

Background and Aims

Agrochemicals

- Agrochemicals currently needed to meet the global food demand (UN SDG 2), but has harmful effects on the environment and non-target organisms (UN SDG 14 & 15) making agrochemical a wicked problem
- Analysis of structure required for understanding structural-activity relationship (SAR)
- Better analysis method required to fully understand the impacts of agrochemical application to achieve the UN SDGs

Ion Mobility-Mass Spectrometry (IM-MS)

- Additional dimension to the analysis
- Ability to resolve coeluting analytes and isobaric species
- Reduction of false positive detections
- Allows structural characterisation and SAR studies

Project Aims

- Structural characterisation and SAR investigation of agrochemicals



Methods

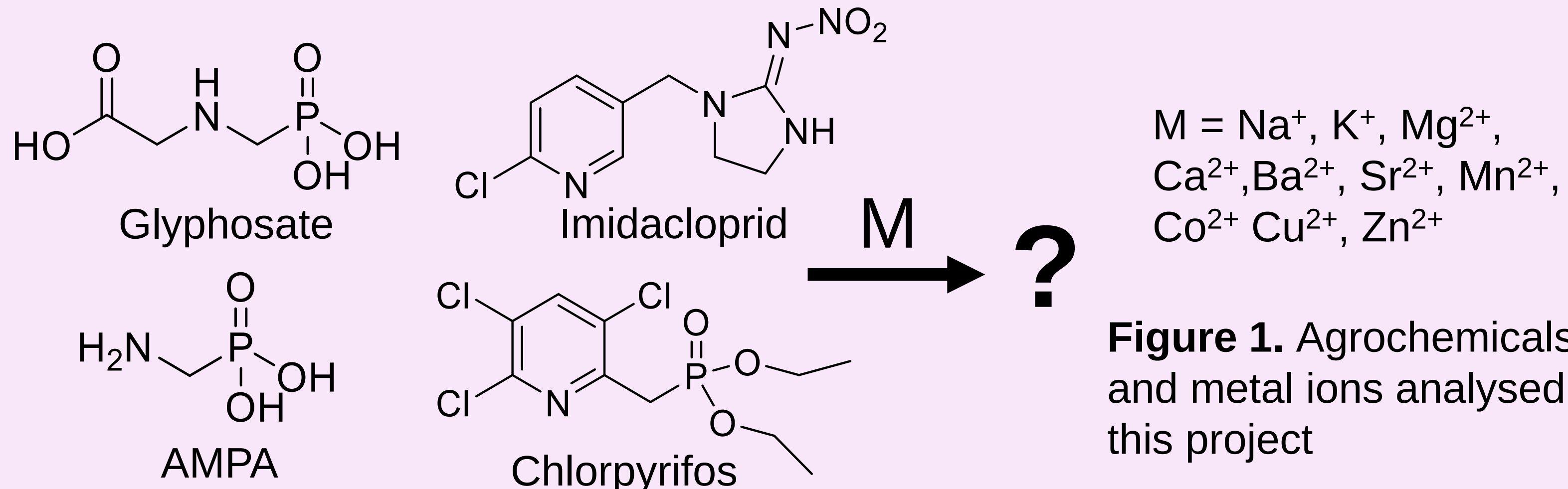


Figure 1. Agrochemicals and metal ions analysed in this project

- Sample analysed using electrospray ionisation (ESI) IM-MS on 3 different types of ion mobility instruments: drift tube (DTIMS), trapped ion (TIMS) and travelling wave (TWIMS)
- Density functional theory (DFT) applied for computational geometry optimisation prior to collisional cross section (Ω) calculation
- Comparison of experimental and computational Ω to characterise structures of agrochemical-metal complexes

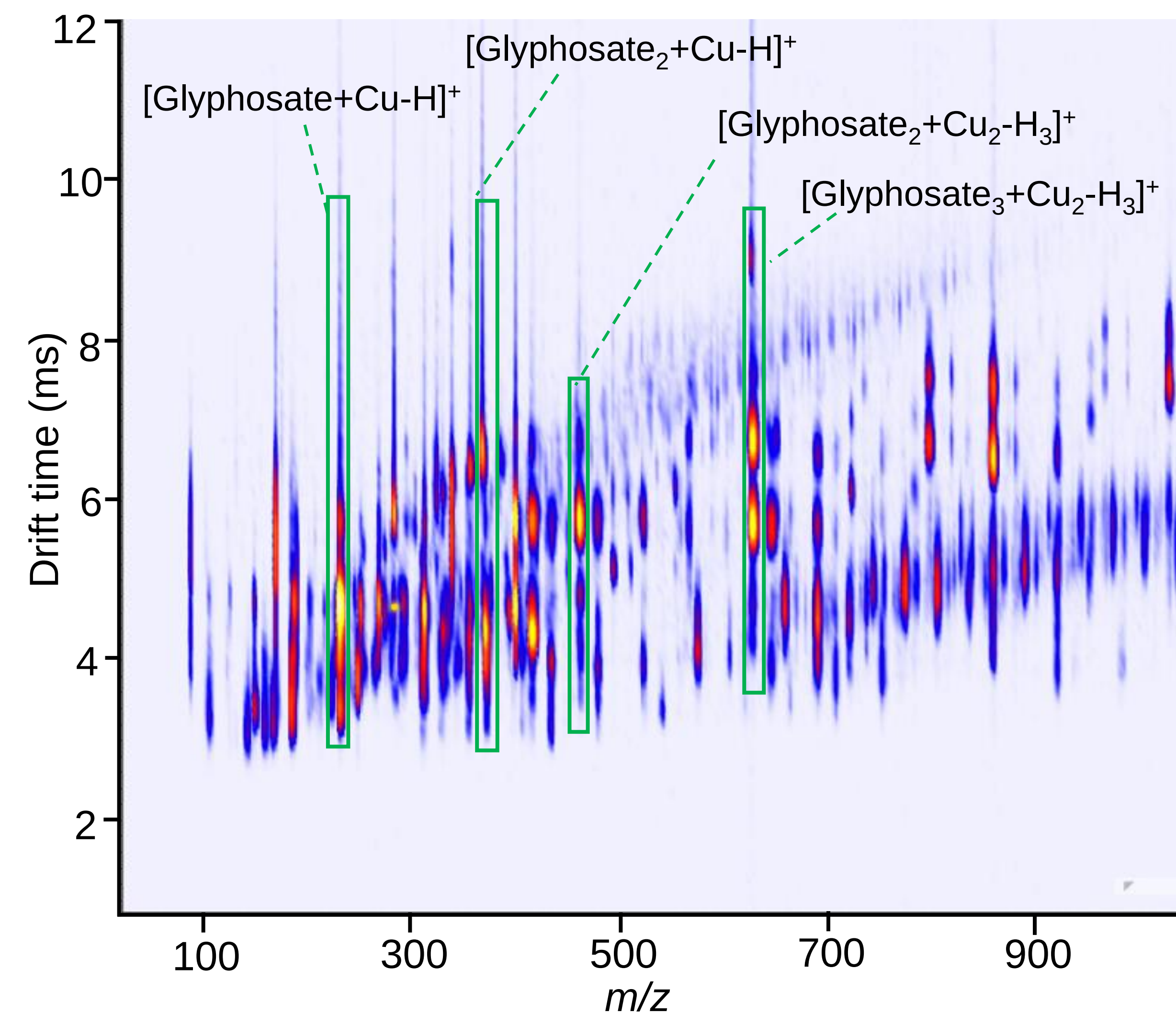


Figure 2. ESI-TWIMS-MS mobilogram of Glyphosate + Cu^{2+} with some assigned assemblies.

Table 1. Experimental and calculated Ω_{N_2} values of $[Glyphosate+Cu-H]^+$ and $[Glyphosate_2+Cu-H]^+$

	DTIMS	TIMS	TWIMS		Calculated
			Vion	Synapt	
$[Glyphosate+Cu-H]^+$	139.5	152.6	135.05	134.58	132.6
	158.5	170.8	167.98		
	171.5	177.6	198.68		
$[Glyphosate_2+Cu-H]^+$	161.7	166.7	170.18	162.81	178.1
	168.4		228.02		

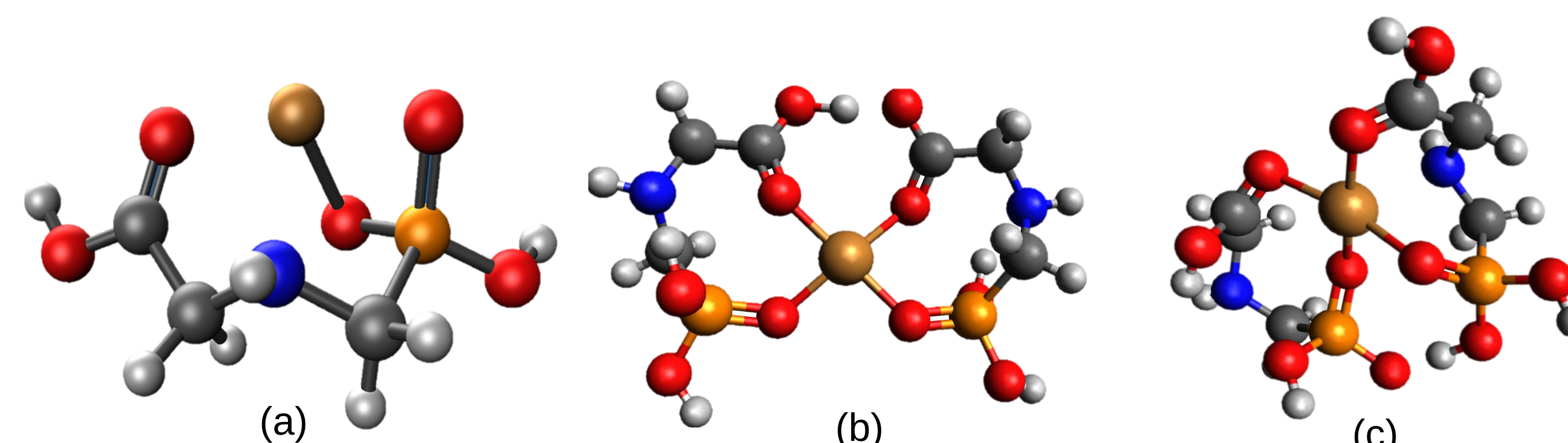


Figure 3. DFT optimised structures of possible $[Glyphosate+Cu-H]^+$ (a) and $[Glyphosate_2+Cu-H]^+$ (b and c) geometries.

Discussion

- Glyphosate readily complexes with divalent metal cations ubiquitous in the environment forming multiple structural assemblies (Figure 2)
- Similar results observed on other types of agrochemicals
- Concentration of agrochemicals present as complexes are currently neglected in routine analysis
- Analysis method capable of identifying complexes with different structure is important
- ESI-IM-MS combined with computational method allow structural characterisation of these complexes by comparing the experimental and calculated Ω values
- Structural characterisation of these complexes is the first step to understanding its characteristics and behaviours and would lead to better analysis and regulations that would be more aligned to the UN SDGs

Conclusions

- Established framework for measuring Ω of agrochemical metal complexes using IM-MS
- Predicted structures of agrochemical complexes using computationally
- Successfully obtained consistent results across different types of ion mobility instruments
- More assignments and calculations required to characterise more structural assemblies

Future Works

- DTIMS Ω library of agrochemicals
- High-throughput agrochemical screening and in-depth SAR studies
- Workflow automation for agrochemical analysis

References

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