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Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA

Andrew B. Lindstrom,*,† Mark J. Strynar,† Amy D. Delinsky,† Shoji F. Nakayama,§ Larry McMillan,‡ E. Laurence Libelo,∥ Michael Neill,^ and Lee Thomas^

†U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, North Carolina 27711, United States

‡National Caucus & Center on Black Aged, Inc., Durham, North Carolina, United States

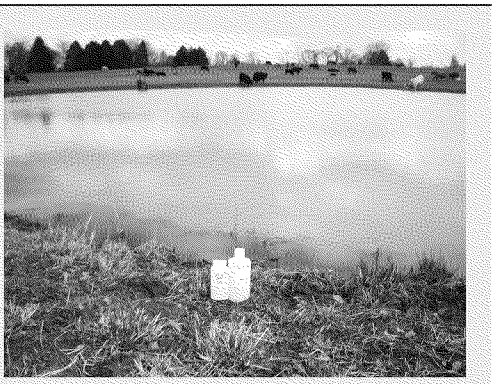
§U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio 45268, United States

∥U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, DC 20460, United States

^U.S. Environmental Protection Agency Region IV, Atlanta, Georgia, United States

Supporting Information

ABSTRACT: Perfluorinated chemicals (PFCs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been produced and used in a wide range of industrial and consumer products for many decades. Their resistance to degradation has led to their widespread distribution in the environment, but little is known about how humans become exposed. Recent studies have demonstrated that the application of PFC contaminated biosolids can have important effects on local environments, ultimately leading to demonstrable human exposures. This manuscript describes a situation in Decatur, Alabama where PFC contaminated biosolids from a local municipal wastewater treatment facility that had received waste from local fluorochemical facilities were used as a soil amendment in local agricultural fields for as many as twelve years. Ten target PFCs were measured in surface and groundwater samples. Results show that surface and well water in the vicinity of these fields had elevated PFC concentrations, with 22% of the samples exceeding the U.S. Environmental Protection Agency's Provisional Health Advisory level for PFOA in drinking water of 400 ng/L. Water/soil concentration ratios as high as 0.34 for perfluorohexanoic acid, 0.17 for perfluoroheptanoic acid, and 0.04 for PFOA verify decreasing mobility from soils with increasing chain length while indicating that relatively high transport from soils to surface and well water is possible.



INTRODUCTION

Perfluorinated chemicals (PFCs) have been produced and used in a wide range of industrial and consumer applications for the past five decades. This class of compounds has a number of unusual characteristics, including water and oil repellency, thermal stability, and surfactant properties that make them extremely useful. The terminal degradants in this class are extraordinarily stable, and this has contributed to their widespread presence in environmental and biological matrices worldwide.[1] Perfluorocarboxylic acids (PFCAs), which include perfluorooctanoic acid (PFOA), and perfluorosulfonates (PFSAs), which include perfluorooctane sulfonate (PFOS), are now found in human blood worldwide at concentrations in the ng/mL serum range.[2] Some of the PFCs have been found to be toxic in tests with laboratory animals,[3] and epidemiological studies have shown correlations with human health effects, such as a negative association between PFOS and PFOA with birth weight and size,[4] higher blood levels of PFOS and PFOA being related to current thyroid disease,[5] and elevated cholesterol levels among PFOA-exposed individuals.[6] The U.S. Environmental Protection Agency (EPA) issued provisional short-term health advisories (PHA) for PFOS and PFOA in drinking water and action levels for dermal exposure to soils and biosolids. The drinking water PHA levels are at 200 ng/L for PFOS and 400 ng/L for PFOA, estimating that short-term consumption of drinking water below these levels will safeguard public health.[7] No exposure limits for other PFCs have been developed by U.S. federal regulators to date, but chronic and cumulative health guidelines are under development. Despite an increasing amount of research in this area, the sources of the

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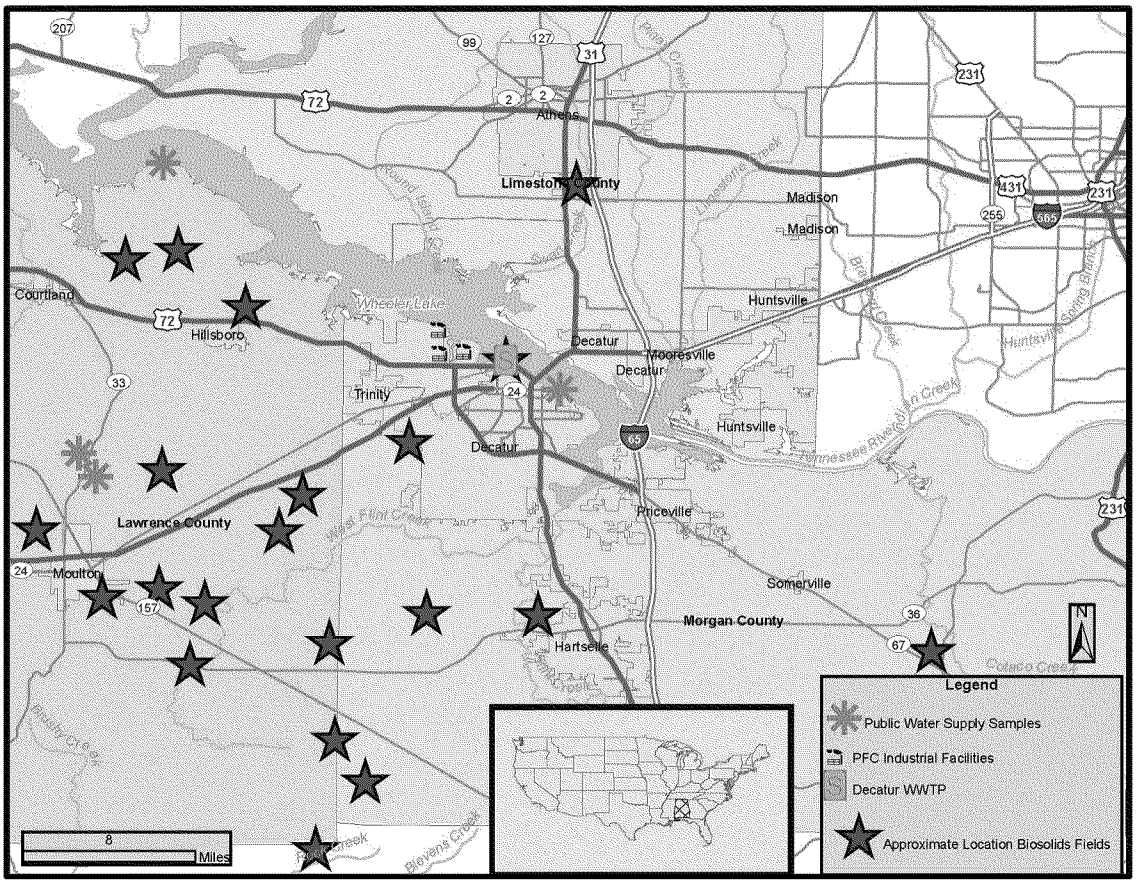

Figure 1. Locations of fields that received applications of biosolids from the Decatur Utilities Dry Creek Waste Water Treatment Plant.

PFCs in the environment remain poorly characterized, their transport and fate are still largely a matter of conjecture, and the relative importance of the potential routes of human and ecological exposure remain obscure.

Although there has been a great deal of research about persistent organic pollutants in wastewater treatment plant (WWTP) effluents and biosolids, the presence of PFCs in WWTP effluents is a relatively recent concern. Research has demonstrated that biosolids from WWTPs with no known specific industrial sources of fluorochemicals typically contain PFCs at concentrations in the ng/g level. For example, Sinclair et al.[8] found PFOS ranging from <10 to 65 ng/g and PFOA from 18 to 241 ng/g in biosolids collected from two New York State WWTPs in 2005. Perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnA) also ranged as high as 91 and 115 ng/g, respectively. In a similar study involving WWTPs from the Eastern U.S., Loganathan et al. found PFOS and PFOA concentrations in biosolids ranging from 8.2 to 990 ng/g and 8.3 to 219 ng/g, respectively, from one plant selected to be representative of rural conditions in Kentucky.[9] It has also been observed that mass flows of many PFCs increase significantly during treatment, suggesting that labile precursor materials break down to form the highly stable PFCAs and PFSAs during treatment processes.[8,10,11] It appears that the ubiquitous use of PFC containing materials in the residential, commercial, and industrial sectors along with the apparent inability of typical WWTP processes to effectively remove these materials leads to the presence of PFCs in WWTP effluents and biosolids.

The discharge of this effluent waste, either as liquid or treated biosolid material may therefore lead to the distribution of PFC material in the environment. Our knowledge of the potential impact of typical WWTP effluents on soils, surface water, groundwater, wildlife, or crops is extremely limited. However, at least two sets of studies have been conducted describing the consequences of inadvertent land application of fluorochemical industry impacted biosolids. One series of studies in Germany documented contamination of agricultural fields and surface water reservoirs, with correspondingly elevated levels of PFCs found in the blood of people drinking water from this region.[12,13] Another set of studies has documented contamination of surface soils in the U.S. after application of fluorochemical industry impacted biosolids.[14,15] The current study adds new information to this situation in the U.S.

Since the 1990s, the Decatur Utilities Dry Creek WWTP in Decatur, Alabama (Decatur Utilities) has processed permitted wastewater effluent from a number of local industries engaged in the production of PFC materials, and others that may use or emit PFC containing materials. Between 1995 and 2008, Decatur Utilities supplied over 34 000 dry metric tons of fluorochemical industry impacted biosolids to local farmers who used this material as a soil amendment on approximately 2000 ha of agricultural fields in Lawrence, Morgan, and Limestone counties in Alabama (Figure 1). Over this time period, as more has been learned about transport, fate, and persistence of the PFCs, interest about the potential impact of this practice has been increasing. In an effort to gauge the potential environmental

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effects of their operations and discharge to the Decatur Utilities WWTP, the 3M Company conducted a study that measured PFCs in a variety of matrices collected from 6 test cities (Multi-City study), including Decatur, AL from 1999 to 2001.[16] Results indicated that PFOS ranged from 58 to 159 ng/g in sludge from four wastewater treatment plants but it was about 3000 ng/g from the Decatur Utilities plant. PFOS was detected in all liquid effluent samples between 50 and 960 ng/L at five plants, but the Decatur effluent was about 5000 ng/L. Perfluorooctane sulfonamide (FOSA) was detected in sludge from four plants (<44 ng/g) with the Decatur Utilities plant having about 100 ng/g. PFOA was also detected in sludge from four plants (<17 ng/g) with concentrations at Decatur being as high as 244 ng/g. 3 M also conducted a separate study in late 2000 to measure PFOS and PFOA in the Tennessee River, both up- and downstream of the waste outfall of their Decatur area facility at Baker's Creek.[17] Using a new LC/MS/MS method, PFOS levels were found to range from about 32 ng/L upstream of the plant to approximately 114 ng/L after the point of discharge into the river. PFOA concentrations increased similarly, with all measurements being below the limit of quantitation (<25 ng/L) upstream, and a mean of 394 ng/L downstream of their facility.

Despite clear indications of elevated PFC concentrations in the Decatur area, the Multi-City study found no detectable levels of PFOS (LOD = 2.5 ng/L), FOSA, or PFOA (LOD = 7.5 ng/L) in the Decatur public drinking water system.[16] However, follow-up sampling in 2005 and 2006 at five municipal drinking water systems which have source water intakes on the Tennessee River found PFOA in most finished water samples at approximately 30 ng/L, with one sample ranging as high as 155 ng/L.[18] As awareness of this situation became more widespread and established sampling methods became more available, one company that discharged waste to the Decatur WWTP tested its effluent stream in 2007. After EPA was notified of potentially large discharges of PFCs to the WWTP by this company, an investigation of the PFC levels in biosolids and biosolids land application areas began. Initially, EPA developed methods for the measurement of many different PFCs in soil and biosolids, and preliminary results of soil samples collected from this area in 2007 indicated that a range of different PFCs were present, with total PFC concentrations >1000 ng/g.[19] These data, coupled with the previous results from other studies in this area, suggested the possibility that surface and well water in the Decatur area could be contaminated with PFCs as a result of land application of contaminated biosolids.

For this investigation, surface and well water samples were collected from areas associated with historical land application of fluorochemical industry impacted biosolids from the Decatur Utilities WWTP to determine if and to what extent local water supplies had been affected. The primary objective was to determine if water supplies exceeded the recently issued PHA guidelines for drinking water for PFOS (200 ng/L) and PFOA (400 ng/L). Additional goals included characterizing the concentrations of other related PFSAs and PFCAs, providing data for the evaluation of the relationships between biosolids treated soils and water concentrations, and describing a rigorous quality assured protocol that can be used for sampling, long distance transport, and analysis of water samples.

MATERIALS AND METHODS

Target compounds were purchased in premixed ampules prepared by Wellington Laboratories, (Guelph, Ontario, Canada, PFCA MXA standard) containing the following compounds: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate, (PFHxS), and perfluorooctane sulfonate (PFOS). For internal standards (IS), the following compounds were purchased from Wellington Laboratories: 1,2-$^{13}C_2$-labeled perfluorohexanoic acid ($^{13}C_2$ PFHxA), 1,2-$^{13}C_2$-labeled perfluoroundecanoic acid ($^{13}C_2$ PFUnDA), and $^{18}O_2$ sodium perfluorohexanesulfonate($^{18}O_2$ PFHxS). 1,2,3,4,5,6,7,8-$^{13}C_8$-labeled PFOA ($^{13}C_8$ PFOA) solution was purchased from Cambridge Isotope Laboratories, (Andover, MA), and $^{18}O_2$ ammonium perfluorooctane sulfonate ($^{18}O_2$ PFOS) was purchased from Research Triangle Institute (Research Triangle Park, NC). Analyte/IS pairs are listed in Table S1 of the Supporting Information (SI). Glacial acetic acid, sodium acetate, ammonium hydroxide (NH_4OH, 28% in water), and ammonium acetate were purchased from Sigma-Aldrich (St. Louis, MO). Methanol and methyl tertiary butyl ether (MTBE) were purchased from Honeywell Burdick & Jackson (Muskegon, MI). Five-mL ampules of 35% nitric acid were purchased from EP Scientific Products (Miami, OK).

Sample Collection. EPA Region 4 personnel collected 51 different water samples, including private drinking water wells (n = 6), wells used for other purposes (livestock, watering gardens, washing, n = 13) (PW = private well), and surface water (ponds and streams, n = 32) (SW = surface water). These samples were collected from 21 separate farms that had received application of fluorochemical industry impacted biosolids (Figure 1). In most cases the water sources were either on or within 500 m of a biosolid applied field. All known water supply wells in the area were sampled along with surface water bodies (ponds, lakes, springs) in or near fields with the highest recorded rates of biosolid application. Farms ranged in size from 9 to 308 ha, with a total area of more than 2000 ha receiving WWTP biosolids for as long as 12 years. Although field-specific application rate information was available, chemical analysis of biosolids was not conducted during the period of application, making it difficult to focus on the locations that were most likely to be contaminated.

Sample collection materials were shipped to the field team in 5 large containers in February 2009. Each container consisted of one field blank containing laboratory-grade deionized (DI) water, two field spikes (one with each target analyte at 200 ng/L and another with each target analyte at 400 ng/L), and 12 precleaned (triple rinsed with methanol and dried) 1-L high-density polyethylene (HDPE) sampling bottles (Nalgene Labware, Rochester, NY). The sampling procedure involved rinsing the collection bottle with three volumes of water followed by filling on the fourth iteration and adding 5 mL of 35% nitric acid as a preservation agent. Samples were shipped at ambient temperature to the laboratory where they were stored at room temperature for less than three weeks prior to analysis.

Sample Analysis. A method previously developed for trace level analysis[20] was modified to measure midlevel concentrations (10 1000 ng/L) of the target analytes to allow for more accurate comparison with the PHA levels for PFOA and PFOS (400 and 200 ng/L, respectively). Briefly, exact sample volumes were determined by pouring the sample into a 1-L polypropylene graduated cylinder, after which the original sample container was thoroughly rinsed with 10 mL of methanol. The sample was then

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returned to the original sample container with the methanol rinsate, and 50 µL of an internal standard (IS) solution containing 500 ng of each IS was added and thoroughly mixed. The sample was then passed through a glass fiber filter cup (1.6 µm; Whatman, Florham Park, NJ) and again returned to the original container.

Solid phase extraction (SPE) was conducted using a dual piston syringe pump (SepPak Concentrator, Waters Corporation, SPC10-C) operating at a flow of 10 mL/min. Waters Oasis WAX SPE Plus cartridges (225 mg) were first conditioned by passing 10 mL of methanol and 10 mL of DI water through the cartridge. A 500-mL aliquot of each sample was then loaded onto the SPE cartridge. The cartridges were then transferred to a vacuum manifold and washed with 10 mL of 25 mM sodium acetate buffer (pH 4) followed by 10 mL of methanol at a rate of one drop per second. Cartridges were then purged with a gentle stream of nitrogen gas long enough remove all indications of moisture. The cartridges were then returned to the vacuum manifold in the reverse direction from sample loading (this elution will therefore "back-flush" the sample) and eluted with 6 mL of ammonium hydroxide (NH_4OH, 28% in water)/methanol/MTBE solution (v:v:v, 1:2:27) at a flow rate of approximately 1 drip/second. The eluate was then mixed with 2 mL of methanol and concentrated to approximately 3 mL (at 35 ¬C) using a TurboVap LV (Caliper Life Sciences, Hopkinton, MA). A 100-µL aliquot of the concentrated eluate was mixed with 100 µL of 2 mM ammonium acetate buffer (pH 6.5) to approximate the initial mobile phase conditions.

Instrumental Analysis. Samples were analyzed using a Waters Acquity ultraperformance liquid chromatography system coupled with a Waters Quatro Premier XE triple quadrupole mass spectrometer (UPLC-MS/MS; Waters Corporation). A 20-µL aliquot of each sample was injected onto an Acquity UPLC BEH C18 column (1.7 µm, 2.1 L 50 mm; Waters Corporation) that was maintained at 50 ¬C. The mobile phase consisted of solvent A: 2 mM ammonium acetate buffer with 5% methanol and solvent B: 2 mM ammonium acetate in 95% methanol and 5% DI water at a flow rate of 500 µL/min, starting with 60% solvent A for 30 s and then increasing to 90% solvent B at 3.5 min and 100% solvent B at 3.6 min and held for 0.9 min. At 4.6 min the gradient was returned to the original conditions and held until 6.0 min. Electrospray negative ionization was used in the mass spectrometer source. The capillary voltage was set at negative 0.4 kV. Cone gas and desolvation gas flows were 2 and 1200 L/h, respectively. The source temperature was 150 ¬C and the desolvation temperature was 350 ¬C. Transitions for all ions were observed using multiple reaction monitoring (MRM) and analyte-specific mass spectrometer parameters were optimized for each compound. One primary transition was used for quantitation and the ratio of the primary transition ion to a secondary ion was used for confirmation (Tables S1 and S2 contain the details of the instrumental analysis). Quantitation was performed using an 8-point calibration curve between 10 and 1000 ng/L and stable-isotope internal standards using the response of the analyte (peak area counts) divided by the response of the internal standard to calculate unknown concentrations. The limit of quantitation (LOQ) for the method, defined as the lowest point on the standard curve which back-predicted within (30% of the theoretical value, was determined to be 10 ng/L for all compounds except PFHpA and PFDA, which were 50 ng/L. If samples were found to exceed 1000 ng/L, the second aliquot of sample was diluted to approximate the midpoint of the calibration curve using DI water with nitric acid and the IS mixture at the same concentration as the initial sample. Subsequent determination of analyte concentrations included a correction for the dilution factors used for each adjusted sample.

Quality Control (QC). Field blanks were prepared by filling precleaned 1-L collection bottles with laboratory DI water, previously determined to be PFC-free. Travel spikes containing all target anlaytes were prepared at low (200 ng/L) and high (400 ng/L) concentrations in 1 L of DI water. These QC samples were preserved with the addition of 5 mL of 35% nitric acid and shipped into the field with the empty containers designated for collection of field samples. Low and high level field spikes and field blanks were included at a rate of 10% of all planned samples. Field duplicates were also collected at a rate of 10% of all planned samples.

Laboratory QC procedures included the following: Solvent blanks, consisting of 1:1 unprocessed methanol and 2 mM ammonium acetate, were used to ensure that the mobile phase materials and analytical instrumentation remained free of contamination during analysis. Matrix blank samples, prepared from 1 L of deionized laboratory grade water with 5 mL of 35% nitric acid and the IS mixture, were used to ensure that sample processing materials and procedures were free of contamination. After the successful analysis of the first 500-mL portion of selected samples, fortified samples were prepared by spiking the remaining portion with a native standard solution containing all of the target analytes such that the fortified sample received an additional 400 ng/L of each target analyte. Fortified samples provide assurance that retention times, quantitiation and qualification ions, and calibration procedures were consistent between unknown and fortified samples. Additionally, to provide assurance that target analytes were correctly identified, quantitiation and qualification ions were monitored and compared with the quantitiation and qualification ion ratios observed in the standards used to construct the standard curves. If the quantitiation/qualification ion ratio of the field samples differed by more than 2 standard deviations from the standard curve points, the sample was flagged and examined for potential errors associated with inappropriate peak integration, retention time, or ion suppression/enhancement.

Statistical Analysis. Summary statistics were calculated using Microsoft Office Excel (version 2003, Microsoft Corporation, Redmond, WA) and correlation analysis was done with R-2.9.0 software (Vienna, Austria).

' RESULTS

Quality Control Samples. All of the target compounds measured in the field blanks were determined to be less than the LOQ for each sample (Table S3). The mean accuracy of the low (200 ng/L) and high level (400 ng/L) field spikes was in all cases within (25% of the theoretical spiked concentration (Table S3). Of the five duplicate samples that were collected, three had analyte concentrations that were near or below the LOQ with good agreement between duplicates (Table S4). Samples W36SW and W36SW Dup, for which most of the target analytes were above the LOQ, had relative percent difference values in most cases of <20%. Duplicate values for PFOS in these samples had a relative difference of 42%, but the concentrations were at the lowest portion of the calibration curve. Of the 570 separate analyses conducted for the field samples, 14 (2.5%) were flagged because of quantitation/qualification ion

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ratio inconsistencies. This occurred at relatively low concentrations (mean = 28 ng/L) and in each case integrations were reviewed and manually adjusted, if necessary, before final quantitation was accepted. To help evaluate the response of the analytical assay at the midrange of the calibration curves, an additional 400 ng/L of each analyte was added to five selected field samples. As summarized in Table S5, the average % recovery of standard addition at this level was within (12% of the theoretical value for all compounds except PFDA and PFOS, which showed 188% and 157% recovery, respectively. Sample storage could have been related to this issue as this evaluation was performed some time after all unknown samples had been run. The internal standards for PFDA and PFOS had approximately 50% of the response recorded in the original analysis, which could cause apparently elevated recoveries for these target compounds in this part of the evaluation. However, the good performance of PFDA and PFOS in the field blanks and spikes (Table S3) and the precision of duplicate samples (Table S4) help to provide an indication of overall method performance.

Field Samples. Table S6 summarizes the data from the well (Table S6A) and surface water (Table S6B) samples collected in this effort. Of the 51 unique field samples collected, PFOA was detected in 29 (57%) of the samples at concentrations ranging from < LOQ to a high of 11 000 ng/L, with 11 samples out of 51 (22%) above the PHA level of 400 ng/L. Two additional samples (389 and 397 ng/L) were not appreciably different from the PHA. PFOA occurred in two drinking water samples: W54PW at 2070 ng/L and WP14PW at 594 ng/L. PFOS was measured in 15 samples (29%) at concentrations ranging from < LOQ to a high of 151 ng/L, but all concentrations were below the 200 ng/L PHA level. PFOS was measured in two drinking water samples: W11PW at 12.0 ng/L and W14PW at 14.1 ng/L.

Of the 51 samples, 42 (82%) had at least one target compound at concentrations above the LOQ. Five of the target compounds were measured in more than half of the samples, with PFBA in 39 samples (77%), PFHxA and PFOA in 29 (57%), PFBS in 27 (53%), and PFPeA in 26 (51%). PFNA was detected in 10 (20%) samples with the highest concentration being 286 ng/L and PFDA was detected in 6 (12%) samples with a high value of 838 ng/L. Neither compound was observed in drinking water samples.

DISCUSSION

Results of field blanks, field spikes (Table S3), field duplicates (Table S4), standard curve back-prediction, and standard addition indicate that the methods used in this assessment generally provide data of acceptable precision and accuracy. Spearman correlation analysis among target compounds (Figure S1) suggests two groups of related compounds in these samples. PFOA, PFHpA, PFHxA, PFPeA, PFBA, and PFBS were generally well correlated, suggesting similar mobility from the biosolids and/or a common specific industrial source. PFOS was not significantly related to any of the other target compounds, suggesting at least one distinct source of this material as well. Review of National Pollutant Discharge Elimination System data indicates a variety of sources discharging to the Decatur WWTP, including facilities engaged in production and use of fluoropolymers, fluorocarbon fibers, polymers, polymer films and resins. Unfortunately, there are only very limited data on the PFC concentrations in any of these effluent streams, making it very difficult to characterize specific sources.

Data detailing how the concentrations of the various PFCs in the biosolids changed over the 12-year application period do not exist. Moreover, given the large size of some of these fields, it is impossible to pinpoint which specific locations actually received applications. However, to help gain some understanding of the water measurements made in this study, it is useful to examine the distributions of the target compounds among surface and well water samples (Figure S2). While there were no statistically significant differences noted between surface and well water, the longer-chain compounds were rare in the well water samples, with only one sample having measurable levels of PFNA and no samples having measurable PFDA. In contrast, Figure S2 also indicates that well water tended to have higher and more variable concentrations of the shorter-chain compounds (e C8) in comparison to surface water samples, suggesting greater mobility of the low molecular weight materials. This is consistent with the data presented in Figure S3 which show the correlations between dry metric tons of biosolids applied per hectare and PFC concentrations in water samples from adjacent ponds, streams, or wells. Only concentrations of the shorter-chain compounds were significantly related to biosolids application rates, with PFOA ($r = 0.49$, $p < 0.010$), PFHxA ($r = 0.46$, $p < 0.05$), PFPA ($r = 0.30$, $p < 0.05$), and PFBA ($r = 0.57$, $p < 0.001$).

In a study of soils from a subset of these Decatur fields, Washington et al. found PFOS from 30 to 410 ng/g and PFOA from 50 to 320 ng/g, but the highest level contaminants were PFDA and perfluorododecanoic acid (PFDoA), which ranged from 130 to 990 ng/g and from 30 to 530 ng/g, respectively.[14] Moreover, the 10:2 and 12:2 fluorotelomer alcohols (FTOHs) were found at concentrations from <5.6 to 166 and 2 to 133 ng/g, respectively.[15] These FTOHs are known to break down or be metabolized to corresponding carboxylic acids. Washington et al. also found that PFCAs in these fields were significantly related to total mass of biosolids applied, with longer-chain PFCAs more highly correlated with total mass applied, whereas shorter-chain PFCAs were more highly correlated with the time since last application of biosolids. Both observations suggest long-chain materials persist in the soil longer and that shorter-chain materials may be more mobile.

To more fully evaluate the issue of mobility from soil to ground and surface water, we examined the relationships between the six fields reported in Washington et al.[14] and 16 corresponding water measurements from the current study. A simple regression of individual PFC water concentrations with average reported soil levels failed to show any significant relationships (data not shown), indicating that the mere presence of a water source in the vicinity of a biosolid applied field did not lead to predictable contamination. This is not surprising, as a variety of factors will influence whether contamination from soil is transported to water. For example, consider two separate ponds at differing elevations that are the same distance from a biosolid applied field. A pond at a lower elevation would be much more likely to receive overland flow from a contaminated field than a pond at a higher elevation. In a similar manner, because of the complex karst geology in the Decatur region, transport of surface-applied materials to groundwater is also likely to be specific to each different situation. To overcome difficulties associated with interpreting the aggregated data set, we examined specific situations where water/soil relationships could be more definitely established. In Figure 2, selected water/soil concentration ratios from fields where both were measured at higher levels are plotted against the carbon chain length of the PFCAs. It is

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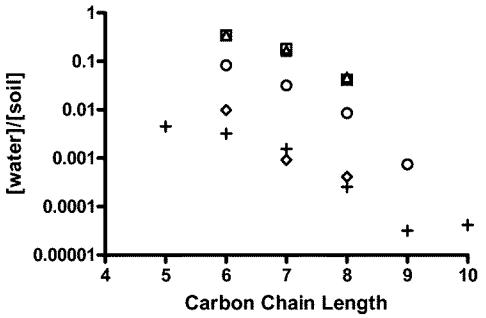

Figure 2. PFCA [water]/[soil] ratios by carbon chain length for selected Decatur fields (concentration in water [water] in ng/mL, concentration in soil [soil] in ng/g). (Δ) Field 1-4, soil 09D*, surface water sample W44SW ([water]/[soil] = (0.1478 └ chain length) þ 1.219; r^2 = 0.9865; p = 0.0741). (O) Field 15-3, soil 09E*, surface water sample W50SW ([water]/[soil] = (0.02696 └ chain length) þ 0.2332; r^2 = 0.8851; p = 0.0592) ( )) Field 17-1a, soil 09F*, surface water sample W64SW ([water]/[soil] = (0.004728 └ chain length) þ 0.03683; r^2 = 0.7900; p = 0.3031). (0) Field 14-1-10, soils 09B*, 09C*, well water sample W12PW ([water]/[soil]= (0.1510 └ chain length) þ 1.246; r^2 = 0.9984; p = 0.0258). (þ) Field 04-07, soil 07A*, surface water sample W36SW ([water]/[soil] = (0.000954 └ chain length) þ 0.00876; r^2 = 0.8841; p = 0.0052) (*) Soil concentrations are mean levels from Washington et al., Tables SI 9 and 10[14].

interesting to note that in the two fields with the highest overall [water]/[soil] ratios (Fields 1-4 and 14-1-10), PFHxA was measured in a pond (W44SW) and a well water sample (W12PW) at approximately 0.34 of the soil concentration of the nearby field. In both cases progressively longer chain materials give lower [water]/[soil] ratios, with PFHpA giving 0.16 0.18, and PFOA giving 0.04 0.05. These relationships were modeled with the linear regression equations listed in Figure 2 making it possible to quantitatively predict how carbon chain length influences this ratio. For example, the 9-carbon carboxylate, PFNA, was measured in the soils of both of these fields with average concentrations above 80 ng/g soil, but the regression predicts that PFNA would have no mobility to water. This is consistent with the detection of no PFNA in either of the corresponding water samples. Also, while the Washington et al. study did not include soil measurements of PFPeA and PFBA in field 14-1-10, these compounds were measured at 2330 and 1260 ng/L, respectively, in the well water sample from the present study. Using these concentrations as input, the [water]/[soil] ratio generated from the regression equation for this field leads to a prediction of 4.75 ng/g of PFPeA and 1.96 ng/g of PFBA in the soil from this field. Also, if these equations represent reasonable upper bound predictions of the relationship between [water]/[soil] and carbon chain length, they may be useful for predicting expected water contamination from studies that only included soil measurements. For example, data from the regressions in the present study give a maximum [water]/[soil] ratio for PFOA of 0.038, suggesting that a soil concentration of 11 ng/g could lead to waterborne PFOA at 418 ng/L, above the current health advisory for PFOA in drinking water (i.e., 11 ng/g soil └ 0.038 = 0.418 ng/mL water = 418 ng/L).

Although the slopes of these relationships in Figure 2 are different for each water source/field combination, these data clearly indicate that the potential for migration from soil to water is a function of chain length. Moreover, while PFOS was routinely measured in the soil samples at concentrations above 100 ng/g, paired water/soil measurements only occurred three times leading to water/soil ratios from 0.00003 to 0.01136, suggesting limited mobility of PFOS from these soils.

The higher mobility of the shorter-chain materials is consistent with a previous study which found that the sediment/water partition coefficient for the PFCs increase with chain length.[21] It is interesting to note that as the industry shifts from C8 and longer compounds to reduce problems associated with bioconcentration and toxicity, it is becoming increasingly clear that the shorter-length compounds are more mobile and more likely to cause water contamination issues.

The clear documentation that this study provides, indicating the extent to which land application of fluorochemical industry impacted biosolids can lead to contamination of ground and surface water resources, has a range of important implications. First, it is evident that direct consumption of the contaminated water could directly lead to human exposures.[12,13] In this specific case, the individuals using private wells that were contaminated at levels above the PHA were immediately informed and given access to a municipal water system. However, the mobility of PFCs from soil documented in this study raises questions about the potential impacts of more typical WWTP biosolids. Fujii et al. show that there is essentially a one-to-one correspondence between concentrations in surface water and finished drinking water supplies in a wide range of locations worldwide, providing evidence that standard treatment options do not effectively remove PFCs from drinking water.[22] Given that biosolids from conventional WWTP appear to routinely contain PFCs,[8 11] the data from this study suggest that source and finished water supplies in areas potentially impacted by land application of more typical WWTP biosolids should be evaluated to determine the possibility of PFC contamination.

Although PFCs are obviously present in the water resources of the Decatur region, it is not clear to what extent these contaminants are available for transfer to local crops, livestock, and wildlife. Analysis of plants collected from these same Decatur fields has shown grass/soil accumulation factors of 0.25 for PFOA, 0.75 for PFHpA, and 3.8 for PFHxA.[23] Moreover, in a small preliminary investigation in May of 2009, the U.S. Food and Drug Administration found PFOS at 170 ng/L in a bulk milk tank sample from the Decatur biosolids application area.[24] This concentration is very close to the PHA level for PFOS in drinking water (200 ng/L) and it suggests that contamination may be transferred to livestock. Additionally, data from studies of freshwater fish conducted elsewhere clearly indicate that lakes and rivers contaminated at the same levels documented in the current study contain fish with levels of PFOS high enough to warrant issuance of fish consumption advisories.[25] It is therefore reasonable to hypothesize that PFCs from biosolids in Decatur may be taken up by local livestock and wildlife and that this may give rise to a number of different exposure pathways that are relevant for humans.

Data from this study show that land application of fluorochemical industry impacted biosolids can lead to water resource contamination above the drinking water PHA for PFOA (400 ng/L) recently issued by the EPA. Other PFCs, for which PHAs have not been issued, were also found in local water resources at levels from the 100s to 1000s of ng/L. In a more general context, the fact that PFC contamination of biosolids appears to be common, and that soil PFC levels can directly influence contamination of surrounding water resources indicates that a more complete evaluation of the potential impact of all types of biosolids would be helpful. Land application of

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biosolids is the dominant method of disposal in many parts of the world, with approximately 50% of U.S. biosolids being disposed of in this manner.[26] It is reasonable to hypothesize that land application of biosolids is an important factor in the distribution of PFCs in the environment and this may in turn influence human exposure.

' ASSOCIATED CONTENT

b Supporting Information. Additional method description, tables showing UPLC-MS/MS conditions, mass transitions of each analyte, and detailed results. This material is available free of charge via the Internet at http://pubs.acs.org.

' AUTHOR INFORMATION

Corresponding Author
*Phone: 919-541-0551; fax: 919-541-0905; e-mail: lindstrom.andrew@epa.gov.

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' REFERENCES

(1) Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K. R.; Muir, D. C. Biological monitoring of polyfluoroalkyl substances: A review. Environ. Sci. Technol. 2006, 40 (11), 3463–73.

(2) Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Van Wouwe, N.; Yang, J. H.; Aldoust, K. M. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ. Sci. Technol. 2004, 38, 4489–95.

(3) Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl acids: A review of monitoring and toxicological findings. Toxicol. Sci. 2007, 99 (2), 366–94.

(4) Apelberg, B. J.; Witter, F. R.; Herbstman, J. B.; Calafat, A. M.; Halden, R. U.; Needham, L. L.; Goldman, L. R. Cord Serum Concentrations of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Relation to Weight and Size at Birth. Environ. Health Perspect. 2007, 115 (11), 1670–1676.

(5) Melzer, D.; Rice, N.; Depledge, M. H.; Henley, W. E.; Galloway, T. S. Association between Serum Perfluorooctanoic Acid (PFOA) and Thyroid Disease in the US National Health and Nutrition Examination Survey. Environ. Health Perspect. 2010, 118 (5), 686–692.

(6) Steenland, K.; Tinker, S.; Frisbee, S.; Ducatman, A.; Vaccarino, V. Association of Perfluorooctanoic Acid and Perfluorooctane Sulfonate With Serum Lipids Among Adults Living Near a Chemical Plant. Am. J. Epidemiol. 2009, 170 (10), 1268–1278.

(7) U.S. Environmental Protection Agency. Provisional Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS). http://www.epa.gov/region4/water/documents/final_pfoa_%20pfos_memo_oswer.pdf.

(8) Sinclair, E.; Kannan, K. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 2006, 40, 1408–14.

(9) Loganathan, B. G.; Sajwan, K. S.; Sinclair, E.; Senthil Kumar, K.; Kannan, K. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res. 2007, 41 (20), 4611–20.

(10) Schultz, M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F.; Field, J. A. Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. Environ. Sci. Technol. 2006, 40 (23), 7350–7357.

(11) Becker, A. M.; Gerstmann, S.; Frank, H. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere 2008, 72 (1), 115–21.

(12) Skutlarek, D.; Exner, M.; Färber, H. Perfluorinated surfactants in surface and drinking waters. Environ. Sci. Pollut. Res. 2006, 13 (5), 299–307.

(13) Holzer, J.; Midasch, O.; Rauchfuss, K.; Kraft, M.; Reupert, R.; Angerer, J.; Kleeschulte, P.; Marschall, N.; Wilhelm, M. Biomonitoring of perfluorinated compounds in children and adults exposed to perfluorooctanoate-contaminated drinking water. Environ. Health Perspect. 2008, 116 (5), 651–7.

(14) Washington, J. W.; Yoo, H.; Ellington, J. J.; Jenkins, T. M.; Libelo, E. L. Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA. Environ. Sci. Technol. 2010, 44 (22), 8390–8396.

(15) Yoo, H.; Washington, J. W.; Ellington, J. J.; Jenkins, T. M.; Neill, M. P. Concentrations, Distribution, and Persistence of Fluorotelomer Alcohols in Sludge-Applied Soils near Decatur, Alabama, USA. Environ. Sci. Technol. 2010, 44 (22), 8397–8402.

(16) 3M Environmental Monitoring Multi-City Study Water, Sludge, Sediment, POTW Effluent and Landfill Leachate Samples; 3M Environmental Laboratory: St. Paul, MN, 2001.

(17) Hansen, K. J.; Johnson, H. O.; Eldridge, J. S.; Butenhoff, J. L.; Dick, L. A. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. Environ. Sci. Technol. 2002, 36, 1681–5.

(18) Weston Solutions, Inc. Data Assessment Report, 3M Decatur, Alabama Facility, PFOA Site-Related Environmental Monitoring Program; Prepared for 3M Company, St. Paul, MN, 2008 (USEPA docket number: EPA-HQ-OPPT-2004-0112-0108.2).

(19) Washington, J. W.; Ellington, J. J.; Evans, J. J.; Jenkins, T. M.; Yoo, H.; Strynar, M. J. Results of Analyses of Sludge and Sludge-Applied Soils From the September 2008 Decatur, AL Reconnaissance Study. http://www.epa.gov/region04/water/documents/Soil%20and%20Sludge%20Sampling%20Decatur%20AL%20September%202008.pdf.

(20) Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B. Determination of Perfluorinated Compounds in the Upper Mississippi River Basin. Environ. Sci. Technol. 2010, 4103–4109.

(21) Higgins, C. P.; Luthy, R. G. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 2006, 40 (23), 7251–6.

(22) Fujii, S.; Polprasert, C.; Tanaka, S.; Lien, N. P. H.; Qiu, Y. New POPs in the water environment: Distribution, bioaccumulation and treatment of perfluorinated compounds - a review paper. J. Water Supply Res. Technol.-Aqua 2007, 56 (5), 313–326.

(23) Yoo, H.; Washington, J. W.; Jenkins, T. M.; Ellington, J. J. Quantitative Determination of Perfluorochemicals and Fluorotelomer Alcohols in Plants from Biosolid-Amended Fields using LC/MS/MS and GC/MS. Environ. Sci. Technol. 2011No. DOI: 10.1021/es102972m.

(24) USEPA. Perfluorochemical (PFC) Contamination of Biosolids Near Decatur, Alabama. http://www.epa.gov/region4/water/documents/fact_sheet_decatur_july_2010.pdf.

(25) Delinsky, A. D.; Strynar, M. J.; Nakayama, S. F.; Varns, J. L.; Ye, X.; McCann, P. J.; Lindstrom, A. B. Determination of ten perfluorinated compounds in bluegill sunfish (Lepomis macrochirus) fillets. Environ. Res. 2009, 109 (8), 975–984.

(26) USEPA. Biosolids-Frequently asked questions. http://www.epa.gov/OW-OWM.html/mtb/biosolids/genqa.htm.

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Supporting Information

Title:
Application of WWTP Biosolids and Resulting Perfluorinated Compound Contamination of Surface and Well Water in Decatur, Alabama, USA

Authors:

Andrew B. Lindstrom, Mark J.Strynar, Shoji F. Nakayama, Amy D. Delinsky, Larry McMillan, E. Laurence Libelo, Michael Neill, and Lee Thomas

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Figure S2. Comparison of target compounds in well and surface water samples in (ng/L)

Figure S3. Correlation of target compound concentration and dry metric tons of biosolids applied

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Table S1. Perfluorinated analytes, abbreviations, internal standards, mass transitions, confirmation ions, and ion ratios monitored in analysis

Target Analyte	Quantitation transition	Confirmation transition	IS	ion ratio† (mean)	ion ratio (SD)	LOQ (ng/L)
Perfluorobutanoic acid (PFBA)	212.80 → 168.75	NA*	$^{13}C_2$-PFHxA	NA	NA	10
Perfluoropentanoic acid (PFPeA)	262.85 → 218.75	NA				10
Perfluorohexanoic acid (PFHxA)	312.70 →268.70	312.70 →118.70		16.26	2.05	10
Perfluoroheptanoic acid (PFHpA)	362.65 → 318.70	362.65 → 168.65		4.81	0.23	50
Perfluorooctanoic acid (PFOA)	412.60 → 368.65	412.60 → 168.70	$^{13}C_8$-PFOA	3.63	0.26	10
Perfluorononanoic acid (PFNA)	462.60 → 418.60	462.60 → 218.75		3.89	0.27	10
Perfluorodecanoic acid (PFDA)	512.60 → 468.55	512.60 → 468.55	$^{13}C_2$-PFUnDA	6.31	0.50	50
Perfluorobutane sulfonate (PFBS)	298.70 → 98.80	298.70 → 79.90	$^{18}O_2$-PFHxS	0.62	0.04	10
Perfluorohexane sulfonate (PFHxS)	398.65 → 98.80	398.65 → 79.90		1.15	0.10	10
Perfluorooctane sulfonate (PFOS)	498.65 → 98.80	498.65 → 79.90	$^{18}O_2$-PFOS	0.62	0.03	10
1,2-$^{13}C_2$- Perfluorohexanoic acid ($^{13}C_2$-PFHxA)	314.75 → 269.75	Internal Standards (IS) ‡				
$^{18}O_2$-Sodium perfluorohexanesulfonate ($^{18}O_2$-PFHS)	402.65 → 83.90					
1,2,3,4,5,6,7,8-$^{13}C_2$-Perfluorooctanoic ($^{13}C_8$-PFOA)	429.65 → 375.75					
$^{18}O_2$-Ammonium perfluorooctanesulfonate ($^{18}O_2$-PFOS)	502.60 → 83.90					
$^{13}C_2$ Perfluoroundecanoic acid ($^{13}C_2$-PFUnDA)	564.60 → 519.65					

* Mass spectrometer conditions did not produce secondary qualification ions that can be used for compound confirmation
† Ratio of quantitation ion to confirmation ion, used to help confirm the identity of target compounds
‡ Parameters not used with internal standards

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Table S2. Summary of the UPLC/MS/MS method including target and qualifier ions

Reservoirs: A: 2 mM ammonium acetate in deionized water with 5% methanol,
B: 2 mM ammonium acetate in 95% methanol 5% DI water
Column: BEH C18 reverse phase, 2.1×50 mm, 1.7 μm particle size
Flow rate: 500 μL/min
Column temperature: 50°C
Injection Volume: 40 μL
Gradient mobile phase program:

Time	A	B	curve
0.00	75	25	initial
0.50	75	25	6
3.50	10	90	6
3.60	0	100	6
4.50	0	100	6
4.60	75	25	6
6.00	75	25	6

The Quatro Premier mass spectrometer is operated in the multiple reaction monitoring (MRM) mode using negative-ion-spray ionization under the following conditions:

Instrument Parameters	
Capillary (kV)	−0.40
Source temperature	150°C
Desolvation temperature	350°C
Cone gas flow	2 L/hr
Desolvation gas flow	1200 L/hr
Cone voltage	Optimized for
Collision energy	each compound

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Table S2. (Continued) Compound specific parameters for Quatro Premier XE (MS/MS)

Compound	Quantitation MRM	Qualification MRM	Cone Voltage	Collision Energy
PFBS	298.70 > 98.80	298.70 > 79.90	40	28 (30)
PFHxS	398.65 > 98.80	398.65 > 79.90	50	32 (38)
PFOS	498.65 > 98.80	498.65 > 79.90	60	38 (48)
PFBA	212.80 > 168.75		15	10
PFPeA	262.85 > 218.75		15	9
PFHxA	312.70 > 268.70	312.70 > 118.70	13	10 (21)
PFHpA	362.65 > 318.70	362.65 > 168.65	14	10 (17)
PFOA	412.60 > 368.65	412.60 > 168.70	15	11 (18)
PFNA	462.60 > 418.60	462.60 > 218.75	15	11 (17)
PFDA	512.60 > 468.55	512.60 > 218.75	16	12 (18)
Internal Standards				
$^{18}O_2$-PFHS	402.65 > 83.90		50	38
$^{13}C_2$-PFOS	502.65 > 83.90		60	48
$^{13}C_2$-PFHxA	314.75 > 269.75		13	9
$^{13}C_8$-PFOA	420.65 > 375.75		15	11
$^{13}C_2$-PFUnDA	564.60 > 519.65		17	12

Note: Collision energies for qualification ions are in parenthesis

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Table S3. Summary of Field Blanks, Low Level Field Spikes, and High Level Field Spikes in ng/L

Sample Type	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
Field Blanks*	< 50	< 10	< 10	< 50	< 10	< 10	< 10	< 10	< 10	< 10
Low Level Trip Spike (SD) *	210 (17)	156 (45)	162 (36)	171 (31)	195 (23)	217 (33)	218 (60)	172 (39)	198 (18)	205 (22)
Percent Accuracy (%RSD)	105 (8.2)	78.1 (28.8)	80.9 (22.5)	85.5 (18.3)	97.3 11.9)	108 (15.4)	109 (27.5)	86.1 (22.7)	98.9 (9.1)	103 (10.6)
High Level Trip Spike (SD) *	448 (56.8)	301 (59.7)	318 (51.1)	339 (58.0)	388(29.3)	393 (41.5)	382 (19.2)	364 (30.9)	386 (26.5)	387 (24.2)
Percent Accuracy (%RSD)	112 (12.7)	75.2 (19.9)	79.4 (16.1)	84.7 (17.1)	97.1 (7.6)	98.3 (10.6)	95.4 (5.0)	90.9 (8.5)	96.6 (6.9)	96.8 (6.2)

* Mean of 5 determinations; Low Level Field Spikes prepared at 200 ng/L; High Level Field Spikes prepared at 400 ng/L

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Table S4. Summary of Duplicate Field Samples in ng/L

	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
W06PW	*	*	*	*	*	*	*	*	*	*
W06PW dup	*	*	*	*	*	*	*	*	*	*
Rel % Diff	---	---	---	---	---	---	---	---	---	---
W53SW	*	*	18.4	*	*	*	*	51.1	*	*
W53SW dup	*	*	14.8	*	*	*	*	56.1	*	*
Rel % Diff	---	---	21.3	---	---	---	---	9.26	---	---
W24SW	*	*	*	*	22.1	56.6	62.6	*	*	*
W24SW dup	*	*	33.7	*	18.7	72.0	77.9	*	*	*
Rel % Diff	---	---	---	---	16.8	23.9	21.8	---	---	---
W36SW	54.2	12.4	389	393	505	333	236	30.3	16.7	38.2
W36SW dup	*	21.8	397	407	511	369	274	19.8	17.7	41.2
Rel % Diff	---	54.8	2.04	3.52	1.11	10.1	15.2	42.2	5.42	7.67
W17PW	*	*	*	*	*	*	13.2	*	*	*
W17PW dup	*	*	*	*	*	*	13.8	*	*	*
Rel % Diff	---	---	---	---	---	---	4.33	---	---	---

Rel % Diff = Relative percent difference between duplicate samples:
Absolute value of [(conc 1- conc 2)/ (mean of conc 1 and conc 2) x 100%]
* Values below LOQ.

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Table S5. Standard Addition (SA†) of 400 ng/L of Each Analyte to Selected Field Samples (ng/L)

	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
W06PW-SA†	614	433	477	460	386	369	393	551	450	420
W63PW-SA†	677	412	471	489	405	427	412	646	485	504
W02PW-SA†	1030	301	339	347	392	459	444	688	420	401
W13SW-SA†	628	403	653	731	515	480	426	595	422	450
W34SW-SA†	805	318	559	512	451	520	558	663	396	426
W06PW	*	*	*	*	*	*	*	*	*	*
W63PW	*	*	*	*	*	*	*	*	*	*
W02PW	*	*	*	*	*	*	*	*	*	*
W13SW	*	27.7	321	234	182	76.4	62.5	*	*	13.4
W34SW	*	16.2	204	73.6	103	162	234	*	*	*
(W06PW-SA†) – (W06PW)	614	433	477	460	385	369	393	551	450	420
(W63PW-SA†)- (W63PW)	677	412	471	489	405	427	412	646	485	504
(W02PW-SA†)- (W02PW)	1030	301	339	347	392	459	444	688	420	401
(W13SW-SA†)- (W13SW)	628	375	332	498	333	403	364	595	422	437
(W34SW-SA†)- (W34SW)	805	302	355	439	348	358	324	663	396	426
% recovery for W06PW	153	108	119	115	96.0	92.0	98.0	138	113	105
% recovery for W63PW	169	103	118	122	101	107	103	161	121	126
% recovery for W02PW	257	75.0	85.0	87.0	98.0	115	111	172	105	100
% recovery for W13SW	157	94.0	83.0	124	83.0	101	91.0	149	105	109
% recovery for W34SW	201	76.0	89.0	110	87.0	90.0	81.0	166	99.0	107
Ave % Recovery	188	91.1	98.8	112	93.2	101	96.9	157	109	109
SD % Recovery	43.2	15.4	18.2	15.1	7.70	10.3	11.5	13.8	8.50	9.80

SA† = Sample received laboratory spike equivalent to 400 ng/L of each compound
* Values below the limit of quantitation, assumed to be 0 for the calculation of difference

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Table S6A. Perfluorinated compound concentrations in well water samples in ng/L

Sample Name	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
W06PW	*	*	*	*	*	*	*	*	*	*
W14PW β	*	25.7	594	619	570	333	180	14.1	20.7	25.4
W63PW	*	*	*	*	*	*	*	*	*	*
W07PW	*	*	*	*	9.72	*	45.8	*	*	*
W101PW	*	*	*	*	*	*	14.6	*	*	22.9
W58PW	*	*	*	*	*	*	*	*	*	*
W09SW	*	*	*	*	*	*	10.4	*	*	*
W02PW	*	*	*	*	*	*	*	*	*	*
W54PW β	*	*	2070	2100	2150	1180	680	*	46.4	56.5
W15PW	*	*	*	*	15.8	12.2	42.6	*	*	*
W62PW β	*	*	*	*	*	*	*	*	*	*
W22PW β	*	*	*	*	*	*	*	*	*	*
W11PW β	*	*	*	*	*	*	34.6	12.0	12.7	26.4
W60PW	*	*	149	77.2	150	57.2	98.1	151	56.5	33.9
W12PW	*	*	6410	5220	3970	2330	1260	*	87.5	76.6
W08PW	*	*	*	*	*	*	*	*	*	*
W01PW β	*	*	*	*	*	*	24.1	*	*	10.1
W17PW	*	*	*	*	*	*	13.2	*	*	*
W19PW	*	*	*	*	*	*	11.6	*	*	*
Max =	*	25.7	6410.0	5220.0	3970.0	2330.0	1260.0	150.6	87.5	76.6
Min =	*	25.7	149.2	77.2	9.7	12.2	10.4	12.0	12.7	10.1

* Values below the limit of quantitation (LOQ)
β indicates sample from a well used for drinking water

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Table S6B. Perfluorinated compound concentrations in surface water samples in ng/L

Sample Name	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
W51SW	*	*	29.5	*	12.0	*	*	*	*	*
W27SW	*	*	134	81.5	65.9	68.4	72.7	11.6	*	*
W10SW	*	*	13.6	*	20.2	20.8	52.7	*	*	30.9
W28SW	*	*	94.8	127	153	91.1	70.8	*	*	15.6
W46SW	838	286	1100	491	205	192	188	83.9	*	10.4
W42SW	125	93.3	993	777	729	434	303	16.5	17.5	40.8
W43SW	68.0	54.4	396	216	201	180	152	14.6	*	10.0
W32SW	230	70.9	750	839	961	571	439	66.3	20.6	90.2
W53SW	*	*	18.3	*	*	*	*	51.1	*	*
W03SW	*	*	*	*	*	*	19.4	13.2	*	20.9
W33SW	*	*	*	*	*	*	30.4	*	*	23.9
W61SW	*	*	*	*	*	*	*	*	*	*
W52SW	*	*	2230	3180	3750	1970	1030	*	12.1	91.3
W24SW	*	*	*	*	22.1	56.6	62.6	*	*	*
W102SW	*	*	*	*	*	*	*	*	*	*
W64SW	*	*	758	1200	1730	1060	825	*	12.3	56.7
W36SW	54.2	12.4	389	393	505	333	236	30.3	16.7	38.2
W29SW	*	*	*	*	*	*	*	21.1	*	14.8
W31SW	*	*	30.1	*	*	*	44.6	31.7	*	26.0
W30SW	*	*	24.1	*	13.7	*	40.0	31.5	*	13.5
W35SW	*	*	*	*	*	*	14.4	*	*	9.51
W48SW	*	*	26.0	*	16.4	17.2	33.0	*	*	*
W13SW	*	27.7	321	234	182	76.4	62.5	*	*	13.4
W34SW	*	16.2	204	73.6	103	162	234	*	*	*
W26SW	*	*	67.9	30.0	141	305	394	*	*	11.2
W57SW	*	*	32.2	*	*	*	10.7	*	*	*
W47SW	*	*	1250	1360	1310	478	330	*	40.6	63.9
W50SW	*	40.0	1160	715	762	354	199	*	*	54.5
W44SW	*	*	11000	8250	6710	3770	1750	*	218	208
W45SW	129	26.4	176	61.0	69.4	143	194	38.2	*	*
W41SW	*	*	90.5	*	50.6	90.7	102	*	*	*
W49SW	*	*	35.7	*	42.3	28.3	29.4	*	*	*
Max =	838.2	285.6	11000.0	8250.0	6710.0	3770.0	1750.0	83.9	217.5	208.0
Min =	54.2	12.4	13.6	30.0	12.0	17.2	10.7	11.6	12.1	9.5

* Values below the limit of quantitation (LOQ)

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Figure S1. Spearman correlation coefficients (rho) for all target compounds

	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	PFBA	PFOS	PFHxS	PFBS
PFDA	1.000	0.7143	0.5429	0.3714	0.0857	0.0857	0.0857	0.8286	1.000	0.2000
PFNA		1.000	0.6727 *	0.5030	0.3818	0.3697	0.0546	0.5000	0.2000	−0.0238
PFOA			1.000	0.9338 ***	0.9535 ***	0.9017 ***	0.8407 ***	0.0000	0.3091	0.6782 **
PFHpA				1.000	0.9744 ***	0.8947 ***	0.7068 ***	−0.0667	0.3000	0.8676 ***
PFHxA					1.000	0.9610 ***	0.8851 ***	0.0303	0.2545	0.8281 ***
PFPeA						1.000	0.9528 ***	−0.0833	0.2364	0.8328 ***
PFBA							1.000	0.4396	0.2308	0.7217 ***
PFOS								1.000	0.6000	0.1329
PFHxS									1.000	0.1608
PFBS										1.000

Significance is indicated with asterisks: $p < 0.05$ =*, $p < 0.01$ = **, $p < 0.001$ = ***

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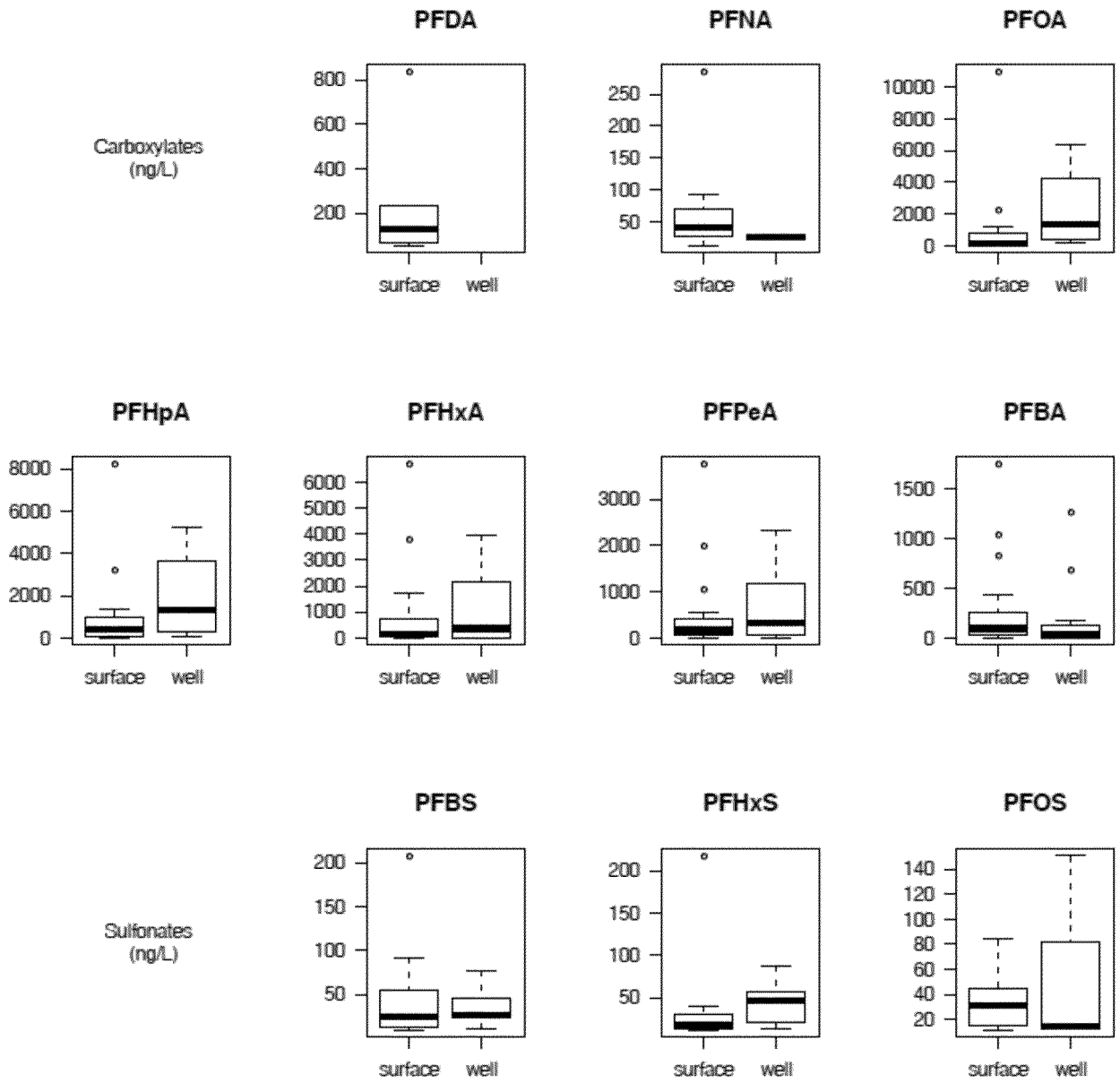
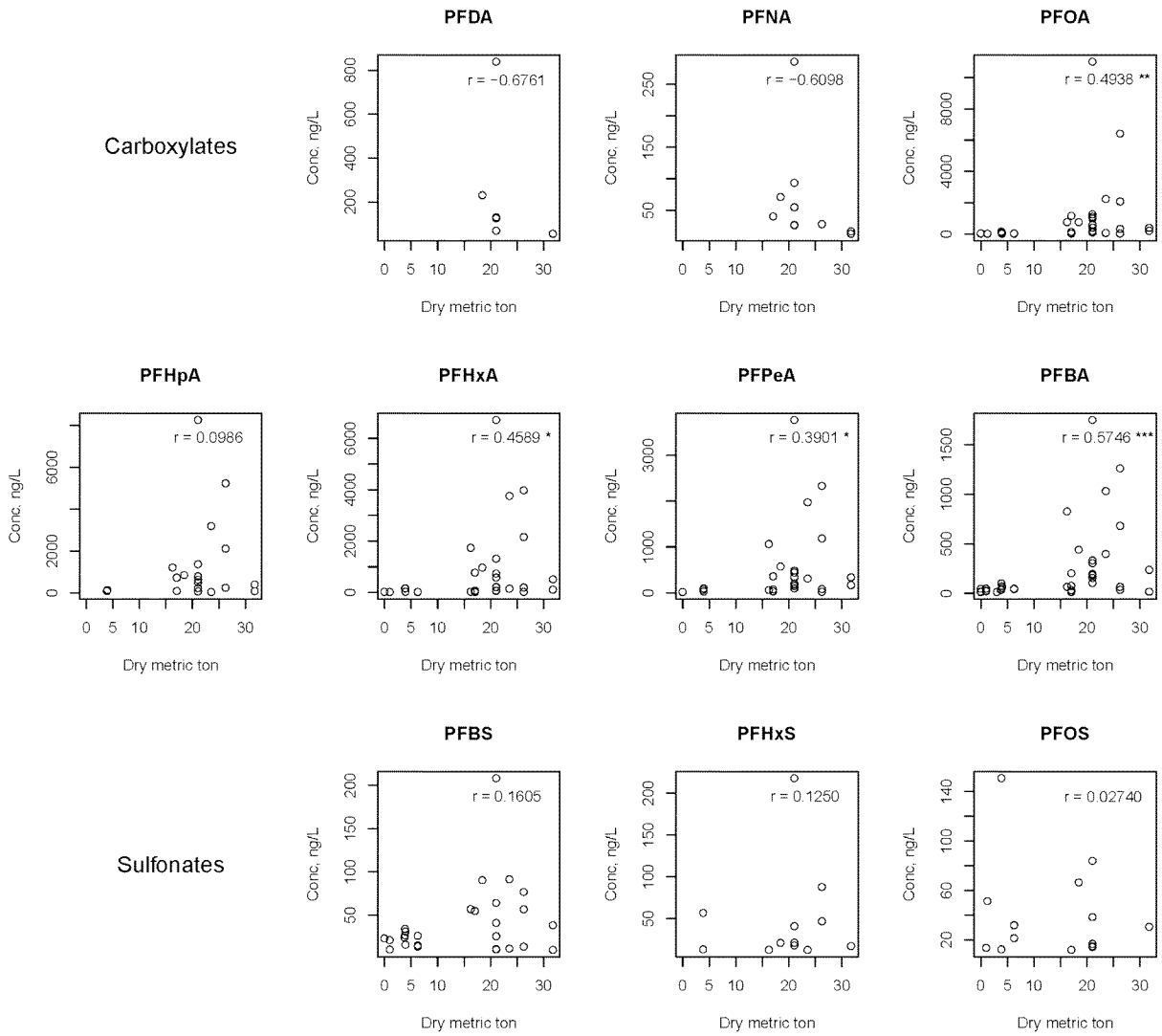
Figure S2. Comparison of target compounds in well and surface water samples in (ng/L)



Midline = median; top and bottom of box = 75th and 25th percentiles, respectively; top and bottom whiskers = 75th and 25th percentiles +/- 1.5 times the interquartile range, respectively. Open circles represent outliers.

Figure S3. Correlation of target compound water concentration and dry metric tons of biosolids applied



Significance is indicated with asterisks: p< 0.05 = *, p < 0.01 = **, p < 0.001 = ***