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Environ. Sci. Technol. Lett., **Just Accepted Manuscript** • Publication Date (Web): 16 Jun 2015

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Quantum yields for direct photolysis of neonicotinoid insecticides in water: Implications for exposure to non-target aquatic organisms

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ABSTRACT

Environmental fate processes of neonicotinoid insecticides are of significant interest, given the serious threats these chemicals can pose to non-target organisms such as pollinators (e.g., bees). Direct photolysis was investigated using a laboratory photoreactor approximating full-spectrum sunlight to predict the aquatic fate of neonicotinoids. Quantum yields (ϕ_c) were 0.019±0.001, 0.013±0.001, 0.0092±0.0005, 0.0022±0.0003 and 0.0013±0.0002 for thiamethoxam, clothianidin, imidacloprid, acetamiprid and thiacloprid, respectively. Based on these values, estimated half-lives were 0.2-1.5 days for different seasons in surface waters at temperate latitudes for thiamethoxam, consistent with the 0.98 day half-life observed experimentally outdoors at Winnipeg, Manitoba, Canada (50°N) for thiamethoxam in summer. Light attenuation through shallow clear surface waters (e.g., by natural organic matter) indicated that photolysis of thiamethoxam at depths greater than 8 cm was negligible, which may help explain reports of their environmental persistence.

INTRODUCTION

Neonicotinoid insecticides are widely used in agriculture to protect against a variety of pests such as whiteflies, beetles and termites.[1] Neonicotinoids act by selectively binding with the nicotinic acetylcholine receptor to disrupt neural transmission.[2] They are applied as seed coatings or as foliar sprays, and released via seed leaching, spray drift, surface run-off, and wind or animal-mediated dispersal of contaminated pollen and nectar from treated plants.[3] Consequently, they are widely detected in environmental media such as plants,[4] soil and water.[5] Neonicotinoids are of great environmental concern because they exhibit adverse effects on pollinators (e.g., bees),[1,6,7] non-target invertebrates,[8] vertebrates[9,10] and even humans.[11] Furthermore, the controversial nature of neonicotinoids and their possible link to major bee die-offs globally has increased pressure to phase out this class of insecticides,[12] as exemplified by a recent two-year moratorium in Europe.[13, 14] However, it is not clear if neonicotinoids are responsible for declines in bees, or if other variables are in play, as pollinating species can experience complex and confounding environmental stressors. That, combined with the paucity in data characterizing exposure via realistic field studies, makes it difficult to isolate the issue just to neonicotinoids.[12,14] It is thus essential to understand the environmental processes controlling the fate of neonicotinoids to inform better decisions relating regulations of these insecticides.

Direct photolysis is an important factor affecting the environmental fate of many organic contaminants, including neonicotinoids.[15,16] The quantum yield (ϕ_c) is a characteristic parameter defining how efficiently a compound degrades upon absorption of a photon,[15,17] facilitating the modeling and prediction of direct photolysis rate constants (k_p) and half-lives ($t_{1/2}$).[17] Although the photodegradation of neonicotinoids using either laboratory photoreactors or natural sunlight has been investigated,[16,18-20] to our knowledge there exists no peer-reviewed literature reporting ϕ_c values under environmentally relevant conditions (i.e. λ>290 nm). Some internal reports,[21-29] including those from the European Commission [21-24] and the U.N. Food and Agriculture Organization (FAO),[25-28] report ϕ_c

values for acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam. However the experimental conditions and reliability of these values are unknown, and independent verification is required. For example, the *p*-nitroanisole (1×10^{-5} M)/pyridine (2.5×10^{-3} M) actinometer system, which could not provide a similar half-life of all target compounds (from 3.5 min to 254 h) and consequently correct photon flux monitoring, was used for the determination of ϕ_c of several neonicotinoids in various unpublished phototransformation experiments.[29]

Thus, our objective was to determine ϕ_c values of the frequently used neonicotinoid insecticides thiamethoxam, clothianidin, imidacloprid, acetamiprid, and thiacloprid in water with a laboratory photoreactor under environmentally relevant light conditions. These results were further evaluated (for thiamethoxam only) under natural sunlight to investigate indirect photolysis and biotic degradation processes, as well as effects of light attenuation through the water column. This will allow prediction of the persistence of these chemicals in surface waters, and aid in ascertaining exposure levels to vulnerable non-target species (e.g., pollinators).

MATERIALS AND METHODS

/Details on chemicals and reagents used, including structures and basic physical-chemical parameters of the studied neonicotinoids, are listed in Supporting Information (SI). All irradiations were performed using a Rayonet Merry-Go-Round Photochemical Reactor (model RPR-100, The Southern New England Ultraviolet Company, Branford, CT). The photoreactor had 16 medium-pressure mercury lamps with spectral emission ranging from 250 to 400 nm, centered at 300 nm (Figure S1 and Table S2).[30] Cylindrical Pyrex tubes (50mL) which filtered wavelengths <290 nm were used as irradiation vessels.

The *p*-nitroanisole/pyridine and *p*-nitroacetophenone/pyridine actinometer systems[31] were used to monitor photon flux in the photoreactor, with 4.6×10^{-5} M *p*-nitroanisole and 0.01 M pyridine for ϕ_c

determination of thiamethoxam, clothianidin and imidacloprid, while 6.0×10^{-5} M *p*-nitroacetophenone and 0.01 M pyridine were used for experiments with acetamiprid, thiacloprid and the outdoor experiment of thiamethoxam. Actinometers were included in all irradiation and dark experiments.

Triplicate laboratory irradiations (10 mg/L, high concentrations were used to facilitate photoproduct identification) were conducted with 40 mL solutions of each individual insecticide in 50 mM borate buffer at pH 7.4 in Pyrex tubes. Given the pK_a values for these five neonicotinoids are well above or below (>2 pH units) this pH (Table S1),[32] each compound is present only as a single species during the duration of these experiments. Dark experiments were carried out in an oven that matched the maximum temperature (45°C) and time reached in the photoreactor.[30] Experiments were performed in triplicate over 45 min for thiamethoxam, clothianidin and imidacloprid, and 36 h for acetamiprid and thiacloprid. Chemical concentrations were determined using high performance liquid chromatography (HPLC) with diode array detection, while photoproducts were measured using HPLC tandem mass spectrometry and time-of-flight high resolution mass spectrometry (QTOF) as detailed in SI.

Detailed methods for calculating molar absorptivity and ϕ_c (290-360 nm) using our actinometers, as well as natural sunlight estimations (SI) were published previously.[17,30] The solar irradiance parameter (L_λ) used for the $t_{1/2}$ estimation of neonicotinoids under sunlight was obtained from the literature.[33]

Degradation of thiamethoxam under natural sunlight conditions was assessed at the Prairie Wetland Research Facility at the University of Manitoba in July 2014. Details of this facility are published elsewhere.[34] Briefly, sealed Pyrex tubes containing thiamethoxam and nanopure water were deployed in three randomly-selected 3500 L mesocosms containing approximately 2000 L of water, natural uncontaminated sediments, macrophytes, and invertebrates typical of Canadian Prairie wetlands, at different depths (0 cm, 8 cm, 18 cm and 28 cm). Photon flux was measured using *p*-nitroacetophenone/pyridine at these depths, along with dark controls as above. In order to clarify whether other environmental degradation processes such as non-photolytic abiotic transformation (e.g., hydrolysis), microbial biotransformation and indirect photolysis were involved in removing thiamethoxam during the experiment, other control tubes were deployed in triplicate (see SI for details).

RESULTS AND DISCUSSION

Photolysis kinetics and quantum yields

The photolysis of neonicotinoid insecticides, which absorb photoreactive light (Figure S2) followed pseudo-first-order kinetics (Figure 1). No loss of these insecticides was observed in the dark (Figure 1). Imidacloprid, clothianidin, thiamethoxam, acetamiprid, and thiacloprid exhibited direct photolysis half-lives of 12±0.4 min, 12±1.1 min, 22±1.3 min, 26±1.0 h and 42±1.6 h, respectively (Figure 1). Direct photolysis ϕ_c were calculated as 0.019±0.001, 0.013±0.001, 0.0092±0.0005, 0.0022±0.0003 and 0.0013±0.0002 (290-360nm) for thiamethoxam, clothianidin, imidacloprid, acetamiprid and thiacloprid, respectively (Figure 1). The averaged photon flux of the photoreactor ranged from 8.8×10^{14} to 1.1×10^{15} photons×cm^{-2} sec^{-1} over the course of the entire experiment. The half-life for thiamethoxam under natural sunlight (300-360nm) at the surface of the mesocosm water was 0.98±0.03 days (Table 1 and Figure S3A). In comparison with the surface water photodegradation, the light flux decreased 89% to 7.9×10^{13} and 98% to 1.1×10^{13} photons×cm^{-2} sec^{-1} at depths of 8 cm and 18 cm, respectively.

Given the paucity of data existing for published neonicotinoid quantum yields, it was necessary to rely on the few unpublished values from technical documents to place our results in context. The ϕ_c of direct photolysis of thiamethoxam in water was reported as 0.013±0.002 in an unpublished European Commission document (experimental conditions unknown),[21] similar to our result (0.019). The half-life of thiamethoxam was predicted to be 0.20-1.5 days at 50°N (Table 1) for different seasons based on the measured ϕ_c in the present study, which corresponds well with our measured half-life. Discrepancies are possibly due to specific weather conditions (e.g., cloudy) during the outdoor irradiations. The very similar half-life in poisoned tubes in mesocosms of 1.1±0.2 days (Figure S3B) indicates that direct photolysis dominated transformation processes for thiamethoxam. However, screening of UV light in the mesocosm water column (e.g., by natural organic matter; total organic carbon was measured as 16.5±3.1 mg/L in the present study) resulted in considerably longer half-lives at depth.[35] The pseudo-first order rate constant for thiamethoxam in tubes at the surface (0.71 ± 0.02 d^{-1}) of the mesocosm tanks decreased to 0.02 ± 0.008 d^{-1} and 0.01 ± 0.003 d^{-1}, respectively, at 8 and 18 cm depth (Figure S4). In contrast, FAO[25] reported a photolytic $t_{1/2}$ for thiamethoxam of 2.3-3.1 days in phosphate buffered aqueous solutions (pH=5) using xenon arc light irradiation. That report noted that samples were exposed to light for 12 h at an average intensity of 410 W/m^2 per day followed by 12 h dark intervals with a total reaction time for 30 days.[25] Moreover, Bonmatin et al.[32] estimated that the aqueous photolysis $t_{1/2}$ of thiamethoxam under sunlight at pH 7 to be 2.7 days. However, details of experimental conditions were not clear. Experimental designs that were inconsistent (e.g., different light sources) and/or problematic (e.g., involvement of cosolvent and inappropriate actinometer) may help explain the variability in ϕ_c and $t_{1/2}$ reported throughout the peer-reviewed and grey literature for environmental contaminants, a topic that has been fully reviewed previously.[15]

An outdoor sunlight experiment conducted in March 2012 in Zürich (47° N latitude) reported a $\phi_c = 0.0073$ and $t_{1/2} = 3.3$ h for clothianidin,[29] similar to the ϕ_c value reported by European Commission (0.014)[22] and measured in the present study (0.013 ± 0.001). The outdoor $t_{1/2}$ of clothianidin was predicted as 0.35-3.3 days for different seasons at 50° N latitude based on our measured ϕ_c. FAO[26] reported a $t_{1/2}$ of 0.6 days of summer solar exposure for clothianidin at Phoenix, Arizona (33°N latitude).

Studies by Redlich et al.[36] report laboratory measured ϕ_c values for imidacloprid determined at wavelengths <290 nm, which are not environmentally relevant. Von Gunten[29] conducted quantum yield measurements for imidacloprid under natural sunlight in March 2012 in Zürich and observed a ϕ_c = 0.0055 and $t_{1/2}$ = 2 h, comparable with our results (ϕ_c = 0.0092; Figure1 and Table 1). The environmental $t_{1/2}$ of imidacloprid in surface waters at 50°N latitude was calculated as 4.2 h at the equinox,[27] whereas our estimation was 0.36 d (8.6 h) and 0.83 d (19.9 h) in spring and autumn, respectively.

Again, good agreement is observed when comparing our results to those of von Gunten[29] who reported quantum yields from outdoor sunlight experiments (March 2012 in Zürich). Von Gunten[29] observed a ϕ_c = 0.0046 and $t_{1/2}$ = 254 h for acetamiprid under natural sunlight, which agree reasonably well with our values: ϕ_c = 0.0022 and $t_{1/2}$ (predicted) = 9.7 days in summer (232 h). In contrast, the study by the European Commission reported the ϕ_c of acetamiprid as 0.10 at λ>290 nm (experiment condition unknown), [23] which was much higher than our results (0.0022) and those values from von Gunten (0.0046).[29] However, the $t_{1/2}$ determined in this European Commission report (34 days under xenon lamp, irradiation: 12 hours/day) [23] was comparable with our estimation (9.7-68 days in different seasons), again pointing to experimental inconsistencies surrounding quantum yield determinations

The FAO[28] and European Commission[24] reported the ϕ_c of thiacloprid as 0.00035 and estimated an 80 days $t_{1/2}$ with simulated sunlight and 324 days under natural sunlight at Phoenix. Their ϕ_c was lower than our measured number (0.0013±0.0002) and the $t_{1/2}$ was higher than our results (8.8-60 days), but the reasons were not clear.

Photoproduct identification

It was evident from the HPLC-MS/MS analysis that the irradiations generated photoproducts and the abundance of these products increased with reaction time (Figure S5-S9). The mass spectra from these total ion chromatograms (TIC) were used to identify potential photoproducts, with further analysis, structural elucidation, and confirmation done using QTOF. It should be noted that chromatographic separation of photoproducts was neither attempted nor necessary for the purposes of this study, and thus, single chromatographic peaks observed in Figures S5-S9 may represent multiple photoproducts. Two photoproducts of thiamethoxam were identified, corresponding to *m/z* 247.0417 and 168.0767 (Table S3, Figures S10 and S11). Both of these masses and proposed structures correspond to major photoproducts previously identified for thiamethoxam.[20] Two photoproducts were identified for clothianidin, *m/z* 206.0149 (Figure S12) and *m/z* 205.0307 (Figure S13), both previously reported by Gong et al.,[18] however the proposed structure for *m/z* 206 in the current study differs. QTOF evidence from the fragmentation pattern of the *m/z* 206 ion supports our proposed structure (Figure S12). Please see SI for further details. Three major photoproducts were identified for imidacloprid, two of which are strongly supported by the literature and a third that has not been previously reported (Table S3). Photoproducts *m/z* 212.0586 and 211.0741 and their corresponding structures (Figures S14 and S15) have been observed multiple times in the literature.[36-39] The imidacloprid photoproduct *m/z* 189.0769 was observed for the first time in the present study (Figure S16). However, it is not clear what the structure of this observed ion is.

Photoproduct identification for both acetamiprid and thiacloprid was markedly more challenging than the other neonicotinoids, likely because of their relatively recalcitrant nature towards photolysis. Acetamiprid showed a photoproduct at *m/z* 205.1081 that corresponded to a logical structure shown in Figure S17. Alternatively, the structure of the thiacloprid photoproduct at *m/z* 235.0646 could not be confidently determined. Three plausible, very similar structures are proposed in Figure S18. Both of these photoproduct masses have not been previously reported in the literature. It should be noted that masses for acetamiprid and thiacloprid were observed in the irradiated samples at exactly 4 mass units greater than the parent masses, 227.0905 and 257.0469, respectively (Figures S17 and S18). No plausible chemical formula information was generated from the QTOF software and thus structure elucidation was not attempted, however this may warrant further investigation.

IMPLICATIONS

Thiamethoxam, clothianidin and imidacloprid will quickly undergo direct photolysis in surface waters, resulting in decreased exposure of non-target organisms consuming or exposed to water at these depths. However, light screening in waters can rapidly decrease photodegradation, as evidenced by the significant light attenuation observed in our deployments in mesocosm waters, which were clear in appearance. While those experiments were for thiamethoxam only, it is very likely that other neonicotinoids would be similarly affected. This would increase exposure of biota to these chemicals, and may help to explain their observed persistence in shallow surface waters.[5,32] In any event, acetamiprid and thiacloprid are relatively stable toward sunlight degradation in aquatic systems.

ASSOCIATED CONTENT

--Supporting information

Supporting Information available: details of experimental work, Tables S1-S3 and Figures S1-S18. This material is available free of charge via the Internet at http://pubs.acs.org.

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--Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Natural Sciences and Engineering Research Council of Canada, a University of Manitoba Graduate Fellowship (to JKC), and the Canada Research Chairs Program. The authors would like to thank Gregg Tomy for access to the QTOF instrument, Thor Halldorson for assistance running the instrument and operating the software, and Mark Hanson for technical assistance with mesocosms. We also thank Adrian Challis for technical assistance in the design and construction of the photolysis deployment racks for the mesocosm experiments.

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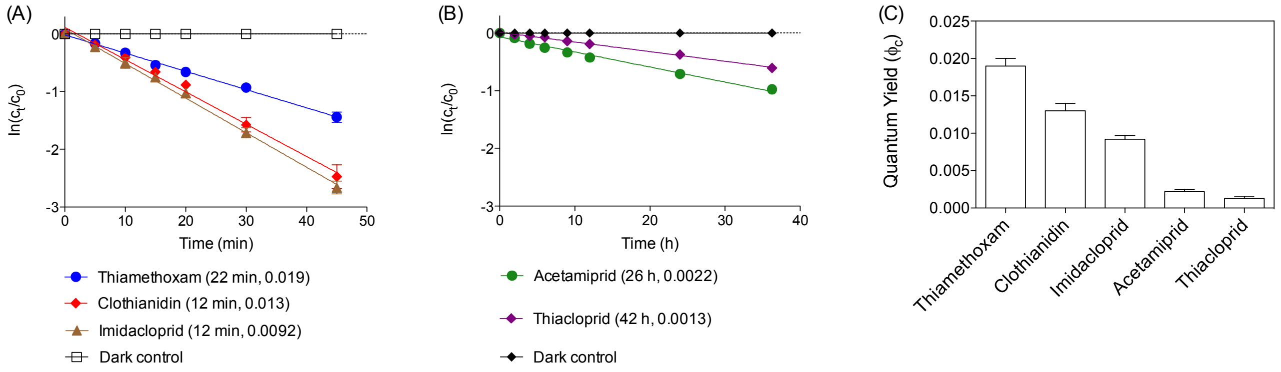
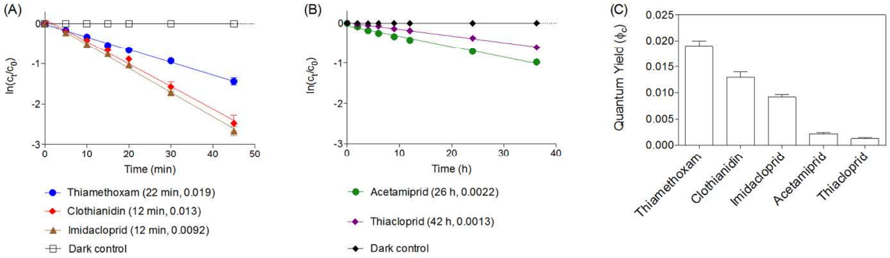


Figure 1 First-order direct photolysis (A and B) and quantum yield (ϕ_c) (C) of neonicotinoid insecticides in water for irradiations in a laboratory photoreactor. Error bars in (A) and (B) represent standard deviations (SD) of the mean. The correlation coefficients (r^2) for the pseudo first-order kinetic plots ranged from 0.982-0.994. Average half-lives and ϕ_c of each neonicotinoid insecticide are shown in brackets in the legend. Errors in (C) were calculated through error propagation.

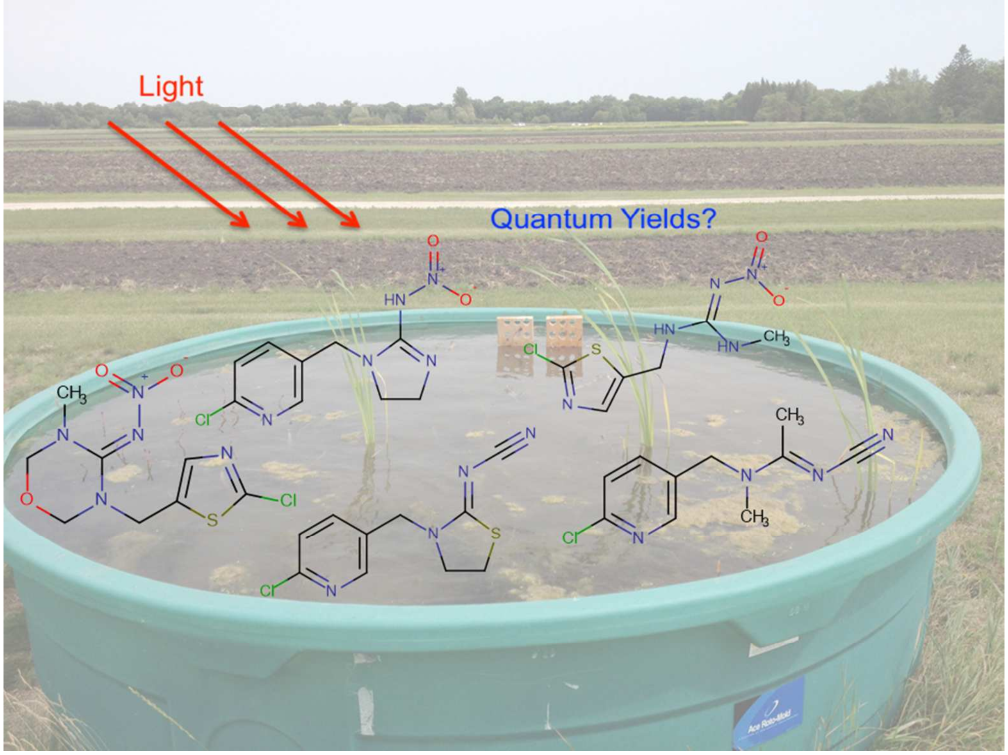
Table 1 Estimated photolysis rate constants (k_{dcE}) (days^{-1}) and half-lives ($t_{(1/2)E}$) (days) for neonicotinoid insecticides in surface water at 50° N latitude for spring, summer, autumn and winter by sunlight on clear days.

Compounds	Spring		Summer		Autumn		Winter	
	k_{dcE}	$t_{(1/2)E}$	k_{dcE}	$t_{(1/2)E}$	k_{dcE}	$t_{(1/2)E}$	k_{dcE}	$t_{(1/2)E}$
Thiamethoxam	2.17	0.32	3.46 (0.71)[a]	0.20 (0.98)[a]	1.10	0.63	0.46	1.49
Clothianidin	1.31	0.53	1.98	0.35	0.56	1.23	0.21	3.31
Imidacloprid	1.94	0.36	2.93	0.24	0.84	0.83	0.31	2.22
Acetamiprid	0.04	16.5	0.07	9.67	0.02	29.7	0.01	67.9
Thiacloprid	0.05	14.3	0.08	8.75	0.03	26.6	0.01	60.3

[a] Numbers in brackets were measured under natural sunlight in Winnipeg, Manitoba, Canada in July 2014.



254x190mm (300 x 300 DPI)



254x190mm (96 x 96 DPI)