DOI: 10.1556/CRC.37.2009.Suppl.4

PHYTOREMEDIATION OF PERSISTENT ORGANIC POLLUTANTS

Tamas KOMIVES [1] – *Gabor GULLNER* [1] – *Andras BITTSANSZKY* [1] – *Sophie PASCAL* [2] – *Francois LAURENT* [2]

[1] Plant Protection Institute, Hungarian Academy of Sciences, Herman Otto ut 15, 1022 Budapest, Hungary, e-mail: tkom@nki.hu
[2] INRA, UMR Xénobiotiques, 180 ch. de Tournefeuille, BP3, 31931 Toulouse Cedex 9 France

Abstract: Toxicity, chemical stability, bioaccumulation, and long-range transport of persistent organic pollutants (POPs) cause environmental and human health hazards, and demand the cleanup of remnants from previous applications. Phytoremediation uses living higher plants for the removal and biochemical decomposition of environmental pollutants and became a front-runner among cleanup technologies. The efficiency of plants as detoxifiers, filters or traps has been proven in cleaning up soils polluted with crude oil, explosives, landfill leachates, metals, pesticides, and solvents. Although phytoremediation of POPs is made very difficult by their low bioavailability, recent literature indicated that some plants (primarily those belonging to the Cucurbitaceae family) are capable of taking up significant amounts of POPs and accumulate them in their tissues. A joint French-Hungarian research project will investigate the possibility of phytoremediation of POPs.

Keywords: Persistent organic pollutants, POPs, phytoremediation, uptake, translocation, metabolism

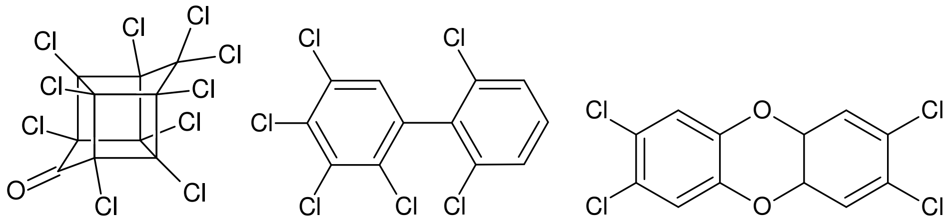
Introduction

Chlorinated insecticides and polychlorinated biphenyls representing groups A and B of persistent organic pollutants (POPs, Table 1 and Figure 1) have been developed in the first half of the twentieth century. Group C relate to polychlorinated dioxins and furans (Table 1 and Figure 1) that are generated as bye-products of industrial processes and incineration [Inui *et al*. 2008, White 2009].

Table 1. Groups of persistent organic pollutants (POPs)

Group	POPs
A. Chlorinated insecticides	A family of seven insecticide active ingredients
B. Polychlorinated biphenyls	A family of 209 individual compounds used as industrial chemicals
C. Polychlorinated dioxins and furans	A family of 75 compounds formed as by-products of industrial processes (primarily combustion)

After decades of intensive production of POPs the damaging consequences became evident and showed that they are a global threat [Oldal *et al*. 2006, Inui *et al*. 2008, White 2009]. Environmental and human health hazards demand the cleanup of sites polluted by POPs. Phytoremediation, *i.e.* the use of plants for removing, sequestering, or chemically decomposing environmental pollutants, has become one of the most rapidly developing fields of environmental restoration. The efficiency of plants as detoxifiers, filters or traps has been proven in cleaning up soils polluted with crude oil, explosives, landfill leachates, metals, pesticides, and solvents [Komives and Gullner 2000, Uzinger and Anton 2008]. Although information on the phytoremediation of POPs is rather scanty, very recent literature has indicated that some plants (primarily those belonging to the Cucurbitaceae family) are capable of taking up significant amounts of POPs and accumulate them in their tissues [Inui *et al.* 2008, White 2009].



chlordecone **2,2',3,4,5,6'-hexachlorobiphenyl** **2,3,7,8-tetrachlorodiphenyl dioxin**

A B C

Figure 1. Examples of POP chemicals belonging to groups A, B, and C

The collaborative study between our laboratories will focus on the possibility of phytoremediation of soils contaminated by POPs.

Uptake and Translocation of POPs in plants

Uptake and translocation of a POP molecule in plant tissues depends on the pollutant's concentration in the soil solution, its ability to enter the root system, and the rate of transpiration in the plant [Komives and Gullner 2000]. Binding of most POPs to soil particles is practically irreversible and usually very little desorption occurs: only low concentrations of POPs can be detected in the soil solution and POPs seldom reach the groundwater. Therefore, efficacy of the phytoremediation of POPs is limited by the bioavailability of the pollutant. Bioavailability is determined by the physical and chemical properties of the POP molecule, as well as those of the soil. Uptake of aqueous solutions of POPs and their translocation within plant tissues are usually passive processes, regulated by the water transport into the cells. Thus, removal of POPs from soil is possible only by increasing their apparent water-solubility. A new approach takes advantage of the ability of cyclodextrins to increase the elution of organic compounds from soils. Cyclodextrins have dual solubilizing potency: they may act as surfactants as well as complexing agents that form inclusion complexes with hydrophobic compounds.

Metabolism of POPs in plants

An efficient phytoremediation of POPs would include the conversion of the pollutants by the plant tissues into harmless derivatives. Unfortunately, very little is known about the rates of transformation and the structure of the metabolites derived from individual POP molecules by plant cells [Campos *et al.* 2008], although plants are capable of transforming a number of xenobiotics by a wide variety of chemical/biochemical metabolic pathways. These biotransformation reactions are generally referred to as *Pha-*

ses I and *II*, where *Phase I* includes oxidative transformations and *Phase II* deals with the conjugation of *Phase I* products to amino acids or sugars.

Xenobiotic (hydrophobic)

↓ ***Phase I***

Functionalized derivative (less hydrophobic)

↓ ***Phase II***

Conjugate (hydrophilic)

↓ ***Phase III***

Terminal metabolite (compartmentized)

Figure 2. Metabolic scheme of the biotransformations of xenobiotics in plants

In plants, the oxidative metabolism in the *Phase I* system is usually mediated by cytochrome P-450-containing mixed function oxygenases (CYP, E.C.1.14.-.-). These enzymes support the oxidative, peroxidative and reductive metabolism of both endogenous and xenobiotic substrates. In plants there are a surprisingly high number of CYP genes: 246 in *Arabidopsis* (representing approximately 1% of the plant's gene complement) compared with less than a 100 in humans. CYP enzymes are characterized by the high diversity of reactions that they catalyze and the high range of their chemically divergent substrates. Increasing emphasis on functional genomic approaches to CYP research recently has greatly advanced our understanding of CYP-mediated reactions in plants. In the *Phase II* systems hydrophobic xenobiotics functionalized by the *Phase I* system are converted to more hydrophilic forms *via* conjugation with sugars or sulfhydryl (-SH) group-containing tripeptides, such as glutathione (γ-L-glutamyl-L-cysteinyl-glycine, GSH). Plants lack the excretion system of animals. In plant cells toxic metabolites and pollutants are sequestered into the cell vacuole. This *Phase III* type process is an active one and is catalyzed by membrane-bound ATP-driven pumps [Komives and Gullner 2004].

Discussion and conclusions

The questions the unique ability of some Cucurbitaceae plants to take up and accumulate POPs raises are very interesting. Most importantly, the key factors influencing the uptake are not known and should be investigated. In practical application, the high-uptake plants will be very useful in phytoremediation of POPs and they can also serve as possible hosts for phytomonitoring of these contaminants in soils. On the other hand, the findings show that non-cucurbit crops make good substitute crops in fields contaminated with POPs. Also, low-uptake *Cucurbita* biotypes will be useful in the breeding of substitute rootstocks for grafting commercial cucumber and melon cultivars.

Another intriguing aspect of the phytoremediation of POPs is the dependence of the uptake and translocation processes on the chemical structure of the pollutants.

Quantitative structure-activity relationships describing their behavior in the soil-soil solution-plant system will provide us information on key biological mechanisms determining the efficiency of phytoremediation.

With advances in plant biology and soil science, phytoremediation has become one of the most rapidly developing fields of environmental restoration. Our knowledge of the factors that determine the efficiency of the phytoremediation of organic pollutants has expanded greatly in recent years. It became evident that this process is determined by a highly complicated sequence of events, elements of which may play a significant role, depending on the plant-soil-pollutant system (Jolánkai *et al*. 2008). In case of POPs the key role of the solubilization of the pollutant has been clearly established. However, much is yet to be learned about the systems regulating the uptake of POPs by plant roots, especially, with respect to their specificity and their mechanism of regulation. Genetic variability studies of Cucurbitaceae [Szabó *et al*. 2005] and investigations to follow the fate of POPs in hyperaccumulating plants will provide us with exciting challenges for further research.

Acknowledgements

Financial support of this work was provided by OTKA (PD5169) and the Balaton project (TET F-35/2006) jointly supported by the National Research and Technology Agency of Hungary and the Centre National de la Recherche Scientifique of France.

References

Campos, V. M. – I. Merino – R. Casado – L. F. Pacios – L. Gómez.: 2008. Review. Phytoremediation of organic pollutants. Spanish Journal of Agricultural Research 2008, **6**: 38-47

Inui, H. – T. Wakai – K. Gion – Y.-S. Kim – H. Eun: 2008. Differential uptake for dioxin-like compounds by zucchini subspecies. Chemosphere **73**: 1602–1607

Jolánkai, M. – F.H. Nyárai – A. Tarnawa – H. Klupács – I. Farkas: 2008. Plant and soil interrelations. Cereal Researh Communication **36**:(Supplement) 7-10.

Komives, T. – G. Gullner: 2000. Phytoremediation. In “Plant-Environment Interactions” (Ed. Wilkinson, R. E.), New York, Marcel Dekker, Inc. pp. 437-452.

Komives, T. – G. Gullner: 2004. Dendroremediation. In: I Láng, M Jolánkai, T Komives (ed.) Pollution Processes in Agri-Environment, Budapest: Akaprint, pp.13-21.

Komives, T. – G. Gullner: 2005. Phase I xenobiotic metabolic systems in plants, Zeitschrift für Naturforschung C **60:** 179-185.

Láng, I. – M. Jolánkai –T. Komives (Editors): 2004. Pollution Processes in Agri-Environment, pp. 277. Akaprint Publishers, Budapest

Oldal, B. – E. Maloschik – N. Uzinger – A. Anton – A. Székács: 2006. Pesticide residues in Hungarian soils. Geoderma **135**: 163–178.

Szabó, Z. – G. Gyulai – M. Humphreys – L. Horváth – A. Bittsánszky – R. Lágler – L. Heszky: 2005. Genetic variation of melon (C. melo) compared to an extinct landrace from the Middle Ages (Hungary) I. rDNA, SSR and SNP analysis of 47 cultivars. Euphytica 146:87-94.

Uzinger, N – A. Anton. 2008. Chemical stabilization of heavy metals on contaminated soils by lignite. Cereal Research Communications **36**:1911-1914.

White, J.C.: 2009. Optimizing Planting Density for *p,p*-DDE Phytoextraction by *Cucurbita pepo*. Environmental Engineering Science **26:** 1-7.