Supporting Information

Detection of Active Microbial Enzymes in Nascent Sea Spray Aerosol: Implications for Atmospheric Chemistry and Climate

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Supporting Material and Methods (M)

M1. Measurement of Enzymatic Activities During the Microcosm Bloom Experiments and at Coastal Ocean

Surface seawater was collected off the end of the Ellen Browning Scripps Memorial Pier (Scripps Pier), La Jolla, California (32° 52.02' N, 117° 15.43' W, USA) with an acid clean carboy. The seawater was pre-filtered through 50 μm acid-washed Nitex to remove larger herbivores and kept protected from light. Within 1 h, the water was brought into the laboratory and the Marine Aerosol Reference Tank (MART)[1] was filled. Three MART experiments were set-up in November 2013 (MART-A), in December 2013 (MART-B), in January 2014 (MART-C, Table S1). Nutrients[2] as in f/20 (MART-A, -B) and as in f/2 (MART-C) were added to stimulate a phytoplankton bloom under constant light (cool, white light 100 μE m^{-2} s^{-1}, 5700 K).

In MART-A, -B, -C, a suite of parameters was measured either every day in the bulk water (*in vivo*, not presented in this paper, and extracted chlorophyll *a* (Chl *a*), and dissolved organic carbon, DOC) or every 2 days (bacteria, viral abundance and enzymatic activities) in the bulk seawater (SW), sea surface microlayer (SSML) and impinged sea spray aerosol (SSA) fractions. Seawater was collected using a lateral port on the MART into a sterilized 50 mL tube and immediately processed. Sea surface microlayer (SSML) was sampled with an acid-washed and precombusted glass plate.[3] The glass plate, 45.5 x 33 x 0.6 cm, with an effective sampling area of 33 x 33 cm was dipped 5 times to recover 20 mL equal to 115 μm SSML thickness. 2.5 mL were aliquoted and diluted by a factor of 10 for the determination of bacterial and viral abundances and enzyme assays. SSA were impinged into midget impingers (Chemglass) containing 0.2 μm filtered autoclaved seawater (FASW) at a flow rate of 1 SLPM. Details can be found in Lee et al. 2015.[4]

MART SSA size distributions measured by Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS) with different aerosol size metrics were unified by converting both d_m and d_a to the physical diameter (d_p),[5] assuming all particles were spherical and had a density (ρ_p) of 1.8 g cm^{-3} and a reference density (ρ_0) of 1 g cm^{-3}.[6] It is important to note that SSA particles were dried prior analysis and so the spherical particle assumption may not be accurate in all cases. SSA is an external mixture of particles with different compositions,[7,8] including size

dependent differences in morphology.[9] Caution is therefore encouraged when making quantitative comparisons between SSA size distributions reported using different methods. Calculated SSA volume from these two instruments were used to normalize the enzymatic activities measured in the MART to the total SSA sampled for the given sample.

As discussed in the main text, marine aerosols were sampled from the Scripps Pier to probe for the presence of active enzymes in the marine aerosols. Note that size distribution measurements were not performed during this sampling periods, thus the enzymatic activities are normalized by the total volume of air sampled (Table S4).

M2. Chlorophyll *a* and Dissolved Organic Carbon Measurements

Extracted Chl *a* was determined fluorometrically[10] in duplicates. Samples (100–200 mL) were filtered onto Whatman GF/F filters, extracted in 90% acetone and their fluorescence was measured and corrected for phaeopigments using a Turner Design 700 fluorometer. *In vivo* Chl *a* was determined fluorometrically in triplicates using a hand-held fluorometer (Aquafluor, Turner Design).

For the determination of DOC concentrations, seawater was filtered through precombusted (450 °C for 6 h) GF/F filters in a precombusted metal-glass filtration tower system with a hand-pump (pressure differential 12.5 cm Hg; during high Chl *a* days filters were changed frequently to minimize cell breakage). The filtrate was transferred into precombusted 40-mL glass vials and immediately acidified with two drops of trace metal-free concentrated 12 N HCl (final pH 2). Samples were stored at 4 °C in the dark. DOC analyses were conducted as per standard high-temperature combustion procedures on a Shimadzu TOC 5000A.[11,12]

M3. Bacterial and Viral Abundance in SW, SSML, and SSA Fractions

Seawater samples from the SW, SSML, and SSA fractions were fixed with a 0.2 μm filtered 37 % formaldehyde solution (final concentration 2 %) and stored at 4 °C for 30 min and then filtered onto 0.02 μm Anodisc (Whatman) membrane and stained with SYBR Green I (Thermo Fisher Sci.) following the protocol of Noble and Fuhrman (1998).[13] For SW and SSML fractions, duplicate filters were analyzed on an Olympus BX71 epifluorescence microscope at 1000 x final magnification with a 480 nm excitation and 520 nm emission filter set. More than 200 cells or viruses were counted in random fields. For the SSA fraction, that was more challenging due to the dim signal, duplicate filters were imaged at Wide-Field Nikon TE2000-U inverted microscope using a Plan Apochromat VC 100x, 1.4 NA oil immersion objective (Nikon Instruments, Japan) and with a CoolSNAP HQ CCD Camera (Photrometric). SYBR Green I filter set was 490 nm excitation and 528 nm emission. The exposure time ranged from 100 ms to 1 s depending on the sample. Undiluted SSA-impinged solution volumes (10 and 50 μL) were plated on ZoBell medium[14] to estimate the colony forming units (CFU), thus surveying the SSA bacterial viability.

M4. Enzymatic Activities

In addition to enzymatic activities described in the materials and methods section in the main text, we measured in the MART experiments chitinase activities (4-methyl-umbelliferone-N-acetyl-β-D-glucosaminide, 20 µM), and in marine aerosols, lipase-butyrate and protease-serine activities (4-methylumbellifreyl butyrate and L-serine-7-amido-4-methylcoumarin hydrochloride (20 µM both respectively).

M5. Statistical Analysis for Scaling Enzymatic Activities

All statistical analyses were done in R programming language (R Core Team 2013; http://www.R-project.org/) using the package »nlme« (Jose Pinheiro, Douglas Bates, Saikat DebRoy, Deepayan Sarkar) and the R Development Core Team (2013) for the Linear and Nonlinear Mixed Effects Models. The enzymatic activity data were log 10 transformed. The model was set to predict the log 10 enzymatic activities from the enzymatic activity of the three fractions (SW, SSML, in comparison to SSA), Chl *a*, DOC and the time from the beginning of the experiment. The differences among the three MART experiments were taken as sources of random effects. A p-value of 0.05 or less was taken as an indicator for a statistically significant relation between the predictor variables and the log 10 enzymatic activity values.

NMDS analyses: Enzymatic activities were expressed as percentage of the diverse activities per day. The data fed the Non-Metric Multi Dimensional Scaling (NMDS) analysis in Primer 5 (version 5.2.9).[15] A similarity matrix was constructed with the Bray-Curtis similarity coefficient for all pairs of samplings. NMDS plots degradation patterns. Stress level <0.1 or lower indicate a little data distortion.

Please note that DOC, bacteria and virus abundance in SW, SSML and SSA data of MART-C experiments have been published in Lee et al.[4]

T1. Chlorophyll *a* and Dissolved Organic Carbon Dynamics in MART-A, -B, -C

During the MART experiments, intense phytoplankton blooms developed within 9 to 10 days after initiation (MART-A: 30 µg L^{-1}, MART-B: 35 µg L^{-1}, MART-C: 39 µg L^{-1}, Chl *a*; Figure S1). In MART-C, a secondary bloom developed after 10 days (25 µg L^{-1}, Figure S1A). Diatoms dominated the phytoplankton community during all four blooms. DOC, sampled in seawater (SW), accumulated during the growth phase as well as during the demise of the phytoplankton blooms, and concentrations remained above pre-bloom levels through the termination of each experiment (Figure S1B).

T2. Bacteria and Virus Dynamics in SW, SSML and SSA of MART-A, -B, -C

In the SW and sea surface microlayer (SSML) compartments, a bloom of heterotrophic bacteria developed following the peak in the phytoplankton bloom (Figure S1C, D), whereas viral abundance increased during the decaying phase of the phytoplankton bloom (Figure S1E, F). The

SSML was enriched in bacteria and viruses relative to the bulk seawater after the collapse of the bloom, with the exception of MART-C (Figure S1C, D). In SSA, bacteria abundance normalized per liter of impinged air was variable in the three experiments with maximum values reaching 7.4 x 10^4, 5.4 x 10^6 and 9.3 x 10^3 cells L^{-1}, respectively, in MART-A, MART-B and MART-C (Figure S1G). In SSA, viral abundance normalized per liter of impinged air, was the same order of magnitude in MART-A and MART-C but was one order of magnitude lower in MART-B (Figure S1H). The observed variability in abundances reflects differences in the efficiency of the mechanisms that regulate the "ejection" of bacteria and viruses into the SSA from the SW and SSML (bacteria and virus abundance in SSA did not correlate with the relative stocks in SW and SSML). Differences in SSA abundances of bacteria and viruses could not be attributed to variability in air-flow into the MART or the impinger (Table S1). We plated SSA onto ZoBell solid medium to test for bacterial viability. Some bacteria formed colonies, evidencing that at least a part of the microbes was still viable once ejected into SSA.

Bacteria and virus abundances in SSA varied across the three experiments and did not directly correspond to the abundances in SW or SSML (Figure S1C-H). Given the bacterial abundance in SSA, not all particles contained a bacterium, but most SSA particles likely contained dissolved or vesicle-associated enzymes. As shown in Patterson et al.,[16] SSA produced during mesocosm blooms can contain vesicles which likely contain enzymes that were enriched in the SSML.

T3. Enzymatic Activities in SW and SSML of MART-A, -B, -C

During the phytoplankton bloom experiments, intense protease, lipase, alkaline phosphatase, chitinase activities were measured in the SW and in the SSML (Figure S2A-E). Enzymatic activity rates in the SW and SSML were normalized using cell abundance data as commonly done for marine microbial ecology.[17,18] Given the short timeframe between SSA sampling and enzymatic assay, one can rule out bacterial over expression of SSA enzymes. In SW and SSML, protease and alkaline phosphatase trends reflected Chl *a* trends ($p<0.01$; $p= 0.05$, Table S5). This suggests that the bacterial enzymatic intensity likely was correlated with the phytoplankton bloom. Enzymatic activities in SSML were greater than those in SW by factors ranging from 1 to 7.7 times.

As MART phytoplankton bloom experiments are isolated systems, marine aerosols at coastal ocean were impinged to demonstrate that these marine aerosols have enzymes that stay enzymatically active in the atmosphere (Figure 1, Table S4). As it is known for the natural seawater, but this is the first time SSA is assayed, microbial activities in SSA are diverse and can vary on a daily and hourly base due to the diverse bacteria ecotypes present in the sea (different gene expression) and the diverse organic matter pool present in the water that can be explored by bacteria. Overall, in natural SSA, protease-leucine, lipase-stearate, and lipase-oleate presented higher enzymatic activities. We speculate that in freshly released SSA, the enzyme activities of lipases, proteases, and alkaline phosphatases are unlikely to be diffusion limited: that is, on the order of 10^9–10^{10} $M^{-1}s^{-1}$.[19] When we compare natural SSA with MART rates, natural values are

lower in the range of pre-bloom MART and are in agreement as natural ambient aerosols were produced during period of low biological activity. This result demonstrates that aerosols from MART and ambient marine environment remain enzymatically active and studies of MART particles are atmospherically relevant.

T4. Statistical Analysis on Enzymatic Activities of MART-A, -B, -C

Pooling the temporal patterns of enzyme activities and analyzing the three compartments (SW, SSML and SSA), we conclude that: 1) In SSA, protease, lipase, alkaline phosphatase and chitinase varied inversely to the respective SW activities (Table S5B, see negative coefficient sign); 2) In SW and SSML, phosphatase and lipase activities showed similar trends (Table S5B, see positive coefficient sign); 3) SSML activities were always >> SW, as one would expect for enzymes acting at the interface, especially lipase[20,21] (Table S5B, where SSML coefficient values compared to SW are <1, $p<0.01$); 4) In SSA, only protease showed inverted trends *(e.g.* anti-correlated) to DOC (sampled in SW) after the bloom's demise (Table S5C). These results show major contributions of SSML lipase and alkaline phosphatase to SSA in quantitative terms.

We qualitatively analyzed the composition of SSA based on the enzymatic patterns of organic matter degradation in SW, SSML (Figure S2F-H). We found that SSA is qualitatively unique in the enzyme composition and based on the Non-Metric Multi Dimensional Scaling (NMDS) analysis, we hypothesized that SSA enzymes are first generated in SW, and then primed in SSML before being released in SSA.

T5. Particle Coagulation Simulations

Figure 3 and SI S7 illustrate that, in principle the ejected enzymes in the SSA can further transform the composition of organic aerosols in the atmosphere. The particle resolved-coagulation simulations show that for all three background concentration cases, the smaller Aitken mode particles are coagulated onto the larger SSA particles (Figure 2A and S4). Increased concentration of the background aerosol led to faster rate of coagulation, but independent of the simulated case, the coagulated particles had a number size distribution ranging from 100 nm to 2 μm, with peak of the distribution at approximately 300 nm.

The ratio of coagulated particles to the sum of coagulated and background ($\phi_3 = N_{coag} / (N_{coag} + N_{backg}$), where N_{backg} and N_{coag} are the total number of background aerosol and background aerosol coagulated with at least one SSA particle, respectively) quantifies the change the background particles experience by coagulating with SSA. The higher the background number concentrations, the lower ϕ_3 will be, but after 24 h of simulation, 16%, 40%, and 57% of 300-nm particles (peak of the mixed particle distribution) for high, medium, and low background cases, respectively, had coagulated with potential enzyme-containing SSA (Figure 2 and S4). These results demonstrate the significance of this new proposed atmospheric reaction pathway.

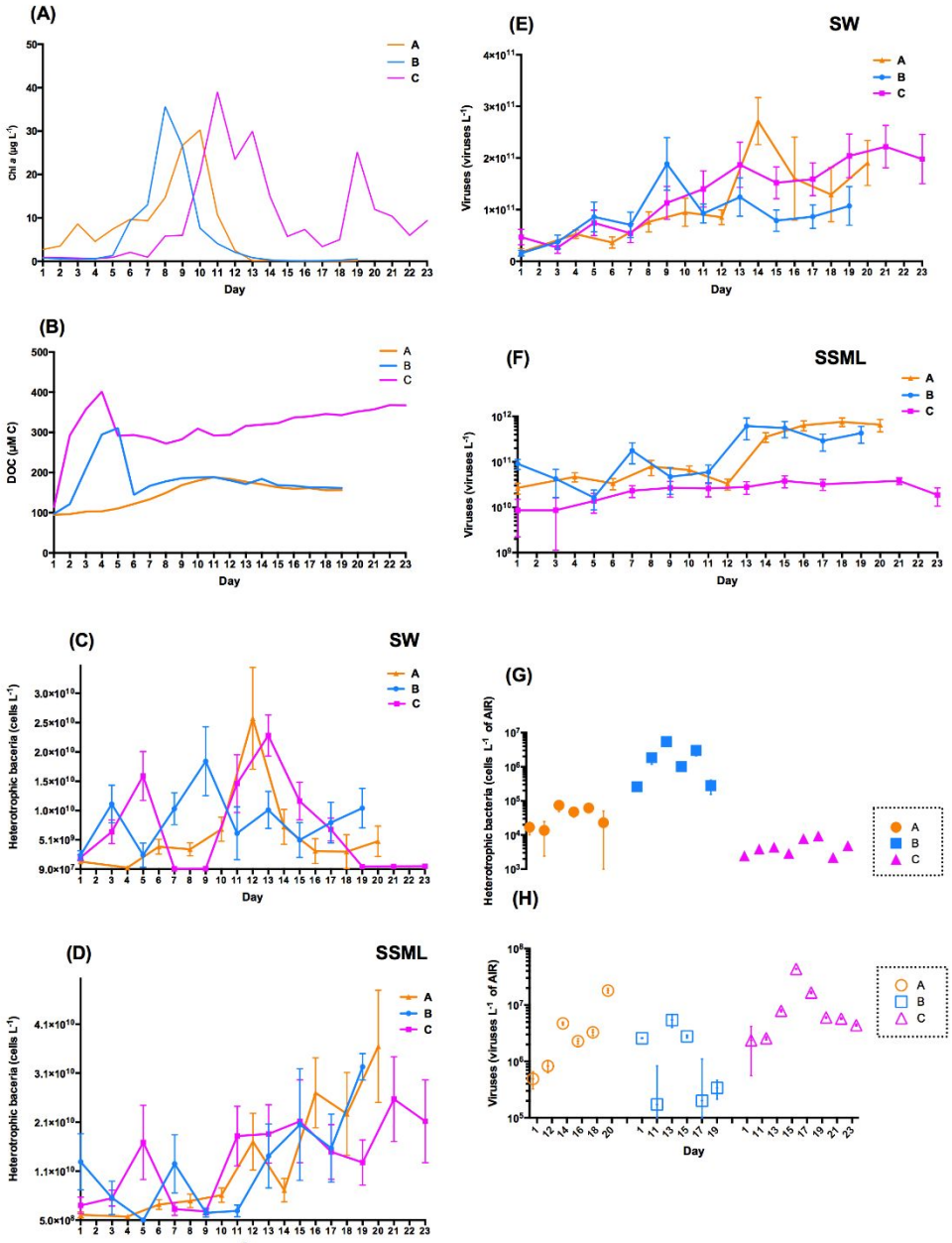

Figure S1. Chlorophyll *a* in µg L^{-1}(A), Dissolved organic carbon (DOC) in µM C (B), heterotrophic bacteria abundance in cells L^{-1} in SW (C), in SSML (D), virus abundance (viruses L^{-1}) in SW (E), and in SSML (F), heterotrophic bacteria (G), and virus (H) abundance in SSA per liter of air during the MART experiments. X-axis indicates the day of the experiment. MART-A in orange (circle), MART-B in blue (square), and MART-C in magenta (triangle).

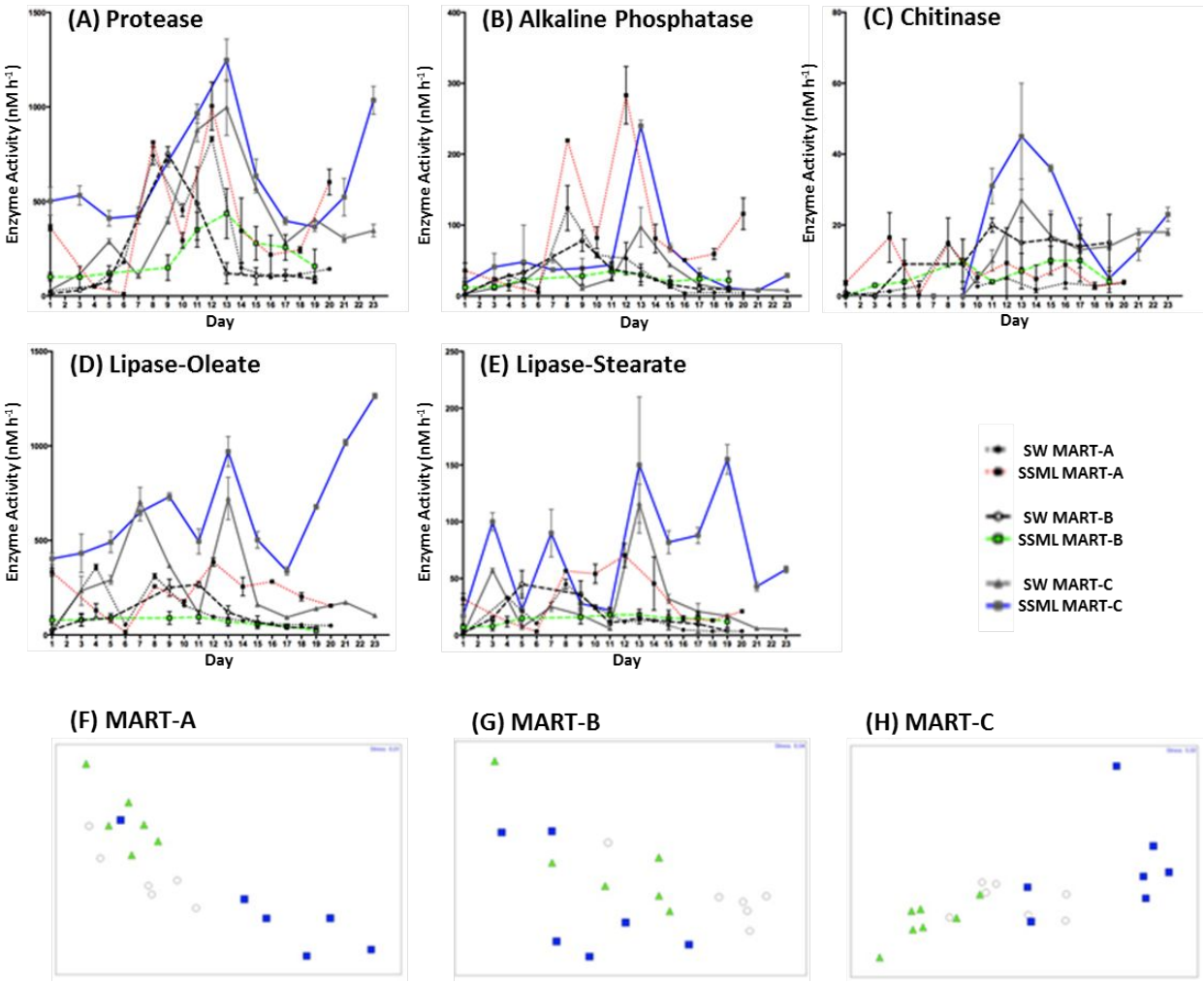

Figure S2. Enzyme activities in SW, SSML and SSA (in red) during MART experiments, expressed in nM h^{-1}. Protease (A), chitinase (B), alkaline phosphatase (C), lipase-oleate (D), and lipase-stearate (E). X-axis indicates the day of the experiment. Non-metric multidimensional scaling (NMDS) plots of enzymatic activities of MART-A (F), -B (G), -C (H) show qualitative enzymatic fingerprint of the SW samples (triangle), SSML samples (circle), and SSA (square). Stress level 0.01, 0.04, and 00.2 for MART-A, -B, and -C respectively.

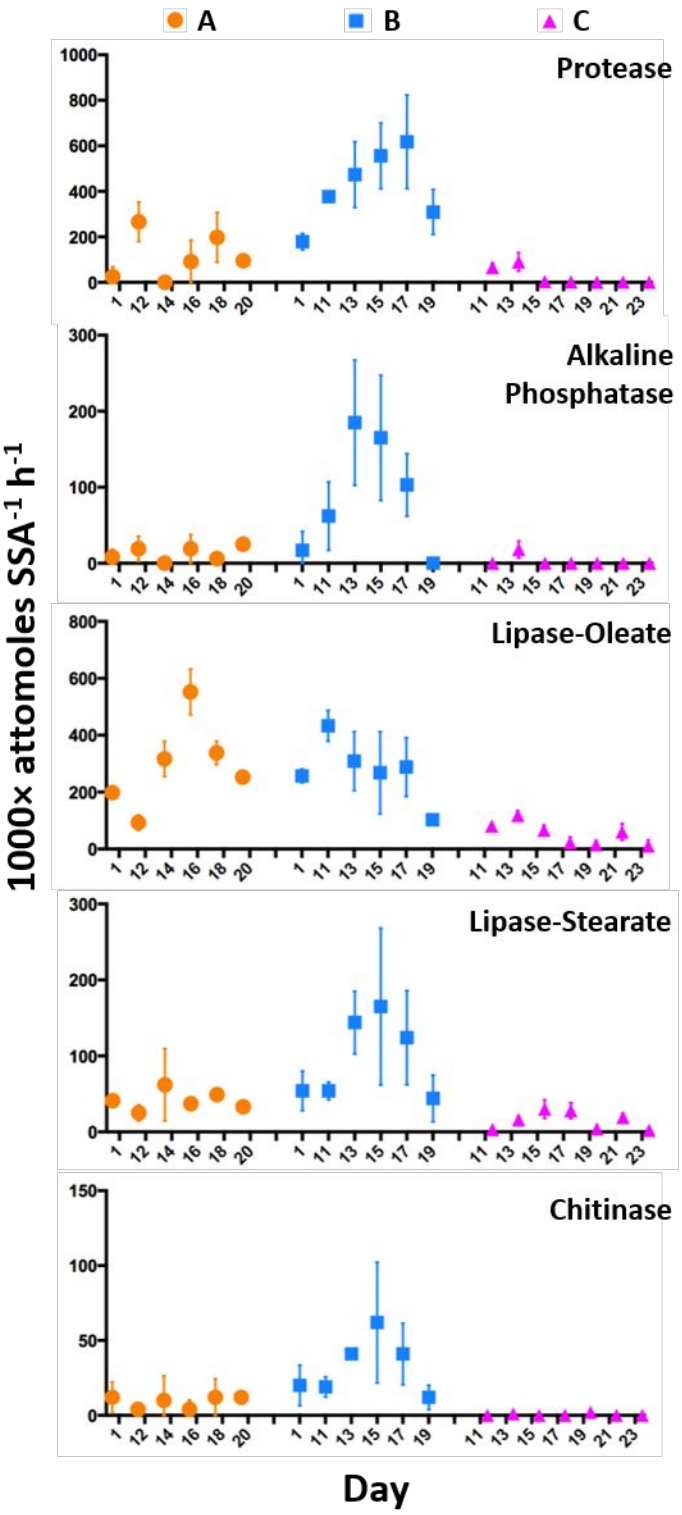

Figure S3. SSA enzyme activities over the course of three separate phytoplankton bloom microcosm experiments (x-axis, SSA production day, error bars represent 1σ). Protease, alkaline phosphatase, lipase-oleate, lipase-stearate, and chitinase normalized per total SSA volume over the course of each microcosm experiment. MART-A (orange circle), MART-B (blue square), and MART-C (magenta triangle).

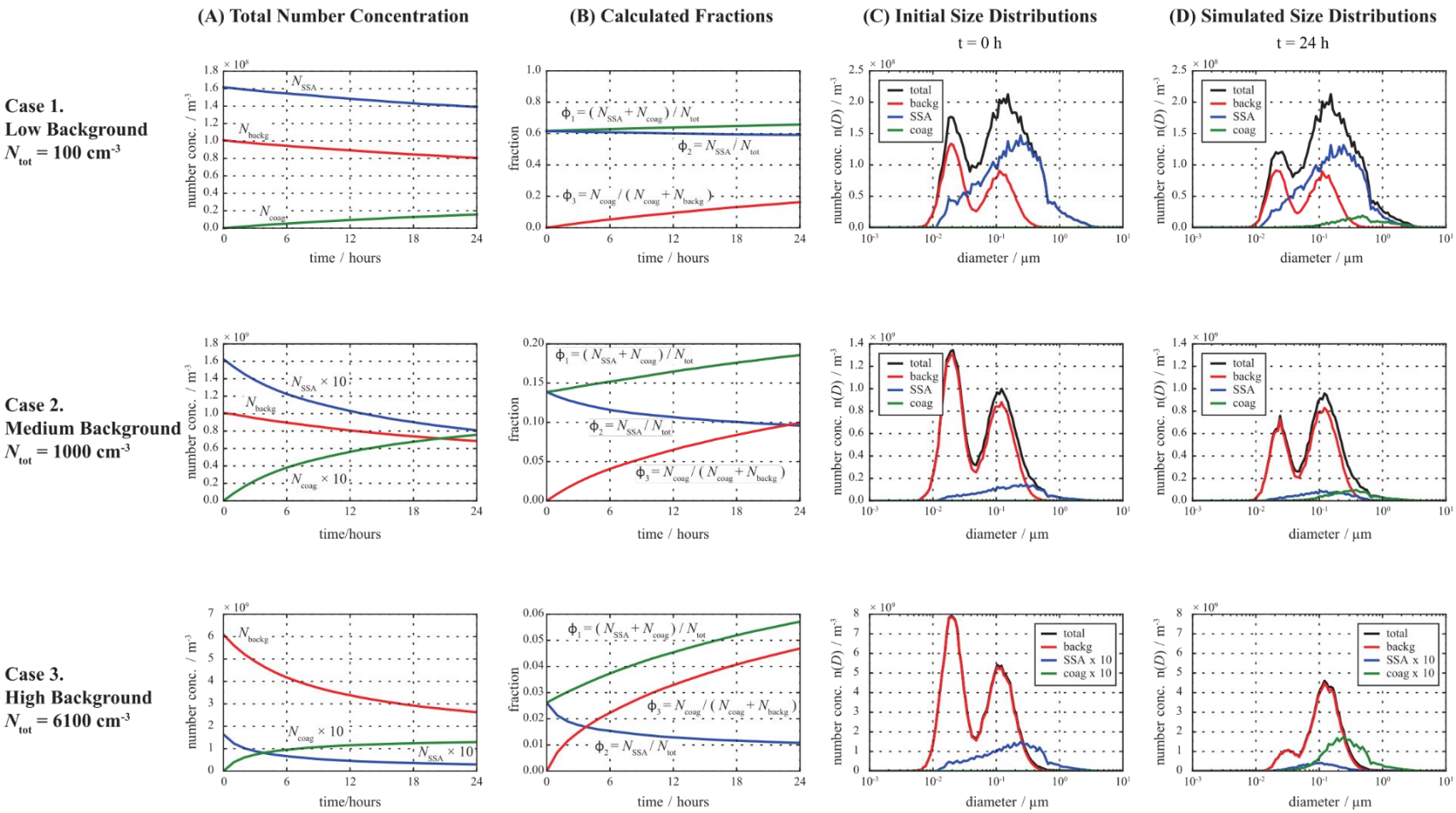

Figure S4. Coagulation simulations of nascent SSA particles with prescribed initial background particle distributions at three background concentrations (Case 1 = 100 cm^{-3}, Case 2 = 1000 cm^{-3}, Case 3 = 6100 cm^{-3}). Panels under (A) show the evolution of total particle concentration over time, (B) shows the calculated ratios, (C) show input particle size distributions, and (D) simulated particle size distribution after 24 h. Total: total particles, backg: background particles, SSA: sea spray aerosols, coag: SSA-background coagulated particles.

Table S1. MART experiment summary. MART experiment details and SSA production day, impinging rate in (LPM), number of SSA particles and SSA particle volume estimated by APS and SMPS. SSA on first day on MART-C has not been analyzed for enzyme activities.

MART	Month	Year	# of days	Nutrients	Tank Volume (L)	Days of SSA production	Impinger Flow (LPM)	Impinging Time (min)	SSA Number Impinged average	SSA Volume average (μm^3)	Single Particle Volume average (μm^3)	Flow into MART (LPM)
A	Nov	2013	20	f/20	60	1, 12-20	1	30	4.09E+07	2.06E+07	0.50	5.8
B	Dec	2013	19	f/20	60	1,9-19	1	30	4.09E+07	2.06E+07	0.50	5.8
C	Jan	2014	23	f/2	100	1,13-23	0.3	120	4.59E+07	4.71E+06	0.10	3.1
E	Sep	2016	N/A	f/20	100	N/A	1	60	1.59E+10	2.31E+05	1.45E-05	2

Table S2. Cell specific enzyme activities in MART experiments. The values indicate the enzymatic activities per cell per hour of protease (L), chitinase (N), alkaline phosphatase (A), lipase-oleate (O) and lipase-stearate (S) in SW and SSML.

	attomoles/cell hr		1	4	6	8	10	12	14	16	18	20
MART-A	SW	L	187.3	1612.2	456.4	2137.1	655.7	321.5	203.2	311.1	373.0	295.3
		N	1.5	37.9	7.1	43.5	3.9	1.9	2.4	11.5	9.4	7.5
		A	23.3	845.5	28.1	357.4	83.8	20.5	31.7	12.5	16.0	8.7
		O	59.8	10449.0	138.9	896.0	226.3	37.2	104.2	185.3	172.5	101.3
		S	8.0	970.8	26.8	129.9	35.7	4.6	17.7	15.0	11.4	7.4
	SSML	L	2302.3	403.6	31.4	1830.4	523.3	608.1	521.3	82.4	109.7	167.5
		N	23.6	133.2	0.8	32.9	9.3	5.6	7.3	3.3	1.2	1.1
		A	227.7	121.1	14.1	494.0	146.1	171.4	122.4	19.1	26.7	32.3
		O	2119.9	1049.2	45.0	579.4	316.7	233.1	386.6	106.6	91.3	43.0
		S	204.1	96.9	8.9	127.4	96.5	42.6	68.9	5.5	5.9	5.9

			1	3	5	7	9	11	13	15	17	19
MART-B	SW	L	4.9	2.7	31.5	40.6	78.6	11.7	20.7	13.7	8.5	5.4
		N	0.3	0.0	3.5	0.5	3.2	1.5	3.2	1.7	1.4	0.8
		A	0.7	2.1	13.3	4.2	6.1	2.9	3.2	1.2	1.0	0.9
		O	10.1	7.0	35.9	13.5	42.9	11.7	13.2	5.0	3.6	3.0
		S	0.8	1.3	18.2	1.9	1.8	1.5	2.4	1.2	0.4	0.5
	SSML	L	8.2	19.8	240.2	75.1	146.3	32.0	14.0	16.9	4.9	5.2
		N	0.0	0.6	8.0	5.0	1.8	0.5	0.5	0.7	0.1	0.0
		A	1.0	2.6	46.0	14.0	14.6	2.2	1.0	1.6	0.7	0.6
		O	6.3	15.8	178.1	45.0	39.7	5.1	2.8	3.0	0.7	0.9
		S	0.6	1.6	30.0	8.0	7.5	1.3	0.8	1.0	0.4	0.3

			1	3	5	7	9	11	13	15	17	19	21	23
MART-C	SW	L	15.1	17.8	17.9	690.7	2136.7	59.5	43.6	48.8	40.9	753.5	545.1	594.2
		N	0.0	0.0	0.0	2.6	0.0	0.7	1.2	1.5	1.8	25.7	32.5	31.0
		A	1.3	1.6	1.3	339.2	57.5	1.6	4.2	3.8	2.3	17.0	16.1	13.1
		O	12.9	142.6	18.2	4552.3	1964.8	7.6	31.6	13.7	13.5	258.2	308.9	176.8
		S	0.5	8.9	0.4	161.9	95.7	0.4	5.1	2.8	3.1	31.5	11.5	8.4
	SSML	L	142.9	106.5	25.1	154.3	312.2	54.7	68.9	30.7	27.5		42.6	41.1
		N	0.0	0.0	0.0	0.0	0.0	1.8	2.5	1.8	1.2	Missing Data	1.1	0.9
		A	5.1	8.2	2.9	13.5	17.3	2.5	13.3	3.3	2.1		0.6	1.1
		O	114.6	381.7	30.0	536.8	321.5	28.0	53.6	24.3	23.4		82.9	50.2
		S	4.9	20.1	1.3	32.6	12.3	1.2	8.3	4.0	6.1		3.5	2.3

Table S3. MART-C size-fractionated enzymatic activities for day 1, 11 and 23. Protease (L), chitinase (N), alkaline phosphatase (A), lipase-oleate (O) and lipase-stearate (S) were measured in SW, in SSML and in SSA. TOT, <1 µm and <0.2 µm refer respectively to the total (not filtered) sample fraction, bacterial fraction and dissolved fraction. The percentage expresses the contribution of the bacterial and dissolved fractions relative to the total activity.

	Day		TOT		<1		<0.2			
			Av	St Dev	Av	St Dev	Av	St Dev	%<1	%<0.2
SW	1	L	31.00	4.49	1.60	8.01	0.30	0.00	4	1
		N	0.00	0.00	0.00	0.00	0.00	0.00	0	0
		A	2.60	0.52	2.00	0.00	1.60	0.11	16	63
		O	26.40	0.55	19.40	1.89	10.00	3.20	36	38
		S	1.00	1.01	0.30	1.50	0.00	0.00	29	0
	11	L	877.00	61.33	800.00	31.76	2.60	0.30	91	0
		N	10.00	3.18	9.00	0.90	0.00	0.00	90	0
		A	23.70	1.03	19.10	2.30	5.00	0.51	59	21
		O	112.40	5.04	96.40	2.74	24.00	2.91	64	21
		S	5.60	0.13	4.00	0.31	0.70	0.64	59	13
	23	L	346.00	32.85	225.30	5.78	0.00	0.00	65	0
		N	18.00	0.55	6.00	0.50	0.00	0.00	33	0
		A	7.60	0.58	4.30	0.08	1.60	0.30	36	20
		O	103.00	4.85	92.50	4.30	25.00	2.59	66	24
		S	4.90	0.65	3.80	0.25	0.50	0.77	68	10
SSML	1	L	502.30	73.59	277.80	68.11	0.50	0.03	55	0
		N	0.00	0.00	0.00	0.00	0.00	0.00	0	0
		A	18.00	10.65	7.60	0.00	2.00	0.30	31	11
		O	402.90	29.63	385.50	20.51	9.00	4.00	93	2
		S	17.30	3.58	13.40	1.14	2.00	5.00	66	12
	11	L	965.30	50.39	768.00	100.16	5.00	1.00	79	1
		N	31.40	5.16	4.10	7.78	2.00	1.00	7	6
		A	43.60	8.62	14.20	7.19	7.00	8.89	17	16
		O	495.20	66.05	341.70	32.75	50.00	15.27	59	10
		S	21.50	3.24	16.50	2.81	3.00	0.90	63	14
	23	L	1035.40	74.08	375.70	3.94	0.00	0.00	36	0
		N	1201.00	1021.00	4.80	1.69	0.00	0.00	21	0
		A	28.70	2.69	12.80	2.13	4.00	1.20	31	14
		O	1264.10	14.36	1202.50	22.23	168.40	25.96	82	13
		S	57.90	3.35	55.50	6.75	2.00	1.38	92	3
SSA	1	L	Missing Sample							
		N								
		A								
		O								
		S								
	11	L	14.00	3.68	10.00	8.70	3.00	0.60	50	21
		N	0.00	0.00	0.00	0.00	0.00	0.00	0	0
		A	0.10	0.80	0.00	0.00	0.00	0.00	0	0
		O	17.30	0.63	15.00	2.37	2.00	0.30	75	12
		S	0.70	0.57	0.40	0.19	0.10	0.08	46	15
	23	L	0.30	0.00	0.30	0.00	0.00	0.00	100	0
		N	0.00	0.00	0.00	0.00	0.00	0.00	0	0
		A		0.00	0.00	0.00	0.00	0.00	0	0
		O	2.40	4.36	1.00	0.50	0.50	0.03	21	21
		S	0.50	0.55	0.00	0.00	0.00	0.00	0	0

	air, L	water temp, °C	chl a, µg/L	enzyme activities normalized to volume of air sampled, pM h^{-1} L^{-1}															
				leucine	sd	chitinase	sd	alk. phos.	sd	oleate	sd	stearate	sd	serine	sd	butyrate	sd	b-glucos.	sd
MART A																			
11/8/2013		15.9	3.7, 2.74*	40.0	70.0	20.0	16.7	13.3	16.7	320.0	33.3	66.7	10.0	-	-	-	-	-	-
11/19/2013		-	10.72*	430.0	140.0	6.7	6.7	30.0	26.7	150.0	43.3	40.0	16.7	-	-	-	-	-	-
11/21/2013	30	-	0.11*	0.0	0.0	16.7	26.7	0.0	0.0	513.3	100.0	100.0	76.7	-	-	-	-	-	-
11/23/2013		-	0.10*	146.7	153.3	6.7	10.0	30.0	30.0	893.3	130.0	60.0	13.3	-	-	-	-	-	-
11/25/2013		-	0.04*	320.0	176.7	20.0	20.0	10.0	13.3	546.7	66.7	80.0	13.3	-	-	-	-	-	-
11/27/2013		-	0.14*	153.3	0.0	20.0	0.0	40.0	0.0	410.0	3.3	53.3	6.7	-	-	-	-	-	-
MART B																			
12/2/2013		nm	nm, 1.54*	290.2	57.8	32.3	22.0	28.3	40.3	416.6	38.6	87.6	41.9	-	-	-	-	-	-
12/12/2013		-	4.07*	610.4	0.0	30.8	10.8	100.5	72.8	700.1	87.1	87.1	18.8	-	-	-	-	-	-
12/14/2013	30	-	0.86*	766.7	233.3	66.7	0.0	300.0	133.3	500.0	166.7	233.3	66.7	-	-	-	-	-	-
12/16/2013		-	0.12*	900.0	233.3	100.0	65.3	266.7	133.3	433.3	233.3	266.7	166.7	-	-	-	-	-	-
12/18/2013		-	0.12*	1000.0	333.3	66.7	33.3	166.7	66.7	466.7	166.7	200.0	100.0	-	-	-	-	-	-
12/20/2013		-	0.53*	500.0	159.7	19.5	13.3	0.0	0.0	166.7	6.2	72.0	49.4	-	-	-	-	-	-
MART C																			
1/16/2014		15.1	1.3, 0.93*	388.7	102.3	0.0	8.0	2.6	22.3	480.2	17.6	18.7	15.8	-	-	-	-	-	-
1/18/2014		-	39.02*	531.2	236.8	7.4	0.8	103.9	66.2	697.0	95.5	96.7	24.1	-	-	-	-	-	-
1/20/2014		-	29.97*	22.2	0.0	0.0	0.0	0.0	0.0	388.7	103.2	179.3	70.8	-	-	-	-	-	-
1/22/2014	36	-	3.40*	11.1	0.0	0.0	0.0	0.0	0.0	130.0	115.5	167.0	61.4	-	-	-	-	-	-
1/24/2014		-	25.17*	8.3	0.0	9.8	7.3	0.0	0.0	85.7	80.2	24.0	0.0	-	-	-	-	-	-
1/26/2014		-	10.36*	11.1	0.0	0.0	0.0	0.0	0.0	355.2	173.0	110.7	29.9	-	-	-	-	-	-
1/28/2014		-	12.78*	8.3	0.0	0.0	0.0	0.0	0.0	66.6	121.0	13.8	15.3	-	-	-	-	-	-
coastal air																			
6/8/2017	60	19.2	2.8	29.0	46.4	nm	nm	nm	nm	14.7	29.1	1.4	3.5	111.1	242.4	645.3	91.4	nm	nm
6/9/2017	113	19.1	3.5	1.8	3.6	nm	nm	nd	nd	0.0	0.0	2.4	3.8	11.0	13.3	417.6	38.1	nd	nd
6/10/2017	113	19.1	4.3	18.0	30.4	nm	nm	nd	nd	11.8	26.0	2.5	3.8	26.6	39.4	334.4	59.2	nd	nd
7/1/2017	88	17.6	6.2	40.7	33.2	nm	nm	1.7	4.1	32.5	22.6	3.0	3.4	54.3	23.1	59.5	145.9	1.0	1.4
7/7/2017	146	19.3	7.0	12.0	16.2	nm	nm	nd	nd	12.6	5.2	14.0	7.6	nd	nd	240.3	44.4	1.6	0.0
7/14/2017a	45	21.5	9.3	0.0	0.0	nm	nm	nd	nd	38.0	25.4	22.9	23.3	nd	nd	1558.9	241.9	nd	nd
7/14/2017b	170	22.1	7.9	21.7	15.1	nm	nm	7.2	6.3	6.2	8.3	1.1	1.3	32.4	17.5	nd	nd	nd	nd

(A)

		Value	St Dev	t-value	p-value
Protease	**SW_SSML**	0.215	0.089	2.417	**0.023**
	Chl *a*	0.016	0.005	3.146	**0.005**
	Sampling Time	0.054	0.021	2.601	**0.016**
Chitinase	SW_SSML	0.065	0.108	0.597	0.557
	Chl *a*	0.01	0.006	1.726	0.101
	Sampling Time	0.066	0.025	2.642	**0.016**
Alkaline Phosphatase	**SW_SSML**	0.301	0.094	3.219	**0.003**
	Chl *a*	0.012	0.006	2.039	**0.053**
Lipase-Oleate	**SW_SSML**	0.255	0.093	2.747	**0.011**
	Chl *a*	0.003	0.005	0.538	0.0596
	Sampling Time	-0.025	0.021	-1.217	0.236
Lipase-Stearate	**SW_SSML**	0.345	0.09	3.812	**0.001**
	Chl *a*	0.008	0.006	1.398	0.176
	Sampling Time	-0.001	0.024	-0.048	0.962

(B)

			Value	St Dev	t-value	p-value
Protease	SW	**DOC**	0.002	0.001	4.891	**0.001**
		Sampling Time	-0.127	0.032	-3.872	**0.002**
	SSML	**DOC**	0.001	0.001	2.737	**0.017**
		Sampling Time	-0.051	0.035	-1.473	0.165
	SSA	**DOC**	-0.006	0.001	-5.769	**0.001**
		Sampling Time	-0.158	0.065	-2.426	**0.032**
Chitinase	SW	**DOC**	0.002	0.001	2.309	**0.038**
		Sampling Time	-0.021	0.053	-0.404	0.693
	SSML	**DOC**	0.003	0.001	3.712	**0.003**
		Sampling Time	-0.068	0.043	-1.575	0.139
	SSA	DOC	-0.002	0.002	-1.004	0.342
		Sampling Time	0.027	0.082	0.334	0.746
Alkaline Phosphatase	SW	**DOC**	0.001	0.001	2.348	**0.035**
		Sampling Time	-0.225	0.035	-6.347	**0.001**
	SSML	DOC	-0.001	0.001	-0.709	0.491
		Sampling Time	-0.139	0.062	-2.241	**0.043**
	SSA	DOC	0.001	0.005	0.123	0.906
		Sampling Time	-0.077	0.164	-0.465	0.658
Lipase-Oleate	SW	**DOC**	0.003	0.001	4.586	**0.001**
		Sampling Time	-0.133	0.031	-4.335	**0.001**
	SSML	**DOC**	0.005	0.001	4.865	**0.001**
		Sampling Time	-0.043	0.054	-0.792	0.443
	SSA	DOC	-0.001	0.001	-1.588	0.136
		Sampling Time	-0.079	0.047	-1.68	0.117
Lipase-Stearate	SW	**DOC**	0.006	0.001	4.381	**0.001**
		Sampling Time	0.049	0.091	0.539	0.56
	SSML	**DOC**	-0.001	0.001	-2.789	**0.016**
		Sampling Time	0.004	0.001	6.521	**0.001**
	SSA	**DOC**	-0.001	0.001	-0.416	**0.684**
		Sampling Time	-0.074	0.056	-1.326	0.207

(C)

		Value	St Dev	t-value	p-value
Protease	Fixed Effects: log10(EnzRate) ~ EnzLoc * Sampling Time				
	SW_SSML	0.09	0.325	0.278	0.783
	SW_SSA	-1.026	0.333	-3.086	**0.004**
	Sampling Time	-0.069	0.06	-1.149	0.271
	SW_SSML:Sampling Time	0.046	0.085	0.541	0.593
	SW_SSA:Sampling Time	-0.203	0.086	-2.362	**0.025**
Chitinase	Fixed Effects: log10(EnzRate) ~ Enz Loc				
	SW_SSML	-0.012	0.097	-0.121	0.904
	SW_SSA	-1.114	0.108	-10.285	**0.001**
Alkaline Phosphatase	Fixed Effects: log10(EnzRate) ~ EnzLoc * Sampling Time				
	SW_SSML	0.435	0.144	3.023	**0.006**
	SW_SSA	-1.077	0.171	-6.297	**0.001**
	Sampling Time	-0.111	0.041	-2.728	**0.017**
Lipase Oleate	Fixed Effects: log10(EnzRate) ~ EnzLoc * Sampling Time				
	SW_SSML	0.373	0.118	3.16	**0.003**
	SW_SSA	-0.975	0.118	-8.254	**0.001**
	Sampling Time	-0.062	0.029	-2.172	**0.049**
Lipase Stearate	Fixed Effects: log10(EnzRate) ~ Enz Loc				
	SW_SSML	0.516	0.107	4.818	**0.001**
	SW_SSA	-0.608	0.107	-5.674	**0.001**

Table S6. Parameters of prescribed idealized urban plume distribution used in the coagulations simulations where N (m^{-3}) is the number concentration, D_{gn} (μm) is the geometric mean diameter, σ_g (dimensionless) is the geometric standard deviation, and N_{total} is the sum of number concentration of Aitken and accumulation modes. The data in the table are from Riemer et al. 2009.[22]

	Aitken Mode			Accumulation Mode			
Case	N (m^{-3})	D_{gn} (μm)	σ_g (1)	N (m^{-3})	D_{gn} (μm)	σ_g (1)	N_{total} (m^{-3})
1	$5.25 \cdot 10^7$	0.02	1.45	$4.75 \cdot 10^7$	0.116	1.65	$1 \cdot 10^8$
2	$5.25 \cdot 10^8$	0.02	1.45	$4.75 \cdot 10^8$	0.116	1.65	$1 \cdot 10^9$
3	$3.2 \cdot 10^9$	0.02	1.45	$2.9 \cdot 10^9$	0.116	1.65	$6.1 \cdot 10^9$

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