Dynamic spatiotemporal changes of per- and polyfluoroalkyl substances (PFAS) in soil and eggs of private gardens at different distances from a fluorochemical plant[☆]

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ABSTRACT

Homegrown food serves as an important human exposure source of per- and polyfluoroalkyl substances (PFAS), yet little is known about their spatiotemporal distribution within and among private gardens. This knowledge is essential for more accurate site-specific risk assessment, identification of new sources and evaluating the effectiveness of regulations. The present study evaluated spatiotemporal changes of legacy and emerging PFAS in surface soil from vegetable gardens ($N = 78$) and chicken enclosures ($N = 102$), as well as in homegrown eggs ($N = 134$) of private gardens, across the Province of Antwerp (Belgium). Hereby, the potential influence of the wind orientation and distance towards a major fluorochemical plant was examined. The $\sum$short-chain PFAS and precursor concentrations were higher in vegetable garden soil (8.68 ng/g dry weight (dw)) compared to chicken enclosure soil (4.43 ng/g dw) and homegrown eggs (0.77 ng/g wet weight (ww)), while long-chain sulfonates and C_{11-14} carboxylates showed the opposite trend. Short-term (2018/2019–2022) changes were mostly absent in vegetable garden soil, while changes in chicken enclosure soils oriented S-SW nearby (<4 km) the fluorochemical plant were characterized by a local, high-concentration plume. Moreover, soil from chicken enclosures oriented SE and remotely from the plant site was characterized by a widespread, diffuse but relatively low-concentration plume. Long-term data (2010–2022) suggest that phaseout and regulatory measures have been effective, as PFOS concentrations nearby the fluorochemical plant in soil and eggs have declined from 25.8 to 2.86 ng/g dw and from 528 to 39.4 ng/g ww, respectively. However, PFOS and PFOA concentrations have remained largely stable within this timeframe in gardens remotely from the plant site, warranting further rapid regulation and remediation measures. Future monitoring efforts are needed to allow long-term comparison for multiple PFAS and better distinction from potential confounding variables, such as variable emission outputs and variability in wind patterns.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a very diverse group of synthetic aliphatic compounds, in which the alkyl chain is partly and completely fluorinated, respectively (Buck et al., 2011). Since the 1940s, these compounds have been used in many industrial applications and commercial products due to their exceptional water-, oil- and stain-repellent properties (Kissa, 2001). The widespread and intensive usage of PFAS combined with their highly persistent, bioaccumulative and mobile properties have resulted in global contamination of virtually every environmental compartment and organism on earth (Cousins et al., 2020; Giesy and Kannan, 2002).

Over the past two decades, growing biomonitoring and experimental evidence has associated elevated exposure to PFAS, in particular perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), with various toxic health effects on organisms (De Silva et al., 2021; Letcher et al., 2010), including humans (Fenton et al., 2021). Consequently, the main fluorochemical producing companies have phased-out PFOS, PFOA and related long-chain compounds from 2002 onwards (3M Company, 2000). Moreover, formal restriction of PFOS and PFOA was

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imposed in 2009 and 2015, respectively, at the Stockholm Convention and has currently been ratified by 152 countries (UNEP, 2019). In response, the fluorochemical industry has shifted its production strategy towards the increased manufacturing of short-chain PFAS, precursor chemicals (Dhore and Murthy, 2021), and the development of new substitute emerging PFAS which are considered to be as similarly persistent and toxic as the legacy PFAS (Brendel et al., 2018; Munoz et al., 2019). Currently, the European Chemicals Agency is evaluating a broad restriction proposal of several countries to ban all PFAS in production and usage purposes across Europe (ECHA, 2023). However, even if emissions would cease in the future, it will still take decades to centuries for degradation and reversal of PFAS contamination in the environment (Cousins et al., 2022; Wang et al., 2015). Therefore, monitoring and evaluating temporal trends in the environment and biota will remain important for their accurate risk assessment.

Within this context, the soil is such an important environmental compartment to monitor as it represents a major sink and long-term reservoir for many PFAS (Brusseau et al., 2020; Liu et al., 2015). In parallel, the soil represents an important cultivation medium in many countries for the production of food, which is generally the most important exposure source of PFAS to the human population (Roth et al., 2020; Vestergren and Cousins, 2013). Therefore, both short-term and long-term monitoring of PFAS in soil and in food is essential to characterize the potential ongoing risks of human exposure to PFAS. Furthermore, it is imperative to evaluate the effectiveness of regulatory measures for some long-chain PFAS and the possible consequences of PFAS industrial production shifts towards short-chain PFAS and precursors on their potential accumulation in these matrices (Land et al., 2018). To the best of our knowledge, no studies to date have examined spatiotemporal trends in self-cultivated food and in garden soil, despite its utter direct importance regarding human risk assessment of PFAS. Moreover, potential differences of PFAS contamination within gardens due to functionally different areas (e.g., chicken enclosure versus vegetable segment) have not been studied.

Previous monitoring studies in Flanders (Belgium) have reported globally among the highest PFAS concentrations in environmental media and biota, including homegrown chicken eggs, nearby a main fluorochemical plant in Antwerp (Groffen et al., 2017; Lasters et al., 2022; Lasters et al., 2023; Lopez-Antia et al., 2019). However, potential spatiotemporal trends and wind orientation in function of this major point source may greatly affect the exposure risk to biota and humans, while it may improve the accuracy of risk assessment. Additionally, it may help to unravel potential new point sources, which is crucial in a densely populated and strongly industrialized region such as Flanders (Verbruggen, 1997), and can enhance our understanding of the environmental fate and distribution of PFAS. Furthermore, few data exist on spatiotemporal trends in (a)biotic matrices across Europe and the study designs are often limited, both in terms of spatiotemporal scale and selected targeted analytes (Land et al., 2018).

In the present study, the PFAS profile and concentrations within private gardens was examined with respect to vegetable garden soil, chicken enclosure soil and homegrown eggs. Secondly, potential short-term (2018/2019–2022) spatiotemporal changes of 29 targeted PFAS (legacy-, emerging-, and precursor PFAS) were investigated in these matrices, nearby and remotely from a major fluorochemical plant, throughout the Province of Antwerp (Belgium). Hereby, it was also tested whether private gardens oriented towards the dominant wind direction from this plant site, during the examined time period (2018–2022), were associated with higher egg concentrations. Moreover, potential local changes in PFAS soil concentrations were examined in repeatedly sampled private gardens before and after major road infrastructure works (i.e. Oosterweel Link, henceforth abbreviated as OW). This road infrastructure project is among the largest road work projects ever undertaken in Flanders (Belgium) and a major part of it has been conducted within vicinity (<4 km) of the 3M fluorochemical plant (Peters et al., 2022). Recent air deposition measurements during the

road works have suggested spreading of PFAS via blowing dust from the OW site (Peters et al., 2022). Lastly, long-term (2010–2022) temporal changes of PFOS and PFOA concentrations in chicken enclosure soil and in homegrown eggs were investigated.

2. Materials and method

2.1. Data collection

Five subsamples from the top soil layer (0–5 cm), each consisting of ±20 g soil, were collected with a stainless steel gouge drill. This resulted in approximately 100 g of pooled soil samples in private gardens across the Province of Antwerp (Belgium) from both the chicken enclosure and vegetable garden segment during the summer period of 2019 (resp. $N = 34$ and $N = 20$), 2021 (resp. $N = 58$ and $N = 45$) and 2022 (resp. $N = 10$ and $N = 13$). Pools of whole egg content from two individual eggs were sampled from free-ranging laying hens in 2019 ($N = 34$), 2021 ($N = 58$) and 2022 ($N = 10$) at the same moment. All the soil samples were collected from uncovered outdoor areas and the eggs originated from free-ranging laying hens with unlimited access to an outdoor enclosure.

The sampling locations were selected along a distance gradient from a known major fluorochemical point source in Antwerp (3M). The PFAS production at this fluorochemical plant started in 1976 using both continuous and batch production cycles. PFOS production took place continuously from 1976 until 2002, while production of PFOA was done sporadically (usually one week per year) via batch production cycles from 1980 until 2007 (3M Company, 2022). The C6 compounds (PFHxSA, PFHxS and PFHxA) have been manufactured until 2001 and production of C8 compounds (PFOSA, PFOS and PFOA) stopped between 2002 and 2007, depending on the compound. From 2001 onwards, the production has shifted towards C4 compounds (FBSA, PFBS and PFBA) (3M Company, 2022). Furthermore, it cannot be excluded that other PFAS have been produced unintentionally as by-products and impurities.

Private gardens were selected both nearby (<4 km range) this fluorochemical plant and remotely (>4 km range) from it across the province of Antwerp (Fig. S1). The distance boundary of 4 km was based on previous monitoring studies in this area showing that most of the variation in PFAS concentrations falls within 4 km from this point source (Groffen et al., 2017; Lasters et al., 2022; Lopez-Antia et al., 2019). Moreover, top layer (0–5 cm) soil samples from repeatedly sampled chicken enclosures ($N = 7$) and vegetable gardens ($N = 6$) were collected in 2019 and 2021 nearby (<4 km range) this point source (Fig. S1). This provided the opportunity to test whether local intensive road infrastructure works of the OW, which have begun in 2020, could be associated with temporal changes within these gardens. Moreover, the interactive PFAS map of Flanders (Department Environment and Health, 2022) was consulted to verify private gardens that were situated within vicinity of any known local PFAS source (e.g., firefighting facilities, military training sites and airports), which was not the case.

In addition to the sample collection, additional data were adopted from published monitoring studies of the same study area to increase the robustness of the later statistical analyses and to enable examination of long-term (2010–2022) trends for PFOS and PFOA. To this end, data of D'Hollander et al. (2011) on topsoil PFOS concentrations from chicken enclosures ($N = 29$) were adopted along with data of PFOS and PFOA concentrations in homegrown eggs ($N = 29$) from 2010. Moreover, data of 16 PFAS in homegrown eggs ($N = 35$) from 2018 were adopted from Lasters et al. (2022). The soil and egg samples in these studies were collected and pre-treated in the same standardized way as in the current study, which resulted in statistically comparable datasets.

2.2. Sample pre-treatment

The fresh soil samples were transferred to polypropylene (PP) tubes and oven-dried at 70 °C. The whole egg content of the homegrown eggs

was beaten and homogenized in a PP container (rinsed a priori with acetonitrile (ACN) with a stainless steel kitchen mixer and pooled into one homogenate sample. The kitchen mixer was thoroughly rinsed with ACN in between every location. All the samples were stored at −20 °C for further chemical analyses of all targeted PFAS (see Table S1).

2.3. PFAS chemical extraction

About 0.30 g of soil or egg sample was weighed on a precision balance to the nearest 0.01 g (Mettler Toledo, Zaventem, Belgium). Briefly, the weighed samples were spiked with 10 ng of mass-labelled internal standard mixture (ISTD, MPFAC-MXA, Wellington Laboratories, Guelph, Canada). Details on the chemical composition of the ISTD are provided in Table S1. Then, 10 ml of the extraction solvent (HPLC-grade ACN) was added to each sample, after which they were thoroughly vortex-mixed and sonicated during three times 10 min. After shaking over-night on a shaking plate (135 rpm, room temperature, GFL3 020, VWR International, Leuven, Belgium), the samples were centrifuged (4 °C, 10 min, 2400 rpm, 1037g, Eppendorf centrifuge 5804R, rotor A-4-44) and the supernatant was brought over to a new 15 mLPP tube. The soil samples were extracted using solid-phase extraction based on the principle of weak-anion exchange, according to the protocol described by Groffen et al. (2019b) with small adjustments. The egg samples were extracted with a clean-up step extraction using graphitized carbon powder following the protocol described by Powley et al. (2005) with minor modifications. Full descriptions of both extraction methodologies are provided in the supplementary information (SI section 1).

2.4. PFAS chemical analysis

For the PFAS analyses, in total 29 analytes were targeted in all the samples. Ultrahigh performance liquid chromatography (ACQUITY, TQD, Waters, Milford, MA, USA) coupled to a tandem quadrupole (TQD) mass spectrometer (UPLC-MS/MS), operating in negative electrospray ionization-mode was used for detection of peak signal for all the targeted analytes. The different targeted PFAS were separated using an ACQUITY UPLC BEH C18 VanGuard Precolumn (2.1 × 50 mm; 1.7 μm, Waters, USA). The mobile phase solvents consisted of ACN and HPLC grade water, which were both dissolved in 0.1% HPLC-grade formic acid. The solvent gradient started at 65% of water to 0% of water in 3.4 min and back to 65% water at 4.7 min. The flow rate was set to 450 μL/min and the injection volume was 6 μL (partial loop). PFAS contamination that might originate from the LC-system was retained by insertion of an ACQUITY BEH C18 pre-column (2.1 × 30 mm; 1.7 μm, Waters, USA) between the solvent mixer and the injector. The targeted PFAS analytes were detected and quantified based on multiple reaction monitoring (MRM) of the diagnostic transitions, which are displayed in Table S1 as validated by Groffen et al. (2019b, 2022).

2.5. Quality control and quality assurance

During the homogenization of the biotic samples, solvent blanks (=10 mL of ACN) were included every 10 samples to check for cross-contamination between the samples. During the extraction, one procedural blank (=10 mL ACN spiked with 10 ng of ISTD solution) was included per 15 samples to verify any contamination during the extraction. During instrumental analysis, solvent blanks (ACN) were regularly injected to rinse the columns and prevent cross-contamination across injections. In the case of batch contamination, the procedural blank values were subtracted from the subsequently measured samples. For the clean-up of the egg samples, 50 mg of graphitized activated carbon powder was used per 0.30 g egg sample to remove the PFOS-interferent analyte taurodeoxycholic acid (TDCA) from the extract, as validated by Sadia et al. (2020).

Calibration curves were prepared by adding a constant amount of the ISTD to varying concentrations of an unlabelled PFAS mixture. The

serial dilution of this mixture was performed in ACN. A linear regression function with highly significant linear fit (all $R^2 > 0.98$; all $P < 0.001$) described the ratio between concentrations of unlabelled and labelled PFAS. The individual compounds were quantified using their corresponding ISTD except for compounds of which no ISTD was present. These analytes were all quantified using the ISTD of the compound closest in terms of functional group and size (Table S1), which was validated by Groffen et al. (2019b, 2021).

2.6. Data processing

Limits of quantification (LOQs) were calculated in matrix for each detected analyte and considered as the concentration corresponding to a peak signal-to-noise ratio of 10. For all the compounds, LOQs are provided for chicken enclosure soil, vegetable garden soil and homegrown eggs in Tables S2–S4, respectively. For every matrix, a common LOQ was assigned among the sampling years which corresponded to the maximum LOQ among all the years combined to reduce bias in studying the actual temporal trends, following Jouanneau et al. (2020). For PFAS that were <LOQ, replacement concentration values were assigned according to the maximum likelihood estimation method (De Solla et al., 2012; Villanueva, 2005). For the linear discriminant analysis (see section 2.7.), concentration values of the various detected PFAS compounds were centred and standardized to obtain equal mean and standard deviations.

The distance of the private gardens from the point source was considered as a categorical variable and divided into two sub-categories: ≤4 km from the plant site and >4 km from the plant site, henceforth also referred to as "nearby the plant site" and "remotely from the plant site", respectively. The precise geographical location of the adopted data from private gardens of 2010 could not be verified as these data were reported at sub-municipal level by D'Hollander et al. (2011). Hence, the distance from the plant site could not be accurately quantified for these samples. In the results and discussion section, "large-scale" refers to both distance categories, while "small-scale" refers only to private gardens "nearby the plant site". The orientation of each private garden relative to the plant site in Antwerp was assessed following the conventional eight-division classification system of wind direction (Yannopoulos, 2011), resulting in the following wind orientation sectors: N (337.5°–22.5°), NE (22.5°–67.5°), E (67.5°–112.5°), SE (112.5°–157.5°), S (157.5°–202.5°), SW (202.5°–247.5°), W (247.5°–292.5°) and NW (292.5°–337.5°).

2.7. Statistical analysis

All the statistical analyses and data visualizations were performed in the R program version 4.2.3 (R Core Team, 2023) and in GraphPhad Prism version 9. The threshold level for significance testing was set at $P \leq 0.05$ for statistical significance testing. Descriptive statistics (geometric mean and min.-max. range) were computed for all detected PFAS in the top soil (chicken enclosure and vegetable garden) and in homegrown eggs for every sampling year and considering the distance category from the major fluorochemical point source in Antwerp. The Shapiro Wilk's test was conducted to verify normality assumptions of the data, and the data were log($x° +° 1$) transformed to meet normality assumptions of the residuals.

Firstly, multivariate linear discriminant analysis (LDA) was conducted to better understand the general PFAS profile and concentration characterization across the three matrices, but also to explore whether separate clusters could be identified according to the wind orientation towards the plant site, based on the explained variation in PFAS concentrations by the two first linear discriminant functions (i.e., LD1 and LD2). Compounds that were <50% of the LOQ in any matrix were excluded from the linear discriminant analysis to enable valid matrix comparisons for commonly detected compounds.

Then, several two-way ANOVA models with distance category from the plant site and matrix type were ran to evaluate specific significant

differences in PFAS concentrations among the matrices according to the distance from the plant site. Another two-way ANOVA model, with sampling year and distance category from the major fluorochemical plant both as fixed factors, was constructed to test specific temporal differences for each matrix. After formal ANOVA testing, post-hoc Tukey's HSD multiple comparison tests were conducted to examine which specific pairs of sub-variables were significantly different. The variable sampling year was considered as a factor in these analyses as it could not be assumed that time behaved linear between the relatively large time gap of the period from 2010 to 2018 and the relatively small sample size. For private gardens that were repeatedly sampled among the years, only the measurement from the first sampling year was included to avoid pseudoreplication in this analysis.

For each matrix, spatiotemporal differences were tested with ANCOVA linear models, containing the wind orientation towards the plant site and sampling year as a fixed factor, as well as the distance from the plant site as a continuous covariate. Then, significant differences in the spatiotemporal distribution of PFAS concentrations among the three matrices were further interpreted by means of the package "openair" in R (Carslaw, 2019; Carslaw and Ropkins, 2012). Hereby, the function windRose was firstly used to plot the frequency of both wind direction and wind speed in the study area during the sampling years 2019, 2021 and 2022. To this end, meteorological time-series data of these wind parameters were adopted from the open-source databank of the Flanders Environment Agency (VMM, 2022). Then, the polarPlot function was used to visually plot the PFAS concentrations of each matrix towards the plant site using Gaussian kernel smoothing, which apportions the observed mean concentration of a pollutant to sectors defined by distance and orientation towards the plant site (Henry et al., 2009). Furthermore, it is also an effective way to visualize spatiotemporal trends while anonymizing the individual location of the private gardens.

Lastly, to test the hypothesis whether the OW road works may influence local soil concentrations in nearby private gardens, repeated paired data of private gardens from 2019 to 2021 nearby the plant site were selected from the original dataset. Then, paired t-tests were conducted to test for potential differences between both sampling years within the same private gardens. Lastly, Pearson correlation tests were conducted for the paired data between the nearest distance from the OW road works site and the soil PFAS concentrations.

3. Results & discussion

3.1. PFAS profile and concentration patterns within private gardens

For clarification and readability reasons, the terms "chicken enclosure soil", "vegetable garden soil" and "homegrown eggs" are henceforth referred to as "chicken soil", "garden soil" and "eggs", respectively.

From the 29 targeted PFAS, up to 15 and 20 analytes could be detected in the chicken soil and garden soil, respectively (Tables S2 and S3). In every soil sample, at least five PFAS compounds could be detected which strongly varied in terms of composition among the samples, regardless of the distance from the major fluorochemical plant. This widespread and heterogeneous presence of PFAS in soil is in agreement with other large-scale PFAS monitoring studies in surface soil, demonstrating that this environmental compartment is a major reservoir for PFAS, both in residential areas that are industrially impacted and in sites without any known nearby source (Brusseau et al., 2020; Sörengard et al., 2022).

Compared to general soil data at non-suspected sites across Europe, the mean concentrations for the $\sum$PFCAs and $\sum$PFSAs in the chicken soil ($\sum$PFCAs = 3.58 ng/g dw; $\sum$PFSAs = 7.66 ng/g dw) and garden soil ($\sum$PFCAs = 7.38 ng/g dw; $\sum$PFSAs = 7.99 ng/g dw) largely exceeded the mean concentrations of soil for the same $\sum$PFCAs and $\sum$PFSAs in Europe, respectively 1.00 ng/g dw and 0.808 ng/g dw (Rankin et al., 2016). For most compounds, the soil concentration range fell within the same order of magnitude compared to previous local soil measurements

in nature areas nearby the fluorochemical plant site in Antwerp (Groffen et al., 2019a,c).

In the eggs, up to 16 compounds could be detected (Table S4) including PFHpA, PFHxS and PFDS, whereas these compounds were <LOQ in the chicken soil. The egg concentrations of the present study were among the highest ever reported in homegrown chicken eggs (Gazzotti et al., 2021; Su et al., 2017; Wang et al., 2019), especially for PFBS and PFOS (Table S4). This confirms earlier findings that homegrown egg consumption can be a major PFAS exposure source presenting potential health risks to humans (Lasters et al., 2022). Together, these results indicate that the general PFAS contamination burden in the Province of Antwerp is among the highest compared to other regions in Europe, which is in agreement with the recently established PFAS pollution map of Europe (Le Monde, 2023) and may be linked with the large degree of industrialization in the densely populated Flanders (Verbruggen, 1997).

The linear discriminant analysis showed that most variation in PFAS concentrations for soil and eggs could be explained by the linear discriminant function 1 (LD1) and linear discriminant function 2 (LD2), which together explained >84% of the total variation in PFAS concentrations (Fig. 1). Clearly, the variation in PFAS concentrations was better explained by the matrix type than the distance (nearby or remotely) from the fluorochemical plant site, indicated by the large overlap of clusters between samples nearby the plant site and remotely from the plant site (Fig. 1). Importantly, regardless of the matrix type, increased concentrations in private gardens nearby the fluorochemical plant site in Antwerp were primarily caused by significantly higher concentrations of FBSA, PFBA, PFBS, PFHxS, and PFOS (Fig. 1, Tables S2–S3). This finding supports the outcome of earlier PFAS monitoring studies in this area which also found indications that historical industrial emissions have been an important source of phased-out PFHxS and PFOS (Groffen et al., 2019a, 2019c). Moreover, the present study affirms early indications that precursor compounds, such as FBSA, as well as short-chain PFBS and PFBA can also be linked with recent industrial emissions (Dhore and Murthy, 2021).

The multivariate analysis revealed large differences between the garden and chicken soil, in terms of PFAS profile and concentrations (Fig. 1). The vector loadings emphasized that garden soil was distinguished from the chicken soil by distinct clustering of significantly higher concentrations for PFBA, PFHpA, PFHxA, FBSA, and 6:2 FTS (all $P < 0.01$, Figs. 1 and 2). This supports our hypothesis that vegetable gardens are enriched with these compounds through intensive soil management and frequent addition of soil amendment products (compost and potting mixes) by gardeners, which are known to be enriched with short-chain PFCAs and precursors of PFCAs (Sivaram et al., 2022). Additionally, these PFCA precursors (FTSs, di-PAPs and FOSA) can be partly transformed into various short-chain PFCA end-products under ambient soil conditions (Lazcano et al., 2020), especially in the presence of root exudate associated microorganisms in the plant rhizosphere (Just et al., 2022). Lastly, the typical PFAS profile in the garden soil can also be explained through the frequent supply of irrigation water, which is known to largely contain short-chain PFCAs and precursors, due to their relatively high water solubility and mobility (Scher et al., 2018; Zhang et al., 2021). To the best of our knowledge, the present study is the first that examined and identified relatively large differences in PFAS contamination within private garden sections (Figs. 1 and 2), depending on their functional usage. Therefore, comparisons with literature data should be interpreted with caution as the precise origin of the soil is rarely specified.

Except for FBSA, which was found at low concentrations and only nearby the plant site, no targeted precursor compounds were detected in the eggs (Table S4). Moreover, from the precursor compounds that were primarily detected in the present study (i.e. 6:2 FTS and FBSA), significantly lower concentrations were consistently observed in the chicken soil compared to the garden soil ($P < 0.01$, Fig. 2a and b). On the other hand, end-degradation products of these precursors, which are PFBS and
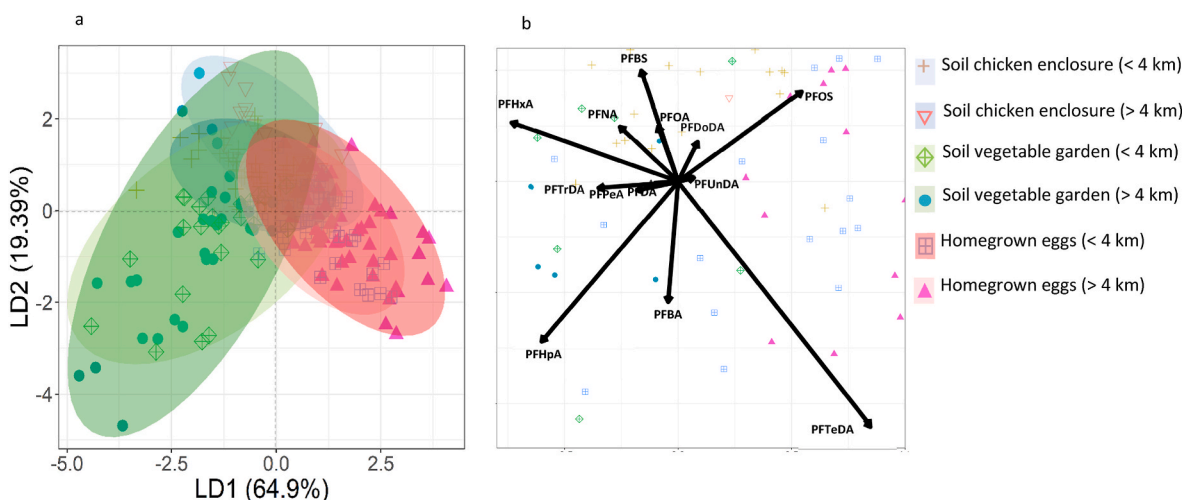
Fig. 1. (a) Multivariate linear discriminant analysis of PFAS concentrations clustered according to the matrix type (soil chicken enclosure, soil vegetable garden and homegrown eggs) and distance from the plant site (<4 km or > 4 km range from the fluorochemical plant site in Antwerp (Belgium)), based on the two first linear discriminant functions LD1 and LD2, which explained 64.9% and 19.4% of the total variation in PFAS concentrations, respectively. (b) Biplot showing the factor loadings and scores of each PFAS compound, indicated by the vector arrows. Symbols and colours represent different matrix types and different distance categories. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

a mixture of $C_{4\text{-}6}$ PFCAs for FBSA and 6:2 FTS, respectively (Méndez et al., 2022; Sivaram et al., 2022), were frequently found in the chicken soil and eggs, while PFBS was the main compound that could be attributed for the distinct cluster of chicken soil from the multivariate analyses. Together, these results suggest that these precursor compounds can be readily biotransformed to their respective end products, which has been demonstrated experimentally for related precursors of PFSAs (Kowalczyk et al., 2020) and PFCAs (Chen et al., 2020) in laying hens.

In contrast to the garden soil, higher PFBS and PFOS concentrations were related with the separate clustering of chicken soil and eggs (Fig. 1b) and significantly higher concentrations were found in eggs for $C_{9\text{-}14}$ PFCAs and most PFSAs, especially PFOS (all $P < 0.05$, Fig. 2c). This suggests that chicken enclosure soil is an important exposure source of long-chain PFSAs and PFCAs to the laying hens. Free-ranging laying hens are geophageous animals that are known to be particularly susceptible for exposure to pollutants via ingestion of contaminated soil particles (Waegeneers et al., 2009). PFSAs and long-chain PFCAs generally exhibit stronger sorption affinity towards the soil and larger bioaccumulation potential compared to short-chain PFAS (Brendel et al., 2018).

3.2. Short-term spatiotemporal trends (2018/2019–2021)

3.2.1. Large-scale changes in PFAS concentrations

Dynamic short-term temporal increases in PFAS concentrations were most evident in the chicken soil and eggs for short-chain compounds (PFBA, PFHxA and PFBS) and long-chain PFCAs (C_{10} and $C_{12\text{-}14}$), as well as for the precursors FBSA and 6:2 FTS (all $P < 0.01$, Fig. 2a and c). On the other hand, almost no differences were observed among years for PFOA and PFOS. In fact, apart from decreasing concentrations of PFOA and PFDS in the chicken soil remotely from the plant site and in the garden soil, respectively, concentrations of most compounds increased (i.e., chicken soil and eggs) or remained stable (i.e., garden soil) from 2018/2019–2022, depending on the matrix type (Fig. 2a–c).
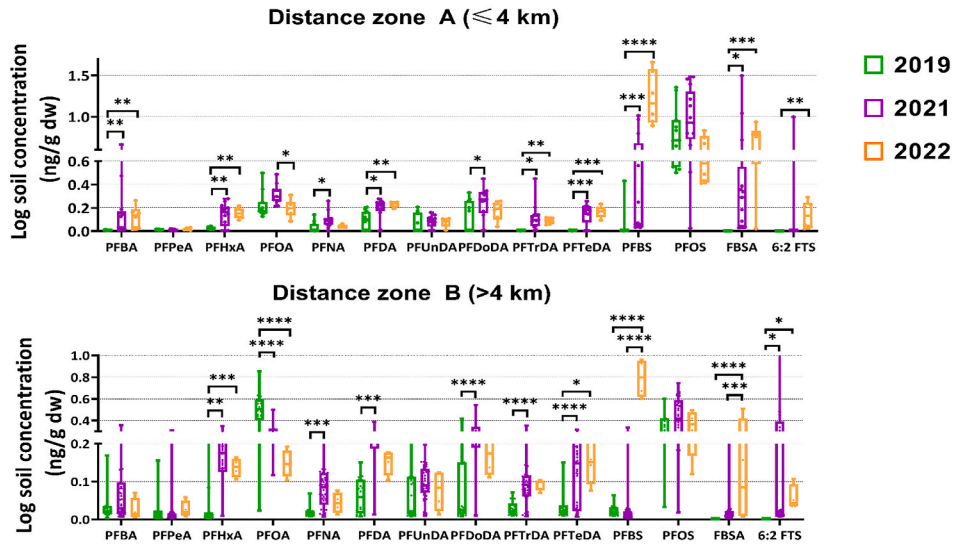
The majority of temporal studies in abiotic matrices, which are mainly limited to sediment and water, as reviewed by Land et al. (2018), have reported similar increasing trends of long-chain PFCAs and precursors over time, while no clear trends have been observed for PFOS and PFOA. The observed temporal changes in eggs are partly in line with other monitoring studies in free-living birds, which observed no clear

changes in PFOS and PFOA concentrations over time, while increased concentrations were reported for some long-chain PFCAs in predatory birds of relatively high trophic levels (Bustnes et al., 2022; Miller et al., 2015), including in buzzard liver samples from Flanders (Groffen et al., 2023). However, these changes are often less consistent and for fewer compounds than those found in the present study. While dynamic changes of PFAS have also been observed in other studies within a small time frame (Meng et al., 2022), the present study supports the earlier proposed hypothesis that ecosystems show a lagged response to environmental changes in pollutant concentrations (De Silva et al., 2021), according to the trophic level of organisms. In other words, organisms on lower trophic levels which have closer exposure to environmental media (e.g. dust, water and soil), such as free-ranging laying hens, seem to respond relatively fast to environmental PFAS changes, while organisms which are on a relatively high trophic level, such as apex predatory birds, have a lagged response.
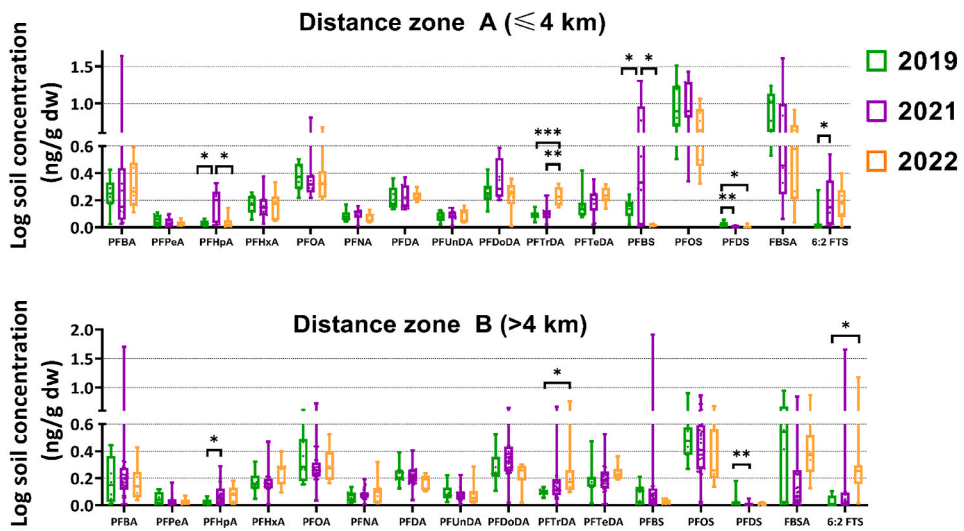
Both nearby and remotely from the plant site, the concentrations of most short-chain PFAS and the precursors significantly increased in chicken soil (PFBS, PFHxA, FBSA and 6:2 FTS), garden soil (PFHpA and 6:2 FTS) and eggs (PFHxA) over time (all $P < 0.05$, Fig. 2a–c), which is in line with the recent shift of the fluorochemical industry towards increased production of these compounds (Dhore and Murthy, 2021; Munoz et al., 2019). Interestingly, the relative increase of these compounds tended to be larger in private gardens nearby the fluorochemical plant site in Antwerp (Fig. 2a–c), which further supports that the PFAS production shift may be an important driver of the observed temporal trends for these PFAS. Notably, PFBS was the short-chain compound with the largest, relative increase over time in chicken soil, both nearby and remotely from the plant site (Fig. 2a). Likewise, FBSA (i.e. precursor of PFBS) concentrations also strongly increased in chicken soil. On the other hand, FBSA was only sporadically detected in eggs while PFBS concentrations did significantly decrease only in this matrix (all $P < 0.05$, Fig. 2c). This finding confirms the earlier findings that biotransformation of FBSA to PFBS is probable (Chen et al., 2020) and may explain this specific temporal pattern.

The long-chain PFCAs (C_{12}–C_{14}) significantly increased from 2019 to 2022 in chicken soil and eggs both nearby and remotely from the plant site (all $P < 0.05$, Fig. 2a and c). Apart for PFTrDA, no such trends were observed for long-chain PFCAs in the garden soil (all $P > 0.05$, Fig. 2b). Contrarily to the short-chain PFCAs and precursor compounds, the relative increases for these long-chain PFCAs were rather uniform over
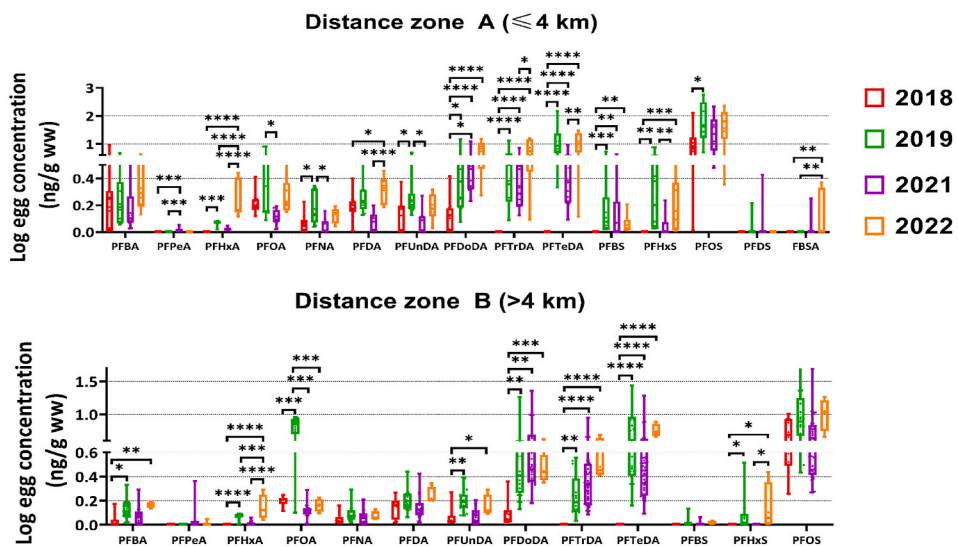
(a)

(b)

(c)

(caption on next page)

time between private gardens nearby the plant site and those located remotely from it. Moreover, the majority of samples for every matrix fell within the range of 1/1 to 6/1 ratio for both the homologue pairs of PFDA/PFUnDA and PFDoDA/PFTrDA in every sampling year at private gardens further away from the plant site and, with few exceptions, also for private gardens nearby the fluorochemical plant site (Table S5). Fluorotelomer degradation typically leads to relatively consistent homologue ratios of deposited PFCAs over time and can be a useful tool for further elucidation of potential precursor degradation (Rankin et al., 2016; Prevedouros et al., 2006). Homologue ratios of PFCAs ranging between 1/1 and 6/1 are typical for atmospheric transport of FTOHs precursors and subsequent oxidation, while ratios above 8/1 are indicative for direct PFCA emissions and/or biological degradation (Rankin et al., 2016). Therefore, it is likely that atmospheric oxidation of PFCA precursor compounds, such as fluorotelomer alcohols (FTOHs), may be an important driving pathway for explaining the increase of long-chain $C_{10\text{-}14}$ PFCAs (Styler et al., 2013).

Ratios above 8/1 for the homologue pair PFOA/PFNA were observed for chicken soil and egg samples, with a decreasing mean ratio from 2019 to 2022 in chicken soil (Table S5). These results further strengthen the hypothesis that atmospheric oxidation of precursors is a plausible mechanism for the elevated C_{10-14} PFCA concentrations found in the present study. On the other hand, PFOA and PFNA probably originate from historical emissions and consumer products, but also from biological transformation of precursors as often high PFOA/PFNA concentration ratios were found for chicken soil and eggs. Since the scope of the present study was restricted to two precursor compounds (FBSA and 6:2 FTS), future monitoring efforts should include FTOHs as targeted analytes to further elucidate this hypothesis.

In contrast to what is observed for chicken soil, short-term temporal changes were largely absent in the garden soil (Fig. 2b). This difference may be explained by functional differences in human soil management practices between these two garden segments. Frequent physical disturbance of the top soil layer and addition of soil amendments in the garden soil may mask environmental changes in PFAS concentrations (Sivaram et al., 2022; Gerardu et al., 2023), while such soil manipulations and disturbances are limited in chicken enclosures. Consequently, the chicken soil may provide a better reflection of potential environmental changes in PFAS concentrations than garden soil. Regarding the eggs, similar directions of temporal changes were observed as for the chicken soil in the present study, although the magnitude of change was often larger and more explicit (Fig. 2a and c). This finding also provides evidence that free-ranging laying hens, due to their close relatively small home-range and close proximity to humans, can be ideal bioindicators of pollutants in residential areas (Lasters et al., 2022; Zergui et al., 2023).

3.2.2. Influence wind orientation towards point source

Meteorological data showed dominant NW-N and N-NE wind currents (>50%) in the region near the fluorochemical plant in Antwerp from 2019 to 2021, respectively (Fig. S2). Nearby the plant site, concentrations of soil and eggs, in private gardens oriented S-SW from the plant site, were often significantly higher for PFBA, PFBS, PFHxS, PFOS and FBSA in recent years (2021 and 2022) (all $P < 0.05$, Figs. S2–S4). These high but relatively local pollution plumes sharply decreased with increasing distance from the plant site (Figs. S2–S4). Recently, aerial and dust deposition measurements in the same distance zone from this plant

site also confirmed strong but local distance gradients for some of these compounds (Peters et al., 2022). Moreover, a similar spatial pattern has been described by monitoring studies within the same study area in soil (Groffen et al., 2019c), isopods (Groffen et al., 2019a) and bird eggs (Lasters et al., 2022). Together, these findings strongly indicate that direct historical emissions from the fluorochemical plant, followed by atmospheric deposition, likely explain the typical plume pattern for these compounds.

For 2021, consistently elevated concentrations of long-chain PFCAs ($C_{11\text{-}14}$) were observed downwind in chicken soil remotely from the plant site in S-SE direction (all $P < 0.05$, Fig. S2), suggesting long-range atmospheric transport and oxidation of precursor compounds. It is difficult to fingerprint potential sources to explain this pattern. Nevertheless, it is likely that these elevated concentrations originate from distant, diffuse constant sources rather than local stack sources, given that the contamination area is relatively widespread (Gerardu et al., 2023; Peters et al., 2022). Moreover, the ratios of PFCA homologue pairs fell within the typical range for precursor oxidation (Rankin et al., 2016), both nearby and remotely from the fluorochemical plant site (Table S5; chicken soil 2021). Unfortunately, no private gardens could be sampled in 2019 and 2022 from these areas to evaluate whether these trends would be confirmed. Therefore, future PFAS monitoring programs in these particular areas would be helpful for further identification of potential source types.

Remarkably, a strong peak of PFOA concentrations in 2019 was followed by a steep decrease in 2021 (Fig. 2a and c). This could be attributed to a cluster of private gardens which were sampled ±9 km away and oriented N-NE from the fluorochemical plant site (soil chicken enclosure, Fig. S2b; homegrown eggs, Fig. S4b). It is not possible to identify the precise source of this elevated PFOA concentration, based on the present study data. However, this pattern was observed in both the soil and the eggs, which may suggest a common source. Although speculative, it should be noted that these private gardens were all situated E-SE within 3 km from a large waste incineration plant. Waste incinerators, such as the one in the study area of the present study (Department Environment and Health, 2022) and elsewhere (Gerardu et al., 2023; Liu et al., 2021), have been identified as active sources of diffuse environmental contamination of complex PFAS mixtures. Indeed, the input material for incineration can range diversely from PFAS-containing household and consumer products to industrial waste products. Hence, emissions can strongly vary in terms of concentrations and compounds (Liu et al., 2021). It would be useful to install passive air samplers in private gardens within a E-SE distance gradient from this potential source to continuously monitor PFAS in circulating air and dust samples to evaluate whether this hypothesis would be supported.

It should be noted that, on the long-term, wind currents in Flanders are mainly originating from the S-SW directions, implying that private gardens located N-NE nearby the plant site would also have relatively higher PFAS concentrations compared to other private gardens at comparable site distance, but in another orientation. Recent investigations in this study area, based on dust deposition data (Peters et al., 2022), have indeed found indications that N-NE located sites from the fluorochemical plant may receive relatively larger PFAS inputs via historical aerial deposition. However, it was practically impossible to investigate such long-term wind effect in the present study for private gardens as the N-NE region nearby the plant site almost exclusively

consists of industrial area and is also intersected by the Scheldt river. Finally, it cannot be ruled out that short-term changes in industrial emission releases may also affect the interpretation of the results. However, if emissions would have been variable, then one might expect variable statistical effects (mix of increases and decreases of concentrations) or no differences among the years, which was not the case based on the data of the present study (Fig. 2). Nonetheless, systematic air measurements with passive air sampling stations during one year, within vicinity of point (e.g., fluorochemical plant) and diffuse PFAS sources (e.g., waste incinerator), would be helpful to quantify potential emission variation and to further disentangle this potential confounding variable.

3.2.3. Small-scale changes in PFAS concentrations (2019–2021)

For repeatedly sampled chicken enclosures nearby the plant site in 2019 and 2021, mean soil concentrations were significantly higher in 2021 compared to 2019 for FBSA, PFOS, PFHxA and C_{10-14} PFCAs (all $P < 0.05$, Fig. 3). For PFBA, a similar trend was observed, albeit just not significant ($P = 0.06$). For repeatedly sampled gardens in 2019 and 2021 nearby the plant site, mean soil concentrations were significantly higher for PFHpA and 6:2 FTS in 2021 compared to 2019 (both $P < 0.05$, Fig. 3), while an increasing trend was observed for PFBS ($P = 0.08$). On the other hand, FBSA concentrations were significantly lower in 2021 than in 2019 ($P < 0.05$, Fig. 3). For all the other compounds, no significant changes in garden soil concentrations between both years were observed (all $P > 0.05$). Importantly, the temporal changes in long-chain PFCA and precursor concentrations were largely in line with those observed in the large-scale dataset (see previous section 3.2.1) and mostly for the chicken soil (Fig. 3), which may be due to previously discussed differences in soil management and practices between these two garden segments.

Moreover, further correlation analyses of the repeatedly sampled

chicken enclosures in 2021 revealed that PFBA concentrations were strongly and significantly negatively correlated with the nearest distance from the OW road work site ($P < 0.05$, $R_{2021} = -0.83$; Fig. S5), while this trend was absent in 2019. The same pattern could also be observed for the soil PFOS concentrations (both $P < 0.001$, $R_{2019} = -0.93$ and $R_{2021} = -0.98$, Fig. S5) and the precursor compounds FBSA and 6:2 FTS (Fig. S5; FBSA: $P < 0.05$, $R_{2021} = -0.85$ and 6:2 FTS: $P < 0.05$, $R_{2021} = 0.98$; Fig. S5), both which were not detected in 2019. The other compounds did not show any significant correlations (all $P > 0.05$).

Together, these results suggest that soil disturbance and transfer activities on the OW road work site may be associated with higher local soil concentrations. Peters et al. (2022) conducted atmospheric air and dust measurements near this OW road work site and also demonstrated elevated concentrations of PFBS and PFOS closer to the site compared to background measurements. Moreover, higher amounts of PFAS deposition were observed on rainy days, indicating that wet deposition is an important route of atmospheric deposition (Peters et al., 2022; Pfotenhauer et al., 2022). PFAS can be adsorbed onto fine and coarse dust fractions, which can act as vehicles for both long-range and short-range transport of PFAS, if these fractions become airborne due to physical disturbance (Liu et al., 2021; Peters et al., 2022). This implies that OW could contribute to this process. Moreover, construction of asphalt roads have been intensively conducted on the OW site, which have also been associated with increased volatilization of PFAS into the air (Bastow et al., 2022). This may also explain the finding that correlations with distance from the road work site were mostly found for short-chain PFAS, which are more volatile than their long-chain homologues (Brunn et al., 2023). Evidently, the wind orientation of the private gardens towards the OW construction site can also play a significant role hereby. Unfortunately, this could not be properly investigated due to the irregular shape of this area and the limited sample size of this repeated
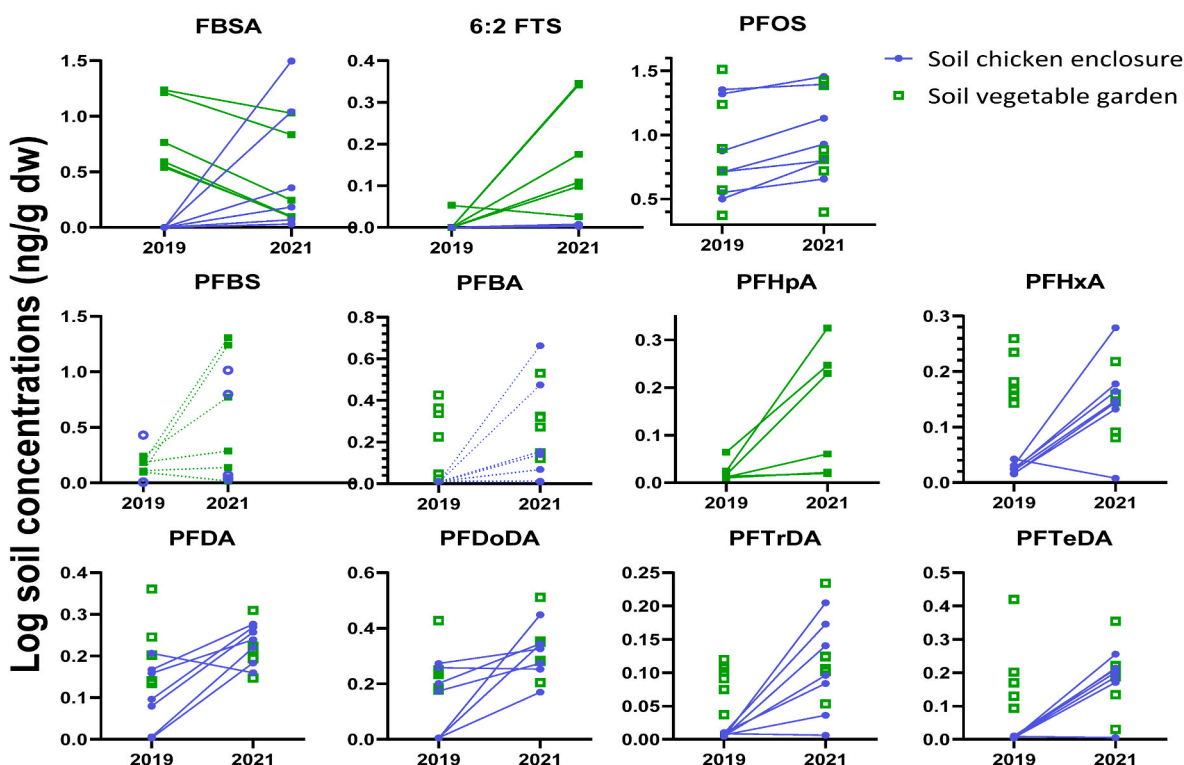

Fig. 3. Local short-term temporal changes in soil PFAS concentrations (in ng/g dw) of repeatedly sampled private gardens in 2019 (before the Oosterweel road works) and in 2021 (during the Oosterweel road works) within 4 km from the fluorochemical plant site in Antwerp (Belgium). The blue circles and green rectangles represent top soil layer data of repeatedly sampled chicken enclosures ($N = 7$) and vegetable gardens ($N = 6$), respectively. Solid lines denote statistically significant ($P < 0.05$) concentration changes from 2019 to 2021. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
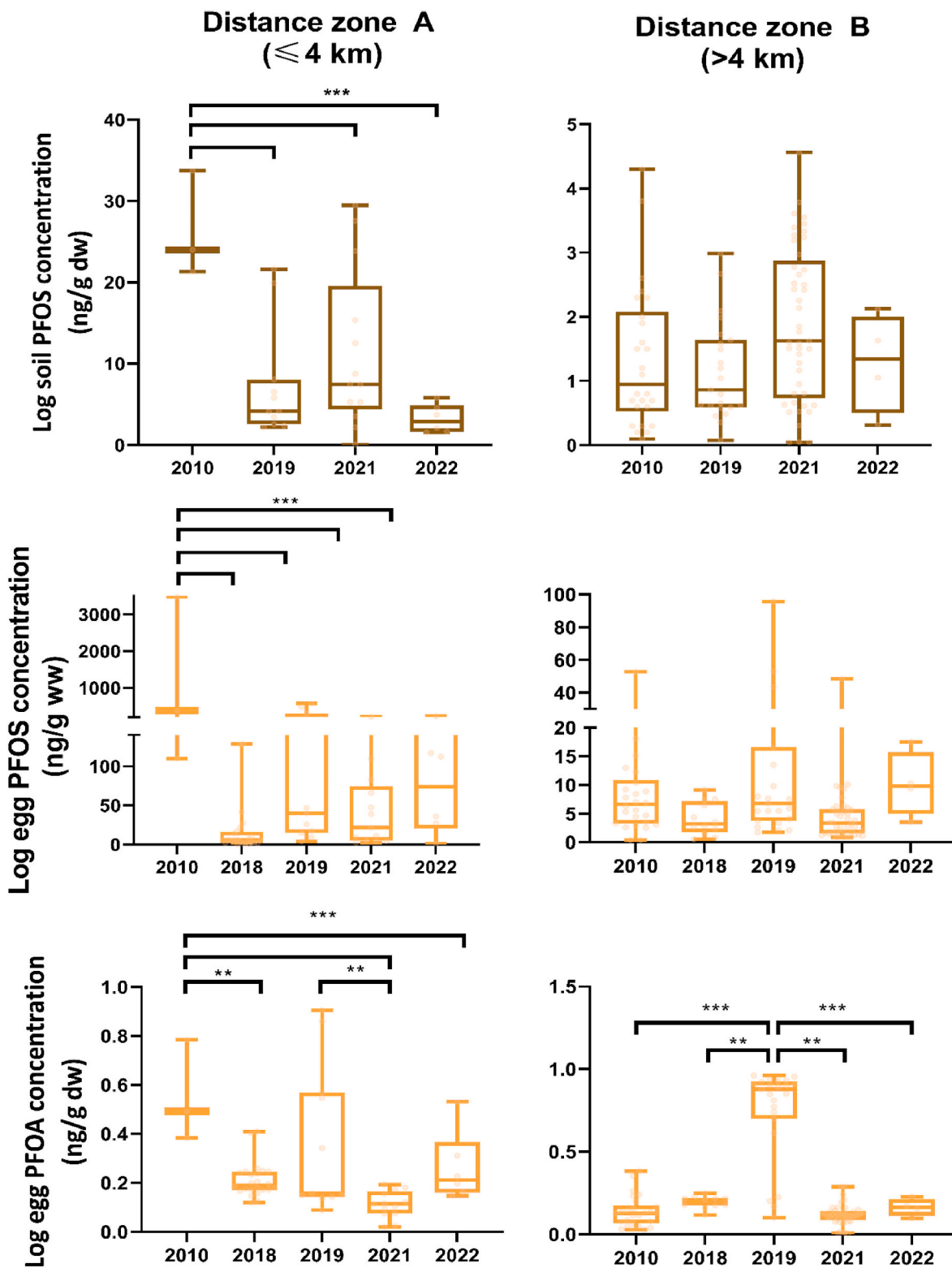
Fig. 4. Long-term temporal trends of PFOS and/or PFOA concentrations in the top soil layer of chicken enclosures (in ng/g dry weight; upper graphs) and homegrown eggs (in ng/g wet weight; lower graphs) within 4 km and outside 4 km range from the major fluorochemical point source in Antwerp (Belgium) from the time period 2010–2022. Box whiskers denote the log min.-max. concentrations and significant differences between years are shown with asterisks (*: $P \leq 0.05$, **: $P \leq 0.01$; ***: $P \leq 0.001$).

dataset.

3.3. Long-term spatiotemporal trends: Soil and homegrown eggs (2010–2022)

Nearby the fluorochemical plant site, a clear significant decline of PFOS concentrations in chicken soil, and for both PFOS and PFOA in eggs, was found for the long-term dataset from 2010 to 2022 (all $P <$ 0.05, Fig. 4). However, remotely from the plant site, PFOS and PFOA concentrations in these matrices remained unchanged during this time period (all $P > 0.05$, Fig. 4). Consequently, the industrial phase-out of these compounds and regulatory measures (3M Company, 2000) did not appear to have an effect further away from the plant site, but only largely affected private gardens nearby the plant site. Moreover, based on the short-term dataset, PFOS and PFOA concentrations nearby the plant site remained unchanged during the last years (2018/2019–2022), which may also indicate that the effect of the regulatory measures and phase-outs on environmental and biota concentrations may have faded over recent years, similar to what other temporal studies have reported for long-term (>10 year timeframe) datasets (Jouanneau et al., 2020; Land et al., 2018; Pereira et al., 2021).

Long-term temporal monitoring studies of PFOS and PFOA at non-suspect sites have often reported mixed results. The majority also shows an absence of changes over the long-term for soil (Land et al., 2018), while unchanged (Eriksson et al., 2016), decreasing (Wang et al., 2022) or even increasing trends (Land et al., 2018) have been observed in bird eggs. Differences in site-specific environmental conditions and historical PFAS emissions, both in terms of quality and quantity, are likely to explain these contrasting results across countries as well as the species' ecology, e.g. marine vs terrestrial birds (Jouanneau et al., 2020; Land et al., 2018). Moreover, a temporal investigation of PFAS in buzzard livers, randomly sampled across Flanders, also did not find any significant concentration changes of PFOS and PFOA from 2000 to 2021 (Groffen et al., 2023). Therefore, in densely populated and industrialized areas with large historical emission outputs, such as Flanders (Verbruggen, 1997), it remains important to continuously monitor temporal trends for PFOS and PFOA, which are still widespread and abundant in the environment.

Remarkably, the rate of decrease for PFOS from 2010 to 2022 in chicken soil and eggs was very similar (Fig. 4), suggesting again that soil is a major PFAS exposure source for laying hens and strongly correlates with PFAS accumulation in the eggs (Lasters et al., 2022). Although median PFOA concentrations in eggs were five times lower than PFOS in 2010, the decrease over time was proportionally slower than for PFOS while the reverse could be expected. Provided that the soil is a dominant exposure source of PFAS to the laying hens and that PFOA leaches much faster from the surface soil to the groundwater than PFOS (Gerardu et al., 2023), one would expect a faster decrease in PFOA concentrations over time in eggs. This could imply that other sources than the soil are important for PFOA exposure to laying hens, e.g. rain water (Cousins et al., 2022) and vegetable leftovers which can contain considerable concentrations of PFOA (Li et al., 2019). Alternatively, this relative difference in decreasing rate can also be explained by the fact that PFOS had already been phased-out much earlier in 2002, while this was only the case for PFOA in 2015 (UNEP, 2019).

Evidently, biological factors, such as inter-individual age differences, may also affect egg PFAS concentrations and could also hinder the interpretation of temporal changes in egg concentrations. However, age had only a minor influence on egg concentrations (Lasters et al., 2022) and more than 70% of the laying-hens in the present study was distributed between one and three years old, thus effects of age differences is expected to be negligible. Moreover, the present study showed that dynamic, short-term temporal trends observed for the chicken soil were often very similar compared to those in eggs, especially for long-chain PFCAs (C_{11-14}). Importantly, these specific compounds are actual by-products of PFOA production and should therefore, in parallel,

have remained stable or decreased over time, which was clearly not the case. Based on the current body of evidence, it is obvious that former restrictions are not sufficient to further reduce the environmental concentrations of these persistent and toxic substances. Therefore, in view of the ongoing and, for some PFAS, even increasing impact on the environment and related health concerns of PFAS, rapid regulatory actions are crucial, particularly in regions with a relatively high chemical footprint, such as Flanders.

4. Conclusions

To the best of our knowledge, our study is the first to demonstrate large differences within private gardens, both in terms of PFAS profile and concentrations. Apparently, vegetable garden soils were being much less affected by environmental changes of PFAS concentrations compared to chicken enclosure soil, probably due to functional differences in soil management processes. Dynamic short-term temporal trends, taking into account wind orientation towards a major PFAS point source, were observed in soil and eggs across a relatively large spatial scale. However, further monitoring efforts are needed in the coming years to allow long-term comparison and better distinction from potential confounding variables, which could not be ruled out due to the relatively small-time frame of the present study.

Long-term data show that PFOS and PFOA concentrations in soil and homegrown eggs have declined within 4 km range from a major fluorochemical plant compared to 2010, probably due to phase-out and regulatory measures. However, concentrations of these two major PFAS remained largely unchanged further away from the plant site and generally stagnated during recent years. The present study provided various lines of indications that temporal changes may be caused by direct recent and historical emissions of legacy PFAS as well as atmospheric precursor oxidation and subsequent degradation to legacy PFAS, as well as precursor biotransformation. These short-term changes appeared to be partly dependent on the wind orientation towards potential point sources, which requires further investigation. Future measurements of precursors via Total Oxidizable Precursor Assay (TOPA) in abiotic and biotic matrices, combined with non-target and suspect screening, would be insightful to further elaborate these hypotheses.

in their private gardens. The authors would like to thank Wendy D'Hollander for adoption of the dataset for egg and soil from 2010, which enabled us to include a section on long-term temporal trends. We would like to thank Stefan Van Dongen for his insightful comments on the statistical analyses. Finally, the authors acknowledge Tim Willems for PFAS analyses with the UPLC-MS/MS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.123613.

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