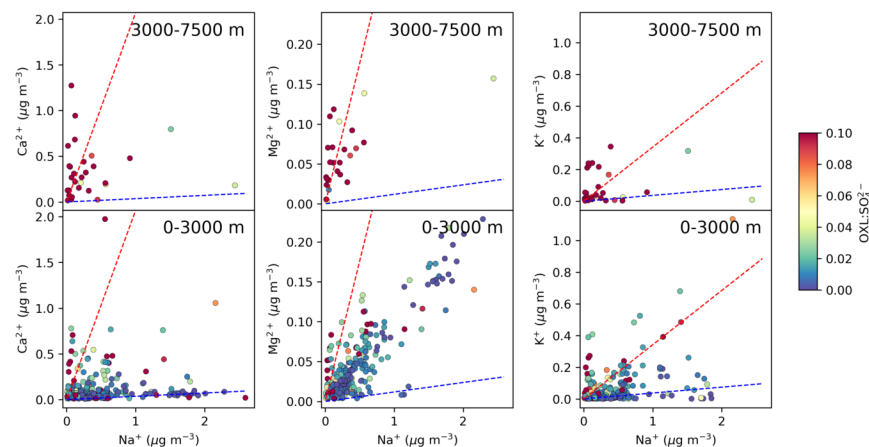


Figure 2 . Altitude-resolved linear regressions of dust species collected by the PILS during CAMP²Ex (BB samples excluded) colored by OXL:SO₄²⁻. Red and blue dashed lines denote literature-based ratios for dust (Park et al., 2004; Švédová et al., 2019; Q. Wang et al., 2018) and sea salt (Chesselet et al., 1972), respectively.

3.3. Impact of biomass burning on OXL:SO₄²⁻

Although strong OXL and SO₄²⁻ correlations may be interpreted as a signal of aqueous processing (Sorooshian, Varutbangkul, et al., 2006; Yao et al., 2003; Yu et al., 2005), the presence of BB emissions must also be considered as a source of both SO₄²⁻ and OXL (Narukawa et al., 1999; Yang et al., 2014). When present, BB emissions led to enhanced OXL:SO₄²⁻ ratios and correlations (Fig. 1). Size-resolved OXL:SO₄²⁻ show similar enhancements during BB periods (Fig. S3b). In the presence of BB emissions, the OXL:SO₄²⁻ ratio is known to increase from 0.05 (non-BB) to 0.18 (BB) in Sydney (Swan & Ivey, 2021) and from 0.03 – 0.069 (non-BB) to 0.072 – 0.15 (BB) in Hong Kong (Zhou et al., 2015). Differences in BB-related OXL:SO₄²⁻ between environments may be attributed to factors including biomass type (Christian et al., 2003), wet scavenging during transport (Marelle et al., 2015), combustion phase (Kondo et al., 2011; Pósfai et al., 2003), and sampled size range (i.e., PM₄ for CAMP²Ex, PM₁ for NiCE, PM₁₈ for CHECSM). During CAMP²Ex, BB-impacted data suggested two subpopulations that differ slightly in their OXL:SO₄²⁻ slopes (Fig. 1h). Both populations were sampled during a large biomass burning event (15 Sep 2019; RF9) but differ in terms of location (~330 km apart), composition, and number concentration (not shown), pointing to clear differences within the CAMP²Ex BB-impacted population left for future work. Regardless of BB differences between campaigns, such a pronounced impact on the OXL:SO₄²⁻ ratio in those respective datasets demonstrates the importance of accounting for BB when exploiting the OXL:SO₄²⁻ ratio for analysis and modeling purposes relevant to secondary aerosol formation processes.

4 Conclusions

Using composition data from multiple campaigns spanning a variety of environments, we calculated statistics of the OXL:SO₄²⁻ mass ratio (median: 0.0217; R = 0.76; N = 2948), with 95% confidence interval bounds indicating a relative uncertainty range of ~±30% about the median (0.0154 – 0.0296). Ground-based size-resolved measurements show overall agreement with the proposed range, specifically within the sub-micrometer mode, suggesting our results are robust within the mixed layer for PM₁. Results from remote marine measurements from ATOM over the Pacific and near-surface Atlantic Oceans also corroborate the bootstrapped OXL:SO₄²⁻ range. As analyzed environments span continental and coastal North America; west, east, and central Pacific Ocean; and west and central Atlantic Ocean, the confidence interval of the ratio is proposed to be robust to a wide range of factors that can impact the formation and removal of both OXL and SO₄²⁻. Furthermore, remarkable similarity between our 95% confidence interval (0.0154 – 0.0296)

and the ratio of yields between SO_4^{2-} and aqueous SOA ($\sim 0.008 - 0.033$) (Ervens et al., 2011) supports the hypothesis of a generalizable range of OXL: SO_4^{2-} .

One exception to the hypothesized OXL: SO_4^{2-} range was the occurrence of gas-phase OXL and/or its precursors partitioning onto dust aloft during CAMP²Ex. Additionally, BB emissions as a source of both OXL and SO_4^{2-} may produce a strong correlation and greatly elevate their ratio. Thus, we caution against interpreting a strong OXL and SO_4^{2-} correlation as a standalone signature of aqueous processing when coarse particle types (e.g., dust) and/or BB emissions are present.

Given its relative uncertainty range ($\sim \pm 30\%$ about the median) when taken across multiple environments, the 95% confidence interval of the OXL: SO_4^{2-} ratio could be used to assess the relative extent of aqueous processing by comparing inferred OXL concentrations between air masses, with the implicit assumption that sampled SO_4^{2-} mainly originates from aqueous processing, which is expected to be particularly true but not limited to near clouds. We emphasize that the OXL: SO_4^{2-} ratio applies specifically to aqueous-processed aerosol (including via clouds or wet aerosol particles) and that an estimation of total SOA from this ratio requires additional information about the ratio of OXL and SOA. Furthermore, gas-phase oxidation is an important source of uncertainty in the ratio as it can be the dominant SO_4^{2-} pathway at times and may partly explain OXL: SO_4^{2-} variability between campaigns.

Examining the OXL: SO_4^{2-} ratio in other parts of the world and seasons would be beneficial to further gauge its variability as well as to identify other potentially confounding factors. Future analysis employing the multi-seasonal ACTIVATE campaign will provide a valuable dataset for investigations of this nature.

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Particulate Oxalate-to-Sulfate Ratio as an Aqueous Processing Marker: Similarity Across Field Campaigns and Limitations

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Key Points:

- Oxalate-sulfate mass ratios show similarity across multiple environments (95% confidence interval: 0.0154 – 0.0296; $R = 0.76$; $N = 2948$)
- Oxalate-sulfate mass ratio is biased towards higher values in presence of coarse aerosol particles and/or biomass burning
- Ground-based, size-resolved measurements reveal that the ratio can be robust within the mixed layer for the submicrometer mode
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Abstract

Leveraging aerosol data from multiple airborne and surface-based field campaigns encompassing diverse environmental conditions, we calculate statistics of the oxalate-sulfate mass ratio (median: 0.0217; 95% confidence interval: 0.0154 – 0.0296; $R = 0.76$; $N = 2948$). Ground-based measurements of the oxalate-sulfate ratio fall within our 95% confidence interval, suggesting the range is robust within the mixed layer for the submicrometer particle size range. We demonstrate that dust and biomass burning emissions can separately bias this ratio towards higher values by at least one order of magnitude. In the absence of these confounding factors, the 95% confidence interval of the ratio may be used to estimate the relative extent of aqueous processing by comparing inferred

oxalate concentrations between air masses, with the assumption that sulfate primarily originates from aqueous processing.

Plain Language Summary

The extent of atmospheric chemical processing remains an uncertain aspect of air mass characterization. Addressing this uncertainty is important because chemical reactions in the atmosphere in the presence of water (aqueous processing) produce a large fraction of global aerosol mass. The oxalate-to-sulfate ratio has been proposed as an indicator of aqueous processing, where higher values point to increased processing of an air mass. In this study, we quantify a range in the oxalate-to-sulfate mass ratio ($0.0154 - 0.0296$) using data from multiple field campaigns encompassing a diverse set of environments. This range is robust near the surface for particles below 1 micrometer in diameter. Larger particles, especially dust, and biomass burning particles significantly affect the oxalate-to-sulfate ratio and thus may confound the interpretation of a high oxalate-to-sulfate ratio as a signal of aqueous processing. In the absence of dust and biomass burning particles, the oxalate-to-sulfate ratio range may be used to compare the relative extent of aqueous processing between different air masses.

1 Introduction

Organic aerosol (OA) account for a major fraction of atmospheric aerosol particles (Hallquist et al., 2009; Kanakidou et al., 2005; Q. Zhang et al., 2007) comprising between 20 – 50% of fine aerosol mass in the continental mid-latitudes (Putaud et al., 2004; Saxena & Hildemann, 1996), 30–80% in the free troposphere (Murphy et al., 2006), and over 80% in tropical forests (Andreae & Crutzen, 1997; Roberts et al., 2001). Secondary organic aerosol (SOA) are derived from gas-to-particle conversion processes, including aqueous processing (Blando & Turpin, 2000; Ervens et al., 2011; Warneck, 2003), wherein oxidized volatile organic compounds (VOCs) partition into cloud droplets or wet aerosol particles and undergo chemical reactions to form low-volatility products that remain in the condensed phase (Ervens, 2015; Ervens et al., 2011; McNeill, 2015). The formation of SOA through aqueous processing has been estimated to serve as a global SOA source comparable to the gas-phase pathway, with 90% of aqueous-phase SOA formed in-cloud (Fu et al., 2008). Using the scheme from Fu et al. (2008), Heald et al. (2011) found contributions of SOA to total OA ranging between 20 – 80% across environments. Oxygenated organic species comprise 60 – 95% of total organic aerosol mass across urban and remote sites (Q. Zhang et al., 2007), while SOA from VOCs explains up to 70% of global organic carbon mass (Hallquist et al., 2009). However, despite improvements in modeling organic aerosol (Heald et al., 2005, 2011), atmospheric chemistry models still underestimate SOA (Schroder et al., 2018) due partly to an incomplete understanding and representation of aqueous processes, resulting in poor model parameterization (Hallquist et al., 2009; McNeill, 2015). The inclusion of SOA formation has been shown to decrease model bias (–64% to –15%) and increase model correlations with observations ($R = 0.5$ to 0.6) (Carlton et al.,

2008); thus, improving SOA estimates is a key area of development for models to more accurately evaluate the impacts of atmospheric aerosol particles and reduce uncertainties regarding the net effect of aerosol particles on health and climate (IPCC, 2014).

Oxalic acid is the most abundant organic acid in tropospheric aerosol particles across different regions (Cruz et al., 2019; Yang et al., 2014; Ziemba et al., 2011). The dissociated ion oxalate (OXL) is a well-established tracer of aqueous processing, contributing 1 – 10 % of total particulate mass (Ervens, 2015; Myriokefalitakis et al., 2011) and 3 – 4% of total organic mass over marine/continental areas (Sorooshian et al., 2010). OXL is often used in combination with other secondary tracers such as SO_4^{2-} to assess the extent of aqueous processing in a region (Crahan et al., 2004; Hilario, Cruz, Bañaga, et al., 2020; Sorooshian, Varutbangkul, et al., 2006; G. Wang et al., 2012; Yu et al., 2005). Direct sources are thought to be minor relative to production via aqueous processing (Ervens, 2015; Huang & Yu, 2007; Myriokefalitakis et al., 2011) and photochemistry (C. Zhang et al., 2020). Sources of gaseous OXL precursors include biomass burning (BB) (Narukawa et al., 1999; Yang et al., 2014) and biogenic emissions (Boone et al., 2015). Early model simulations overestimated OXL by an order of magnitude (Crahan et al., 2004) while global simulations by Myriokefalitakis et al. (2011) showed better agreement over marine/rural environments between observed and modeled OXL (modeled:observed slope = 1.16 ± 0.14 ; $R = 0.60$) but could not capture OXL over urban regions (weak correlation; $r \approx 0$). More recent work reports reduced discrepancy between models and observations for SOA concentrations (Hodzic et al., 2016; Pai et al., 2020; Zhu & Penner, 2019).

The OXL: SO_4^{2-} ratio has been suggested in past work to be an indicator of aqueous processing (Ervens et al., 2014; Wonaschuetz et al., 2012; Yu et al., 2005). The usage of the ratio as an aqueous processing marker implies that OXL and SO_4^{2-} are entirely sourced from aqueous-phase oxidation, whether it be in cloud droplets or wet aerosol particles, and does not account for gas-phase oxidation in cloud-free air (Ervens, 2015; D. D. Huang et al., 2020; Zhan et al., 2021). This is a good assumption for OXL as there is thought to be no gas-phase reaction that would produce OXL (i.e., an aqueous medium is required for OXL production) (Warneck, 2003); however, OXL is influenced by gas-particle partitioning equilibrium and can exist in the gas-phase as oxalic acid (Nah et al., 2018; Tao & Murphy, 2019). For SO_4^{2-} , gas-phase oxidation is an important source of uncertainty as it can dominate over aqueous processing at times (D. D. Huang et al., 2020). Though we also note that oxidation in the gas-phase is much slower than in the aqueous-phase (Cautenet & Lefeuvre, 1994) and aqueous-phase oxidation explains 60 – 90% of SO_4^{2-} in global models (Barth et al., 2000; Faloona, 2009; Fu et al., 2008).

The OXL: SO_4^{2-} ratio can serve as an aqueous processing marker because aqueous media (including clouds and wet aerosol particles) facilitate the production of both OXL and SO_4^{2-} at rates dependent on liquid water content for SO_4^{2-} formation and droplet surface area for OXL (Ervens et al., 2011). These two cloud

parameters correlate within growing clouds (Kim et al., 2003), which connects in-cloud OXL and SO_4^{2-} production such that their ratio may lie within some range. The OXL: SO_4^{2-} ratio has been observed to correlate well with cloud fraction and fall within 0.01 – 0.03 between 0 – 4 km above ground level (AGL) when cloud fractions are high (Wonaschuetz et al., 2012). Therefore, identifying a range in the OXL: SO_4^{2-} ratio across different environments can be useful for comparing relative extents of aqueous processing with higher ratios suggesting more processed air. This comes with the assumptions outlined above that SO_4^{2-} is mainly sourced from aqueous processing, which may not hold for certain environments. However, this ratio is expected to be particularly applicable near clouds. It is important to note that this ratio likely exhibits a seasonal cycle as observed in Tao & Murphy (2019). Work by Yao et al. (2004) also demonstrated seasonal shifts in the relative contributions of primary and secondary OXL.

Laboratory experiments are often relied on for mechanistic details of aerosol particles (e.g., Hennigan et al., 2010; Pang et al., 2019) but sometimes disagree with aircraft measurements (May et al., 2014). Thus, aircraft campaigns provide a valuable opportunity to study aerosol particles influenced by cloud processes in their most natural environment (Sorooshian et al., 2020). This study leverages composition data from multiple field campaigns, predominantly based on airborne measurements, to investigate the following questions: (1) Is there a generally consistent range of OXL: SO_4^{2-} across different regions?; (2) does this ratio depend on particle size?; and (3) what conditions can significantly affect OXL: SO_4^{2-} values?

2 Methods

This work relies mostly on airborne field datasets, with the focus predominantly being on particle-into-liquid sampler (PILS) data. The PILS converts sampled aerosol particles into droplets sufficiently large to be collected via inertial impaction, with the resultant liquid transported to vials on a rotating carousel for post-collection chemical analysis via ion chromatography (IC) (Sorooshian, Brechtel, et al., 2006; Weber et al., 2001).

Table 1 summarizes relevant details across campaigns, namely: the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT), the Marine Stratus/Stratocumulus Experiment (MASE-I), the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), the Marine Stratus/Stratocumulus Experiment II (MASE-II), the Nucleation in California Experiment (NiCE), the Atmospheric Tomography Mission (AToM), the Cloud, Aerosol, and Monsoon Processes-Philippines Experiment (CAMP²Ex), the ground-based CAMP²Ex weatHER and CompoSition Monitoring (CHECSM) study, and the Aerosol Cloud meTeorology Interactions oVer the western ATlantic Experiment (ACTIVATE). Note that species from AToM were collected by Soluble Acidic Gases and Aerosol (SAGA) filters (Dibb et al., 2002, 2003). We use ground-based data from Metro Manila, Philippines during CHECSM collected by a micro-orifice uniform deposit impactor (MOUDI) and analyzed via IC to assess how the OXL: SO_4^{2-} ratio may vary within the mixed

layer and across particle sizes. We examined a total of 53 MOUDI sets that were collected on a weekly basis with a sample duration of ~48 hours per set. Six of those sets were impacted by BB based on the criteria presented by Gonzalez et al. (2021) for the same dataset.

As we analyze a CAMP²Ex case study in Section 3.2, we summarize the campaign here with more details provided in Hilario et al. (2021). CAMP²Ex took place over the Western Pacific and aimed to study the influence of radiation, convection, and meteorology on aerosol and gas species. With 19 research flights between August to October 2019, CAMP²Ex provided a rich composition, radiation, and convection dataset spanning 0 – 9 km AGL. In this study, we analyze submicrometer non-refractory aerosol from the aerosol mass spectrometer (AMS; Aerodyne) (Canagaratna et al., 2007; DeCarlo et al., 2006) and size distributions collected by a laser aerosol spectrometer (LAS; TSI Model 3340) for particle diameters 50 – 3162 nm. A comparison of SO_4^{2-} from the PILS and AMS during CAMP²Ex shows good agreement (AMS:PILS slope = 0.81; R = 0.88), suggesting that SO_4^{2-} was predominantly in the submicrometer size range given the size ranges of the AMS (PM_{10}) and PILS ($\text{PM}_{2.5}$). Based on sea salt SO_4^{2-} calculations, less than 5% of SO_4^{2-} during CAMP²Ex originated from sea salt.

During ATOM, CAMP²Ex, and ACTIVATE, the aerosol sampling inlet likely limited the upper size to approximately 4 μm (McNaughton et al., 2007) although there may have been additional impaction losses in the sampling lines internal to the aircraft that further smoothed the particle transmission curve near this upper bound. This higher cutoff size allowed for sampling of sea salt and dust.

To meaningfully compare OXL: SO_4^{2-} ratios between campaigns, we separated out samples impacted by strong point sources (e.g., ship plumes, cattle feedlots, smoke) as identified using flight scientist notes and clear enhancements in particle concentration data. When calculating species ratios, we excluded instances when the denominator value was below its 5th percentile to reduce the uncertainty caused by low denominator values. Ratios of species in this study refer to mass ratios unless otherwise indicated (e.g., molar ratios). To quantify an all-campaign statistic and uncertainty, median and 95% confidence intervals of the OXL: SO_4^{2-} ratio were derived via bootstrapping of all campaigns using different combinations of sample size and number of iterations, excluding samples with confounding influence (further details are provided in Table S1).

Table 1. Details of aircraft campaigns analyzed. Statistics of oxalate (OXL) and sulfate (SO_4^{2-}) collected by PILS from Figure 1 are listed (R = Pearson correlation, N = number of samples). Median absolute deviation (MAD) is provided as a measure of slope uncertainty (e.g., slope \pm MAD; r, N). Statistics are presented separately for biomass burning (BB) and non-biomass burning (non-BB) samples.

	Location	Location Characteristics	Years Analyzed	Maximum Altitude (km AGL)	Size Range			Campaign Reference
ICARTT	Ohio River Valley, USA	Continental	August 2004		PM ₁	\pm 0.0311 (0.85; 142)	-	Fehsenfeld et al. (2006) Sorooshian, Varutbangkul, et al. (2006)
MASE-I	Northeast Pacific Ocean	Coastal	July 2005		PM ₁	\pm 0.0092 (0.51; 214)	-	Lu et al. (2007) Sorooshian, Lu, et al. (2007)
GoMACCS	Texas, USA	Continental	August – September 2006		PM ₁	\pm 0.0253 (0.63; 867)	-	Parrish et al. (2009) Sorooshian, Ng, et al. (2007)
MASE-II	Northeast Pacific Ocean	Coastal	July 2007		PM ₁	\pm 0.0085 (0.31; 438)	-	Lu et al. (2009) Sorooshian et al. (2009)
NiCE	Northeast Pacific Ocean	Coastal	July – August 2013		PM ₁	\pm 0.0039 (0.42; 67)	\pm 0.0037 (0.25; 27)	Sorooshian et al. (2015)

AToM	Pacific Ocean (50 °S to 50 °N; 155 °E to 235 °E) Atlantic Ocean (50 °S to 50 °N; 310 °E to 0 °E)	Marine	– 2018	PM ₋₄	± 0.0052 (0.72; 124)	-	Wofsy et al. (2018)
CHECSM	Metro Manila, Philippines	Coastal/Urban	2019	Surface (85 m AGL) PM ₁₈	± 0.0255 (0.73; 47)	± 0.0778 (0.82; 6)	Stahl et al. (2020a)
CAMP ²	West Pacific Ocean	Marine/Coastal	August – October 2019	PM ₋₄	High-OXL: 0.3497 ± 0.063 (0.27; 109) High-SO ₄ ²⁻ : 0.0035 ± 0.0106 (0.43; 447)	± 0.0462 (0.84; 94)	Hilario et al. (2021)
ACTIVATION	Northwest Atlantic Ocean	Coastal	August – September 2020	PM ₋₄	± 0.0132 (0.42; 273)	-	Sorooshian et al. (2019)

3 Results

3.1. Statistics of the OXL:SO₄²⁻ Ratio

Across multiple environments (Fig. 1), we observe similarities in the range of the $\text{OXL}:\text{SO}_4^{2-}$ ratio (i.e., slope) across campaigns except for CAMP²Ex (discussed in Section 3.2). A combined plot of all campaigns suggests a common range of $\text{OXL}:\text{SO}_4^{2-}$ across different environments (Fig. S1). Visually, the range in $\text{OXL}:\text{SO}_4^{2-}$ (Fig. S1) decreases with increasing concentrations, perhaps from a clearer signal of aqueous processing at higher concentrations.

Bootstrapping across all campaigns reveals a stable median $\text{OXL}:\text{SO}_4^{2-}$ of 0.0217 ($R = 0.76$; $N = 2948$) (details in Table S1) with 95% confidence interval bounds (0.0154 – 0.0296) indicating a relative uncertainty range of $\sim\pm 30\%$ about the median. The bootstrapped statistics are supported by averaging the $\text{OXL}:\text{SO}_4^{2-}$ slopes between campaigns in Fig. 1 (mean: 0.0184, standard deviation: 0.007, median absolute deviation (MAD): 0.004), which, similar to our bootstrapping method, weights all campaigns equally and removes the statistical bias towards larger datasets. The bootstrapped 95% confidence interval of our observed $\text{OXL}:\text{SO}_4^{2-}$ (0.0154 – 0.0296) is in excellent agreement with the ratio of yields between aqueous SOA (0.008 – 0.033; Ervens et al., 2011) and SO_4^{2-} (approximately unity), corroborating the hypothesis of a general range in $\text{OXL}:\text{SO}_4^{2-}$. Numerous studies spanning a diverse set of environments have reported $\text{OXL}:\text{SO}_4^{2-}$ values (Table S2) with several falling within our bootstrapped range.

Cumulative probability functions (CDFs) were plotted to more easily compare $\text{OXL}:\text{SO}_4^{2-}$ between campaigns (Fig. S2). As point-by-point ratios are sensitive to background levels of OXL and SO_4^{2-} , we plotted CDFs of their enhancement ratio ($\Delta\text{OXL}/\Delta\text{SO}_4$) where values were subtracted by their 10th percentile to approximate background levels per campaign. The resulting CDFs showed similar curves between multiple campaigns and revealed that approximately 20% of point-by-point $\text{OXL}:\text{SO}_4^{2-}$ values fall within our bootstrapped 95% confidence interval (0.0154 – 0.0296) while $\sim 50\%$ of $\text{OXL}:\text{SO}_4^{2-}$ values fall within 0.010 – 0.050. In comparison with the linear regression slope, point-to-point ratios are more susceptible to differences in background, resulting in differences in agreement with our 95% confidence interval (e.g., CHECSM). This is a consequence of the point-by-point calculation: although the dataset as a whole may have a mean slope within our confidence interval, there may still be variability in the $\text{OXL}:\text{SO}_4^{2-}$ ratios of individual points. Thus, as the 10th percentile merely accounts for campaign backgrounds, the linear regression slopes (Fig. 1) may better handle different environments by implicitly accounting for individual background levels via non-zero intercepts.

Surface $\text{OXL}:\text{SO}_4^{2-}$ values from CHECSM agree with the bootstrapped 95% confidence interval for non-BB samples for PM_{18} (0.0264; Fig. 1g) and PM_1 (0.0196) modes ($R = 0.73$ for both). Size-resolved data show that this agreement is greatest between 0.32–1 μm (Fig. S3a), where OXL and SO_4^{2-} masses mostly reside (Cruz et al., 2019). An increase in supermicrometer $\text{OXL}:\text{SO}_4^{2-}$ (Fig. S3a) suggests the enhancement of OXL via gas-particle partitioning of OXL and/or its precursors onto coarse particles as documented for the CHECSM

region (Stahl et al., 2020b; Stahl et al., 2021). These results suggest the ratio may be applicable to the mixed layer for submicrometer particles.

AToM provides insight into the $\text{OXL}:\text{SO}_4^{2-}$ ratio over remote marine environments in both hemispheres. The Pacific and Atlantic Oceans (< 3 km AGL) have a combined $\text{OXL}:\text{SO}_4^{2-}$ ratio of 0.0207 ($R = 0.51$) (Fig. 1f). Separately, the Pacific and Atlantic have ratios of 0.0180 ($R = 0.36$) and 0.0251 ($R = 0.72$), respectively, remarkably similar to other environments (Fig. 1). Across altitudes (Fig. S4), $\text{OXL}:\text{SO}_4^{2-}$ values for the Pacific between 0 – 7.5 km AGL are within our 95% confidence interval (Fig. S4a) but only near-surface Atlantic samples fall within our confidence interval (Fig. S4c), possibly due to OXL and/or its precursors undergoing gas-particle partitioning onto Saharan dust.

Variability in $\text{OXL}:\text{SO}_4^{2-}$ across campaigns was most evident in MASE-II (Fig. 1d) and CAMP²Ex (Fig. 1h), which had instances of very low $\text{OXL}:\text{SO}_4^{2-}$, attributable to (1) fresher plumes that have not had time to form OXL (Wonaschuetz et al., 2012), (2) the degradation of OXL into CO_2 (Zhou et al., 2020), (3) the formation of OXL-metal complexes (Sorooshian et al., 2013; Tao & Murphy, 2019), and (4) the presence of high SO_4^{2-} backgrounds. Correlation coefficients below 0.50 (Fig. 1) signify the presence of confounding sources, an expected result given the diversity of environments analyzed. Seasonal factors may also influence the ratio (Tao & Murphy, 2019). Variability between campaigns (Fig. 1) may be suggestive of SO_4^{2-} from cloud-free photochemistry and gas-phase oxidation (Ervens, 2015), which are important sources of uncertainty when using the $\text{OXL}:\text{SO}_4^{2-}$ ratio to assess aqueous processing, as our proposed range implies that SO_4^{2-} is mainly from aqueous processing.

The main utility of this ratio is to gauge relative rather than absolute extents of aqueous processing between air masses via a comparison of inferred OXL. Considering the differences between OXL and SO_4^{2-} in terms of their precursors, formation mechanisms, and sinks, the consistency of the $\text{OXL}:\text{SO}_4^{2-}$ ratio across multiple environments implies a convergence towards a fairly narrow range, which is assisted in part by the large sample sizes used in this study.

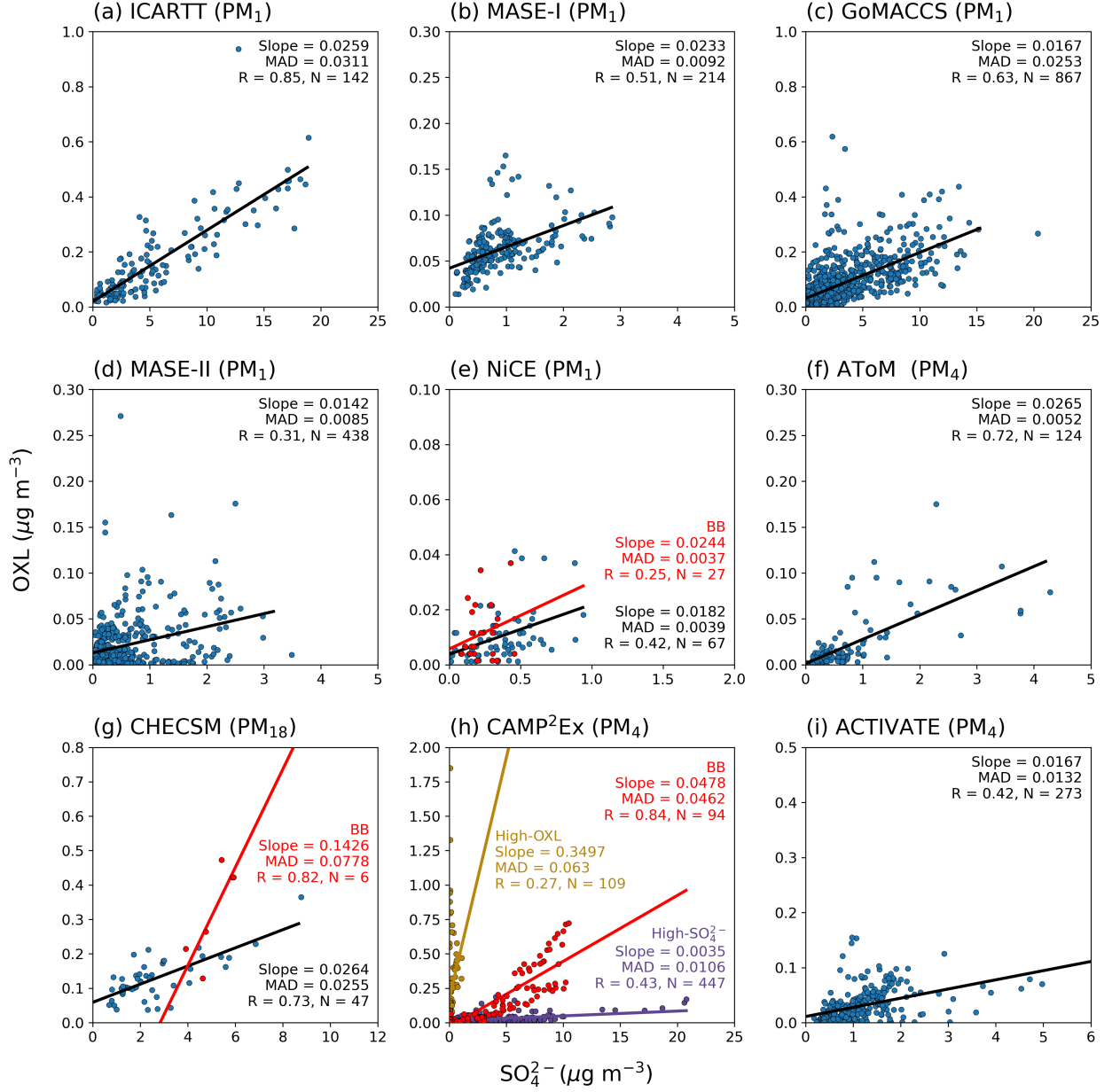


Figure 1. Linear regressions of OXL and SO_4^{2-} mass concentrations across different field campaigns sorted chronologically. All campaigns are aircraft-based except for CHECSM, which was ground-based. Statistics for BB-impacted samples are presented separately in red. CAMP²Ex high-OXL and high- SO_4^{2-} populations are colored in yellow and purple, respectively, in (h). Axes limits are not standardized across panels. In addition to Pearson's R, the median absolute

deviation (MAD) was used as a measure of slope goodness-of-fit.

3.2. Source of the CAMP²Ex high-OXL population

Oxalate and SO_4^{2-} from CAMP²Ex show three populations: high-OXL, high- SO_4^{2-} , and BB-impacted, each characterized by a distinct OXL: SO_4^{2-} slope (Fig. 1h). BB-impacted samples are defined as data collected during RFs 9 and 10 (15 and 16 September 2019, respectively), which targeted smoke emissions. The high-OXL population was defined with $\text{OXL}:\text{SO}_4^{2-} > 0.3$ and the high- SO_4^{2-} population with $\text{OXL}:\text{SO}_4^{2-} < 0.06$; varying the high-OXL ratio lower threshold within 0.10 – 0.30 and high- SO_4^{2-} upper threshold within 0.06 – 0.10 does not impact results of the analyses presented below. Ensuing discussion about these three populations points to important influences on the OXL: SO_4^{2-} ratio.

The high-OXL population during CAMP²Ex (Fig. 1h) was not observed in the other field campaigns. These high-OXL samples were mostly sampled within the free troposphere (> 5 km) (Fig. S5b), altitudes of which were rarely sampled in other field campaigns with AToM being the exception. A few reasons can explain the high-altitude, high-OXL samples during CAMP²Ex: (1) OXL’s lengthier chemical formation pathways compared to SO_4^{2-} (Ervens, 2015; Sorooshian, Lu, et al., 2007), (2) inefficient scavenging of gaseous precursors as air masses are transported upward (Heald et al., 2005), and (3) gas-phase OXL and/or its precursors partitioning onto dust particles (Stahl et al., 2020b; Stahl et al., 2021; Sullivan & Prather, 2007). As the PILS sampled PM_{10} during CAMP²Ex, we hypothesize that the enhanced OXL is due to gas-particle partitioning of OXL and/or its precursors onto coarse mode particles such as dust or sea salt (Mochida et al., 2003; Rinaldi et al., 2011; Sullivan & Prather, 2007; Turekian et al., 2003), evidenced by a prominent coarse mode peak ($D_p \sim 2.5$ μm) in the size distributions of high-OXL samples (Fig. S5). Among the two sources, dust is more likely based on the higher affinity of OXL and/or its precursors to partition onto dust particles compared to sea salt particles (Stahl et al., 2020b). Furthermore, efficient wet scavenging of sea salt reduces its free troposphere concentrations as compared to those of the marine boundary layer (Murphy et al., 2019; Schlosser et al., 2020).

Though both AToM and CAMP²Ex sampled a wide range of altitudes, no high-OXL population was observed during AToM. This is because CAMP²Ex operated near major dust sources such as the Maritime Continent (Hilario, Cruz, Cambaliza, et al., 2020) and continental Asia (Matsumoto et al., 2003) while data from AToM represent more remote marine environments (Table 1). Though the OXL: SO_4^{2-} ratio from AToM is indeed slightly enhanced aloft over the Atlantic (Fig. S4c), this is still a full order of magnitude lower than that of the high-OXL population from CAMP²Ex (Fig. 1h).

To more deeply characterize the high-OXL population, we compared several key variables between the CAMP²Ex high-OXL and high- SO_4^{2-} populations (Table S3), all of which showed statistically significant differences based on the Mann-Whitney U-test (99% confidence level; $p < 0.01$). The following char-

acteristics hint to gas-particle partitioning of OXL and/or its precursors onto dust aloft as has been documented in other studies (e.g., Stahl et al., 2020b; Sullivan & Prather, 2007): (1) dust species such as Ca^{2+} (Kchih et al., 2015) had approximately double the mass concentration in high-OXL air as compared to high- SO_4^{2-} air (Table S3), (2) high-OXL air was mostly sampled in the free troposphere (Fig. S5), (3) ionic crustal ratios in the free troposphere (> 5 km) were more similar to dust values than those for sea salt based on literature (Park et al., 2004; Švédová et al., 2019; Q. Wang et al., 2018) (Fig. 2), and (4) a prominent coarse mode peak is observed for high-OXL samples (Fig. S6). Among the other two campaigns sampling PM_4 , elevated $\text{OXL}:\text{SO}_4^{2-}$ values at higher altitudes were also observed during AToM (Fig. S4); during ACTIVATE, dust was not prevalent at the altitudes sampled (< 5 km).

We next compared m/z 44_{AMS} and OXL (from PILS) to assess the possibility of gas-particle partitioning of OXL and/or its precursors onto coarse mode particles such as dust. m/z 44_{AMS} indicates the mass concentration of oxygenated/aged organic aerosol with the functional group CO_2^+ (Q. Zhang et al., 2005), of which OXL is a subcomponent. As the AMS sampled PM_1 and the PILS sampled PM_4 in CAMP²Ex, their comparison lends insight into how coarse mode particles (i.e., 1–4 μm) may affect PILS observations. Furthermore, because OXL is one component of m/z 44_{AMS}, comparing PILS OXL (PM_4) to m/z 44_{AMS} (PM_1) can serve as an indicator of coarse mode OXL if $\text{OXL}:m/z$ 44_{AMS} > 1 as a highly conservative threshold. The high-OXL population has an $\text{OXL}:m/z$ 44_{AMS} molar ratio of 2.84 ± 3.95 (Table S3), which provides strong evidence for coarse mode OXL (1–4 μm). This is supported by a high $\text{OXL}:\text{Org}_{\text{AMS}}$ ratio in the high-OXL population (0.84 ± 0.98) compared to the high- SO_4^{2-} population (0.01 ± 0.01). Interestingly, $\text{Org}_{\text{AMS}}:\text{SO}_4^{2-}$ is similar between the high-OXL (1.08 ± 1.34) and high- SO_4^{2-} populations (1.27 ± 1.02). Since the AMS samples PM_1 , these findings offer more evidence that differences between populations lie in the coarse mode.

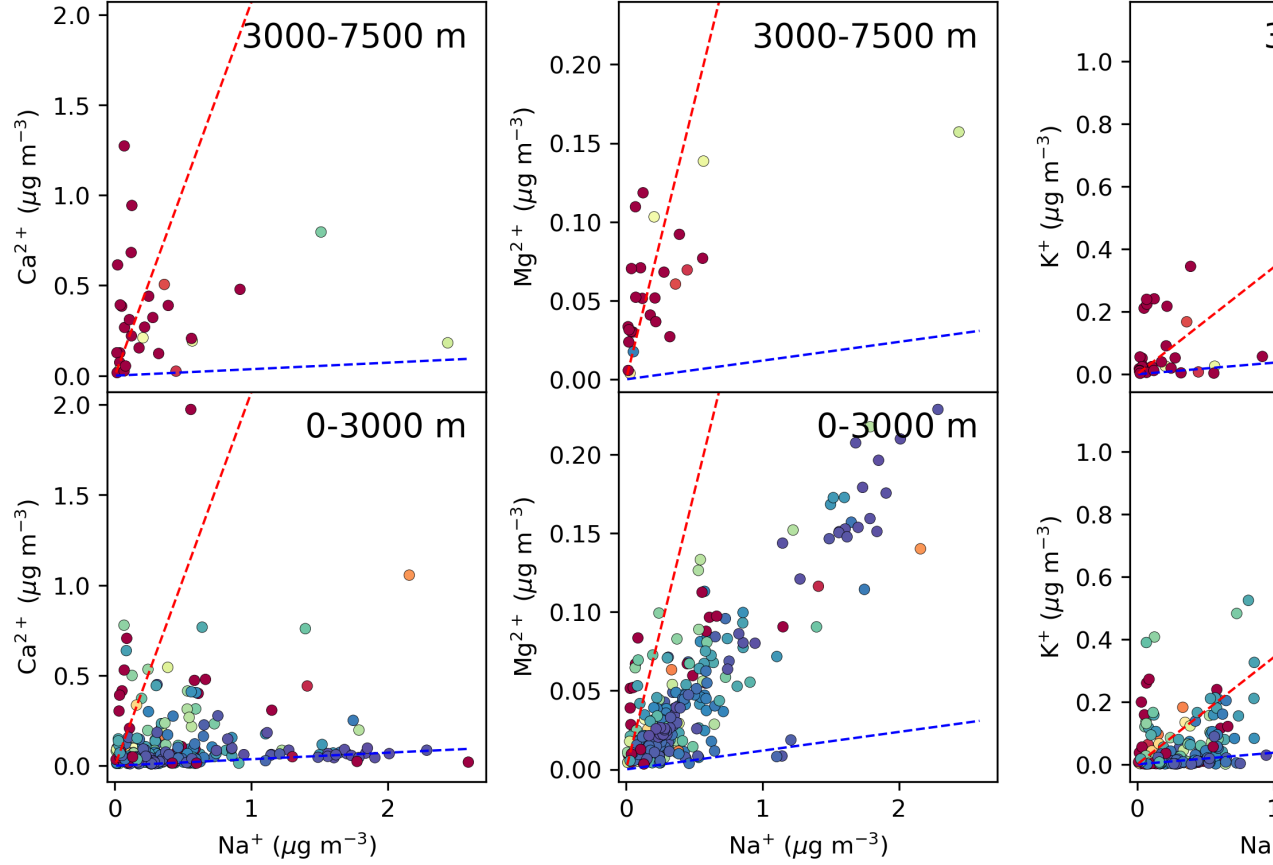


Figure 2. Altitude-resolved linear regressions of dust species collected by the PILS during CAMP²Ex (BB samples excluded) colored by OXL:SO₄²⁻. Red and blue dashed lines denote literature-based ratios for dust (Park et al., 2004; Švédová et al., 2019; Q. Wang et al., 2018) and sea salt (Chesselet et al., 1972), respectively.

3.3. Impact of biomass burning on OXL:SO₄²⁻

Although strong OXL and SO₄²⁻ correlations may be interpreted as a signal of aqueous processing (Sorooshian, Varutbangkul, et al., 2006; Yao et al., 2003; Yu et al., 2005), the presence of BB emissions must also be considered as a source of both SO₄²⁻ and OXL (Narukawa et al., 1999; Yang et al., 2014). When present, BB emissions led to enhanced OXL:SO₄²⁻ ratios and correlations (Fig. 1). Size-resolved OXL:SO₄²⁻ show similar enhancements during BB periods (Fig. S3b). In the presence of BB emissions, the OXL:SO₄²⁻ ratio is known to increase from 0.05 (non-BB) to 0.18 (BB) in Sydney (Swan & Ivey, 2021) and from 0.03 – 0.069 (non-BB) to 0.072 – 0.15 (BB) in Hong Kong (Zhou et al., 2015). Differences in BB-related OXL:SO₄²⁻ between environments may

be attributed to factors including biomass type (Christian et al., 2003), wet scavenging during transport (Marelle et al., 2015), combustion phase (Kondo et al., 2011; Pósfai et al., 2003), and sampled size range (i.e., PM_4 for CAMP²Ex, PM_1 for NiCE, PM_{18} for CHECSM). During CAMP²Ex, BB-impacted data suggested two subpopulations that differ slightly in their $\text{OXL}:\text{SO}_4^{2-}$ slopes (Fig. 1h). Both populations were sampled during a large biomass burning event (15 Sep 2019; RF9) but differ in terms of location (~ 330 km apart), composition, and number concentration (not shown), pointing to clear differences within the CAMP²Ex BB-impacted population left for future work. Regardless of BB differences between campaigns, such a pronounced impact on the $\text{OXL}:\text{SO}_4^{2-}$ ratio in those respective datasets demonstrates the importance of accounting for BB when exploiting the $\text{OXL}:\text{SO}_4^{2-}$ ratio for analysis and modeling purposes relevant to secondary aerosol formation processes.

4 Conclusions

Using composition data from multiple campaigns spanning a variety of environments, we calculated statistics of the $\text{OXL}:\text{SO}_4^{2-}$ mass ratio (median: 0.0217; $R = 0.76$; $N = 2948$), with 95% confidence interval bounds indicating a relative uncertainty range of $\sim \pm 30\%$ about the median (0.0154 – 0.0296). Ground-based size-resolved measurements show overall agreement with the proposed range, specifically within the submicrometer mode, suggesting our results are robust within the mixed layer for PM_1 . Results from remote marine measurements from ATOM over the Pacific and near-surface Atlantic Oceans also corroborate the bootstrapped $\text{OXL}:\text{SO}_4^{2-}$ range. As analyzed environments span continental and coastal North America; west, east, and central Pacific Ocean; and west and central Atlantic Ocean, the confidence interval of the ratio is proposed to be robust to a wide range of factors that can impact the formation and removal of both OXL and SO_4^{2-} . Furthermore, remarkable similarity between our 95% confidence interval (0.0154 – 0.0296) and the ratio of yields between SO_4^{2-} and aqueous SOA ($\sim 0.008 - 0.033$) (Ervens et al., 2011) supports the hypothesis of a generalizable range of $\text{OXL}:\text{SO}_4^{2-}$.

One exception to the hypothesized $\text{OXL}:\text{SO}_4^{2-}$ range was the occurrence of gas-phase OXL and/or its precursors partitioning onto dust aloft during CAMP²Ex. Additionally, BB emissions as a source of both OXL and SO_4^{2-} may produce a strong correlation and greatly elevate their ratio. Thus, we caution against interpreting a strong OXL and SO_4^{2-} correlation as a standalone signature of aqueous processing when coarse particle types (e.g., dust) and/or BB emissions are present.

Given its relative uncertainty range ($\sim \pm 30\%$ about the median) when taken across multiple environments, the 95% confidence interval of the $\text{OXL}:\text{SO}_4^{2-}$ ratio could be used to assess the relative extent of aqueous processing by comparing inferred OXL concentrations between air masses, with the implicit assumption that sampled SO_4^{2-} mainly originates from aqueous processing, which is expected to be particularly true but not limited to near clouds. We emphasize that the $\text{OXL}:\text{SO}_4^{2-}$ ratio applies specifically to aqueous-processed aerosol

(including via clouds or wet aerosol particles) and that an estimation of total SOA from this ratio requires additional information about the ratio of OXL and SOA. Furthermore, gas-phase oxidation is an important source of uncertainty in the ratio as it can be the dominant SO_4^{2-} pathway at times and may partly explain OXL: SO_4^{2-} variability between campaigns.

Examining the OXL: SO_4^{2-} ratio in other parts of the world and seasons would be beneficial to further gauge its variability as well as to identify other potentially confounding factors. Future analysis employing the multi-seasonal ACTIVATE campaign will provide a valuable dataset for investigations of this nature.

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