



Concentrations of hormones, pharmaceuticals and other micropollutants in groundwater affected by septic systems in New England and New York



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HIGHLIGHTS

- Demographic factors affect micropollutants in groundwater near septic systems.
- Elevated TBEP concentrations downgradient of an extended care facility likely reflect use of cleaning formulations
- Pharmaceuticals and hormones occur in groundwater along a shoreline downgradient of septic systems
- Micropollutant concentrations increase with specific conductance values

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form 9 December 2014

Accepted 9 December 2014

Available online xxx

Editor: D. Barcelo

Keywords:

Septic systems

Micropollutants

Endocrine active compounds

Groundwater

Pharmaceuticals

ABSTRACT

Septic-system discharges can be an important source of micropollutants (including pharmaceuticals and endocrine active compounds) to adjacent groundwater and surface water systems. Groundwater samples were collected from well networks tapping glacial till in New England (NE) and sandy surficial aquifer New York (NY) during one sampling round in 2011. The NE network assesses the effect of a single large septic system that receives discharge from an extended health care facility for the elderly. The NY network assesses the effect of many small septic systems used seasonally on a densely populated portion of Fire Island. The data collected from these two networks indicate that hydrogeologic and demographic factors affect micropollutant concentrations in these systems.

The highest micropollutant concentrations from the NE network were present in samples collected from below the leach beds and in a well downgradient of the leach beds. Total concentrations for personal care/domestic use compounds, pharmaceutical compounds and plasticizer compounds generally ranged from 1 to over 20 µg/L in the NE network samples. High tris(2-butoxyethyl phosphate) plasticizer concentrations in wells beneath and downgradient of the leach beds (>20 µg/L) may reflect the presence of this compound in cleaning agents at the extended health-care facility.

The highest micropollutant concentrations for the NY network were present in the shoreline wells and reflect groundwater that is most affected by septic system discharges. One of the shoreline wells had personal care/domestic use, pharmaceutical, and plasticizer concentrations ranging from 0.4 to 5.7 µg/L. Estradiol equivalency

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quotient concentrations were also highest in a shoreline well sample (3.1 ng/L). Most micropollutant concentrations increase with increasing specific conductance and total nitrogen concentrations for shoreline well samples. These findings suggest that septic systems serving institutional settings and densely populated areas in coastal settings may be locally important sources of micropollutants to adjacent aquifer and marine systems.

Published by Elsevier B.V.

1. Introduction

Septic system discharges can be an important source of micropollutants (including pharmaceuticals, personal care products, and endocrine active compounds [EACs]) to adjacent groundwater and surface-water systems. Many areas in the United States are served by on-site septic systems that discharge treated wastewater to groundwater (USEPA, 2002). Nationally, approximately 20% of residential wastewater in the United States is disposed of through septic systems (US Census Bureau, 2006). In some areas of the northeastern United States, over 85% of wastewater disposal is by septic systems (Swartz et al., 2006).

Wastewater discharged from septic systems can reflect differing inputs based on the facility discharging wastewater to the septic system. Concentrations of a disinfectant, antimicrobial compound, and surfactants associated with detergents have been found to be higher in septic system samples from commercial settings than residential ones (Conn et al., 2006), due to the intensive use of cleaning products in commercial settings. Similarly, wastewater from medical facilities may have greater concentrations of pharmaceuticals than residential wastewater due to higher use of pharmaceuticals (Conn et al., 2006). Treatment type can also affect the concentration of micropollutants. Conn et al. (2006) found that the addition of aerobic treatment to septic systems decreased the concentrations of micropollutants; Stanford and Weinberg (2010) found that removal of micropollutants and EACs was promoted through the use of multiple treatments, including the use of aerobic filters. Thus, traditional residential one-tank or drainage pit (cesspool) systems have a potential for contaminating downgradient groundwater systems with micropollutants and other EACs (Stanford and Weinberg, 2010; Stuart et al., 2012).

Septic systems have been identified as the source of a variety of micropollutants and EACs in groundwater. Nonylphenols and octylphenols have been found in groundwater downgradient from septic systems in concentrations as high as 30 µg/L (Rudel et al., 1998). Although Hinkle et al. (2005) found several micropollutants at high (>10 µg/L) concentrations in onsite wastewater samples, relatively few were present downgradient, and concentrations of several (including including tris(2-chloroethyl) phosphate [TCEP], tonalide, caffeine and cholesterol [CHO]) were less than 1 µg/L in groundwater within 7 m of a leach bed. Hinkle et al. also noted a wide variability in micropollutant concentrations in different onsite wastewater samples. Recently, Del Rosario et al. (2014) identified several micropollutants in groundwater downgradient from onsite treatment systems and found a positive correlation between total dissolved nitrate and micropollutant concentrations, and decreasing micropollutant concentrations with increasing distance from the septic system; these results indicate the potential for use of such surrogates as nutrients for indicating the presence of micropollutants.

Reported differences in the presence and concentrations of micropollutants have been associated with hydrogeologic and biogeochemical aquifer characteristics, and chemical properties of the micropollutants. Aquifers in sandy sediments can be highly vulnerable to septic contamination: the naturally occurring estrogens E1 (estrone) and E2 (17β-estradiol) were present in groundwater samples affected by septic systems in the Cape Cod region of New England (Swartz et al., 2006). A separate study of a groundwater plume of treated effluent from a wastewater treatment plant in this region indicated maximum concentrations of nonylphenol and sulfamethoxazole

(SMX) of 2.4 µg/L and 1.5 µg/L, respectively (Barber et al., 2009). Thin unsaturated zones beneath infiltration beds have been identified as promoting the transport of micropollutants to underlying groundwater (Carrara et al., 2008; Swartz et al., 2006). However, some micropollutants are readily removed from septic discharges even in settings with unsaturated zone thickness of less than 1.5 m (Nielsen et al., 2002). Settings such as sandy surficial aquifers in which the potential for biodegradation has been reported to be low (Swartz et al., 2006; Barber et al., 2009; Carrara et al., 2008) may be particularly vulnerable to micropollutant discharges from septic systems. Several studies have suggested that micropollutant concentrations are highest in anoxic zones, as oxic conditions promote the removal of many micropollutants (Swartz et al., 2006; Carrara et al., 2008). Carrara et al. (2008) found the highest concentrations (1–10 µg/L) of pharmaceuticals (including ibuprofen, gemfibrozil, and naproxen) occurred in the anoxic portions of the septic discharge plume.

The introduction of micropollutants to groundwater systems from septic systems is of concern due to the possibility of downgradient transport to adjacent drinking water supplies, and potential for effects on non-target biologic organisms in surface waters receiving groundwater discharge (Schneider et al., 2014; Standley et al., 2008; Underwood et al., 2011; Writer et al., 2010). Hormones, antidepressants, antimicrobials, and other micropollutants associated with septic discharges have been identified as having multiple effects on aquatic species, including impairing the ability of native bacteria in groundwater discharge zones to reduce nitrogen concentrations (Underwood et al., 2011), and affecting physiological and behavioral aspects of fish (Barber et al., 2007; Vajda et al., 2008; Hinck et al., 2009; Painter et al., 2009). In eastern New York, for example, recent declines in fisheries and shellfish in the coastal waters of Long Island (Kraeuter et al., 2005) along with higher ratios of female to male fish in nearshore populations have been observed in sewage-impacted areas of Long Island Sound (Duffy et al., 2009). These observations have been attributed to the presence of hormones in sewage effluent, yet to date there has been no specific study of the presence of hormones in groundwater discharging to coastal waters of Long Island. Despite these concerns, research on micropollutants has focused more on surface-water systems than groundwater systems (Stuart et al., 2012).

1.1. Purpose and scope

This paper consists of an investigation of two well networks (one in New England [NE] and the other in New York [NY]) where septic systems were expected to contribute micropollutants to adjacent groundwater. In both locations, the occurrence of elevated nitrogen concentrations in groundwater downgradient of septic systems led to studies to assess the potential for migration of EACs from these septic systems to nearby water resources. These two areas were chosen for study because they span a range of different demographic sources and system sizes. The purpose of this study is to 1) document micropollutants downgradient of these different systems, 2) assess the relation between micropollutant concentrations and surrogate measures including nutrient concentrations and specific conductance, and 3) relate these findings to different demographics, septic system types, and chemical characteristics of micropollutants.

The NE network includes an assessment of micropollutants in groundwater downgradient of a septic system serving an elderly

population in an extended health-care facility in a glacial till setting where the shallow aquifer is a silty sand. In this area, the primary water quality concern is the migration of nitrate from the septic system towards adjacent properties. For the NE network, the expected high use of pharmaceuticals in the health-care facility discharging to the septic system has also led to concerns over the migration of micropollutants to the downgradient groundwater.

The NY network includes an assessment of micropollutants in groundwater in a coastal setting. Unlike the NE network, this setting has multiple septic systems in a densely populated area (10 dwellings/ha) on a barrier island with an unconfined aquifer overlying brackish water at depth, bounded on the surface by marine waters (Schubert, 2010a, 2010b). Most of the NY systems provide minimal treatment of wastewater before discharging to the sandy surficial aquifer, as these systems are generally cesspools consisting of covered pits lined with cement blocks, but no material covering the pit bottom. The proximity of sensitive estuarine waters of Great South Bay (GSB) to septic system discharges has led to concern over the migration of micropollutants and EACs from these systems to GSB.

The scope of this study includes an assessment of the occurrence of micropollutants in groundwater downgradient of septic systems in both networks during a single sampling round in 2011. Although these two studies were of short duration, these results constitute an initial assessment that will identify potential problem areas where elevated micropollutant concentrations can occur in silty sand in a glacial till setting and sandy surficial aquifer.

2. Methods

2.1. Well networks

The NE network was sampled once in 2011 to assess the effects of a septic system receiving waste from food preparation, laundry, bathrooms and all other sources from a 65-bed extended health care facility for the elderly that has a staff of 60. Daily water use at this site is 2300 L/d (data on water use and other factors in the facility were provided by the maintenance staff). The septic system is over 20 years old and consists of a holding tank designed to trap solids and enable limited anaerobic treatment. Excess water is conveyed to a splitter box through a gravity feed, which then sends water to four small septic tanks that enable additional anaerobic treatment. Water from these septic tanks flows to one of the two leach beds; (each around 500 m²) these leach beds receive flow on alternating basis, generally for two to three days. The overall retention time of the system is approximately one day.

Samples in the NE well network were collected from six wells and at a location within the septic system (Table S-1, Fig. S1). These wells were finished near the base of the shallow surficial aquifer, which consists of silty sand and is underlain by fractured bedrock. Three types of groundwater wells were sampled in the NE network: 1) two wells finished below the leach beds (wells L1, L2); 2) three wells downgradient of the leach beds (wells D1, D2, and D3; wells D1 and D3 are both 30 m downgradient from the nearest leach bed, whereas well D3 is 50 m downgradient from the nearest leach bed); and 3) a well finished upgradient of the leach beds (well B). The upgradient well was sampled to provide an indication of shallow groundwater that is representative of conditions unaffected by septic system discharge. The sample collected in the septic system (site T) was included to indicate the presence and typical concentrations of micropollutants within the septic system itself. NE well depths range from 3.6 to 7.6 m (Table S1).

Samples in the NY network were collected from seven wells once in 2011, and are classified by the well location with respect to shallow groundwater flowpaths in the study area (Fig. S2a, Table S2). All of these wells are finished in the surficial aquifer, which consists of sand interspersed with layers of peat, silt and clay (Schubert, 2010a, 2010b). The shoreline wells consist of three shallow wells (S1, S2, and S3) which range in depth from 1 to 2 m that are on the GSB shoreline

of the Kismet community. This area corresponds to a zone of groundwater discharge to GSB (Schubert, 2010a, 2010b) so these wells were sampled to characterize the micropollutant concentrations in groundwater discharging from septic-affected areas to adjacent GSB. Two wells at the east (S1) and central (S2) portion of the developed area were hand-driven, temporary wells. The third well (S3) located on the west end of the developed is a monitoring well.

The four upgradient wells were generally finished at the top of the aquifer, and had depths generally ranging from 1 to 6 m; one well (U2) is finished near the base of the freshwater flow system, and so is much deeper (32.9 m) than the other wells. Upgradient wells in this study refer to all wells that are not located on the shoreline, regardless of their locations relative to septic systems. Two of the four upgradient wells are adjacent to the Kismet community, one is in undeveloped parkland near the community of Robins Rest, and one well is at a park visitor's center in Watch Hill (Fig. S-3), in an area downgradient of a leach bed serving the visitor's center. Additional information on the Upgradient wells can be found in the Supplementary Information.

2.2. Sample collection and handling

Samples were collected from the NE network in July 2011, and the NY network in October and November 2011, using methods outlined in U.S. Geological Survey (variously dated). Samples were generally collected by using a peristaltic pump, however a submersible pump was used to collect samples from the NY upgradient wells and the NY shoreline well S3. Samples were collected after purging when either field parameters were stabilized or when three casing volumes were pumped from the well. Field parameters were collected onsite, and included temperature, dissolved oxygen, specific conductance, and pH. All samples were filtered by using 0.7- μ m glass-fiber filters in the field and shipped overnight on ice to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Additional information on Sample Collection and Handling is provided in the Supplementary Information.

2.3. Methods of analysis

Samples from both networks were analyzed by using a method developed for analysis of 59 micropollutants associated with domestic and industrial wastewater as described by Zaugg et al. (2007); this method is hereafter referred to as the SH1433 method. Samples were extracted using solid-phase extraction (SPE), with vacuum filtration through 500-mg OASIS-HLBSPE cartridges for this method, and extracts were analyzed by capillary gas chromatography/mass spectrometry (GC/MS). The analytes present in the SH1433 method are listed in Table S3; reporting limits for these compounds ranged from 0.01 to 5 μ g/L. Samples from both networks were analyzed for a modified version of the SH1433 method, hereafter referred to as the LC8144 method. This method uses the same method preparation and analysis steps as the SH1433 method and is described in Zaugg et al. (2014). The LC8144 method includes analysis of 42 compounds, most of which are pharmaceuticals. Reporting limits range from 0.007 to 0.14 μ g/L (Table S4).

Samples collected as part of the NE and NY networks were also analyzed for additional pharmaceuticals using the LC9017 method. The LC9017 method includes analysis for 105 compounds (all but 6 of which are pharmaceuticals; see Table S5) using high-performance liquid chromatography coupled to a triple quadrupole mass spectrometer using an electrospray ionization source operated in the positive ion mode (Furlong et al., 2014). Reporting limits range from 0.00045 μ g/L to 0.19 μ g/L for this method.

Samples collected in the NY network were also analyzed using the SH2434 method, which uses solid-phase extraction combined isotope-dilution quantification method for analysis (Foreman et al., 2012). Analysis is performed using gas chromatography with tandem mass spectrometry. The SH2434 method includes 20 analytes including

estrogens, androgens, and additional micropollutants, with reporting limits that range from 0.0004 to 0.004 µg/L for hormones, from 0.100 µg/L for bisphenol A (BPA), and 0.200 µg/L for 3β-coprostanol (COP) and CHO (Table S6).

Samples from both studies were also submitted for selected analysis of inorganic compounds. Samples collected from the NE site were analyzed for chloride, nitrate plus nitrite, and nitrite using the USEPA method 200.7 (U.S. Environmental Protection Agency, 1994), by a state-certified contract laboratory. Samples collected in the NY network were analyzed for ammonium, nitrite, nitrate plus nitrite and orthophosphate at the NWQL using methods described by Fishman (1993) and Patton and Kryskalla (2011). Samples from both networks were analyzed for nitrate using a cadmium reduction method. Inorganic samples were not stored and were analyzed by laboratories within holding times.

Additional information detailing the SH1433, LC8144, LC9017, and SH2434 methods, including laboratory method performance, can be found in the Supplementary Information.

2.4. Quality assurance

Field blank and replicate samples were collected in the NE study. The field blank (a sample prepared with reagent grade water and processed using the same equipment used to collect environmental samples) was analyzed using the SH1433 and LC8144 methods; analysis of these blank samples showed no detections. Replicate sample percent difference for SH1433, LC8144, and LC9017 methods ranged from 23 to 50%; these high replicate values likely reflect the low (<0.1 µg/L) concentrations present in this sample.

A field blank sample collected during NY network sampling was analyzed for the SH1433, LC8144, LC9017, SH2434, and inorganic analytes; there were no detections for any of the analytes present in all of these methods but SH1433. One analyte (DEET) was detected in the blank sample analyzed using the SH1433 method at a concentration of 0.044 µg/L. DEET concentrations less than 0.4 µg/L were censored in this study to reflect the presence of DEET in this blank. Comparisons for the two nutrients (ammonium and orthophosphate) detected in a replicate sample from the NY network had a 5% difference in concentrations. Additional information on field quality assurance can be found in the Supplementary Information.

2.5. Calculations

Most of the concentration data presented in this analysis is based on concentrations for groups of compounds. Aggregating concentrations of multiple analytes into fewer groups makes it easier to summarize overall differences in concentrations for the large number of analytes presented in these samples. The SH1433 and LC8144 analytes are divided into six different groups based on the use or origin of the compound (Tables S3, S4). These groups include CPG (combustion, pavement, and gasoline-derived compounds, $n = 10$), PAB (plant- or animal-derived biochemical, $n = 5$), PCDU (personal care/domestic use compounds, $n = 24$), PLA (plasticizers and phosphorus-based flame retardants, $n = 5$), PHA (pharmaceutical compounds, $n = 40$) and OTH (compounds not included in the other five other categories, $n = 17$). Concentrations for each of these groups are equal to the sum of detected concentrations for those micropollutants included in each group; concentrations for analytes that are not detected or detected but not quantified are set to zero. An additional pharmaceutical concentration (PHB, $n = 103$) is calculated based on pharmaceuticals detected using the LC9017 method (Table S5). Concentrations reported between the method detection limit and the reporting limit are considered quantitative for this analysis and are included in the calculations. Only pharmaceuticals present in the LC9017 method were used to calculate the PHB concentration; non-pharmaceutical analytes present in the LC9017 method

were not used for any calculations of concentrations of aggregated compounds.

For NY network samples, total nitrogen was calculated as the sum of ammonium and nitrite plus nitrate. Total nitrogen could not be calculated for the NE network samples, as ammonium data were not collected for these samples. Estradiol equivalency quotients (EEq, in ng/L of E2) are calculated for samples with detections of EACs and are used to summarize the chemical estrogenicity of samples included in the NY study (Table S7); details are provided in the Supporting Information.

The non-parametric correlation test (Spearman's r) is used in this paper to indicate general correlations between micropollutant compounds and nitrate and specific conductance values. Non-parametric statistical analysis is commonly used in statistical analysis of water quality due to the log-normal characteristics of water-chemistry data (Helsel and Hirsch, 2002).

3. Results and discussion

3.1. Concentrations of micropollutants in samples in the New England Network

The highest PCDU, PHA, PLA, and PHB concentrations in groundwater at the New England Network were present in the samples collected in the well below leach bed 1 (L1) and in the well downgradient of this leach bed (well D1 in Fig. 1; Tables S8, S9, S10). Concentrations for these groups ranged from 3.8 to over 20 µg/L in the D1 sample and 1.3 to 9.3 µg/L in the L1 sample. PHA and PLA concentrations were also high in the well below leach bed 2 (well L2). PCDU, PHA, PLA, and PHB concentrations were lower for the other two downgradient wells (D2 and D3); with the exception of the PHA and PHB concentrations (>1 µg/L) for the D2 sample, none of these concentrations exceeded 0.5 µg/L. The upgradient well (well B) had no detections of any of the micropollutant compounds included in the study, indicating the lack of septic influence on water quality at this location. These results show that micropollutants are present in groundwater downgradient of the leach beds at this facility, and that the concentrations of micropollutants can vary widely in downgradient groundwater.

Concentrations of most compound groups were higher in the sample collected from the septic system (site T) compared to the groundwater samples (Fig. 1). PAB, PCDU, and PHB total concentrations for the T sample were generally 100 times higher than the concentration from the leach bed or downgradient wells. For example, PAB concentration in the T sample exceed 7 µg/L, whereas no PAB compounds were detected in any of the groundwater samples (Fig. 1). The lack of detection of PAB compounds in groundwater samples is not surprising, as all but one (3-methyl-1(H)-indole) of these compounds have a high $\log K_{ow}$ values (>6), so their high sorption potential likely results in these compounds being trapped on solids in the septic system. By contrast, PHA and PLA concentrations in samples from wells D1 and L1 were around half or more of the concentrations in the T sample. The similarity in PHA and PLA concentrations for the septic system and leach bed and downgradient wells (Fig. 1) indicates a relatively high persistence for these compounds compared to PAB and PCDU compounds. The higher concentrations of pharmaceutical concentrations compared to PAB concentrations for groundwater samples may be related to the difference in $\log K_{ow}$ between these two types of compounds. Pharmaceuticals have a low $\log K_{ow}$ (<3) and so are not as likely to be sorbed to solids within the septic system or during transport in the aquifer as PAB compounds.

Other factors, including biodegradation, also play a role in controlling the presence of micropollutants in groundwater samples. Although caffeine is present in the T sample (>50 µg/L) and has a low $\log K_{ow}$ (<1), it is not detected in any of the groundwater samples, presumably due to the high degree of biodegradation that can occur with caffeine in either the septic system or between the leach beds and the underlying groundwater. Many compounds are likely to be well removed, as the total PHB concentration for the septic-system sample (2800 µg/L) is

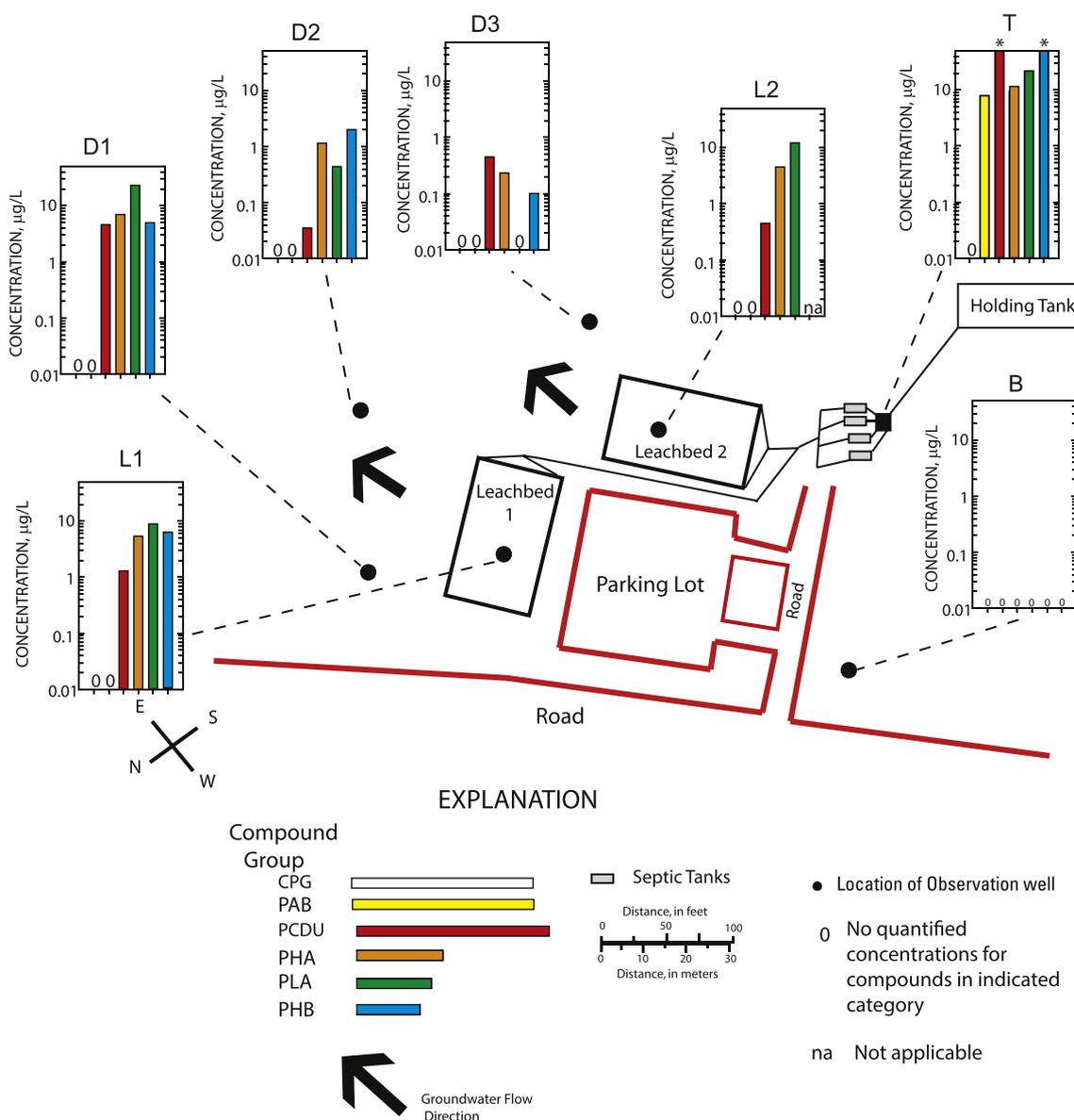


Fig. 1. Location of wells and micropollutant concentrations for the SH1433 method for samples from New England Network, July 2011. Schematic does not show septic system above holding tank. CPG (combustion, pavement, or gasoline), PAB (plant or animal derived biochemicals), PCDU (personal care/domestic use), PHA (pharmaceuticals determined using LC8144 method), PLA (plasticizers and phosphorus-based flame retardants), and PHB (pharmaceutical compounds determined using the LC9017 method) compounds.

over 100 times higher than the PHB concentration for wells D1 and L1 (5.7 and 6.4 $\mu\text{g/L}$, respectively). Although the short duration of the study limits the ability to make conclusive statements about removals of micropollutants in the septic system, these data indicate that there is considerable variability in the degree of removal for different micropollutants and that the PHA and PLA compounds may not be as well removed as other compounds.

Seven pharmaceuticals included in the PHA method were detected at concentrations greater than 0.1 $\mu\text{g/L}$ in samples collected from both wells L1 and D1 (Table S-9). These pharmaceuticals include a barbiturate (butalbital), a muscle relaxant (carisoprodol), an anti-inflammatory (celecoxib), a topical anesthetic (lidocaine), a sedative (phenobarbital), an antiepileptic (phenytoin), and an opioid analgesic (tramadol). Six pharmaceuticals included in the PHB method were detected at concentrations greater than or equal to 0.1 $\mu\text{g/L}$ in both samples from L1 and D1 (Table S10). These include two pharmaceuticals also detected using the PHA method (carisoprodol and lidocaine), an antifungal (fluconazole), an anxiolytic (meprobamate), an antiepileptic (phenytoin), and an antibiotic (SMX). Concentrations of SMX

were particularly high in samples collected from D1 (1.33 $\mu\text{g/L}$) and L1 (0.52 $\mu\text{g/L}$). SMX is commonly detected in groundwater affected by septic effluent, and can persist for long distances downgradient of these systems (Barber et al., 2009; Godfrey et al., 2007). Both pharmaceutical methods indicated that carisoprodol, lidocaine, and phenytoin concentrations from wells D1 and L1 were greater than or equal to 0.1 $\mu\text{g/L}$.

Most of the PLA concentration in the NE samples was contributed by tris(2-butoxyethyl) phosphate (TBEP; Table S8). TBEP concentrations ranged from 8 to over 20 $\mu\text{g/L}$ for samples collected from L1, L2, and D1, and represented more than 85% of the PLA concentration in these samples. The TBEP concentration in the septic holding tank sample was also high (20 $\mu\text{g/L}$). These TBEP concentrations are much higher than those typically found in groundwater (Katz et al., 2010; Barnes et al., 2008) and even higher than most commonly found in treated wastewater effluent (Fries and Puttmann, 2003; Marklund et al., 2005; Phillips et al., 2012). The presence of elevated TBEP concentrations in this setting may reflect conditions that are unique to an institutional setting, as TBEP is a component of floor polishing mixtures used at

this facility. Thus, the use of TBEP-containing mixtures and potential disposal of their residues in the septic system at this facility are the most likely causes of elevated concentrations of TBEP in the NE network groundwater.

These data show that elevated concentrations of micropollutants can persist in groundwater underneath leach beds up to 30 m downgradient (at well D1). Because this well is near a property boundary and within 30 m of a domestic water supply well finished deeper into bedrock, there may be some potential for migration of micropollutants to nearby drinking water sources. Further study will be needed to assess the extent to which these micropollutants are migrating to nearby properties and (or) drinking water sources.

3.2. Concentrations of micropollutants and specific conductance and nitrate in the New England Network

Concentrations of PCDU, PHA, PLA, and PHB were compared to specific conductance and nitrate to assess whether these two measures are correlated to concentrations of micropollutants in the NE network. Specific conductance (Table S11) was used in this analysis because septic effluent can be expected to have high specific conductance, and so

this measure may act as a surrogate for septic discharge. Nitrate (Table S11) is of particular importance in this setting, because local water management officials use 10 mg/L of nitrate as a threshold to indicate when groundwater downgradient of a septic system is adversely affected by septic system discharges.

Specific conductance is well correlated with the PHA, PLA, and PHB concentrations for samples collected from the two wells beneath the leach beds and the three wells located downgradient of leach beds (Fig. 3), with an r^2 value greater than 0.8. If specific conductance is considered to be a more conservative indicator of sewage inputs than nitrate, then these correlations indicate that the pharmaceuticals and plasticizers are transported conservatively at this site. PCDU concentrations are not correlated with specific conductance or nitrate. Although chloride concentration is high (900 mg/L) in the sample from the upgradient well (B), this is not due to septic tank discharges, but reflects the effect of deicing salts leaching into the aquifer at this site, as this site is adjacent to a parking lot (Fig. 1). By contrast, chloride concentrations for all other groundwater samples are all <200 mg/L.

Nitrate concentration is not significantly correlated with PHA, PLA, or PHB concentrations (Fig. 3). The poor correlations with nitrate are attributable to low nitrate in the L1 and D1 samples (0.65 and 1.7 mg/L,

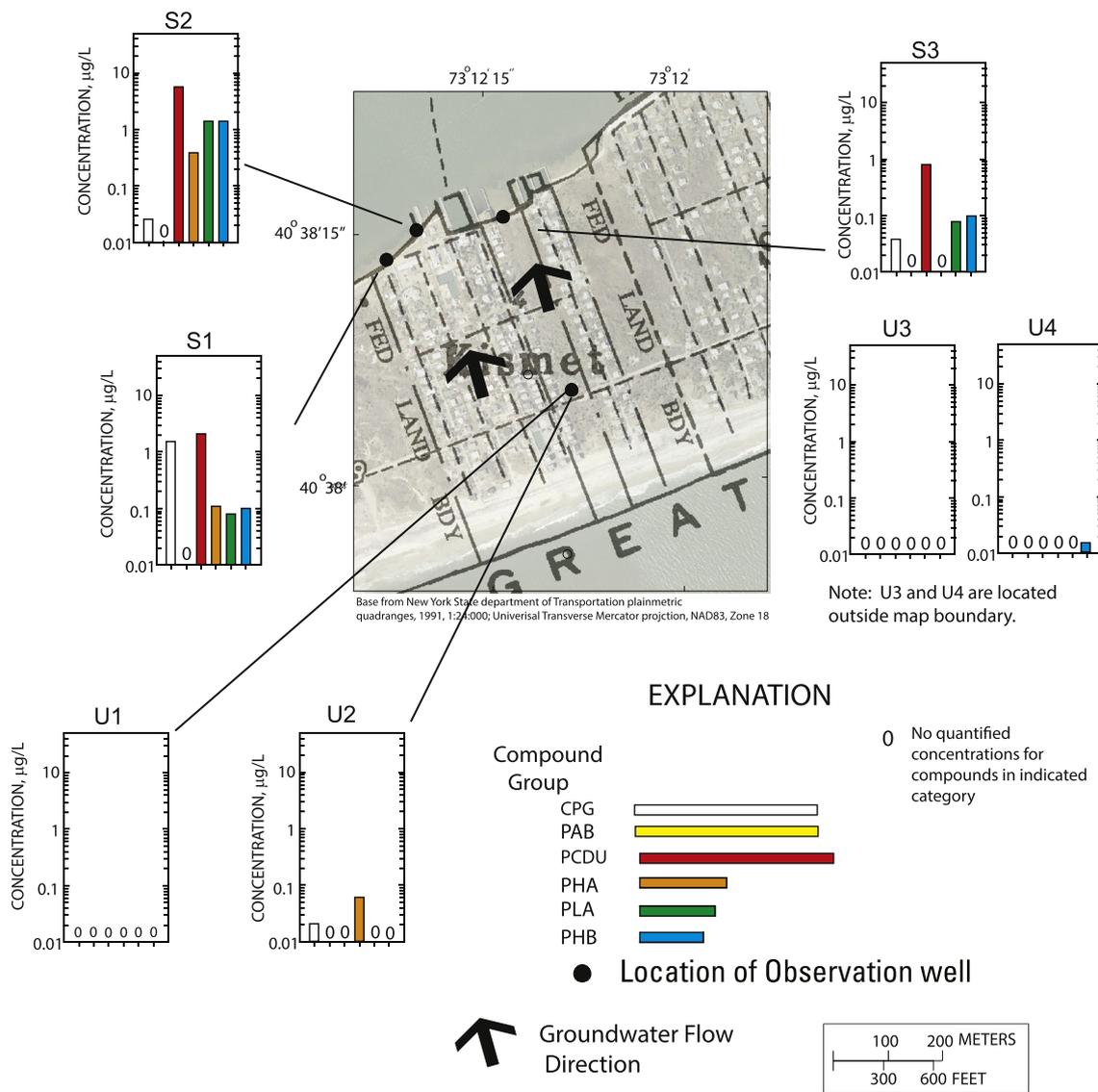


Fig. 2. Location of wells and concentrations for micropollutants from New York Network samples, October–November 2011. CPG (combustion, pavement, or gasoline), PAB (plant or animal derived biochemicals), PCDU (personal care/domestic use), PHA (pharmaceuticals determined using the LC8144 method), PLA (Plasticizers and phosphorus based flame retardants), and PHB (pharmaceuticals determined using the LC9017 method) compounds.

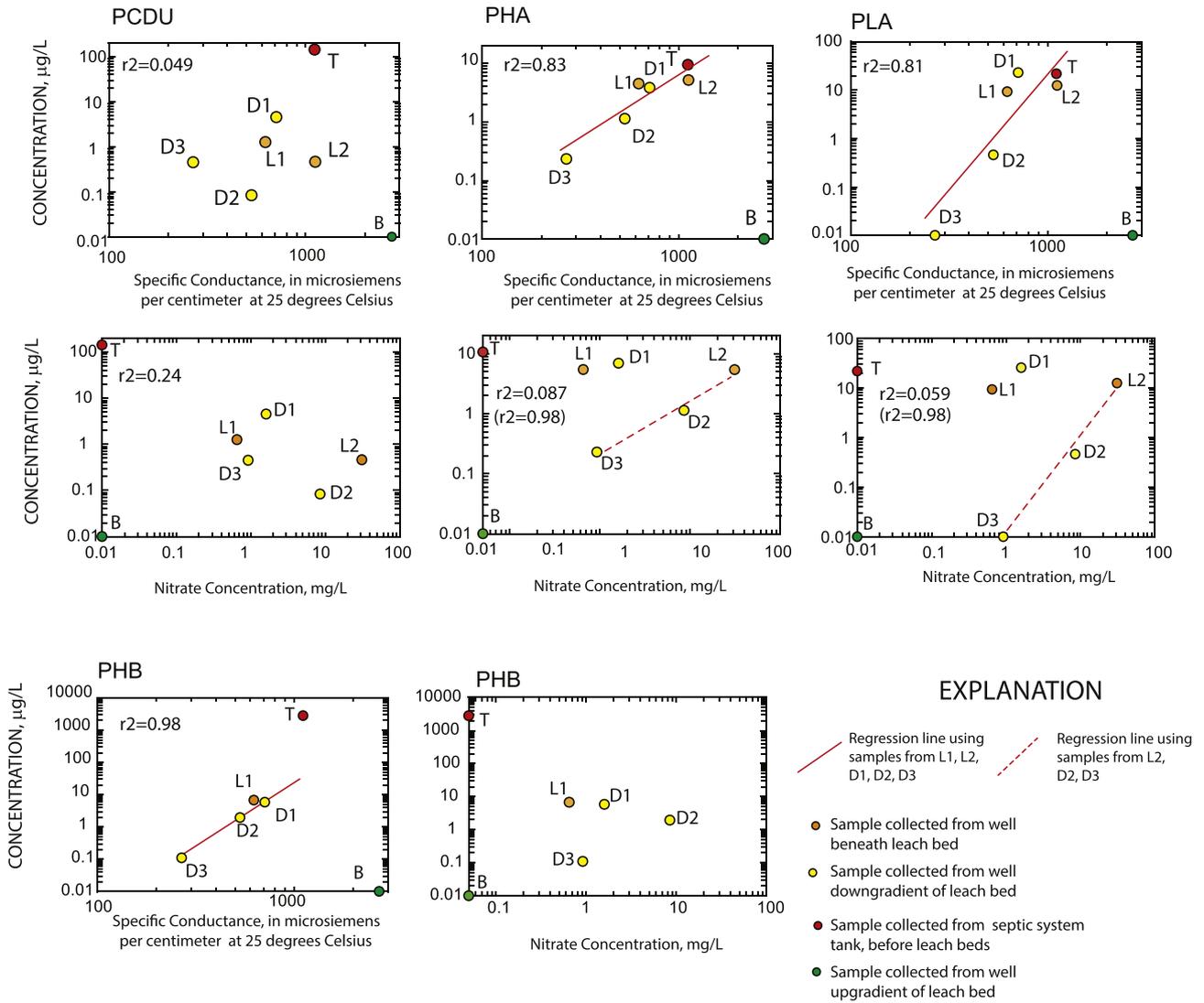


Fig. 3. Concentrations of PCDU (personal care/domestic use), PHA (pharmaceuticals determined using the LC8144 method), PLA (plasticizers and phosphorus-base flame retardants), and PHB (pharmaceuticals determined using the LC9017 method) compounds in samples from New England Network, July 2011, with specific conductance and nitrate concentrations. r^2 = coefficient of determination. PCDU and PLA concentrations analyzed using the SH1433 method; PHA concentrations analyzed using the LC8144 method, PHB concentrations analyzed using the LC9017 method. Well locations shown in Fig. 1 and Supporting Fig. S1.

respectively). By contrast, nitrate concentrations for L2 and D2 are 31 mg/L and 8.5 mg/L respectively, and both of these samples have lower PCDU and PLA concentrations than the L1 and D1 samples. The high micropollutant concentrations and specific conductance values in samples from L1 and D1 indicate a strong septic discharge effect on water quality in these two samples. The lack of high nitrate concentrations, along with the presence of low dissolved oxygen concentrations (less than 0.3 mg/L) in these samples suggests that the predominant form of nitrogen in these two samples could be ammonium, which was not measured in this study. Monitoring ammonium and organic nitrogen at this site will be needed to fully indicate total nitrogen concentrations in this setting, as previous studies have shown correlations between micropollutant concentrations and nitrogen occurrence (Del Rosario et al., 2014).

Several factors at the NE network may promote the transport and persistence of micropollutants in the shallow aquifer. Water-level monitoring at the leach bed wells by a local regulatory agency indicates that the unsaturated zone is thin, generally around 1.5 m. Thin unsaturated zones beneath infiltration beds promote the transport of micropollutants to underlying groundwater (Carrara et al., 2008). Although the limited data collected during this study did not adequately

delineate anoxic zones in this setting, dissolved oxygen concentrations for the leach bed and downgradient wells were extremely low, ranging from 0.1 to 0.4 mg/L. The absence of nitrate in the L1 and D1 samples further indicates that the aquifer in these portions of the surficial aquifer may be anaerobic. Thus, the relatively high micropollutant concentrations observed in the L1 and D1 samples may also be related to the presence of anoxic conditions at these sites, as many studies have indicated that micropollutants tend to be more resistant to removal in anaerobic conditions than aerobic conditions (Swartz et al., 2006; Carrara et al., 2008; Garcia et al., 2013). Distance from the leach beds does not seem to be an important factor controlling micropollutant concentrations for these samples, as the well with the highest micropollutant concentrations (D1) and the well with the lowest micropollutant concentrations (D3) are both 30 m from the nearest leach bed.

3.3. Concentrations of micropollutants in the New York Network

The highest micropollutant concentrations for samples in the NY network were present in the shoreline wells (Fig. 2); the sample collected from S2 had the highest micropollutant concentrations of any well in

this network. PCDU, PHA, PLA, and PHB concentrations were substantially higher for samples from S1, S2, and S3 than in the samples collected from the upgradient wells (U1, U2, U3, and U4; see Fig. 2, Tables S12, S13, S14). PCDU, PLA and PHB concentrations for the S2 sample were >1 µg/L, respectively, and the PHA concentration 0.4 µg/L; corresponding concentrations for samples from the other two shoreline wells were half or less than these concentrations.

Several PCDU compounds equaled or exceeded 0.1 µg/L in the S2 sample (Table S-12), including two detergent degradates (4-*tert*-octylphenol and *p*-nonylphenol), the fragrance GAL, the insect repellent DEET, the ultraviolet fixative benzophenone, and the food additive triethyl citrate. Three of these compounds (4-*tert*-octylphenol, galaxolide, and DEET) were also present in the S1 sample at concentrations greater than 0.1 µg/L (Table S-12). The presence of GAL in the S2 sample demonstrates that compounds with high log K_{ow} values (5.8 for GAL) can be present downgradient from septic systems. The PLA compounds TBEP and TCEP were present in the S2 sample at concentration >0.1 µg/L (Table S-12). Two pharmaceuticals analyzed using the LC9017 method (lidocaine and desvenlafaxine) exceeded 0.5 µg/L in the S2 sample (Table S-14).

The sum of CPG compounds in the S1 sample was much higher (>1.5 µg/L) compared to the other two samples collected from shoreline wells (both <0.05 µg/L) (Fig. 2). The relatively high CPG concentrations in this sample could reflect several nearby sources, including a decommissioned gas plant in the community, localized spills associated with the use of off-highway vehicles on the barrier island, and the use and fueling of two-stroke boat engines in nearby waters. These various uses may result in highly localized sources that can affect groundwater concentrations of compounds included in the CPG group in the shoreline setting.

Few micropollutants were detected in the upgradient wells (Fig. 2; Tables S12, S13), and the two pharmaceuticals detected in upgradient wells (at well U2 and U4) were present at concentrations <0.1 µg/L, despite their proximity to Kismet septic systems (<30 m). These results suggest that the upgradient Kismet wells (U1 and U2) are less affected by septic systems than the shoreline wells, so that the location of these wells on the periphery of Kismet may result in lower concentrations than the shoreline wells. The upland wells in Kismet are located less than 30 m from septic systems, whereas the shoreline wells are located between 20 m and 500 m directly downgradient from the septic systems in Kismet.

The lack of any detected micropollutants in the U3 sample reflect the location of this well in an area of undeveloped park land, and give further indication that the micropollutants present in groundwater in this area are attributable to septic systems. In general, groundwater times of travel are relatively short on Fire Island (Schubert, 2010a, 2010b), so septic-affected groundwater—recharged predominantly during the summer (visitor) season—may have already migrated downgradient of well U4 by the fall when this well was sampled, resulting in low observed concentrations at this location.

The high micropollutant concentrations in the shoreline wells show that groundwater in this portion of the surficial aquifer is affected by septic-system discharges. The shoreline wells are located between 20 and 500 m downgradient of Kismet septic systems, in an area where groundwater recharged in the upgradient areas discharges to GSB (Schubert, 2010a, 2010b). The proximity of these sampling points to GSB suggests that septic systems in this portion of Fire Island are potential sources of micropollutants to the adjacent estuary. These results indicate that the shoreline wells reflect varying amounts of septic discharges. The highest concentrations occurred in the S2 well, which lies in the middle of the developed area. By contrast, the other two wells (S1 and S3) lie on the margins of the developed area and had correspondingly lower micropollutant concentrations.

As was the case with the NE setting, the thin unsaturated zone and presence of anoxic conditions at the NY site may promote the transport of micropollutants in this aquifer. The thickness of the unsaturated zone

in the NY setting is generally less than 1.5 m, which promotes the transport of micropollutants from septic systems to the underlying surficial aquifer. In addition, the presence of ammonium in the shoreline samples (Table S15) indicates that the surficial aquifer is anoxic, which promotes the micropollutant transport (Swartz et al., 2006; Carrara et al., 2008). Finally, the low degree of treatment in the septic systems in the Kismet location also promotes the transport of micropollutants to the underlying groundwater system, as previous studies have shown that systems with little to no treatment discharge relatively higher amounts of micropollutants than septic systems with more advanced treatment (Stanford and Weinberg, 2010; Stuart et al., 2012).

3.4. Estrogenicity in the New York Network

EACs were detected in two of the three shoreline wells (S1 and S2). Five EACs were present in one or more of these samples; two EACs (4-*t*-octylphenol and BPA) were present in both of these samples, and the remaining three EACs (E1, estriol [E3], and 4-nonylphenol) were only quantified in the S2 sample (Tables S-12 and S-16). None of the upgradient wells had detections for any EACs. Concentrations of E1 and E2 found in the S2 sample are similar to those reported in ponds receiving groundwater discharge on Cape Cod in New England (Standley et al., 2008), but higher concentrations (10 times or more) of E1 and E2 have been measured in groundwater near leach beds on Cape Cod (Swartz et al., 2006). Concentrations of E1 and E3 (0.0042 and 0.0025 µg/L, respectively) in the S2 sample are similar to or greater than those present in treated effluent from a wastewater treatment plant using activated sludge for treatment (Phillips et al., 2012; Barber et al., 2012) but lower than estrogen concentrations associated with sewage effluent from a WWTP with trickling filter treatment (Vajda et al., 2008; Vajda et al., 2011).

EEq concentrations ranged from 3.1 ng/L for the S2 sample to 0.11 ng/L for the S1 sample. These results show that the highest EEq concentrations corresponded to the shoreline well in the area with the highest septic density and highest micropollutant concentrations. The EEq value for the sample from well SK-2 is similar to levels found to cause biological effects in fish (Van Den Belt et al., 2004). Linking observed EAC concentrations to effects on biota in nearby receiving waters is well beyond the scope of this study, but these results indicate that EACs are present in groundwater discharging to GSB.

3.5. Concentrations of micropollutants and specific conductance and nitrate in New York Network

PCDU, PHA, and PLA concentrations generally increase with specific conductance and total nitrogen concentration for shoreline well samples collected in the New York Network (Fig. 4). Correlations in this discussion and shown in Fig. 6 are based solely on samples collected from shoreline wells, as these are the samples that are most affected by septic effluent. Although the low number of shoreline well samples ($n = 3$) make it difficult to assess correlations of micropollutant compound groups, correlations between total nitrogen and PCDU and PLA and specific conductance were significant at the 0.10 level; other plots indicated a general increase in concentrations of micropollutants with these variables. Well S2 had the highest concentrations of PCDU, PHA, PHB, PLA, and Eeq value, as well as the highest total nitrogen concentrations (18 mg/L ammonium as nitrogen) and orthophosphate concentration (4.6 mg/L as phosphorus) of any of the shoreline wells; thus sewage impact in this well is reflected in both micropollutant concentrations and nutrient concentrations.

Although specific conductance and total nitrogen both show potential for predicting micropollutant concentrations in shoreline wells, they do not appear to be correlated with these concentrations in the upgradient wells, as the highest specific conductance in any of the samples occurs in well U3 (Fig. 4), which is in an undeveloped area. Similarly, the total nitrogen concentrations (2 mg/L) for some of the upgradient

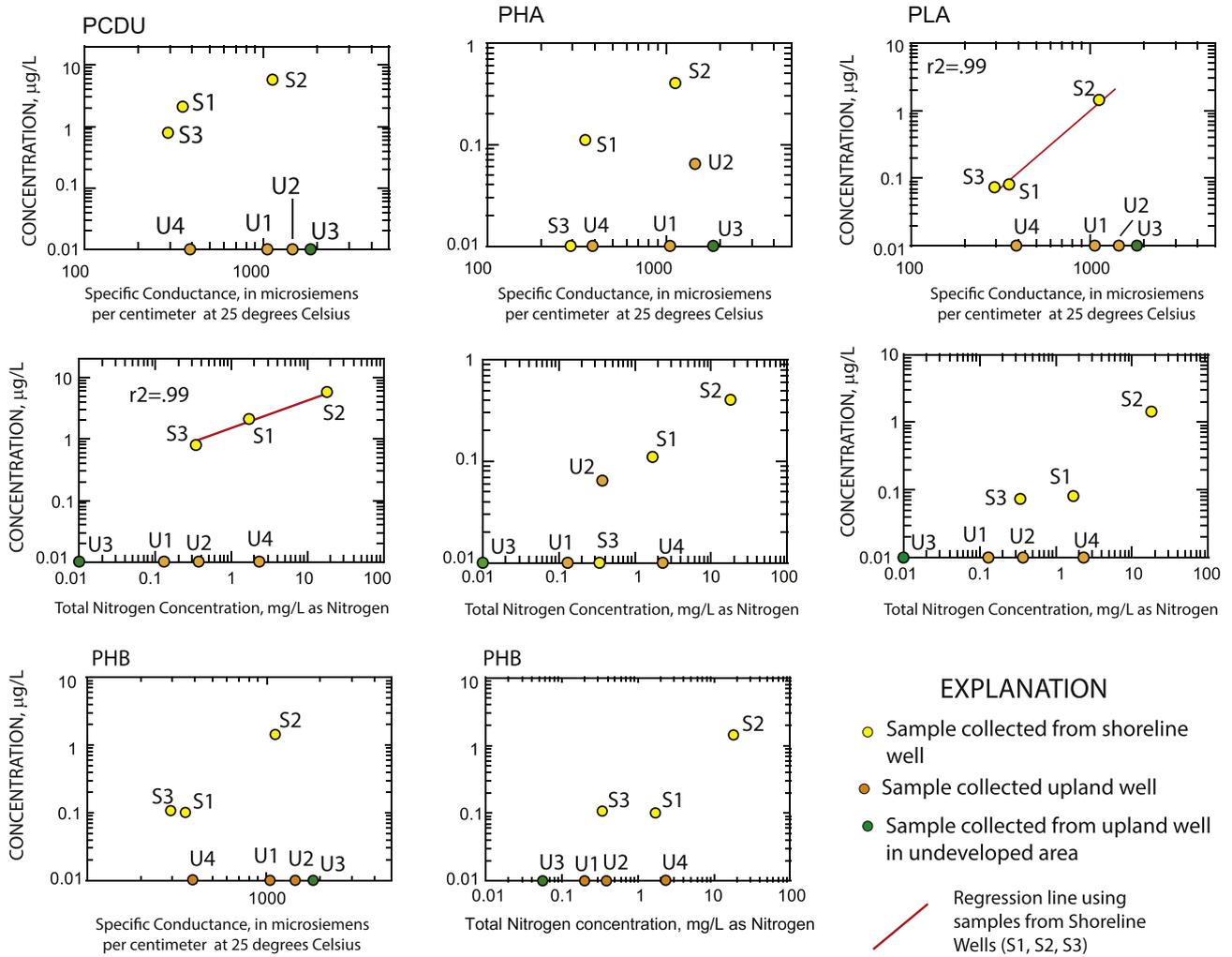


Fig. 4. Concentrations of PCDU (personal care/domestic use), PHA (pharmaceuticals determined using the LC8144 method), PLA (plasticizers and phosphorus-based flame retardants), and PHB (pharmaceuticals determined using the LC9017 method), in samples from New York Network, October–November 2011 with specific conductance and nitrate concentrations. r^2 = coefficient of determination. Well locations shown in Fig. 2 and Supporting Figs. S2a and S2b. Regressions are based on shoreline wells (S1, S2, and S3). Regression line only shown for regressions with p value < 0.10.

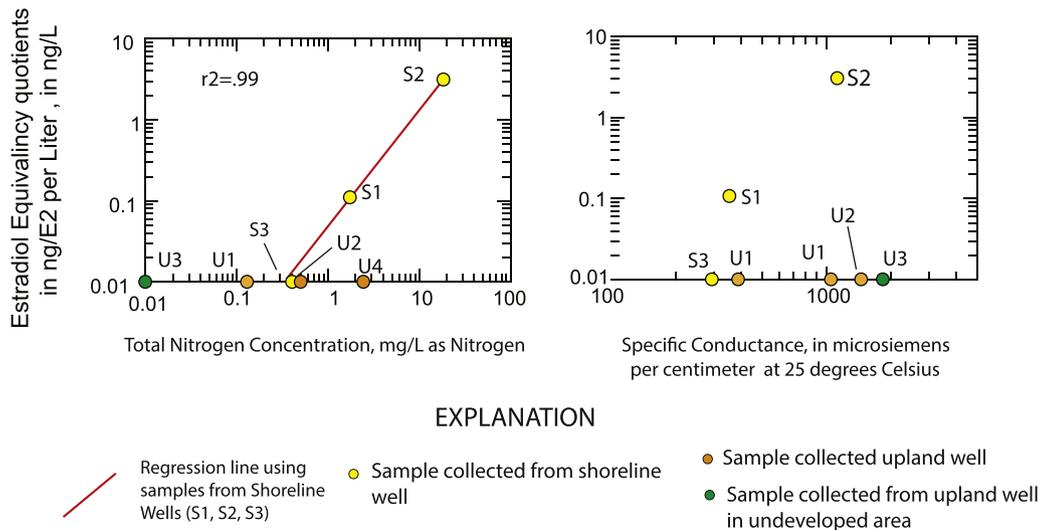


Fig. 5. Estradiol equivalency quotients in ng/E2 per liter with total nitrogen and specific conductance for samples from New York Network. r^2 = coefficient of determination. For well locations, see Fig. 2 and Supporting Figs. S2a and S2b. Regressions are based on shoreline wells (S1, S2, S3). Regression line only shown for regressions with p value < 0.10.

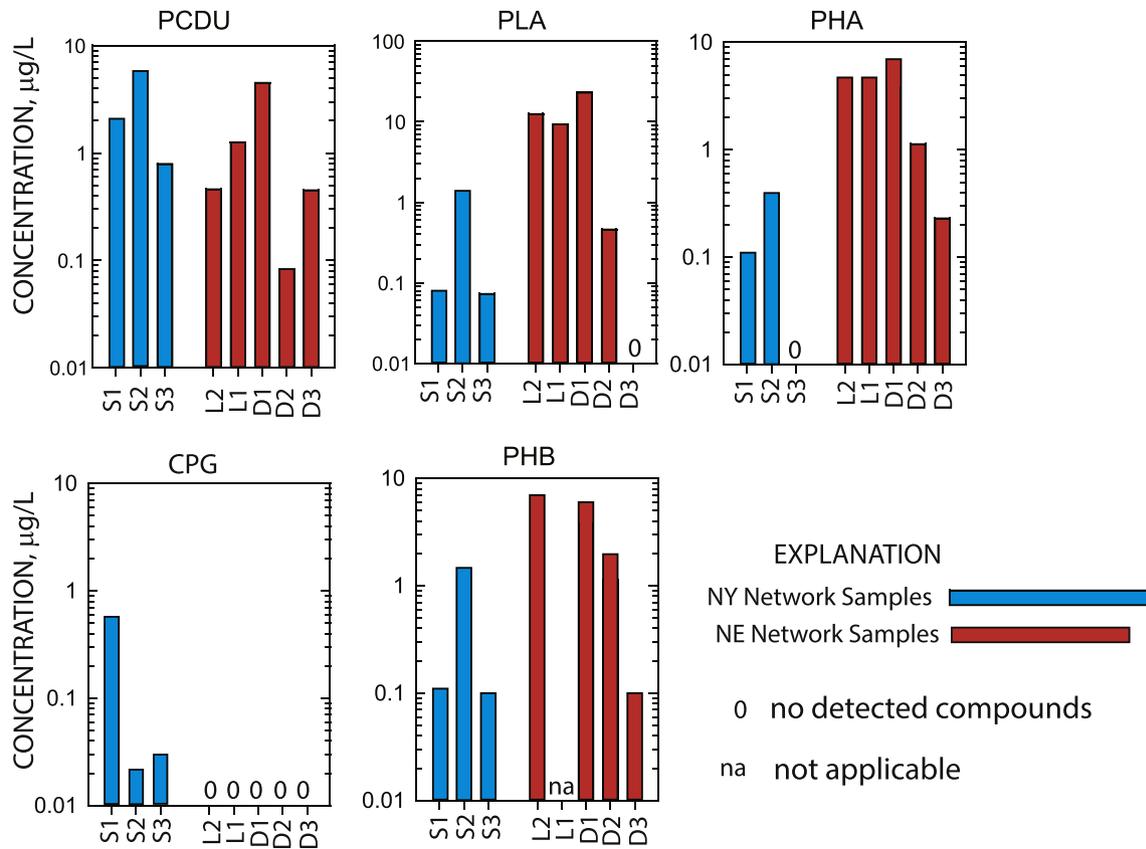


Fig. 6. Concentrations of PCDU (personal care/domestic use), PLA (plasticizers and phosphorus-based flame retardants), PHA (pharmaceuticals determined using the LC8144 method), CPG (combustion, pavement or gasoline), and PHB (pharmaceuticals determined using the LC9017 method) compounds for select samples collected from New England and New York Networks.

wells with no detections for micropollutants were comparable to total nitrogen concentrations found in two of the three shoreline wells. Thus, the positive relation between the micropollutants and specific conductance and total nitrogen concentrations may only apply to areas such as the shoreline wells in developed areas directly affected by septic-system effluent.

As with other micropollutants included in this study, there is a general increase in EEq values for shoreline wells with increasing total nitrogen and specific conductance (Fig. 5). Although the limited temporal and spatial scope of this study make it difficult to extrapolate these findings to other areas on Fire Island, the correspondence between EEq concentrations and nitrogen concentrations indicate that efforts to reduce the migration of nitrogen from septic systems to GSB may also aid in diminishing the transport of EACs to GSB. Additional sampling is needed to confirm these patterns for other developed areas and geochemical settings on Fire Island.

3.6. Comparison of results between NE and NY sampling networks

Comparison of PLA, PHA, PCDU, CPG, and PHB concentrations between the NE and NY samples illustrate how differences in land use and other factors contribute to differences in micropollutant concentrations in these two settings (Fig. 6). The comparison in this section is limited to NE leach bed and downgradient samples (wells L1, L2, D1, D2) and NY shoreline samples (wells S1, S2, and S3), as these samples represent groundwater affected by septic system discharges. Data from the HOR method was not available for both networks, so comparisons of analytes from these methods were not possible.

PLA concentrations were generally higher in the NE samples compared to the NY samples (Fig. 6). PLA concentrations in three NE samples ranged from 9.3 to over 20 µg/L; by contrast, shoreline well PLA

concentrations ranged from <0.1 µg/L to 1.4 µg/L. The high PLA concentrations in the NE samples are attributable to high TBEP concentrations (which generally comprised more than 85% of the PLA concentrations), which presumably reflect the presence of this compound in floor polishing agents or other products used in the extended care facility. TBEP use in the residential setting in NY would be expected to be lower than in the NE setting, resulting in the lower observed groundwater concentrations in NY samples.

PHA and PHB concentrations in the NE samples are higher than those found in the NY samples (Fig. 6), and may reflect the high amount of pharmaceutical use by the residents of the extended health care facility assessed in the NE network. PHA and PHB concentrations for the NE samples typically are >1 to 5 µg/L, whereas shoreline well PHA and PB concentrations are generally <0.5 µg/L (Fig. 6), and the pharmaceutical concentrations in the NE samples are 5–10 times higher than the NY samples. In particular, three of the NE wells had concentrations of celecoxib (an anti-inflammatory pharmaceutical frequently prescribed for arthritis) exceeding 0.4 µg/L, whereas none of the NY groundwater samples had a detection for celecoxib. Similarly, the antibiotic sulfamethoxazole was present at concentrations above 0.5 µg/L in two groundwater samples from the NE network, but was not detected in NY network samples. The NE septic system serves a population that is disproportionately elderly and presumably has higher pharmaceutical use due to age and health concerns (National Center for Health Statistics, 2014). By contrast, the NY septic systems serve an area with a presumably younger population that has lesser pharmaceutical use due to fewer health concerns.

CPG concentrations were much higher in the NY shoreline well samples compared to the NE wells (Fig. 6). The exact cause of these elevated concentrations in the NY samples is unknown, but may be due to proximity to nearby sources unique to the NY setting, including a

decommissioned gas plant and fuel handling areas for vehicles and boats. Not all of the concentrations of compound groups had large differences between the samples collected at the two networks. PCDU concentrations did not greatly differ between the two studies (Fig. 6).

These results indicate that some micropollutant concentrations can vary based on suspected patterns of use of cleaning products and pharmaceuticals associated with particular settings or demographics. The differences in PLA concentrations between the sites is consistent with the findings of Conn et al. (2006) who noted that the use of cleaning products is more intensive in commercial than in residential settings. Although the results of this study are limited by the short duration, the differences in pharmaceutical and TBEP concentrations between these two sites indicate that septic discharges from systems serving the elderly in institutional settings can have different types and concentrations of micropollutants than systems serving a younger population in a non-institutional setting. By contrast, the similarity in PCDU concentrations between samples from the two sites indicates that differences in treatment and hydrogeologic conditions between the two sites may not affect all micropollutant concentrations.

4. Conclusions

Groundwater samples were collected from two groundwater networks in the northeastern United States in 2011 to assess the effect of septic systems on micropollutant concentrations in nearby groundwater. The NE septic system receives discharge from an extended health care facility for the elderly. The NY network includes wells in an upgradient area near septic systems and in shoreline wells in an area where groundwater affected by septic systems discharges to an estuary. Unlike the single septic system present in the NE network, the NY network includes many septic systems that serve individual, seasonal residences in a densely populated area.

The highest total micropollutant concentrations in the NE network were present in samples collected from below the leach beds and in a well downgradient of the leach bed. Elevated TBEP concentrations (exceeding 20 µg/L) in these samples are much higher than typically found in groundwater or wastewater samples, and may reflect the use of TBEP in cleaning agents used at the health-care facility. Specific conductance is generally positively correlated with micropollutant concentrations in the NE network. However, the lack of positive correlation for nitrate with micropollutant concentrations may reflect the presence of nitrogen in the form of ammonium in the wells with the highest micropollutant concentrations in this network. This suggests that future monitoring at this site should include analysis of both nitrate and ammonium.

The highest micropollutant concentrations for samples in the NY network were present in the shoreline wells, which are directly downgradient from the septic systems and adjacent to marine waters. EEq concentrations (which represent the combined estrogenicity of all EACs in the sample) were also highest in the shoreline wells. Pharmaceutical and plasticizer concentrations for groundwater in the NY network were less than those observed in the NE samples, whereas PCDU concentrations were similar. The difference in micropollutant concentrations in these networks could reflect demographic differences between the sites.

These findings as well as other studies suggest that it is reasonable for resource managers to prioritize human or animal medical facilities and commercial facilities that have associated intensive chemical use for monitoring micropollutants downgradient of septic systems. Evaluation of different housing densities on the occurrence of micropollutants may be useful for resource managers to determine if there is a threshold of septic-system densities at which micropollutants can be expected to occur at levels of concern in downgradient groundwater.

Acknowledgments

This research was funded by the US Department of Interior, US Geological Survey Cooperative Water Program and the US Department of Interior, National Park Service. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. The draft manuscript was improved by comments by Tia-Marie Scott and Jennifer Morace, US Geological Survey.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.12.067>.

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