## Author

Joshua Klobas' interest in the implications of climate change and the physical basis for the feedback mechanisms involved led him to the AirUCI organized research unit. He found an undergraduate opportunity in Professor Nizkorodov's Aerosol Photochemistry group and was fortunate enough to be given some degree of self-direction. Joshua's project was a proof of concept of a method for measuring photo-induced dissociation of organic molecules. As the project matured, the tens of thousands of data points offered him the opportunity to learn new statistical techniques and treatments that he will be able to apply to many different types of problems in the future. Joshua is now pursuing a Ph.D. in chemical physics at Harvard University.

### Key Terms

- Photochemistry
- Photodegradation
- Photolysis
- Quartz Crystal Microbalance (QCM)
- Secondary Organic Aerosols (SOA)

# New Approach for Probing Photodegradation of Organic Aerosols Using Quartz Crystal Microbalance

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## Abstract

Atmospheric oxidation of volatile organic compounds from biogenic sources is responsible for a large fraction of the aerosol particles in the atmosphere. The resulting secondary organic aerosol (SOA) particles contribute to many processes implicated in climate change. A challenge in describing SOA-climate interactions is the constant evolution of SOA particles. Photodegradation by solar UV radiation is one of the most important processes in this evolution; therefore, it is important to know how efficient these processes are and understand the major mechanisms responsible for them. We describe a new quartz crystal microbalance (QCM) technique for characterizing SOA photodegradation. We detect the loss of mass in the process of UV irradiation of microgram quantities of SOA particles collected on a substrate using the high mass sensitivity of QCM. Limonene and other compounds were reacted with ozone and deposited directly on quartz crystal by impaction. A scanning mobility particle sizer provided quantitative information on the mass distribution and allowed the calculation of deposited mass. Photolysis experiments were conducted on films of SOA and representative compounds deposited on the quartz crystal. Mass loss was observed as a function of UV flux. This approach has promise for investigating photodegradation of aerosols and other environmental samples.

## Faculty Mentor

Atmospheric particles have a disproportionally strong effect on the Earth's climate despite their small abundance. Elevated concentrations of particulate matter pose significant health risks in heavily urbanized areas. The climate and health effects of atmospheric particles remain poorly understood because their chemical composition changes in complicated ways in response to various environmental factors. Joshua's research addresses a question of whether particles can shrink in size in the presence of solar radiation. He succeeded in putting together a unique instrument to study this phenomenon and demonstrated that organic particles do become smaller when irradiated. This is an important finding because smaller particles scatter light less efficiently compared to larger ones, and they are also less efficient in nucleating cloud droplets.

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## Introduction

### *Organic Aerosols*

Volatile organic compounds (VOCs) are of great interest to atmospheric scientists because of their ability to oxidize into condensable organic compounds that form organic particles. Most contemporary climate models assume that aerosols are composed predominantly of inorganic sulfate particles. Field measurements, however, have convincingly demonstrated that atmospheric particles exist in diverse forms, such as black carbon (soot), inorganic sulfates and nitrates, mineral dust, and, most commonly, organic carbon. The insufficient understanding of organic particles contributes substantially to the error of climate models; however, the complex chemistry of airborne particles has thus far precluded a more complete understanding (Finlayson-Pitts, 2000).

All particles, including organic particles, can serve as cloud condensation nuclei (CCN), impacting regional climates and weather significantly. When more particles can function as CCN, a cloud's lifetime is increased because water vapor is distributed into a larger number of smaller droplets instead of fewer larger droplets. Besides impacting the lifetime of the cloud, the particles themselves contribute directly to changes in radiative forcing, either via scattering, or by absorbing of solar radiation (Wang, 2007). The Intergovernmental Panel on Climate Change (IPCC) 2007 report assigns large errors to the direct and indirect effects of aerosols on climate, stating that much of this uncertainty comes from a poor understanding of organic aerosols (Solomon, et al., 2007).

Apart from climate effects, inhalation of particles has been directly associated with human morbidity. This is evidenced by the fact that differential human lifespans are dependent on the proximity of one's dwelling to various emission sources. Particulate matter (PM) concentrations have been directly correlated with mortality rates from cardiovascular and pulmonary diseases. A 10 $\mu g/m^3$ increase in $PM_{10}$ (particles ranging below 10 μm in diameter) has been correlated to as much as a 2% increase in hospital admissions for pneumonia. $PM_{2.5}$ (particles below 2.5 μm in diameter) concentration increases of 10 $\mu g/m^3$ have been associated with a 16% increase in long-term mortality (Zanobetti, 2009).

The majority of VOCs emitted to the atmosphere are biogenic; these include isoprene ($C_5H_8$) and monoterpenes ($C_{10}H_{16}$). Emissions of biogenic VOCs are on the order of 600 TgC/yr worldwide, an amount dwarfing that of all other families of organic compounds. These VOCs have a short lifetime, on the order of an hour, and are efficiently converted to secondary organic aerosol (SOA) in the troposphere (Chen, 2009). Such particles are called secondary organic aerosol in order to distinguish them from primary organic aerosol (POA) generated by mechanical suspension of dust and ocean water. The yields of SOA from various sources are well characterized in literature; however, the further chemical fates of SOA are much less well understood.

Due to their large emissions, biogenic SOA played a large role in global climate and cloud dynamics for most of preindustrial history. Recent anthropogenic changes in ratios of particle composition due to evolving industrial technologies only serve to complicate and amplify the chemistry of these biogenic aerosols (Carlton, 2010; Karl, 2009). Indeed, increased anthropogenic $NO_x$ emissions from industrialization (primarily from combustion engines) have resulted in elevated tropospheric ozone concentrations. This fuels the generation of additional tropospheric SOA from otherwise biogenic sources, linking SOA formation intimately with broader processes associated with climate change (Ebi, 2008).

This project studied SOA produced from limonene, a monoterpene partially responsible for the characteristic odor of many citrus plants. The formation of SOA from limonene has been studied by several research groups, and it has been shown that these compounds are primarily multifunctional species containing carbonyl, carboxyl, and hydroxyl functional groups which make the SOA susceptible to further chemical reactions in the atmosphere (Bones, 2010). Our goal is to understand the efficiency of photochemical "aging" reactions occurring within limonene SOA. Here, "aged" SOA are defined as those modified through chemical or photochemical pathways, such as further oxidation, photodegradation, or oligomerization.

### *Oscillating Mass Balances*

This project relies on the adaptation of the quartz crystal microbalance (QCM) for the direct measurement of mass lost upon UV irradiation of sample compounds. Günter Sauerbrey first described the QCM in his doctoral thesis "Application of Oscillating Quartz Crystals for the Weighing of Thin Films" (Sauerbrey, 1959). The QCM exploits the piezoelectric properties of quartz to derive a frequency to mass load relationship. An approximate mathematical description of QCM can be derived from treating the system as a physical spring-mass oscillator. Sauerbrey's treatment of these parameters in a first-order solution to the small-load approximation resulted in what is now widely known as the Sauerbrey Equation:

$$\frac{\Delta f}{f_0} = -\Delta d / d = \frac{-\Delta m_q}{\rho_q A d} \qquad (1)$$

where $f_0$ is the characteristic frequency of the quartz crystal, $d$ is the thickness of the quartz crystal, $\Delta m_q$ is the mass of a thin layer of film of thickness $\Delta d$, $\rho_q$ is the density of the quartz crystal, and $A$ is the surface area of the crystal covered with the film. This relationship, when applied to a thin film of a material evenly distributed over the crystal surface is commonly expressed in a more convenient form as:

$$\Delta f = f - f_0 = -C_f \frac{m_f}{Area} \qquad (2)$$

where $f$ is the actually observed oscillation frequency in the presence of a load, $m_f$ is the mass deposited onto the crystal, and $C_f$ is the Sauerbrey sensitivity constant (56.6 $\text{Hz}\bullet\mu\text{g}^{-1}\bullet\text{cm}^2$).

The QCM can distinguish very small changes in mass over a relatively short time scale. The typical sensitivity achieved in environmental QCM applications is equivalent to just a few nanograms of matter deposited on (or removed from) the crystal over a 1-second time interval. QCM sensitivity to temperature and pressure may be reduced by environmental noise. The extreme mass-sensitivity of the balance coupled with its fast response make the system ideal for surface photochemistry techniques. To our knowledge, this work represents the first application of QCM for the characterization of photodegradation of organic aerosols.

## Experimental Approach

Our approach comprised SOA generation, quantitative SOA deposition on a QCM crystal, and photodegradation of the deposited SOA particles, as depicted in Figure 1.

### *SOA Generation and Deposition*

It is common to collect aerosol particles on flat substrates by a process called impaction, in which a stream of air containing particles collides with the surface of the substrate at high speed. Most particle impactors, however, are not compatible with QCM substrates, and we needed a method that did not require removing QCM crystals from the QCM resonator during particle collection to prevent unwanted changes in the crystal frequency. SOA was deposited from an aerosol reactor directly onto the crystal without removing the crystal from the resonator holder. We then determined the mass deposited on a crystal from the measured aerosol mass flux, and calibrated deposition efficiency. An apparatus was designed to characterize and control aerosol mass flux, a function of aerosol mass distribution, aerosol flow rate, and flow time over the crystal surface. The deposition efficiency was determined from analysis of particle mass distributions at sampling points before and after impaction.

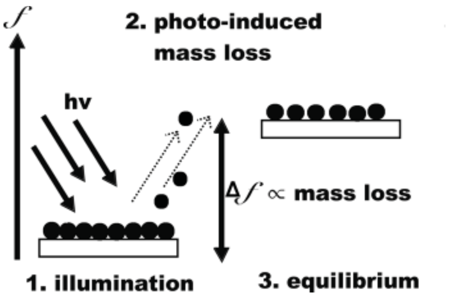

Figure 1

Experimental Approach. Mass loss during photolysis is derived from the observed frequency change of the QCM.

Test aerosol was generated in an aerosol flow tube reactor (Figure 2), in which limonene was oxidized by ozone to form SOA. Ozone was produced in an ozone generator and mixed with carrier gas and limonene in the 17 L flow tube reactor. In these experiments a 1:5 limonene:n-butanol (V:V) mixture was delivered to the flow tube reactor via syringe pump at a rate of 1 μL limonene/hour. The ozone concentration in the flow tube was controlled at 7.2 ppm, and the flow-tube reactor, with a 17 L volume, allows for an average of 6 minutes of reaction at a 3.5 L/min flow rate. Variations in carrier gas flow rate modulated by a mass-flow control unit dictated the VOC-ozone chemistry reaction rate. An ozone/VOC-denuder effectively quenched the reaction by removing residual ozone from the mixture after the flow-tube reactor. The *in-situ* generated SOA was then allowed to flow through the rest of the apparatus. The overall system pressure was kept steady through a manifold of bleed valves.

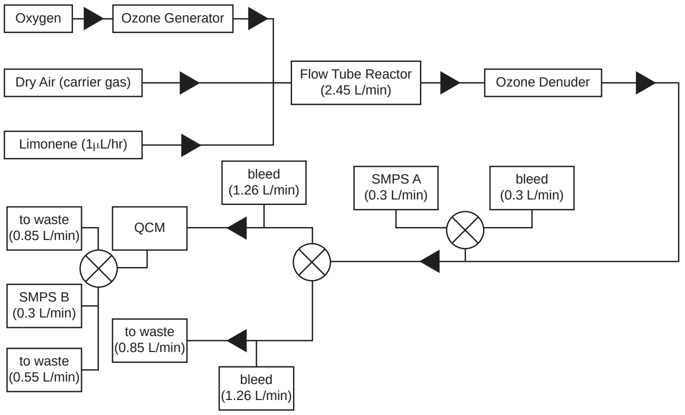

Figure 2

Flow system for the generation and deposition of SOA onto QCM crystals. Arrows show the direction of the flow. The "x-in-a-circle" symbols designate three-way valves. Typical flows are specified in standard liters of air per minute.

The size distribution and number density of the particles leaving the flow tube are quantified with a scanning mobility particle sizer (SMPS). The SMPS is a multi-component instrument, including a differential mobility analyzer (DMA) and condensation particle counter (CPC). The function of the DMA is to separate particles by their electrical mobility, which is correlated with particle size via Stokes' law. An applied DMA potential is chosen to transmit a specific particle size. By increasing the potential from 0–10 kV, the number density of particles of each size can be measured, giving the particle diameter distribution in the 20–1000 nm range.

SOA generation is a sensitive function of reaction conditions, and our goal is the quantitative determination of mass deposited on the quartz crystal; therefore, care was taken to ensure that aerosol mass distribution remained constant over time. With the QCM three-way valve directing flow to the QCM bypass, sampling was first conducted at point SMPS-A (Figure 2) to observe the time evolution of the aerosol size distribution as the flow reactor reached a steady state. Figure 3 shows that a steady state is established after approximately 40 minutes of reaction time.

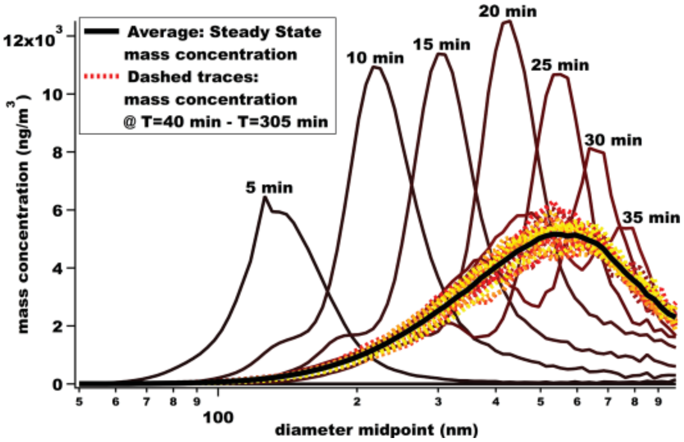

Figure 3

Evolution of the aerosol particle size distribution during aerosol generation. Each trace corresponds to a 5-minute sampling interval. After about 40 minutes, the flow reactor reaches steady state conditions, and the distribution no longer changes.

The SMPS sampler operates with a flow of 0.3 L/min. To account for various SMPS sampling locations, an auxiliary three-way valve was installed at each point alongside a needle valve to maintain a constant 0.3 L/min loss of flow regardless of SMPS sampling configuration. Additionally, in order to allow the establishment of a steady state aerosol distribution without impacting the QCM system, a QCM bypass was constructed from two needle valves and attached to the main flow with a three-way valve. The QCM bypass was designed to duplicate the QCM flow resistance, so as to maintain constant pressure, and therefore constant aerosol concentration, regardless of flow direction (over QCM or through QCM bypass).

### *Particle Impaction*

Once the steady state is reached, the three-way QCM/bypass valve directs the flow over the QCM crystal. The impaction system is a commercial flow-cell intended for liquid flow (Stanford Research Systems), custom-adapted for aerosol flow over a QCM crystal. Aerosol is impacted on the crystal until the desired frequency response is obtained. During this procedure, size distributions are determined by the SMPS at sampling points SMPS-A and SMPS-B. The direct comparison of the mass-distributions observed at sampling points A and B makes it possible to quantify the particle deposition efficiency factor.

In selected experiments, aerosol was collected on a QCM crystal with the help of commercial particle impactors, such as the micro-orifice uniform-deposit impactor (MOUDI). A series of nozzles, arranged such that the nozzle diameter decreases in the direction of aerosol flux, traps particles on suitable substrates (QCM crystal for this experiment). Using the same particle generation parameters as used in the depo-

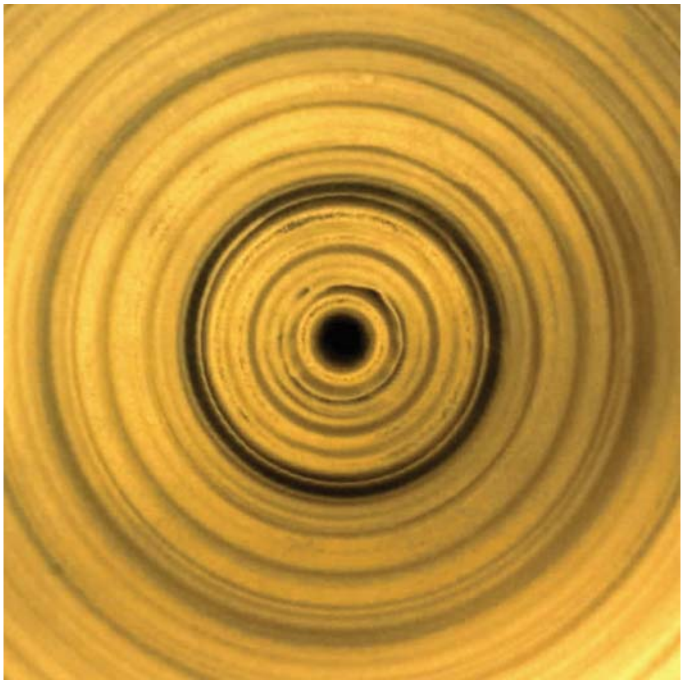

Figure 4

MOUDI deposited limonene SOA (2.5x). The SOA particles are distributed in the concentric circles. An old QCM crystal was used for this imaging experiment, resulting in visible scratch marks (which do not affect the photodegradation experiments presented in this manuscript).

sition apparatus, the QCM cell was bypassed and the flow was directed through a MOUDI apparatus. Particles were collected in the 150–290 nm diameter range on a partially masked quartz crystal insert. Because of the crystal's rotation during deposition as a result of the MOUDI operation, the particles settled in concentric circles on the gold electrode surface (Figure 4). These SOA impacted crystals were then installed in the photolysis apparatus and subjected to UV irradiation.

### *Photolysis*

Figure 5 shows the photolysis apparatus. A QCM crystal holder was placed within a sealed container and a quartz window on the top of the sample chamber allowed for transmission of UV radiation. A 75 W xenon arc lamp was the radiation source and a dichroic mirror reflected UV radiation (300–400 nm) toward the window. A Schott-BG filter (280–480 nm) absorbed the residual radiation, eliminating heat build-up on the crystal surface. An iris aperture served to restrict illumination to only the crystal surface. The relative humidity of the sample chamber can be controlled through the addition of nitrogen or water vapor flow. To minimize temperature fluctuations, the QCM crystal holder and QCM crystal were insulated with foam rubber. For the photolysis experiments, the total flow of purge gas was constant at 100 cubic centimeters per minute. The maximum radiation power density incident on the crystal was 10 mW/cm$^2$.

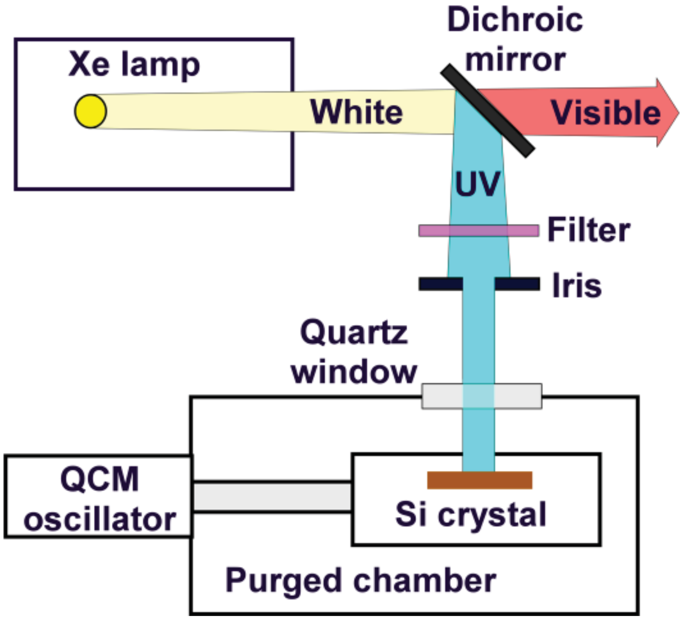

Figure 5

Photolysis Apparatus. The QCM silicon crystal is placed in a purged chamber, where it is irradiated with filtered UV radiation from a broadband Xe-lamp source. Visible radiation is filtered away to prevent unnecessary sample heating.

## Results and Discussion

### *Deposition Apparatus Operation*

Initial experiments were performed to determine the optimal parameters for the particle deposition. Using a fixed aerosol reactor flow rate of 3.5 L/min, a thorough optimization of all the other flows was performed through analysis of steady state particle concentrations with respect to the reaction time. Prior to the start of the experiment, a flow calibrator was used to verify the flow at each bleed point.

After the steady state particle concentration was achieved (Figure 3), the aerosol flow was directed over the QCM instrument. SOA particles began depositing on the QCM, resulting in a steady frequency response (Figure 6). The particle concentration distribution was characterized with SMPS at regular intervals throughout the deposition process. We monitored the flow-tube and post-QCM particle concentration distributions throughout the process.

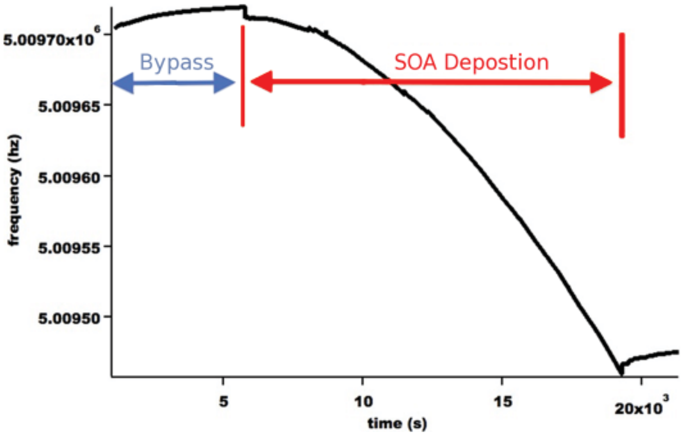

Figure 6

QCM response during SOA deposition. As particles deposit on the QCM surface, the mass of the organic surface film increases, and the oscillation frequency drops.

### *SEM Investigation of Particle Deposition*

As stated earlier, the use of the classical Sauerbrey's equation requires a uniform deposition of a thin film on the resonator surface. We employed scanning electron microscopy (SEM) techniques to determine whether or not our deposited film fits this criterion. SEM is suitable for imaging the SOA adsorbate on the quartz crystal due to the resonator's conductive gold electrode surface.

Figures 7 and 8 show non-uniform islanding of the coalesced particles with anisotropic density tending toward the center, indicating that the Sauerbrey's relation is unlikely to be applicable to our samples. The linear mass-frequency relationship can still be obtained; however, the proportion-

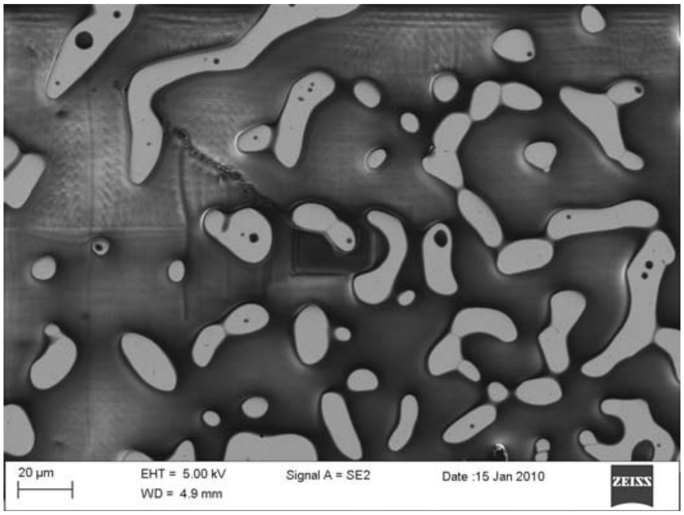

Figure 7

SEM Micrograph–QCM Impacted SOA (950x). Following the deposition, individual SOA particles coalesce into a liquid film.

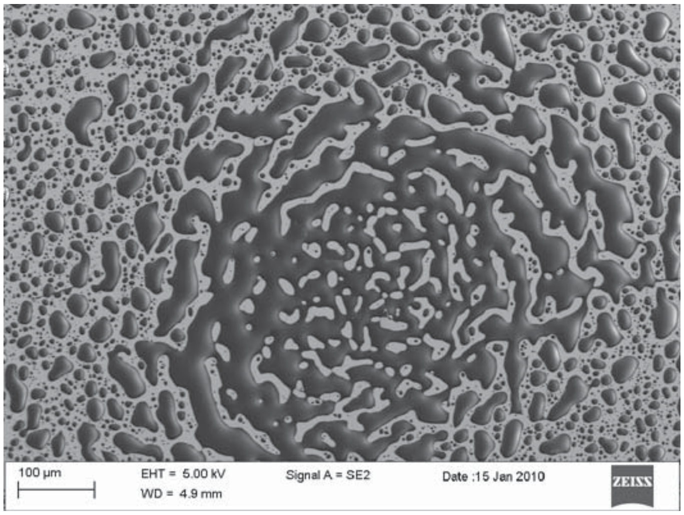

Figure 8

Micrograph-QCM Impacted SOA (95x).

ality constant may differ from the theoretical value appropriate for rigid films. This requires careful calibration of the QCM frequency response for each specific set of aerosol generation and deposition conditions.

### *Determination of Deposition Efficiency*

With knowledge of the particle concentration before and after the QCM impactor cell, it is possible to determine the particle deposition efficiency. A higher flow rate or higher aerosol concentration will result in a faster accumulation of mass on the crystal. To account for this, deposition efficiency, $\eta$, was calculated explicitly for each experiment from the ratio of the measured integrated particle mass distributions:

$$\eta = 1 - \frac{\int_0^\infty \frac{\mathrm{dM}\{\mathrm{SMPS}\text{–}B\}}{\log(\mathrm{Dp})}\, d\log(\mathrm{Dp})}{\int_0^\infty \frac{\mathrm{dM}\{\mathrm{SMPS}\text{–}A\}}{\log(\mathrm{Dp})}\, d\log(\mathrm{Dp})} \tag{3}$$

Additionally, the impaction selectivity of the QCM impactor with respect to the particle size was characterized. Two-variable ANOVA analysis was conducted on the particle mass distribution, the particle median diameter, the particle mean diameter, and various other parameters. The ANOVA analysis confirmed that the QCM impactor does not selectively collect smaller or larger particle sizes, *i.e.*, the measured collection efficiency applies over the entire particle size range of interest (20 nm–1000 nm).

We can now calculate the mass of the aerosol material deposited on the crystal as follows:

$$\mathrm{Mass} = TV\eta \int_0^\infty \frac{\mathrm{dM}\{\mathrm{SMPS}\text{–}A\}}{\log(\mathrm{Dp})}\, d\log(\mathrm{Dp}) \tag{4}$$

In this equation, $T$ is the time elapsed during deposition, $V$ is the aerosol flow rate, $\eta$ is the deposition efficiency (Equation 3), and the integration extends over the entire mass distribution.

In order to verify this approach, the mass of the collected aerosol material was also determined explicitly by removing the crystal from the oscillator holder and weighing it with a microbalance. The calculated value from Equation 4 compared well with the values obtained using explicit weighing. In all trials, the values differed by less than 5% (for example, aerosol flux calculation determined 157.8 µg of SOA was deposited during analysis depicted in Figure 6, while 152 µg of deposited SOA was determined by post-deposition weighing).

A constant of proportionality between the frequency shift and the mass deposited was then derived. This value, due to the non-uniformity of the aerosol film on the crystal, was not constant between experiments, but was reproducible when determined and applied to a specific set of deposition conditions. Typical values lay in the range of 0.5–1.0 Hz/µg. Because the sample was distributed over a surface area of about 0.2 $\mathrm{cm}^2$, this yielded an effective sensitivity constant between 5 and 10 $\mathrm{Hz \cdot cm^2 \cdot \mu g^{-1}}$. This value was smaller than the 56.6 $\mathrm{Hz \cdot cm^2 \cdot \mu g^{-1}}$ expected for a uniform rigid film, due to the softness and non-uniformity of the SOA material.

### *Photolysis of Deposited SOA*

Upon UV-irradiation, the SOA film may undergo photochemical reactions and photodegrade, producing gas-phase byproducts. The decrease in mass due to the loss of volatile compounds formed will be measured as an increase in QCM frequency. By carefully measuring the lamp power and the fraction of the radiation absorbed by the film one can determine the efficiency of the photochemistry (*i.e.*, the number of photolysis events triggered by each absorbed photon).

Initial photolysis experiments involved SOA collected with the MOUDI. Limonene SOA (171 µg) was deposited on a quartz crystal, which was then removed from the MOUDI and installed in the QCM oscillator holder. After placing the crystal in the holder, the frequency drifted upward linearly, suggesting that SOA was evaporating from the surface (Figure 9). When the frequency drift was monotonic and steady, the SOA was irradiated with UV for forty-five minutes. The change in frequency upon photolysis was correlated with the mass lost.

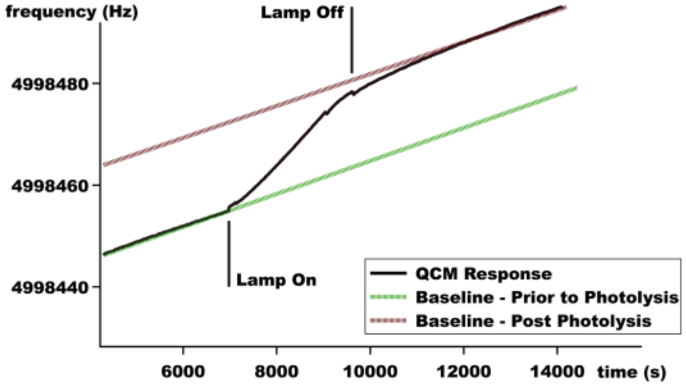

Figure 9

Photodegradation of MOUDI-deposited limonene. The frequency increases with time even in the absence of UV irradiation due to the slow SOA evaporation. In the presence of UV light, the frequency increase accelerates significantly. This image shows how the effect of the spontaneous evaporation and photodegradation can be separated from each other.

Assuming the previously obtained sensitivity constant of ~5 Hz•cm$^{2}$•µg$^{-1}$, the effective mass loss rate from the crystal during the irradiation period was 43 ng/min. This represents 1.1% of mass loss during the 45-min irradiation period. Illumination power was of the same order of magnitude as solar power from a 300–400 nm incident on the Earth's surface at a zenith angle of 0°, indicating that the experimental SOA UV exposures are similar to atmospheric SOA UV conditions. If we assume that the loss rate remains constant at approximately 1% mass per hour, a significant fraction of the material in the particle (>60%) will be photodegraded after remaining in the atmosphere for 10 days (about 100 hours of exposure to light). This indicates that photodegradation is an efficient loss mechanism for biogenic organic aerosols.

The initial experiments with SOA photodegradation were revealing, but they were complicated by the poor baseline behavior due to aerosol evaporation. Additionally, the frequency still exhibits slow drift due to temperature changes (visible in Figure 6, for example). In future experiments, the QCM crystal will be temperature controlled through a thermostat.

Once these limitations are overcome, photochemical properties of the sample compounds will be measurable using the combined deposition-photolysis apparatus. Mass loss upon irradiation as a function of time and irradiation power will allow for the determination of quantum yields for photodissociation chemistries.

## Conclusion

This paper describes the first application of QCM in investigating SOA photochemical aging. We developed methods for deposition of SOA on the resonator surface in a controlled manner. An apparatus was constructed for the real-time characterization of *in situ* generated SOA and its deposition properties. This apparatus was shown to be reasonably robust. Future improvements, such as a machined QCM flow-cell impactor and a higher-quality temperature-controlled QCM resonator, could improve the accuracy of the instrument beyond that of the order-of-magnitude range currently obtained. Additionally, a temperature controlled QCM resonator will solve the issue of the temperature-dependent baseline drift.

Although this is a work in progress, we also describe the use of the quartz crystal microbalance to characterize mass loss upon UV irradiation of SOA. We also demonstrated the competition of evaporative processes with photodegradation processes in limonene SOA. Atmospherically relevant mass loss due to photodegradation on the order of 1% per hour was observed under conditions approximating typical solar flux for the 300–400 nm wavelength range. We demonstrated that special care must be taken in avoiding artifacts such as frequency change induced by the redistribution of sample over the crystal area.

If such effects are appropriately controlled, QCM can be a useful tool for the quantification of photodegradation of SOA and related organic compounds. This apparatus will be useful for the further understanding of the lifecycle of SOA in the atmosphere, possibly leading to better modeling parameterization of particles, and more generally, the role of SOA photo-dissociation products in atmospherically relevant processes. Although climate change concerns motivate this project, it should be stressed that we describe an analytical technique useful beyond this paradigm.

## Acknowledgements

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