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Urban Pesticides Risk Assessment and Management

Review

QUANTITATIVE ANALYSIS OF OVER 20 YEARS OF GOLF COURSE MONITORING STUDIES

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Abstract—The purpose of the present study was to comprehensively evaluate available golf course water quality data and assess the extent of impacts, as determined by comparisons with toxicologic and ecologic reference points. Most water quality monitoring studies for pesticides have focused on agriculture and often the legacy chemicals. There has been increased focus on turf pesticides since the early 1990s, due to the intense public scrutiny proposed golf courses receive during the local permitting process, as well as pesticide registration evaluations by the U.S. Environmental Protection Agency under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Results from permit-driven studies are frequently not published and knowledge about them is usually not widespread. Forty-four studies involving 80 courses from a 20-year period passed our quality control and other review criteria. A total of 38,827 data entries (where one analysis for one substance in one sample equals a data entry) from pesticide, pesticide metabolite, total phosphorus, and nitrate analyses of surface water and groundwater were evaluated. Analytes included 161 turf-related pesticides and pesticide metabolites. Widespread and/or repeated water quality impacts by golf courses had not occurred at the sites studied, although concerns are raised herein about phosphorus. Individual pesticide database entries that exceed toxicity reference points for groundwater and surface water are 0.15 and 0.56%, respectively. These percentages would be higher if they could be expressed in terms of samples collected rather than chemicals analyzed. The maximum contaminant level ([MCL]; 10 mg/L) for nitrate-nitrogen was exceeded in 16/1,683 (0.95%) of the groundwater samples. There were 1,236 exceedances of the total phosphorus ecoregional criteria in five ecoregions for 1,429 (86.5%) data entries. (This comparison is conservative because many of the results in the database are derived from storm flow events.) Thus, phosphorus appears to present the greatest water quality problem in these studies. Pesticides detected in wells had longer soil metabolism half-lives (49 d) compared with those not detected (22 d), although the means were not significantly different. Environ. Toxicol. Chem. 2010;29:1224–1236. © 2010 SETAC

Keywords—Pesticide Nitrate Phosphorus Golf Water

INTRODUCTION

The subject of golf course design, construction, and management raises many environmental issues that are frequently discussed among government officials and the general public, particularly in the context of reviews of land development permit applications. This issue has practically no limitation in scope, geographically or in subject matter. For example, comprehensive environmental impact assessments are required for proposed golf courses in China and Korea [1]. Avian impacts had been noted for turf insecticides whose turf use has since been banned in the USA (e.g., [2]). Concerns about aquatic macroinvertebrate impacts have been documented in Canada [3] (although these investigators did not use upstream reference points), and analogous concerns about amphibians have been studied elsewhere [4–6]. Pesticide use on golf courses has been examined in comparison with agricultural pesticide use on more than 80 crops [7]. Proactive environmental stewardship approaches for golf course development and management have been written and recommended for overall environmental protection (e.g., [8–10]), as well as for protection of amphibians and their habitats [11]. A key focus of many discussions regarding known or potential golf course impacts has been water quality.

Thus comprehensive data and assessments of golf course water quality impacts in several regulatory and scientific contexts are needed. Regulatory decisions regarding environmental permitting at the local scale, as well as pesticide registration decisions at the state and national scales, could be better advised by such an analysis. Researchers could use such information to guide the filling of data gaps and/or could use the data as one component of ecosystem impact analyses.

We had previously obtained water quality monitoring data from 17 studies of 36 golf courses, and conducted a meta-analysis of the data [12]. The previous review did not include phosphorus (P), and the U.S. Environmental Protection Agency (U.S. EPA) has since published ecoregional criteria for total phosphorus (TP) and total nitrogen (TN) that are very low, i.e., typically 0.2 ppm or less for TP in lakes and reservoirs (U.S. Environmental Protection Agency, Office of Water; http://www.epa.gov/waterscience/criteria/nutrient/ecoregions), concentrations that are often below background in our experience. Data from large areas of the North American continent were also lacking. Finally, data were insufficient for evaluating temporal trends of the analytes. Many more monitoring studies were in progress at the time of our 1999 paper. Thus, the purpose of the present study is to update the data collection from the previous effort [12] and expand the analyses of the data to include TP, as well as the evaluation of temporal and spatial trends in the data.

The original data set had several limitations. A number of these limitations were mentioned in the 1999 publication [12], such as the inability to conclude that the reported concentrations provided true national estimates for golf course impacts on

All Supplemental Data may be found in the online version of this article.

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water quality due to the analytical and spatial limitations of the data, as well as the fact that the results do not arise from a single, comprehensive statistically based monitoring survey (e.g., stratified random sampling). This current effort still lacks a unified statistical design, but it is more spatially representative. It contains data from more golf courses in the mid-continent, as well as more areas known to have large numbers of golf courses (Fig. 1). This analysis also includes an attempt to capture data from the analyses of pesticides that were actually applied to golf courses, based on a questionnaire administered to participating superintendents (golf course managers). Thus, we attempted to include analytical results only for pesticides that were definitely or likely used on a particular golf course. Finally, the publication of rather strict TN and TP ecoregional criteria allows for a more meaningful interpretation of the nutrient results.

MATERIALS AND METHODS

Solicitation and review of studies

Results of surface water and groundwater studies conducted on golf courses throughout the United States and Canada were solicited through a variety of sources. Initially, press releases were issued requesting information, followed by articles in six golf course trade magazines. These are publications read by golf course superintendents and turf researchers. Letters requesting information were sent to all 104 chapter heads of the Golf Course Superintendents Association of America (GCSAA; Lawrence, KS, USA), all 50 state environmental water quality regulatory agencies, and 22 contacts in the U.S. EPA's headquarters and 10 regional offices. The response rate was 36% from the state agencies and 100% from the U.S. EPA. Furthermore, attempts were made to contact all golf course superintendents and/or lead investigators from the 17 studies used for the original 1999 research effort to obtain monitoring data subsequent to 1996. Finally, the peer network (word of mouth) was used. Thus, it is likely we identified most of the completed golf course water quality monitoring studies as of June 2007 for which individual sample results and adequate documentation were available (Supplemental Data, Tables S1 and S2).

Analytes

The focus was pesticides, pesticide metabolites, nitrate-N, and TP. Often, analytical results were reported for pesticides that were not known to be used on golf course turf. Those pesticide results were almost always nondetects (ND), and an effort was made to exclude these pesticides. We had previously included solvents used as pesticide product carriers [12]. We did not include solvents in this analysis because of the lack of detections in the previous study, and the fact that most golf turf pesticide products are applied either in aqueous solutions or as dry granular materials.

Total organic analytes initially consisted of 194 pesticides and pesticide metabolites. Organic chemicals that were almost certainly never applied to golf courses were deleted from this list, for a total of 161 turf-related pesticides and metabolites that were analyzed in at least one of the studies included in the present study. We estimate that fewer than 120 pesticide active

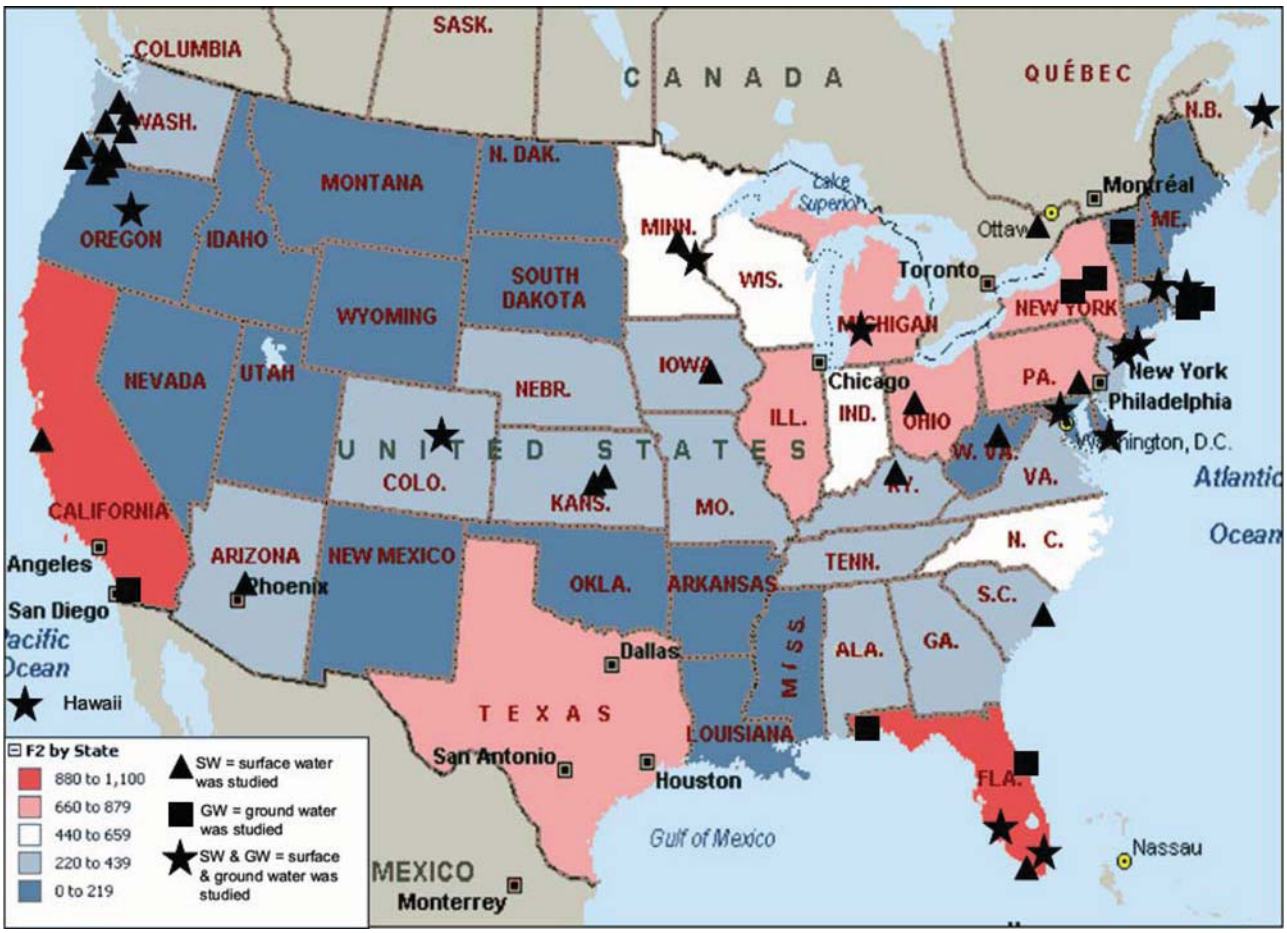

Fig. 1. Golf course facilities distribution in the United States and location of study sites (adapted from J. Kass, Director of Research, National Golf Foundation, Jupiter, FL, USA, personal communication, 2007).

ingredients are currently registered for use on turf, but other turf pesticides have also been registered during the period covered by the various studies and have since been withdrawn from the market. Further, some pesticides may be applied to nonturf areas at golf courses—ornamental plants and water features.

Part of the effort to identify whether golf courses actually used or applied the pesticides that were being analyzed included a questionnaire. Pesticide-use information was requested from all golf course superintendents in the studies; the response rate was 50%, and on average 71% of pesticides analyzed had actually been applied to the golf courses. The 71% value should be regarded as a lower limit because, at many golf courses, records of pesticide applications more than two years prior to the study were not readily accessible or did not exist.

Quality control

Each study was subject to a two-stage quality control (QC) review. First, study directors and/or laboratory staff were contacted to ensure that adequate quality control measures were followed by the participating laboratories, including proper state certification and assurance that blank, matrix spike, and duplicate analyses were run. Second, approximately 10 to 20% of the data entered for each study (generally closer to 20%) was checked for completeness and accuracy in an in-house QC review prior to statistical evaluation. In addition, a third, nonsystematic level of QC review was also implemented; detailed internal data queries and spot checks for data entry errors were done in the preparation of the manuscript.

Twenty-nine new studies were initially reviewed for potential inclusion in this meta-analysis. The new studies included 46 additional golf courses. Twenty-seven of these 29 new studies passed our QC review criteria and were included with the original 17 studies, yielding a total of 44 studies that include 80 golf courses in the database (Supplemental Data, Tables S1 and S2); all but two of these golf courses were located in the USA (two studies were conducted in Canada). Most of the studies were unpublished contractor reports.

Data entry and statistical analyses

After the preliminary review for content and data quality, data were entered into Microsoft Access 2003 (Microsoft Corporation©). Data from the 1999 effort had been previously entered into Borland Paradox Version 5.0 (Borland International); these data were transferred into the new Access database. Statistical analyses were conducted using SigmaPlot® v10.0 (Systat Software©).

The data contained a large number of NDs; that is, the substance analyzed was not detected above the detection limit (DL) or, more appropriately, the method reporting limit ([MRL]; analogous to the practical quantitation limit [PQL]). It is not clear how these data should be entered when calculations are done, particularly considering the fact that the DLs or PQLs were not consistent. The actual concentration represented by ND is some value below the DL/PQL/MRL, however, the analytical method cannot determine whether the ND is truly zero or some unquantifiable value between zero and the MRL/PQL. We used the U.S. EPA's accepted method of replacing the ND with half DL/PQL [13,14] for the two datasets that contain less than 20% NDs, nitrates in groundwater and TP in surface water. This method is also known as the substitution method, where a specific number is substituted for each ND. Although it is expedient, it can impact the reliability of standard deviation estimates (e.g., [15]), particularly when the DL is not extremely low. The substitution method should not be used when uncertainty/error analysis will be important, nor when the NDs exceed 20% of the data set.

A Winsorized mean was computed (i.e., the data at the tails were censored; U.S. EPA [14]; section 4.7.2.1) for those datasets where the number of NDs are greater than 20% but less than 40% of the dataset. The Winsorized mean method was applied to the nitrate in surface water and TP in groundwater results. Thus, all nitrate or TP NDs in surface water or groundwater, respectively, were replaced at the low end of the concentration distribution by the next highest value. An analogous replacement was made at the high end. This allows reasonable estimates of the mean and median, but sacrifices the ability to reliably estimate the standard deviation, a key to any uncertainty analysis. One frequently cited approach for evaluating databases with 15 to 50% NDs is Cohen's method (e.g., [13,14]); however, this cannot be used with this database due to the requirement that all DLs must be the same.

For datasets with greater than 40% NDs (all pesticide analyses), neither the substitution method nor the Winsorized mean approach is appropriate. For these data, a range of the mean was computed, i.e., the lower end of the range assumes ND = 0.0, and the upper end of the range assumes ND equals the DL for the particular pesticide in the particular study.

Mann-Kendall test. The Mann-Kendall (M-K) test was used to determine if there were increasing TP and nitrate-N trends. The M-K is a nonparametric test that tests for trends within a dataset [16]. Basically, an S value is calculated using the dataset. Through a series of equations, this S value is then used to calculate a variance that considers *tied* data (i.e., values that appear more than once, like NDs), which is then used to calculate a Z value. The calculated Z value is compared to a table Z value for a selected level of significance (e.g., $\alpha = 0.05$, or 95% confidence limit [CL]) to determine if there are any trends: increasing, decreasing, or none. Unlike the regression analyses, the data need not conform to any distribution pattern.

Regression analysis. The M-K test does not discriminate very well between weak and strong trends. Therefore, a regression analysis was also used to discern trends in the multiyear data, because the regression analysis provides a better sense of the relationship between concentration and time, e.g., if $r^2 = 100\%$ for a plot of concentration versus time, then 100% of the variability in the concentrations is fully explained by increasing time. Anything less than 100% indicates that there are other influences affecting the analyte concentrations.

Toxicity reference points

Drinking water. Groundwater and surface water pesticide results were compared with chronic (lifetime) drinking water standards or guidelines, and surface water pesticide results that exceeded lifetime limits were compared with acute reference points. The maximum contaminant levels (MCLs) legally enforceable by U.S. EPA were only available for seven of the pesticides, and nonenforceable lifetime drinking water health advisory levels (HALs) were available for an additional seven pesticides ([17]; http://www.epa.gov/waterscience/health). The remainder of the lifetime HALs were calculated as follows, generally following the approach used by the U.S. EPA's Office of Ground Water and Drinking Water. Chronic reference doses (cRfDs) adjusted with the Food Quality Protection Act (FQPA) uncertainty factors (the maximum unit dose in mg chemical/kg body wt/d calculated that one could consume without suffering any adverse effects) were generally obtained from the U.S. EPA's Office of Pesticide Programs Registration Eligibility Decision documents (http://www.epa.gov/oppsrrd1/

reregistration/status.htm) or food tolerance notices published in the Federal Register. A secondary source was the U.S. EPA's Integrated Risk Information System [IRIS]. (The first two sources are preferred because IRIS information can be less up-to-date.) The lifetime HAL was calculated using the following formula for nonneurotoxic endpoints:

$$\text{lifetime HAL} = \text{cPAD} \cdot 70\text{kg body wt}/2\text{L/day} \times \text{food factor}$$

where cPAD (chronic population adjusted dose) = cRfD divided by the FQPA uncertainty factor (usually 1, 3, or 10) and the food factor = 0.2 if there are tolerances registered for the subject pesticide on any foods other than a limited number of minor crops. Equation 1 is modified for neurotoxic agents by substituting 10 kg body weight/1 L/d as the consumption rate multiplier appropriate for toddlers.

Acute HALs were calculated using the same basic approach, except the acute PAD and the 10 kg/1 L/d consumption factor were used.

Maximum allowable concentrations for aquatic organisms. The aquatic toxicity reference points (MACs) have two sources. The U.S. EPA Office of Pesticide Program's Aquatic Life Benchmark Table (http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm) contains criteria (Aquatic Life Benchmarks) for 21 of the detected pesticides. The remaining pesticide MACs were calculated using 1/10th the LC50 or EC50 of the most sensitive freshwater species listed in the U.S. EPA's Ecotoxicity Database (http://cfpub.epa.gov/ecotox) or obtained from other available sources (Table 1). These MAC values are not meant to be definitive but are presented for comparison purposes.

Golf course environment

There are approximately 18,331 golf courses in the United States (K. McClendon, National Golf Foundation, Jupiter, FL, USA, personal communication, 2008) and 2,390 in Canada (T. Yamada, Royal Canadian Golf Association, ON, Canada, personal communication, 2008). (Note that this type of statistic can also be expressed as golf facilities, which would yield a lower number.) The area of an average 18-hole U.S. golf course is 61 ha (150 A; [18]). Golf courses consist of several types of management zones. The four types of playing surfaces are, in descending order of management intensity (average percentages of total area and average areas): greens and tees (3.9% and 2.4 ha); fairways (20% and 12 ha) and driving range/practice areas (4.6% and 2.8 ha); roughs (34% and 21 ha); and out-of-play areas [18]. Thus, the average 18-hole golf course consists of approximately 38 ha (74 A) of managed turf, but only 28% of the total area typically consists of the more intensively managed playing surfaces, tees, greens, and fairways.

Typically, the most dominant or troublesome pest pressures are weeds in warm climates, diseases in cooler climates, and a combination of weeds, diseases, and insect larvae in the transition zone (mid-latitudes). Herbicides are used mostly on fairways and roughs, fungicides are applied more intensively to greens and tees, and insecticides are often used throughout the course. Roughs, which constitute the largest area of golf courses, receive the fewest and least intensive pesticide and fertilizer treatments. Probably fewer than 10 golf courses throughout the United States and Canada are truly pesticide free.

Golf courses are irrigated based on evapotranspiration needs. Greens almost always have underdrain systems, and good drainage is a key factor in golf course design and construction.

Turfgrass is a living filter that is often used as part of phytoremediation (e.g., [19,20]) and as a best management practice (BMP) to treat stormwater runoff (e.g., [21]). This filtration efficacy is likely due partly to its extensive shoot and root density [22].

Figure 1 depicts the distribution of golf facilities in the U.S. and the location of study sites. A golf facility may include more than one golf course, and, at this scale, a single symbol may denote more than one golf facility. Note that multiple study sites may be represented by a single symbol, due to the small scale of the figure.

Study descriptions

Locations, sampling sites, objectives, and other key information for all studies in the database are shown in Supplemental Data, Tables S1 and S2.

RESULTS

Overview

In the USA, approximately 55 possible combinations of climate zones (CZs) and groundwater (GW) regions occur, and approximately 48 possible surface runoff/water (SW) and CZ combinations [23–25]. The studies that were evaluated spanned seven GW regions, eight CZs, and 14 level III aggregate ecoregions (Table 2; http://earth1.epa.gov/waterscience/criteria/nutrient/ecoregions/index.html). Level III ecoregions are defined by the patterns and composition of biotic and abiotic phenomena (e.g., geology, physiography, vegetation, climate, soils, land use, wildlife, and hydrology) that reflect or affect differences in ecosystem quality and integrity. Thus, it is still desirable to have results from many more areas of the United States.

The database included 38,827 entries, prior to refinement, where one entry is one analysis for a single analyte in one sample (Table 3). The numbers in this table were reduced (refined) by deleting from further analysis pesticides and their metabolites that were almost certainly not used on the subject golf courses (Table 4). This action resulted in the omission of 726 database entries. There was only one detection among the deleted data: aldrin. Statistical analyses were completed for the dataset categories in Table 4.

Supplemental Data, Figure S1 summarizes pesticide detections by use class. Some of these pesticides were detected more than once. Approximately 3.7% of all surface water organic database entries were detections (quantifiable concentrations) and approximately 1.2% of the groundwater organic entries were quantified detections.

Surface water results

Pesticides and metabolites. There were 15,752 surface water pesticide/metabolite entries, of which 590 (3.7%) were detections. The highest number of pesticides that were detected was from the insecticide class (26), followed by herbicides (17) and fungicides (14) (Supplemental Data, Fig. S1).

Table 5 lists all pesticide analytes that were included in the database. An effort was made to exclude pesticides that were almost certainly never used at a golf course—either on turf, in ponds (lakes), or in related golf property areas (see *Materials and Methods* section). Those chemicals with a strikethrough represent chemicals that have been eliminated from the data-

Table 1. Pesticides detected in surface water with maximum contaminant level/health advisory level and maximum allowable concentration exceedances[a]

Surface water pesticides	Total entries	Total No. of detections	No. of detections exceeding MAC	No. of detections exceeding MCL or chronic HAL	MAC U.S. EPA Aquatic Life Benchmark or calculated by ETS (ppb)[b,c]	Chronic HAL/MCL (ppb)	Acute HAL (ppb)	Max concn. (ppb)
2,4-D	761	52	0	0	12,500	70[d]	—	34.35
Acephate	29	2	0	1	130[e]	7.5[e]	35	19
Ametryn	66	2	0	0	1,800	60	—	0.06
AMPA (glyphosate metab.)[f]	23	11	N/A	N/A	N/A	N/A	—	21.6
Atrazine	77	22	0	0	360	3[d]	—	2.5
Azoxystrobin	113	2	0	0	8.4[e]	1,260[e]	—	5.8
Bentazon	48	1	0	0	50,000	20	—	2.4
Beta-BHC	240	2	N/A	0	N/A	0.0091	—	0.085
Carbaryl	251	7	1	0	2.55	40[g]	—	227
Chlorothalonil	544	14	0	2	11.5	2[g]	200[d]	6.5
Chlorpyrifos	449	21	17	0	0.05	2[d]	30[d]	0.4
3,5,6-Trichloro-2-pyridinol	55	11	0	0	1,000[h]	7[e]	—	0.9
Clopyralid	32	2	0	0	1,722 (MAC VT)	3,500[e]	—	0.42
DDD	223	4	N/A	4	N/A	0.00031[i]	—	0.051
DDE	223	2	N/A	2	N/A	0.00022[i]	—	0.0093
DDT	223	4	4	4	0.001	0.00022[i]	—	0.059
Delta-BHC	240	2	N/A	N/A	N/A	N/A	—	0.16
Diazinon	248	19	15	1	0.05[e]	1.0[d]	20	1.4
Dicamba	561	12	0	1	14,000	4,000/200[e,j]	2,000	200
Dieldrin	220	2	0	0	0.2[i]	1.75	—	0.007
Disulfoton	184	1	0	0	1.95	0.3	—	0.21
Dithiopyr	89	1	0	0	46[e]	122	—	0.1
Diuron	30	7	0	0	80	2[e]	—	1.4
Endosulfan I	238	1	1	0	0.22[i]	3[e]	—	0.055
Endosulfan II	232	1	0	0	0.22[i]	3[e]	—	0.0065
Ethofumesate	45	1	0	0	50	8,750[e]	—	0.65
Ethoprop	114	2	0	2	22	0.2	0.5	7.7
Fenamiphos sulfone[f]	22	2	1	0	0.2[e]	2[e]	20 (est.)	0.36
Fenamiphos sulfoxide[f]	22	7	2	0	0.9[e]	2[e]	20 (est.)	3.2
Fenamifos	77	7	1	0	0.13[e]	0.7[d]	—	0.13
Fenarimol	100	5	0	0	90[e]	4,200[e]	—	0.24
Fonophos	2	2	N/A	0	N/A	10	—	0.32
Glyphosate	253	13	0	0	27,500	700	—	170
Heptachlor	270	1	0	0	0.37[e]	0.4	—	0.07
Imidacloprid	48	6	0	0	8300[e]	399[e]	—	8.95
Iprodione	298	27	4	0	2.4[e]	280[e]	—	4
Isofenphos	30	1	0	0	0.43[e]	35[e]	—	0.046
Lindane	271	8	2	0	0.17[e]	0.2	1,000[d]	0.25
Malathion	405	3	0	0	0.25	100	—	0.21
MCPP	417	1	N/A	0	N/A	1,400[e]	—	0.3
Metalaxyl	106	5	0	0	910[e]	400[e]	—	0.84
Methamidophos	29	1	0	0	2.6[e]	46	—	1.1
MSMA (as arsenic)[k]	3	3	0	3	1,200[e]	0.02	—	7
Myclobutanil	45	17	0	0	240[e]	175[e]	—	1.6
Oryzalin	65	1	0	0	700	46	—	2.2
Oxadiazon	57	3	0	0	53[e]	40	—	0.13
PCNB	464	25	0	0	24[e]	21	—	13
Pronamide	30	2	0	0	2,800	50	—	1
Propiconazole	169	16	0	0	425	9.2[e]	—	1.1
Propiconazole-a	56	19	N/A	0	—	9.2[e]	—	2.7
Propiconazole-b	55	20	N/A	0	—	9.2[e]	—	3.8
Simazine	252	67	0	39	500	4	1,000	152
Triadimefon	198	2	0	0	100[e]	210[e]	—	4.7
Triadimenol[f]	42	15	0	0	250[e]	27[e]	—	3
Triclopyr	139	18	0	0	180	140	—	1.1
Vinclozolin	73	2	0	0	284[e]	2[e]	—	0.5

[a] AMPA = aminomethylphosphonic acid; BHC = benzene hexachloride; 2,4-D = dichlorophenoxyacetic acid; DDD = dichlorodiphenyldichlorethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; DSMA = disodium monomethylarsenate; ETS = Environmental & Turf Services, Inc.; HAL = health advisory level; MAC = maximum allowable concentration; VT = Vermont; MCL = maximum contaminant level; MCPP = methylchlorophenoxypropionic acid; MSMA = monosodium methane arsonate; N/A = not available or not applicable; PCNB = pentachloronitrobenzene; U.S. EPA = U.S. Environmental Protection Agency; — = calculation not necessary.

[b] U.S. EPA Aquatic Life Benchmarks from www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm.

[c] The lower of the acute fish or invertebrate benchmarks was used.

[d] U.S. EPA [17].

[e] Values calculated by the authors.

[f] Pesticide metabolite.

[g] Based on 1×10^{-6} chronic drinking water cancer risk derived from the U.S. EPA [17].

[h] Screening level MAC estimated by dividing the lowest end of the toxicity range for the chemical by 10; i.e., the classification MT (moderately toxic) would indicate a screening level of 1 mg/L/10 = 100 μg/L.

[i] U.S. EPA Water Quality Criteria (www.epa.gov/waterscience/criteria/wqcriteria.html).

[j] The 1988 U.S. EPA HAL is 4,000 ppb. We calculated 200 ppb using more recent data.

[k] Arsenic is a component of the organoarsenical herbicides MSMA and DSMA. It can also arise from natural sources, as well as from historic use of inorganic arsenicals such as lead arsenate. Researchers usually did not, or were not able to, distinguish among the various potential arsenic sources when they reported their results.

Table 2. Draft aggregate level III ecoregions for the National Nutrient Strategy[a]

Ecoregion No.	Name of ecoregion
I	Willamette and Central Valleys
II	Western forested mountains
III	Xeric West
IV	Great Plains grass and shrublands
V	South central cultivated Great Plains
VI	Corn belt and Northern Great Plains
VII	Mostly glaciated dairy region
VIII	Nutrient-poor largely glaciated upper Midwest and Northeast
IX	Southeastern temperate forested plains and hills
X	Texas–Louisana coastal and Mississippi alluvial plains
XI	Central and Eastern forested uplands
XII	Southern coastal plain
XIII	Southern Florida coastal plain
XIV	Eastern coastal plain

[a] http://epa.gov/waterscience/criteria/nutrient/ecoregions/index.html.

base. None of the chemicals deleted were detected, with the exception of a single detection of aldrin. Inclusion of these results would have diluted the meta-analysis.

Table 1 provides information on pesticides detected in surface water, including water quality reference point exceedances. Two main categories of drinking water reference points are listed in Table 1, MCLs and lifetime HALs developed for chronic exposures, and acute HALs for short-term exposures. The HALs were calculated as described in the *Materials and Methods* section. Concentrations of pesticides in surface water were initially compared with the MCLs and lifetime HALs. Any concentration exceedances were then compared with acute HALs. Surface water contamination by golf course pesticides tends to be episodic, therefore acute HALs are more appropriate toxicologic reference points for this exposure pattern.

Ten pesticides exceeded their respective enforceable drinking water standard (i.e., MCL) or their lifetime drinking water HAL at least once. The number of detections that exceeded their respective enforceable drinking water standard was 60. The exceedance rate was 0.38% of pesticide entries (Supplemental Data, Fig. S2), 12.5% of the detections (481). The lifetime HAL/MCL is an overly conservative but convenient comparison with infrequent episodic concentrations, because the HAL is usually established from a lifetime exposure of an adult drinking two liters of water per day. Only ethoprop appeared to exceed its acute HAL, a more appropriate reference point. We found that 28 of the 481 detections exceeded an MAC (an exceedance rate of 5.8% of the detections, and 0.18% of total surface water pesticide entries) (Supplemental Data, Fig. S3). Nine different active ingredients yielded the 42 exceedances.

The range of average concentration of pesticides in surface water was 0.16 to 4.14 μg/L. As explained above, the lower end of the range assumes ND = 0.0, and the upper end of the range assumes ND = DL, for the particular pesticide in the particular study. The 95th percentile concentration range was between 0.07 and 0.44 μg/L, depending on whether ND = 0.0 or ND = DL. The 99th percentile concentration range was between 0.09 and 0.58 μg/L depending on whether ND = 0 or ND = DL.

We documented, from the participating golf courses surveyed, that an average of 60% of the pesticides (ranging from 21 to 100% for each golf course) analyzed in surface water samples were actually used during the monitoring period. (This percentage should be regarded as a lower limit due to the discontinuity in records and/or superintendents.) The response rate for surface water pesticide use surveys was 48% (12 received out of 25 sent). Supplemental Data, Table S3 provides a list of pesticides that were used on at least one golf course in the present study. (The distribution of survey responses was skewed to the West coast of the country for the surface water studies—50% of responses were from the West coast, 3% from the mid-continent, 1% from the Southeast.)

Table 3. Total number of database entries from all accepted studies

	Organics[a]	Nitrate-N	Total phosphorus	Total
Groundwater	15,807	1,683	970	18,460
Surface water	16,445	2,493	1,429	20,367
Total	32,252	4,176	2,399	38,827

[a] Organics refers to pesticides and metabolites.

Table 4. Net database entries (following removal of pesticides/metabolites that would never be applied to a golf course)

	Organics[a]	Nitrate-N	Total phosphorus	Total
Groundwater	15,774	1,683	970	18,427
Surface water	15,752	2,493	1,429	19,674
Total	31,526	4,176	2,399	38,101

[a] Organics refers to pesticides and metabolites.

Nitrate-nitrogen. Of the 2,493 surface water nitrate-N entries, 1,809 (72%) were detections. The MCL (10 mg/L) for nitrate-N in surface water was exceeded in 20 detections. The Winsorized mean nitrate-N concentration was 0.23 mg/L (25% NDs) (Fig. 2).

Figure 2 depicts nitrate-N concentrations in surface water. The box represents the two mid-quartiles (upper 75th and lower 25th). The *whiskers* represent the upper 90th and lower 10th percentiles; there are a number of outliers and the data are not normally distributed.

Nitrate-N detections were compared to the ecoregional criteria for TN. It is important to note that this is not a conservative comparison, because the TN ecoregional criteria are composed of inorganic-N and TKN (organic-N plus ammonia). Nitrate-N detections occurred in 12 of the 14 ecoregions: I–III, V–IX, and XI–XIV (Table 2). The average number of detections per ecoregion was 151, with detections ranging from 1 (in ecoregion VIII) to 503 (in ecoregion VI). Total nitrogen ecoregional criteria ranged from 0.12 to 2.18 mg/L for rivers and streams, and 0.1 to 1.27 mg/L for lakes and reservoirs. The 553 TN ecoregional criteria exceedances by nitrate-N were 22% of the nitrate-N surface water analyses. There was an average of approximately 46 ecocriteria exceedances in the ecoregions with exceedances, ranging from none (ecoregions VIII, XIII) to more than 150 (ecoregion II). An average of two golf courses per ecoregion were responsible for the exceedances, ranging from 1 (ecoregions I, V, VIII, XI, XIII) to 12 (ecoregion II). There were detections in five CZs (4–6, and 8–10), with an average of approximately 229 detections, ranging from 1 (CZ 10) to 554 (CZ 5). Approximately five golf courses were responsible for these detections, ranging from 1 (CZ 10) to 10 (CZ 8).

Total phosphorus. The number of surface water TP entries was 1,429, with 1,379 (96.5%) detections (Fig. 3). The average TP concentration was 0.43 ± 0.66 mg/L (± SD; ND = half DL,

Table 5. Pesticides and pesticide metabolites analyzed in one or more of the studies in groundwater and surface water[a]

Analyte[a]	GW	SW	Analyte[a]	GW	SW	Analyte[a]	GW	SW	Analyte[a]	GW	SW	Analyte[a]	GW	SW
1,2 Dichloropropane	*Y*	*N*	Bromacil	Y	Y	Endosulfan II	Y	Y	Lindane	Y	Y	Propiconazole-a	Y	Y
cis-1,3 Dichloropropene	*Y*	*N*	*Butachlor*	*N*	*Y*	Endosulfan sulfate[b]	Y	Y	Linuron	Y	Y	Propiconazole-b	Y	Y
trans-1,3 Dichloropropene	*Y*	*N*	Captan	N	Y	Endrin	Y	Y	Malathion	Y	Y	Propoxur	Y	N
3,5,6-Trichloro-2-pyridinol[b]	Y	Y	Carbaryl	Y	Y	Endrin aldehyde[b]	Y	Y	Mancozeb	N	Y	*Prothiofos/tokuthion*	*N*	*Y*
3-Hydroxy-carbofuran[b]	Y	N	Carbofuran	Y	Y	Endrin ketone[b]	Y	Y	MCPA	Y	Y	Quinclorac	N	Y
1-Naphthol[b]	N	Y	Carfentrazone-ethyl	Y	Y	*EPN*	*N*	*Y*	MCPP	Y	Y	Ronnel	N	Y
2,4,5-T	*Y*	*Y*	Chlordane	Y	Y	EPTC/eptam	N	Y	Merphos	N	Y	Siduron	Y	N
2,4,5-TP	*Y*	*Y*	*Chlordecone*	*N*	*Y*	Ethalfluralin	N	Y	Metalaxyl	Y	Y	Siduron (A)	Y	N
2,4-D	Y	Y	Chloroneb	Y	Y	Ethion	Y	Y	Methamidophos	Y	Y	Siduron (B)	Y	N
2,4-DB	Y	Y	Chloropicrin	Y	N	Ethofumesate	Y	Y	Methomyl	Y	N	Simazine	Y	Y
DDD	Y	Y	Chlorothalonil	Y	Y	Ethoprop	Y	Y	Methoxychlor	Y	Y	Simetryn	N	Y
DDE	Y	Y	Chlorpyrifos	Y	Y	Ethyl parathion	Y	Y	Methyl bromide	Y	N	*Sulfotep*	*N*	*Y*
DDT	Y	Y	Chlorpyrifos ethyl	Y	Y	Ethylene dibromide	Y	N	Methyl isothiocyanate	Y	N	Sulprofos	N	Y
Acephate	Y	Y	Cis-permethrin	N	Y	Etridiazole	Y	N	Methyl parathion	Y	Y	*Terbacil*	*N*	*Y*
Acetochlor	*N*	*Y*	Clopyralid	Y	Y	Fenamiphos sulfone[b]	Y	Y	Metolachlor	N	Y	*Terbufos*	*Y*	*Y*
Alachlor	*Y*	*Y*	*Coumaphos*	*N*	*Y*	Fenamiphos sulfoxide[b]	Y	Y	Metribuzin	Y	Y	Terbuthylazine	N	Y
Aldicarb	*Y*	*N*	*Cyanazine*	*N*	*Y*	Fenamiphos	Y	Y	Mevinphos	Y	Y	*Terbutryn*	*N*	*Y*
Aldicarb sulfone[b]	*Y*	*N*	Cyfluthrin	Y	N	Fenarimol	Y	Y	*Mirex*	*N*	*Y*	Tetrachloroethylene	Y	N
Aldicarb sulfoxide[b]	*Y*	*N*	Dacthal diacid[b]	Y	N	Fenoxaprop ethyl	Y	Y	Inorganic arsenic (as a surrogate for MSMA)[c]	Y	Y	*Tetrachlorvinphos*	*N*	*Y*
Aldrin	*Y*	*Y*	DCPA	N	Y	Fensulfothion	N	Y	*MTBE*	*Y*	*N*	Thiophanate-methyl	Y	Y
Alpha-BHC	Y	Y	Dalapon	Y	Y	Fenthion	N	Y	Myclobutanil	Y	Y	Thiram	Y	Y
Alpha-chlordane	N	Y	Delta-BHC	Y	Y	Fludioxonil	N	Y	Naled	Y	Y	*Toxaphene*	*Y*	*Y*
Ametryn	Y	Y	Deltamethrin	Y	Y	Flutolanil	Y	Y	Oryzalin	Y	Y	Trans-permethrin	N	Y
AMPA[b]	N	Y	Demeton	N	Y	Fluvalinate	Y	N	Oxadiazon	Y	Y	Triadimefon	Y	Y
Anilazine	Y	Y	Demeton-O	N	Y	Fonophos	Y	Y	*Oxamyl*	*Y*	*N*	Triadimenol[b]	Y	Y
Arsenic[b,c]	Y	Y	Demeton-S	N	Y	Gamma-chlordane	Y	Y	Paclobutrazol	Y	N	Tribufos	N	Y
Atraton	*N*	*Y*	Diazinon	Y	Y	Gamma-BHC	Y	Y	Parathion-methyl	N	Y	Trichlorfon	Y	N
Atrazine	Y	Y	DBCP	Y	N	Glufosinate	N	Y	PCNB	Y	Y	*Trichloronate*	*N*	*Y*
Azinphos-methyl	*N*	*Y*	Dicamba	Y	Y	Glyphosate	Y	Y	Pendimethalin	Y	Y	Triclopyr	Y	Y
Azoxystrobin	Y	Y	Dichlobenil	N	Y	Halofenozide	Y	N	Phorate	Y	Y	Trifloxystrobin	N	Y
Bendiocarb	Y	Y	Dichlorprop	Y	Y	Halosulfuron-methyl	Y	N	Picloram	Y	Y	Trifluralin	Y	Y
Benefin	Y	Y	Dichlorvos	N	Y	Heptachlor	Y	Y	Prodiamine	N	Y	Trinexapac-ethyl	N	Y
Benfluralin	N	Y	*Dieldrin*	*Y*	*Y*	Heptachlor epoxide[b]	Y	Y	Prometon	N	Y	Vernolate/Vernam	N	Y
Benomyl	Y	N	*Dinoseb*	*N*	*Y*	*Hexachlorobenzene*	*N*	*Y*	Prometryn	Y	Y	Vinclozolin	Y	Y
Bentazon	Y	Y	Dimethoate	N	Y	Hexazinone	Y	Y	Pronamide	Y	Y			
Beta-BHC	Y	Y	Diquat	N	Y	Imidacloprid	Y	Y	Propachlor	N	Y			
Bifenthrin	Y	Y	Disulfoton	Y	Y	Iprodione	Y	Y	Propamocarb	Y	N			
Bispyribac-sodium	Y	N	Dithiopyr	N	Y	Isofenphos	Y	Y	Propanil	N	Y			
Boscalid	Y	N	Diuron	Y	Y	Isoxaben	N	Y	Propazine	N	Y			
Butylate	*N*	*Y*	Endosulfan I	Y	Y	Lambda-cyhalothrin	Y	Y	Propiconazole	Y	Y			

[a] AMPA = aminomethylphosphonic acid; BHC = benzene hexachloride; 2,4-D = dichlorophenoxyacetic acid; 2,4-DB = 4-(2,4-dichlorophenoxy) butyric acid; DBCP, dibromochloropropane; DCPA = dimethyl tetrachloroterephthalate; DDD = dichlorodiphenyldichlorethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; DSMA = disodium monomethylarsenate; EPN = *O*-ethyl *O*-(4-nitrophenyl) phenylphosphonothioate; EPTC = *S*-ethyl dipropylthiocarbamate; GW = groundwater; MCPA = 4-chlor-*o*-tolyloxyacetic acid; MCPP = methylchlorophenoxypropionic acid; MSMA = monosodium methane arsonate; MTBE = methyl-*tert*-butyl ether; PCNB = pentachloronitrobenzene; SW = surface water; 2,4,5-T = 2,4,5-trichlorophenoxy acetic acid; 2,4,5-TP = 2,4,5-trichlorophenoxy propionic acid. Chemicals in italics were initially included in the database after the quality control (QC) review, but then deleted due to the low probability of use at the subject golf courses.

[b] Pesticide metabolite.

[c] Arsenic is a component of the organoarsenical herbicides MSMA and DSMA. It can also arise from natural sources, as well as from historic use of inorganic arsenicals such as lead arsenate. Researchers usually did not, or were not able to, distinguish among the various potential arsenic sources, nor between the different forms of arsenic, when they reported their results.

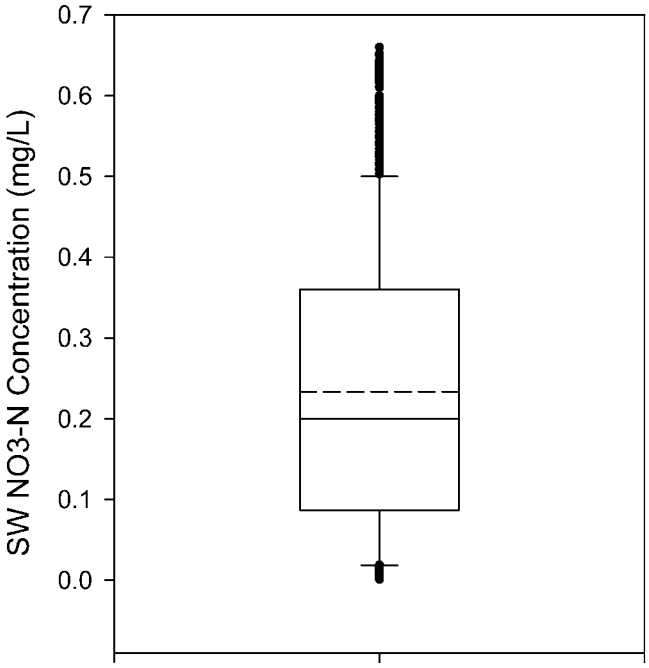

Fig. 2. Nitrate-N (NO3-N) detections in surface water (SW; Winsorized). Dashed line (- - -) = mean; solid line (—) = median.

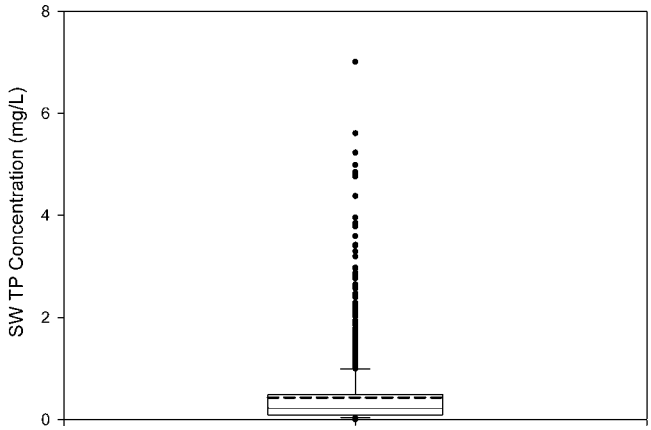

Fig. 3. Total phosphorus (TP) detections in surface water (SW). Nondetects (ND) = 0.5 practical quantitation limit (PQL); dashed line (- - -) = mean; solid line (—) = median.

NDs <20% of the entries). There were 1,227 exceedances of TP ecoregional criteria in five ecoregions—1,083 in rivers and streams, and 153 in lakes and reservoirs. The 1,227 TP ecoregional criteria exceedances are 86% of the TP surface water analyses.

The U.S. EPA has created two TP criteria for each ecoregion: one for lakes and reservoirs and one for streams and rivers. Each detection was compared to the appropriate criteria based on the type of the sample (e.g., flowing stream vs. grab pond sample) and location. Detections of TP occurred in ecoregions II, V, VI, XII, and XIV. There was an average of approximately 215 detections per ecoregion with detections, ranging from 9 (ecoregion XII) to 832 (ecoregion VI). There was an average of 185 ecocriteria exceedances in the ecoregions with exceedances, ranging from 0 (ecoregion XII) to 693 (ecoregion VI). The majority of these exceedances per ecoregion occurred at one golf course, with the exception of ecoregion II, where two golf courses were responsible for the exceedances. Total phosphorus was detected in surface water in three CZs (5, 6, and 8), with an average of 358 detections, ranging from 17 (CZ 8) to 832 (CZ 5). Two golf courses were responsible for these detections, which ranged from one (CZ 6) to four (CZ 6). Note that this comparison of TP detections and ecoregional criteria was done on the regional scale (i.e., aggregate level III) and not on the local scale, where TP criteria may or may not exist. Apparently, these ecoregional criteria were developed based on baseflow conditions, i.e., storm events were excluded (I. Davis, U.S. Environmental Protection Agency, Office of Science and Technology, personal communications, January 14 and 28, 2010). A significant fraction of these results in this database is obtained from storm flow events. Therefore, this is a conservative comparison.

Groundwater results

Pesticides and metabolites. There were 15,774 groundwater pesticide/metabolite entries, of which 191 (1.2%) were detections. Detections by categories are herbicides (11), followed by insecticides (8) and fungicides (8). Most samples were from monitoring wells. (Lysimeter samples were not used in the analyses of groundwater impacts.) Twenty-four detections (12.6% of detections, 0.15% of the total entries) exceeded an MCL standard or lifetime HAL, representing eight different pesticides (Supplemental Data, Fig. S4 and Table 6).

The range of average concentration of pesticides in groundwater was 0.08 to 6.32 μg/L, depending on whether ND = 0.0 or ND = DL. The 95th percentile concentration was between 0.03 and 0.86 μg/L, depending on whether ND = 0.0 or ND = DL. The 99th percentile concentration was between 0.04 and 1.13 μg/L, depending on whether ND = 0.0 or ND = DL.

There were pesticide detections in four GW regions (7, 9–11). The average number of detections per GW region was 46, with detections ranging from 2 (GW region 7) to 74 (GW region 9). There was also an average of two golf courses per GW region responsible for the detections, ranging from one (GW region 7) to three (GW region 9). Additionally, an average of approximately nine different pesticides was detected per GW region, ranging from 1 pesticide (in GW region 7) to 14 (in GW region 9).

Pesticides were detected in six CZs (4 and 6–10) with an average of approximately 31 detections, ranging from 1 (CZ 8) to 98 (CZ 6). There was also an average of five golf courses responsible for the detections, ranging from 1 (CZ 4, 8, 10) to 15 (CZ 6). The majority of the CZs had one pesticide detected, with the exception of CZ 6, which had three pesticides detections.

On average, 69% (range 0 to 100%) of pesticides analyzed in groundwater were documented to be used during the monitoring period (Supplemental Data, Table S4). However, this may underestimate actual pesticide use in the two years prior to the beginning of sampling, as noted above. The pesticide use survey response rate for the groundwater studies was 46% (6 received of 13 sent). (Four of the golf course superintendents that responded are located in New England, one is from the Midwest, and one is from the mid-continent region.)

Nitrate-nitrogen. There were 1,683 groundwater nitrate-N entries, of which 1,377 (82%) were detections. The DLs ranged from 0.005 to 0.5 ppm, and were typically 0.1 ppm. There were 16 (1.2%) detections exceeding the 10 mg/L MCL in groundwater. The average concentration of nitrate-N was 1.08 mg/L (ND = half DL, 18% NDs) (Fig. 4).

Table 6. Pesticide detections in groundwater and maximum contaminant level/health advisory levels exceedances[a]

Pesticides	Total entries	No. of detections	No. of detections that exceed MCL or HAL	HAL/MCL	Max concn. detected (ppb)
2,4-D	1,024	18	0	70	50
3,5,6-Trichloro-2-pyridinol[b]	76	2	0	7[c]	0.76
Acephate	147	2	2	7.5[c]	8.8
Arsenic[b,d]	150	14	14	10	126
Atrazine	163	2	1	3	7.9
Azoxystrobin	47	3	0	1,260[e]	5
Bentazon	146	8	1	200	120
Bromacil	158	1	0	70	0.85
Chlordane	247	19	2	2	7.2
Chlorothalonil	532	6	2	2[c]	3.1
Chlorpyrifos	750	3	0	2	0.1
Dacthal diacid[b]	75	4	0	4,000[c]	1.07
Diazinon	163	1	0	1	0.05
Dicamba	605	2	0	4,000[c,e]/200[c,e]	1.9
Diuron	166	9	1	2	5.8
Fenamiphos sulfoxide[b]	142	6	0	2	0.79
Fenamiphos	160	19	1	0.7	0.71
Heptachlor epoxide[b]	245	11	0	2	0.16
Imidacloprid	106	2	0	399[c]	1.7
Iprodione	839	14	0	280[c]	55
Isofenphos	701	1	0	35[c]	1.17
Myclobutanil	168	12	0	175[c]	0.9
Oxadiazon	1	1	0	40[c]	0.05
Paclobutrazol	140	3	0	460[c]	4.2
Propiconazole	386	3	0	9.2[c]	0.72
Simazine	162	6	0	4	3.3
Triadimefon	1,030	13	0	210[c]	90.2
Triadimenol[b]	272	6	0	27[c]	8.4

[a] 2,4-D, dichlorophenoxyacetic acid; HAL, health advisory levels; MCL, maximum contaminant level.
[b] Pesticide metabolite.
[c] Values calculated by authors.
[d] The element arsenic is a component of the organoarsenical herbicides MSMA and DSMA. Inorganic arsenic can also arise from natural sources, as well as from historic use of inorganic arsenicals such as lead arsenate. Researchers usually did not, or were not able to, distinguish among the various potential arsenic sources when they reported their results.
[e] The 1988 U.S. Environmental Protection Agency HAL for dicamba is 4,000 ppb. We calculated 200 ppb using more recent data.

Nitrate-N was detected in GW regions 6, 7, 9–13 (Table 7). There was an average of 155 detections per GW region, ranging from 6 (GW region 11) to 577 (GW region 9). There was also an average of approximately two golf courses per GW region responsible for the detections, ranging from one (GW regions 6, 12, 13) to four (GW region 9). There were detections in four CZs (5–7, 9, and 10). In these CZs with detections, there was an average of approximately 207 detections, ranging from 2 (CZ 9) to 745 (CZ 6), and two golf courses responsible for these detections, ranging from 1 (CZ 9, 10) to 5 (CZ 6).

Total phosphorus. The number of groundwater TP entries was 970, of which 688 (71%) were detections (Fig. 5). The average TP concentration in groundwater was 0.12 mg/L (Winsorized mean). There were approximately 101 TP detections in five GW regions (6, 7, 9–11), ranging from 8 (GW regions 10, 11) to 334 (GW region 7). A majority of these detections were from one golf course in each region, the exception being from GW region 7, where two golf courses were responsible for the exceedances. Detections in CZs ranged from 5 to 7 and 10, with an average of approximately 127 detections, ranging from 8 (CZ 10) to 342 (CZ 7).

DISCUSSION

Pesticides: Mobility and persistence

The previous meta-analysis of turf pesticide impacts compared pesticide degradation rates and soil binding trends with an earlier U.S. EPA analysis of data from a national groundwater study [26]. The hypothesis was that pesticides detected in surface water and groundwater are more mobile and persistent than those pesticides not detected. Cohen et al. [12] used soil aerobic metabolism $t½$ (half-life) as the persistence parameter, and the mobility parameter was K_{OC} (the potential for neutral organics to bind to soil organic carbon). The trends supported the hypothesis, but differences were not statistically significant.

In the present study, we attempted to refine this comparison by limiting the analysis to those pesticides known to be used on the golf courses as reported by study participants. Thus, we calculated the means of the natural logarithms (ln) for $t½$ and K_{OC} for 11 pesticides applied and detected in groundwater, 19 pesticides that were analyzed and applied but not detected in groundwater, 13 pesticides applied and detected in surface water, and 19 pesticides that were applied and analyzed but not detected in surface water samples. The ln K_{OC} values for nondetected pesticides were nearly identical for surface water (6.20) and groundwater (6.22), and higher than the ln K_{OC} values for detected pesticides in surface water (6.08) and groundwater (5.95)— although the differences are not significant—which did not support the hypothesis. The $t½$ for detected pesticides versus nondetects supported the hypothesis in groundwater (i.e., longer half-lives for detected pesticides). However, the difference in means was only weakly significant. For groundwater, ln $t½$ (days) is 3.90 for detected pesticides compared with 3.08 for nondetected pesticides, with $p = 0.18$ at

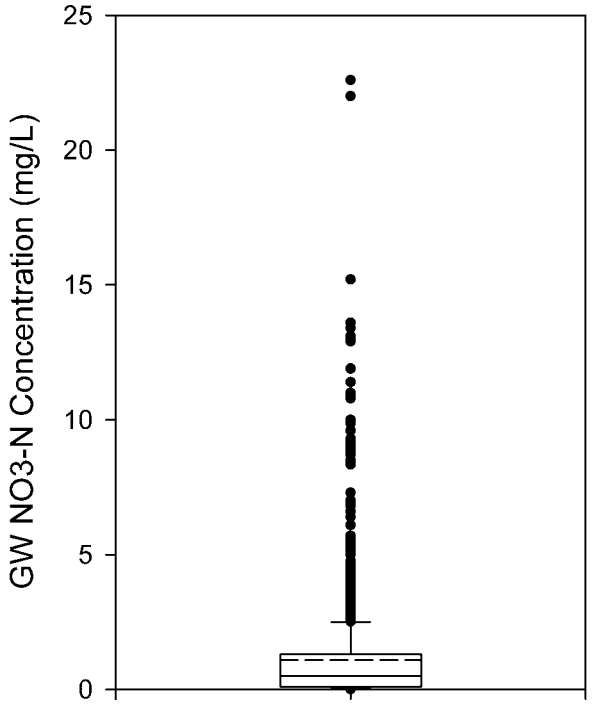

Fig. 4. Nitrate-N (NO3-N) detections in groundwater (GW). Nondetects (ND) = 0.5 practical quantitation limit (PQL); dashed line (- - -) = mean; solid line (—) = median.

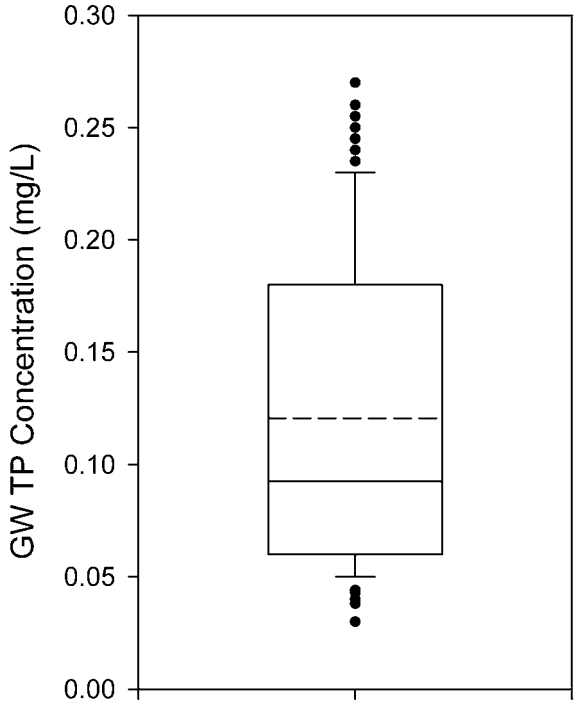

Fig. 5. Total phosphorus (TP) detections in groundwater (GW; Winsorized). Dashed line (- - -) = mean; solid line (—) = median.

the 95% CL. The difference for surface water detections was also not significant: $t½$ (days) was 3.27 for detects and 4.09 for nondetects ($p = 0.18$).

In summary, the K_{OC} is not a key independent variable for predicting ground and surface water detections in our database in this simple analysis. The most intriguing result is the groundwater/pesticide aerobic soil metabolism half-life analysis. Although the means were not statistically significantly different ($p = 0.18$, 95% CL), the mean half-life for detected pesticides, 49 d, is larger than the mean half-life for pesticides reported as used at the site but not detected in wells, 22 d.

This type of analysis should be pursued further, but with the following improvements. If this database or a similar database is used, some sort of weighting scheme should be applied to assign greater weight to the pesticides that are detected more frequently in relationship to their prevalence of use. A further analysis of analogous results should also not be as simplified as our approach. Many factors are related to pesticide characteristics: hydrology, land cover, application method, slope length, climate, and erosive tendencies that determine detection likelihood in groundwater and surface water [27–30]. Not all of these factors need to be considered in a simple assessment of the relative importance of soil metabolism and soil organics partitioning, but some of this knowledge could be integrated. For example, perhaps a simple analytic solution that integrates some of these factors, such as the Attenuation Factor described by Rao et al. [31], could be used.

Table 7. Groundwater regions[a]

Region	Description
1	Western mountain ranges
2	Alluvial basins
3	Columbia lava plateau
4	Colorado plateau and Wyoming basin
5	High plains
6	Nonglaciated central
7	Glaciated central
8	Piedmont and Blue Ridge
9	Northeast and superior uplands
10	Atlantic and Gulf coastal plain
11	Southeast coastal plain
12	Hawaii
13	Alaska

[a] R.C. Heath [25].

Pesticides: Reference point exceedances

Fourteen of the 24 groundwater exceedances were due to arsenic. The specific form of arsenic (As) detected (i.e., inorganic, organic, As^{3+}, or As^{5+}) was not determined in these studies. Most environmental analyses convert the molecule into inorganic As prior to detection and quantitation. The arsenic-containing herbicide that is currently heavily used on turf, monosodium methane arsonate, is an organoarsenical. The organoarsenicals have lower toxicity than inorganic arsenic and they are not considered carcinogenic to humans [32]. The extent to which the 14 As exceedances represent use of organoarsenical turf herbicides, old inorganic pesticides, or natural sources, is unknown.

Only 0.15% of the groundwater data entries for pesticides exceeded an HAL or MCL, slightly higher than we found previously (0.07%) with 25% fewer data points [12].

It is generally not appropriate to compare pesticide concentrations in surface water with lifetime drinking water HALs due to their episodic nature. (An exception would be the more unusual scenario of pesticide-laden groundwater base flow.) Therefore, we calculated acute HALs (see *Toxicity reference points* section above) to compare with surface water detections. This is a precedent, to our knowledge. However, we also compared the results with lifetime HALs because we had done that in 1999 [12], and because it is still standard practice.

The data showed that 0.40% of the surface water pesticide entries exceeded a chronic HAL/MCL, only one detection

exceeded an acute HAL, and 0.20% of the data entries exceeded an MAC. The MAC exceedance frequency was significantly lower (0.2% vs 0.6–0.9%), but the exceedance frequency for lifetime HALs/MCLs in surface water was slightly higher than what was found previously (0.4% vs 0.29%; [12]). Acute HALs were not derived for the previous work.

The relatively low rates of pesticide detections and exceedances in surface water is likely due to a combination of two factors: the fact that the turf system (verdure, thatch, dense roots) acts as a living filter, and the practice of applying minimal pesticides to the roughs, which typically surround the more intensively managed tees, greens, and fairways. Thus, it could be said that golf courses are inherently designed with built-in best management practices (BMPs), to a certain extent, in addition to the BMPs typically required during the permitting process for stormwater management.

Nutrients: Temporal trends

Overall inorganics database. The annual average concentrations of nitrate-N in groundwater ($n = 1{,}683$) show a slight increasing trend ($y = 0.0425X–83.888$, $r^2 = 0.29$, $p = 0.021$, where X is time in years). There was no significant annual trend for concentrations of nitrate-N in surface water. There were no statistically significant annual trends for TP in groundwater or surface water. Below are two examples of these specific trends analyses.

Two New York golf courses. Temporal trends for the NY-3 nitrate-N well results were analyzed using two statistical tests: Mann-Kendall (M-K) and simple linear regression. According to M-K and regression tests, nitrate-N concentrations increased in 11 wells at the 95% confidence limit (CL) over a seven-year period, *including the background well,* and decreased in three wells. There were no increasing nitrate-N trends for two of the 11 wells at the 99% CL using the M-K test. When $r^2 = 0.7$ was used as a cutoff, only three of the 14 wells demonstrated an increasing seven-year trend. In any case, all mean N concentrations were just fractions of the 10 mg/L drinking water MCL. Consequently, this suggests there have been no significant impacts of nitrate-N on groundwater quality from the golf course, and the increasing trends in nitrate-N are difficult to interpret due to the increase in the background well.

Only the M-K tests were run for the NY-2 groundwater dataset. The M-K test was run for two wells to determine if there were any increasing TP trends at the 95 and 99% CLs. The data indicated a decreasing TP trend (i.e., lower TP concentrations) at the 95 and 99% CLs in one well, and an increasing TP trend in the other well at the 95% CL, but not at the 99% CL. The M-K analysis for the NY-2 golf course shows an increasing nitrate-N trend in one well through 2005, however, nitrate-N has declined since 2005 (i.e., the calculated Z value in 2005 was 4.6 and it was 3.02 for the 2006/2007 data). The M-K test for nitrate-N in the other well shows that its concentration is stable, i.e., it is neither increasing nor decreasing. Overall, the nitrate-N concentration has decreased since 2001 at the NY-2 golf course.

The M-K test for the NY-2 surface water dataset shows that there are no increasing TP trends at any of the seven stations monitored at the 95 and 99% CLs for 12 years of monitoring. This includes the TP concentration spikes that occur during storm flow sampling events.

The M-K tests (both the 95 and 99% CLs) show no increasing nitrate-N trends at the seven surface water stations in 12 years of monitoring. However, there were decreasing trends (lower nitrate-N concentrations) at five stations, and several concentration spikes during both storm and/or baseflow sampling events.

Basic time-series comparisons (surface water). Basic time-series comparisons of the entire database were done for pesticides, nitrate-N, and TP (pre- and post-1997). There were a greater number of detections, more golf courses with pesticide detections, and more pesticides detected, in the pre-1998 data compared with the post-1997 time period. There were a greater number of detections, and more golf courses with nitrate-N detections, in the pre-1998 time period compared to the post-1997 time period. The time-series analyses for TP showed there were more detections, and a greater number of golf courses with TP detections, in the pre-1998 time period (including 1997) compared to the post-1997 time period. It is important to note that these comparisons are skewed because many of the golf courses that participated in the initial meta-analysis did not submit additional data for this new effort, and many of the new golf courses were added after 1997 to the overall study.

Basic time-series comparisons (groundwater). A time-series comparison for analytes in groundwater was done that is similar to the basic time-series comparison for surface water. There were fewer pesticide detections, fewer golf courses with pesticide detections, and fewer pesticides detected in the pre-1998 data compared with the post-1997 time period. The time-series analyses for nitrate-N (pre- and post-1997) showed there were fewer nitrate-N detections and fewer golf courses with nitrate-N detections pre-1998 (including 1997) compared with the post-1997 time period. The time-series analysis for TP (pre- and post-1997) showed there were more TP detections and a greater number of golf courses with TP detections in the pre-1998 (including 1997) compared to the post-1997 time period. (Again, it is important to note that these comparisons are skewed because many of the golf courses that participated in the initial meta-analysis did not submit additional data for this new effort, as well as many of the new golf courses were new to the overall study.)

In our experience, a small increase in nitrate-N can be expected, typically 1 ppm above baseline in the shallow part of the aquifer, at sites where a golf course is built and the previous land use is unmanaged vegetation. Part of this increase can manifest as an initial spike that results from land clearing and/or preemergent fertilization. Increases in TP concentrations in groundwater may or may not occur.

Nutrients: Exceedances

An overwhelming majority of the TP surface water results exceeded their respective ecoregional criteria. This could be a function of overfertilization and/or very strict criteria (i.e., they are often less than 0.04 ppm). Additionally, the U.S. EPA ecoregional criteria are based on baseflow data representing a regional scale, however, the results in this database were derived from storm flow and baseflow. As a result, many of the background samples exceed these regional criteria. In our experience, the irreducible concentrations from vegetated areas, including unfertilized areas, can often yield TP concentrations greater than the ecoregional criteria. Thus, we recommend that golf course superintendents base their P applications on soil tests conducted at least annually. This conclusion and recommendation may have applicability in other agronomic applications as well.

Nitrate-N MCL exceedances in groundwater were low (1.4%), and the average concentration (1.08 ± 1.87 mg/L) was in the typical background range for many/most regions

of the country. Surface water nitrate-N concentrations were often elevated relative to ecoregional criteria for TN; the Winsorized mean was 0.23 mg/L, and TN ecoregional criteria vary from 0.10 to 2.18 mg/L.

Database coverage

More data are needed from U.S. states with large numbers of golf courses including Texas, Illinois, Michigan, Ohio, and Pennsylvania, as well as the mid-continent region in general. However, the present study increased the number of data points in the central, western, and southwestern states compared to the previous study [12].

We attempted to remove from consideration those pesticides not likely to have been applied to the golf courses, but some of these results may still be diluted with meaningless nondetects.

Summary

The present study addresses the large data gap in the availability of reliable water quality data for golf course environments, which has been a key focus of many discussions regarding known or potential golf course impacts. There is a continued need for additional high quality, reliable data on the water quality impacts by golf courses. The present study expands the existing database [12] of 36 golf courses from 17 studies with the addition of 44 golf courses from 29 studies encompassing over 20 years of data collection, and adds the critical parameter TP to the analysis. The present effort has greatly increased the spatial and temporal coverage of the dataset. Exceedances of pesticide water quality criteria in surface and groundwater were infrequently observed. Total phosphorus concentrations in surface water appear to be the analyte of greatest concern, based on this database. It is appropriate for golf course superintendents to implement BMPs to reduce TP loading to the surrounding environment (e.g., [33,34]).

SUPPLEMENTAL DATA

Figure S1. Use class of pesticides detected in surface water (□) and groundwater (■) as reported in the monitoring studies.

Figure S2. Pesticides detected in surface water that exceed a Maximum Contaminant Level/Health Advisory Level (MCL/HAL).

Figure S3. Pesticides detected that exceed a Maximum Allowable Concentration (MAC) in surface water.

Figure S4. Pesticides detected in groundwater with Maximum Contaminant Level/Health Advisory Level (MCL/HAL) exceedances. (357 KB PDF)

Table S1. Types of sampling and analytical parameters for each study.

Table S2. Summary of golf course studies accepted for inclusion of the present study.

Table S3. List of pesticides that were applied to turfgrass to at least one golf course (GC) monitoring surface water.

Table S4. List of pesticides that were applied to turfgrass to at least one golf course (GC) monitoring groundwater. (24 KB DOC)

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