Chemical Mixtures

Executive Summary from a SETAC Pellston Workshop®
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Background and Objectives

Assessing the impacts of chemical mixtures in the environment is challenging largely because of high variation: diverse sources and constituents; routes of environmental exposure; taxa-specific sensitivities. This complexity and uncertainty leads to concerns that current prospective risk assessment (RA) methods are insufficient for appropriate environmental protection. Likewise, there is scope to better understand impacts of mixtures from retrospective impact assessments.

There are RA frameworks applicable to chemical mixtures but they appear to be too complicated for verification and forecasting for risk managers. A key question for the workshop was "can we develop a testable framework to navigate through the uncertainties and complexities of assigning causality and that provides tools for iterative forecasting of risks based on probable exposure scenarios?" The workshop addressed this need by exploring whether we can simplify the exposure-response morass into typical exposure scenarios without losing scientific credibility.

One of the overall aims that emerged was to propose an approach for deriving a likely chemical profile to help explain field observations or to provide a background against which the toxicity of a new product might be assessed.

Workshop Approach and Participants

Each group addressed a number of "big-picture" questions (appendix 1) to aid in developing specific scientific guidance for such a framework as well as a range of scenario specific questions to help develop representative mixture profiles for use in prospective risk assessment and retrospective impact assessment. The state-of-the-science precludes definitive solutions to many of these issues - but acknowledging them and their role in decision-making should result in a more scientifically based framework being developed.

The workshop consisted of 38 invited experts covering key areas of agriculture, urban, municipal, and complex watershed assessments. The key SETAC sectors were represented as follows: 15 from business and industry, 11 from government, and 11 from academia. These included hydrologists, ecologists, ecotoxicologists, and environmental chemists from 10 countries from Europe, North America, and Asia. As per previous Pellston Workshops, most time was spent in working groups with regular plenary feedback and discussion. Each group consisted of a multidisciplinary team with exposure, toxicity and risk or impact assessment expertise pertinent to the scenario.

General Achievements and Conclusions

Agricultural scenario

The agricultural land use scenario generated field and catchment-scale exposure and effects estimates using procedures that are recognized and used in regulatory schemes in the U.S., Europe, and other parts of the world. Two types of scenarios were defined including a single unit (e.g., feed lot, agricultural field, pasture, aquaculture production areas, biosolids applications, etc.). The second scenario was multi-unit, combining several single unit scenarios within a single catchment or watershed. These assessments considered inputs from spray drift, surface runoff and erosion, and from tile drainage systems. Septic tanks and municipal wastewater discharges were not considered in the initial tier. Both scenarios followed an event-driven approach, e.g. rain events, and required a description of hydrology to get the correct timing of the discharges with a focus on the lower end of the watershed. Approaches were spatially organized as: single field unit (200 ha), small catchment (10 km2, 5 stream segments, 5 field units), medium catchment (100 km2, 10 small catchments, 50 stream segments), and large catchment. A risk assessment decision tree looked at 13 active substances on a daily basis and the risks were summed and evaluated as described below in the Effects approach. Two case studies are now being developed to illustrate the approach.

Municipal wastewater discharge scenario

A simple scenario for municipal wastewater treatment plant (WWTP) discharges was based on emissions to small or mid-size streams where upstream has reference-quality biological condition and the habitat quality downstream of each discharge is unimpaired and where the WWTP discharge is the only input of chemicals to the stream. The WWTPs were assumed to treat domestic waste only. This workgroup evaluated both prospective and retrospective methods to estimate and verify potential mixture effects of domestically sourced chemicals.

Environmentally relevant chemicals were identified based on concentrations at which representatives have been reported in product classes along with their aquatic toxicity. Priority was given to chemicals that may be released from products and articles where they have been detected in domestic wastewater effluents and have potential to pose an environmental risk to aquatic life. Using standard prospective risk assessment methods (e.g., the E.U.'s Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), the U.S.'s Toxic Substances Control Act (TSCA), Canada's New Substances Notification (NSN), and guidance issued by Japan's Ministry of Economy, Trade and Industry), individual chemical risks were estimated and summed using reasonable worst-case, component-based mixture toxicity principles, i.e. concentration addition.

The key to understanding the voracity of prospective methods is to conduct retrospective impact assessments of mixtures emanating from domestic wastewater treatment plant discharges. Retrospective methods provide an opportunity to evaluate individual contaminants or highly complex mixtures in real-world settings. They provide an ecological reality check. We developed a process in which the risk assessment of mixtures from domestic WWTPs are assessed by incorporating both prospective and retrospective methods.

Urban scenario

Urban regions are the fastest growing areas globally. Infrastructure for collection and treatment of industrial and domestic wastewater is expanding, but is often outstripped by urban growth. The growing area of impervious surfaces in an urban environment can represent a direct source of contaminants to surface waters during rain and storm events. Urban storm water runoff presents one of the greatest challenges to ensuring clean water for human and ecological health. Storm water overflows from combined sewer systems are additional sources of chemicals, particularly in older cities. The urban scenario also has to consider non-treated or partially treated point sources from industrial origin, as well as diffuse inputs from dry and wet atmospheric deposition.

The urban land use scenario focused on "chemical signatures" typical of urban point and nonpoint sources. These included those from common industrial sectors and impervious areas such as buildings (e.g., Cu, Zn, PAHs,), gardens and parks (e.g., pesticides, nutrients), vehicles (e.g. metals, tire particles), sewage (e.g., nutrients, plasticizers, surfactants), and combustion processes (e.g., PAH). By combining monitoring data available in the literature, using established scenarios such as REACh - Specific Environmental Release Categories, and drawing on our knowledge of urban hydrology, we are able to estimate the expected emissions and concentrations in receiving waters. The toxic units associated with these chemicals were prioritized using the multisubstance Potentially Affected Fraction approach (ms-PAF) of the RIVM (Netherlands), and compared to the River Invertebrate Prediction and Classification System (RivPACs).

Effects approach

During the workshop an ad hoc group was formed to develop a tiered framework decision tree for both retrospective and prospective studies of chemical mixtures. The approach is based on developing appropriate acute and chronic exposure concentrations that consider spatial and temporal variations. These are done for each chemical in the mixture followed by considering possible chemical interactions such as antagonism, concentration addition, and synergism of the associated toxic units (TUs). If the summation of the TUs suggest a mixture concentration above an acceptable threshold concentration, then a refined effects assessment is conducted, which may include accounting for bioavailability, calculating SSD ms-PAFs, micro/mesocosm testing, mixture toxicity testing, and field assessments. These studies will allow for refinement of exposure determinations or possible risk mitigation and risk management actions.

Integrated scenarios

A suite of common typologies representing different land uses and the associated chemical mixtures were developed and used to provide an integrated scenario approach. The associated chemical profile of each land use was "blended" to construct a chemical profile. The result of integrating the exposure scenarios is a series of time-course concentration profiles for the chemical mixtures. The framework provides a flexible, tiered approach for interpreting acute and chronic toxic pressures utilizing established mixture-toxicity models and various refinement options. Since this process is relatively complex, it is important to formulate clear questions before undertaking an assessment.

Translating the integrated scenario mixtures from loadings or concentrations in surface waters into toxic pressure and risk requires assessing the appropriate temporal scale. This is possible by assessing the weighted average exposures (e.g., runoff mean concentrations) to match typical acute or chronic toxicity test durations, e.g., 7 d average for acute and 28 d for chronic. The risk acceptability of the toxic pressure over time should consider the magnitude and frequency of the threshold exceedances. Such thresholds may be described by a range of metrics such as TUs, msPAF or PECs<EQSs. Predicting long-term impact of mixture profiles may require complex mechanistic models.

Assessing mixture toxicity can be for both prospective and retrospective purposes. If prospective, it is important to note the simplifications and uncertainties associated with the assessment could result in either over- or under-protection. Therefore, it is important to confirm or refine the predicted toxic impacts prior to management decisions. This can be done using retrospective methods.

Recommendations

- Further work is needed to provide additional details on associated methods and guidance on the approach.
- Always watch Flamenco dancing in Valencia - it inspires creativity in feedback sessions!
- Case studies should be used to illustrate the approaches.

Publications and Presentations

The workshop products consist of four papers to be published in IEAM, and will include those from the breakout groups as described above: agricultural, domestic wastewater and urban runoff, as well as an integration paper that includes an effects assessment framework and a quantitative integration of selected urban, domestic and agricultural scenarios.

Moreover, a workshop summary has been published in the Globe, and several presentations were given at preceding SETAC annual meetings in Barcelona (May 2015, poster corner discussion) and Salt Lake City (November 2015, plenary session).

Appendix I

"Big picture" questions

1. Do previously constructed frameworks (e.g., WERF, ECETOC TF, CWN, etc.) serve as a starting point for Pellston Workshop discussions? What aspects of those are useful and not useful? Some of these approaches utilize "Weight-of-Evidence" based approaches, but WoE approaches can vary widely in their scope and usefulness. Can a basic WoE approach be recommended for higher Tier evaluations? How can this be used to rank stressors, chemical and sites?
2. Habitat (or some aspects of habitat, e.g., flow, geomorphology, substrate) has been recognized as a common and often major stressor of biotic communities. How can assessments of mixtures best separate ecological impacts of habitat from chemical mixtures?
3. How is reference condition best established in human dominated waterways? There are approaches using AQEM and RivPACs for example that consider this, but it can be challenging in some regions where "natural" conditions do not exist.
4. How is scale dealt with? For example, significant ecological impacts from mixtures are observed in a effluent mixing zone of 50 meters downstream - but are not significant elsewhere. How does one determine the ecological significance of this impact on the waterway's ecosystem? Is this a policy decision? On a related note - How are stressor inputs from upstream dealt with? How does one deal with fish migration and benthic drift between upstream and downstream reaches outside of the site-of-concern in regards to exposures and resilience?
5. How can the cumulative effect of upstream discharges be dealt with? Could this be similar to the U.S. EPA's Total Maximum Daily Loading (TMDL) approach that considers waste load allocations of mixtures?
6. How can the "bad actors" in mixtures be determined and ranked in a manageable manner that does not require extensive research endeavors? Could a small number of "surrogate" chemicals be selected to more easily assess the loadings and significance of the "bad actors"?
7. How are stressors common in these exposure scenarios (e.g., nutrients and metals) best linked back to dominant source inputs? What are some useful chemical signatures (e.g., stable isotopes, chemical fingerprint) to help link to sources?
8. While most regulatory focus on the water column, aquatic ecosystems have interacting compartments critically important to various communities, such as surficial sediments, periphyton/biofilms, flocs, hyporheic zones, and riparian zones. How are these compartments best integrated into a mixture based framework? Instream-based approaches that acknowledge the importance of bioavailability, changing exposures, fate processes, and compensatory mechanisms for example, in the proper ecological context are superior to overly simplistic lab and literature based models. Can a framework be designed for different ecosystem-based exposure scenarios (such as headwaters vs. large river mouths - see AQEM classifications) that consider real-world conditions?