Environmental Science & Technology

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Ecological and Landscape Drivers of Neonicotinoid Insecticide Detections and Concentrations in Canada's Prairie Wetlands

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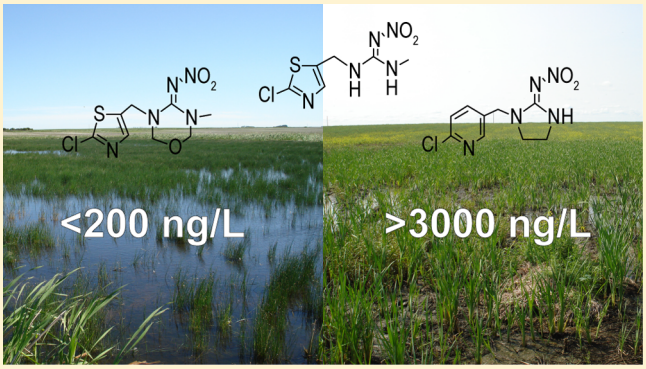
Supporting Information

ABSTRACT: Neonicotinoids are commonly used seed treatments on Canada's major prairie crops. Transported via surface and subsurface runoff into wetlands, their ultimate aquatic fate remains largely unknown. Biotic and abiotic wetland characteristics likely affect neonicotinoid presence and environmental persistence, but concentrations vary widely between wetlands that appear ecologically (e.g., plant composition) and physically (e.g., depth) similar for reasons that remain unclear. We conducted intensive surveys of 238 wetlands, and documented 59 wetland (e.g., dominant plant species) and landscape (e.g., surrounding crop) characteristics as part of a novel rapid wetland assessment system. We used boosted regression tree (BRT) analysis to predict both probability of neonicotinoid analytical detection and concentration. BRT models effectively predicted the deviance in neonicotinoid detection (62.4%) and concentration (74.7%) from 21 and 23 variables, respectively. Detection was best explained by shallow marsh plant species identity (34.8%) and surrounding crop (13.9%). Neonicotinoid concentration was best explained by shallow marsh plant species identity (14.9%) and wetland depth (14.2%). Our research revealed that plant composition is a key indicator and/or driver of neonicotinoid presence and concentration in Prairie wetlands. We recommend wetland buffers consisting of diverse native vegetation be retained or restored to minimize neonicotinoid transport and retention in wetlands, thereby limiting their potential effects on wetland-dependent organisms.



INTRODUCTION

Global pesticide use is forecast to more than double by the year 2050, which, together with agricultural intensification, could lead to unprecedented losses in both ecosystem services and species richness.[1] Agricultural intensification relies heavily on pesticide use in which prophylactic and repeated applications across large spatial scales may create the potential for long-term effects at the landscape level.[2] Between 1 to 10% of pesticides are transported from croplands to wetlands, with even greater losses if rainfall events occur shortly after application.[3,4] Frequent and widespread insecticide applications allow for buildup of high concentrations in natural aquatic systems, including wetlands.[5] Wetland contamination affects nontarget organisms such as aquatic insects and their vertebrate predators (e.g., amphibians, birds) on local and landscape scales. Therefore, to understand the distribution of pesticides in the environment and their effects on biological communities, it is important to conduct locally intensive surveys across the scales at which pesticides are found.[6]

Pesticide concentrations in the wetland environment can be highly variable[7−10] as their fate is likely influenced by the interplay of numerous physical, chemical, and biological variables. Physico-chemical properties of pesticides such as water solubility, molecular weight, soil adsorption, and half-life are well described.[11,12] However, environmental persistence of pesticides in surface water is influenced by numerous processes which include: transport, leaching, transfer between environmental compartments (e.g., air, water, sediment), and transformation processes that can change or degrade the compound (e.g., photolysis).[11−15] Moreover, both biotic and abiotic environmental factors as well as landscape characteristics can significantly affect the strength persistent contaminants have on biological communities.[16] Few studies have examined features

Received: March 13, 2015
Revised: June 16, 2015
Accepted: June 22, 2015
Published: June 22, 2015

ACS Publications © 2015 American Chemical Society

DOI: 10.1021/acs.est.5b01287
Environ. Sci. Technol. 2015, 49, 8367−8376

which may influence detection and concentration of pesticides in aquatic systems such as wetlands.

This knowledge gap is especially true of neonicotinoid insecticides, which are extensively used across agro-wetland landscapes (e.g., Canadian Prairies, Great Plains, and Midwestern, United States).[5,10,17,18] Neonicotinoids are frequently applied in spring as soil or seed treatments or in summer as a foliar spray. As seed treatments, they act as a systemic which protects the roots and shoots of young plants against piercing-sucking insects such as aphids, thrips, and some Coleopteran pests (e.g., wireworm).[19,20] Together, the three most commonly used neonicotinoids—thiamethoxam, clothianidin, and imidacloprid—are registered for use in 120 countries on 295 crops, including canola, cereals, corn, rice, vegetables, and soybeans.[21] Application rates vary between crops and neonicotinoid active ingredient (e.g., corn−imidacloprid, 11−96 g a.i./ha; wheat−thiamethoxam, 36−63 g a.i./ha).[22]

Abiotic factors such as surrounding soil or topography (e.g., organic matter, slope), water (e.g., depth and temperature), dissolved organic carbon, and admittance of solar ultraviolet light may play a role in neonicotinoid fate and persistence in surface waters.[23] Biotic factors such as submerged or emergent plant growth could provide opportunities for surface adsorption, chemical sequestration in plant tissues, or even increased exposure to solar irradiance for photolysis.[13] Numerous other factors such as depth, pH, turbidity, and surficial cover through algal bloom formation are speculated to affect neonicotinoid persistence in surface waters.[24] Field margin vegetation and other plants may draw up neonicotinoids from arable soils.[19] Persistence of systemic pesticides in aquatic environments will necessarily vary with field conditions.[25] There is an immediate need to better understand the fate of neonicotinoids in the aquatic environment—especially the less studied clothianidin and thiamethoxam[26,27]—as these and other neonicotinoids will impact ecosystem services and functions[28] with potential consequences for wetland environments and communities.

In this paper, neonicotinoids are presented as a case study through examination and modeling of the numerous variables that may affect pesticide detections and concentrations in wetlands. Previous wetland studies, although limited, have found neonicotinoids to be prevalent in the environment;[5,10] however, a range of neonicotinoid concentrations have been consistently detected across these and other surface water systems worldwide.[24] Main et al. (2014) found little accumulation of neonicotinoids in wetland sediments; however, neonicotinoids were shown to both accumulate[29] and persist in agricultural soils for extensive periods of time.[19,30,31] Higher latitudes will experience longer half-lives due to lower light intensity as well as lower annual temperatures overall.[25] As wetlands are the transition zone between aquatic and terrestrial ecosystems, they may be at greater risk for potential pesticide contamination. Neonicotinoids are highly water-soluble and have low soil adsorption and lipophilicity which increases the likelihood of their movement into aquatic systems via surface and subsurface runoff.[32,33]

Here, we present an exploratory analysis demonstrating the potential for modeling both neonicotinoid detection and concentration in a large number of wetlands in Canada's Prairie Pothole Region using a set of 59 biotic and abiotic variables collected as part of a field-validated rapid wetland assessment system. We hypothesized that landscape features such as crop type and topography, and wetland features such as surficial or surrounding plant cover could predict neonicotinoid detections and concentrations. Ultimately, our objective was to determine those features which may be most useful to mitigate neonicotinoid contamination to aid management and conservation decisions regarding wetland ecosystems.

METHODS

Study Sites and Wetland Selection. Fieldwork was conducted in 2012 and 2013 on 238 wetlands embedded within intensive agricultural cropland or grass/hay fields located near 10 rural communities across central Saskatchewan (Supporting Information, SI, Figure S1). Agricultural fields were selected using a stratified random design to encompass a wide range of land use and crop types, including: barley, canola, chemfallow (herbicide-treated fallow fields), flax, field pea, grassland (including pasture and prairie), oat, and wheat. We sampled wetlands of varying size and permanency (= class). Where possible, we sampled three wetland replicates per agricultural quarter section (= 65 ha field)[5] across a range of wetland classes (temporary, seasonal, semipermanent, and permanent).[34] Prairie Pothole wetlands are often highly disturbed due to surrounding land use activities (e.g., crop production). Consequently, vegetation communities are commonly dominated by disturbance-tolerant species such as broadleaf cattails (*Typha latifolia*). Since the wetland hydrology of the Prairie Pothole Region is reliant upon the accumulation of snowmelt during spring runoff, the size, depth, vegetation communities, and range of available wetland class often differed among the 10 sampling areas based on local-scale variation in snowfall.[35,36]

Water Sampling. A single water sample was collected during a 10 day period (late-June to early July) to capture effects of the agricultural growing season and growth and diversity of wetland vegetation, but not necessarily peak pesticide concentrations. A detailed description of the water sampling methods used in this study is outlined in Main et al.[5]

Rapid Wetland Assessment Criteria. Our rapid wetland assessment method was modified from published Prairie Pothole Region classification systems,[34,37] rapid assessment criteria,[38−40] and vegetation evaluation techniques[41−44] that included both quantitative and qualitative indicators. Field-validated criteria were based on 59 environmental predictor variables grouped into five categories (see SI Table S1 for full list of variables measured). Wetland water depth was measured in the central portion of the pond and width of vegetation zonation was recorded at the four major compass points of each wetland.[38] Vegetation in Prairie Pothole wetlands typically exhibit classic patterns of zonation with individual species distribution along a moisture or water depth gradient.[42] Classification of plant zones was chosen based on the majority of species that fall within categories from outer to inner zones—wet meadow, shallow marsh, emergent deep marsh, and shallow open water.[34,37] The boundary of study wetlands was based on the edge extent of the wet meadow zone, i.e., areas that contain water for several weeks after snowmelt. We only included plant communities equaling >10% of the plant zone area, thus rare plant species were not included.[41] Wetland coordinates and area calculations of all wetlands were completed using a hand-held GPS unit (Garmin Montana 650). Visual estimations of variables such as percent cover of surficial vegetation or vegetation disturbance levels were obtained by the same surveyors in both years to reduce observer error or bias. Landowner rotation schedules and/or plant identification were used to identify surrounding crops.

DOI: 10.1021/acs.est.5b01287
Environ. Sci. Technol. 2015, 49, 8367−8376

Neonicotinoid application rates were not available for individual fields. Instead, surrounding crop was used as a proxy given the known frequency and standard rates of application.[5]

Neonicotinoid Analysis: Water Samples. Wetland water samples were analyzed at the National Hydrology Research Centre, Environment Canada in Saskatoon, SK. Methods described herein were previously adapted from Xie et al.[45] A description of the analytical details is presented in the SI Methods. As 34% of our wetlands contained >2 neonicotinoid mixtures, we used the sum of total neonicotinoid concentrations per wetland as the overall response variable in our models. We treated samples with neonicotinoid concentrations all below the limit of quantification (LOQ) as nondetections (zeroes). LOQs in wetland water were as follows: thiamethoxam, 1.6 ng/L; imidacloprid, 1.1 ng/L; clothianidin, 0.9 ng/L; and acetamiprid, 0.7 ng/L.

Boosted Regression Tree (BRT) Models. Boosted regression trees (BRTs) are a machine-learning method used in ecology and conservation biology for analysis and modeling, particularly in exploratory contexts.[46−49] We used BRTs to examine the relative influence of 59 different biotic and abiotic wetland and landscape predictors on neonicotinoid analytical detections >LOQ (hereafter detections) and total neonicotinoid concentrations. Classification and regression trees are ideal for ecological modeling because they accommodate complex linear and nonlinear responses to multiple categorical and continuous predictors, are relatively insensitive to collinearity and outliers, allow complex interactions, can accommodate missing data, and allow the model to be developed from the data rather than predetermined.[47] However, single classification or regression trees may not represent the optimal model, can be difficult to interpret, and may produce biologically unrealistic models. BRTs improve upon single classification and regression trees by incorporating "boosting," in which a large number of trees are built and combined in an iterative process to improve model performance.[47,48] A full description of boosted regression tree model parametrization, model building, and evaluation is detailed in the SI Methods.

The relative influence of wetland and landscape predictor variables are presented as variable importance (VI) scores. VI scores are calculated based on the number of times the variable occurs in the set of trees, weighted by how much the variable improves the fit of each tree, averaged across the entire model. Variables with higher VI scores have a stronger influence on the response (neonicotinoid detection or concentration); all VI scores sum to 100.[47,49] Because these VI scores are relative and do not indicate whether given variables are useful for modeling a response, we added a random number between 1 and 100 as an additional predictor variable.[49] Including a random number allows the identification of variables that have stronger influences on neonicotinoid detection and concentration than random. We retained predictor variables with higher VI scores than the random number in the final models. All analyses were conducted in package *dismo*[50] in R version 3.0.1 (R Development Core Team 2014).

RESULTS

Neonicotinoid Concentrations in Wetland Water. We sampled water from 134 wetlands in June of 2012 and 145 wetlands in June of 2013. Only those wetlands still holding water in early July were included in our rapid wetland assessments: (2012:126 wetlands and 2013:112 wetlands). In 2012, 83 of 134 wetlands (62%) contained at least one neonicotinoid versus 123 of 145 wetlands (85%) in 2013 (see Main et al;[5] Table 1). All four neonicotinoids assessed were detected in at least one sample. Detection frequency was ranked in both years as follows: clothianidin > thiamethoxam > imidacloprid > acetamiprid. Mean and maximum concentrations by active ingredient varied in both years (Table 1) and thus sampling year was included in BRT models. Mean and maximum total neonicotinoid concentrations decreased with wetland permanence as follows: temporary (mean: 272.4 ng/L; max: 590); seasonal (mean: 198.6 ng/L; max: 3110); semipermanent (mean: 96.8 ng/L; max: 520.4); and permanent (mean: 22.6 ng/L; max: 129.3).

Table 1. Summary of Detections, Arithmetic Means and Maximum Concentrations of Total Neonicotinoids and Active Ingredients in Water from Prairie Wetlands of Central Saskatchewan (June to July, 2012−2013)

sampling period	neonicotinoid	% detection	mean (ng/L)	max. (ng/L)
Summer 2012	clothianidin	51	142	3110
n = 134	thiamethoxam	19	40.3	1490
	imidacloprid	8.2	15.9	256
	acetamiprid	1.5	1.1	54.4
	total neonic.	62	76.8	3110
Summer 2013	clothianidin	76	59.7	498
n = 145	thiamethoxam	52	40.6	476
	imidacloprid	12	7.1	196
	acetamiprid	0.7	0.6	13.4
	total neonic.	85	108	595

BRT Model Performance. The BRT models accounted for 62.4% of the deviance in neonicotinoid detections and 74.7% of the deviance in total neonicotinoid concentrations (SI Table S3). Neonicotinoid detections were explained by 21 variables, including the top four which explained the majority of variance: dominant shallow marsh plant species identity (importance value = 34.8, indicating that it explained 34.8% of model deviance); current crop type (13.9%); vegetation disturbance (13.0%); and dominant wet meadow plant species identity (5.0%; Figure 1A). Within the shallow marsh zone, the dominant plant species identity (n = 28) was associated with neonicotinoid detection probability. A high neonicotinoid detection probability (marginal effect ≥1.0) was predicted by the presence of four dominant plant species: *Thlaspi arvense*, *Agrostis scabra*, *Poaceae spp.*, and *Avena fatua*. A low detection probability (marginal effect ≤1.0) was predicted by the presence of four dominant plant species: *Aster borealis*, *Sium suave*, *Carex bebbii*, and *C. atherodes* (Figure 2A). Wetlands surrounded by crops including oat, canola, and barley had a higher detection probability, whereas neonicotinoids were rarely detected in wetlands within pasture and grasslands (Figure 2B). Neonicotinoid detections increased nonlinearly with vegetation disturbance with two thresholds (sharp increases) at approximately 45% and 80% disturbance levels (Figure 2C). Dominant wet meadow species also influenced detections. Fourteen dominant plant species were associated with a higher probability of neonicotinoid detection (marginal effect >0), including *Plantago major*, *Juncus torreyi*, and *A. fatua*, while seven species, including *Scolochloa festucacea* and *Equisetum hyemale* were associated with a lower detection probability (Figure 2D).

DOI: 10.1021/acs.est.5b01287
Environ. Sci. Technol. 2015, 49, 8367−8376

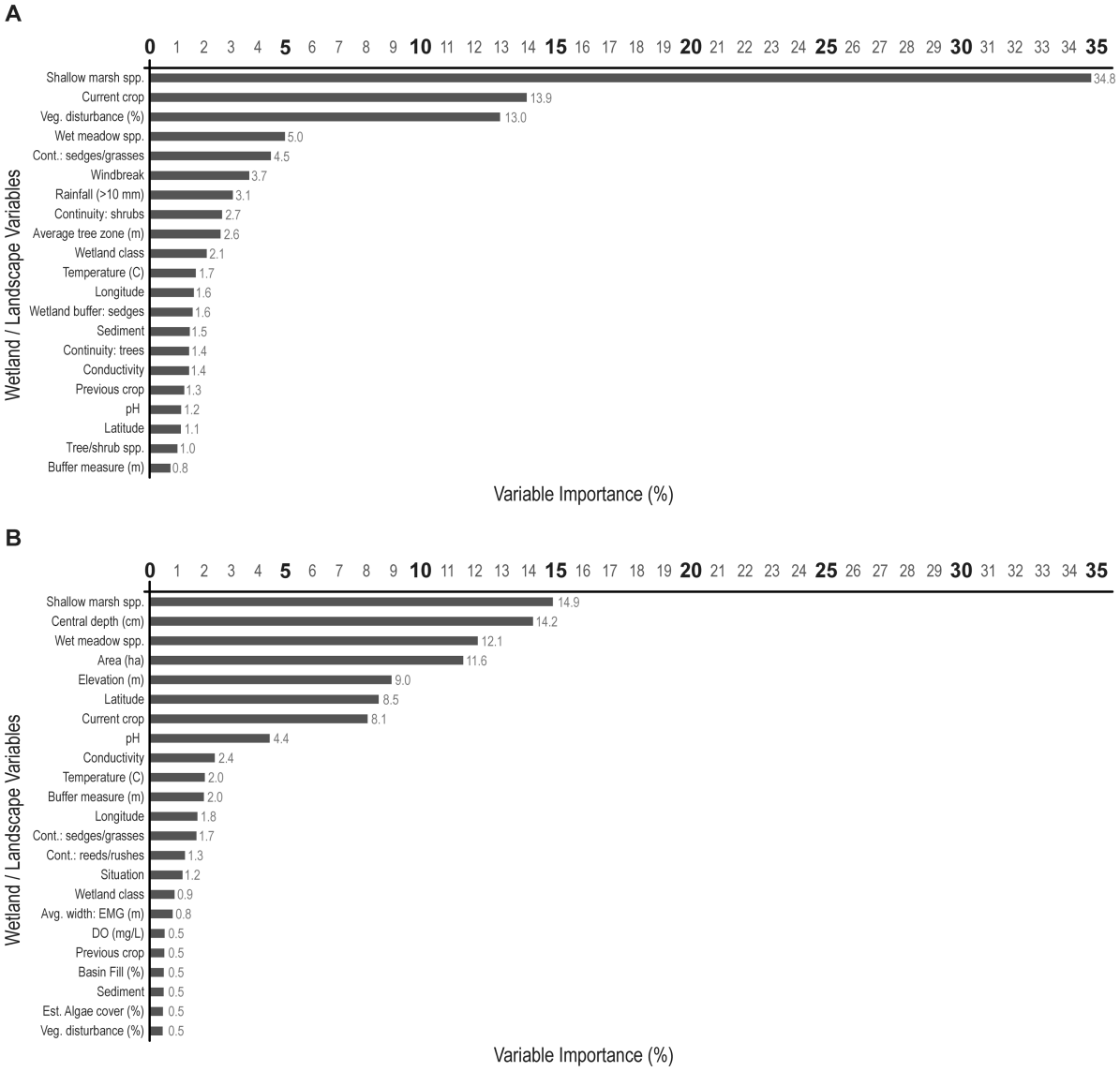


Figure 1. Variable importance (VI) scores of key wetland and landscape predictor variables affecting neonicotinoid detection (A) and concentration (B) in Prairie wetlands. The sum of scores is equal to 100 with percentages of predictor variables indicating the importance of that variable contributing to the overall deviance of the model.

Neonicotinoid concentrations were explained by 23 variables, including the top seven which explained the majority of variance: dominant shallow marsh plant species (14.9%), wetland central depth (14.2%), dominant wet meadow plant species (12.1%), area (11.6%), elevation (9.0%), latitude (8.5%) and current crop (8.1%; Figure 1B). We found higher neonicotinoid concentrations (marginal effect >0), were predicted by dominant shallow marsh plant species identity (n = 11) including *T. arvense*, *Scirpus validus*, and *Carex aquatilis*. Lower neonicotinoid concentrations were predicted by ten species, including *Scirpus acutus* and *Mentha arvensis* (Figure 3A). Wetland central depth had a negative nonlinear effect on neonicotinoid concentration, with sharp concentration declines at depths of 25 and 40 cm (Figure 3B). Neonicotinoid concentrations were also predicted by wet meadow dominant plant species identity (n = 18), with the presence of six species associated with higher neonicotinoid concentrations (marginal effect >0.2), including: *A. fatua*, *Calamagrostis canadensis*, and *E. fluviatile* (Figure 3C). Wetlands which were missing wet meadow plant communities (= "none") were also associated with higher neonicotinoid concentrations. Wetlands smaller than ∼1ha in size (Figure 3D) and those wetlands situated at lower elevations (450 m to ∼525 m) were more likely to have higher total neonicotinoid concentrations, whereas concentrations decreased sharply at elevations above 550 m (SI Figure S2A). Concentrations exhibited a regional pattern in which they peaked at latitudes near 52.6°N (SI Figure S2B). Consistent with neonicotinoid seed treatment use and rotation patterns, wetlands surrounded by the crops of canola, oat, and barley had higher concentrations than wetlands surrounded by wheat and field pea (SI Figure S2C).

DISCUSSION

Here we present a modeling approach that effectively explains neonicotinoid detections and concentrations in Prairie wetlands based on locally collected and remotely sensed environmental variables. To our knowledge, we are the first to simultaneously assess the relative effects of multiple vegetative and biogeophysical characteristics on neonicotinoid fate in wetlands

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Environ. Sci. Technol. 2015, 49, 8367−8376

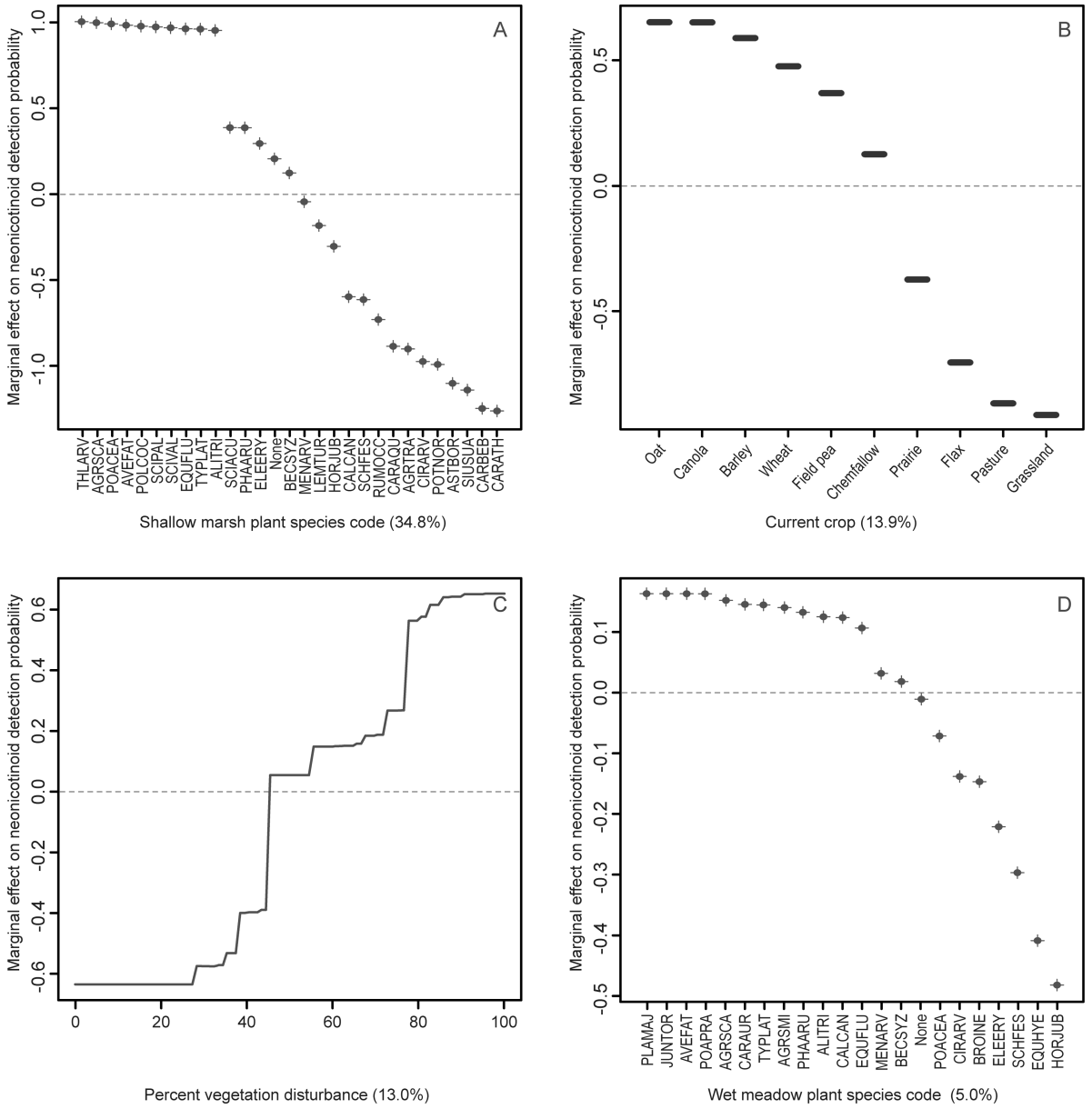

Figure 2. Relationships between detection of total neonicotinoids in Prairie wetlands and key predictor variables: (A) shallow marsh plant species, (B) current crop, (C) percent vegetation disturbance, and (D) wet meadow plant species. Plots are presented as dimensionless transformations of the response variables with variable importance (VI) scores listed for each variable. Plant species codes are defined in SI Table S4.

across multiple scales. Three variables, dominant shallow marsh plant species, crop type, and percent vegetation disturbance, accounted for over half (62%) of the variation in neonicotinoid detection probability; three variables (dominant shallow marsh, wet meadow plant species, and wetland depth) also accounted for over 40% of the variation in neonicotinoid concentration.

Of the 59 variables included in our model set, vegetation community structure in the shallow marsh zone best explained both neonicotinoid detections (34.8%) and concentrations (14.9%). However, shallow marsh species presence was a more important predictor of detections than concentrations, as the greater species richness in the detection model equated to more variation explained. The shallow marsh zone is often described as a "buffer zone" for wetlands and, in the case of neonicotinoids, has an overwhelming effect on the transport and persistence of this pesticide class. Detection of neonicotinoids was highest in wetlands containing select dominant plant species in the shallow marsh, including: *T. arvense*, *Scirpus paludosus*, *T. latifolia*, and *Alisma triviale* (SI Table S4). All four species have some ability to tolerate disturbance. *T. arvense* is resistant to soil disturbance; *S. paludosus* and *T. latifolia* can be pioneering species after disturbance often withstanding even slightly brackish conditions; and *A. triviale* is typically prevalent in wetlands adjacent to cultivated fields.[51] Conversely, wetlands dominated by sedge species such as *C. atherodes* were likely to be devoid of neonicotinoids. Similar to the detection model, neonicotinoid concentrations were highest in wetlands containing species such as *T. arvense*, *Carex aquatilis*, and *S. validus*. The lowest neonicotinoid concentrations were detected in wetlands where *M. arvensis* or *S. acutus* dominated plant communities in the shallow marsh.

It is unclear as to why certain plant species are associated with higher or lower neonicotinoid detections or concen-

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Environ. Sci. Technol. 2015, 49, 8367−8376

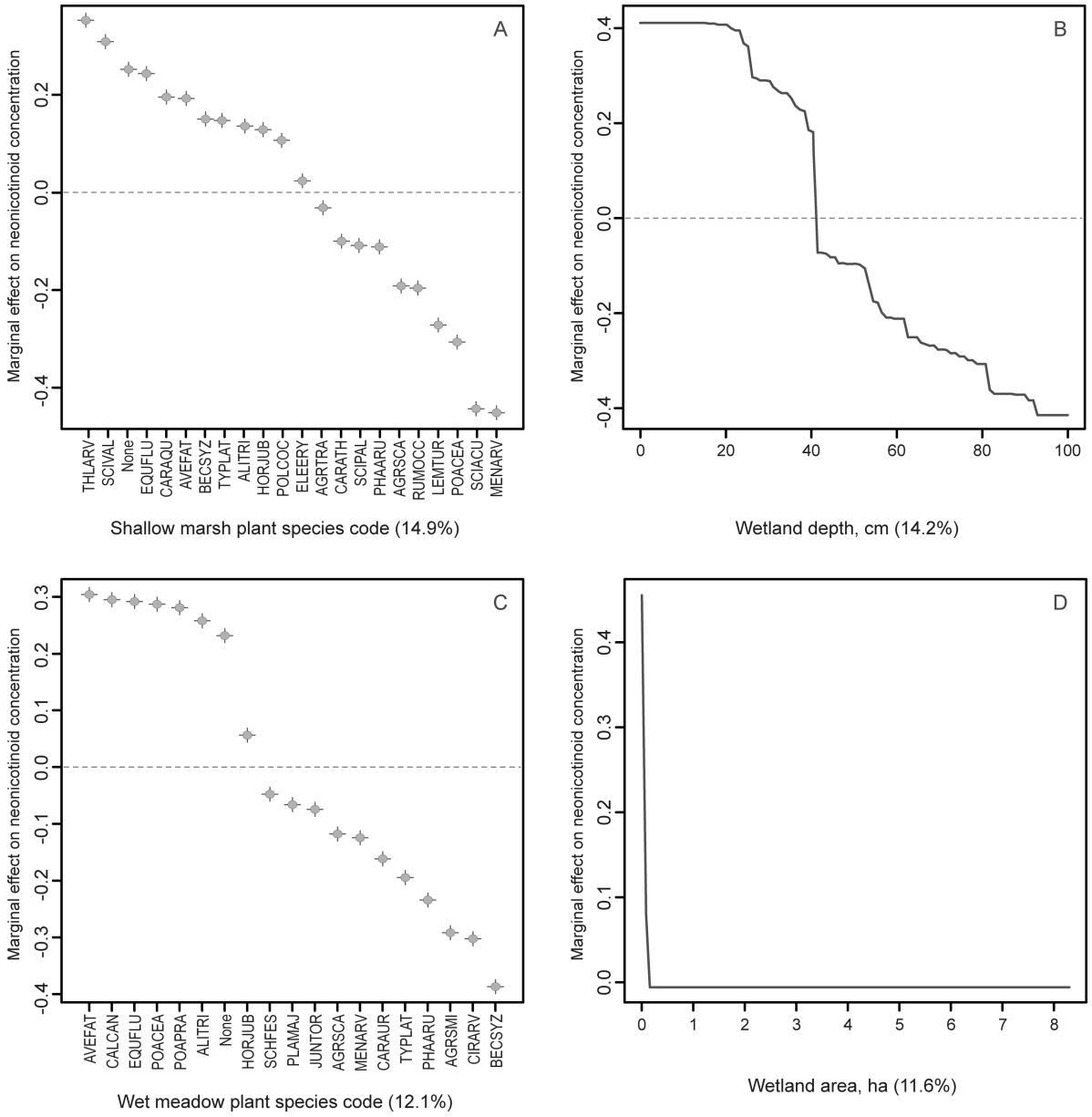

Figure 3. Relationships between concentration of total neonicotinoids in Prairie wetlands and key predictor variables: (A) shallow marsh plant species, (B) wetland depth, (C) wet meadow plant species, and (D) wetland area. Details are the same as listed in Figure 2. Plant species codes are defined in SI Table S4.

trations in these wetlands; however, wetlands and their associated vegetation have been documented to increase the removal of a range of pesticides through plant uptake, root sorption, and hydrolysis.[52−54] We speculate that some of these dominant species may also have phytoremediation potential or may alter their abiotic environment leading to increased/decreased persistence. In later wetland hydroperiod stages, plants such as *A. triviale* and *P. arundinacea* have greater surface area (e.g., roots, shoots, and leaves) within the water, which may increase sorption to plants and create biofilms that promote microbial activity and pesticide degradation.[55] The presence of specific dominant plant species may also be representative of geophysical characteristics of certain study wetlands including landscape position, water depth, and water quality. Although we measured each of these variables separately and the model ranks them with VI scores, we cannot rule out the possibility that plant species identity could act as a surrogate for the complex ecological interactions between numerous individual variables.

We also cannot rule out the possibility that the causality of the association between neonicotinoid detection and concentration and plant species composition is reversed. Neonicotinoids may be acting as a stressor that affects some plant species more than others, leading to altered plant community compositions. For example, *T. arvense*—a member of the Brassicaceae family—is indicative of wetlands with both high concentration and high probability of neonicotinoid detection. A non-native and noxious weed, *T. arvense*, is likely tolerant to a variety of stressors, potentially including neonicotinoids, as it is known to be resistant to soil disturbance and some herbicides.[56] Further experimental study of the relationship between neonicotinoids and individual and community plant responses is needed.

DOI: 10.1021/acs.est.5b01287
Environ. Sci. Technol. 2015, 49, 8367−8376

Aquatic plants also provide physical structure to wetlands and are able to alter the wetland's abiotic environment both physically (e.g., light levels) and chemically (e.g., pH, nutrient levels).[57] This feature could influence neonicotinoid fate and persistence in Prairie wetlands. However, our findings reveal that plant species composition, more so than density, affects neonicotinoid detections and concentrations. We assessed plant density in two ways: (1) actual measurements of vegetation zones (e.g., width); and (2) cover type, which identifies the ratio of plants to open water.[34,37] Cover type was not retained in our final models and less than 2% of model variance was accounted for by actual vegetation zone measurements.

Presence of intact wet meadow and shallow marsh zones is an important indicator of healthy wetland condition.[42] Although detection of neonicotinoids was strongly influenced by certain dominant plant species in the shallow marsh and wet meadow zones, high total neonicotinoid concentrations were frequently found in wetlands where those zones had been removed or cultivated. The sharpest increases in neonicotinoid detection probability were found at 45% vegetation disturbance and ∼80% disturbance. This factor was not important to our concentration model possibly indicating a trade-off between disturbance, which facilitates chemical transport, while also enhancing dilution from runoff. Due to their rich, moisture-retaining soils, wet meadow and shallow marsh zones tend to be cultivated during dry years which create coarse-grained vegetation mosaics with fewer native plants.[41] In our study, 62% of 238 wetlands were missing an outer wet meadow community. Removal of these buffer vegetation zones likely increased their susceptibility to neonicotinoid contamination from adjacent cultivated row crops. Presence of wet meadow grasses may trap and degrade various pesticide compounds.[58] Further research has shown that plant buffer strips or vegetated treatment systems are the most important characteristic influencing the retention performance of pesticides leading to degradation via hydrolysis or photolysis.[59] The presence or absence of buffer zones has important implications for protection of aquatic organisms such as wetland macro-invertebrates. Buffered wetland sites are known to hold significantly greater aquatic macroinvertebrate abundance than nonbuffered wetlands.[60]

Our model indicated that depth accounted for 14.2% of variation in neonicotinoid concentration, with the highest concentrations in shallow wetlands <40 cm deep. Wetland size and depth are frequently correlated, such that many of these shallow high-concentration wetlands were <1 ha in size. Indeed, wetland area accounted for 11.6% of variation in neonicotinoid concentration. The highest concentration detected in our study (3110 ng/L)[5] was in a seasonal wetland of 0.3 ha in size and 12 cm depth; whereas, our largest study wetland (83 ha and >1m deep) had a concentration of 5.8 ng/L. Although orders of magnitude lower, likely due to dilution, many of these larger more permanent waterbodies contain detectable levels of neonicotinoids, indicating movement into water bodies of all sizes. Deeper wetlands frequently have less sunlight penetration which may slow neonicotinoid degradation, facilitating persistence, despite low concentrations. Indeed, thiamethoxam underwent a slower degradation process in the absence of light.[23] Our finding of high concentrations in shallow wetlands seemingly contradicts the prediction of rapid neonicotinoid degradation in shallow waters due to extensive light penetration and photolytic breakdown.[13] However, many Prairie wetlands are highly turbid, contain a high variability of dissolved organic carbons, or are heavily disturbed which likely reduces light penetration and, consequently, degradation. Neonicotinoid persistence in natural environments could potentially be influenced by dissolved organic matter acting as a photo-sensitizer.[61]

Crop type is known to influence neonicotinoid concentration in Prairie Pothole wetlands.[5] Current crop type accounted for 13.9% of variation in neonicotinoid detection and 8.1% of variation in concentration. Over 95% of canola grown in Canada is treated with a neonicotinoid active ingredient.[5] Although registered for use, most Canadian cereal (e.g., oat, barley) and legume (e.g., field pea) crops are less frequently treated with neonicotinoids; however, treated-seed options continue to grow in spatial extent and frequency of use. Wetlands in untreated grassland (including prairie and pasture) and chemfallow fields still contain trace neonicotinoids likely from previous crop treatments.[19,31]

Year effects including time since planting and rainfall may also influence concentrations of neonicotinoids within wetland water. We sampled wetlands during the same 10 day time period (late June to early July) in both years. We did not aim to capture peak water concentrations which typically occur within 24 h postseeding, followed by rapid breakdown via first-order kinetics over the next 48 h and slower degradation over the subsequent 192 h time period.[24,62] In Prairie wetlands, rainfall events can strongly increase the potential for surface water contamination.[63] Although rainfall and temperature patterns differed between years, year effects did not explain detection or concentration in either model. We did not specifically target our wetland sampling to include precipitation events, but did include time since last rainfall (defined as a precipitation event ≥10 mm) as a variable in our model. Similarly, time since last rainfall had a minimal effect (3.1%), with peak detection probabilities between ∼3 and 12 days postrainfall. Rainfall did not contribute to the neonicotinoid concentration model.

Several biotic variables (e.g., surficial plant and algal cover) and abiotic variables (e.g., pH) had minimal to no effect on neonicotinoid detection and concentration, despite the fact that plant community structure in emergent and submerged aquatic zones can influence water temperature and light diffusion.[57] We hypothesized that surficial plant cover may be associated with higher detection probability and concentration due to reduced photolysis. However, % algal cover did not contribute to the detection model and accounted for only 0.5% of the variation in neonicotinoid concentrations. Although clothianidin rapidly degrades through photolysis in the lab, this is less likely to occur in natural systems unless they hold clear, irradiated water.[26] Conversely, algal cover may increase pesticide degradation despite reductions in light levels. Algae decreased the persistence of atrazine and lindane through pesticide sorption or algae-facilitated degradation in a lab environment,[64] and algal blooms reportedly rapidly degrade pesticides under field conditions.[65] Plant growth generally increases a wetland's overall surface area relative to its water volume which may further increase opportunities for surface adsorption, sequestration in plant tissues, microbial degradation, and improved exposure of compounds on leaves to sunlight for photolysis.[13,52,54]

Interestingly, landscape features such as topography and wetland density, although speculated to have an influence on presence and concentration of neonicotinoids, were found to account for minimal to no variance in our models. We found no effect of wetland density on neonicotinoid detection and

DOI: 10.1021/acs.est.5b01287
Environ. Sci. Technol. 2015, 49, 8367−8376

concentration, contrary to previous studies showing that numerous small "pothole" wetlands interspersed with intensive agriculture have high probabilities of chemical contamination.[66] We used wetland situation (isolated, overflow, channel, and terminal) as a topographic proxy measurement of a wetland's position in the landscape or watershed.[37] Wetland situation accounted for only 1.2% (concentration) of the overall variance in our models. The highest concentrations in our study were found in isolated wetlands or those receiving water from surrounding uplands, but never overflow.[37] Although we anticipated terminal wetlands—found in topographically low areas—to have the highest concentrations, isolated wetlands (245 ± 60 ng/L) had higher mean (±SE) concentrations than terminal connected wetlands (53.7 ± 7.4 ng/L). Elevation did account for 9.0% of concentration model variance, and lower-elevation (~450−550m) wetlands had higher overall neonicotinoid concentrations. Many of our study wetlands appear biologically unique and independent of one another; therefore, wetland density and landscape situation were less important features.

Implications for Wetland Ecosystem Conservation. Numerous plant species in the shallow marsh and wet meadow zones were indicative of both detection and concentration of neonicotinoids. However, wetlands lacking these two zones had the highest neonicotinoid concentrations, further indicating the importance of preserving healthy vegetation communities in agricultural wetlands. Cultivation of both wet meadow and shallow marsh vegetation communities can increase the potential for chemical inputs such as pesticides.[41]

Neonicotinoids are implicated in declines of a variety of animals, most notably bees.[67−70] In wetlands and other surface water systems, numerous nontarget aquatic insect species may experience direct toxic effects or sublethal effects (e.g., reduced emergence), which inhibits critical ecosystem functions such as leaf litter breakdown and nutrient cycling.[71−73] Long-term neonicotinoid concentrations in water that exceed 35 ng/L can affect sensitive aquatic invertebrate populations through chronic effects.[24] Importantly, over half (52%) of the wetlands in our study surpassed the critical value above which invertebrates are affected. Our research, combined with previous documentation of pervasive use and frequent wetland occurrence of neonicotinoids throughout the Canadian Prairies,[5] reveals that agriculturally embedded wetlands and their associated communities are impacted. Pothole wetlands are chronically exposed based on growing neonicotinoid use across the Canadian Prairies,[5] with potential for negative effects of aquatic macroinvertebrates and the insectivorous birds, fish, amphibians, and mammals that rely upon them.[74]

Part of the objective of wetland ecotoxicology should be to determine management strategies to ameliorate impacts on these chemically stressed systems.[75] Our study highlights the value of using robust techniques to analyze complex multivariate data sets including a wide range of biotic and abiotic wetland and landscape characteristics. Our findings reveal that neonicotinoid presence and concentration in surface water are largely affected by the presence and composition of vegetated wetland buffers, whereas many abiotic and landscape variables show limited influence. This observation is timely and important for understanding how an extensively used chemical class like neonicotinoids behaves under field conditions. Temporary and seasonal wetlands are most often disturbed and seem to be under the greatest impact from chemical contamination, despite their importance for supporting biodiversity including invertebrates and their vertebrate predators.[41,42] Mechanistic explanations of the patterns described herein are beyond the scope of this exploratory study. Further research, particularly experimental approaches, is encouraged to identify the processes and causality. We recommend research to examine the individual contribution of key wetland habitat variables highlighted here on pesticide fate. Regardless of the mechanism, our research has clear and important implications for management of agricultural landscapes. To reduce neonicotinoid concentrations in wetlands—and their concomitant effects on aquatic insects, and other organisms—buffers consisting of diverse native vegetation should be retained.

■ ASSOCIATED CONTENT

Supporting Information

A table outlining the variables collected as part of the wetland assessment criteria (Table S1); the boosted regression tree correlation matrix (Table S2); BRT model parameters (Table S3); dominant plant species table indicating which species are associated with neonicotinoid detection and concentration (Table S4); a figure outlining our study area (Figure S1); plots of predictor variable relationships to neonicotinoid concentration (Figure S2A-C) and detailed descriptions of analytical and statistical methods. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01287.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the numerous field/lab technicians involved with this study: M. Cavallaro, M. Hauck, K. Majewski, B. White and A. Zahara. We are grateful for the continued involvement and advice of: A. Cessna, R. Clark, J.-M. DeVink, J. Devries, K. Drake, K. Liber, F. Messier and I. Phillips. Thank you to the generous Saskatchewan farmers and landowners for access to their land. This work was funded by a NSERC Strategic Project Grant to C.A. Morrissey and scholarship funding from the University of Saskatchewan and the Saskatchewan Innovation and Opportunity Scholarship to A.R. Main.

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