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Cite this: *Environ. Sci.: Processes Impacts*, 2025, 27, 729

Soil contamination by environmentally persistent free radicals and dioxins following train derailment in East Palestine, OH†

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The Norfolk Southern train derailment on February 3, 2023, in East Palestine, Ohio, prompted concerns about the health impacts from the chemical spills and open-air combustion. We hypothesize that the combustion of chemicals, including vinyl chloride, in the presence of transition-metal oxides from the train, tracks, and soil minerals were conducive to the formation of hazardous byproducts including environmentally persistent free radicals (EPFRs), dioxins, and furans. We also hypothesize that these harmful byproducts of combustion have a shared origin and thus will have elevated concentrations in soil samples collected close to the derailment site when compared to concentrations in background soils. This study examined the co-occurrence of these soil contaminants from samples collected August 14–17, 2023, within a two-mile radius of the incident site to assess the concentration of EPFRs, dioxins, and furans. We measured elevated levels of EPFRs (average: 3.00×10^{17} spins per g) and dioxin/furan toxic equivalence (TEQ) (average: 32.8 pg g⁻¹) near the derailment area compared to background levels (EPFRs: 1.33×10^{17} spins per g; TEQ: 10.7 pg g⁻¹). Significant positive correlations ($p < 0.002$) between EPFRs and specific dioxin/furan congener concentrations (0.63–0.74) indicated robust associations between EPFRs and dioxin/furan congeners, the first such observations in field-collected soil samples. These results highlight the environmental health impact of the derailment and associated combustion, underscoring the need for comprehensive longitudinal monitoring and remediation efforts in the affected area and similar industrial accident sites. This study also offers insights into the formation mechanisms and persistence of EPFRs, dioxins, and furans.

Received 10th October 2024
Accepted 17th February 2025

DOI: 10.1039/d4em00609g

rsc.li/espi

Environmental significance

Combustion and spillage of vinyl chloride in East Palestine, Ohio in the aftermath of the February 3, 2023, train derailment may have led to the production of environmentally persistent free radicals (EPFRs), dioxins, and furans. Dioxins are known to be carcinogenic, while furans are classified as likely carcinogens. EPFRs have been shown to produce cardiovascular and respiratory effects in laboratory studies. This work detected elevated levels of EPFRs and dioxins/furans in soil samples collected near the site of the derailment and subsequent burn. This work represents the first study of these compounds together in soil samples, observing a significant positive correlation between EPFR concentration and numerous dioxin/furan congeners.

Introduction

On February 3, 2023, in East Palestine, Ohio, a Norfolk Southern train derailment resulted in a significant spill of hazardous materials including vinyl chloride, ethylene glycol, butyl acrylate, and isobutylene,^{1,2} initially resulting in fires at the derailment site and chemical spills into nearby soils and streams. On February 6th, 2023, a decision was made to begin a vented burn which led to the two-day release and burn of vinyl chloride from derailed cars on site.³ The spill and subsequent vented burn of chemicals were conducive to the formation of hazardous combustion byproducts including environmentally persistent free radicals

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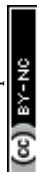
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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4em00609g>



(EPFRs) and dioxins/furans. In this study, soil samples were collected and analyzed for the presence of these contaminants in relation to their proximity to the derailment site.

The term EPFR refers to a resonance-stabilized organic radical complex commonly associated with combustion processes.^{4–7} The persistent nature and toxicological effects of EPFRs on human health and ecosystems underscore the urgency of investigating their presence following environmental disasters. In recent years, EPFRs have become of increased interest in air pollution and toxicology research. EPFRs form primarily through combustion processes that result in the interaction of chemical compounds and transition metals.^{5,8–10} The structure of these radicals allows for resonance stabilization, thereby substantially increasing the observed lifetime, resulting in radicals that are stable in soils for up to years.^{7,11} The presence of these radicals in soils provides a vehicle for human interaction, as soil is a primary component of both indoor and outdoor dust,¹² which is commonly inhaled.^{13,14} Additionally, EPFRs and dioxins/furans present in soils were once airborne particles that deposited onto the soil, indicating the risk of inhalation prior to deposition was also present. Upon inhalation, EPFRs are commonly associated with several adverse health conditions, including pulmonary^{15–18} and cardiovascular^{16,19–21} ailments. It has also been found that EPFRs play a role in the radical cascade that results in the formation of reactive oxygen species (ROS), a class of highly reactive free radicals directly associated with oxidative stress.^{22–25} Because our understanding of exposures and health effects related to EPFRs is still emerging, there are currently no reference or baseline concentration levels for EPFR toxicity. Previous studies of contaminated soil provide EPFR concentration levels for comparison.^{26–32}

Dioxins and furans belong to a class of chemical compounds known to be very toxic to biological systems.^{33,34} Dioxin and furan exposures have been linked directly to reproductive and developmental issues,^{35–38} thyroid disease,^{36,39} and cancers.^{40–42} With high chemical stability, these compounds can enter the body and be stored in fat tissue over many years (half-life: 7–11 years^{43–45}). Dioxins and furans are typically generated during incomplete combustion associated with industrial processes like waste incineration,^{46–49} smelting^{50,51} and herbicide production,^{52,53} but can also be produced through natural processes such as wildfires^{54,55} and volcanic eruptions.^{34,56–58} Previous studies have also identified high concentrations of dioxin/furans generated as byproducts of vinyl chloride monomer production.⁵⁹ These observations provide further justification for the hypotheses proposed here.

Previous research on combustion-related byproducts has suggested a connection between EPFRs and common congeners of dioxins and furans.^{4,60,61} During combustion processes, products of incomplete combustion are formed either from oxygen-starved pockets or poor heat transfer and unbalanced flame conditions. The presence of halogens in the combustion feed gives rise to halogenated organic compounds (including halogenated aromatics) at the interface of the post-flame zone. When passing to the cool zone of the combustion system and in the presence of transition-metal oxides, surface-mediated reactions produce

EPFRs.⁶² It has been reported that stable free radicals like EPFRs are intermediates in the formation of highly toxic dioxins in thermal systems.^{62–65} Laboratory studies have demonstrated the simultaneous production of EPFRs, dioxins, and furans with precursors of 2-monochlorophenol^{60,66} and 1,2,3-trichlorobenzene.⁶⁷ Vinyl chloride, the primary chemical treated through the vented burn process in East Palestine, is a known chlorine donor in the formation of dioxin/furans under combustion conditions.⁶⁸ However, the direct correlation between EPFRs and dioxin/furan concentrations in the environment, especially post-industrial accidents, remains underexplored. This study aims to bridge this knowledge gap by investigating soil samples from the vicinity of the East Palestine derailment site.

We hypothesized that concentrations of EPFRs, dioxins, and furans have a shared origin and thus will be elevated close to the derailment site when compared to background levels given the combustion of vinyl chloride in the presence of transition-metal oxides from the train, train tracks, and soil minerals. We further hypothesize that a positive correlation between the concentrations of EPFRs and dioxins/furans in soil samples collected near the East Palestine derailment site will be observed, based on this shared origin. This work will test these hypotheses by investigating correlations between measured EPFR content and dioxin/furan concentrations to further elucidate chemical connections between the two classes of pollutants. We analyzed soil samples collected in August 2023, after the February 3, 2023, derailment, and associated vented burn for their EPFR and dioxin/furan content. A preliminary analysis of EPFR and dioxin/furan distribution in soils near the derailment provides valuable insights into the spatial extent of contamination and potential hazards to the affected community. Additionally, by testing the correlation between EPFRs and dioxins/furans, we aim to improve our understanding of potential relationships between these pollutants. This work provides a snapshot of the spatial distribution of EPFR and dioxin/furan concentrations in soils near the derailment site to identify areas with the potential for elevated health risks associated with exposure to these compounds for further study.

Materials and methods

Sample collection

Soil sample collection was completed August 14–17, 2023. Whole soil samples were collected from 27 locations (public and private properties) throughout East Palestine, OH, and within a two-mile radius surrounding the train derailment site. Private property samples were collected after receiving consent from landowners. At the time of sample collection, EPA implemented restricted access to an area containing the derailment location as they conducted remediation efforts. Six of the 27 soil samples in this work were collected from within this area and thus are designated as “restricted zone” samples (EP-019–EP-024). Of the six “restricted zone” samples, one site (EP-024) had been excavated and replaced with imported fill dirt prior to sample collection. All sample locations were anonymized, and residents were given assurance that no identifying information would be reported. Locations were selected based on proximity to the



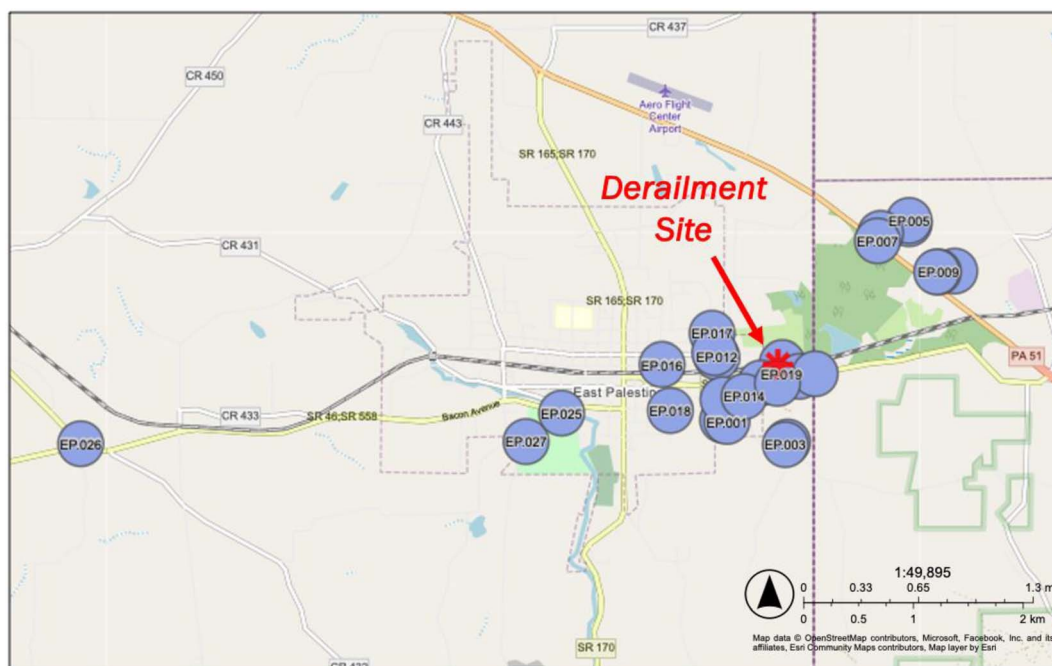


Fig. 1 Sampling locations used in this work. Location markers were intentionally shifted and enlarged to maintain privacy. Asterisk denotes the derailment site.

derailment site, prevailing wind directions post-incident, and areas identified by preliminary assessments as potentially high-risk for chemical deposition. Some sites were located on commercial property or along a roadside and were not on residential property. Sample locations used in this work are illustrated in Fig. 1.

In addition to the 27 sampling locations in and around East Palestine, 10 soil samples were obtained for use as a location-specific background level determination. These background samples were collected before the derailment (December, 2022) as part of a separate study at an agricultural field approximately 10 miles from the derailment site. Given their distance from East Palestine and the fact that they were obtained prior to the derailment, these pre-incident samples are considered background for this study and are not included in the presented East Palestine dataset averages.

Samples were collected using a drill-powered auger in combination with a bucket modified with a hole in the bottom allowing the auger to pass through and into the ground, so that the soil was simultaneously collected inside the bucket. After a site was selected, the auger was used to collect approximately 750 g of soil at a depth of 0–15 cm (0–6 inches). This sampling was designed to match sampling protocols used in East Palestine by the U.S. EPA and Norfolk-Southern.^{69–71} Samples were placed into individual collection bags, labeled by a sample identification number, and latitude/longitude coordinates. Collection tools were emptied and wiped between samples. After collection, sealed sample bags were placed into a cooler and shipped to Louisiana State University (Baton Rouge, LA) for analysis. All soil samples used in this study were stored in a -20°C freezer prior to preparation for analysis.

Sample analysis

Aliquots taken from the collected samples were air-dried to account for any variability in moisture levels. Dry samples were then homogenized using a mortar and pestle. Ground soil was passed through a 425 micrometer sieve to ensure uniform size for analysis. The grinding tools and sieve were wiped free of visible particles and cleaned using compressed air between samples to avoid cross-contamination.

Soil characterization was done using total organic carbon analysis (TOC) and inductively-coupled-plasma ionization paired with optical emission spectroscopy (ICP-OES) for detection. TOC analysis was completed using a Shimadzu TOC-L total carbon analyzer with parameters modified from previous soil studies.^{72,73} For this work, the furnace temperature was set to 900°C to ensure complete sample combustion using sucrose standard as a calibration reference.⁷⁴ The carrier gas used in TOC analysis was pure O_2 . ICP-OES analysis was carried out using methodology modified from previous work⁷⁵ on a Varian Vista MPX simultaneous analyzer. Soil samples were dissolved using 5 ml concentrated trace metal-grade nitric acid (approx. 70%) diluted to 50 ml with double deionized water ($18.3\text{ M}\Omega$) and 1 ml trace metal-grade H_2O_2 , before aerosolization and introduction to the plasma ionization source. For ICP analysis, the use of internal metal standards was employed.

Electron paramagnetic resonance (EPR) spectroscopy was used to identify EPFR presence, location of the radical, and concentration. A brief description of EPR is presented in ESI Text S1.[†] EPR analyses were performed using a Bruker EMX-20/2.7 EPR spectrometer (X-band) with dual cavities using the following parameters modified from previous studies involving contaminated soils:^{26–32} microwave frequency of 9.735 GHz,



power of 0.641 mW, 3 scans, modulation amplitude of 4.000 G, modulation frequency of 100.000 kHz, center field of 3479.060 G, sweep width of 100.000 G, time constant of 0.640 ms, conversion time of 20.480 ms, sweep time of 41.943 s, resolution of 2048 points, and receiver gain of 6.32×10^3 . Measurements were performed at room temperature. A Levenberg–Marquardt⁷⁶ curve fitting macro inside IGOR PRO 9.0.2 data processing software was used to obtain spectral information. EPR calibration standard $\geq 95\%$ pure 2,2-diphenyl-1-picrylhydrazyl (DPPH) was purchased from Thermo Scientific and used as a quantification and calibration standard. The EPR analysis, as carried out, yielded two important pieces of information: (i) the concentration of EPFR in the sample, reported (mass normalized) as spins per gram, *via* the area of the EPR signal and (ii) the atoms within the molecule that harbor the paramagnetic center as indicated by the spectra position of EPFR signal, reported as the *g*-value.

For dioxin and furan analysis, sample aliquots from the 27 East Palestine sampling locations were sent to Eurofins Test America (Knoxville, TN). Analysis was carried out using a Thermo Scientific DSF Magnetic Sector gas chromatograph coupled with high-resolution mass spectrometry. The U.S. EPA standard Method SW846 8290A⁷⁷ was used for this analysis to ensure that our results were comparable to those collected by U.S. EPA and Norfolk Southern in their assessment efforts.⁷⁸ The 17 congeners measured in this analysis are as follows: 1,2,3,4,6,7,8-heptachlorodibenzo-*P*-dioxin (HpCDD); 1,2,3,4,6,7,8-heptachlorodibenzo-*P*-furan (HpCDF); 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,7,8-hexachlorodibenzo-*P*-dioxin (HxCDD); 1,2,3,4,7,8-hexachlorodibenzo-*P*-furan (HxCDF); 1,2,3,6,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDD; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8-pentachlorodibenzo-*P*-dioxin (PeCDD); 1,2,3,7,8-pentachlorodibenzo-*P*-furan (PeCDF); 2,3,4,7,8-PeCDF; 2,3,7,8-tetrachlorodibenzo-*P*-dioxin (TCDD); 2,3,7,8-tetrachlorodibenzo-*P*-furan (TCDF); octachlorodibenzodioxin (OCDD); octachlorodibenzofuran (OCDF).

Since the term “dioxin/furan” commonly refers to a class of compounds, analysis of multiple congeners is possible. The concentrations of each measured dioxin/furan congener are assigned a representative toxic equivalency factor (TEF) that relates each congener to the most toxic species, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) by applying a weighting factor.⁷⁹ The products of the weighting factors and concentrations (*C*) for each congener (*i*) are summed over the measured congeners to generate the toxic equivalency (TEQ), a value to describe the total toxicity of the sample regarding all measured dioxins and furans (eqn (1)):

$$\text{TEQ} = \sum(\text{TEF}_i \times C_i) \quad (1)$$

The U.S. Environmental Protection Agency (U.S. EPA) compares the dioxin/furan TEQ to make informed decisions about remediation at an incident site.⁸⁰ The Regional Screening Level (RSL) corresponds to a risk of 1-in-1 000 000 for a given health outcome with 30 years of exposure, and values have been set for cancer and noncancer effects.⁸¹ For evaluating risks of cancers associated with dioxin and furan exposures in soils, the

RSL is 4.8 pg g^{-1} . For noncancer effects, the RSL is 51.0 pg g^{-1} .⁸⁰ We calculated TEQ values based on the dioxin and furan congeners and their TEFs⁷⁹ and compared them with the cancer and noncancer RSLs.

Meteorological data

Data were obtained from the National Oceanographic and Atmospheric Administration Integrated Surface Database for the Youngstown Municipal Airport in Youngstown, OH (USAF-WBAN code 725250-14852) for February 6–7, 2023, coinciding with the vented burn. Data retrieval and wind rose production was performed for each day of the vented burn using the R (v.4.4.2) statistical software with the openair, worldmet, and tidyverse packages.

Statistical analysis

Relationships between EPFR concentration (spins per g) and dioxins/furans were tested to identify potential associations of EPFRs with dioxin and furan congeners among the compounds for the 27 soil samples. First, Grubb's test⁸² was used to test if the most extreme value for any given parameter was an outlier. Only one data point was considered for removal to maintain $n = 26$ or $n = 27$. To establish a balance between over-culling the dataset and avoiding the regressions being controlled by one point, we selected $p < 0.0001$. Hence, for a given parameter, one data point was removed if it skewed the data distribution substantially enough that it would change the regression. If the data point did not meet this stringent significance requirement for removal, then it was retained. For most parameters, one outlier was removed. We also performed the regressions without the removal of any outliers. Next, linear regression tested the relationships between each dioxin congener and EPFR concentration. We accounted for 17 congeners of dioxins/furans as well as seven aggregate concentrations, TOC, and 11 metals (36 total comparison groups) by applying a significance level of $p < 0.00139$ ($\alpha = 0.05/36$) in accordance with Bernoulli's multiple comparisons testing.⁸³ For regressions meeting the significance criterion, the associations were visualized and presented in figures below. Analyses were performed using the R statistical programming software (v.4.4.2) using the tidyverse and dplyr packages for data organization and the stats and ggplot2 packages for statistical analysis.

Sample quality assurance

During the sampling conducted in this work, all materials used for soil collection were wiped clean of any previous soils before a new sample was collected. All sample sites were identified with precise GPS locations at the time of sampling and given unique identification numbers to maintain resident's privacy. All soil characterization (ICP-OES and TOC) analyses were performed using triplicate measurements with average values reported. ICP analysis employed the use of internal target metal standards for sample calibration. Concentrations measured in the ICP analysis were well above method detection limits calculated using EPA-defined procedures.⁸⁴ EPR measurements were conducted using calibration standard DPPH, tested



initially and after every 5th sample, to ensure center-field accuracy for g -value reporting. All measurements of soil-bound EPFRs including background samples returned radical signals well above the EPR detection limits. Values observed outside of two standard deviations from the statistical mean concentration were re-analyzed ($n = 2$). Dioxin and furan analysis was completed by a certified testing laboratory. Samples were analyzed using U.S. EPA Method SW846 8290A for sampling dioxins and furans by high-resolution gas chromatography/high-resolution mass spectrometry.⁷⁷ Dioxin/furan analyses employed the use of standard addition detection as well as the use of method blank and lab control samples.

Results and discussion

EPFR analysis

EPR analysis of the collected soils generated complex radical signals, suggesting a multi-radical system (ESI Fig. S2†). These complex signals were deconvoluted for both quantitative and qualitative analysis: to determine the radical concentration (spins per g), and the radical identity (g -value). Quantitative analysis of the post-incident East Palestine soil samples exhibited EPFR presence at varying concentration levels

(approximately 0.4×10^{17} – 6×10^{17} spins per g, complete results are reported in Table 1).

These survey samples exhibited concentration values of up to five times higher than the average background concentration. These elevated concentrations are notable as it has been demonstrated that EPFRs are connected to significant health impacts.^{15–21} Though environmentally stabilized through resonance,^{7,11} the activity of EPFRs changes dramatically once introduced to aqueous conditions^{22–24} like those found in the human body. The presence of elevated levels of EPFRs in the soil near the derailment site could signify potential exposure risk to the disaster responders (cleanup and assessment) and the surrounding community at large. When compared to previously studied contaminated soils, some samples collected in the “restricted zone” (area near the derailment site) contained radical concentrations comparable to or greater than those seen at types of facilities where EPFRs have been observed, including wood treatment facilities²⁸ (5.83×10^{17} spins per g) and past coking sites³⁰ (3.00×10^{17} spins per g). Radical values observed outside of the restricted zone throughout the East Palestine community (average = 1.33×10^{17} spins per g) were consistently lower than the value observed on the imported fill dirt sample (1.95×10^{17} spins per g) collected after spill zone remediation. These concentrations are comparable to those measured on previously studied non-contaminated soils.²⁸

Via deconvolution, the characteristic g -values for each of the three radicals involved in the multi-radical system were identified as ~ 2.001 , ~ 2.003 , and ~ 2.007 . Measured g -values of 2.0010 ± 0.002 and 2.0070 ± 0.002 were consistent for all post-incident samples, possibly indicating the presence of lead-organometallic radical complexes and sulfur-centered radicals respectively.⁸⁵ An example of the deconvolution output can be found in ESI Fig. S3.† For this study of EPFRs, the primary focus is on the radical at g -value ~ 2.003 , which is associated with the organic radical.^{4,7,86} As this component is the focus of this work, further discussion of g -value will be in reference to the organic radical of the observed EPR signals. Samples in this dataset had g -values of 2.0024–2.0035 (Table 1). Values seen in this dataset below 2.0030 correspond to carbon-centered radicals, with those above 2.0030 representing carbon-centered radicals that are adjacent to an oxygen atom.

The g -values observed in the EPFR analysis (2.0024–2.0035) align with the g -values of other contamination events. Samples reported by Dela Cruz *et al.* studying Superfund soils from wood treatment sites had carbon-centered radical g -values ranging from 2.0027 to 2.0030.²⁸ Previous work on samples collected from combustion and/or industrial sites has also reported g -values consistent with those observed in this sampling effort.^{30–32} The range of g -values seen across the East Palestine soil samples is consistent with the hypothesis that events occurring during and after the burn of hazardous chemicals from the train derailment could play a role in the formation of EPFRs. There is the potential that the carbon-centered radicals observed through this study are connected to the deposition of carbon-rich ash related to the vented burn. The g -values in this dataset are also consistent with those measured in studies

Table 1 Sample ID, distance from derailment site, radical concentration, organic radical g -values, and TEQ values for each soil sample collected in the East Palestine sampling effort

Sample ID	Distance from derailment site (miles)	Radical concentration (spins per g)	Organic radical g -value	TEQ (pg g ⁻¹)
EP-001	0.42	1.73×10^{17}	2.0026	1.2
EP-002	0.44	7.46×10^{16}	2.0029	0.6
EP-003	0.52	5.27×10^{16}	2.0032	4.5
EP-004	0.53	1.01×10^{17}	2.0033	1.5
EP-005	1.11	1.08×10^{17}	2.0034	0.8
EP-006	1.17	1.25×10^{17}	2.0030	0.8
EP-007	0.98	9.82×10^{16}	2.0030	3.1
EP-008	0.91	8.37×10^{16}	2.0033	1.8
EP-009	1.14	1.53×10^{17}	2.0032	1.7
EP-010	1.20	1.24×10^{17}	2.0031	0.7
EP-011	1.09	1.37×10^{17}	2.0030	34.3
EP-012	0.29	1.75×10^{17}	2.0029	3.4
EP-013	0.27	1.64×10^{17}	2.0028	5.5
EP-014	0.20	2.93×10^{17}	2.0027	59.4*
EP-015	0.33	1.10×10^{17}	2.0027	4.2
EP-016	0.57	2.74×10^{17}	2.0025	23.5
EP-017	0.31	9.06×10^{16}	2.0035	2.4
EP-018	0.59	2.90×10^{17}	2.0026	50.1
EP-019^a	0.11	2.83×10^{17}	2.0025	6.7
EP-020	0.08	1.55×10^{17}	2.0026	30.9
EP-021	0.11	1.85×10^{17}	2.0028	88.2^{a,b}
EP-022	0.20	4.27×10^{17}	2.0027	26.0
EP-023	0.27	5.56×10^{17}	2.0025	31.3
EP-024	0.11	1.93×10^{17}	2.0029	13.4
EP-025	1.17	1.39×10^{17}	2.0023	18.8
EP-026	1.30	4.00×10^{16}	2.0027	0.2
EP-027	1.39	1.26×10^{17}	2.0030	10.3

^a Bold italicized text indicates samples obtained in the “restricted zone”. ^b Asterisk indicates TEQ values above RML (51 pg g⁻¹).



where radical recombination to form dioxins and furans was observed.^{60,63,64}

Dioxin/furan analysis

Analysis of dioxin and furan concentrations resulted in a range of TEQs across the dataset ($0.19\text{--}88.2\text{ pg g}^{-1}$) that vary from below the cancer RSL of 4.8 pg g^{-1} to those above the noncancer RSL of 51.0 pg g^{-1} . Table 1 contains the calculated dioxin/furan TEQ values for each of the East Palestine samples. Of the 27 post-incident samples collected by this group, 13 sites had dioxin

TEQ values at or above the cancer RSL, including two of those samples containing TEQs that exceeded the noncancer RSL.

TEQ values of the dioxin and furan data from the East Palestine soil samples collected in this work were compared with publicly available data reported by the U.S. EPA (32% of samples with TEQ values above the cancer RSL, 7.9% above the noncancer RSL) and Norfolk Southern (33% of samples with TEQ values above the cancer RSL, 4.6% above the noncancer RSL).^{69,70,87} Values observed in this sampling campaign (48% of samples with TEQ values above the cancer RSL, 7.4% above the noncancer RSL) had similar proportions above the cancer and noncancer RSLs when compared with the other collected data in the immediate area. The three datasets are visualized in Fig. 2 with the U.S. EPA-designated cancer and noncancer RSLs as overlaid reference lines.

Measured TEQ values were found to be elevated in proximity to the site of the derailment and vented burn. The spatial distribution of the TEQ values measured in this dataset is shown in Fig. 3. All TEQ values measured in the restricted zone (average TEQ = 32.8 pg g^{-1} ; median TEQ = 31.1 pg g^{-1}) were above the cancer RSL of 4.8 pg g^{-1} , with this area also containing the highest calculated TEQ (88.2 pg g^{-1}). This finding is consistent with previous studies connecting the formation of dioxins and furans to combustion processes.^{46–49} These data also support previous research associating the burning of vinyl chloride with the formation of these toxic compounds.⁶⁸ The levels of dioxins and furans observed in the East Palestine dataset suggest that further remediation efforts may be necessary to properly address the associated risk in the community.

Dioxin and furan concentrations observed in this dataset suggest an elevated level of contamination present. Urban *et al.* generated a review of available dioxin data to determine background dioxin TEQ values present in rural and urban/suburban soils throughout the United States.⁸⁸ Using census data as

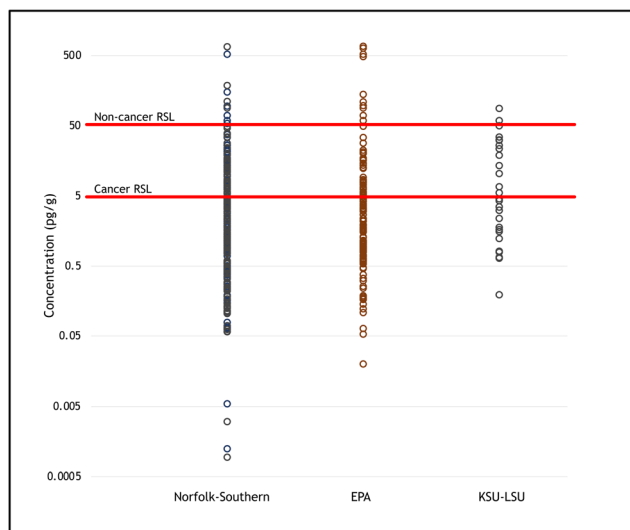


Fig. 2 Dioxin/furan TEQ values for samples collected by Norfolk Southern and U.S. EPA as well as the samples collected by LSU/KSU. Cancer RSL (4.8 pg g^{-1}) and noncancer RSL (51.0 pg g^{-1}) are included for visualization, and TEQ data are presented on a log scale.

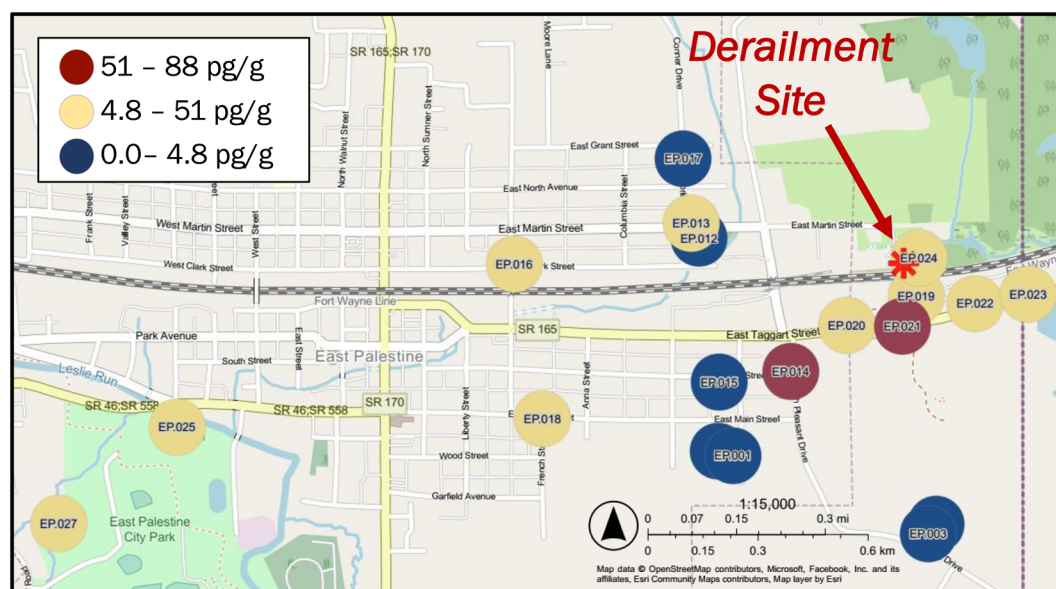


Fig. 3 Map of TEQ values observed on samples collected in the East Palestine sampling effort. Location markers were intentionally enlarged to maintain privacy. The asterisk denotes the derailment site.



a guide, the East Palestine samples were found to be comparable to the urban/suburban soil sites reported by Urban *et al.*⁸⁸ The urban/suburban data reported within the Urban *et al.* study,⁸⁸ along with the East Palestine sample results are reported in ESI Table S4.† Samples collected by the authors for the East Palestine post-incident dataset presented a mean TEQ value of 15.8 pg g⁻¹, a median TEQ of 4.5 pg g⁻¹, a minimum TEQ of 0.2 pg g⁻¹, and a maximum TEQ of 88.2 pg g⁻¹. Mean and median TEQ values for the East Palestine soil samples were higher than the values reported at 75% of the locations included in the Urban *et al.* review.⁸⁸

Correlation between EPFRs and dioxin/furan congeners

Relationships were determined for the concentration of EPFRs with dioxin/furan congeners, as well as with TEQ. These analyses were conducted as previous research has suggested a link between EPFRs and dioxins, particularly polychlorinated-dibenzo furans (PCDFs).^{4,60–64} Our results show that EPFRs were significantly ($p < 0.00139$) correlated with TEQ, five

congeners, five aggregate congener types including hexa-chloro-dibenzo dioxins and furans and penta-chloro-dibenzo furans, and two metals, Na and Zn. Table 2 contains Pearson correlation values for the 17 congeners and 7 aggregates measured. Statistically significant correlations are illustrated in ESI Fig. S5.† All significant correlations were positive and ranged from 0.62 (total HxCDF) to 0.77 (Zn). These positive correlations between EPFR concentration and dioxin congeners are the first to be observed on field-collected soil samples, to the knowledge of the authors. Regressions performed without outlier removal are provided in ESI Table S6.†

Our findings highlight the complex dynamics of EPFR and dioxin/furan contamination following the East Palestine derailment, offering new insights into pollution dispersal mechanisms and potential health impacts. Results from the EPFR analysis in this work are consistent with previous work studying Superfund or other contaminated soils.^{26–30} Notably, samples nearest to the derailment site in the restricted zone displayed elevated radical concentration levels (average = 3.00×10^{17} spins per g) when compared to the remainder of the

Table 2 Relationships of dioxin congeners or aggregate values with EPFR concentration ($\times 10^{17}$). Accounting for Bernoulli's multiple comparisons, the level of significance is $p < 0.002$. No more than one outlier was removed in each model

Dependent variable	Slope	<i>p</i> -Value	Correlation	Adjusted <i>R</i> ²	Outlier removed
TEQ^a	11.38	0.0008	0.628	0.368	Yes
2,3,7,8-TCDD	204.01	0.0051	0.693	0.433	Yes
Total TCDD	41.50	0.0062	0.333	0.071	Yes
2,3,7,8-TCDF	2.990	0.0024	0.577	0.299	Yes
Total TCDF	5.770	0.0006	0.701	0.469	Yes
1,2,3,7,8-PeCDD	6.380	0.0001	0.542	0.260	Yes
Total PeCDD	10.39	0.0005	0.705	0.475	Yes
1,2,3,7,8-PeCDF	6.040	0.0066	0.696	0.456	No
2,3,4,7,8-PeCDF	14.63	0.0084	0.738	0.523	Yes
Total PeCDF	3.470	0.0076	0.703	0.474	Yes
1,2,3,4,7,8-HxCDD	1.940	0.0007	0.646	0.391	Yes
1,2,3,6,7,8-HxCDD	2.560	0.0001	0.657	0.406	Yes
1,2,3,7,8,9-HxCDD	0.420	0.0086	0.515	0.233	Yes
Total HxCDD	1.810	0.0050	0.671	0.427	Yes
1,2,3,4,7,8-HxCDF	1197.00	0.0118	0.727	0.506	Yes
1,2,3,6,7,8-HxCDF	69.90	0.0069	0.538	0.258	Yes
Total HxCDF	457.70	0.0228	0.617	0.354	Yes
1,2,3,4,6,7,8-HpCDD	86.27	0.0092	0.543	0.264	Yes
Total HpCDD	120.75	0.0002	0.445	0.165	Yes
1,2,3,4,6,7,8-HpCDF	107.22	0.0010	0.532	0.251	Yes
1,2,3,4,7,8,9-HpCDF	55.37	0.0001	0.602	0.332	Yes
Total HpCDF	109.73	0.0001	0.510	0.228	Yes
OCDD	5.240	0.1113	0.496	0.213	Yes
OCDF	81.91	0.0001	0.526	0.245	Yes
TOC	1.000	0.0027	0.565	0.291	Yes
B	1.520	0.0569	0.378	0.107	Yes
Ca	7618.00	0.0223	0.446	0.166	Yes
Cu	9.690	0.0312	0.557	0.282	Yes
Fe	2182.00	0.1422	0.296	0.050	Yes
K	−109.70	0.4205	0.165	−0.013	Yes
Mg	543.90	0.2662	0.226	0.012	Yes
Mn	206.10	0.1352	0.301	0.053	Yes
Na	28.870	0.0005	0.633	0.376	Yes
P	86.770	0.1729	0.276	0.037	Yes
S	175.81	0.0035	0.551	0.274	Yes
Zn	56.910	4.42×10^{-6}	0.769	0.574	Yes

^a Bold italicized text indicates statistical significance.



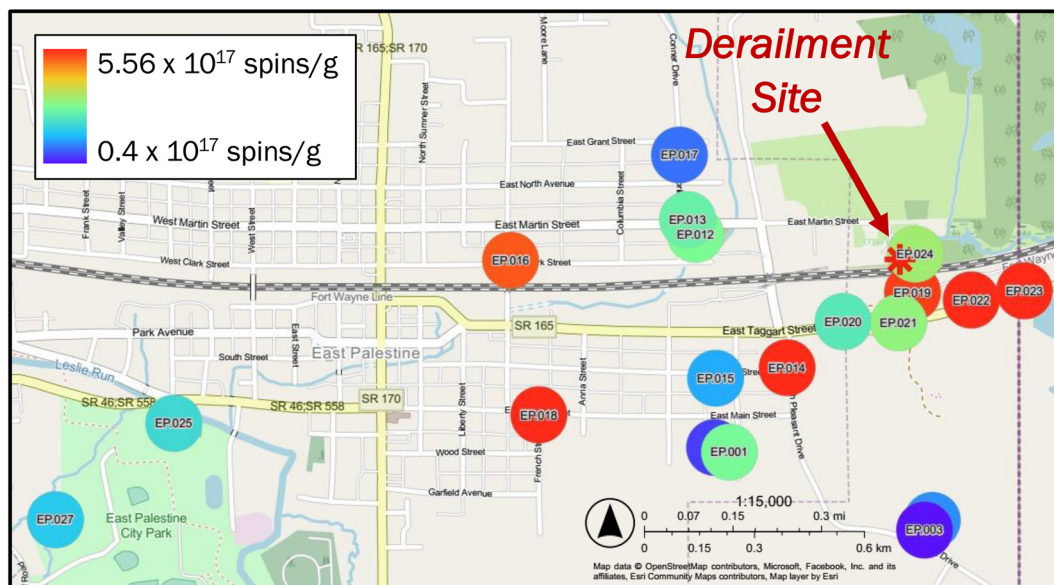


Fig. 4 Map of EPFR concentrations observed on samples collected in the East Palestine sampling effort. Location markers were intentionally enlarged to maintain privacy. The asterisk denotes the derailment site. Sites EP.019–EP.024 are referred to as the “restricted zone”.

sample set (average = 1.33×10^{17} spins per g) (Fig. 4). EPFR levels in restricted zone compared with the remaining samples were not significantly higher ($p = 0.11$), due to the small sample size in the restricted zone. The average radical concentration seen on the ten background soil samples collected before the derailment was 1.10×10^{17} spins per g. Total EPFR analysis results of the background samples are reported in ESI Table S7.† Sample locations displaying the highest radical concentrations were located just southeast of the derailment site (EP-022 and EP-023). This finding is consistent with our hypothesis that EPFRs were formed during the combustion processes utilized in the response efforts for two reasons. First, it is known that combustion processes result in the formation of EPFRs.^{5,8–10} Second, winds moved toward the southeast during the first day of the prescribed burn, and they shifted to flow towards the northwest on the second day. Wind speeds ranging from 0 to 7.7 m s^{-1} indicate a potential for some deposition near the burn site for calm winds and some transport several km downwind for higher winds (ESI Fig. S8†). Observed EPFRs near the combustion site in the restricted zone are consistent with expected results for deposited combustion products in calm conditions and for a burn at ground level. Predicted soot deposition based on the Interagency Modeling and Atmospheric Assessment Center (IMAAC) model (ESI Fig. S9†) is consistent with the latter condition showing the deposition pathway resulting from the vented burn.⁸⁹

The positive statistical correlations observed between EPFR concentration and dioxin/furan congeners are consistent with previous laboratory research showing the formation of dioxins and furans from EPFR-containing precursors.^{4,60–63} The α -values of the EPFRs seen here are also consistent with radicals previously shown to recombine into these dioxins and furans.^{60,63,64} In the East Palestine dataset, correlations between the EPFR concentration and the total measured concentrations of PeCDD

and PeCDF had the greatest statistical significance, suggesting a chemical connection between these compounds. The pentachlorinated character of the congeners that exhibited the strongest correlations supports previous field and laboratory research connecting the precursor chemicals in the vented burn processes (vinyl chloride) to the formation of dioxin/furans *via* chlorine contribution.⁶⁸ These findings suggest a shared source, although we recognize that our regression estimates are designed to identify relationships between EPFRs and dioxin/furan congeners rather than confirming any causality.

The observations of elevated levels of both EPFRs and dioxin/furans near the derailment site (<0.30 mi) (Table 1) and their correlations are noteworthy. These findings point toward a two-pronged risk to the community of East Palestine, as it is known that both EPFRs and dioxin/furans are persistent compounds, directly connected to significant health impacts.^{15–21,33–42} This work shows statistically significant correlations between soil concentrations of EPFRs and TEQ, along with statistically significant associations between EPFR concentration and some dioxin/furan congeners. The previous findings showing stable EPFRs undergoing recombination resulting in the formation of more toxic dioxin/furans,^{60,63,64} are supported by the correlations seen in this research. Based on these findings, it is necessary to conduct further research on the co-formation between toxic compounds, especially in complex native substrates such as soils.

It is important to note that soil remediation efforts have been carried out by the U.S. EPA and Norfolk Southern, some of which had not been concluded at the time of this sampling. The site sampled after remediation EP-024, in which the contaminated soil was excavated, removed, and replaced with imported fill soil, still showed higher concentrations of EPFRs and dioxins/furans when compared to background levels. Additional remediation efforts may have addressed some of the elevated levels seen in



this work, however, the EPFR and TEQ values observed through this sampling effort indicate that additional sampling research is necessary to properly assess any potential remaining risk levels from these contaminants in East Palestine. The exact nature of the EPFRs measured in this work is unknown, and thus the lifetimes of these radicals cannot be pinpointed. Additionally, the specific generation pathway of these EPFRs cannot be determined as it is known that EPFRs can be formed through combustion processes and chemical interaction with soil components.^{90,91} These samples, collected six months after the derailment, could present radical concentrations lower than those present during the initial days of the incident, as it is known that some radicals exhibit shorter lifetimes than others,^{7,11} however sample concentrations relative to one another should be consistent as these radicals are suspected to be generated by the same source. All samples collected in this data set were obtained from the surface 0–15 cm. Surface samples do not provide any information about legacy concentrations in the area, therefore additional sampling of deeper soils is needed. Industrial operations have historically taken place in East Palestine and potentially could have been a source of soil contamination. While this remains an uncertainty, there is no reason to believe that contamination due to legacy sources would be greater at the site of the derailment compared with elsewhere in the community. A more comprehensive analysis of potential contaminating compounds is also necessary to address the limited hazard assessment completed in this work. An additional limitation of this work was the small sample size, particularly inside the derailment area. This will be addressed through future sampling campaigns to further investigate deposition influences from the vented burn. Simulations by the IMAAC High-Resolution Numerical North American Model (Fig. S8†) suggest potential deposition along a swath of land at least 50 miles long, where the maximum deposition is expected to be approximately 10 miles southeast of East Palestine.⁸⁹ Because EPFRs, dioxins, and furans are persistent compounds with long lifetimes, we anticipate seeing a signature of these materials in soil collected from the identified deposition area even if the controlled burn only produced PM that deposited to the area over a few hours.

The analysis of the soil samples collected from the East Palestine community and the surrounding area, both before and after the February 3, 2023, derailment and subsequent vented burn supported our initial hypotheses that EPFRs and dioxins/furans will be co-located. Observed EPFR concentrations and *g*-values were consistent with previous research related to contamination events.^{26–32} TEQ values observed in this study were higher than many areas reported in the Urban *et al.* review,⁸⁸ but in a similar range as other dioxin/furan data from East Palestine measured by Norfolk Southern and U.S. EPA.^{69,70,87}

Conclusion

A key finding from this report is that EPFR concentrations and dioxin/furan TEQ values were elevated in soil samples collected closer to the derailment when compared to the remainder of the dataset, suggesting the controlled vented burn of February 6th, 2023, as a potential source. The findings in this work indicate

that additional research is necessary in the East Palestine region to systematically investigate the spatial distribution of EPFRs and dioxins/furans with respect to other sources in evaluating the potential risks that remain. This study also found a positive correlation between EPFR radical concentration and the measured congeners of dioxins/furans. Previous research has shown that EPFR radical recombination can lead to the formation of dioxins/furans,^{46–49} and significant positive correlations found in this study between the EPFR concentrations and dioxin/furan congener concentrations are consistent with those reports.

To the best of our knowledge, this study is the first to demonstrate a direct link between EPFRs and dioxin/furan concentrations in real-world soil, providing critical insights into environmental contamination and public health risks. Our findings underscore the urgent need for comprehensive environmental monitoring and stricter regulations to mitigate the long-term impacts of industrial accidents on the ecosystem and human health. Future studies should explore the mechanistic pathways through which EPFRs contribute to the formation of dioxins/furans, utilizing longitudinal studies to assess their long-term environmental and health impacts.

Data availability

All data enclosed in this work can be accessed *via* an online dataset.⁹²

Conflicts of interest

The authors have no known conflicts of interest to report.

Acknowledgements

This research kindly acknowledges Mr Mark Durno and the U.S. EPA for their cooperation and assistance in this soil sampling effort and data collection. We would also like to acknowledge Dr Randall Hall for the creation of the macro used in the deconvolution process, and Ms. Sandra Morgan for her coordination efforts. This work was supported by the National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program grant (P42ES013648), the NIEHS-funded North Carolina State University Center for Human Health and the Environment (P30ES025128), the National Institute of Environmental Health Sciences of the National Institutes of Health under Award Number R21ES036033, and the Herbert W. Hoover Foundation (KSU Index Number 411844). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health or the Herbert W. Hoover Foundation.

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