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RPPR Final Report

as of 24-Jun-2022

Agency Code: 21XD

Proposal Number: 71600CH

Agreement Number: W911NF-18-1-0085

INVESTIGATOR(S):

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Report Date: 30-Sep-2021

Date Received: 24-Jun-2022

Final Report for Period Beginning 01-Feb-2018 and Ending 30-Jun-2021

Title: Environmental Chemistry: Surface Films as Active Environmental Interfaces

Begin Performance Period: 01-Feb-2018

End Performance Period: 30-Jun-2021

Report Term: 0-Other

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STEM Degrees: 1

STEM Participants: 1

Major Goals: This project's major goals included: 1) Collecting and characterizing passively sampled, native environmental films, 2) developing model films representative of their native counterparts, and 3) investigating the adsorption/desorption behaviours of smaller, (semi)volatile species. All three of the goals were addressed under this award, leading to significant new insights, publications, presentations, and dissertations. Goals 1 and 2 were particularly well explored. Goal 3 was limited in scope to addressing ad/desorption of water, which also led to several unexpected and impactful findings.

Accomplishments: Goal 1 Work to collect and characterize environmental films continued through this project period. We continue to identify and explore new environments and conditions for film collection and have continued to write and publish manuscripts that describe the varying chemical and physical properties of the films we collect. The most recent manuscript (currently addressing minor revisions for Chemosphere) examined the differences in environmental films formed on vertical and horizontal surfaces at the same location data attached. An additional manuscript to be submitted in coming weeks evaluates the changes to environmental films collected as a function of distance from a road during the winter season, and tracks differences in road-salt coverage within the film.

Goal 2 This goal has been successfully addressed. We have developed a reasonable model film system based on mixtures of organic and inorganic compounds which can be drop cast or spin-cast onto flat substrates. While the models can always be improved, this work has been successful in that it provides an excellent platform for creating generic models that can be tailored as desired.

Goal 3 Final progress on this goal was focused mostly on adsorption-desorption of water with some limited results for nitrite-nitrate and phosphate-phosphite. The results from water adsorption were very informative and constituted a significant section of a recent publication. The water acts as a significant film maturation pathway through deliquescence-efflorescence cycling. It also advances chemical mixing of water-soluble film species. The adsorption behaviours of nitrite and phosphite was tracked initially with secondary ion mass spectrometry and later in bulk with ion-chromatography. These results have been linked to the growth of microorganisms within the films identified by our group and linked to local air quality reports published by other groups.

We did not make as much progress in examining the adsorption or desorption of persistent organic pollutant species as we originally proposed. The original goal was complicated by the significant changes induced by water adsorption. We spent most of the effort for this goal focusing on water uptake, and could likely spend significantly more effort on water. The work to understand water's role in these films is foundational to develop insights to the

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adsorption-/desorption of any other molecular species within environmental films.

Training Opportunities: This project supported training of four graduate students and four undergraduate students. While not all were paid directly from this award, they all benefitted from the research activities and resources provided by this funding. Three graduate students who did receive funding from this award have graduated with Ph.D.s. Two are in industrial positions and a third is working at Argonne National Laboratory. The fourth graduate student is entering year two of her Ph.D. program.

The undergraduate students have all graduated with bachelors degrees, and are all employed in STEM areas.

This funding inspired several collaborations which led to training opportunities that would otherwise not have been possible. These included several visits to PNNL's EMSL facility to use advanced analytical methods, and a DOE-SCGSR fellowship for one of the project's graduate students to work at PNNL for ~9 months.

Results Dissemination: Results of this work were presented at several ACS National and Regional meetings, the Pacificchem 2021 meeting, and in numerous invited University lectures. Results of this work have been included in two Ph.D. dissertations, and in four peer reviewed publications. There are an additional three manuscripts which have been drafted, and we hope to submit these for review and publication in the coming months.

Honors and Awards: Prof. Shaw was invited to present the results of this work at the 2021 Pacific Chem meeting. The meeting was switched to virtual format due to the COVID pandemic, but an invitation to Pacificchem is noteworthy of a high interest in this work and its results. Prof. Shaw was also awarded tenure and promotion to associate professor during this award, and recognized as the Dean's Scholar of 2019.

Protocol Activity Status:

Technology Transfer: A student supported by this award was awarded a DOE-SCGSR fellowship and visited PNNL's EMSL facility for most of the 2021-22 academic year. This student engaged in research directly stemming from the ARO award, and exchanged data and analyses with the PNNL scientists.

Our group also collaborated with Dr Erin Durke and Dr Jason Edmonds (DTRA and ECBC) on a collaborative funding proposal application (unfunded) in 2019.

PARTICIPANTS:

Participant Type: PD/PI

Participant: Scott K Shaw

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Jessica L DeYoung

Person Months Worked: 11.00

Project Contribution:

National Academy Member: N

Funding Support:

ARTICLES:

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Earth and Space Chemistry
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acsearthspacechem.8b00158
Volume: 3 **Issue:** 2 **First Page #:** 305
Date Submitted: 8/28/19 12:00AM **Date Published:** 1/1/19 6:00AM
Publication Location:

Article Title: Physical and Chemical Morphology of Passively Sampled Environmental Films

Authors: Jacob S. Grant, Zihua Zhu, Christopher R. Anderton, Scott K. Shaw

Keywords: Thin Film, Environmental Surface, Microscopy, Imaging, SIMS, Particulate Matter

Abstract: This work presents spatially resolved physical and chemical surface characterization of passively sampled environmental films developed in urban, suburban, and metropolitan locations. Environmental surface films are important mediators of atmospheric particulate matter (PM) and persistent organic pollutants (POPs) fate and transport. The films are developed via dry deposition onto silicon wafer substrates for time scales ranging from 1 to 52 weeks. Spatial and chemical morphologies of the films are analyzed by bright-field, scanning electron, and atomic force microscopies. Surface feature sizes span 6 orders of magnitude, from the millimeter to nanometer regimes, indicative of super- and sub-micrometer PM as well as conformal films of nanoscale PM and semivolatile molecules. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging data are analyzed to report the films' chemical morphology and speciation which include a range of organic and inorganic species. Increases in surfa

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Acknowledged Federal Support: Y

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Earth and Space Chemistry
Publication Identifier Type: DOI **Publication Identifier:** 10.1021/acsearthspacechem.9b00234
Volume: 3 **Issue:** 12 **First Page #:** 2726
Date Submitted: 12/18/20 12:00AM **Date Published:** 10/1/19 5:00AM
Publication Location:

Article Title: Passively Sampled Environmental Films Show Geographic Variability and Host a Variety of Microorganisms

Authors: Jacob S. Grant, Patrick M. Richards, Christopher R. Anderton, Zihua Zhu, Timothy E. Mattes, Scott K. S

Keywords: Physical and Chemical Morphology of Passively Sampled Environmental Films

Abstract: ABSTRACT: This work presents spatially resolved physical and chemical surface characterization of passively sampled environmental films developed in urban, suburban, and metropolitan locations. Environmental surface films are important mediators of atmospheric particulate matter (PM) and persistent organic pollutants (POPs) fate and transport. The films are developed via dry deposition onto silicon wafer substrates for time scales ranging from 1 to 52 weeks. Spatial and chemical morphologies of the films are analyzed by bright-field, scanning electron, and atomic force microscopies. Surface feature sizes span 6 orders of magnitude, from the millimeter to nanometer regimes, indicative of super- and sub-micrometer PM as well as conformal films of nanoscale PM and semivolatile molecules. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging data are analyzed to report the films' chemical morphology and speciation which include a range of organic and inorganic species. Increas

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Volume: 5 **Issue:** 12 **First Page #:** 3407
Date Submitted: 6/21/22 12:00AM **Date Published:** 11/1/21 5:00AM
Publication Location:

Article Title: What Are the Differences between Two Environmental Films Sampled 1 km Apart?

Authors: Jessica L. DeYoung, Evangeline A. Holyoake, Scott K. Shaw

Keywords: environmental films grime microscopy particles water pollution

Abstract: Environmental films are atmospheric materials that passively deposit and form coatings on most outdoor surfaces. Film heterogeneity in the chemical makeup and physical form often makes understanding their contributions to the environment difficult. It is well known that cities or rural areas produce unique films. To study how this trend changes with a known distance, we characterize two films, collected at the same time, separated by ~1 km: representing city (CB) and suburban (CP) areas. The chemical analysis shows that the urban (CB) film, in comparison to its suburban (CP) counterpart, has higher surface coverage (+4.8%) and higher elemental diversity in metals. The physical form and roughness show that the urban (CB) sample collects more particulate than the suburban (CP) sample. This accumulation increases the surface area suggesting that the urban (CB) sample forms faster and maintains higher adsorption capacity than the suburban sample. The urban (CB) sample has metals often associated

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Journal: ACS Earth and Space Chemistry
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Volume: 5 **Issue:** 3 **First Page #:** 645
Date Submitted: 6/21/22 12:00AM **Date Published:** 3/1/21 6:00AM
Publication Location:

Article Title: Evaluating Environmental Film Maturation through a Deliquescence–Efflorescence Model

Authors: Jessica DeYoung, Scott K. Shaw

Keywords: environmental films, deliquescence/efflorescence cycling, morphology, particle size, ripening, quartz crystal microbalance, optical microscopy, image analysis

Abstract: As atmospheric particulate and (semi)volatile molecules gradually deposit on outdoor surfaces, they create heterogeneous coatings known as environmental films. The unique chemical environments within these films will impact local environmental chemistry. We report the effects of water vapor and deliquescence/efflorescence cycling on particles incorporated into these films within three model systems created in our laboratory: pure salt, pure organic, and mixed salt-organic films, ranging from 1 to 5 μm thickness. To do this, we monitor morphology changes to inorganic and organic particles that comprise each film type before and after relative humidity (%RH) cycling. We track the model film behaviors by quartz crystal microbalance and optical microscopy, including detailed image analysis to track particle sizes, shapes, and number density. Our results show maximum particle diameter and shape distributions (~100 nm to hundreds of μm and circular to elongated), as well as the number of fil

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Date Published:

Conference Location: Chicago

Paper Title: An automated system to study deliquescent properties of model environmental films

Authors: Evangeline Holyoake, Jessica DeYoung, Scott K. Shaw

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Conference Name:

Date Received:

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Date Published: 01-Mar-2022

Conference Location: San Diego, CA

Paper Title: Chemical Differences of Passively Collected Environmental Films on Surfaces with Different Hydrophilicity

Authors: Jessica DeYoung, Zezhen Cheng, Swarup China, Gregory Vandergrift, Yadong Zhou, Zihua Zhu, Scott

Acknowledged Federal Support:

DISSERTATIONS:

Publication Type: Thesis or Dissertation

Institution: University of Iowa

Date Received: 18-Dec-2020

Completion Date: 5/15/19 8:45PM

Title: MORPHOLOGICAL STUDIES OF MODEL AND NATIVE ENVIRONMENTAL SURFACE FILMS

Authors: Grant, Jacob S.

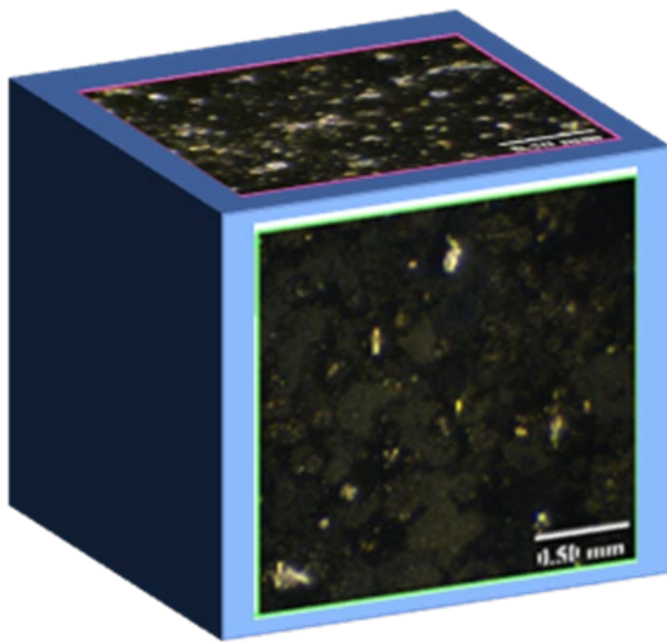
Acknowledged Federal Support: **N**

Partners

I certify that the information in the report is complete and accurate:

Signature: Scott Shaw

Signature Date: 6/24/22 12:21PM



TOC Graphic

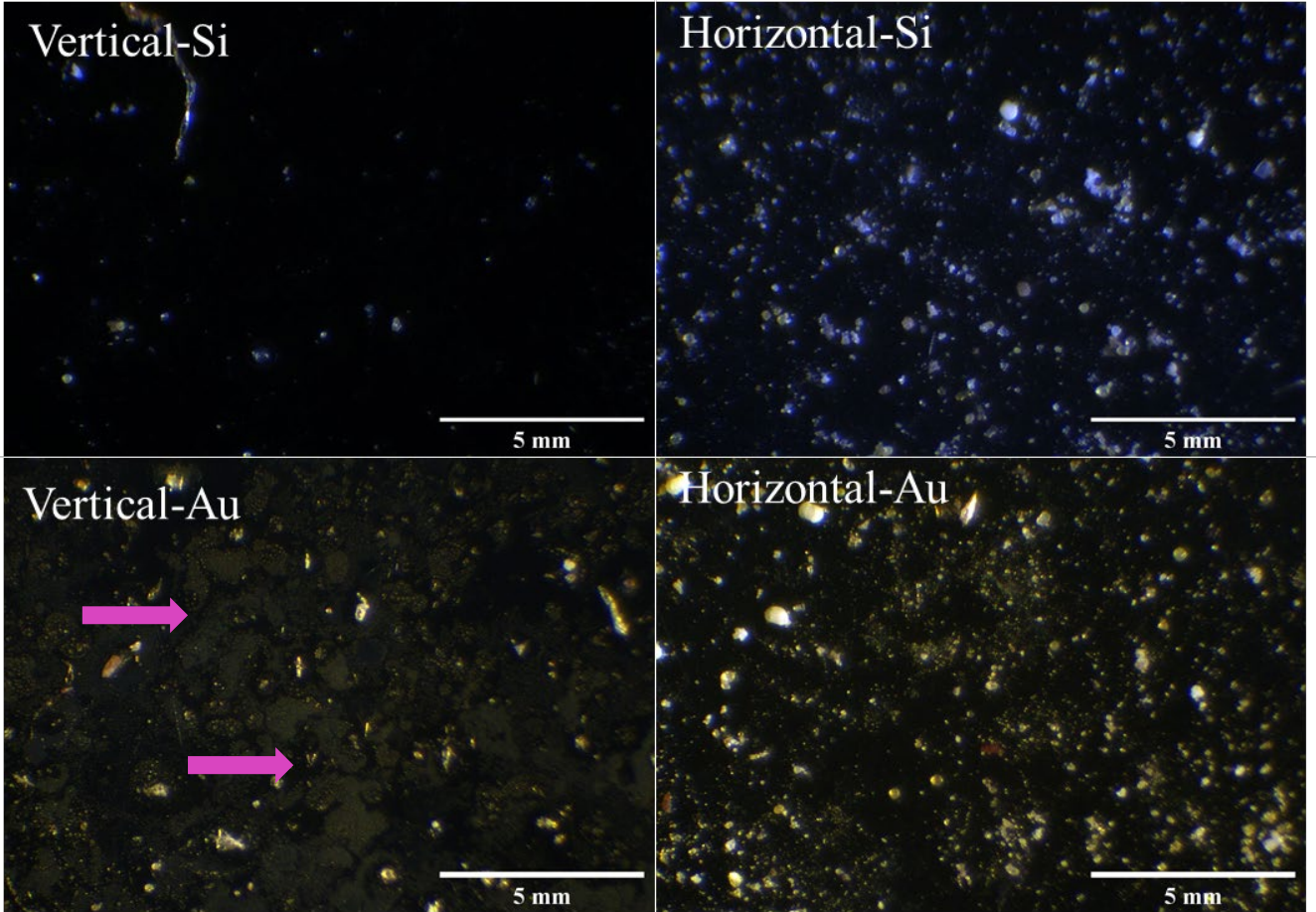


Figure 1: Bright field microscopy images showing the vertical (left column) and horizontal (right column) surface films. Two silicon wafers are shown in the top row and two gold pieces are shown in the bottom row. The scalebar is 5 mm.

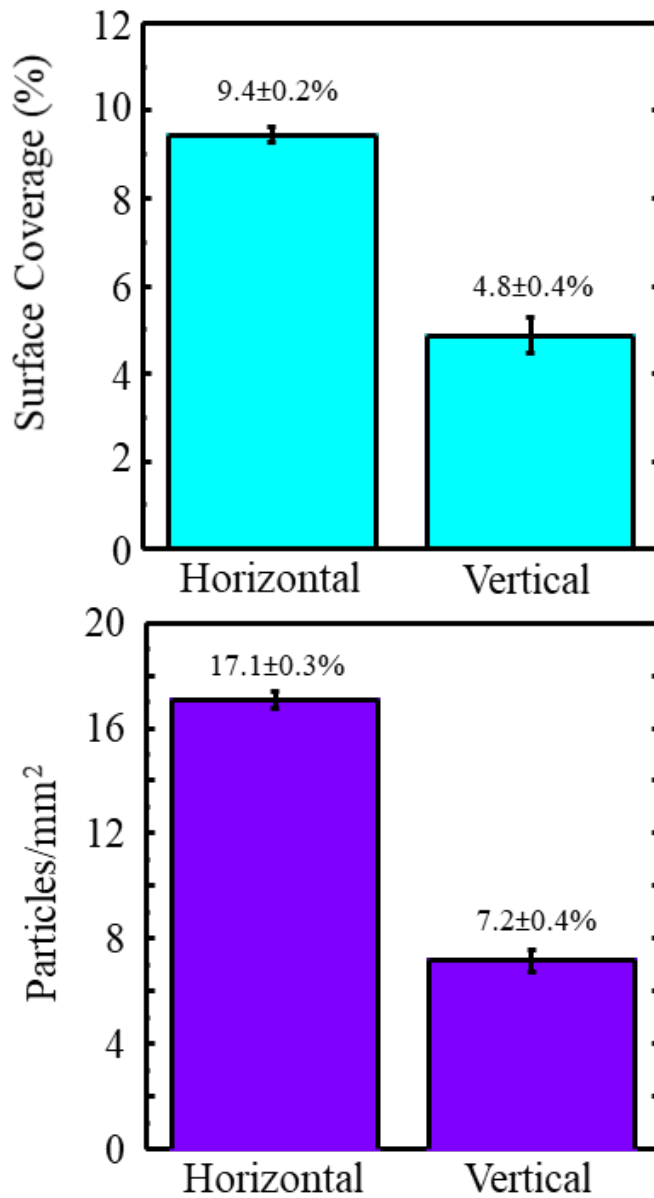


Figure 2: The surface coverage (top) and particle concentration (bottom) for the two surfaces. The error bars shown here are the standard error of the measurements.

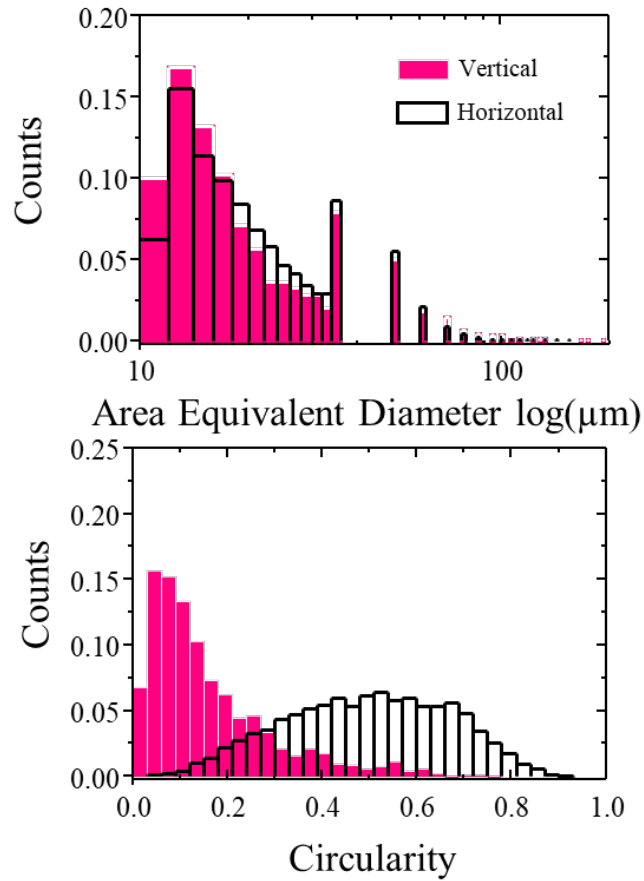


Figure 3: The size analysis and morphologic parameters for the higher magnification images (90x). The top histogram shows the vertical (pink) and horizontal (hollow black) for the two distributions.

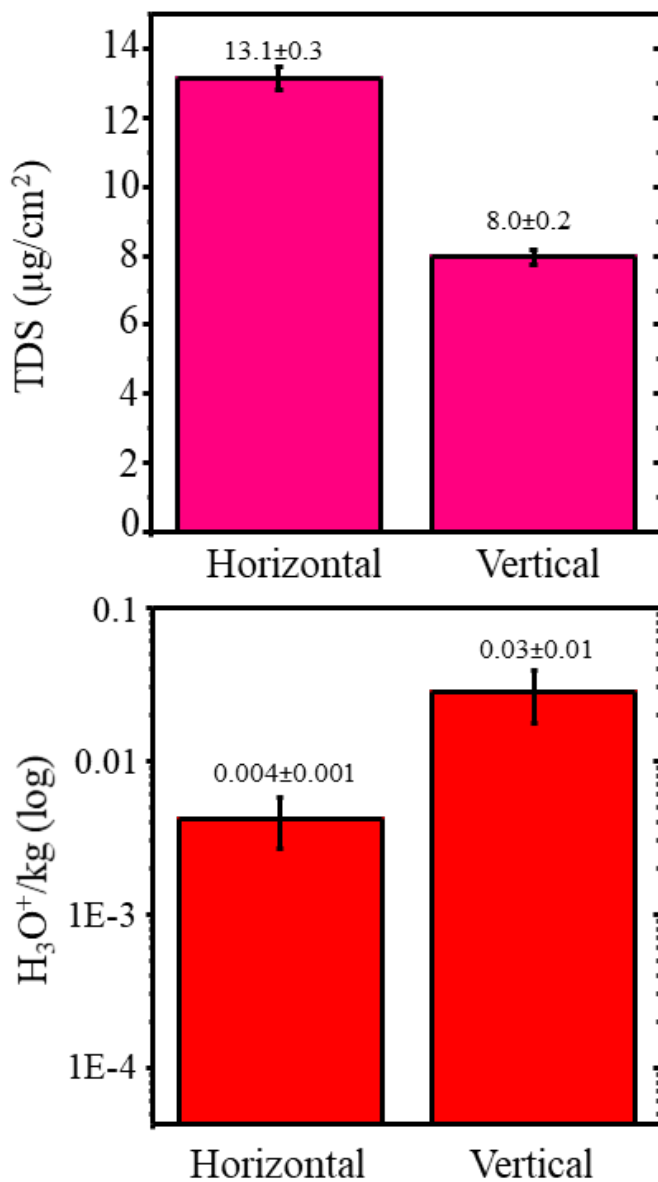


Figure 4: TDS values (top) for each film sample showing the amount of extracted material for horizontal and vertical species. Also, the hydronium ion concentrations, normalized per microgram of dissolved species, for the horizontal and vertical samples (bottom). Reported errors are the standard error of the measurements.

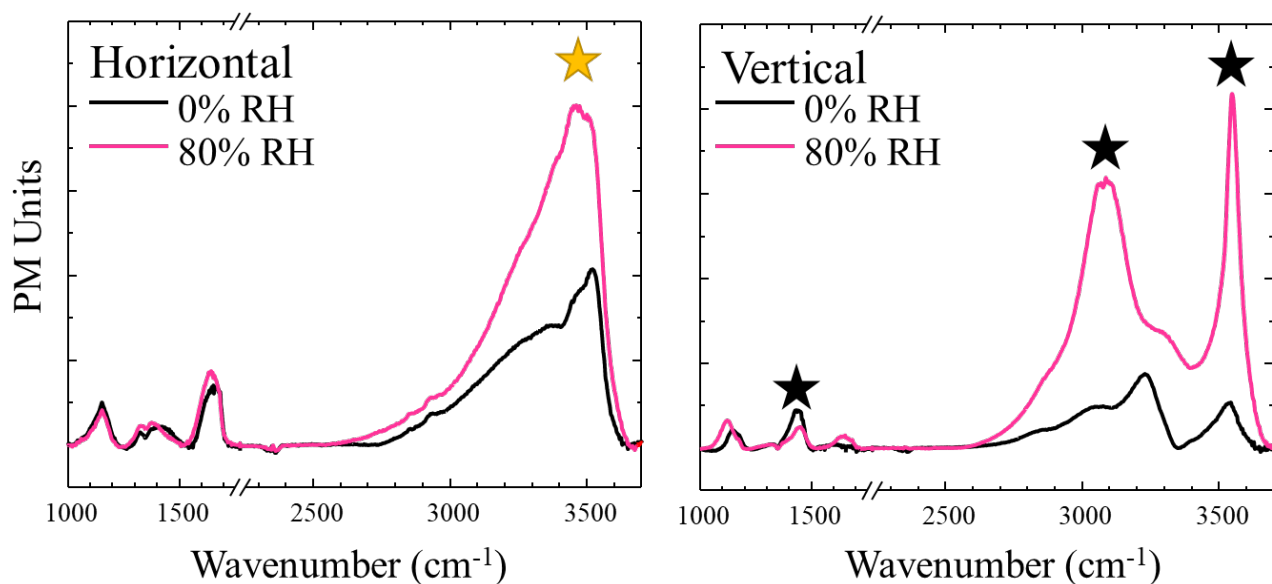


Figure 5: PMIRRAS spectra of environmental films collected on gold-coated substrates in horizontal (top) and vertical (bottom) orientations for low (red trace at 0%) and high (black trace at 80%) relative humidity environments.

Table 1: Values of contact angle for each of the surfaces listed with the standard error of the measurements.

Surface	Contact angle (°)
Vertical (n=16)	50±1
Horizontal (n=16)	30.9±0.6
Clean gold w/ water (n=8)	67±1