Investigating Concentration and Composition of Aerosol Particles of Seawater with Different Conditions by Atomizing and Bubbling

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Abstract. The way particles get into the atmosphere and effect albedo and climate change is studied by many groups. This group used methods and procedures to sample liquid and solid particles from the atmosphere. The purpose was to use the same methods and procedures and test two different processes to collect particles from an aqueous source on Teflon filters: atomizing and bubbling. This project is important because it can help show how the particles get from the oceans into the atmosphere. Atomizing blasts sample solutions into droplets which are then able to be collected on the filters. Bubbling produces bubbles that reach the surface of the solution and burst. The resulting particles are then injected into the air and can then be collected on filters. Fourier Transform Infrared (FTIR) spectroscopy was used to scan the filters and get the spectral data of absorbance at each wavenumber to determine the organic mass (OM) collected on each filter. Seawater was collected and stored under three different conditions: in the sun, in a dark cabinet, and in the freezer. In addition, one seawater sample was used immediately. The bubbled and atomized seawater solutions produced very different absorbance spectra and compositions to other “aged” seawater samples using the two different techniques. The bubbled samples are representative of the bubbles bursting at the ocean surface and producing particles, where the atomized samples are more representative of the composition of the solution being sampled. The bubble bursting in the bubbler enriches the organic concentration in the particles collected on the filter where the atomizer does not.

Introduction. Changes in future climate result from both, anthropogenic and natural sources. The burning of fossil fuels in heating, transportation, and agriculture all lead to climate change, but natural processes are also a factor in climate change (Russell et al., 2010). Particles in the atmosphere may increase the planetary albedo. Albedo is the fraction of short wave radiation emitted from the sun that is reflected from earth back to space. Some organic particles have been shown to increase the fraction of reflected radiation from earth. Marine aerosols are formed from bubbles bursting at the surface of the ocean, which loft particles into the atmosphere. Bubbles are formed due to the entrapment of air caused from waves breaking. These particles in the atmosphere have lifetimes that range from a couple seconds to many years. Fresh particles can become aged in the atmosphere. When they reach the end of their life cycle, the particles either fall out of the air by coagulation (they become too heavy), condense as rain, or they are chemically removed by reactions in the atmosphere (Riedel & Lassey, 2008). Analyzing how and what particles get into the atmosphere and impact albedo is currently being studied by many groups. The Aerosols Group, at Scripps Institute of Oceanography (SIO) analyze particles and develop models to understand the role aerosol particles play in
radiative forcing in the atmosphere which affects the climate. The “Marine Aerosols” project had two goals to investigate. The first goal was to use procedures developed for liquid or solid particles suspended in a gas, and test two different types of aerosol-producing instruments to collect particles from various aqueous samples and analyze their composition and concentrations. The second goal was to compare fresh seawater sampled by the atomizer and bubbler, to the results of seawater that was allowed to “age” in a freezer, a dark cabinet and in the sunlight for two days and then sampled. Physical and chemical processes react at different temperatures in seawater. When solutions are stored in different conditions, the sampled solutions could give different results even if the samples are all from the same source and collected at the same time. The two techniques give ways to study different processes to see which particles get into the atmosphere and could live long enough to affect the albedo. This project is also important because it can help to show that particles do interact and change overtime in seawater samples, under different conditions.

**Research Methods.** Designing a project to collect particles on Teflon filters from an aqueous source is difficult. Teflon is a hydrophobic and non-polar material which causes the water and its solutes to roll off. Teflon filters work well to collect particles that are suspended in the gas phase. To be able to collect particles from aqueous sources, there are two different techniques: atomizing and bubbling. Atomizing the solution takes fluid samples and sprays the fluid into a mist. Particles then are able to be collected on the Teflon filters. Bubbling is similar to the ocean waves; a non-reactive gas is passed through the solution creating air bubbles in the sample. When the bubbles pop, particles are produced and then collected on the filters.

The lab in which I worked used a Clean Room with regulated humidity and temperature to limit the amount of particles that could come into contact with the Teflon filters during analysis. The humidity was set at 55% but fluctuated depending on the weather. The temperature limit was set at 20.0°C and did not fluctuate.

Pre-scanning and weighing the filters produced baseline weights and scans to compare to after the particles have collected on the filters. Collecting the weights for each of the filters, a microbalance in the clean room uses a program that records weights. Once a weight was recorded ten times, this was repeated for all 22 sets. A set is a pair of filters; one filter is the sampled filter, which collects all the sampled particles, and the second filter is the backup, used to back up the collection of particles, if some were to get past the sampled filter.

The filters were scanned using a Fourier Transform Infrared Spectroscopy (FTIR) to determine the absorbance in the infrared region. The FTIR is connected to a N₂ source to purge the sample compartment. Nitrogen purges the sample compartment for 10 minutes at 1L/min. After the ten minutes the flow rate is dropped to 160 mL/min. Purging the sample compartment removes other gases which have IR absorbance from the sample compartment. A program that controls the FTIR runs two background scans to set a baseline. If the humidity changes through the scanning, the conditions in the
compartment change and a background scan is needed again. Filters are placed in a holder for FTIR. The holder is placed in the FTIR the same way for all scans to be able to have reproducible data. Scanning the filter there is a 180 second delay to purge the compartment. The FTIR starts scans and runs 128 scans of the filter. This was completed for all 22 sets of filters.

Once the filters were all pre-weighted and pre-scanned they were placed in petri dishes and wrapped with Teflon tape to limit contaminants.

The standards were made by using a 1L volumetric flask and the specified compound for each of the standards. The compounds were weighed and transferred to the volumetric flask quantitatively. De-ionized (DI) water was added to the volumetric flask. Each solution was transferred to two cleaned mason jars. The standards of sucrose, fructose, glucose, and cellobiose were all on the order of nanomolar (nM) in concentration. The standards were made and sampled to be able to compare the sampled seawater, but are random carbohydrates standards that could potentially be in the seawater, to see differences in the spectra and absorbances. The total organic carbon (TOC) with sea salt solution (artificial seawater) was based on table S4 (Russell et al., 2010 Supplement). Using the average Pacific TOC which is 7.42E-4 TOC/Na and calculations assuming Na is 35g per 1000g of H20. Sucrose and glucose and sea salt were added to a 1L volumetric flask and DI water was added. The artificial seawater solution was stored until sampled. The reason to use the artificial seawater solution is to compare to the seawater collected from the pier and what has been found to be an average of the Pacific Ocean’s TOC. All the standard solutions were placed in a cabinet until ready to be sampled.

Seawater was collected on February 8, 2011 from the end of the Scripps Institution of Oceanography pier using a five qt. bucket and a rope. The collected seawater was poured into eight mason jars that were pre-cleaned. The sun, cabinet, and freezer seawater samples were put in their prospective locations and let sit for two days. The fresh sampled seawater was immediately bubbled and atomized. The seawater samples that were placed in different locations were to test to see if bacteria enzymes or other mechanisms will produce different organic compositions.

For the bubbling of the samples and standards, the solutions went into a glass bubbler with a frit. The frit is a porous glass that is used in the bubbler to allow the gas to create bubbles that burst at the surface of the solution. The bubbler used was 25cm tall. The solutions poured into the bubbler all measured 13.5 cm from the bottom of the bubbler; this allowed all the solutions to have the same amount of volume to keep the process of sampling the same. The middle of the frit where the bubbles were produced was 11.5 cm from the surface. There was 11.5 cm for the bubbles to form and grow. Nitrogen was used as the gas source to create the bubbles because nitrogen is unreactive. The filter set for each sample was placed in a filter holder with a hole for the air to pass through the filter. A flow rate of 2.09±0.03 L/min through the filter was the starting volume for each of the samples, on average. These solutions were bubbled for an hour and then the flow rates were recorded before turning off the vacuum and N2. After running the solution through the bubbler, the solution is replaced in the jar and
placed back into the cabinet. The bubbler and frit were rinsed between each run.

For atomizing, the standards and samples were poured into an atomizing jar. The propellant, nitrogen, is passed over a hole that is attached to a tube creating a venturi effect. The venturi effect creates a vacuum in the tube and draws the solutions up and into the flow of the propellant and atomized and collected on the filter (Carboni, 2002). A flow rate of 2.10 ± 0.02 L/min through the filters was the average. The atomizer was run for 30 minutes for all solutions except one, 25 minutes for the sea salt in DI water. The atomizer and jar was cleaned with DI, acetone, and then rinsed three times with DI water, repeated for all 11 solutions.

For both the bubbling and atomizing, the sampled filters placed into their petri dishes wrapped with Teflon tape and placed into the freezer until ready to be moved back into the clean room to be scanned and weighed. The filters sit in the clean room for 24 hours before scanning or weighing in order for the filters to reach equilibrium.

The filters’ post scans and weights were collected the same way as the pre-scanning. Then scans both pre-scanned and post scanned spectra were run through automated algorithms for peak fitting and integration to minimize bias. The absorption is converted to mass by using reference absorptivities specific to different peak locations (Russell, L., 2010).

**Results.** Table 1 gives the 22 sets of filters with description of the sampled solution. In Table 2 the total percent OM, the mass on filters was calculated by subtracting the pre weight from the post weights and are recorded in µg. The pre-scan filter weights average was 103.0251 ± 3.9672 µg. The post-sampling the average filter weight was 104.2897 ± 4.3928µg. The filters were weighed three times for both the pre and post weights. This result shows that there were particles that were collected on the filters from the sampling of the solutions. Table 2 shows the percent OM of the total mass from the seawater sampled filters. These were calculated by taking the OM of the filters and dividing it by the total mass of the filters and multiplying by one hundred to get the percent of OM on each of the filters.

When the filters are new and have no sampled material on them, air easily passes through them, so using a flow rate while sampling gives a general representation of the amount of particles collected on the filter. The starting flow rates for atomizing averaged 2.10 ± 0.02 L/min, and the ending flow rate average was 1.11 ± 0.88 L/min. All except one of the atomizing solutions went the whole thirty minutes. The only one that did not was the sea salt in DI water standard. The average starting flow rate for the bubbled solutions was 2.09 ± 0.03 L/min and the average ending flow rate is 2.05±0.03L/min. All of the bubbled...
solutions were sampled for sixty minutes. The starting and ending flow rates show that the flow through the filters was hindered through the sampling process.

We are interested in all of the organic functional groups, but acids, amines, carbonyl, and alcohols are the functional groups we observed above the detection limits from our algorithm. Four infrared energy locations are used to identify functional groups in infrared spectra. The four groups have different wavelengths, at which they absorb infrared light at different amounts. Figure 1 and Figure 2 give the spectrum of each of the different filters with the 4 functional groups that were detected. Both the atomizing and bubbling filter colors in the figures are the same based on the sampled solutions.

In Figure 3, the four different conditioned atomized seawater samples are compared with the artificial seawater made in the lab. The artificial seawater and the freshly sampled seawater have very similar absorbance and spectra. In Figure 4, the bubbled seawater samples and the artificial seawater show very different absorbances than the atomized graph. In the bubbled spectrum, the freshly sampled seawater sample looks very similar to the frozen sampled seawater, where the artificial seawater has a shape and
absorbance that resembles the seawater sample that sat in the sun. The absorbances of the atomized solutions are also 4 times larger than the absorbance to the bubbled solutions, even though they were sampled for half of the time.

**Discussion.** The uncertainties from the DI water (bubbled and atomized) were larger than the amount of OM concentration calculated, showing that the organic mass of these samples was below detection limit. This happens because with just DI water there shouldn’t be any OM on the filter. In Table 1, there was 1 filter that was negative percent of OM, it was bubbled. This demonstrates that the mass of particles collected on the bubbled filters is so small that the weight change of the humidity in the clean room has a larger impact than the miniscule amount of mass on each of the bubbled filters.

When bubbling and atomizing the different solutions, the bubbled solutions with the sea salts and sampled ocean water created smaller and more abundant bubbles compared to the solutions that did not contain sea salts, based on my observations. The smaller bubbles created a foam-like substance above the water which did not burst quickly. The non-sea salt standards produced larger bubbles which burst shortly after making contact with the surface. When looking at the spectra, the atomized samples have larger absorbance than the bubbling spectra. This is because the atomizer takes the solution and blasts it into tiny droplets allowing more mass to be collected on the filters. The bubbler uses the bursting of bubbles to loft small amounts of OM into the air above the solution and then collected on the filters. The flow rates for the atomizer from start to finish had a larger drop than the bubbling flow rates. This is because

In the infrared spectrum alcohols absorb at approximately 3300-3500 cm\(^{-1}\) and is a very broad peak (Volland, 1999). On some of the spectra, there are noticeable sharp peaks around 3500 cm\(^{-1}\) (Figure 5). This sharp peak has been previously observed as the Phenol functional group (Bahadur et al., 2010). Phenol functional groups have rarely been observed in filter samples of ambient aerosol particles. Phenols are similar to alcohols in that they are hydroxyl groups but the phenols are bonded to an aromatic benzene ring. The hydroxyl radical (OH\(^{\cdot}\)) quickly reacts with the phenol group and removes them from the atmosphere by bonding to the benzene ring in the -ortho and -para positions. Further oxidation of the phenols with the OH\(^{\cdot}\) finally forms lower molecular weight acids, carbon dioxide and water (Bremner et al., 2006). The reason the sectra have such large absorbances is because there was not enough time for the phenols to react with the hydroxyl radical. The primary particles collected were fresh and
there was not a lot of time for aging or reacting with other compounds.

When looking at both Figures 3 and 4, there are some differences as well as similarities in the absorbance of the sampled solutions. In the atomized figure, the freshly sampled seawater spectrum has a very low absorbance compared to the other three sampled seawater samples. The fresh seawater also has a spectrum that looks similar to the artificial seawater. Using the comparison that artificial seawater made was an average of the TOC calculated for the Pacific Ocean. The freshly sampled seawater shows that the fresh seawaters’ TOC is close to the average. In both figures, the spectra have phenol peaks, but the atomized solutions peaks are more distinguished than the bubbled samples. The reason that the atomized phenol functional groups are more distinguished is because the amount of OM that is able to be sprayed into aerosol form is greater with the atomized technique than from the bubbling technique.

In the bubbling of the sampled ocean water, the freshly bubbled and the frozen spectra have very similar peaks, which mean in the frozen sample, the bacteria or other contributors to reactions were possibly hindered by the colder environment and resulted in a very similar absorbance and peaks. The bubbled sunlight sample did not absorb as much compared to the fresh but does have similar spectrum to the TOC but the fresh seawater did not. This is possibly due to the fact that sample sat in the sun and was affected by the changing temperatures and allowed the compounds in the seawater to be altered by bacteria and reactions with other compounds.

The varying temperatures changed the rates at which the compounds were changed.

The bubbled cabinet solution was in an area where the temperature was more constant which allowed more of the compounds to be processed and changed. The atomized solutions had a different output. The fresh had a lot of alcohol absorbance and very little phenol absorbance where the sunlight had a very high absorbance of phenols and a smaller absorbance of alcohols. The frozen and cabinet samples have similar peaks to the sunlight seawater, but with less absorbance. The fresh seawater sample had a smaller phenol peak than the cabinet and frozen. This shows that in the fresh water there is no breakdown of plant materials in solution. As the others sat, reactions occurred and broke down the plant material to be sampled later. This was a good experiment to see how the atomizer and bubbler represented and produced the aerosol particles from their specific solution and what the differences were.

Conclusion. Bubbling and atomizing seawater and standards are efficient ways to collect particles on Teflon filters. Both processes are slightly different in their approach to generating aerosol particles which are collected on a filter. Unique results were observed with the large absorbances at $3500\text{cm}^{-1}$ in both the bubbled and atomized samples indicative of phenol functional groups. The bubbled and atomized sampled seawater spectra had very different absorbances for the two different techniques used. Varying the conditions in which the samples are stored and sampled (fresh, sunlight, cabinet, and frozen) give different results depending on the technique used. The atomizing technique is more representative of what the composition of the solutions are, and the bubbling is more representative of the
actual way the bubbles are formed and burst when waves break on the surface of the oceans. The freshly atomized sampled seawater had very similar peaks and absorbance to the artificial seawater made in lab, where the bubbled sun and frozen seawater samples had similar peaks and absorbance and the artificial seawater had completely different looking peaks. The spectra from both the bubbled and atomized showed that reactions did occur and changed compositions of the sampled seawater, however it was not determined if it was chemical or physical that caused the change.

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Reference