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VOCs, Pesticides, Nitrate, and Their Mixtures in Groundwater Used for Drinking Water in the United States

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Samples of untreated groundwater from 1255 domestic drinking-water wells and 242 public supply wells were analyzed as part of the National Water-Quality Assessment Program of the U.S. Geological Survey between 1992 and 1999. Wells were sampled to define the regional quality of the groundwater resource and, thus, were distributed geographically across large aquifers, primarily in rural areas. For each sample, as many as 60 volatile organic compounds (VOCs), 83 pesticides, and nitrate were analyzed. On the basis of previous studies, nitrate concentrations as nitrogen ≥ 3 mg/L were considered to have an anthropogenic origin. VOCs were detected more frequently (44%) than pesticides (38%) or anthropogenic nitrate (28%). Seventy percent of the samples contained at least one VOC, pesticide, or anthropogenic nitrate; 47% contained at least two compounds; and 33% contained at least three compounds. The combined concentrations of VOCs and pesticides ranged from about 0.001 to 100 μg/L, with a median of 0.02 μg/L. Water from about 12% of the wells contained one or more compounds that exceeded U.S. Environmental Protection Agency drinking-water standards or human health criteria, primarily because of nitrate concentrations exceeding the maximum contaminant level in domestic wells. A mixture is defined as a unique combination of two or more particular compounds, regardless of the presence of other compounds that may occur in the same sample. There were 100 mixtures (significantly associated with agricultural land use) that had a detection frequency between 2% and 19%. There were 302 mixtures (significantly associated with urban land use) that had a detection frequency between 1% and <2%. Only 14 compounds (seven VOCs, six pesticides, and nitrate) contributed over 95% of the detections in these 402 mixtures; however, most samples with these mixtures also contain a variety of other compounds.

Introduction

All humans are exposed concurrently and sequentially to many contaminants via several exposure routes (for example, inhalation of air, ingestion of food and water, and dermal contact). Everyone has hundreds of measurable contaminants in their bodies (*1*); however, the preponderance of toxicology studies to date have dealt with single, pure compounds (*2*). Some health effects result from exposure to large concentrations (e.g., concentrations greater than current standards and health criteria) of a single compound; however, there is increasing evidence that exposure at much lower concentrations also can be harmful (*2*−*4*). Endocrine disruption, particularly at low concentrations, is an area of intensive current research.

The effects of multicontaminant exposure on humans are uncertain, and additional work is needed to reduce this uncertainty. There are an enormous number of mixtures of commonly used chemicals, and this poses a daunting prioritization problem for toxicologists. This difficulty is confounded by the possibility that contaminant mixtures can have additive, antagonistic, or synergistic interactions or may not interact at all because they affect totally different systems within the body (*5*). Mixtures of contaminants having similar modes of action are generally of most interest; however, this may not always be the best approach for two reasons. First, recent animal studies have shown that compounds with different modes of action (for example, atrazine and nitrate) can interact (*6*, *7*). Second, the modes of action for all compounds, especially volatile organic compounds (VOCs), are not known.

Defining human exposure to mixtures of contaminants and their potential effects is an enormous task that likely will continue for decades. Nevertheless, identification of common mixtures of contaminants in water can be viewed as a first step toward defining exposure. Common mixtures on a national scale may differ from those on a regional or local scale; consequently, there is also a need to conduct smaller-scale studies such as was done in southern New Jersey (*8*). Common mixtures in groundwater may not be the most toxic from a health perspective, but human exposure to these mixtures is prevalent. Contaminants in water could be considered with additional information such as blood analyses, toxicology assays, and screening for estrogenic activity to identify the most important mixtures for further study.

The purpose of this paper is to (1) describe VOCs, pesticides, nitrate, and their most common mixtures in untreated groundwater used for drinking water in the United States, and (2) present a preliminary analysis of associations and possible explanatory variables for VOCs, pesticides, nitrate, and their most common mixtures. Detections among compound groups and individual mixtures are analyzed for frequency of occurrence and their relation to selected explanatory variables. The analysis of compound groups provides background information so that the analysis of mixtures can be fully understood within its context.

Methods

Groundwater samples were collected between 1992 and 1999, as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. A total of 1497 sampled wells were distributed across the United States (Figure 1); 1255 domestic wells and 242 public water-supply wells. Well depths ranged from 1.8 to 823 m, with a median depth of 46 m. Domestic wells had a median well depth of 43 m, and public supply wells had a median depth of 77 m. At the time of sampling, all wells were used as a source of drinking water.

There are three important characteristics of NAWQA's sampling design that can make NAWQA data different from

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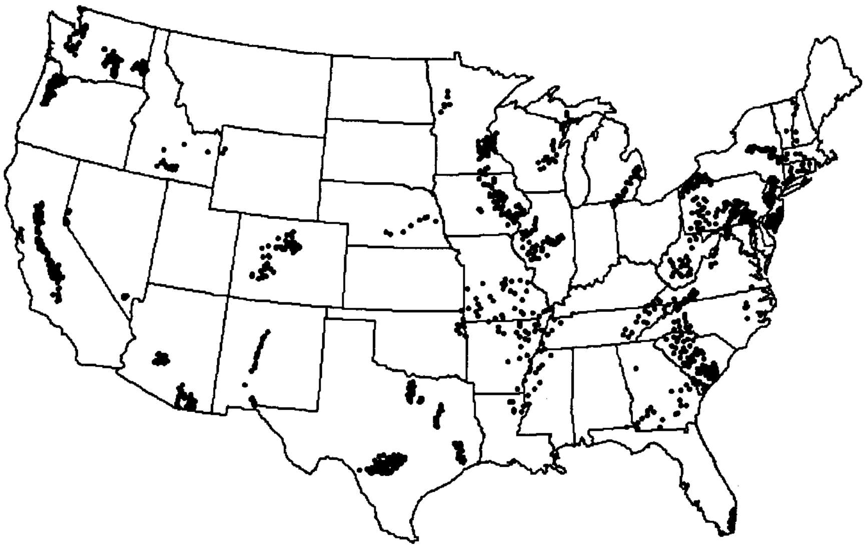

FIGURE 1. Location of 1497 wells in the conterminous United States sampled between 1992 and 1999.

many other drinking-water surveys. First, samples were collected to define the quality of water in the aquifer; therefore, they were collected before any treatment. Chlorination is the most common treatment and often the only treatment provided for public supplies in the United States (*9*); less than 5% of the public water suppliers use treatment processes that are designed to reduce concentrations of organic compounds in water (*9*). Chlorination is intended for the reduction of pathogens and is not considered a treatment for the removal of VOCs, pesticides, or nitrate. Nevertheless, under some conditions, chlorination can result in the oxidation of some VOCs and pesticides (*10*) and also can add VOCs, such as trihalomethanes. Almost 99% of individual domestic water supplies in the United States use groundwater (*11*), and the water normally is untreated. For these supplies, concentrations of some VOCs may be reduced by pressure tanks, or some VOCs may be added to the water from glue and plastic used in some plumbing systems; however, the concentrations of pesticides and nitrate in domestic water supplies at the tap are expected to be similar to concentrations in the aquifer.

Second, sampled wells for NAWQA's groundwater resource assessments resulted in data that were biased toward rural domestic wells because of the dominance of rural to urban population density areas in the United States. Consequently, these data likely do not provide a representative assessment of the quality of the water where it is used most intensively. For example, about 55% of the people dependent on groundwater live in urban population density areas (*12*); however, only 8% of the wells sampled were from areas with urban population density, assuming 386 people/km^2 (1000 people/mi^2) as the division between rural and urban (*12*). In a 1-km^2 area around the sampled wells used in the analysis, the overall median population density was 20 people/km^2, with the median being 17 people/km^2 around wells in rural areas and 863 people/km^2 around wells in urban population density areas.

Third, most of the samples were collected from domestic wells, and the water quality from these wells can be different from public supply wells for a number of reasons, including their generally shallower depth, lower pumping rates, and variable construction. Among the groundwater users in the United States, about 70% use public water supplies, and 30% use domestic water wells (*11*). Among the wells sampled by NAWQA, only 16% were public water supplies.

Samples were analyzed for 60 VOCs, 83 pesticides, and nitrate, although not all samples were analyzed for every compound (Table A1 in the Supporting Information). Sampling protocols and quality-control/assurance plans are described by Koterba (*13*) and Martin et al. (*14*). Source solution blanks, equipment blanks, field blanks, trip blanks, laboratory blanks, replicate samples, and spike samples are some of the types of quality-control/assurance samples that are collected on a routine basis. The results of the field blank samples were reviewed to identify any systematic contamination. If contamination occurred, the concentration data were not used for this analysis. All analyses were done at the USGS National Water-Quality Laboratory in Denver, CO. VOCs and pesticides were analyzed using capillary-column gas chromatograph/mass spectrometry (*15*−*17*). The long-term method detection limits for VOCs and pesticides varied by compound and with time but generally were less than 0.10 μg/L, with the exception of 720 VOC samples collected and analyzed from 1992 to 1996. These samples had a method reporting level of 0.2 μg/L. Some of the very low concentrations were estimated, indicating some quantitative uncertainty; however, this uncertainty was not related to the identification of the compound (*15*). Nitrate analysis is described by Fishman (*18*) and Patton and Truitt (*19*). Nitrite-plus-nitrate concentrations are based on elemental nitrogen (e.g., NO_2^- plus NO_3^- as N) and are referred to in this paper as "nitrate" because the nitrite contribution generally is negligible in groundwater.

Although all pesticides analyzed in this study are considered to have an anthropogenic source, some VOCs and nitrate can be derived from both anthropogenic and natural sources (*20*, *21*). VOCs can originate from spills, nonpoint-source contamination, and degradation of parent compounds. A few VOCs can occur naturally (e.g., trichloromethane, (*20*)), particularly if concentrations are in the small ng/L level. In North America, nitrate is an ubiquitous compound in groundwater with variable background concentrations (*22*−*24*). Previous regional and national investigations have defined background nitrate concentrations from less than 1 to 3 mg/L (*22*−*24*). For the purpose of this national-scale analysis, nitrate concentrations of $\geq$3 mg/L were assumed to have anthropogenic sources (and treated as "detections"), which is consistent with several earlier studies (*21*, *23*, *25*). Background concentrations for nitrate are currently being evaluated for groundwater samples collected as part of the NAWQA program.

A mixture is defined as a unique combination of two or more particular compounds, regardless of the presence of other compounds that may occur in the same sample. Thus, a sample with three detected compounds (A−C) contains four different mixtures (AB, AC, BC, and ABC). This approach is most useful if a particular mixture is found to be toxic even if it occurs with a variety of other compounds. The number of mixtures within a data set can be very large, and samples with the largest numbers of compounds contribute most of the mixtures. For example, a sample with two compounds has one mixture, a sample with five compounds has 26 mixtures, and a sample with 30 compounds (the largest number in one sample) has 1.07×10^9 mixtures. There were more mixtures in this one sample than all other samples combined.

A preliminary analysis of possible explanatory variables was performed for compound groups and the most common mixtures. Statistical analysis was done by dividing the samples into two groups (on the basis of the presence/absence of common mixtures or compounds) and then testing for differences. When comparing two nominal variables, a contingency table following the Pearson's χ^2 distribution was used. When comparing two groups with continuous variables, the Wilcoxon rank sum test was used. The test is used to determine if one group tends to produce larger observations when compared to the second group. An α value of 0.05 was used to evaluate the significance of all statistical tests.

Explanatory variables included well depth, well type, aquifer type, population density, dissolved oxygen concentration, and land use. Shallower wells generally are considered more prone to anthropogenic contamination than deeper wells. Public supply wells can have high pumping rates and large capture zones, which can increase the number of potential contamination sources (*8*). Unconfined aquifers generally are considered more prone to contamination than confined aquifers. There were 1030 wells at which aquifer type was identified; 198 wells were finished in confined aquifers, which includes some semiconfined aquifers and 832 wells in unconfined aquifers. Population density (which was based on a 1-km^2 area around each well) is related to many potential sources of VOCs (for example, underground storage tanks, runoff from parking lots, and sewer lines). Dissolved oxygen can be associated with recently recharged shallow groundwater where microbes have not utilized the dissolved oxygen and organic carbon as a source of energy. Recently recharged groundwater can carry anthropogenic contaminants to shallow groundwater.

Multi-Resolution Land Characteristics land-cover data (*26*), which has a 30-m resolution, was used to classify the general land use in a 1-km^2 area around a well. Urban land use included areas identified as low and high-intensity residential, commercial, industrial, transportation, and urban/recreational grasses. Agricultural land use included areas identified as orchards/vineyards, row crops, or small grains.

Because a univariate analysis was performed, the significance of the explanatory variables were tested without trying to account for multiple variables. For example, it has been shown that VOC detections are associated with population density (*12*). Sometimes, simple variables (such as well depth) may be obscured because the sources of VOCs are not being considered in these associations.

Results and Discussion

Seventy percent of the samples contained at least one VOC, pesticide, or anthropogenic nitrate; 47% contained at least two analyzed compounds; and 33% contained at least three compounds (Figure 2). VOCs were the most frequently detected compound group (44%), followed by pesticides (38%) and anthropogenic nitrate (28%). Concentrations of many VOCs and pesticides were low; in fact, if the concentrations are censored at 0.2 μg/L the detection frequency of VOCs is 18% and pesticides is 9%. The combined concentration of VOCs and pesticides in a single sample ranged from about 0.001 to 100 μg/L (Figure 3), with a median concentration of 0.02 μg/L. The summed concentration was significantly correlated with the number of compounds detected (Spearman's $\rho = 0.85$, $p < 0.01$). The Lowess smooth line (locally weighted scatterplot smoother) shows the trend of this relation (Figure 3). VOC concentrations were generally greater than pesticide concentrations (Figure 4).

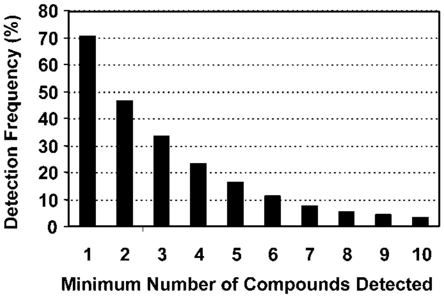

FIGURE 2. Detection frequency of one or more compounds in groundwater samples.

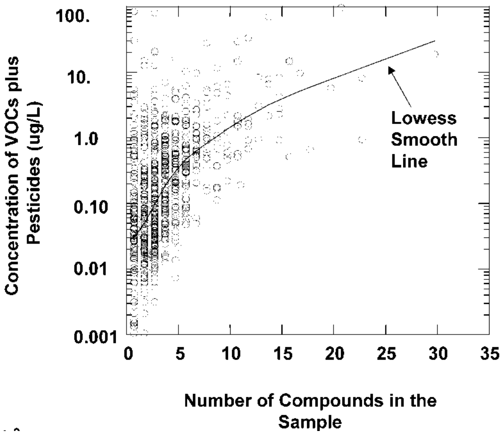

FIGURE 3. Comparison of the total concentration of all VOCs and pesticides with the number of compounds in the sample.

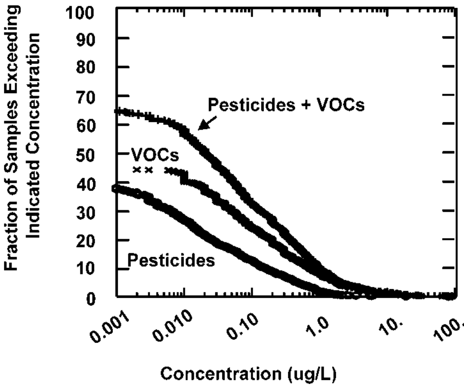

FIGURE 4. Quantile plot of the concentrations of VOCs and pesticides.

Of the 1497 samples, water in 11.6% did not meet current drinking water standards or human health criteria established by the U.S. Environmental Protection Agency; samples from 12.8% of the domestic wells and 5.4% of the public supply wells exceeded standards or health criteria. Preference was given to the drinking-water standards and health criteria in the following order: (1) the maximum contaminant level (MCL), (2) health advisory (HA) level, and (3) the risk-specific dose (RSD5). RSD5 is the concentration associated with a risk of one additional person in 100 000 contracting cancer over a 70-year life span (27). Table 1 lists compounds that exceeded standards or health criteria. Nitrate was the

TABLE 1. Compounds Exceeding Maximum Contaminant Level (MCL), Health Advisory (HA), or the Risk-Specific Dose (RSD5; the Risk of One Additional Person in 100 000 Contracting Cancer over a 70-Year Life Span)

compound	standard, μg/L	standard or criteria	well type	no. of exceedences	no. of analyses	exceedence percentage
1,2-dibromo-3-chloropropane	0.2	MCL	domestic	18	1255	1.4
1,2-dibromoethane	0.05	MCL	domestic	3	1255	0.2
			public	1	240	0.4
1,2-dichloropropane	5	MCL	domestic	2	1255	0.2
alachlor	2	MCL	domestic	1	1250	0.1
chloroethene	2	MCL	public	2	242	0.8
diazinon	0.6	HA	domestic	1	1249	0.1
dieldrin	0.02	RSD5	domestic	6	1249	0.5
			public	3	240	1.3
dinoseb	7	MCL	domestic	1	963	0.1
			public	1	187	0.5
nitrate	10 000	MCL	domestic	136	1242	11.0
			public	5	242	2.1
tetrachloroethene	5	MCL	domestic	3	1228	0.2
trichloroethene	5	MCL	domestic	1	1255	0.1
			public	1	242	0.4

TABLE 2. Top 25 Most Frequently Detected Mixtures

rank	compounds in mixture				column A no. of samples (out of 1497) with mixture	percentage of samples in column A that only contain this mixture
1	atrazine	deethylatrazine			284	5.6
2	deethylatrazine	nitrate			214	2.8
3	atrazine	nitrate			198	3.0
4	atrazine	deethylatrazine	nitrate		179	14.5
5	atrazine	simazine			138	4.3
6	deethylatrazine	simazine			127	0.0
7	atrazine	deethylatrazine	simazine		120	5.0
8	nitrate	simazine			111	4.5
9	atrazine	metolachlor			103	0.0
10	deethylatrazine	metolachlor			99	0.0
11	deethylatrazine	trichloromethane			97	4.1
12	atrazine	prometon			96	1.0
13	atrazine	deethylatrazine	metolachlor		95	2.1
14	atrazine	nitrate	simazine		92	1.1
15	deethylatrazine	nitrate	simazine		92	1.1
16	deethylatrazine	prometon			90	0.0
17	atrazine	deethylatrazine	prometon		87	5.7
18	nitrate	trichloromethane			86	5.8
19	tetrachloroethene	trichloromethane			86	2.3
20	atrazine	deethylatrazine	nitrate	simazine	86	14.0
21	atrazine	trichloromethane			78	1.3
22	metolachlor	nitrate			76	0.0
23	nitrate	prometon			73	4.1
24	deethylatrazine	metolachlor	nitrate		71	0.0
25	atrazine	metolachlor	nitrate		70	1.4

compound most frequently exceeding a standard or health criteria in both domestic and public supply samples.

Occurrence of Mixtures. There were millions of unique mixtures in the 699 samples with two or more compounds; however, only 402 mixtures (Table A2 in the Supporting Information) were detected at least 15 times (>1% detection frequency). Although these 402 common mixtures constitute less than 0.002% of the total number of mixtures, they were detected in 88% of the samples that had mixtures. Samples containing the 402 most common mixtures most often contained a variety of other compounds. For example, atrazine and deethylatrazine were found together 284 times in 1497 samples, but only 16 samples (5.6%) contained only atrazine and deethylatrazine (Table 2). Samples with at least one of the 402 common mixtures had higher concentrations of VOCs (Wilcoxon rank-sum test $p < 0.01$), pesticides ($p < 0.01$), and nitrate ($p < 0.01$) than those samples without these mixtures. Even if samples that had no detections of VOCs, pesticides, or anthropogenic nitrate are excluded, the results are the same. The 402 common mixtures contained a maximum of six compounds. There were more unique mixtures with three compounds (155) than any other group, and the number of mixtures with four compounds (99) was almost as large as the number with two compounds (118).

Table A2 (in the Supporting Information) ranks the 402 most common mixtures by the number of samples containing the mixture. Mixtures with pesticides and nitrate generally rank higher than mixtures with VOCs. This observation was verified by grouping the 402 mixtures into quartiles (about 100 mixtures/quartile) based on their detection frequency. The detection frequency among the top 100 mixtures (fourth quartile) ranges from 2% to 19% and the remaining 302 mixtures (first through third quartiles) have a detection frequency that ranges from 1% to <2% (Figure 5). The top 100 mixtures have a different composition than the remaining 302 mixtures (Figure 5). Pesticides contributed about 30% of the detections for the first three quartiles and then increase to more than 60% in the fourth quartile. VOCs contributed

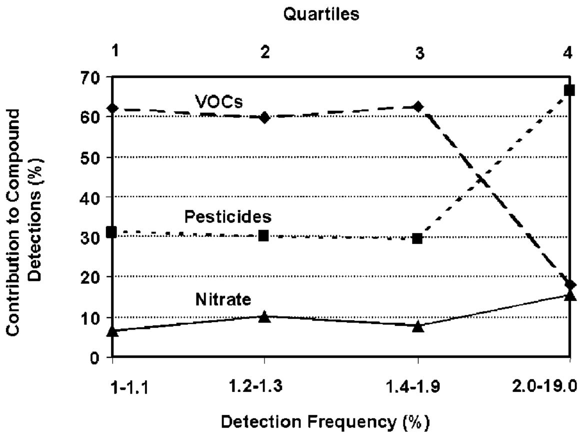

FIGURE 5. Comparison of VOC, pesticide, and nitrate contribution to compound detections within the 402 most common mixtures. There were about 100 mixtures in each of the four quartiles.

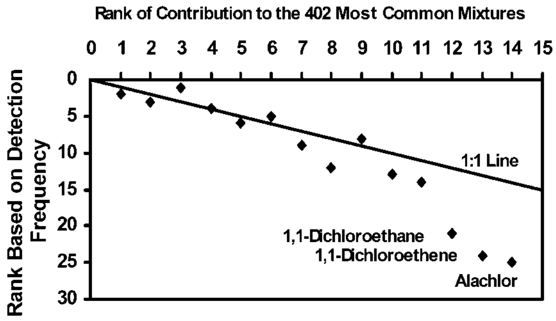

FIGURE 6. Comparison of ranks based on detection frequency and contribution to mixtures for the 14 compounds listed in Table 3.

TABLE 3. Rank Order of 14 Compounds That Contributed to more than 95% of Detections in the 402 Most Common Mixtures

rank	compound	type
1	deethylatrazine	pesticide
2	atrazine	pesticide
3	nitrate	
4	trichloromethane	VOC
5	tetrachloroethene	VOC
6	simazine	pesticide
7	metolachlor	pesticide
8	1,1,1-trichloroethane	VOC
9	prometon	pesticide
10	methyl *tert*-butyl ether	VOC
11	trichloroethene	VOC
12	1,1-dichloroethane	VOC
13	1,1-dichloroethene	VOC
14	alachlor	pesticide

about 60% of the compounds for the first three quartiles and then decrease to about 20% for the fourth quartile. Nitrate contributed 5−15% of the compounds in the mixtures.

There are 31 compounds in the 402 most common mixtures, but only 14 (Table 3) contributed more than 95% of the detections. Frequently detected compounds were generally those found in the 402 common mixtures. The ranks of the first 11 compounds in mixtures (Table 3) mimics ranks based on individual detection frequency (Figure 6), indicating that these compounds may have been important contributors to mixtures simply because they were ubiquitous. The last three compounds listed in Table 3 (1,1-dichloroethane, 1,1-dichloroethene, and alachlor) were found more frequently in mixtures than would have been expected based on their detection frequency (Figure 6).

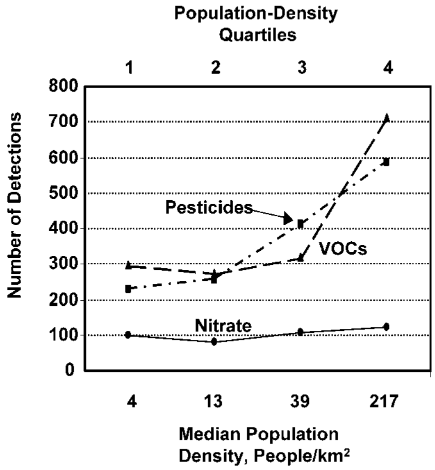

FIGURE 7. Comparison of the number of samples with VOCs, pesticides, and nitrate within quartiles of population density that are based on a 1-km^2 area around the sampled well. There were about 375 samples in each of the four quartiles.

Examination of the composition of the 402 most common mixtures indicates that there are at least four reasons why these mixtures occur. First, persistent pesticides and nitrogen fertilizer applied together, or sequentially, can result in the co-occurrence of pesticides and nitrate even if they were applied during different seasons or years. Second, if degradation is slow and the degradation products are persistent, parent compounds can co-occur with their degradation products. Third, products that contain mixtures of compounds (for example, gasoline) can contaminate the groundwater with multiple compounds from the same source. Fourth, compounds can co-occur because they have wide distributions in groundwater and their distributions overlap (for example, methyl *tert*-butyl ether and trichloromethane).

Analysis of Potential Explanatory Variables. Groundwater that had pesticides, anthropogenic nitrate, or one of the 402 common mixtures was associated with higher dissolved oxygen concentrations, shallower depths, and unconfined aquifers (conditions normally associated with vulnerable aquifers). VOCs were associated with higher dissolved oxygen concentrations but not with well depth or aquifer type (Table 4), indicating that an abundant source of VOCs is more important than hydrogeologic factors. For example, VOCs generally would not be expected in areas where there were no sources even if the aquifer is shallow and unconfined.

Land use has a significant effect on the detection of the compound groups and the 402 most common mixtures (Table 4). Urban land use was associated with the detection of VOCs, pesticides, and the 402 common mixtures but was not associated anthropogenic nitrate. This is somewhat perplexing because there are sources of nitrate in areas with urban land use (nitrogen fertilizer), and other compounds (pesticides and VOCs) are being transported to drinking water wells in these areas. Furthermore, well depth was not correlated with urban land use (Spearman's $\rho = 0.047$). Agricultural land use was associated with pesticides, anthropogenic nitrate, and the 402 common mixtures and was negatively associated with VOCs, indicating that agricultural practices are not a significant source of VOCs.

Population density was an important explanatory variable for the detection of all compound groups and the 402 common mixtures (Table 4). To better understand the effect of population density, samples were divided into quartiles ($\sim$375 samples/quartile) based on population density around the sampled well. Pesticides and VOCs did not increase linearly over the entire range of population densities but

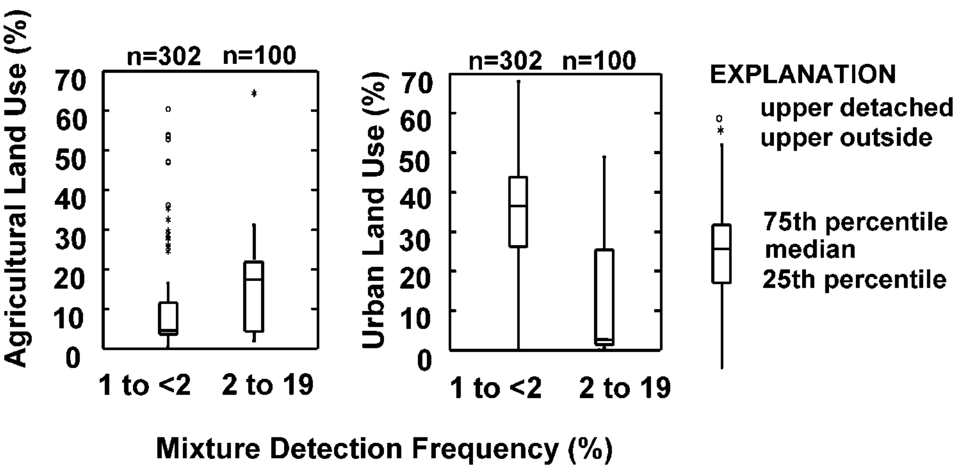

FIGURE 8. Comparison of land use activity in a 1-km^2 area around the sampled well and the detection frequency of the 402 most common mixtures.

TABLE 4. Relations between Selected Explanatory Variables and the Presence of Compound Groups and Any of the 402 Most Common Mixtures

detection of	explanatory variable	type of variable	*p* value	detections more strongly associated with
any VOC	well depth	continuous	0.38	
	well type (public/domestic)	binary	<0.01	public supply wells
	aquifer type (confined/unconfined)	binary	0.09	
	population density	continuous	<0.01	higher population density
	dissolved oxygen	continuous	<0.01	higher dissolved oxygen
	urban land	continuous	<0.01	more urban land
	agricultural land	continuous	<0.01	less agricultural land
any pesticide	well depth	continuous	<0.01	shallow depths
	well type	binary	0.01	public supply wells
	aquifer type	binary	<0.01	unconfined aquifers
	population density	continuous	<0.01	higher population density
	dissolved oxygen	continuous	<0.01	higher dissolved oxygen
	urban land	continuous	0.03	more urban land
	agricultural land	continuous	<0.01	more agricultural land
anthropogenic nitrate	well depth	continuous	<0.01	shallow depths
	well type	binary	<0.01	domestic wells
	aquifer type	binary	<0.01	unconfined aquifers
	population density	continuous	<0.01	higher population density
	dissolved oxygen	continuous	<0.01	higher dissolved oxygen
	urban land	continuous	0.71	
	agricultural land	continuous	<0.01	more agricultural land
any of the 402 most common mixtures	well depth	continuous	<0.01	shallow depths
	well type	binary	0.02	public supply wells
	aquifer type	binary	0.04	unconfined aquifers
	population density	continuous	<0.01	higher population density
	dissolved oxygen	continuous	<0.01	higher dissolved oxygen
	urban land	continuous	<0.01	more urban land
	agricultural land	continuous	0.02	more agricultural land

increased only after a threshold level was obtained (Figure 7). Detections of the 402 common mixtures follow a similar pattern with population density as pesticides and VOCs, except that the number of detections increased by a factor of 8 from about 950 detections in the first population density quartile to 7500 in the fourth quartile.

Public supply wells were associated with VOCs, pesticides, and the 402 common mixtures (Table 4). The median well depth for public supply wells (77 m) is deeper than domestic wells (43 m); however, public supply wells are more prone to anthropogenic contamination, partly because they are located in areas where there is more urban land use (Wilcoxon rank sum test, $p < 0.01$). Domestic wells were associated with anthropogenic nitrate because they were generally located in agricultural land use areas (Wilcoxon rank sum test, $p < 0.01$), where the transport of nitrate to drinking water wells is more common and the wells are shallower.

The 402 most common mixtures were divided into two groups: (1) the top 100 mixtures having detection frequencies that range from 2% to 19%, and (2) the subsequent 302 mixtures having detection frequencies that range from 1% to <2% (Figure 8). Agricultural land use was significantly larger (Wilcoxon rank sum test, $p < 0.01$) around sampled wells that contained any of the top 100 mixtures; in contrast, urban land use activity was significantly larger (Wilcoxon rank sum test, $p < 0.01$) around sampled wells that contained any of the remaining 302 mixtures (Figure 8). Consequently, agricultural land use yields fewer mixtures, but these mixtures tend to have higher detection frequencies. Urban land use yields more mixtures, but these mixtures tend to have lower detection frequencies. These detection frequencies are based on aquifer resource assessments (that are strongly biased toward rural domestic wells) and probably would be substantially different for other sampling strategies.

Implications

Some groundwater monitoring programs may want to consider including VOCs, pesticides, nitrate, and emerging compounds rather than focusing on one or two contaminant groups; in fact, both VOC and pesticide analyses are necessary to delineate compounds present in samples, and nitrate is a poor screening tool. If the analysis were limited to only VOCs or pesticides, there would have been incomplete knowledge in about 40% of the samples. VOCs or pesticides were detected without anthropogenic nitrate in 43% of the samples; if anthropogenic nitrate had been used as a screening tool, these samples would have been overlooked. Commonly detected VOCs and pesticides are the better screening tools for these compound groups. For example, the presence of atrazine or deethylatrazine correctly identifies the presence of other pesticides in about 82% of the samples, and trichloromethane correctly identifies the presence of other VOCs in about 72% of the samples.

High nitrate concentrations may be a concern because about 11% of the samples from domestic wells and 2% of the samples from public supply wells exceeded the MCL. Routine monitoring for nitrate is mandated for public supply wells, but there is no required monitoring for domestic water supplies. There are more than 15 million wells used for domestic water supply in the United States with an average of 3−4 people using water from each well (*28*). Adverse health effects potentially related to nitrate concentrations greater than 10 mg/L, as nitrogen, in drinking water include methemoglobinemia (*29*) and spontaneous abortions (*30*). Nitrate concentrations of 4 mg/L or more in drinking water from community supply wells in Nebraska were associated with increased risk of non-Hodgkin's lymphoma (*31*). A recent study in Iowa also showed a positive trend between municipal water nitrate levels and risk of bladder and ovarian cancers (*32*).

Although the purpose of this work was not to differentiate between potentially toxic and benign mixtures, one of the most common mixtures identified in this investigation has been shown to have an adverse effect on laboratory animals. The occurrence of atrazine with nitrate was the third most frequently detected mixture in this study (Table 2), and this mixture (at concentrations of the same order of magnitude as current MCLs) was found to alter thyroid levels, decrease the ability to make antibodies to foreign proteins, and to alter aggressive behavior in outbred white mice and wild deer mice (*7*).

Associations between selected explanatory variables and the common mixtures have been identified, providing an initial characterization of the population most likely exposed to these mixtures. For example, land use activity was determined to affect mixtures of compounds. In agricultural land use areas, anthropogenic activity typically involves the consistent ubiquitous use of a few persistent mobile compounds. These compounds tend to co-occur with discrete cohorts resulting in the frequent detection of some mixtures. In urban land use areas, anthropogenic activity is diverse, involving the localized use of many different persistent compounds. These compounds tend to co-occur with a variety of cohorts.

Wells for this analysis were sampled to assess the water quality of large aquifers and were not stratified based on water use. This sampling strategy provides a fair representation of water quality of domestic wells in rural areas but under represents water quality of public supply wells in urban areas. Analysis presented in this paper indicates that urban development has a significant impact on groundwater quality and the composition of mixtures; consequently, redoing this analysis as more NAWQA data become available in urban areas is essential.

Analyses and information presented in this paper were designed to assist others in selecting mixtures and compound concentrations for toxicity studies. Mixtures that occur frequently in domestic and public wells used for drinking water have been identified, making it possible to prioritize toxicology testing based on potential human exposure. Mixtures that ranked high among the 402 most common mixtures (Table 2 and Table A2) may be of interest because of the larger potential for human exposure through ingestion in drinking water. Additionally, mixtures containing the 14 compounds listed in Table 3 may be of particular interest because these compounds are ubiquitous in mixtures. Combined concentration of VOCs and pesticides in a sample is related to the number of compounds detected and can be estimated from Figure 3. The statistical summary of concentrations of individual compounds is listed in Table A1.

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Supporting Information Available

Table A1 is a statistical summary of VOC, pesticide, and nitrate concentrations in untreated groundwater samples, Table A2 is the most common 402 mixtures detected in rank order, Table A3 is the chemical data for the sampled wells. This material is available free of charge via the Internet at http://pubs.acs.org.

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