Introducing Field Environmental–Analytical Chemistry in the Quantitative Analysis Laboratory

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Abstract: Advances in instrumentation and technology now provide the ability to perform many quantitative determinations in the field. Additionally, the potential for sample degradation and analyte decomposition make it necessary to determine certain analytes (e.g., dissolved oxygen) in the field when conducting environmental analyses. Unfortunately, field environmental–analytical chemistry is not a substantial portion of the analytical chemistry curriculum at many institutions. Students in lower-level analytical chemistry courses are often non-chemistry science majors, particularly at institutions with small chemistry departments. We report here on an experiment in which field environmental-analytical chemistry is introduced in the quantitative analysis laboratory. In the context of a water quality assessment of a local river, students determine temperature, pH, ORP, nitrate nitrogen, and ammonia nitrogen at several points in the river. The experimental objective is to determine the potential effects local agricultural practices and treated wastewater discharge may be having on the water composition. The pedagogical objective is to expose these students to the difficulties involved in making analytical determinations in unfamiliar and/or disruptive settings.

Introduction

Environmental chemistry has become an increasingly important component of many undergraduate programs. As of Fall 2000, seventeen institutions had environmental chemistry options that were approved by the American Chemical Society [1]. Numerous other schools have alternatives that range from specialized degree tracks and options to environmental chemistry components in traditional chemistry courses. The need for trained professionals in environmental chemistry [2] is a result of a number of factors, including an increasingly stringent regulatory environment and the realization that historical practices were often insensitive to potential environmental impacts. In designing new laboratory experiments, and adding an environmental emphasis to existing experiments, the course instructor should attempt to focus on real-world issues with practical applications that relate to students' observations in the course of their daily lives or professional careers. This can be accomplished via many different routes. In the case of environmental fields, the call has been made for an experiential approach to educating students that includes fieldwork [3] and the need for a more multidisciplinary approach to solving environmental problems has been expressed [4].

A great deal of work has gone into designing new experiments with an environmental emphasis or component for undergraduate laboratories. Numerous experiments have been published that apply a specific analytical technique to the study of an environmentally significant analyte [5–8] while others investigate environmental bioassay procedures or biotoxicity [9, 10]. Many other papers detail experiments with substantial environmental sampling components [11, 12], an emphasis on quality assurance and quality control [13] and the study and preparation of regulatory documents such as environmental impact statements [14]. Additional papers have described application of environmental-analytical chemistry in the field for examining environmental issues [15], and long-term projects in which environmental–analytical chemistry is a major component of interdisciplinary projects [16] or a quantitative analysis laboratory course [17]. These are just a few examples of the great volume of material available. Regardless of the mechanism for introducing environmental chemistry into the curriculum, one should strive to incorporate context-based curricula, undergraduate research or miniprojects, cooperative and problem-based learning. and appropriate use of technology [18–23].

It is also important to note that many academic departments fulfill some service role within their college or university, sometimes resulting in more nonmajors than majors enrolled in their courses. Analytical and environmental chemists in academia often meet their service requirement via lower-division analytical chemistry courses in which the primary audience is nonchemistry science majors. While it is vital that chemical educators continue to demonstrate basic chemical phenomena and principles to these students, it is also an important consideration that these students are more likely to become nonchemical scientific professionals than professional chemists. Non-chemistry majors likely to be enrolled in the traditional sophomore- or junior-level quantitative analysis course include biochemistry, biology, ecology, environmental science, environmental engineering, and other fields. Faculty teaching these courses should consider modifying the curriculum to include an environmental component that is applicable to these majors. While a modified curriculum can include many of the same principles as the traditional analytical chemistry curriculum, adding an environmental

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emphasis requires greater attention to issues such as dealing with complex matrices, sample preparation/preservation, quality control/quality assurance, sampling techniques, and others. This paper describes an experiment in field environmental analytical chemistry, adopted for a laboratory course in quantitative analysis in which the majority of students are juniors majoring in zoology, general biology, microbiology, biochemistry, and secondary-school science education.

Experimental Section

The scenario presented to students for this experiment is that they are members of a local civic group charged with monitoring water quality in a river impacted by wastewater treatment systems and agricultural runoff. This is a common occurrence in many municipalities in the U.S. Students determine temperature, pH, oxidation-reduction potential (ORP), nitrate nitrogen concentrations, and ammonia nitrogen concentrations in the river. In our case, the impacted river is the Palouse River, in Whitman County, Washington. Students are free to select specific sampling locations, based on their interpretation of the location of activities that would impact water quality (e.g., wastewater treatment, application of agrochemicals to recreational fields, etc.). At the same time, restrictions based on public access and the desire of the instructor to have them sample both upstream and downstream of the local wastewater treatment plant are made clear. The experiment covers two, three-hour laboratory periods and a field trip. We visit four sites during a six-hour field trip. The prelaboratory discussion of experimental procedures (available in the supporting material). includes pointing out to students potential sources and sinks of the analytes of interest, and how to design and execute an appropriate sampling plan. The prelaboratory discussion also addresses matrix effects, and particularly, how complicated matrices can impact the quality of analytical determinations. In our case, the specific example of the need to adjust the ionic strength of sample solutions using ammonium sulfate to match that of the standards when using the nitrate-ion-selective electrode (ISE) is used. Furthermore, the relevance of measurements such as ORP in the context of complex systems with many analytes (e.g., natural waters that contain dissolved oxygen, Fe^{2+}, Fe^{3+}, etc.) is stressed. Also during the prelaboratory discussion, the instructor alerts students that since this is a true field experiment, they will be required to bring all apparatus, accessories, consumables, etc. with them. We deemed it unacceptable to return to the laboratory if students forgot important materials.

The first laboratory period is used for student preparation. Students come to the laboratory after being given instruction on how to locate and copy a United States Geological Survey topographic map of the study area. During this first period students are also given a demonstration on each apparatus and use the remainder of the class period to prepare standards and calibrate each apparatus. Successful demonstration of their ability to perform selected measurements is important if their field analyses are to be of adequate quality. There is limited time in the field for additional training on how to use instruments. Students are instructed on how to correctly sample waters from the river without disturbing the sediments by using a “dipper” sampling device (essentially a 4-meter polyethylene pole with a 500-mL beaker at the end) (Figure 1).

In our specific laboratory experiment, temperature and pH are measured using a Hanna portable pH meter, while nitrate and ORP were determined using two Corning portable pH/mV/ISE meters equipped with nitrate ISE and Ag/AgCl–Pt combination electrodes. Portable battery powered stirrers were used for the nitrate ISE, pH, and ORP measurements. Ammonia was determined by colorimetry using Hach test kits. While at best semiquantitative, the relatively simple ammonia determination allows us to expose the students to a variety of types of measurements that can be made in the field (potentiometric, colorimetric, etc.) without the need for a portable colorimeter. During this period, we also include instruction on how to use the global positioning system (GPS) receiver. GPS is employed so students can accurately plot the locations of their analyses on the topographical map, with the goal of clarifying the relationship between sampling locations, potential contaminant sources, and the analytical results obtained. A requirement of their laboratory report is that they turn in a copy of this map with the sampling locations clearly marked, and with the results of their analyses listed (mean ± standard deviation) at the locations marked on the map.

A checklist of materials that each group of students is required to bring is given to them in the written experimental procedures (available in the supporting material). Each group goes through the checklist and, with the close supervision of the instructor, ensures that they have all of the items needed before the end of the first laboratory period. They are provided a small basket in which to store their solutions, goggles, etc. In addition to laboratory apparatus (pH meters, electrodes, etc), the instructor ensures that each student has packed safety goggles, and the instructor packs a first-aid kit. While in practice, wearing safety goggles in the field may not be common, our students who work with chemical reagents are required by law to wear goggles. An additional consideration is the collection of waste. A 20-L waste container is used in this experiment to collect all chemical waste, including reagents such as ammonium sulfate.

“Fieldwork day” is coordinated as a one-day field trip and is spent traveling to the various field locations and conducting the analyses. The lone luxury allowed on the trip is a portable, albeit somewhat unstable, table. While an important objective is to simulate field conditions as much as possible, one has to practically consider the costs involved if equipment were to be damaged, particularly the nitrate ISE. The table was used to setup portable stirrers and was the center location for performing analyses. At each location, students rotate among the different instruments, calibrating each with the standards from their group. The latitude and longitude of each site is recorded using the GPS receiver. Students collect and analyze multiple samples from each site so that they can evaluate the uncertainty in their results. This portion of the experiment takes approximately six hours, with approximately one hour spent traveling from site to site and setting up the apparatus. For many of the students, working outside for six hours, while not physically demanding, left them exhausted. The potential for exhaustion, dehydration in hot weather, and excessive exposure to the sun are important considerations in this type of experiment, and instructors should be prepared to deal with them as necessary. An additional consideration, if working near deep or turbulent waters, is water safety. Indeed, if working near a deep lake, or deep, fast-moving river, it would be prudent to have the students who collect samples wear a personal flotation device.

The third period of the experiment occupies the next regularly scheduled laboratory time. It is spent cleaning and storing the apparatus, and assisting students with their calculations and data interpretation. It provides a good opportunity to review results with the whole class, provide assistance with dilution calculations (e.g., correcting data for dilution of water samples for nitrate determinations), and helping the students identify the sampling locations on their topographic maps.

Results and Conclusions

This experiment has been performed three times during the summer session of quantitative analysis laboratory at Washington State University (WSU). In general, students found the equipment and apparatus simple to use, yet they did encounter some recurring problems. The first widespread problem was difficulty interpreting the latitude–longitude data collected using the GPS receiver. Most of the students had no prior cartography skills. These difficulties were corrected by

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Table 1. Student Data for Field Analyses of Temperature, pH, ORP, Nitrate, and Ammonia in the Palouse River ($n = 3$)[a]

	Upstream of Pullman, WA	Downtown, Upstream of Pullman, WA Playfields	Immediately Upstream of Pullman, WA Wastewater Treatment Plant	Immediately Downstream of Pullman, WA Wastewater Treatment Plant
Temperature (°C)	22.9 ± 0.4	25.5 ± 0.1	24.6 ± 0.4	27.4 ± 0.3
pH	7.44 ± 0.02	8.06 ± 0.02	7.71 ± 0.02	8.67 ± 0.05
ORP (mV)	192.9 ± 1.7	140.4 ± 6.5	193.5 ± 2.9	141.2 ± 0.4
Ammonia N (ppm)	1.2	0.8	2.0	0.6
Nitrate N (mM)	1.2 ± 0.2	1.2 ± 0.1	1.0 ± 0.1	4.6 ± 0.8

[a] The sampling sites are listed in order starting from the upstream site to the last site sampled along the river downstream from wastewater treatment plant.

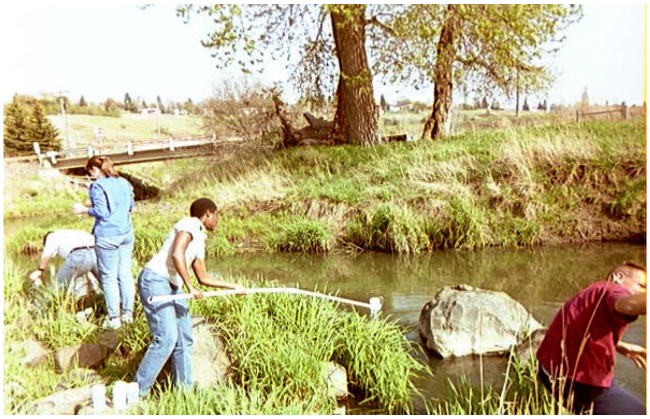

Figure 1. Students use the dipper sampler to collect midchannel water samples from a local river.

additional discussions during the third laboratory period. Additional problems encountered in the field included student complaints regarding the instability of their working surface and a backlog at the pH/mV/ISE meter used to determine nitrate. A sample of data collected by students is shown below in Table 1. These results can be used to demonstrate that the impacts of agriculture and the discharge of treated sewage can have on local water quality.

Temperature and pH measurements were completed with relatively ease, although students did eventually realize that the water temperature measurements needed to be made immediately after sampling to avoid changes due to the relatively hot outdoor temperatures (generally 30–32 °C). There was also great variation in the measured ORP values from site to site. The prelaboratory session included a discussion regarding the consideration of ORP as less of a quantitative measurement and more as a qualitative evaluation of the overall condition of a water body (e.g., generally oxidizing versus generally reducing). Most students commented on this during their laboratory reports. Though semiquantitative (the field color scale has graduations of 0.2 ppm ammonia), ammonia nitrogen tests were quite revealing; most students recognized that the high values (as shown above) obtained upstream of the sewage treatment plant were likely the result of ammonia-based fertilizer application to, or direct ammonia injection into, local agricultural fields. The lower value found downstream from the sewage treatment plant is likely due to dilution of existing river water from wastewater treatment plant discharge. Nitrate nitrogen concentrations were highest downstream of the sewage treatment plant, likely the result of nitrate in discharge from the plant. Students realized that in the field that they had to dilute their field samples for nitrate determination using deionized water that was supplied by the instructor, and then perform a 1:1 dilution with ammonium sulfate solution to adjust the ionic strength of the samples so that they matched that of the standards.

In general, student comments regarding the experiment were positive. For example, students were asked what they liked and disliked about the experiment, and we requested that they respond to this inquiry in writing when writing in their laboratory reports. Popular responses included comments such as " I really enjoy working outdoors, and if I could I would work outdoors all of the time." and "It was fun to go outside to do experiments rather than do routine work inside the lab." One student commented that it "was a nice change from the daily lab work. However, working outdoors was more of a hassle, for instance having to take down and setup the equipment at each site." When questioned about the difficulties in collecting samples and analyzing them in the field, most students felt that the "dipper" sampler was simple to use, yet that it took a while to get accustomed to handling it. The greatest interest in changing the experiment was a desire to "be able to measure for lead, arsenic and other heavy metal contaminants, as well as nitrite." Clearly, if concentrations of trace element contaminants are high enough (e.g., in an area affected by acid mine drainage), either colorimetric tests or the use of additional metal-ion selective electrodes could be employed. To enhance the connection between this laboratory and the accompanying lecture course, postlaboratory questions also asked students to elucidate the details of potentiometric measurements and the various types of ISEs available. With classes of 15–16 students working in groups of three, two instructors (faculty member and TA) were required for close supervision. In our case, we covered a sampling area representing 4 km of the river, and used two vans to transport students. With the time constraints and the desire to make the experience last for an entire day in the field, we found it easiest to perform this experiment in the summer, when most of our students are enrolled in only quantitative analysis and quantitative analysis laboratory.

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Supporting Material. The student laboratory handout is available as an Adobe Acrobat PDF file (http://dx.doi.org/10.1007/s00897000477b).

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