



Pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds in public drinking water wells in a shallow sand and gravel aquifer



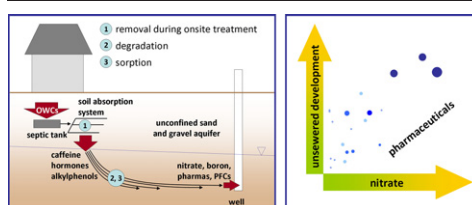
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HIGHLIGHTS

- We tested 20 public wells in a sand and gravel aquifer for 92 OWCs.
- Pharmaceuticals and perfluorosurfactants were frequently detected.
- Septic systems are the primary sources of OWCs into the aquifer.
- Maximum concentrations of two pharmaceuticals are as high as other U.S. source waters.
- Nitrate, boron, and extent of unsewered development correlate with OWC presence.

GRAPHICAL ABSTRACT



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ABSTRACT

Approximately 40% of U.S. residents rely on groundwater as a source of drinking water. Groundwater, especially unconfined sand and gravel aquifers, is vulnerable to contamination from septic systems and infiltration of wastewater treatment plant effluent. In this study, we characterized concentrations of pharmaceuticals, perfluorosurfactants, and other organic wastewater compounds (OWCs) in the unconfined sand and gravel aquifer of Cape Cod, Massachusetts, USA, where septic systems are prevalent. Raw water samples from 20 public drinking water supply wells in Cape Cod were tested for 92 OWCs, as well as surrogates of wastewater impact

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oxazole (115 ng/L) and the anticonvulsant phenytoin (66 ng/L) matched or exceeded maximum reported concentrations in other U.S. public drinking water sources. The sum of pharmaceutical concentrations and the number of detected chemicals were both significantly correlated with nitrate, boron, and extent of unsewered residential and commercial development within 500 m, indicating that wastewater surrogates can be useful for identifying wells most likely to contain OWCs. Septic systems appear to be the primary source of OWCs in Cape Cod groundwater, although wastewater treatment plants and other sources were potential contributors to several wells. These results show that drinking water supplies in unconfined aquifers where septic systems are prevalent may be among the most vulnerable to OWCs. The presence of mixtures of OWCs in drinking water raises human health concerns; a full evaluation of potential risks is limited by a lack of health-based guidelines and toxicity assessments.

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1. Introduction

Pharmaceuticals, personal care product ingredients, hormones, and other organic wastewater compounds (OWCs) are commonly found in aquatic systems (Barnes et al., 2008; Benotti et al., 2009; Kolpin et al., 2002). Some OWCs, including hormones, alkylphenols, and

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other endocrine disrupting compounds (EDCs), have been linked to reproductive effects in fish and other freshwater organisms (Brian et al., 2007). In addition, there are concerns about human health effects from OWCs in drinking water. While some assessments conclude that human health effects are unlikely at current exposure levels (Bruce et al., 2010; WHO, 2011), there are significant uncertainties in these assessments (Kumar et al., 2010) and growing evidence of EDC activity at low levels of exposure that are not apparent at higher levels (Vandenberg et al., 2012; WHO/UNEP, 2013).

Although 40% of U.S. residents rely on groundwater for drinking water (US Census Bureau, 2011; US EPA, 2009a), the presence of OWCs has been much more thoroughly characterized in surface waters than in groundwater. Shallow unconsolidated sand and gravel aquifers, which are prevalent through many parts of the U.S. (Miller, 1999), are especially vulnerable to OWCs because their high hydraulic conductivity and lack of confining layers permit infiltration from pollution sources. This vulnerability is compounded in regions with onsite wastewater treatment systems (e.g., septic systems and cesspools), which serve 20% of U.S. households (US Census Bureau, 2011) and discharge OWCs into the subsurface (Carrara et al., 2008; Godfrey et al., 2007). OWC removal by septic systems is highly variable and depends on treatment conditions and OWC characteristics (Stanford and Weinberg, 2010; Wilcox et al., 2009).

In order to investigate the influence of OWCs from septic systems on drinking water in a vulnerable aquifer, we have studied sources and transport of OWCs in groundwater on Cape Cod, Massachusetts, USA. Cape Cod's sand and gravel aquifer is impacted by contamination from septic systems, which serve about 85% of residences (Massachusetts EOE, 2004), and from groundwater discharge of wastewater treatment plant (WWTP) effluent via rapid infiltration beds. Studies of the Cape Cod aquifer have shown a high degree of persistence and long-range transport for some OWCs. Cape Cod's aquifer contains glacial deposits of fine- to coarse-grained sand and gravel with low organic carbon (OC) content (0.001–1%) (Barber, 1994). We previously found hormones, alkylphenol ethoxylates (detergent metabolites), and other OWCs up to 6 m downgradient of a septic system, especially under anoxic conditions (Swartz et al., 2006). We found four hormones and six pharmaceuticals in Cape Cod kettle ponds, which are primarily fed by groundwater, with greater detection frequencies and maximum concentrations in ponds downgradient of more densely populated residential areas (Standley et al., 2008). U.S. Geological Survey studies of a 6-km long plume of WWTP effluent in the western part of Cape Cod (reviewed by Barber, 2008) have shown persistence and minimal retardation of some organic pollutants such as tetrachloroethylene, 1,4-dichlorobenzene, and sulfamethoxazole, while sorption and biodegradation limit the mobility of some non-polar organic compounds and surfactants such as 4-nonylphenol (Barber et al., 1988, 2009).

The persistence of OWCs in the Cape Cod sole source aquifer has implications for drinking water quality and public health, but there has been limited study of OWCs in the region's drinking water. We previously detected bisphenol A and two alkylphenol ethoxylate metabolites in a study of alkylphenols and other phenolic compounds in Cape Cod private wells (Rudel et al., 1998). Thirteen OWCs, including three pharmaceuticals and six organophosphate flame retardants/plasticizers, were detected in a study of eight wastewater-impacted drinking water wells (public and private) (Zimmerman, 2005). The presence of EDCs and other OWCs in drinking water is of particular concern on Cape Cod, where breast cancer incidence is elevated relative to other parts of Massachusetts and the U.S. (Silent Spring Institute, 1997; State Cancer Profiles, 2013). While estimated historical concentrations of nitrate in drinking water, an indicator of wastewater infiltration, were not associated with increased breast cancer risk in a Cape Cod-wide epidemiological study (Brody et al., 2006), a more recent study with improved exposure modeling suggested wastewater-impacted drinking water was a risk factor for breast cancer in one region of Cape Cod (Gallagher et al., 2010). A limitation of these studies is that they relied

on proxy exposure measures or models; direct measurements of EDCs and other OWCs are necessary to more thoroughly evaluate potential exposures to OWCs through drinking water and to better understand the processes influencing OWC transport in sand and gravel aquifers, such as on Cape Cod.

With cooperation from nine Cape Cod public water supply districts, we tested raw water samples from 20 public wells for 92 OWCs, including pharmaceuticals, hormones, and consumer product chemicals. Our objectives were: (1) to evaluate the presence of OWCs in Cape Cod public drinking water supply wells and compare their concentrations to other U.S. public drinking water sources; and (2) to evaluate whether surrogates of wastewater impact (nitrate, boron, and unsewered development) can be used to inexpensively identify wells most impacted by OWCs. Characterizing the presence of OWCs in Cape Cod drinking water wells can improve our understanding of the processes controlling OWC fate and transport in groundwater systems.

2. Experimental

2.1. Site selection

Nine of 17 public water supply districts in Barnstable County, Massachusetts, USA, participated in this study. In 2009, these nine districts operated a total of 80 wells, with 4 to 21 wells per district. For each of these wells, nitrate (NO_3^-) data (2005–2009) were obtained from Massachusetts Department of Environmental Protection (MassDEP) as a surrogate of wastewater impact. Nitrate concentrations were available at least once per year for each well. Wells were classified as “low nitrate” if all reported NO_3^- concentrations from 2005 to 2009 were ≤ 0.5 mg/L and “high nitrate” if they exceeded 0.5 mg/L at least once during those five years. Background [NO_3^-] in unimpacted Cape Cod groundwater is ≤ 0.2 mg/L (Silent Spring Institute, 1997); concentrations of ≤ 0.5 mg/L are considered minimally-impacted, and concentrations of > 2.5 mg/L are considered highly-impacted (Massachusetts EOE, 2004). In this paper, [NO_3^-] is expressed as mg/L $\text{NO}_3\text{--N}$.

The extent of residential development in well recharge areas was also considered as a surrogate of wastewater impact, since 85% of Cape Cod residences rely on septic systems. GIS-based 2005 land cover/land use data, which included 33 land use types and had a 0.5 m resolution, were obtained from MassGIS (Massachusetts IT Division, 2012). ArcMap (ESRI, Redlands, CA) was used to analyze land use within zones of contribution (ZOCs) established by MassDEP to represent the maximum extent of recharge areas under extreme conditions (six months drought, maximum pumping rate). Wells with $\leq 20\%$ residential development were designated as having less-developed ZOCs and wells with $> 20\%$ residential development were designated as having more-developed ZOCs.

Among the 74 wells for which we had [NO_3^-] and land use data, we selected 20 wells with the goal of achieving a distribution of [NO_3^-] and residential land use that mirrored the available wells within the nine participating districts, while selecting an equal number of wells (2 or 3) per district (Fig. 1). The classification of the 20 selected wells (and of the 74 available wells in parentheses) was: 10% (8%) low NO_3^- /less developed; 15% (11%) low NO_3^- /more developed; 30% (32%) high NO_3^- /less developed; and 45% (49%) high NO_3^- /more developed. 2008 annual pumping rates for the 20 selected wells ranged from 30.7 to 174 million gal per well, with the exception of one well that was offline. Table S1 provides additional information about the selected wells.

2.2. Sample collection

Raw (untreated) water samples were collected from spigots at each wellhead, prior to any treatment, from 20 public supply wells in October 2009. Samples were also collected from two distribution systems. Raw water from Cape Cod public wells undergoes pH adjustment and, in some cases, filtration and chlorination. Prior to sample collection, each

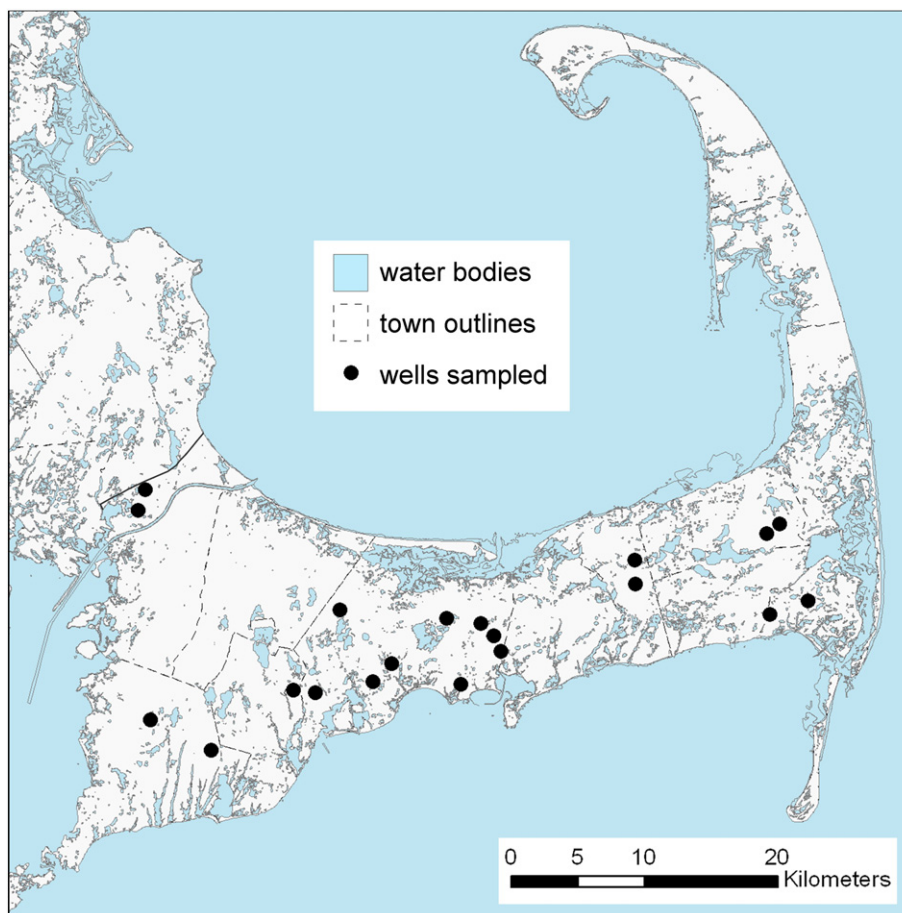


Fig. 1. Map of Cape Cod, Massachusetts, USA, showing the location of 20 public wells sampled in October 2009.

well was run for at least 1 h and each spigot was flushed for at least 10 min. For OWC analyses, water samples were collected in 500-mL or 1-L silanized, amber glass bottles that contained Na_2SO_3 for dechlorination (although just one sample from a distribution system was chlorinated) and were subsequently acidified with HCl. No additives were used for alkylphenol analyses. Samples for nitrate and boron analyses were collected in 125-mL HDPE bottles without preservatives. Twenty percent of samples were QA/QC samples (two field blanks, two duplicates, one matrix spike). Samples were immediately placed on ice in coolers and shipped overnight to the laboratory.

2.3. OWC analyses

Target OWCs were selected based on previous detections in aquatic systems, especially groundwater and drinking water, evidence of endocrine disruption, and/or availability of an analytical method. Method reporting limits (MRLs) for OWC analyses varied by four orders of magnitude, ranging from 0.1 to 1500 ng/L. Concentrations between limits of detection (LODs) and MRLs were reported only for alkylphenols. A complete list of target analytes and MRLs is provided in Table S2.

Details of analytical methods are provided in Appendix A Supplementary data. All analyses were conducted by Underwriters Laboratories (South Bend, IN, USA), except alkylphenol analyses, which were conducted by AXYS Analytical Services (Sidney, BC, Canada). In short, samples collected for OWC analyses were extracted with a solid phase extraction (SPE) cartridge prior to analysis with either liquid chromatography or gas chromatography followed by mass spectrometry. Isotopically-labeled surrogate compounds were used to assess compound recovery and accuracy. Nitrate was measured

using ion chromatography and boron was measured using inductively coupled plasma mass spectrometry.

2.4. Surrogates of wastewater impact

We evaluated correlations between OWCs and several surrogates of wastewater impact: NO_3^- , boron (B), well depth, and land use metrics. Boron, which is present in soaps and detergents, has been used as a wastewater tracer (Schreiber and Mitch, 2006) and exhibits conservative transport in the Cape Cod aquifer (Barber et al., 1988). Previous studies suggest background [B] in Cape Cod groundwater is below $\sim 10 \mu\text{g/L}$; LeBlanc (1984) reported $7 \mu\text{g/L}$ in an uncontaminated groundwater well, while Swartz et al. (2006) reported a minimum of $16 \mu\text{g/L}$ in septic system-impacted groundwater with detectable levels of detergent compounds. Well depth may be an indicator of wastewater impact, since deeper wells tend to be better protected from contamination sources (Verstraeten et al., 2005). Well depth data were obtained from MassDEP.

The extent of residential and commercial development was characterized within well ZOCs and within a 500-m radius circular zone around each well. Although actual recharge areas are larger and elongated in an upgradient direction (Barlow, 1994), 500-m radius circles have been used successfully to correlate agricultural land use with $[\text{NO}_3^-]$ (Kolpin, 1997) and urban land use with volatile organic compounds in supply wells (Johnson and Belitz, 2009). For each ZOC and 500-m radius zone, we used ArcMap to calculate the extent of residential (%RES) and commercial (%COM) development. We calculated residential development in two ways: as the sum of all residential land use regardless of density and as a weighted average that incorporated

average parcel sizes across multiple development densities (very low, low, medium and high densities and multi-family), expressed as an estimated number of septic tanks per acre. Total residential development was highly correlated with the weighted average (Spearman correlation coefficients >0.95) and both metrics yielded similar correlations with other parameters, so for simplicity, only results based on total residential development are presented. We used an online GIS-based planning tool, WatershedMVP (Cape Cod Commission, 2013b), to calculate the fraction of residential and commercial parcels connected by sewer to a WWTP, and adjusted %RES and %COM to include only parcels served by onsite wastewater treatment. For correlation analyses, we evaluated %RES and %DEV (%RES + %COM) in both ZOCs and 500-m radius zones.

2.5. Statistical analyses and chemical databases

Correlations between parameters were tested using the non-parametric Spearman's rank sum correlation test. Correlations were considered significant for $p < 0.05$. To compare likelihood of sorption, octanol–water partitioning coefficients ($\log K_{ow}$) were calculated for

each OWC using the KOWWIN program within U.S. EPA's EPI Suite package Version 4.0 (Meylan and Howard, 1995; US EPA, 2000).

3. Results and discussion

3.1. Nitrate and boron concentrations

Among the 20 wells tested, our 2009 NO_3^- measurements suggested that six wells had background or minimal impact ($<0.5 \text{ mg/L NO}_3^-$), ten showed moderate impact ($0.5\text{--}2.5 \text{ mg/L NO}_3^-$), and four were highly impacted ($>2.5 \text{ mg/L NO}_3^-$). $[\text{NO}_3^-]$ varied from <0.1 to 5.3 mg/L and $[\text{B}]$ ranged from <5 to $37 \text{ }\mu\text{g/L}$ (Table S1). In all wells with background $[\text{NO}_3^-]$, $[\text{B}]$ was also consistent with background ($<10 \text{ }\mu\text{g/L}$). Median $[\text{NO}_3^-]$ was 1.0 mg/L , which is higher than the 0.69 mg/L median among all the wells in participating districts (2008 and 2009 data).

3.2. OWC occurrence

Eighteen OWCs were detected in at least one well (Table 1). Antibiotics, perfluorosurfactants, organophosphate flame retardants, and non-antibiotic prescription drugs were the most frequently detected

Table 1
Organic wastewater compounds detected in 20 public supply wells on Cape Cod, Massachusetts.

Chemical name	CAS number	Method reporting limit (ng/L)	Number of times detected (% of wells)	Maximum concentration (ng/L)	Health-based guideline values (ng/L)	Maximum in other U.S. public source waters (raw water) (ng/L)*
<i>Prescription drugs</i>						
<i>Non-antibiotics</i>						
Antipyrine	60-80-0	1	1 (5%)	1	NA	$<1^e$
Atenolol	29122-68-7	0.1	1 (5%)	0.8	70,000 ^b	36 ^a
Carbamazepine	298-46-4	1	5 (25%)	72	12,000 ^b , 40,000 ^j	$<11^f$, 2 ⁿ , 9 ^e , 51 ^a , 156 ^d , 190 ^c
Gemfibrozil	25812-30-0	0.5	1 (5%)	1.2	14,000 ^b	$<13^f$, $<15^f$, 4 ⁿ , 17 ^e , 24 ^a
Meprobamate	57-53-4	0.1	4 (20%)	5.4	260,000 ^b	73 ^a
Phenytoin	57-41-0	2	4 (20%)	66	2000 ^b	29 ^a
<i>Antibiotics</i>						
Sulfamethizole	144-82-1	1	1 (5%)	1	NA	$<50^a$
Sulfamethoxazole	723-46-6	0.1	12 (60%)	113	18,000,000 ^b	2 ⁿ , 12 ^e , 41 ^f , 58 ^f , 110 ^a
Trimethoprim	738-70-5	0.1	1 (5%)	0.7	6,700,000 ^b	$<13^f$, 1 ⁿ , 4 ^e , 11 ^a , 20 ^c
<i>Other OWCs</i>						
DEET	134-62-3	5	1 (5%)	6	200,000 ^j	$<500^f$, 16 ^e , 110 ^a , 410 ^c
<i>Organophosphate flame retardants</i>						
TBEP	78-51-3	50	1 (5%)	50	NA	300 ^f , 400 ^f , 960 ^c
TCEP	115-96-8	20	3 (15%)	20	3300 ^p	$<500^f$, $<500^f$, 260 ^f , 530 ^a
TCPP	13674-84-5	10	4 (20%)	40	150,000 ^p	720 ^a
TDCPP	13674-87-8	10	1 (5%)	10	NA	$<500^f$, 170 ^f , 260 ^c
TEP	78-40-0	10	5 (25%)	20	NA	NA
<i>Perfluorosurfactants</i>						
PFOA	335-67-1	10	2 (10%)	22	40 ^k , 300 ^g , 400 ^q	31 ^m
PFOS	1763-23-1	1	8 (40%)	97	200 ⁿ , 300 ^h	16 ⁿ , 41 ^m
<i>Alkylphenols</i>						
4-Nonylphenol	Isomer mix	250	1 of 7 (14%)	20 J	NA	$<5000^f$, 130 ^a , 4100 ^c

Abbreviations: NA = not available; J = estimated value, below method reporting limit; TBEP = tris(2-butoxyethyl) phosphate; TCEP = tris(2-chloroethyl) phosphate; TCPP = tris(chloropropyl) phosphate; TDCPP = tris(1,3-dichloro-2-propyl) phosphate; TEP = triethyl phosphate; PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonate.

References:

- ^a Benotti et al. (2009).
- ^b Bruce et al. (2010).
- ^c Focazio et al. (2008).
- ^d Guo and Krasner (2009).
- ^e Illinois EPA (2008).
- ^f Kingsbury et al. (2008).
- ^g Minnesota DOH (2008a).
- ^h Minnesota DOH (2008b).
- ⁱ Minnesota DOH (2012).
- ^j Minnesota DOH (2011).
- ^k Post et al. (2009).
- ^m Quiñones and Snyder (2009).
- ⁿ Tabe (2010).
- ^p US EPA Region 3 (2012).
- ^q US EPA (2009b).
- ^r Zimmerman (2005).

* Source waters suspected to be contaminated by sources other than WWTPs or domestic wastewater sources, such as chemical production facilities, were not included.

types of chemicals (Fig. 2). The most frequently detected chemicals were sulfamethoxazole (antibiotic, detected in 60% of wells; MRL 0.1 ng/L), perfluorooctane sulfonate (PFOS; perfluorosurfactant, 40%; MRL 1 ng/L), carbamazepine (anticonvulsant, 25%; MRL 1 ng/L), and triethyl phosphate (flame retardant/plasticizer, 25%; MRL 10 ng/L). Of the 20 wells tested, 15 contained detectable concentrations of at least one OWC, as did both distribution system samples. Nine wells contained multiple OWCs, with up to 12 OWCs per well.

3.2.1. Pharmaceuticals

Sixty percent of wells contained detectable concentrations of at least one pharmaceutical (most MRLs ≤ 5 ng/L), with maximum concentrations ranging from 0.7 ng/L (trimethoprim) to 113 ng/L (sulfamethoxazole) (Table 1). Nine of the 54 target pharmaceuticals were detected, comprising three antibiotics and six other prescription medications. The average total concentration of detected pharmaceuticals in each sample ($\Sigma[\text{pharma}]$) was 24 ng/L (median, 0.6 ng/L; maximum, 131 ng/L). These $\Sigma[\text{pharma}]$ values likely underestimate actual pharmaceutical concentrations because they do not include chemicals that were not included in the laboratory analysis or those present below the MRL. To our knowledge, this is the first time that antipyrene (analgesic for ear infections) and sulfamethizole (antibiotic) have been detected in a drinking water source, whereas the other detected pharmaceuticals have previously been reported in other U.S. public drinking water sources. Notably, concentrations of two pharmaceuticals exceeded any previously reported concentration in U.S. public drinking water sources. The maximum sulfamethoxazole concentration exceeded maximum concentrations in five other studies (Benotti et al., 2009; Focazio et al., 2008; Illinois EPA, 2008; Tabe, 2010; Zimmerman, 2005), and two wells had higher phenytoin (anticonvulsant) concentrations than those found in the only other study that tested for phenytoin (Benotti et al., 2009).

Pharmaceutical concentrations in groundwater were highly variable across wells. The well with the highest sulfamethoxazole concentration did not have detectable concentrations of any other pharmaceutical, whereas the well with the highest carbamazepine concentration contained detectable concentrations of seven other pharmaceuticals. These results may indicate a high degree of heterogeneity in loading from local sources and/or spatial differences in hydraulic conductivity and biogeochemical conditions, such as OC levels and redox status, that affect OWC transport.

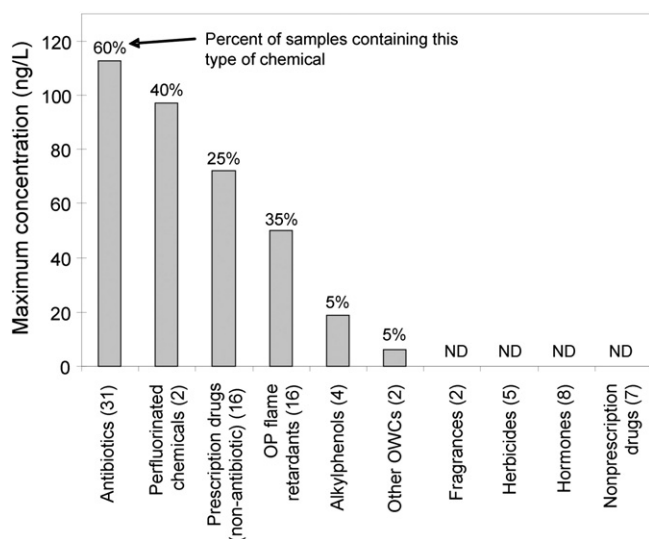


Fig. 2. Detection frequencies and maximum concentrations of individual OWCs in 10 chemical categories. The number in parentheses after each category name indicates the number of target analytes in that category. The numbers above each bar represent the percent of samples that contained each chemical type. ND = not detected.

Septic system effluent from residential and commercial development is likely the primary source of pharmaceuticals in groundwater, although other sources are possible. Cape Cod has five centralized WWTPs, all of which discharge into groundwater; four of the wells we tested may receive effluent from one of these WWTPs. Other potential sources of pharmaceuticals include onsite wastewater treatment for medical facilities and nursing homes. None of the 10 Cape Cod medical facilities and nursing homes with groundwater discharge permits (23,660–165,610 L/d design flow; Cape Cod Commission, 2013a) are located within the ZOCs for any of our wells, although there may be smaller facilities that discharge within the ZOCs for some tested wells.

3.2.2. Perfluorosurfactants

Samples from four wells contained >10 ng/L PFOS (MRL 1 ng/L); two of these also contained >10 ng/L perfluorooctanoic acid (PFOA; MRL 10 ng/L). Perfluorosurfactants are highly persistent in the environment and are used in a range of consumer products, including food packaging, non-stick cookware, stain resistant textiles, paints and lubricants, and have numerous commercial and industrial applications. PFOA and PFOS were detected in 66% and 48% of samples, respectively, in a survey of European groundwater (Loos et al., 2010). In the U.S., elevated concentrations of perfluorosurfactants in groundwater have typically been associated with production facilities (NJDEP, 2007; Shin et al., 2011), although WWTPs are also sources (Quiñones and Snyder, 2009).

The sample from one well had relatively high PFOS (97 ng/L) and PFOA (22 ng/L) levels despite moderate $[\text{NO}_3^-]$ and $[\text{B}]$ (0.9 mg/L and 16 $\mu\text{g/L}$, respectively), and a second well had moderately elevated PFOS (16 ng/L) and PFOA (14 ng/L) despite nearly background levels of $[\text{NO}_3^-]$ and $[\text{B}]$ (0.3 mg/L and 11 $\mu\text{g/L}$, respectively), suggesting a source other than domestic wastewater. Possible sources include a municipal airport and fire training academy that lie within the ZOCs of these two wells. PFOS, PFOA and other perfluorosurfactants are used in some aqueous film-forming foams for extinguishing hydrocarbon fires and have been detected in groundwater and surface waters down-gradient of fire-training areas (Moody et al., 2003) and airports (Saito et al., 2004).

3.2.3. Organophosphate flame retardants

Samples from 35% of tested wells contained at least one organophosphate flame retardant (OPFR; MRLs 10–100 ng/L), with maximum concentrations among the five detected OPFRs ranging from 10 to 50 ng/L. OPFRs are used in many household products (e.g., plastics, textiles, furniture, electronics, and construction materials) and have been found in the low $\mu\text{g/L}$ range in WWTP effluent (Reemtsma et al., 2008). Some OPFRs are persistent in the environment; for example, tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) have been frequently detected in drinking water sources (Focazio et al., 2008; Kingsbury et al., 2008). Domestic wastewater is likely the primary source of OPFRs into the aquifer, although there may be additional sources, such as runoff from construction sites (Andresen et al., 2004).

3.2.4. Compounds not detected

Although hormones, alkylphenols, musk fragrances, and caffeine are all typically found in wastewater, we did not detect any chemicals belonging to these classes (LODs for alkylphenols: 0.7–9 ng/L; MRLs for hormones, musk fragrances, and caffeine: 0.1–10 ng/L), aside from a single detection of 4-nonylphenol (4-NP; estimated concentration 20 ng/L). We also did not find 45 of 54 pharmaceuticals or 11 of 16 OPFRs that we tested for, even though many of these have been detected in other aquatic systems.

Hormones and alkylphenols have been previously detected in groundwater and surface water on Cape Cod (Standley et al., 2008; Swartz et al., 2006) and other regions (Benotti et al., 2009; Loos et al., 2010) but were generally absent from the wells in this study. While Standley et al. (2008) reported androstenedione, estrone, and progesterone in

groundwater-fed ponds on Cape Cod at maximum concentrations of 3.0–6.5 ng/L, we did not detect any of the eight hormones that we included in our analysis (including estrone and progesterone) above their respective MRLs (0.1–0.5 ng/L). Similarly, although 4-NP, octylphenol, and two NP ethoxylates (NP1EO, NP2EO) were found in Cape Cod groundwater near a septic system leach pit (concentrations up to 84 µg/L; Swartz et al., 2006) and in other groundwater studies (concentrations up to 11 µg/L; Loos et al., 2010), we detected 4-NP just once, at a relatively low concentration, and we did not detect any other alkylphenols. We did not test for NP ethoxycarboxylates (e.g., NP1EC), which are the most common environmental degradation products of long-chain NP ethoxylates (Ahel et al., 1987). Loos et al. (2010) found higher maximum concentrations of NP1EC than of NP in European groundwater, and Swartz et al. (2006) observed formation of NP1EC, NP2EC, and NP in groundwater near a septic system.

Although caffeine has been among the most frequently detected OWCs in other groundwater studies (Barnes et al., 2008; Focazio et al., 2008; Loos et al., 2010; Verstraeten et al., 2005) and has been suggested as a marker of wastewater impacts in shallow drinking water wells (Seiler et al., 1999), we did not detect caffeine (MRL 10 ng/L) or its metabolite paraxanthine (MRL 5 ng/L). While surveys of groundwater in the U.S. and Europe have reported caffeine concentrations up to 130 ng/L, caffeine has typically not been detected above ~15 ng/L in groundwater (Barnes et al., 2008; Focazio et al., 2008; Zimmerman, 2005). In previous studies of Cape Cod groundwater, oxic groundwater samples within 6 m of a septic system leach pit contained <5 ng/L caffeine, whereas groundwater with dissolved oxygen of <3 mg/L contained caffeine concentrations up to 1710 ng/L (Swartz et al., 2006). Seiler et al. (1999) did not detect caffeine (MRL 40 ng/L) in wastewater-impacted wells deeper than 10 m, even those with [NO₃⁻] above 10 mg/L. By contrast, caffeine has been detected much more frequently and at higher concentrations (up to 6000 ng/L) in rivers and streams (Kingsbury et al., 2008; Kolpin et al., 2002), suggesting greater attenuation under oxic subsurface conditions than in oxic surface waters.

3.3. Factors influencing likelihood of OWC detection in groundwater

Evaluating the characteristics of the chemicals detected in the public wells may provide insight into the factors that control OWC persistence in the Cape Cod aquifer. The absence of certain OWCs indicates one or more of the following factors: (1) relatively high MRLs; (2) relatively low concentrations in domestic wastewater; (3) effective removal during onsite treatment; (4) degradation in aquifer sediments; or (5) sorption to solid phases during subsurface transport. MRLs varied over four orders of magnitude (Table S2), and chemicals with relatively high MRLs are less likely to be detected. Other factors are discussed below.

Some chemicals may not have been detected because of relatively low loading into domestic wastewater effluent. In some cases, this may reflect low household usage. For instance, nonylphenol ethoxylates have been phased out of many laundry detergents (McCoy, 2007). For some OWCs excreted in human waste, primarily hormones and pharmaceuticals, the dominant forms in domestic wastewater may be hydrophilic metabolites rather than the parent compounds analyzed in this study (Reddy et al., 2005; Celiz et al., 2009). For instance, concentrations of the antilipidemic simvastatin were lower than concentrations of its hydroxy acid metabolite in WWTP influent (Vanderford and Snyder, 2006). Similarly, endogenous estrogens are primarily excreted as more hydrophilic glucuronides and sulfates, which undergo varying degrees of deconjugation or degradation during wastewater treatment (Reddy et al., 2005). These transformations may partially explain why we did not detect any of the eight hormones, nor 45 of 54 pharmaceuticals, that we tested in this study.

Treatment of septic tank effluent through soil absorption systems and aerobic sand filters may promote degradation of caffeine, paraxanthine, alkylphenols, hormones, and other OWCs before effluent

reaches groundwater. Soil absorption systems were shown to remove >99.9% of caffeine and paraxanthine (Godfrey et al., 2007) and >97% of total nonylphenols (Huntsman et al., 2006), and aerobic sand filters were shown to remove >90% of three steroid estrogens (Stanford and Weinberg, 2010). Many Cape Cod septic systems include sand-based soil absorption systems that may effectively reduce loading of caffeine, alkylphenols, and hormones into the aquifer.

While the relatively low OC content of the Cape Cod aquifer may limit microbial activity, some OWCs in this study likely undergo substantial biodegradation. In simulated groundwater recharge experiments, microbial communities became more efficient at degradation of pharmaceuticals after several months of exposure, even with low levels of biodegradable dissolved OC (Hoppe-Jones et al., 2012). Losses of caffeine, hormones, and alkylphenols were observed in a septic system plume on Cape Cod, with estimated transformation rates for caffeine of 0.07–0.14 d⁻¹ (Swartz et al., 2006). Mass loss of 17β-estradiol and branched-chain 4-NP was apparent in a WWTP effluent plume on Cape Cod, whereas sulfamethoxazole showed only minor mass loss (Barber et al., 2009). Measured mineralization rates in related microcosm experiments designed to estimate maximum biodegradation potential were 0.011 d⁻¹ for 17β-estradiol and 0.039 d⁻¹ for straight-chain 4-n-NP (Barber et al., 2009). Assuming first-order kinetics and a groundwater flow velocity of 0.42 m d⁻¹ (Barber et al., 2009), these degradation rates correspond to >95% removal of 17β-estradiol and >99.9% removal of 4-NP and caffeine during groundwater transport across 120 m, the minimum protective radius around public wells in Massachusetts with approved yields over 380 m³ d⁻¹.

Sorption to OC in aquifer sediments may retard movement of some hydrophobic OWCs, reduce dissolved concentrations, and enhance biodegradation. Barber et al. (1988) observed that partitioning of non-polar organic compounds into the solid phase could be predicted by log K_{ow} and %OC. Hormones (log K_{ow} mostly >3) and alkylphenols (log K_{ow} of >4 for NP, OP, NP1EO and NP2EO) are more hydrophobic, and therefore more likely to partition into the solid phase, than most of the pharmaceuticals and personal care products we detected (log K_{ow} mostly <3). Two relatively hydrophobic musk fragrances, galaxolide (log K_{ow} 5.9) and tonalide (log K_{ow} 5.7), were not detected in this study above the MRL of 10 ng/L; a study of U.S. source waters detected these two compounds more frequently in surface waters than in groundwater (Focazio et al., 2008). Based on typical values in the Cape Cod aquifer for grain density (ρ = 2.6 g/cm³), OC content in <125 µm sediments (f_{OC} = 0.001), fraction <125 µm sediments (f = 0.05) and porosity (ε = 0.3) (Barber et al., 1988), we estimated retardation factors (R_f) above 2 (i.e., groundwater velocity is at least twice contaminant velocity) for OWCs with log K_{ow} values above 4.2. Nevertheless, some relatively hydrophobic OWCs were found in this study, including PFOA (log K_{ow} 4.81) and gemfibrozil (log K_{ow} 4.77). Their persistence may be related to ionization state, since both PFOA (maximum pK_a 3.8) and gemfibrozil (maximum pK_a 4.42) are expected to be primarily present as anions in Cape Cod groundwater (pH 5–7; Barber et al., 1988) and ionized species tend to have lower log K_{ow} values (US EPA, 2000). While retardation may enhance degradation of biologically labile compounds, chemicals that do not readily undergo biodegradation may still persist in groundwater, even when substantial retardation is expected.

Overall, our results suggest that regulations requiring buffer areas around public supply wells and use of septic systems with soil absorption systems have the potential to prevent hormones, alkylphenols, fragrances, and some other classes of relatively hydrophobic and readily-degradable OWCs from reaching public wells at levels detectable in this study.

3.4. Surrogates of OWC presence

The expense of OWC analyses often precludes routine monitoring by public water suppliers, especially those serving small communities. Identifying inexpensively-measured surrogates of OWC presence would help

water suppliers prioritize wells for OWC sampling and source water protection. We evaluated correlations between predictors of wastewater impact ($[\text{NO}_3^-]$, $[\text{B}]$, well depth, and two metrics of residential and commercial land use) and OWC presence in public wells, as well as correlations among these surrogates.

3.4.1. Correlations among surrogates

Strong correlations were found among $[\text{NO}_3^-]$, $[\text{B}]$, and land use. Concentrations of NO_3^- and B were strongly correlated (Spearman correlation coefficient $\rho = 0.80$; $p < 0.001$), suggesting a common source. Domestic wastewater from septic systems is the major source of NO_3^- to Cape Cod groundwater (Cole et al., 2006), although fertilizers associated with landscaping and agriculture may also be sources. Boron is commonly used as a marker of wastewater (Schreiber and Mitch, 2006). $[\text{NO}_3^-]$ was also significantly correlated with $\% \text{DEV}_{\text{ZOC}}$ ($\rho = 0.54$; $p < 0.05$) and $\% \text{DEV}_{500 \text{ m}}$ ($\rho = 0.65$; $p < 0.01$); $[\text{B}]$ was also correlated with $\% \text{DEV}_{500 \text{ m}}$ ($\rho = 0.50$, $p < 0.05$), while not significantly correlated with $\% \text{DEV}_{\text{ZOC}}$ ($\rho = 0.33$, $p = 0.16$). Using $\% \text{RES}$ instead of $\% \text{DEV}$ yielded similar ρ values with $[\text{NO}_3^-]$ and slightly lower ρ values with $[\text{B}]$. Both $[\text{NO}_3^-]$ and $[\text{B}]$ were more strongly correlated with $\% \text{DEV}_{500 \text{ m}}$ than with $\% \text{DEV}_{\text{ZOC}}$, reflecting the relative importance of land use sources in closest proximity to the wells.

3.4.2. Correlations between surrogates and OWCs

We used two aggregate measures of the presence of OWCs: $\Sigma[\text{pharma}]$ and the number of OWCs detected (n_{detects}). $\Sigma[\text{Pharma}]$ provides a measure of impact specifically from wastewater, since non-wastewater sources of pharmaceuticals are not expected on Cape Cod, while n_{detects} may include OWCs from other sources.

Both n_{detects} and $\Sigma[\text{pharma}]$ increased with higher levels of wastewater impact and development (Fig. 3, Table S3). For instance, average $\Sigma[\text{pharma}]$ was over 100 times higher in wells with $[\text{B}] > 10 \mu\text{g/L}$, indicative of wastewater impact, compared to wells with $\leq 10 \mu\text{g/L}$ B. $[\text{NO}_3^-]$,

$[\text{B}]$, and $\% \text{DEV}_{500 \text{ m}}$ were all strongly correlated with $\Sigma[\text{pharma}]$ and n_{detects} . $\Sigma[\text{Pharma}]$ was most strongly correlated with $[\text{NO}_3^-]$ and n_{detects} was most strongly correlated with $[\text{B}]$. As with NO_3^- and B, $\Sigma[\text{pharma}]$ and n_{detects} were both more strongly correlated with $\% \text{DEV}_{500 \text{ m}}$ than with $\% \text{DEV}_{\text{ZOC}}$. It is not surprising that $\Sigma[\text{pharma}]$ and n_{detects} were most strongly correlated with chemical wastewater indicators (NO_3^- , B) since $\% \text{DEV}$ does not reflect the relative proximity between sources and wells, nor the temporal variability in loading, which may be especially pronounced in this region where the population more than doubles in the summer.

Well depth was negatively, although not significantly, correlated with measures of OWC presence. The strongest correlations were observed between well depth and $\Sigma[\text{pharma}]$ ($\rho = -0.33$) and with n_{detects} ($\rho = -0.26$). The relatively narrow range of well depths (12–39 m) may have limited our ability to find a significant relationship. Deeper wells pull water with longer flow paths, allowing for greater chemical retardation and degradation. Well depth was negatively correlated with n_{detects} in a study of 47 wells (depths 8–223 m; Barnes et al., 2008) and negatively associated with ammonia concentrations in a study of 26 shallow wells impacted by septic systems (depths 5–30 m; Verstraeten et al., 2005).

3.5. Implications

Our results provide new insight into the transport of OWCs from septic systems into groundwater and ultimately into public drinking water wells. Overall strengths of our study include the fact that we tested for a wide range of OWCs across a region where groundwater is primarily impacted by septic systems. Analyzing multiple surrogates of wastewater impact allowed us to evaluate the ability of each to predict the presence of OWCs. Exploring many chemicals with a range of sources and characteristics (biodegradability, hydrophobicity) provides insight into key processes controlling fate and transport.

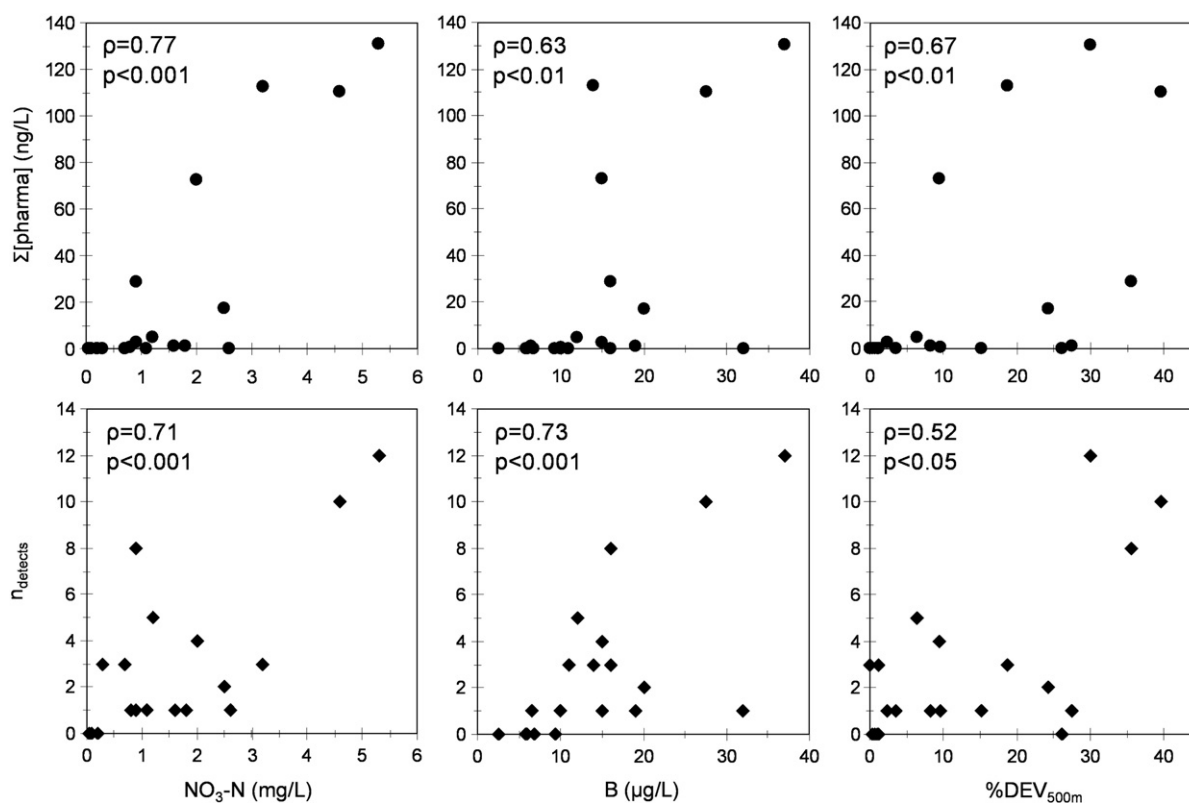


Fig. 3. Sum of detected pharmaceutical concentrations ($\Sigma[\text{pharma}]$) and number of OWCs detected (n_{detects}) as functions of nitrate, boron, and $\% \text{DEV}_{500 \text{ m}}$. Each graph shows the Spearman correlation coefficient (ρ) and corresponding p value. $\% \text{DEV}_{500 \text{ m}}$ is the sum of unsewered residential and commercial development within a 500-m radius zone around each well.

Additional sampling of the Cape Cod aquifer would provide greater insight into drivers of spatial and temporal variability. Our results, based on one-time sampling, do not reveal seasonal or interannual trends driven by variations in the number of residents and biogeochemical conditions. Repeated sampling would provide a more representative assessment of drinking water quality and more integrated measure of exposure for Cape Cod residents over time. While the presence or absence of specific OWCs provides some insight into the dominant factors controlling transport, this study was not designed to distinguish among multiple mechanisms controlling OWC fate and transport. Additional sampling and groundwater modeling that incorporates heterogeneity in the composition of aquifer sediments and groundwater velocities, as well as chemical properties of individual OWCs, would allow better characterization of OWC transport and prediction of other OWCs that may also be present.

$[\text{NO}_3^-]$ and $[\text{B}]$ were correlated with the presence of OWCs in the Cape Cod aquifer and may be useful OWC surrogates in other regions where sand and gravel aquifers are impacted by domestic wastewater. However, results cannot be generalized to areas where contributions from natural and non-residential anthropogenic sources of B and NO_3^- approach or exceed contributions from residential sources. In some regions, $[\text{B}]$ in groundwater is elevated due to saltwater intrusion, geological sources, or metal-working operations (Waggott, 1969; Barrett et al., 1999). Background $[\text{NO}_3^-]$ can vary regionally and non-residential anthropogenic sources include fertilizers and N-rich wastes from feedlot operations. Furthermore, NO_3^- may display non-conservative behavior due to denitrification and other biogeochemical transformations, especially in groundwater systems with higher levels of OC. Stable isotopes of N and B have been used to distinguish multiple pollution sources (Vengosh et al., 1994), but isotopic analyses are less frequently conducted by commercial laboratories and data interpretation requires characterization of end member isotopic composition. Other chemicals that have been suggested as wastewater indicators in groundwater include individual OWCs such as artificial sweeteners (Buerge et al., 2009), although these are not routinely analyzed by commercial laboratories. Many surveys of OWCs in the environment do not report information about inorganic wastewater markers or land use patterns. Including such ancillary data would help evaluate the usefulness of these surrogates more broadly.

Several aspects of our results raise human health concerns. First, concentrations of perfluorinated chemicals and some pharmaceuticals in this study approached published health-based guidelines. Concentrations of PFOA (22 ng/L) and PFOS (110 ng/L) in one distribution system sample were within a factor of two of the lowest drinking water advisory level for these compounds (Table 1; Post et al., 2009; US EPA, 2009b). Furthermore, a recent epidemiological study suggested that current drinking water limits for PFOS and PFOA are not sufficiently protective for immunotoxicity endpoints in children (Grandjean and Budtz-Jørgensen, 2013). In addition, our highest phenytoin concentration (66 ng/L) was only 30 times lower than the health-based drinking water equivalent level developed by Bruce et al. (2010).

We were not able to evaluate potential health implications for the other OWCs detected in this study because for many OWCs, health-based guidelines are not available at all or are inadequate because of a lack of toxicity information (Stephenson, 2009) and limited toxicity testing requirements. In addition, older studies that are available for some chemicals, such as OPFRs, did not investigate effects during sensitive periods of development (Dishaw et al., 2011). Furthermore, while this study included a diverse list of nearly 100 OWCs, there are about 80,000 chemicals currently in use, suggesting that other OWCs, as well as their metabolites, were also present in our samples.

Interpretation of low concentrations of OWCs in drinking water has been controversial. Some risk assessments have suggested that few or no health risks are associated with commonly-reported drinking water exposures from pharmaceuticals, since such exposures are generally far below therapeutic levels or levels where adverse health effects have

been reported in animal or human studies (Bruce et al., 2010; WHO, 2011). Similarly, for chemicals present in consumer products, exposures associated directly with product use or other exposure pathways (e.g., food consumption) are expected to be much higher than via consumption of drinking water, except in cases of highly contaminated drinking water (Egeghy and Lorber, 2011; Lorber, 2008; Trudel et al., 2008; Vestergren and Cousins, 2009). However, this interpretation does not address our limited understanding of potential effects from low-dose exposures or interactions among multiple chemicals.

Relatively high doses of pharmaceuticals are given to individuals with expectation of a significant health benefit, but safety evaluation is not conducted for the purpose of evaluating health risks of widespread population exposure to low doses. Some published approaches to setting health-based limits for pharmaceuticals divide the minimum therapeutic dose by a standard safety factor (NRMMC, 2008; WHO, 2011), but pharmaceuticals often have target and non-target effects well below the therapeutic dose and sensitivity can vary widely among individuals, as in the case of antibiotic allergies (Bruce et al., 2010). For example, a recent study showed that acetaminophen inhibits testosterone production at concentrations approximately 100 times lower than the therapeutic plasma concentration (Kristensen et al., 2011). Hormones in particular can be active over a very wide range of concentrations, so dividing a therapeutic dose by 1000 or even 10,000 may still result in a biologically active dose, and effects of EDCs can be more apparent at lower doses than higher doses (Vandenberg et al., 2012).

While some guidelines for pharmaceuticals are based only on therapeutic dose, other guidelines have been developed based on results of toxicity studies (e.g., Bruce et al., 2010). However, few of these studies are available and their usefulness may be limited by endpoints considered, since assessment for drugs may not include toxicity data or rigorous assessment of developmental toxicity, neuro- or immunotoxicity, endocrine toxicity, and carcinogenicity (ICH, 2013). Environmental risk assessments of pharmaceuticals often focus on the most frequently-detected chemicals in environmental waters; however, a prioritization method based on number of prescriptions, toxicity information, metabolism information, and predicted WWTP removal showed that some of the pharmaceuticals with the greatest potential human health risk have not been studied in the environment (Dong et al., 2013). Trimethoprim and atenolol, which were both detected in our study, were among the 20 (of the 200 most frequently prescribed) pharmaceuticals that received the highest priority scores. Risks from mixtures of pharmaceuticals also need to be addressed. For example, the common antibiotic sulfamethoxazole inhibits metabolism of the commonly-detected drug phenytoin (US FDA, 2008); these drugs commonly co-occur in wastewater-impacted drinking water, so the presence of sulfamethoxazole could increase the effects of phenytoin.

The presence of antibiotics in groundwater also raises concerns about potential effects on microbial communities, including the development of antibiotic resistance. Shifts in microbial community structure and biogeochemical transformations of nitrogen have been observed following exposure to sulfamethoxazole, with the lowest concentration tested, 5 nM (1266 ng/L), resulting in a 47% decrease in nitrate reduction potential (Underwood et al., 2011). Microbial communities exposed to 240–520 µg/L sulfamethoxazole showed changes in composition and sulfamethoxazole sensitivity, especially in the absence of prior exposure (Haack et al., 2012). While these effects were observed at much higher concentrations than observed in public wells on Cape Cod, these findings demonstrate the potential for sulfamethoxazole and other antibiotics entering sand and gravel aquifers to affect in situ microbial communities, especially in close proximity to effluent discharges.

4. Conclusions

This study found organic wastewater compounds, including pharmaceuticals, perfluorosurfactants, and organophosphate flame retardants,

in public drinking water wells in a sand and gravel sole source aquifer where septic systems are prevalent. Maximum concentrations of two pharmaceuticals matched or exceeded maximum concentrations found in other U.S. drinking water sources. The presence of OWCs in drinking water raises human health concerns, but a full evaluation of potential risks is limited by a lack of health-based guidelines and toxicity assessments. While many OWCs were not present at detectable levels in these public wells, other OWCs persisted through onsite and centralized wastewater treatment and during subsurface transport. Concentrations of nitrate and boron and extent of unsewered development may be used to identify wells most likely to be impacted by OWCs. Our results demonstrate the vulnerability of drinking water supplies in sand and gravel aquifers where groundwater discharges of wastewater are prevalent. Future studies are needed to identify the major sources of some OWCs, such as perfluorosurfactants, into domestic wastewater and to determine primary fate and transport processes in impacted aquifers.

Nutrients are a major cause of impairment in surface waters across the U.S. In watersheds where a substantial portion of nutrient pollution comes from domestic wastewater, loading of pharmaceuticals, hormones, and other OWCs is also expected to occur. Management efforts aimed at reducing nutrient loading can alter the extent and locations of OWC loading into surface waters and groundwater. While groundwater is often considered to be better protected from pollution than surface water, public and private wells may still be vulnerable. Even deep wells are not entirely protected from pollution; pathogens leaching from leaking sewers were recently detected in wells up to 300 m deep (Bradbury et al., 2013). While most OWCs are not currently regulated in drinking water, integrated wastewater planning should anticipate the impacts of wastewater on drinking water supplies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.08.067>.

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