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Environmental Pollution 124 (2003) 375–378

ENVIRONMENTAL POLLUTION

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Concurrent plant uptake of heavy metals and persistent organic pollutants from soil

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Received 15 January 2003; accepted 5 February 2003

"Capsule": *Heavy metals and organic pollutants aged in soil are both taken up by some plants, suggesting the possibility of phytoremediating two different contaminant types simultaneously.*

Keywords: Phytoremediation; Persistent organic pollutants; Heavy metals in soil

1. Introduction

The extent of anthropogenic environmental pollution—in the United States (Black, 1999; Glass, 1999), in the European Union (Chaudhry et al., 2002), and in the third world is well documented. For example, the Food and Agriculture Organization of the United Nations has estimated that at a minimum 10^5 t of unwanted pesticides are in "storage" in undeveloped countries, with at least 2×10^4 t in African countries (Chaudhry et al., 2002). The potential for negative impacts of these stocks on humans and the environment is of major concern. In situ remediation techniques, such as phytoremediation—the attenuation of pollution through the use of plants—which impose minimal environmental disturbance, offer economic, agronomic, and societal benefits to all countries.

Up to the present time phytoremediation of soil-borne heavy metals and of organic contaminants has been pursued as two distinct disciplines. This compartmentalized approach applies to fundamental studies of the mechanisms of action, as well as to the development of remediation technologies. Based on data from the authors' laboratories over the preceding several years we propose that far more convergence as opposed to divergence in the underlying plant physiology and soil science impacts the soil/vegetation microcosm to attenuate both soil-borne heavy metals and organic pollutants. For example, our published research has established that zucchini (*Cucurbita pepo* L.) and spinach (*Spinacia oleracea*) bioaccumulate soil-bound persistent organic pollutants (POPs) (Mattina et al., 2002). Other published reports have shown that spinach bioaccumulates heavy metals from soil (Römer and Keller, 2001). The data which are presented here demonstrate that these two plants simultaneously bioconcentrate and translocate both categories of weathered, soil-bound pollutant. Such simultaneous uptake and translocation of heavy metal and organic pollutants, if confirmed and optimized, could have enormous implications for plant/soil interaction mechanisms, and impact on practical remediation approaches, and ultimately on risk to human health.

2. Materials and methods

Using a well characterized field plot (Mattina et al., 1999), a variety of crops were grown during the summer months in 2000 through 2002. Plants were grown either directly in the contaminated soil or in 100 l plastic tubs filled with the contaminated soil and buried in the field

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doi:10.1016/S0269-7491(03)00060-5

plot up to one inch of their top edge. A listing of the plants examined is presented in Table 1. Canada thistle is a common weed and was an opportunistic plant.

2.1. Analysis for chlordane

Vegetation samples were rinsed thoroughly, chopped, and stored frozen in amber glass jars until analysis. Soil samples were collected using a 1 inch stainless steel corer to a depth of 6 inches. The extraction and clean-up procedures have been described in detail previously (Mattina et al., 2002). Quantitation of all samples was done using internal standard calibration on a Saturn 2000 Ion Trap GC/MS system (Varian, Sugar Land, TX, USA) equipped with a 30 m×0.25 mm i.d. × 0.25 μm film thickness γ-DEX120 column (Supelco, Bellefonte, PA, USA). GC/MS conditions, calibration, and data reduction have been detailed previously (Mattina et al., 2002).

2.2. Analysis for heavy metals

All samples were dried at 95 °C for 24 h. Soils, 1.0 g, and vegetation, 0.5 g, were digested with 10 ml conc. HNO_3 on a hot plate for 30 min. Lead and zinc concentrations were determined by Inductively Coupled Plasma Emission Spectroscopy (ICP OES) using the Atom Scan 16 (Thermo-Jarrell Ash, Franklin, MA, USA). The digests were analyzed also for arsenic and cadmium with a PE 51 OOPC graphite furnace atomic absorption spectrometer (GFAAS) (Perkin-Elmer Corp., Welisley, MA, USA). Further details may be found in an earlier publication (Stilwell and Graetz, 2001).

3. Discussion

Two bioconcentration factors, as defined in Eqs. (1) and (2), computed from the compartment concentrations, will be used in discussing the results from this study. Concentrations in all compartments were calculated on a dry weight basis. Typical soil chlordane concentrations ranged from 3000 to 6000 ng/g; ranges for chlordane concentrations in roots were 2500–25 000 ng/g; and for chlordane in leaves, 81–760 ng/g (Mattina et al., 2002). Concentrations of the metals in soil and plant tissues in mg/kg are provided in Table 2.

$$\mathrm{BCF} = \frac{C_{\mathrm{roots}}}{C_{\mathrm{soil}}} \tag{1}$$

$$\mathrm{BCF}' = \frac{C_{\mathrm{aerial}}}{C_{\mathrm{soil}}} \tag{2}$$

In Fig. 1 are shown the BCF values for weathered chlordane and several heavy metals for the plants studied. As we have well documented in previous studies (Mattina et al., 2002), *C. pepo* L. (zucchini) is an exceptionally good bioaccumulator of soil-bound chlordane. We present here for the first time that zucchini also accumulates zinc and cadmium in an amount comparable to their bioaccumulation in spinach. It has been previously established that spinach uptakes and translocates copper, zinc, and cadmium from soil (Römer and Keller, 2001).

In addition to determining BCF values, we also calculated BCF′ values and summarize these data in

Table 1
Plants examined

Common name	Scientific name	Culitvar
Lettuce	*Lactuca sativa*	Black Seeded Simpson
Pumpkin	*Cucurbita pepo*	Triple Treat
Zucchini	*Cucurbita pepo*	Black Beauty
Cucumber	*Cucumis sativus*	Marketmore 76
Tomato	*Lycopersicon esculentum*	Marglobe
Canada thistle	*Cirsium arvense*	n/a (weed)
White lupin	*Lupinus albus*	A.U. Homer
Spinach	*Spinacia oleracea*	Winter Bloomsdale

Table 2
Concentration of metals analysed in soil and tissue compartments (mg/kg)

Description	As	Cd	Pb	Zn
Soil				
Spinach	125.9	0.7	501	102
Lettuce 1	90.9	0.9	428	122
Lettuce 2	145.05	1.1	749	162
Tomato	67.4	0.28	252	50
Pumpkin	53.8	0.31	188	63
Zucchini	66.45	0.5	339.35	113.35
Lupin	65.05	0.4	320.75	127.45
Cucumber	79.2	0.38	327	71
Canada Thistle	34.05	0.44	294	76
Vegetation				
Spinach leaves	1.55	5.3	<10	144
Spinach roots	13.6	4.4	226	140
Lettuce leaves 1	9.8	2.9	<10	31
Lettuceroots l	6.575	2	<10	28
Lettuce leaves 2	4.67	2.2	<10	38
Lettuce roots 2	10.31	1.1	83	28
Tomato stems	0.935	0.98	45	164
Tomato roots	15.65	0.83	106	182
Pumpkin leaves	3.53	0.15	<10	74
Pumpkin roots	17.45	0.34	53	71
Zucchini Leaves	2.775	1	<20	369.1
Zucchini Roots	68.9	4	227.35	140.15
LupinTops	30.85	<0.1	<20	51.105
LupinRoots	42.55	0.4	<20	78.105
Cucumber leaves	2.905	0.1	<10	54
Cucumber roots	24.3	0.33	<10	113
Canada Thistle shoots	0.84	1.9	<10	70
Canada Thistle roots	2.265	1.29	<10	30

Table 3. Once again zucchini occupies a notable position among the data provided in this table.

If we now define a translocation factor (TF) as shown in Eq. (3)

$$TF = \frac{BCF'}{BCF} = \frac{C_{aerial}}{C_{root}} \quad (3)$$

we can then graph TF values as shown in Fig. 1B for the same group of plants. Lettuce, spinach, thistle, tomato, and zucchini show TF values greater than 1 for one or more of the examined analytes.

These data suggest the intriguing possibility that plant factors which impact phytoremediation of one category of soil-bound pollutants may also impact the other

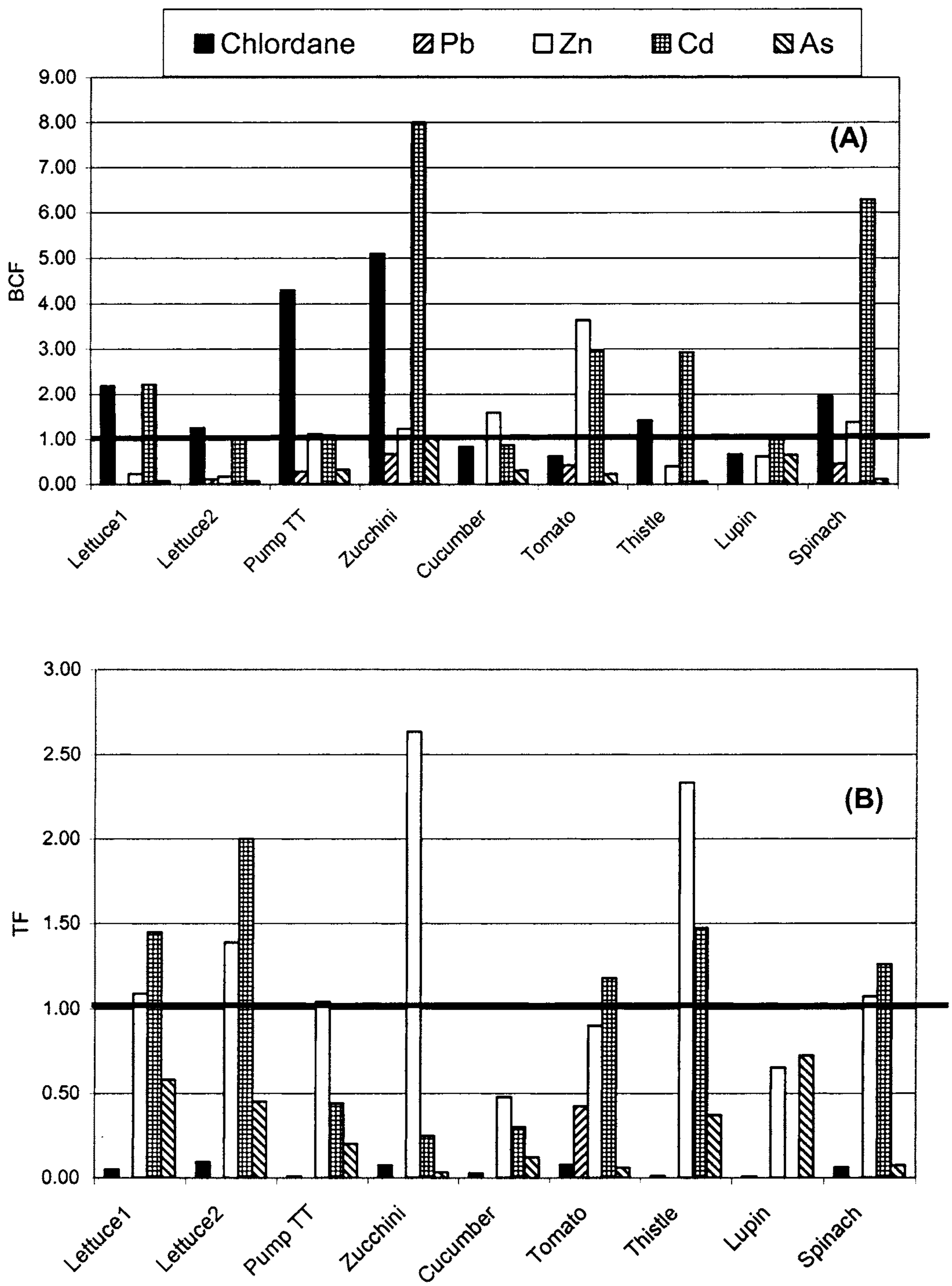

Fig. 1. (A) Bioconcentration factors for several analytes in a variety of plants; (B) translocation factors for the same set of analytes and plants.

Table 3
BCF′ values[a]

Soil Contaminant	Lettuce1	Lettuce2	Pumpkin	Zucchini	Cucumber	Tomato	Thistle	Lupin	Spinach
Chlordane	0.11	0.12	0.04	0.38	0.02	0.05	0.02	0.01	0.12
Pb	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00
Zn	0.25	0.24	1.17	3.26	0.76	3.28	0.92	0.40	1.47
Cd	3.22	2.00	0.48	2.00	0.26	3.50	4.32	0.00	7.93
As	0.04	0.03	0.07	0.04	0.04	0.01	0.03	0.47	0.01

[a] BCF′ was determined from leaf tissue in all cases except for tomato, for which stem tissue was used.

category. We have hypothesized previously that the notable accumulation of weathered POPs by *C. pepo* derives from the plant's release of low molecular weight organic acids (LMWOAs) as a fundamental nutrient acquisition strategy (White et al., 2003). Both spinach (Römer and Keller, 2001) and lupins (Egle et al., 2001) have been shown to exude LMWOAs such as citrate in response to phosphorus deficiency. These acids increase nutrient availability by chelating inorganic soil constituents that routinely bind to phosphorus, such as Fe, Ca, and Al (White et al., 2003). We speculate that as the soil matrix, including both mineral and organic portions, is deconstructed by the organic acids, the availability of sequestered organic and heavy metal pollutants is increased. Citric and malic acids, both constituents of root exudates, have been shown to increase the solubility of Cu, Zn, and Cd in the soil solution (Römer and Keller, 2001). Experiments are in progress to characterize the exudates of *C. pepo* and to determine the various steps in the soil chemistries which impact the mechanism of pollutant uptake and transfer. If complementarity between the uptake of heavy metals and organic pollutants can be confirmed and optimized, such complementarity will impact soil/plant interactions, practical remediation approaches, and ultimately, human health assessment.

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