

EFFECT OF DESORPTION-RESISTANCE ON PLANT UPTAKE OF PAH'S FROM SEDIMENTS

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ABSTRACT

Two types of wetland plants; *Salix nigra* and *Scirpus olneyi* were used in laboratory studies to evaluate relationships between sorption, plant uptake, translocation and transpiration of phenanthrene and chlorobenzene. Previous studies have evaluated the plant uptake of non-ionic organics from hydroponic systems; however, little information exists for plant uptake of “aged” desorption-resistant contaminants in sediments. The objective of this study was to determine phenanthrene plant uptake from three different treatments: 1) sediment artificially contaminated, aged and resistant to desorption, 2) chemical in a fully bioavailable sand matrix and 3) sediment freshly contaminated. The laboratory results were compared against those predicted by a mathematical model to predict plant uptake taking into account sorption hysteresis, which has not been considered in all previous plant uptake models. Plant uptake was observed in all three treatments. Despite the lowest uptake observed, the “aged” chemical was bioavailable to plants. Uptake is primarily in the belowground plant portion, and is consistent with a repartitioning from sediment to plant tissue via a simple sorption reaction.

INTRODUCTION

The uptake and transformation of a number of classes of organic compounds by plants has been reported (e.g., Burken & Schnoor 1998). Structure activity relationships developed over the past decade (Trapp, 1995, Burken & Schnoor, 1998) for non-ionic organics suggest that uptake is only effective for compounds with Kow's from 0.5 to approximately 4, below that of many of the more hydrophobic (petroleum-related) organic contaminants such as polycyclic aromatic hydrocarbons (PAHs). These relationships have been developed for plants grown hydroponically without regard for complex sorption-desorption behavior in the rhizosphere. As a result, the relationship between plant uptake and contaminant partitioning in soils and sediment is poorly understood.

Sorption irreversibility or "desorption-resistance" of organic compounds in soils and sediments has been reported (Fu et al., 1994; Kan et al., 1997; Kan et al., 1998; Wei et al., 1999) often in the context of contaminant "aging". These studies suggest that a significant fraction of the contaminant is slowly desorbed from the sediment (i.e., the desorption rate is slower than the adsorption rate). A number of explanations have been published to explain this phenomenon (Kan et al. 1997; Kan et al. 1998; Wei et al. 1999, Weber et al. 1998, Pignatello and Xing, 1996) but no agreement exists on the mechanism at this date. In one explanation, the soil or sediment has a finite sized desorption-resistant compartment that, once full, adsorption and desorption become completely reversible processes (Kan et al., 1994). If contaminant desorption from this resistant fraction is sufficiently slow, it may be possible to leave the residual in place and save on clean-up costs with no risk to the environment (Wei et al., 1999). To date, the bioavailability of contaminants found in this desorption-resistant compartment has not been investigated for plants. Relationships between contaminant aging and plant uptake have implications both for risk assessment, where vegetation is often a component of an exposure pathway and for the phytoremediation, the remediation of contaminants using vegetation.

The objective of this study was to assess the effect of desorption-resistance on plant uptake. Sediment and sand were prepared to maintain different concentrations of phenanthrene in the porewater including an artificially "aged" treatment that contained only the desorption-resistant contaminant. Plant uptake studies were conducted in the greenhouse to test the hypothesis that desorption-resistant phenanthrene, a model PAH, is not bioavailable to vegetation.

MATERIALS AND METHODS

Plants.

The wetland plant species used throughout the experimentation were: a tree, black willow (*Salix nigra*) and a sedge, three-square bulrush (*Scirpus olneyi*). The trees were obtained from cuttings of larger trees, these cuttings were grown hydroponically in a greenhouse and were continuously flooded until roots and leaves were developed. The sedges were obtained from a nursery.

Chemicals; ¹⁴C-labeled and non-labeled.

Radiolabeled chlorobenzene (Sigma Chemical Co. St. Louis, MO., 27 mCi/ mmol) as well as radiolabeled [9,10-¹⁴C] phenanthrene (Sigma Chemical Co. St. Louis, MO., 8.3 μCi/ μmol) were used as tracers. The [¹⁴C] compounds were further diluted with a corresponding non-labeled chemical; Chlorobenzene (Sigma Chemical Co. St. Louis, MO., >99.9%) and Phenanthrene (Sigma Chemical Co. St. Louis, MO., >96% HPLC) in the reactors. [9,10-¹⁴C] phenanthrene (ChemSyn Laboratories, Lenexa, KS., 56.7 μCi/ μmol) was used to prepare the desorption-resistant sediment.

Soil Sources.

Three different soil types were used in this study: a) commercial silica sand (rinsed with de-ionized water, oven-dried and then autoclaved), b) soil indigenous to the superfund site “Petro Processor Inc.” (PPI) and c) Bayou Manchac sediment, collected from Bayou Manchac (Baton Rouge, LA) The soil/sediment were sieved through a 2 mm mesh sieve (No. 10).) and then frozen and thawed twice in a 4°C freezer in order to eliminate the native macro life (worms, snails, etc.). After this preparation, the water content of the sediment was adjusted to desired conditions (20%) for the experiments. One batch of the soil/sediment was contaminated and decontaminated to leave only the desorption-resistant fraction using the isopropanol extraction protocol provided by Liu et al. (2000) for establishing known amounts of organics in the reversible and irreversible compartments. After the sieving process, another batch of the soil/sediment was dried, stored and prior to inoculation it was autoclaved.

Experimental protocol.

Glass plant-uptake reactors based on the working principle of those described previously (Burken & Schnoor 1998) were fabricated for this study. Three different treatments were utilized: a) fully available treatment (FA) where a phenanthrene or chlorobenzene solution was added to a reactor containing the plant and silica sand. b) a desorption-resistant treatment (DR) where sediment was artificially “aged” using the protocol of Liu et al. (2000), and c) a freshly contaminated (FC) treatment where the sediment was contaminated with one of the chemicals just before sealing the reactor. For treatments FA and FC, ¹⁴C-phenanthrene was added with the activity and conditions shown in Table 1. The activities and conditions for chlorobenzene are shown in Table 2. Treatment DR had the amount of contaminated soil shown in Tables 1 and 2 without additional contaminant amendments. Following this, a tree or sedge was placed in the lower portion of the reactor and the amount of sand or soil shown in the respective tables was added. The reactors were assembled, separating the bottom portion of the plant from the top with a sealed Teflon-lined septum carefully sealed with Teflon tape to avoid contaminant migration between the reactor top and bottom. Once the setup was finished, the lower part of the reactor was covered with aluminum foil to discourage algal growth. An air-flow of about 30 ± 5 cc/min was supplied to the top of the reactor to remove any contaminant that may have been transpired by the plant. This air was passed through a Supelco ORBO™ -32 standard charcoal tube and then into 20 mL 1N NaOH solution to trap the CO₂ transpired by the plant. When necessary, ¼ strength modified Hoagland’s solution was added as plant nutrient.

RESULTS AND DISCUSSION

Effect of desorption resistance on plant uptake

The distribution of ^{14}C phenanthrene in belowground and aboveground plant parts by both *Salix* and *Scirpus* is shown in Figure 1. As expected, uptake was greater for the sand treatment (not shown) followed by the freshly contaminated sediment and the desorption-resistant sediment. In each case, total uptake (measured as a percent) was statistically different between the three treatments with sand > freshly contaminated > desorption-resistant (Dunnett's mean test at 5% level of significance).

On a percent uptake basis, plants incubated with "aged" desorption-resistant phenanthrene accessed less than 5% of the contaminant load when compared with ~15% in the freshly contaminated sediment. Results demonstrated that plant uptake of desorption-resistant phenanthrene was measurable and while the bioavailability was significantly lower, plants were able to access this material in sediments. Correlations between water uptake and contaminant uptake were used to estimate the transpiration stream concentration (Figure 2 for phenanthrene and figure 3 for chlorobenzene). There was no statistical difference between estimated transpiration stream concentrations of *Salix* and *Scirpus* for the desorption-resistant treatment. There was also no statistical difference between *Salix* and *Scirpus* in sand and freshly added treatments; however, these two treatments were statistically different from the desorption-resistant treatment. The estimated transpiration stream concentrations were statistically lower for the desorption-resistant treatments (at the 5% level of comparison using Bonferroni's inequality). Decreased transpiration stream concentrations are expected in the desorption-resistant treatments because of the low porewater concentrations that are observed once the sediment is artificially aged.

Measurements of total uptake and the distribution of ^{14}C in the plant indicate that the majority of mass resides in the root zone (both roots and the stem), which is in contact with the sediment or sand. The mechanism of plant uptake is unknown although two possibilities exist: uptake is driven by the movement of porewater containing phenanthrene into the plant (the "transpiration stream") or "uptake" is the result of a simple partitioning process to the roots and stem that occurs in the sediment. Simple models exist to predict uptake by both of these mechanisms. Plant uptake from transpiration can be expressed as:

$$\text{Plant uptake} = TS * TSCF * C * t \quad (1)$$

where: Plant uptake is the mg of phenanthrene present in the plant, TS is the water uptake in L/day, TSCF is a transpiration stream concentration factor (dimensionless) that is the ratio of the concentration of phenanthrene in the transpiration stream to the concentration of phenanthrene in porewater, C is the porewater concentration in mg/L, and t is the time (days) of plant exposure to the contaminant. Plant uptake due to sorption can be determined from a simple linear isotherm.

$$Uptake\ due\ to\ sorption = r_m * K_r * C_w \quad (2)$$

where:

r_m = mass of roots (kg)

K_r = root partition coefficient [(mg/kg)/(mg/L)]

C_w = porewater concentration (mg/L).

By adding these equations we get the predicted plant uptake due to translocation and sorption:

$$Plant\ uptake_{t_1-t_2} = TSCF \cdot Trans_{(t_1-t_2)} \cdot \frac{(C_{t_1} + C_{t_2})}{2} + [r_m \cdot K_r \cdot C_w] \quad (3)$$

The model was calibrated using experimental data. A batch measurement of the root-water partition coefficient, K_r , was conducted for *Salix* and *Scirpus*. The root-water partition coefficient for phenanthrene was 193.1 L/kg for *Salix* roots and 155.3 L/kg for *Scirpus* roots; the chlorobenzene coefficient was 162.0 L/kg for *Salix* and 138.6 L/kg for *Scirpus*. Porewater concentrations for the DR treatments were below detection limits. Therefore, porewater concentrations were estimated using the biphasic isotherm described by Kan et al. (1997) used for the desorption-resistant phase.

Model predictions were made and the relative magnitude of both terms (translocation and sorption) calculated. Translocation was a very minor component and the sorption term dominated for phenanthrene. This is consistent with the small activity of ^{14}C measured in the aboveground biomass. In Figure 4, we can see that equation 3 predicts the total uptake of desorption-resistant phenanthrene ($\log K_{ow} = 4.46$ (Reible 1999)) in both types of wetland plants. For a hydrophobic compound like phenanthrene, the major contribution to the model is by the sorptive portion of the equation. This demonstrates the strong association of these hydrophobic compounds with the root, while the hydrophilic compounds are carried upwards with the water and maybe outside of the plant as shown in figure 5 which tends to over predict the plant concentration for a more hydrophilic compound chlorobenzene ($\log K_{ow} = 2.84$ (Reible 1999))

The study results have implications for the remediation of sediments using vegetation and the fate of contaminants in wetland systems. The effect of sediment: water partitioning on wetland plant uptake of phenanthrene and chlorobenzene has been demonstrated. Lower porewater concentrations resulted in lower uptake of the contaminant. The total uptake of phenanthrene by this wetland vegetation could be best modeled as a partitioning process rather than a process driven by the translocation of porewater through the plant, while the opposite stands for chlorobenzene. Submerged roots and plant stems represent a “clean” organic sorptive phase for the contaminant. Desorption of contaminants from sediments and subsequent sorption on the root tissue is the mechanism observed in these studies. Plant uptake was also observed in the artificially “aged”, desorption-resistant treatment. If this sediment preparation mimics the actual aging process in the environment, these results suggest that contaminants in this

phase have lower bioavailability but it is still measurable. Plant-based remediation of compounds in the desorption-resistant phase will be slower but still possible. Due to the physiological and morphological adaptations of wetland plants, they may be able to take up more hydrophobic contaminants than the terrestrial plants which makes the wetland plants a likely candidate for phytoremediation of oil contaminated soils

TABLE 1. Initial conditions for the Phenanthrene uptake treatments.

Media	DR		FA		FC	
	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>
Plant species						
Sediment or sand dry weight in each reactor	68	68	85	85	100	100
mL of 1ppm phenanthrene solution per reactor	0	0	75	75	50	75
mg of phenanthrene per reactor	0.921	0.921	0.075	0.075	0.05	0.075
μCi of ^{14}C phenanthrene per reactor	0.156	0.156	0.012	0.023	0.209	0.058

TABLE 2. Initial conditions for the chlorobenzene uptake treatments.

Media	DR		FA		FC	
	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>
Plant species						
Sediment or sand dry weight in each reactor	90	90	100	100	75	75
Concentration (ppm) of the solution added	0	0	11.6	10	11	10.1
mL of CB solution per reactor	0	0	100	100	100	100
mg of chlorobenzene per reactor	0.91	0.91	1.16	1.0	1.1	1.01
μCi of ^{14}C chlorobenzene per reactor	0.0177	0.0177	0.0245	0.0177	0.025	0.0176

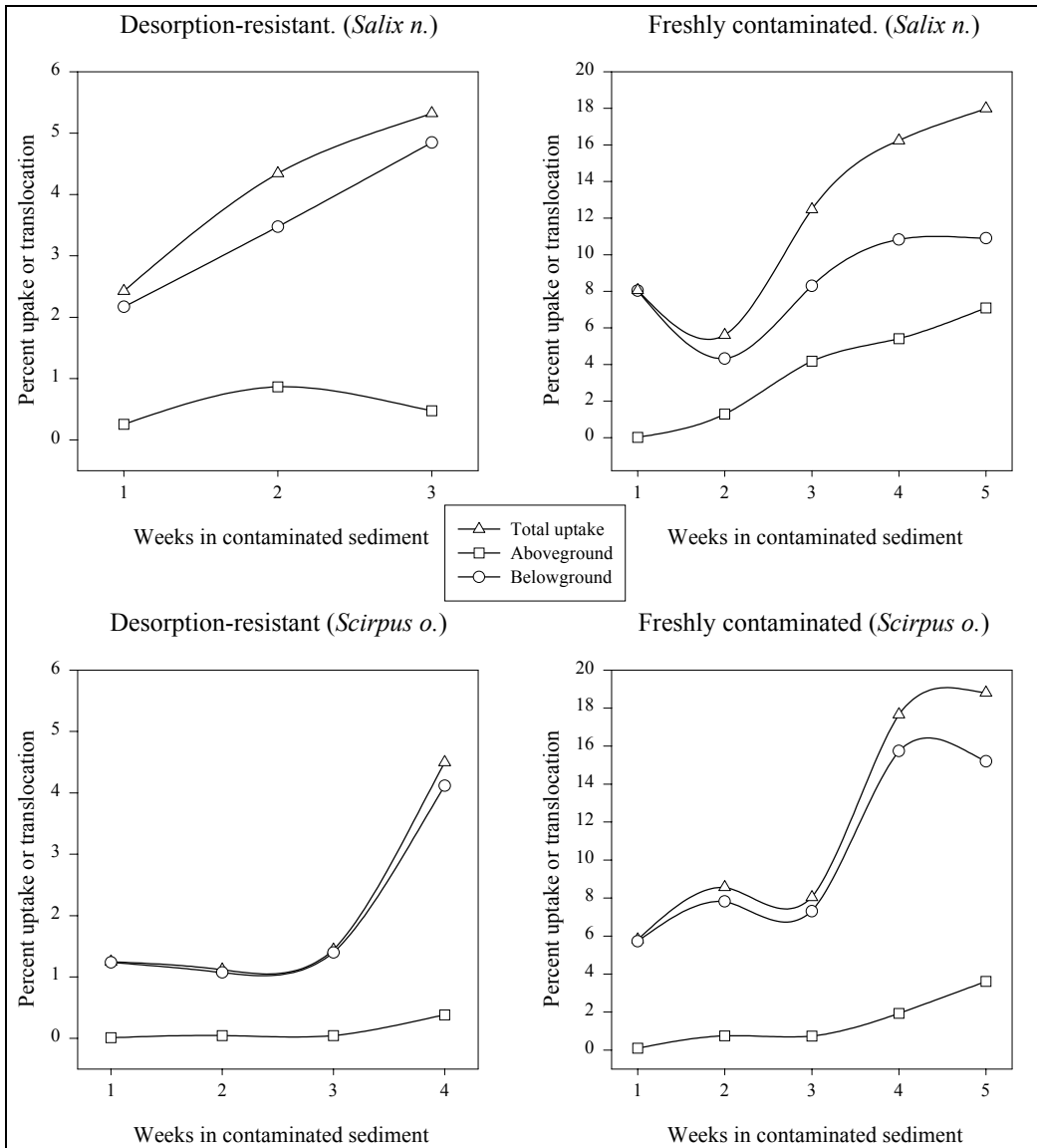


FIGURE 1. Distribution of ^{14}C -phenanthrene in plants (as percent) above and belowground.

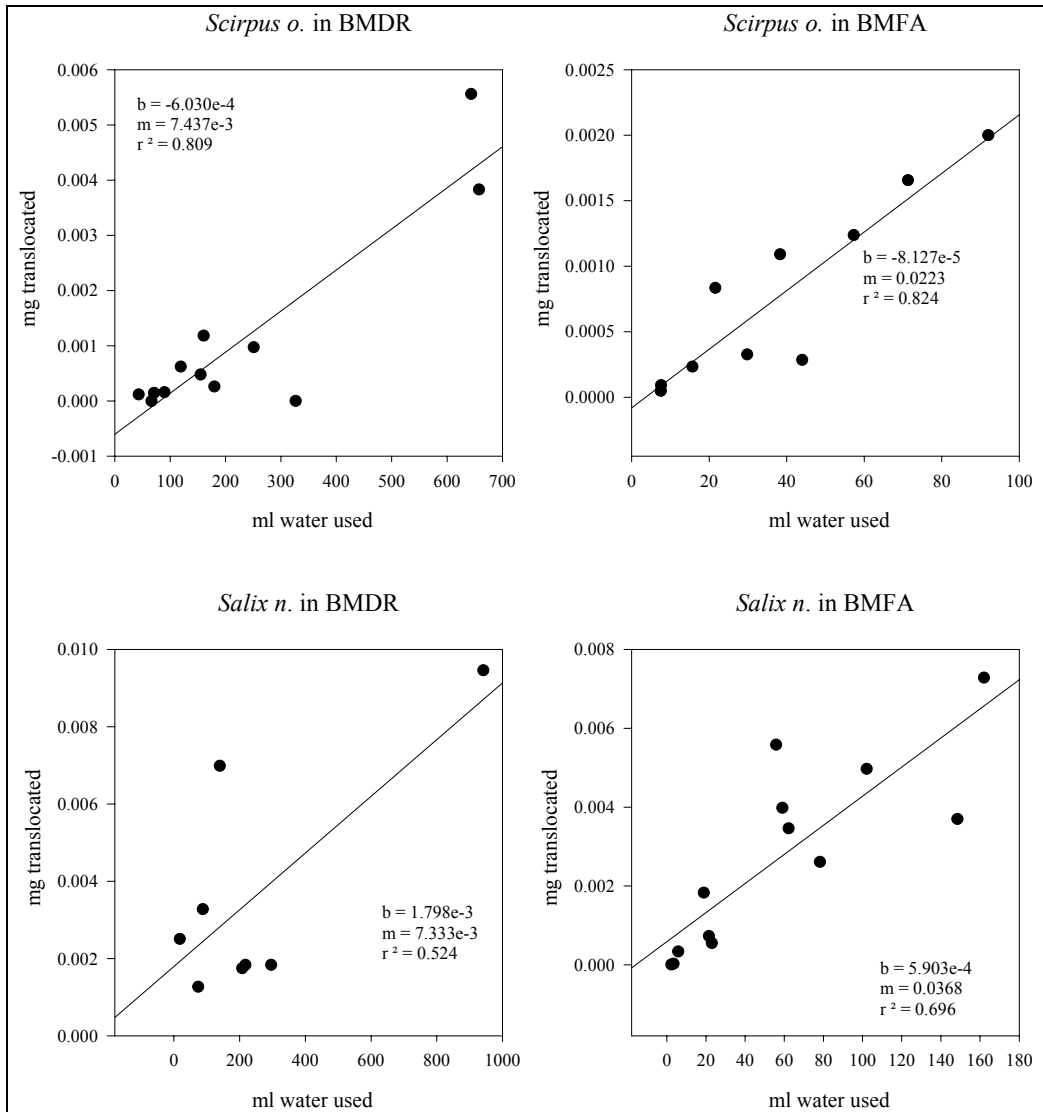


FIGURE 2. Correlation between water uptake and mg ¹⁴C-phenanthrene uptake.

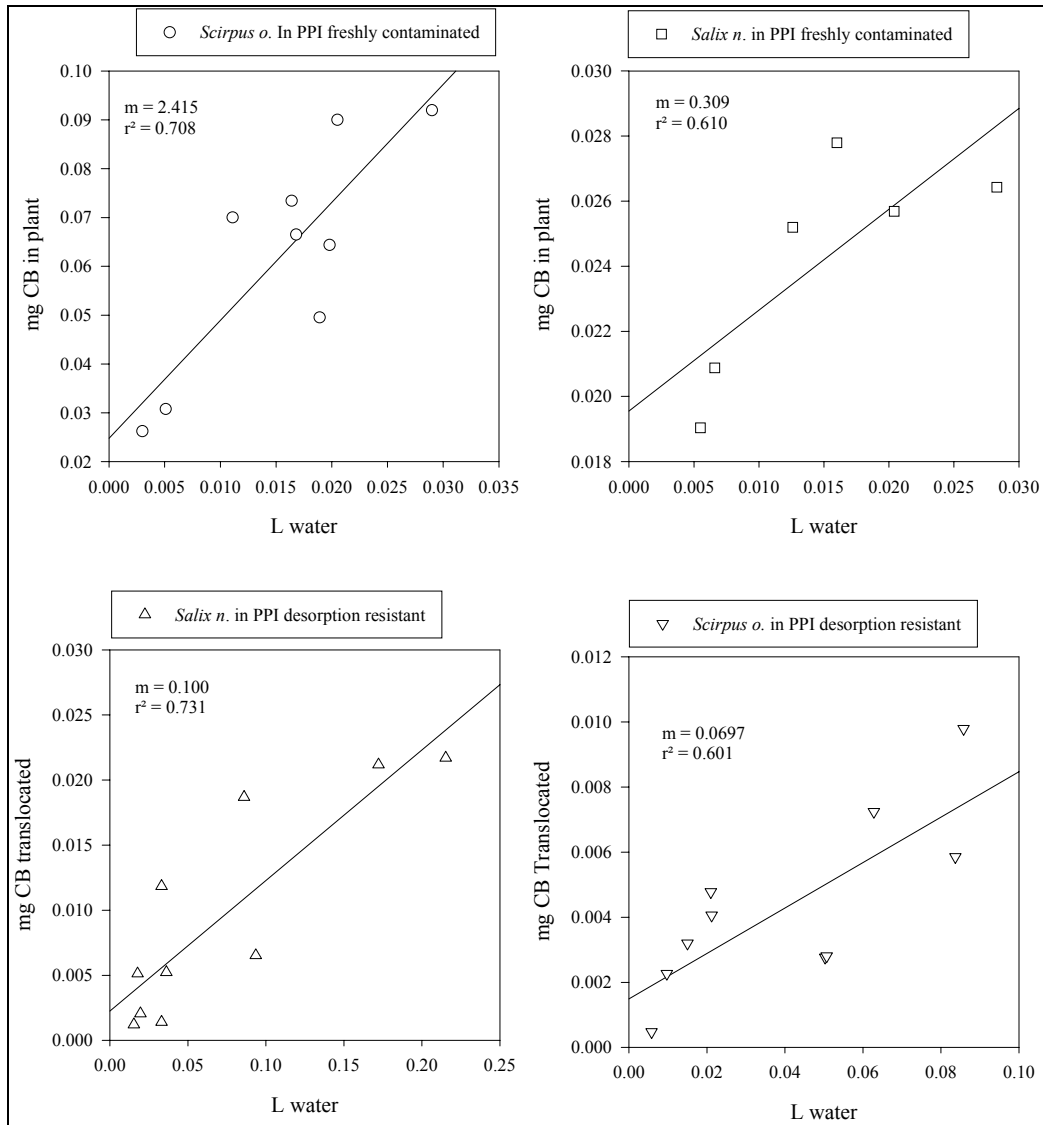


Figure 3. Correlation between water uptake and mg ¹⁴C-chlorobenzene uptake.

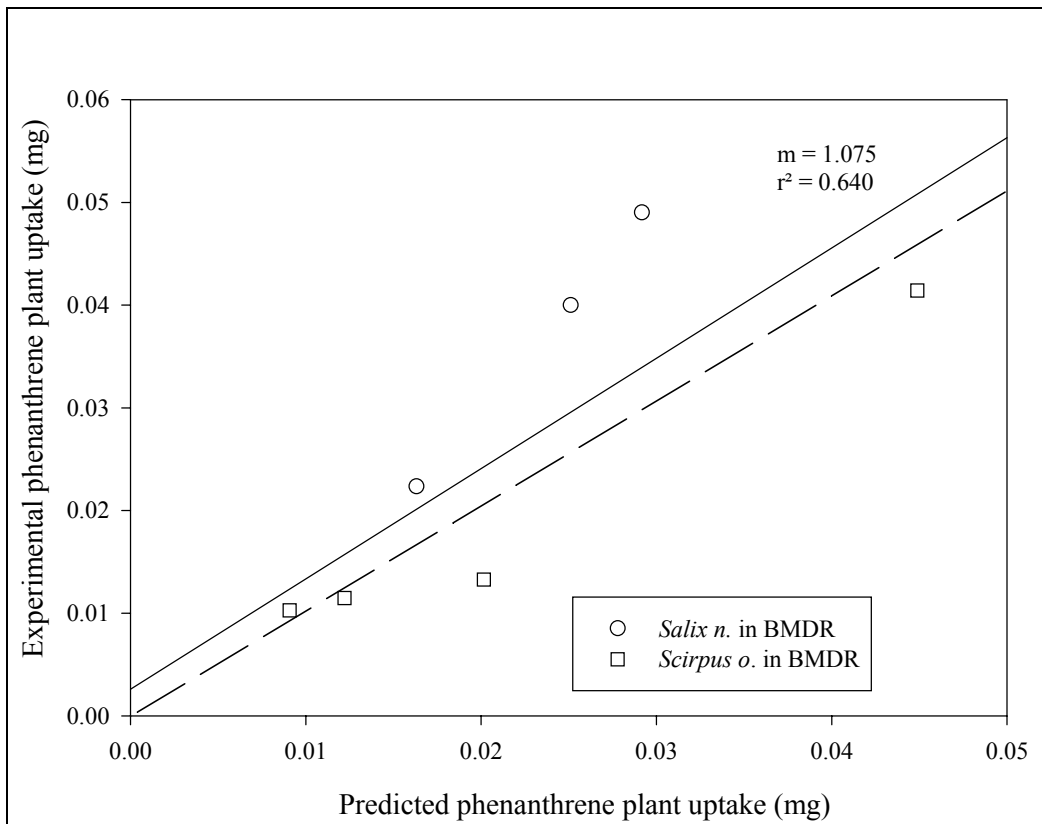


Figure 4. Plot of the predicted phenanthrene plant uptake versus observed experimental plant uptake. The solid line is a regression line for all the data in the figure, while the dashed line has a slope = 1 and represents complete agreement between the model and observations.

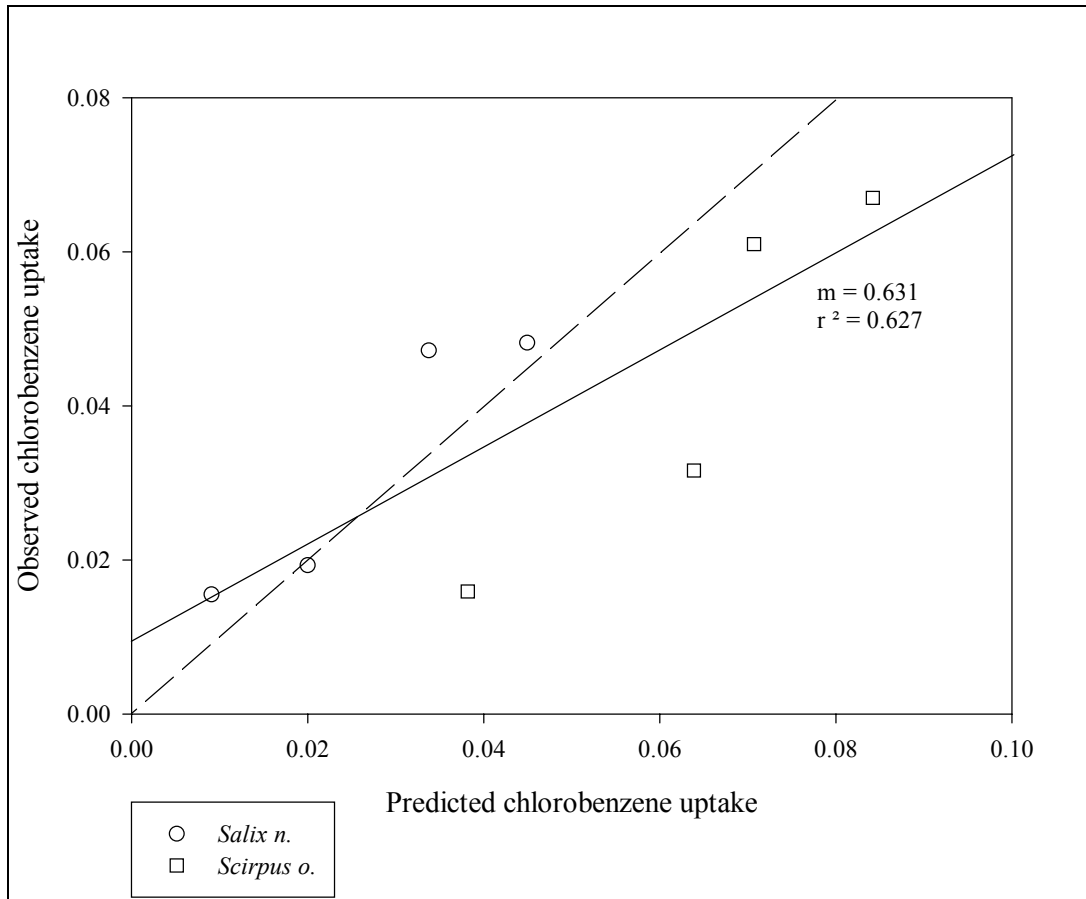


Figure 5. Plot of the predicted chlorobenzene uptake by the whole plant using equation 19. The solid line is a regression line for all the data points, while the dashed one has a slope of 1 and is included for easier comparison

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