STRUCTURAL CHARACTERISATION OF GLYPHOSATE AND AMPA METAL COMPLEXES USING ION MOBILITY-MASS SPECTROMETRY

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N-(phosphonomethyl)glycine or Glyphosate is the most used herbicide globally. First developed in the 1970s, it quickly gained popularity due to its extreme efficacy and its non-selective trait in exterminating weeds. Recent studies have also linked Glyphosate and its primary metabolite, aminomethylphosphonic acid (AMPA), to multiple adverse health effects from metalloenzyme inhibiting activities to non-Hodgkin's lymphoma. Both Glyphosate and AMPA are zwitterionic and have multiple reactive functional; groups that can readily participate in coordination bonding, and polymerisation, (Figure 1) allowing them to easily form various complexes with divalent metal cations, including multiply charged species. The metal complexes formed possess extraordinarily rich structural variability. Structural characterisation of these complexes is highly desirable as that would provide better mechanistic understanding of their behaviour, characteristics, interactions, and biological and environmental fate. Ion mobility is an analytical technique where ions are separated based on their interaction with an inert drift gas under the influence of an electric field. In addition to the separation, ion mobility also allows users to access an additional analytical dimension which is ions' collisional cross sections. In tandem with mass spectrometry, the technique is fit for this purpose as it can separate isomers that are cannot be resolved over mass spectrometry. alone. Here, target $[Glyphosate+M-H]^+$ and $[AMPA+M-H]^+$ complexes where M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} were structurally characterised. Multiple IMS-MS techniques including drift tube (DTIMS), trapped (TIMS) and travelling wave (TWIMS) were used to robustly characterise the Glyphosate and AMPA metal complexes under different instrumental conditions. Density functional theory (DFT) structures were generated to computationally predict potential collisional cross sections. These theoretical values were compared to the experimentally obtained values to gain further structural insight. Experimental results have confirmed that there is a common structure preferred by the complexes across the different metals investigated. However, there are also additional isomers with different CCS values indicating the capriciousness of Glyphosate and AMPA which is supported by the computational results and hints at the origins of adverse events and fate in the environment.

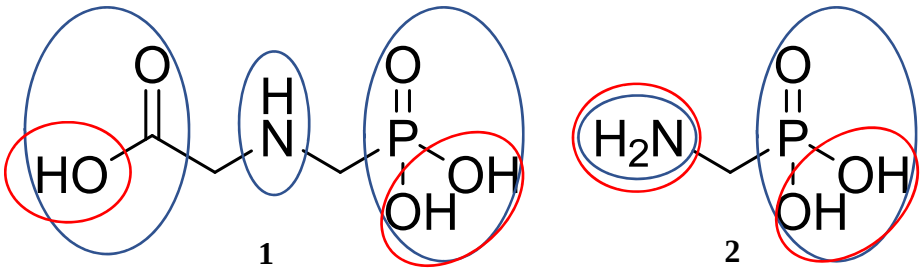

Figure 1. Structures of Glyphosate (1) and AMPA (2) with coordination sites circled in blue and polymerisation circled in red