Characterization of Sea Surface Microlayer and Marine Aerosol Organic Composition using STXM-NEXAFS Microscopy and FTIR Spectroscopy

Savannah L. Lewis[1], Lynn M. Russell[1], Georges Saliba[2], Patricia K. Quinn[3], Timothy S. Bates[3, 4], Craig A. Carlson[5], Nicholas Baetge[6], Lihini I. Aluwihare[1], Emmanuel Boss[6], Amanda A. Frossard[8], Thomas G. Bell[9,10], and Michael J. Behrenfeld[6]

[1]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA,
[2] California Air Resource Board, Sacramento, California, USA
[3] Pacific Marine Environmental Laboratory, NOAA, Seattle, Washington, USA
[4] Cooperative Institute for Climate, Oceans, and Ecosystem Studies (CICOES), University of Washington, Seattle, Washington, USA,
[5] Department of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, CA, USA
[6] Department of Botany and Plant Pathology, Oregon State University, Corvallis, Oregon, USA
[7] School of Marine Sciences, University of Maine, Orono, ME, USA
[8] Department of Chemistry, University of Georgia, Athens, GA, USA
[9] Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth, PL1 3DH, UK
[10] Department of Earth System Science, University of California, Irvine, CA, USA

Sharp carbonate peak in many extracted samples

Mcarb and Macid particle types had carbonate absorptions and contained a large fraction of extracted particles (21 out of 21 and 17 out of 25, respectively). The extraction method used water, so it is possible that the fairly water insoluble carbonate (K_{sp} = 3.36 x 10^{-9} at 25^{o} C) precipitated out and had an enhanced signal. Crilley et al., [2013] used a 45 minute water sonication extraction method on Teflon filters and ran the solution through an Aerodyne Mass Spectrometer (AMS). When these results were compared with real-time AMS spectrums from 5 sites, excellent agreement was found between the extracted organic mass and the real-time AMS organics with r^2 values ranging from 0.89 and 0.98, supporting the fidelity of the extraction method for representing the ambient particle population.

The carbonate could be enhanced in particles by the drying process, but prior observation of this same category of particles suggest that it is not an artifact of the extraction method [*Saliba et al.*, 2021]. However, the widespread presence of carbonate in all Mcarb and most Macid particles needs verification with directly-collected single particle samples.

Persistent NEXAFS aromatic/alkene peak in all sample types

All sample types had the aromatic/alkene NEXAFS peak: three of three seawater samples, six of six SML samples, two of four Sea Sweep samples, and five of six ambient samples. Six of the eight clusters (d, g, j, l, m, and Macid) contain this aromatic/alkene peak. The 285 eV NEXAFS peak in aerosol samples has been associated with alkenes and aromatics [*Shakya et al.*, 2013]. This peak has also been frequently attributed to soot [*Knopf et al.*, 2014; *Moffet et al.*, 2010; *Takahama et al.*, 2007], due to the known C 1s → $\pi^*_{C=C}$ transition in elemental carbon. Ault et al., [2013] found that the aromatic peak (285.4 eV) was not in a wave-flume experiment initially, but was present after the addition of bacteria, phytoplankton, and growth media (Supplemental Figure 2). This absorption was attributed to chlorophyll, which has both aromatic and alkene bonds. Chlorophyll was present at all sampling locations in average concentrations ranging from 0.11 – 68 mg C m^{-3} (Table 1). Polycylic aromatic hydrocarbons (PAH) are another possible source of the absorption at 285 eV which can come from biomass burning that can be transferred to seawater and sediments [*Rogge et al.*, 1998; *Samburova et al.*, 2016; *Zhang et al.*, 2016]. Lastly, nanoplastics are an option with poly(ethylene terephthalate) (PET) displaying clear peaks at both 284.4 and 285.1 eV [*Yang et al.*, 2021] and many other common nanoplastic polymers showing aromatic/alkene absorptions at 285 eV [*Foetisch et al.*, 2021].

Tables:

Table S1: Detailed information about every particle that was above the detection limit for STXM-NEXAFS

SampleID	Sample Type	Cluster Type	Morphology	AirMassCategory	Alkene/Aromatic	Ketonic Carbonyl	Alkyl	COOH Carbonyl	Carbonate	Potassium
532_190909129	SML	1	spherical	-	1	1	0	1	1	1
532_190912111	Ambient	1	oblong	Mixed	1	1	0	1	0	0
532_190913010	Ambient	1	multi-clump	Mixed	1	0	0	1	0	0
532_190913036	SeaSweep	1	multi-clump	-	1	1	0	1	0	0
532_190913052	SeaSweep	1	multi-clump	-	0	0	0	1	0	1
532_190913052	SeaSweep	1	multi-clump	-	0	0	0	0	0	0
532_200930123	SML	1	oblong	-	1	1	1	0	0	0
532_201001050	SML	1	oblong	-	1	1	1	0	0	1
532_201001093	SML	1	spherical	-	1	1	0	1	0	0
532_201002186	Seawater	1	oblong	-	1	1	0	0	0	0
532_201002190	Seawater	1	spherical	-	1	1	0	1	0	0

532_210628040	Ambient	1	oblong	Marine	1	1	0	1	1	0
532_210629116	Ambient	1	oblong	Marine	1	1	0	1	0	1
532_190909089	SML	2	irregular	-	0	0	0	0	0	0
532_190909158	SML	2	multi-clump	-	1	0	0	0	0	0
532_190909213	SML	2	coatedcubic	-	1	0	0	0	0	0
532_190911021	SML	2	coatedcubic	-	0	0	0	0	0	0
532_190911028	SML	2	multi-clump	-	1	1	0	1	1	0
532_190912126	Ambient	2	multi-clump	Mixed	0	0	0	1	1	1
532_190912126	Ambient	2	multi-clump	Mixed	0	0	0	1	1	1
532_200927144	SeaSweep	2	irregular	-	0	1	0	1	1	1
532_200927180	SeaSweep	2	multi-clump	-	0	1	0	1	1	1
532_200928028	SeaSweep	2	multi-clump	-	1	0	1	1	1	0
532_200928030	SeaSweep	2	coatedcubic	-	1	0	0	1	0	0
532_200930083	SML	2	irregular	-	1	0	0	0	0	0
532_201001081	SML	2	spherical	-	1	1	0	0	0	0
532_201001123	Ambient	2	spherical	Mixed	0	0	0	1	1	1
532_201002045	Ambient	2	coatedcubic	Mixed	1	0	0	0	0	0
532_210629081	Ambient	2	multi-clump	Marine	0	0	0	1	1	1
532_210629125	Ambient	2	multi-clump	Marine	1	0	0	1	0	0
532_210629136	Ambient	2	spherical	Marine	0	0	0	1	1	1
532_210629181	SML	2	spherical	-	0	0	0	0	0	0
532_210629185	SML	2	coatedcubic	-	1	0	0	1	0	0
532_210629195	SML	2	spherical	-	1	0	0	1	0	0
532_210629222	SML	2	spherical	-	1	0	0	1	1	0
532_210630000	SML	2	irregular	-	0	0	0	0	0	0
532_210630010	SML	2	spherical	-	0	0	0	0	0	0
532_190911080	Ambient	3	film	Mixed	0	0	0	1	1	1
532_190911086	Ambient	3	oblong	Mixed	0	0	0	0	1	1
532_190911088	Ambient	3	irregular	Mixed	0	0	0	0	1	1
532_190909223	SML	4	oblong	-	1	1	0	1	1	0
532_190912199	Ambient	4	multi-clump	Mixed	1	1	0	0	0	0
532_190913042	SeaSweep	4	spherical	-	1	1	0	0	0	0
532_200925008	Ambient	4	irregular	Marine	0	0	0	0	1	0

532_200925021	Ambient	4	halo	Marine	0	0	0	0	0	0
532_200925039	Ambient	4	multi-clump	Marine	1	0	0	0	0	0
532_200927040	Ambient	4	spherical	Continental	1	0	0	0	0	0
532_200927087	Ambient	4	spherical	Continental	1	1	0	1	1	1
532_200928048	SeaSweep	4	spherical	-	1	0	0	0	0	0
532_200930038	SML	4	oblong	-	1	1	0	0	0	0
532_201001045	SML	4	coatedcubic	-	1	0	0	0	0	1
532_201001097	SML	4	spherical	-	1	1	0	0	0	0
532_201002109	Seasweep	4	irregular	-	1	1	0	0	0	0
532_201003059	Ambient	4	spherical	Continental	1	0	0	0	0	0
532_210628052	Ambient	4	irregular	Marine	1	0	0	0	0	1
532_210629106	Ambient	4	oblong	Marine	1	0	0	1	0	0
532_210629162	Ambient	4	irregular	Marine	1	0	0	0	0	0
532_190909085	SML	5	multi-clump	-	0	0	0	1	1	1
532_190909102	SML	5	halo	-	1	0	0	1	1	1
532_190909117	SML	5	spherical	-	0	0	0	1	1	1
532_190911071	Ambient	5	irregular	Mixed	1	1	1	0	1	1
532_190912036	Ambient	5	irregular	Mixed	0	0	1	1	1	1
532_190912045	Ambient	5	halo	Mixed	0	0	1	1	1	1
532_190912055	Ambient	5	halo	Mixed	0	0	0	0	1	1
532_190912058	Ambient	5	multi-clump	Mixed	0	0	0	0	1	1
532_190912062	Ambient	5	halo	Mixed	0	0	0	0	1	1
532_190912075	Ambient	5	irregular	Mixed	0	0	0	0	1	1
532_190912169	Ambient	5	multi-clump	Mixed	0	1	1	1	1	1
532_200925058	Ambient	5	spherical	Marine	1	1	0	0	1	1
532_200926033	SeaSweep	5	spherical	-	0	0	0	1	1	1
532_200927054	Ambient	5	coatedcubic	Continental	1	0	0	0	1	1
532_200928039	SeaSweep	5	coatedcubic	-	0	0	0	1	1	1
532_200930006	SML	5	spherical	-	1	0	0	0	0	1
532_200930010	SML	5	coatedcubic	-	0	0	1	0	1	1
532_200930032	SML	5	spherical	-	1	0	0	0	0	1
532_201002027	Ambient	5	coatedcubic	Mixed	0	0	0	1	1	1
532_201002088	Seasweep	5	coatedcubic	-	0	1	1	1	1	1

532_201002118	Seasweep	5	spherical	-	0	0	0	0	1	0
532_210628011	Ambient	5	coatedcubic	Marine	0	1	0	1	1	0
532_210629087	Ambient	5	irregular	Marine	1	0	0	0	1	0
532_210630061	Seawater	5	irregular	-	1	0	0	0	1	1
532_210630109	Seawater	5	halo	-	1	0	0	0	1	1
532_190909122	SML	6	oblong	-	1	0	1	0	0	0
532_190909137	SML	6	film	-	1	0	1	0	0	0
532_190910039	SML	6	coatedcubic	-	1	1	0	1	0	1
532_200930087	SML	6	irregular	-	1	0	0	0	0	0
532_201001034	SML	6	irregular	-	1	1	0	1	0	0
532_201002010	Ambient	6	spherical	Mixed	1	1	0	1	0	0
532_210629189	SML	6	oblong	-	1	0	0	1	1	0
532_210630014	SML	6	spherical	-	0	0	0	0	0	0
532_210630073	Seawater	6	spherical	-	0	0	0	0	0	0
532_210630162	Seawater	6	multi-clump	-	1	0	0	1	0	0
532_190911097	Ambient	7	spherical	Mixed	0	0	1	0	1	1
532_190912003	Ambient	7	spherical	Mixed	0	0	1	0	1	1
532_190912031	Ambient	7	multi-clump	Mixed	0	0	1	0	1	1
532_190912041	Ambient	7	coatedcubic	Mixed	0	0	1	1	1	1
532_190912121	Ambient	7	multi-clump	Mixed	0	0	1	0	1	0
532_190912131	Ambient	7	spherical	Mixed	0	0	1	0	1	1
532_190912162	Ambient	7	multi-clump	Mixed	0	0	1	0	1	0
532_190912179	Ambient	7	halo	Mixed	0	0	1	0	1	0
532_190912189	Ambient	7	multi-clump	Mixed	0	0	0	0	1	0
532_190913049	SeaSweep	7	multi-clump	-	0	0	0	0	1	1
532_200925031	Ambient	7	halo	Marine	0	0	1	1	1	0
532_200926041	SeaSweep	7	spherical	-	0	0	1	0	1	1
532_200927027	Ambient	7	spherical	Continental	0	0	1	1	1	1
532_200927104	Ambient	7	multi-clump	Continental	0	0	0	1	1	1
532_200927188	SeaSweep	7	spherical	-	0	0	1	0	1	1
532_201002006	Ambient	7	coatedcubic	Mixed	0	1	1	1	1	1
532_201002036	Ambient	7	multi-clump	Mixed	0	1	0	0	1	1
532_201002042	Ambient	7	irregular	Mixed	0	1	0	1	1	1

532_201002070	Seasweep	7	spherical	-	0	1	0	0	1	1
532_201003021	Ambient	7	irregular	Continental	0	0	0	1	1	1
532_201003048	Ambient	7	irregular	Continental	0	0	0	0	1	1
532_190909111	SML	8	oblong	-	1	1	0	0	0	0
532_190911040	SML	8	spherical	-	1	1	0	0	0	0
532_200927049	Ambient	8	spherical	Continental	1	1	0	0	0	0
532_200927098	Ambient	8	spherical	Continental	1	1	0	0	0	0
532_200927113	Ambient	8	spherical	Continental	1	0	0	0	0	0
532_201001023	SML	8	halo	-	1	1	0	1	0	0
532_201002103	Seasweep	8	oblong	-	1	1	0	1	0	0
532_210630021	SML	8	multi-clump	-	1	0	0	0	0	0
532_210630177	Seawater	8	multi-clump	-	1	1	0	0	0	0

Figures

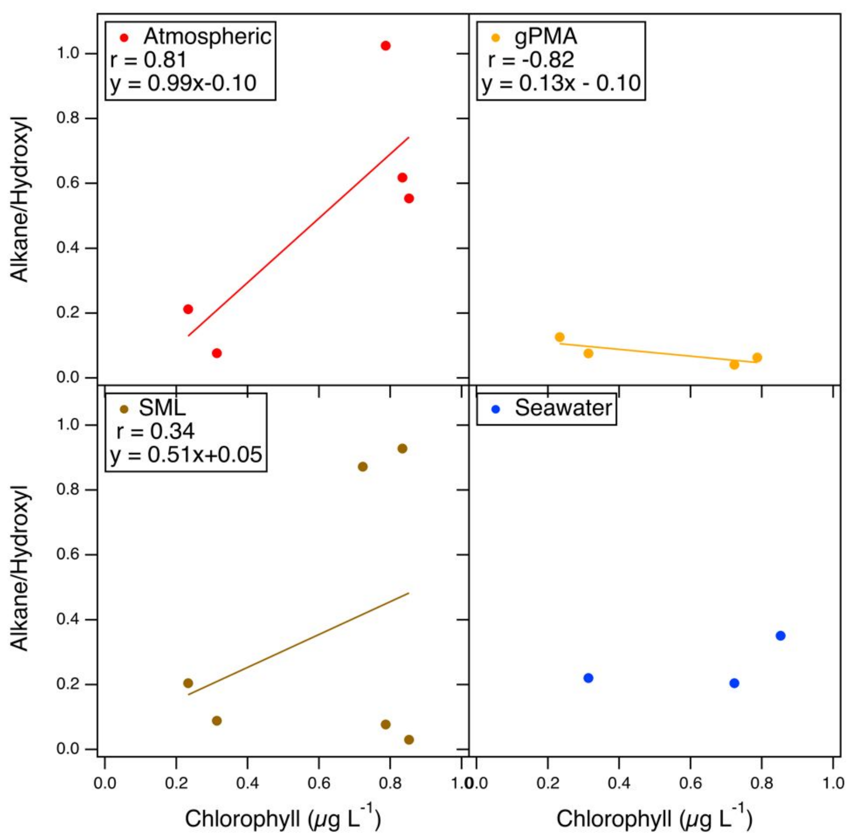

Figure S1: The alkane to hydroxyl ratio of concurrently sampled ambient (top left), SML (bottom left), Sea Sweep (top right), and seawater (bottom right) filters compared to 5 m in-line

Chlorophyll A concentrations averaged to the ambient filter time. SML and ambient filters show much more alkane/hydroxyl variability and a positive slope whereas Sea Sweep and seawater samples exhibit relatively constant alkane/hydroxyl values resulting in a slope of ~0.

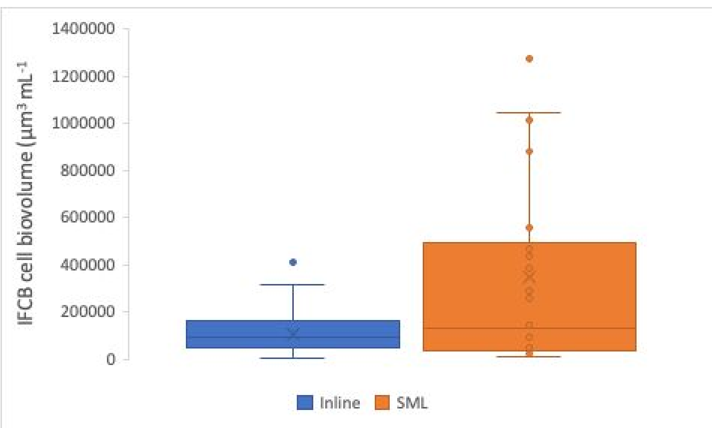

Figure S2: Box and whisker plot of IFCB cell biovolumes from 2 different sampling sources with median values of: 9.22×10^4 $\mu m^3 mL^{-1}$ (Inline, blue) and 1.29×10^5 $\mu m^3 mL^{-1}$ (SML, orange). The SML had a much more variable biovolume and was statistically distinct from the inline data ($p<0.05$).

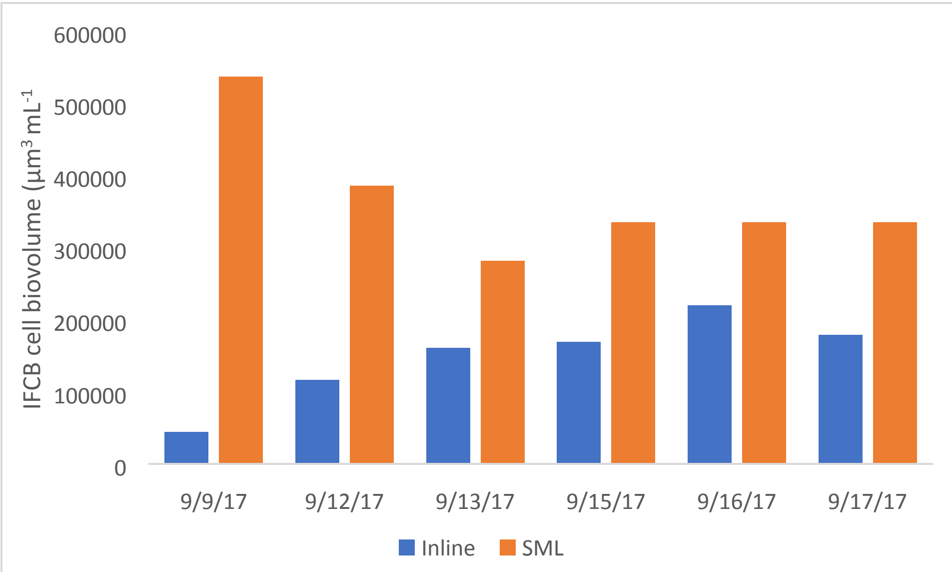

Figure S3: IFCB cell biovolume on 6 of the sample days during NAAMES 3 comparing inline data with SML data. The SML cell biovolume data is consistently larger than the inline data.

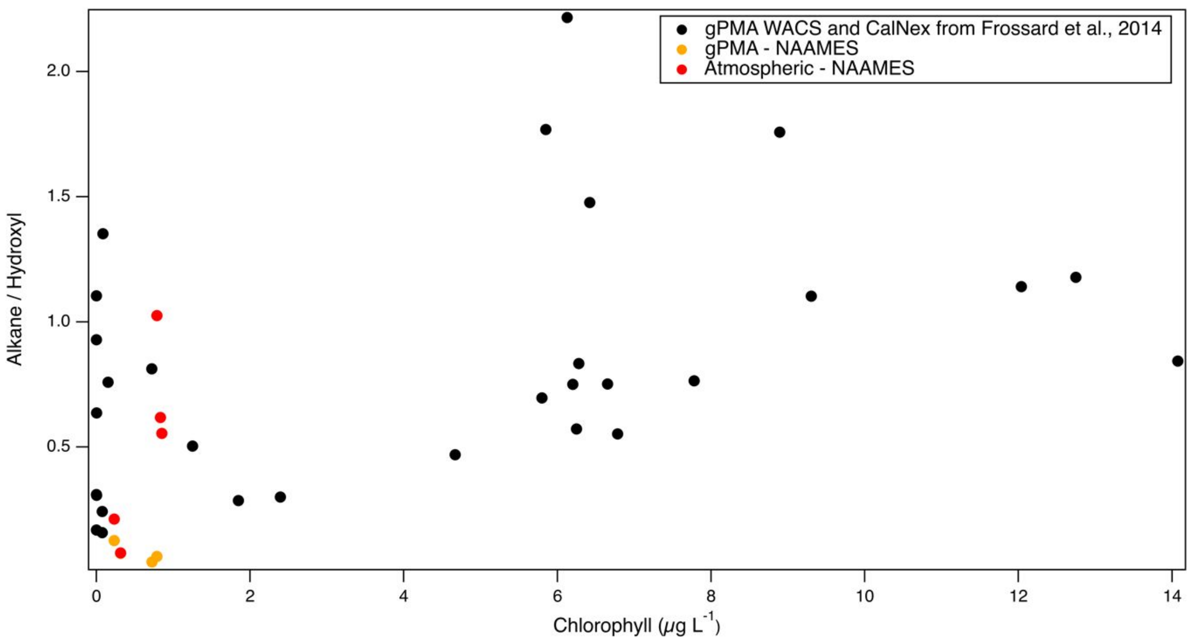

Figure S4: Alkane to hydroxyl ratios from 3 campaigns: NAAMES (red (ambient) and orange (gPMA) and a combined gPMA dataset of WACS and CalNex from Frossard et al., 2014. The gPMA data had a lower alkane / hydroxyl ratio that what was seen previously, possibly due to more tumultuous sampling conditions that inhibited the formation of the SML during sampling.

References

Ault, A. P., et al. (2013), Size-Dependent Changes in Sea Spray Aerosol Composition and Properties with Different Seawater Conditions, *Environmental Science & Technology*, *47*(11), 5603-5612, doi:10.1021/es400416g.

Crilley, L. R., G. A. Ayoko, and L. Morawska (2013), Analysis of organic aerosols collected on filters by Aerosol Mass Spectrometry for source identification, *Analytica Chimica Acta*, *803*, 91-96, doi:https://doi.org/10.1016/j.aca.2013.07.013.

Foetisch, A., M. Filella, B. Watts, L.-H. Vinot, and M. Bigalke (2021), Identification and characterisation of individual nanoplastics by scanning transmission X-ray microscopy (STXM), *Journal of Hazardous Materials*, 127804, doi:https://doi.org/10.1016/j.jhazmat.2021.127804.

Knopf, D. A., P. A. Alpert, B. Wang, R. E. O'Brien, S. T. Kelly, A. Laskin, M. K. Gilles, and R. C. Moffet (2014), Microspectroscopic imaging and characterization of individually identified ice nucleating particles from a case field study, *Journal of Geophysical Research: Atmospheres*, *119*(17), 10,365-310,381, doi:https://doi.org/10.1002/2014JD021866.

Moffet, R. C., T. Henn, A. Laskin, and M. K. Gilles (2010), Automated Chemical Analysis of Internally Mixed Aerosol Particles Using X-ray Spectromicroscopy at the Carbon K-Edge, *Analytical Chemistry*, *82*(19), 7906-7914, doi:10.1021/ac1012909.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1998), Sources of Fine Organic Aerosol. 9. Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces, *Environmental Science & Technology*, *32*, 13-22.

Saliba, G., et al. (2021), Organic composition of three different size ranges of aerosol particles over the Southern Ocean, *Aerosol Science and Technology*, *55*(3), 268-288, doi:10.1080/02786826.2020.1845296.

Samburova, V., J. Connolly, M. Gyawali, R. L. N. Yatavelli, A. C. Watts, R. K. Chakrabarty, B. Zielinska, H. Moosmüller, and A. Khlystov (2016), Polycyclic aromatic hydrocarbons in biomass-burning emissions and their contribution to light absorption and aerosol toxicity, *Science of The Total Environment*, *568*, 391-401, doi:https://doi.org/10.1016/j.scitotenv.2016.06.026.

Shakya, K. M., et al. (2013), Similarities in STXM-NEXAFS Spectra of Atmospheric Particles and Secondary Organic Aerosol Generated from Glyoxal, α-Pinene, Isoprene, 1,2,4-Trimethylbenzene, and d-Limonene, *Aerosol Science and Technology*, *47*(5), 543-555, doi:10.1080/02786826.2013.772950.

Takahama, S., S. Gilardoni, L. M. Russell, and A. L. D. Kilcoyne (2007), Classification of multiple types of organic carbon composition in atmospheric particles by scanning transmission X-ray microscopy analysis, *Atmospheric Environment*, *41*(40), 9435-9451, doi:10.1016/j.atmosenv.2007.08.051.

Yang, T., J. Luo, and B. Nowack (2021), Characterization of Nanoplastics, Fibrils, and Microplastics Released during Washing and Abrasion of Polyester Textiles, *Environmental Science & Technology*, *55*(23), 15873-15881, doi:10.1021/acs.est.1c04826.

Zhang, A., S. Zhao, L. Wang, X. Yang, Q. Zhao, J. Fan, and X. Yuan (2016), Polycyclic aromatic hydrocarbons (PAHs) in seawater and sediments from the northern Liaodong Bay, China, *Marine Pollution Bulletin*, *113*(1), 592-599, doi:https://doi.org/10.1016/j.marpolbul.2016.09.005.