Chapter

Plant Uptake, Translocation and Metabolism of PBDEs in Plants

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Abstract

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in concentrations up to 30 w% of the total mass of the products. Worldwide consumption of technically relevant PBDE mixtures was about 7500 tons (penta-BDEs), 3790 tons (octa-BDEs) and 56,100 tons (deca-BDE) in 2001 and about 50–60% of this total volume was discharged into environment only by agricultural use of sewage sludges. The use of PBDEs was strictly regulated from 2004 onwards due to their high emission load and their effect as endocrine disrupters, neurotoxins, and fertility reducing agents. Nevertheless, soils worldwide are contaminated by gaseous and particle-bound transport of PBDEs. Therefore, the uptake of PBDEs from contaminated agricultural land via crops and the food chain is a major human exposure pathway. However, uptake and intrinsic transport behavior strongly depend on crop specifics and various soil parameters. The relevant exposure and transformation pathways, transport-relevant soil and plant characteristics and both root concentration factor (RCF) and transfer factor (TF) as derivable parameters are addressed and quantified in this chapter. Finally, based on available crop specific data a general statement about the transport behavior of PBDEs in twelve different crops according to relevant PBDE congeners is given.

Keywords: Plant uptake, translocation, root concentration factor, PBDE, shoot concentration factor, food industry, crops

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used for decades as flame retardants in a wide variety of products. Notable among these are building insulations, upholstered furniture, electrical goods, vehicles and aircrafts, foams, textiles, electrical insulations, and a variety of technical plastics such as acrylonitrile-butadiene-styrene copolymers (ABS), high impact polystyrene (HIPS), polybutylene terephthalate (PBT), or plain paper (PAP), where PBDEs were used in concentrations of 5–30 percent by weight. Despite a spectrum of 209 PBDE congeners, only three formulations were of technical relevance, namely pentabromodiphenyl ether (penta-BDEs), octabromodiphenyl ether (octa-BDEs), and perbrominated diphenyl ether (deca-BDE, BDE-209). The global demand (EU demand) of these mixtures in 2001 was about 7500 tons (EU:150 tons), 3790 tons (EU: 610 tons), and 56,100 tons (EU: 7600 tons) [1]. The use of BDE-209 reached its peak in 2003–2006 with 30,000 tons (China), 9600 tons (EU), 5000–10,000 tons (Northern

America), and 1600 tons (Japan) [2]. Because of their endocrine-disrupting properties, neurotoxicity, and negative impacts on fertility as well as their high environmental persistence, the use of these mixtures was strictly regulated by the Stockholm Convention of 2001 and finally banned in 2004 (penta-BDEs, octa-BDEs) and severely restricted for BDE-209 in 2019 according to the lower toxicity in case of higher degree of bromination [3, 4].

As former high-volume chemicals PBDEs are ubiquitous in environment today, but are mainly detectable in soil and dust samples. E-waste sites and waste water sludge were identified as main sources with BDE-209 as dominant congener [5, 6]. Hence, BDE-209 levels of 6.3–12,194.6 ng g DM^{-1} (dry matter) at a ratio of 35–89.6% of the total PBDE where detected on e-waste recycling sites [7–9], while currently highest ∑PBDE levels of 8.70–18,451 ng g DM^{-1} were reported for soil at an industrial production site of plastic parts in electrical industry in Changzhou [10]. PBDE levels of 7240–10,469 ng g DM^{-1}, 180–370,000 ng g DM^{-1}, and 270–110,000 ng g DM^{-1} were also reported as currently highest levels in dust of industrial environment, house dust, and office dust samples in the UK, respectively [11]. In sludge samples of both municipal and industrial waste water treatment plants (WWTPs) in the USA, Turkey, and Hessian (Germany) levels of 85.5 ng g DM^{-1} up to 2.5 w% of ∑PBDE were reported [12–14]. The annual input of PBDEs into the environment in the USA was quantified as 47.9–60.1 tons, where 24.0–36.0 tons were located in sewage sludge [6].

As WWTP sludge is commonly used as fertilizer in agriculture, PBDE contamination is not restricted to hotspots like e-waste sites, and ubiquitous spread is further increased by gaseous and particulate-based transport of PBDEs. Consequently, soil samples were positively tested towards PBDE contaminations in grassland and forest soils of UK and Norway (∑PBDE: 65–12,000 pg. g DM^{-1}) [15], Western Austria (∑PBDE: 10.4–2744 pg. g DM^{-1}) [16], Germany (BDE-47: <27–505 pg. g DM^{-1}, BDE-209: <156–461 pg. g DM^{-1}) [17], and the Artic (∑12PBDEs ex BDE-209: 120 pg. g DM^{-1}, and ∑PBDE: 1.7–416 pg. g DM^{-1}) [17, 18].

Given the widespread distribution of PBDEs in soils, it can be assumed that they are absorbed by plants to a significant extent and are then introduced into humans via the food chain. The following sections are intended to show the factors influencing the plant uptake of PBDEs and their degradation products and to examine in detail the uptake and transport behavior of twelve selected crops. From these data, generally valid relationships for other crops will be derived using simple key parameters.

2. Physical characteristics and their effect on transport pathways and plant uptake

Because PBDEs show a wide range of molecular weight (328–959 g mol^{-1}), lipophilicity (log K_{OW} = 6–10), and volatility (log K_{OA} = 9–16) [19, 20], BDE congener specific transport and plant uptake mechanisms (soil-air-plant vs. soil–soil moisture-root-plant) are highly different and dependent on specific substance parameters (vapor pressure, Henry coefficient, air-plant partition coefficient, K_{OW} value, K_{OA} value), meteorological parameters (temperature, wind rate, precipitation, temporal rainfall distribution, deposition kinetics of gaseous and particulate BDEs), long range transport, plant specific characteristics (species, lipid content, carbohydrate content, fiber content, foliage morphology, non-lipid plant parts, rind consistency), and rhizosphere factors [18, 21–23]. Under aspects of transport, low brominated BDEs (Br_2-Br_3) are mainly and medium brominated BDEs (Br_4-Br_5), depending on the study, are minorly to dominantly distributed as gaseous compounds (BDE-15: 100%; BDE-28: 35–60%), while transmission and deposition of higher brominated congeners (Br_6-Br_{10}) are obligatorily characterized by adsorption of BDEs on a particulate phase [17, 22–25]. As a result of the particle-bound lower-range transport of the latter PBDEs, the PBDE pattern in soil and plant samples from densely populated regions and near hotspots shows high agreement with the present PBDE emission spectrum, while in sparsely populated regions the PBDE spectrum is dominated by low brominated congeners [7, 23]. Additionally, a significant concentration gradient of ∑PBDEs from both densely populated to sparsely populated regions and from emission sites to adjacent region can be observed [7, 26]. Hence, various studies around the world showed a wide range of PBDE concentrations in dust samples of 4.33–370,000 ng g DM^{-1} [11, 20, 27–31] with a clear domination of BDE-209 in the range of 69.2–99.6% [11, 20, 25].

Due to the high molar mass and the lipophilicity of high brominated BDEs, plant uptake by the soil–soil moisture-root-plant pathway is of low relevance and restricted to low and medium brominated BDEs (Br_2-Br_5) like BDE-47, BDE-99 and BDE-100 [21, 32], even though intrinsic transport of BDE-209 was reported by single studies [33–35], but disproved by Wu et al. [36], where plant availability of BDE-209 was quantified as 0.3–0.5% of the initial soil concentration and 99.5–99.7% of BDE-209 are solely adsorbed on the soil matrix and the outer side of the roots. Hence, atmospheric uptake of high brominated BDEs is the dominant pathway, even though BDE-209 reveals a low ratio of 0.1% of the atmospheric PBDE pattern [24, 37].

3. Human exposure to PBDE contaminations and uptake

As a result of the presence of gaseous and particulate PBDEs in air, the human PBDE uptake is dominated by inhalation, but the relevance of this pathway is strongly affected by atmospheric PBDE levels. Hites and Sjödin et al. reported concentrations of 5.27–301 pg. m^{-3} in ambient air and 0.06–67 ng m^{-3} at indoor air, but increased levels up to 312.1 ng BDE-209 m^{-3} at a Swedish e-waste recycling site [38, 39]. Average BDE-209 levels of 0.13 ng m^{-3} (gaseous) and 140 ng m^{-3} (particulate) were reported by Li et al. in 14 Chinese air samples and total BDE-209 uptake by inhalation was quantified as 3000 ng d^{-1} (respiration) and 69 ng d^{-1} (dust uptake), equivalent to 84% of the total daily uptake [40]. This finding was validated by multiple studies. As a consequence, 16% of daily PBDE uptake, and even higher ratios in case of lower ambient PBDE levels, are assigned to dietary uptake underlining the relevance as second dominant pathway.

4. Transformation and detoxification of PBDEs in plants

While PBDEs in the atmosphere are photolytically transformed by hydroxylation und subsequent transformation to lower brominated congeners or ring closure to the corresponding dibenzofurans [41, 42] and PBDEs in soil and sediments are mainly mineralized by stepwise debromination or detoxified by hydroxylation (OH-BDE) or methoxylation reactions (MeO-BDE) in the rhizosphere, strongly affected by the degree of bromination, concentration of oxygen, organic matter and microorganisms [43], intrinsic PBDEs in plants can be transformed by the same three transformation pathways. Exemplarily, transformation of BDE-28 and BDE-47 in maize was analyzed in detail by Wang et al. [44]. BDE-47 (Br_4) was dominantly converted to 6-MeO-BDE-47 (275 ng•g^{-1} DM) in the root phase, followed by 5-MeO-BDE-47 (40 ng•g^{-1} DM), ∑Br_2-BDEs (23 ng•g^{-1} DM), ∑Br_3-BDEs (20 ng•g^{-1}

DM), and small quantities of two unidentified hydroxylated BDEs (8 ng•g^{-1} DM) with continued decrease over time, similar to the transformation behavior against BDE-28 (Br_3). Similar results were observed in plants of pumpkins, rice, wheat and soybean for BDE-47 and BDE-99 with formation of 5-OH-BDE-47, 6-OH-BDE-47, 4'-OH-BDE-49, 4'-OH-BDE-42, 4-MeO-BDE-42, and BDE-28 in case of BDE-47 as parent congener, and with formation of 4-OH-BDE-99 and 4-MeO-BDE-99 in case of BDE-99 as soil contaminant [45, 46]. The total PBDE levels clearly dropped in all studies. In liver cells, transformation of both low and moderate brominated BDEs was shown by cytochrome P450 monooxygenases and glutathione-S-transferase, two enzyme complexes also found in plants, where they can potentially catalyze the same reactions. However, both enzyme sets were induced by BDE-209, but this congener was not converted [47]. In difference, various study showed comparable PBDE patterns both in soil and plant tissues at almost unchanged concentration levels over time, underlining negligible metabolism of PBDEs in plants [6]. In summary, PBDEs might be transformed in plants by debromination, hydroxylation and methoxylation reactions, but transformation behavior strongly depends on the plant species and the established microbial consortium in the rhizosphere [48].

5. Soil-root transport: RCF and TF value

5.1 RCF value of PBDEs

As a result of high bromination, high molecular weight, low mobility and high lipophilicity, BDE-209 as the dominant PBDE in soil is only marginally available for plants at levels of 0.3–0.5% of the initial concentration [36]. Despite the apparently low relevance, the soil – soil moisture – root uptake pathway is still of high relevance as tests with living and non-living roots of different plants showed 3.5–6 times higher BDE-209 levels in the living tissues [49]. Additional analysis of small-scale soil-based BDE gradients within the root plexus underlined the assumption of active BDE-209 uptake by plants [9] and was clearly proved by greenhouse experiments cultivating six different plant species in contaminated and non-contaminated soil in parallel [50]. In comparison to BDE-209 levels in contaminated soil, BDE-209 levels reached 5.2–10.4 ng g DM^{-1} and, therefore, less than 5%, i.e. more than 95% of BDE-209 contamination in plants could be attributed to root uptake and intrinsic plant transport. Both processes are coupled to plant transpiration elevating PBDE levels in shoots and leaves at dry weather conditions [51].

To increase comparability of PBDE uptake and intrinsic transport, both the root concentration factor (RCF) and the translocation factor (TF) were introduced in literature and correlated to the log K_{OW} value of PBDEs [9]. Both parameters can be correlated in a clearly negative way, i.e. higher RCF values were detected in case of lower brominated PBDEs and, therefore, compounds with lower log K_{OW} values than in case of higher log K_{OW} values [9]. In detail, plant specific RCFs of BDE-209 were up to ten times lower than the RCFs of BDE-28 [7, 9, 19]. This observation may be explained both by the lack of water solubility and thereby restricted root uptake with the soil moisture phase, and the strong adsorptive behavior of higher brominated PBDEs in soil. Hence, with exception of some plants like radish, green squash, and soft-stem bulrush, which are well adapted for phytoremediation processes, RCFs are clearly less than 1 for all PBDE congeners [52]. However, PBDE uptake is significantly affected by the presence of organic solubilizers in the soil like extracts of wheat straw or pig manure, where BDE-47 uptake by wheat as an example was elevated by a factor of 3.1 (wheat manure) and 1.9 (pig maure), respectively [53]. Hence, PBDE uptake increases with increasing surfactant activity, whereas decreases at weak surfactant activity and thereby increase of the organic content in soil [54]. Furthermore, PBDE uptake and RCFs as consequence are strongly affected by plant species specifics, physical and chemical soil properties, initial concentration levels of PBDEs, relevance of both gaseous and particulate atmospheric uptake, duration of the growth period, and organic soil content. Details will be described in Section 6.

In contrast, a positive correlation of both RCF and TF value was observed for maize in case of BDE-15, BDE-28, and BDE-47, which can be explained by an increased transpiration of the plants as these low-brominated congeners reveal higher water solubility [51].

5.2 TF value of PBDEs

The ratio of PBDE levels in shoots to the levels in roots is defined as translocation factor (TF). In contrast to the RCF, a general statement about the correlation of log K_{OW} and TF is not appropriate, since no clear positive or negative correlation occurs as the TF value depends on numerous parameters like plant species specifics, initial PBDE levels in soil, the lipid content of the shoots, plant age, distance of the plant issue from the root plexus, and the hardly quantifiable effect of the soil-air-plant exposure pathway. In principle, a negative correlation may be assumed as lower log K_{OW} values correlate with higher water solubility and, hence, higher intrinsic transport. As PBDE accumulate in the root area, stem and shoots show significantly lower contamination levels and relevance of atmospheric PBDE uptake significantly increases [51]. Nevertheless, the bioaccumulation and translocation behavior of PBDE in plants is not conclusively clarified and depends on numerous, partially insufficiently determined parameters.

6. Factors of PBDE plant uptake

Numerous studies focused on both physico-chemical and substance specific properties affecting plant uptake and biodegradation behavior of PBDE, where PBDE specifics (vapor pressure, K_{OW} value, air-water distribution K_{AW} value, air-plant distribution K_{AP} value), environmental parameters (temperature, wind rate, precipitation, temporal rain distribution, kinetics of both gaseous and particle-bound deposition), plant properties (species, lipid content, foliage morphology, ratio of non-lipid plant parts, rind thickness, contents of both sugar and fibers), as well as the presence of an microbial active rhizosphere were generally found to be highly germane. For bioavailability and thus biodegradability of PBDEs pH value and soil composition are of particular importance [18, 22, 23]. In detail, relevant parameters are:

6.1 Excretion of plant solubilizers

Easy metabolizable intermediates as amino acids, organic acids, sugars and exozenzymes are excreted by plants as detoxification strategy to improve microbial bioavailability and biodegradability of PBDE in the rhizosphere [33]. For example, hexose was excreted by *Kandelia obovate* to enhance microbial debromination of BDE-99 to Br_2-BDEs and Br_3-BDEs in soil [55].

6.2 Plant specifics

Plant specifics like plant morphology, wax layers of bay leaves and the lipid content of both leaf and roots strongly affect both atmospheric and soil-based uptake of PBDEs. Hence, accumulation of Br_3-BDEs to Br_{10}-BDEs in the wax layer of wheat was determined as 29–93% of the total plant uptake [25], while BDE-209 accumulation in six different plant species at initial soil levels of 4700 ng g DM^{-1} ranged 1822–10,933 ng $plant^{-1}$ with alfalfa showing lowest and maize showing highest levels [56].

6.3 Rhizosphere and mycorrhiza

The release of plant eluates into the mycorrhizal is part of the symbiosis between the plant and the mycorrhizal fungi promoting the plant's uptake of nutrients and the growth of microorganisms in the mycorrhizal area. Its secondary effect of enhanced microbial biodegradation and detoxification of PBDEs in the mycorrhizal area was shown several times in literature. As an example, increased depletion of 470 ng g DM^{-1} towards 2250 ng g DM^{-1} was observed for BDE-209 comparing rice plants with and without mycorrhizal fungi [57].

6.4 Specific root and leaf surface

A correlation between accumulation of PBDEs and high specific plant surface was clearly shown for BDE-209 in roots of radish, lettuce and taro [58, 59] and for Br_2-BDE to Br_{10}-BDE in both pine needles and eucalyptus leaves [60].

6.5 Lipid content

The lipid content of a plant, especially of the roots, shows strong effects on PBDE uptake and was successfully evaluated for various mosses, lichens, ryegrass, alfalfa, maize, radish, squash, and pumpkin. A positive correlation between lipid content and PBDE uptake (RCF), as well as a negative correlation in lipid content and intrinsic PBDE mobility (TF) was observed [19, 22, 61, 62].

6.6 Organic content of the soil

Similar to the lipid content an increase in organic content of soil evokes higher PBDE accumulation in the soil and, therefore, reduced PBDE plant uptake [20, 33, 63]. Exemplarily, PBDE uptake in carrots was reduced by 31.5–69.8% and soil-based biodegradation increased by 8.6–28.5% by addition of 1–4 w% of swine manure to the soil fraction [63]. Differentiation between TOC and DOC showed a clear improvement in adsorption of PBDE in the soil matrix at higher TOC levels, whereas no effect was observed in case of increased DOC levels [54].

6.7 Biochar

Since biochar is insoluble and thus is considered as a TOC increase of the soil, elevated accumulation of PBDE in the soil phase may occur [64].

6.8 Sewage sludge

As sewage sludge reveals a high TOC content, but also enhanced contamination levels with PBDE or their detoxification and degradation products, sewage sludge is a dominant PBDE exposure pathway. Hence, using contaminated sludges as agricultural fertilizers, increasing concentration levels and accumulation of PBDE in the soil phase and, finally, elevated PBDE plant uptake are observed. However, relevance of this effect strongly depends on the original PBDE contamination levels of the sludge. An overview of PBDE levels in different sewage sludges was previously presented [52]. Similar to both lipid content and TOC content, a negative correlation between BDE-209 uptake and organic content, implemented by sewage sludge out, was observed [37].

6.9 Compost and digestate

In difference to sewage sludge, the PBDE load of compost and digestates is rather low as confirmed by various studies due to the low contamination levels of the plant educts (leaves, green waste, fruit and food residues). For instance, a broadly based study of biocompost, green waste compost and digestates in Baden-Wuerttemberg showed comparable median concentrations of 13 ng g DM^{-1}, 5.4 ng g DM^{-1}, and 13.7 ng g DM^{-1} and confirmed to low relevance of these materials as PBDE emissions sources [65].

6.10 Soil humidity

As a result of the low water solubility of PBDE, high soil moisture effectively prevents evaporation of BDEs as well as plant uptake [64]. Correspondingly, a longer PBDE load may be expected at wet locations.

6.11 Plastic particles

Plastics may reveal partition coefficients of PBDEs of several orders of magnitude higher than those towards sewage sludge or soil at levels of 0.04–1.6 w% [66, 67]. In detail, accumulation of PBDEs in low density polyethylene films (LDPE), an adequate and commonly accepted model for diffusive transport phenomena across biomembranes, showed accumulation factors against the aqueous phase (K_{PEW}) of 10^5–10^7 in case of 23 BDE congeners covering the total spectrum of bromination [68]. Furthermore, a curvilinear correlation between the log K_{PEW} and log K_{OW} factor, very similar to the correlation of BCF and log K_{OW} shown in **Figure 1** was observed and explained by energy barriers for diffusive transport into the LDPE structure [68]. The statement of rising K_{PEW} levels at higher lipophilicity of BDE congeners was further confirmed [67]. However, K_{PEW} levels are strongly affected

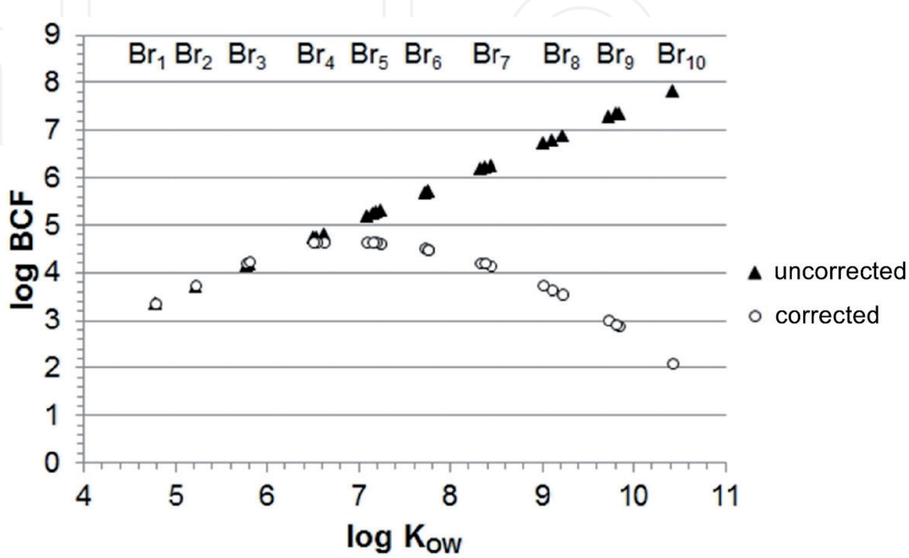

Figure 1.
Correlation of log K_{OW} and log BCF of 25 BDEs of high environmental relevance (−3, −7, −17, −28, −30, −47, −49, −66, −85, −99, −100, −123, −153, −154, −155, −183, −184, −191, −197, −201, −202, −206, −207, −208, −209) applying simple mathematical models with/without correction.

by the type of plastic and the temperature level during test conditions as adsorption is an endothermic process. While enhanced accumulation of BDE congeners was observed for polyethylene, polypropylene, polystyrene, and polyamide, low accumulation levels were observed for polyvinylchloride [66–68]. Hence, the hypothetical potential of injection of plastic particles into the soil as sink for PBDE and thereby soil remediation was positively investigated.

6.12 Other additives

Additional additives like graphene, TiO_2, Al_2O_3, Ag, and carbon nanotubes were considered as relevant for BDE-209 uptake in spinach, pumpkin, cucumber, corn and water spinach [36]. Indeed, an increased plant uptake was observed for all of these additives. Combinations of clay minerals like bentonite and oxidizing agents like sodium persulfate have also been positively tested for increased bioavailability of Br_3-Br_{10} – BDEs [69].

6.13 Solubilizers

The addition of surfactant-active additives elevates both mobility of PBDE in the soil matrix and plant uptake as previously described.

6.14 Macro- and trace elements

Apart from undisputed relevance of macro- and trace elements both in the development of the microflora in the rhizosphere and in plant growth, positive effects on the degradation of BDEs were observed in individual cases. Exemplarily, nitrate as additive caused intensified desorption and biodegradation of BDE-99, but might cause inhibition in case of high levels [70, 71].

6.15 Heavy metals

Presence of elevated concentrations of heavy metals shows ambivalent effects. Metals like Ni or Fe cause an enhanced uptake of PBDE, which was justified by chemical debromination of BDE-209 and enhanced mobilization, uptake and transport of Br_8- to Br_{10}-BDEs in the roots and shoots of the plants [64]. Enhanced plant uptake of low brominated BDEs like BDE-47 was also observed (24.76% vs. $< 1.5\%$) [72]. In contrast, reduced BDE-209 uptake of up to 50% by pumpkins was reported after addition of 300 mg Cu kg DM^{-1} and microbial mineralization was negatively affected at more elevated levels [70, 73]. Similar effects were shown for lead, where BDE-209 uptake was reduced by a factor of 2.9–3.7 by tall fescue at levels up to 1950 mg Pb kg DM^{-1} [74]. Heavy metal induced effects on PBDE plant uptake are also plant specifics as shown for cadmium, where levels of up to 14,800 ng g DM-1 had no effect on BDE-209 uptake in case of black nightshade, but lifting effects in case of amaranth [75, 76].

In summary, presence of essential heavy metals like iron or copper at adequate concentrations might have a positive effect on PBDE degradation, while non-essential heavy metals at non-toxic levels reveal no effect.

7. Predictive mathematical models

Due to the broad spectrum of food plants, attempts were made to develop simple but sensitive models to predict PBDE plant uptake based on simple chemical conditions and input variables as distribution equilibria, lipid content, organic matter, and initial PBDE soil-water concentration to achieve predictive statements about RCF, SCF (shoot concentration factor) or TF.

While these models provide comparatively good correlations for the RCF, they commonly fail in prediction of the TF, because this value is strongly influenced by intrinsic and atmospheric transport of BDEs in addition to the plant specific uptake of PBDE in the root plexus. Therefore, deviations in the range of two decades can be observed comparing model and real situation [77, 78]. Even after restriction of models to single pollutant situations instead of congener mixtures with variable concentration levels, and after focusing on single and simplified plants like lettuce, where differentiations between shoot and fruit or over the height of the shoot are not applicable, deviations of 25.3–58.2% of the model compared to real situation were reported for the insecticide chlorpyrifor [79].

Another highly relevant error is caused by incorrect analysis of intrinsic PBDE levels in roots in contrast to adsorptive fractions at the outer root surface affecting quality of environmental data. Hence, Briggs et al. [80] showed a significant decrease in BCF levels and thus RCF values of PBDE starting at a log K_{OW} value of approx. 6.5 (corresponds to a log BCF value of approx. 4.6) after elimination of externally adsorbed congeners (see **Figure 1**). This chart corresponds to Bintein's bilinear model [81], which was confirmed by Meylan et al. [82] for 610 non-ionic pollutants. This negative correlation at high log K_{OW} values and thus high lipophilicity bases on three restrictions of lipophilic compounds as follows:

- **Equilibrium kinetics**: The higher the lipophilicity of a pollutant, the longer it takes to achieve equilibrium state between two phases or compartments. The life span of annual crops might be too short to establish equilibria between soil and root or root and shoot [83].

- **Solubility:** Water solubility decreases with increasing lipophilicity and strongly lipophilic substances are primarily adsorb onto particles or surfaces. However, for absorptive root uptake of pollutants, a phase transition from soil to the liquid phase as well as from the liquid phase to the intrinsic root is required without adsorptive elimination at the tissue [80, 83]

- **Membrane permeability and cellular transport mechanisms**: The membrane-based cellular uptake of pollutants takes place by passive permeation [80]. The membrane permeability and thus bioavailability of contaminants is concisely described by Lipinski's 'Law of 5′, stating out low absorption or membrane permeability at log K_{OW} values higher than 5, molecular weight higher than 500, more than 5 hydrogen bond donors and more than 10 $(= 2 \cdot 5)$ hydrogen bond acceptors. The former two requirements are fulfilled even in case of Br_4- to Br_5 – BDEs. By means of known transport mechanisms into the cell, PBDE plant uptake may be affected by co-transport phenomena of biomolecules like amino acids.

8. RCF and TF values of specific crops

Following the extensive literature evaluation by Dobslaw et al. [52] twelve crops with the highest documented data density were selected and the occurring RCF and TF values for BDE-47 and BDE-209 were compared. The highest data density regarding the transition of PBDEs from soil to root or from root to plant was available for BDE-209 followed by BDE-47. In contrast to lower brominated

BDEs the concentrations of BDE-209 found in literature range over several decades, which facilitates an evaluation of the literature data concerning transition rates. In particular, the following species were selected: Rice (*Oryza sativa* L.), maize (*Zea mays* L.), prince's-feather (*Amaranthus hypochondriacus* L.), the group of bok choy, Chinese cabbage, broccoli, and filder cabbage (*Brassica* sp.), lettuce (*Lactuca sativa sp.), spinach* (*Spinacia oleracea* L.), sweet potato vine (*Ipomoea batatas* L.), radish (*Raphanus sativus* L.), carrot (*Daucus carota* L.), taro root (*Colocasia esculenta* L. Schott), pea (*Pisum sativum* L.), and pumpkin (*Cucurbita pepo ssp. pepo*).

Figure 2 shows the concentrations of BDE-209 in the roots of these crops as a function of the corresponding soil concentrations (RCF), indicating the dependency of BDE-209 uptake on the soil concentration with a ratio of about 1:10 (c_{root}:c_{soil}). Comparing shoots and corresponding soil a similar dependency on soil concentration with a ratio of about 1:18 (c_{root}:c_{soil}) was found (**Figure 3**). This representation was chosen because of the higher data density being available. However,

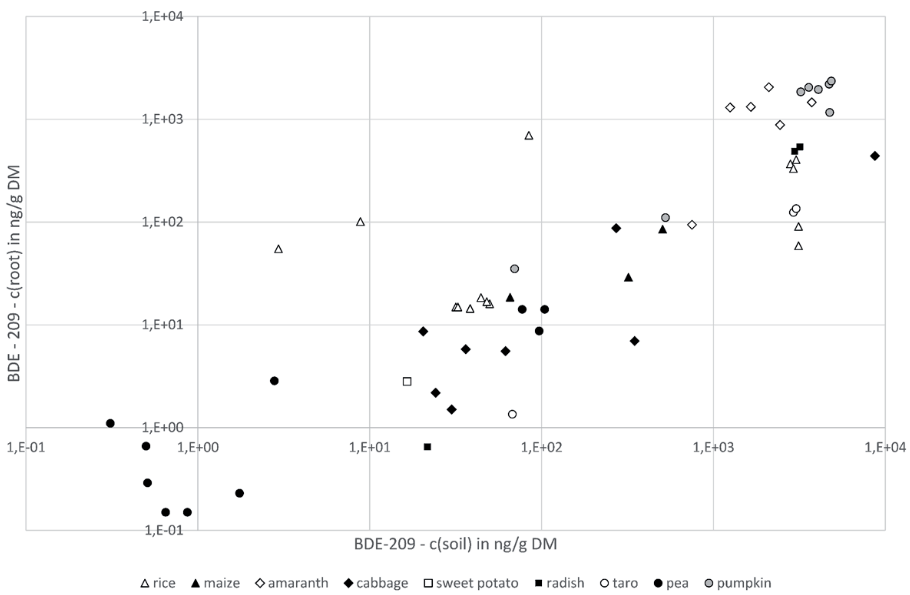

Figure 2.
BDE-209 – Root concentration factor (RCF), concentration in root as function of corresponding soil concentration.

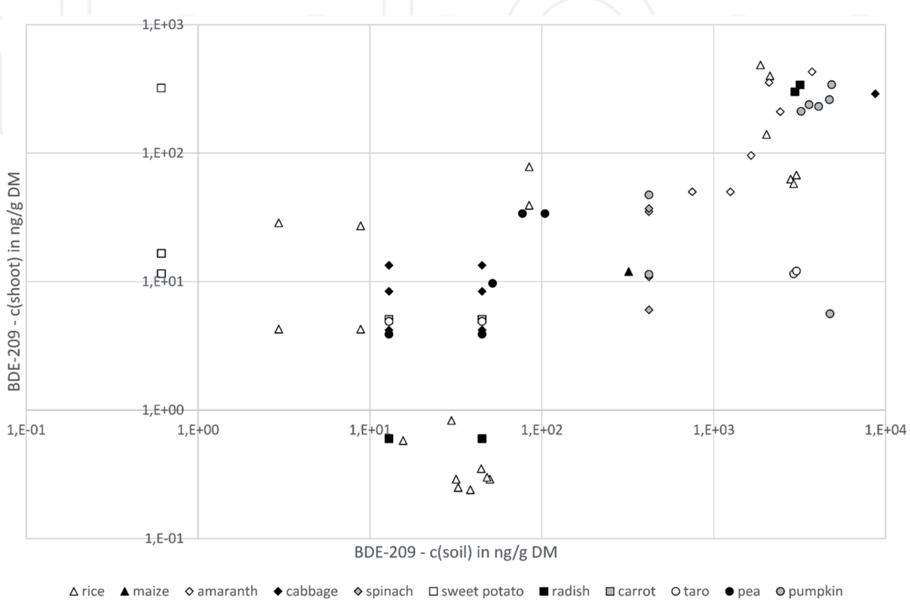

Figure 3.
BDE-209 – Concentration in shoot as function of corresponding soil concentration.

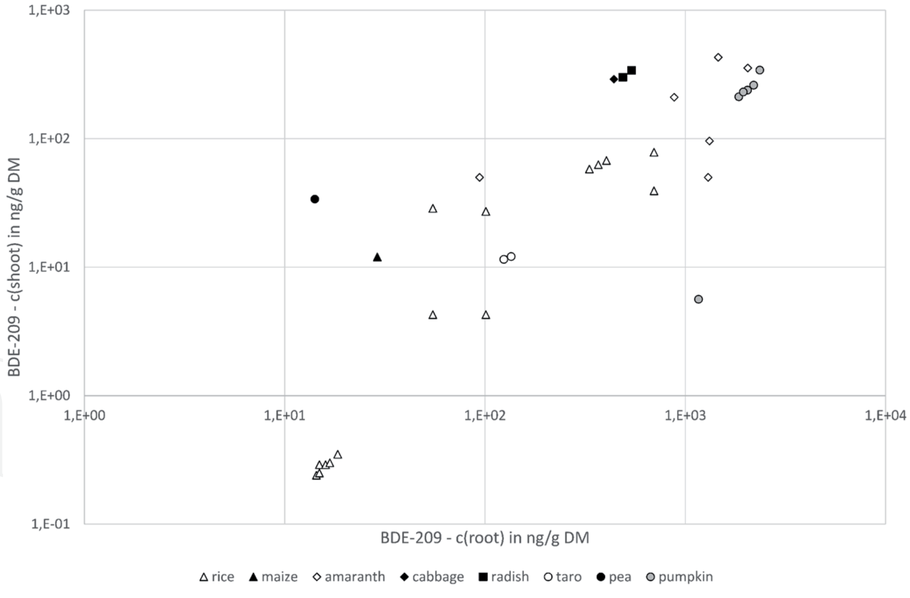

Figure 4.
BDE-209 – Translocation factor (TF), concentration in shoot as function of corresponding root concentration.

a TF could be derived from the comparison of the existing data pairs, which points to the dependence of the shoot concentrations on the concentrations in the root (**Figure 4**) with a ratio of about 1:9 (c_{shoot}:c_{root}).

The extent of transition of the tetrabrominated BDE-47 from soil to root and shoot was also determined by the concentration of the flame retardant in the soil (**Figures 5** and **6**). For BDE-47, despite its lower logK_{OW} in comparison to BDE-209, the transition rates are higher with about 1.1:1 (c_{root}:c_{soil}) and 1:6 (c_{shoot}:c_{soil}). Too few corresponding data pairs were available for the representation of the TF. A graphical summary of the results for the congeners 47 and 209 is given in **Figure 7**. The results are consistent with the prediction models described in Section 7 (see also **Figure 1**). Due to its high log K_{OW}, BDE-209 is expected to have a lower uptake compared to BDE-47. With the models mentioned above, it is possible to adequately describe the uptake behavior of lipophilic PBDEs. Of particular interest is the trend that the uptake of the substances is primarily determined by the

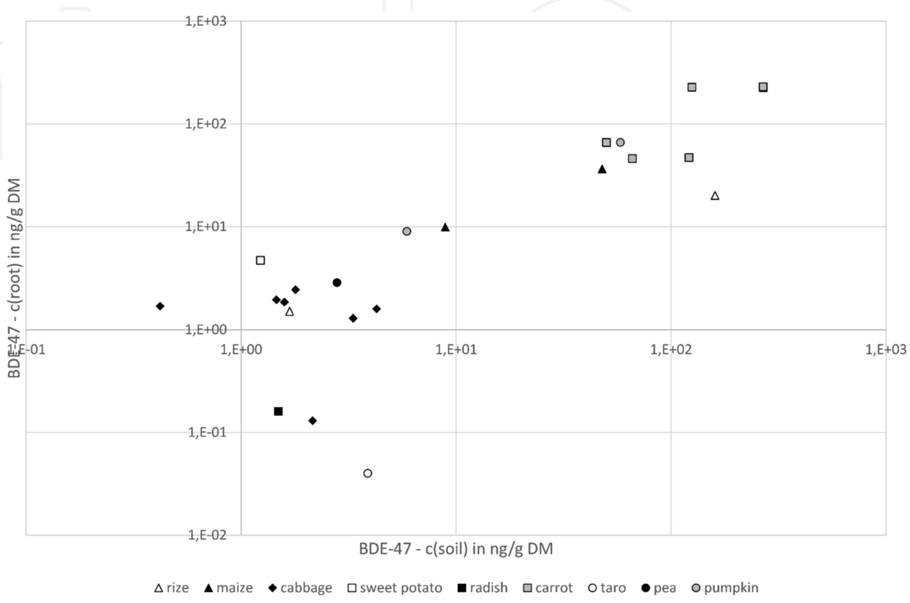

Figure 5.
BDE-47 – Root concentration factor (RCF), concentration in root as function of corresponding soil concentration.

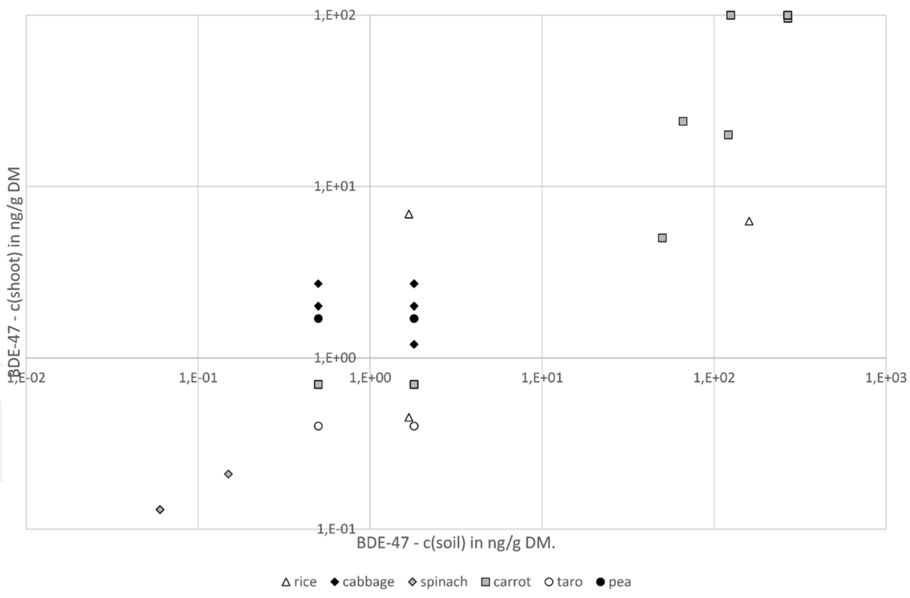

Figure 6.
BDE-47 – Concentration in shoot as function of corresponding soil concentration.

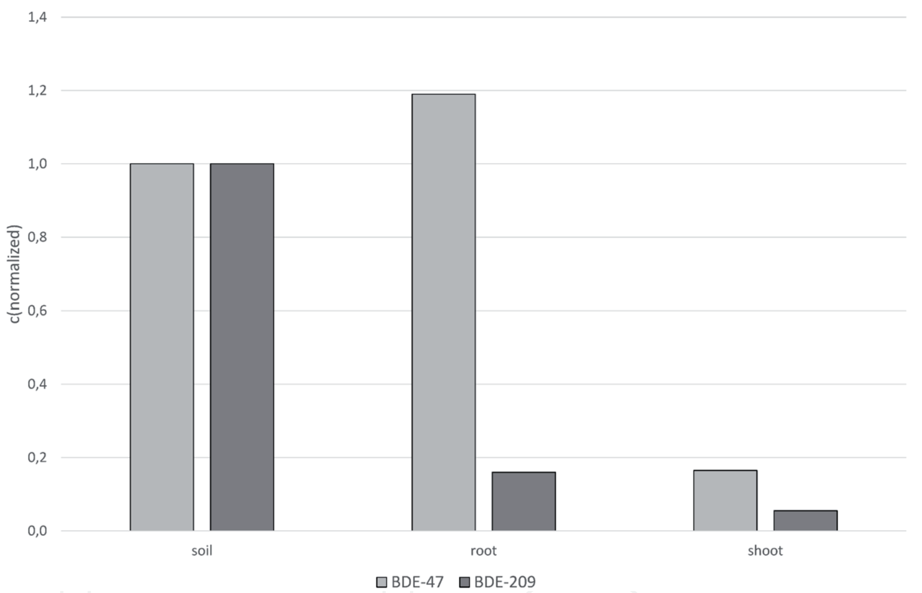

Figure 7.
BDE-47 and BDE-209 – Comparison of concentrations in soil, root and shoot (normalized, c(soil) =1).

concentration of the compounds in soil. A dependency of the uptake on the crop species might have been expected, but cannot be proven by the present data set.

9. Conclusion

PBDEs were widely used as flame retardants. Due to their effects as endocrine disruptors, neurotoxins, and on reproductive capacity as well, knowledge of terrestrial accumulation behavior and, in particular, their uptake by plants for food production is highly relevant. Uptake can occur viasoil-air-plant pathway as well as soil–soil water-root-plant pathway. Transport and plant uptake behavior strongly depend on physical and chemical properties of the BDEs, environmental factors, large-scale atmospheric transport processes, plant properties as well as terrestrial rhizospheres. During both atmospheric and terrestrial transport PBDEs are subject to UV-induced (atmospheric) or microbial induced (terrestrial) transformation and degradation processes like debromination, hydroxylation, methoxylation and ring closure to dibenzofurans. As PBDEs reveal high lipophilicity they tend to adsorption on lipophilic soil matrices and thereby show low uptake via soil–soil water-root-plant pathway and subsequent intrinsic transport. Hence, uptake and intrinsic transport are only expected for low brominated BDEs. Therefore, declining concentrations of PBDEs could be detected from soil via roots to shoots and final fruits, i.e. RCF and TF show negative correlation with their log K_{OW} values. Consistent with this statement, 84% of the human PBDE intake are attributed to respiration and inhalation of dust, while only 16% were correlated with dietary uptake. The actual exposure of vegetarian foods to PBDEs depends on the following parameters:

- Both microbial degradation and plant uptake of PBDE are elevated by release of easily biodegradable plant extracts like amino acids, organic acids, sugars and exoenzymes as commonly observed in symbiosis with rhizobia.

- The presence of rhizobia enhances microbial degradation and plant uptake of PBDE.

- Both atmospheric and terrestrial PBDE uptakes are strongly affected by the morphology of the plant (specific surface of leaves and roots) and the increasing lipid content of plant tissues accelerating PBDE uptake.

- PBDE immobilization and accumulation in soil is promoted by increasing TOC levels caused by implementation of compost, sewage sludge, digestates, or biochar.

- In contrast, increasing levels of DOC show no effect on plant uptake of PBDEs as long as there is no solubilizing effect by surfactants.

- As sewage sludge shows PBDE contamination up to 2.5 w%, it is an important emission source of PBDEs affecting soil contamination. In contrast, PBDE loads of compost and digestates are very low and commonly pollution effects are negligible.

- A decrease in evaporation losses and an enhanced immobilization tendency of PBDE can be observed in case of raising soil moisture.

- Solubilizers, ionic additives and nanoscale organic substances act as mobilizing agents increasing mobilization and plant uptake of PBDEs.

- Macroelements as nitrate favor terrestrial PBDE degradation through its function as alternative electron acceptor. Hence, plant's load is reduced.

- The presence of trace elements supports microbial transformation of PBDE in soil and therefore causes lower contamination of plants. In contrast, heavy metals seem to enforce PBDE uptake by plants by inhibition of terrestrial biodegradation processes.

- Current mathematical models allow high quality in prediction of the RCF value with a minimum of input parameters. In opposite, the prediction of SCF and TF values is not suitable due to the insufficient coverage of plant-specific parameters.

- According to Lipinski's 'Law of 5' Br_4- and Br_5-BDE congeners reveal the highest RCF levels. Higher polarity is required to gain high TF factors. Within the same isomers, even small differences in lipophilicity significantly change these values.

- Available PBDE data only show a linear correlation between soil concentration and plant uptake. Plant specific uptake effects cannot be observed.

10. Outlook

The poor biodegradability of PBDEs means that both the accumulation of PBDEs in the food chain and inhalation exposure will continue to be highly relevant issues in the next few decades. Problems comparable to those described for PBDEs are also expected for alternative brominated flame retardants such as hexabromobenzene, pentabromotoluene, 1,2-bis-(2,4,6-tribromophenoxy)ethane, or decabromodiphenylethane due to the likewise high degree of bromination, high persistence and thus a high bioaccumulation potential [20, 84]. A ubiquitous presence of these compounds was already proven [19].

Especially remarkable is the partial lack of metadata in existing publications, which makes an comprehensive evaluation, as it was tried in this publication, difficult. This concerns, for example, more detailed information about the soil composition, the content of organic carbon, lipid, and water of roots and shoots. Thinning of data, such as the aggregation of single congener data to sums (e.g. ∑PBDE) without further information about the composition makes a valuable data set useless.

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Conflict of interest

The authors declare that they have no conflict of interest.

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