Analysis of the mixture toxicity burden in 17 rivers in north eastern Australia – implications for the Great Barrier Reef.

The Great Barrier Reef (GBR) is a protected ecosystem, listed as a UNESCO World Heritage site since 1981. It runs for approximately 3000km along the coastline in north-eastern Australia. A total of thirty-five major river basins discharge to the GBR and many transport large loads of pesticides, suspended sediment, nutrients from agricultural land. Over the past 6 years an extensive program has been conducted by the Queensland Government to monitor concentrations of 51 pesticides and their breakdown products in 17 rivers that discharge to the GBR. To explore the potential impact that the pesticides pose to the riverine environments and to the GBR we analysed the risk posed by the individual pesticides and their mixtures. Australia currently does not have water quality guidelines for 17 of the 38 pesticides detected. For those, we calculated ecotoxicity thresholds using a simplified version of the Australian methodology for determining water quality guideline values, based on species-sensitivity distributions. In all rivers, multiple pesticides were routinely detected at concentrations greater than their level of reporting. All rivers had at least one sample where the combined toxicity was greater than 1 toxic unit (TU), i.e. exposure situations where the total pesticide concentration exceeded acceptable levels. In a number of rivers more than 50% of samples had a combined toxicity greater than 1 TU. Average TU's per river ranged from 13.47 to 0.10, with substantial fluctuations over the seasons but without clear trends between years. The patterns indicate that specific events such as severity of wet/dry seasons and cyclone events impact the combined toxicity found. We also found land use patterns affected the combined toxicity in the river ecosystems. In each of the rivers, 90% of the expected mixture toxicity was caused by only between 2 and 6 pesticides, although the individual pesticides that dominated the combined toxicity differed between rivers.

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Analysis of the Pesticide Mixture Toxicity Burden in 17 Australian Rivers that Discharge to the Great Barrier Reef

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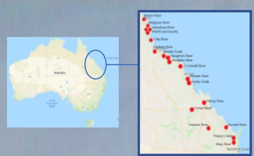
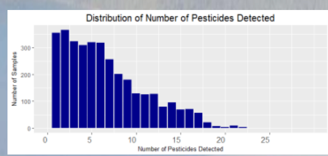
1. The Great Barrier Reef Catchment Loading Monitoring Program (GBRCLMP):

Pesticide concentration data were analysed from an environmental monitoring program conducted in Queensland, Australia from 2011 – 2016.

- 17 Rivers that discharge to the Great Barrier Reef.
- 3757 samples collected and analysed for pesticide concentration.
- 45 pesticides and 6 breakdown products included in the screen – 51 compounds in total.
- 38 different pesticides detected.
- All rivers have at least one sample with pesticides detected above the limit of reporting (LOR).
- Median number of pesticides detected per sample was 5.
- 81.8% of samples contained a mixture of 2 or more pesticides.

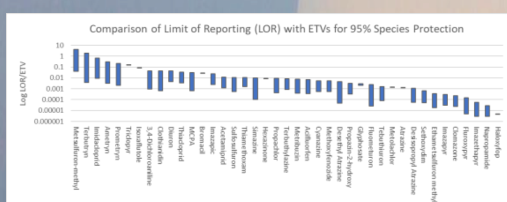




2. Data treatment for ETV estimation and the consideration of Non-Detects

- Australia currently only has default (national) guideline values (DGVs) for 21 of the 38 different pesticides detected in Queensland rivers (King *et al*, 2017).
- Australian national guidelines use Species Sensitivity Distributions (SSDs) to determine ecotoxicological thresholds (ETV) protective of 95% of species (Warne, 2015).
- Based on the Warne *et al.* (2015) method, threshold limits were calculated for 20 pesticides that did not have DGV.
- 73.4% of analytes were below their analytical limit of reporting (LOR).
- Non-detects (ND) can be problematic for mixture risk assessment. They might bias the final risk estimate if the chemical-analytical power is insufficient (Gustavsson, 2017).
- However, in the presented data, the ratio between the limit of reporting and the (LOR/ETV) is sufficiently low (0.1 or lower) for most pesticides.
- Consequently, the impact of different strategies on how to handle non-detects (such as ND = 0, Kaplan Meier method or ND = LOR) is negligible for mixture risk estimates.

n= 1583 Samples, ETV = PC95	Median RQ_{SUM}	Mean RQ_{SUM}
Non-detects = ZERO	1.988	5.892
Kaplan-Meier method	2.005	5.915
Non-detects = LOR	2.742	6.704

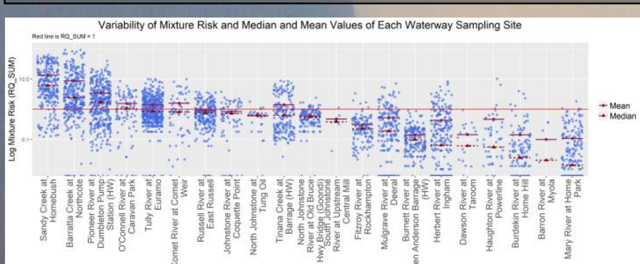


3. Risk of individual compounds and pesticide mixtures

of samples calculated as the sum of risk quotients (RQ_{SUM}):

$$\text{Pesticide Mixture Risk} = RQ_{SUM} = \sum \frac{\text{Environmental Conc.}}{ETV}$$

- The concentration protective of 95% of species (PC95) DGV and ETV values were used.
- Highest mixture toxicity recorded at Sandy Creek, with a RQ_{SUM} of 117.
- 17 of the 19 rivers had at least one sample with a RQ_{SUM} >1.
- 4 Rivers have a median RQ_{SUM} >1 and can be considered to be at risk. (i.e. >50% of the samples from those rivers have a mixture risk that exceeds the 95% species protection threshold).

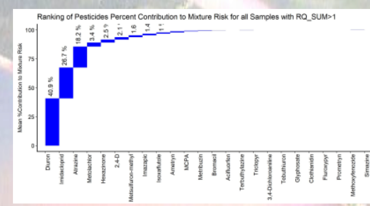


4. Relative contributions to mixture toxicity

Pesticides were ranked by relative contribution to the total pesticide mixture risk, calculated for 966 "at risk" samples with a mixture toxicity of RQ_{SUM} >1 (25.7% of all samples).

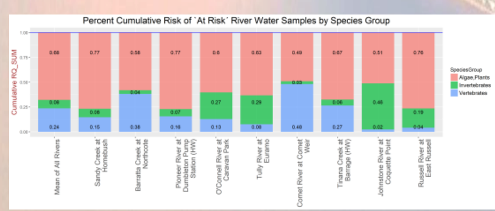
$$\text{Relative contribution to toxicity of pesticide mixture} = \frac{RQ_{IND.PESTICIDE}}{RQ_{SUM}}$$

- In all rivers, 90% of the toxicity of mixture is attributable to 6 individual pesticides or less.
- Herbicides, in particular photosystem II inhibitors, were the main drivers of the toxicity of pesticide mixtures.
- Averaged across all rivers, the main contributors to mixture toxicity risk were 10 pesticides that consisted of 9 herbicides (4 of them PSII inhibitors) and 1 insecticide.



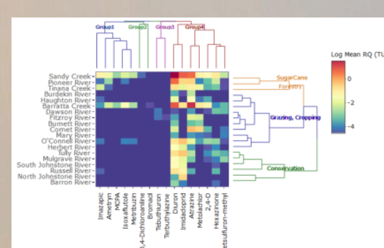
5. Impacts for different taxonomic groups and risk profiles of pesticide mixtures for individual rivers

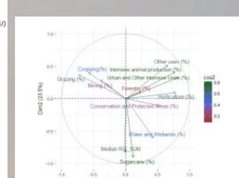
- The impact of the pesticide mixture on different trophic levels was estimated by generating taxonomic group-specific ETVs from SSD. The taxonomic groups were: plants; invertebrates and vertebrates.
- Different rivers with different pesticide uses in their catchment areas reflect different degrees of risk for the three taxonomic groups.
- For all rivers at least 50% of the risk from the mixture of pesticides is borne by algae and plants.
- The average risk proportion for all rivers is 68% for algae and plants, 24% vertebrates and 8% for invertebrates.



6. Land use patterns and river pesticide profiles used to identify priority pesticides, land use categories and rivers

- Catchment areas upstream from the sampling sites were characterised by 11 different land use categories (mostly agricultural).
- Hierarchical cluster analysis of pesticide data indicated there were 3 main land use patterns: grazing and cropping; conservation; and sugarcane and forestry.
- River pesticide profiles were used to group 16 pesticides by common co-occurrence (4 groups).
- Sugarcane farming and forestry land use were hotspots for diuron, imidacloprid and atrazine.
- Principal component analysis of land use categories indicated a relationship between percentage of catchment area used for sugarcane farming and mixture toxicity (RQ_{SUM}).





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Background Photo: Flood plume from the Johnstone River, 2011 (credit: Australian Broadcasting Corporation)

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