Report as of FY2006 for 2006ME83B: "A sequential time-weighted average approach for monitoring pesticide levels in Maine surface waters "

Publications

Project 2006ME83B has resulted in no reported publications as of FY2006.

Report Follows

A SEQUENTIAL, TIME-WEIGHTED AVERAGE MONITORING APPROACH TO DETECT PESTICIDE LEVELS IN MAINE SURFACE WATERS

1. Background

This project aims at addressing the concerns of Maine environmental stakeholders about pesticide concentrations that may negatively impact Atlantic Salmon (*Salmo solar*) habitats in surface waters. In Washington and Hancock Counties watersheds, the pesticides of interest are: phosmet, chlorothalonil, propiconazole and hexazinone. A pilot experiment in summer 2004 showed that the Polar Organic Chemi-cal Integrative Sampler (POCIS) can be effective in measuring pesticide levels in water, thus, offering an alternative to the methods (grab sampling and ISCO autosampler) currently used by the Maine Department of Agriculture. However, there is a need to further the POCIS study both qualitatively and quantitatively by collecting a larger amount of data in the field and by generating, in the laboratory, calibration parameters specific to the pesticides previously mentioned.

2. Objectives

The proposed work for the period of September 2006 to April 2007 was as follows:

1. Trip to Columbia , Missouri, to work with USGS experts on POCIS experiment designs;
2. Perform laboratory studies in order to determine sampling rate data in low and high flow conditions for hexazinone, phosmet, chlorothalonil and propiconazole. Generating specific sampling rates of these chemicals will allow more accurate water concentration calculations, not only within the context of this study, but in future field experiments as well.
3. Progress report including sampling rate data generated for the pesticides.

3. Work carried out

1. September to December 2006

The first semester was devoted to academic formalities like the formation of an advisory committee and presentation of a thesis proposal to the committee. The administrative procedures for the release of the federal match of the project funding were also undertaken during that semester. In the meantime, the literature gathering was initiated. Many articles about pesticide sampling, analysis and modeling in the field and laboratory were collected from different environmental journals.

2. January to April 2007

During the month of February 2007, I traveled to the USGS research center in Columbia (Missouri) in order to meet with Dr. David Alvarez (the designer of the POCIS device) and other staffs. I toured their laboratories and had some fruitful discussions about experimental designs with the POCIS. One important feature of the project is the identification and quantification of the pesticides used on the blueberries from water and the POCIS matrices. This analytical aspect

usually takes up a large part of the budget when carried out by commercial laboratories. Therefore, during the spring semester, I took a class in advanced analytical chemistry that will allow me to carry out the analysis of the pesticides at the University of Maine once the procedures for the extraction and pre-concentration of the samples are optimized.

4. Future work (May to August 2007)

The different constraints related to academic, technical and financial planning delayed the start of the calibration experiments scheduled for the period of January to April 2007. The process will be initiated in May 2007 with the following activities:

1. Analytical methods optimization

Gas chromatography mass spectrometry (GC/MS) will be used for the qualitative and quantitative analyses of the pesticides. Therefore, analytical methods for analyte extraction in surface water and the POCIS sorbent need to be optimized prior to laboratory experiments. Pesticide extraction in POCIS and water matrices will be done according to SOPs provided respectively by the EST laboratory (Saint Joseph, MO) and the Hitchner Hall laboratory at the University of Maine. The analytical method optimization will be undertaken up to the third week of May. Once the whole procedure (extraction, QA/QC, analyte quantitation) is mastered, the POCIS calibration experiment will be set up in the laboratory.

2. Laboratory-controlled experiments

The parameter that will be measured in the laboratory is the sampling rate (R_s). It is an expression of the volume of water cleared of the target analyte per day and is used for estimating pesticide concentration in water from the concentration measured in POCIS deployed in the field. The sampling rate is calculated from laboratory-deployed POCIS by the formula:

$R_s\,(Ld^{-1}) = C_{POCIS} / C_w * t$

Where, C_{POCIS} is the analyte concentration in the POCIS device, C_w is the analyte concentration in the test water, t is the deployment time in day. This model assumes integrative sampling of the test chemicals by the device and requires that their concentrations remain fairly constant throughout the experiment. However, a drop in pesticide concentration can result from physical and chemical processes in the experimental setup (sorption on the walls of test container, metal component of the POCIS, volatilization etc). Therefore, I will conduct some preliminary studies to determine some parameters for the actual experiment.

1) Preliminary studies

The experiments will be conducted in stirred and quiescent conditions. The experimental unit is a ten-gallon glass aquarium (20” x 10” x 12”). Six gallons of water will be put in the tank as a reaction medium. The ideal experimental setup to model river flow would be a flow-through system that ensures water recycling and mixing while maintaining constant concentration of the tested compounds in water (C_w). It takes time to set up such a system, and keeping analyte concentration constant can be difficult. Thus, a simpler and quicker static stirred system will be set up for this first experiment , consisting of one submersible pump placed at the bottom of the tank to stir the system and recycle water inside the tank at a flow rate of $153gh^{-1}$ (flow-through systems may be considered for further experiments)

a. Half-lives determination

Some documents report relatively short half-lives for some of the targeted pesticides (for example 9 hours for phosmet). There is no clear indication as to the conditions under which the experiments have been conducted. I will determine the hydrolysis half-lives ($t_{1/2}$) of the compounds (*without the POCIS device*) according to a 14/10 L/D cycle, using a store-bought timer and light source. The pesticides will be spiked in four tanks at a concentration of $5\mu gL^{-1}$, while four other tanks containing unfortified water will serve as controls. Water samples (500 mL) will be taken every day for one week and analyzed for pesticides.

b. Determination of water renewal schedule

Keeping constant water concentrations with these hydrophilic pesticides can be quite challenging. In order to do so, the test water needs to be replaced periodically. Thus, another exploratory test (*with the POCIS device*) will be conducted at 25 ^{o}C (using heaters) over a seven day-period to roughly determine the timing in concentration decrease and set up a renewal schedule of test water for the actual calibration experiment. Four tanks will be used to conduct this preliminary trial as follows:

(1) The water in two tanks will be spiked with the appropriate amount of stock solutions to maintain a nominal concentration of $5\mu gL^{-1}$. $NaHCO_3$ will be used as pH buffer and $CaCl_2$ will be used to adjust ionic strength. The devices will be put in the tanks a few hours after spiking the water with pesticides.

(2) Six POCIS devices will be placed in each tank. Water in the two other tanks will not contain pesticide and will be used as background controls.

(3) Pesticide concentrations in the tanks will be monitored daily (from day 0 to day 7) by collecting and analyzing 500 mL of water.

(4) Two POCIS will be retrieved and replaced 24 hours, 3 days and 7 days after the deployment for pesticide analysis.

2) Calibration experiments

The actual calibration experiment will be done according to the same procedure described for the renewal schedule. The only change will be that eight tanks will be used in this experiment; that is, four tanks with fortified water and four tanks as blanks.

5. Field experiment

Field deployments of the POCIS are still scheduled to take place in July. However, the actual timing, method and extent of these experiments will depend on the following factors:

- The timing of the laboratory experiments;
- The recommendations of project partners (DEP, ASC, DA) and committee members;
- The cooperation of blue berry growers;
- The collaboration of local organizations in the study locations.

6. Conclusion

The first three trimesters of the project were devoted to academic, technical and financial activities in preparation of the calibration experiments. Beginning in May, The analytical method for pesticide pre-concentration in water sample POCIS sorbent will be optimized, and the experiments will start the first week of June. If the laboratory experiments go as scheduled, field deployments of POCIS will be carried out during the summer.