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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Tap water fingerprinting using a convolutional neural network built from images of the coffee-ring effect

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Table SI-1. Measured water chemistry data from tap water samples collected across Michigan and treatment information from annual municipal water quality reports and system operators. Averages and standard deviations are listed for values conducted in replicate.

City	**F^- (mM)**	**NO_3^- (mM)**	**Zn (mM)**	**TOC (ppm)**
MSU - academic hall	0.04	BD	2.3×10^{-3}	3.1
Durand	0.03	0.02	BD	1.3
Kalamazoo	0.04	0.03	BD	BD
Portland	0.03	BD	BD	2.1
Battle Creek site A	0.05	BD	3.9×10^{-3}	0.79
Battle Creek site B	0.05	0.02	BD	1.2
Charlotte	0.02	0.01	1.1×10^{-4}	1.4
Fowlerville	0.04	BD	BD	1.4
Lansing site A	0.01	0.01	1.2×10^{-4}	1.5
Lansing site B	0.03	0.01	9.1×10^{-4}	1.5
East Lansing	0.02	0.03	6.3×10^{-4}	1.3
Howell	0.03	BD	1.5×10^{-4}	BD
MSU - residence hall	0.05	BD	4.2×10^{-4}	3.2
Williamston	0.03	BD	3.5×10^{-4}	2.2
Genoa Twp soft	BD	BD	1.7×10^{-4}	2.2
Genoa Twp	BD	BD	1.1×10^{-4}	2.0
Rest stop Okemos	0.03	BD	BD	1.1
Rest stop Zeeland	0.04	BD	2.8×10^{-3}	1.0
Rest stop I96/M66	0.03	BD	4.9×10^{-4}	3.3
Rest stop Fenton	0.06	0.02	1.0×10^{-3}	1.0
Allegan	0.03	BD	5.5×10^{-4}	BD
Genoa Twp	BD	BD	1.2×10^{-4}	BD
Detroit	0.03	0.07	3.2×10^{-3}	1.6
Flint	0.04	0.03	7.5×10^{-4}	BD
Swartz Creek	0.03	0.03	1.2×10^{-4}	BD
Grand Rapids	0.03	0.03	2.3×10^{-4}	BD
Holland	0.04	0.03	8.9×10^{-4}	BD
Wyoming	0.03	0.03	BD	BD

Table SI-2. Composition of synthetic tap water solutions.

Chemicals	Detroit (mM)	Lansing (mM)	MSU hard water (mM)
$NaHCO_3$	0.23	0.50	0.55
Na_2SO_4	-	1.20	-
$MgCl_2(H_2O)_6$	0.25	0.53	0.40
$MgSO_4(H_2O)_7$	0.10	-	0.80
$MgCO_3$	-	-	0.50
$CaCl_2$	-	0.56	-
$CaSO_4$	0.16	-	-
$CaCO_3$	0.50	-	2.60
KCl	-	0.100	0.027
KH_2PO_4	0.0152	0.0100	0.0113
$NaNO_3$	0.0725	0.0140	-
$KF(H_2O)_2$	0.0325	0.0270	0.0430
$FeCl_3$	0.0016	-	0.0190
$CuCl_2(H_2O)_2$	0.0006	0.0005	0.0020

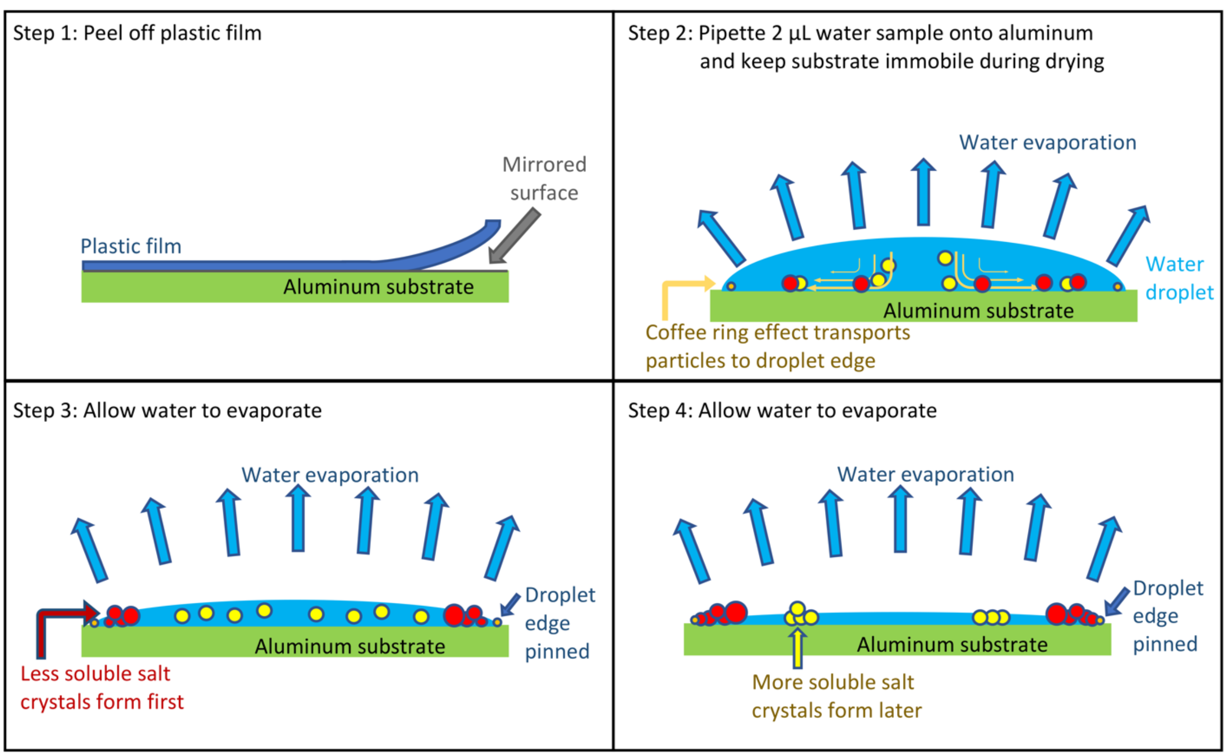


Figure SI-1. The experimental procedure includes depositing two microliter droplets of an aqueous solution onto an aluminum substrate and allowing it to dry without movement.

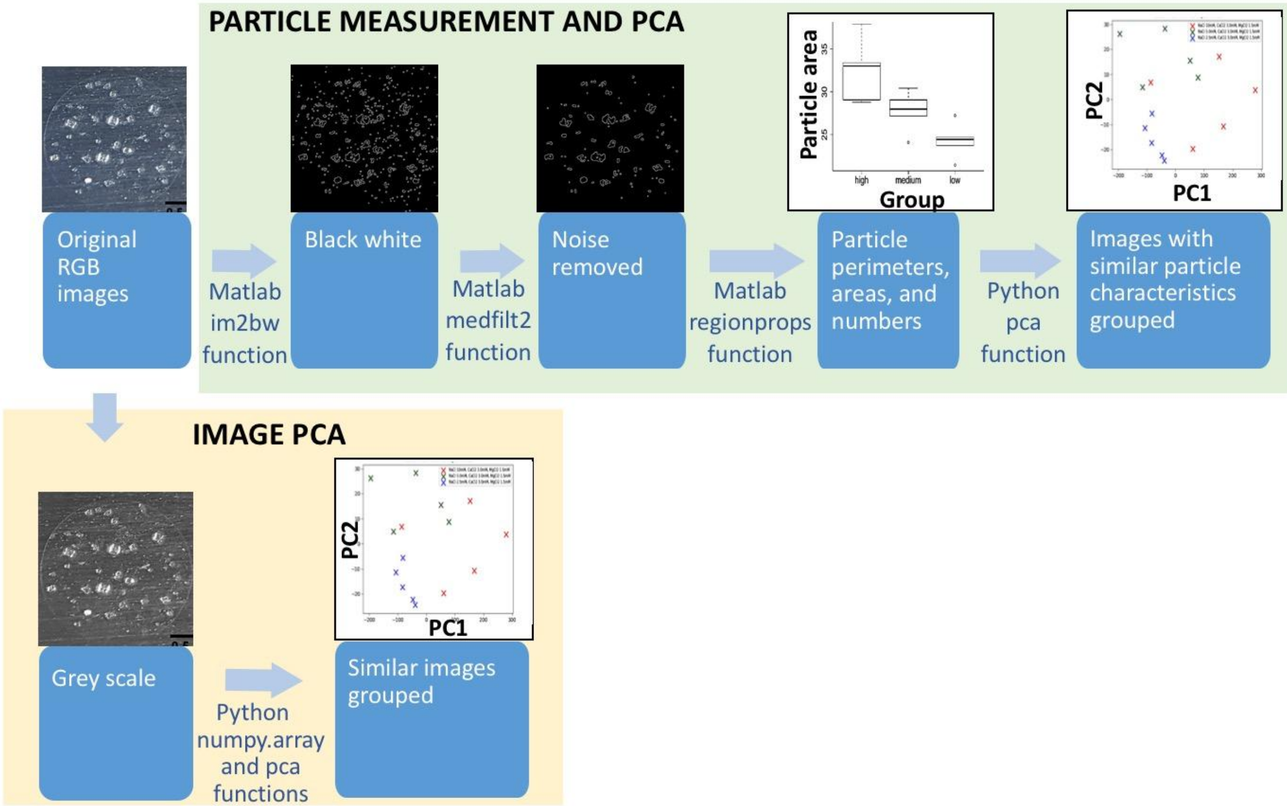
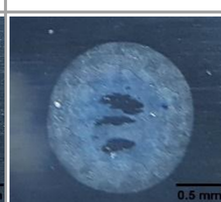
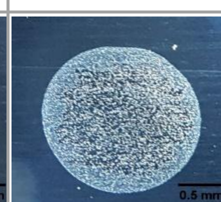
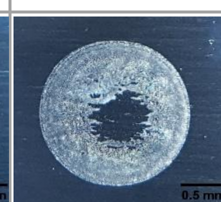
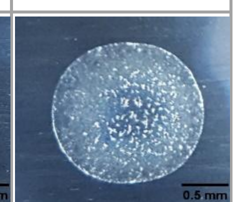
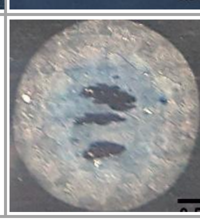


Figure SI-2. Image analysis pipeline in Matlab and Python.

Table SI-3. Examples of raw and pre-processed images used for the convolutional neural network (CNN) model.

Water sample	Detroit	Genoa Township well RO	Genoa Township private well untreated	Howell	Williamston
Raw image					
Pre-processed image					

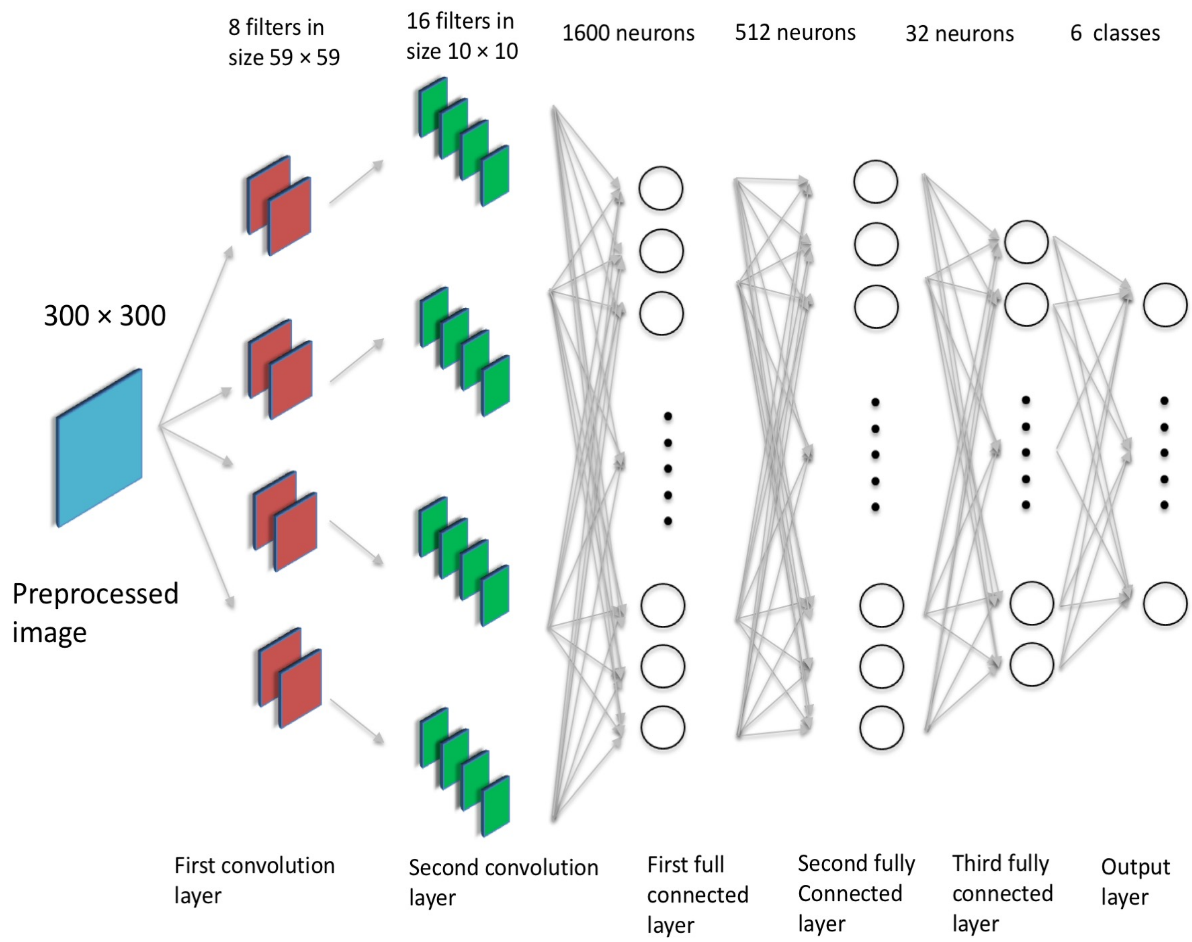
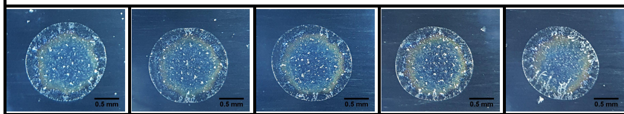
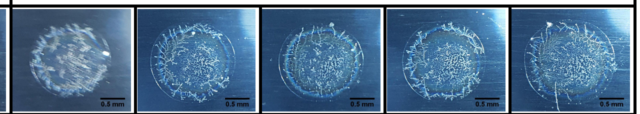
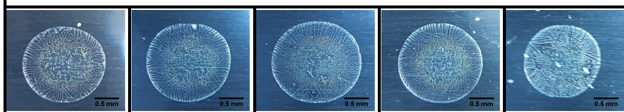
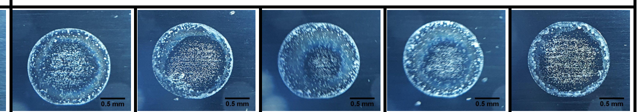
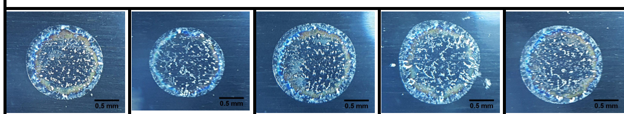
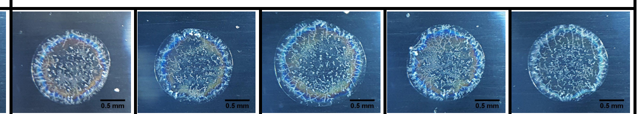
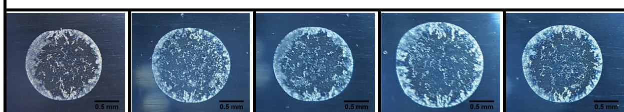
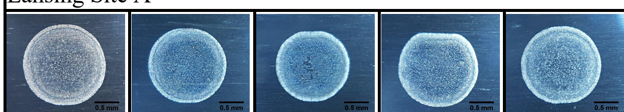
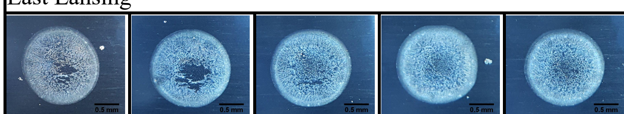
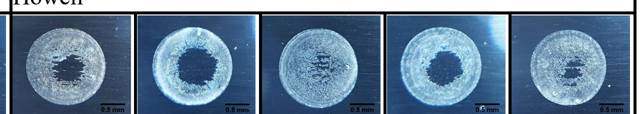
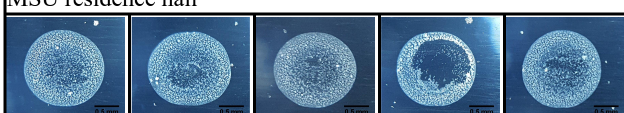
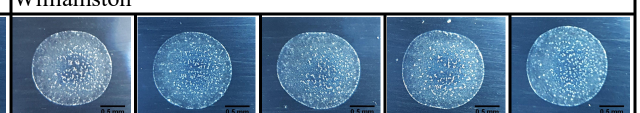
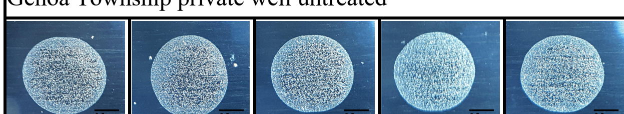
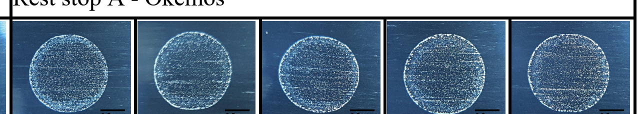
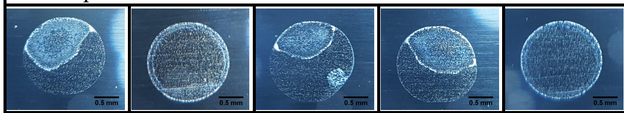


Figure SI-3. A schematic of the convolutional neural network (CNN) model.

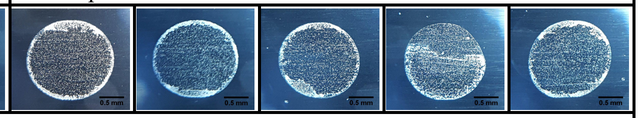
Table SI-4. Five replicates of each freshly collected water sample (stored less than one week). The lab temperature was 24-25 °C and relative humidity 52% for this experiment.

MINIMALLY TREATED GROUNDWATER	
MSU academic hall	Durand
	
Kalamazoo	Portland
	
Battle Creek Site A	Battle Creek Site B
	
Charlotte	Fowlerville
	
LIME SOFTENED	
Lansing Site A	Lansing Site B
	
East Lansing	Howell
	
ION EXCHANGE	
MSU residence hall	Williamston
	
Genoa Township private well softened	
	
UNTREATED GROUNDWATER	
Genoa Township private well untreated	Rest stop A - Okemos
	

Rest stop C - Zeeland

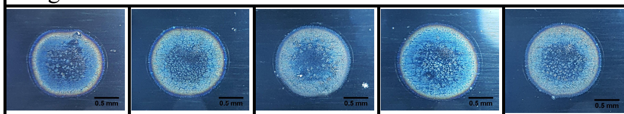


Rest stop D - M66/I96 East

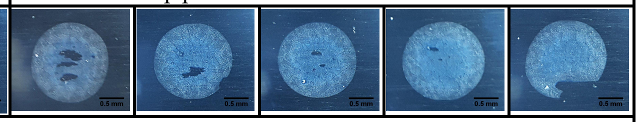


REVERSE OSMOSIS

Allegan



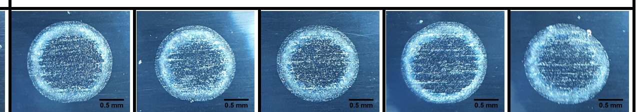
Genoa Township private well RO



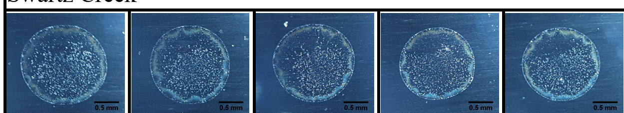
SURFACE WATER

Detroit

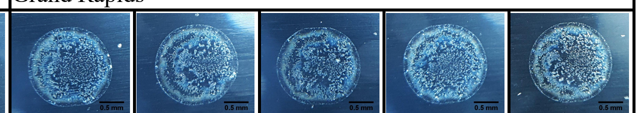
Flint



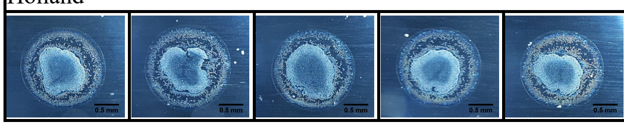
Swartz Creek



Grand Rapids



Holland



Wyoming

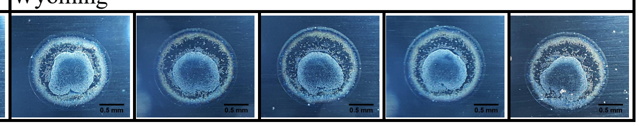
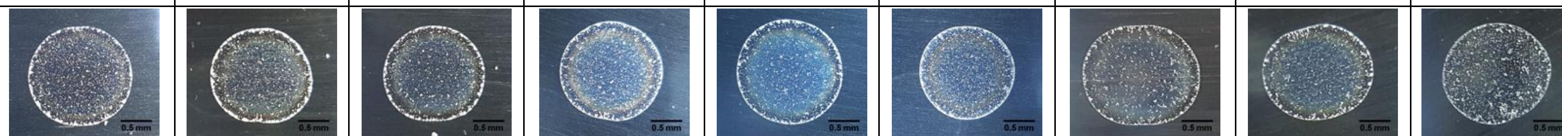
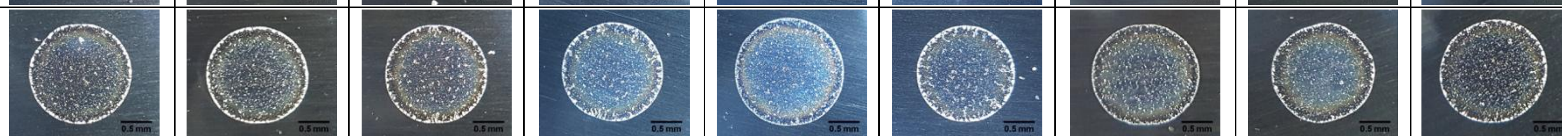
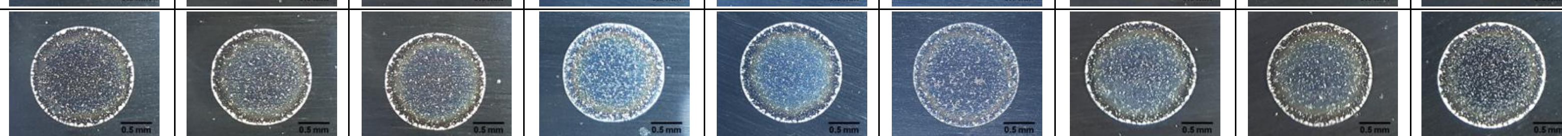


Table SI-5. Consistency of tap water residue patterns on different mirrored aluminum slides prepared by different researchers, with nanopure water and synthetic hard freshwater controls. The lab temperature was 24 °C and relative humidity 47%.

	Analyst 1 - Experienced (1 year)			**Analyst 2 - Moderate Experience (2.5 months)**			**Analyst 3 - Least Experienced (1 week)**		
	MSU academic hall Slide 7	MSU academic hall Slide 8	MSU academic hall Slide 9	MSU academic hall Slide 7	MSU academic hall Slide 8	MSU academic hall Slide 9	MSU academic hall Slide 1	MSU academic hall Slide 2	MSU academic hall Slide 3
Replicate 1									
Replicate 2									
Replicate 3									
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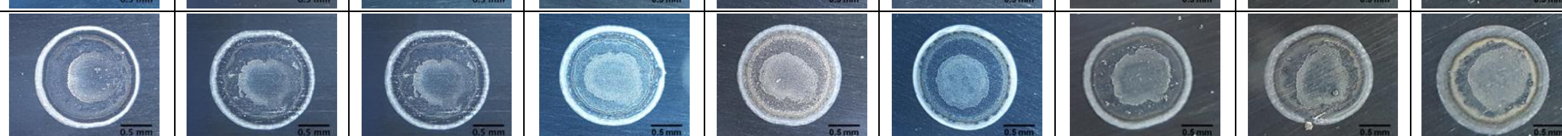
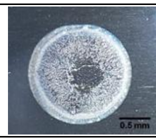
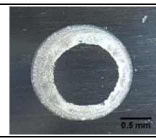
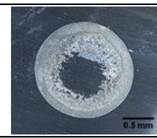
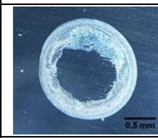
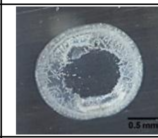
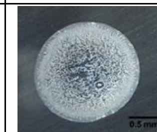
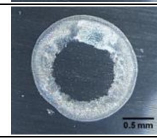
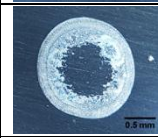
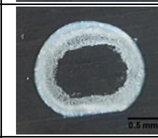
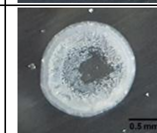
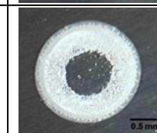
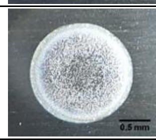
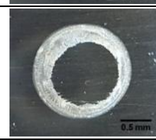
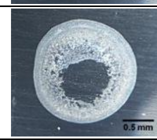
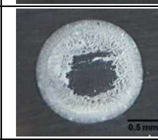
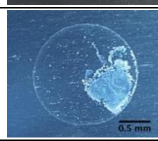
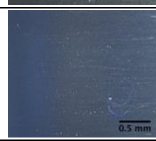
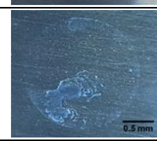
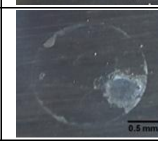
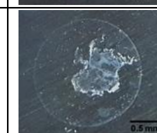
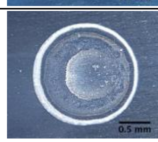
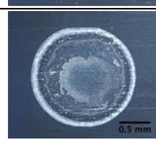
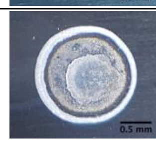
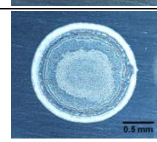
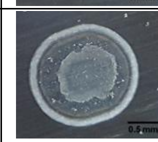
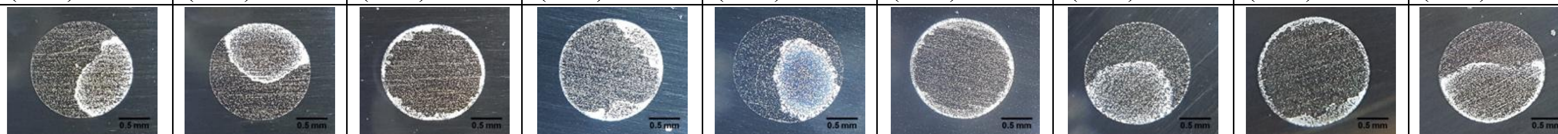
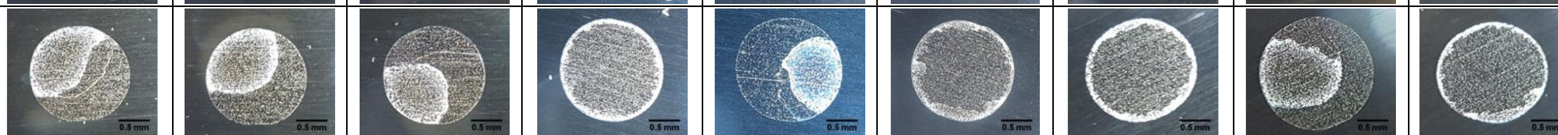
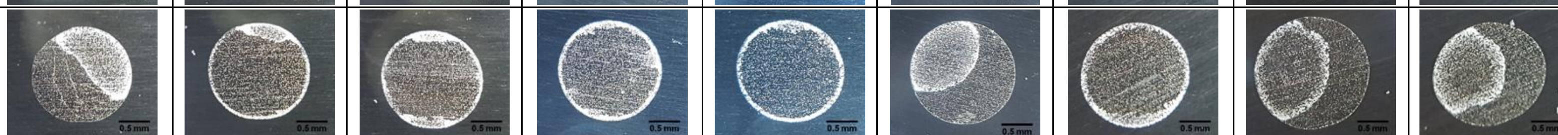
Synthetic Hard									

	Analyst 1 - Experienced (1 year)			**Analyst 2 - Moderate Experienced (2.5 months)**			**Analyst 3 - Least Experienced (1 week)**		
	East Lansing Slide 1	East Lansing Slide 2	East Lansing Slide 3	East Lansing Slide 1	East Lansing Slide 2	Slide Damaged	East Lansing Slide 1	East Lansing Slide 2	East Lansing Slide 3
Replicate 1									
Replicate 2									
Replicate 3									
Blank									
Synthetic Hard									

	Analyst 1 - Experienced (1 year)			**Analyst 2 - Moderate Experienced (2.5 months)**			**Analyst 3 - Least Experienced (1 week)**		
	Rest Stop (M66) Slide 4	Rest Stop (M66) Slide 5	Rest Stop (M66) Slide 6	Rest Stop (M66) Slide 4	Rest Stop (M66) Slide 5	Rest Stop (M66) Slide 6	Rest Stop (M66) Slide 1	Rest Stop (M66) Slide 2	Rest Stop (M66) Slide 3
Replicate 1									
Replicate 2									
Replicate 3									
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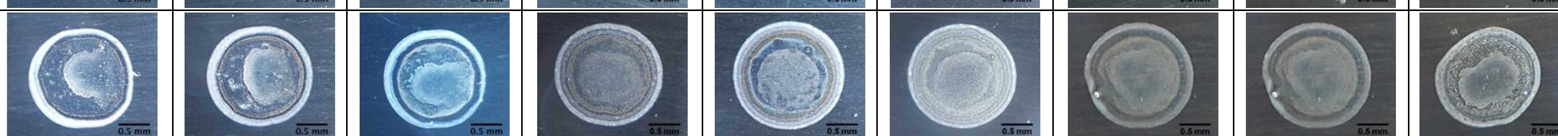
Synthetic Hard									

	Analyst 1 - Experienced (1 year)			Analyst 2 - Moderate Experienced (2.5 months)			Analyst 3 - Least Experienced (1 week)		
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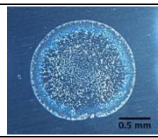
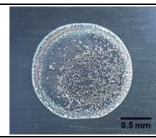
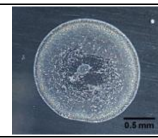
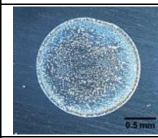
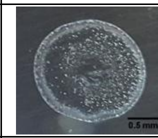
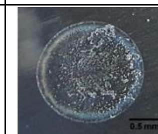
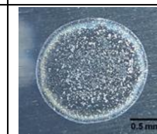
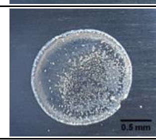
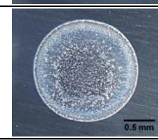
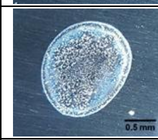
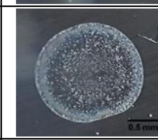
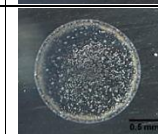
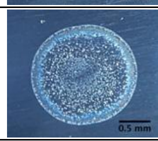
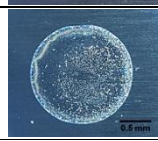
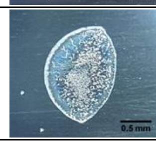
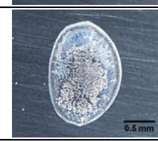
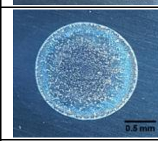
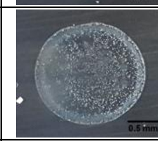
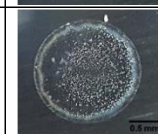
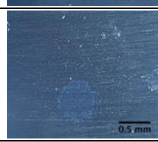
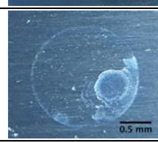
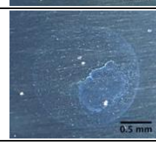
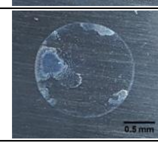
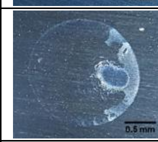
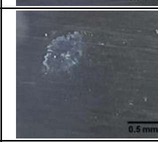
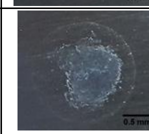
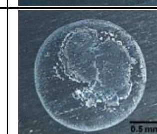
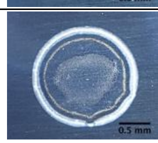
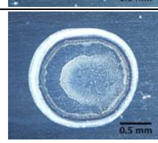
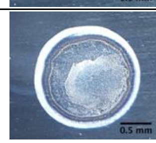
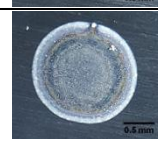
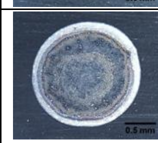
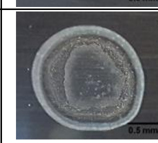
Replicate 1									
Replicate 2									
Replicate 3									
Blank									
Synthetic Hard									

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(1 year)</td><td colspan="3">Analyst 2 - Moderate Experienced
(2.5 months)</td><td colspan="3">Analyst 3 - Least Experienced
(1 week)</td></tr>
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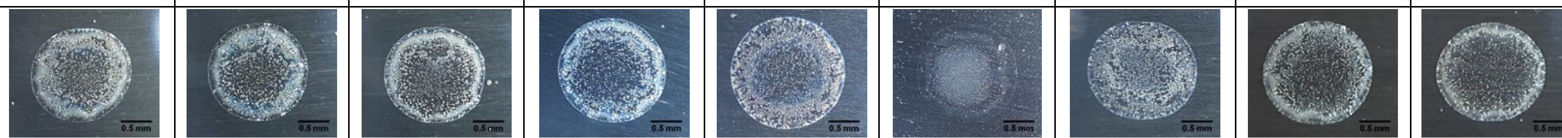
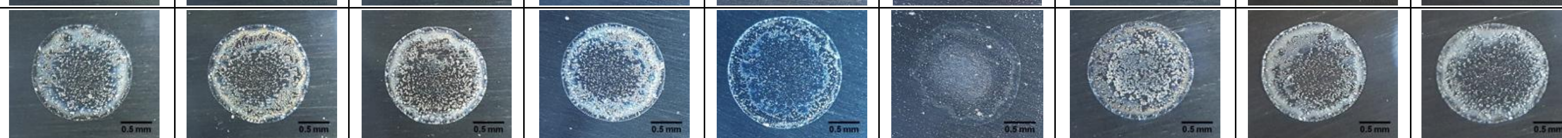
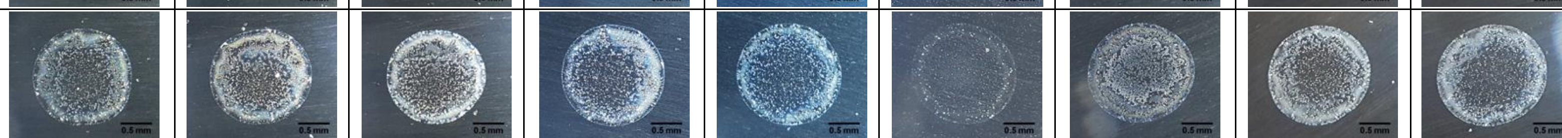
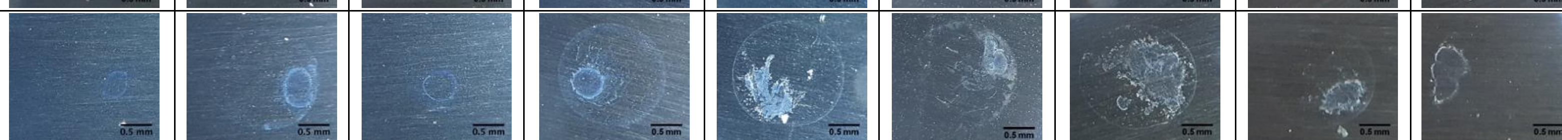
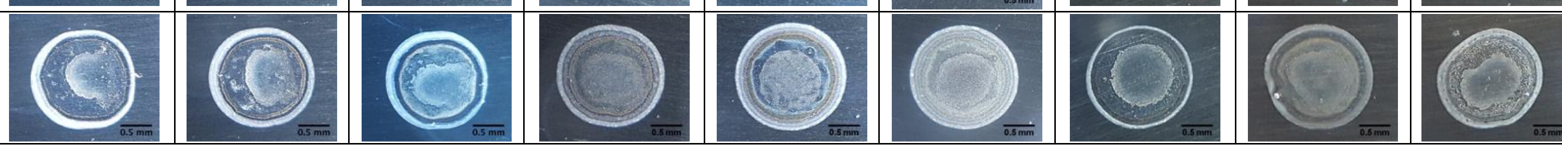
<tr><td>Replicate 1</td><td colspan="9"></td></tr>
<tr><td>Replicate 2</td><td colspan="9"></td></tr>
<tr><td>Replicate 3</td><td colspan="9"></td></tr>
<tr><td>Blank</td><td colspan="9"></td></tr>
<tr><td>Synthetic Hard</td><td colspan="9"></td></tr>
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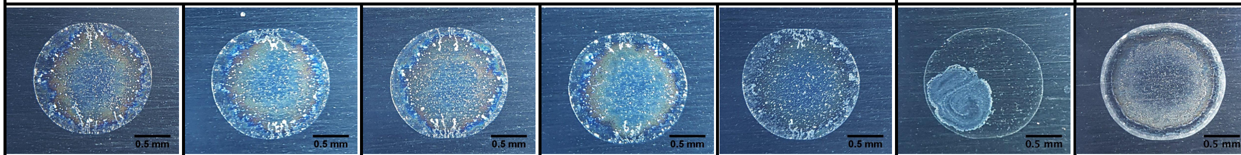
Table SI-6. Nanochromatography patterns of Michigan tap waters (stored for two months at 4 °C) dried on slides cut from the same sheet of aluminum. Nanopure water synthetic hard water served as controls. The lab temperature was 24 degrees °C and relative humidity was 47-48% for this experiment.

Minimally treated groundwater		
MSU academic building	Nanopure	Synthetic
		
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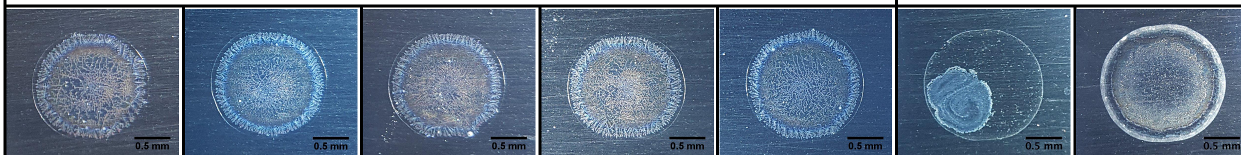
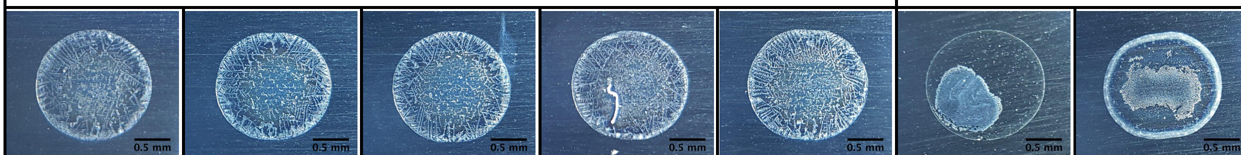
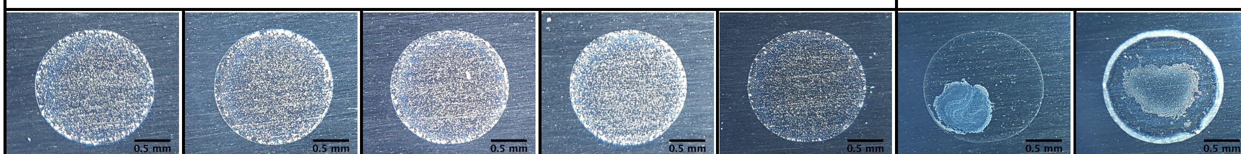
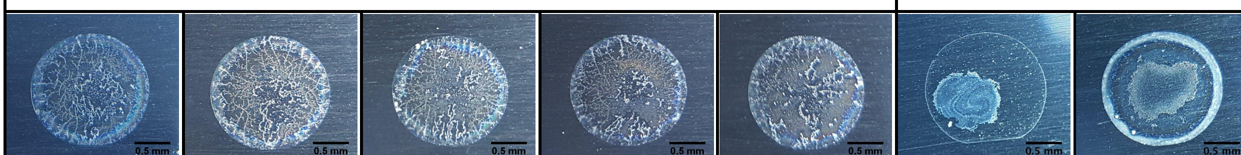
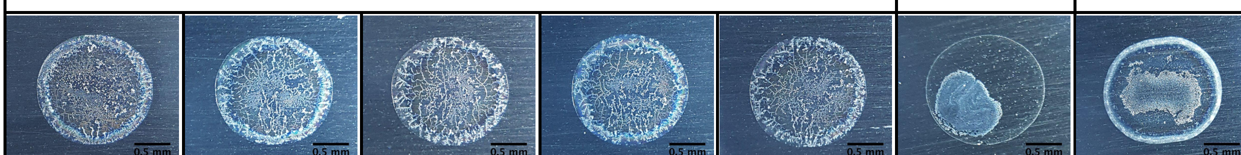
		
Kalamazoo		
		
Portland		
		
Battle Creek Site A		
		
Battle Creek Site B		
		
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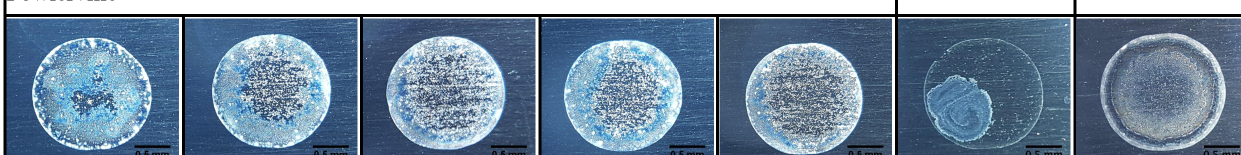
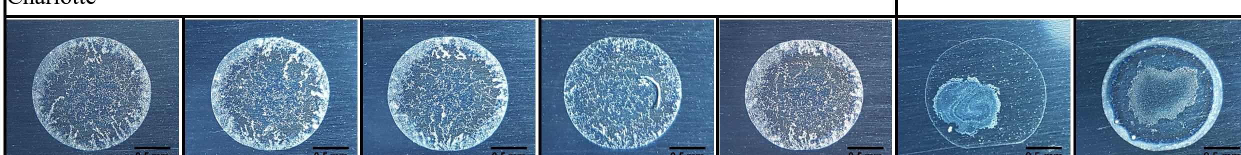
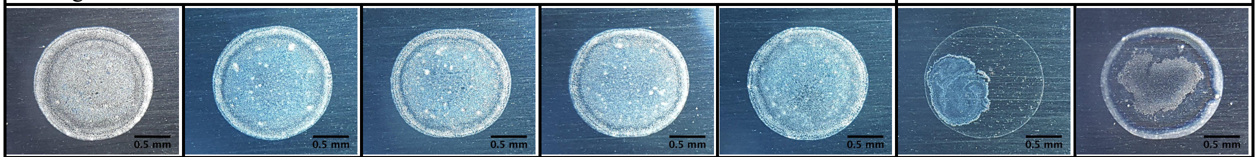
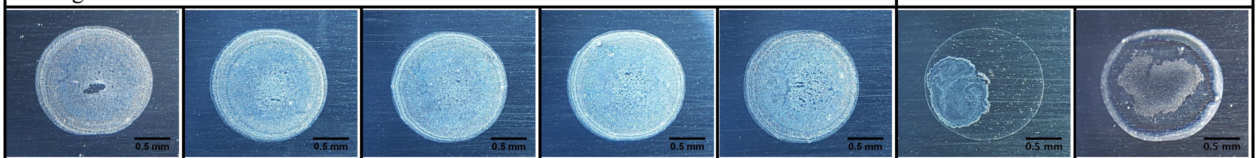
		
Charlotte		
		

Lime softened

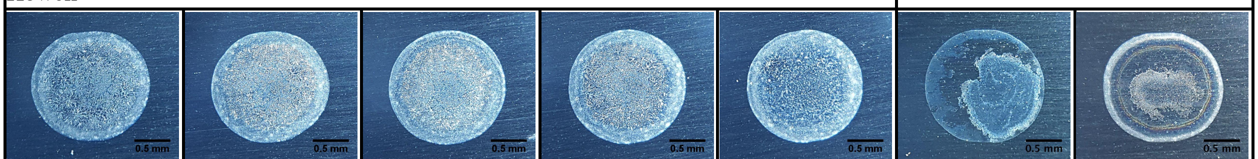
Lansing Site A



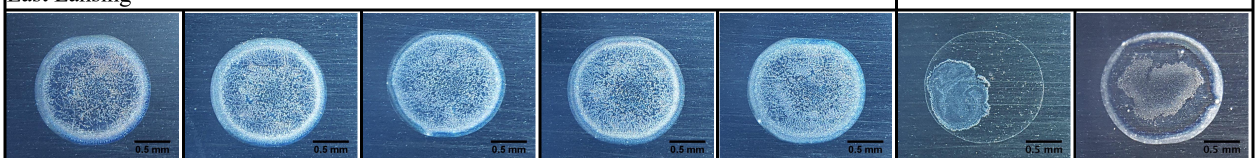
Lansing Site B



Howell

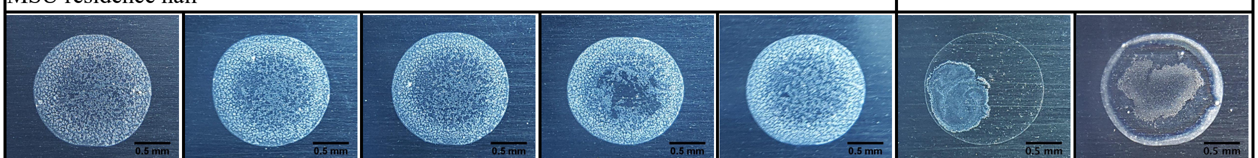


East Lansing

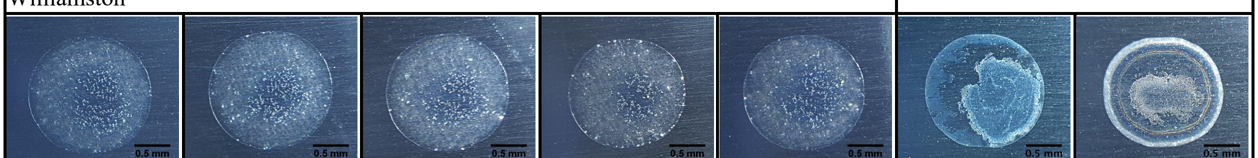


Ion exchange

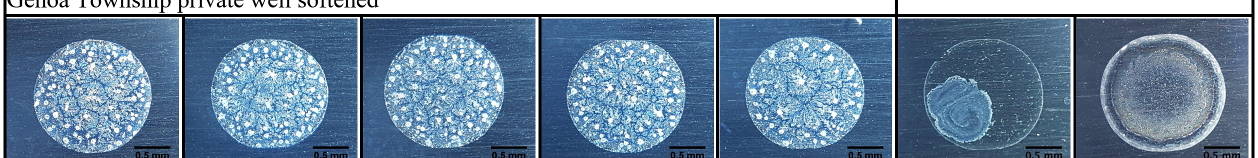
MSU residence hall



Williamston

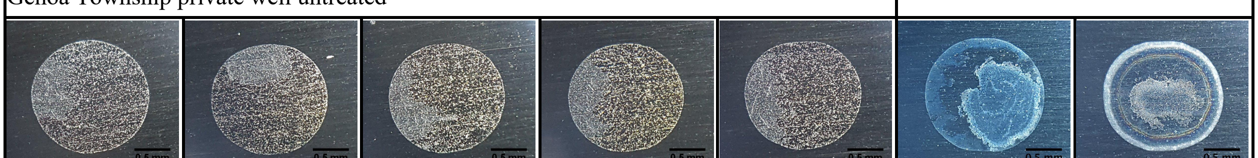


Genoa Township private well softened

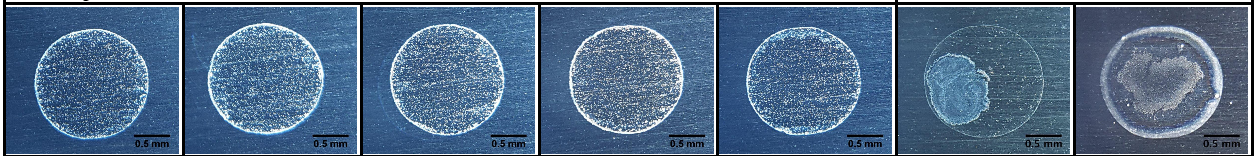


Untreated groundwater

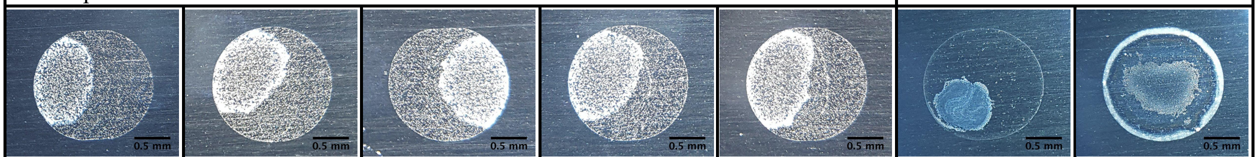
Genoa Township private well untreated



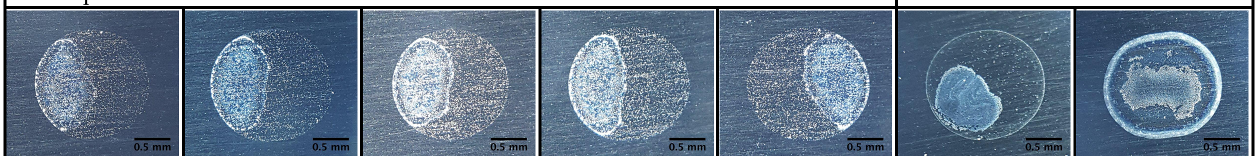
Rest stop A - Okemos



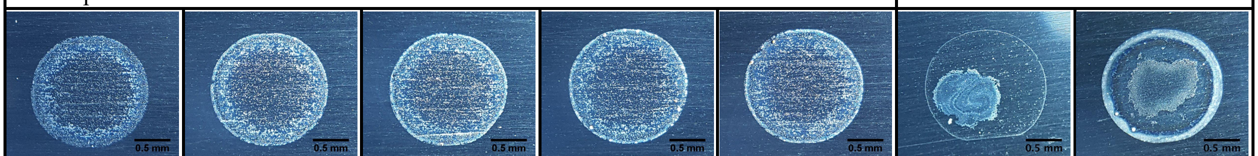
Rest stop D - M66/I96 East



Rest stop C - Zeeland

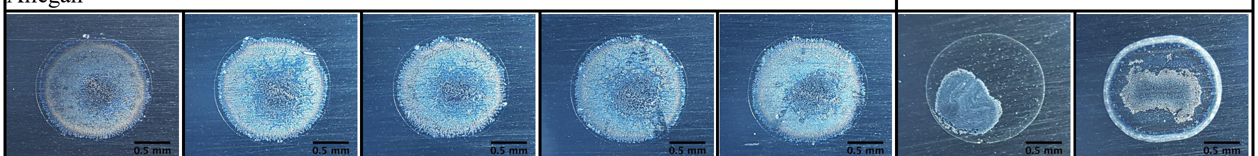


Rest stop B - Fenton

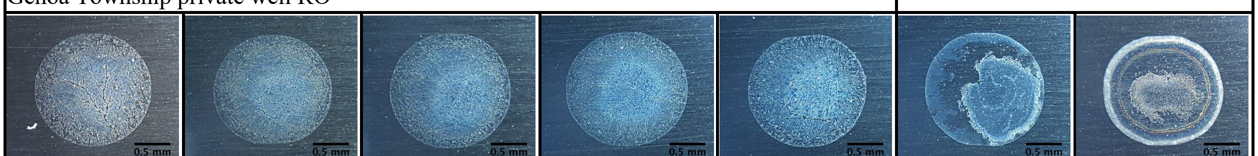


Reverse osmosis

Allegan

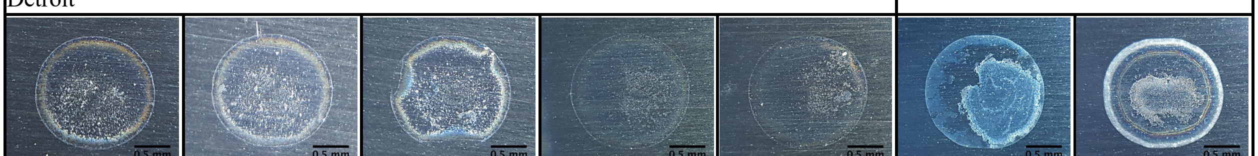


Genoa Township private well RO

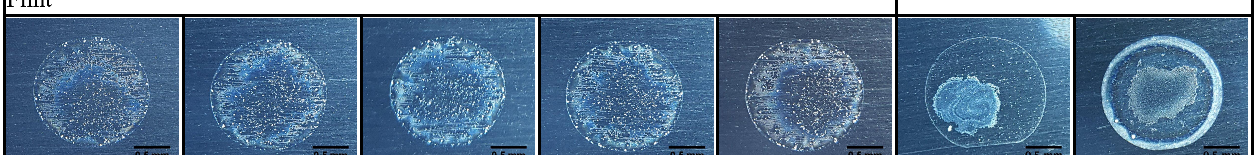


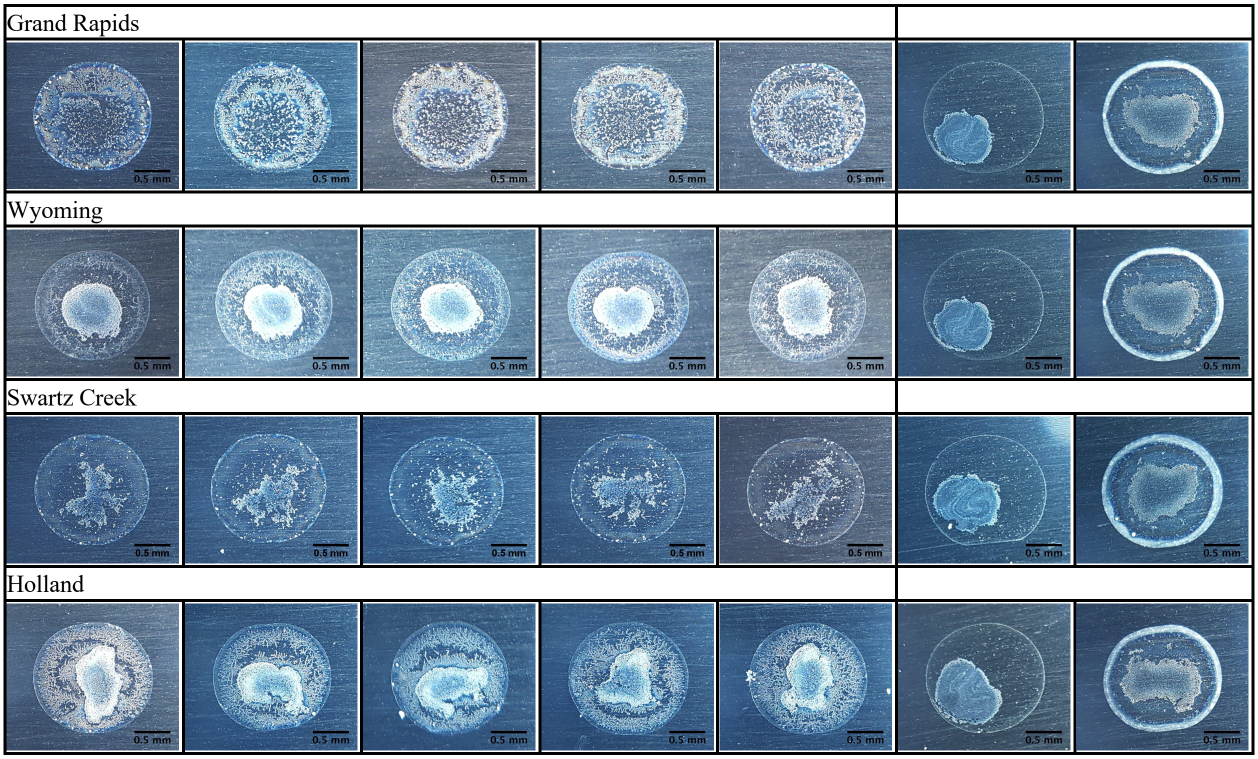
Surface waters

Detroit



Flint

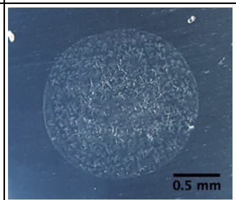
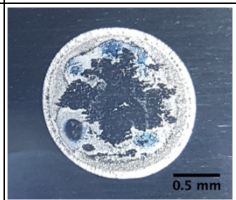
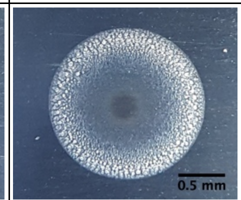
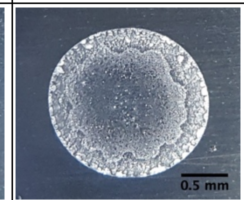
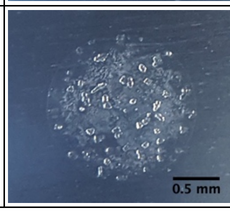
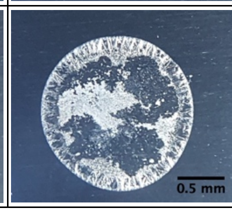
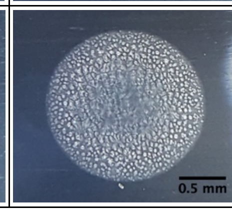
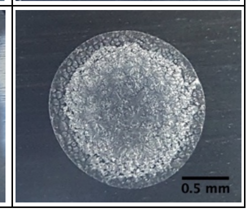




Durability of the proposed protocol

Experiments have been conducted and published elsewhere to document the effects of various parameters on the coffee-ring effect, including the substrate hydrophobicity,[1–4] humidity,[5–7] temperature,[6,8] evaporation rate,[9] volume of droplet,[10] concentration,[2,3,7,8,10,11] and chemical characteristics of the solute.[1,9] In this work, one widely available substrate was used for all measurements, the volume of droplet held constant, the experiments conducted at room temperature and 50% relative humidity, and the lab benches were relatively level (± 1°). The variations in the coffee-ring effect caused by concentration and chemical characteristics of the solute were harnessed to identify differences in the water chemistry of the sample. The effect of humidity on salt mixtures with four different water chemistries was analyzed, and some samples were more durable to the environmental condition than others (Table SI-6). The frequency of battery changes in the loupe also influences the brightness of the image collected; normalization of image brightness was applied during image processing to alleviate this issue.

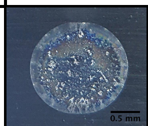
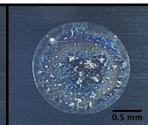
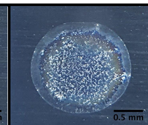
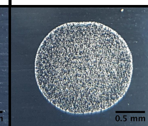
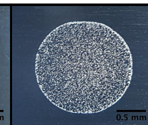
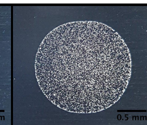
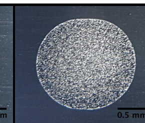
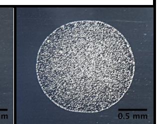
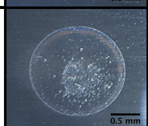
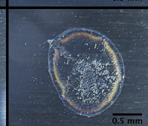
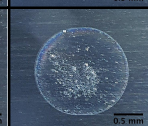
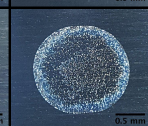
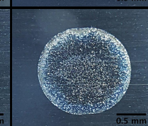
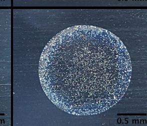
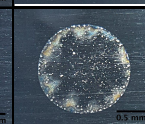
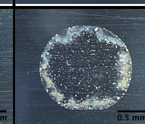
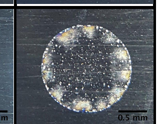
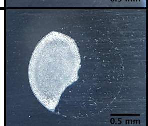
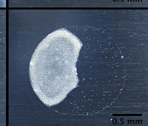
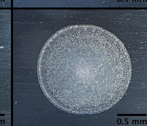
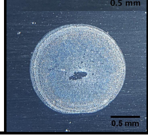
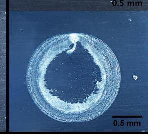
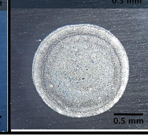
Table SI-7. Temperature and humidity effect on residue pattern for four salt mixtures.

Temperature and relative humidity	Drying time (min)	3 mM $CaCl_2$ 1.5 mM $MgCl_2$ 10 mM NaCl	0.5 mM $CaSO_4$ 0.25 mM $MgSO_4$ 5 mM Na_2SO_4	0.5 mM $CaSO_4$ 0.25 mM $MgSO_4$ 10 mM $NaHCO_3$	0.5 mM $CaCl_2$ 0.25 mM $MgCl_2$ 10 mM $NaHCO_3$
24 °C < 20% RH	20				
23 °C 46-48% RH	25				

Applications of this protocol more broadly would require either control of environmental conditions (e.g., temperature, humidity, and leveled surfaces), generation of an extensive library with residue patterns collected at a variety of temperature and humidity values such that user data could be matched to the appropriate library, or creation of a CNN model that has been trained with a dataset that encompasses variability expected by a broader user base. Additional experiments must be conducted to characterize the extent of control required to produce comparable data, evaluate the cost required for control of experimental conditions, and to harness the environmental conditions to further differentiate between similar tap water chemistries.

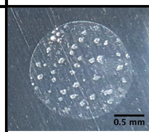
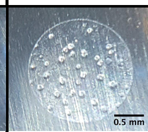
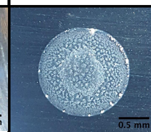
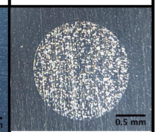
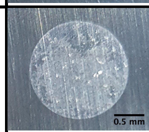
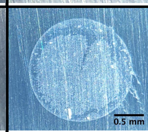
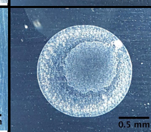
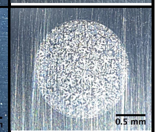
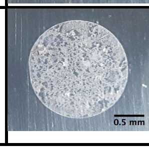
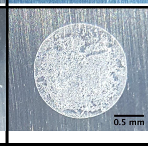
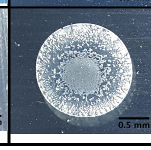
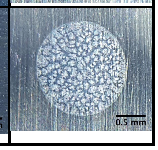
In order to further verify that differences exist between tap water residue patterns due to differences in water chemistry and not variation in substrates, all the collected tap waters were tested again on a single set of substrates cut from the same sheet, with more nanopure water and synthetic hard water controls. Samples with different water chemistry still displayed different patterns from each other when tested on the same aluminum sheet, proving that the unique patterns were not obtained simply due to variability in the low-cost substrates. The tap waters had aged for approximately two months at 4 °C, so differences are expected in the patterns due to storage; as samples age, chlorine is consumed, phosphates absorb to plastic bottles, etc. Most of the samples were similar but not identical between the fresh and stored samples, and several samples changed including lime softened water and Swartz Creek (**Figure 3** and **Table SI-7**). Future samples should be tested fresh to reduce variability.

Table SI-8. Residue patterns of synthetic tap water solutions compared to real tap water at 24 °C and relative humidity of 47%.

	Collected tap water			Simplified synthetic (Calcium, magnesium, sodium, chloride, sulfate, bicarbonate)			Complex synthetic (simplified synthetic plus iron, copper, nitrate, fluoride, phosphate)		
MSU									
Detroit									
Lansing*									
									

*The residue pattern for Lansing water was sensitive to the substrate; the second row of patterns for the collected sample shows the range of additional patterns observed for Lansing water.

Table SI-9. Simple synthetic mixtures on a separate slides analyzed at 24 °C and 48% relative humidity. The low concentration mixtures that are not the same as the previous table are indicated by bold font.

	NaCl 10 mM	NaCl 5.0 mM	$NaHCO_3$ 10 mM	$NaHCO_3$ 5.0 mM
3 mM $CaCl_2$, 1.5 mM $MgCl_2$				
1 mM $CaCl_2$, 0.5 mM $MgCl_2$				
0.1 mM $CaCl_2$, 0.05 mM $MgCl_2$				

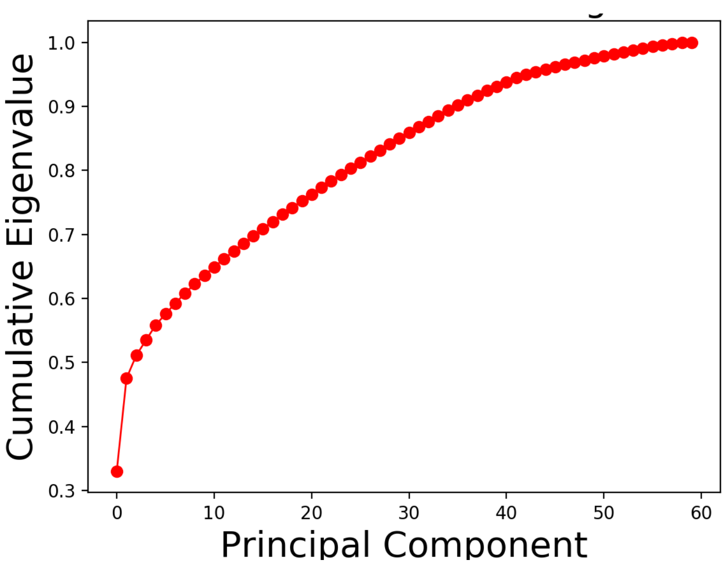


Figure SI-4. PCA on the nanochromatography image files for simplified synthetic waters (five replicates of twelve mixtures of salts).

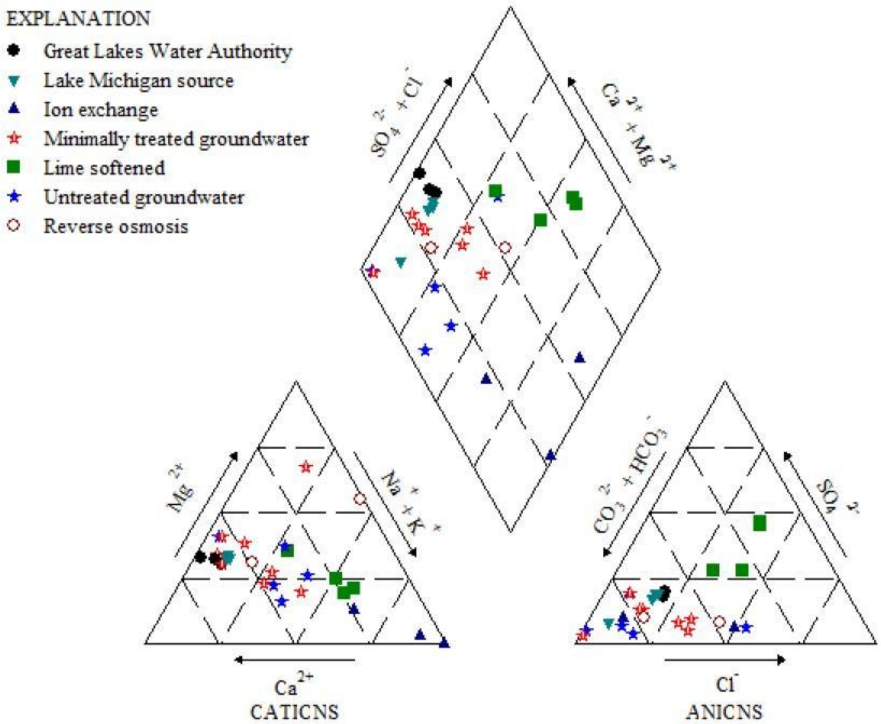
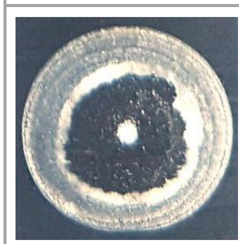
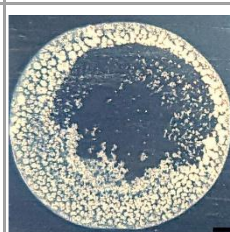
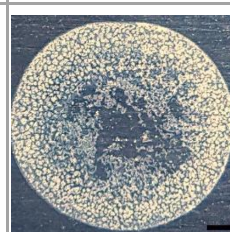
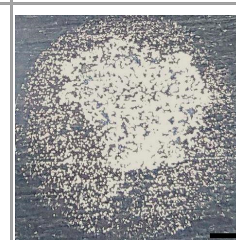
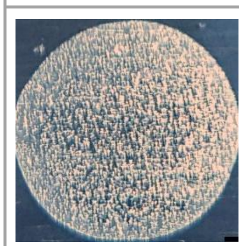


Figure SI-5. Trilinear classification of tap water samples organized by treatment technology.

Table SI-10. Images with mis-classification percentage above 70%.

Image is different from other replicates				
Lansing site B	MSU residence hall	MSU residence hall	Portland	Portland
				
Reason not clear			**Images in class two**	
Genoa Township private well untreated	Genoa Township private well untreated	Battle Creek site B	Genoa Township private well softened	Genoa Township private well softened
				

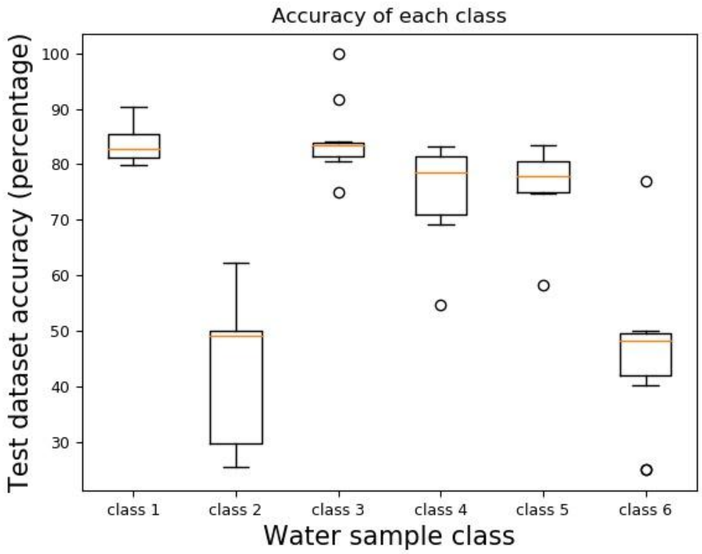


Figure SI-6: Test dataset accuracies by class

References

1 N. Shahidzadeh, M. F. Schut, J. Desarnaud, M. Prat and D. Bonn, Salt stains from evaporating droplets, *Sci. Rep.*

2 X. Zhong, J. Ren and F. Duan, Wettability Effect on Evaporation Dynamics and Crystalline Patterns of Sessile Saline Droplets, *J. Phys. Chem. B*, 2017, **121**, 7924–7933.

3 D. Zhang, Y. Xie, M. F. Mrozek, C. Ortiz, V. J. Davisson and D. Ben-Amotz, Raman Detection of Proteomic Analytes, *Anal. Chem.*, 2003, **75**, 5703–5709.

4 C. Ortiz, D. Zhang, Y. Xie, V. J. Davisson and D. Ben-Amotz, Identification of insulin variants using Raman spectroscopy, *Anal. Biochem.*, 2004, **332**, 245–252.

5 V. Chhasatia, A. Joshi and Y. Sun, Effect of relative humidity on contact angle and particle deposition morphology of an evaporating colloidal drop, *Appl. Phys. Lett.*, 2011, **97**, 231909–231909.

6 Y. Li, Q. Yang, M. Li and Y. Song, Rate-dependent interface capture beyond the coffee-ring effect, *Sci. Rep.*, 2016, **6**, 24628.

7 D. Kaya, V. A. Belyi and M. Muthukumar, Pattern formation in drying droplets of polyelectrolyte and salt, *J. Chem. Phys.*, 2010, **133**, 114905.

8 P. Takhistov and H.-C. Chang, Complex Stain Morphologies, *Ind. Eng. Chem. Res.*, 2002, **41**, 6256–6269.

9 B. Shin, M.-W. Moon and H.-Y. Kim, Rings, Igloos, and Pebbles of Salt Formed by Drying Saline Drops, *Langmuir*, 2014, **30**, 12837–12842.

10 C. Ortiz, D. Zhang, Y. Xie, A. E. Ribbe and D. Ben-Amotz, Validation of the drop coating deposition Raman method for protein analysis, *Anal. Biochem.*, 2006, **353**, 157–166.

11 T.-S. Wong, T.-H. Chen, X. Shen and C.-M. Ho, Nanochromatography driven by the coffee ring effect, *Anal. Chem.*, 2011, **83**, 1871–1873.