ANALYTICAL CHEMISTRY

Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils

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The toxicity and environmental persistence of anthropogenic per- and poly-fluoroalkyl substances (PFAS) are of global concern. To address legacy PFAS concerns in the United States, industry developed numerous replacement PFAS that commonly are treated as confidential information. To investigate the distribution of PFAS in New Jersey, soils collected from across the state were subjected to nontargeted mass-spectral analyses. Ten chloroperfluoropolyether carboxylates were tentatively identified, with at least three congeners in all samples. Nine congeners are $\geq (CF_2)_7$. Distinct chemical formulas and structures, as well as geographic distribution, suggest airborne transport from an industrial source. Lighter congeners dispersed more widely than heavier congeners, with the most widely dispersed detected in an in-stock New Hampshire sample. Additional data were used to develop a legacy-PFAS fingerprint for historical PFAS sources in New Jersey.

Per- and poly-fluoroalkyl substances (PFAS) are anthropogenic compounds used to impart surfactant, antistaining, antisticking, and related properties to a wide array of consumer and industrial products. Spurred by concerns regarding potential toxicity and environmental persistence of long-chain PFAS (1–5), in 2006 the U.S. Environmental Protection Agency (EPA) and eight leading PFAS manufacturers and users negotiated a voluntary "PFOA Stewardship Program" in which the companies agreed to work toward the elimination of perfluorooctanoate acid (PFOA, or C8), as well as C8 precursors and related longer-chain homologs from emissions and product content by 2015. With establishment of the PFOA Stewardship Program, numerous PFAS manufacturers and users initiated efforts to develop substitute compounds for legacy long-chain PFAS, commonly settling on structures that are treated as confidential business information. With proliferation of these substitute PFAS, environmental chemists have set about attempting to identify them using nontargeted, high-resolution mass spectrometry (HRMS) to assemble formulas and likely structures from molecular-precursor and -fragment data (6). High mass-resolution

enables chemists to identify those molecular formulas that have exact masses within a user-specified mass-error threshold, and molecular-fragment masses and spectra of the molecules help narrow possible formulas further, ideally informing molecular structure as well (7).

Among participants in the PFOA Stewardship Program, several have operated industrial facilities, ongoing or in the past, in or near densely populated New Jersey. As part of efforts to elucidate industrial chemical sources, chemical species, and distribution of legacy and possible substitute PFAS in New Jersey, in late 2017 the New Jersey Department of Environmental Protection (NJDEP) collected soil samples. For this survey, samples primarily were collected in southern New Jersey, where two PFOA Stewardship Program signatories are located: Solvay, in West Deptford Township, and DuPont (now Chemours), in Pennsville
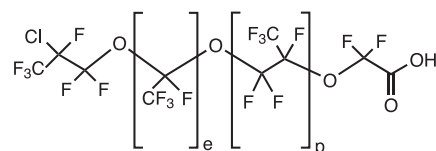
Fig. 1. A chloroperfluoropolyether carboxylate (ClPFPECA) identified by nontargeted MS analyses in soil samples from New Jersey. In the New Jersey samples, perfluoroethyl (e) plus perfluoropropyl (p) groups were observed to range in sum from one to four. The example congener depicted here would be designated (e,p) = 1,1. Isomers likely include an alternative terminal structure of $ClCF_2CF(CF_3)O-$ (13, 14) as well as relative positions for the perflluoroethyl and perfluoropropyl groups.

Township. Historically, Solvay produced polyvinylidene fluoride (PVDF), which entailed use of Surflon, a surfactant that contains C9, C11, and C13 (perfluorononanoate, perfluoroundecanoate, and perfluorotridecanoate) perfluorocarboxylates (PFCAs) (8). By contrast, the DuPont/Chemours facility manufactured and used fluorotelomers [compounds synthesized from perfluoroalkyl iodide, composed of perfluorinated-carbon straight chains such as $F(CF_2)_6-$, and usually two-hydrogen-bearing carbons, such as $-CH_2CH_2-$] from 1962 until no later than 2014 (9). Sampling transects were collected in the dominant downwind directions as recorded at nearby Philadelphia International Airport, and remote locations around the state were sampled as well (sampling campaign details are available in the supplementary materials). These samples were sent to the EPA, Office of Research and Development (ORD) laboratory in Athens, Georgia.

At the ORD laboratory, soil samples were extracted (supplementary text, fig. S1, and table S1) in triplicate and selected samples analyzed (supplementary text) for PFAS unknown to our research team by using an ultraperformance liquid chromatograph (UPLC) coupled to a quadrupole time-of-flight (QToF) mass spectrometer operating in negative electrospray ionization (ESI), MS^e (no mass filtering) mode. Output data were sorted by signal intensity, high-intensity molecular features were plotted on mass-defect plots (7) ranging in defect from –0.10 to +0.05 Da, and molecular features appearing in the plots of multiple samples were selected for further scrutiny. Using low-collision-energy precursor masses, high-collision-energy fragment masses, a distinctive mono-chloro M+2 spectral feature, and carbon-isotopic ratios (10), we tentatively identified a molecular feature as a chloroperfluoropolyether carboxylate (ClPFPECA) that is described in the literature as "Solvay's product (CAS No. 329238-24-6)" (11), as reported in a product assessment by the European Food Safety Authority (EFSA) at the request of "Solvay Solexis, Italy" (12). With these reports, together with compound-synthesis papers by Solvay chemists (13, 14), the structure of these ClPFPECAs appears to be as shown in Fig. 1 for 70% of production, with 30% having an alternative terminus of $ClCF_2CF(CF_3)O-$.

We have not had access to a standard of the Solvay product. However, on the basis of tentative identification of one Solvay product congener in our data, and the literature report that ClPFPECA congeners can include 0 to 2 perfluoroethyl groups (Fig. 1, e) and 1 to 4 perfluoropropyl groups (Fig. 1, p) (11, 12) separated by ether linkages, we carried out suspect screening of our MS^e data by extracting hypothetical masses to determine what other congeners might be present. After

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this effort, all tentatively identified congeners were further elucidated on the QToF operating in MS/MS mode, in which the quadrupole magnets were focused on suspected precursor mass/charge ratio (m/z) values and fragmented with ramped collision energy; then, precursors and fragments were isolated and detected in the ToF (supplementary text). Results for the nine ClPFPECA congeners tentatively identified on QToF are depicted in Fig. 2 and fig. S2. Within conventional HRMS-identification confidence context (15, 16), these compounds fall at level 2b (diagnostic probable structure) and level 3 (tentative candidate), but considering the nine congeners together, confidence of their general identity is high.

Having tentatively identified nine congeners in these New Jersey soil samples as Solvay's product, we reexamined in-house nontargeted results for a water sample from the Bormida di Spigno River, downstream of Solvay Specialty Polymers Italy (Spinetta Marengo, Alessandria, Italy). In this Italian water sample, we identified five ClPFPECA congeners (fig. S3) that were consistent with our New Jersey soil samples, bolstering confidence still further in our identification of these compounds as Solvay's product.

Informed by the fragmentation patterns of the QToF suspect screening, we developed a method for routine analysis of the detected congeners on a conventional-resolution tandem mass spectrometer [liquid chromatography (LC)–MS/MS], adding monitoring for a possible ethyl,propyl (e,p)=1,0 congener (fig. S4 and table S2). Whereas this method was not developed with the benefit of authentic standards, it was informed by masses for ~30 precursors and fragments uniformly having mass error <4 mDa when the MS signal is $\geq 10^5$ (fig. S5). With an objective of assessing relative concentrations among samples, we performed analyses on the triplicate soil extracts with a matrix internal standard labeled with five heavy carbons, $^{13}C_5$-perfluorononanoic acid ($^{13}C_5$-PFNA; $^{13}C_5$-C9), then reported ClPFPECAs "as C9," by simple peak-area ratios (supplementary text). We also performed LC-MS/MS analyses on the triplicate soil-extract replicates for legacy PFCAs, quantitating on mass-labeled internal matrix standards (supplementary text). Results of ClPFPECA analyses are summarized in table S4, and PFCA analyses are summarized in table S5.

Of the 10 congeners we identified by means of QToF or tandem MS, (i) six were expected on the basis of EFSA information (e,p=0,1; 1,1; 0,2; 2,1; 1,2; and 0,3 congeners) (11, 12); (ii) four were not included as congeners in the EFSA information (1,0; 2,0; 3,0; and 4,0 congeners); and (iii) six congeners anticipated on the basis of EFSA information were not detected (2,2; 1,3; 2,3; 0,4; 1,4; and 2,4 congeners) (fig. S6). In fig. S7, we summarize the fractional composition of the 10 ClPFPECA congeners detected in our study in terms of mean, maximum, and minimum fraction observed among our soil samples. Addressing the mean fractions, at roughly 40% each, the e,p = 0,1 and 1,1 congeners are dominant, followed by ~15% for the 0,2 and lesser to trace amounts of all other congeners (fig. S7).

Several ClPFPECAs eluted as split peaks (Fig. 2 and fig. S2). We investigated whether this splitting reflected the presence of isomers by extracting spectral patterns of visually distinct chromatographic peak ranges, looking for unique fragmentation patterns across aggregate peaks (supplementary text, qualitative examination for isomers, and figs. S8 to S10). On the basis of these efforts, we suspect the presence of group-regioisomerism for congeners having both ethyl and propyl groups as well as regioisomers based on chlorine position (Fig. 1).

These New Jersey soil samples generally were elevated in legacy PFCAs relative to global background soil estimates (17) and particularly
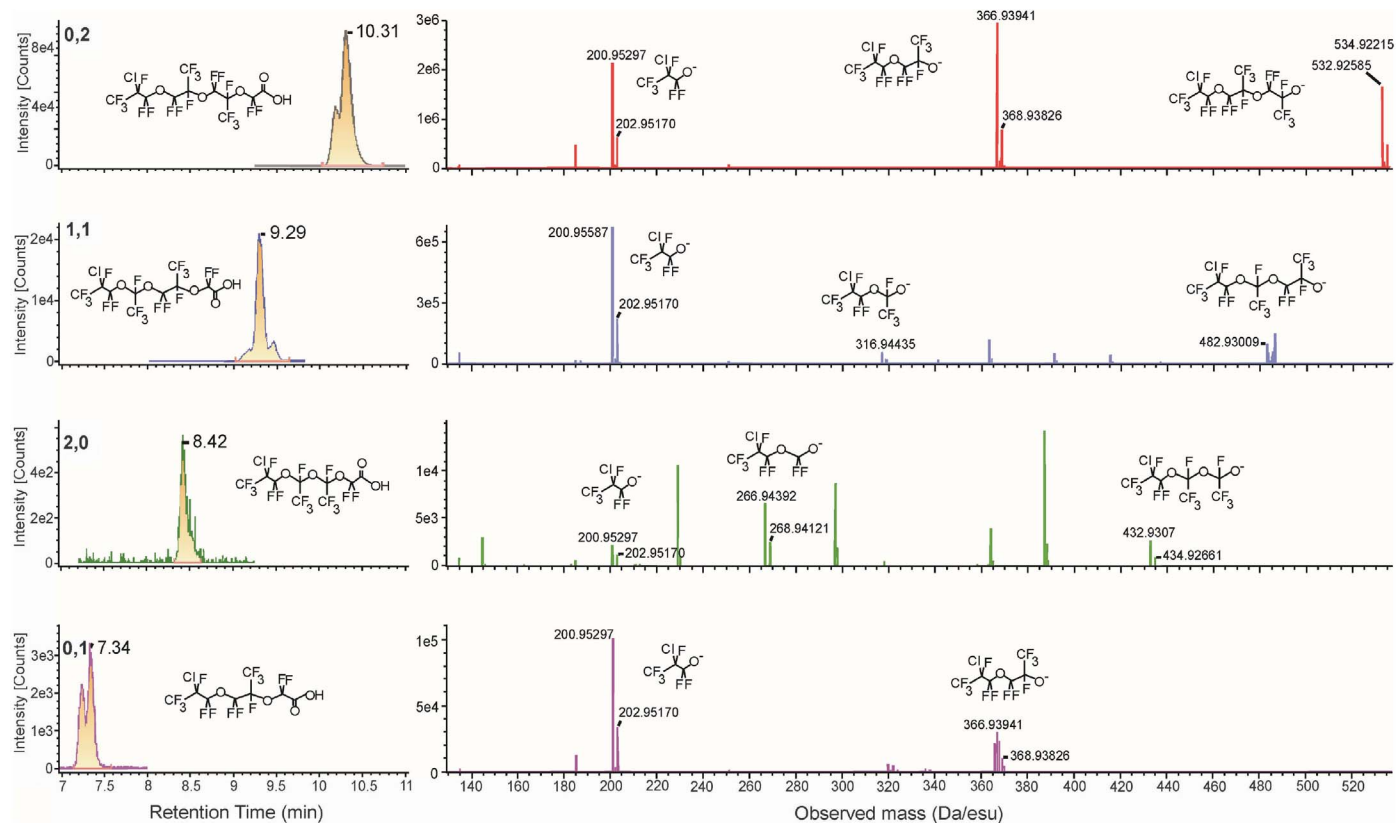
Fig. 2. Mass chromatograms (MS/MS mode), spectra, and precursor and fragment structures of four smaller ClPFPECA congeners detected in New Jersey samples. These are identified in the top left of the chromatograms by ethyl#,propyl#. Results for larger congeners are shown in fig. S2. Chromatogram peaks consist of signal from precursors and selected major fragments. Congeners elute in order according to molecular mass, small to large. On major spectra, the diagnostic monochlorine signal is 3:1 for ^{35}Cl:^{37}Cl.

elevated in C9 and longer homologs. For example, the mean C9 in our New Jersey soils is 785 pg/g dry soil (table S5) [compared with global background of 18 pg/g (17)]; mean C10 = 437 pg/g (perfluorodecanoate; background = 11 pg/g); mean C11 = 1618 pg/g (background = 9.6 pg/g); mean C12 = 167 pg/g (perfluorodecanoate; background = 9.0 pg/g); and mean C13 = 222 pg/g (background not reported). Also, the lowest New Jersey soil concentrations in our study for C9 through C12 PFCAs (table S5) were 5- to 30-fold that of mean global background values (17). These increased long-chain concentrations resulted in an anomalous PFCA-homolog profile for the New Jersey samples relative to global background. Whereas the PFCA profile for global background soils tended to be highest in C6, C7, and C8 PFCAs (perfluorohexanoate, perfluoroheptanoate, and perfluorooctanoate), in this order, these New Jersey samples were most highly represented by C11 and C9, in this order (fig. S11).

Taken altogether, these data for ClPFPECAs and the elevated levels of legacy PFAS strongly suggest the presence of regional PFAS sources.

Probing for possible relationships suggested by variation in the data, we performed principal component analysis (PCA) to guide directed testing (fig. S12). Principal component 1 (PC1) and PC2 account for 96.8% of variation in the data, with PC1 alone accounting for 90.6%. The 95% confidence interval ellipsoids in the PCA score plot (fig. S12) encompass the two chemical families almost exclusively: the ClPFPECAs and the legacy PFCAs. The major ellipsoidal axis of the ClPFPECA cluster is oriented more closely parallel to PC1, reflecting considerable variance among these data that can be characterized dominantly by a single component, as might be expected for a single physical source. Additionally, C11 and C13 fall within the ClPFPECA ellipsoid (fig. S12), suggesting similarities in the pattern of variation for C11 and C13 with at least some of the ClPFPECAs.

Exploring variation in the ClPFPECA data (fig. S12), we regressed the eight ClPFPECA congeners detected in most samples (excluding rarely detected 1,0 and 4,0 congeners) against distance from Solvay in log-transformed space (Fig. 3A). All eight congeners decreased with distance from Solvay with high degrees of significance ($P < 0.0002$) (Table 1). Examining the data in three dimensions, the ClPFPECA concentration contours form a concentric focus on Solvay, which is consistent with Solvay being the source of these compounds (Fig. 4). The slope of diminishing concentration with distance from Solvay (Table 1) also increases with molecular mass ($P < 0.001$) (Fig. 3B), suggest-ing that smaller congeners were dispersed more widely than larger congeners. This sorting by mass might be a factor in the absence of our detection of several of the largest ClPFPECA congeners expected for the Solvay product (fig. S6) (12); the heaviest congener we detected is the e,p = 0,3 at 792.9 Da, and the lightest of the six congeners expected, but not detected (fig. S6), was the 2,2, with a mass of 858.9 Da.

Considering that these soil samples chiefly are from positions that are not hydraulically downgradient in the watershed of any Solvay wastewater discharge (Fig. 4 and fig. S1), aqueous discharge cannot explain these observations, so these correlations strongly suggest atmospheric release from Solvay as the principal mode of occurrence for these soils.

The observation that three of the lightest congeners (0,1; 1,1; and 0,2) were detected in all study samples, including the most remote New Jersey sample near the northern state border (sample SS22) (fig. S1), suggests that light congeners might be dispersed beyond New Jersey state boundaries. To explore this possibility, we analyzed an in-stock sample from Merrimack, New Hampshire, that falls roughly parallel with the downwind transect extending northeasterly from Solvay (fig. S13). To determine whether unrelated samples might have ClPFPECAs, we also analyzed an in-stock

Fig. 3. Concentration profile. (**A**) Log 0,1-congener soil concentration (picograms/gram) versus log distance from Solvay (kilometers). The regression statistics are for the New Jersey soil samples (blue) located as far as 150 km removed from Solvay (table S1). Other ClPFPECA congeners are still more highly correlated with distance from Solvay (Table 1). Also shown is the 0,1 congener detected in a soil from Merrimack, New Hampshire, at 12.1 pg/g (orange), some 460 km distant from Solvay (table S1), falling closely proximate to the regression line for New Jersey 0,1 congeners. The 0,1 congener is the most widely dispersed of the ClPFPECAs (B) and the only ClPFPECA detected in the New Hampshire soil. Inclusion of the New Hampshire data point in the regression [coefficient of determination (R^2) = 0.55; $P = 10^{-5}$] increases the significance of the relationship roughly an order of magnitude beyond that of New Jersey data alone. (**B**) Regression slope (log [ClPFPECA] versus log distance from Solvay) for each of eight ClPFPECA congeners versus congener molecular mass. Given the statistically significant relationship ($P = 0.001$), this observation suggests sorting by molecular mass in an atmospheric plume, with lighter molecules generally being dispersed more remotely than heavier molecules. Mechanisms of atmospheric mass sorting remain uncertain, but the regression slope also is correlated with congener-acid vapor pressure ($R^2 = 0.91$; $P < 0.001$) and congener-anion octanol-water partition coefficient ($R^2 = 0.92$; $P < 0.001$), as estimated by the EPA Chemical Transformation Simulator (25).

A

Log [0,1] = -0.662Log (km) + 2.71
$R^2 = 0.47$ P=0.0001

B

Slope = -0.0031Mass + 0.77
$R^2 = 0.92$ P<0.001
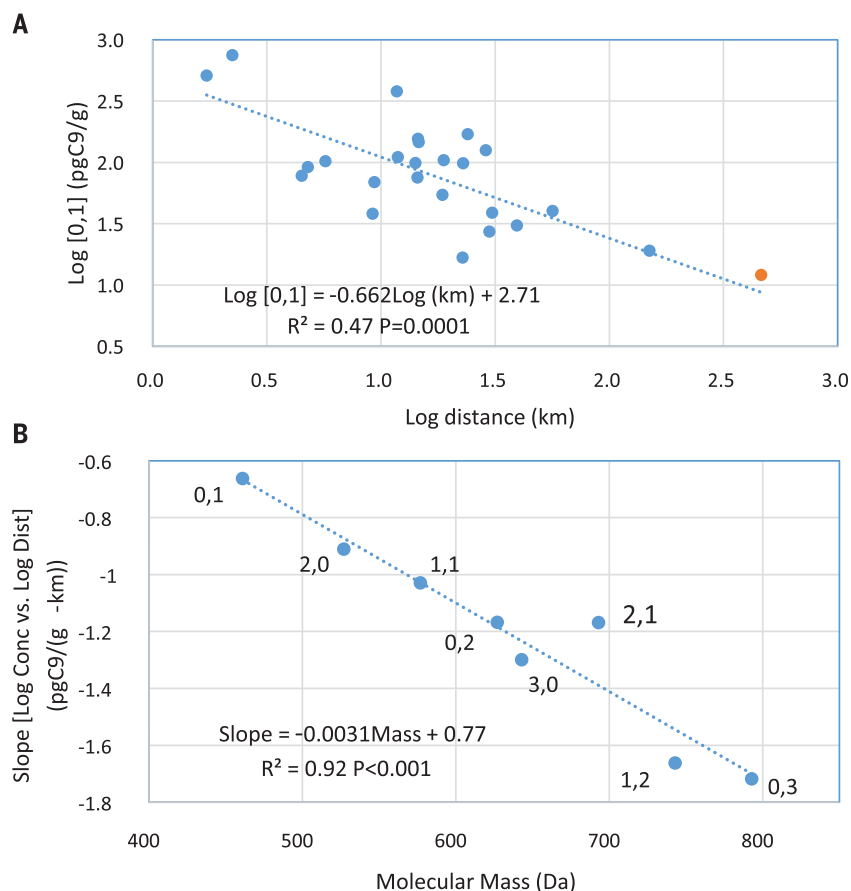
Table 1. Regression statistics for chemical data (picograms/gram) against distance from selected facilities in log-transformed space. ND, not detected; n, sample count; Nonsig., nonsignificant; PFUA, perfluoroundecanoic acid; PFDA, perfluorodecanoic acid; PFDoA, perfluorododecanoic acid; PFTeA, perfluorotetradecanoic acid.

Analyte atmospheric precursor*	Distance from Solvay (km) (maximum n = 24)				Distance from Chemours (km) (anomalous background SS22 excluded; n = 23)			
	Compound(s)	Pearson R	P†	Slope	Compound(s)	Pearson R	P†	Slope
	0,1 (ND = 0, n = 24)	0.688	2.0×10^{-4}	−0.662				
	2,0 (ND = 2, n = 22)	0.766	3.2×10^{-5}	−0.911				
	1,1 (ND = 0, n = 24)	0.791	4.1×10^{-6}	−1.029				
	0,2 (ND = 0, n = 24)	0.845	2.0×10^{-7}	−1.167				
	3,0 (ND = 3, n = 21)	0.822	4.9×10^{-6}	−1.300				
	2,1 (ND = 2, n = 22)	0.831	1.7×10^{-6}	−1.169				
	1,2 (ND = 7, n = 17)	0.846	1.9×10^{-5}	−1.662				
	0,3 (ND = 4, n = 20)	0.849	2.2×10^{-6}	−1.718				
	ΣCongeners (ND = 0, n = 24)	0.796	3.3×10^{-6}	−0.937				
8:2FTOH	PFNA (C9)	0.130	Nonsig.		PFOA (C8)	0.202	Nonsig.	
10:2FTOH	PFUA (C11)	0.620	1.2×10^{-3}	−0.464	PFDA (C10)	0.514	1.2×10^{-2}	−0.404
12:2FTOH	PFTrA (C13)	0.482	1.7×10^{-2}	−0.356	PFDoA (C12)	0.478	2.1×10^{-2}	−0.394
14:2FTOH	(C15 not analyzed)				PFTeA (C14)	0.426	4.3×10^{-2}	−0.337
	(C9 + C11 + C13)	0.519	4.7×10^{-3}	−0.324	(C8 + C10 + C12)	0.204	Nonsig.	
	(C11 + C13)	0.604	1.8×10^{-3}	−0.449	(C10 + C12)	0.519	1.1×10^{-2}	−0.402
	(C9 + C11 + C13) – (C8 + C10 + C12)	0.383	Nonsig.					
	(C11 + C13) – (C10 + C12)	0.660	4.5×10^{-4}	−0.608				

*Source, Ellis et al. (20).   †Significance level.

sample from Conyers, Georgia, which is roughly 1000 km southwest from Solvay (fig. S13). We detected the 0,1 congener in the downwind Merrimack sample (Fig. 3A) and no other congeners, and we detected no ClPFPECAs in the remote Conyers sample. The 0,1 congener is the most widely dispersed (Fig. 3B and Table 1), and the New Hampshire sample, some 450 km removed, plots closely proximate to the regression line for the 0,1 congener in New Jersey samples as a function of distance to Solvay (Fig. 3A). However, whether this New Hampshire 0,1-congener detection is from Solvay or some unknown source requires more study.

Given the role of Solvay as potentially the dominant or sole source of ClPFPECAs in our study, plots of legacy PFCAs against ClPFPECAs potentially guide which, if any, legacy PFCAs remain diagnostic of pre-Stewardship Solvay releases. Plotting concentrations of each legacy PFCA, chain lengths C4 (perfluorobutanoic acid) through C13 [perfluorotridecanoic acid (PFTrA)], against the sum of ClPFPECAs in fig. S14 shows three samples from closely proximate to Solvay that are high in ClPFPECAs also are high in C9, C11, and C13 PFCAs. On the basis of this observation, C9, C11, and C13 were regressed against distance from Solvay. Results of these regressions indicated that C9 is not correlated with distance from Solvay, but consistent with the PCA (fig. S12), C11 (P = 1.2 × 10^{-3}) and C13 (P = 1.7 × 10^{-2}) were statistically related with distance from Solvay (Table 1 and

fig. S15). The seeming inconsistency of C9 plotting anomalously in fig. S14 but not being statistically related to distance from Solvay is likely due in large part to the relatively much higher mobility of C9 than C11 and C13 in soils. For example, in a study of PFCAs in Decatur, Alabama, soils, Washington et al. (18) reported deep-to-surface soil ratios for C9 as high as 50-fold that of C11 or C13, suggesting much higher rates of loss for C9 than C11 and C13 from surface soils through leaching and percolation.

Although figs. S14 and S15 and Table 1 suggest a relationship of C11 and C13 with Solvay, considerable spread remains in the data (fig. S15), perhaps reflecting noise imparted from other sources. The majority of all environmental releases of PFCAs longer than C8 from 1951 to 2015 arose from fluorotelomer- and C9-based products (19). According to smog-chamber experiments (20) and global-scale modeling that used a complex suite of kinetic constants estimated from literature (21), atmospheric oxidation of n:2FTOHs (where n is an even integer and FTOHs are fluorotelomer alcohols) yields roughly equimolar nPFCAs and (n+1)PFCAs or preferentially nPFCAs in urban areas where nitrogen oxides can be elevated. In soils, microbially mediated degradation of n:2FTOHs has been shown to proceed through beta oxidation to yield dominantly nPFCAs (22, 23). Consistent with these studies, in their global soil survey, Rankin et al. (24) reported that C8/C9

[nPFCA/(n+1)PFCA] ratios commonly fall in roughly equimolar to dominantly C8 (nPFCA) range and argued atmospheric or soil degradation of fluorotelomers as a dominant mode of PFCAs occurrence globally. Given (i) historical production and use of fluorotelomers at the large-scale New Jersey Chemours facility, (ii) the generally prevalent contribution of fluorotelomers to C10 and C12, and (iii) atmospheric and soil fluorotelomer-degradation stoichiometry favoring roughly equimolar or dominantly even-chain PFCAs, the difference of nPFCAs minus (n+1)PFCAs, (C11 + C13) – (C10 + C12), has the potential to deconvolute potential signals from Solvay and Chemours for these legacy PFAS. Large positive excesses in this difference suggest direct release of C11 and C13 PFCAs, whereas near-zero or negative values of this difference would be consistent with atmospheric or soil degradation of fluorotelomer precursors as a source.

Applying the difference (C11 + C13) – (C10 + C12) to our New Jersey soil data accentuates signal to noise in that the strength of correlation with distance from Solvay (fig. S16) increases nearly an order of magnitude beyond that of C11 or C13 alone, with P = 4.5 × 10^{-4} (Table 1). (C11+C13) – (C10+C12) is plotted in fig. S17 as a function of the sum of ClPFPECAs, illustrating a relationship significant at P = 4.0 × 10^{-5} and bolstering that these parameters reflect a common mode of occurrence: airborne transport.
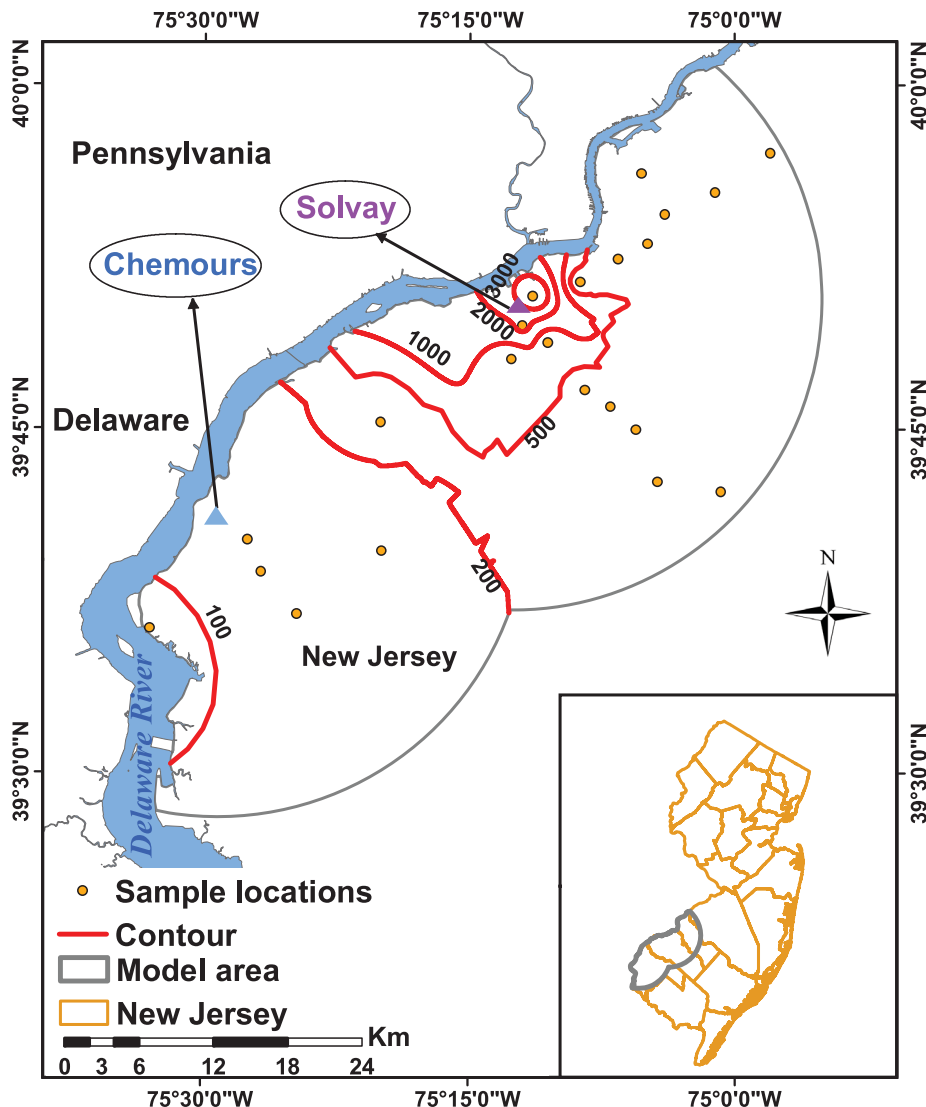
Fig. 4. Geographic distribution. Shown are ΣClPFPECAs in surface soils (picograms/gram). Contour lines were generated by using an algorithm in ArcMAP 10.6.1 that weighted the five nearest data points according to inverse-square distance. Despite some geographic sporadicity in the data and numerical artifacts where data are sparsely spaced, taken as a group the contours depict a clear pattern of increasing ΣClPFPECAs with proximity to Solvay.

Contours of the difference (C11 + C13) – (C10 + C12) are mapped in fig. S18. The resulting pattern depicts a strongly expressed positive anomaly focusing on Solvay as well as a negative anomaly proximate to Chemours, a pattern that is consistent with the reasoning above (fig. S18). These results are consistent with values reported in Rankin et al. (24) in that three of four samples collected ~20 km southeast of Chemours calculate to negative values for the difference (C11 + C13) – (C10 + C12). Taken altogether then, the difference (C11 + C13) – (C10 + C12) evidently fingerprints two potential PFAS sources in concert by accentuating differences in mode of occurrence: direct odd-chain PFCA release from the Solvay facility versus fluorotelomer degradation in the atmosphere or soil from the Chemours facility.

Here, we have reported tentative identification of 10 ClPFPECA congeners distributed across an expansive breadth of soils in densely populated New Jersey and likely beyond. In light of these findings, numerous near-term pressing uncertainties merit investigation, including the presence and mobility of the congeners in soil profiles, in surface and ground waters, in vegetation (such as agricultural crops), and in animals including humans, as well as whether there is evidence that these ClPFPECAs degrade in the environment. In the longer term, investigation of whether these ClPFPECAs might be toxic is prudent.

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SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/368/6495/1103/suppl/DC1
Materials and Methods
Supplementary Text
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Tables S1 to S5
References (27, 28)

Science

Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils

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Perfluorocarbons' path into soils

Covering carbon chains with fluorines has produced a variety of useful nonstick coatings. However, growing concern about the toxicity and extraordinary environmental persistence of the underlying compounds is spurring a search for alternatives. The precise structure of these next-generation alternatives often remains a trade secret. Washington *et al.* sampled soils in New Jersey and then used mass spectrometry to assign plausible structures—incorporating chlorine and ether segments into the CF$_2$ chain—to compounds that appear to have emanated from their manufacture (see the Policy Forum by Gold and Wagner). The data can inform in-depth studies of these compounds' environmental transport and persistence.
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