Evaluating a novel oxidation process for the environmental fate of pesticides (Ref IAP2-18-145)

Newcastle University, School of Engineering
In partnership with Durham University

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Key Words
Emerging contaminants, oxidation, minerals

Overview

Anthropogenic activities intentionally and unintentionally release a multitude of organic contaminants to the environment. These contaminants are often present in very low concentrations in the environment, and hence are called ‘micropollutants’, yet they are highly potent and can persist over decades in water bodies, soils, and sediments, affecting surface and groundwater quality, ecosystem and human health [1].

In this context, chemicals used in agriculture, and here mostly pesticides, are a particular concern as their application over large areas can lead to large scale contamination of entire watersheds. Although their use is highly regulated in the UK, surface runoff and leaching into the subsurface can still lead to pesticide concentrations in surface and subsurface water resources that compromise them for use as drinking water supply and negatively affect non-target organisms [2]. In developing countries, the threat to water resources and human health posed by pesticides is often even more dire as the use of pesticides is pervasive, regulations are enforced only patchily due to lack of resources, and pesticides banned in the UK are still widely used owing to their low price and high effectiveness [2].

Pesticides are designed to be stable for application on agricultural land, and thus are degraded only slowly by natural processes such as microbial activity or light-induced transformations. Just recently, a previously unknown process involving naturally occurring minerals was discovered and has yet to be evaluated for the fate of micropollutants such as pesticides. Because this novel process is proposed to lead to the formation of highly reactive oxidizing species such as hydroxyl radicals [3] this process might be an important irreversible sink for pesticides in subsurface environments that undergo cycles of reducing and oxidizing conditions [4].

This project will thus assess whether and to what extent interactions of ferrous iron-bearing clay minerals with pesticides affect their environmental fate. We will explore the interactions of model pesticides with iron-bearing clay minerals during cycles of reducing and oxidizing conditions to monitor the effect of the newly discovered oxidation process. In addition, we will also probe whether sorption of pesticides to the minerals is a prerequisite for pesticide transformation and to this end will use pesticides that differ in their sorption extent and mechanism. To provide profound understanding of the governing processes, we will complement wet-chemical experiments and mineral characterization with microscopic approaches and molecular modeling.

Methodology

The student will be based in the School of Engineering at Newcastle University (supervised by A. Neumann) and spend significant time at the University of Durham for the relevant parts of the project (microscopy – supervised by K. Voitchovsky, molecular modeling – supervised by C. Greenwell).

The project will involve mainly lab experiments with well-characterized clay minerals, which will be studied in batch and column experiments. Sorption and oxidation reactions will be studied separately as well as
in combination to delineate their relative importance. The pesticides will be chosen based on their propensity to oxidation reactions, the knowledge of transformation products and the ability to quantify them, as well as their likely sorption mechanism (positive specific interactions, positive non-specific interactions, repulsion).

The minerals will be characterized before and after reaction with pesticides using X-ray diffraction (XRD), infrared spectroscopy (FT-IR), and Mössbauer spectroscopy, to provide insights into pesticide sorption (XRD, FT-IR) and clay mineral iron speciation (Mössbauer). Sorption and transformation of the pesticides will be monitored by quantifying the parent pesticide as well as the main transformation products with liquid chromatography methods (HPLC and/or LC-MS).

The binding mechanism and type of interactions involved in sorption of pesticides to the clay minerals will be evaluated by combining microscopic approaches (atomic force microscopy – AFM) with molecular modeling. AFM enables in-situ visualization of the mineral-liquid interface with single ion/molecule resolution [5] and will be used to gain atomistic insights into the binding of pesticides to the minerals. Simultaneously, the interaction force between single pesticide molecules and the mineral will be accurately measured by force spectroscopy to assess the effect of cycles of reducing and oxidizing conditions. This will be complemented by studying bulk adsorption binding energies, using molecular mechanics and employing the widely recognised ClayFF parameter set. To further understand redox reactions of bound pesticide species, density functional theory calculations will be undertaken using the CASTEP code.

Timeline

Year 1: Detailed literature review; training in laboratory techniques and development of analytical methods; commencement of batch reactor experiments
Year 2: Continuation with batch reactor experiments; training in and application of microscopy and modeling; preparation of 1st journal article and conference presentation towards end of year
Year 3-3.5: Column experiments (to be concluded by end of third quarter); writing up of thesis and preparation of journal article(s)

Funding ceases after 3.5 years

Training & Skills

The student will be trained in all laboratory skills, analytical techniques, and modeling approaches required for this project. Training in all aspects of laboratory work, from planning over implementing to critically assessing, will be provided at Newcastle University (NCL). Here, the student will also receive training in experimenting and working with samples under the exclusion of oxygen, be trained in FT-IR and Mössbauer spectroscopy, as well as become familiar with the routine analysis method of HPLC for organic contaminants. Specialized training in the advanced analytical method LC-MS will be provided, if and when necessary, by experienced technical staff who are dedicated to this state-of-the-art analytical instrument (NCL). Specialized training in clay mineralogy and techniques and approaches for their characterization will be delivered through an established 1-week course at the James Hutton Institute in Aberdeen (https://hutton.ac.uk/events/clay-mineralogy-and-its-application-oil-industry). Similarly, the student will receive training at the University of Durham (UoD) in state-of-the-art microscopy (AFM) and force spectroscopy, as well as molecular modeling approaches. Further training needs will be assessed during the first three months of the PhD, involving the PhD student and the entire supervisory team, and a detailed training plan will be developed. This training plan might also include relevant taught MSc modules at NCL or UoD. Furthermore, the PhD student will be encouraged to make use of the broad suite of training opportunities in transferable skills provided at NCL. The supervisory team will build on these skills trainings and consolidate and deepen the student’s critical analysis and writing skills, their proficiency in preparing manuscripts for publication in peer-reviewed journals, and their competency at delivering conference presentations.

References & Further Reading

[4] Zeng, Q.; Dong, H.; Wang, X.; Yu, T.; Cui, W., Degradation of 1, 4-dioxane by hydroxyl radicals
produced from clay minerals. *J Hazard Mater* *2017, 331*, 88-98.


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**Further Information**

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