# WHAT ARE THE MAIN DRIVERS THAT CONTRIBUTE TO HERBICIDAL MIXTURE TOXICITY IN A HIGHLY AGRICULTURALLY INFLUENCED LANDSCAPE

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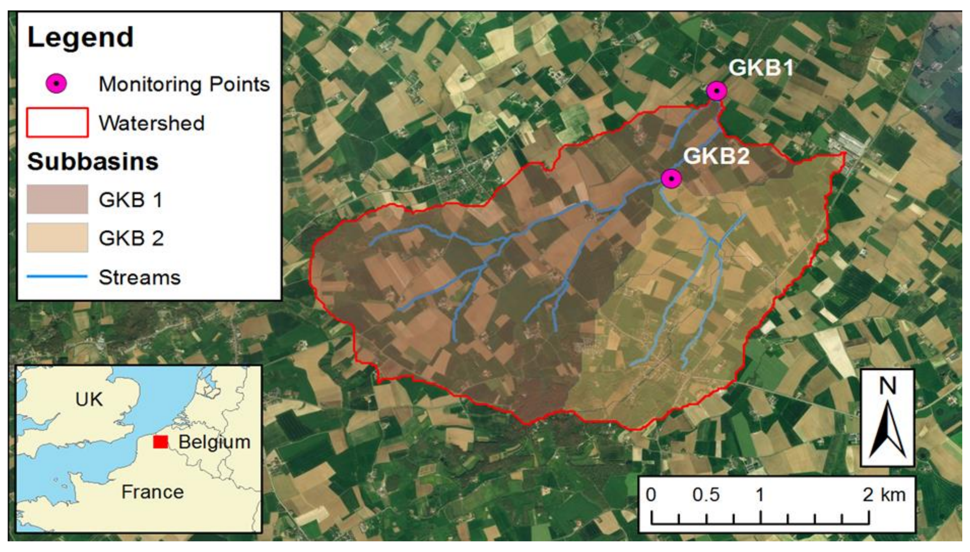
CAMBRIDGE ENVIRONMENTAL ASSESSMENTS




## BACKGROUND ON CHEMICAL MIXTURES IN WATER BODIES

- In the aquatic environment chemicals rarely occur as single entities but in undetermined mixtures.
- Environmental risk assessments for pesticides focus on mixture assessments for intended but not for unintended mixtures
- The assessment and regulation of unintended mixtures has raised concerns and prompted discussions by researchers, the public and regulators.
- Discussions included the implementation of a mixture assessment factor (MAF), but also addressing potential risks by managing critical compounds in spatio-temporal hotspots and their common mode of action (MOA).
- Only a limited number of chemicals drive the mixture toxicity, i.e., mixtures are not equitoxic.
- For photosynthetic organisms, mixture toxicity is primarily related to herbicides.

**BOX 1:**

Risk Quotient (RQ) – calculated for each herbicide and sampling occasion

- ***RQ = Measured Concentration/RAC***

Risk Quotient sum (RQsum) – calculated to assess mixture by assuming concentration addition

- ***RQsum= ΣRQi***

Maximum Risk Quotient (RQmax) – the highest RQ within a mixture of a given compound

Multiple chemical ratio (MCR; also termed maximum cumulative ratio)

- ***MCR=RQsum/Rqmax***

A MCR of 2 indicates that the chemical with the RQmax contributes 50% to the overall toxicity of the mixture.

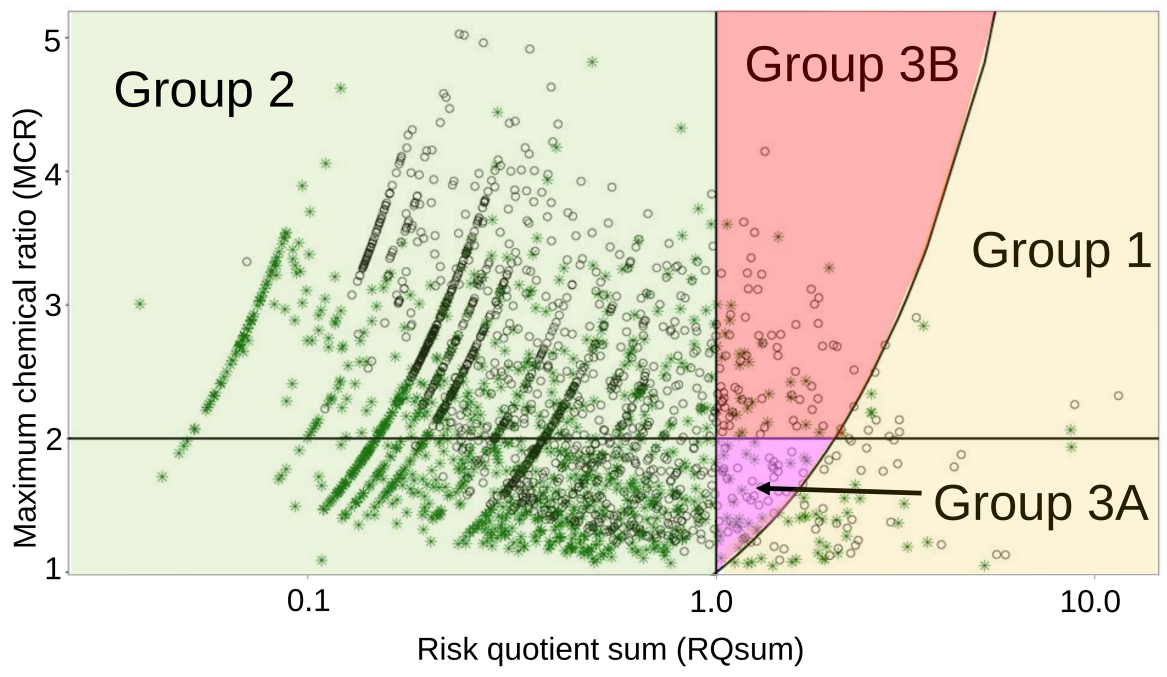



Figure 1: Algae (green stars) and macrophytes (black circles) MCR plotted against RQsum, vertical line indicates RQsum = 1, horizontal line indicates MCR = 2; the curved line indicates where RQsum= MCR, visible lines formed by data points on the left side of the graph are artefacts of the values for the limit of quantification (LOQ) and limit of detection (LOD); MCR cannot be <1 therefore the y-axis cut off at 1.

Table 1: Overview on the criteria for the grouping of sampling days based on RQsum, MCR and RQmax

| Group | RQsum | MCR | RQmax | Potential Risk | Potential Cumulative Effect | Covered by Current ERA | Results for total study period [%] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Algae | Macro phytes |
| 1 | RQsum >1 | MCR <RQsum | RQ >1 | Yes | Yes/No | Yes | 3 | 3 |
| 2 | RQsum <1 | MCR >RQsum | RQ <1 | No | Yes/No | Yes | 93 | 90 |
| 3A | RQsum >1 | RQsum <MCR <2 | RQ <1 | Yes | No | No | 2 | 2 |
| 3B | RQsum >1 | MCR >2 | RQ <1 | Yes | Yes | No | 2 | 5 |

## MONITORING AND DATA ANALYSIS

- 12 herbicides and 1 metabolite were monitored for, sub-daily for 3.5 years, following applications in a highly agriculturally influenced catchment (2010 – 2013)
- A stewardship programme was conducted alongside as of 2011
- The measured herbicide concentrations were analysed for their exceedance of regulatory requirements as individual compounds and mixtures, by using the RAC as threshold value and assuming additive toxicity for mixtures (BOX 1)
- Sampling occasions were grouped into 4 categories: Group 1, 2, 3A and 3B (Fig. 1 and Table 1).
- Category 3B would be decisive in identifying how much potential mixture toxicity may not be covered by a single substance risk assessment, as no single compound dominates the mixture.
- Algae and macrophytes were analysed separately to highlight the differences in sensitivities to the compounds.

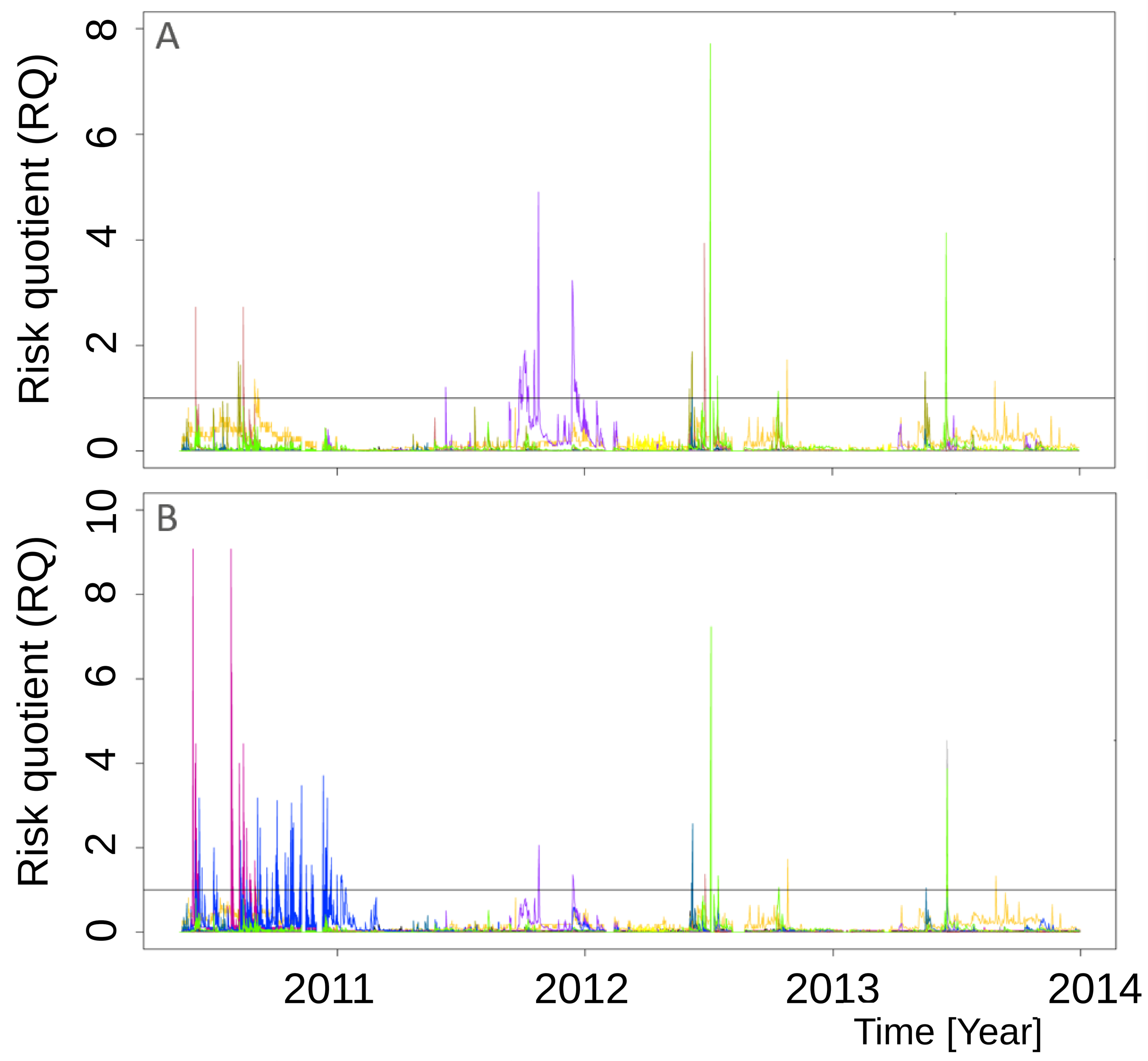



Figure 2:Algae (A) and Macrophytes (B) RQs of individual compounds (each compound is represented by one colour) plotted over time (using sub-daily samples); RQ >1 horizontal line

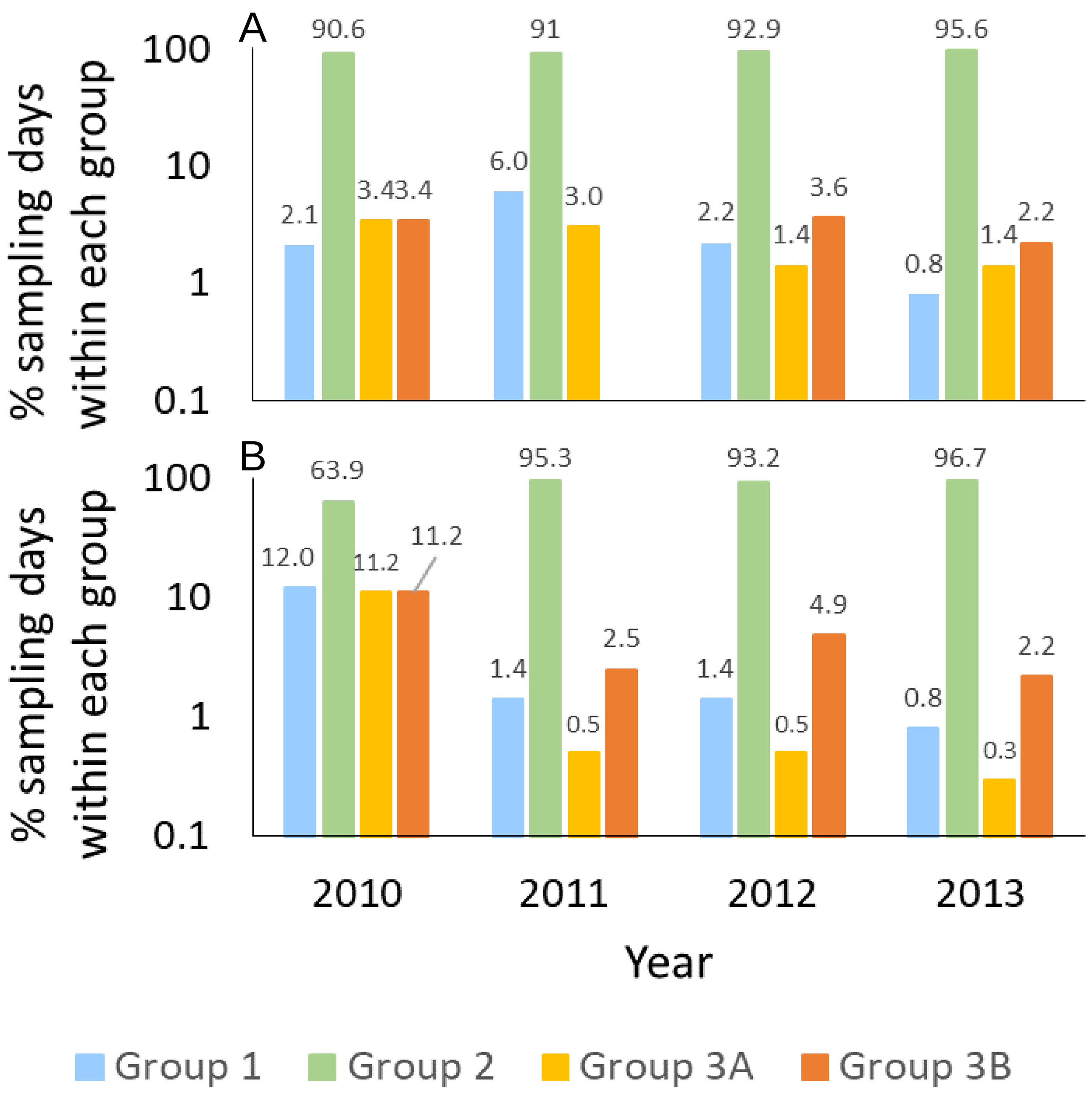



Figure 3:Algae (A) and Macrophytes (B): Distribution of the sampling days in each study year

## RESULTS AND DISCUSSION

- Exceedance events were driven by different herbicides in algae and macrophytes (Fig. 2)
- Mixtures are dominated by 3-5 herbicides depending on the organism group (Fig.2)
- Most sampling days are classed as Group 2 (no exceedance event)
- Over the total study duration of almost 4 years potential mixture toxicity events in group 3B account for 2% and 5% in algae and macrophytes, respectively (Table 1)
- There is a strong seasonal clustering of exceedance events corresponding to the spray calendar (Fig. 2)
  - 2011 is an exception to this pattern due to very low rainfall particularly in spring/summer
  - This also may have resulted in the lack of sampling occasions within group 3B for algae in 2011
- Large reductions of exceedance events were observed over the course of the study (Fig. 3):
  - In 2013 group 2 accounted for 96 and 97% for algae and macrophytes, respectively
  - This reduction was more pronounced for macrophytes than for algae (Fig. 3)
  - The reduction of the exceedance events coincided with the onset of the stewardship programme
- The largest reduction of exceedance events was observed in Group 1 followed by Group 3A
- Group 3B showed the least reduction of exceedance events
  - This confirms that the stewardship played a role in reducing large peaks (e.g. by reducing point sources) and thereby reducing the concentration of the dominating chemical in Group 1 and 3A.

## CONCLUSIONS AND RECOMMENDATIONS

- Potential mixture toxicity events in group 3B account for 2% and 5% over the whole study duration in algae and macrophytes, respectively
- Hotspot management to stick to good agriculture practice was very effective in reducing the frequency of potential mixture effects even further
- The results suggest that an additional mixture assessment factor would not improve the risk assessment given this low percentage
- Efforts should rather concentrate on point-source management, which would not be addressed by risk assessment and/or mixture toxicity assessment