

2001

Plant Uptake of Desorption Resistant Organic Chemicals From Sediments.

Cesar Miguel Gomez hermosillo
Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation

Gomez hermosillo, Cesar Miguel, "Plant Uptake of Desorption Resistant Organic Chemicals From Sediments." (2001). *LSU Historical Dissertations and Theses*. 339.
https://digitalcommons.lsu.edu/gradschool_disstheses/339

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]

**PLANT UPTAKE OF DESORPTION
RESISTANT ORGANIC CHEMICALS
FROM SEDIMENTS**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

**The Department of Civil and
Environmental Engineering**

**By
Cesar Gomez
B.S., University of Guadalajara, 1989
M.S., University of Guadalajara, 1993
August 2001**

UMI Number: 3021427

UMI[®]

UMI Microform 3021427

Copyright 2001 by Bell & Howell Information and Learning Company.

All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

Bell & Howell Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

ACKNOWLEDGMENTS

My sincere gratitude to Dr. John H. Pardue for his guidance and support through all these years. I thank Dr. Danny D. Reible for his help and always-optimistic approach toward my research. I also want to thank Drs. David Constant and William Moe for their valuable help, support and advice.

I want to thank my beloved wife Guillermina for being so patient with me and for being a "single mother" through the time I spent attending school. Thanks to my kids Cesar, Karen and Brenda for all the joy they bring to my life.

I also want to thank everyone from Guadalajara, Mexico who in one way or another made possible for me to attend Louisiana State University.

Most important, I thank GOD

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
ABSTRACT.....	x
1. INTRODUCTION.....	1
2. PLANT UPTAKE OF ORGANIC CONTAMINANTS: SEDIMENT- WATER PARTITIONING AND THE TRANSPIRATION STREAM. A LITERATURE REVIEW.....	7
2.1 Introduction.....	7
2.2 Theory of Water and Material Uptake by Plants.....	7
2.3 Sediment-water Partitioning.....	15
2.4 Phytoremediation.....	20
2.5 Plant Uptake Modeling.....	25
2.6 Conclusions.....	31
3. EFFECT OF DESORPTION-RESISTANCE ON PLANT UPTAKE OF PHENANTHRENE FROM SEDIMENT.....	33
3.1 Introduction.....	33
3.2 Materials and Methods.....	34
3.3 Results and Discussion.....	40
3.4 Conclusions and Implications.....	50
4. EFFECT OF DESORPTION-RESISTANCE ON WETLAND PLANT UPTAKE OF CHLOROBENZENE AT A LOUISIANA SUPERFUND SITE.....	55
4.1 Introduction.....	55
4.2 Materials and Methods.....	56
4.3 Results and Discussion.....	62
4.4 Conclusions.....	76
5. DEVELOPMENT OF A MATHEMATICAL MODEL RELATING DESORPTION RESISTANCE TO PLANT UPTAKE.....	79
5.1 Introduction.....	79
5.2. Model Development.....	86
5.3. Results and Discussion.....	92
5.4 Conclusions.....	94
6. CONCLUSIONS.....	96

REFERENCES.....	100
APPENDIX; EXPERIMENTAL REACTORS.....	109
VITA.....	116

LIST OF TABLES

Table	Page
2.1 Adaptations presented by hydrophytes to compensate the oxygen deficiency in the root system due to continuous flooding, adapted from (Mitsch & Gosselink 2000).....	14
3.1 Summary of the initial conditions for each experiment.....	37
3.2 Mass balances (^{14}C) for all the plants and soils in the experimentation. BM_F (Bayou Manchac freshly added), BM_irr (Bayou Manchac desorption resistant).....	45
4.1 Summary of the initial conditions for each experiment.....	60
4.2 Percent CB recovery for all experiments.....	66

LIST OF FIGURES

Figure	Page
2.1 Diagram of root hairs (one-celled extensions of epidermal cells) in soil. Root hairs are used by plant to improve the contact between root and soil, they also help prevent the formation of air filled cavities while water is being removed from the soil by the plant. In this longitudinal section view of root hairs we can also see: (p) plasma tube, cell sap volume or vacuole (v); soil particles (s); hydration water (w_1); capillary water (w_2) and, (l) represents air spaces. From (Mohr & Schopfer 1995).....	8
2.2 Schematic section of a plant showing the xylem and the phloem, usually, the transpiration stream flows upward through the xylem and the assimilation stream flows downwards through the phloem, from (Mohr & Schopfer 1995).....	9
2.3 Longitudinal section of a root showing some of the major parts, modified from (Mohr & Schopfer 1995).....	10
2.4 Diagrams showing three developmental stages of an endodermal root cell. (a) The endodermal cell is characterized by the presence of a casparian strip in its anticlinal walls. (b) Later, a suberin lamella covers all wall surfaces. (c) Finally, the suberin is covered by a thick cellulose layer. Modified from (Raven et al. 1992).....	12
2.5 Three possible pathways for the movement of water and its components from the outside of the roots into the tracheary elements (water conducting elements) of the roots. (a) apoplastic, (b) symplastic and (c) transcellular. Modified from (Raven et al. 1992).....	13
2.6 Atrazine degradation mechanism by Poplar trees as proposed by (Burken & Schnoor 1997). DEA, deethylatrazine; HA, hydroxyatrazine; DIA, deisopropylatrazine; DEHA, deethylhydroxyatrazine; DDA, didealkylatedatrazine; HDAP, hydroxylated dealkylated products.....	23

3.1	Block diagram of the artificial aging process used to leave only the desorption-resistant fraction of contaminant in the sediment.....	38
3.2	Comparison between total phenanthrene uptake and translocation by <i>Scirpus O.</i> from the three different treatments applied.....	41
3.3	Comparison between total phenanthrene uptake and translocation by <i>Salix</i> from the three different treatments applied.....	42
3.4	Correlation between water uptake and phenanthrene translocated above ground.....	46
3.5	Mass balance for phenanthrene uptake, translocation and mineralization by <i>Salix n.</i> in the sand treatment.....	47
3.6	Biodegradation in the rhizosphere in two different soils.....	48
3.7	Phenanthrene sorption into live roots of the two plant species.	51
3.8	Predicted phenanthrene uptake by the translocation model.....	52
3.9	Predicted phenanthrene uptake by the sorption model.....	53
4.1	Block diagram of the desorption process used to leave only the desorption-resistant fraction of contaminant in the sediment.....	61
4.2	Total chlorobenzene uptake (as %) by both plant species in the three different soils.....	63
4.3	Comparison between total chlorobenzene uptake and its translocation above ground by <i>Scirpus o.</i> in three different contaminated soils	64
4.4	Comparison between total chlorobenzene uptake and its translocation above ground by <i>Salix n.</i> in three differently contaminated soils.....	65

4.5	Graphic representation of the concentration in the transpiration stream. The line slope is considered to be the chlorobenzene concentration in the transpiration stream (mg/L).....	68
4.6	Comparison between ^{14}C detected as VOC (from the ORBO trap) and translocated aboveground for Scirpus in PPI freshly contaminated treatment.....	69
4.7	Mineralized $^{14}\text{CO}_2$ trapped during chlorobenzene experiments.....	70
4.8	Partition of chlorobenzene between plant roots and water.....	73
4.9	Predicted chlorobenzene uptake by the translocation model...	74
4.10	Predicted chlorobenzene uptake by the sorption model.....	75
4.11	Changes in the TSCF calculated from the equations proposed by (Briggs et al. 1982) and by (Burken & Schnoor 1998).....	78
5.1	Plot of the predicted phenanthrene plant uptake using equation 17. 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.....	93
5.2	Plot of the predicted chlorobenzene uptake by the whole plant using equation 17. 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.....	94
A1	Top part of the closed reactors used for the plant uptake studies.....	110
A2	Bottom (or lower) part of the glass reactors used in the plant uptake experiment. During the experimentation, both parts keep separated from each other by a teflon lined septa in the cap of the bottom part.....	111

A3	Modified Erlenmeyer flask used to determine the capability of the rhizosphere to biodegrade the chemicals. In this picture we can see plant roots (the stem was cut out before the picture), contaminated liquid, and silica sand.....	112
A4	Modified Erlenmeyer flask used for the biodegradation studies, the reservoir where the NaOH is placed can be seen in the middle of the flask.....	113
A5	Setup used to test contaminant sorption to plant roots.....	114
A6	Setup to test sorption of chemicals into roots.....	115

ABSTRACT

Two types of wetland plants, a woody species, black willow (*Salix nigra*), and a non-woody, the macrophyte three-square bulrush (*Scirpus olneyi*), were used in laboratory studies to evaluate relationships between sorption, plant uptake, translocation and transpiration of phenanthrene, a model polycyclic aromatic hydrocarbon and chlorobenzene, a model chlorinated benzene from the reversible and desorption-resistant compartment of a sediment for Phenanthrene (PHEN) and a wetland soil for chlorobenzene (CB). The wetland soil is from The Petro Processors Inc. site (PPI), a 77-acre CERCLA facility located about 10 miles north of Baton Rouge, Louisiana.

Other 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. Structure activity relationships for non-ionic organics suggest that plant uptake is only effective for compounds with log K_{ow} 's from 0.5 to approximately 4, below the log K_{ow} of 4.4 reported for PHEN. The objective of the study was to determine the potential for plant uptake of PHEN and CB. Three treatments were utilized for studies: 1) sediment with PHEN and CB aged and resistant to desorption, 2) PHEN and CB in a sand-water matrix, presumed to be fully bioavailable and 3) sediment with freshly contaminated PHEN and CB. Wetland plants were exposed to these treatments using ^{14}C -labeled chemicals as tracers. The ^{14}C -chemical in the plant was converted to $^{14}\text{CO}_2$ using a biological oxidizer and the radioactivity was determined with scintillation counting. The

laboratory results were compared against those produced by a mathematical model to predict plant uptake taking into account sorption hysteresis which has not been considered in all previous plant uptake models.

Uptake is primarily in the root and stem tissue in the sediment, and is consistent with a repartitioning from sediment to plant tissue via a simple sorption reaction. Clean, fresh wetland plant tissue represents an effective sorption phase. Results were confirmed by measuring root-water partition coefficients and computing the potential uptake based on simple partitioning.

1. INTRODUCTION

U.S. coastal waters contain large volumes of contaminated sediments with potential hazards to public health and the environment (National Research Council [NRC] 1997). Sediments are loose particles of sand, clay, silt and other substances created by various erosional processes and delivered to stream channels. These particles come from eroding soil and from decomposing plants and animals which settle at the bottom of a water body (U.S.E.P.A. 1999). Sediments can be carried long distances by wind water and ice. Sediments can also be resuspended by storms or boat propellers. As consequence of resuspension of the sediments, all of the living organisms in the water, and not just the bottom-dwelling organisms will be directly exposed to the contaminants present in the sediments (U.S.E.P.A. 1999).

As a result of urbanization and industrialization, sediments have been contaminated with a variety of substances. The contaminants found in sediments can be categorized as toxic when they adversely affect the living organisms either by direct or indirect contact with the contaminated waters (National Research Council [NRC] 1997). Toxic contaminants can be classified as inorganic (e.g., heavy metals, radionuclides, nitrogen or phosphorus.) or organic (e.g., pesticides, polycyclic aromatic hydrocarbons {PAHs}, organochlorides.).

Two important classes of organic contaminants are PAHs and chlorobenzenes. PAHs are universal environmental contaminants and are largely derived from petroleum products (Steudle & Paterson 1998). The following major routes of entry into the aquatic environment have been proposed by (Steudle &

Paterson 1998) for bi- and tricyclic PAHs; spillage and seepage of fossil fuels, and for high molecular weight PAHs; discharge of domestic and industrial wastes, fallout, and land runoff. Whether the PAHs are in air or water, they are, in general, quickly adsorbed onto particulate matter. Eventually, these contaminants tend to enter the sediments of water bodies [(Steudle & Paterson 1998), (Sims & Overcash 1983),(Takada et al. 1990)]. Similarly, the widely used chlorinated solvents such as chlorinated benzenes are ubiquitous sediment contaminants. Chlorobenzenes can be detected in all media and are highly persistent in aerobic and anaerobic environments (Lorenz 1998). Extensive soil and groundwater contamination has been caused by the improper handling and storage of these chlorinated benzenes (Becvar et al. 1998).

Traditional ex-situ methods used to remediate contaminated sediments include dig and haul, dredging, and incineration. These techniques are expensive due to the large amounts of sediments that require treatment and environmentally disruptive because the surrounding habitat is usually destroyed. This case is most commonly observed in sensitive wetland areas. Phytoremediation, the use of vegetation to treat contaminants, may provide an *in situ*, cost-effective, alternative for the clean-up of large volumes of contaminated sediments.

Phytoremediation is the “use of plants (trees, grasses and aquatic plants) and their associated rhizospheric microorganisms to remove, degrade or accumulate environmental contaminants found in soils, sludges, sediments and waters” (Cunningham et al. 1995). Within the past decade, studies have demonstrated that vegetation can play an active role in remediating contaminated

soils (Cunningham et al. 1995; Burken & Schnoor 1996; Chappell 1997; Chang & Corapcioglu 1998; Doucete et al. 1998; Gordon et al. 1998), and that the rhizosphere was special due to its capability to provide an ideal environment for microorganisms that biotransform organic compounds (Nair et al. 1993; Anderson et al. 1994; Ferro et al. 1994; Anderson et al. 1995; Reilley et al. 1996; de Souza et al. 1999). Over the past decade, phytoremediation has undergone evolution from an interesting concept into a field-scale remediation technology (Burken & Schnoor 1998). This technology can be used to remediate contaminants such as organics, inorganics, metals and radionuclides (Glass 1999)

Phytoremediation is a broad term used for the following mechanisms (or combinations of mechanisms) that plants can use to clean-up soils, sediments or waters: a) *rhizospheric biodegradation*; where organic contaminants present in the sediment are biodegraded by the microorganisms found near the plant roots, b) *phytoextraction and phytodegradation* where organic contaminants are taken up into the plant via the transpiration stream and subsequently degraded by plant enzymes; c) *phytoaccumulation* that involves the uptake and translocation of heavy metals via the transpiration stream to the aboveground part of the plant d) *phytostabilization* where vegetative cover over the contaminated sediment serves to immobilize the contaminants through adsorption, absorption and accumulation by roots and physical stabilization of the sediment and e) *rhizofiltration*, an ex situ application where plant roots are used to sorb and concentrate contaminants from surface water

The fate of contaminants in systems including sediment (or soil) and water depends on the partition properties of the chemical in question with both mineral and organic portions of the sediment, as well as with the organic matter present in the water column. Sorption of contaminants onto these particles, affects the availability. The sorption mechanisms governing the partitioning between the organic pollutants of interest and the sediments, depend on chemical and physical properties of the sediment and the chemical (Karickhoff 1980). Sorption irreversibility or hysteresis of organic compounds from sediments has been proposed [(Goring & Hamaker 1972), (Karickhoff 1980), (Di Toro & Horzempa 1982), (Pignatello 1989), (Fu et al. 1994), (Kan et al. 1994), (Kan et al. 1997)]. They suggest that a significant fraction of the contaminant is slowly desorbed from the sediment (i.e., desorption rate is slower than the adsorption rate). The soil's irreversible compartment has a finite capacity and once it is full, adsorption and desorption become completely reversible processes (Kan et al. 1994). If contaminant desorption from this resistant fraction is completely irreversible, or even sufficiently slow, it may be possible to leave the residual in place and save on clean-up costs with no risk to the stakeholders (Wei et al. 1999).

Although there is still controversy over the mechanism responsible for this desorption-resistant fraction, the bioavailability of organic contaminants found in the desorption resistant (or "irreversible") compartment of sediments has not been investigated to date for plants.

The bioavailability of organic contaminants is very important for remediation of waste sites. The Petro Processors Inc. site (PPI) is a 77-acre

CERCLA facility comprised of two former petrochemical disposal areas situated about 1.5 miles apart. The disposal of organic waste dates back to 1969 at these locations. The sites' principal contaminants are "hex" wastes (hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD)), chlorinated solvents, polycyclic aromatic hydrocarbons (PAH's) and oils. Of recent interest is the remediation of the Devil's Swamp portion of the site, a bottomland hardwood wetland that was impacted by an historical spill (*ca.* 1970) of free-phase waste material containing HCB, HCBD and a variety of other chlorinated and petroleum hydrocarbons. Since this portion of the site is heavily vegetated, wetland plants may play a significant role in the natural attenuation of contaminants at this portion of the site.

Based on this introduction, the studies proposed here have the following objectives:

1. To determine the influence that desorption resistance has on organic chemicals in their availability to wetland plants.
2. Identify the mechanisms by which wetland plants take up organics, and compare whether these are the same as the proposed for terrestrial plants commonly used in phytoremediation projects and investigations
3. To determine the ability of vegetation to uptake phenanthrene, a model PAH compound with an octanol-water partitioning coefficient ($\log K_{ow} = 4.46$) that lies outside the limits proposed by (Briggs et al. 1982) and almost at the end limit of the values proposed by (Burken & Schnoor 1998) for plant uptake.

4. Apply the experimental results to the available mathematical models and if the current models do not explain the plant uptake, propose a new mathematical model that would represent the uptake of organics from desorption resistant soils by wetland plants.
5. Estimate the benefits of wetland plants on the clean-up processes of a Superfund site, specifically the PPI site.

Experiments were conducted to determine the ability of two classes of wetland plants, a tree species; Black willow (*Salix nigra*) and a sedge; Three-cornered grass (*Scirpus olneyi*) to uptake phenanthrene, a model polycyclic aromatic hydrocarbon and chlorobenzene, a model chlorinated benzene from the reversible and desorption-resistant compartment of a sediment are reported here. Also, a mathematical model has been proposed for uptake and subsequent translocation of chemicals from the reversible and irreversible soil compartments, this model can help on quantifying the role vegetation plays on the clean-up process at PPI and other contaminated sites.

The dissertation is organized as follows: a literature review of processes affecting plant uptake is presented as Chapter 2. The effect of desorption-resistance on wetland plant uptake of phenanthrene is presented as Chapter 3. The uptake of chlorobenzene at the PPI site is described in Chapter 4. A mathematical model relating plant uptake of desorption-resistant compounds is presented as Chapter 5. Finally, some conclusions are presented as Chapter 6.

2. PLANT UPTAKE OF ORGANIC CONTAMINANTS: SEDIMENT-WATER PARTITIONING AND THE TRANSPIRATION STREAM. A LITERATURE REVIEW

2.1 Introduction

The mechanisms responsible for water uptake by plants and the limitations for organic compounds to move into the plant vascular system are reviewed. The relationship between sediment contamination, contaminant aging and bioavailability of the contaminants sequestered by the sediment is also discussed. Establishing a relationship between plant uptake and the partitioning of compounds found in sediment is important when trying to implement phytoremediation as a remediation process. The focus of the review is to summarize what is known about uptake of compounds in vegetated systems and the relationship between partitioning and uptake.

2.2 Theory of Water and Material Uptake by Plants

Water evaporation (transpiration) from the surface of plant cells exposed to the air is a continuous process. Plant roots have to absorb water from the soil to make up this "transpirational" loss. Therefore, we can consider a continuous water flow from the soil to the atmosphere, the so-called "transpiration stream".

The root system of higher plants has two primary functions, to take up the water and mineral nutrients needed for growth and survival and for anchorage (Fitter 1996). The vast majority of the water that a plant takes from the soil, enters via direct absorption into the epidermis of younger roots. The root hairs (Figure 2.1) provide most of the area needed for this absorption (Raven et al. 1992).

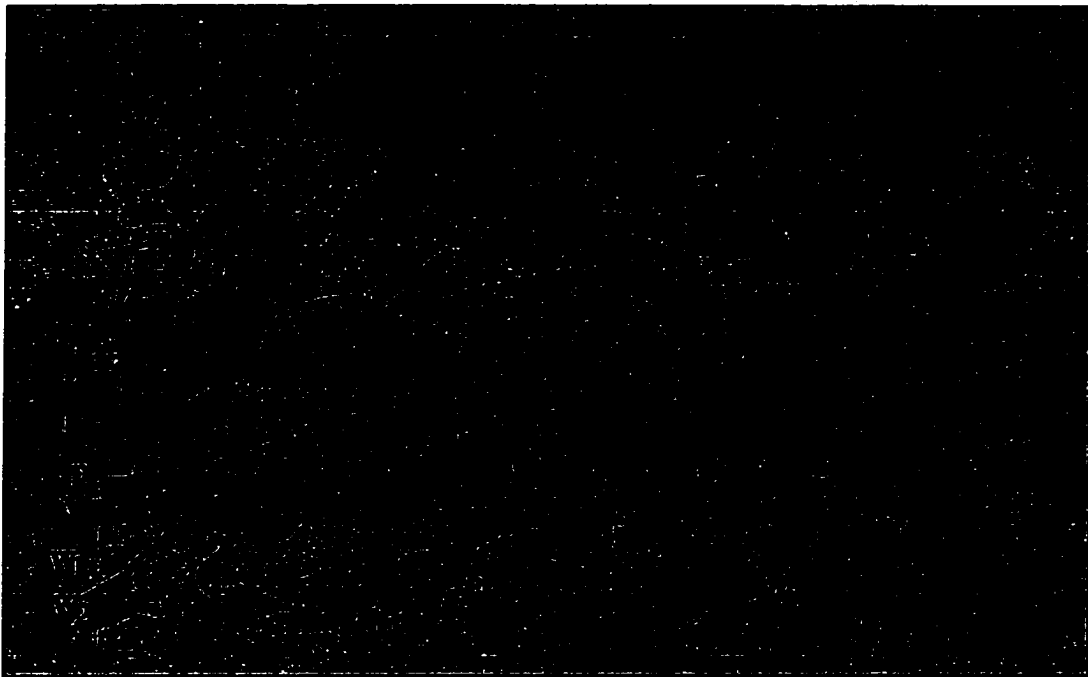


Figure 2.1. Diagram of root hairs (one-celled extensions of epidermal cells) in soil. Root hairs are used by plant to improve the contact between root and soil, they also help prevent the formation of air filled cavities while water is being removed from the soil by the plant. In this longitudinal section view of root hairs we can also see: (p) plasma tube, cell sap volume or vacuole (v); soil particles (s); hydration water (w_1); capillary water (w_2) and, (l) represents air spaces. From (Mohr & Schopfer 1995).

In general, we can say that from the root hairs, the water, and chemicals solubilized in it, move through the cortex (Figure 2.2) through the endodermis (the innermost layer of cortical cells) and finally into the vascular cylinder.

Since water evaporation occurs mainly in the leaves due to their large surface area and the presence of stomates, the transpiration stream flux has to be upwards. Photosynthesis occurs also mainly in the leaves and the organic molecules produced by photosynthesis are needed by every part of the plant including roots. This is provided by another stream moving upwards and downwards, the “assimilation” stream. The transpiration stream uses the xylem for transport, while

the assimilation stream uses the phloem (Figure 2.3). Using the proper terminology for these tissues, the transpiration stream is in the apoplast while the assimilation stream is in the symplast (Mohr & Schopfer 1995).

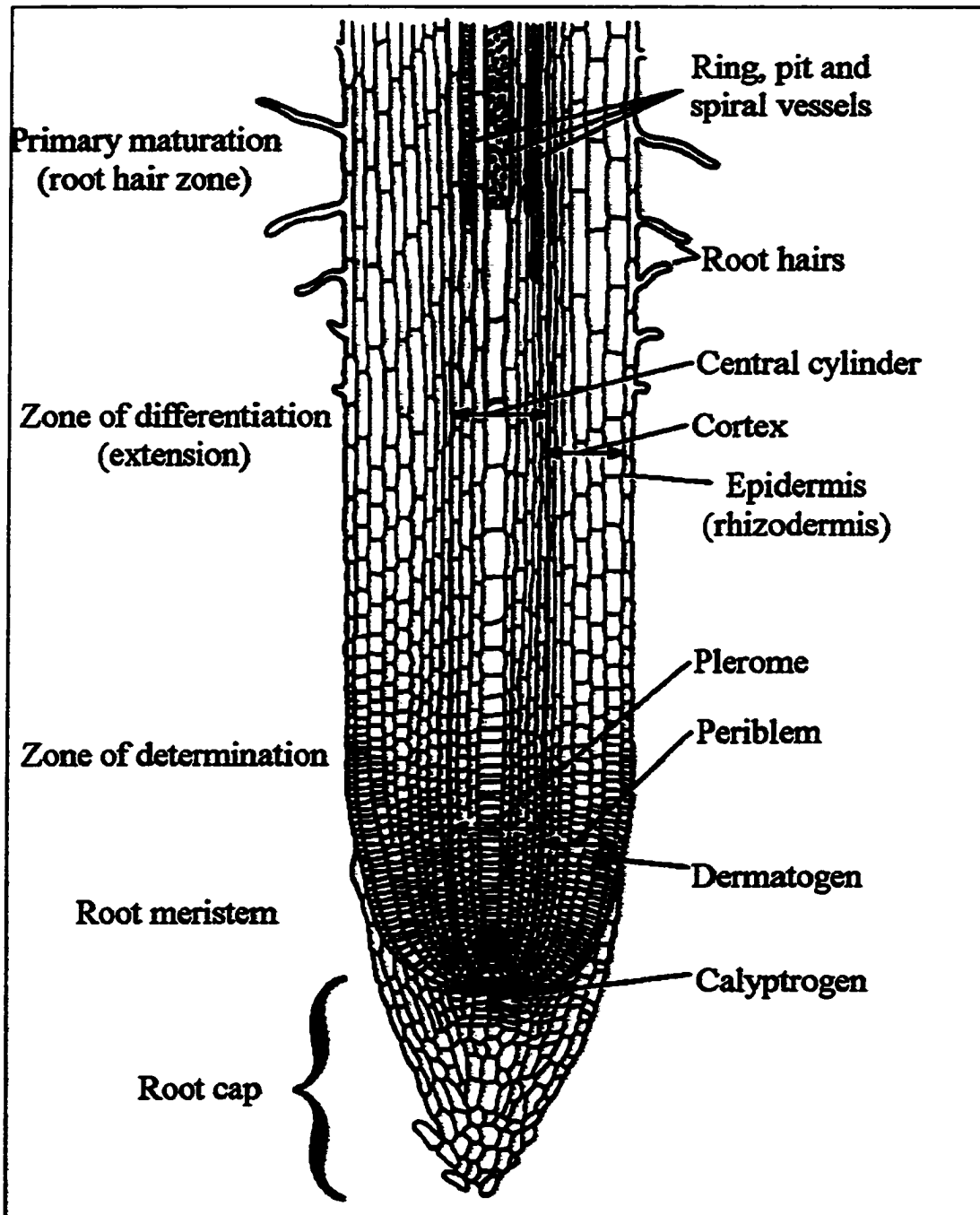


Figure 2.2. Longitudinal section of a root showing some of the major parts, modified from (Mohr & Schopfer 1995).

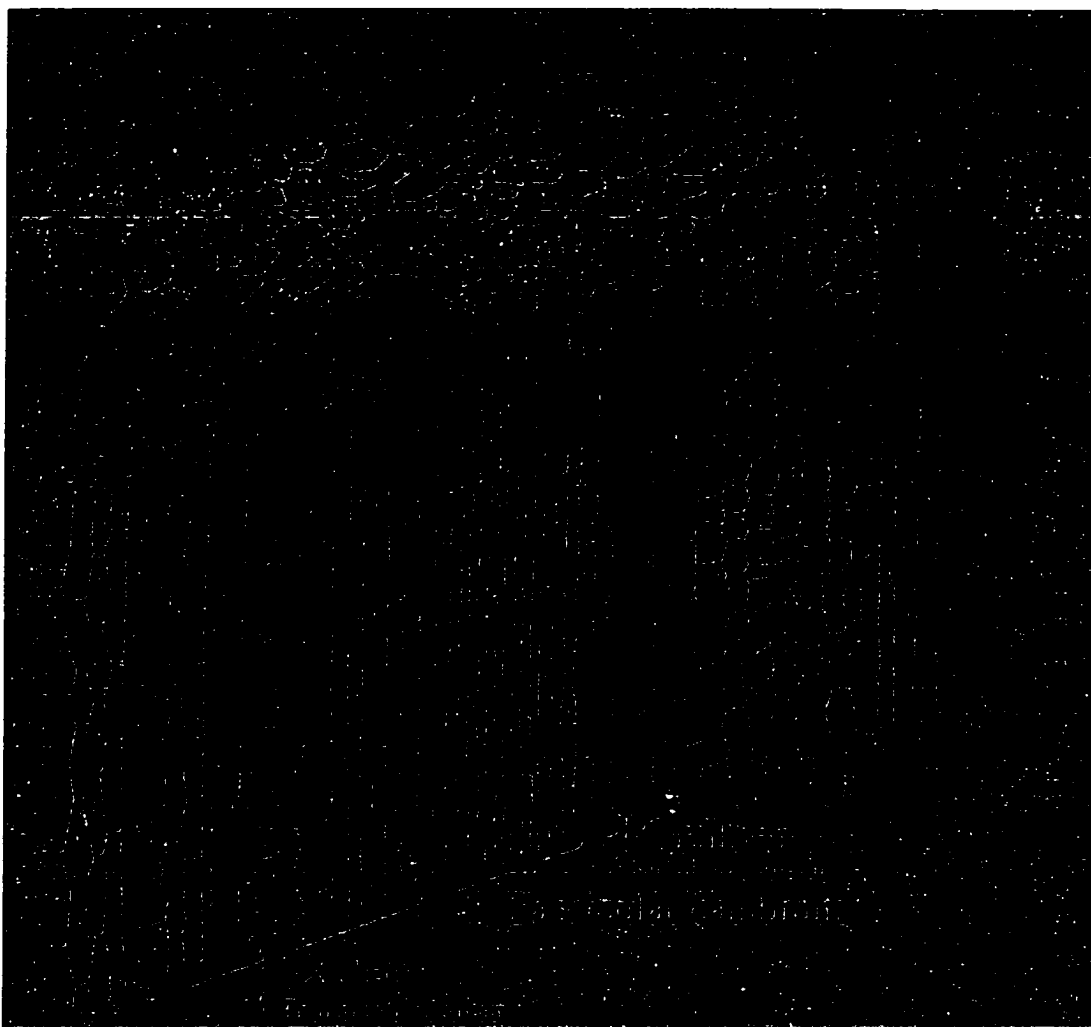


Figure 2.3. Schematic section of a plant showing the xylem and the phloem, usually, the transpiration stream flows upward through the xylem and the assimilation stream flows down via the phloem, from (Mohr & Schopfer 1995).

Water and solutes move freely from soil solution to the interior of roots in the capillary spaces between these cells. This free movement is stopped at the endodermis by a bandlike layer that is impregnated by a fatty substance called suberin (a complex mixture of hydrophobic long-chain fatty acids and alcohols). This layer of waxy material is called the casparian strip, which is only a portion of the primary wall layer around the anticlinal walls (the walls perpendicular to the surface of the root) of these cells, (Raven et al. 1992) (Figure 2.4). The

hydrophobic, space-filling nature of the casparian band along with its attachment to the plasma membrane, greatly reduces the possibility that ions or small hydrophilic molecules can pass between the cortex and stele without first passing through the endodermal protoplast. (Hopkins 1995). Here the only way for the compounds to pass through the endodermis is to enter the symplast (making use of some carrier or channel). This may occur either in the outer tangential wall of the endodermal cell itself or through any of the epidermal or cortical cells. (Hopkins 1995).

There is uniform agreement in the literature that there are at least two major pathways for the transport of a molecule from the root periphery to the xylem vessels: (a) apoplastic, e.g., via the cell wall space and transported across cell membranes only twice at the endodermis region to get past the casparian strip barrier and (b) symplastic where transport occurs across cell membranes and tonoplast membranes (a membrane binding the vacuole, also called vacuolar membrane) many times (Figure 2.5) (Mohr & Schopfer 1995, Hopkins 1995, Trapp & McFarlane 1995).

It is important to note that many authors like (Raven et al. 1992, Weatherley 1982) among others consider a vacuolar or extracellular pathway as a third option. These authors also note that this movement can only constitute a small fraction of the total flow. Even other authors like (Oertli 1996) consider up to six different water/nutrients pathways.

The apoplastic pathway is favored by less lipophilic compounds, whereas the symplastic pathway is favored by more lipophilic compounds. The frequency of membrane crossing depends on the affinity of the compound towards the membrane

which, in turn, is dictated by its log K_{ow} value (Trapp & McFarlane 1995). The only root volume that can be entered without crossing a membrane is referred to as the “apparent free space”. This “apparent free space” stops at the endodermis where the Casparian strip is developed (Hopkins 1995).

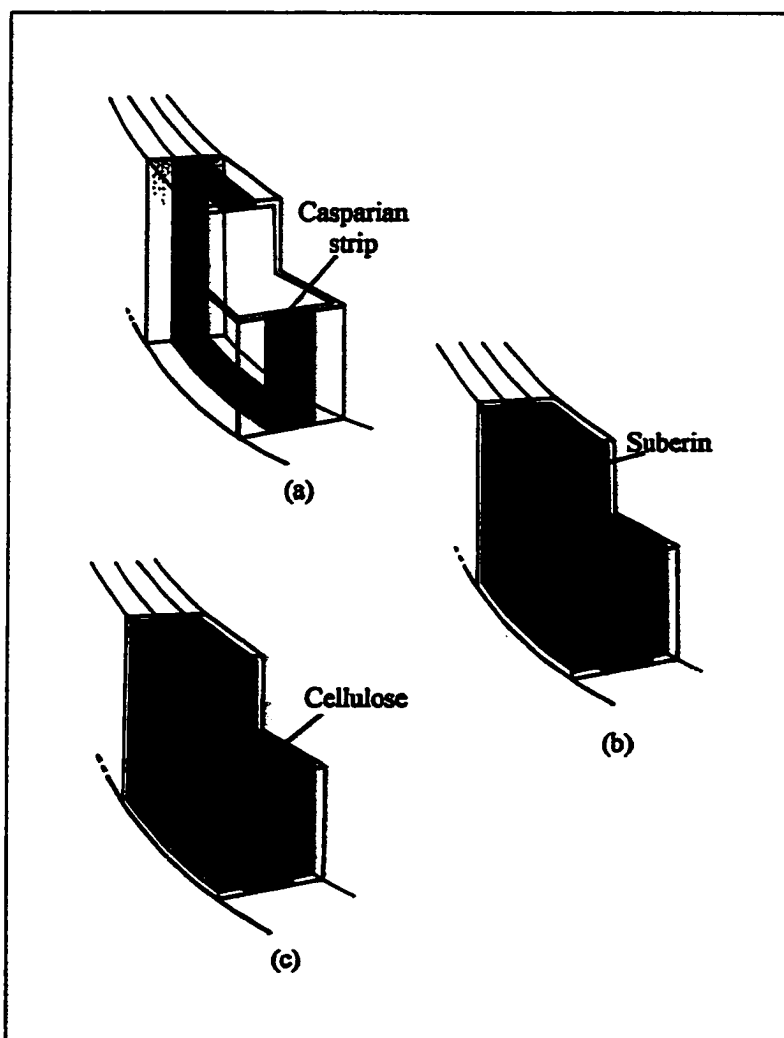


Figure 2.4. Diagrams showing three developmental stages of an endodermal root cell. (a) The endodermal cell is characterized by the presence of a casparian strip in its anticlinal walls. (b) Later, a suberin lamella covers all wall surfaces. (c) Finally, the suberin is covered by a thick cellulose layer. Modified from (Raven et al. 1992)

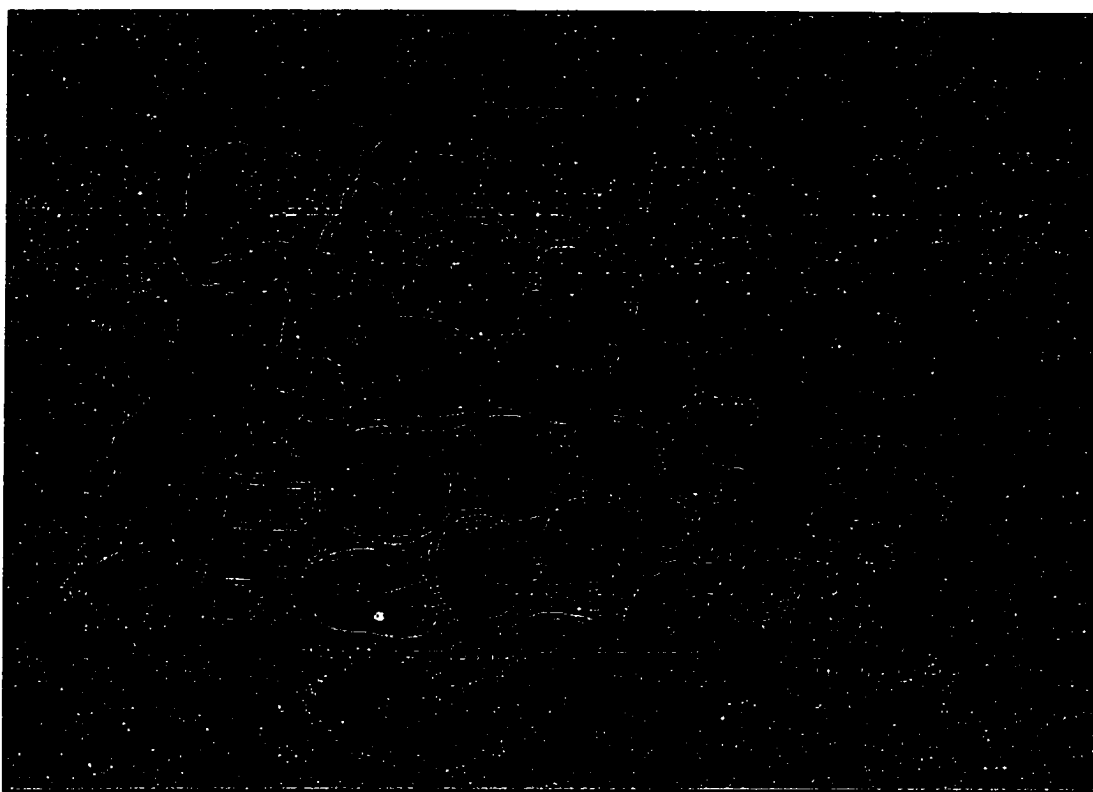


Figure 2.5. Three possible pathways for the movement of water and its components from the outside of the roots into the tracheary elements (water conducting elements) of the roots. (a) apoplastic, (b) symplastic and (c) transcellular or vacuolar. Modified from (Raven et al. 1992)

Compounds with low $\log K_{ow}$ values may pass from the root periphery to the xylem predominantly through the apoplastic pathway with little retention by root tissue, thus reaching a steady state very quickly. Compounds with higher lipophilicity would tend to take the more lipophilic symplastic pathway, and be partitioned into root tissues along the whole pathway. (Hsu et al. 1990). In a work presented by Shone (Shone et al. 1974), the compounds taken up by the plants were characterized as lipophilic and lipophobic, and they concluded that the lipophilic compounds are able to penetrate the cortical cells of the root and could reach the

shoots more easily than the lipophobic compounds which may be confined to the free space in the roots.

Flood-tolerant wetland plants like the ones used in this study have the ability to adapt to the harsher, usually anoxic flooded environment by several adaptation mechanisms (Table 2.1). The development of aerenchyma, the air spaces inside the roots and stems, helps these plants acquire the needed oxygen by diffusion from the aerial parts of the plant into the roots (Mitsch & Gosselink 2000). Once a plant develops aerenchyma, it does not depend any longer on the soil oxygen supply, due to the high porosity (up to 60% volume compared to 2-7% for flood intolerant plants) (Mitsch & Gosselink 2000). Uptake mechanisms for wetland plants are poorly understood. In particular, the role of aerenchyma is not understood.

Table 2.1. Adaptations presented by hydrophytes to compensate the oxygen deficiency in the root system due to continuous flooding, adapted from (Mitsch & Gosselink 2000).

Type of adaptation	Adaptation	
Structural or morphological	Aerenchyma	
	Special organs or responses	Adventitious roots
		Stem elongation
		Lenticels
		Pneumatophores
	Pressurized gas flow	
Physiological	Anaerobic respiration	
	Malate production	

2.3 Sediment-water Partitioning

The uptake mechanisms discussed above all rely on the contaminant reaching the porewater around the root. Desorption must proceed before any plant uptake would be observed. The results of many laboratory and field observations indicate that a significant fraction of sediment-bound contaminants desorb slowly, are not biodegraded and are difficult to remove by extraction with surfactants or cosolvents. For example, (Pereira et al. 1988) found that the concentration of halogenated organic compounds in native water, suspended sediments and biota of Bayou d'Inde, Louisiana was far below the predicted values with respect to concentration in the contaminated bottom sediments. Similarly, (Mcgroddy & Farrington 1995) observed that a fraction of PAHs in river sediments is not available for partitioning. For most of these sediments, the contamination had ceased for periods of many years, yet the sediment-bound contaminants persisted over tens of years without significant reduction in concentration or loss of the hydrocarbon fingerprint.

Other studies, (Chung & Alexander 1998) showed that for dissimilar soils, the diminution of contaminant bioavailability with respect to time was completely different for each type of soil. The effects on phenanthrene aging on sequestration and bioavailability in different types of soil under different environmental conditions were studied by (White et al. 1997). One important finding of this report was that the decrease in a compound's bioavailability with aging was present regardless of a lack of change in its recovery by vigorous extraction procedures. Keeping these findings in mind, is easy to understand why remediation efforts over

the last several decades have revealed that the time scale for complete cleanup of contaminated porous media can be extremely long because of diffusion-limited sorption and desorption processes (Wittmann et al. 2000).

While most sorption studies in environmental soil chemistry have focused on the adsorption of molecules to the soil, the desorption process is also extremely important. It is often observed that desorption is more difficult than adsorption and that not all of the contaminant can be desorbed (Sparks 1995). This "irreversibility" or desorption resistance is referred to as "hysteresis". Hysteresis is inconsistent with classical equilibrium models where the sorption process is assumed to be completely reversible. (Hatzinger & Martin 1995) showed for lab samples as well as contaminated field samples that chemical compounds become less bioavailable and more resistant to biodegradation with time. Sorption irreversibility from sediments has been proposed by (Kan et al. 1994; Fu et al. 1994; Kan et al. 1997; Kan et al. 1998; Wei et al. 1999). They have conducted adsorption-desorption experiments and found adsorption to be fast and predictable from available values of organic carbon normalized partition coefficient (K_{oc}) and K_{ow} (Kan et al. 1994; Fu et al. 1994). Adsorption is reported to be at equilibrium within 4 days, and linear isotherms could be easily constructed with K_p values consistent with the corresponding values for K_{oc} and K_{ow} . On the other hand, after desorption periods lasting up to 5 months, they found 30-50% of the adsorbed fraction to resist desorption.

Xing & Pignatello (Xing & Pignatello 1998) have proposed for polar and non-polar compounds, a "dual-mode" sorption mechanism into soil organic matter. This mechanism explains that dissolution into the solid phase takes place

simultaneously with an adsorption-like process called “hole-filling” in which the holes are a number of sites dispersed in the soil matrix where specific sorption takes places with the behavior of a Langmuir isotherm.

Weber and Huang (Weber Jr et al. 1991; Huang et al. 1996; Huang & Webber Jr. 1997; Huang et al. 1997b; Huang & Webber Jr 1998; Huang et al. 1998; Weber Jr et al. 1998; Lueking et al. 2000), attribute the hysteretic phenomenon to the particle-scale heterogeneity of the soil organic matter and introduced the dual reactive domain model (DRDM) which postulates basically, that the soil organic matter is comprised of two principal domains, one highly amorphous, swollen or “soft” and the other which is condensed, tightly cross linked or “hard”. They suggest that each fraction exhibits a different type of sorption behavior; in the soft part it is linear and fast and in the hard part is nonlinear and slow. In one of their reported experiments (Weber Jr et al. 1998), they used diagenetically altered kerogene (a highly condensed natural organic matter) which has a three dimensional structure with aromatic nuclei cross linked by aliphatic bridges. They stated that the nuclei seems to be mainly formed by clusters (about 100 nm in diameter) of 2, 4 or more parallel aromatic sheets which have a gap about 30-40 nm, this gap is big enough to trap inside small molecules such as phenanthrene. Based on this, they propose that the deeper (far from the surface) a contaminant diffuses into an increasingly glassy region of the condensed soil organic matter, the more difficult it is for a solute to have access to it, thus, the more difficult it will be to desorb.

Using batch reactors, (Pardue & Shin 2000) conducted sorption-desorption experiments in wetland soils. The experimental data were fitted to three models,

which consider different mechanistic explanations for the desorption-resistant fraction. The results of these three models consistently indicate that a desorption-resistance fraction exists in highly organic wetland soils and that aging of the organic matter increases the size of that fraction. Clearly desorption-resistance can be a key process in wetland sediments.

In general, investigators have reported that as organic compounds age in soils they become less and less available either for organisms' uptake (bioremediation and biodegradation) or to exert toxic effects. (Cunningham & Ow 1996) suggest that the bioavailability of organic contaminants decreases with time. (Huang & Webber Jr. 1997) stated in their hypothesis that the quality of organic matter determines the degree of hysteresis in sorption-desorption experiments. These findings suggest that the size of the soil compartment where "irreversible" sorption takes place may be related to the age of the organic matter. Three different soil samples as well as laboratory prepared soils were used by (Hatzinger & Martin 1995) to test the effect of aging on extractability. They found that the extractable portion of the aged material to be up to 30% less compared to freshly contaminated material. (Connaughton et al. 1993), studied the desorption kinetics of naphthalene with time and found that as the incubation time (aging) increased, the organic compounds could sorb to compartments or regions in the soil that exhibit slow adsorption/desorption kinetics.

Nam and Alexander (Nam & Alexander 1998) proposed the hypothesis that sequestration and reduced bioavailability occur when hydrophobic compounds enter soil nanopores with hydrophobic surfaces. They suggest that once a molecule enters

a nanopore with a diameter less than 100 nm, it is probably unavailable to any living organism since even the smallest bacteria are larger. The same observation relating pore size to bacteria size was made by (Zhang et al. 1998). An intraparticle diffusion model was analyzed by (Grathwohl & Reinhard 1993). It suggests that intraparticle porewater limits mass transfer from the internal sorption sites under the assumption that diffusion occurs in water-filled pores among homogeneous particles. (Steinberg et al. 1987) showed on their study that the persistence of 1,2-Dibromoethane (EDB) in soils after 19 years of its last known application was due to entrapment in soil micropores instead of soil interlayers. (Kelsey & Alexander 1997) conducted a study to determine if compounds with different hydrophobicity ($\log K_{ow}$ 2.75, 3.37 and 4.46) exhibited different sequestration and bioavailability behaviors in soils as residence time in soil increased. They concluded that bioavailability decreased as time increased.

In summary, a number of investigators have discussed a phenomenon which can be described as irreversible or slow desorption. It is clear that the fraction of contaminants that is "difficult" to extract from soils remains in some kind of compartment which authors have not agreed upon yet, the contaminants in this compartment (either interlayer, gaps or pores) find their way out only at an extremely slow rate. There are numerous explanations for this phenomenon and none of these are agreed upon to date. Clearly, sediment contaminants that are "desorption resistant" may be difficult to remediate. To date, no one has studied the relationship between irreversible sorption and plant uptake.

2.4 Phytoremediation

In the past decade, phytoremediation of inorganic and organic contaminants has been extensively studied and the "concept" has evolved into a well-established technique with field applications and even commercialization has been possible. In many of the phytoremediation studies, the factor limiting the effectiveness of the technology has been the transport of the substances from the bulk solution across the root surface and into the plant sap. (Paterson et al. 1990) report three factors that affect root uptake of organics: 1) physicochemical properties of the compound, 2) environmental conditions and 3) plant characteristics.

Root uptake has been shown to be proportional to the n-octanol/water partition coefficient (K_{ow}) for the target chemical (Zhang et al. 1998), that is, compounds that exhibit high hydrophobicity can better partition into roots and be transported to the rest of the tree. However, if the compound is too hydrophobic it may remain bound to the mucigel (polymeric carbohydrates) associated with the root surface and lipid membrane of the roots epidermis (Clarkson 1996) In order for a compound to be translocated from the roots, it must pass the symplast of the endodermis (Trapp et al. 1994). These studies and others (Briggs et al. 1982, Burken & Schnoor 1998), have resulted in the development of structure-activity relationships for uptake . These will be discussed later.

One of the key concerns while trying to implement phytoremediation is the possible transfer of compounds into the food chain. Wild (Wild & Jones 1992) studied the uptake of PAH by carrots from soils containing sewage sludges containing PAHs and found that atmospheric deposition was the dominant

mechanism that provides PAH's to the foliage. Root uptake was considered by the authors as insignificant and independent from soil concentration, compared to atmospheric deposition.

The uptake and transformation of a number of classes of compounds has been documented. Compton (Compton et al. 1998), conducted field tests with 183 hybrid poplar trees to assess the uptake of volatile organic compounds (VOC's). Compton's results indicated the presence of VOC's and their degradation products, implying the uptake of these compounds by the poplar trees. Watkins (Watkins et al. 1994) studied the volatilization of naphthalene from soil-microcosms planted with Bell Rhodegrass, and observed an enhanced volatilization and suppressed mineralization from the planted soil in comparison to the non-planted soil, this apparent contradiction can be explained by the fact that naphthalene removal from the rhizosphere by plant uptake reduces the amount of available contaminant for biodegradation. (Schnoor et al. 1995) reported that benzene and toluene would be suitable for phytoremediation. Based on their findings of enhanced biodegradation in the rhizosphere of anthracene and pyrene, (Reilley et al. 1996) suggests that degradation and further uptake of PAH's with four or more aromatic rings is possible.

Atrazine plant uptake has also been widely studied. Burken (Burken & Schnoor 1996, Burken & Schnoor 1997) showed the uptake, hydrolyzation and dealkylation of atrazine by hybrid poplar trees and proposed a degradation mechanism as shown in Figure 2.6. It was also shown that after root uptake, the pesticide could be rapidly translocated to the leaves through the stem.

Inorganic contaminants have also been widely used in plant uptake studies. Heavy metal-contaminated soil can be remediated using plants known as hyperaccumulators [plants that accumulate >0.01-1% (depending on the element) by weight of heavy metals into plant tissues]. Kirkman (Kirkham 2000) as well as Hooda (Hooda et al. 1997) studied the effects of different chelators on heavy metal uptake from sewage sludge. Huang (Huang et al. 1997a) also studied the effect of chelators on Pb uptake from soils, this work showed that chelators are effective in solubilizing lead from the soil, and Pb plant concentration increased from less than 500 mg/kg plant w/o chelators to more than 10000 mg/kg plant after chelators addition. The extraction capacity of Cd, Cu and Zn by willow was demonstrated by (Greger & Landberg 1999) and by (Punshon & Dickinson 1999). Selenium can be scavenged by plants from contaminated soils, bioconcentrated, and then harvested for a completely elimination of that fraction from the soil. Zayed (Zayed et al. 1998) reported that selenium could ultimately be volatilized into a harmless form (dimethyl selenide).

One of the organic compounds most widely studied in plant uptake experiments is TCE, one of the most common compounds found in Superfund sites. A very good example of how well studied TCE plant uptake is the report presented by (Chappell 1997), in a general way, this report covers all the way from phytoremediation overview to field studies. Anderson and Walton (Anderson & Walton 1995) studied the fate of readily available [^{14}C]TCE in the rhizosphere using closed reactors. They demonstrated the different distribution patterns between leaf, stem and root and also report the increased mineralization in vegetated soil as opposed to non-vegetated

soils. They suggest a direct relationship between water uptake and contaminant translocation into the roots.

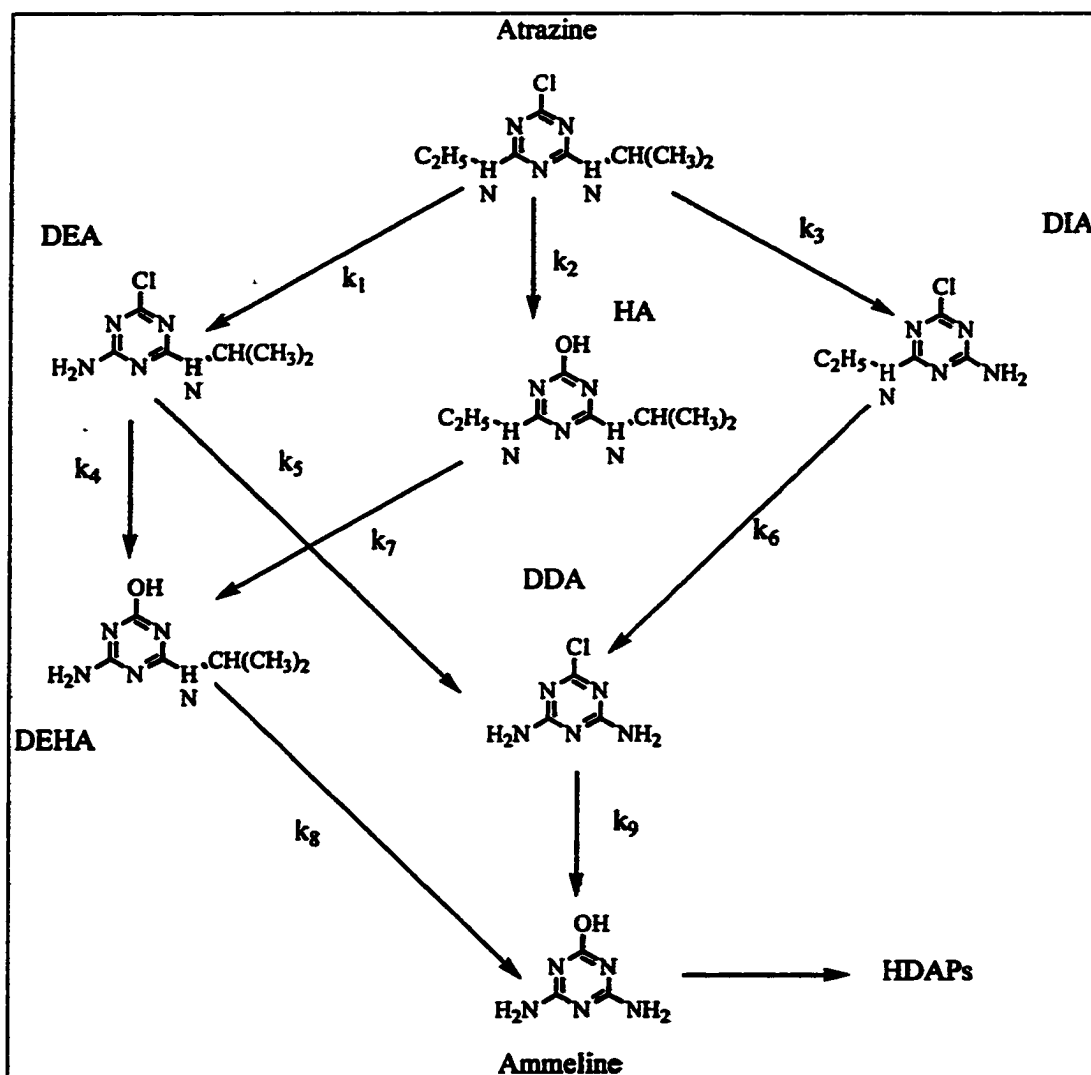


Figure 2.6. Atrazine degradation mechanism by Poplar trees as proposed by (Burken & Schnoor 1997). DEA, deethylatrazine; HA, hydroxyatrazine; DIA, deisopropylatrazine; DEHA, deethylhydroxyatrazine; DDA, didealkylatedatrazine; HDAP, hydroxylated dealkylated products.

Tree cores were taken and further analyzed by (Vrobley et al. 1999). They determined that TCE was present in trunks of the six different tree species growing

above contaminated shallow groundwater. They also showed that the concentration changed vertically upward. Narayanan (Narayanan et al. 1999) also studied the potential for TCE removal from groundwater using a laboratory scale chamber.

A key complication in the use of vegetation for treatment of VOCs is the potential for volatilization. Davis (Davis et al. 1998) measured the transfer rate of several VOC's (trichloroethylene (TCE), trichloroethane, chloroform and dichloromethane among others) from contaminated water to the gas phase above the plants. These authors reported that the chlorinated hydrocarbons used in their experiments moved readily through plants and were transported in their original form to the gas phase. Using 11 different chemicals with log K_{ow} 's ranging from 0.9 to 5.04, (Burken & Schnoor 1999) determined that different chemicals can be volatilized from the leaves in different amounts which depends on the compounds' vapor pressure. In a field scale project at the Aberdeen proving grounds in Maryland, (Compton et al. 1998) determined that 1,1,2,2 tetrachloroethylene (TCA) and TCE are transpired from the leaf tissues of hybrid poplar trees.

In addition to the processes discussed above, several other processes are important benefits for phytoremediation. These include:

- I. Increases in soil microbial population and activity by the release of root exudates, build up of organic carbon due to root necromass (Anderson et al. 1994, Schnoor et al. 1995) and improved aeration by the release of oxygen to the root zone as well as the formation of more oxygen paths through the root necromass (Nye & Tinker 1977; Shimp et al. 1993).

- II. Interception and retardation of the movement of hydrophobic organic chemicals and also some metals (Nair et al. 1993).
- III. Stimulated cometabolic transformations of recalcitrant chemicals to less toxic metabolites (Nair et al. 1993, Briggs et al. 1982, McCrady et al. 1987, Burken & Schnoor 1997).
- IV. Uptake of volatile hydrocarbons by leaves from the air, playing the role of a cap for contaminated sites (Sabljic et al. 1990, McCrady & Maggard 1993).

2.5 Plant Uptake Modeling

For long time, investigators have reported equations to correlate the plant uptake of ions from external solutions, Russell (Russell & Shorrocks 1959) defined the transpiration stream concentration factor (TSCF) for barley and sunflower plants in rubidium and phosphate solutions as follows:

$$TSCF = \frac{\text{Concentration of ion in transpiration stream}}{\text{Concentration of ion in external solution}} \quad (1)$$

In 1974, Shone (Shone & Wood 1974) moved ahead the TSCF concept from inorganic ions to herbicides and a fungicide, they also introduced the root concentration factor (RCF) concept:

$$RCF = \frac{\mu\text{g compound / g fresh weight root}}{\mu\text{g compound / ml ambient solution}} \quad (2)$$

The importance of this new concept is that it can be shown that some saturation of the roots is necessary before the maximum value of TSCF can be

reached, and as shown by Shone, the concentration in the root of most of the chemicals exceeded the concentration in the surrounding medium, the authors suggested the possibility of sorption into cell constituents for this increased value. All the compounds, except 2,4-dichlorophenoxyacetic acid (2,4-D) reported by Shone, showed a TSCF value less than one, as compared to those reported for inorganic ions obtained by Russell, which ranged from 0.3 to 155.7 (over 60 different values in this range).

In another work presented by Shone (Shone et al. 1974), the compounds were characterized as lipophilic and lipophobic, and they concluded that the lipophilic compounds are able to penetrate the cortical cells of the root and could reach the shoots more easily than the lipophobic compounds which may be confined to the free space in the roots. Taking these correlations and concepts a step further, (Briggs et al. 1982) presented an equation to relate the plant uptake to the n-octanol/water partition coefficient, K_{ow} as follows:

$$TSCF = 0.784 e^{\left[\frac{-(\log K_{ow} - 1.78)^2}{2.44} \right]} \quad (3)$$

The empirical equation 3 was developed for barley, and has an uptake optimum for slightly lipophilic compounds whose $\log K_{ow} = 1.78$. The transpiration stream concentration factor (TSCF), controls the amount of a given compound that can be taken into the plant and further transported along the xylem.

The TSCF concept has been used to estimate plant uptake based on the fugacity of the chemical in the soil and shoot. With the maximum concentration of

the transpiration stream being that of the water (Z_w), the contaminant flux into shoots (N_{Rsh}) can be calculated with the following equation given by (Trapp et al. 1990):

$$N_{Rsh} = TST \cdot TSCF \cdot Z_w \cdot (f_s - f_{sh}) \quad (4)$$

where:

TST = transpiration stream (m^3/s),

f_s = fugacity of the soil,

f_{sh} = fugacity of the shoot.

Numerous fully developed mathematical models exist for the plant uptake of organic compounds (Dowdy & McKone 1997, Burken & Schnoor 1996; Burken & Schnoor 1998, Trapp et al. 1994; Trapp & McFarlane 1995; Trapp & Matthies 1995, Boersma et al. 1988, Behrendt & Brüggemann 1993; Chang & Corapcioglu 1998 among others. An excellent example is the model by (Trapp & McFarlane 1995), which is an extensive report on modeling and simulation exploring all the possible transport mechanisms from root uptake to transpiration from leaves, as well as the metabolic pathways of contaminants. This work provides simple equations to evaluate the uptake of contaminants in soil by roots, the root concentration factor (RCF), the translocation from roots to shoots, the movement within shoots as well as the transpiration from leaves among other transport mechanisms.

Using equation 3 and partition coefficients as the one shown in equation 5, (Behrendt & Brüggemann 1993) studied the fate of three pesticides in plants with $\log K_{ow}$ values ranging from an almost optimum for equation 1 (1.82) up to 3.06

which is approaching the end of the effective uptake zone proposed by equation 1.

These authors used a system of simulation models called SNAPS (Simulation model network atmosphere-plant-soil). Their results show that after 3-4 months, less than 1% of the applied pesticide should remain in the plants while the rest was either degraded by the plant or volatilized.

$$K_{LA} = \frac{(WC + L_p (K_{aw})^b \rho_l)}{(\rho_w K_{aw})} \quad (5)$$

where:

K_{LA} = Partition coefficient leaf/atmosphere

WC = water content of the leaf

L_p = Lipid fraction of the leaf

ρ = Density

K_{aw} = Partition coefficient air/water

Boersma (Boersma et al. 1988) produced a theoretical model for the coupled transport of water and organic solutes based on transport across simple thin membranes, this model describes the mechanisms that control uptake, accumulation, and degradation of xenobiotic organic chemicals in terrestrial plants. A drawback of this model is that some anatomical properties of leaf and root tissues for each particular plant are needed as show in equation (6).

$$\frac{dM_1}{dt} = \left(\frac{D_1}{\Delta x_1} \left\{ K_{1,1} C_0 - K_{1,2} \frac{M_1}{V_1(1+B_1)} \right\} + K_{1,1} q_1(1-\sigma_1)C_0 + J_s \right) A_1 - \left(\frac{D_2}{\Delta x_2} \left(K_{2,1} \frac{M_1}{V_2(1+B_2)} \right) + K_{3,1} q_2(1-\sigma_2) \frac{M_1}{V_1(1+B_1)} \right) A_2 - \lambda_1 V_1 \frac{M_1}{V_1(1+B_1)} \quad (6)$$

where:

A_i = Contact area between compartments (cm^2)

B_i = Sorption coefficient for compartment i (dimensionless)

C_i = Solute concentration in compartment i (mol/cm^3)

J_s = Rate of active uptake of solute (s^{-1})

$K_{i,1}$ = Partition coefficient for transport into compartment i; is the ratio solubility in the membrane/solubility in water (dimensionless)

$K_{i,2}$ = Partition coefficient for transport out of compartment i (dimensionless)

M_i = Mass of solute in compartment i (g)

V_i = Volume of compartment i (cm^3)

q_i = Flux ($\text{cm}^3/\text{cm}^2 \text{ s}$)

Δx_i = Thickness of membrane separating compartments (cm)

σ_i = Reflection coefficient for compartment i (dimensionless)

λ_i = Rate constant for first order processes in compartment i (s^{-1})

A root growth model has been presented by Chang (Chang & Corapcioglu 1998) for nonvolatile hydrocarbons. This model suggests that plant characteristics (such as root radius), are more important than contaminant properties for a phytoremediation operation.

Burken (Burken & Schnoor 1997) studied the uptake and further metabolism of Atrazine using poplar trees. A mathematical model was developed to estimate the rate constants for the degradation mechanism they proposed. The following two equations presented by the authors can be used to calculate the atrazine concentration in bulk pore water solution and in poplar leaf tissue:

$$\left(\frac{d[Atra]_w}{dt} \right) = -k_{1w}[Atra]_w - k_{2w}[Atra]_w - k_{3w}[Atra]_w - TSCF_{Atra} \frac{T[Atra]_w}{V_w} - k_s \left([Atra]_w - \frac{[Atra]_{RS}}{RCF} \right) \quad (7)$$

$$\left(\frac{d[Atra]_L}{dt} \right) = \frac{T[Atra]_R}{V_L} - k_{1L}[Atra]_L - k_{2L}[Atra]_L - k_{3L}[Atra]_L \quad (8)$$

where:

W = pore water/bulk solution

R = root xylem

RS = root surface

L = leaf

T = time (days)

Trapp (Trapp & Matthies 1995) shows an analytical solution (with sample calculations) for plant uptake considering uptake from soil, gaseous deposition, leaves transpiration, degradation, and tree growth as a "one compartment" calculation.

An empirical fugacity-based model to predict uptake by leaves of Organic chemicals in gaseous phase is presented by Paterson (Paterson & Mackay 1991) this

model is based in the octanol-air and water-air partition coefficients for the chemical. Equation 9 is what they proposed to calculate the uptake.

$$BCF_v = 0.19 + 0.7K_{WA} + 0.05K_{OA} \quad (9)$$

where:

BCF_v = Ratio of volumetric concentrations $\frac{g/m^3 \text{ wet leaf}}{g/m^3 \text{ air}}$

K_{WA} = Water-air partition coefficient

K_{OA} = Octanol-air partition coefficient

No model has been developed which describes the relationship between irreversible sorption of organics in the sediment and plant uptake. To date, all models have assumed that sorbed organics in the sediment are completely reversible and fully available. In chapter four, a model for plant uptake is presented, this model is basically a modification to some of the above discussed models so the desorption resistant fraction of contaminant could be fitted into the equation.

2.6 Conclusions

Based on the literature discussed above, the following data gaps are identified. Currently there are no scientific publications citing the influence of desorption resistance on plant uptake, either terrestrial or aquatic. All the studies consider that the contaminant even if it has been in the soil for long time, it will be fully available for plant uptake. The great majority of the studies on plant uptake have been done with terrestrial plants, but very few have considered aquatic or wetland plants as a potential remediation tool. There is little or no information

available on how wetland plants take up chemicals and transport them to the above-ground parts of the plant.

The currently available models, have been formulated for agricultural plants like barely and for other terrestrial plants such as poplar trees. None of the current models has been applied to wetland plants which have a different morphology than these previously mentioned plants, so there is a need for a model which could be useful to predict the uptake by wetland plants. Finally, there is also no information on how wetland plants can help on the clean-up processes at contaminated sites. Many current CERCLA or Superfund sites across US involve wetlands.

3. EFFECT OF DESORPTION-RESISTANCE ON PLANT UPTAKE OF PHENANTHRENE FROM SEDIMENT

3.1 Introduction

The uptake and transformation of a number of classes of organic compounds by plants has been reported (Burken & Schnoor 1998, Burken & Schnoor 1996, Chaineau et al. 2000, Davis et al. 1998, Hughes et al. 1997, Newman et al. 1997, Thompson et al. 1998). Structure activity relationships developed over the past decade (Trapp et al. 1990, Trapp 1995; Burken & Schnoor 1998) for non-ionic organics suggest that uptake is only effective for compounds with K_{ow} 's from 0.5 to approximately 4, below that of many of the more hydrophobic organic contaminants such as 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. 1994, Kan et al. 1997, Kan et al. 1998, Wei et al. 1999, Weber Jr et al. 1998, Pignatello 1989, Luthy et al. 1997) 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 a treatment that contained only the desorption-resistant contaminant. Plant uptake studies were conducted in the greenhouse to test the hypothesis that contaminant in the desorption-resistant compartment is not bioavailable to vegetation.

3.2 Materials and Methods

Plants. Two different wetland plant species were used throughout the experimentation: a tree, black willow (*Salix nigra*) and a sedge, three-square bulrush (*Scirpus olneyi*). The trees used in the experimentation were obtained from cuttings of larger trees, which were grown hydroponically in a greenhouse. The sedges were obtained from a nursery, and from there, a large "stock" population was created, from these, individual plants were transplanted into reactors. The plants remained in the reactors until they showed positive growth, and when at least 15 plants (enough

for 5 sampling points with triplicate) showed positive growth, the experiment was initiated.

¹⁴C-labeled and non-labeled phenanthrene. The [¹⁴C] compound was further diluted with a non-labeled phenanthrene solution (Sigma Chemical Co. St. Louis, MO., >96% HPLC) in the reactors. High specific activity radiolabeled [9,10-¹⁴C] phenanthrene (ChemSyn Laboratories, Lenexa, KS., 56.7 µCi/ µmol) was used to prepare the desorption-resistant sediment. Radiolabeled [9,10-¹⁴C] phenanthrene (Sigma Chemical Co. St. Louis, MO., 8.3 µCi/ µmol) was used in the remaining treatments.

Sediment. Two porous media were used in this study: a) commercial silica sand (rinsed with de-ionized water, oven-dried and then autoclaved) and b) Bayou Manchac sediment. The sediment used was collected from Bayou Manchac (Baton Rouge, LA) on October 28, 1998. The sediment was collected using an Ekman grab sampler and passed through a 10 mm coarse sieve to remove large objects such as branches, matted leaves, clams, rocks, glass, etc. before returning to the lab. Back in the lab, the sediment was 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 was complete, the water content of the sediment was adjusted to desired conditions (20%) for the inoculation and made consistent between the different batches. One batch of the sediment was contaminated and decontaminated to leave only the desorption-resistant fraction using the isopropanol extraction protocol (Liu et al. 2000) developed for establishing known amounts of organics in the reversible and irreversible

compartments. After the sieving process, another batch of the sediment was dried and autoclaved prior to inoculation.

Experimental protocol. Plant uptake reactors similar in design to those described in (Burken & Schnoor 1998) were fabricated for this study. Three different treatments were utilized a) fully available treatment, where a phenanthrene solution was added to a reactor containing the plant and silica sand. b) a desorption-resistant treatment where sediment was artificially "aged", and c) a freshly contaminated treatment where the sediment was very recently contaminated with phenanthrene. For the fully available (sand) experiments, a solution of ^{14}C -phenanthrene (with the load shown in Table 3.1) plus non-labeled phenanthrene dissolved in deionized water (with a final concentration of 1 mg/L) was added to the lower part of the glass reactors. Following this, a tree or sedge was placed in the lower portion of the reactor and 100 g dry weight of sand 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 avoid any algae 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 followed by a 20 mL 1N NaOH solution to trap CO_2 . When necessary, $\frac{1}{4}$ strength modified Hoagland's solution was added as fertilizer.

Table 3.1. Summary of the initial conditions for each experiment.

Media	Bayou Manchac desorption resistant		Bayou Manchac freshly contaminated		Sand	
	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>
Sediment 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

For the desorption-resistant treatment, sediment from Bayou Manchac, LA was prepared using the following procedure. A large volume of sediment (20 kg dry weight) was placed in jars in which phenanthrene and ^{14}C -phenanthrene had previously been uniformly spiked and the solvent evaporated. The inoculation targets were 480 mg/kg unlabeled phenanthrene, 10 $\mu\text{Ci/kg}$ ^{14}C labeled phenanthrene and 4550 mg/kg sodium azide as a microbial inhibitor. Once all of the jars had been identically prepared, they were thoroughly sealed, the jar exterior was covered with duct tape, and placed on a continuous axial tumbler for one month. After the aging month, the sediment was desorbed using the protocol of (Liu et al. 2000)(see the block diagram on figure 3.1). In short, the extraction procedure was:

a). The sediment was extracted with a 50% v/v isopropanol and electrolyte solution (0.01 M NaCl, 0.01 M CaCl_2) for 24 h in a rotary tumbler with a solid/water ratio of 20/80 (wt/wt). b). The slurry was centrifuged at 5,500 rpm for 50 minutes and the

supernatant decanted, c). The remaining isopropanol was washed from the soil with electrolyte solution (two times) maintaining the same solid/water ratio described above, d). The entire washing process was repeated. This resulting sediment has a load of 13.61 mg/kg of desorption-resistant phenanthrene, and the concentration in the free-phase water was of 0.046mg/L. From this sediment, 68 g dry weight was added to the lower portion of the reactor, and spiked with ¼ strength Hoagland's solution. The rest of the set-up procedure was the same as for the sand experiment.

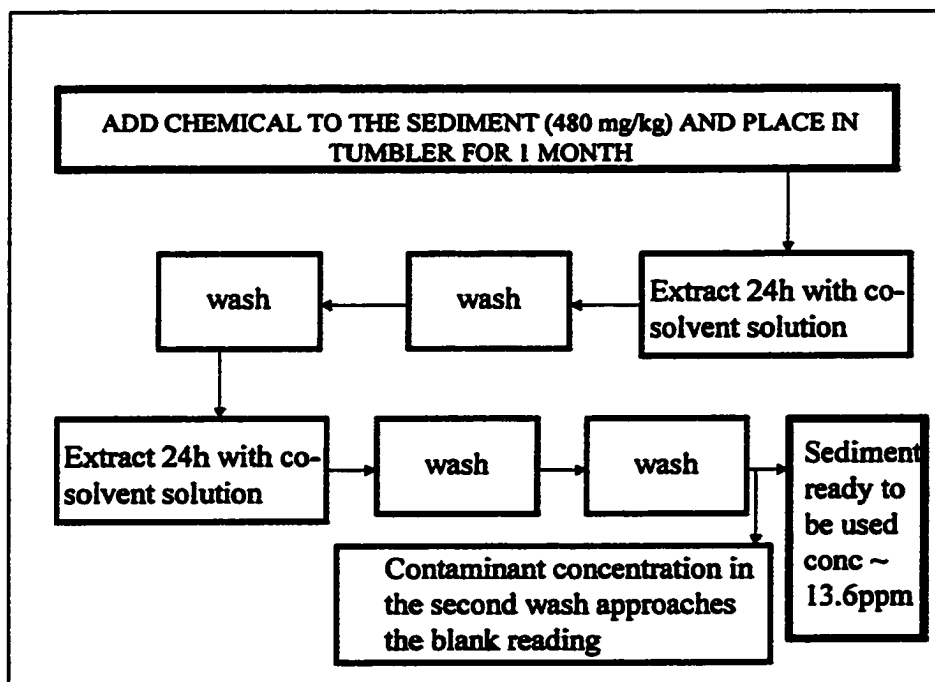


Figure 3.1. Block diagram of the artificial aging process used to leave only the desorption-resistant fraction of contaminant in the sediment.

For the freshly contaminated treatment 85 g dry weight of clean Bayou Manchac sediment was added to the reactor followed by the phenanthrene solution containing 1 mg/L of unlabeled phenanthrene and the amount of ^{14}C -phenanthrene shown in Table 5.1 was added prior to closing the reactor. Again, the rest of the set-up was the same as for the two previous experiments.

At weekly time intervals, three plants of each species were removed from the reactor, the roots leaves and stem separated and cut into small pieces (approximately 0.5 g each) and oxidized to $^{14}\text{CO}_2$ using a biological oxidizer (OX600 R. J. Harvey Instrument Co.) The efficiency of the oxidizer was checked periodically using ^{14}C -labeled mannitol and was consistently over 90%. To complete the mass balance, the ORBO tube, liquid and soil remaining in the reactor were also analyzed for ^{14}C . A liquid scintillation counter (LS 6000SC; Beckman Instruments) was used to quantify the ^{14}C present in the solution from the biological oxidizer and from the flasks and NaOH solutions. Based on these measurements "plant uptake" was defined as the measured ^{14}C activity associated with vegetation regardless of the physical mechanism responsible for uptake. "Translocation" was defined as the ^{14}C activity measured in the above-ground plant parts not in direct contact with the sediment or sand that was presumed to have resulted from ^{14}C transport in the transpiration stream of the plant. The "bioavailable" portion of contaminant in this context is the ^{14}C that is taken up by the plant regardless of mechanism and is synonymous with plant uptake.

Biodegradation studies. To confirm that biodegradation was occurring in the rhizosphere, modified Erlenmeyer respirometry flasks were used. These flasks have inside them a 5 mL capacity tube attached to the bottom. The setup was similar to the plant uptake experiments, but in this case, 2 mL 1N NaOH was placed in the inner glass tube so we could trap any CO_2 produced inside the reactor, sampling was also done at weekly intervals.

Sorption experiments. Partition, or sorption to the plant was tested with the following setup: vials with a known amount of live roots were filled with a 2 mg/L phenanthrene solution, which also included ^{14}C -phenanthrene as tracer. After 24 hours in a shaker, the solution was exchanged for a new one and the amount sorbed into the plant was calculated, this procedure was repeated until the uptake showed to have reached a saturation point.

3.3 Results and Discussion

Effect of desorption resistance on plant uptake

The total uptake of phenanthrene by both *Salix* and *Scirpus* is shown in Figures 3.2 and 3.3. As expected, uptake was greater for the sand treatment 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 (Dunnet'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.

Distribution of ^{14}C phenanthrene in belowground and aboveground plant parts is presented in Figures 3.2 for *Scirpus* and Figure 3.3 for *Salix*. Relatively small differences were observed between *Scirpus* and *Salix* despite differences in water uptake (transpiration rate) and plant morphology.

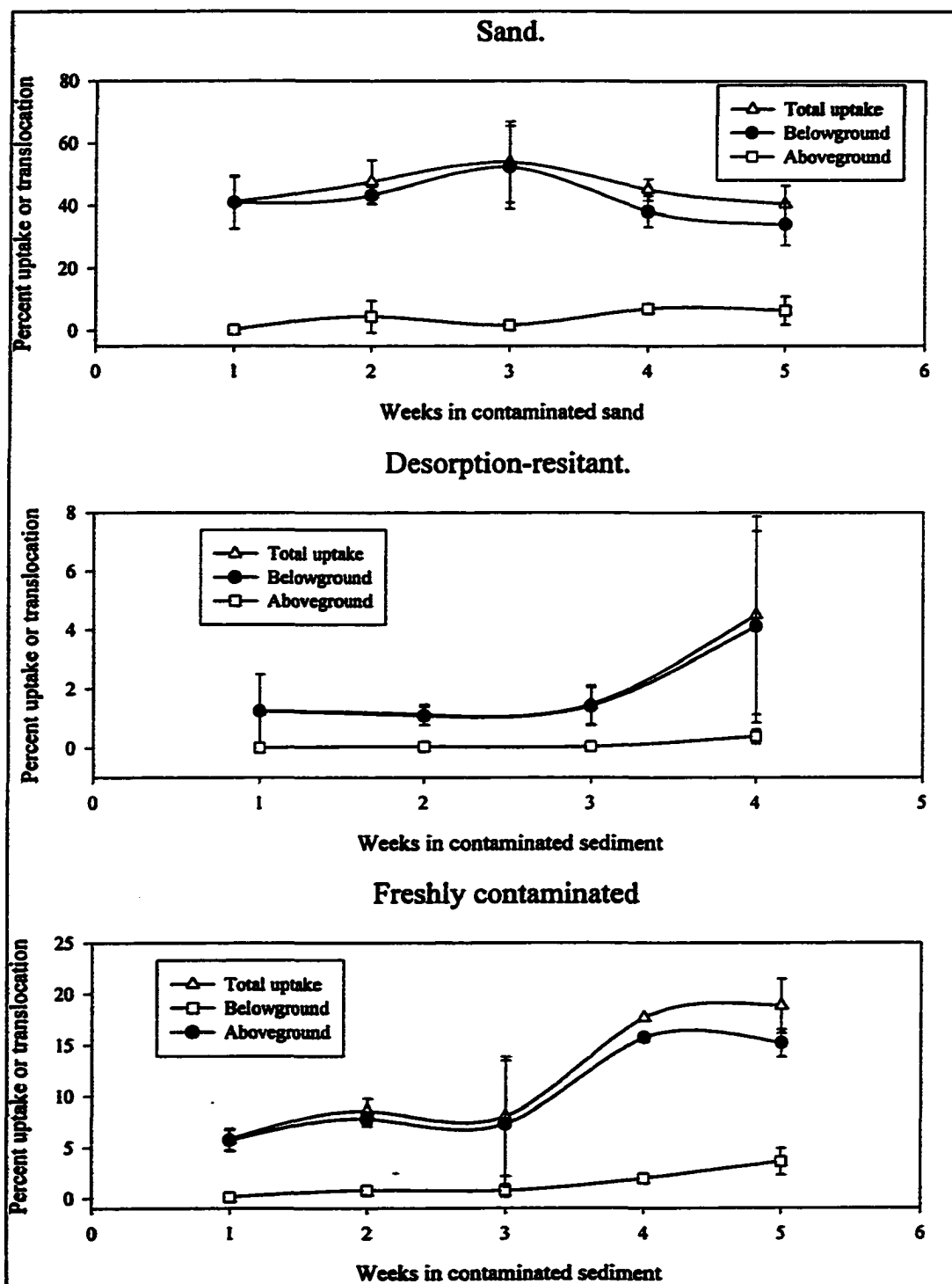


Figure 3.2. Comparison between total phenanthrene uptake and translocation by *Scirpus o.* from the three different treatments applied.

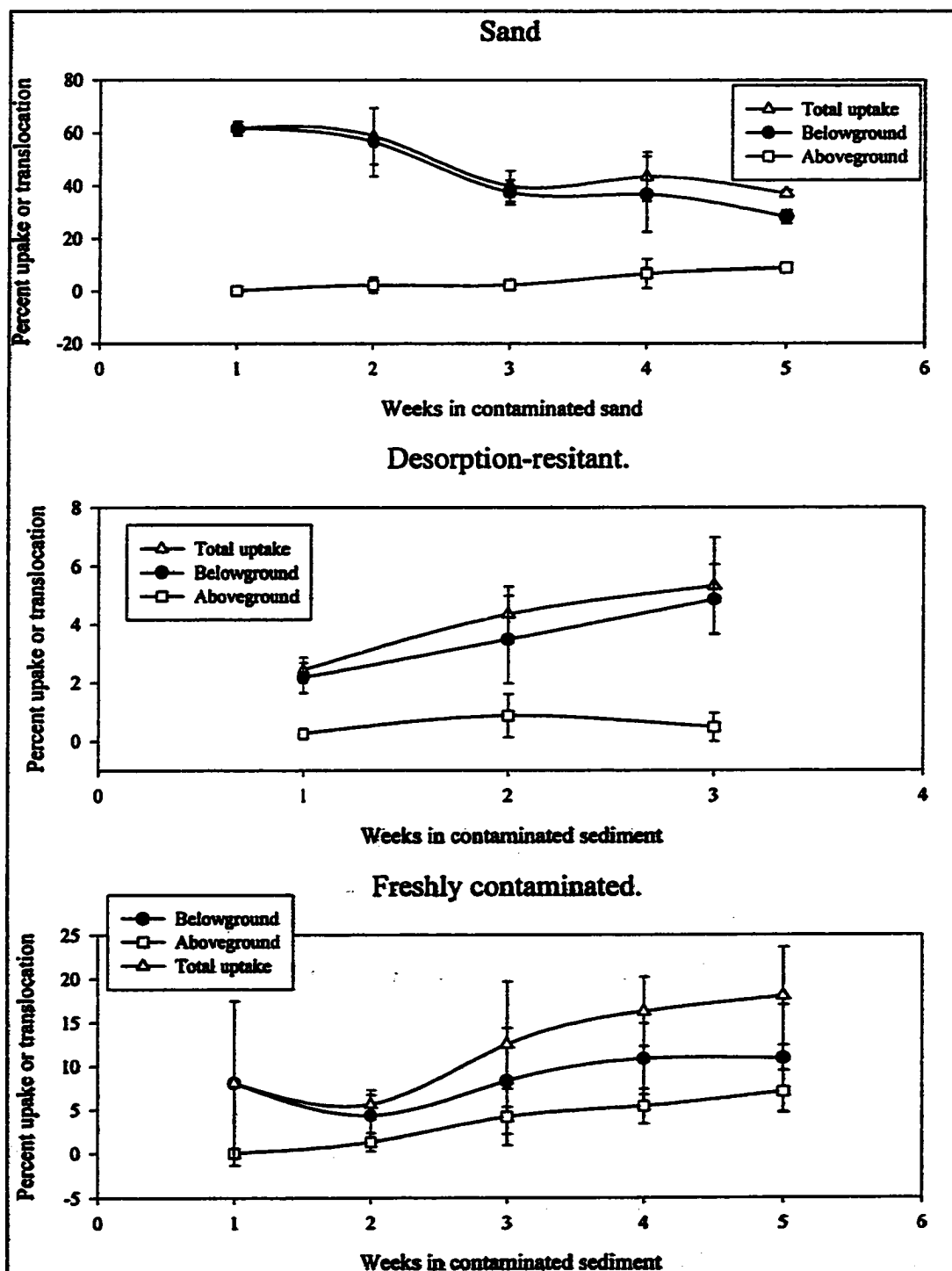


Figure 3.3. Comparison between total phenanthrene uptake and translocation by *Salix* from the three different treatments applied.

The percentage measured as total uptake was similar for each plant.

Statistical comparisons were made between *Salix* and *Scirpus* for ^{14}C uptake in aboveground and belowground plant parts for the data measured at the conclusion of the experiment. Results indicated no statistical difference in the total ^{14}C uptake for the sand treatment and the freshly-added treatment. For the desorption-resistant treatment, total uptake was higher in *Salix* (Dunnet's means test at 0.05 level of significance). No statistical differences were observed for ^{14}C in the aboveground portion between the two plants while belowground concentrations of ^{14}C were higher for *Salix* in the desorption-resistant treatment. These differences are attributed to greater root mass in the *Salix* reactors.

Since aboveground plant parts were not in direct contact with contaminated sediment or water, ^{14}C detected in aboveground plant parts was assumed to be the result of translocation. As expected, ^{14}C in the upper plant parts increased over time as water use proceeded. Overall translocation was a small fraction of the total uptake for all treatments. Accumulation of ^{14}C in the aboveground portion of the plants was plotted versus water uptake (Figure 3.4). The slope of the curve of accumulation versus water uptake was used as an estimate of the concentration of phenanthrene in transpiration stream of the plant. Slopes ranged from 7×10^{-3} mg/mL to 0.02 mg/mL. There was no statistical difference between estimated transpiration stream concentrations of *Salix* and *Scirpus* for 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.

Mass balances closed very well with all mass balances >70% and most >85% (Table 3.2). A significant portion of the mass was accounted for as CO₂, presumably from microbial biodegradation in the rhizosphere. CO₂ was routinely trapped in base traps connected with air leaving the top and bottom of the reactors. A breakdown of the mass balance is presented in Figure 3.5. Initial below-ground uptake decreases over time as CO₂ production increases suggesting that as biodegradation proceeds, desorption of phenanthrene occurs to maintain equilibrium. The source of this CO₂ is unknown although similar concentrations of CO₂ were measured when traps were placed in the base of the reactors (Figure 3.6). Based on the similarities between activities of CO₂ in two experiments, it was concluded that microbial degradation in the rhizosphere was responsible. Transport of gases through wetland plants is commonly observed (Grosse & Mevi-Shutz 1987; Mitsch & Gosselink 2000) and the difficulty ensuring a complete seal around a growing plant must be noticed. Mass balances for the desorption-resistant treatments were essentially 100% without any contribution from rhizospheric degradation suggesting that it may be a less significant process in "aged" contamination.

The mortality rate of the plants in these experiments, was 1/15 for both plants in silica sand, and for *Salix* in Bayou Manchac freshly contaminated and 3/15 also for *Salix* in Bayou Manchac Sediment desorption resistant and for *Scirpus* in Bayou Manchac sediment freshly contaminated, the rest of the set-ups had no losses.

Table 3.2. Mass balances (^{14}C) for all the plants and soils in the experimentation. BM_F (Bayou Manchac freshly added), BM_irr (Bayou Manchac desorption resistant)

	Week 1	Week 2	Week 3	Week 4	Week 5
<i>Scirpus</i> in BM_F					
mean	104.8	97.3	103.5	99.4	111.6
Std dev	6.8	10.5	12.4	1.7	17.4
<i>Salix</i> in BM_F					
mean	91.9	89.2	83.6	86.2	89.9
Std dev	17.0	5.4	6.5	15.1	32.7
<i>Salix</i> in silica sand					
mean	86.5	87.6	86.0	97.4	102.9
Std dev	5.3	5.9	2.3	1.9	11.7
<i>Scirpus</i> in silica sand					
mean	77.3	75.9	77.0	72.8	75.0
Std dev	1.7	4.2	3.2	1.7	5.5
<i>Salix</i> in BM_irr					
mean	103.2	101.9	98.3		
Std dev	9.5	1.5	1.5		
<i>Scirpus</i> in BM_irr					
mean	105.2	106.1	101.8	98.9	
Std dev	5.9	5.7	3.8	4.1	

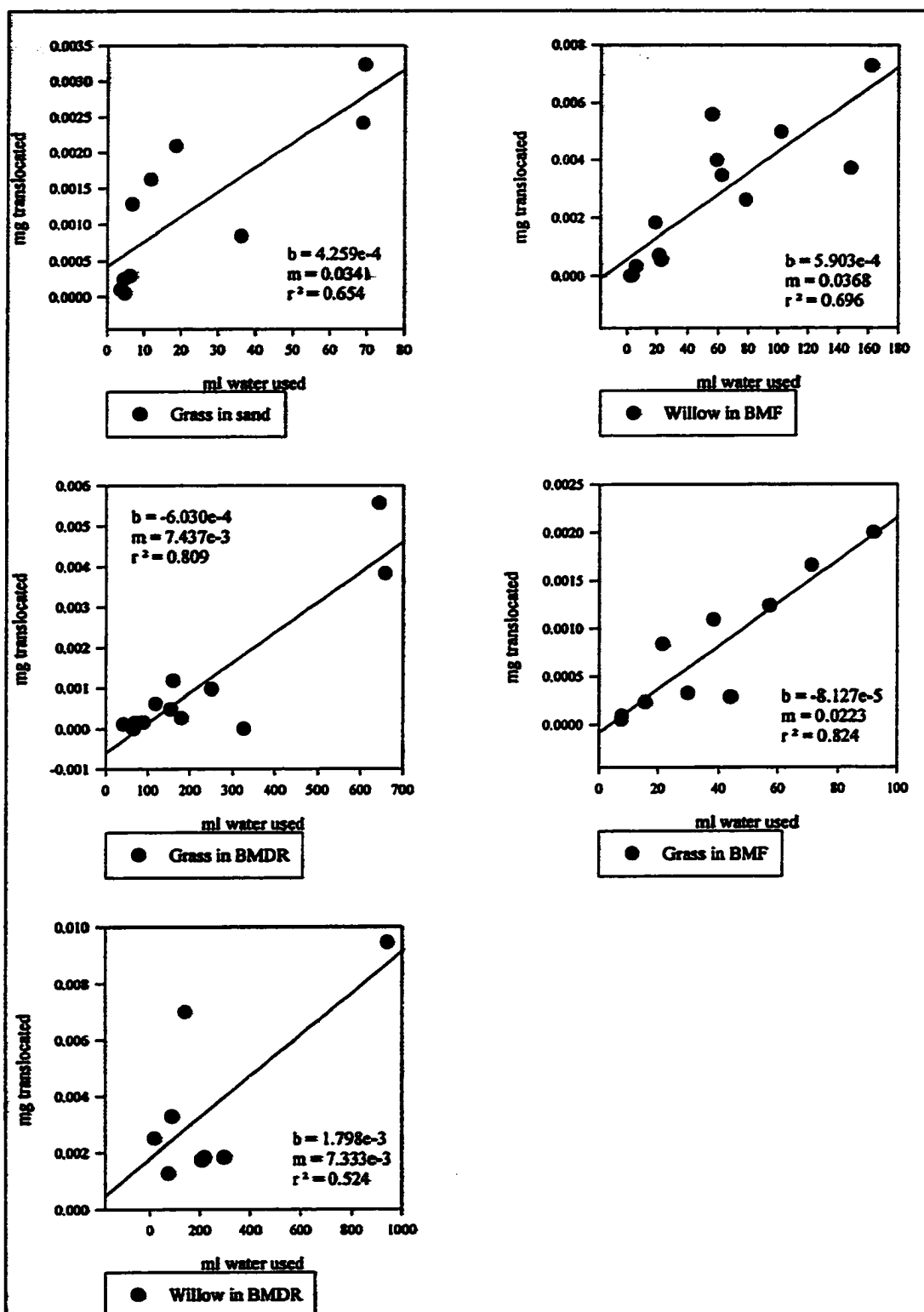


Figure 3.4. Correlation between water uptake and phenanthrene translocated above ground.

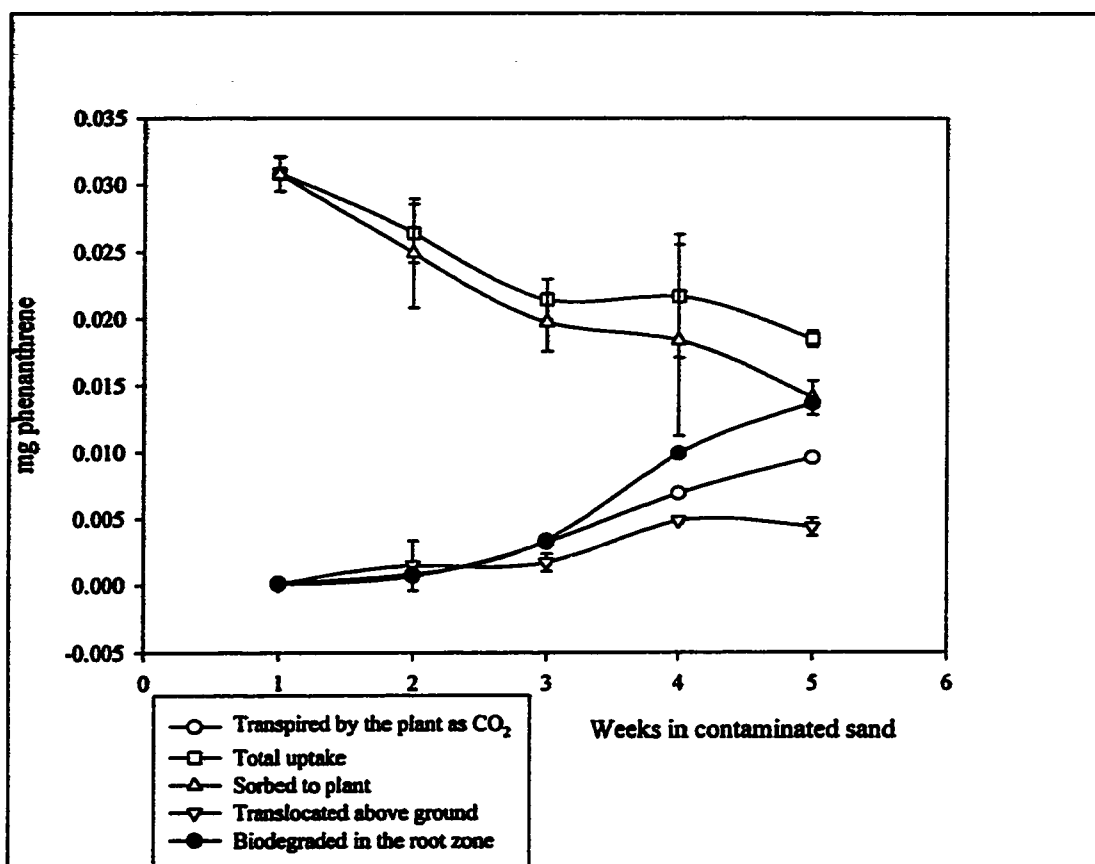


Figure 3.5. Mass balance for phenanthrene uptake, translocation and mineralization by *Salix n.* in the sand treatment.

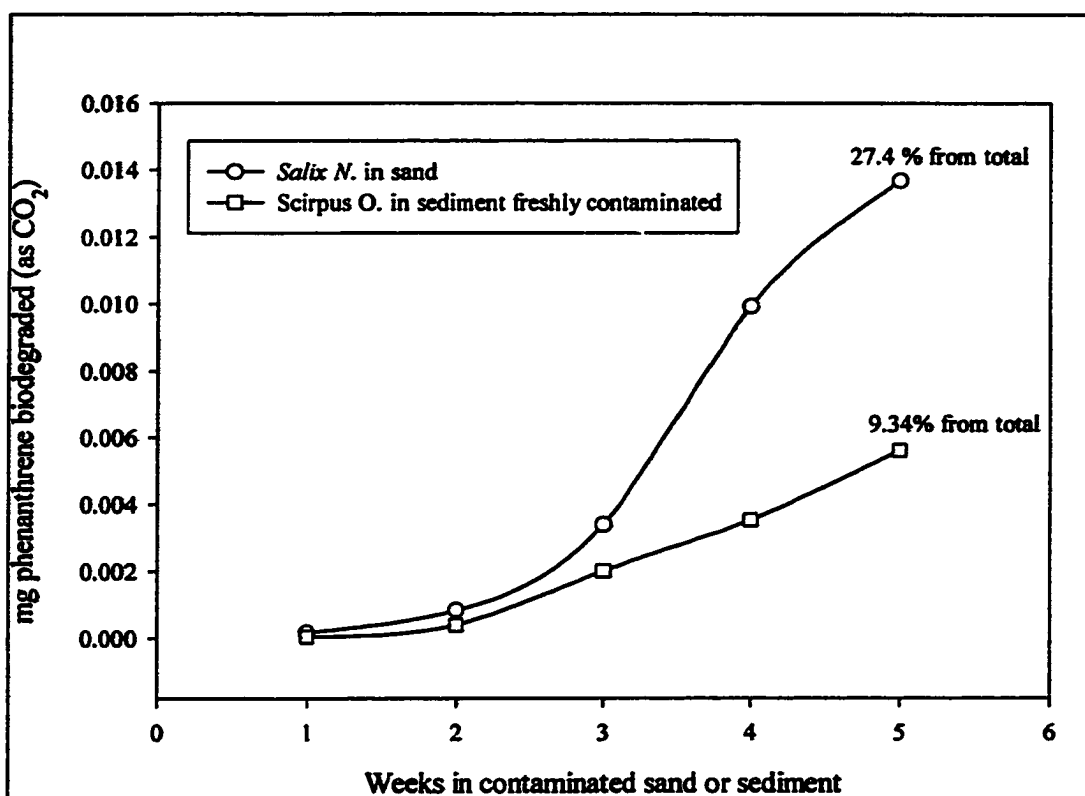


Figure 3.6. Biodegradation in the rhizosphere in two different soils.

Mechanisms for plant uptake of phenanthrene

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.

Uptake from the transpiration stream can be predicted from the following equation:

$$\text{Plant uptake} = TS * TSCF * C$$

where:

Plant uptake = phenanthrene present in the plant (mg)

TS = water uptake (L)

TSCF = 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 and

C = porewater concentration (mg/L)

For TSCF, structure-activity relationships exist for several plants (Briggs et al. 1982), (Burken & Schnoor 1998).

$$TSCF = 0.784e^{\left[\frac{-(\log K_{OW} - 1.78)^2}{2.44} \right]} \quad (\text{Briggs})$$

$$TSCF = 0.75e^{\left[\frac{-(\log K_{OW} - 2.50)^2}{2.4} \right]} \quad (\text{Schnoor})$$

Uptake from sorption can be predicted from a simple partitioning equation:

$$\text{Plant uptake} = S * K_r * C$$

where:

S = root mass (kg)

K_r = root partition coefficient for phenanthrene (L/kg)

C = porewater concentration (mg/L).

A batch measurement of the root-water partition coefficient was conducted for *Salix* and *Scirpus* and is presented in Figure 7. The root-water partition coefficient for phenanthrene was 193.1 L/kg for *Salix* roots and 155.3 L/kg for *Scirpus* roots.

Comparison of the predictive value of the two approaches is presented in Figure 3.8 and 3.9. Because of the relatively high octanol-water partition coefficient, K_{ow} , of phenanthrene, the sorption mechanism is expected to dominate. Clearly, the results from the simple modeling approach demonstrate that uptake can be better predicted from a sorption mechanism. Differences in the observed and predicted values can be due to a number of factors including the distribution and morphology of the root system and the variable surface area not accounted for in the batch measurement. In contrast, the translocation model substantially under-predicted the uptake for most treatments.

Based on these results, it can be hypothesized that "aged" contaminants in sediments with a high proportion of mass in the desorption-resistant phase can be taken up by wetland vegetation, albeit slowly. "Clean" root tissue represents a new organic phase in these sediments to which phenanthrene can partition. Since the sorption mechanism appears to be dominant, plants with very high root mass will be more effective at removing phenanthrene from sediments.

3.4 Conclusions and implications

The study results have implications for the remediation of sediments using vegetation and the fate of contaminants in sediment systems. The effect of sediment-water partitioning on wetland plant uptake of phenanthrene 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.

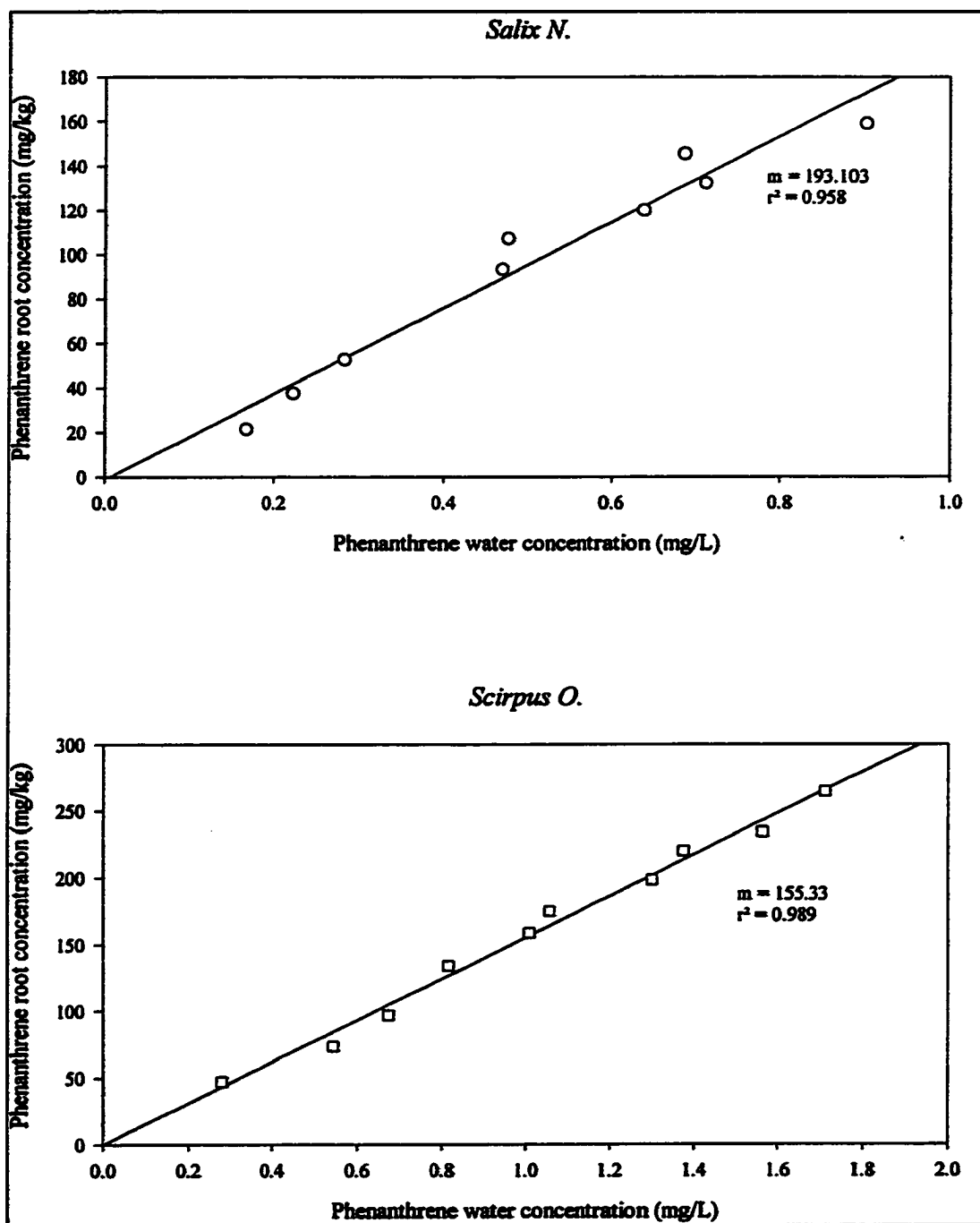


Figure 3.7. Phenanthrene sorption into live roots of the two plant species.

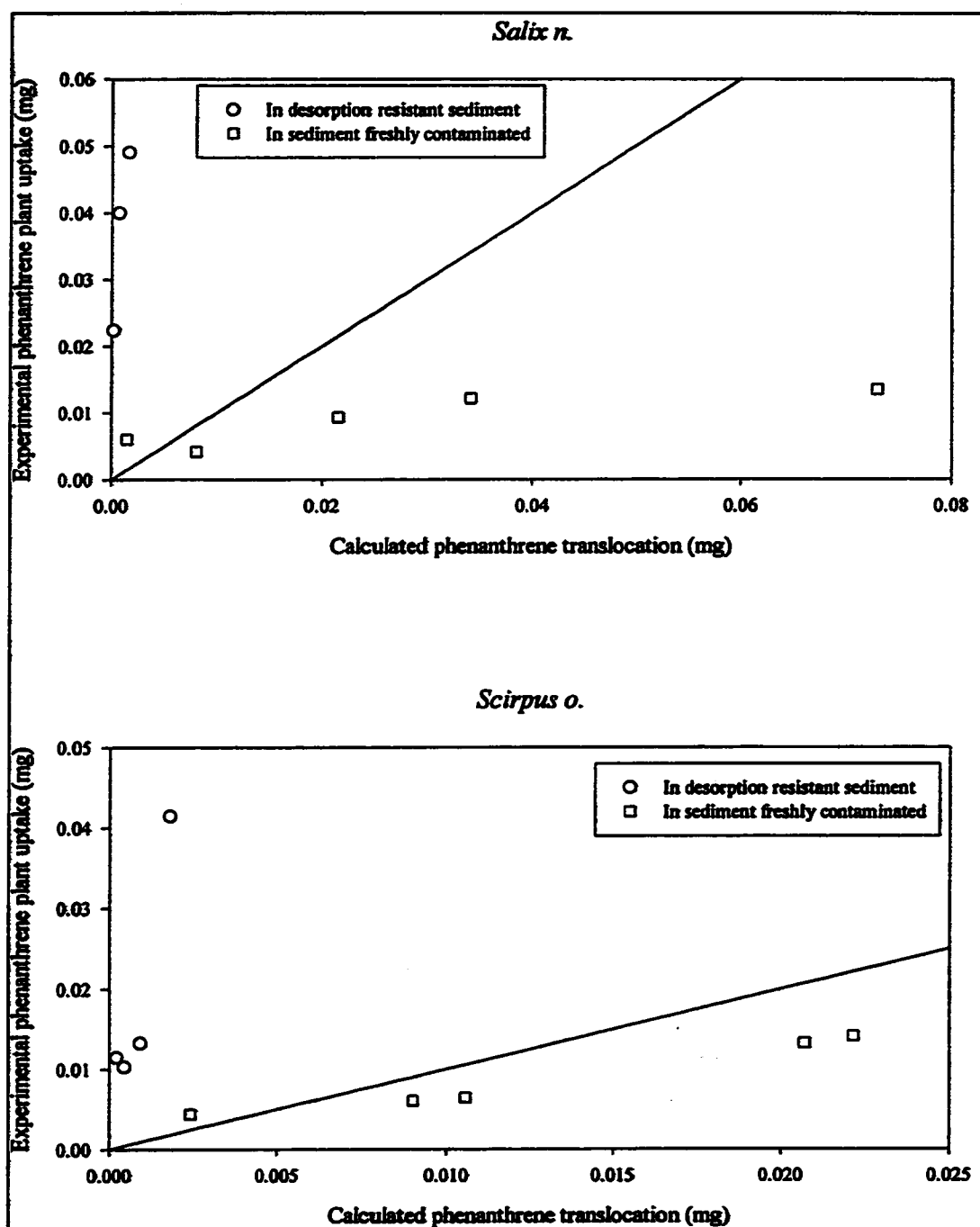


Figure 3.8. Predicted phenanthrene uptake by the translocation model.

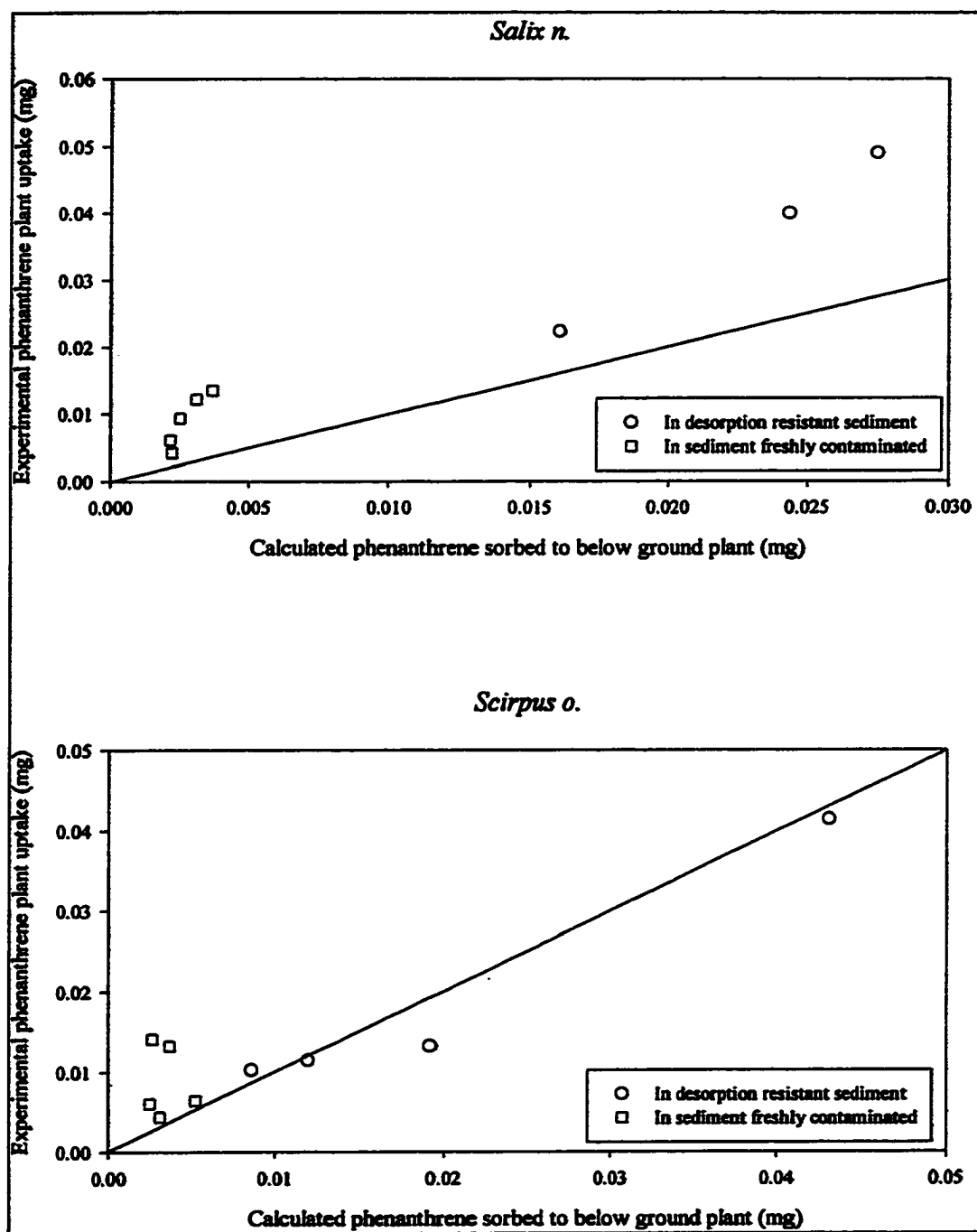


Figure 3.9. Predicted phenanthrene uptake by the sorption model.

Submerged roots and plant stems represent a "clean" organic sorptive phase for phenanthrene. 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.

4. EFFECT OF DESORPTION-RESISTANCE ON WETLAND PLANT UPTAKE OF CHLOROBENZENE AT A LOUISIANA SUPERFUND SITE

4.1 Introduction

Phytoremediation is an emergent *in situ* remediation technology which makes use of plants (trees, grasses and aquatic plants) and their associated rhizospheric microorganisms to remove, degrade, accumulate or stabilize environmental contaminants found in soils, sludges, sediments and waters. Over the past decade, phytoremediation has undergone evolution from an interesting concept into a field-scale remediation technology (Burken, 1998; Glass, 1999). The effectiveness of the technology for organic contaminants is poorly understood. In particular, the relationship between bioavailability and plant uptake of organic contaminants present in the rhizosphere has not been established.

The presence of a desorption-resistance phenomenon for organic compounds from sediments has been observed (Goring and Hamaker, 1972; Karickhoff, 1980; Di Toro, 1982; Pignatello, 1989; Kan et al., 1994, 1994a, 1997). These studies demonstrated that a significant fraction of the contaminant is slowly desorbed from the sediment (i.e., the desorption rate is slower than the adsorption rate). In one explanation, the desorption resistant compartment has a finite capacity and once it is full, adsorption and desorption become completely reversible processes (Kan et al. 1994). If contaminant desorption from this resistant fraction is completely irreversible, or even sufficiently slow, it may be possible to leave the residual in place and save on clean-up costs with no risk to the stakeholders (Wei et al. 1999). Although there is still controversy over the mechanism responsible for

this desorption-resistant fraction, the bioavailability of contaminants found in the irreversible compartment has not been investigated to date for plants.

The bioavailability of "aged" organic contaminants is very important for remediation of waste sites where plant uptake may be a significant fate process. The Petro Processors Inc. site (PPI) is a 77-acre CERCLA facility comprised of two former petrochemical disposal areas situated about 1.5 miles apart. The disposal of organic waste dates back to 1969 at these locations. The sites' principal contaminants are "hex" wastes (hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD)), chlorinated solvents, polycyclic aromatic hydrocarbons (PAH's) and oils. Of recent interest is the remediation of the Devil's Swamp portion of the site, a bottomland hardwood wetland that was impacted by an historical spill (*ca.* 1970) of free-phase waste material containing HCB, HCBD and a variety of other chlorinated and petroleum hydrocarbons. Since this portion of the site is heavily vegetated, wetland plants may play a significant role in the natural attenuation of contaminants at this portion of the site.

The objective of this study was to measure plant uptake of the site contaminant, chlorobenzene from a PPI wetland soil. Two classes of wetland plants, a tree species; black willow (*Salix nigra*) and a sedge; three-square bulrush (*Scirpus olneyi*) were used as model vegetation. A second objective was to compare and contrast uptake from treatments that resulted in different porewater concentrations of chlorobenzene including a treatment that was artificially "aged".

4.2 Materials and Methods

Plants. Two different wetland plant species were used throughout the experimentation: a tree, black willow (*Salix nigra*) and a sedge, three-square

bulrush (*Scirpus olneyi*). The trees used in the experimentation were obtained from cuttings of larger trees, which were grown hydroponically in a greenhouse. The sedges were obtained from a nursery, and from there, a large "stock" population was created, from these, individual plants were transplanted into reactors. The plants remained in the reactors until they showed positive growth, and when at least 15 plants (enough for 5 sampling points with triplicate) showed positive growth, the experiment was initiated.

¹⁴C-labeled and non-labeled chlorobenzene. Radiolabeled chlorobenzene (Sigma Chemical Co. St. Louis, MO., 27 mCi/ mmol) was used as a tracer. The [¹⁴C] compound was further diluted with a non-labeled chlorobenzene solution (Sigma Chemical Co. St. Louis, MO., >99.9%) in the reactors. These two chemicals were used in all three treatments.

Soil Sources. Two different soil types were used in this study: a) commercial silica sand (rinsed with de-ionized water, oven-dried and then autoclaved) and b) soil indigenous to the PPI site. The soil used was collected from a "clean" location at the PPI site. Back in the lab, the soil was dried for about four days at 98 °C, then meshed through a sieve #28, autoclaved and kept in closed containers until needed. One batch of the sediment was contaminated and decontaminated to leave only the desorption-resistant fraction using the isopropanol extraction protocol developed for establishing known amounts of organics in the reversible and irreversible compartments (Liu et al. 2000) and the rest was kept closed until used.

Experimental protocol. Plant uptake reactors similar in design to those described in (Burken & Schnoor 1998) were fabricated for this study. Three different treatments were utilized a) fully available treatment, where a chlorobenzene solution was added to a reactor containing the plant and silica sand. b) a desorption-resistant treatment where chlorobenzene was artificially "aged", and c) a freshly contaminated treatment where the sediment was very recently contaminated with chlorobenzene. For the fully available (sand) experiments, a solution of ^{14}C -chlorobenzene (with the activity shown in Table 4.1) plus non-labeled chlorobenzene dissolved in deionized water (with a final concentration of 11.6 mg/L for *Salix*, and 10 mg/L for *Scirpus*) was added to the lower part of the glass reactors. Following this, a tree or sedge was placed in the lower portion of the reactor and 100 g dry weight of sand 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 prevent any algae 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 followed by a 20 mL 1N NaOH solution to trap CO_2 . When necessary, $\frac{1}{4}$ strength modified Hoagland's solution was added as fertilizer.

For the desorption-resistant treatment, soil from the PPI site was prepared using the following procedure. One kg dry soil was added to a 3 different clean 4L glass pickle jars and then filled all the way to the top with chlorobenzene solution

(100 ppm chlorobenzene solution and 600 μ L 14 C-chlorobenzene). Once all of the jars had been identically prepared, they were thoroughly sealed, the jar exterior was covered with duct tape, and placed on a continuous axial tumbler for one month. After the aging month, the sediment was desorbed using the protocol of (Liu et al. 2000)(Figure 4.1) In short, the extraction procedure was: a). the sediment was extracted with a 50% v/v isopropanol and electrolyte solution (0.01 M NaCl, 0.01 M CaCl_2) for 24 h in a rotary tumbler with a solid/water ratio of 20/80 (wt/wt). b). the slurry was centrifuged at 5,500 rpm for 50 minutes and the supernatant decanted, c). the remaining isopropanol was washed from the soil with electrolyte solution (two times) maintaining the same solid/water ratio described above, d). the entire washing process was repeated. After this procedure, the soil had a load of 10.1 mg/kg of desorption-resistant chlorobenzene, and the concentration in the porewater was 0.007 mg/L. From this sediment, 90 g dry weight was added to the lower portion of the reactor, and spiked with $\frac{1}{4}$ strength Hoagland's solution. The rest of the set-up procedure was the same as for the sand experiment.

For the freshly contaminated treatment, 75 g dry weight clean soil was added to the reactor. This was followed by the chlorobenzene solution (11 and 10.1ppm for *Salix* and *Scirpus* respectively) that was added prior to closing the reactor. Again, the rest of the set-up was the same as for the two previous experiments

At weekly time intervals, three plants of each species were removed from the reactor, the roots leaves and stem separated and cut into small pieces (approximately 0.5 g each) and oxidized to $^{14}\text{CO}_2$ using a biological oxidizer (OX600 R. J. Harvey Instrument Co.) The efficiency of the oxidizer was checked

periodically using ^{14}C -labeled mannitol and was consistently over 90%. To complete the mass balance, the ORBO tube (when available), liquid and sediment remaining in the reactor were also analyzed for ^{14}C . A liquid scintillation counter (LS 6000SC; Beckman Instruments) was used to quantify the ^{14}C present in the solution from the biological oxidizer and from the flasks and NaOH solutions. Based on these measurements "plant uptake" was defined as the measured ^{14}C activity associated with vegetation regardless of the physical mechanism responsible for uptake. "Translocation" was defined as the ^{14}C activity measured in the aboveground plant parts not in direct contact with the sediment or sand that was presumed to have resulted from ^{14}C transport in the transpiration stream of the plant. The "bioavailable" portion of contaminant in this context is the ^{14}C that is taken up by the plant regardless of mechanism and is synonymous with plant uptake.

Table 4.1. Summary of the initial conditions for each experiment.

Type of "soil"	PPI Desorption resistant		PPI Freshly contaminated		Sand	
Plant species	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>	<i>Salix</i>	<i>Scirpus</i>
Grams "soil" dry weight in each reactor	90	90	75	75	100	100
mL of chlorobenzene solution per reactor	0	0	100	100	100	100
Concentration (ppm) of the solution added.	0	0	11	10.1	11.6	10
mg of chlorobenzene per reactor	0.91	0.91	1.1	1.01	1.16	1.0
μCi of ^{14}C chlorobenzene per reactor	0.0177	0.0177	0.025	0.0176	0.0245	0.0177

Biodegradation studies. To confirm that biodegradation was occurring in the rhizosphere, modified Erlenmeyer respirometry flasks were used. These flasks have inside them a 5 mL capacity tube attached to the bottom. The setup was similar to the plant uptake experiments, but in this case, 2 mL 1N NaOH was placed in the inner glass tube so we could trap any CO₂ produced inside the reactor, sampling was also done at weekly intervals.

Sorption experiments. Partition, or sorption to the plant was tested with the following setup: vials with a known amount of live roots were filled with a 10 mg/L chlorobenzene solution, which also included ¹⁴C-chlorobenzene as tracer. After 24 hours in a shaker, the solution was exchanged for a new one and the amount sorbed into the plant was calculated, this procedure was repeated until the uptake showed to have reached a saturation point.

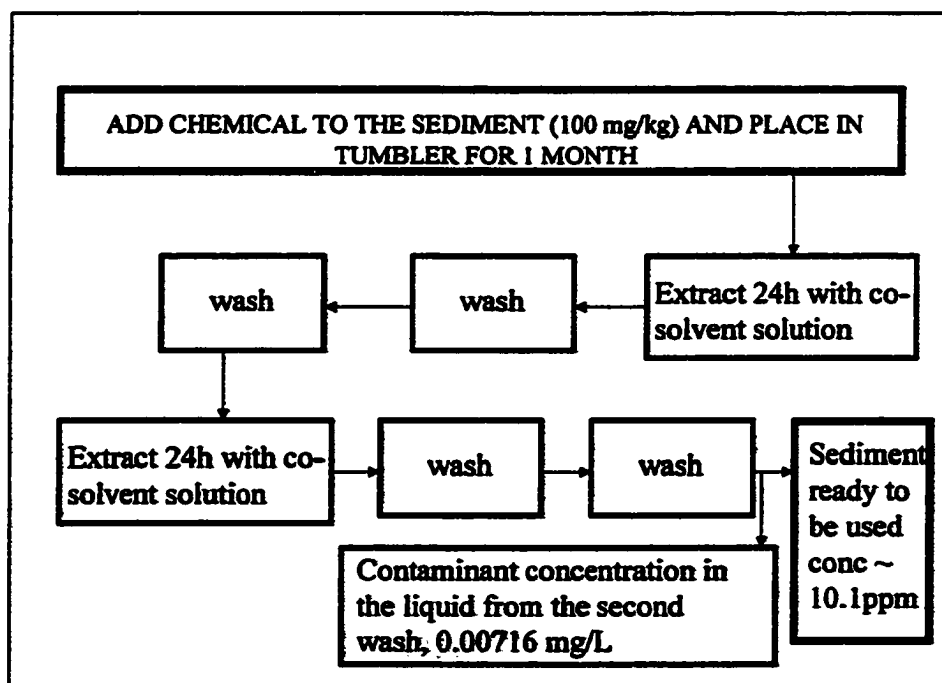


Figure 4.1. Block diagram of the desorption process used to leave only the desorption-resistant fraction of contaminant in the sediment.

4.3 Results and Discussion

Plant uptake of chlorobenzene

The total uptake of ^{14}C -chlorobenzene by both *Salix* and *Scirpus* is shown in Figure 4.2. As defined above, *uptake* is the ^{14}C activity associated with the total plant tissues at any time. Uptake ranged from 1-12% for *Scirpus* and from 1.5-5.5% for *Salix* over the 5 weeks of the study. For both plant species, uptake in the freshly contaminated and the sand treatment decreased over time while uptake in the desorption-resistant treatment increased over time. At the conclusion of the study, uptake was statistically higher in the desorption-resistant treatment. Previous studies with phenanthrene discovered a relationship between porewater concentration and uptake. Based on this the expected uptake order is sand > freshly contaminated > desorption-resistant. In this case, we found the trend to be the opposite with plants grown in the desorption-resistant treatment having statistically higher plant burdens of ^{14}C at the conclusion of the study.

The number of plants that died was 1/15 for each *salix* treatment, and for *Scirpus* in sand. For the rest of the treatments, all plants survived.

Distribution of ^{14}C chlorobenzene in belowground and aboveground plant parts is presented in Figures 4.3 for *Scirpus* and Figure 4.4 for *Salix*. Relatively small differences were observed between *Scirpus* and *Salix* despite differences in water uptake (transpiration rate), contaminant availability and plant morphology. The amount of mass present in the aboveground plant tissues was small compared with the total uptake. Most of the ^{14}C in chlorobenzene was recovered in the belowground plant tissues.

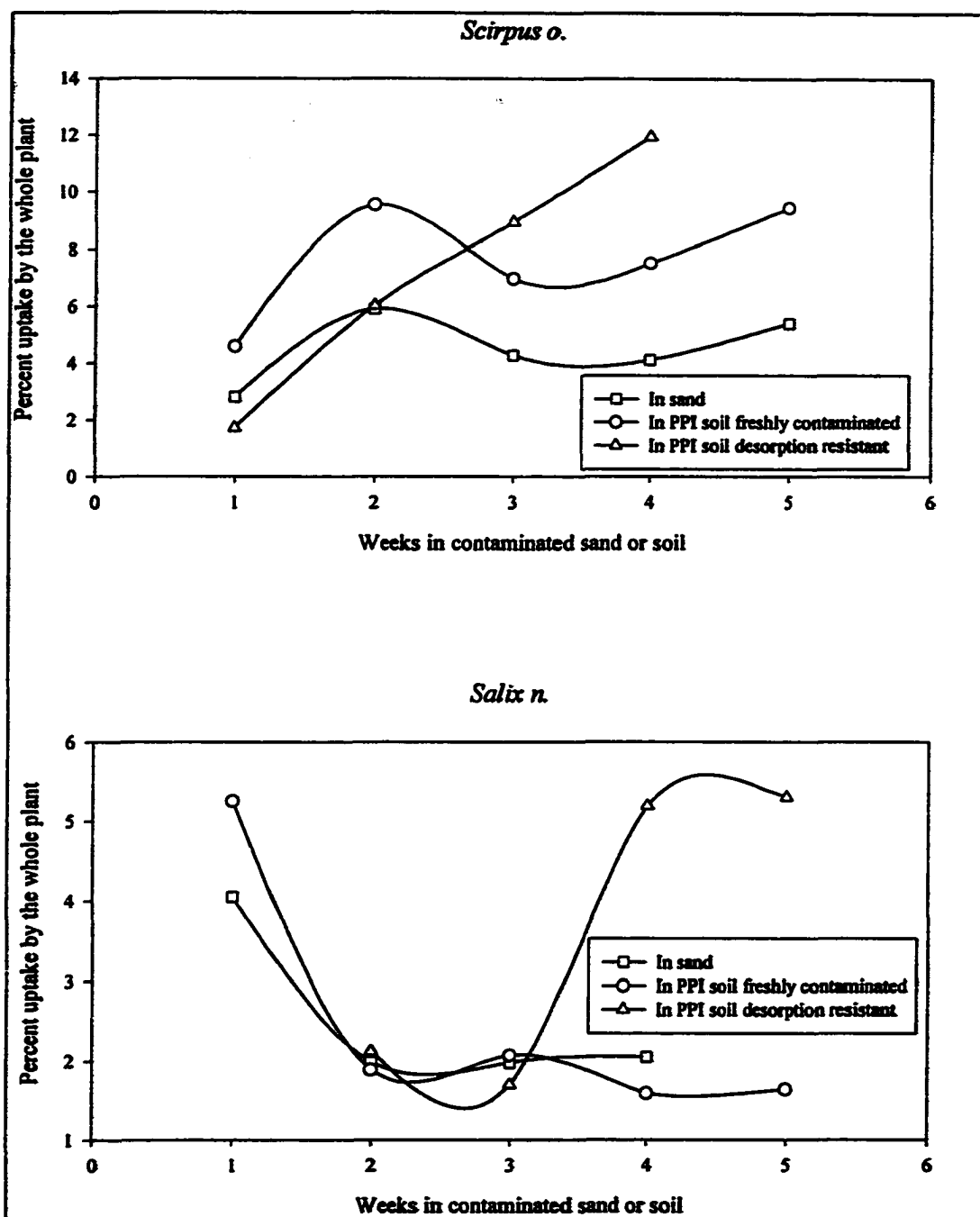


Figure 4.2. Total chlorobenzene uptake (as %) by both plant species in the three different soils.

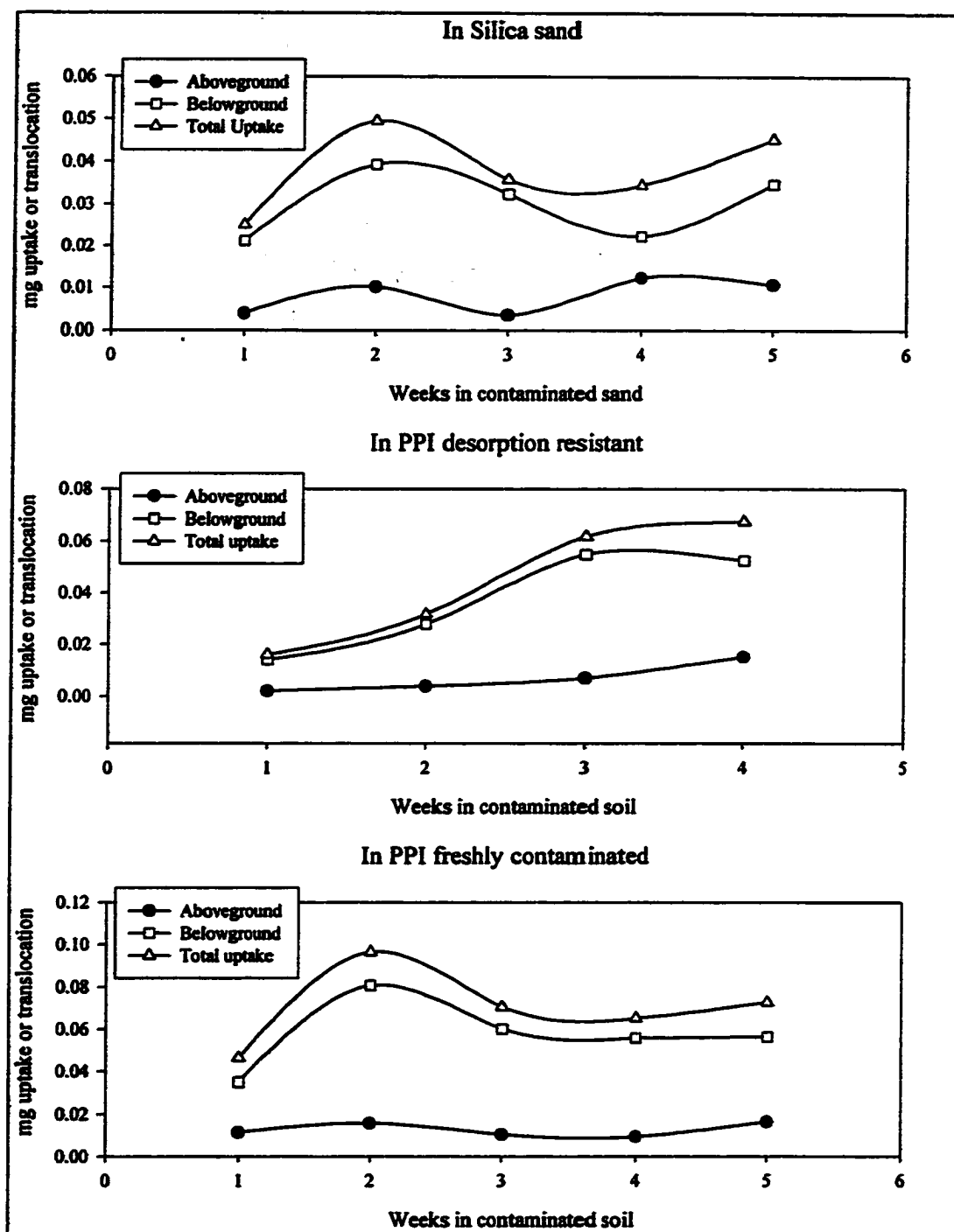


Figure 4.3. Comparison between total chlorobenzene uptake and its translocation above ground by *Scirpus o.* in three different contaminated soils.

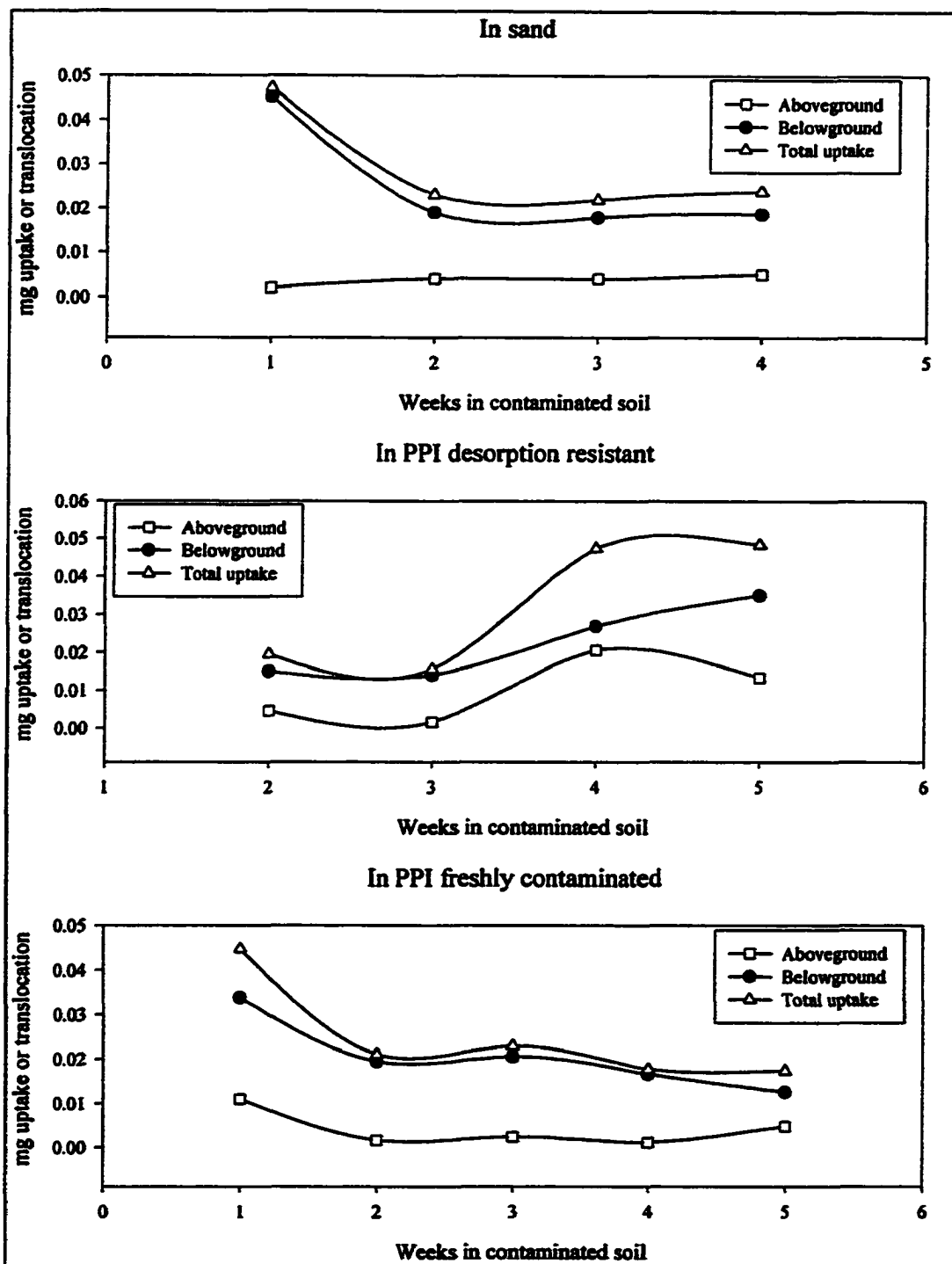


Figure 4.4. Comparison between total chlorobenzene uptake and its translocation above ground by *Salix n.* in three differently contaminated soils.

Mass balance

Mass balances closed very well for the desorption-resistant treatment (78 to 100% recovery) (Table 4.2). For the remaining treatments, mass balances were generally poor ranging from 8 to 75 % recovery). ORBO tubes were used to trap VOCs leaving the top of the reactors on a single treatment (freshly added for *Scirpus*). Since this recovered a large amount of mass (40-60%) it was concluded that volatilization through the plant was a significant mechanism and accounted for much of the missing ^{14}C in the other treatments. Since mass balance was effectively closed in the desorption-resistant treatment, it was concluded that volatilization was not a significant fate mechanism in this treatment. Processes contributing to the mass balance are discussed below.

Table 4.2. Percent CB recovery for all experiments.

	Week 1	Week 2	Week 3	Week 4	Week 5
<i>Salix N. in PPI DR</i> Mean		98.17	91.26	78.49	85.72
Std dev		4.21	5.46	5.05	5.35
<i>Scirpus O. in PPI DR</i> Mean	84.59	102.98	82.74	97.68	
Std dev	3.92	6.40	7.40	9.83	
<i>Salix N. in sand</i> Mean	53.15	19.57	8.79	10.86	
Std dev	41.14	19.98	9.84	12.50	
<i>Scirpus O. in sand</i> Mean	33.32	27.80	27.58	16.91	19.72
Std dev	10.05	6.20	4.01	2.05	2.71
<i>Salix N. in PPI FA</i> Mean	25.07	41.02	32.92	9.51	9.05
Std dev	5.09	7.82	18.11	3.85	3.38
<i>Scirpus O. in PPI FA</i> Mean	63.23	48.66	75.53	38.62	51.58
Std dev	12.05	15.25	7.03	5.27	12.07

Translocation/volatilization

Since aboveground plant parts were not in direct contact with contaminated sediment or water, ^{14}C detected in aboveground plant parts was assumed to be the result of translocation. As expected, ^{14}C in the upper plant parts increased over time as water use proceeded. Overall the ^{14}C present in the above-ground plant tissues

was a small fraction of the total mass balance for all treatments, even though it was concluded that a significant translocation and volatile loss occurred in the experiment (Figures 4.3 and 4.4). Accumulation of ^{14}C in the aboveground portion of the plants was plotted versus water uptake (Figure 4.5). The slope of the curve of accumulation versus water uptake was used as an initial estimate of the concentration of chlorobenzene in transpiration stream of each plant. Slopes ranged from 0.06 mg/L for the desorption-resistant treatment to 2.4 mg/L for the freshly added treatment. Since quantitative structure activity relationships (Briggs et al. 1982; Briggs et al. 1987; Burken & Schnoor 1998) predict that the plant root should not discriminate for compounds like chlorobenzene. Therefore transpiration stream concentrations should mimic measured porewater concentrations relatively closely. In both cases, transpiration stream concentrations predicted from the regressions are greater than the average porewater concentrations (~ 1 mg/L in the freshly added treatment and $7\text{e-}3$ in the desorption-resistant treatment). Additional mass in the aboveground plant tissues strongly suggests a second mechanism such as volatilization of chlorobenzene through the aerenchymal spaces in the wetland plant. Since the VOC volatilized is not included in the calculation, this mechanism may be the dominant mechanism in this system.

VOCs leaving the top of the plants were trapped in a single experiment to better close the mass balance. The amounts trapped are presented in Figure 4.6 and compared with the activity of ^{14}C measured in the aboveground plant parts. The magnitudes of the amount volatilized are similar to the masses remaining in the aboveground plant tissues.

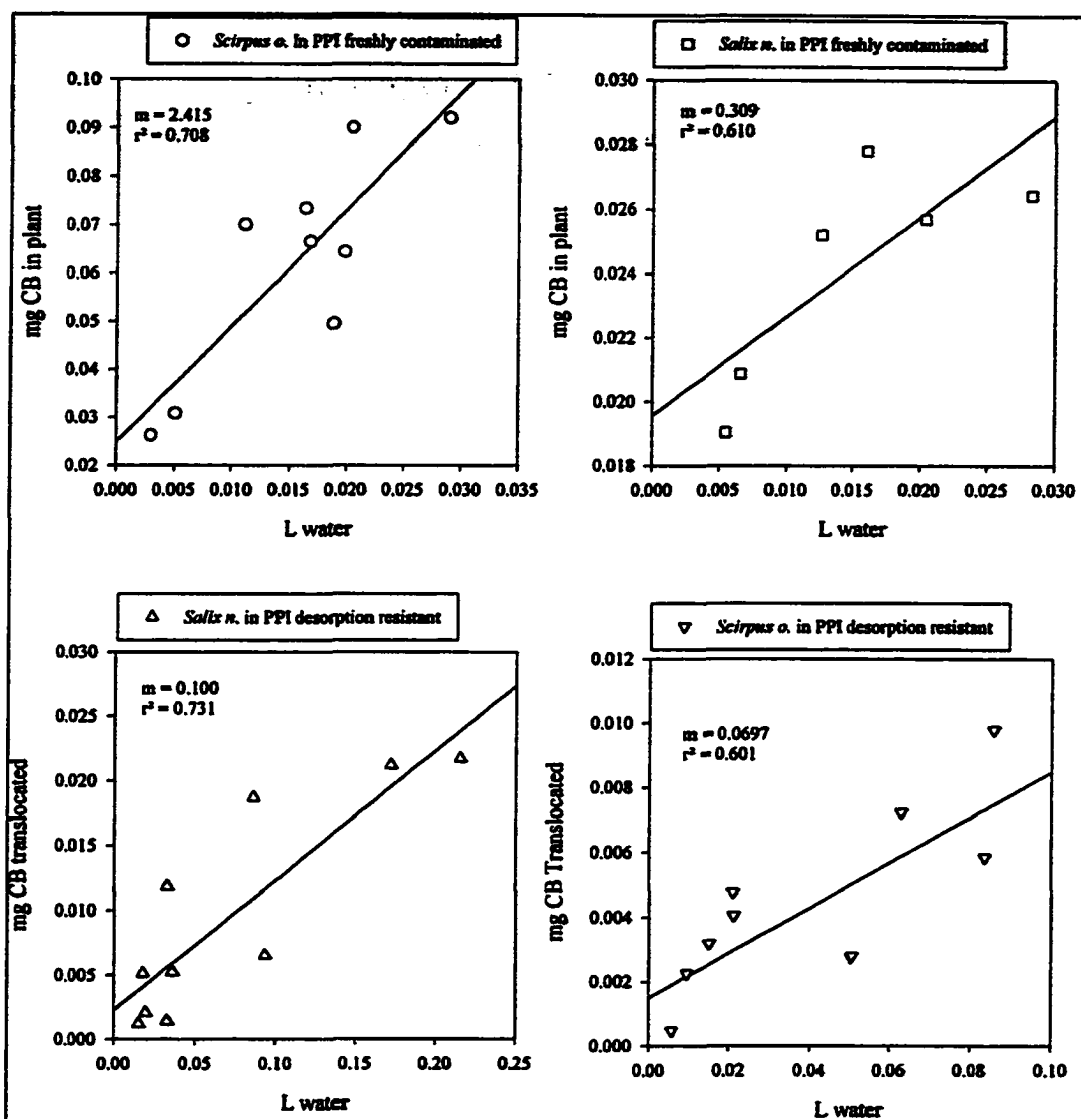


Figure 4.5. Graphic representation of the concentration in the transpiration stream. The line slope is considered to be the chlorobenzene concentration in the transpiration stream (mg/L)

Mineralization

CO₂ leaving the tops of the reactors was continuously trapped in NaOH traps (Figure 4.7). A relatively minor portion (between 0.2 and 4% of the initial load) of the mass was accounted for as CO₂, presumably transpired from the plant. A smaller amount (0.6 to 1.8 %) was measured when traps were placed in the base of

the reactors. This amount was accounted as presumably from microbial biodegradation in the rhizosphere. Based on the similarities between activities of CO₂ in two experiments, it was concluded that microbial degradation in the rhizosphere was responsible. Transport of gases through wetland plants is commonly observed (Grosse & Mevi-Shutz 1987; Mitsch & Gosselink 2000) and the difficulty ensuring a complete seal around a growing plant must be noticed.

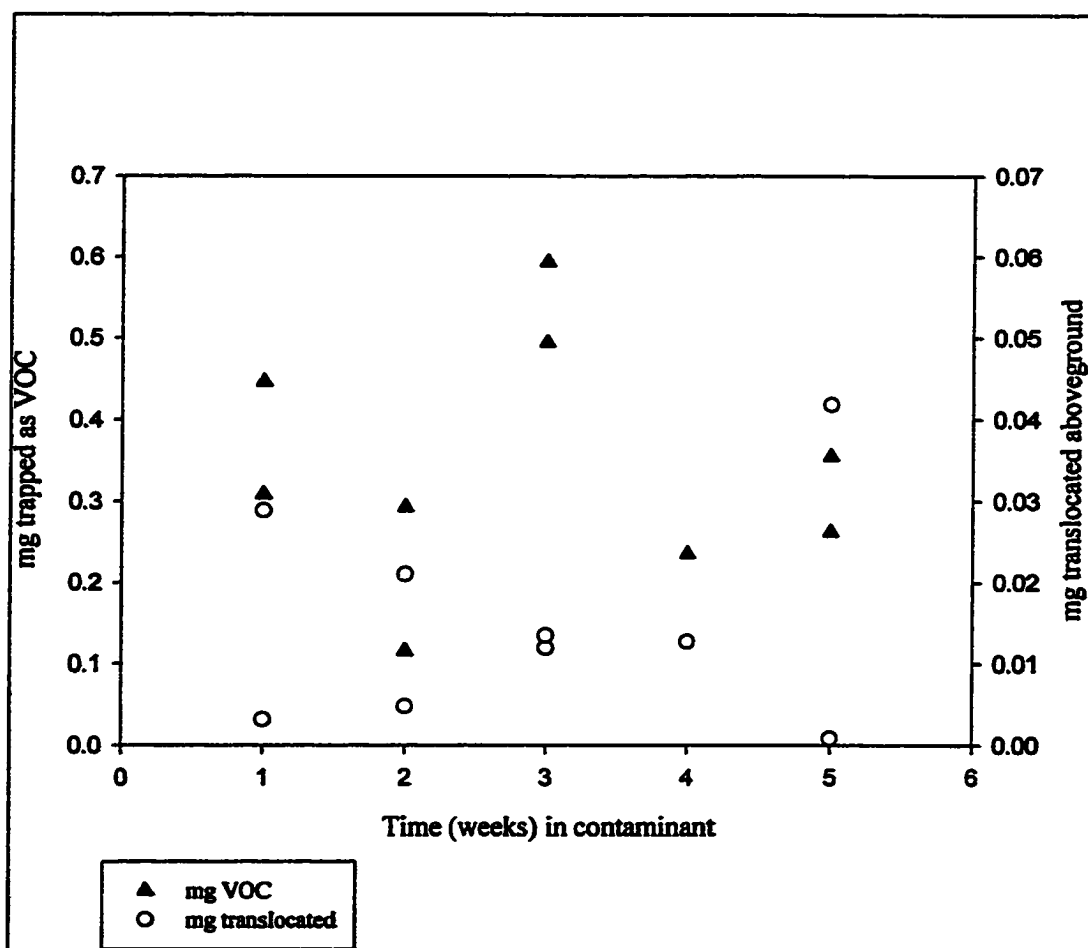


Figure 4.6. Comparison between ¹⁴C detected as VOC (from the ORBO trap) and translocated aboveground for *Scirpus* in PPI freshly contaminated treatment

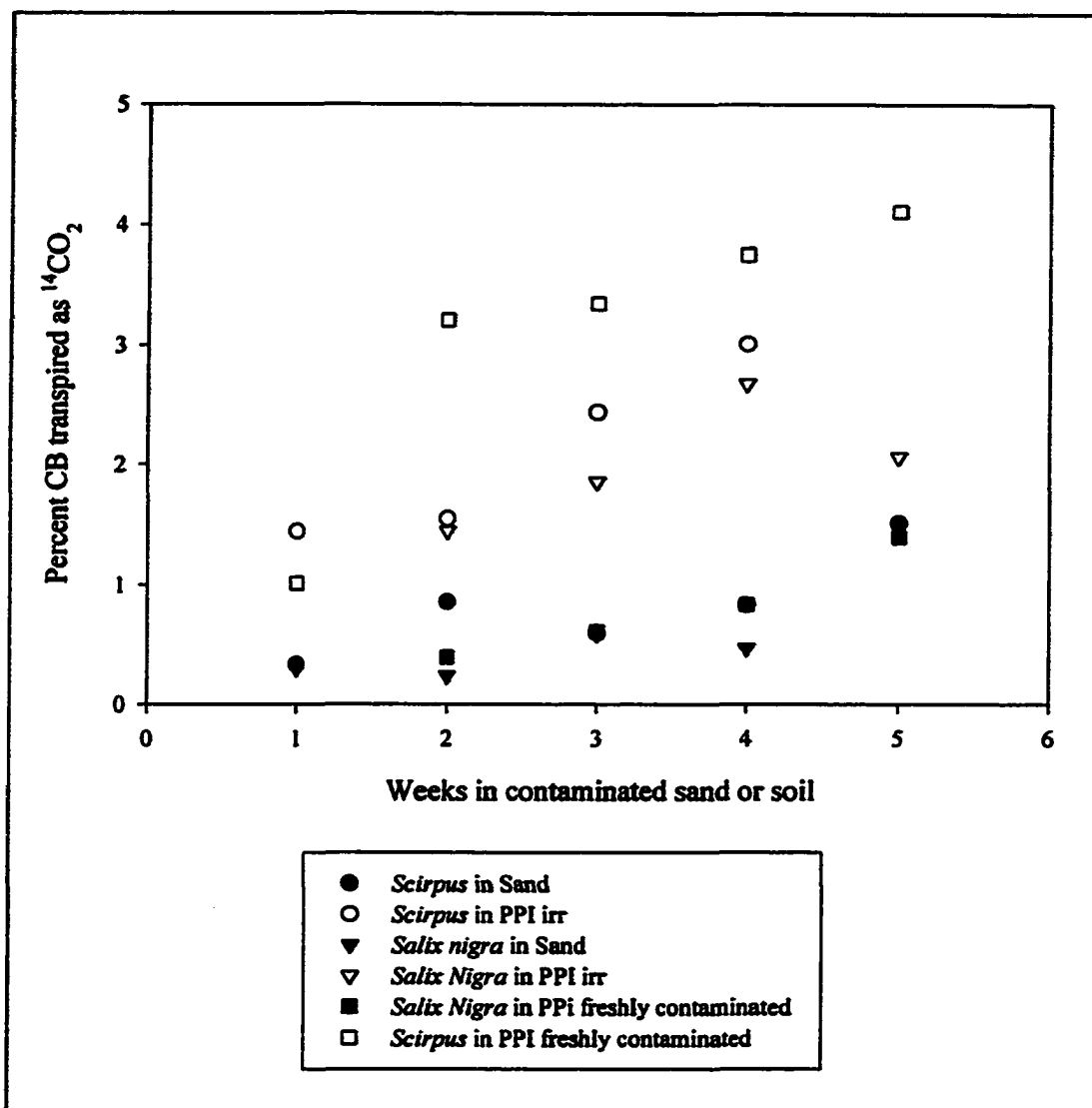


Figure 4.7. Mineralized $^{14}\text{CO}_2$ trapped during chlorobenzene experiments

Mechanisms for plant uptake of desorption-resistant chlorobenzene

Measurements of total uptake and the distribution of ^{14}C in the plant indicate that the majority of mass remaining in the plant 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.

Uptake from the transpiration stream can be predicted from the following equation:

$$\text{Plant uptake} = TS * TSCF * C$$

where:

Plant uptake = chlorobenzene present in the plant (mg)

TS = water uptake in L

TSCF = transpiration stream concentration factor (dimensionless) that is the ratio of the concentration of chlorobenzene in the transpiration stream to the concentration of chlorobenzene in porewater

C = porewater concentration (mg/L)

For TSCF, structure-activity relationships exist for several plants (Briggs et al. 1982; Burken & Schnoor 1998).

$$TSCF = 0.784e^{\left[\frac{-(\log K_{ow} - 1.78)^2}{2.44}\right]} \quad (\text{Briggs})$$

$$TSCF = 0.75e^{\left[\frac{-(\log K_{ow} - 2.50)^2}{2.4}\right]} \quad (\text{Schnoor})$$

Uptake from sorption can be predicted from a simple partitioning equation:

$$\text{Plant uptake} = S * K_r * C$$

where:

S = root mass (kg)

K_r = root partition coefficient for chlorobenzene (L/kg)

C = porewater concentration (mg/L)

A batch measurement of the root-water partition coefficient was conducted for *Salix* and *Scirpus* and is presented in Figure 4.8. The root-water partition coefficient for chlorobenzene was 162 L/kg for *Salix* roots and 138 L/kg for *Scirpus* roots.

Comparison of the predictive value of the two approaches is presented in Figure 4.9 (translocation) and 4.10 (sorption). For the desorption-resistant treatment, the sorption approach predicted the uptake reasonably well while the translocation method underpredicted uptake of the desorption-resistant chlorobenzene. In contrast, the sorption approach *underpredicted* uptake of chlorobenzene in the freshly added treatment for *Scirpus* and *Salix*. The translocation model predicted *Salix* reasonably while overpredicting uptake for *Scirpus*. Again, these graphs include only uptake. Since a significant amount of mass went through the plant in the freshly added treatment, it can be concluded that both models underpredict uptake since they do not consider this third mechanism.

Based on these results, it can be hypothesized that "aged" contaminants in sediments with a high proportion of mass in the desorption-resistant phase can be taken up by wetland vegetation, albeit slowly. "Clean" root tissue represents a new organic phase in these sediments to which chlorobenzene can partition. Since the sorption mechanism appears to be dominant, plants with very high root mass may be ideal agents for phytoremediation of these contaminants. Translocation and volatilization is a real phenomenon for these wetland plant species when the porewater concentration is high. The "driving force" measured as the difference in concentration between the porewater and the root tissue is much higher in the

freshly added treatment, resulting is faster diffusion to the aerenchymal tissues. This may encourage the volatilization observed.

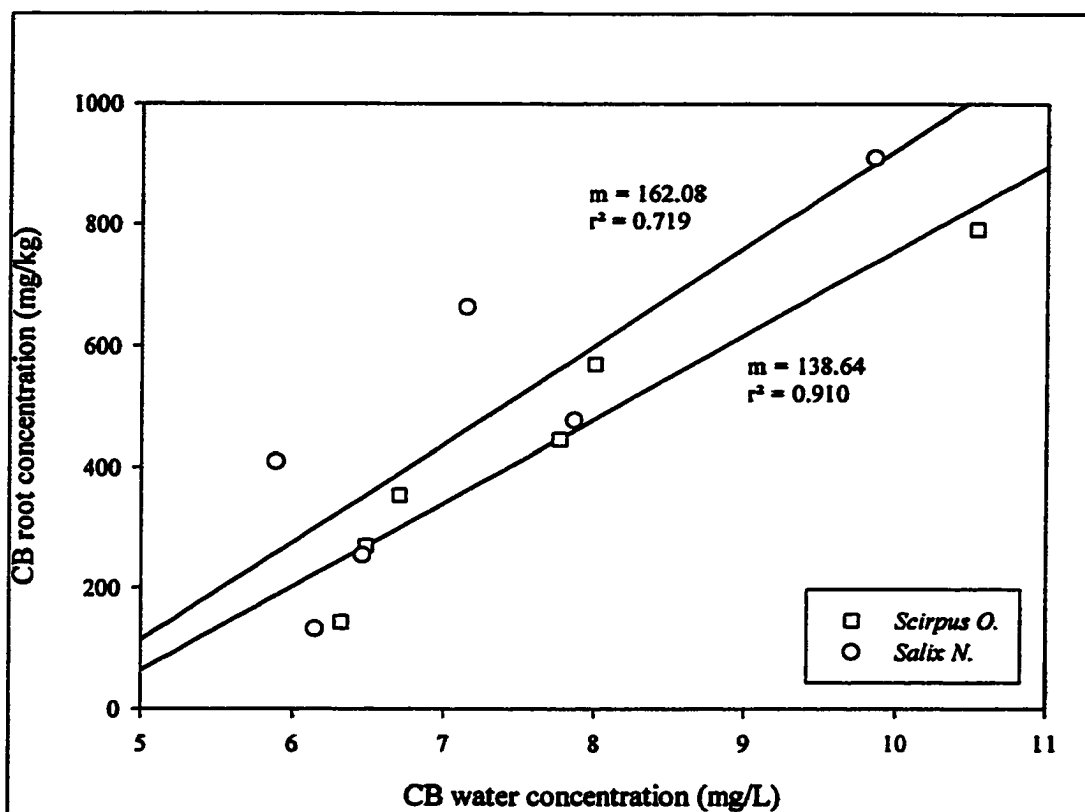


Figure 4.8. Partition of chlorobenzene between plant roots and water.

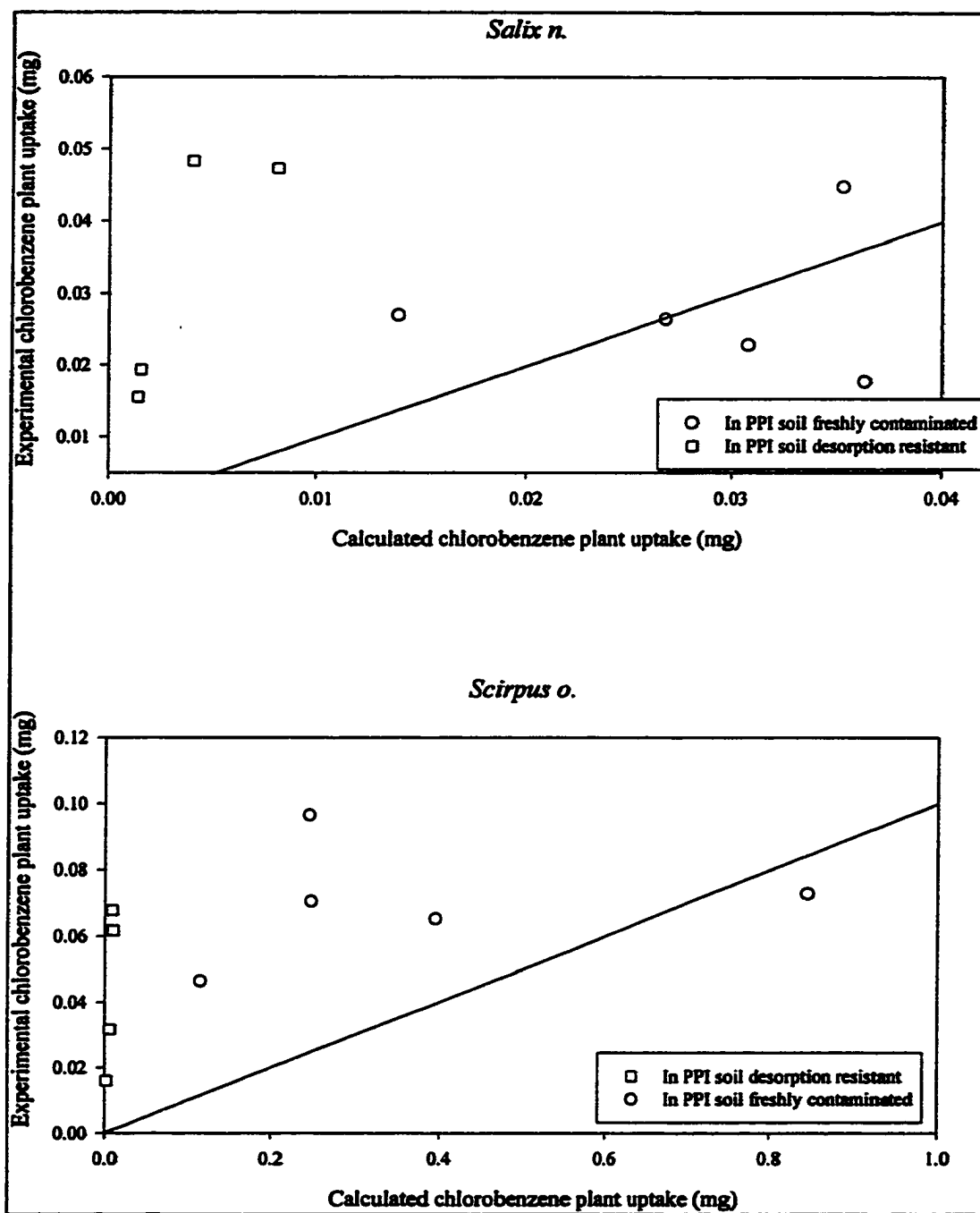


Figure 4.9. Predicted chlorobenzene uptake by the translocation model

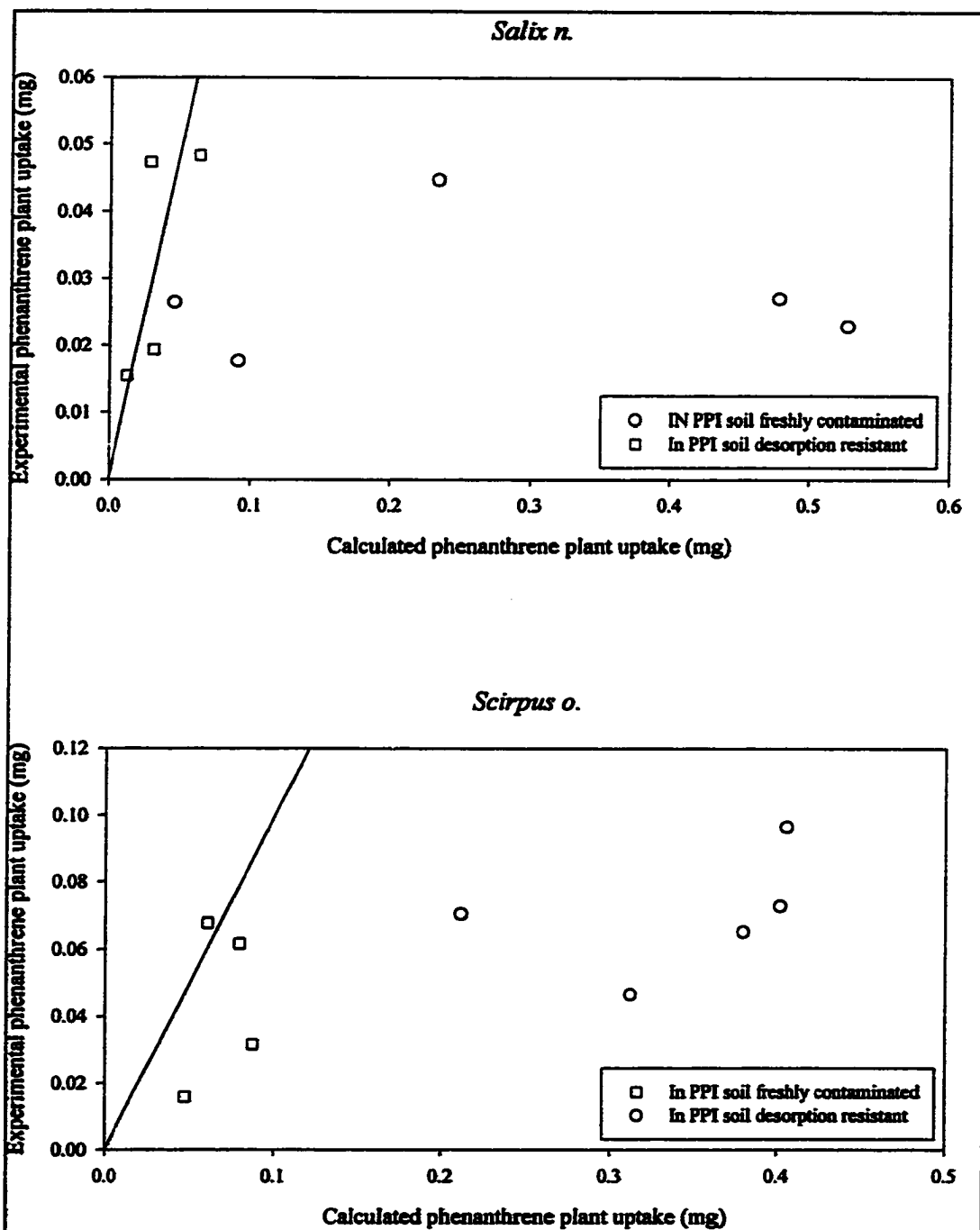


Figure 4.10. Predicted chlorobenzene uptake by the sorption model

4.4 Conclusions

Implications for remediation of the PPI site

Devil's Swamp and the Baton Rouge Bayou area adjacent to the PPI site is characterized by periodically flooded conditions and the swamp is highly vegetated with willow, cypress and various grass and sedge species. Soil is contaminated with concentrations of HCB and HCB_D. Previous studies have documented dechlorination of HCB to chlorobenzene and to CO₂ under anaerobic conditions in Baton Rouge Bayou sediment (Pardue et al. 2001). Chlorobenzene and dichlorobenzenes are routinely detected that were not part of the original waste. There is laboratory and field evidence of ongoing reductive dechlorination of HCB to lower chlorinated benzenes through sequential removal of chlorines.

Structure-activity relationships developed for plant uptake (Burken & Schnoor 1998; Briggs et al. 1982) predict very low potential for translocation of chlorinated benzenes with 3 or more chlorines (Figure 4.11). Utilizing the transpiration stream concentration factor (TSCF), only when mono- and dichlorobenzenes are present does the TSCF exceed 0.5. In other words, at a TSCF of 0.5, the transpiration stream concentration inside the plant is ½ the porewater concentration of the sediment. Dechlorination will have to precede plant uptake and translocation for there to be a significant portion of the HCB waste to be effectively remediated by the existing vegetation.

The effect of desorption resistance or aging is more difficult to predict. Clearly, results indicate that desorption-resistance will slow the plant uptake of chlorobenzene. In some respect this may be valuable since it also slows the

volatilization of chlorobenzene. Even though the existing spill is over 30 years old, it is not known whether the lower chlorinated benzenes are present in an aged state. The presence of lower chlorinated benzenes in surface sediments in the swamp strongly suggests relatively recent dechlorination, since these compounds are relatively poorly sorbed and volatile. Periodic flooding by the Mississippi River would rapidly deplete these lower chlorinated benzenes from sediments. Results demonstrate that regardless of their partitioning in sediments, chlorobenzene is accessible by vegetation types present in Devil's Swamp. Coupled dechlorination and plant uptake may represent an important component of the natural attenuation of this contaminated wetland.

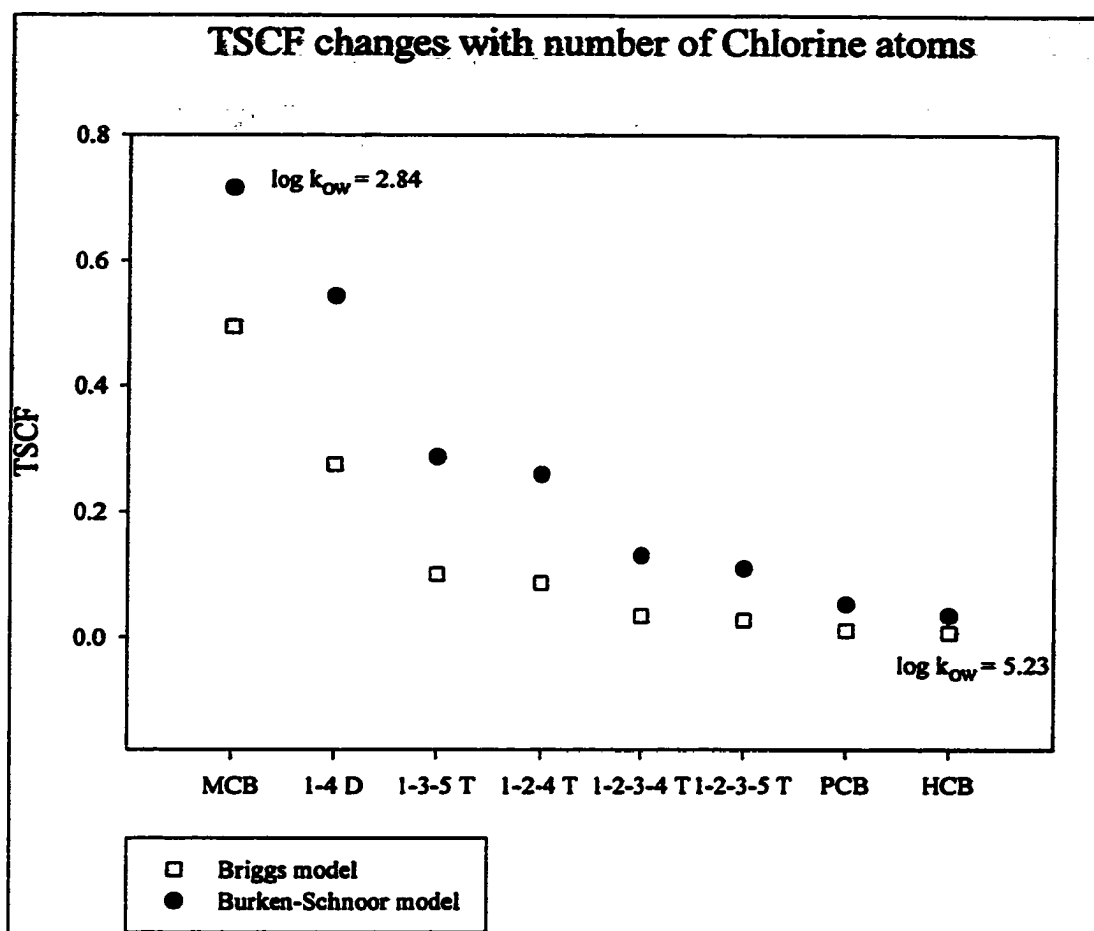


Figure 4.11 Changes in the TSCF calculated from the equations proposed by (Briggs et al. 1982) and by (Burken & Schnoor 1998).

5. DEVELOPMENT OF A MATHEMATICAL MODEL RELATING DESORPTION RESISTANCE TO PLANT UPTAKE

5.1 Introduction

One of the most important factors affecting the fate of organic chemicals in sediment/water systems is their chemical interactions with both mineral and organic portions of the sediment (Luthy et al. 1997). These interactions, which include mechanisms as adsorption, partitioning and diffusion-limited mass transport result in strong binding and extremely slow release rates (Luthy et al. 1997; Pignatello 1989; Kan et al. 1994). These extremely slow release rates, have suggested sorption irreversibility or hysteresis of organic compounds from sediments (Goring & J.W. Hamaker 1972; Karickhoff 1980; Di Toro & Horzempa 1982; Pignatello 1989; Fu et al. 1994; Kan et al. 1994; Kan et al. 1997). In other words, the hysteresis phenomenon suggests that a significant fraction of the contaminant is slowly desorbed from the sediment (i.e., desorption rate is slower than the adsorption rate). An understanding of contaminant sequestration is necessary to better predict the fate, availability and sediment toxicity of organic chemicals. This will yield a better basis to assess exposure risk, and to define more realistic remediation endpoints.

For long time, investigators have reported equations useful to correlate the plant uptake of ions from external solutions, Russell (Russell & Shorrocks 1959) defined the transpiration stream concentration factor (TSCF) for barley and sunflower plants in rubidium and phosphate solutions as follows:

$$TSCF = \frac{\text{Concentration of ion in transpiration stream}}{\text{Concentration of ion in external solution}} \quad (1)$$

In 1974, Shone (Shone & Wood 1974) moved ahead the TSCF concept from inorganic ions to herbicides and a fungicide, they also introduced the root concentration factor (RCF) concept:

$$RCF = \frac{\mu\text{g compound / g fresh weighth root}}{\mu\text{g compound / ml ambient solution}} \quad (2)$$

The importance of the RCF over the TSCF concept is that it can be shown that some saturation of the roots is necessary before the maximum value of TSCF can be reached, and as shown by Shone, the concentration in the root of most of the chemicals exceeded the concentration in the surrounding medium. The authors suggested the possibility of sorption into cell constituents for this increased value. From the chemicals reported in the work by (Shone & Wood 1974), all the compounds, except 2,4-dichlorophenoxyacetic acid (2,4-D), showed a TSCF value less than one, as compared to those previously reported for inorganic ions obtained by Russell, which ranged from 0.3 to 155.7 (with 60 different values in this range).

In another work presented by Shone (Shone et al. 1974), the compounds were characterized as lipophilic and lipophobic, and they concluded that the lipophilic compounds are able to penetrate the cortical cells of the root and could reach the shoots more easily than the lipophobic compounds which may be confined to the free space in the roots. Taking these correlations and concepts a step further,

(Briggs et al. 1982) presented an equation to relate the plant uptake to the n-octanol/water partition coefficient, K_{ow} as follows:

$$TSCF = 0.784 e^{\left[\frac{-(\log K_{ow} - 1.78)^2}{2.44} \right]} \quad (3)$$

The empirical equation 3 was developed for Barley, and has an uptake optimum for slightly lipophilic compounds whose $\log K_{ow} = 1.78$.

The transpiration stream concentration factor (TSCF), controls the amount of a given compound that can be taken into the plant and further transported along the xylem. The TSCF concept has been used to estimate plant uptake based on the fugacity of the chemical in the soil and shoot. With the maximum concentration of the transpiration stream being that of the water (Z_w), the contaminant flux into shoots (N_{Rsh}) can be calculated with the following equation given by (Trapp et al. 1990):

$$N_{Rsh} = TST \cdot TSCF \cdot Z_w \cdot (f_s - f_{sh}) \quad (4)$$

where:

TST = transpiration stream (m^3/s),

f_s = fugacity of the soil,

f_{sh} = fugacity of the shoot.

Numerous fully developed mathematical models exist for the plant uptake of organic compounds (Dowdy & McKone 1997; Burken & Schnoor 1996; Burken & Schnoor 1998; Trapp et al. 1994; Trapp & McFarlane 1995; Trapp & Matthies 1995; Boersma et al. 1988; Behrendt & Brüggemann 1993; Chang & Corapcioglu

1998 among others). An excellent example is the model by (Trapp & McFarlane 1995), which is an extensive report on modeling and simulation exploring all the possible transport mechanisms from root uptake to transpiration from leaves, as well as the metabolic pathways of contaminants. This work provides simple equations to evaluate the uptake of contaminants in soil by roots, the root concentration factor (RCF), the translocation from roots to shoots, the movement within shoots as well as the transpiration from leaves among other transport mechanisms.

Using equation 3 and partition coefficients as the one shown in equation 5, (Behrendt & Brüggemann 1993) studied the fate of three pesticides in plants with $\log K_{ow}$ values ranging from an almost optimum for equation 1 (1.82) up to 3.06 which is approaching the end of the effective uptake zone proposed by equation 1.

These authors used a system of simulation models called SNAPS (Simulation model network atmosphere-plant-soil). Their results show that after 3-4 months, less than 1% of the applied pesticide should remain in the plants while the rest was either degraded by the plant or volatilized.

$$K_{LA} = \frac{(WC + L_p (K_{ow})^b \rho_l)}{(\rho_w K_{aw})} \quad (5)$$

where:

K_{LA} = Partition coefficient leaf/atmosphere

WC = water content of the leaf

L_p = Lipid fraction of the leaf

ρ = Density

K_{AW} = Partition coefficient air/water

Boersma (Boersma et al. 1988) produced a multi-compartmental theoretical model for the coupled transport of water and organic solutes based on transport (and further equilibrium) across simple thin membranes, this model describes the mechanisms that control uptake, accumulation, and degradation of xenobiotic organic chemicals in terrestrial plants. A drawback of this model is that some anatomical properties of leaf and root tissues for each particular plant are needed as show in equation (6).

$$\frac{dM_1}{dt} = \left(\frac{D_1}{\Delta x_1} \left\{ K_{1,1} C_0 - K_{1,2} \frac{M_1}{V_1(1+B_1)} \right\} + K_{1,1} q_1(1-\sigma_1)C_0 + J_s \right) A_1 - \left(\frac{D_2}{\Delta x_2} \left(K_{2,1} \frac{M_1}{V_2(1+B_2)} \right) + K_{3,1} q_2(1-\sigma_2) \frac{M_1}{V_1(1+B_1)} \right) A_2 - \lambda_1 V_1 \frac{M_1}{V_1(1+B_1)} \quad (6)$$

Instantaneous time rate of change of chemical in mass in compartment 1 ($\mu\text{g} / \text{h}$)	=	Mass transport of chemical into compartment 1 via diffusive and mass flow, from compartment 0 ($\mu\text{g} / \text{h}$)	-	Mass transport of chemical out of compartment 1 via diffusive and mass flow, to compartment 2 ($\mu\text{g} / \text{h}$)	-	All first order loss processes that occur in compartment 1 ($\mu\text{g} / \text{h}$)
---	---	--	---	--	---	---

Where:

0 = Soil

1 = Root apoplast

2 = Root symplast

3 = Root xylem

A_i = Contact area between compartments (cm^2)

B_i = Sorption coefficient for compartment i (dimensionless)

C_i = Solute concentration in compartment i (mol/cm^3)

J_s = Rate of active uptake of solute (s^{-1})

$K_{i,1}$ = Partition coefficient for transport into compartment i ; is the ratio solubility in the membrane/solubility in water (dimensionless)

$K_{i,2}$ = Partition coefficient for transport out of compartment i (dimensionless)

M_i = Mass of solute in compartment i (g)

V_i = Volume of compartment i (cm^3)

q_i = Flux ($\text{cm}^3/\text{cm}^2 \text{ s}$)

Δx_i = Thickness of membrane separating compartments (cm)

σ_i = Reflection coefficient for compartment i (dimensionless)

λ_i = Rate constant for first order processes in compartment i (s^{-1})

A root growth model has been presented by (Chang & Corapcioglu 1998) for nonvolatile hydrocarbons. This model suggests that plant characteristics (such as root radius), are more important than contaminant properties for a phytoremediation operation.

Burken (Burken & Schnoor 1997) studied the uptake and further metabolism of Atrazine using poplar trees. A mathematical model was developed to estimate the rate constants for the degradation mechanism they proposed. The following two equations presented by the authors can be used to calculate the atrazine concentration in bulk pore water solution and in poplar leaf tissue:

$$\left(\frac{d[Atra]_w}{dt} \right) = -k_{1w}[Atra]_w - k_{2w}[Atra]_w - k_{3w}[Atra]_w - TSCF_{Atra} \frac{T[Atra]_w}{V_w} - k_s \left([Atra]_w - \frac{[Atra]_{RS}}{RCF} \right) \quad (7)$$

$$\left(\frac{d[Atra]_L}{dt} \right) = \frac{T[Atra]_R}{V_L} - k_{1L}[Atra]_L - k_{2L}[Atra]_L - k_{3L}[Atra]_L \quad (8)$$

where:

W = pore water/bulk solution

R = root xylem

RS = root surface

L = leaf

T = time (days)

(Trapp & Matthies 1995) showed an analytical solution (with sample calculations) for plant uptake considering uptake from soil, gaseous deposition, leaves transpiration, degradation, and tree growth as a "one compartment" calculation.

An empirical fugacity-based model to predict uptake by leaves of organic chemicals in gaseous phase is presented by (Paterson & Mackay 1991) this model is based in the octanol-air and water-air partition coefficients for the chemical.

Equation 9 is the model equation they proposed to calculate the uptake.

$$BCF_v = 0.19 + 0.7K_{WA} + 0.05K_{OA} \quad (9)$$

where:

BCF_v = Ratio of volumetric concentrations $\frac{g/m^3 \text{ wet leaf}}{g/m^3 \text{ air}}$

K_{WA} = Water-air partition coefficient

K_{OA} = Octanol-air partition coefficient

All the previous models have in common the assumption that the contaminants in soil are fully available and reversible bound (or they have been developed under hydroponic conditions). No model has been developed which describes the relationship between desorption-resistance of organics in the sediment/soil and plant uptake. We are introducing a model to predict plant uptake of chemicals found in the desorption-resistant compartment of the sediment. This model combines concepts of desorption-resistance and plant uptake of organic contaminants in a unique equation.

5.2. Model Development

Once sediment is contaminated and the contaminant is sorbed, three mechanisms or processes have to occur in order for a contaminant to be taken up by plants:

- 1) Desorption from the sediment and the pore water**
- 2) Sorption to the roots from the porewater**
- 3) Translocation of the contaminant to the aboveground portion of the plant.**

From the three previous processes, is obvious that if we want to predict the whole plant uptake of a given chemical, the model has to include a translocation term and a sorption term.

a) Sediment sorption model

A linear isotherm with the following equilibrium expression is assumed to model the reversible sorption of chemicals to sediments:

$$q = K_p C \quad (1)$$

where:

q ($\mu\text{g/g}$) = concentration of sorbed compound in the solid phase,

C ($\mu\text{g/mL}$) = solution phase concentration,

K_p = linear partition coefficient (mL/g)

Considering a labile (readily desorbed or reversible) and a non-labile phase (slow-desorbing phase or irreversible), a biphasic irreversible adsorption model has been proposed by (Kan et al. 1997):

$$q = q^{rev} + q^{irr} \quad (2)$$

where:

q^{rev} ($\mu\text{g/g}$) = the concentration of sorbed compound in the labile (or reversible) fraction

q^{irr} ($\mu\text{g/g}$) = the concentration of sorbed compound in the desorption-resistant (or "irreversible") fraction.

The sorption to the labile (readily desorbing) compartment is described by a linear isotherm:

$$q^{rev} = K_p C \quad (3)$$

where:

K_p (mL/g) = linear partition coefficient

C (μg/mL) = solution phase concentration.

If equation 3 is normalized to the organic carbon content in sediment we obtain:

$$q^{rev} = K_{oc} \cdot OC \cdot C \quad (4)$$

where:

K_{OC} (mL/g) = organic carbon normalized partition coefficient ($=K_p/OC$)

OC = organic carbon content (as a fraction)

The sorption to the non-labile (desorption-resistant, or slow-desorbing) fraction is represented by a Langmuir-type sorption isotherm:

$$q^{irr} = \frac{K_{oc}^{irr} \cdot OC \cdot q_{max}^{irr} \cdot f \cdot C}{q_{max}^{irr} \cdot f + K_{oc}^{irr} \cdot OC \cdot C} \quad (5)$$

Combining the linear sorption isotherm for labile fraction and the Langmuir-type sorption isotherm for the desorption-resistant (non-labile, or slow-desorbing) fraction yields:

$$q = K_{oc} \cdot OC \cdot C + \frac{K_{oc}^{irr} \cdot OC \cdot q_{max}^{irr} \cdot f \cdot C}{q_{max}^{irr} \cdot f + K_{oc}^{irr} \cdot OC \cdot C} \quad (6)$$

where:

K_{oc}^{irr} (mL/g) = partition coefficient of the desorption-resistant fraction

f = fraction of the compound residing in the desorption-resistant compartment
(percentage of the compartment that has been filled)

q_{\max}^{irr} ($\mu\text{g/g}$) = maximum capacity of the desorption-resistant fraction.

A semi-empirical relationship was obtained to represent q_{\max}^{irr} by (Kan et al. 1998):

$$q_{\max}^{irr} \approx A \cdot K_{ow}^n \quad (7)$$

where:

$$A = 37765 \cdot OC$$

K_{ow} = octanol/water partition coefficient

$$n = -0.23$$

The second term on the right-hand side of Eq. (5) can be rearranged as a Langmuir isotherm:

$$q^{irr} = \frac{bQ^o C}{1 + bC} \quad (8)$$

where:

$$Q^o = q_{\max}^{irr} f \quad (9)$$

When the aqueous solution concentration, C ($\mu\text{g/mL}$) is relatively large, the second term becomes a constant, q_{\max}^{irr} . If C is small, the second term reduces to $K_{oc}^{irr} \cdot OC \cdot C$.

b) Plant uptake model; translocation term

Numerous models to predict plant uptake exist, however, no model has been developed to describe the relationship between the desorption-resistant contaminants in the sediment and plant uptake. To date, all models have assumed that sorbed organics in the sediment are completely reversible. In this approach, the Kan-Tomson model for sorption irreversibility (Kan et al. 1998) and the Schnoor-Burken structure-activity relationship (Burken & Schnoor 1998) are coupled to model plant uptake from desorption-resistant fraction.

Considering only the desorption-resistant phase, Eq. (2) becomes:

$$q^{irr} = \frac{K_{oc}^{irr} \cdot OC \cdot q_{max}^{irr} \cdot f \cdot C^{irr}}{q_{max}^{irr} \cdot f + K_{oc}^{irr} \cdot OC \cdot C^{irr}} \quad (10)$$

After simple algebraic operations, the bulk solution concentration for the reversible and irreversible phase can be defined as:

$$C_{bulk\ solution}^{irr} = \frac{q^{irr} \cdot q_{max}^{irr} \cdot f}{K_{oc}^{irr} \cdot OC \cdot q_{max}^{irr} \cdot f - q^{irr} \cdot K_{oc}^{irr} \cdot OC} \quad (11)$$

$$C_{bulk\ solution}^{rev} = \frac{q^{rev}}{K_{oc} \cdot OC} \quad (12)$$

From the transpiration stream concentration factor (TSCF) defined by (Russell & Shorrocks 1959), we get:

$$TSCF = \frac{C_{transpiration\ stream}}{C_{bulk\ solution}} \quad (13)$$

where:

$C_{Transpiration\ stream}$ can be estimated from the slope of figures 3.4 and 4.5

$C_{bulk\ solution}$ can be estimated from equation 11

Plant uptake has been defined by (Burken & Schnoor 1998) to be directly proportional to TSCF, the amount of water transpired and the porewater concentration:

$$Plant\ uptake\ (mg) = TSCF \cdot Trans \cdot C_{bulk\ solution} \quad (14)$$

where:

Trans = amount of water transpired (L).

According to (Burken & Schnoor 1998) plant uptake between time 1 and time 2 can be defined as:

$$Plant\ uptake_{t1-t2} = TSCF \cdot Trans_{(t1-t2)} \cdot \frac{(C_{bulk\ solution,t1} + C_{bulk\ solution,t2})}{2} \quad (15)$$

where:

$C_{bulk\ solution}$ = concentration in bulk solution, (mg/L).

c) Plant uptake model; sorption term

Equation 15, predicts the plant uptake, but it considers that the contaminant has already been sorbed by the plant roots and that it also has already passed all the

cell walls and membranes separating the external solution from the stem xylem solution, thus another term which will consider sorption into the roots is needed for a better prediction of the total plant uptake from a desorption resistant sediment, the term is:

$$Uptake\ due\ to\ sorption = r_m \cdot K_r \cdot C_w \quad (16)$$

where:

r_m = mass of roots (kg)

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

C_w = Bulk water concentration (according to equation 11)

Adding equations 15 and 16 we get the predicted plant uptake due to translocation and sorption:

$$Plant\ uptake_{t1-t2} = TSCF \cdot Trans_{(t1-t2)} \cdot \frac{(C_{bulk\ solution, t1} + C_{bulk\ solution, t2})}{2} + \left[r_m \cdot K_r \cdot \left(\frac{q^{hr} \cdot q_{max}^{hr} \cdot f}{K_{oc}^{hr} \cdot OC \cdot q_{max}^{hr} \cdot f - q^{hr} \cdot K_{oc}^{hr} \cdot OC} \right) \right] \quad (17)$$

5.3. Results and Discussion

From Figure 5.1, we can see that the equation predicts the total uptake of desorption-resistant phenanthrene ($\log K_{ow} = 4.46$ (Reible 1999)) by both types of wetland plants. The raw data used to calculate the points in Figure 5.1 is presented in the appendix. 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 outside of the plant.

In Figure 5.2, the same model is applied to chlorobenzene ($\log K_{ow} = 2.84$ (Reible 1999)) for both types of wetland plants. In this case, the model well predicted several data points but generally overpredicted the uptake for chlorobenzene. Several reasons may account for this overprediction including additional loss mechanisms such as volatilization.

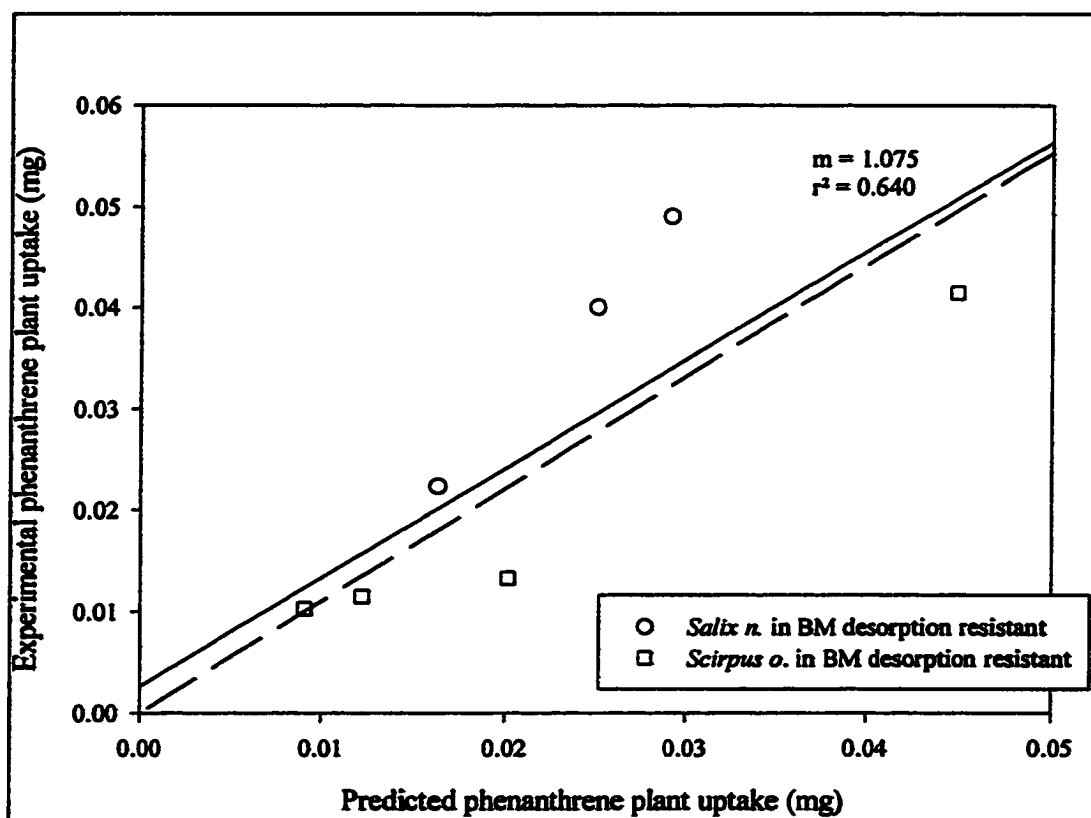


Figure 5.1. Plot of the predicted phenanthrene plant uptake using equation 17. The solid line is a regression line for all the data in the figure, while the dashed line has a slope = 1 and represents complete agreement between the model and observations.

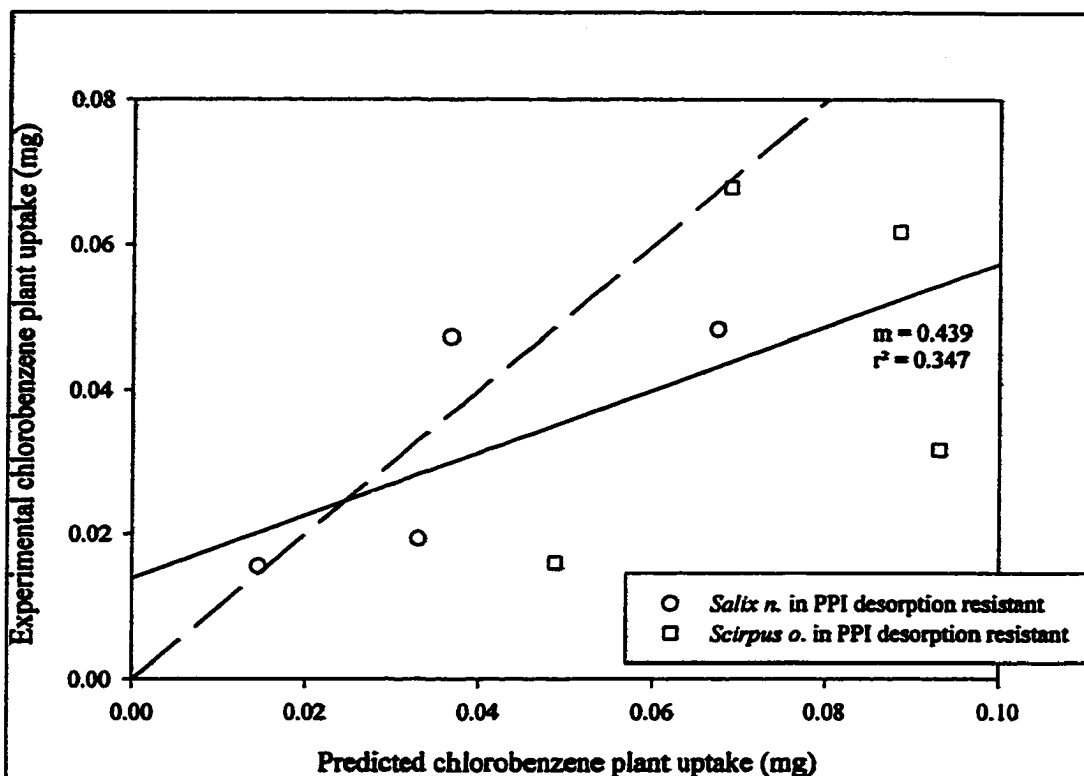


Figure 5.2. Plot of the predicted chlorobenzene uptake by the whole plant using equation 17. The solid line is a regression line for all the data points, while the dashed one has a slope of 1 and is included for easier comparison.

The relative contribution from each term in the model is of interest. The transpiration stream concentration factor concept represents the most widely utilized predictive tool for phytoremediation applications, these predicted translocated quantities are relatively small compared with the predicted by the sorption term.

5.4 Conclusions

A model was developed which combines mathematical concepts of desorption-resistance with simple plant-uptake relationships. The model presented is an effective tool to predict the amount of chemical that will be found in the whole plant when the compound present has a significant desorption-resistant fraction. This

model is more effective for hydrophobic than for hydrophilic compounds due to the fact that hydrophilic compounds can be volatilized and lost in the balance.

It has been shown that when dealing with desorption resistant soils, it is very important to consider the partitioning process, either water-soil, water-root or root-soil. It is also important to note that when dealing with chemicals only slightly lipophilic and which can be easily translocated, it is likely that they will be translocated all the way out of the plant. Thus a simple estimation of how much is inside the plant is not a good measure of plant uptake due to the large amount that will be transpired outside the plant. It has also been shown that the uptake from the desorption resistant soils cannot be accurately predicted by the current models, and a sorptive term is necessary for a better prediction of the total plant uptake of lipophilic compounds such as phenanthrene.

6 CONCLUSIONS

We generated results to start filling up the gaps found on Chapter 2. Results were generated to cite the influence of desorption resistance on plant uptake, either terrestrial or aquatic. All the previous studies consider that the contaminant even if it has been in the soil for long time, it will be fully available for plant uptake. We have studied the use of wetland plants as potential remediation tool opposed to the great majority of the studies on plant uptake which have been done with terrestrial plants. There is little or no information available on how wetland plants take up chemicals and transport them to the above-ground parts of the plant. There is also no information on how wetland plants can help on the clean-up processes at contaminated sites. Many current CERCLA or Superfund sites across US involve wetland

The study results have implications for the remediation of sediments using vegetation and the fate of contaminants in sediment systems. The effect of sediment: water partitioning on wetland plant uptake of phenanthrene 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. Submerged roots and plant stems represent a "clean" organic sorptive phase for phenanthrene. 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 and since the contaminant release from this fraction is too slow, it is advisable to use vegetation as a barrier.

Structure-activity relationships developed for plant uptake (Burken & Schnoor 1998) (Briggs et al. 1982) predict very low potential for translocation of chlorinated benzenes with 3 or more chlorines (Figure 4.11) which are more commonly found contaminants than mono and dichlorobenzenes. Based on this TSCF approach, dechlorination will have to precede plant uptake and translocation for there to be a significant portion of the HCB waste to be effectively remediated by the existing vegetation.

The effect of desorption resistance or aging is more difficult to predict. Clearly, results indicate that desorption-resistance will slow the plant uptake of chlorobenzene. In some respect this may be valuable since it also slows the volatilization of chlorobenzene. Even though the existing spill is over 30 years old, it is not known whether the lower chlorinated benzenes are present in an aged state. The presence of lower chlorinated benzenes in surface sediments in the swamp strongly suggests relatively recent dechlorination, since these compounds are relatively poorly sorbed and volatile. Periodic flooding by the Mississippi River would rapidly deplete these lower chlorinated benzenes from sediments. Results

demonstrate that regardless of their partitioning in sediments, chlorobenzene is accessible by vegetation types present in Devil's Swamp. Coupled dechlorination and plant uptake may represent an important component of the natural attenuation of this contaminated wetland.

The currently available models, have been formulated for agricultural plants like barely and for other terrestrial plants such as poplar trees. None of the current models has been applied to wetland plants, which have a different morphology than these previously mentioned plants, so there is a need for a model which could be useful to predict the uptake by wetland plants.

A model was developed which combines mathematical concepts of desorption-resistance with simple plant-uptake relationships. The model presented is an effective tool to predict the amount of chemical that will be found in the whole plant when the compound present has a significant desorption-resistant fraction. This model is more effective for hydrophobic than for hydrophilic compounds due to the fact that hydrophilic compounds can be volatilized and lost in the balance.

It has been shown that when dealing with desorption resistant soils, it is very important to consider the partitioning process, either water-soil, water-root or root-soil. It is also important to note that when dealing with chemicals only slightly lipophilic and which can be easily translocated, it is likely that they will be translocated all the way out of the plant. Thus a simple estimation of how much is inside the plant is not a good measure of plant uptake due to the large amount that will be transpired outside the plant. It has also been shown that the uptake from the desorption resistant soils cannot be accurately predicted by the current models,

which only consider the amount translocated above ground, and a sorptive term is necessary for a better prediction of the total plant uptake of lipophilic compounds such as phenanthrene.

REFERENCES

- Anderson Tod A., White DC, Walton Barbara T. (1995) Degradation of hazardous organic compounds by rhizosphere microbial communities. *Biotechnology and Bioengineering*, 23: 205-225
- Anderson TA, Kruger EL, Coats JR (1994) Enhanced degradation of a mixture of three herbicides in the rhizosphere of a herbicide-tolerant plant. *Chemosphere*, 28: 1551-1557
- Anderson TA, Walton BT (1995) Comparative fate of [^{14}C]trichloroethylene in the root zone of plants from a former solvent disposal site. *Environmental Toxicology and Chemistry* 14: 2041-2047
- Becvar ESK, Fisher A, Sewell G, Magar V, Gosset J, Vogel CM. Enhanced in situ reductive dechlorination. Wickramanayake, Godage B. and Hinchee, Robert E. C1-4, 121-127. 1998. Columbus, OH, Battelle press. The first international conference on remediation of chlorinated and recalcitrant compounds.
Ref Type: Conference Proceeding
- Behrendt H, Brüggemann R (1993) Modeling the fate of organic chemicals in the soil plant environment: Model study of root uptake of pesticides. *Chemosphere* 27: 2325-2332
- Boersma L, Lindstrom FT, McFarlane C, McCoy EL (1988) Uptake of organic chemicals by plants: A theoretical model. *Soil Science* 146: 403-417
- Briggs GG, Bromilow RH, Evans AA (1982) Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. *Pesticide Science* 13: 495-504
- Briggs GG, Rigitano RLO, Bromilow RH (1987) Physico-chemical factors affecting uptake by roots and translocation to shoots of weak acids in barley. *Pesticide Science* 19: 101-112
- Burken JG, Schnoor JL (1996) Phytoremediation: Plant uptake of atrazine and role of root exudates. *Journal of Environmental Engineering* 122: 958-963
- Burken JG, Schnoor JL (1997) Uptake and metabolism of atrazine by poplar trees. *Environmental Science and Technology* 31: 1399-1406
- Burken JG, Schnoor JL (1998) Predictive relationships for uptake of organic contaminants by hybrid poplar trees. *Environmental Science and Technology* 32: 3379-3385

Burken JG, Schnoor JL (1999) Distribution and volatilization of organic compounds following uptake by hybrid poplar trees. International Journal of Phytoremediation 1: 139-151

Chaineau CH, Morel JL, Oudot J (2000) Bioremediation and Biodegradation. Biodegradation of Fuel Oil Hydrocarbons in the Rhizosphere of Maize. Journal of Environmental Quality 29: 569-578

Chang Y-Y, Corapcioglu MY (1998) Plant-Enhanced subsurface bioremediation of nonvolatile hydrocarbons. Journal of Environmental Engineering 124: 162-169

**Chappell J. Phytoremediation of TCE using *Populus*. Status report. 1997.
Ref Type: Report**

Chung N, Alexander M (1998) Differences in sequestration and bioavailability of organic compounds aged in dissimilar soils. Environmental Science and Technology 32: 855-860

Clarkson DT (1996) Root structure and sites of ion uptake. In Y Waisel, A Eshel, U Kafkafi, eds Plant roots the hidden half, Ed. 2. Marcel-Dekker Inc., New York, pp 483-510

Compton HR, Haroski DM, Hirsh SR, Wrobel JG (1998) Pilot-Scale use of trees to address VOC contamination. In GB Wickramanayake, RE Hinchee, eds Bioremediation and Phytoremediation. Battelle Press,

Connaughton DF, Stedinger JR, Lion LW, Shuler ML (1993) Description of time-varying desorption kinetics: Release of naphthalene from contaminated soils. Environmental Science and Technology 27: 2397-2403

Cunningham SD, Berti WR, Huang JW (1995) Phytoremediation of contaminated soils. Trends in Biotechnology 13: 393-397

Cunningham SD, Ow DW (1996) Promises and prospects of phytoremediation. Plant Physiology 110: 715-719

Davis LC, Vanderhoof S, Dana J, Selk K, Smith K, Goplen B, Erickson LE (1998) Movement of chlorinated solvents and other volatile organics through plants monitored by fourier transform infrared (FT-IR) spectrometry. Journal of Hazardous Substance Research 4-1-4-26

de Souza MP, Huang CPA, Chee N, Terry N (1999) Rhizosphere bacteria enhance the accumulation of selenium and mercury in wetland plants. Planta 209: 259-263

Di Toro DM, Horzempa AM (1982) Reversible and resistant components of PCB : Adsorption isotherms. Environmental Science and Technology 16: 594-602

- Doucete WJ, Plaehn WA, Downey DC, Taffinder SA, Edwards R (1998) Phytoremediation of dissolved-phase trichloroethylene using mature vegetation. In GB Wickramanayake, RE Hinchee, eds *Bioremediation and Phytoremediation*. Battelle Press, Columbus, pp 233-237
- Dowdy DL, McKone TE (1997) Predicting plant uptake of organic chemicals from soil or air using octanol/water and octanol/air partition ratios and a molecular connectivity index. *Environmental Toxicology and Chemistry* 16: 2448-2456
- Ferro AM, Sims RC, Bugbee B (1994) Hycrest crested wheatgrass accelerates the degradation of pentachlorophenol in soil. *Journal of Environmental Quality* 23: 272-279
- Fitter A (1996) Characteristics and functions of root systems. In Y Waisel, A Eshel, U Kafafi, eds *Plant roots the hidden half*, Ed. 2. Marcel-Dekker Inc., New York, pp 1-20
- Fu G, Kan AT, Tomson M (1994) Adsorption and desorption hysteresis of PAHs in surface sediment. *Environmental Toxicology and Chemistry* 13: 1559-1567
- Glass DJ (1999) Special commentary: Current market trends in phytoremediation. *International Journal of Phytoremediation* 1: 1-8
- Gordon M, Choe N, Duffy J, Gordon E, Heilman P, Muiznieks I, Ruszaj M, Shurtleff BB, Strand S, Wilmoth J, Newman LA (1998) Phytoremediation of trichloroethylene with hybrid poplars. *Environmental Health Perspectives* 106: 1001-1004
- Goring CAI, J.W.Hamaker (1972) *Organic chemicals in the soil environment*.
- Grathwohl P, Reinhard M (1993) Desorption of trichloroethylene in aquifer material: Rate limitation at the grain scale. *Environmental Science and Technology* 27: 2360-2366
- Greger M, Landberg T (1999) Use of willow in phytoextraction. *International Journal of Phytoremediation* 1: 115-123
- Grosse W, Mevi-Shutz J (1987) A beneficial gas transport system in nymphoides peltata. *American Journal of Botany* 74: 947-952
- Hatzinger PB, Martin A (1995) Effect of aging of chemicals in soil on their biodegradability and extractability. *Environmental Science and Technology* 29: 537-545
- Hooda PS, McNulty D, Alloway BJ, Aitken MN (1997) Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. *Journal of Science in Food and Agriculture* 73: 446-454

- Hopkins WG (1995) Introduction to plant physiology. John Wiley & Sons, Inc.,
- Hsu FC, Marxmiller RL, Yang AYS (1990) Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using a pressure chamber technique. *Plant Physiology* 93: 1573-1578
- Huang JW, Chen J, Berti WR, Cunningham SD (1997a) Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction. *Environmental Science and Technology* 31: 800-805
- Huang W, Schlautman MA, Webber Jr WJ (1996) A distributed reactivity model for sorption by soils and sediments. 5. The influence of near-surface characteristics in mineral domains. *Environmental Science and Technology* 30: 2993-3000
- Huang W, Webber Jr WJ (1998) A distributed reactivity model for sorption by soils and sediments. 11. slow concentration-dependent sorption rates. *Environmental Science and Technology* 32: 3549-3555
- Huang W, Webber Jr. WJ (1997) Thermodynamic considerations in the sorption of organic contaminants by soils and sediments. 1. The isosteric heat approach and its applications to model inorganic sorbents. *Environmental Science and Technology* 31: 3238-3243
- Huang W, Young TM, Schlautman MA, Yu H, Webber Jr WJ (1997b) A distributed reactivity model for sorption by soils and sediments. 9. general isotherm nonlinearity and applicability of the dual reactive domain model. *Environmental Science and Technology* 31: 1703-1710
- Huang W, Yu H, Webber Jr WJ (1998) Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments 1. A comparative analysis of experimental protocols. *Journal of Contaminat Hydrology* 31: 129-148
- Hughes JB, Shanks J, Vanderford M, Lauritzen J, Bhadra R (1997) Transformation of TNT by aquatic plants and plant tissue cultures. *Environmental Science and Technology* 31: 266-271
- Kan AT, Fu G, Hunter M, Chen W, Ward CH, Tomson MB (1998) Irreversible sorption of neutral hydrocarbons to sediments: Experimental observations and model predictions. *Environmental Science and Technology* 32: 892-902
- Kan AT, Fu G, Hunter MA, Tomson MB (1997) Irreversible adsorption of naphthalene and tetrachlorobiphenyl to Lula and surrogate sediments. *Environmental Science and Technology* 31: 2176-2184
- Kan AT, Fu G, Mason BT (1994) Adsorption/desorption hysteresis in organic pollutant and soil/sediment interaction. *Environmental Science and Technology* 28: 859-867

Karickhoff SW (1980) Sorption kinetics of hydrophobic pollutants in natural sediments in contaminants and sediments. Ann Arbor Press,

Kelsey JW, Alexander M (1997) Declining bioavailability and inappropriate estimation of risk of persistent compounds. Environmental Toxicology and Chemistry 16: 582-585

Kirkham MB (2000) EDTA-facilitated phytoremediation of soil with heavy metals from sewage sludge. International Journal of Phytoremediation 2: 159-172

**Liu W, Kan AT, Mason T, Wei C, Joe H, Danny Reible . Protocol for assessment of biological available pollutant concentration in soil. Symposia paper presented before the division of environmental chemistry of the American Chemical Society. New Orleans, LA. American Chemical Society. 2000. 8-22-1999.
Ref Type: Conference Proceeding**

**Lorenz A . Medium optimization for the cultivation of bacteria reductively dechlorinating trichlorobenzenes. Wickramanayake, Godage B. and Hinchee, Robert E. C1-4, 77-82. 1998. Battelle press. The first international conference on remediation of chlorinated and recalcitrant compounds.
Ref Type: Conference Proceeding**

Lueking AD, Huang W, Soderstrom-Schwarz S, Kim M, Webber Jr WJ (2000) Relationship of soil organic matter characteristics to organic contaminant sequestration and bioavailability. Journal of Environmental Quality 29: 317-323

Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Webber Jr. WJ, Westall JC (1997) Sequestration of hydrophobic organic contaminants by geosorbents. Environmental Science and Technology 31: 3341-3347

McCrary JK, McFarlane C, Lindstrom FT (1987) The transport and affinity of substituted benzenes in soybean stems. Journal of experimental botany 38: 1875-1890

McCrary JK, Maggard SP (1993) Uptake and photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin sorbed to grass foliage. Environmental Science and Technology 27: 343-350

McGroddy SE, Farrington JW (1995) Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston harbor Massachusetts. Environmental Science and Technology 29: 1542-1550

Mitsch WJ, Gosselink JG (2000) Wetlands. John Wiley & Sons, Inc.,

Mohr H, Schopfer P (1995) Plant physiology. Springer, Berlin

Nair DR, Burken JG, Licht LA, Schnoor JL (1993) Mineralization and uptake of triazine pesticide in soil-plant systems. *Journal of Environmental Engineering* 119: 842-853

Nam K, Alexander M (1998) Role of nanoporosity in sequestration and bioavailability: Tests with model solids. *Environmental Science and Technology* 32: 71-74

Narayanan M, Russel NK, Davis LC, Erickson LE (1999) Fate and transport of trichloroethylene in a chamber with alfalfa plants. *International Journal of Phytoremediation* 1: 387-411

National Research Council [NRC] (1997) Contaminated sediments in ports and waterways. Cleanup strategies and technologies. National Academy Press, Washington, D.C.

Newman LA, Strand SE, Choe N, Duffy J, Ekuan G, Ruszaj M, Shurtleff BB, Wilmoth J, Heilman P, Gordon MP (1997) Uptake and biotransformation of trichloroethylene by hybrid poplar trees. *Environmental Science and Technology* 31: 1062-1067

Nye PH, Tinker P.B. (1977) Studies in ecology volume 4: Solute movement in the root system. In University of California press, ed. Blackwell Scientific Publications,

Oertli JJ (1996) Transport of water in the rhizosphere and in roots. In Y Waisel, A Eshel, U Kafkafi, eds *Plant roots the hidden half*, Ed. 2. Marcel-Dekker Inc, New York, pp 607-633

Pardue J, Clover C, Jackson A (2001) Reductive dechlorination of chlorobenzenes in a contaminated wetland. In press

Pardue JH, Shin WS . Desorption resistance of organic compounds in wetland soils. Means J and Hinchee R. 25-32. 2000. Battelle Press. Wetlands & remediation an International conference.

Ref Type: Conference Proceeding

Paterson S, Mackay D, Tam D, Shiu WY (1990) Uptake of organic chemicals by plants: a review of processes, correlations and models. *Chemosphere* 21: 297-331

Paterson S, Mackay D (1991) Correlation of the equilibrium and kinetics of leaf-air exchange of hydrophobic organic chemicals. *Environmental Science and Technology* 25: 866-871

Pereira EW, Rostad CE, Chiou CT, Brinton TI, Barber II LB, Demcheck DK, Demas CR (1988) Contamination of estuarine water, biota and sediment by halogenated organic compounds: A field study. *Environmental Science and Technology* 22: 772-778

Pignatello JJ (1989) Slowly reversible sorption of aliphatic hydrocarbons in soils. 1. Formation of residual fractions. Environmental Toxicology and Chemistry 9: 1107-1115

Punshon T, Dickinson N (1999) Heavy metal resistance and accumulation characteristics in willows. International Journal of Phytoremediation 1: 361-385

Raven PH, Evert RF, Eichhorn SE (1992) Biology of plants. Worth Publishers, Inc., New York

Reible DD (1999) Fundamental of environmental engineering. Lewis Publishers, Boca Raton

Reilley KA, Banks MK, Schwab AP (1996) Organic chemicals in the environment: Dissipation of polycyclic aromatic hydrocarbons in the rhizosphere. Journal of Environmental Quality 25: 212-219

Russell RS, Shorrocks VM (1959) The relationship between transpiration and the absorption of inorganic ions by intact plants. Journal of experimental botany 10: 301-316

Sabljić A, Güsten H, Schönherr J, Riederer M (1990) Modeling plant uptake of airborne organic chemicals. 1. Plant cuticle/water partitioning and molecular connectivity. Environmental Science and Technology 24: 1321-1326

Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carreira LH (1995) Phytoremediation of organic and nutrient contaminants. Environmental Science and Technology 29: 318A-323A

Shimp JF, Tracy JC, Davis LC, Lee E, Huang W, Erickson LE, Schnoor JL (1993) Beneficial effects of plants in the remediation of soil and groundwater contaminated with organic materials. Environmental Science and Technology 23: 41-47

Shone MGT, Bartlett BO, Wood AV (1974) A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley II. Relationship between uptake by roots and translocation to shoots. Journal of experimental botany 25: 401-409

Shone MGT, Wood AV (1974) A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley I. Absorption in relation to physico-chemical properties. Journal of experimental botany 25: 390-400

Sims RC, Overcash MR (1983) Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems. Residue Reviews 88: 1-68

Sparks DL (1995) Environmental soil chemistry. In Academic Press Inc, ed.

Steinberg SM, Pignatello JJ, Sawhney BL (1987) Persistence of 1,2-dibromoethane in soils: Entrapment in intraparticle micropores. Environmental Science and Technology 21: 12-1201

Steudle E, Paterson CA (1998) How does water get through roots? Journal of experimental botany 49: 775-788

Takada H, Onda T, Ogura N (1990) Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography. Environmental Science and Technology 24: 1179-1186

Thompson PL, Ramer LA, Schnoor JL (1998) Uptake and transformation of TNT by hybrid poplar trees. Environmental Science and Technology 32: 975-980

Trapp S (1995) Model for uptake of xenobiotics into plants. In S Trapp, C McFarlane, eds Plant Contamination. Modeling and Simulation of Organic Chemical Processes. Lewis Publishers, pp 107-151

Trapp S, Matthies M (1995) Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environmental Science and Technology 29: 2333-2338

Trapp S, Matthies M, Scheunert I, Topp EM (1990) Modeling the bioconcentration of organic chemicals in plants. Environmental Science and Technology 24: 1246-1252

Trapp S, McFarlane C (1995) Plant contamination: Modeling and simulation of organic chemical processes. Lewis Publishers,

Trapp S, McFarlane C, Matthies M (1994) Model for uptake of xenobiotics into plants: Validation with bromacil experiments. Environmental Toxicology and Chemistry 13: 413-422

U.S.E.P.A. (1999) Protocol for developing sediment TMDLs. Washington D.C.

Vroblesky DA, Nietch CT, Morris JT (1999) Chlorinated ethenes from groundwater in tree trunks. Environmental Science and Technology 33: 510-515

Watkins JW, Sorensen DL, Sims RC (1994) Volatilization and mineralization of naphthalene in soil-grass microcosms. In Bioremediation through Rhizosphere Technology. pp 123-133

Weatherley PE (1982) Water uptake and flow in roots. In OL Lange, PS Nobel, CB Osmond, H Ziegler, eds Physiological plant ecology II: Water relations and carbon assimilation Vol 12 B. Springer-Verlag, Berlin, pp 79-109

Weber Jr WJ, Huang W, Yu H (1998) Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments 2. Effects of soil organic matter heterogeneity. Journal of Contaminat Hydrology 31: 149-165

Weber Jr WJ, McGinley PM, Katz LE (1991) Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. Water Research 25: 499-528

Wei C, Kan AT, Gongming Fu, Vignona LC, Tomson MB (1999) Adsorption-desorption behaviors of hydrophobic organic compounds in sediments of Lake Charles, Louisiana, USA. Environmental Toxicology and Chemistry 18: 1610-1616

White JC, Kelsey JW, Hatzinger PB, Alexander M (1997) Factors affecting sequestration and bioavailability of phenanthrene in soils. Environmental Toxicology and Chemistry 16: 2040-2045

Wild SR, Jones KC (1992) Organic chemicals in the environment: polynuclear aromatic hydrocarbon uptake by carrots grown in sludge-amended soil. Journal Environment Quality 21: 217-225

Wittmann C, Suominen KP, Salkinoja-Salonen MS (2000) Evaluation of ecological disturbance and intrinsic bioremediation potential of pulp mill-contaminated lake sediment using key enzymes as probes. Environmental Pollution 107: 255-261

Xing B, Pignatello JJ (1998) Competitive sorption between 1,3-dichlorobenzene or 2,4-dichlorophenol and natural aromatic acids in soil organic matter. Environmental Science and Technology 32: 614-619

Zayed A, Lytle CM, Terry N (1998) Accumulation and volatilization of different chemical species of selenium by plants. Planta 206: 292

Zhang W, Bouwer EJ, Ball WP (1998) Bioavailability of hydrophobic organic contaminants: Effects and implications of sorption-related mass transfer on bioremediation. Ground Water Monitoring and Remediation 126-138

APPENDIX: EXPERIMENTAL REACTORS

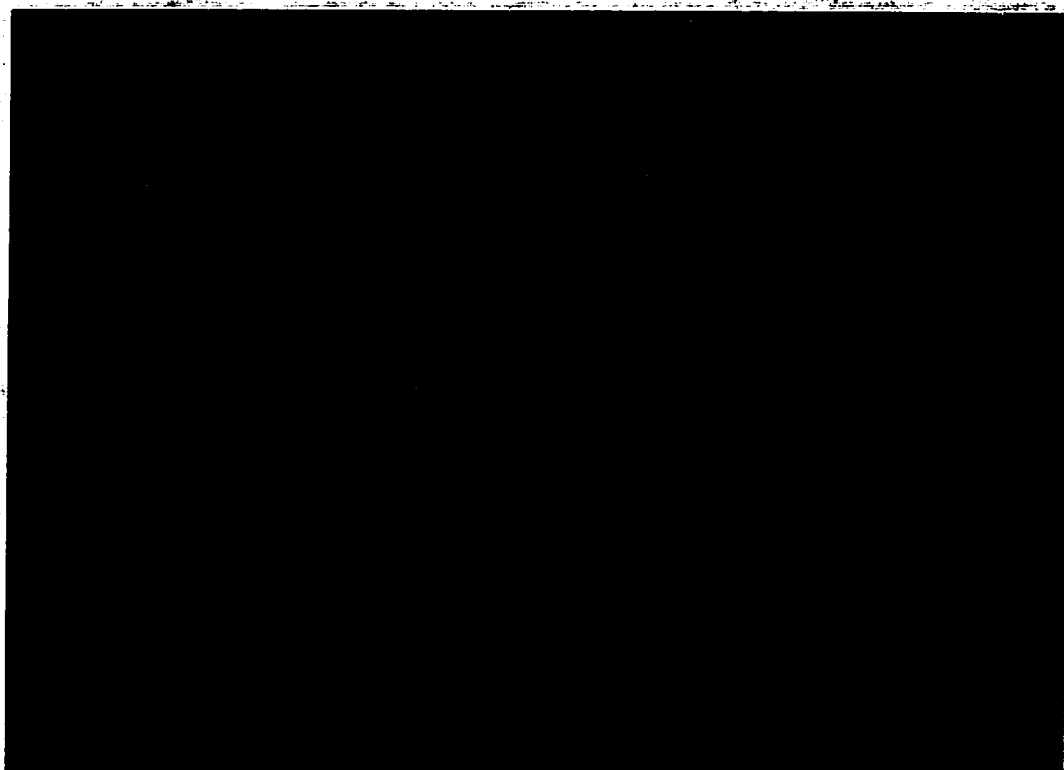


Figure A1. Top part of the closed reactors used for the plant uptake studies.

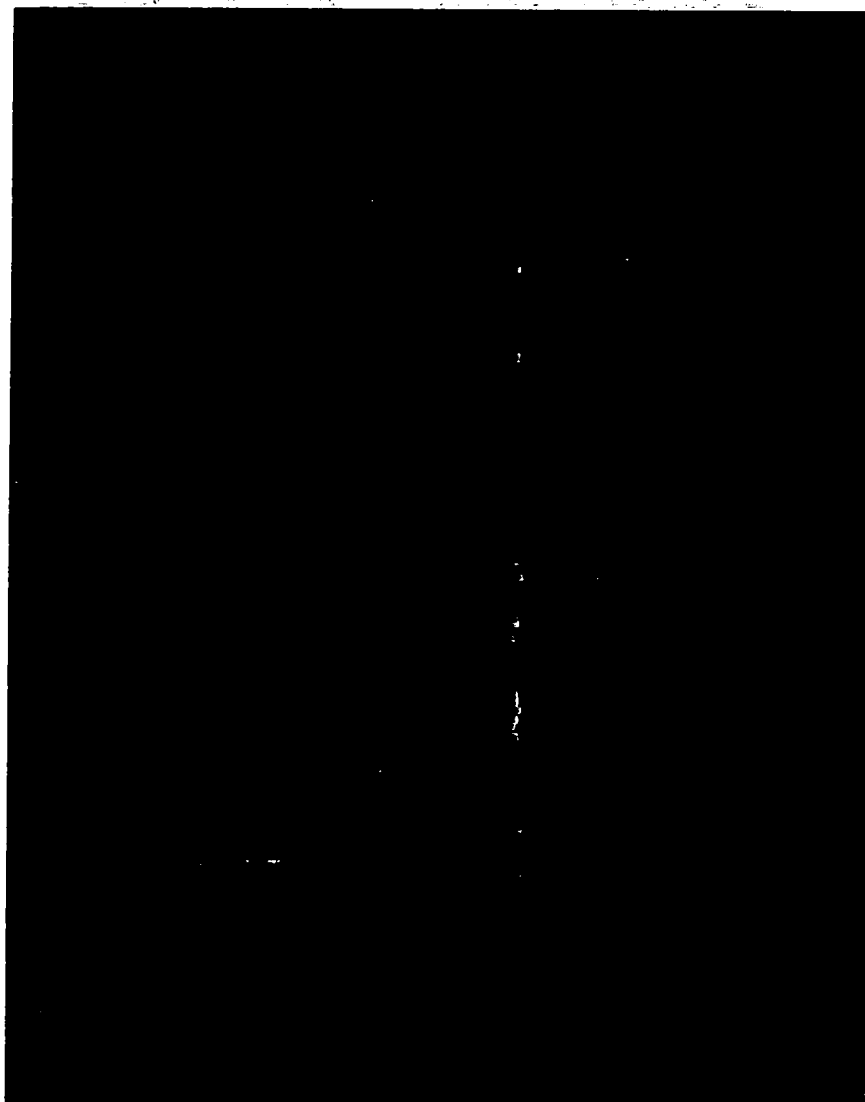


Figure A2. Bottom (or lower) part of the glass reactors used in the plant uptake experiment. During the experimentation, both parts keep separated from each other by a teflon lined septa in the cap of the bottom part.



Figure A3. Modified Erlenmeyer flask used to determine the capability of the rhizosphere to biodegrade the chemicals. In this picture we can see plant roots (the stem was cut out before the picture), contaminated liquid, and silica sand.

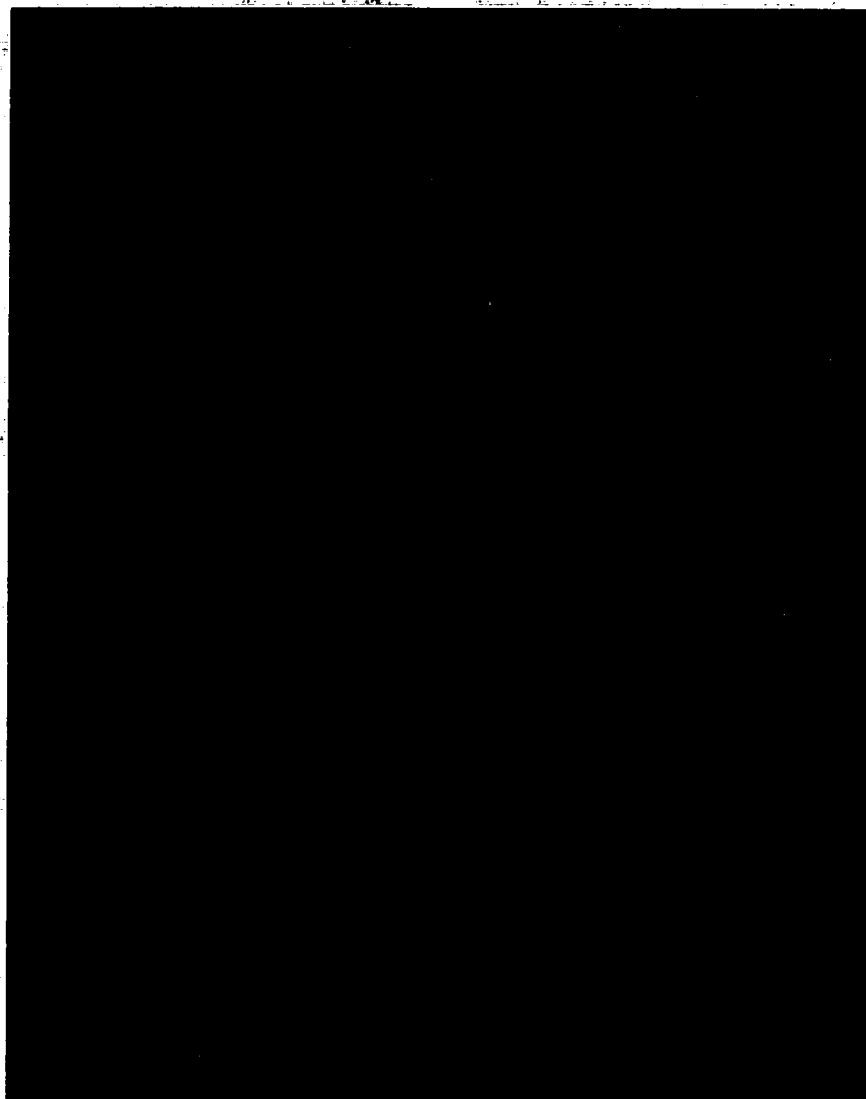


Figure A4. Modified Erlenmeyer flask used for the biodegradation studies, the reservoir where the NaOH is placed can be seen in the middle of the flask.



Figure A5. Setup used to test contaminant sorption to plant roots.

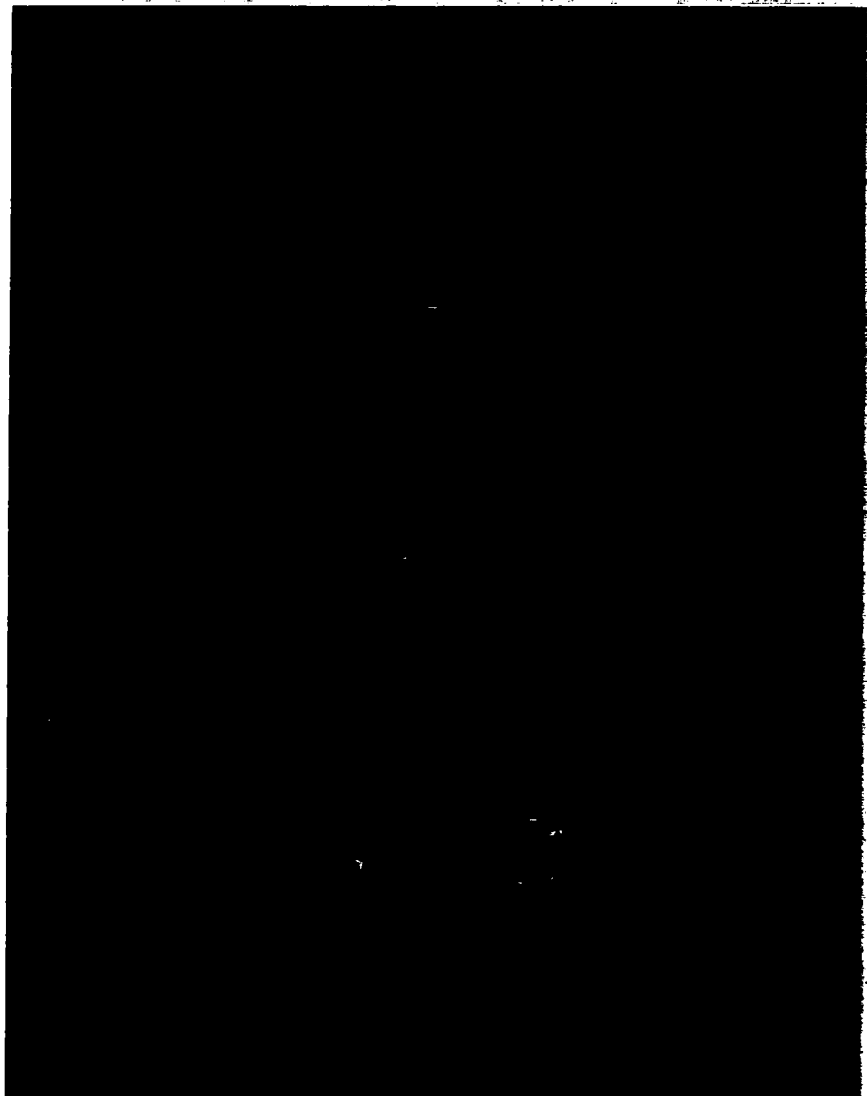


Figure A6. Setup to test sorption of chemicals into roots.

VITA

Cesar Miguel Gomez Hermosillo was born in Guadalajara, Mexico, on September 29, 1964. He attended the University of Guadalajara where he obtained a bachelor's degree in chemical engineering in 1989. He later (1990) got a scholarship from the German government to attend courses on water-wastewater treatment. In 1993 He got a master's degree from the University of Guadalajara, and later he attended Louisiana State University where he will receive the degree of Doctor of Philosophy in August 2001.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Cesar Gomez

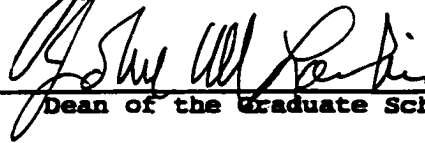
Major Field: Civil Engineering

Title of Dissertation: Plant Uptake of Desorption Resistant Organic Chemicals from Sediment

Approved:



Major Professor and Chairman

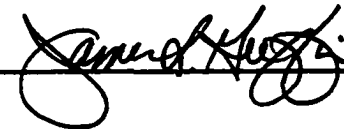


Dean of the Graduate School

EXAMINING COMMITTEE:



William Moe



Date of Examination:

17 May 2001