

MODELING TRACE ORGANIC CONTAMINANTS IN
COMMERCIAL AND HIGH-DENSITY RESIDENTIAL
URBAN STORMWATER RUNOFF

by
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ABSTRACT

Urbanization can dramatically alter stormwater, both the quantity and quality, by engendering larger peak flows and through the introduction of contaminants into stormwater runoff. This study builds upon previous research that developed relationships between a suite of nonpoint source contaminants, known as trace organic contaminants (TOrcs), and hydrologic measurements for a series of storms in Madison, WI, by creating statistical and deterministic models. Stormwater runoff from both a commercial site and a high-density residential site was characterized for TOrcs in a previous study. Correlations and regressions were calculated between TOrc loads and hydrologic measurements for both sites. Regressions were possible for all but two contaminants. From the regressions, it became evident that loading responses to precipitation were not the same between the two land covers for some TOrcs. The regressions were transferred to the Source Loading and Management Model for Windows (WinSLAMM), an event-based hydrologic and water quality model, to demonstrate how it can be used to model novel contaminants. The regressions were also used to estimate mean annual loads of TOrcs from all commercial and high-density residential areas in Madison, WI. This work will ultimately allow managers to simulate the presence and mitigation of TOrcs through stormwater best management practices.

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LIST OF SYMBOLS

COMM	commercial
HDRES	high-density residential
EMC	event mean concentration
EML	event mean load
EPA	United States Environmental Protection Agency
KTRL	Kendall-Theil Robust Line
NAIP	National Agricultural Imagery Program
NURP	National Urban Runoff Program
OLS	ordinary least-squares
PAH	polycyclic aromatic hydrocarbon
RMSE	root mean square error
TMDL	total maximum daily load
TOrC	trace organic contaminant
USDA	United States Department of Agriculture
USGS	United States Geological Survey
WinSLAMM	Source Loading and Management Model for Windows

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CHAPTER 1

INTRODUCTION

As lands become urbanized a plethora of potential issues begin to manifest. The process of urbanization generally results in an increase in impervious surfaces. Such a phenomenon can adversely affect both hydrology and water quality of urban stormwater runoff [1]. A reduction in pervious surfaces decreases the water retention in a given area, which can increase peak flows from precipitation events [2]. It can also lead to water quality degradation because there are fewer sites at which infiltration, a process that can help remove pollutants, occurs. Furthermore, contaminants are part of the makeup of the built environment and are introduced through numerous pathways such as car brakes, pavement materials, and pesticide application [3].

After enacting the Clean Water Act in the United States in 1972, point source pollutants became a priority target for study and reduction. In the 1980s the United States Environmental Protection Agency (EPA) undertook the Nationwide Urban Runoff Program (NURP) to study urban stormwater and non-point source pollution. The NURP projects established that urban stormwater and non-point source pollution contribute significantly to contaminant loads in receiving waters [2]. Metals and nutrients were the primary focus of many NURP projects. This paper specifically focuses on a class of contaminants known as trace organic contaminants (TOrcs), sometimes also referred to as emerging contaminants or micropollutants [4]. Used herein, TOrcs are comprised of a multitude of organic contaminants, such as pesticides, herbicides, flame retardants, and petroleum

products. The TOrCs in this study are all detrimental to human and environmental health. Their effects range from mild skin, nose, throat, and eye irritation to toxicity to aquatic life [5]-[23]. .

The current study characterizes the response of TOrC event mean loads (EMLs) in urban stormwater runoff from non-point sources to precipitation events in various urban land covers. It is a first step in understanding the prevalence and magnitude of TOrCs in stormwater runoff from urban areas. According to Title 33 of the U.S. Code, Chapter 26, Subchapter III, Section 1314 (f), one must be able to identify and evaluate the nature and extent of non-point source pollutants in order for total maximum daily loads (TMDLs) to be established [24]. Once TMDLs are established various methods can be used to comply with them, such as installing stormwater best management practices (BMPs) and street sweeping. TOrC modeling will help identify and evaluate the nature and extent of the TOrCs studied in this project. This work enables managers to predict where the TOrCs will be and thus use appropriate measures to mitigate their loads. Furthermore, the statistical and deterministic prediction methods can be easily used for other contaminants and regions if the data is available.

Many studies to date have associated categories of TOrCs with specific land covers, such as residential, commercial or industrial, as well as their concentrations. Burant et al., 2018, whose data set is the focus of this paper, establishes seasonal trends for some TOrCs; they also establish that concentrations of TOrC can vary by land cover, where some are generally higher in a commercial site and others are higher in a high-density residential site. Other

TOrCs show no difference in concentrations between the two sites [25]. Brown and Peak, 2006, sampled runoff from an urban catchment and a river in an adjacent rural community in New Zealand and found that polycyclic aromatic hydrocarbons (PAHs) and metals are detected at higher concentrations in the urban catchment than in the rural catchment. They also found that road debris is the dominant source of metals in the rural catchment, whereas traffic, building materials, and industrial activities are the dominant sources in the urban catchment [3]. Gasperi et al., 2014, sampled urban stormwater for 77 pollutants in one industrial and two residential sites in France. They found that the pollutant distributions between dissolved and particulate contaminants are not dissimilar between the sites and that PAH fingerprints are similar between rain events, regardless of the site. They found, too, that the distribution between dissolved and particulate phases are highly dependent on the contaminant's chemical and physical properties. [26]. Burkhardt et al., 2011, studied TOrCs in stormwater that originated from construction materials. They found that the age of the material highly influences the concentrations in stormwater runoff, particularly for biocides [27].

There are a scarce number of studies relating TOrCs to hydrologic measurements. There are, however, studies that indicate a connection between other contaminants and hydrologic measurements, such as rainfall intensity and season. Macrae et al., 2010, conducted a study at Strawberry Creek in Ontario, CA, and determined that antecedent hydrologic conditions – season, discharge/pre-event flow, and precipitation – do not exhibit strong relationships with nutrient exports [28]. Liu et al., 2013, also studied various hydrologic

conditions in the Gold Coast, Queensland, Australia, for residential sites and road surfaces from commercial, residential, and industrial areas. They concluded that precipitation intensity and duration generally exhibit more influence than antecedent dry days on stormwater quality. They also deduced that while land cover is an important factor, site-specific characteristics such as the percentage of impervious surfaces also significantly influence pollutant build-up and wash-off [29].

Connections have not only been established between contaminants and hydrologic indicators, but they have also been established between contaminants, different land covers, and different source areas. Sekhar and Reddy, 2013, made regression models to predict water quality in the Krishna River in India. They found that various contaminants are, in fact, correlated with land cover in their study area [30]. Sun et al., 2013, studied the relationship between land use intensity (and complexity) and nitrogen in the Haihe River Basin in China. They found that nutrient loadings are influenced by land cover changes, with human-induced changes having the most significant effects [31]. Steuer et al., 1997, establish that some contaminants are more prevalent in stormwater runoff when coming from different source areas in different land covers, such as commercial paved parking or residential lawns [32]

There is a dearth of models for the prediction of loads or concentrations of TOrCs. While many deterministic and statistical models exist to predict nutrients and metals, among other contaminants, few exist for TOrCs. The need to predict TOrCs will become increasingly important as urbanization continues and more

contaminants are discovered in or introduced into the environment. This study uses two types of models, one statistical and the other deterministic. The statistical models were made from regressions. There is precedent for statistical water quality models: Marsalek, 1990, compared and used various probabilistic methods to determine various non-point source pollutants in urban stormwater and found that such methods of prediction are often consistent with reported results [33]. The deterministic model used in this study is the Source Loading and Management Model for Windows (WinSLAMM). WinSLAMM is both a hydrologic and water quality model developed by PV & Associates [34]. It was originally developed in the 1970s after extensive small-storm urban hydrologic studies were conducted by the EPA. WinSLAMM is ideal for practitioners in urban areas because it allows the study of specific source areas and different land covers. The model allows BMPs to be placed in source areas, watersheds, and between junctions and an outfall point to determine how they would both water quality and quantity.

The objective of this study is to predict TOC loads given specific land covers and precipitation event characteristics. This study aims to answer the following questions: (1) Which hydrologic measurements, if any, are correlated to EMLs of TOCs? (2) Can statistical relations be built between TOC loads and hydrologic measurements? (3) Do TOC loads respond differently to precipitation events in different land covers? (4) Can regressions between TOC EMLs and hydrologic measurements be used in a deterministic model, like WinSLAMM, to simulate TOC loads? Answering these questions will be vital in predicting TOC loads if one desires both establish and comply with TMDLs.

CHAPTER 2

MATERIALS & METHODS

2.1 Study sites

Hydrologic data and water-quality samples were measured and collected by the United States Geological Survey (USGS), then shipped to the Colorado School of Mines and USGS National Water Quality Laboratory for determination of TOC concentrations [25]. Samples were collected from two urban catchments in Madison, WI. Precipitation in Madison, WI, generally follows seasonal patterns typical of Midwest: it is driest in the winter (December-February) and wettest in the summer (June-September). The mean annual rainfall, based on a 30-year normal (1980-2010), was 34.48 inches [35].

The land cover and source areas of the two sites were analyzed using a tax parcel map available from the City of Madison, National Land Cover Database (NLCD) 2011, and aerial photography over the City of Madison from the 2015 National Agriculture Imagery Program (NAIP) from the United States Department of Agriculture (USDA) Farm Service Agency (FSA) [36] [37] [38]. The Anderson Land Cover Classification Scheme, coupled with both NLCD and tax assessor parcels, guided the land cover classification for both of the two urban catchments [36] [37] [39]. All spatial analysis was performed in ArcGIS 10.4.1 [40]. From NLCD it was determined that both sites were developed. From the tax parcel map, it was determined that one site was over 80% commercial and the other was over 80% residential. Thus, based on the prevalent land cover designations, the two sites

were classified as: commercial (COMM), with an Anderson Land Cover classification of (I) Urban or Built-Up Land and (II) Commercial and Services, and high-density residential (HDRES), with an Anderson Land Cover classification of (I) Urban or Built-Up Land, (II) Residential, and (III) High-Density. According to NLCD, the two sites encompassed

- COMM
 - 0.42% open space, 6.35% low intensity, 67.9% medium intensity, and 24.4% high intensity developed areas;
 - 0.10% deciduous forest; and
 - 0.83% pasture/hay according [37].
- HDRES
 - 2.47% open space, 58.3% low intensity, 33.3% medium intensity, and 5.93% high intensity developed areas according [37].

Runoff from COMM discharges to Lake Mendota; HDRES discharges to Lake Monona (Figure 2.1) [25].

To further characterize the sites and to parameterize WinSLAMM, source areas within the two sites (Figure 2.1) were defined and digitized as: building, driveway, miscellaneous, parking, sidewalk, street, and vegetation. NAIP imagery over the two sites was used for source area digitization. COMM encompassed an area of 46.02 acres, of which 7.36 acres were buildings, 0.09 acres were miscellaneous, 19.72 acres were parking, 5.57 acres were streets, 1.29 acres were

sidewalks, and 11.99 acres were vegetation. HDRES encompassed an area of 21.03 acres, of which 5.35 acres were buildings, 2.30 were driveways, 0.38 acres were miscellaneous, 0.29 acres were parking, 1.27 acres were sidewalks, 3.01 acres were streets, and 8.43 acres were vegetation.

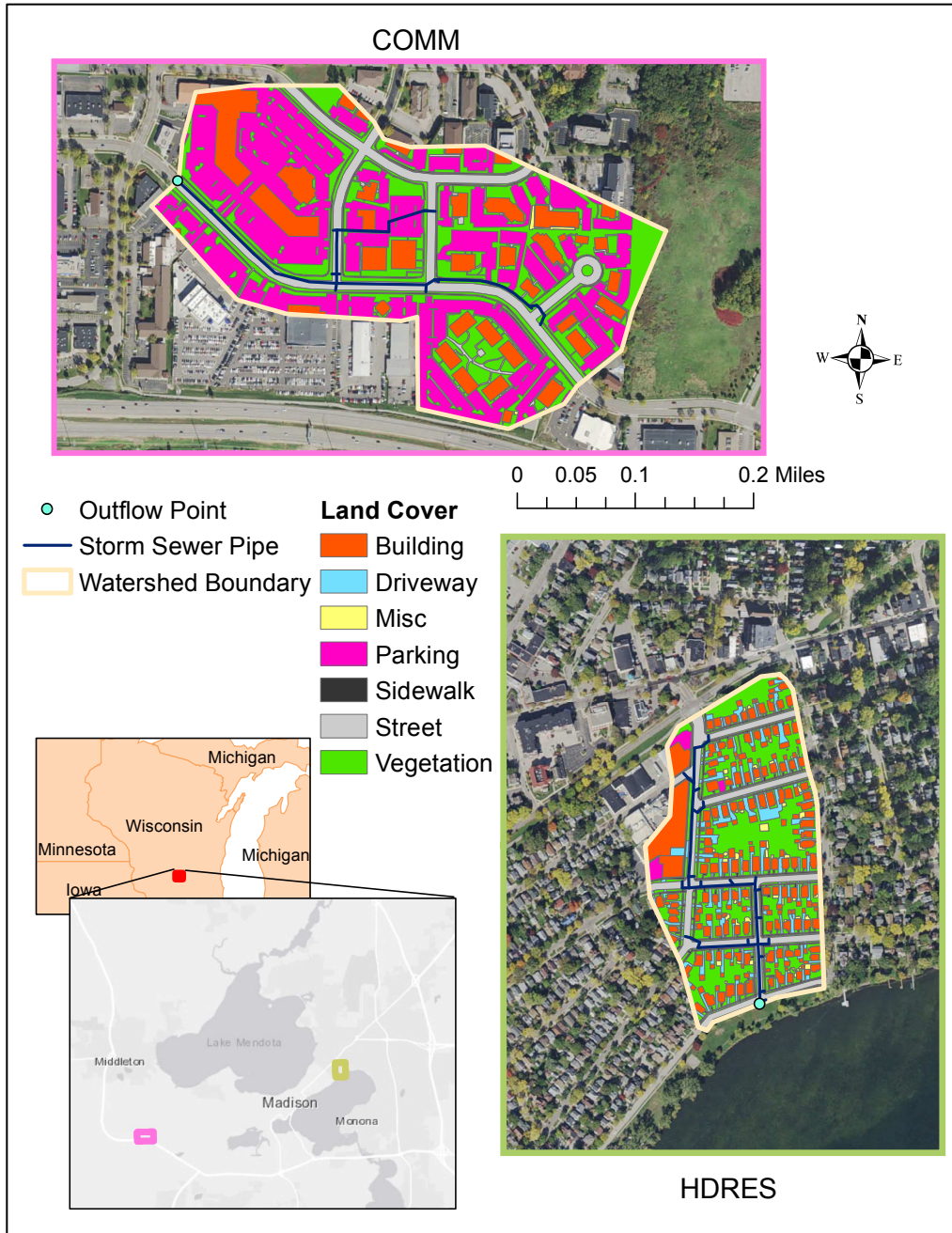


Figure 2.1 Site maps for COMM and HDRES

2.2 Hydrologic and contaminant data

2.2.1 Hydrologic measurements

Both sewer outfalls were equipped with automated water-quality samplers to collect aqueous water quality samples and discern hydrologic conditions. Each was equipped with a low-profile sensor to measure water depth and velocity to calculate discharge. Tipping buckets, calibrated to 0.25 mm per tip, were used to collect precipitation data. The information collected pertained only to stormwater surface runoff in the sewer. There were no other hydrologic contributors, such as wastewater runoff and streams, within either site.

Hydrologic measurements were collected for 15 precipitation events in COMM and 19 precipitation events in HDRES. Hydrologic measurements consisted of event duration, total precipitation depth, maximum rainfall intensity at 15 minutes, maximum rainfall intensity at 30 minutes, antecedent dry days, and peak flow. The events for COMM took place from 06/14/2016-09/21/2016 and the events for HDRES took place from 04/06/2016-08/19/2016. The events for both sites in this study were not sequential; there were precipitation events between those measured and analyzed in this study. The data were reported for the total event, not as a time series.

2.2.2 Contaminants

The automated water quality samplers in the sewer networks were activated once water depth exceeded 1.2 cm from the bottom of the pipe. Flow-weighted composite samples were used to calculate event mean concentrations (EMCs).

Sample laboratory analyses are discussed in a companion paper by Burant et al., 2018, and the TOrcs are described in Table 2.1 [25].

The methods employed to process the samples had a limit of quantitation (LOQ). Since the statistics conducted herein require observations for all elements in a set, and since practices like substitution and deletion should be avoided when analyzing censored data as it produces spurious and skewed result, the contaminants studied were limited to those that had no censored values [41]. Of the original 82 TOrcs analyzed from the samples, 13 in COMM and 13 in HDRES had no censored data for every storm (Table 2.1). No data were collected for the second storm in COMM for anthraquinone, caffeine, fluoranthene, DEET, and phenanthrene. This presented a different situation than that for censored data, however, because there was no reported value for that event, be it a number or LOQ. The number of events for the aforementioned TOrcs were thus one less than that of the others in COMM.

2.3 Empirical data analysis

Area-normalized EMLs, rather than EMCs, were utilized in the current study because of regulatory reasons (total maximum daily loads, not total maximum daily concentrations) and because preliminary correlation analyses showed TOrc EMCs were not consistently well-correlated with any of the considered hydrologic metrics. An area-normalized load is calculated as the EMC multiplied by the outfall volume and divided by the study site area. All of the statistical analyses for this project were done using R, version 3.3.1 [45].

Table 2.1 TOrcs analyzed in this study, where they were detected, their uses, their health and ecological effects, log K_{ow}, molecular weight, and solubility in water

Name	Detected in COMM	Detected in HDRES	Use	Health & Ecologic Effects	Log K _{ow}	Molecular Weight [g/mol]	Solubility in water at 25 °C [mg/L]
2,4-D ^a [5]	Yes	Yes	Herbicide	Used in agent orange, acute oral and dermal toxicity	2.81	221.033	677
Anthraquinone [6]	Yes	No	Manufacture of dyes, textiles, and pulp	Skin and eye irritation, urine discoloration	3.39	208.216	1.353
Atrazine [7] [42]	No	Yes	Herbicide	Slightly-to-moderately toxic to humans and animals	2.61	215.658	34.7
Benzotriazole [8]	Yes	Yes	Corrosion inhibitor and anti-scaling agent	Explosive particles, acute oral toxicity, serious eye irritation	1.44	119.127	1.98*10 ⁴
Caffeine [43]	Yes	Yes	Food and beverages	Diuretic, stimulant	-0.07	194.194	2.16*10 ⁴
DEET ^b [9]	Yes	Yes	Repellant	Acute oral toxicity, eye and skin irritation, harmful to aquatic life	2.02	191.274	912
Diuron [10]	No	Yes	Biocide, herbicide, pesticide	Irritation of nose, throat, eyes, and skin	2.68	233.029	42
Fluoranthene [11]	Yes	No	Coal tar, petroleum derived asphalt	Contact burns to skin and eyes, nausea, tachycardia, cardiac arrhythmias, liver injury, pulmonary edema, and respiratory arrest	5.16	202.256	0.20-0.26
Imidacloprid [12] [13]	Yes	Yes	Insecticide	Acute oral toxicity, harmful to aquatic life	0.57	255.662	6.1*10 ^{2 9}
Mecoprop [16] [15]	Yes	Yes	Herbicide, pesticide	Acute oral and dermal toxicity, eye damage, harmful to aquatic life	3.13	214.645	880
Oryzalin [17][18]	Yes	Yes	Herbicide	Very toxic to aquatic life	3.73	346.358	2.5
Phenanthrene [19]	Yes	No	Coal tar	Very toxic to aquatic life	4.46	178.234	1.15
TCEP ^c [20] [21] [22]	Yes	Yes	Flame retardant	Acutely toxic, highly carcinogenic, highly adverse to development	1.78	285.482	7.8*10 ^{3 9}
TCPP ^d [21]	Yes	Yes	Flame retardant	Highly adverse to reproduction and development	2.59	327.563	1.6*10 ³
TDCPP ^e [23]	Yes	Yes	Flame retardant	Highly carcinogenic, highly adverse neurologically, highly and acutely toxic to aquatic life	3.65	430.889	7 ^h
TPP ^f [44]	No	Yes	Flame retardant	High and acute chronic toxicity to aquatic life	4.59	326.288	1.9

^a 2,4-D = 2,4-dichlorophenoxyacetic acid

^b DEET = N,N-diethyl-meta-toluamide

^c TCEP = tris(2-carboxethyl)phosphine

^d TCPP = tris(chloropropyl)phosphate

^e TDCPP = tris(1,3-dichloro-propyl)phosphate

^f TPP = triphenyl phosphate

⁹ the solubility was measured at 20°C

^h the solubility was measured at 24 °C

2.3.1 Outliers

Tukey's Boxplot Method was used to look for outliers in TOrC EMLs [46]. Only extreme outliers were analyzed because of the small number of events in which TOrCs were detected. Few of the TOrC EMLs had extreme outliers in COMM and HDRES. Removing the outliers did not significantly affect the analysis results. Furthermore, according to Helsel and Hirsch, there is no reason to remove outliers [47]. Outliers were thus included to maximize the number of events analyzed.

2.3.2 Data distributions, correlations, & regressions

The Shapiro-Wilks test, with $\alpha = 0.05$, was used to test for the normality of the data [48] [49]. Results of the Shapiro-Wilks test indicate that not all of the data were normally or log-normally distributed. Kendall's tau was used to measure correlations between area-normalized TOrC EMLs and the hydrologic measurements listed in Chapter 2.2.1. Kendall's tau was used because of the small sample size and non-normality of the data [47] [50]. Kendall's tau-b was used rather than Kendall's tau-a because of how it treats tied ranks. Even though Kendall's tau only measures the strength of a monotonic relationship between two variables; a Kendall's tau of 0.7 or above corresponds with a Pearson's r of 0.9 or above, indicating a very strong connection between two variables [47]. These correlations were calculated as data-exploration measures and to determine which variables would be most appropriate for hypothesis testing and use in models.

Regressions were calculated after computing the aforementioned explanatory correlations. Area-normalized loads were the dependent variables and precipitation depth was the independent variable (Chapter 3.1). Two types of regressions were used in this study: the Kendall-Theil Robust Line (KTRL) and ordinary least-squares (OLS). KTRL is a non-parametric regression method that uses median values to compute line slopes and intercepts [47] [51]. OLS produces the best-fit linear regression (it minimizes the sum of the squared errors) if there is a linear relationship between two variables, if the residuals of the regression have a mean of zero, and if the residuals are heteroscedastic. OLS is viable even if the residuals are not normal and not independent of the independent variable. In this study, KTRL was used to establish the significance of a linear relationship between TO_rC EMLs and precipitation depth. OLS regressions were then computed for those TO_rC EMLs that exhibited linear relationships with precipitation depth to establish the best-fit line. The OLS regressions whose residuals did not have a mean of zero and/or were not heteroscedastic were not used in this study. Not all residuals were normal, so the slopes and the intercepts of the regressions were not tested statistically for randomness and/or for cross-site comparisons. If the regression has a negative intercept the model becomes a step-wise function: the model predicts a value of 0 if the precipitation is less than $-\frac{\textit{intercept}}{\textit{slope}}$ because it is not possible to have a negative load.

2.3.3 Cross-site analysis & regression validation

The OLS regressions' fits were analyzed both visually and with explanatory statistics for their goodness-of-fit and predictive powers. The regressions for TO_rC EMLs that were measured in both COMM and HDRES were also analyzed visually to determine how they reacted to precipitation events in both land covers. The slopes and intercepts were studied to determine their similarities and differences between sites. Root mean square error (RMSE), percent bias, index of agreement, modified index of agreement with $j=1$, and visual checks were to determine their goodness-of-fit [52]. The index of agreement was used to establish the fit of higher values and the modified index of agreement was used for lower values.

2.4 Scaling regression results to Madison, WI

The OLS regressions were used to estimate total annual loads from all commercial and high-density residential areas for the watersheds to which Madison, WI, discharges its stormwater. This analysis may inform environmental managers on potential TO_rC loads throughout the city so that they may begin to plan for TMDL establishment, compliance, and treatment through installation of stormwater treatment practices. The mean annual rainfall depth was calculated from records from 1981-2010 at the airport and is reported in Chapter 2.1 [35]. The total commercial area in Madison was calculated from the tax assessor parcels available from the City of Madison where the property class was commercial [36]. The total high-density residential area in Madison was calculated as the intersection between tax assessor parcels whose property class was residential

and NLCD developed, low-intensity, medium-intensity, and high-intensity areas [36] [37]. The Wisconsin Department of Natural Resources has delineated watersheds based on drainage and management criteria and has made them available to the public [53]. Once all of the commercial and high-density residential areas were defined they were clipped to the watersheds using ArcGIS [40]. Mean annual loads for each watershed were then calculated from both land covers for the TOrCs described herein.

2.5 WinSLAMM

2.5.1 WinSLAMM hydrology & water quality

WinSLAMM is an event-based water quality and rainfall-runoff model that routes water through various source areas in watersheds first to a junction and then to an outfall point. Each watershed has a designated land cover, and there may be more than one watershed that has the same land cover that routes to the same junction. The user defines source areas within each watershed, such as buildings, parking, and streets, and their parameters, such as pitched or thatched roofs, direct connectivity to drains, and soil types if water drains to soils. WinSLAMM is a Type I rainfall-runoff model [54] [55]. Rather than having one runoff coefficient for a given basin, however, there are different runoff coefficients for source areas for various storm sizes. Since WinSLAMM is a Type I model, the duration of the event does not affect the outfall volume; it does, however, affect the simulated peak flow and intensity as WinSLAMM constructs a synthetic hydrograph for each event.

WinSLAMM has built-in modules to calculate the mass and concentration of particulate solids, particulate pollutants, and filterable pollutants in runoff. The model calculates particulate solid concentrations and loadings in much the same way that it calculates runoff volume: there are defined concentrations for different storm sizes, for different source areas, and for different land covers. There is, however, a unique particulate solids build-up function for streets. The model assumes that streets have a default initial amount of particulate solids and that particulate solids accumulate on the streets as a linear function of inter-event times [55].

2.5.2 WinSLAMM configuration

Both COMM and HDRES were studied in separate WinSLAMM configurations; each contained only one watershed routed to a junction, which was then routed to an outfall. The source areas for both COMM and HDRES outlined in Chapter 2.1 were used to characterize the WinSLAMM model at both sites. Buildings for both sites were assumed to have pitched roofs, and all impervious areas were directly connected to drainages. Both sites have silty soil [56].

WinSLAMM allows users to define custom impervious and pervious source areas with their own runoff coefficients, particulate solids, and pollutant files. The users may do this if their source area is not found within the model or if they want to examine a particular aspect of a source area without legacy interference from the model. As will be explained in Chapter 2.5.4, particulate solids were used as proxies for TOrCs. Other Impervious Area (#84) was used in lieu of streets

because the particulate solids initial loads and build-up function for streets were not suitable for modeling TOrCs in this project. All of the runoff coefficients parameterized for Other Impervious Area (#84) were the same as those for streets.

2.5.3 WinSLAMM hydrologic calibration & validation

WinSLAMM was calibrated and validated hydrologically with storm event outfall volume for COMM and HDRES using a split sample of the storms from each site. The calibration and validation storms were chosen randomly from the available data. The initial runoff coefficients were deduced by the USGS [57]. The models were manually calibrated to minimize percent bias by altering initial source area runoff coefficients. Because hydrology was measured only in the downstream pipe rather than from source areas directly, the models were calibrated by adjusting each runoff coefficient for each source area for each storm size by the same percentage. Once the runoff coefficients for the source areas were adequately calibrated, the other half of the split sample was run for validation purposes. Percent bias, RMSE, and the Nash-Sutcliff Efficiency (NSE) were used to assess the validation runs.

2.5.4 Integrating TOrC regressions into WinSLAMM

OLS regressions were used to calculate TOrC loads for storms at varying precipitation depths (as required by WinSLAMM). WinSLAMM was run, post-calibration and post-validation, with the same storm depths to calculate outfall volumes for each storm. The loads and volumes were converted into

concentrations for the same storm depths by dividing the predicted loads by the predicted outfall volumes for each respective storm depth. Since no source areas were sampled for water quality (i.e. just the stormwater runoff at the outlet was sampled) it was assumed that each TOrC had a uniform distribution across each site. That is, the concentrations for each storm depth for each source area were the same; the loads from each source area, however, were different because source areas exhibit different runoff volumes for each event due to different runoff coefficients. New .pscx files (the file extension indicating particulate solids) were used to predict TOrC loads by using particulate solid loads as proxies for TOrC loads. New .pscx files were created and subsequently edited to include the aforementioned concentrations for the different storm depths. WinSLAMM was then run using these .pscx files to model TOrC loads in urban stormwater runoff.

Particulate solids were chosen as the proxy contaminant for modeling TOrC loads because WinSLAMM allows for parametrization of concentrations at different storm depths, whereas particulate and filterable pollutants only use the mean and coefficient of variance of observed loads to predict loads. The agreements between the regressions and WinSLAMM were analyzed in much the same way as the cross-site analyses. RMSE, percent bias, index of agreement, and modified index of agreement with $j=1$ were all calculated between WinSLAMM and the observed values. These were then compared with the same statistics for the regressions against the observed values.

CHAPTER 3
RESULTS & DISCUSSION

3.1 Relations between hydrologic controls and TOrC loads

Due to consistent non-normality of the data, as established from the Shapiro-Wilks test, correlations between TOrC EMLs and hydrologic measurements were calculated with Kendall's tau-b (Table 3.1 on p. 22).

TOrC EMLs are most highly and consistently correlated with precipitation depth and peak flow for both COMM and HDRES (Table 3.1 on p. 22). The fact that TOrC EMLs are highly correlated with hydrologic events, but TOrC EMCs are not, indicates that these contaminants are transport limited, not supply or source limited, in these urban areas. In other words, there will always be TOrC loads during precipitation events, though they may be beneath an instrument's LOQ. The lack of correlation between these TOrCs EMLs and antecedent dry days is a further indication that there is no supply limitation of these TOrCs in these urban areas: there is no apparent build-up between precipitation-runoff events, yet there are detectable loads given enough precipitation. This finding agrees with what Burkhardt et al., 2011, found in studying contaminants leaching from construction materials: there will be a continuous release of contaminants from the materials as precipitation occurs [27]. This also agrees with what Macrae et al., 2010, found for nutrient export and Liu et al., 2013, found for total suspended solids, total organic carbon, total phosphorous, and total nitrogen: antecedent hydrologic conditions have little-to-no influence on their export [28] [29]. However, this runs counter to

what others have found about other water quality parameters, such as heavy-metals and phosphorous: many studies have established a correlation between antecedent dry days and non-TOrC loads [1] [58] [59]. This may be indicative of different accumulation processes for these TOrCs than many metals and nutrients. They are, in effect, ever-present in these urban areas and likely do not experience significant build-up. They are in the construction materials and are consistently applied to the land cover through pesticides, herbicides, and the likes in large enough quantities that they will be flushed throughout the wet season. There was weak-to-no evidence that the TOrCs in this study were correlated with intensity in both watersheds (Table 3.1 on p. 22), indicating that they are readily scoured from the environment given enough rain: there is no threshold of intensity that must be met before they are removed from their sources.

3.2 Hypothesis testing & regression development

Precipitation depth was the explanatory variable used in the regressions in this study because TOrC EMLs exhibit the strongest and most consistent correlations with precipitation depth; 92% of TOrC EMLs have $\tau > 0.5$ with precipitation depth at both sites, whereas 81% of TOrC EMLs have $\tau > 0.5$ with the next best metric (peak discharge) at both sites. However, since a correlation analysis of the data indicate a strong relationship between precipitation depth and peak flow, and since there is a relationship between precipitation depth and peak flow, peak flow was not used to create multi-variate regressions [60].

To test the hypothesis that TOrC loads and precipitation depth exhibit a linear relationship, every TOrC EML was regressed against precipitation depth using the KTRL. The KTRL p-values and OLS regression parameters are provided in Table 3.2. Twelve out of 13 TOrC EMLs in COMM exhibit linear relationships with precipitation depth and 12 out of 13 TOrC EMLs in HDRES exhibit linear relationships with precipitation depth. There is no linear relationship between imidacloprid and precipitation depth in COMM and between atrazine and precipitation depth in HDRES. The residuals for every valid OLS regression have a mean of zero and are heteroscedastic. Eight of 13 residuals in COMM do not reject the Shapiro-Wilks test and 2 of 13 residuals in HDRES do not reject the Shapiro-Wilks test. This indicates that it is impossible to statistically test the regression parameters for the majority of the OLS regressions (e.g. statistically compare them to zero or other values). The analyses for these regressions, comparing them to zero and to each other, were therefore done visually and arithmetically. While cross-site and individual regression statistical analyses would strengthen the validity of this, graphical and arithmetic analyses are necessary and add much explanatory power [59].

OLS regressions were calculated for all TOrCs, except for imidacloprid in COMM and atrazine in HDRES. OLS is advantageous to use when the minimum assumptions and requirements are met because OLS minimizes the squared sum of errors between the regression line and the observed values. This, in effect, minimizes statistical model errors and creates a best-fit line.

Table 3.1 Kendall tau-b correlation coefficients between TOrCs and hydrologic event measurements. Greyed out numbers indicate low correlations ($|\tau| < 0.50$).

Name	COMM: Duration [hr]	COMM: Precip [cm]	COMM: Intensity – 15 min [in/hr]	COMM: Intensity – 30 min [in/hr]	COMM: Antecedent Dry Days [days]	COMM: Peak Flow [cfs]	HDRES: Duration [hr]	HDRES: Precip [cm]	HDRES: Intensity – 15 min [in/hr]	HDRES: Intensity – 30 min [in/hr]	HDRES: Antecedent Dry Days [days]	HDRES: Peak Flow [cfs]
2,4-D	0.27	0.64	0.56	0.51	0.073	0.55	0.33	0.53	0.38	0.27	-0.077	0.48
Anthraquinone	0.20	0.91	0.33	0.47	-0.18	0.58	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
Atrazine	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	0.36	0.25	-0.039	-0.14	0.00	0.14
Benzotriazole	0.055	0.64	0.64	0.70	0.29	0.70	0.15	0.61	0.32	0.22	0.15	0.56
Caffeine	0.20	0.64	0.42	0.56	0.18	0.67	0.21	0.61	0.22	0.22	0.26	0.51
DEET	0.20	0.64	0.33	0.47	0.090	0.18	-0.18	0.55	0.43	0.40	0.18	0.64
Diuron	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	0.18	0.64	0.46	0.35	0.13	0.64
Fluoranthene	0.16	0.87	0.38	0.51	0.22	0.63	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
Imidacloprid	0.20	0.27	-0.018	0.11	-0.11	0.26	0.23	0.68	0.30	0.30	0.23	0.54
Mecoprop	0.24	0.67	0.60	0.55	0.11	0.59	0.15	0.55	0.22	0.22	0.26	0.51
Oryzalin	0.20	0.71	0.49	0.62	0.29	0.62	0.23	0.58	0.20	0.19	0.28	0.48
Phenanthrene	0.11	0.91	0.33	0.38	0.18	0.58	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ
TCEP	0.16	0.82	0.53	0.66	0.26	0.73	-0.10	0.55	0.33	0.27	0.21	0.61
T CPP	0.16	0.82	0.53	0.66	0.26	0.73	0.026	0.58	0.35	0.25	0.13	0.64
TDCPP	0.16	0.75	0.60	0.73	0.18	0.81	-0.051	0.68	0.51	0.48	0.10	0.72
TPP	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	0.15	0.81	0.48	0.43	0.10	0.67

Table 3.2 Kendal-Theil Robust Line slope significance p-values, OLS slopes, and OLS intercepts for TOrcs in both COMM and HDRES, as well as the ratios of slopes and absolute difference of intercepts between the two land covers. ^{a b c}

Name	COMM: <i>KTRL</i> <i>Slope</i> <i>p-</i> <i>value</i>	COMM: <i>OLS Slope</i> <i>[ng/m²*cm]</i>	COMM: <i>OLS</i> <i>Intercept</i> <i>[ng/m²]</i>	HDRES: <i>KTRL</i> <i>Slope</i> <i>p-</i> <i>value</i>	HDRES: <i>OLS Slope</i> <i>[ng/m²*cm]</i>	HDRES: <i>OLS</i> <i>Intercept</i> <i>[ng/m²]</i>	Slope Ratios (COMM/HDRES)	Intercept Differences (COMM- HDRES)
2,4-D	0.0064	1300	3200	0.012	3500	1000	0.37	2200
Anthraquinone	0.00025	2500	-640	-	-	-	†	†
Atrazine	-	-	-	0.24	**	**	†	†
Benzotriazole	0.0064	600	-240	0.0039	1100	600	0.55	-840
Caffeine	0.0095	2200	1500	0.0039	5800	-730	0.38	2230
DEET	0.0095	7300	-200	0.0083	1300	130	5.6	-330
Diuron	-	-	-	0.00047	13	14	†	†
Fluoranthene	0.00049	950	-330	-	-	-	†	†
Imidacloprid	0.24	**	**	0.0011	24	15	†	†
Mecoprop	0.0040	450	1100	0.0083	330	-140	1.4	1240
Oryzalin	0.0024	500	160	0.0057	410	330	1.2	-170
Phenanthrene	0.00025	420	-93	-	-	-	†	†
TCEP	0.00046	610	-240	0.0083	1200	360	0.51	-600
TCP	0.00046	2000	-1200	0.0057	1800	1100	1.1	-2300
TDCPP	0.0011	440	-280	0.0014	98	16	4.5	-296
TPP	-	-	-	0.00011	740	530	†	†

^a - indicates that the TOrc was not detected in that land cover

^b ** indicates that there was not an established linear relationship between the TOrc and precipitation depth, meaning that the TOrc could not be modeled.

^c † indicates that the ratios or differences were not calculable.

Table 3.3 RMSE, % bias, index of agreement (d), and a modified index of agreement for the regressions in both COMM and HDRES for the regressions. ^{a b}

Name	COMM: RMSE	COMM: % bias	COMM: d	COMM: modified d	HDRES: RMSE	HDRES: % bias	HDRES: d	HDRES: modified d
2,4-D	6900	0	0.39	0.29	10000	0	0.57	0.47
Anthraquinone	680	-0.60	1.0	0.93	-	-	-	-
Atrazine	-	-	-	-	**	**	**	**
Benzotriazole	510	0	0.96	0.73	2300	0	0.72	0.57
Caffeine	3400	0	0.87	0.65	6600	0	0.90	0.75
DEET	4500	-0.74	0.98	0.82	2000	0	0.83	0.67
Diuron	-	-	-	-	41	0	0.56	0.46
Fluoranthene	270	-1.1	0.99	0.93	-	-	-	-
Imidacloprid	**	**	**	**	40	0	0.82	0.64
Mecoprop	2600	0	0.33	0.29	170	-5.1	0.98	0.84
Oryzalin	750	0	0.88	0.74	900	0	0.72	0.57
Phenanthrene	260	-0.45	0.98	0.84	-	-	-	-
TCEP	340	-2.6	0.98	0.85	2500	0	0.71	0.57
TCPP	850	-4.5	0.99	0.86	3400	0	0.76	0.58
TDCPP	200	-5.3	0.99	0.86	140	0	0.85	0.70
TPP	-	-	-	-	1600	0	0.70	0.56

^a - indicates that the TOrc was not detected in that land cover

^b ** indicates that there was not an established linear relationship between the TOrc and precipitation depth, meaning that the TOrc could not be model

3.3 Statistical model evaluation

As indicated in Table 3.3, the regressions tend to fit the observed values quite well: there are small percent biases in both COMM and HDRES hovering about or equal to zero for the majority of regressions, and never exceeding -5.3; the indices of agreement for COMM are consistently 0.9 or higher and for HDRES are consistently 0.7 or higher, indicating that the regressions predict higher values well; the modified indices of agreement for COMM were consistently 0.7 or higher and for HDRES are consistently 0.5 or higher, indicating a relatively good fit for low values. The differences between the indices and modified indices of agreement shows that these statistical models tend to predict higher values better than lower values. The better prediction for higher values is likely due to the fact that some OLS regressions have negative intercepts; in the cases where the regression produces negative intercepts the model underestimates loadings for smaller precipitation events up until it rains $-\frac{\text{intercept}}{\text{slope}}$ cm.

The regressions tend to fit the observed values better in COMM than they do in HDRES. This could be for many reasons but is likely due to more consistent uses of many of these contaminants in COMM than in HDRES. For example, to apply pesticides in Wisconsin one must become a licensed applicator in both commercial and private settings [61]. So, while institutions in commercial areas hire professional and licensed applicators to maintain their vegetated areas, those in private and residential settings either hire licensed companies or apply the pesticides themselves. If a private individual is the applicator they may not have the legal requirements to apply the pesticides to begin with or their licensure may

have lapsed. This would result in a more inconsistent application of pesticides in residential than commercial areas. Or, the application regimens differ between residential than commercial areas. Or, the application regimens differ between land covers, engendering different amounts to accumulate in both land covers. However, additional data such as that obtainable through a survey needs to be collected to fully evaluate this explanation. Many of the pesticides and herbicides may be deposited from the atmosphere, but there is no strong evidence to suggest different depositional patterns in COMM and HDRES.

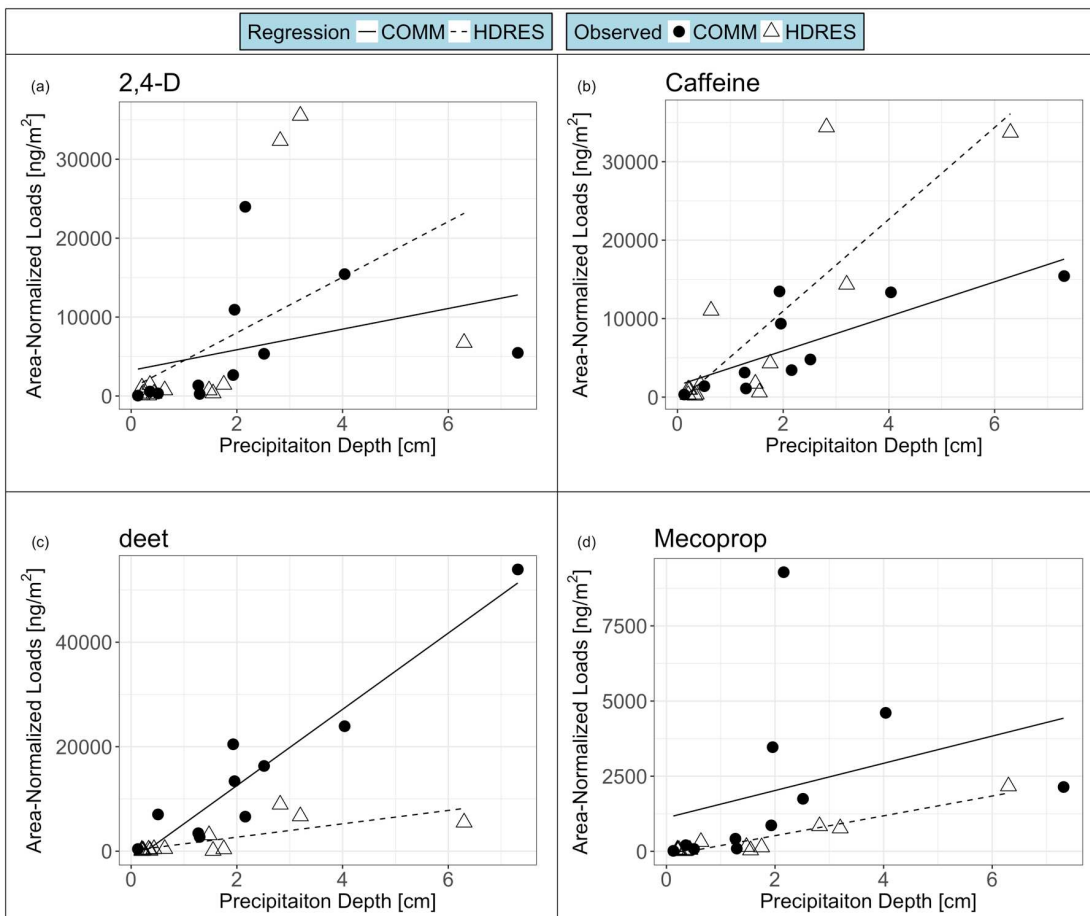


Figure 3.1 Example regressions for (a) 2,4-D; (b) caffeine; (c) deet; and (d) mecoprop in both COMM and HDRES.

As seen in Figure 3.1 and in Table 3.3, 2,4-D's and mecoprop's regressions have poor fits ($d = 0.39$ and modified $d = 0.29$ in COMM and $d = 0.57$ and modified $d = 0.4.7$ in HDRES for 2,4-D; $d = 0.33$ and modified $d = 0.29$ in COMM mecoprop), whereas caffeine's and DEET's exhibit very good fits ($d = 0.87$ and modified $d = 0.65$ in COMM and $d = 0.90$ and modified $d = 0.75$ in HDRES for caffeine; $d = 0.98$ and modified $d = 0.82$ in COMM for deet). The examples shown in Figure 3.1 also indicate how different TOrC loads respond to precipitation depth in both COMM and HDRES.

The differences and similarities in slope values indicate different or similar responses to precipitation depth in COMM and HDRES. From all regressions for TOrCs detected in both sites, as well as the slope ratios and intercept differences in Table 3.2, one sees there is no trend as to which class of TOrC (e.g. flame retardant, pesticide, herbicide) will respond similarly or differently to precipitation in either land cover (see Appendix A, Figures A.1-A.5, for regressions of the other contaminants detected in both sites). Oryzalin's and mecoprop's regressions have similar slopes in both COMM and HDRES, though slightly higher in COMM. 2,4-D, benzotriazole, caffeine, and TCEP all have smaller slopes in COMM than in HDRES, indicating that they have a smaller per-acre loading responses in COMM than HDRES to precipitation events. DEET, TCPP, and TDCPP have higher slopes in COMM than in HDRES, indicating that they have a higher per acre loading in COMM than in HDRES. The negative intercepts of some other TOrCs indicate that it must rain a certain amount before the TOrC can be detected at these two sites;

it must rain more than $-\frac{\textit{intercept}}{\textit{slope}}$ cm. See Appendix A, Figures A.1-A.10, for the fits of regressions that are not shown in this manuscript.

2,4-D, an herbicide, has a smaller slope in COMM than in HDRES, indicating that there will be smaller loadings in COMM than in HDRES. 2,4-D is often applied to gardens, lawns, and roadsides [62]. Since vegetation accounts for a higher relative percentage of the area to paved surfaces in HDRES than it does in COMM, it may be deduced that more 2,4-D is applied to vegetation than to paved surfaces. Benzotriazole has a smaller slope in COMM than in HDRES, and thus, has a smaller per-acre loading in COMM than in HDRES during precipitation events. This may be because benzotriazole leaches from construction materials and buildings are responsible for almost twice the percentage of runoff volume in HDRES than in COMM (Chapter 3.5). DEET, an insect repellent applied directly to the skin or clothes, has a higher slope in COMM than it does in HDRES [63]. Even though DEET is often applied while at home, this result is likely due to differences in human traffic because COMM has a larger area and is more trafficked than HDRES (COMM has a mall and many office buildings, whereas HDRES predominantly has single-family homes). The difference in slopes for caffeine between COMM and HDRES is ambiguous because caffeine is consumed via food and drink; it is introduced to the environment through both food and human waste. It could be that there is more caffeine in HDRES because the individuals who live there dispose of their food and drink (either accidentally or on purpose) in HDRES public areas and/or homeowners in HDRES apply coffee grounds to their vegetated areas. Mecoprop is often used in agriculture with cereal crops and fruit

trees, so any mecoprop present in either site was likely deposited from the atmosphere due to volatilization from surrounding agricultural areas [14]. Since there is no reason to believe that depositional patterns differ for COMM and HDRES there should be similar per-acre load responses to precipitation in both sites. Oryzalin also has very similar slopes in both land covers. Oryzalin is an herbicide that is not very mobile and does not easily volatilize [64]. This indicates that the oryzalin present in either land cover likely originated in those covers and that similar per-acre loadings of oryzalin are applied to both land covers. TCEP, TCPP, and TDCPP are flame retardants used in furniture and are often found in indoor dust [21] [65]. While many flame retardants are sold and utilized as mixtures, these results indicate that furniture in different land covers use different mixtures with different relative concentrations of flame retardants [22]. TCEP has a smaller slope in COMM than in HDRES and TCPP and TDCPP have a higher slope in COMM than in HDRES. So, the flame retardants used most commonly or in high relative amounts to other retardants in furniture in COMM are therefore TCPP and TDCPP and the flame retardant used most commonly or in high relative amounts to other retardants in furniture in HDRES is therefore TCEP.

Burant et al., 2018, used the Mann-Whitney test to compare EMCs between COMM and HDRES [25]. They showed that TDCPP and DEET had higher EMCs in COMM; TCPP, TCEP, and benzotriazole had higher EMCs in HDRES; and all other TORCs had no distinguishable difference in EMCs between the two sites. These findings, in general, agree with the findings in this study. The results from this study deviate from Burant et al., 2018, for 2,4-D, TCPP, and caffeine. This may

be because this study examined EMLs whereas Burant et al., 2018, examined EMCs.

3.4 Scaling regression results to Madison, WI

The total commercial area in Madison, WI, is 12,410 acres, 21% of the city, and the total high-density area in Madison, WI, is 13,900 acres, 23% of the city. See Figure 3.2 for a map of the watersheds around and the COMM and HDRES areas in Madison, WI. The expected annual loads for each TOrC in each watershed to which Madison, WI, discharges its stormwater are found in Table 3.4 on p. 32. Other land covers, such as agricultural and industrial, likely contribute TOrC loads as well, but as no data is available for those studies they cannot be readily calculated. The Yahara River and Lake Monona Watershed, a primarily urbanized area, experiences the largest annual loads for all TOrCs from both land covers in Madison, WI, whereas Upper Koshkonong Creek Watershed experiences the smallest. This indicates that TMDLs should first be established for the former watershed and last for the latter. There are large discrepancies between annual TOrC loads for the different watersheds, ranging from tens of grams per year to tens of thousands of grams per year.

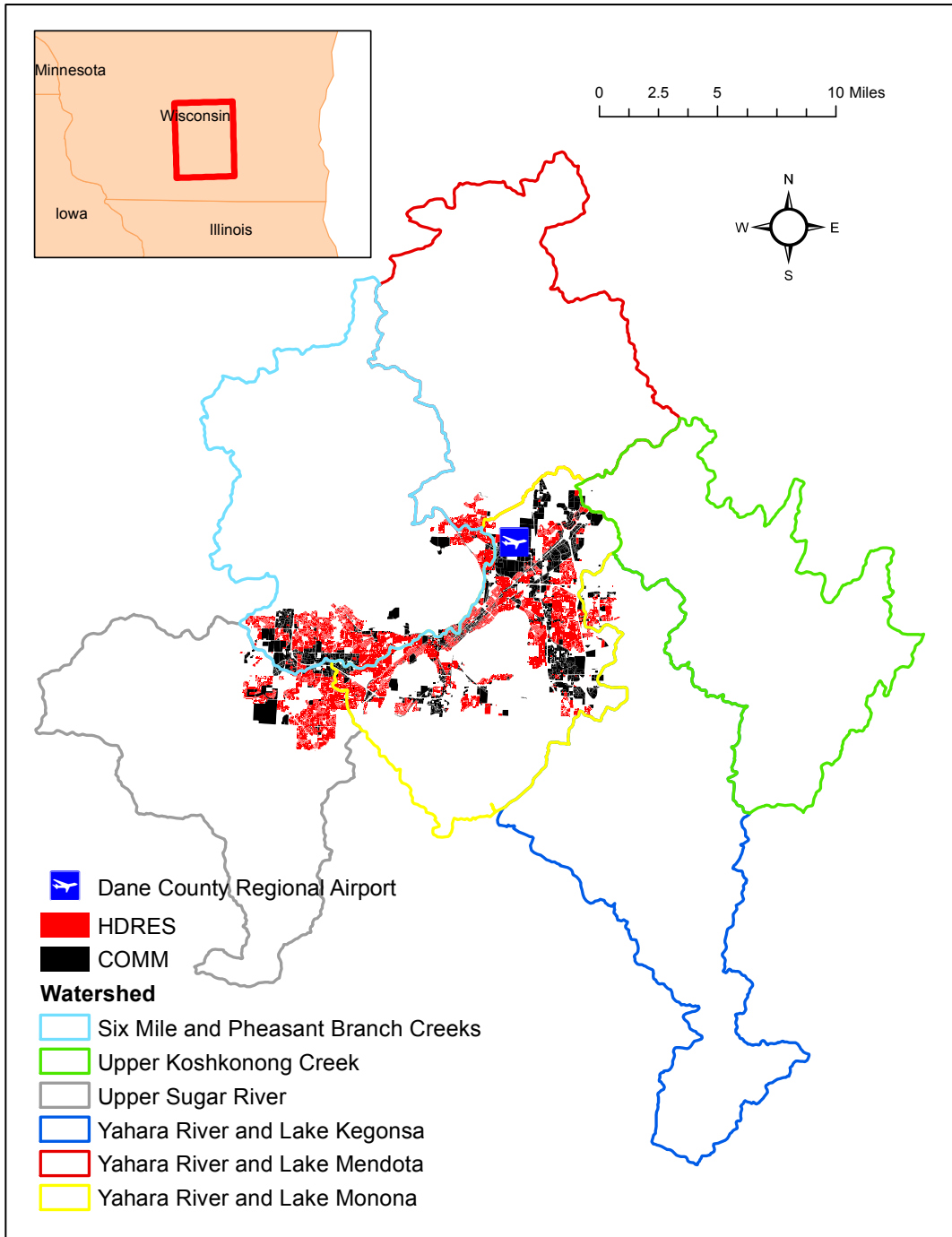


Figure 3.2 A map delineating the total COMM and HDRES areas of Madison, WI, as well as the watersheds to which the city discharges its stormwater.

Table 3.4 Combined mean annual loads for TOrcs from both COMM and HDRES areas in watersheds to which Madison, WI, discharges its stormwater.

Name	Yahara River and Lake Mendota [g]	Upper Sugar River [g]	Yahara River and Lake Kegonsa [g]	Yahara River and Lake Monona [g]	Upper Koshkonong Creek [g]	Six Mile and Pheasant Branch Creeks [g]
2,4-D	910	2480	461	14400	113	4960
Anthraquinone ^a	474	1290	240	7510	58.8	2580
Atrazine ^d	-	-	-	-	-	-
Benzotriazole	311	847	157	4900	38.5	1690
Caffeine	1500	4100	761	23800	186	8190
DEET	1600	4360	808	25300	198	8700
Diuron ^b	2.54	6.92	1.28	40.2	0.314	13.8
Fluoranthene ^a	177	483	89.7	2810	22.0	965
Imidacloprid ^c	4.52	12.3	2.29	71.6	0.560	24.6
Mecoprop	148	404	75.0	2350	18.4	807
Oryzalin	172	470	87.1	2730	21.3	938
Phenanthrene ^a	77.7	212	39.4	1230	9.64	424
TCEP	334	910	169	5290	41.4	1820
T CPP	698	1900	353	11100	86.5	3800
TDCPP	99.4	271	50.3	1580	12.3	542
TPP ^b	140	382	70.9	2220	17.4	763

^a The loads calculated for this TOrc come only from COMM because it was not detected in HDRES

^b The loads calculated for this TOrc come only from HDRES because it was not detected in COMM

^c The loads calculated for this TOrc come only from HDRES because an OLS regression could not be calculated in COMM

^d This TOrc was not detected in COMM and an OLS regression could not be calculated in HDRES

3.5 WinSLAMM hydrologic calibration, validation, & runoff analysis

WinSLAMM hydrology was calibrated well for COMM. The hydrologic calibration and validation results for COMM outfall volumes can be seen in Figure 3.3. The initial runoff coefficients were decreased by 32%. The resulting calibration percent bias was 0.10% and NSE was 0.99. The validation percent bias was -4.2% and NSE was 0.91. The one-to-one line of the observed events passes through the middle of the calibrated and validated volumes, indicating that the model captured both larger and smaller events well (Figure 3.3).

Results of the calibration and validation analyses for HDRES were similar to that for COMM (Figure 3.3). The initial runoff coefficients were decreased by 46%. The calibration percent bias was 2.7% and NSE was 0.13. The validation percent bias was -11% and NSE was 0.91. The poor NSE in the calibration runs was likely due to the presence of an outlier (Figure 3.3, b.i). Percent bias can always be targeted to 0, but such an endeavor may over-fit a model. Were the outlier removed the runoff coefficients would have been calibrated to even smaller values. This would have been detrimental to the validation because, as it stands, the model underestimates the values for the validation runs. Furthermore, with so few events, removing just one data point would have severely weakened this analysis. Outliers should not be removed because doing so spuriously skews the results [41] [47].

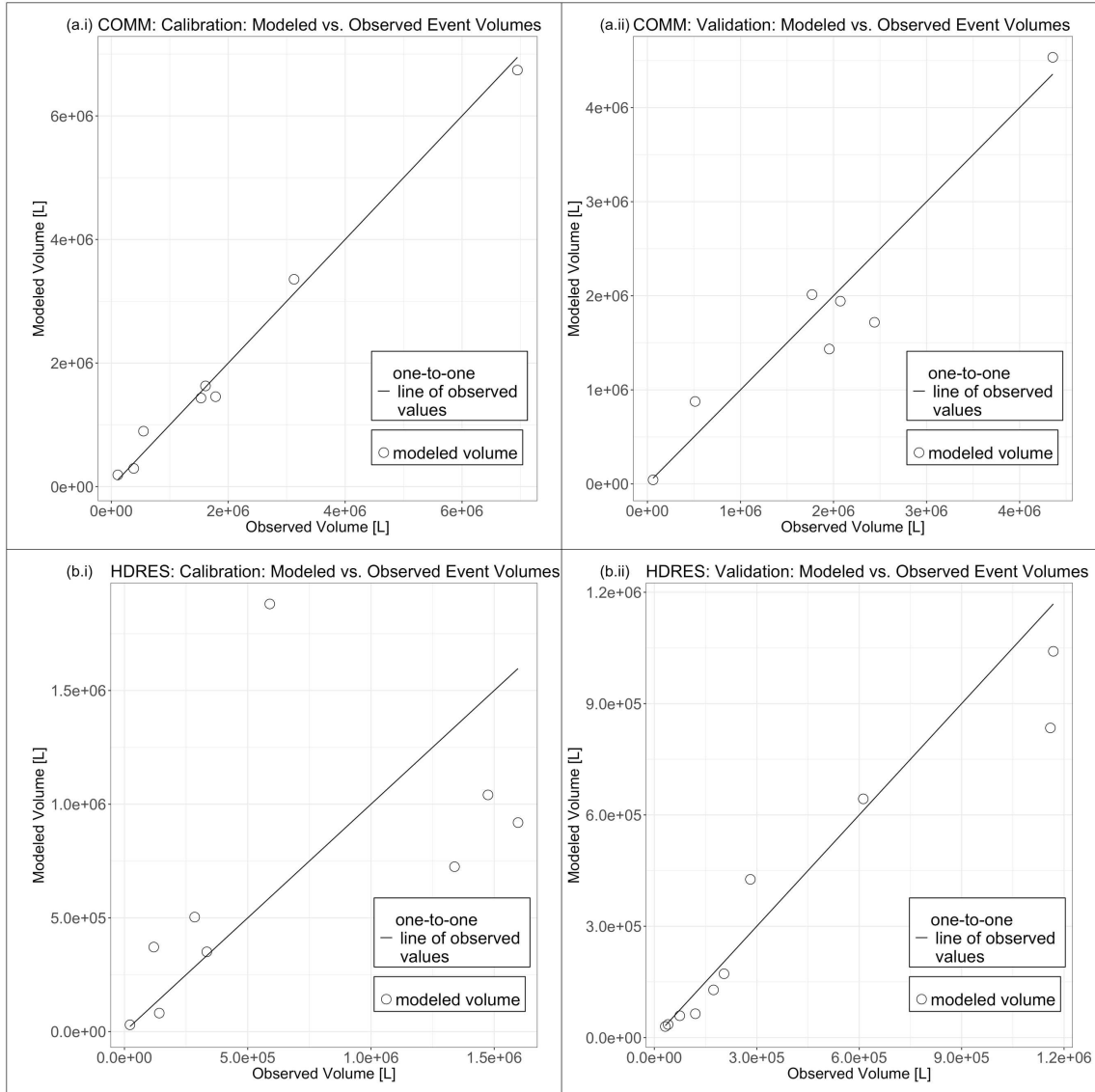


Figure 3.3 WinSLAMM calibration and validation for COMM (a.i and a.ii) and for HDRES (b.i and b.ii). The solid line is a one-to-one line of the observed events.

The largest discrepancies between the two land covers in terms of total runoff volume were roofs, parking, vegetation, and streets (Table 3.5). The discrepancies between source area runoff volume percentages accounted for the greatest discrepancies between the total TOrC loadings for the two land covers because of the assumption of a uniform distribution of TOrC concentration across the sites. It would thus be advantageous to install BMPs around roofs and paved

parking in COMM sites and roofs and streets in HDRES sites in Madison, WI, to attain the greatest loading mitigation.

Table 3.5 Average percentage of total outfall volume for each source area in COMM and HDRES according to WinSLAMM.

Source Area	COMM: Percentage of Total Outfall Volume	HDRES: Percentage of Total Outfall Volume
Driveways	-	15
Paved Parking	54	1.9
Roofs	25	43
Sidewalks	0.6	8.4
Streets	15	21.8
Vegetation	5.4	9.9

3.6 WinSLAMM TOrc EML prediction performance

WinSLAMM predictions for TOrc loads performed in a similar fashion to the OLS regressions on which they were based. After calibrating WinSLAMM hydrologically, the model was run to predict TOrc loads. As can be seen in the examples shown in Figure 3.4, Figures B.1-B.3 in Appendix B, and from the statistics in Table 3.6, WinSLAMM and the OLS regressions on which they are based follow the same trends: WinSLAMM underestimates and overestimates the same events. Not only did WinSLAMM perform in a similar manner to the OLS regressions, but it also had similar statistics for each TOrc. WinSLAMM does, however, predict smaller values for larger storms than the OLS regressions, but the differences are negligible. This shows that regressions can be successfully transferred to WinSLAMM. In the same way OLS minimizes the squared errors, such a transference will lessen the squared errors of the model.

Table 3.6 RMSE, % bias, index of agreement, and a modified index of agreement for the regressions in both COMM and HDRES for WinSLAMM. ^{a b}

Name	COMM: RMSE	COMM: % bias	COMM: d	COMM: modified d	HDRES: RMSE	HDRES: % bias	HDRES: d	HDRES: modified d
2,4-D	7000	-1.1	0.35	0.27	10000	0.63	0.57	0.47
Anthraquinone	690	0.48	1.0	0.93	-	-	-	-
Atrazine	-	-	-	-	**	**	**	**
Benzotriazole	510	-0.51	0.95	0.72	2300	0.25	0.72	0.56
Caffeine	3400	0.08	0.87	0.64	6600	1.4	0.90	0.75
DEET	4600	0.36	0.97	0.82	2000	0.92	0.83	0.67
Diuron	-	-	-	-	41	-0.18	0.55	0.45
Fluoranthene	270	0.077	0.99	0.92	-	-	-	-
Imidacloprid	**	**	**	**	40	0.16	0.82	0.63
Mecoprop	2600	-1.1	0.31	0.27	180	-3.9	0.97	0.83
Oryzalin	750	0.38	0.87	0.74	900	0.033	0.72	0.57
Phenanthrene	260	0.60	0.97	0.84	--	-	-	-
TCEP	340	-1.3	0.98	0.85	2600	0.59	0.71	0.57
TCPP	870	-3.1	0.99	0.86	3400	0.22	0.75	0.58
TDCPP	200	-3.8	0.99	0.86	140	0.81	0.85	0.70
TPP	-	-	-	-	1600	0.097	0.70	0.56

^a - indicates that the TORC was not detected in that land cover

^b ** indicates that there was not an established linear relationship between the TORC and precipitation depth, meaning that the TORC could not be modeled

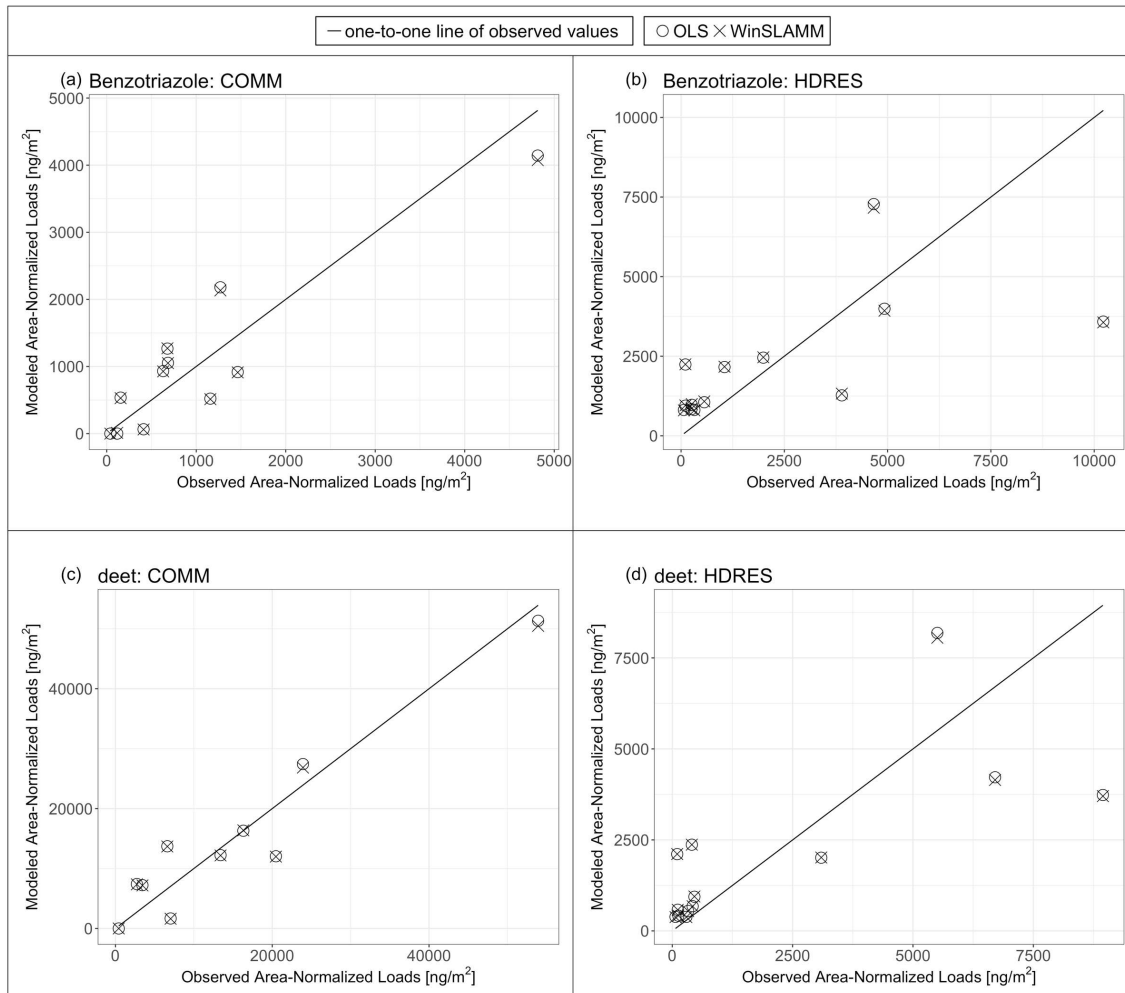


Figure 3.4 Comparisons of WinSLAMM and OLS to each other, as well as to observed values. (a) benzotriazole in COMM; (b) benzotriazole in HRES; (c) deet in COMM; and (d) deet in HDRES.

WinSLAMM is a relatively simple and easy-to-parameterize model. Much of the information required to configure WinSLAMM in the United States is readily available. The model's methods and algorithms are also straightforward, which aids the user in interpreting the results. Such a close fit between WinSLAMM and OLS regressions helps to lay the foundation for further work in contaminant and BMP modeling. This work shows that OLS regression results can be transferred to WinSLAMM, which will enable future users to analyze novel contaminants or BMP mitigations. Furthermore, if source areas are better studied than those results, too,

can be transferred to WinSLAMM and used successfully. Such work would enable very specific areas to be targeted by BMPs to mitigate TOrC loadings and comply with TMDLs.

CHAPTER 4

CONCLUSIONS & FURTHER WORK

TOrC loads were evaluated statistically, using hydrologic measurements as explanatory variables. These results were then transferred to WinSLAMM to exhibit how such statistical models can be transferred to a deterministic model. Precipitation depth is the most highly related hydrologic measurement to these TOrC loads. It is possible to calculate regressions for many of these TOrC loads against precipitation depth in both commercial and high-density residential areas. Regression analysis showed that there is no general trend as to which class of contaminant is more prevalent in either land cover. To further target TOrC loads and know of their sources, source areas should be studied individually and more in-depth. The developed regressions can be used to estimate annual TOrC loads from all commercial and high-density residential areas in Madison, WI, for the watersheds to which the city discharges its stormwater. These regressions can also be successfully imported into models like WinSLAMM to learn about the loadings from different source areas. The transfer of regressions to WinSLAMM allows users to target specific areas to study how BMPs reduce TOrC loads. It also provides users predictive tools for the presence and loads of TOrCs in urban stormwater runoff. With this information, BMPs can be strategically implemented to lessen TOrC loads. For that to be done, however, studies must be conducted to learn more about source area release and which BMPs are most effective in mitigating TOrC loads. This work also helps establish expected loads from different

areas to calculate and establish TMDLs for these TOrCs for different bodies of water.

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APPENDIX A

REGRESSION FIGURES FOR BENZOTRIAZOLE, ORYZALIN, TCEP, TCPP, TDCPP, ANTHRAQUINONE, FLUORANTHENE, PHENANTHRENE, DIURON, AND TPP

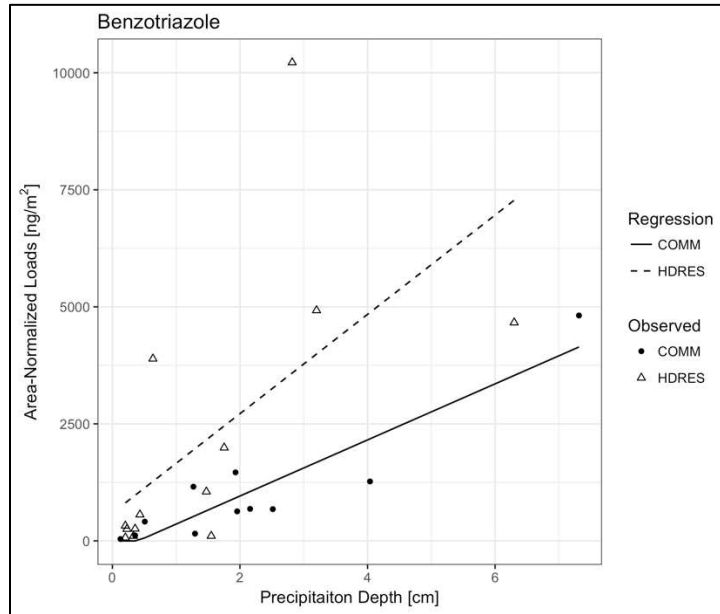


Figure A.1 Regressions for benzotriazole in both COMM and HDRES.

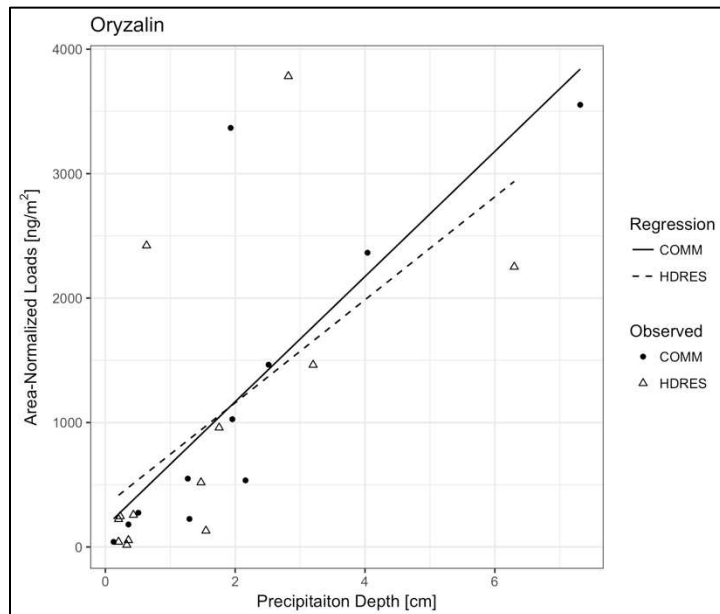


Figure A.2 Regressions for oryzalin in both COMM and HDRES.

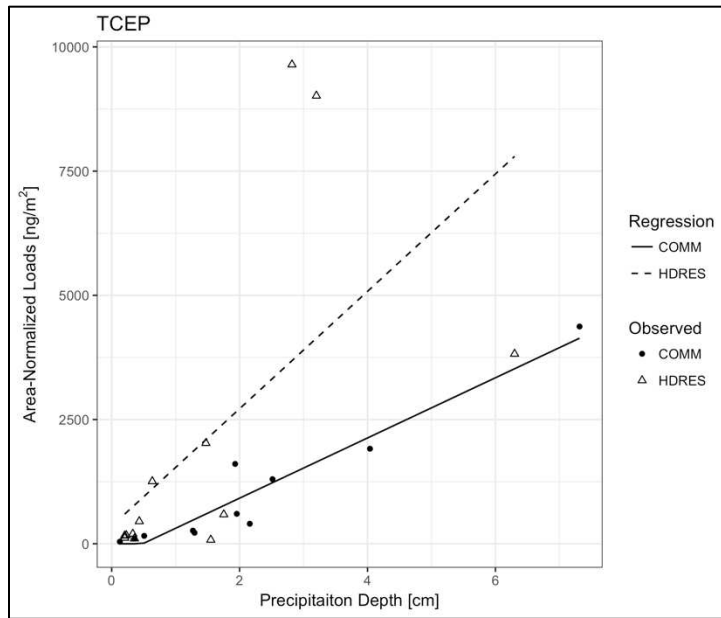


Figure A.3 Regressions for TCEP in both COMM and HDRES.

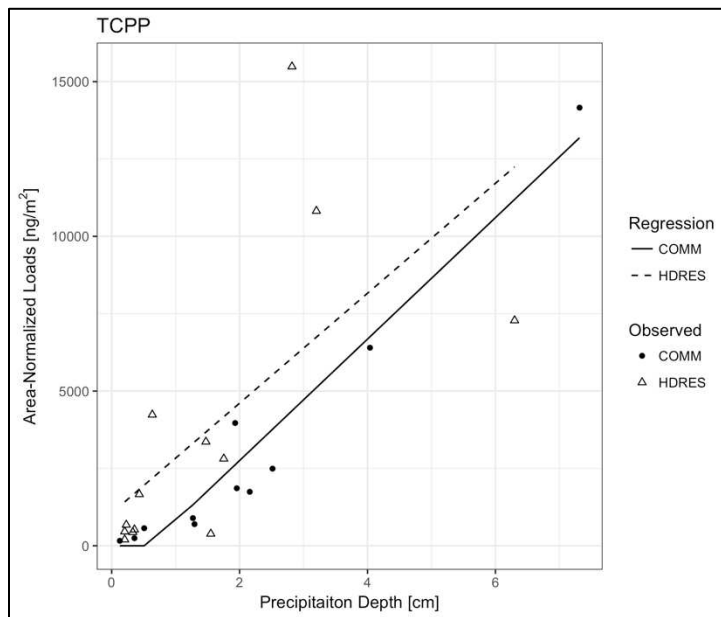


Figure A.4 Regressions for TCPP in both COMM and HDRES.

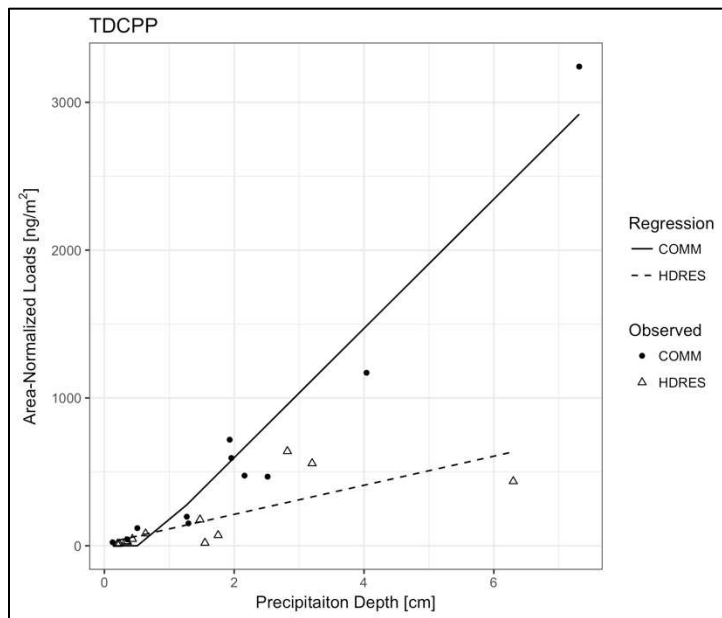


Figure A.5 Regressions for TDCPP in both COMM and HDRES.

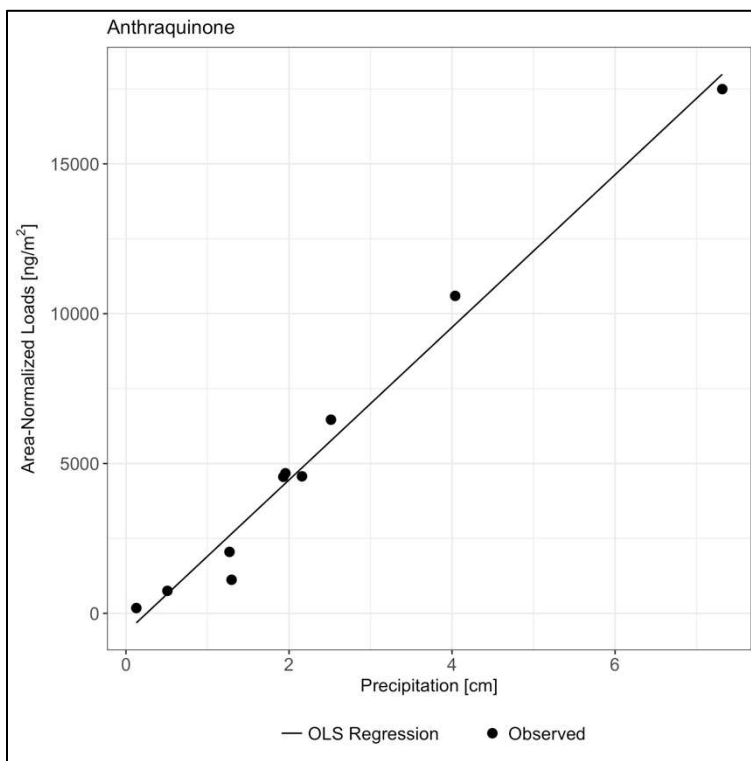


Figure A.6 Regression for anthraquinone in COMM.

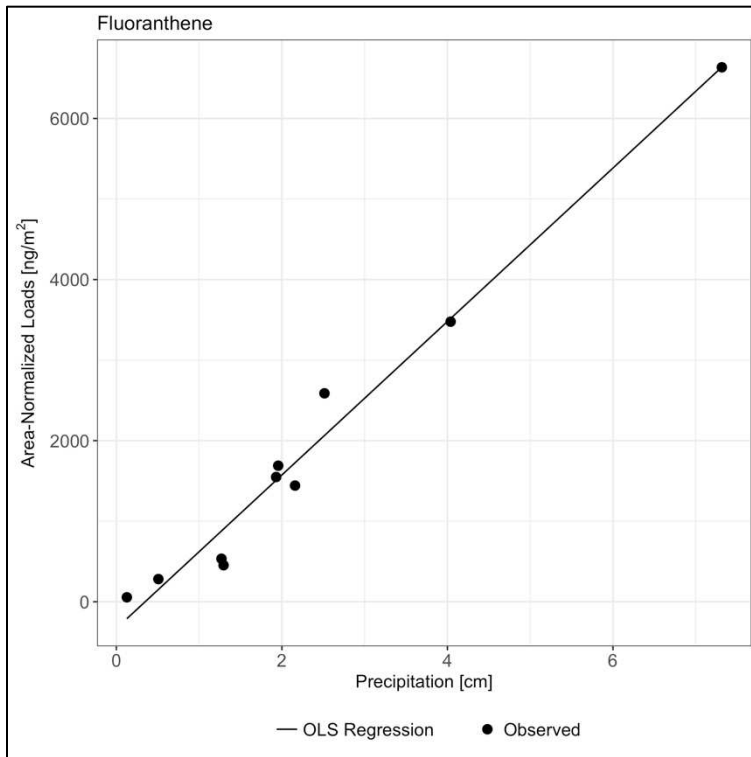


Figure A.7 Regression for fluoranthene in COMM.

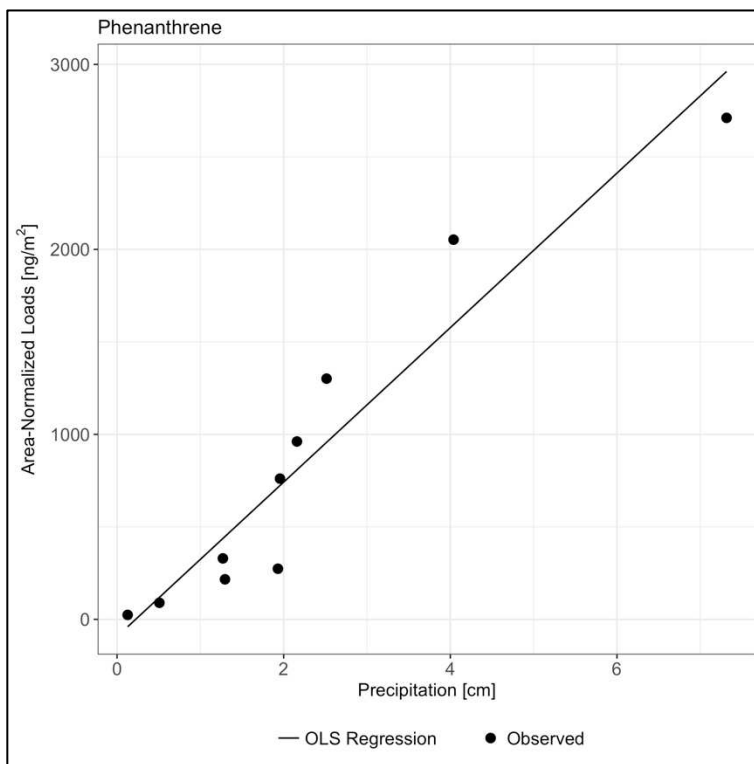


Figure A.8 Regression for phenanthrene in COMM.

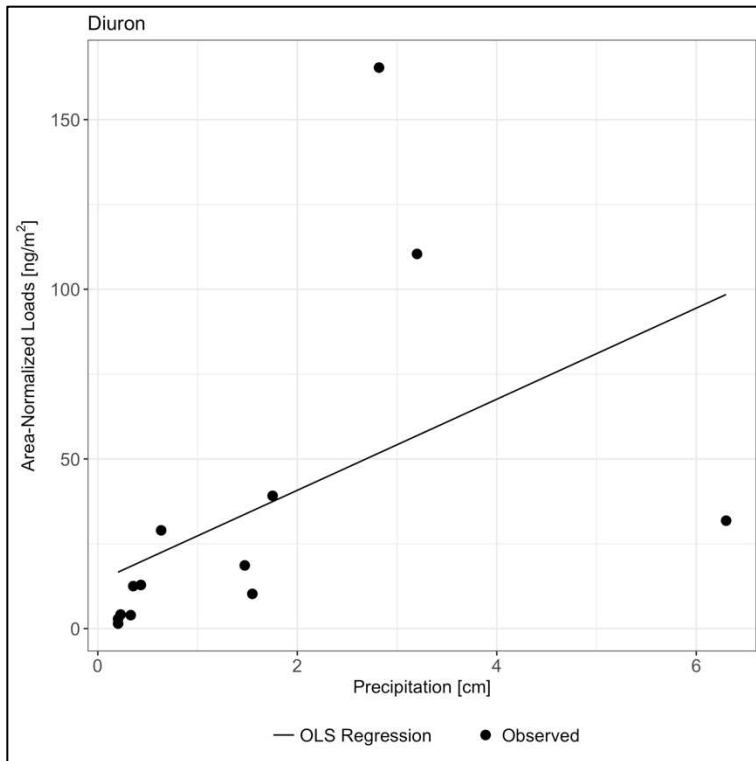


Figure A.9 Regression for diuron in HDRES.

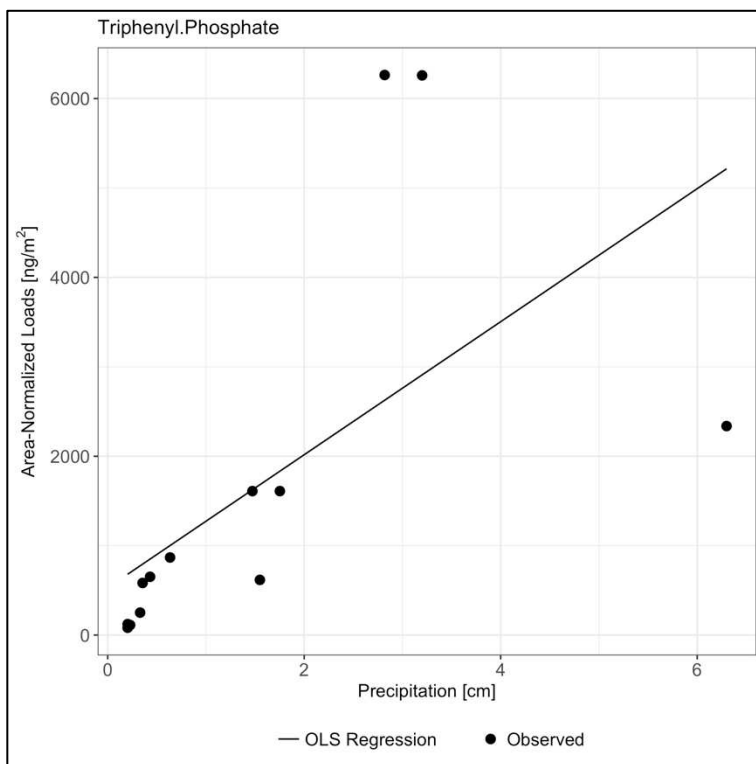


Figure A.10 Regression for TPP in HDRES.

APPENDIX B

WINSLAMM & OLS COMPARISONS TO OBSERVED VALUES FOR 2,4-D, CAFFEINE, MECOPROP, ORYZALIN, TCEP, TCP, TDCPP, ANTHRAQUINONE, FLUORANTHENE, PHENANTHRENE, DIURON, IMIDACLOPRID, AND TPP

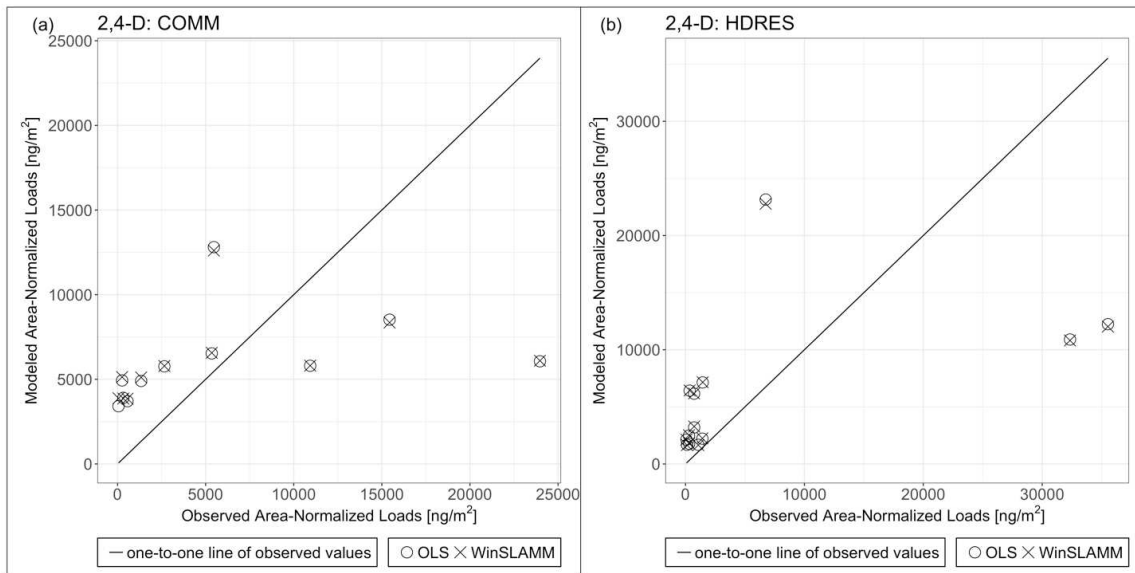


Figure B.1 Comparisons of WinSLAMM and OLS to each other and observed values for 2,4-D for (a) COMM and (b) HDRES.

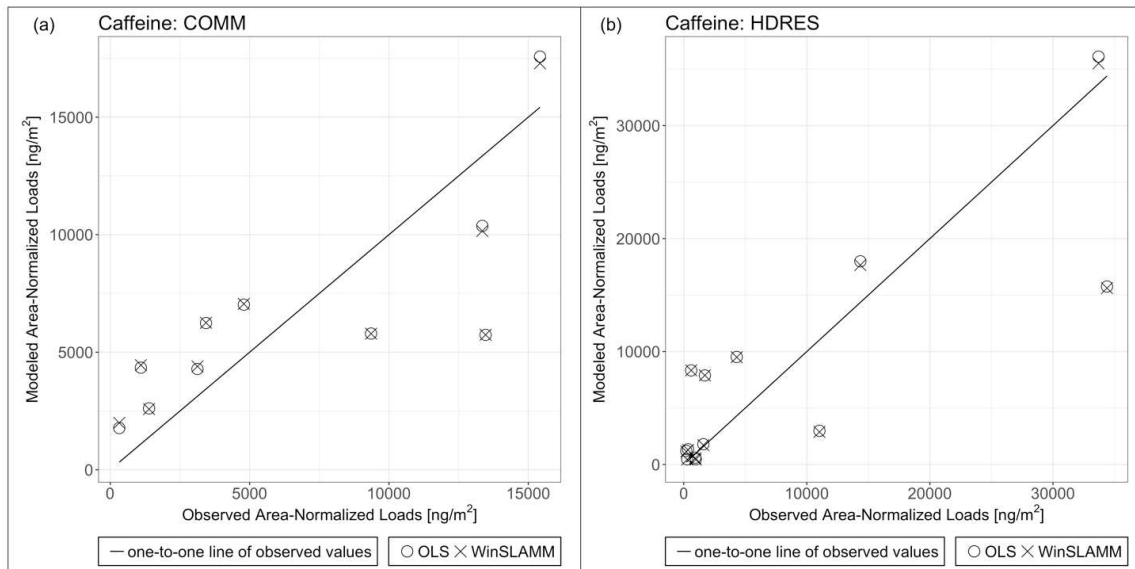


Figure B.2 Comparisons of WinSLAMM and OLS to each other and observed values for caffeine for (a) COMM and (b) HDRES.

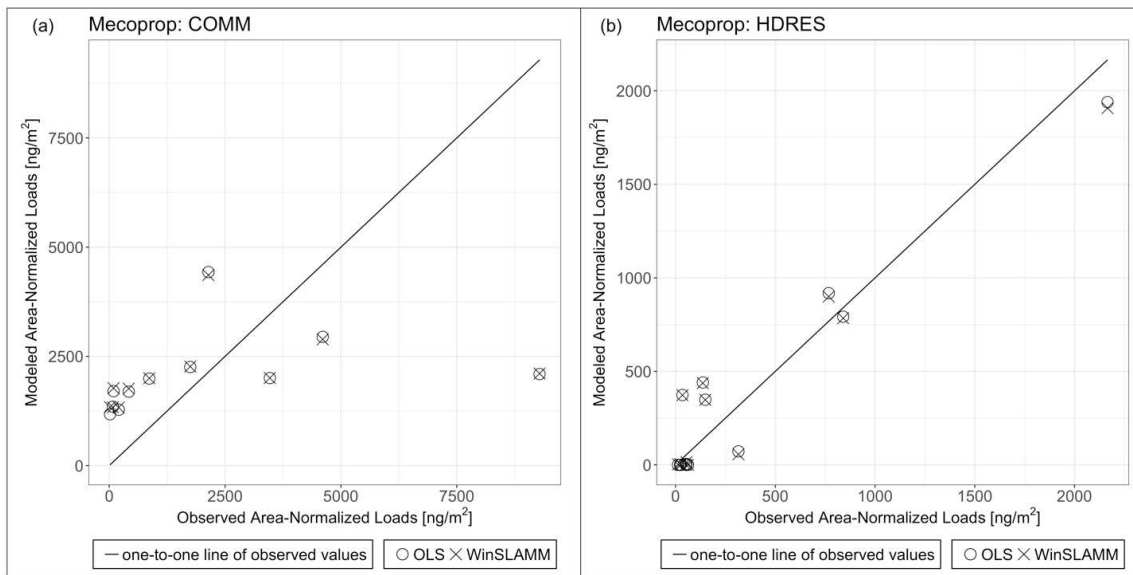


Figure B.3 Comparisons of WinSLAMM and OLS to each other and observed values for mecoprop for (a) COMM and (B) HDRES.

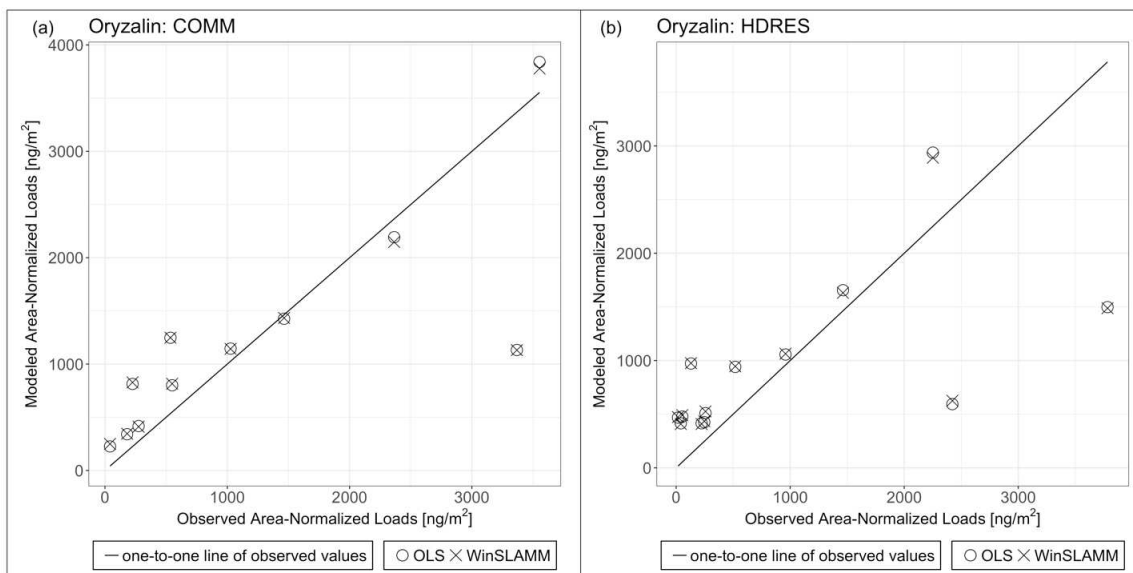


Figure B.4 Comparisons of WinSLAMM and OLS to each other and observed values for oryzalin for (a) COMM and (B) HDRES.

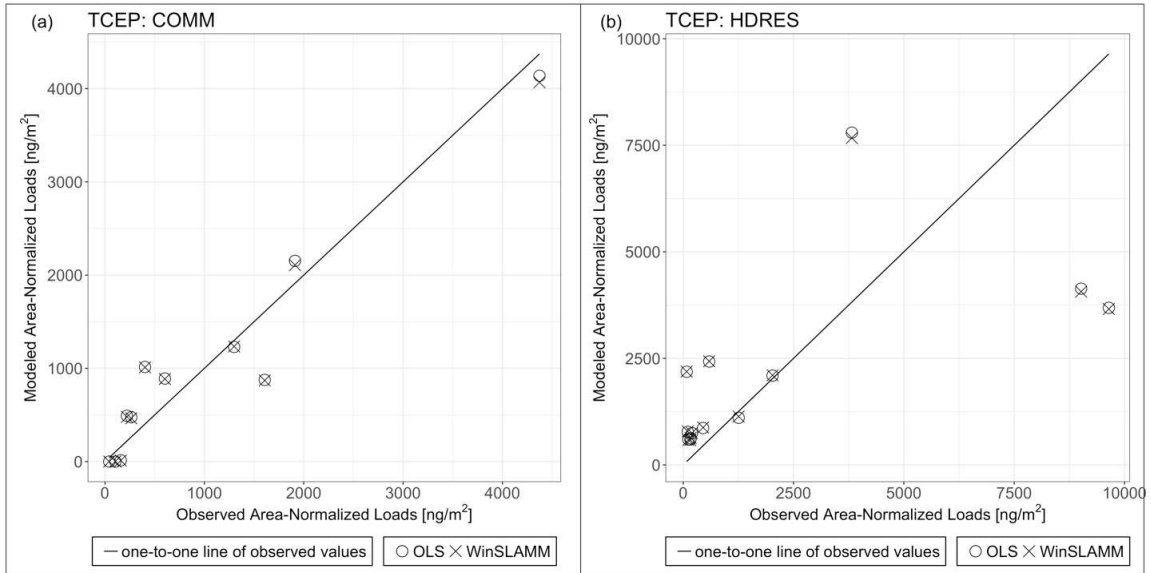


Figure B.5 Comparisons of WinSLAMM and OLS to each other and observed values for TCEP for (a) COMM and (B) HDRES.

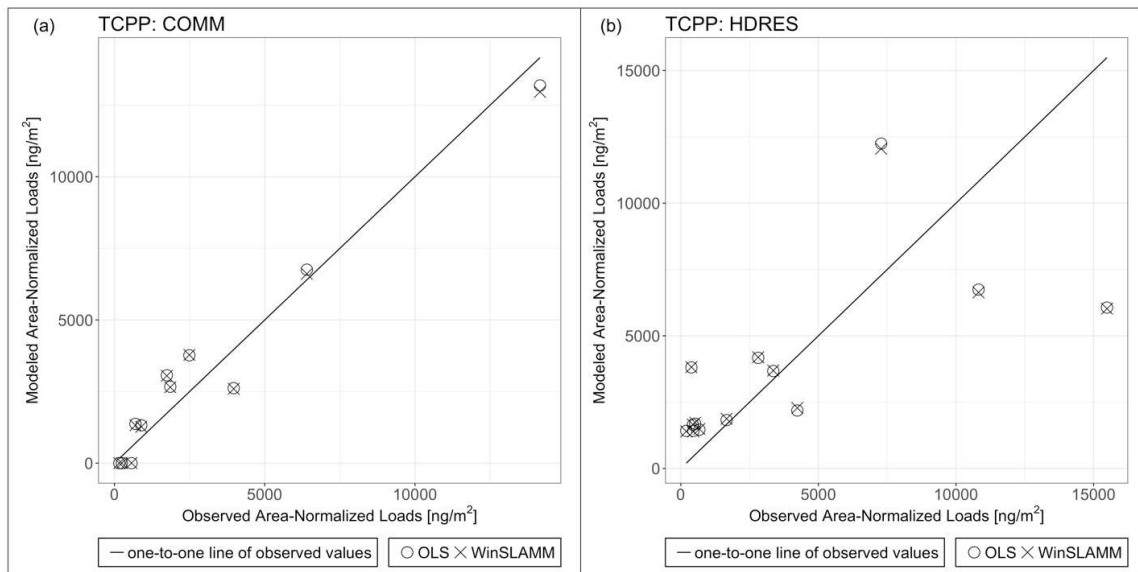


Figure B.6 Comparisons of WinSLAMM and OLS to each other and observed values for TCP for (a) COMM and (B) HDRES.

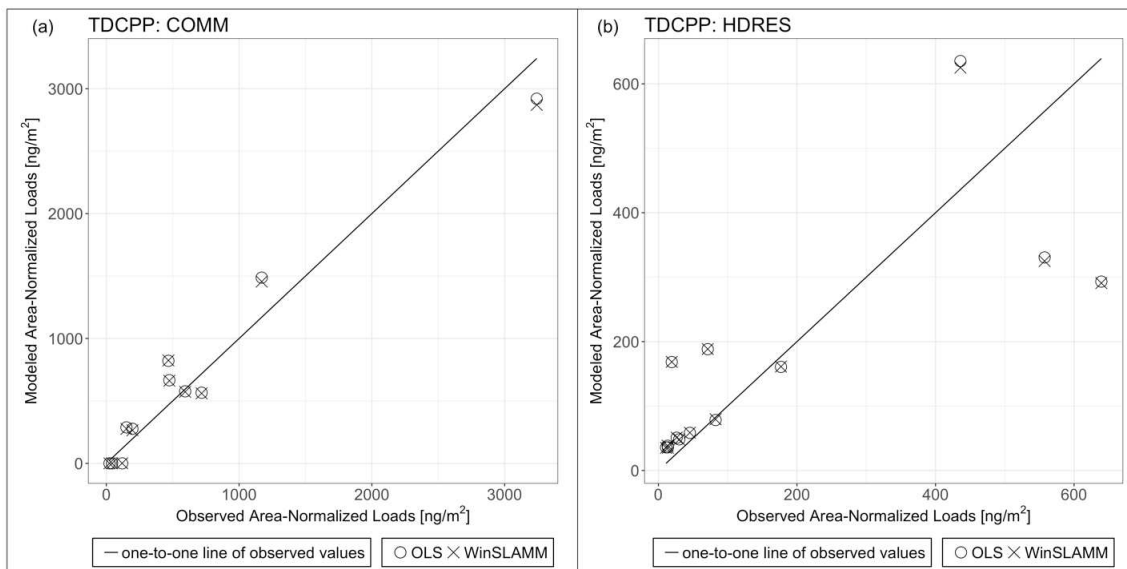


Figure B.7 Comparisons of WinSLAMM and OLS to each other and observed values for TDCPP for (a) COMM and (B) HDRES.

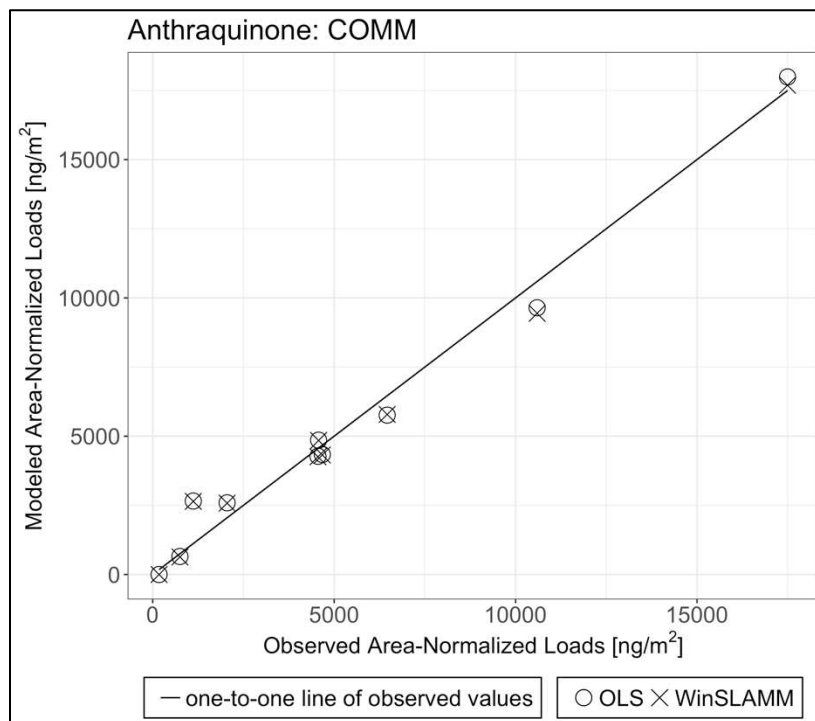


Figure B.8 Comparisons of WinSLAMM and OLS to each other and observed values for anthraquinone for COMM.

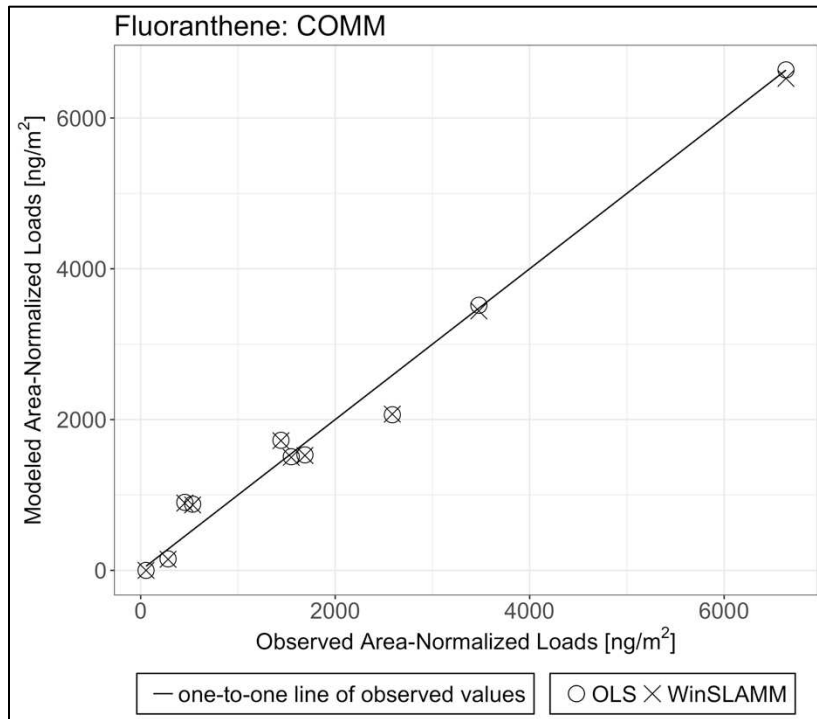


Figure B.9 Comparisons of WinSLAMM and OLS to each other and observed values for fluoranthene for COMM.

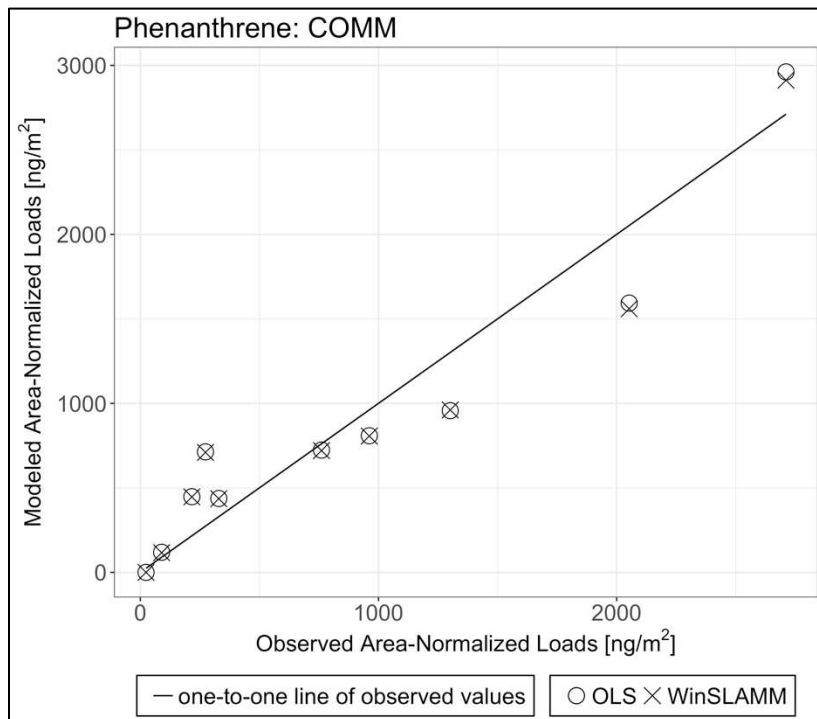


Figure B.10 Comparisons of WinSLAMM and OLS to each other and observed values for phenanthrene for COMM.

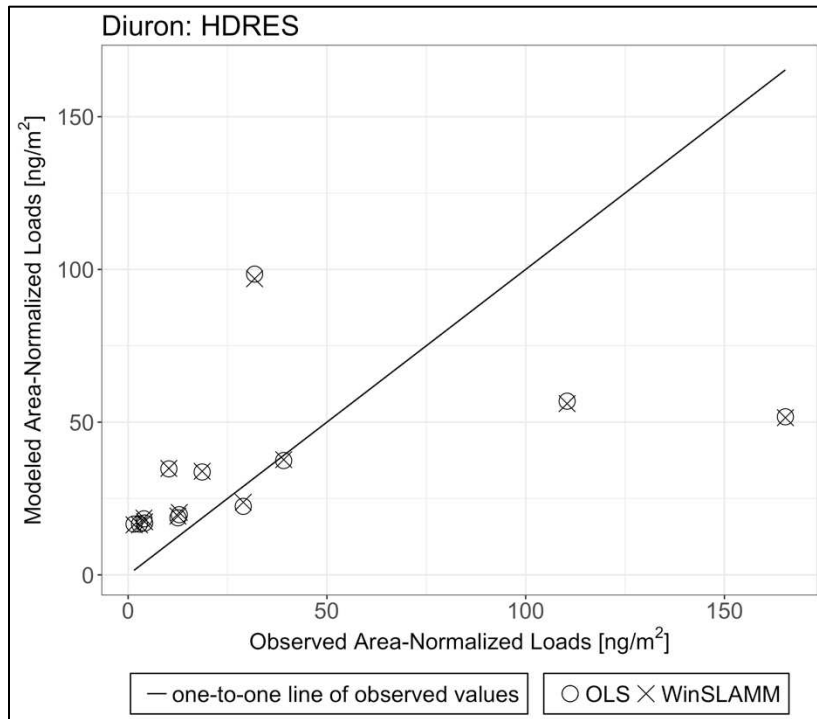


Figure B.11 Comparisons of WinSLAMM and OLS to each other and observed values for diuron for HDRES.

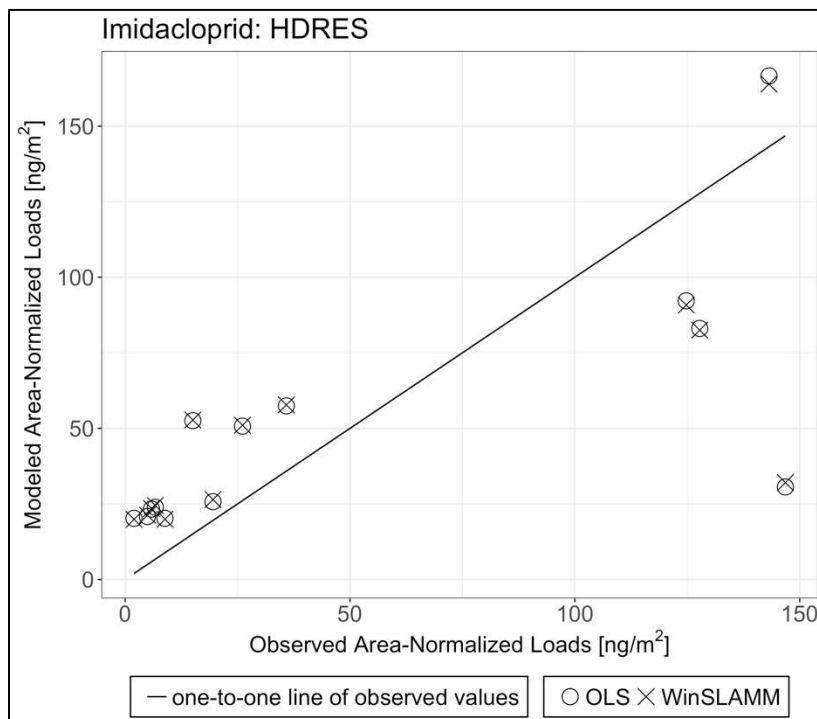


Figure B.12 Comparisons of WinSLAMM and OLS to each other and observed values for imidacloprid for HDRES.

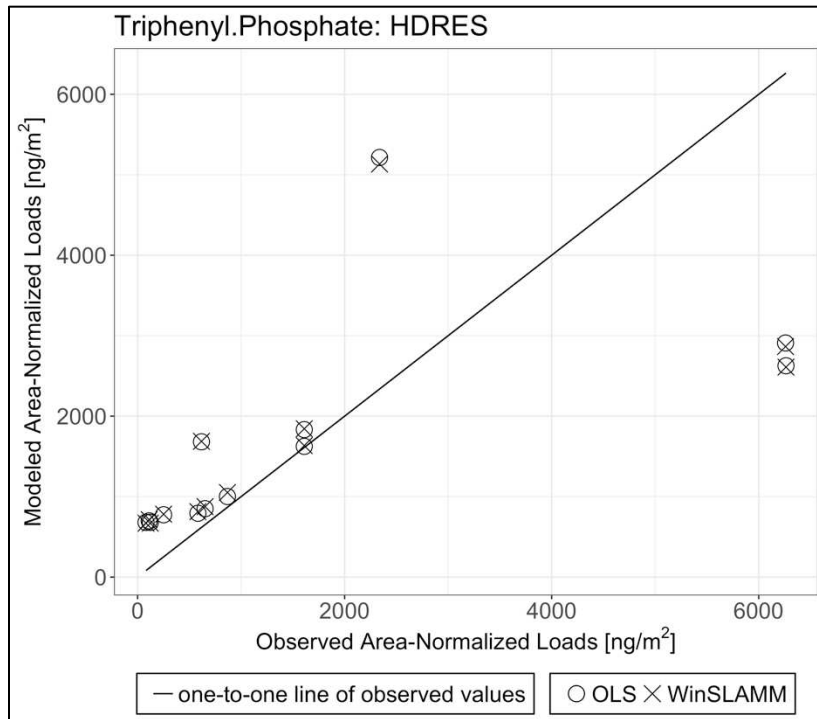


Figure B.13 Comparisons of WinSLAMM and OLS to each other and observed values for TPP for HDRES.