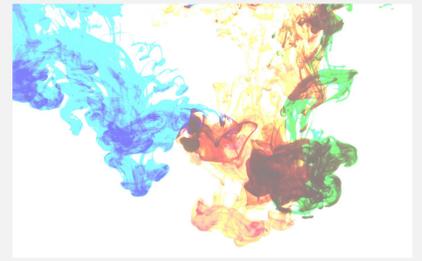


PROSPECTIVE RISK ASSESSMENT FOR MIXTURES OF AGRICULTURAL CHEMICALS IN SURFACE WATER



Christopher Holmes, Waterborne Environmental, Inc., VA, USA
 Mick Hamer, Syngenta, Bracknell, UK
 Colin Brown, University of York, York, UK
 Russell Jones, Bayer CropScience, NC, USA
 Lorraine Maltby, The University of Sheffield, Sheffield, UK
 Eric Silberhorn, US FDA Center for Veterinary Medicine, MD, USA
 J. Scott Teeter, Elanco Animal Health, IN, USA
 Michael Warne, Queensland Government, Brisbane, AU
 Lennart Weltje, BASF SE, Limburgerhof, DE



INTRODUCTION

In 2015 a SETAC Pellston workshop was held to help inform decision making around aquatic mixture risk assessments of chemicals using exposure scenarios and decision trees. The efforts were broadly grouped into three areas of chemical origination: agriculture, domestic, and urban influences (a separate integration group was charged with looking at overarching issues). The agricultural land use combined effect measures with exposure scenarios of chemical mixtures for field and catchment-scale using procedures that are recognized and used in regulatory schemes in the U.S., Europe and other parts of the world.

Chemicals modeled were those used in crop protection and livestock production, and were considered to occur as mixtures (in time and space). Two types of scenarios were defined including a single unit that could represent a variety of typical chemical input locations (e.g., feed lot, agricultural field, pasture, aquaculture, biosolids applications, etc). The second scenario was multi-unit, combining several different uses within a single catchment/watershed. These assessments considered inputs from spray drift, surface runoff and erosion, and/or tile drainage systems on a daily basis over an extended period of time (e.g., from one to 30 years).

AQUATIC TOXICITY ENDPOINTS

- Acute and chronic endpoints for primary producers, invertebrates and fish were collected from available registration documents
- The most sensitive endpoint was selected
- Standard assessment factors were applied to obtain regulatory acceptable concentrations
- UK scenario:** EU review reports and EFSA conclusions. Acute assessment factor: 100, chronic assessment factor: 10, mesocosm assessment factor 3 on NOEC/NOAEC.
- US scenario:** Aquatic benchmark values and the related EPA documents for crop protection, and registration reports for veterinary medicines.
 Crop protection – Acute assessment factor: 2, chronic assessment factor: 1.
 Veterinary Medicines – Acute assessment factor as in registration reports: 100 or 1000.

CASE STUDY 1: UK WHEAT PROBLEM FORMULATION

- Pesticide risk assessments are product based (either individual active substances or co-formulated mixtures of active substances)
- Is there any additional risk associated with exposure of the aquatic environment to any mixtures that arise from the full suite of plant protection products applied to a crop?**
- The risk assessment relates to a single crop and risk is expected to be greatest at field-scale where there is limited potential for dilution within the receiving water body.

SCENARIO DEFINITION

- Modeled as a wheat field in Eastern UK, consisting of PPP applications of 13 substances over the course of the year
- This scenario used standard FOCUS soil, weather and receiving water body
- Modeled over 20 years
- Concentrations based on the stream in the FOCUS R1 scenario, most applicable scenario for this area in UK
- The loadings to water were calculated with FOCUS SWASH/PRZM, then the water fate part with STEPS1234
- Edge-of-field model with UK LERAP no-spray buffer of 5 m

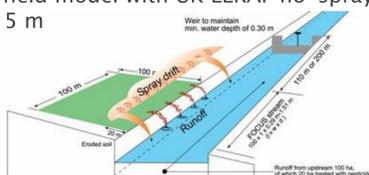


Figure 1. Schematic of FOCUS Scenario (from <http://www.pesticide-models.eu/toxswa/eu-registration>)

| Chemical name | Group | Application date |
|---------------------|-------------|------------------|
| Flufenacet | Herbicide | 14 October |
| Pendimethalin | Herbicide | 14 October |
| Cypermethrin | Insecticide | 6 November |
| | | 9 April |
| Iodosulfuron-methyl | Herbicide | 9 April |
| Mesosulfuron-methyl | Herbicide | 9 April |
| Epoxiconazole | Fungicide | 14 April |
| | | 27 April |
| | | 19 May |
| Boscalid | Fungicide | 27 April |
| Chlorothalonil | Fungicide | 27 April |
| | | 19 May |
| Proquinazid | Fungicide | 27 April |
| Prochloraz | Fungicide | 19 May |
| Pyraclorobin | Fungicide | 19 May |
| Fluoxastrobin | Fungicide | 18 June |
| Prothioconazole | Fungicide | 18 June |

Table 1. Plant protection products and application dates for UK Case Study

UK RESULTS

- Of the 7519 total days modelled, the sum of the RQs exceeded 1 (indicating potential further refinement, mitigation or risk management required) on a total of 391 days, equivalent to 5.2% of the total.
- For 300 of these 391 days, at least one individual compound RQ was > 1, either only one compound (148) or more than one compound (152). This means that 77% of the exceedances over 20 years of simulation would be captured by the current approach for risk assessments for individual compounds.
- The number of instances where the ΣRQ was >1 without any individual RQ >1 was 91 days, or 1.2% of the total days (i.e., the effects of the mixture would exceed the effect(s) of an individual).
- The maximum number of consecutive days ΣRQ >1 was 4 days
- Mitigation on label was used in modeling (LERAP 5m buffer), but there may be additional mitigations on label for individual compounds (e.g., drift reduction technology) that were not taken into account.

CONCLUSIONS

- This study demonstrates situations in both case studies where the sum of the mixture toxicity may produce effects that individual compounds may not.
- Some considerations:
 - The most sensitive endpoint was used for each compound
 - This spanned multiple taxonomic groups
 - E.g., effects to both primary producers and fish taxa combined
 - Concentration addition may not be appropriate in these cases
- Combined both chronic and acute toxicity endpoints across all compounds
- Chronic endpoints should be examined over time
 - We looked at daily peak concentrations
 - TWA using a comparable timeframe to testing (e.g., 21 day, 60 day) may be more appropriate

CASE STUDY 2: US CORN

PROBLEM FORMULATION

- Agricultural fields don't exist in isolation within the landscape
- What is the risk associated with the potential environmental combination of plant protection products and veterinary medicines applied in the same watershed?**
- The risk assessment relates to multiple sources of chemical inputs, where risk is expected to be greatest at watershed-scale where there is greater potential for aggregation within a low-flow water body

SCENARIO DEFINITION

- Simulates a multi-unit watershed scenario consisting of a combination of corn fields, pasture, and feedlot inputs
- Twelve different active substances for PPP at maximum label rate
- These applications ranged from a pre-plant herbicide to a late-year fungicide
- Manure from treated cattle containing two different pharmaceuticals (parasiticide and antibiotic) applied to corn fields as fertilizer
- Direct runoff input from pasture and feedlot
- Based on US EPA's Index Reservoir scenario as modeled with EPA's Surface Water Concentration calculator (SWCC)
- Soil, weather and other parameters based on US EPA Tier II Iowa corn scenario used in pesticide registration evaluations
- Watershed composition: 56.6% corn, 2.3% pasture, 0.09% feedlot based on GIS analysis
- Crop modeling still 'edge-of-field' and adhered to most stringent label buffer requirement
- Modeled for 30 years

| PPP name | Group | Application date |
|-----------------|------------------|-------------------|
| Acetochlor | Pre-herbicide | 1 wk before plant |
| Flumetsulam | Pre-herbicide | 1 wk before plant |
| Clopyralid | Pre-herbicide | 1 wk before plant |
| Atrazine | Pre-herbicide | 1 wk before plant |
| Clothianidin | Seed treatment | At planting |
| Ipconazole | Seed treatment | At planting |
| Trifloxystrobin | Seed treatment | At planting |
| Metaxyl | Seed treatment | At planting |
| Tefluthrin | Soil insecticide | At planting |
| Glyphosate | Post-herbicide | 28 d after emerge |
| Pyraclorobin | Fungicide | 65 d after emerge |
| Metconazole | Fungicide | 65 d after emerge |

| Veterinary Medicine | "Application" date |
|----------------------------------|----------------------------------|
| Tilmicosin | |
| Manured cropland (solid manure) | May 8, Oct 26 |
| Manured cropland (liquid manure) | May 30, June 30, July 30, Aug 30 |
| Pasture | Apr 1 – 14 (14 day excretion) |
| Feedlot | Apr 15 – 29 (14 day excretion) |
| Moxidectin | |
| Manured cropland (solid manure) | May 8, Oct 26 |
| Manured cropland (liquid manure) | May 30, June 30, July 30, Aug 30 |
| Pasture | Apr 1 – 20 (20 day excretion) |
| Feedlot | Apr 1 – 20 (20 day excretion) |

Table 2 & 3. Plant protection products (top) and veterinary medicines (bottom) with application dates for US Case Study

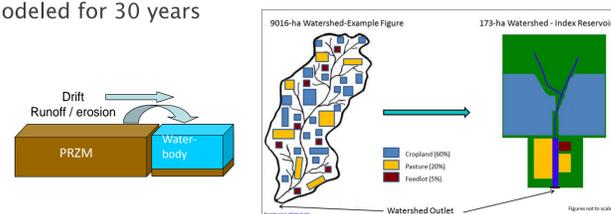


Figure 2. Schematic of 'edge-of-field' model and EPA Index Reservoir scenario

US RESULTS

- Of the 10957 total days modelled, the ΣRQs exceeded 1 (indicating potential further refinement, mitigation or risk management required) on a total of 1296 days, equivalent to 11.8% of the total.
- For 804 of these 1296 days, at least one individual compound RQ was > 1, either only one compound (497) or more than one compound (307). This means that 62% of the exceedances over 30 years of simulation would be captured by the current approach for risk assessments for individual compounds.
- The number of instances where the ΣRQ was >1 without any individual RQ >1 was 492 days, or 4.5% of the total days (i.e., the effects of the mixture would exceed the effect(s) of an individual).
- The maximum number of consecutive days ΣRQ > 1 was much higher than UK scenario which reflects the receiving water body used in modelling – reservoir with very low flow.
- US scenario combined crop protection and veterinary medicines, however these may have very different safety factors when determining LOC. E.g., vet med AF = 100, crop protection AF = 2.

We sincerely acknowledge the following sponsors (<http://pellston.setac.eu/?contentid=824>):



For more information: holmes@waterborne-env.com