Seasonal Variations in Indirect Photolysis Rates in UK Surface Water Bodies

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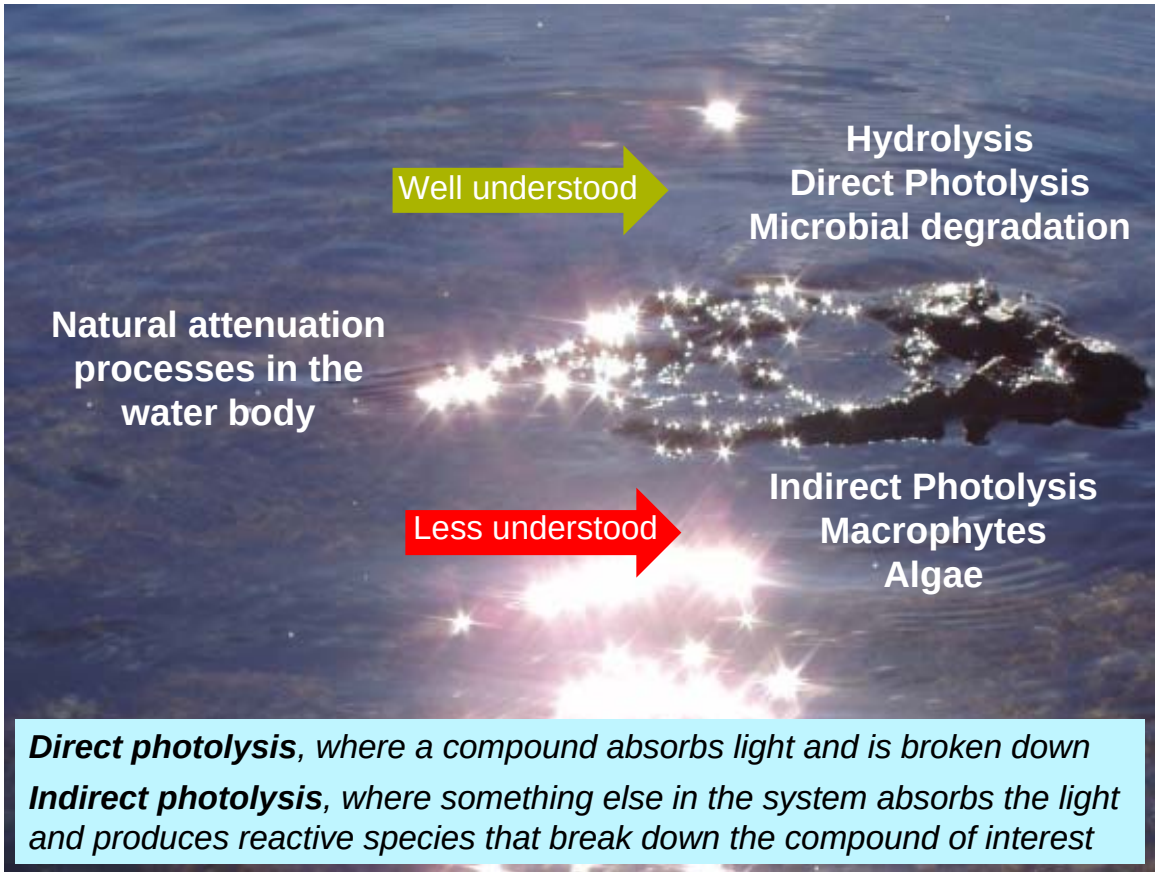
Introduction

- Agriculture faces an ongoing challenge of growing more (food, feed, fibre) from less (land, water)
- Crop Protection Products (CPPs) support agriculture by helping with the management of pests and diseases
- Significant efforts are being made (e.g TOPPS) to avoid CPPs moving to water bodies
- However in some situations some of the applied CPP may reach surface waters (drift, run-off, drainage)

Potato Blight

Low Drift Nozzles



***Direct photolysis**, where a compound absorbs light and is broken down*

***Indirect photolysis**, where something else in the system absorbs the light and produces reactive species that break down the compound of interest*

- Important photosensitizers in natural waters include
  - NO_3^-, CO_3^-, Fe^{3+}, dissolved organic matter (DOM)
- These produce radical species such as
  - hydroxyl, hydrated electron, triplet state DOM, reactive oxygen
- A previous study[1] indicated that indirect photolysis can make a significant contribution to the photodegradation of a range of CPPs
- In most cases, nitrate was the natural water constituent most highly correlated with faster degradation rates

$$NO_3^- \xrightarrow{h\nu} {}^{\bullet}NO_2 + {}^{\bullet}O^- \xrightarrow{H^+} {}^{\bullet}OH$$

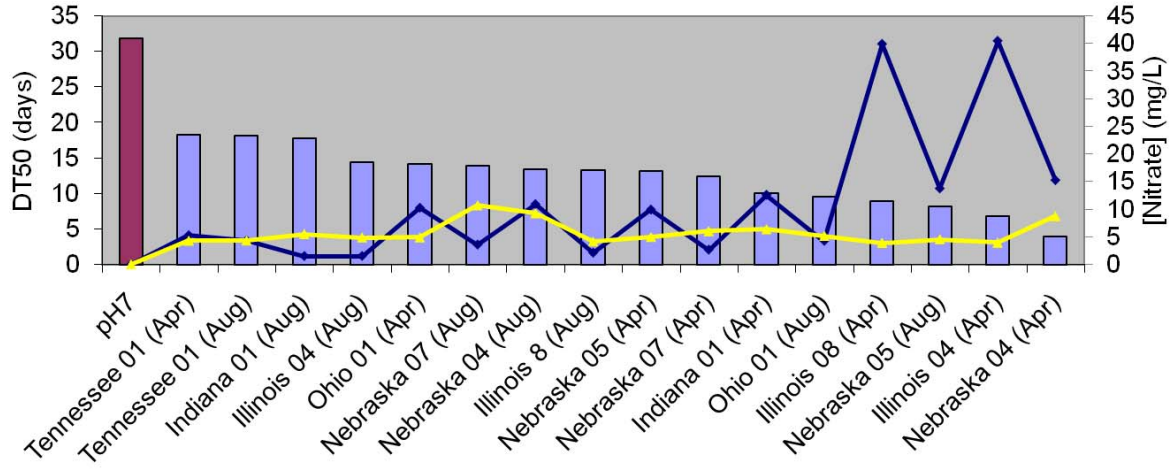
$$NO_2^- \xrightarrow{h\nu} NO + {}^{\bullet}O^- \xrightarrow{H^+} {}^{\bullet}OH$$

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\bullet}OH$$

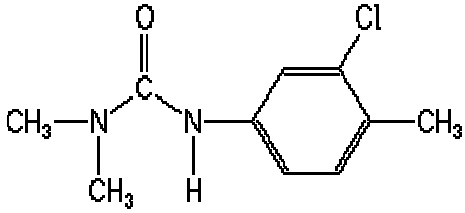
$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + OH^- + {}^{\bullet}OH$$

[1]The role of indirect photolysis in limiting the persistence of Crop Protection Products in Surface Waters, Environmental Toxicology and Chemistry (in press)

Photodegradation rates of chlorotoluron in a range of natural waters



- Moderate direct photolysis rate
- Nitrate was the most highly correlated constituent (Pearson = -0.37)

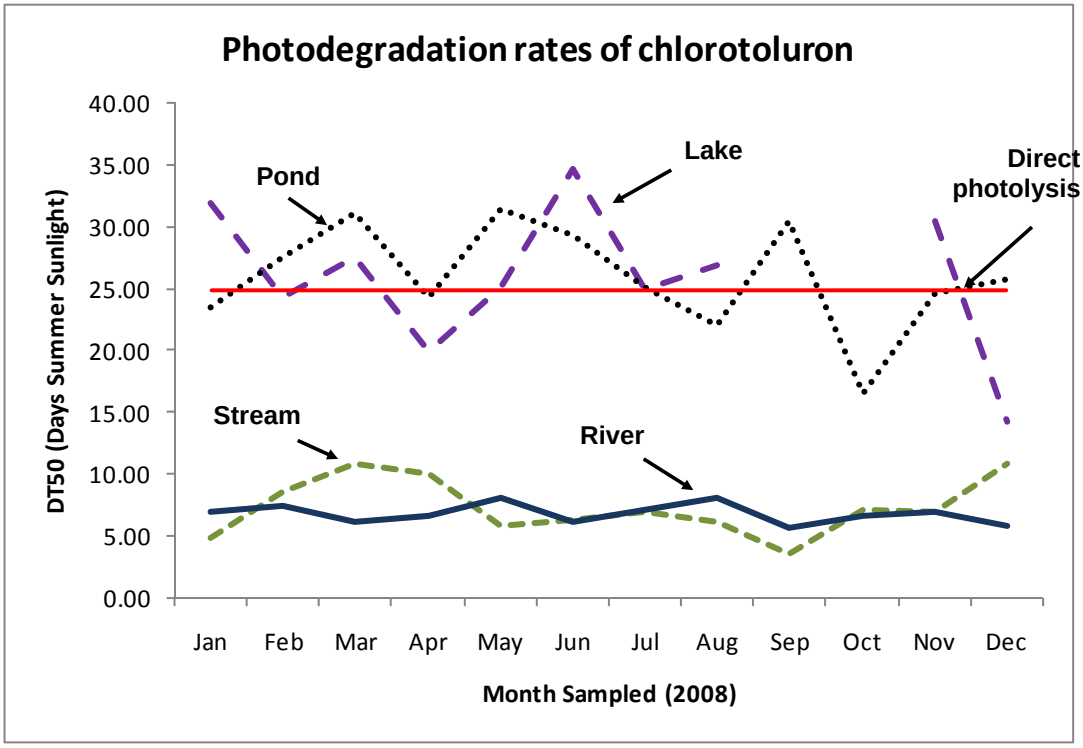


- Given that indirect photolysis is driven by the composition of natural water it is possible that the significance of the process may vary depending on;
  - the type of water body
  - seasonal changes in the composition of the water body
- To investigate these the photodegradation rate of chlorotoluron was investigated in 4 contrasting UK water bodies sampled monthly for a year
- Concentrations of bicarbonate, nitrate, dissolved organic carbon and iron were also determined

Methods

- Waters sterilised by gamma irradiation (25KGy)
- ^{14}C and closed system used to ensure mass balance
- Hanau Suntest system was used to simulate sunlight
- Measure light intensity at each position
- Sterility checked before and after photolysis
- Analysis by radio-HPLC
- Temperature monitoring (approx 25^{o}C ± 2)
- Correct for natural light intensity
- Regression based on 4 data points

Results



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	Nitrate	TOC	Bicarbonate	Iron
Stream	-0.565	-0.22	-0.214	-0.311
River	-0.407	-0.157	-0.046	0.488
Lake	-0.665	-0.479	0.722	0.428
Pond	-0.247	-0.057	-0.06	0.065

Pearson correlations of DT50 with constituents of the waters

- As expected, these data suggest that nitrate is the most important constituent of the waters
- Relationship is probably not linear

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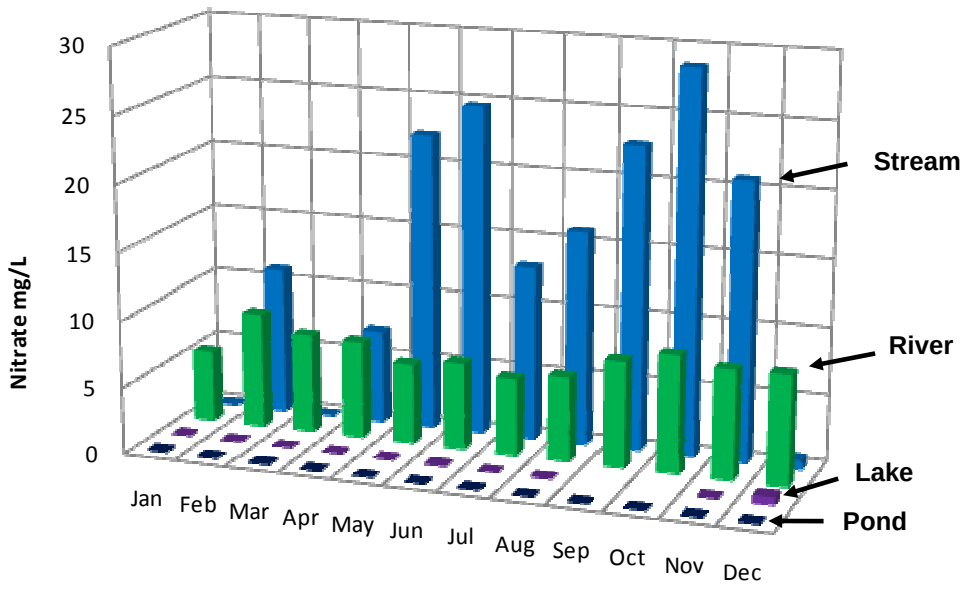
Variation in nitrate concentration in each water body



- Some seasonal variation in nitrate concentrations but doesn't seem to be reflected in degradation rates

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Conclusions

- Indirect photolysis (probably mediated by nitrate) can increase photodegradation rates of chlorotoluron by 4-5 fold
- The type of water body (nitrate concentration) had a greater influence than seasonal variation on the degradation rates observed
- There was no distinct seasonal variation in the photodegradation rate of chlorotoluron in any of waters tested
- Indirect photolysis can be an important process when considering persistence of organic compounds in surface waters

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Further work

- It would be useful to repeat the work with other chemistries
- More work is required to understand the kinetics of indirect photolysis
  - influence of sensitizer concentration
  - influence of temperature
  - relationship with light intensity