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Uptake and translocation of brominated flame retardants in tomato plants (*Solanum lycopersicum* L.): Results from a standard soil-based biotest

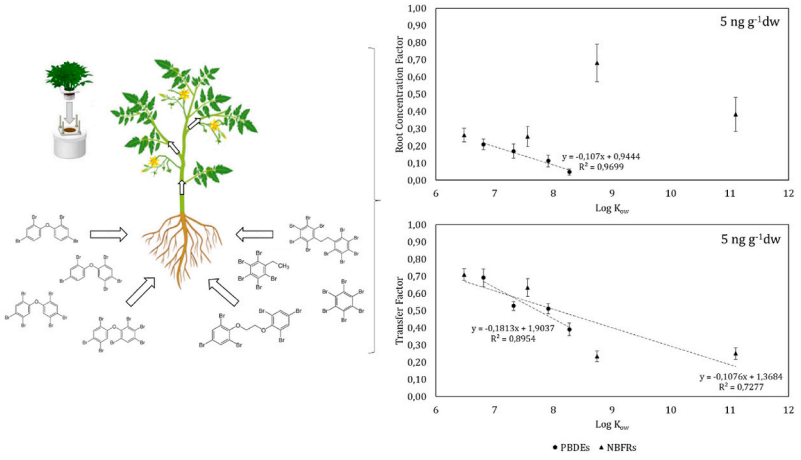
Giovanni Beggio [a,*], Tiziano Bonato [b,c], Simone Marangoni [c], Matthieu N. Bravin [d,e], Edy Fantinato [b], Sebastiano Nigris [f,g], Alberto Pivato [a], Rossano Piazza [b]

[a] Department of Civil, Environmental and Architectural Engineering, University of Padova, Via Marzolo 9, 35131, Padova, Italy
[b] Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino 155, I-30172 Venice, Italy
[c] Società Estense Servizi Ambientali S.E.S.A., Este, PD, Via Comuna, 5/B, 35042 Este, Padova, Italy
[d] CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France
[e] Recyclage et risque, Univ Montpellier, CIRAD, Avenue Agropolis, 34398, Montpellier, Cedex 5, France
[f] Department of Biology, University of Padova, Via U.Bassi 58/ B Italy
[g] Botanical Garden Department of Biology, University of Padova, Via Orto Botanico, 15, 35123 Padova, Italy

HIGHLIGHTS

- RHIZOtest was applied to assess uptake of BFRs in tomato plants.
- Following exposure to spiked soil, all BFRs were detected in roots and shoots.
- Higher concentrations of NBFRs than PBDEs were observed in roots and shoots.
- PBDEs uptake and transfer likely regulated by degree of bromination.
- Root-shoot transfer likely influenced by lipophilicity of BFRs.

GRAPHICAL ABSTRACT



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ABSTRACT

The uptake and translocation of four polybrominated diphenyl ethers (PBDEs) and four novel brominated flame retardants (NBFRs) in tomato plants (*Solanum lycopersicum* L.) were investigated via the RHIZOtest, a standard soil-based biotest, optimized for organic compounds. Tomato plants were exposed to soil samples spiked with 0 (i.e. control), 5.00 or 50.00 ng g^{-1}dw of each compound. Compared of those of the control, exposure to increasing spiking concentrations resulted in average reductions of 13% and 26% (w/w) in tomato plant biomass. Higher concentrations of NBFRs were analyzed both in roots, ranging from 0.23 to 8.01 ng g^{-1}dw for PBDEs and from 1.25 to 18.51 ng g^{-1}dw for NBFRs, and in shoots, ranging from 0.09 to 5.58 ng g^{-1}dw and from 0.47 to

* Corresponding author.
E-mail address: giovanni.beggio@unipd.it (G. Beggio).

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7.78 ng g^{-1}dw for PBDEs and NBFRs, respectively. This corresponded to an average soil uptake of 5% for PBDEs and 9% for NBFRs at the lower soil-spiking level, and 3% for PBDEs and 6% for NBFRs at the higher soil spiking level. Consequently, among both initial spiking levels, the soil-root concentration factor (RCF) values were lower on average for PBDEs (0.13 ± 0.05 g dw soil g^{-1}dw roots) than for NBFRs (0.33 ± 0.16 g dw soil g^{-1}dw roots). Conversely, nondifferent values of the root-shoot transfer factor (TF) were calculated for both PBDEs (0.54 ± 0.13 g dw roots g^{-1}dw shoots) and NBFRs (0.49 ± 0.24 g dw roots g^{-1}dw shoots). The differences and similarities reported in the RCF and TF between and within the two groups of compounds can be explained by their properties. The calculated RCF and TF values of the PBDEs exhibited a decreasing trend as the number of bromine atoms increased. Additionally, a robust negative linear correlation was observed between RCF values and the respective $\log K_{ow}$ values for the PBDEs, at both soil-spiking levels. The root uptake of NBFRs exhibited a negative correlation with their hydrophobicity; however, this was not observed in the context of root-to-shoot transfer. The presence of a second aromatic ring appears to be the key factor influencing the observed variations in NBFRs, with biphenyl NBFRs (BTBPE and DBDPE) characterized by lower uptake and reduced translocation potential than monophenyl PBEB and HBB. Understanding the transfer of these compounds to crops, especially near plastic recycling waste sites, is crucial for understanding the risks of their potential inclusion in the human food chain.

1. Introduction

The presence and fate of so-called "legacy substances" in recycled goods represent a major topic in the discussion on the efficacy of circular economy scenarios. In fact, it has become clear that recycled products may contain more of these substances than nonrecycled products, potentially determining the risks to human health and ecosystems when migrating into environmental compartments. Here, appropriate experimental approaches still need to be optimized to generate useful data for refining risk estimations, while allowing a more reliable comparison of chemical levels in recycled and nonrecycled goods (Johansson et al., 2020). This basic knowledge can further support competent authorities in the definition of thresholds for determining when a recycled material can be considered safe for use as a product (e.g., the so-called end-of--waste criteria as established in European regulation (Johannson, 2022; Johansson and Forsgren, 2020)).

Among legacy substances, brominated flame retardants (BFRs) are chemicals intentionally added to a variety of primary materials (i.e., not recycled furniture, building materials, textiles, and electronics), to reduce flammability and delay fire propagation (Stapleton et al., 2012). As a consequence, BFRs have been detected in a wide range of waste materials (Hennebert, 2020). The persistence of these chemicals in recycled plastic materials has also been demonstrated (Pivnenko et al., 2017).

Among BFRs, polybrominated diphenyl ethers (PBDEs) are considered endocrine disruptors that can led to developmental effects, both neurological and physiological, and are suspected to be carcinogenic to humans (McGrath et al., 2017; Wu et al., 2020). For these reasons, PBDEs have been listed within the POP list under the Stockholm Convention and targeted by bans and minimization strategies (Sharkey et al., 2020). Therefore, novel brominated flame retardants (NBFRs) such as Hexabromobenzene (HBB), Pentabromoethylbenzene (PBEB), 1, 2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiph enyl-ethane (DBDPE), were introduced on the market as substitutes for PBDEs (Covaci et al., 2011).

Ultimately, Cook et al. (2023) suggested that one possible exposure BFR pathway for humans can be represented by the ingestion of crops cultivated in BFR-contaminated land around industrial sites. In particular, the occurrence and distribution of PBDEs and NBFRs in soils around waste recycling facilities have been thoroughly monitored, mainly in China (Wang et al., 2016b; Wu et al., 2019a). The considerable variability in BFR levels monitored in soil samples from different manufacturing zones, ranging from several nanograms per gram of dry weight to more than 50 000 ng g^{-1} dw, is primarily attributed to local scenarios and chosen analytical methodology factors, such as the range of BFR congeners analyzed and the soil sampling depth (Wu et al., 2019b). Furthermore, several studies reported and discussed the presence of BFR in soils from other anthropic and natural areas, suggesting tha these chemicals are ubiquitous in all environmental compartments (Brits et al., 2016; Covaci et al., 2011; Ma et al., 2022; Vecchiato et al., 2021). Additionally, the effects of plant exposure to BFR, in terms of uptake and phytotoxicity, have long been discussed by the scientific community (Zhang et al., 2021). In particular, BFR uptake by several plant species was investigated both in hydroponic solution (Bonato et al., 2022; Meng et al., 2018; Xu et al., 2023) and in soil-based experiments (Sun et al., 2019; Wang et al., 2016a, 2022). The limitations of hydroponic studies are well-known and related to the reduced potential to mimic complex soil environments, notably the impact of soil-solution interactions on contaminant availability. Additionally, the available literature is characterized by a wide set of different experimental conditions for both hydroponic and soil-based studies, allowing for difficult comparisons and data-quality evaluations. These issues highlight the need to generate data through a standardized soil-based methodology able to improve the mechanistic understanding and assessment of plant uptake and ultimately support the decision-making process on substances regulatory control (Doucette et al., 2018).

Responding to these requirements, the present study assessed the transfer of four PBDEs and four NBFRs from the soil to a tomato plant (*Solanum lycopersicum* L.) by using an internationally acknowledged soil-based biotest, standardized under the EN ISO 16198 (CEN, 2015). This biotest, alsoknown as the RHIZOtest (Bravin et al., 2010), allows close contact between the roots and the soil while preventing the roots from penetrating the soil layer by separation through a 30-μm polyamide mesh. In addition to ensuring biological and chemical interactions at the soil−root interface, this method allows for easy recovery of the rhizosphere (i.e., considered as the volume of soil directly affected by root activities) and the prevention of root contamination with soil particles, thereby increasing the reliability of concentration values quantified after exposure. Notably, the standard was initially developed to investigate the role of root-induced chemical processes in the root uptake and root-shoot transfer of inorganic trace elements. In this study, the optimization consisted of expanding the scope of application of the standard to include organic compounds, by replacing the polyamide with a 30-μm stainless steel mesh to avoid possible absorption of BFRs. To the best of the authors' knowledge, this study represents the first application of the optimized RHIZOtest standard method to analyze the uptake of BFRs in tomatoes. Given the presence of tomatoes in global dietary patterns and their widespread cultivation, investigating the possibility of soil-related contamination is instrumental for thoroughly estimating the potential risks associated with the occurrence of BFRs in the human food chain.

2. Materials and methods

2.1. Materials, reagents and standards

Tomato (*Solanum lycopersicum* L. cv. "Cuore di bue") seeds were

purchased from those available on the market. Standard soil was prepared according to ISO 11269–2:2013 (see composition, chemical and physical characteristics in Tables S1, S2 and S3 of the Supplementary Material) (CEN, 2013). Three nutrient solutions were prepared following the EN ISO 16198 standarnd (Table S4, S5 and S6) (CEN, 2015).

Individual solutions of PBEB, HBB, BTBPE, DBDPE, BDE 47, BDE 99, BDE 153 and BDE 183 were purchased from AccuStandard (New Haven, CT, USA). Internal surrogate standards for NBFRs i.e., ^{13}C-BDE-47, ^{13}C-BTBPE, ^{13}C-BDE-209, ^{13}C-BDE-99, ^{13}C-BDE-153 and ^{13}C-BDE-183, were purchased from Wellington Laboratories (Guelf, ONT, Canada), while the standard ^{13}C-BDE-209 was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The purities of all the standards used were higher than 95%. The chemical names, formulas, abbreviations, and CAS numbers of the PBDEs and NBFRs are reported in Tables S7 and S8 of the Supplementary Material, respectively.

Pesticide grade HPLC solvents, including dichloromethane, n-hexane, acetone and ethyl-acetate, methanol, anhydrous sodium sulfate (60 mesh), neutral silica gel (100–200 mesh) and alumina were obtained from Merck KGaA (Frankfurter Strabe, Darmstadt, Germany).

2.2. Soil incubation and plant growth in RHIZOtest

Plant uptake and the consequent root−shoot translocation were investigated for 2 classes of BFRs, namely PBDEs (BDE 47, BDE 99, BDE 153 and BDE 183) and NBFRs (PBEB, HBB, BTBPE, DBDPE). For each compound, three soil concentrations were tested: 0.00 (i.e., control), 5.00 and 50.00 ng g^{-1}dw, resulting in nominal total BFRs concentrations of 40.00 and 400.00 ng g^{-1}dw, respectively. The tested spiking levels were assumed to be representative of BFR concentrations found in contaminated soils worldwide (Wu et al., 2019b). In particular, 5.00 ng g^{-1}dw was assumed to represent the average environmental conditions that were recorded in some agricultural soils around the world (Brits et al., 2016; Covaci et al., 2011; Ma et al., 2022). The 50.00 ng g^{-1}dw treatment was further tested to observe possible trends between the initial spiking level and i) the amount of BFRs absorbed by the exposed plants and ii) possible phytotoxic effects, measured as hindered growth of root and/or shoot biomass.

Plant exposure to BFRs in soil was investigated with the so-called RHIZOtest experimental setup (Bravin et al., 2010), following the related ISO standard (CEN, 2015) with some modifications detailed below. The experiment was carried out stepwise. First, the seeds were superficially sterilized for 30 min using a 5% sodium hypochlorite solution, rinsed with sterile water, and subsequently germinated in plastic pots (40 seeds per pot) closed at the bottom with a 30-μm stainless steel mesh (previously washed with 6% H_2O_2 for 10 min and rinsed with Milli-Q water) for 7 d in hydroponics with the nutrient solution nr.1. Second, the plants were pregrown for 14 d in hydroponics with the nutrient solution nr.2. These two hydroponic phases enabled plants to develop a dense planar root mat.

Two days before the start of the hydroponic phases, fifteen batches of 9 g dw of the standard soil were placed in cylindrical aluminum containers at 70% of the soil water holding capacity with the nutrient solution nr.3, and then incubated in a growth chamber (Caron, Avantor, VWR International, USA) for 2 d to allow them to equilibrate (see below for climatic conditions). Then, five standard soil batches were spiked with a mixture of PBDEs (BDE-47, BDE-99, BDE-153 and BDE-183) and NBFRs (PBEB, HBB, BTBPE and DBDPE) in acetone solutions to reach a nominal concentration of 5.00 or 50.00 ng g^{-1} dw for each compound. Five batches of the standard soil were used as controls, i.e., spiked with the same volume of acetone but without any BFR. The spiked and control batches of the standard soil were then incubated in the aforementioned growth chamber for 21 d.

After hydroponics, the plant pots were transferred onto the spiked and control soils and grown for an additional 8 d (i.e. exposure phase) in the aforementioned growth chamber under the following conditions: 25 ± 3 °C, 75 ± 5% relative humidity; 200–400 μmol photons m^{-2} s^{-1} photosynthetically active radiation and 12:12 h of light/dark conditions. The root mat was in contact through the mesh with the 6-mm thick soil layer (equivalent to 9 g dw), which was itself connected with the nutrient solution nr.3 by filter paper wicks to meet plant requirements for water and major nutrients. The concentrations of each BFR (i.e., 0.00, 5.00 and 50.00 ng g^{-1}dw) were replicated five times for a total of 15 experimental devices. At the end of the exposure period, the plants were harvested and thoroughly rinsed with deionized water. Roots were separated from the shoots. The soil, root and shoot samples were oven-dried for 4 d at 40 °C, weighed and prepared for BFR quantification. The sample dry weight was determined on a randomly collected portion of each sample by oven-drying at 105 °C for 12 h according to the methods of Ahn et al., (2014).

2.3. Test sample preparation, extraction, and purification

After harvesting, the shoot and root replicates were washed thoroughly with distilled water to remove any adhering soil particles that could have passed through the 30-μm stainless steel mesh. Prior to the BFR determination, the root and shoot samples were stored at −20 °C and homogenized through IKA T 50 Digital ULTRA-TURRAX® Dispersers (Germany).

Test sample preparation for BFR determination was carried out according to previous studies (Alonso et al., 2017; Bonato et al., 2022; Sun et al., 2019; Vrkoslavová et al., 2010), with some modifications. In addition to the samples produced during the abovementioned RHIZOtest experiment, solid subsamples (approximately 1.0 g) of previously prepared roots, shoots and soil samples were mixed with anhydrous sodium sulfate and then spiked with 5 and 50 ng of ^{13}C–BDE-47, ^{13}C-BDE-99, ^{13}C-BDE-153, ^{13}C-BDE-183, ^{13}C-BDE-209 and ^{13}C-BTBPE to check the recovery efficiency of the analytical procedure.

Extraction was performed over 30 min with 30 mL of a mixture of dichloromethane and n-hexane (1:1 v/v) in an ultrasonic bath (Bonato et al., 2022). The extract was concentrated to approximately 1 mL using a rotating evaporator, treated with 50 mL of concentrated sulfuric acid in a separating funnel and subsequently purified by a chromatographic column consisting of (from bottom to top) 2.0 g of anhydrous sodium sulfate, 5.0 g of silica gel, and 2.0 g of anhydrous sodium sulfate. The purified extract was then eluted with 50 mL of hexane and concentrated again to 200 μL by gentle nitrogen flow, before further purification via gel permeation chromatography (GPC-Azura DSCSVI Knauer, Germania) instrument equipped with a column SX3 styrene-(divinylbenzene-3%) and40-80 μm mesh, and a final elution with a mixture of cyclohexane and dichloromethane (3:7 vol/vol) at 1 mL min^{-1}. Prior to chromatography, the eluate solvent was exchanged with n-hexane using a Rotavapor and reduced to 50 μL over a nitrogen stream, with the addition of the syringe standard ^{13}C-BDE-169.

2.4. Analytical protocols

The concentrations of NBFRs in the purified extracts were analyzed via gas chromatography (GC system Agilent 7890 A) coupled to mass spectrometry working with negative ion chemical ionization (GC–NCI–MS) connected to a 7000D quadrupole mass spectrometer operating by high EI ionization (5975 C inert XL).

The column used had a 15 m × 180 μm internal diameter with a splitless pulsed injection of 2 μL, and a dimpled ultrainert liner (Agilent). The initial temperature of the injection port was set to 100 °C for 0.2 min before increasing it to 300 °C at a rate of 900 °C min^{-1}. The temperature was set initially at 80 °C for 1 min, then raised first to 230 °C at 37.5 °C min^{-1}, and then to 325 °C at 30 °C min^{-1}. The temperatures of the transfer line, the ionic source and each quadrupole were 325 °C, 280 °C, and 150 °C, respectively. Helium (purity 99.999%) was used as the makeup gas first at a flux rate of 1.8 mL min^{-1} for 8.25 min before

increasing to 100 mL min^{-1} and decreasing to 4 mL min^{-1}. The different analytes were determined according to two ionic transitions and to the retention time.

A DB e 5 ms capillary column (30 m × 0.25 mm i.d. x 0.25 μm) was used with ammonia as the carrier gas at a flow rate 3.0 mL min^{-1}, an ion source pressure of 1.9 × 10^{-4} Torr and a temperature of 250 °C. The temperature program ranged from 140 °C (held for 2 min) to 325 °C (held for 10 min) at 10 °C min^{-1}. Injection was carried out in splitless mode for 1 min with an injector temperature of 250 °C. To determine the concentrations of decabrominated compound (deca-BDE), a shorter DB and 5 ms capillary column (15 m × 0.25 mm i.d. × 0.1 μm) were used due to their thermal instability at higher temperatures. The analytical procedure was carried out to monitor the two most abundant isotope peaks from the mass spectra corresponding to $m/z = 79$ and 81 $[Br]^-$ for all the selected analytes, with the exception of deca-BDE-209, for which m/z = 487 489 and m/z = 497 498 were selected for monitoring the native and ^{13}C-labeled compounds, respectively.

For each of the BFR groups, a compound was assumed to be positively identified when: i) the related retention time did not differ more than 5% from that of the analytical standards, ii) the signal–noise (S/N) ratio of both transitions exceeded 3:1, and iii) the relative abundance between transitions was reported to be within ±20% of the measurements. Quantification was performed by isotopic dilution, by exploiting the most abundant ionic transition. The acquisition parameters of the spectral masses for GC-MS/MS are listed in Table S9 in the Supplementary Material, while the internal standards used are reported in Table S10 of the Supplementary Material, for each measured parameter. Five-point curves were used to calibrate the analyte quantification, and each curve was characterized by a regression coefficient (i.e. r^2) higher than 0.998 (Table S10).

2.5. Quality assurance and control (QA/QC)

Every analytical step was conducted to minimize cross-contamination and degradation of the target compounds. Prior to use, all the equipment was rinsed with acetone and the glassware was thermally treated in an oven for 16 h at 550 °C. Prior to the GC–MS, samples and extracts were stored in dark conditions at −20 °C.

A laboratory control sample (LCS) and a method blank were analyzed every 10 measurements with the same analytical protocols. Method blank analysis consisted of the performance of the entire analytical protocol without the test sample to record possible contamination resulting from the equipment used. The method blanks were all less than half of the MDL (Table S10). LCSs were prepared by adding 50 ng of each target compound dissolved in methanol to 0.5 g of hydromatrix absorbing material. The accuracy and precision of the analytical results were determined by comparing the measured concentrations in LCSs with the expected values (50 ng/0.5 g = 100 ng g^{-1}) (Table S11).

2.6. Statistical analysis and data interpretation

Statistical analysis was performed on the collected data using Microsoft Excel 2016and the statistical software Minitab®18 (Minitab, Inc., USA). The means and standard deviations were calculated from the measured dry weights of the plant parts (five replicates for both roots and shoots per concentration), from the analyzed BFRs concentrations in the hydroponic solutions and from the roots and shoots collected from each treatment concentration (five replicates for both roots and shoots per concentration). Significant differences between the mean concentrations in the roots and shoots at various initial spiking concentrations were also checked using a 2-sample ttest ($p \leq 0.05$) to assess the differential distribution of the BFRs in the plant parts. The variance homogeneity and normality of the data were assessed using the Levene and Kolmogorov–Smirnov tests, respectively.

Furthermore, the following parameters were defined for data interpretation. The root concentration factor (RCF) was calculated at the end of the exposure phase for each BFR and spiked concentration as the ratio between the mean compound concentration measured in roots (C_R expressed as ng of compound per g of root dry weight) and the mean compound concentration measured in the corresponding standard soil samples (C_{soil} expressed as ng of compound per g of dry soil) (Hu et al., 2021):

$$RCF = \frac{C_R\ (ng\ g^{-1}dw)}{C_{soil}(ng\ g^{-1}dw)} \quad (1)$$

The shoot concentration factor (SCF) was calculated at the end of the exposure phase for each BFR and spiked concentration as the ratio between the mean compound concentration measured in the shoots (C_S expressed as ng of compound per g of root dry weight) and C_{soil}(Gao and Zhu, 2004):

$$SCF = \frac{C_S\ (ng\ g^{-1}dw)}{C_{soil}\ (ng\ g^{-1}dw)} \quad (2)$$

The translocation factor (TF) was calculated at the end of the exposure phase for each BFR and spiked concentration as the ratio between the *SCF* and the *RCF* (Hu et al., 2021):

$$TF = \frac{SCF}{RCF} = \frac{C_S\ (ng\ g^{-1}dw)}{C_R\ (ng\ g^{-1}dw)} \quad (3)$$

3. Results and discussion

3.1. Quality control of the experimental equipment and analytical procedures

The recovery values calculated from the measured laboratory control sample (LCS) concentrations for the tested BFRs showed an acceptable degree of accuracy according to the low values of the resulting standard deviations (Table S10). The average recovery values (n = 12) for the BFR concentrations measured in the LCSs varied from 87% to 102%, and from 88% to 101%, for the plant tissues and soil, respectively (Table S10).

No trace-level contaminations were reported in the method blanks for the analyzed compounds. Accordingly, laboratory reporting limits, i.e., method detection and method quantitation limits (MDLs and MQLs), were estimated to allow for the quantification of each tested compound over the average level of contamination of the method blank, with 99% confidence limits (Table S8 of the Supplementary Material). All BFR concentrations in the plants in the control soil were lower than those in the MQL. It could thus be assumed that no cross-contamination occurred due to the materials, reagents or equipment.

The results from replicate analyses performed on the same type of test sample (i.e., shoots or roots) and for each treatment were consistent (see Tables S12–S14). Coefficients of variation were found in an acceptable range from 0.27 to 0.02, with a decreasing variability from the lower to higher dosages of the tested BFRs (Hennebert et al., 2022; Hennebert and Beggio, 2021).

The measured concentrations of PBDEs and NBFRs in the soil were largely similar to the nominal concentrations (within 20%). Therefore, the nominal concentrations were used in the following discussions.

3.2. Exposure to BFRs decreased plant biomass

As shown in Fig. 1, plant mass growth was negatively influenced by the spiked soil concentrations of the tested BFRs during the 8 days of exposure (detailed data are reported in Table S12).

With respect to the control, the biomass of the whole plants decreased by 13 and 26% on average due to exposure to BFRs nominal concentrations of 5.00 and 50.00 ng g^{-1}dw, respectively. This trend was reflected in the impaired growth of both roots and shoots during the exposure phase (Fig. 1).

These results are similar to findings reported in the scientific literature,

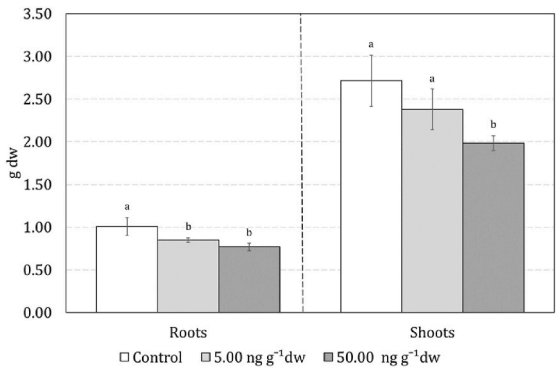

Fig. 1. Dry weights (g dw) of roots and shoots measured after the 8d exposure phase for each tested concentration. Values are expressed as mean between 5 replicates. Error bars represent standard deviations. Mean values that do not share the same letter are significantly different ($p < 0.05$, $n = 5$).

possibly highlighting the phytotoxicity of PBDEs and NBFRs among different plant species (Zhang et al., 2021). These considerations were already reported in hydroponic experiments. For maize, Bonato et al. (2022) reported a total biomass decrease of 29% with respect to the control after 5 days exposure to a total concentration of 330 μg L^{-1} NBFRs and organo-phosphorous flame retardants. Furthermore, after 3 days growth in water contaminated with up to 15 μg L^{-1} of BDE-28, BDE-47, or BDE-99, maize plants had lower dry weights up to 36, 37 and 44%, respectively, compared to those of plants grown in noncontaminated media, revealing negative impacts also on seed germination and root elongation (Xu et al., 2023). Additionally, potential phytotoxic effects were noted in rice, after 15 days exposure to BDE-209 at concentrations up to 500 μg L^{-1}, resulting in significant inhibition of root and shoot lengths of 19% and 9% (expressed as a percentage of the control) (Li et al., 2018). Finally, the exposure of Chinese cabbage seedlings to BDE-47 at concentrations ranging from 10 to 100 μg L^{-1} for 30 days resulted in significant adverse effects, such as inhibited growth, metabolic interference, disruption of biomembranes, and reduced photosynthesis (Meng et al., 2018). According to soil-based studies, exposing tobacco plants to a soil concentration of 50.00 ng g^{-1} BDE47 and BDE209 led to a significant decrease (about 20%) in both aboveground and belowground biomass and a decrease in the length and width of leaves; these effects are likely due to decrease in the chlorophyll content and the levels of chlorophyll forming enzymes ultimately affecting plant photosynthesis (Wang et al., 2022). Furthermore, Chinese cabbage seedlings cultivated in soil contaminated by BDE-209 (i.e., 5–20.00 ng g^{-1}) exhibited growth inhibition after 60 days, likely due to reduced photosynthetic parameters (i.e., decreases in chlorophyll and soluble protein contents) and ineffective self-alleviation of oxidative stress (Meng et al., 2022). Among the responses to PBDE exposure, hindered growth is reported to be significantly related to partial suppression of photosynthetic functions and oxidative stress (Sun et al., 2020).

3.3. BFRs were taken up by the roots

The BFRs in the root samples were quantified after exposure (Table 1), and the results indicated plant uptake from the spiked soil. Indeed, a significantly greater total concentration of BFRs was measured in the roots exposed to 50.00 ng g^{-1}dw (78.54 ± 0.72 ng g^{-1}dw) than in those exposed to 5.00 ng g^{-1}dw (10.51 ± 0.27 ng g^{-1}dw), indicating concentration dependence (Zhang et al., 2021). Both these concentrations and the concentration ranges of single BFRs in roots analyzed in this study, i.e., 0.23–3.40 g g^{-1}dw at the lower spiking level and 3.18–18.51 g g^{-1}dw at the higher spiking level, were consistent, i.e., on the same order of magnitude, with those reported by soil-based studies in several plant species after exposure to a similar concentrations of PBDEs and NBFRs in soils.

In pot experiments, Huang et al. (2011) measured the concentrations of single congeners of PBDEs in the range of 0.10–118 ng g^{-1} in ryegrass, maize, and pumpkin grown in soil samples contaminated with total concentrations of PBDEs ranging from 236 to 1177 ng g^{-1}. After pot cultivation on paddy soil characterized by a total average content of PBDEs (17 congeners), DBDPE and BTBPE of 130, 41.00 and 3.90 ng g^{-1}dw, respectively, rice showed average root concentrations of 25.00 ng g^{-1}dw of total PBDEs, 7.80 ng g^{-1}dw of DBDPE and 0.74 ng g^{-1}dw of BTBPE (Zhang et al., 2015). Wang et al. (2016a) investigated eight congeners of PBDEs and six NBFRs, resulting in total concentrations ranging from 1.16 to 107 ng g^{-1} and 7.08–82.00 ng g^{-1} respectively, in the roots of 14 different plant species grown in agricultural soils around e-waste recycling facilities characterized by soil concentrations ranging from 13.90 to 351 ng g^{-1} of total PBDEs and 11.60–70.80 ng g^{-1} of total NBFRs. Furthermore, Sun et al., 2019 reported average root concentrations of 3.16 g g^{-1}dw for tomatoes and of 3.63 g g^{-1}dw for cucumbers, both of which were exposed to six NBFRs in agricultural soils until fruit maturation, each occurring in the approximate range 0.50–3.75 g g^{-1}dw. Conversely, after hydroponic exposure to different PBDEs and NBFRs, the root concentration resulted on average one order of magnitude greater than that reported in this study (Bonato et al., 2022; Wang et al., 2011; Zhao et al., 2012). Being hydrophobic, BFRs likely tend to be retained by soil organic matter (SOM) partially decreasing their availability for roots uptake (Huang et al., 2011).

It is noteworthy that roots exposed to PBDEs were characterized by lower concentration ranges than those exposed to the same concentrations of NBFRs, for both 5.00 ng g^{-1}dw treatment (0.23–1.04 ng g^{-1}dw and 1.25–3.40 ng g^{-1}dw, for PBDEs and NBFRs, respectively) and 50.00 ng g^{-1}dw treatment (3.18–8.01 ng g^{-1}dw and 9.56–18.51 ng g^{-1}dw, for PBDEs and NBFRs, respectively). This trend is somewhat similar to what has been reported by Wang et al. (2016a), where the root concentrations of several NBFRs were measured to be higher than those of PBDEs, on average among several plant species. Nonetheless, contrary to the findings of this investigation, it was not possible to confirm this difference unequivocally, as the plants were subjected to varying soil concentrations of the two chemical groups (Wang et al., 2016b). Therefore, to the best of our knowledge, this represents the first instance of this

Table 1
BFRs concentrations (ng g^{-1}dw) in the roots and shoots at the end of the test, for tested spiking levels. The results are expressed as the mean and standard deviation ($n = 5$). Within the same initial spiked concentration, the mean concentrations in the roots and shoots that do not share the same letters are significantly different ($p \leq 0.05$). Replicates data are extensively listed in Table S11.

	5.00 ng g^{-1}						50.00 ng g^{-1}					
	Roots			Shoots			Roots			Shoots		
BDE 47	$1.04^{a,b}$	±	0.16	0.72^{a}	±	0.15	$8.01^{a,b}$	±	0.57	5.58^{a}	±	0.45
BDE 99	$0.83^{a,b,c}$	±	0.20	0.44^{b}	±	0.10	$7.04^{b,c}$	±	0.63	$4.10^{b,c}$	±	0.54
BDE 153	$0.55^{b,c}$	±	0.17	$0.28^{b,c}$	±	0.08	6.23^{c}	±	0.57	3.44^{c}	±	0.47
BDE 183	0.23^{c}	±	0.09	0.09^{c}	±	0.03	3.18^{d}	±	0.49	1.07^{d}	±	0.28
PBEB	$1.30^{a,d}$	±	0.19	0.92^{a}	±	0.15	10.38^{e}	±	1.04	7.78^{e}	±	0.43
HBB	1.25^{a}	±	0.28	0.79^{a}	±	0.15	$9.56^{a,e}$	±	0.47	6.85^{e}	±	0.41
BTBPE	3.40^{e}	±	0.55	0.79^{a}	±	0.11	18.51^{f}	±	0.84	5.24^{a}	±	0.72
DBDPE	1.90^{d}	±	0.49	0.47^{a}	±	0.14	15.65^{g}	±	1.18	$4.85^{a,b}$	±	0.71

observed trend between NBFRs and PBDEs.

The RCF values were calculated to describe the observed uptake rate normalized with respect to the initial soil concentration (Fig. 2a). Like what was reported by Huang et al. (2011), the initial soil concentrations of PBDEs were reported to marginally affect (however, significantly) the RCF only for BDE-47, with the RCF calculated to be slightly significantly greater at the lower spiking level than at the higher spiking level (Fig. 2a). Considering NBFRs, significantly higher RCF values at the lower spiking level were determined for BTBPE and, to a lower extent, PBEB (Fig. 2a). Supporting the trend noted for root concentration, significantly higher average values of RCF were calculated for NBFRs than for PBDEs, both at the lower (0.39 ± 0.19 vs. 0.13 ± 0.07, respectively) and at higher initial soil concentrations (0.12 ± 0.04 vs. 0.07 ± 0.08, respectively).

The ranges of RCF values calculated from this study (i.e., 0.05–0.21 for PBDEs and 0.19–0.68 for NBFRs) are within the ranges reported in the literature (Zhang et al., 2021), but are within the lower limits of those reported by other papers discussing results from pot-based or field-based experiments on a variety of plant species (i.e., 0.1–2.5 for PBDEs and 0.5–6.3 for NBFRs) (Huang et al., 2011; Sun et al., 2019; Wang et al., 2016a; Zhang et al., 2015). However, previous works are characterized by a wide set of different experimental conditions, thus preventing a consistent comparison with the results of this study. In addition to the possible influence of soil concentration, root uptake behavior can vary widely and depends on physicochemical properties of the tested BFRs, experimental setup (i.e., exposure time, occurring or imposed abiotic conditions, different or site-specific compositions of real field-scale soil samples) and different responses of crops at the rhizosphere level (i.e., production of plant-specific root exudates and relation to the rhizosphere microbial activity) (Wang et al., 2016a; Zhang et al., 2021). In this context, the optimization of the standardized experimental setups proposed in CEN (2015), as was done by this study for organic compounds, could provide a starting base for the performance of plant uptake testing with different plant species and soil concentrations, thus providing reliable data for comparison in future metanalyses.

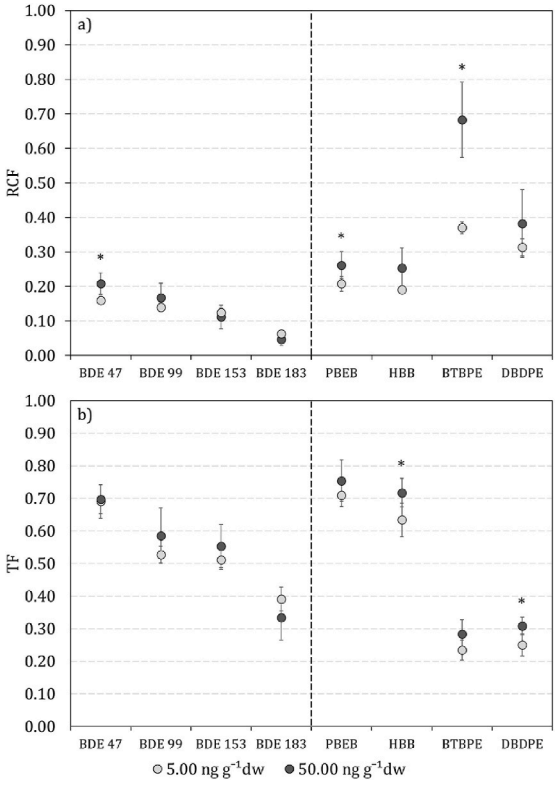

Fig. 2. RCF values (a) and TF values (b) for tomato plants after exposure to different spiked soil concentrations of some PBDEs and NBFRs. Values are expressed as mean ± standard deviation (n = 5). Significant differences ($p < 0.05$) between values calculated at different spiked soil concentrations are marked with asterisks (*).

3.4. BFRs transferred from roots to shoots

At the end of the exposure period, each investigated analyte was quantified in each shoot replicate, confirming the occurrence of BFR transfer from roots to the aerial parts of the tomato plants (Table 1). No BFR concentrations were measured in the shoot replicates of the control soil, indicating negligible foliar uptake from atmospheric air (Table S14). For both spiking levels, the shoot total concentration of BFRs was almost 50% lower than that of the corresponding roots, highlighting the differential distribution in the plant tissues (Table 1) (Huang et al., 2011). The proposed mechanism for root-shoot transfer involves radial movement through the apoplastic or symplastic pathways within the roots, subsequently advancing toward the vascular bundle for further transportation into the shoots. This could be mediated by both the tendency of organic molecules to partition in the root lipids and the blocking action of the Casparian strips (Zhang et al., 2021).

Like in the case of the roots, in the shoot concentration data, the total BFR concentration was reported one order of magnitude greater for the 50.00 ng g^1dw treatment(i.e., 38.90 ± 0.49 ng g^{-1}) than for the 5.00 ng g^{-1}dw treatment (i.e., 4.50 ± 0.11 ng g^{-1}). Supporting the trend observed in the roots, the total shoot concentrations of PBDEs (1.53 ng g^{-1}dw and 14.18 ng g^{-1}dw for increasing spiking levels, respectively) were reported to be almost 50% lower than the sum of shoot concentrations of NBFRs (2.97 ng g^{-1} for the lower spiking level and 24.72 ng g^{-1} for the higher spiking level). To the best of our knowledge, information regarding the translocation behavior of PBDEs and NBFRs to the aerial parts of plants in soil-based studies is limited and poorly comparable with the results of this study, due to the different initial soil concentrations of BFRs and exposure settings. For reference, Wang et al., 2016a reported total shoot concentrations of PBDEs and NBFRs ranging from 10.30 to 164 ng g^1dw and 8.41–69.50 ng g^1dw respectively, among several plant species.

The average TF values were calculated for BFRs in the range of 0.25–0.75 (Fig. 1b). Significant, but minimal, differences were observed, between the different applied spiking levels, for HBB and DBDPE, suggesting that the initial soil concentration has a minor influence on the mechanism of root−shoot transfer for PBDEs. Notably, no clear trend was observed between the TF values of PBDEs and NBFRs, as the average TF values were not significantly different between the two groups at either the lower (0.53 ± 0.12 for PBDEs and 0.46 ± 0.24 for NBFRs) or the higher (0.54 ± 0.15 for PBDEs and 0.52 ± 0.23 for NBFRs) spiking level. A similar stem:root ratio range (0.35–0.62) were noted by Huang et al. (2011) for PBDE uptake in pumpkin, ryegrass and maize. Much wider ranges of fruit bioaccumulation factors, calculated as fruit/soil concentrations for several NBFRs, were calculated for tomatoes (0.30–5.30) and cucumbers (0.57–7.00) by Sun et al. (2019); however, the major contribution was derived from foliar uptake of NBFRs in resuspended soil particles. Remarkably, comparable TF values were calculated for NBFRs in maize during hydroponic experiments by Bonato et al. (2022), who investigated the same range of compounds of this study. This coherence could suggest that root-shoot transfer could be less influenced by the type of exposure (i.e., water or soil-mediated and initial exposure concentrations) and more influenced by specific plant physiology and BFR features. However, a gap in knowledge persists regarding the mechanisms governing the transfer and accumulation of FRs within the aerial components (including shoots, leaves, or edible parts) of plants. Hence, further investigation is needed.

3.5. Influence of BFR properties on uptake and root–shoot transfer behavior

The specific properties of the studied BFRs could have influenced their differential distribution observed at the end of the exposure phase (Fig. 3a and b). In particular, the role of the degree of bromination, the molecular configuration and the hydrophobicity (log K_{ow}) of the compounds can be discussed.

For the PBDEs, the concentrations of the individual compounds were distributed similarly at both spiking levels, i.e., in decreasing order: BDE 47 (39–33% of total PBDE, for lower and higher initial soil concentrations, respectively) > BDE 99 (31–29%) > BDE 153 (21–25%) > BDE 183 (9–13%) for PBDEs (Fig. 3a). The shoot contents of the PBDEs exhibited the same trend, with BDE 47 and BDE 49 being present at higher concentrations than BDE 153 and BDE 183 for both treatments (Fig. 3a). Here, the decreasing number of bromine atoms seems to have enhanced contaminant transport from the soil to the plant tissues, with roots-shoot translocation potentially having a greater influence than root uptake (Fig. 3a). In support of these findings, both the RCF (Fig. 2a) and TF (Fig. 2b) values decreased inversely with increasing number of bromine atoms in the compounds. This trend is also consistent with the increased hydrophobicity (log K_{ow}) of more brominated compounds (Fig. 3a).

The observed trends in root concentration support data discussed by Huang et al. (2011) for the exposure of pumpkin, maize and ryegrass to soil concentrations of lower and higher brominated PBDEs. Similarly, lower brominated species occurred in higher concentrations also in roots and shoots of rice cultivated in paddy soil contaminated by PBDEs with total sediment concentration ranging from 4.44 to 12.25 ng g^{-1}dw; the detected brominated species mostly consisted of lower brominated congeners (i.e., BDE-44 and BDE-99, with 19.5% and 33.6%, respectively) (Wang et al., 2020) Furthermore, a greater tendency of higher brominated species to remain in soil than migrate in roots and shoots was also noted for several other plant species (Wang et al., 2016a). However, an inverse trend was noted for many other vegetal species

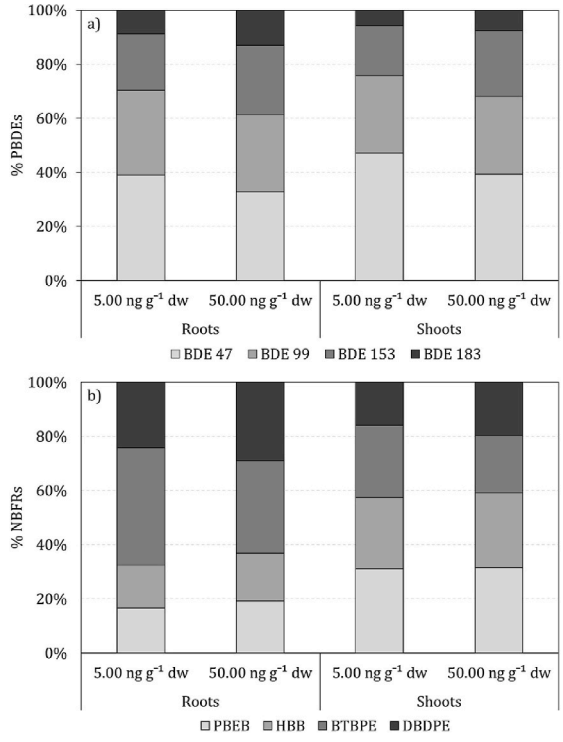

Fig. 3. Concentrations distribution measured in the roots and shoots of tomato plants for PBDEs (Fig.3a) and NBFRs (Fig. 3b) congeners, at both initial spiking levels. Mean values (n ¼ 4) on a dry matter basis are presented.

cultivated in PBDEs contaminated soils and sediments, where a predominance of higher brominated compounds was found in root samples (Hu et al., 2020; Wang et al., 2016a; Yang et al., 2018). In these studies plants were cultivated in soils where higher brominated compounds were present at much higher concentrations than lower brominated species, due to long-term contamination of soils. Here, the initial availability of these compounds could have played a more major role than any other factor related to chemical composition or plant-specific features. In fact, this is in contrast with the experimental design performed in this study, in which both lower and higher brominated PBDEs were spiked at the same initial concentrations.

At the end of the exposure phase, the NBFRs were differentially distributed in the roots and shoots (Fig. 3b). In the roots, the NBFRs were distributed in decreasing order as follows: BTBPE (43- 4% of total NBFR, for lower and higher initial soil concentrations, respectively) > DBDPE (24–29%) > PBEB (17–19%) > HBB (16–18%). These values are consistent with the rankings observed in the RCFs calculated for NBFRs, with BTBPE and DBDPE characterized by higher (significantly for both at 50.00 ng g^{-1}dw) values than PBEB and HBB (Fig. 2a). Conversely, NBFRs exhibited an inverse distribution in shoots at both initial soil concentrations, with PBEB and HBB characterized by higher shoot concentrations than BTBPE and DBDPE (Fig. 3b). In contrast with the RCF values, the corresponding TFs were calculated as three times greater on average for PBEB and HBB than for BTBPE and DBDPE (Fig. 2b), revealing a lower tendency of the former to undergo uptake from soil and of the latter to translocate from roots to shoots. These results suggest that the translocation of PBEB and HBB from the roots of these two shoot types could have led to a lower occurrence in the roots than that of BTBPE and DBDPE. Here, a major role could have been played by the molecular configuration of the tested NBFRs. As suggested in Meng et al. (2018) and Xu et al. (2023), a second aromatic ring could have resulted in greater steric hindrance of biphenyl NBFRs (I.E., BTBPE and DBDPE) which, together with lower water solubility (Table S8), could have limited the transfer within the plants when compared with monophenyl PBEB and HBB, by limiting penetration of cellular membranes. Remarkably, a similar trend was previously found in shoots of maize exposed to the same NBFRs in hydroponic settings (Bonato et al., 2022).

The observed trend can be further discussed considering the specific hydrophobicity (i.e., log K_{ow}) of the spiked BFRs. A strong negative linear correlation can be detected between the RCF and corresponding log K_{ow} values for PBDEs at both lower (Fig. 4a) and higher (Fig. 4b) spiking levels. A negative correlation in soil-root systems generally confirms the trends observed for soil-based studies investigating PBDE uptake among a variety of different tested plants. In particular, the retention potential of PBDEs is thought to be mainly due to competition between root lipid content and soil organic matter. This phenomenon decreases PBDE availability in the soil and hence the transfer of more hydrophobic compounds into the roots (Zhang et al., 2021). Conversely, no clear correlation was detected between the RCF of NBFRs and related hydrophobicity, supporting the findings of Wang et al. (2016a, 2016b), who did not report a correlation between NBFR concentration and organic carbon in soils. For this group of substances, the influence of other properties not considered in this study (e.g., type of soil texture and organic content, plant specific exudates, microbial biomass occurring at the rhizosphere level and cultivation conditions) has still not been discussed in the available literature and should be further investigated.

Finally, negative linear relationships were recorded between the TF values and corresponding log K_{ow} for both compounds categories at both spiking levels (Fig. 4), which is consistent with the findings of previous reports suggesting that highly lipophilic compounds tend to remain absorbed to the lipidic fraction of the root apparatus for several plant species (Huang et al., 2011; Wang et al., 2020; Zhao et al., 2012). In addition, comparison with the literature can be quite problematic because i) TF values are usually calculated referring to different plant

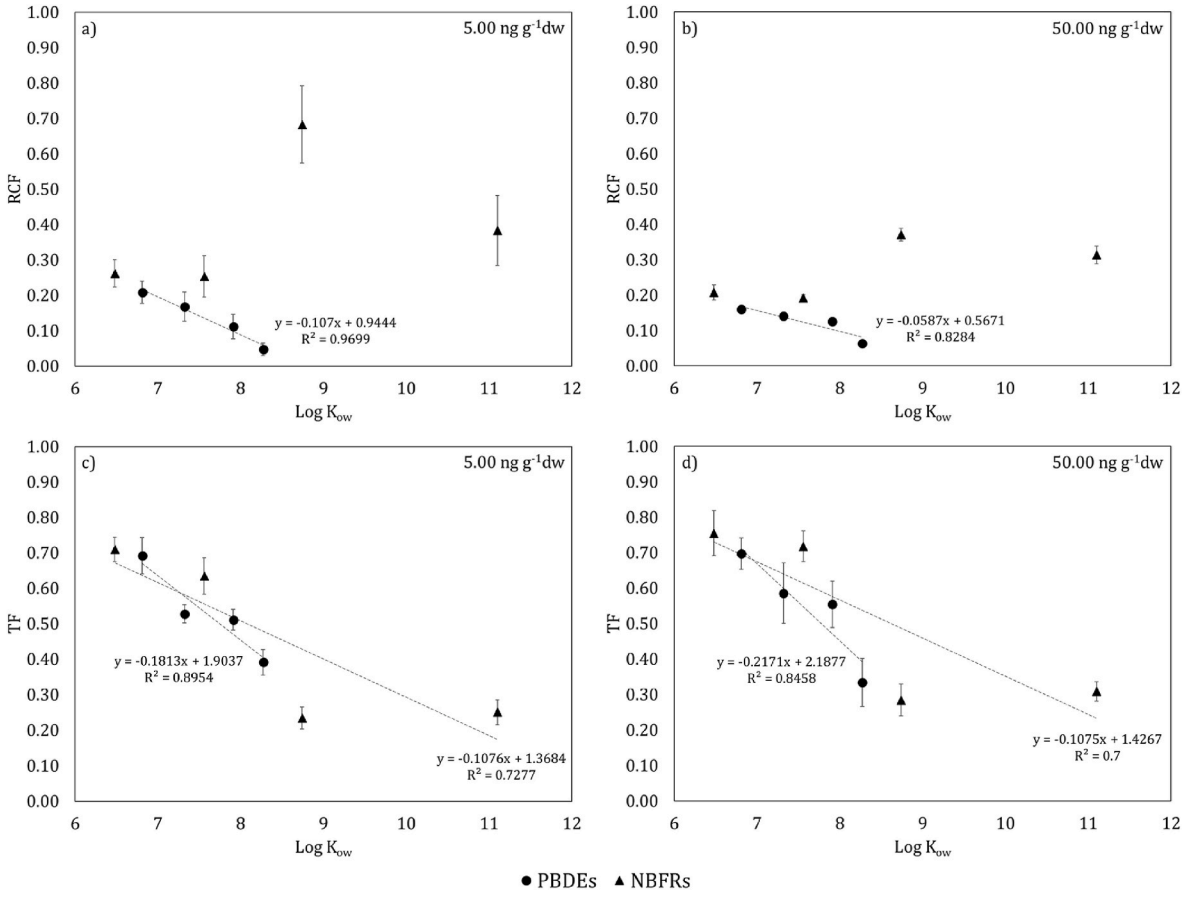

Fig. 4. Relationship between hydrophobicity (Log Kow) and resulting values of RCF (a and b) and TF (c and d) of PBDEs and NBFRs, at the two tested soil spiking level, i.e., 5.00 ng g^{-1}dw and 50.00 ng g^{-1}dw.

parts (i.e., stem, leaf, shoot, fruit) among different studies, ii) the contribution of foliar uptake cannot be excluded and iii) different tested experimental conditions can determine differential response of BFRs translocation within plants (Wang et al., 2020; Zhang et al., 2015, 2021). Standardization of experimental setups is therefore needed to improve comparisons of contaminants transport within plant.

3.6. Plant uptake decreased the soil concentration of BFRs

Significantly decreased soil concentrations of the investigated BFRs were measured in the soil samples after the 8 days exposure period (Table S13), indicating that BFRs were removed from the soil. Plant uptake of the total spiked BFRs in soil was 7 ± 3% on average for the lower spiked concentration, and 4 ± 2% calculated for the higher spiking level. On average, for both spiked concentrations, plant uptake rates were calculated greater for NBFRs (9% and 6% for 5 ng g^{-1} and 50 ng g^{-1} respectively) than for PBDEs (5% and 3% for 5 ng g^{-1} and 50 ng g^{-1} respectively). Consistent with the observed distributions in plant roots and shoots, the BTBPE uptake rate was highest among NBFRs (12.0%–6.0%, according to initial soil concentrations), followed by PBEB (8%–6.0%), HBB (8%–5%) and DBDPE (7%–5%). For PBDEs, higher uptake rate was reported for BDE-47 (7%–5% with respect to different soil spiking levels), BDE-99 (5%–4%), BDE-153 (4%–3%) and BDE-183 (2%–1%).

When accounting for plant part concentrations analyzed at the end of the test (Table 1), mass balance calculations showed minimal discrepancies (i.e., on average < 1% w/w for both treatments). This suggests that losses by adsorption onto the experimental equipment (i.e., stainless steel mesh and HDPE and PP for food contact exposure apparatus), volatilization or soil-degradation were negligible. Therefore, it can be speculated that plant uptake was the main factor determining the disappearance of BFRs from soil. This seems to contrast with previous findings in the literature on PBDEs, which showed mass losses in soil-based experiments due to the degradation of PBDEs in soil performed by the soil microbial community and metabolite formation in plant tissues. In particular, Huang et al. (2010) carried out a 60-day pot experiment involving various plant species. The plants were grown in natural loamy soil spiked with 5000 ng g^{-1} dw of BDE-209 and incubated for four weeks before exposure. The final soil concentrations exhibited a notable decrease ranging from 12% to 38% depending on the different plant species. This decline was primarily attributed to microbial soil degradation, while only a minor fraction was ascribed to occurred plant uptake. Similarly, in another 60-day pot experiment conducted by Huang et al. (2011), when ryegrass, maize, and pumpkin were exposed to PBDE contaminated soil samples, final PBDE soil concentrations decreased by 13%–22%. Here, microbial metabolism in the soil was identified as the primary contributing factor to this reduction, assuming that plant uptake has played a minor role (Huang et al., 2011). NBFRs are also known to be subjected to microbial degradation in soil, although no direct studies concerning such interactions are currently available (Xiong et al., 2019).

Here, the residence time of BFRs in the soil considered in this study (i.e., 22 days) was remarkably shorter than that reported in the cited literature (Huang et al., 2010, 2011). In this context, only PBEB was characterized by a lower (11.2d) biodegradation half-life (BHL), with the remaining BFRs having BHLs in the range of 25 (BDE47, BDE49) – 437d (DBDPE) (Table S7 and Table S8). This, combined with the shorter incubation period, could explain the discrepancy noted in the literature. The possible establishment of anaerobic conditions could also have increased the BHL of the tested compound (Nyholm et al., 2010).

Finally, the use of artificially made soil, instead of real soil samples, could also have hindered the development of a microbial community and the consequent degradation process in the soil test portions. This could represent a baseline scenario where only plant uptake processes are evaluated, thereby avoiding the introduction of additional influencing variables, such as microbial soil degradation. However, these considerations should be corroborated by further characterization of soil microbial community development in the applied experimental setting.

4. Conclusions

This study describes for the first time results on the uptake and translocation of four PBDEs and four NBFRs, spiked at the same initial soil concentrations, in tomato plants. The data were obtained through the use of a standard soil-based biotest, the RHIZOtest, optimized for high K_{ow} organic compounds. Notably, higher concentrations of NBFRs than PBDEs were detected in both the roots and the shoots, irrespective of spiking level. Additionally, in contrast to those for PBDEs, the RCF values for NBFRs were not correlated with log K_{ow}, suggesting that further understanding of the properties of these substitute BFRs is needed. Taken together, these findings raise concerns about the feasibility of substituting legacy PBDEs and highlight the importance of ongoing monitoring for the presence of these compounds in crops, as well as their potential inclusion in the human food-chain. In this context, the experimental apparatus used can provide a consistent and reproducible dataset, representing a step forward compared to less realistic hydroponic studies. Ultimately, these outcomes will aid regulatory authorities in formulating effective proposals for regulating NBFRs, in both new and recycled materials.

CRediT authorship contribution statement

Giovanni Beggio: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Tiziano Bonato:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Simone Marangoni:** Investigation, Methodology, Validation, Writing – original draft. **Matthieu N. Bravin:** Conceptualization, Methodology, Visualization, Writing – review & editing. **Edy Fantinato:** Conceptualization, Writing – review & editing. **Sebastiano Nigris:** Conceptualization, Writing – review & editing. **Alberto Pivato:** Conceptualization, Supervision, Writing – review & editing. **Rossano Piazza:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.141594.

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