SciForum
Mol2Net

Uptake of Different Organic Pollutants by Carrot

Ekhiñe Bizkarguenaga [1,*], Luis Ángel Fernández [1], Olatz Zuloaga [1] and Ailette Prieto [1]

[1] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao (Spain), Address; E-Mail: luis-angel.fernandez@ehu.eus (Luis Angel Fenández), olatz.zuloaga@ehu.eus (Olatz Zuloaga), ailette.prieto@ehu.eus (Ailette Prieto)

* Author to whom correspondence should be addressed; ebizkarguenaga@gmail.com.

Published: 4 December 2015

Abstract: In this study the uptake of different organic pollutants, including musk fragrances (tonalide and galaxolide), polybrominated diphenyl ethers (PBDEs), perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorosulfonamide (FOSA) by carrot samples was compared. The bioconcentration factors (BCFs), defined as ratio of the concentration in the dry plant tissue and the concentration in the compost amended soils, were compared and correlation with the water solubility of the target compounds was studied. A good correlation was obtained between the water solubility and the BCFs in the different plant tissues (carrot root peel, root core and leaves). Besides, while the target analytes with the lowest solubility (musk fragrances and PBDEs) tended to accumulate in the peel of the carrot, the most water soluble target analytes (the perfluorinated compounds) tended to translocate to the carrot leaves.

.

.

Keywords: plant uptake; carrot; musk fragrances; polybrominated diphenyl ethers, perfluorocarboxylic acids; perfluorosulfonic acids; perfluorosulfonamide;

1. Introduction

Under the Urban Wastewater Treatment Directive (UWWTD), towns and cities within the 28 European Union (EU-28) members are required to collect and treat their urban wastewater. The reuse of the sludge is also encouraged, and final disposal to surface waters has been banned (1). However, wastewater treatment plants (WWTPs), also called "biological treatments", are demonstrated not to be effective enough in contaminant removal (2). Not all the chemicals entering the WWPTs are completely degraded and are either removed by sorption and deposition to the final sludge, by volatilization or by discharge onto a surface

water body, if they remain in the wastewater effluent stream (2).

In this sense, contaminants of emerging concern (CECs) have been detected in effluents discharges from municipal and/or industrial wastewater treatment plants (WWTPs), including polybrominated diphenyl ethers (PBDEs), musk fragrances or perfluorinated compounds (2, 3).

Land applications of sewage sludge and/or compost derived of them have been adopted worldwide as an option for sludge management. Crops grown in soils amended or irrigated with wastewater containing CECs are exposed to contaminant uptake (4), which then become and entrance of pollutants in the food chain. Within this context, and taking into account that plants form an essential basis of animal and human diet, an evaluation of the uptake and accumulation of potential harmful organic contaminants in plants is of importance for risk assessment.

In this sense, the aim of the present work is to study the uptake in terms of BCFs of different organic pollutants, including musk fragrances (tonalide and galaxolide), PBDEs, perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs) and perfluorooctanosulfonamide (FOSA) by different carrot compartments (peel, core and leaves) and to evaluate the correlation between BCFs and the target analytes water solubility.

.

2. Results and Discussion

The BCFs for tonalide (water solubility 1200 µg/L), galaxolide (water solubility 1800 µg/L), BDE-138 (water solubility 19 µg/L) and BDE-209 (water solubility 0.14 µg/L), perfluorooctanoic acid (PFOA, water solubility $11 \cdot 10^6$ µg/L), perfluorooctasulfonate (PFOS, water solubility $75 \cdot 10^5$ µg/L), perfluorootanosulfonamide (FOSA, water solubility 0.029 µg/L), perfluoro-n-nonanoic acid (PFNA, water solubility 2.5 10^6 µg/L), perfluoro-n-heptanoic acid (PFHpA, water solubility 5.1 10^7 µg/L), perfluorohexyl phosphonic acid (PFHxPA, water solubility 2.3 10^8 µg/L), perfluoro-n-pentanoic acid (PFPeA, water solubility 9.5 10^8 µg/L) and perfluoro-n-butanoic acid (PFBA, water solubility 10 10^8 µg/L) obtained in our laboratories for the same carrot (*Daucus carota ssp sativus*) specie (Chantenay) were correlated with the logarithm of their water solubilities. According to the results in Figure 1 (a), an exponential correlation between water solubility and $BCF_{Total,}$ as well as BCF_{Peel} (determination coefficients of r^2=0.32), BCF_{Core} (r^2=0.74) and BCF_{Leaves} (r^2=0.60) was observed for all the analytes. The accumulation was higher with the water solubility increment observing a dramatically bioconcentration increased for the analytes (PFHxPA, PFPeA and PFBA) with a water solubility higher than 8. In order to confirm these results, the previously mentioned analytes were discarded and only the rest included in the graphic (see Figure 1 (b)) observing the similar behaviour for all the analytes.

It should also be highlighted, while the target analytes with the lowest solubility (musk fragrances, AHTN and HHCB, and PBDEs, BDE-138 and BDE-209) tended, in general, to accumulate in the peel of the carrot, the most water soluble target analytes (PFOS and PFOA as examples) tended to translocate to the carrot leaves (see BCFs included in Table 1). However, as can be clearly observed from Table 1, while BDE-138 accumulated exclusively in the peel, BDE-209 accumulated mainly in the leaves (BCF_{leaves}) when present at a low concentration.

Accumulation in the leaves could be due to translocation after root uptake or by foliar uptake

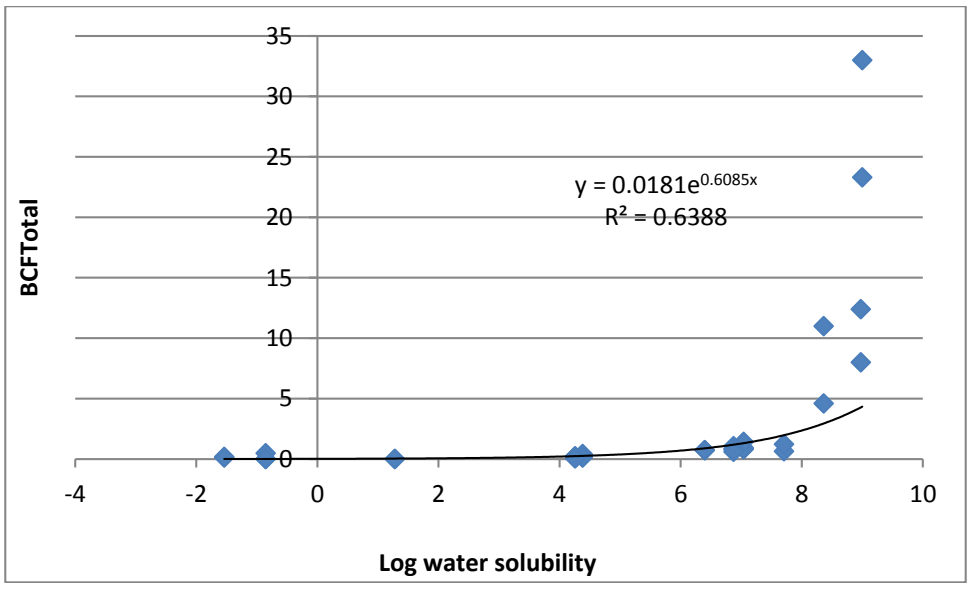
from the air. According to the values obtained from the blanks, no appreciable contribution from foliar uptake was observed for any of the target analytes and, thus, foliar uptake was discarded.

Main text paragraph.

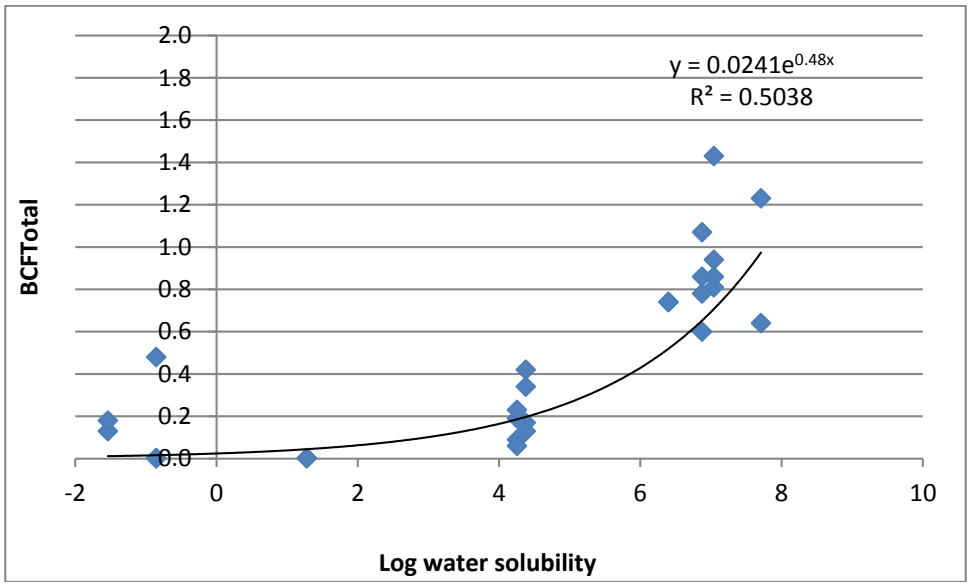
Table 1. Bioconcentration factors (BCFs) of the analytes in the different carrot (*Chantenay* specie) compartments and the total BCFs (BCF_{Total}).

An average nominal concentration of 5000 ng/g (musks fragrances) and 7500 ng/g (BDE-209) (high concentration level) was used as fortification level. As the compost already contained the musks (16-38 ng/g) and BDE-209 (7-20 ng/g) at a low concentration level, fortification was unnecessary. BDE-138 was added in order to adjust to a nominal concentration of 120 ng/g (low level). A nominal concentration of 500 ng/g (low level) was used in the case of PFOA and PFOS. MDLs: method detection limits.

Experiment	Compartment	BCF_{HHCB}	BCF_{AHTN}	$BCF_{BDE-138}$	$BCF_{BDE-209}$	BCF_{PFOA}	BCF_{PFOS}
Low level	Peel	1.25-1.54	0.59-0.67	0.01-0.02	< MDLs	0.12-0.61	0.39-0.43
	Leaves	0.44-0.52	0.30-0.32	< MDLs	1.44	0.81-3.34	1.67-1.93
	Core	<MDLs	<MDLs	< MDLs	< MDLs	0.05-0.36	0.52-0.64
	Total	0.34-0.42	0.19-0.23	0.002-0.003	0.48	0.81-0.94	0.86-1.07
High level	Peel	0.84-0.87	0.42-0.46		0.001-0.009		
	Leaves	0.02-0.02	0.01-0.01		0.003-0.004-		
	Core	0.03-0.04	0.01-0.02		< MDLs		
	Total	0.13-0.17	0.06-0.09		0.001-0.003		



(a)



(b)

Figure 1. BCF_{Total} versus the logarithm of water solubility of (a) BDE-138, BDE-209, PFOA, PFOS, PFOSA, PFNA, PFHpA, PFHxPA, PFPeA and PFBA and (b) all the analytes except PFHxPA, PFPeA and PFBA.

3. Materials and Methods

Plant Cultivation

Pots (n=2) with 2 kg of the (95:5) soil:compost mixtures were sown with previously germinated (~14 days) carrot seeds. For germination, petri dishes were covered with moistened filter paper and the seeds were evenly distributed in the petri dish. Afterwards, seeds were covered with another piece of moistened filter paper. The number of plants per pot was 3−4.

Control (n=1) plants of carrots grown in the non-fortified compost amended soil 2.4 mixture were placed in between the fortified amended soil pots. The cultivation of the carrot was performed under controlled greenhouse conditions.

Temperature was set to 25 °C during the day and at 18 °C during the night with a 14-h day length and a relative humidity of 50 % and 60 % during the day and overnight, respectively, and they were regularly watered with distilled water and Hoagland nutritive solution (5). Carrots were harvested during a period of three months reflecting the minimum time to produce relatively mature crops and all plants per pot were collected and pooled to one sample. Each plant was dissected into roots (peel and core) and leaves. Fresh weight of all plant fractions was recorded, followed by rinsing with tap water. Carrots were peeled with a vegetable peeler (depth of ~2 mm).

Sample treatment and analysis

Carrot samples (peel, core and leaves) were freeze-dried using a Cryodos-50 laboratory freeze-dryer (Telstar Instrumat, Sant Cugat del Valles, Barcelona, Spain). In the case of the compost amended soil, this was air-dried for approx. 48 hours. Both, the dried plant and compost amended soil samples were stored at -20

°C until analysis. Analyses were performed in triplicate under the conditions described in previous works for musk fragrances (6), PBDEs (7) and perfluorinated compounds (8).

4. Conclusions

It has been demonstrated that uptake of several organic pollutants is dependent on their water solubility and that the BCFs in the different carrot compartments is exponentially related to the logarithm of the water solubility of the target analytes. A dramatically bioconcentration increase for the analytes (PFHxPA, PFPeA and PFBA) with a water solubility higher than 8 was observed. In general, while the target analytes with the lowest solubility tended to accumulate in the carrot peel, the most water soluble target analytes tended to translocate to the leaves.

Acknowledgments

The Spanish Ministry of Science and Technology financially supported this work through the CTM2011-24094 project. E. Bizkarguenaga is for her pre-doctoral fellowships Technical and human support by PhD. Azucena González, Phytotron Service, SGIker (UPV/EHU) is gratefully acknowledged.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

1. Kelessidis, A.; Stasinakis, A.S. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Manage.* **2012**, 32, 1186-1195.
2. Ratola, N.; Cincinelli, A.; Alves, A.; Katsoyiannis, A. Occurrence of organic microcontaminants in the wastewater treatment process: A mini review. *J. Hazard. Mater.* **2012,** 239, 1-18.
3. Loos, R.; Carvalho, R.; António, D. C.; Comero, S.; Locoro, G.; Tavazzi, S.; Paracchini, B.; Ghiani, M.; Lettieri, T.; Blaha, L.; Jarosova, B.; Voorspoels, S.; Servaes, K.; Haglund, P.; Fick, J.; Lindberg, R. H.; Schwesig, D.; Gawlik, B. M., EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. *Water Res.* **2013,** 47, 6475-6487.
4. Olofsson, U.; Bignert, A.; Haglund, P. Time-trends of metals and organic contaminants in sewage sludge. *Water Res*. **2012**, 46, 4841-4851.
5. Epstein, E.; Bloom, A.J. Mineral nutrition of plants: principles and perspectives. *second ed. Sinauer Associates, Sunderland, MA* **2005**.
6. Aguirre, J.; Bizkarguenaga, E.; Iparraguirre, A.; Fernández, L.Á.; Zuloaga, O.; Prieto, A. Development of stir-bar sorptive extraction thermal desorption gas chromatography-mass spectrometry for the analysis of musks in vegetables and amended soils. *Anal. Chim. Acta* **2014**, 812, 74-82.
7. Iparragirre, A.; Rodil, R.; Quintana, J.B.; Bizkarguenaga, E.; Prieto, A.; Zuloaga, O.; Cela, R.; Fernández, L.A., Matrix solid-phase dispersion for the extraction of polybrominated diphenyl ethers and their hydroxylated and methoxylated analogues in vegetables and soils. *J. Chromatogr. A* **2014**, 1360, 57-65.

8. Zabaleta I.; Bizkarguenaga E.; Iparraguirre A.; Navarro P.; Prieto A.; Fernández L.A.; Zuloaga O.; Focused ultrasound solid-liquid extraction for the determination of perfluorinated compounds in fish, vegetables and amended soil., *J. Chromatogr. A.* **2014** 1331, 27-37.