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Research Article

Evaluation of Methods to Monitor Per- and Polyfluoroalkyl Substances (PFAS) Contamination in the Environment

—Alexa Kaminski

Beyond my general passion for the environment, I struggled to find a particular area that I wanted to focus on as an environmental engineering major at the University of New Hampshire and in my future career. I have always wanted to do impactful work, but I was pulled by so many environmental issues that I struggled to decide which one I cared most about. So, when the opportunity arose in the summer of 2017 to intern at a company in their analytical chemistry lab, I took it—despite it being outside the realm of environmental engineering. I did not expect to end up loving the chemistry, the instrumentation, and the time working in the lab as much as I did. So, when another opportunity came up to study per- and polyfluoroalkyl substances (PFAS) in a research lab on campus, I knew it would be something I would enjoy.

I first heard about PFAS in a solid- and hazardous-waste class, where I learned that these substances are an emerging global health and environmental problem. Some people may be familiar with the term *PFCs* (perfluorocarbons or perfluorinated chemicals), which is a broader class of chemicals. Although *PFCs* and PFAS are related and sometimes overlapping groups of chemicals, the Environmental Protection Agency and other organizations are now trying to use the term *PFAS* for the particular group of compounds that I studied, rather than the broader *PFC*.



The author, Alexa Kaminski.
(Photo by Olivia Fortna.)

PFAS is the name for a category of thousands of different man-made chemicals that have numerous desirable properties, including oil and water repulsion, temperature resistance, and friction reduction. For these reasons, PFAS were widely used beginning in the 1940s in both industrial applications and commercial products. For example, they were commonly used in nonstick cookware, waterproof clothing and fabrics, stain-resistant furniture and carpeting, food packaging, cleaning products, and ski wax (USEPA, 2017).

The chemical makeup and structure that give PFAS their desirable properties are the same characteristics that cause them to be an environmental and health concern. Once humans are

exposed to these chemicals, the health effects can be wide ranging and severe, even at low exposure levels. Laboratory and epidemiological studies have suggested that exposure to some PFAS are associated with immune system effects, cancers, and thyroid hormone disruption (USEPA, 2016). Concerns surrounding the chemicals began when studies detected PFAS in the blood of occupationally exposed workers in the 1970s, then in the blood of the general population in the 1990s (Buck et al., 2011). Today, trace levels of PFAS are detectable in the blood of most people (Agency for Toxic Substances and Disease Registry, 2017).

Certain PFAS are present throughout the environment in surface and groundwater, sediment, air, and wildlife (Kannan et al., 2004). Because of their chemical properties, they are highly mobile and very difficult to accurately sample and measure. They also bioaccumulate, or build up within the bodies of organisms high in the food chain who consume organisms that have been exposed to the chemicals. Even though the use of PFAS is being phased out because of their toxicity, we need to improve our capacity to manage existing contamination in the environment. An essential first step toward managing and treating the problem is establishing the ability to accurately and reliably measure the current conditions so that appropriate treatment processes can be designed. My Summer Undergraduate Research Fellowship (SURF), funded by the Hamel Center for Undergraduate Research, focused on developing our capabilities in this important monitoring phase of the solution.

PFAS in the Environment

The abundance and persistence of PFAS in the environment is a problem for two main reasons. First, contamination of the groundwater affects drinking water sources, creating a direct exposure route to humans. Many towns get their drinking water from groundwater aquifers, which are underground reservoirs of water. PFAS contamination has caused problems around the country and locally, including at Pease International Tradeport in Portsmouth, New Hampshire, where drinking water wells have been shut down. Pease is a well-known contamination site, as are many other former military bases, because of the PFAS-containing fire-fighting foams that the military commonly used in fire drills. This caused contamination in the local groundwater, which spread to neighboring areas, including the city of Portsmouth, where it caused the shutdown of additional drinking water wells.

Secondly, the presence of PFAS in groundwater and sediment threatens the biological organisms that live in water and soils, like worms, invertebrates, and other small prey, which make up the bottom of the aquatic food web. These organisms are exposed to the chemicals that are both sorbed (attached) to soil particles and dissolved in the water. Since PFAS do not degrade quickly in nature and are not degraded by the organisms themselves, they bioaccumulate up the food chain and eventually reach detectable levels in larger predators that may not have any contact with the contaminated water and sediments. This is another possible exposure route for humans, who are apex predators in the food chain.

The purpose of my summer research was to evaluate passive sampling techniques for quantitatively monitoring PFAS in sediment porewater. Porewater is the free water that exists in the pore spaces between soil particles or rock. It flows at a slow rate and can move into both surface water bodies, like lakes and streams, or into groundwater aquifers. Many processes occur in sediment porewater, including microbial activity and mineral precipitation and dissolution. PFAS are known to be present

in this matrix. Because PFAS are resistant to most types of degradation in the environment and very mobile, contamination is unlikely to disappear on its own.

Passive Sampling Versus Active Sampling

I chose to study in-situ passive samplers for PFAS sampling because this method provides several benefits over active sampling. In-situ passive samplers are placed on-site and are intended to be left in place for a period of time to collect time-averaged samples, often of air or water, at their original locations. This method causes little disturbance to the site. In contrast, active sampling involves taking a sample at one distinct point in time, and usually creates more disturbance at a site. An example of active sampling would be taking a grab sample of surface water, collecting a soil core, or pumping out a groundwater sample.

Passive samplers do not use pumps or electricity to gather samples, but rely on natural molecular diffusion and sorption processes to measure contamination in the environment. They can achieve sampling of only the contamination within the porewater, as opposed to active samplers that often collect both dissolved-phase and sediment-bound contamination because of the disruption of the site that can dislodge and collect particles. This is important because the fraction collected by passive samplers (porewater only) is a better representation of the fraction of contamination that is biologically available to enter and accumulate in the food chain.

Another benefit of passive sampling is that it involves fewer potential sources of contamination that may affect the sample between collection and testing. A sample collected through active sampling must be transferred between the sampling equipment (such as pumps, bailers, or augers) to a sample container, which is then taken back to the lab. The sampling equipment is usually cleaned and reused for multiple samples. This is different from passive samplers, which are usually used just once for each individual sample and act as both the sampler itself and the sample storage container. The compounds of interest are extracted directly from the sampler back in the lab. This eliminates potential sources of contamination, which are of particular concern with PFAS because these compounds are used so widely in different materials and products. A sample may be compromised by anything from a rain jacket worn during sampling to the container it is stored in.

Sample Preparation and Evaluation

My first task was to complete a literature review of previous work surrounding PFAS as well as different passive sampler applications. One paper in particular, written by Kaserzon et al. in 2012, summarized their work testing a PFAS passive sampler for surface water applications. This paper provided us with a number of relevant equations and methods to reference in our project.

I developed an experiment with the goal of evaluating three sorbent materials for potential use in a PFAS passive sampler. These sorbents are made of different polymers that will bond with different types of chemicals and contaminants. The goal was to determine which sorbent would be best, based on its ability to collect a mass of PFAS that could accurately quantify the concentration in the surrounding porewater. The sorbents that we chose to test were Oasis WAX, Oasis HLB, and Strata X-

AW. Each has a slightly different chemical structure that affects how it sorbs contaminants. Another goal was to evaluate the rate at which the PFAS sorbed to each of these sorbents.

We planned to use a tandem mass spectrometer (tandem MS) to quantify PFAS. This instrument is commonly used to measure different compounds in environmental samples and is able to both identify unknown compounds based on their chemical signature and quantify the mass that was in the original sample after being calibrated to that compound. UNH's tandem MS is run by Dr. Anyin Li of the chemistry department. Dr. Li has done extensive research on the methods of quantifying PFAS on this instrument. For this reason, we reviewed our proposed experiment with him before beginning.



Figure 1: The sorbent material is a fine, powdery substance seen in the bottom of each plastic tube. Samples are loaded into the top of the tubes, flow through the sorbent, and exit through the narrow outlet.



Figure 2: Pictured are some of the stock solutions made from the PFAS salts. These were made at a known concentration by dissolving the PFAS salts in water.

Dr. Li suggested that we run blank and recovery samples on the tandem MS before proceeding with the main experiment. Recovery samples are important to test before the real experiment to ensure that our planned procedure works. We used recovery samples to confirm that the same mass of PFAS known to be in the stock solution is being accurately quantified by the tandem MS after sorbing and desorbing from the sorbents. Blank samples are also important, as they were tested and evaluated using the same procedure to ensure there is no PFAS contamination coming from any of our lab materials during the experiment.

To prepare the samples for testing, we first made stock solutions of each of the seven PFAS compounds of interest. We did this by dissolving solid PFAS salts into deionized water (DI water) at a known concentration. These individual solutions were used as stock solutions for each PFAS compound. The solutions were then mixed together and diluted to create six individual one-liter working solutions that each contained a very low concentration of the seven compounds of interest. We ran each of these six solutions through a cartridge containing the sorbent materials. The six working solutions were enough to test each of the three sorbents twice, so that we had duplicate samples of each sorbent. This is important to ensure accuracy in our results.

After each of the one-liter solutions had been passed through the sorbents, we removed the PFAS from the sorbents through a process called elution. We passed a small volume of several different solvents through the sorbents and collected these solvents, called the eluate, afterward. We chose these solvents because we expected them to pull the PFAS off the sorbent and into the eluate. However, the concentration of PFAS in this eluate was too low for the tandem MS to detect, so we dried these eluates using a stream of nitrogen. This caused the liquid solvents to evaporate, leaving the collected PFAS in the container. After this concentration, we added a very small volume of water to the container to redissolve the PFAS in a concentrated state. If our

procedure worked as intended, the mass of PFAS in this final concentrated sample would be the same mass of PFAS that was in the original one-liter working solution for each compound of interest.

We prepared two recovery solutions that were made from the same individual PFAS stock solutions that had been created for each of the seven compounds of interest. These recovery samples did not pass through sorbents and did not go through any manipulation apart from concentration under nitrogen; therefore we expected that after running these samples through the tandem MS, the concentration would be the same as the original stock solution. This was important to ensure, because any error in the creation of the stock solution would affect the samples it was used to produce.

At the same time as we prepared these recovery samples, we also prepared the blank samples. To do this, we also passed two 200 mL samples of DI water through two Strata X-AW sorbent cartridges. We then used the same elution procedure as we used for the recovery samples, and dried the eluate the same way. This was an important step to complete so that we could ensure that there was no PFAS contamination coming from the DI water or from any of the materials that the samples came in contact with (sorbent, sample vials, and so on). We therefore expected these blank samples to have undetectable levels of PFAS.

Results and Sources of Variation

Because of the short time frame for this project, the blank and recovery samples were the only samples tested over the summer. Although we spent time preparing for a more thorough experiment to evaluate the different types of sorbents for their applicability in accurately sampling PFAS, we did not have enough time to complete that step.

Overall, our results were not as expected. We observed significant variation among all samples as well as variation between the duplicate samples for each compound of interest. These results point to instrument error as the main source of unanticipated variation.

Figures 5 and 6 represent the measurements obtained from two compounds out of the seven compounds that were tested: PFAO and PFDoA. The x-axis shows each of the eight total samples run: two replicates for each sorbent tested (Oasis WAX, Strata X-AW, and Oasis HLB), and two replicate recovery samples that did not pass through a sorbent.



Figure 3: Samples were housed in these vials after being passed through the sorbent. These vials went under the nitrogen dryer for concentration.



Figure 4: The sample vials are held in the metal block of the nitrogen dryer, and the needles descend into the vials just above the water surface. The dryer is connected to a nitrogen tank, and the nitrogen is gently blown out of the needles at the surface of the sample to speed evaporation.

One type of error seen in these results is a variation in measured intensity of the internal standards. Internal standards are two compounds that are added in known concentrations to each sample in order to have a reliable compound to compare with the other compounds of interest. The first type of error seen is between Ratio 1 and Ratio 2 for each sample. These ratios were produced by dividing the intensity signal of the compound of interest by the intensity of both internal standards, where intensity is a measure of the detector's response to the number of ions that hit the detector per unit of time. Since the concentration of the two internal standards added was the same, their intensity signals should ideally be the same, and Ratio 1 and Ratio 2 for each sorbent sample should be the same. However, this was consistently untrue in our results.

Figure 5 illustrates this result. This graph displays the results for the compound of interest perfluorooctanoic acid (PFOA). As can be seen with the XAW:2 sample, Ratio 1 is significantly lower than Ratio 2. This implies that the signal intensity detected by the instrument was not consistent even for compounds present in the sample at the same concentration. We believe that these inconsistencies were caused mainly by instrument error, perhaps related to how different samples were loaded manually into the instrument for analysis.

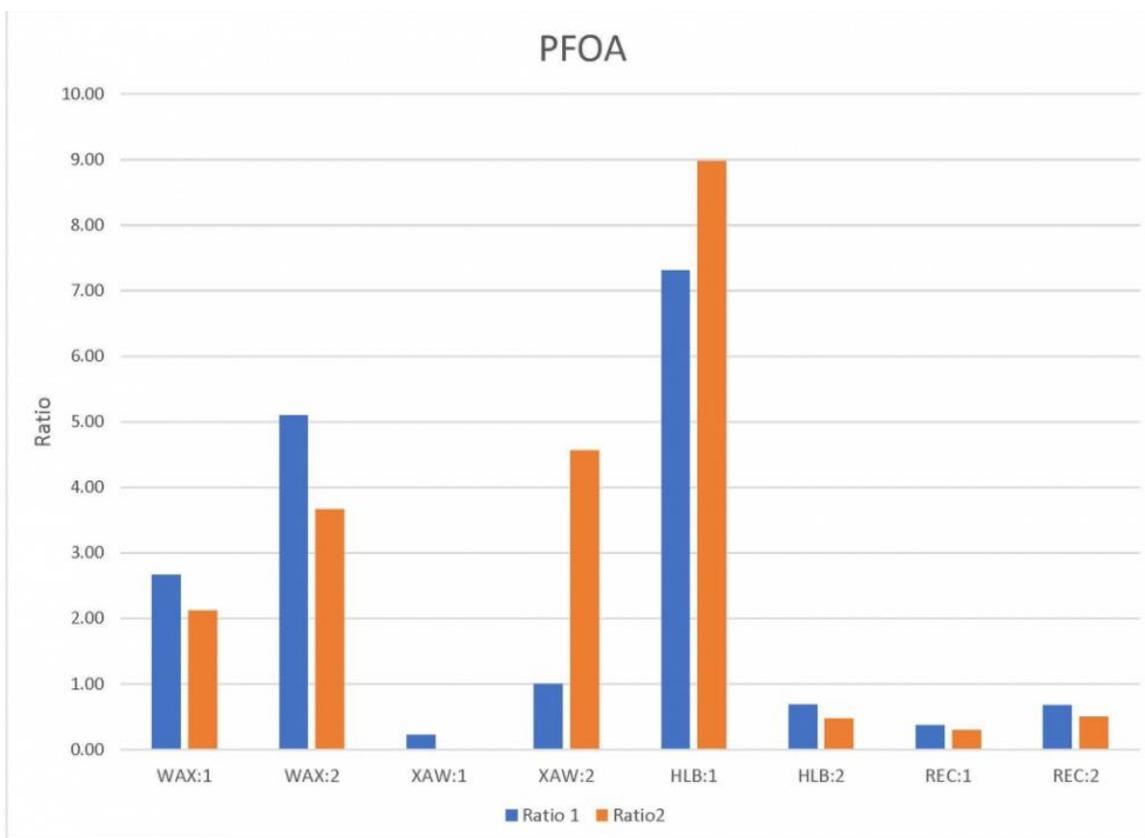


Figure 5: This graph shows the intensity ratios of PFOA to both internal standards in each of the three sorbent samples (WAX, XAW, and HLB) and in the recovery sample (REC). Ratio 1 represents the ratio of PFOA intensity to the intensity of the first internal standard, and Ratio 2 represents the ratio of PFOA intensity to the second internal standard. The variation in the measured intensity of the internal standards is most obvious in the XAW:2 sample. If the instrument had been working more consistently, the ratios in each sample and between duplicate samples would have been more similar to each other.

Another type of error seen in the results is variation between duplicate samples. All samples were produced and run in duplicates, so that there were two separate samples for each type of sorbent. Since duplicates were prepared in the same way, their respective intensities should have been the same. However, this was not the case. Figure 6 shows the results from the compound of interest perfluorododecanoic acid (PFDoA). As can be seen in the graph, both Ratio 1 and Ratio 2 vary greatly between the two HLB samples. Ratio 2 is almost an order of magnitude different between the two duplicates, which shows significant variation between the samples. Since these samples were produced and treated the same way in the lab, instrument error is a likely cause of these inconsistent results.

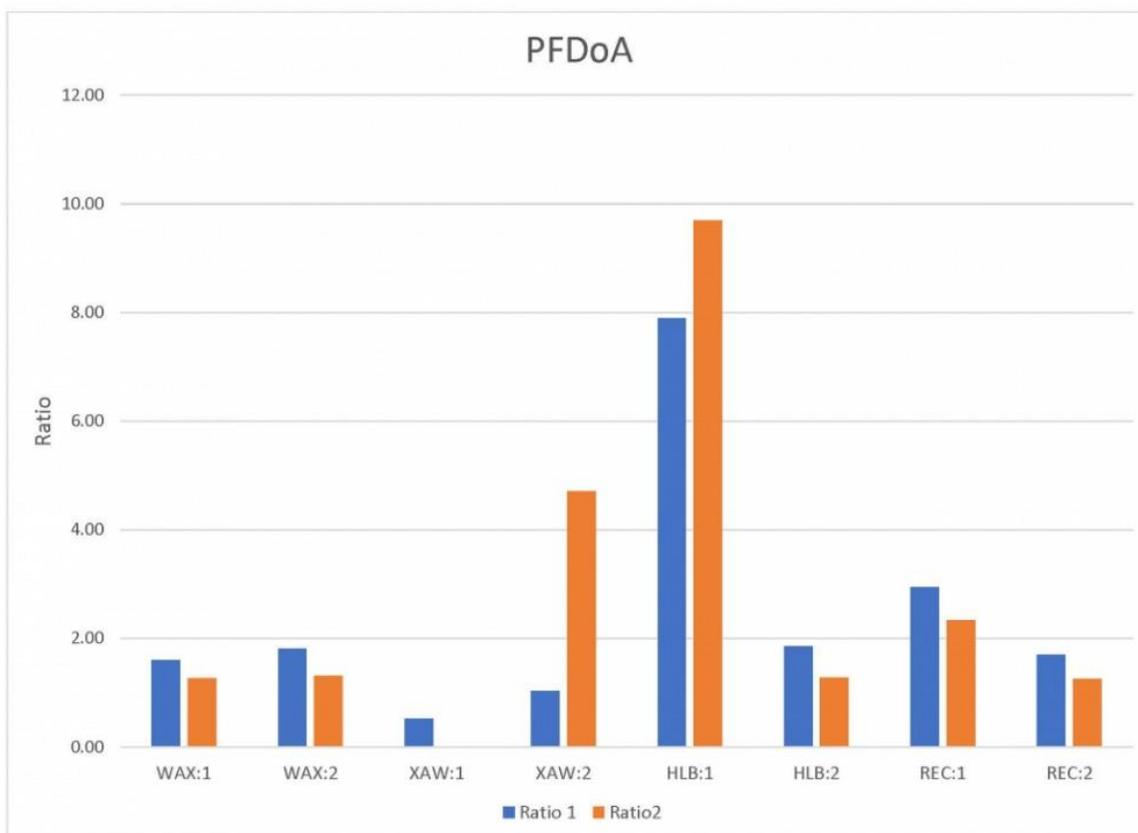


Figure 6: This graph shows the resulting intensity ratios of PFDoA to both internal standards in each of the three sorbent samples (WAX, XAW, and HLB) and in the recovery sample (REC). Ratio 1 represents the ratio of PFDoA intensity to the intensity of the first internal standard, and Ratio 2 represents the ratio of PFDoA intensity to the second internal standard. The variation between duplicate samples can be clearly seen in this sample between HLB:1 and HLB:2. If the instrument had been working more consistently, the ratios in each sample and between duplicate samples would have been more similar to each other.

Although we did not obtain much reliable quantitative data from these tests, we did gain some useful information. We proved that, with some future refinements made to the testing procedure, we are close to developing the capacity to quantify PFAS on campus. Some of these changes might include adjusting the way the samples are added to the instrument for analysis. Currently, the samples are being loaded by hand, but some type of automation may provide more consistent results. The procedure we followed and the data we collected was used in the writing of two grants that UNH has

since received. The first is a core grant for \$30,000 to study emerging contaminants, including PFAS. The second is a \$15,000 grant from the New Hampshire Water Resource Center.

Conclusions and Lessons Learned

My research complements work being done by others both locally and worldwide related to remediation of contaminated sites, such as the groundwater aquifers at Pease International Tradeport and in Portsmouth, New Hampshire. Having the ability to monitor a site and accurately characterize the current conditions is an essential first step toward designing a treatment method.

This research also is important to my professional goals because it taught me a lot about research and analytical methods, as well as about a field I may decide to pursue professionally. I learned a lot about the challenges of research and how to overcome them, such as the tendency for processes to take longer than anticipated and the frequency of unexpected challenges. I also learned about how to be self-motivated and work independently, but also to ask questions when I need help: it is much more efficient to ask a question of someone who has more experience than I do than to spend more time researching on my own.

I also gained skills in presenting and explaining my research. I presented my research at the Summer Research Symposium put on by the UNH Leitzel Center in August 2018, where I explained my work to people with different expertise and levels of experience in scientific fields. This is one of my most important takeaways from this project. The primary client of environmental engineers is often the public, who are commonly not well educated in science or engineering. For this reason, having the skills to explain to the public in understandable terms why such engineering projects are being conducted, despite their limited knowledge of the problems, will be invaluable in my future career.

I am hugely thankful for all the support I received throughout this project. This work would not have been possible without the SURF award funded by Mr. Dana Hamel and the UNH Hamel Center for Undergraduate Research. I'd like to thank Dr. Anyin Li for his input on our experimental design and for allowing us to use his instrument, and Ms. Taoqing Wang for testing our samples. I am also grateful to Mrs. Elham Tavasoli for giving input and participating in lab procedures throughout the project. Lastly, I'd like to thank my mentor, Dr. Kevin Gardner, for his leadership and direction, and Mr. Scott Greenwood for the continuous hands-on assistance and contributions he provided throughout the duration of the project.

References

Agency for Toxic Substances and Disease Registry. "Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in the U.S. Population." 2017. https://www.atsdr.cdc.gov/pfc/docs/PFAS_in_People.pdf

Buck, R. C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." *Integrated Environmental Assessment and Management*, 7, no. 4, 19 Sept. 2011, pp. 513–541, [dx.doi.org/10.1002/ieam.258](https://doi.org/10.1002/ieam.258).

Kannan, K., S. Corsolini, J. Falandysz, G. Fillmann, K. Kumar, G. Loganathan, M. Mohd, J. Olivero, N. Van Wouwe, J. Yang, and K. Aldous. "Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries." *Environmental Science and Technology*, 24 July 2004, pp. 4489–4495. pubs.acs.org/doi/abs/10.1021/es0493446.

Kaserzon, Sarit L, et al. "Development and Calibration of a Passive Sampler for Perfluorinated Alkyl Carboxylates and Sulfonates in Water." *Environmental Science and Technology*, 9 Apr. 2012, doi:10.1021/es300593a.

USEPA. "Basic Information about Per- and Polyfluoroalkyl Substances (PFASs)." 25 July 2017. www.epa.gov/pfas/basic-information-about-and-polyfluoroalkyl-substances-....

Author and Mentor Bios

Alexa Kaminski, from Doylestown, Pennsylvania, is majoring in environmental engineering at the University of New Hampshire (UNH). She conducted her research with a Summer Undergraduate Research Fellowship (SURF) from the Hamel Center for Undergraduate Research. Alexa was first exposed to her research topic during a guest lecture. Later that year, her professor sent an email detailing a research project, and Alexa jumped on the opportunity. She was excited to conduct a project on her own that would have real, significant results, and she liked working each day on something important and worthwhile. Through the research process, Alexa learned that nothing goes as planned and everything takes longer than anticipated. Even when you plan everything out on paper and account for every step and possibility, you can still experience something totally unexpected in the lab. On working with her mentor and other colleagues, Alexa said, "They were always around to answer questions and help when I needed it, but I was able to make choices and do a lot of work on my own."

After graduating from UNH, Alexa hopes to attend graduate school. She plans to study sustainability with a focus on its societal and economic effects. Through her SURF project, she has learned that she has a passion for working with stakeholders and the public, taking concrete steps toward sustainable development.

Kevin H. Gardner is a professor in the Department of Civil and Environmental Engineering and is the vice provost of research. Dr. Gardner began working at the University of New Hampshire (UNH) in 1999 and is focused on mitigating the human impact on the environment. He specializes in sustainability and the remediation of contamination. In recent years, Dr. Gardner has worked to develop samplers for analyzing PFAS/PFOA compounds in soils and groundwater. Because UNH is a land grant institution, he feels a responsibility to conduct research that is relevant and important to the state. Dr. Gardner says that Alexa's project "was super difficult because the analysis is so challenging and we really aren't set up for it yet . . . I certainly gained knowledge and experience from Alexa's work." Dr. Gardner believes that writing for *Inquiry* is a critical experience, because many disciplines interface with the public and clients from diverse businesses, and it is important to be able to recognize your audience and speak and write appropriately.