

The Natural Photo-transformation Process of Pesticides in Atmospheric Droplets

Objectives and Background

When pesticides are sprayed onto crops a significant amount enters the atmosphere. Droplets which land on soil, plants or in water can further also evaporate. However, much of the research conducted on such subjects depict pesticides in "bulk" liquid phases, thus ignoring microdroplets. It is important to analyse microdroplets as they can react differently due to their large specific surface areas, pH gradients, surface electric fields and so on. Hence, some reactions that would proceed quickly in microdroplet phases will not occur in traditional liquid phases.

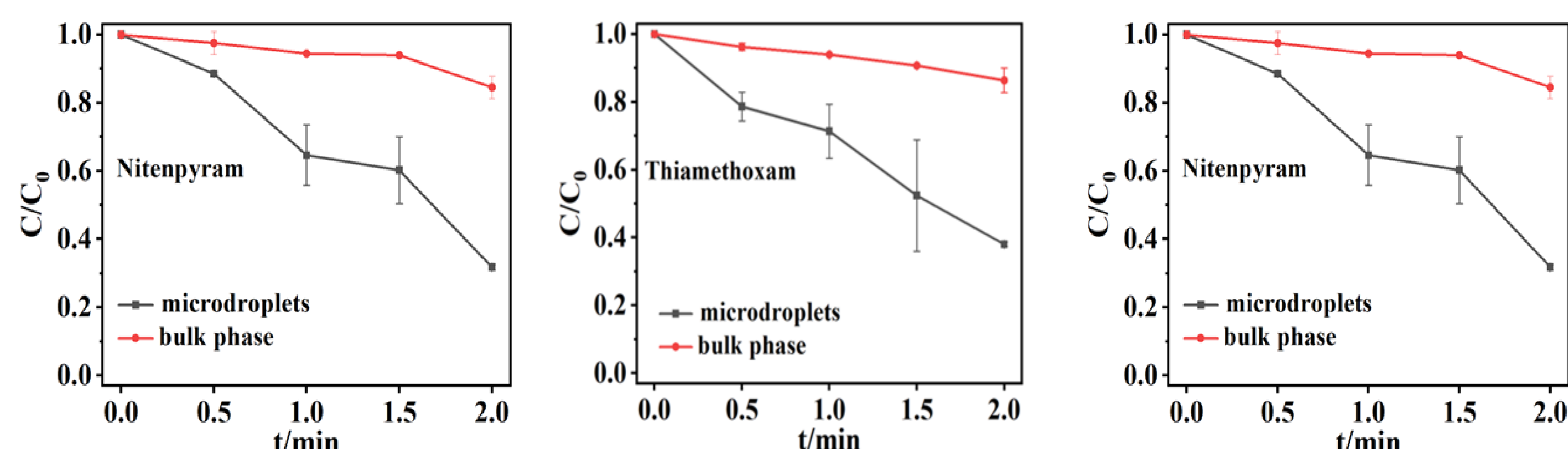
Therefore, our research investigates the photo-degradation of certain pesticides (nitenpyram, imidacloprid and thiamethoxam) in atmospheric microdroplets with different reactants and in bulk phases. We analysed their transformation processes and mechanisms including direct photolysis, radical oxidation, etc.

Methods and Results

For all experiments the setup was: A Xe Lamp set to a 12A current, each pesticide brought to a (20mL) 10ppm concentration with pH4 water ($H_2SO_4/NaOH$).

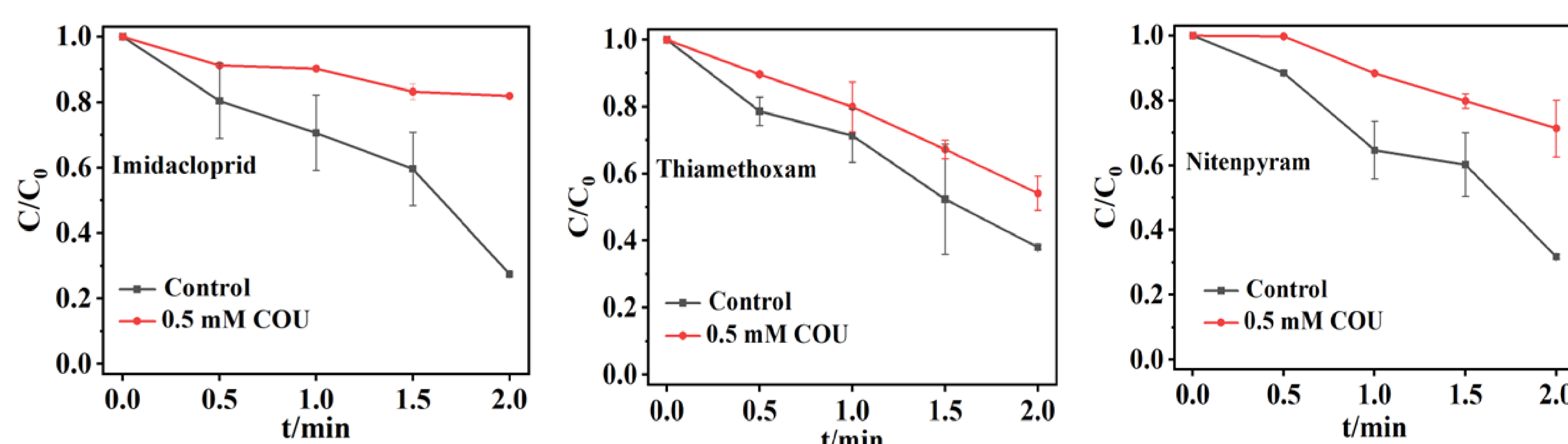
Initial Microdroplet Analysis (IMA) and Bulk Phase Analysis

The solution was sprayed onto a polytetrafluoroethylene membrane and irradiated in a water filled reaction chamber; inhibiting evaporation. Parallel samples (80 μ L) were collected with a glass slide at 30s intervals From 0-2m and stored with pure water (80 μ L). All samples were analysed under HPLC. Leftover solution was poured into a glass bottle and measured following the same time intervals and sampling guidelines as above.



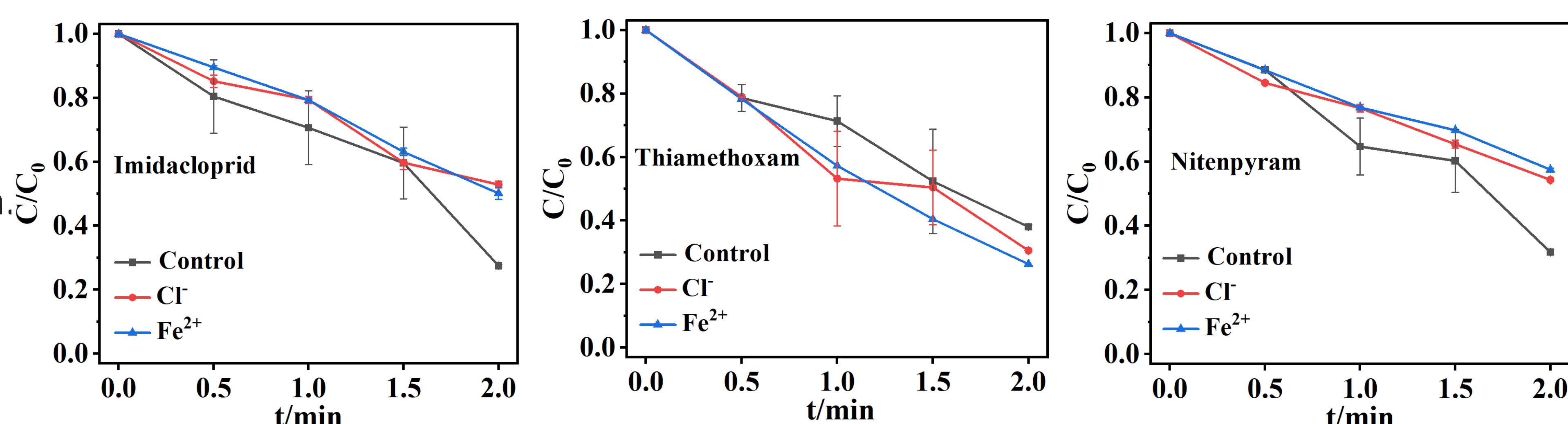
Direct Photolysis vs Free Radical Oxidation

The IMA guidelines were followed however, 20 μ L of coumarin (500mM) was added initially to quench OH^\cdot . Its final concentration was 0.5mM.



Chloride and Iron(III) ions influence

The IMA guidelines were followed but 20 μ L of NaCl (10'000ppm) was added to the initial solution. Then again with 20 μ L of $Fe_2(SO_4)_3$ (10'000ppm) added initially. The final concentration of both ions is thus 10ppm.



Conclusions and Discussion

The rate of degradation in microdroplet phases was significantly faster than that in bulk phases because of the nature of a droplet, for one there is a much larger air-water interface in microdroplets compared to bulk phases.

It is known that hydroxyl radicals (formed from the irradiation of a hydrogen peroxide solution) will quickly convert gaseous pollutants into secondary organic aerosols and nitrates in the atmosphere. Quenching these radicals with coumarin will decline the rate of transformation of our pollutants as this reaction mechanism is limited. Hence, our graphs show decreased reaction rates when quenching.

Although the addition of Fe(III) ions could have increased reaction rate as they could have partaken in the Photo-Fenton reaction (the creation of hydroxyl radicals from hydrogen peroxide and iron under acidic conditions) this was not observed, perhaps due to an insufficient Fe(III) ion concentration for producing an adequate amount of hydroxyl radicals.

References

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