Journal of Environmental Indicators, 9:12-13, 2015

Quantitative Biomonitoring of Water Quality for POPs Using Freshwater Mussels

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Mussels have a long history of use as freshwater and marine biomonitors of water quality. Under passive biomonitoring programs, organisms native to the region are collected from the site of study and contaminant residues measured in their tissues. Environmental quality can be inferred based on spatial patterns of measured tissue residues or in some cases estimates of water concentration extrapolated based on animal/water concentration ratios generated from bioconcentration factors. However, these programs may suffer from several issues. Study species may not be available in abundance at a given location due to excessive contamination or habitat characteristics. Organisms may not be in steady state with their environment with respect to tissue contaminant concentrations as a result of changes to environmental loadings. Lastly, sampling approaches may be difficult in some systems where depth, turbidity or flow conditions make diver-assisted collections difficult or impossible.

In quantitative monitoring, animals of the desired species are obtained from cultures or a reference location and caged at the location of interest for set periods of time. This approach ensures that animals of the same species and in sufficient abundance are available at each location of study. Since the time of deployment is known in these cases, application of toxicokinetic models can be used to steady-state correct-time dependent concentrations measured in the biomonitor followed by estimation of water concentrations using bioconcentration factor approaches. Finally, borrowing methods used in passive sampler technologies (e.g. semi-permeable membrane devices), biomonitors can be pre-dosed with a set of hydrophobic, non-environmental chemicals designated as performance reference compounds (PRCs) prior to their deployment. By tracking the rate of dissipation of PRCs, mussel filtration rates are calibrated in-situ permitting the most accurate steady-state correction and water concentration estimates. This seminar will highlight spatial and temporal observations generated from a long-running quantitative mussel biomonitoring program implemented in the Huron-Erie corridor between 1996 and 2010. Spatial and temporal patterns of polychlorinated biphenyls are discussed as well as selected surveys where PRC compounds were used to track in-situ sampling rates in deployed biomonitors.

Elliptio complanata were collected each year from Balsam Lake near Lindsey, Ontario. Approximately 150 mussels from the reference location were transported to the Great Lakes Institute for Environmental Research, University of Windsor and held in recirculating tanks equipped with active charcoal filters for 2-4 weeks prior to deployment. Animals were placed in minnow traps or custom wire mesh cages equipped with a float and suspended off the sediment approximately 1 m. At some locations, cages were suspended from docks or break wall structures. Mussels were typically deployed for 21, 60-65, 126, 182, 220-250 days beginning in April-May until Nov-Dec each year. Samples were taken prior to deployment in order to measure day zero chemical residues for control correction. After a given deployment period, 5 replicate animals were collected from cages at each sample location.

Standard sampling locations consisted of 6 locations in Canadian waters of the Detroit River utilizing an upstream/downstream sampling design in proximity to two sewage outflows operated by the City of Windsor. At selected years, additional locations were added to provide full coverage of water contamination for the Detroit River Area of Concern that included upstream, midstream and downstream waters in Canadian and United States jurisdictions. After deployment, mussels were frozen and analyzed for organochlorine pesticides and polychlorinated biphenyls using accredited standard analytical operating procedures via a CALA accredited laboratory.

Control and steady correction of contaminant residues in retrieved mussels was performed according

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to:

$$_{(ss)} = _{(t)} - _{(o)} \cdot e^{-ktot \cdot t} / (1 - e^{-ktot \cdot t})$$

Where $C_{m(ss)}$ is the steady state corrected mussel concentration (ng/g wet weight) in the animal; $C_{m(t)}$ is the chemical residues (ng/g wet weight) measured in the mussel at the time of retrieval, $C_{m(o)}$ is the chemical residues (ng/g wet weight) measured in mussels prior to deployment, k_{tot} is the elimination rate coefficient (d^{-1}) for each chemical of study and t is the time in days.

Water concentrations (ng/L) were estimated as:

$$C_w = _{(ss)} / f_{lipid} \cdot K_{OW} \div 1000$$

Where f_{lipid} is the mass fraction of lipid in the shucked mussel sample and K_{OW} is the octanol/water partition coefficient (L/Kg) for the chemical of study.

Strong temporal patterns were evident in the 15 years of routine mussel biomonitoring collections (Fig. 1, A). Although extrapolated PCB concentrations showed no significant long-term trends, multi-year periods of declines and increases in water residues were apparent and consistent across sample locations. Spatial patterns of PCBs in the Detroit River showed a significant increase in concentrations at U.S. locations compared to Canadian locations. The geometric mean U.S. concentration in 2002 was 0.64 ng/L compared to 0.9 ng/L in Canadian waters. In situ PCB toxicokinetics were found to be faster for deployed mussels compared to mussels depurated under laboratory conditions by a mean factor of 4 fold (Fig. 1, B). This indicates that use of laboratory-derived elimination coefficients during steady-state correction results in overestimates of water contamination particularly during short deployment periods. Uncertainty in estimates of $C_{m(ss)}$ arising from variation in k_{tot} values across field locations and between replicate biomonitors is compared using model-based Monte Carlo simulations to recommend optimum biomonitor deployment periods and replicate sizes.

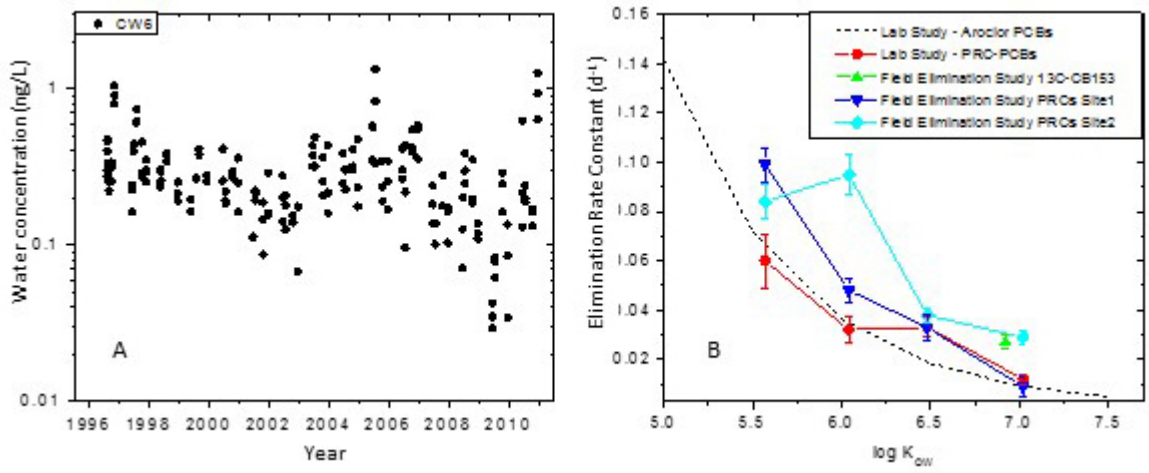

Figure 1. A: Temporal patterns of water PCB concentrations at a biomonitoring station in the Detroit River from 1996-2011. B: Comparison between in-situ elimination of 13C-PCBs and laboratory elimination of the same chemical by *Elliptio complanata*.