River-Sea Systems: Spatial and temporal occurrence of Neonicotinoids, Glyphosate and related transformation products in the Chinese Bohai Sea and 36 surrounding Rivers

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Neonicotinoid insecticides (NNs) and the herbicide glyphosate are systemic pesticides widely used in agriculture and urban environments. They are the most used pesticides worldwide. Their extensive use has led to great social concerns regarding their environmental fate and toxicity to non-target organisms and to human health. Consequently, glyphosate is at risk of being banned in the EU and 3 NNs (imidacloprid, clothianidin and thiamethoxam) have recently been permanently banned for outdoor applications. Nevertheless, their use is still permitted in China. Moreover, NNs have been incorporated in the watch list of substances for the EU monitoring program in surface waters (2015/495/EU) due to possible threats to aquatic organisms. Therefore, these compounds are emerging environmental contaminants of concern.

This study investigates the temporal and spatial occurrence of 7 NNs, as well as other insecticides (fipronil, imidaclothiz, cycloxaprid and sulfoxaflor), the herbicide glyphosate and several of their transformation products in the Chinese Bohai Sea and its surrounding rivers. Water samples were collected in the summer and fall of 2018 from 36 rivers and 47 stations in the Bohai Sea. All samples were immediately stored at -20°C until analysis. All samples were extracted by solid-phase extraction (1L water sample was used for the insecticides, whereas 20 mL water sample was used for glyphosate and its main metabolite AMPA (aminomethylphosphonic acid)), eluted with methanol and further enriched by evaporation. For glyphosate and AMPA, the water samples were first derivatized with FMOC-Cl (9-Fluorenylmethoxycarbonyl chloride). All samples were analyzed by HPLC-MS/MS.

The results show that, from the 18 compounds analyzed, 15 were detected in river samples and 12 in seawater samples. Acetamiprid was detected in all river- and seawater samples. Much higher concentrations were observed in the rivers (<LOD – 4487 ng.L⁻¹) as compared to the Bohai Sea (<LOD – 120.5 ng.L⁻¹). AMPA was the compound detected at the highest concentration for both river- (4487 ng.L⁻¹ – Xiaoqinglong River) and seawaters (120.5 ng.L⁻¹), followed by glyphosate (Xiaoqing River = 463.6 ng.L⁻¹; seawater = 27.4 ng.L⁻¹) and then by acetamiprid (Duliujian River =
127.4 ng.L\(^{-1}\); seawater = 1.7 ng.L\(^{-1}\)). Except for AMPA, all compounds were found at higher concentrations during the summer season.

In conclusion, the ubiquitous presence of acetamiprid and the high concentrations and detection frequencies of AMPA in the sampled waters suggest a high persistence and stability of these compounds in surface waters. Therefore, these compounds may accumulate in aquatic/marine environments and may pose a risk to aquatic/marine organisms. The Bohai and Laizhou Bays presented the highest contamination status, to where most contaminated rivers were flowing, indicating that riverine discharges are important contributors to the pollution status of the marine environment. The higher detection frequencies and concentrations of the transformation products of imidacloprid, fipronil and glyphosate in the marine environment indicate the rapid degradation of their parent compounds during their “journey” from the contaminated rivers to the Bohai Sea. Since evidence shows that these transformation products have similar or even higher persistence and toxicity to non-target organisms, it is important to further monitor these compounds in the marine environment.