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Supplementary Material for

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

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METHODS

Sampling campaign: As part of efforts to elucidate sources and distribution of per- and poly-fluoroalkylate substances (PFAS) in New Jersey, in October and November 2017 the NJ Department of Environmental Protection (NJDEP) collected surface-soil samples. For this survey, twenty-four samples were collected in the vicinity of (mostly along transects) two industrial sites in southern New Jersey, Solvay (West Deptford Township) and Chemours (Pennsville Township), with an additional two soil samples collected in remote locations within the state. The sample transects were oriented parallel to dominant downwind directions, as recorded at nearby Philadelphia International Airport, from each facility (Fig. S1). Sampling sites generally were on public lands that have not experienced obvious disturbance. Two "background samples," intended to represent typical soils in New Jersey that are remote from Solvay and Chemours, were collected from the central and northern areas of the state, including near the northern state border with New York. Sample locations are depicted in Figure S1 and summarized in Table S1.

At each site, surface soil samples were collected, generally ranging over depth from 0 cm to roughly 10 cm, using methanol-washed stainless-steel spades. Each surface soil sample consisted of soil collected at three subsample locations within about a one-meter area; first pre-mixed in the holes prior to transfer to the sample container. The three subsamples were roughly equidistant from each other in a short transect or equilateral triangle and were collected after removal of the surface vegetation. The location of each sample site was recorded using a GPS unit at the time of sample collection. Two QA/QC field duplicates and two field blanks were also collected: field blanks were collected by pouring clean sand over a sampling spade and into an empty sample bottle. Samples were stored in high-density polyethylene sample containers with unlined caps, which were stored in coolers on ice with completed chain-of-custody forms.

These samples were sent to a laboratory at the U.S. Environmental Protection Agency, Office of Research and Development (EPA/ORD) located in Athens, Georgia for analysis.

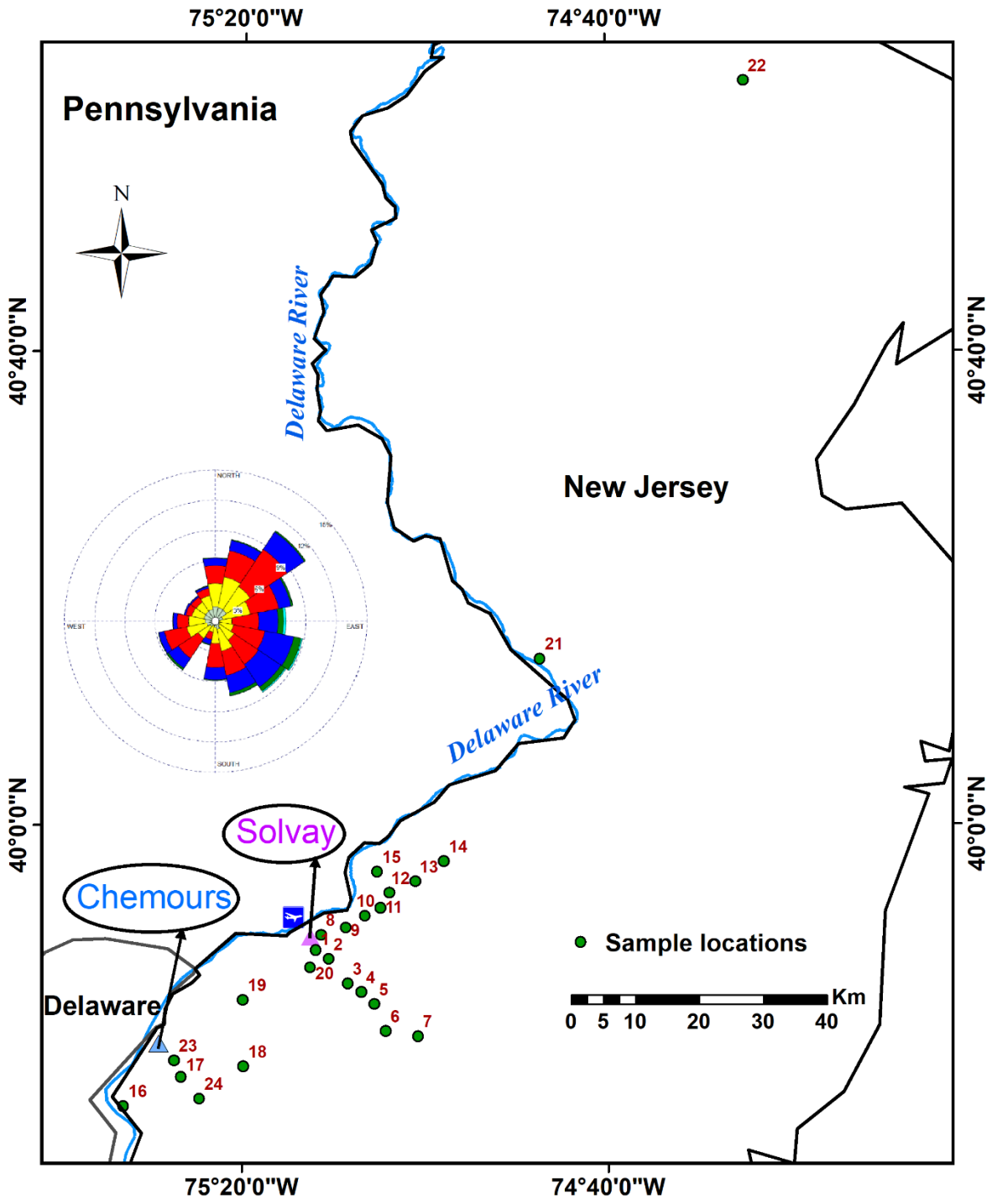


Figure S1: Soil sampling locations. The wind rose depicted in the western field represents data collected from the Philadelphia International Airport (jet icon).

Table S1: Soil sampling locations

Site Designation	Latitude (degrees)	Longitude (degrees)	UTM Distance from Solvay (km)	UTM Distance from Chemours (km)	Municipality or Township	County
1	39.826	-75.200	2.233	28.610	West Deptford Twp.	Gloucester
2	39.813	-75.176	4.498	29.725	West Deptford Twp.	Gloucester
3	39.779	-75.141	9.354	31.073	Deptford Twp.	Gloucester
4	39.767	-75.117	11.718	32.694	Washington Twp.	Gloucester
5	39.750	-75.093	14.499	34.299	Monroe	Gloucester
6	39.712	-75.073	18.802	35.530	Washington Twp.	Gloucester
7	39.705	-75.013	22.892	40.619	Monroe	Gloucester
8	39.847	-75.190	1.723	30.569	West Deptford Twp.	Gloucester
9	39.857	-75.145	5.711	34.401	West Deptford Twp.	Gloucester
10	39.874	-75.110	9.173	37.959	Bellmawr	Camden
11	39.885	-75.082	11.844	40.635	Mt. Ephraim	Camden
12	39.906	-75.066	14.160	43.103	Haddon Twp.	Camden
13	39.922	-75.018	18.562	47.465	Cherry Hill	Camden
14	39.951	-74.966	23.985	52.918	Moorestown	Burlington
15	39.936	-75.088	14.613	43.481	Camden City	Camden
16	39.605	-75.550	39.409	11.209	Pennsville Twp.	Salem
17	39.646	-75.445	29.788	6.274	Mannington Twp.	Salem
18	39.662	-75.332	22.791	13.674	Pilesgrove Twp.	Salem
19	39.755	-75.333	14.441	14.817	Woolwich Twp.	Gloucester
20	39.801	-75.210	4.781	26.519	East Greeenwich Twp.	Gloucester
21 (bkgd)	40.236	-74.790	56.357	84.656	Trenton	Mercer
22 (bkgd)	41.049	-74.410	149.947	176.042	West Milford	Passaic
23	39.669	-75.458	28.759	3.572	Mannington Twp.	Salem
24	39.616	-75.412	30.663	10.717	Mannington Twp.	Salem
New Hampshire	42.901	-71.463	462		Merrimack	Hillsborough
Georgia	33.764	-83.993	1034		Conyers	Rockdale
Solvay	39.845	-75.212	0.000	28.993	West Deptford Twp.	Gloucester
Chemours	39.693	-75.486	28.993	0.000	Pennsville Twp.	Salem

Sample preparation & extraction: The extraction method used in this study is based on previous methods (*24, 26*), that have been shown to recover roughly 100% of PFOA, perfluorodecanoic acid (PFDA; C10) and perfluorododecanoic acid (PFDoDA; C12) in spike-and-recovery experiments (*26*).

Briefly, samples received in the laboratory were sieved in methanol-washed (MeOH-) 2-mm stainless-steel (SS) sieves. Each soil was extracted in triplicate with ~2 g (dry weight) samples transferred into MeOH-washed polypropylene copolymer (PPCO) centrifuge tubes and sealed with PPCO caps. The soil samples were spiked with $^{13}C_8$-labeled perfluorooctanoate (M8C8) as a recovery standard. An aliquot of 2M sodium hydroxide prepared in polished 18 MΩ water (PW) and 90:10 acetonitrile:PW (ACN:PW) solution were mixed into the soils by vortexing for 15 to 30 s, sealed with caps and Parafilm, and then sonicated in an ice bath for 60 min. Next, the samples were mounted onto a LabQuake rotisserie mixer and rotated overnight (~15 h) at 8 revolutions per minute then centrifuged at 36.6 kG (17,500 rpm) and 18 to 22 ºC for 15 min. The supernatants were decanted into glass vials and a second round of 90:10 ACN:PW extraction performed on the soils. The two supernatants were combined in the glass vial and blown to near dryness under 0.2 µm filtered air in a solid-phase-extraction (SPE) manifold. The extract residues were cleaned by dissolution in tetrabutyl ammonium hydrogen sulfate (TBAS), extracted into methyl-tert-butyl ether (MTBE) by vortexing, and stored in a freezer overnight. In the morning, the MTBE was decanted from the frozen TBAS solution into pre-weighed glass vials and the TBAS solution was extracted again with a second aliquot of MTBE. Combining the MTBE fractions, the extracts in the glass vials were blown to dryness in the SPE assembly. The glass vials were re-weighed and the dried extracts reconstituted with a 1 mL aliquot of 60:40 ACN:PW containing 100 pg/g of mass-labeled matrix internal standards as described in previous papers (*26, 18*). The glass vials were weighed a final time prior to filtering with 0.2 µm nylon filters.

Analytical: Samples were first analyzed by liquid chromatography/mass spectrometry using a Waters Corporation (Milford, Massachusetts) Acquity ultra-performance liquid chromatograph (UPLC) flowing to a Waters Xevo quadrupole time-of-flight (QToF) mass spectrometer (MS), introduced through negative electrospray ionization (ESI). The UPLC was operated at Q=0.15 ml/min, linearly ramping from 20/80 ACN/H_2O, having 0.1% formic acid, to 90/10 ACN/H_2O over 20 minutes. Chromatographic separation was performed using an Acquity BEH C18 column (1.7 mm, 2.1 x 50 mm) at 35 ºC. The QToF was mass calibrated the same day as all published results using sodium formate. Leucine enkephalin was injected every 30 seconds during analytical runs as a mass reference. Collision energy was ramped from 11 to 25 V. Initial runs were performed in MS^e mode.

Observing classic ^{35}Cl:^{37}Cl = 3:1 precursor and fragments spectra, and using mass-defect (*7*) and carbon-isotopic (*10*) data filtering, anomalous molecular features were tentatively identified as a PFAS (Figure 1) reported in literature based on patents as the "Solvay compound" (*11, 12*), but not yet reported to be detected in the environment so far as we know. The conceptual model for our interpretation was that the ESI induced in-source loss of –(CF_2)COOH

at the carboxylate terminus (Figure 1), and the detected masses reflected this loss. Based on this tentative identification, and literature reports on molecular structure, suspect screening was performed on the MS^e data to determine whether congeners of the compound might be present. Following this effort, tentatively identified congeners were confirmed on the QToF operating in MS/MS mode wherein the quadrupole was focused on suspected precursor m/z values, fragmented with ramped collision energy, then precursors and fragments isolated/detected in the ToF. Results of these efforts are depicted in Figures 2 and S2 for a soil sample collected from adjacent to the Solvay facility (Soil Sample SS8). As a group we call these compounds chloroperfluoropolyether carboxylates (ClPFPECAs) and we identify specific congeners by their perfluoro-ethyl group, perfluoro-propyl group (e,p) count.

Informed by the fragmentation patterns of the suspected screening, we developed a method for routine analysis on a Waters Corporation (Milford, MA) Acquity UPLC coupled to a Quattro Premier triple-quadrupole mass spectrometer operated in negative electrospray ionization mode. Chromatographic separation was performed using an Acquity BEH C18 column (1.7 mm, 2.1 x 100 mm) at 35 ^{o}C with a Waters frit guard disc (0.2 mm, 2.1 mm). An LC/MS/MS method is desirable for analysis of larger numbers of samples because LC/MS/MS analyses are less labor intensive than QToF or similar high-resolution instruments, data files are less voluminous and these instruments are available in more laboratories than are high-resolution MS instruments. Analytical details of this LC/MS/MS method, which are transferable to similar systems with minor modification, are summarized in Table S2 and an example output is depicted in Figure S3.

Semi-quantitative concentration estimates of ClPFPECAs were generated to allow comparison of relative amounts detected amongst samples by normalizing ClPFPECA LC/MS/MS peaks to the peak area of the mass-labeled internal matrix standard of $^{13}C_5$-PFNA added to all extracts at 99.4 pg/g and expressing sample concentrations as "pg/g as C9." We semi-quantitated these ClPFPECA data following the procedure in Rankin et al. (*24*) in which the three extraction-replicate values of each analyte were compared to the process blanks using a Student's t test. When the t statistic exceeded the critical t(α=0.001) we designated these values as greater than the limit of semi-quantitation and report these values in green fields. When the t statistic exceeded the critical t(α=0.05) but was less than t(α=0.001) we designated these values as greater than the limit of reliability and report these values in yellow fields.

The soil extracts were quantitated for perfluorocarboxylates (PFCAs) using the same Waters Acquity UPLC coupled to a Quattro Premier triple-quadrupole mass spectrometer described above, operated in negative electrospray ionization mode. Instrumental parameters, methods, calibration and mass-labeled matrix internal standards were detailed in earlier work (*26, 27*). We performed quantitation for PFCAs following the method of Rankin et al., as summarized above for the ClPFPECAs, using a t test to compare triplicate extraction reps of each sample to process blanks. When the t test statistic exceeded the critical t(α=0.001) we designated these values as greater than the limit of quantitation and report these values in green fields. When the t test statistic exceeded the critical t(α=0.05) but was less than t(α=0.001) we

designated these values as greater than the limit of detection and report these values in yellow fields.

The analytical concentrations of ClPFPECAs and PFCAs in our soil extracts were expressed as soil concentrations by multiplying extract concentrations by extract mass and dividing by dry soil mass.

Table S2: LC/MS/MS analytical parameters for ClPFPECAs

Parameter	Chloro perfluoro polyether carboxylate congeners by group number of ethyl,propyl										Legacy compounds	
Ethyl,Propyl	**1,0**	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**4,0**	**0,3**	**PFOA**	**PFNA**
Molecular Mass	411.9372	461.9340	527.9257	577.9225	627.9193	643.9142	693.9110	743.9078	759.9028	793.9046	413.9737	463.9705
Anion Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{13}ClF_{24}O_7$	$C_{14}ClF_{26}O_6$	$C_8F_{15}O_2$	$C_9F_{17}O_2$
Precursor Mass	316.9427	366.9395	432.9312	482.9280	532.9249	548.9198	598.9166	648.9134	664.9083	698.9102	412.9659	462.9627
Precursor Formula	$C_5ClF_{10}O_2$	$C_6ClF_{12}O_2$	$C_7ClF_{14}O_3$	$C_8ClF_{16}O_3$	$C_9ClF_{18}O_3$	$C_9ClF_{18}O_4$	$C_{10}ClF_{20}O_4$	$C_{11}ClF_{22}O_4$	$C_{11}ClF_{22}O_5$	$C_{12}ClF_{24}O_4$	$C_8F_{15}O_2$	$C_9F_{17}O_2$
Fragment Mass	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	366.9395	532.9249	368.9761	418.9729
Fragment Formula	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	$C_6ClF_{12}O_2$	$C_9ClF_{18}O_3$	$C_7F_{15}O$	$C_8F_{17}O$
Example Elution Time (m)	2.3	2.6	3.4	3.9	4.6	4.9	5.5	6.1	6.4	6.7	2.35	2.91
Dwell time (s)	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Cone potential (V)	12	12	12	12	12	12	12	12	12	12	14	15
Collision energy (V)	10	10	10	10	10	10	10	10	10	10	10	11

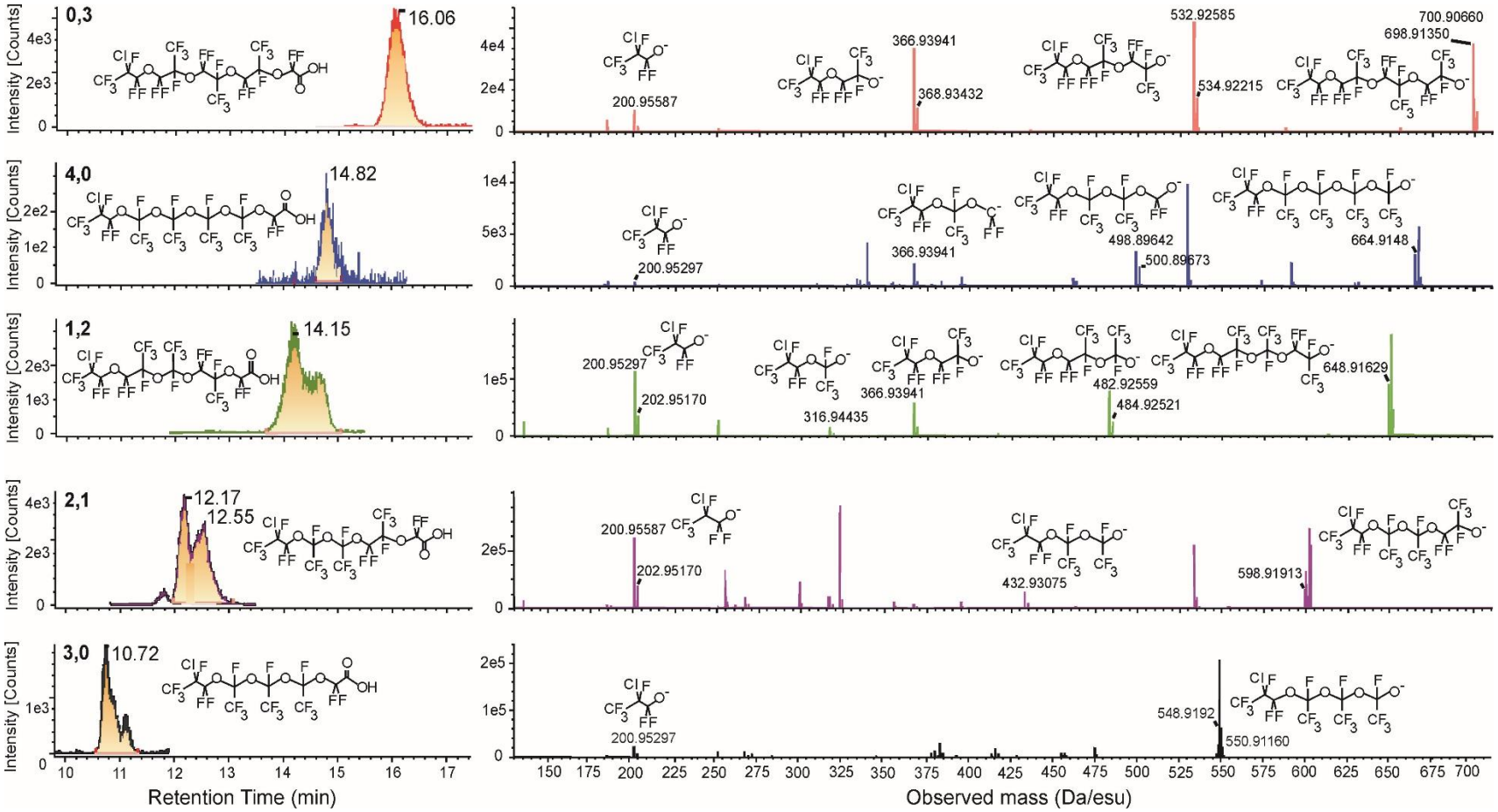


Figure S2: Mass chromatograms (MS/MS mode), spectra and precursor/fragment structures of five larger ClPFPECA congeners detected in NJ samples, identified in the upper left of the chromatograms by ethyl#,propyl#. The smallest congener, 1,0, was not detected in soil samples on QToF but likely was detected in soils on tandem mass spectrometer (see text) and in water samples (report in preparation). Chromatogram peaks consist of signal from precursors and selected major fragments. Note congeners elute in order according to molecular mass, small to large. Also note on major spectra the diagnostic mono-chlorine signal of 3:1 for ^{35}Cl:^{37}Cl.

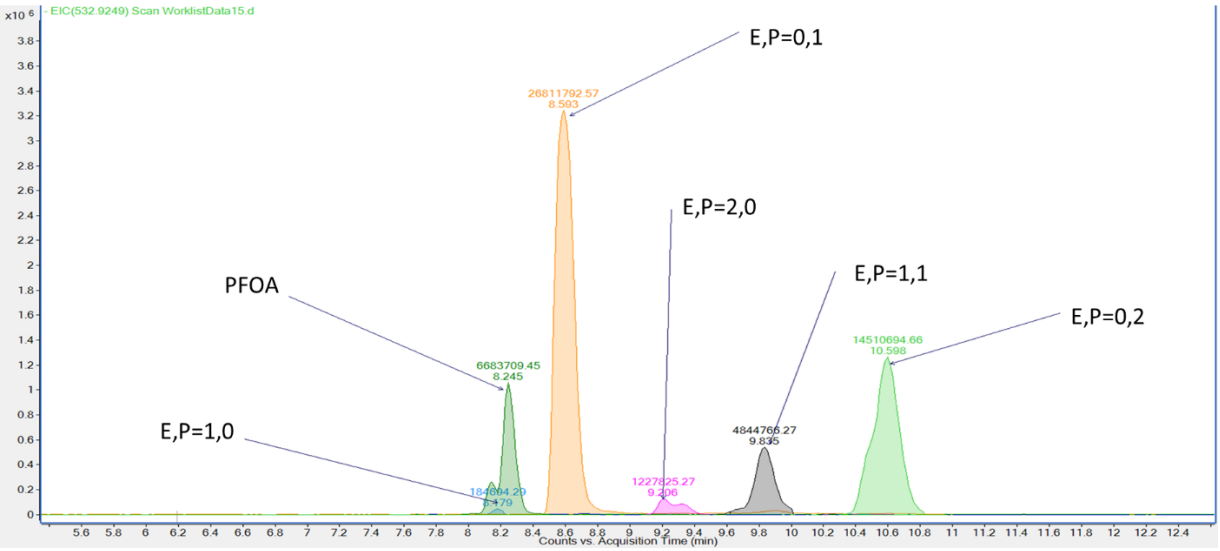


Figure S3: MS^e mass chromatogram for Bormida River, Italy sample: In-house MS^e results for a water sample from the Bormida di Spigno River, downstream of Solvay Specialty Polymers Italy S.p.A. Five ClPFPECA congeners are identified by ethyl#,propyl#, plus perfluorooctanoic acid (PFOA) for reference.

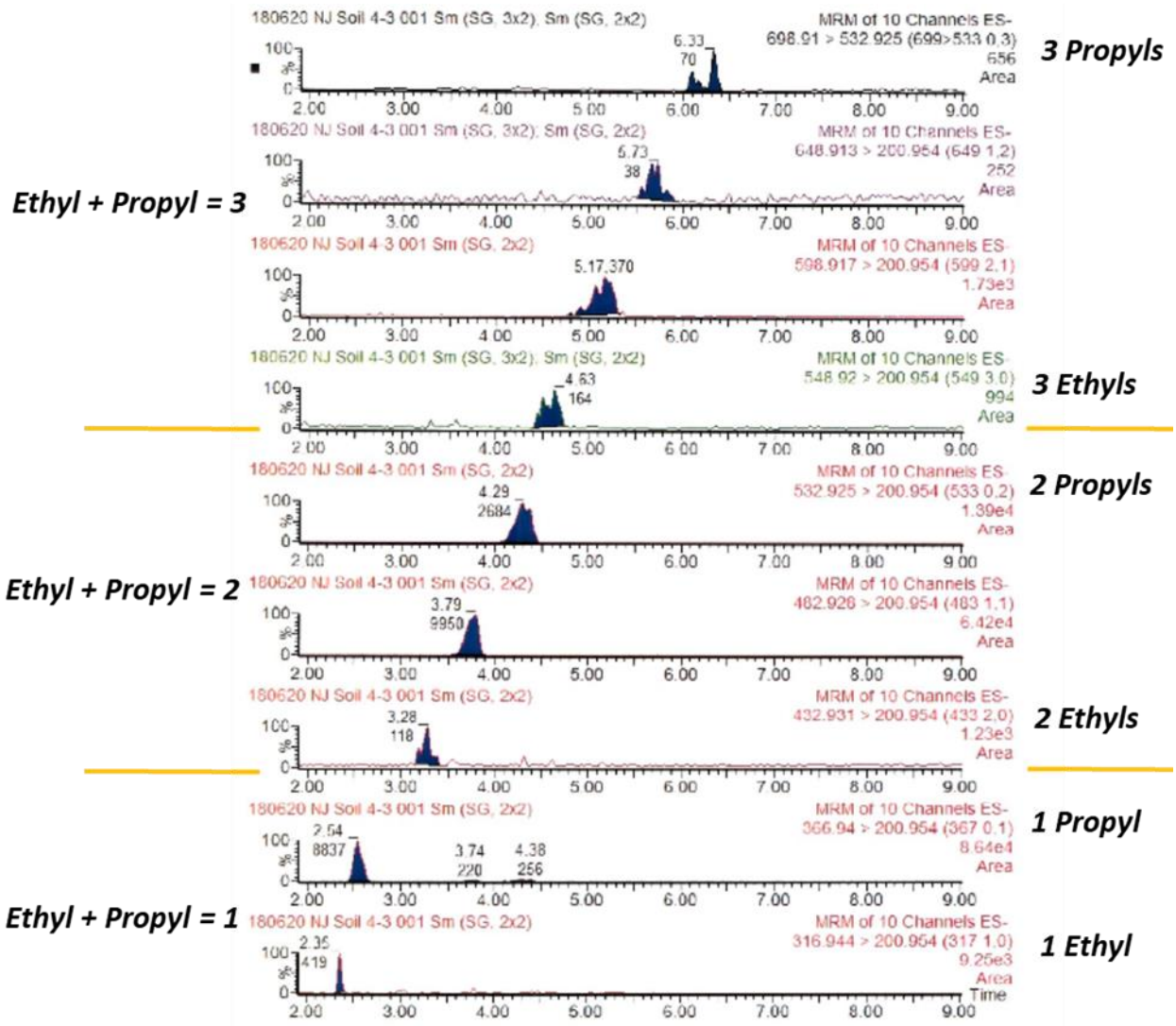


Figure S4: Example tandem mass-spectrometer chromatograms of nine ClPFPECA congeners detected in NJ samples, Soil Sample SS8 shown here. Note congeners elute in order according to molecular mass, small to large.

RESULTS

Quality assessment: The tentative identification of these molecular features as ClPFPECAs on QToF was based upon factors including i) presence of mass spectra of isotopologues differing by two Da at a ratio of 3/1, characteristic of the presence of a single chlorine, ii) presence of mass spectra of isotopologues differing by one Da at ratios consistent with inferred carbon numbers for each congener (*10*), and iii) the primary tool of high-resolution observed masses being closely consistent with theoretical masses of the tentatively identified compounds. Table S3 documents the consistence of precursor observed masses with theoretical masses. In every case except the 4,0 congener, observed and theoretical masses agree within 5 ppm mass error; mass error for 4,0 is less than 10 ppm. Figure SS4 plots mass error of all precursors and fragments as a function of signal intensity and illustrates that the relatively large mass error of 4,0 likely is due to its low signal intensity.

On the tandem mass spectrometer, these ClPFPECA compounds were tentatively identified by criteria including: i) internal consistence among samples for elution time, ii) molecular-precursor mass, iii) molecular-fragment mass, iv) signal-to-noise contrast, and v) temporal continuity of signal.

During the ClPFPECA analytical run we analyzed: i) ten process blanks (empty tubes subjected to the entire extraction process) which returned non-detects for all congeners in all ten blanks; and ii) two field blanks (sand transported to the field opened and returned), both of which were non-detect for all congeners.

To assess the repeatability of our ClPFPECA semi-quantitations, we analyzed one of three reps for all 24 samples ~1/2 year removed from our semi-quantitation values. Of 133 values exceeding the limit of semi-quantitation across all congeners, 122 or 92% fell within 50% (relative percent difference; RPD).

Also a geographic control soil from Conyers, GA, some 1000 km SW of the New Jersey Solvay facility, was analyzed for ClPFPECAs; no congener peaks were detected in the Conyers, GA soil.

To assess quality of our PFCA quantitations:

1) we calculated recovery of our $^{13}C_8$-PFOA recovery internal standard. For all soil extract reps, mean and standard deviation of $^{13}C_8$-PFOA recovery was $\bar{x} \pm 1SD = 0.99 \pm 0.09$ and for the process blanks it was $\bar{x} \pm 1SD = 0.97 \pm 0.18$ indicating excellent recovery.
2) check standards were run during the sample run. Of 91 values across 13 analytes (PFCA chain lengths C4-C14, C16 and C18), 84 values fell within 50% of nominal value, a compliance rate of 92%. Five of the seven check values falling outside of this range were the 11 pg/g (11 parts per trillion) standard, the lowest standard.
3) three reps were subjected to repeated measure. All analytes detected at >LOD fell within 50% (%RPD).

4) two field blanks (consisting of sand taken to the field, poured over a sampling spade into an empty bottle and returned to the laboratory) were analyzed. No analytes were detected in the field blanks in excess of the process blanks.

Table S3: Mass error for tentatively identified precursors run on QToF in MS/MS mode

Congener	Molecular Formula	Molecular Mass	Precursor Formula	Observed Mass	Exact Mass	Mass Error		Spectral Signal
		(Da)		(Da)	(Da)	(mDa)	(ppm)	(Counts)
0,1	$HC_8ClF_{14}O_4$	461.9340	$C_6ClF_{12}O_2$	366.9394	366.9395	0.090	0.245	1.4E+04
2,0	$HC_9ClF_{16}O_5$	527.9257	$C_7ClF_{14}O_3$	432.9307	432.9312	0.500	1.155	2.7E+03
1,1	$HC_{10}ClF_{18}O_5$	577.9225	$C_8ClF_{16}O_3$	482.9301	482.9280	2.090	4.328	5.5E+04
0,2	$HC_{11}ClF_{20}O_5$	627.9193	$C_9ClF_{18}O_3$	532.9259	532.9249	0.950	1.783	1.1E+06
3,0	$HC_{11}ClF_{20}O_6$	643.9142	$C_9ClF_{18}O_4$	548.9192	548.9198	0.580	1.057	1.2E+04
2,1	$HC_{12}ClF_{22}O_6$	693.9110	$C_{10}ClF_{20}O_4$	598.9191	598.9166	2.530	4.224	1.7E+04
1,2	$HC_{13}ClF_{24}O_6$	743.9078	$C_{11}ClF_{22}O_4$	648.9111	648.9134	2.320	3.575	4.5E+03
4,0	$HC_{13}ClF_{24}O_7$	759.9028	$C_{11}ClF_{22}O_5$	664.9148	664.9083	6.473	9.735	2.9E+03
0,3	$HC_{14}ClF_{26}O_6$	793.9046	$C_{12}ClF_{24}O_4$	698.9081	698.9102	2.110	3.019	4.4E+04

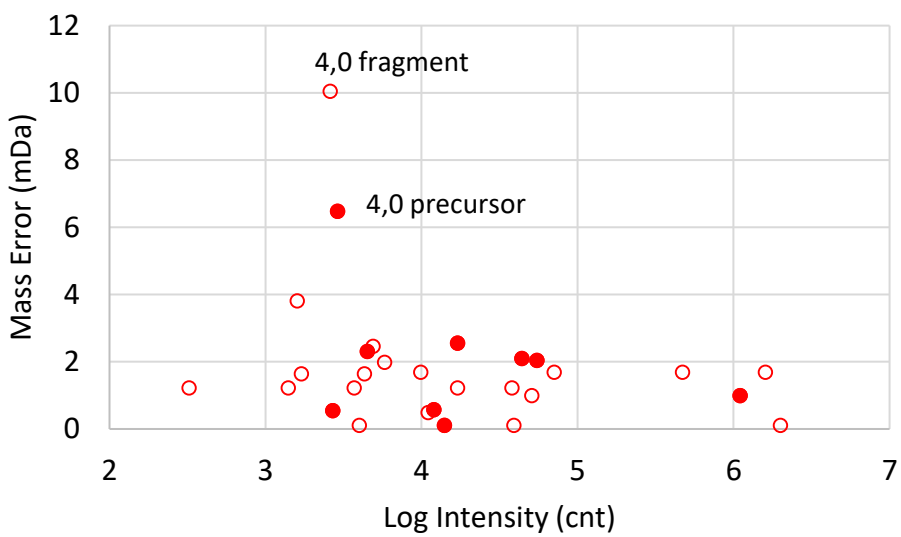


Figure S5: QToF mass error as a function of signal intensity. Filled circles represent precursors, open circles represent fragments. Mass error does not exceed 4 mDa for any data having signal intensity $\geq 10^4$.

Data tabulation: The ClPFPECA data are summarized in Table S4. Values exceeding the limit of semi-quantitation, as defined above, are reported in green fields. Values falling in the range below limit of semi-quantitation but exceeding the limit of reliability are reported in yellow fields. Values that did not statistically exceed process blanks at α=0.05 are reported in red and can be regarded as best estimates for a censored dataset, albeit uncertain in detection status.

The PFCA data are summarized in Table S5. Values exceeding the limit of quantitation, as defined above, are reported in green fields. Values falling in the range below limit of quantitation but exceeding the limit of detection are reported in yellow fields. Values that did not statistically exceed process blanks at α=0.05 are reported in red and can be regarded as best estimates for a censored dataset, albeit uncertain in detection status. Two values for C11 (PFUA) that were detected in excess of our highest standard are reported in blue fields. Note that C16 (PFHxDA) and C18 (PFODA) are considered estimated values. Also note that fraction linearity of C8 (PFOA) and C9 (PFNA) is considered qualitative, consistent with past convention (*24*).

Table S4: Semi-quantitative analytical results for soil ClPFPECAs (pg as C9/g dry soil)

Sample Designation	Summary Statistic	1,0 (pg C9/g)	0,1 (pg C9/g)	2,0 (pg C9/g)	1,1 (pg C9/g)	0,2 (pg C9/g)	3,0 (pg C9/g)	2,1 (pg C9/g)	1,2 (pg C9/g)	4,0 (pg C9/g)	0,3 (pg C9/g)
SS1	Mean	1.8	749.3	14.5	1503.3	668.8	39.9	84.4	7.1	0.0	24.6
	Stand Dev	0.6	100.9	0.5	84.9	28.3	1.4	10.7	1.8	0.0	7.6
	COV	0.353	0.135	0.037	0.056	0.042	0.036	0.127	0.254		0.311
SS2	Mean	0.0	77.9	2.1	216.8	95.4	5.4	11.5	0.9	0.0	3.5
	Stand Dev	0.0	4.5	0.6	40.4	22.2	1.8	2.3	0.4	0.0	0.6
	COV		0.057	0.294	0.186	0.233	0.338	0.203	0.410		0.177
SS3	Mean	1.2	68.9	1.3	107.0	62.6	3.1	13.3	1.7	0.0	4.2
	Stand Dev	2.1	2.8	0.9	8.0	15.4	1.3	1.6	0.1	0.0	1.7
	COV	1.732	0.040	0.729	0.075	0.247	0.414	0.117	0.079		0.407
SS4	Mean	25.6	379.9	5.7	454.5	133.0	6.7	15.2	0.9	0.0	3.7
	Stand Dev	2.5	37.4	0.6	63.7	8.4	0.7	1.9	0.2	0.0	2.1
	COV	0.099	0.099	0.101	0.140	0.063	0.107	0.124	0.276		0.564
SS5	Mean	0.0	156.0	1.2	123.8	41.8	1.5	5.3	0.30	0.0	1.2
	Stand Dev	0.0	13.0	0.5	13.0	9.0	0.7	0.8	0.38	0.0	0.4
	COV		0.083	0.457	0.105	0.215	0.442	0.146	1.254		0.377
SS6	Mean	0.0	104.3	1.6	143.7	53.3	1.6	6.2	0.07	0.04	1.2
	Stand Dev	0.0	9.5	0.2	23.0	8.1	1.3	1.9	0.13	0.06	0.6
	COV		0.091	0.120	0.160	0.152	0.790	0.311	1.732	1.732	0.481
SS7	Mean	0.0	98.3	1.3	44.4	14.3	1.0	1.1	0.0	0.0	0.08
	Stand Dev	0.0	8.0	0.2	2.4	2.6	0.6	0.9	0.0	0.0	0.13
	COV		0.081	0.149	0.055	0.184	0.579	0.868			1.732
SS8	Mean	0.87	510.0	16.5	2234.4	956.0	64.6	159.6	20.3	0.0	47.6
	Stand Dev	1.51	71.1	2.4	251.9	102.1	12.6	15.8	3.5	0.0	6.0
	COV	1.732	0.139	0.143	0.113	0.107	0.195	0.099	0.171		0.125
SS9	Mean	0.49	102.1	1.1	82.1	42.2	1.7	8.3	0.9	0.0	3.8
	Stand Dev	0.85	2.9	0.6	3.9	3.6	0.1	0.9	0.2	0.0	0.3
	COV	1.732	0.029	0.536	0.048	0.084	0.046	0.106	0.175		0.072
SS10	Mean	0.25	38.1	0.51	43.2	24.9	1.2	5.5	0.70	0.0	1.2
	Stand Dev	0.44	5.1	0.60	5.8	5.3	0.1	2.2	0.64	0.0	0.4
	COV	1.732	0.134	1.169	0.134	0.215	0.104	0.393	0.903		0.316
SS11 Mix	Mean	0.0	110.4	1.5	134.5	41.3	2.4	5.0	0.5	0.0	0.89
	Stand Dev	0.0	14.2	0.9	40.2	14.7	2.5	2.5	0.0	0.0	0.84
	COV		0.129	0.604	0.299	0.355	1.035	0.490	0.061		0.950
SS12	Mean	0.0	98.9	1.5	107.7	45.9	2.2	9.2	0.6	0.0	2.2
	Stand Dev	0.0	7.5	0.8	7.4	5.1	0.4	2.3	0.2	0.0	0.6
	COV		0.076	0.504	0.069	0.111	0.184	0.247	0.349		0.253
SS13	Mean	2.6	54.3	0.75	28.9	11.0	0.25	4.7	0.0	0.0	1.0
	Stand Dev	4.5	4.5	1.01	3.1	1.4	0.43	0.7	0.0	0.0	0.3
	COV	1.732	0.082	1.352	0.109	0.129	1.732	0.153			0.266
SS14	Mean	0.0	170.0	1.9	108.1	35.4	1.8	5.4	0.28	0.0	0.82
	Stand Dev	0.0	62.8	0.2	37.0	25.0	1.5	4.6	0.44	0.0	1.34
	COV		0.369	0.101	0.343	0.707	0.852	0.850	1.554		1.639
SS15	Mean	1.1	146.3	2.3	202.9	59.9	3.6	7.0	0.17	0.0	1.5
	Stand Dev	1.0	91.9	1.3	123.3	38.7	1.8	5.1	0.27	0.0	0.6
	COV	0.869	0.628	0.578	0.607	0.646	0.500	0.725	1.567		0.431
SS16	Mean	0.26	30.6	0.31	12.3	2.8	0.0	0.0	0.0	0.0	0.0
	Stand Dev	0.46	2.8	0.27	1.2	1.0	0.0	0.0	0.0	0.0	0.0
	COV	1.732	0.090	0.885	0.100	0.347					
SS17	Mean	0.31	27.3	0.23	23.0	12.2	0.6	1.6	0.0	0.05	0.07
	Stand Dev	0.53	3.3	0.40	3.4	3.0	0.5	1.4	0.0	0.08	0.12
	COV	1.732	0.122	1.732	0.146	0.244	0.868	0.886		1.732	1.732
SS18	Mean	0.11	16.7	0.0	22.8	7.5	0.0	0.8	0.02	0.03	0.11
	Stand Dev	0.20	2.5	0.0	2.8	1.2	0.0	0.7	0.04	0.05	0.20
	COV	1.732	0.147		0.121	0.155		0.867	1.732	1.732	1.732
SS19	Mean	0.28	75.2	1.4	101.5	41.7	2.6	8.3	0.7	0.05	1.7
	Stand Dev	0.48	47.6	0.5	33.9	19.0	1.3	5.0	0.5	0.08	1.0
	COV	1.732	0.633	0.339	0.334	0.455	0.497	0.599	0.666	1.732	0.563
SS20	Mean	0.37	91.6	1.2	124.1	44.5	2.4	9.1	0.4	0.05	1.4
	Stand Dev	0.64	3.2	0.7	14.1	3.0	0.4	1.4	0.1	0.09	0.6
	COV	1.732	0.035	0.620	0.113	0.067	0.153	0.158	0.168	1.732	0.414
SS21	Mean	0.0	40.3	0.13	34.3	10.1	0.27	2.2	0.0	0.0	0.0
	Stand Dev	0.0	4.4	0.22	7.5	2.0	0.48	2.2	0.0	0.0	0.0
	COV		0.109	1.732	0.220	0.202	1.732	1.011			
SS22	Mean	0.0	19.1	0.20	15.5	4.2	0.0	0.0	0.0	0.0	0.0
	Stand Dev	0.0	2.4	0.34	4.0	1.4	0.0	0.0	0.0	0.0	0.0
	COV		0.124	1.732	0.260	0.334					
SS23	Mean	0.0	125.8	2.4	162.0	50.8	2.7	6.8	0.13	0.0	0.44
	Stand Dev	0.0	20.4	1.2	32.5	10.4	1.3	2.9	0.23	0.0	0.48
	COV		0.162	0.511	0.200	0.206	0.491	0.423	1.732		1.089
SS24	Mean	1.7	38.8	0.0	35.0	11.2	0.30	2.27	0.0	0.0	0.0
	Stand Dev	1.0	5.9	0.0	6.2	1.6	0.52	2.03	0.0	0.0	0.0
	COV	0.573	0.151		0.176	0.138	1.732	0.894			

Table S5: Quantitative analytical results for soil PFCAs (pg/g dry soil)

Sample Designation	Summary Statistic	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUA	PFDoA	PFTrA	PFTeA	PFHxDA (*)	PFODA (*)	Percent Linear	
		pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	PFOA	PFNA
SS1	Mean	121.1	142.5	28.1	91.4	398.0	2714.7	381.0	5729.7	99.4	590.1	24.7	ND	ND	0.959	0.993
	St. Dev.	21.3	38.8		40.5	138.7	412.6	18.4		13.7	57.6	8.5			0.009	0.001
	COV	0.176	0.272		0.443	0.349	0.152	0.048		0.138	0.098	0.342			0.009	0.001
SS2	Mean	101.7	52.2	33.6	31.1	195.9	91.2	114.5	1477.2	64.7	153.2	24.9	ND	ND	0.948	0.915
	St. Dev.	75.7	30.5		12.7	100.9	15.3	12.2	162.4	19.9	24.6	5.5			0.006	0.045
	COV	0.745	0.583		0.409	0.515	0.168	0.107	0.110	0.308	0.161	0.220			0.006	0.049
SS3	Mean	148.7	153.5	94.6	159.3	422.2	770.0	580.9	1436.6	244.3	252.3	104.4	21.9	4.9	0.974	0.988
	St. Dev.	41.6	42.6	71.9	17.6	52.7	52.1	35.1	38.5	14.5	8.8	5.1	13.0		0.005	0.001
	COV	0.279	0.278	0.761	0.110	0.125	0.068	0.060	0.027	0.059	0.035	0.049	0.593		0.005	0.001
SS4	Mean	268.6	366.1	295.9	344.8	1068.2	2628.5	625.4	2768.8	183.1	326.3	81.6	ND	ND	0.975	0.995
	St. Dev.	496.6	209.6	283.0	167.8	683.1	1576.9	368.6	1609.4	110.5	189.8	49.7			0.004	0.000
	COV	1.849	0.573	0.956	0.487	0.640	0.600	0.589	0.581	0.604	0.581	0.610			0.004	0.000
SS5	Mean	111.7	178.3	78.7	131.7	243.8	691.1	231.4	824.9	60.9	85.6	28.0	ND	ND	0.976	0.992
	St. Dev.	36.6	31.1	70.6	13.5	49.3	140.5	28.8	91.8	9.9	8.4	7.4			0.001	0.004
	COV	0.328	0.175	0.897	0.103	0.202	0.203	0.125	0.111	0.162	0.099	0.265			0.001	0.004
SS6	Mean	119.0	245.4	62.8	101.7	295.3	765.5	277.9	1372.8	111.4	165.1	46.5	ND	ND	0.969	0.992
	St. Dev.	66.8	30.9	67.5	16.7	92.9	69.0	9.2	138.3	28.7	29.2	10.2			0.007	0.009
	COV	0.561	0.126	1.076	0.164	0.315	0.090	0.033	0.101	0.258	0.177	0.220			0.008	0.009
SS7	Mean	256.7	275.6	186.2	187.6	748.9	1215.1	256.4	810.1	63.3	91.6	39.9	ND	ND	0.970	0.989
	St. Dev.	114.3	28.6	74.6	22.6	145.4	81.6	24.1	41.1	19.5	2.5	3.5			0.007	0.005
	COV	0.445	0.104	0.401	0.121	0.194	0.067	0.094	0.051	0.307	0.028	0.089			0.007	0.005
SS8	Mean	69.4	53.3	6.2	37.7	72.4	295.1	324.4	6557.6	277.1	1277.0	71.5	1.7	3.6	0.968	0.994
	St. Dev.	44.4	15.1		12.9	48.2	26.7	51.6		56.2	292.6	15.5			0.005	0.007
	COV	0.639	0.283		0.341	0.665	0.090	0.159		0.203	0.229	0.216			0.005	0.007
SS9	Mean	102.7	103.6	58.0	91.2	161.6	521.8	207.1	1456.8	84.7	225.8	35.4	ND	ND	0.965	0.992
	St. Dev.	22.1	19.0	69.7	17.9	47.9	25.2	12.6	86.0	6.1	19.2	3.9			0.008	0.004
	COV	0.215	0.184	1.201	0.197	0.297	0.048	0.061	0.059	0.072	0.085	0.111			0.008	0.004
SS10	Mean	45.9	77.7	158.0	151.4	1900.6	286.0	261.8	794.4	100.2	104.1	39.8	ND	ND	0.951	0.984
	St. Dev.	24.7	16.6	70.8	16.9	58.3	19.4	6.6	89.6	6.0	9.2	5.3			0.004	0.013
	COV	0.538	0.213	0.448	0.112	0.031	0.068	0.025	0.113	0.059	0.088	0.134			0.004	0.013
SS11	Mean	191.9	176.3	155.5	100.0	316.8	784.0	421.7	1367.5	116.5	165.9	54.9	8.3	ND	0.958	0.995
	St. Dev.	40.6	137.3	103.8	17.5	115.3	59.3	113.5	423.6	33.9	46.9	21.7	5.1		0.008	0.001
	COV	0.212	0.779	0.668	0.175	0.364	0.076	0.269	0.310	0.291	0.283	0.395	0.607		0.008	0.001
SS12	Mean	88.8	171.0	136.8	130.5	573.4	445.1	268.0	655.4	119.9	97.4	47.5	ND	1.9	0.964	0.992
	St. Dev.	22.3	26.3	74.1	13.5	64.7	29.6	13.8	18.1	3.2	9.3	2.2			0.006	0.002
	COV	0.251	0.154	0.542	0.104	0.113	0.066	0.051	0.028	0.026	0.095	0.047			0.006	0.002
SS13	Mean	159.5	199.5	425.9	134.9	619.4	1145.6	311.9	1249.4	145.8	186.7	69.7	ND	ND	0.967	0.994
	St. Dev.	30.3	47.4	457.5	22.4	77.4	419.2	47.6	193.7	33.7	42.4	14.7			0.004	0.002
	COV	0.190	0.237	1.074	0.166	0.125	0.366	0.153	0.155	0.231	0.227	0.211			0.005	0.002
SS14	Mean	228.3	192.0	228.3	139.2	414.7	886.6	337.2	803.4	102.8	97.9	36.9	ND	0.4	0.988	0.996
	St. Dev.	117.4	57.4	144.6	63.6	230.9	490.0	63.6	61.5	14.0	13.5	12.1			0.007	0.001
	COV	0.514	0.299	0.633	0.457	0.557	0.553	0.188	0.077	0.136	0.138	0.327			0.007	0.001
SS15	Mean	152.9	212.9	254.7	163.1	599.2	614.3	473.0	3967.2	144.9	347.1	50.5	ND	0.1	0.987	0.996
	St. Dev.	126.9	130.8	202.6	125.3	479.6	362.3	303.3	2274.2	101.3	201.6	31.5			0.005	0.003
	COV	0.830	0.614	0.796	0.769	0.800	0.590	0.641	0.573	0.699	0.581	0.623			0.005	0.003
SS16	Mean	91.4	212.8	267.6	172.2	264.3	651.5	295.9	307.2	74.1	54.3	31.5	ND	ND	0.997	1.000
	St. Dev.	22.1	15.2	177.6	14.5	48.6	41.2	36.0	30.9	9.0	12.1	2.4			0.003	0.000
	COV	0.242	0.071	0.663	0.084	0.184	0.063	0.122	0.101	0.122	0.223	0.077			0.003	0.000
SS17	Mean	141.0	295.1	319.8	319.1	404.7	710.6	1458.7	1159.9	448.0	133.6	114.3	39.0	10.9	0.998	0.997
	St. Dev.	27.8	43.0	87.0	61.1	70.2	43.6	106.7	72.0	47.1	17.4	22.0	10.7		0.002	0.003
	COV	0.197	0.146	0.272	0.192	0.174	0.061	0.073	0.062	0.105	0.130	0.193	0.273		0.002	0.003
SS18	Mean	119.0	96.1	72.0	66.3	159.8	356.1	363.8	377.3	113.4	65.1	45.0	1.9	ND	0.994	0.997
	St. Dev.	89.3	19.8	68.3	14.3	46.8	33.1	33.7	27.0	3.2	2.3	7.7	3.6		0.005	0.004
	COV	0.751	0.206	0.949	0.216	0.293	0.093	0.093	0.071	0.029	0.035	0.171	1.910		0.005	0.004
SS19	Mean	143.3	150.0	72.6	68.3	150.5	337.3	192.6	543.5	83.8	78.7	38.0	ND	ND	0.979	0.965
	St. Dev.	89.9	84.3	108.3	36.1	136.3	363.3	28.4	78.3	23.1	21.2	15.4			0.035	0.032
	COV	0.627	0.562	1.491	0.528	0.905	1.077	0.147	0.144	0.276	0.269	0.406			0.036	0.033
SS20	Mean	65.1	121.3	101.9	56.4	92.7	475.0	192.4	1343.0	54.6	111.8	19.1	ND	ND	0.988	0.994
	St. Dev.	21.4	22.7	86.8	15.6	64.6	82.7	36.0	151.7	16.3	23.5	4.0			0.017	0.003
	COV	0.329	0.187	0.852	0.277	0.697	0.174	0.187	0.113	0.298	0.210	0.212			0.017	0.003
SS21	Mean	132.9	247.1	120.4	175.5	689.3	626.3	400.9	895.3	150.1	129.1	71.2	ND	3.3	0.988	0.973
	St. Dev.	48.8	61.8	84.2	46.0	75.5	85.8	33.4	16.2	5.7	7.6	7.4			0.008	0.023
	COV	0.367	0.250	0.699	0.262	0.110	0.137	0.083	0.018	0.038	0.059	0.104			0.008	0.023
SS22	Mean	760.0	621.5	88.6	292.2	1254.8	658.0	697.3	1023.0	447.3	300.5	257.1	75.9	86.5	0.970	0.975
	St. Dev.	120.1	173.0		49.5	74.8	48.6	28.3	29.3	30.0	39.4	44.1	47.3		0.011	0.031
	COV	0.158	0.278		0.169	0.060	0.074	0.041	0.029	0.067	0.131	0.171	0.623		0.011	0.032
SS23	Mean	282.9	380.9	226.1	445.5	330.3	446.3	1055.2	1076.2	525.3	203.2	251.5	105.6	30.8	0.989	0.925
	St. Dev.	203.7	64.5	74.7	108.7	64.3	96.3	127.3	163.9	93.6	36.5	49.3	37.3		0.006	0.049
	COV	0.720	0.169	0.330	0.244	0.195	0.216	0.121	0.152	0.178	0.179	0.196	0.354		0.006	0.053
SS24	Mean	256.7	424.7	493.2	425.9	892.2	731.4	755.3	843.8	199.4	87.3	70.9	1.4	ND	0.984	0.968
	St. Dev.	79.1	35.5	113.6	45.9	120.4	56.3	85.7	71.8	15.1	7.0	10.0			0.009	0.004
	COV	0.308	0.083	0.230	0.108	0.135	0.077	0.113	0.085	0.076	0.080	0.140			0.009	0.005

(*) Due to difficulties in analysis, PFHxDA and PFODA are considered estimates.

Scrutiny of ClPFPECA congeners: Some inconsistency exists in the literature regarding the position of the chlorine in ClPFPECAs. Following a self-reported, condensed structural formula in a Solvay Solexis submission to the European Food Safety Authority (*12*), Wang et al. (*11*) suggested a terminus of $ClFCCF_2CF_2O$-. However, in two synthesis papers, Solvay chemists Tonelli et al. (*13, 14*) describe the chlorine terminal moiety as having two structures, $F_3CCFClCF_2O$- for 70% of production and $ClFCCF(CF_3)O$- for 30% of production. While these moieties are identical in formula to Wang et al. (*11*) and EFSA (*12*), they differ slightly in structure. In our paper, we report the ClPFPECA structure consistently with Tonelli et al. (*13,14*). Also noteworthy, our MS fractionation patterns do not resolve such a minute level of detail as the structural alternatives described here.

Following the EFSA information (*12*), Wang et al. (*11*) reported expected ClPFPECA congeners to include e=(0-2), p=(1-4). In Figure S5, we compare the congeners we detected in our study to those expected based on Solvay self-reporting to EFSA. The congeners expected based on EFSA and detected in our study include e,p = 0,1; 1,1; 0,2; 2,1; 1,2; and 0,3 (green field in Figure S5). Congeners not expected based on EFSA, but evidently detected in our study include e,p = 1,0; 2,0; 3,0; and maybe 4,0 in trace amounts. Congeners expected based on EFSA, but not detected in our study include e,p = 2,2; 1,3; 0,4; 2,3; 1,4; and 2,4. Pairing the observations of, i) our pattern of unexpected-detected/expected-detected/expected-undetected following a general trend of light being detected and heavy not being detected, and ii) an evident pattern in transport distance of light congeners being conveyed farther than heavy (Figure 5), suggests that possibly heaviest congeners were culled from the effluent train short of the distance between the source and our nearest samples, e.g., in a stack or scrubber.

The relative amounts of ClPFPECA congeners detected in our study of New Jersey soils can be depicted by: i) summing the estimated concentrations of all congeners in each sample; ii) expressing the fraction of each congener in each sample by dividing the estimated congener concentration by the total concentration; iii) assembling summary statistics for all soil samples of the mean fraction, maximum fraction and minimum fraction of each congener; and iv) summarizing these results as Figure S6. For our study, the dominant congeners were the e,p=1,1, the 0,1 and the 0,2 congeners, in that order, followed by lesser to trace to nondetect amounts of other congeners. It is noteworthy that, because these congeners evidently sort by mass in the emitted plume as a function of distance, that the relative composition we report (Figure S6) likely is unique to our dataset and not necessarily reflective of the commercial product or the environment in general. If another study had more remote samples than ours, it might well have higher proportions of lighter congeners, and vice versa.

Number of propyl groups (p) \ Number of ethyl groups (e)	0	1	2	3	4
0	Not Detected (ND)	Trace (few samples)	**Intermediate**	Minor	Trace? (<LOR)
1	**MAJOR (widely dispersed)**	**MAJOR (near source)**	**Intermediate**	ND	ND
2	**MAJOR (near source)**	**Intermediate**	ND	ND	ND
3	**Intermediate**	ND	ND	ND	ND
4	ND	ND	ND	ND	ND

Figure S6: Summary of ClPFPECA congeners, tabulated by ethyl (e) and propyl (p) group count. Green field identifies congeners anticipated based on EFSA information reported by Wang et al. (*11*, *12*) and tentatively identified in one or more samples of this study. Yellow field identifies congeners not anticipated based on EFSA and Wang et al. (*11*, *12*), but identified in one or more samples of this study. Red field identifies congeners anticipated based on EFSA and Wang et al. (*11*, *12*), but not detected (ND) in this study. White field identifies congeners not anticipated based on EFSA and Wang et al. (*11*, *12*) and not detected in this study. Descriptor terms for each congener are qualitative assessments of the relative abundances among congeners detected in this study.

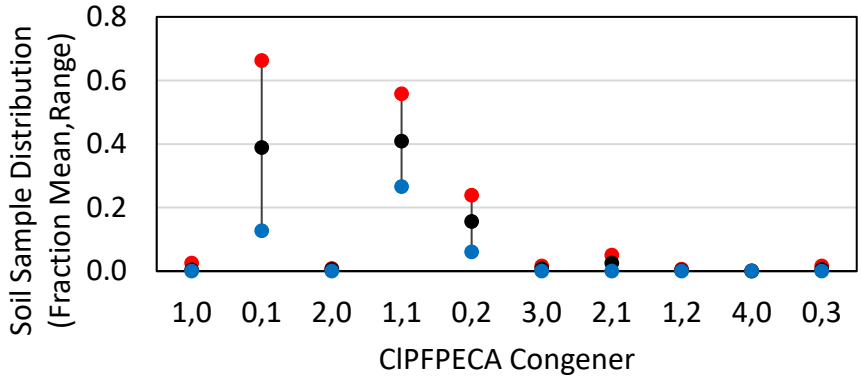


Figure S7: Relative amounts of ClPFPECA congeners (mass of each congener/total mass of congeners) detected in soil samples of our NJ study. Black represents the mean fraction, red represents the maximum detected in any sample and blue represents the minimum in any sample.

Qualitative examination for isomers: Several chromatographic peaks in Figures 2 and S2 exhibit some degree of bimodality (here modality is used in the statistical sense, representing the most abundant occurrence of a value in a set, with peak height interpreted as abundance, so that peaks having two apices are described as bimodal). Whether bimodal or unimodal, for peaks consisting solely of either ethyl or propyl groups, but not both (e,p = 0,1; 0,2; 0,3; 2,0; 3,0; 4,0, i.e., mono-moiety congeners), we have found no spectral evidence of isomers. That is, spectral patterns generated from strategically chosen time periods of bimodal peaks were uniformly closely comparable amongst each other, with no unique spectral peaks in any temporal section of the chromatographic peak. It is important to note that our analyses have not fragmented the chlorine terminal moiety, so while chlorine-position isomers might lead to bimodal chromatograms, we cannot evaluate this with our mass spectra. Consisting entirely of ethyl groups, the 3,0 congener is particularly unsuited to forming isomers that are not grossly deviant from intended structure. So the existence of bimodal chromatographic peaks (Figure S2) such as this might reflect isomers based on chlorine position, see text for details.

The absence of evidence of isomers for the purely propyl-bearing congeners (e,p = 0,1; 0,2; 0,3) (Figures 2 & S2), is consistent with the notion that the orientation of propyl groups does not vary in these molecules.

Spectra for all detected congeners having both ethyl and propyl moieties are depicted in Figures S8-S10, specifically for e,p = 1,1; 2,1 and 1,2. For each of these congeners: i) precursor plus fragments chromatographic peaks present bimodally or as two incompletely resolved peaks, not a unimodal peak; ii) fragment chromatographic peaks vary temporally among each other; and iii) judiciously selected segments of chromatographic peaks fragment to unique spectra.

Addressing the 1,1 congener in detail, extracting across the entire bimodal peak yields a dominant 200.95 mass (ClC3F6O-) which is common to all congener structure and a trace 316.94 mass (ClC3F6OC2F4O-; Fig. S7 and S2). In contrast, the early eluting 1,1-congener lobe yields only the 200.95 mass, and the later eluting lobe yields the 200.95 mass as well as a prominent 316.94 mass which is unique to a structure wherein the ethyl group is closer to the chlorine terminus (which we designate as the EP isomer of the 1,1 congener). Given the unique spectra of the two 1,1-congener chromatographic peaks, these observations suggest ethyl-propyl positional congeners in which the earlier prominent chromatographic peak is the PE isomer and the latter minor chromatographic peak is the EP isomer. The 2,1 congener is less well resolved due at least partly to less intense signal, but similar reasoning suggests EEP and PEE isomers (Fig. S8). Like the 2,1 congener, evidence for the presence of isomers of the 1,2 congener is not compelling, but spectra offer some suggestion of EPP and PEP isomers (Fig. S9). Summarizing, these observations suggest ethyl-propyl positional isomers of ClPFPECAs might be present, but the evidence remains inconclusive. Taken altogether, these observations suggest that these congeners might possess ethyl-propyl sequence isomers.

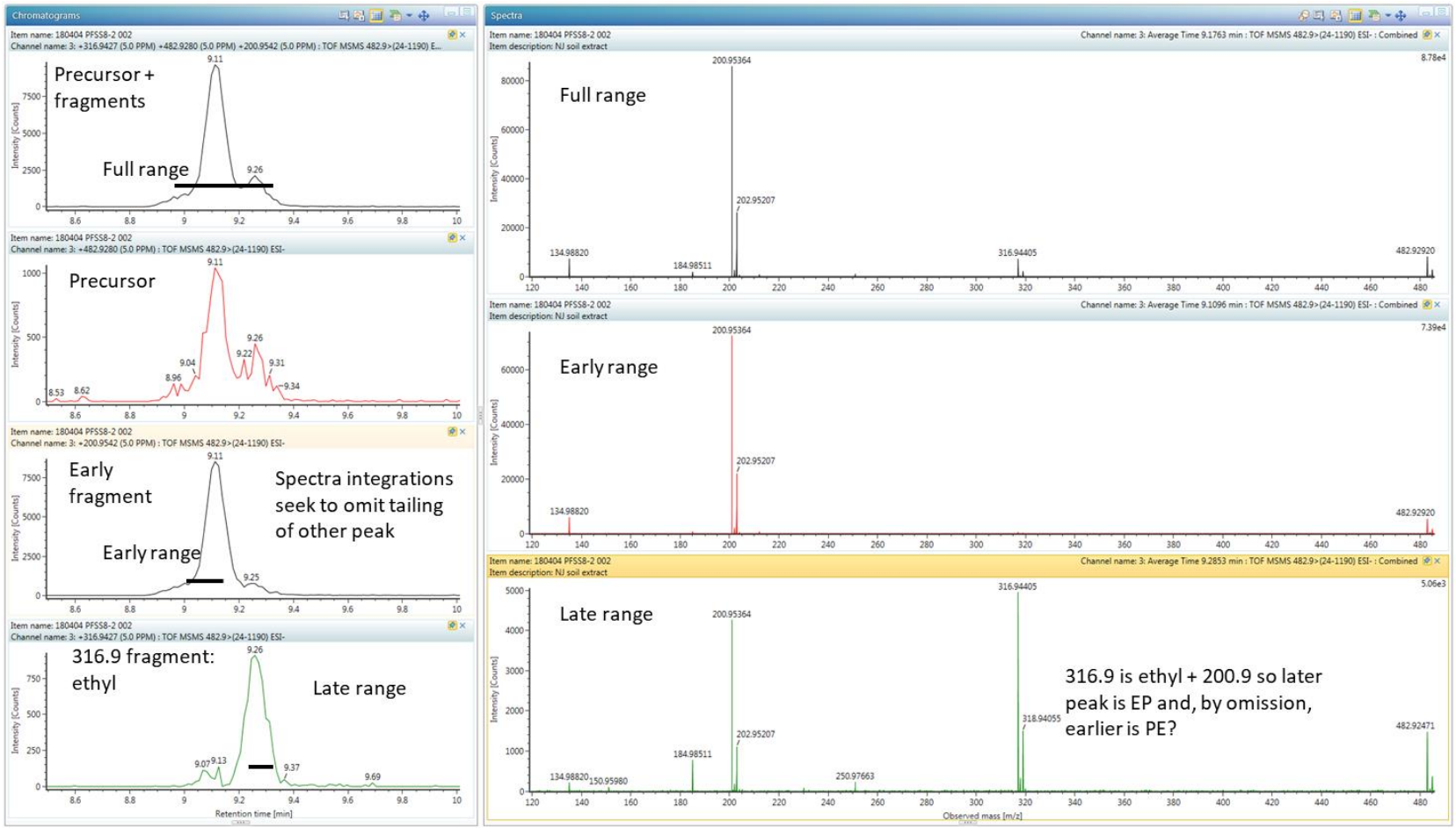


Figure S8: Selected precursor/fragment chromatograms and spectra for the 1,1 congener. The chromatogram for the precursor plus dominant fragments is bimodal. The earlier peak is comprised dominantly of the 200.9 fragment ($Cl(CF_2)_3O$-), which is common to any isomer of this congener. The latter peak is comprised dominantly of the 316.9 fragment ($Cl(CF_2)_3O(CF_2)_2O$-), which is specific to the EP (i.e., Cl terminus-ethyl-propyl-carboxylate terminus) isomer. These combined details of, i) precursor plus fragments peak presents as two peaks, not a unimodal tailing peak, ii) fragment peaks vary temporally among each other, and iii) the peaks ionize to unique spectra, suggest two isomers of the 1,1 congener, i.e., EP and PE. If the suggested isomers are ionized equally efficaciously, the peak shape suggests PE isomer is the dominant isomer.

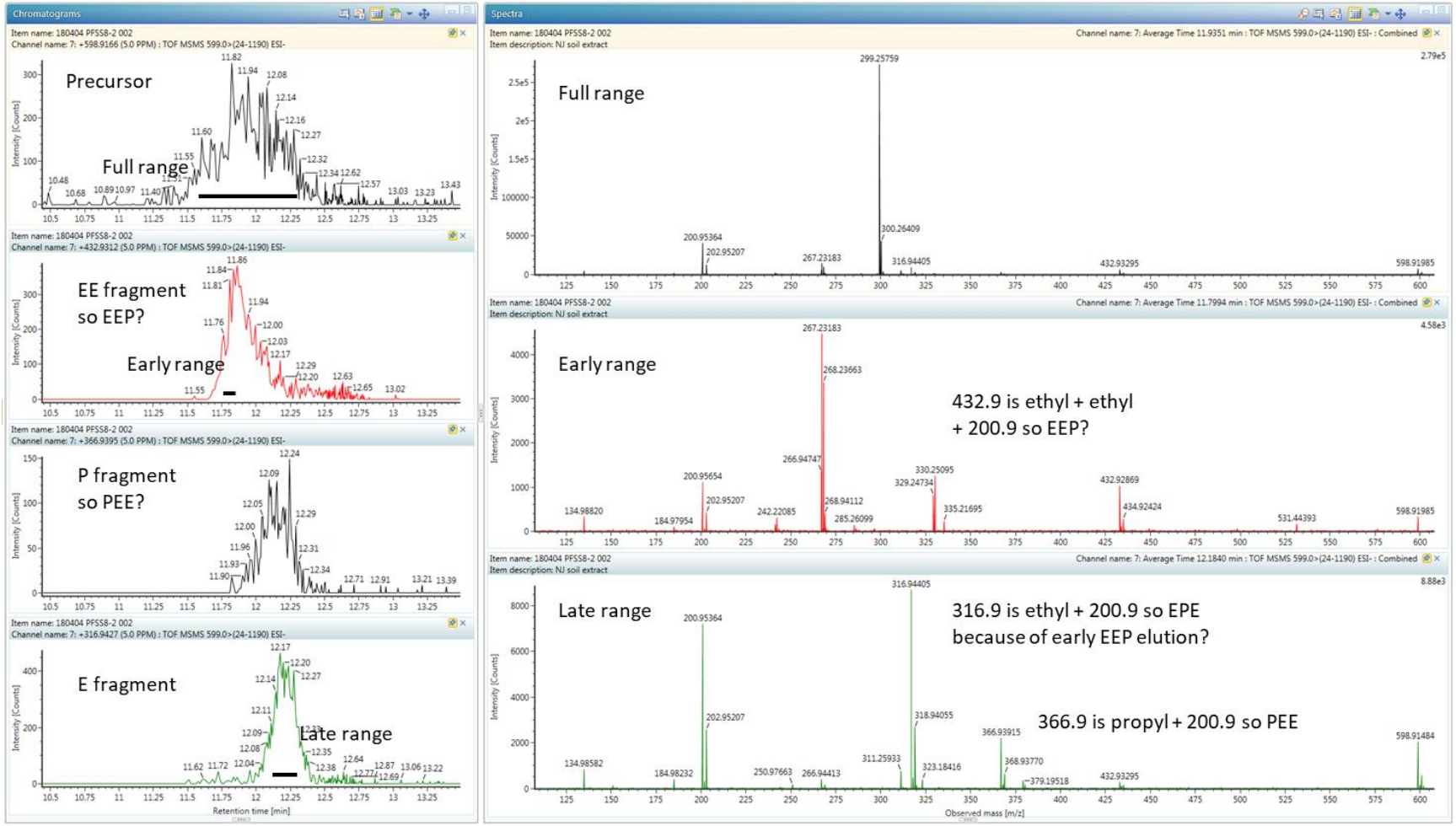


Figure S9: Selected precursor/fragment chromatograms and spectra for the 2,1 congener. The precursor chromatogram presents a broad peak. An EE fragment, 432.9 ($Cl(CF_2)_3O((CF_2)_2)_2O$-), elutes at the front of the precursor peak suggesting EEP. An apparent P fragment, 366.9 ($Cl(CF_2)_3O(CF_2)_3O$-), elutes toward mid-point of the precursor consistent with PEE. And an E fragment, 316.9 ($Cl(CF_2)_3O(CF_2)_2O$-), elutes late in the precursor peak, possibly reflecting EPE. The combined details of, i) precursor plus fragments peak presents as two peaks (Figure 2), not a unimodal tailing peak, ii) fragment peaks vary temporally among each other, and iii) fragment peaks ionize to unique spectra, suggest isomers of the 2,1 congener.

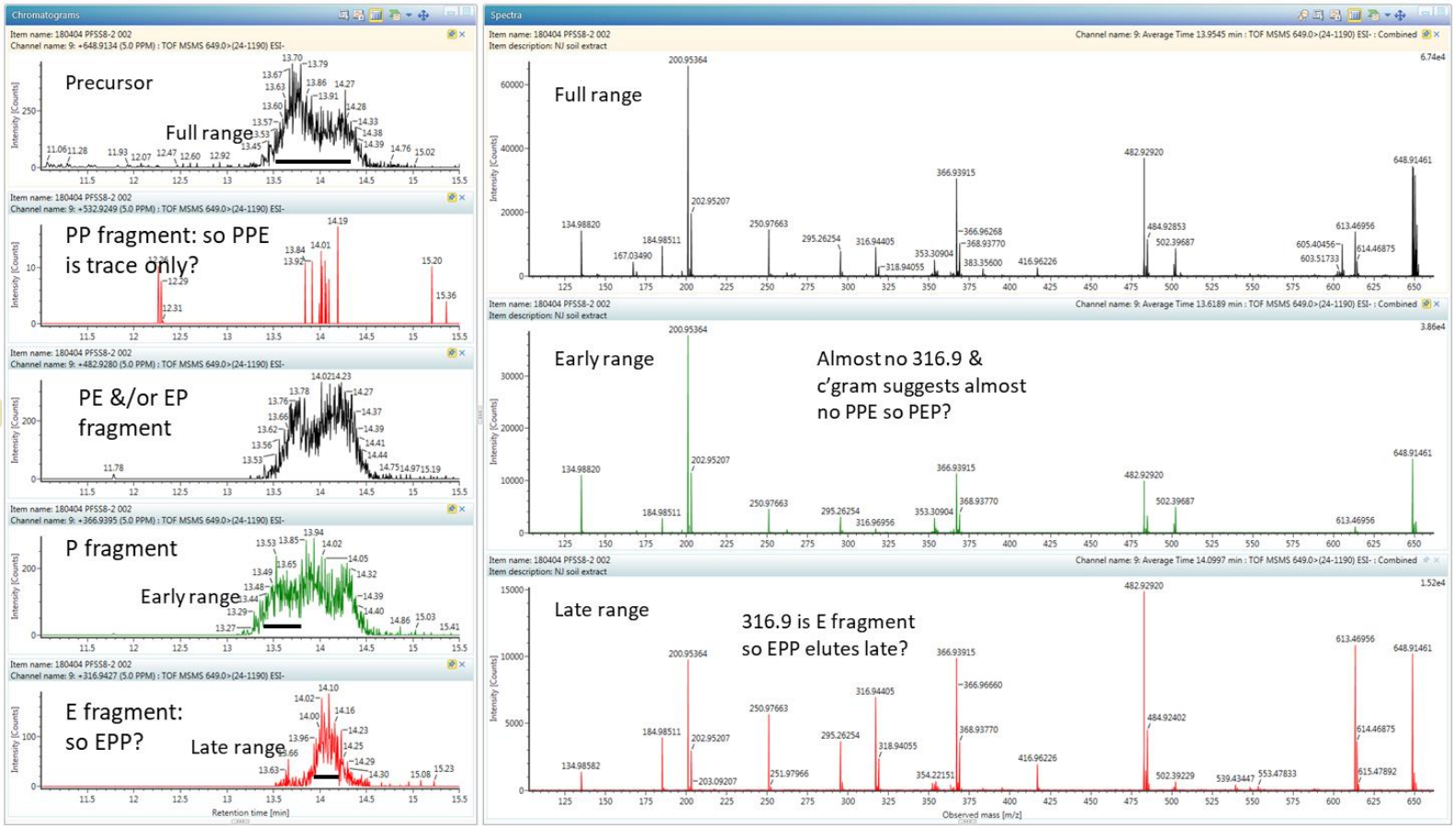


Figure S10: Selected precursor/fragment chromatograms and spectra for the 1,2 congener. The precursor chromatogram presents a broad peak. There is effectively no signal for a PP fragment, 532.9 ($Cl(CF_2)_3O((CF_2)_3)_2O$-), suggesting an absence of a PPE isomer. An ethyl and propyl fragment, 482.9 ($Cl(CF_2)_3O(CF_2)_3O(CF_2)_2$-), elutes bimodally suggesting EPP and/or PEP. An apparent P fragment, 366.9 ($Cl(CF_2)_3O(CF_2)_3O$-), elutes toward mid-point of the precursor consistent with PEE. And a P fragment, 366.9 ($Cl(CF_2)_3O(CF_2)_3O$-), and an E fragment, 316.9 ($Cl(CF_2)_3O(CF_2)_2O$-), both are evident. The combined details of, i) precursor plus fragments peak presents as two peaks (Figure 2), not a unimodal tailing peak, ii) fragment peaks vary temporally among each other, and iii) fragment peaks ionize to unique spectra, suggest isomers of the 1,2 congener. Peak shape and variation of spectra with time is consistent with the presence of PEP and EPP positional isomers, but no or only trace PPE.

Assessment of PFCA data in concert with ClPFPECA data:

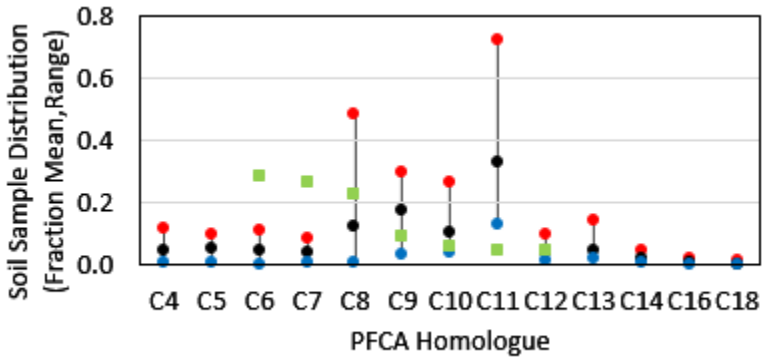


Figure S11: Relative distribution of legacy PFCA homologues in New Jersey soils of this study showing the mean of all 24 samples (black), the lowest observed (blue), and the highest observed (red). Also shown for comparison are the fractions of C6 to C12 PFCAs reported for global background soils (green) by Rankin et al. (*24*).

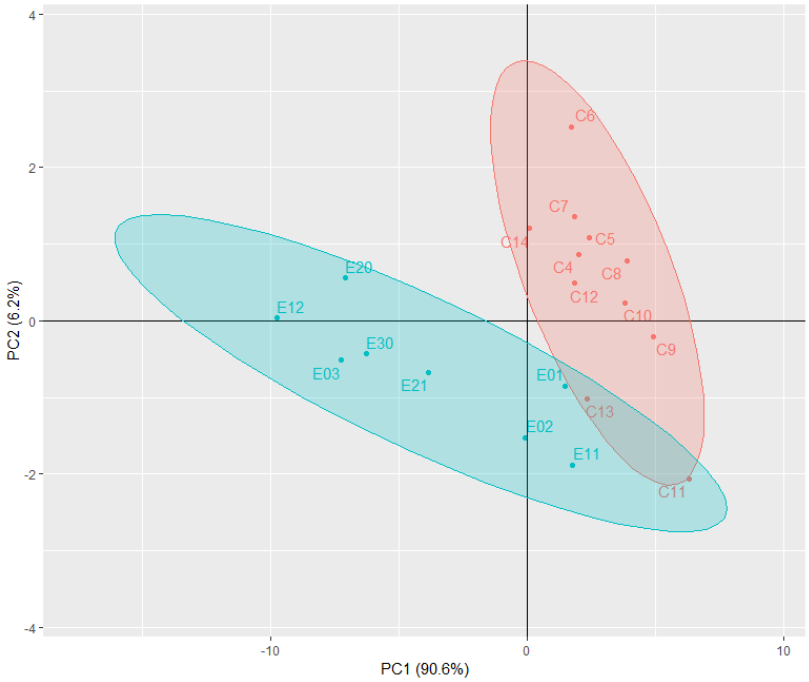


Figure S12: Principal Component Analysis (PCA) score plot of chemical variables: E designates ether, representing the ClPFPECAs, followed by congener ethyl,propyl count. C designates carboxylate, representing the PFCAs, followed by chain length. To normalize data and foster commensurate scaling among variables, all data were log-transformed for the PCA. See text for interpretive details.

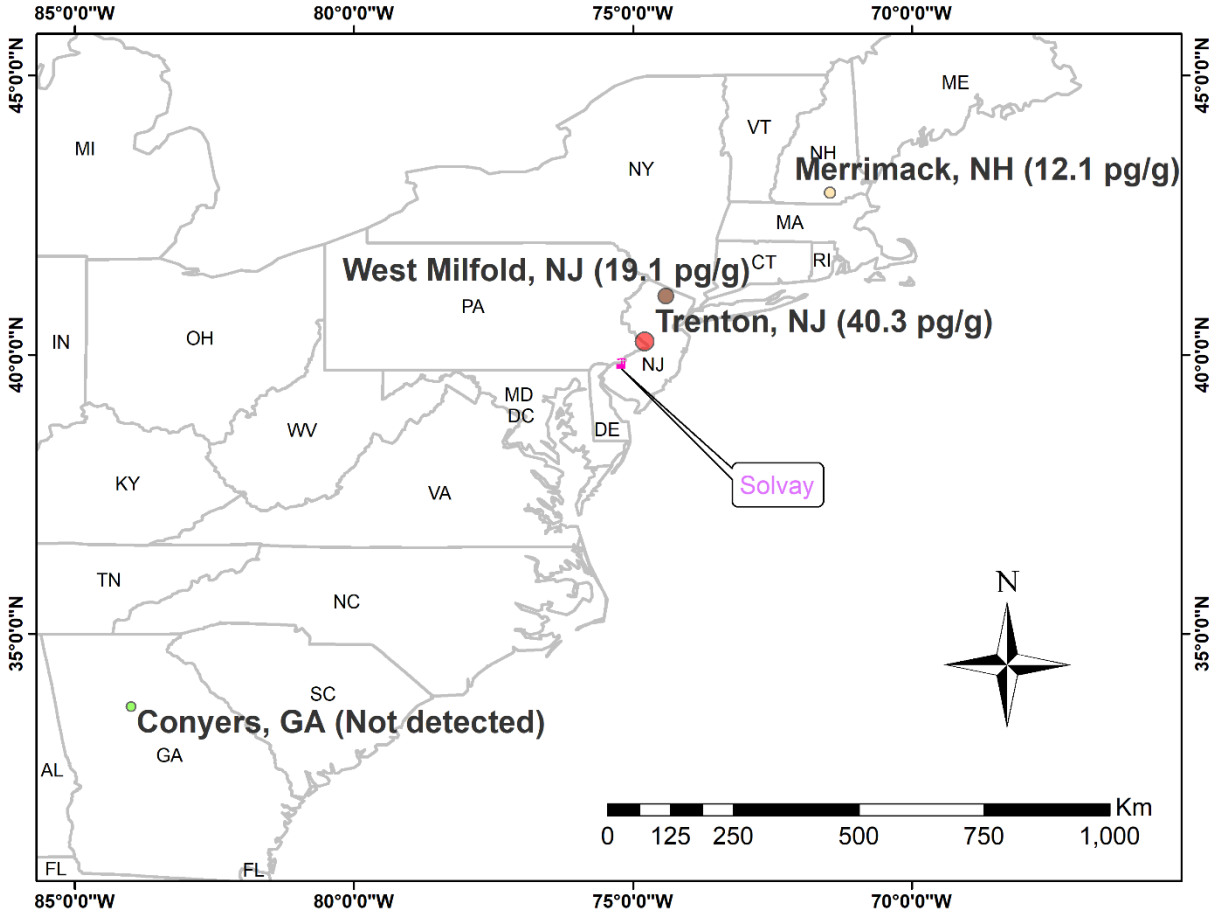


Figure S13: Remote sample locations in Merrimack, NH and Conyers, GA. Concentrations of the 0,1 ClPFPECA congener are reported at selected locations. No ClPFPECAs were detected at Conyers, GA.

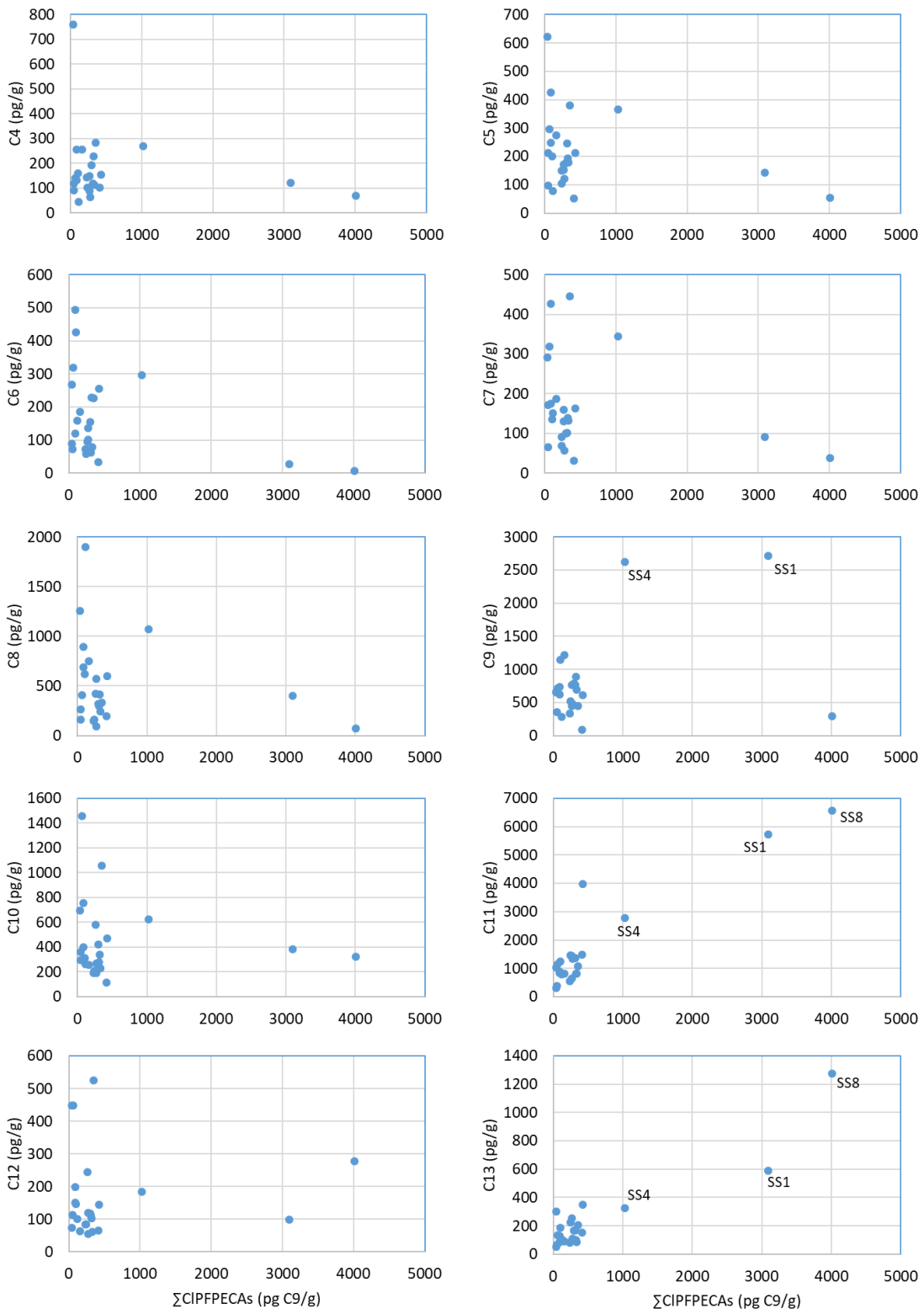
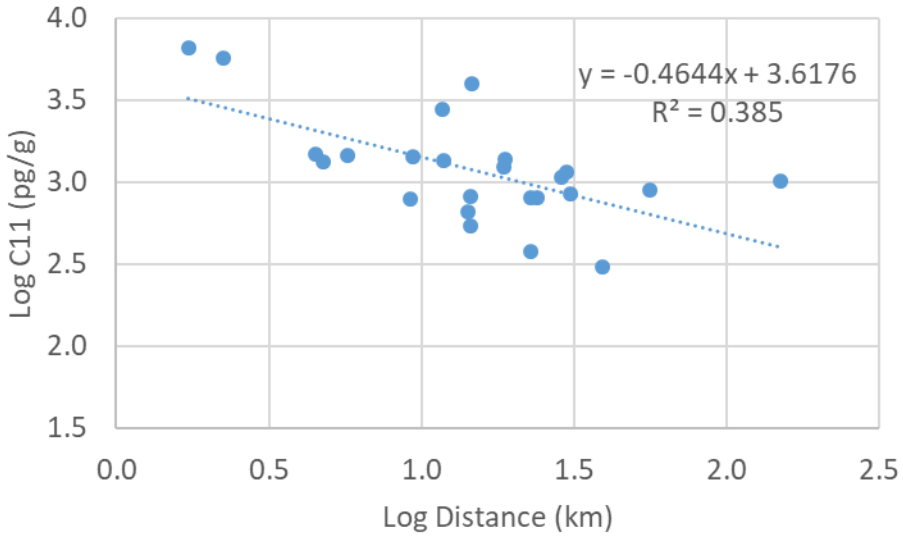


Figure S14: Plots of Legacy PFCAs vs the sum of ClPFPECAs. Some of the highest samples for C9, C11 and C13 PFCAs also are among the highest in ClPFPECAs and were collected from near Solvay.



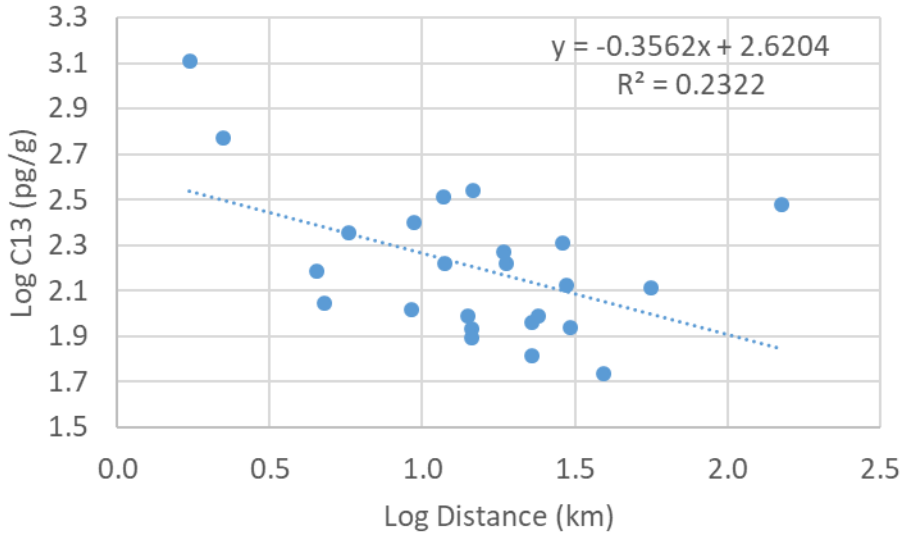


Figure S15: Legacy PFCAs C11 and C13 vs distance from Solvay in log transformed space. Both compounds are highly statistically correlated with distance from Solvay (Table 1).

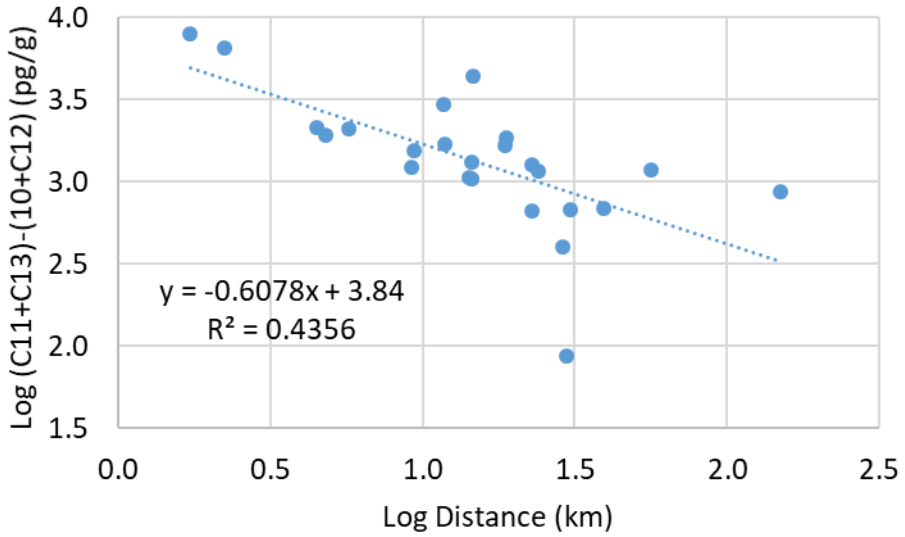


Figure S16: [(C11+C13)-(C10+C12)] vs distance from Solvay in log transformed space. A constant of 700 was added to all these difference values to preclude negatives which cannot be log transformed. Subtraction of (C10+C12), as proxies for FTOH-derived (C11+C13), from total (C11+C13), yields an approximation of (C11+C13) that has not arisen from FTOH-precursor oxidation. This variable is statistically related to distance at roughly an order-of-magnitude greater level than any single of the PFCAs alone (Table 1). The minimum visual outlier (x,y ~ 1.5,2.0) represents sample SS17 (Figure S1), collected from near Chemours, and is high in C10, possibly from 10:2FTOH oxidation in soil as well as atmosphere at this location proximate to Chemours.

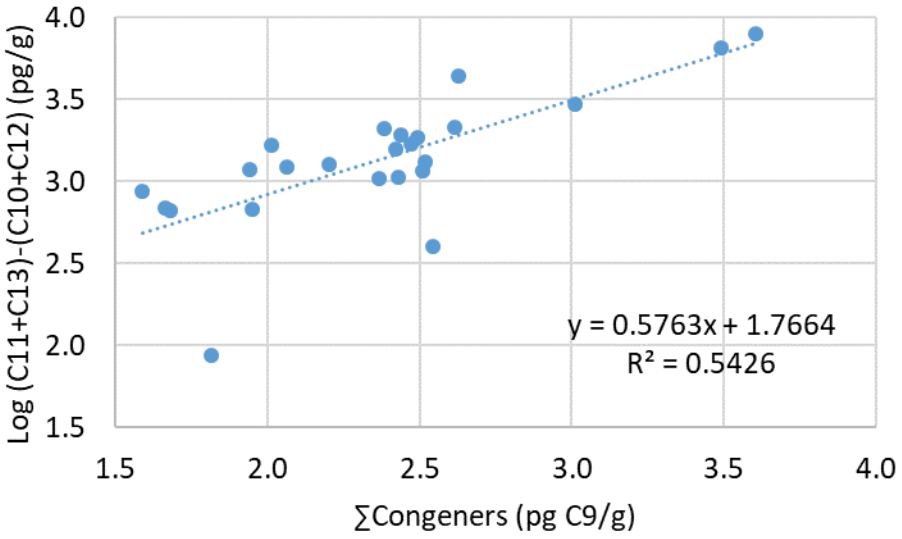


Figure S17: [(C11+C13)-(C10+C12)] vs sum of ClPFPECA congeners. A constant of 700 was added to all the PFCA difference values to preclude negatives which cannot be log transformed. Significant at $P = 4x10^{-5}$, these variables are highly statistically related, strongly suggesting a common mode of occurrence.

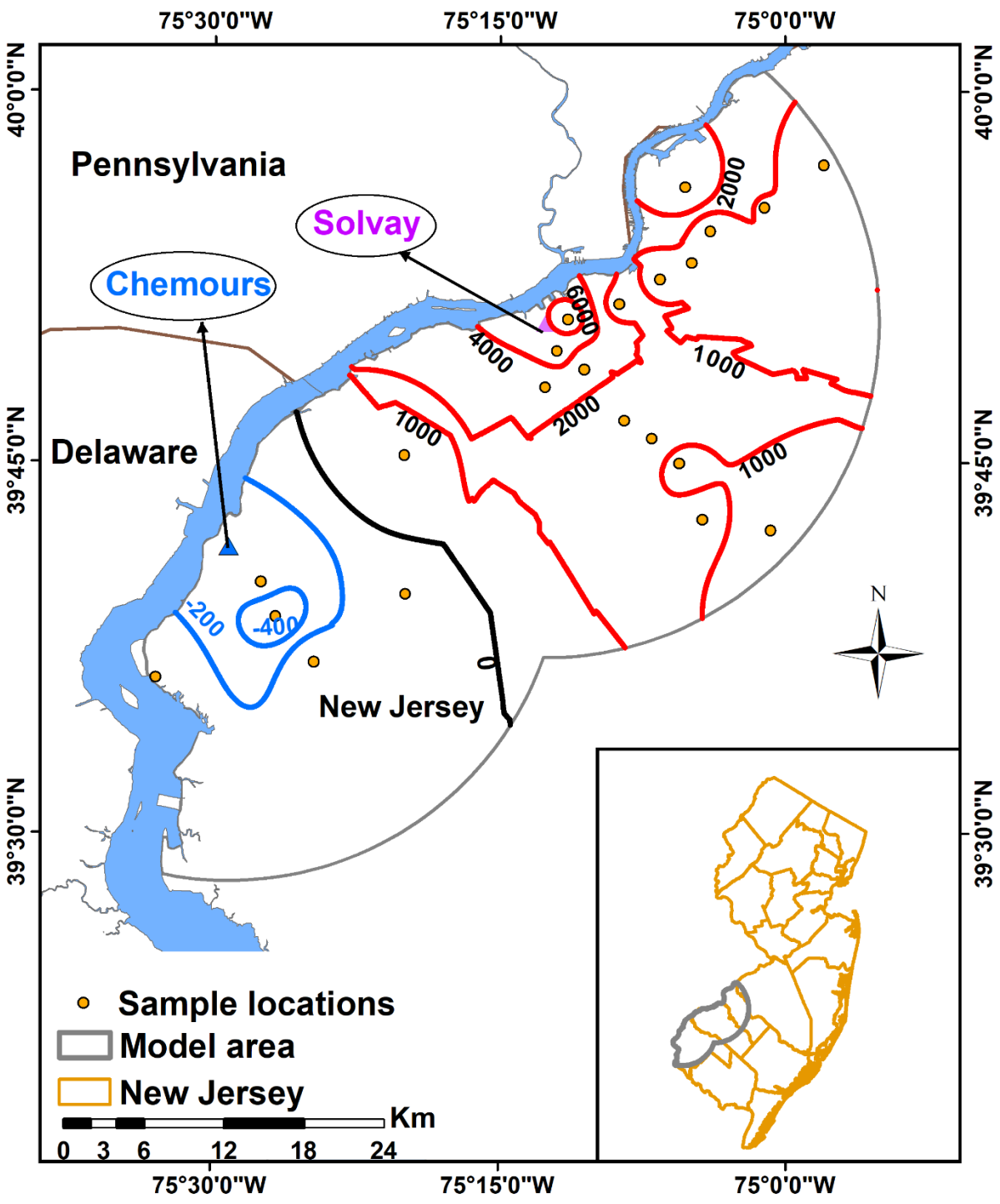


Fig. S18: [(C11+C13)-(C10+C12)] in surface soils (pg/g). Contours lines were generated using an algorthim that weighted the five nearest data points according to inverse-square distance. Despite some geographic sporadicity in the data and numerical artifacts where data are sparse, taken as a group the contours depict a clear positive anomaly focusing on Solvay and a negative anomaly focused near Chemours. See text for details.

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