UPTAKE AND TRANSLOCATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY PLANTS IN SOILS

A Thesis

by

CHRISTOPHER LEE DERMODY

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Arthur P. Schwab
Co-Chair of Committee,	Terry J. Gentry
Committee Members,	Samuel Ma
Head of Department,	David D. Baltensperger

December 2018

Major Subject: Soil Science

ABSTRACT

Polyaromatic hydrocarbons (PAHs) and their interaction with plants have received an abundance of attention from the scientific community, as they are ubiquitous and recalcitrant in the environment. As some PAHs are known carcinogens, understanding how these pollutants bio-accumulate and become available for human consumption is imperative for pollution and exposure prevention. Many of the contaminant pathways associated with PAHs are well understood yet some disagreement exists in the published literature regarding the potential for PAHs to be taken up by plant roots to be subsequently translocated to above ground tissues.

In this thesis, the mobility of PAHs within plant tissues is investigated to assess the significance of this bioaccumulation pathway. Physiochemical parameters, modeling studies, as well as research spanning several decades are reviewed. After examining all of the information in this thesis, it can be concluded that the translocation of PAHs from plant roots to above ground tissues is highly unlikely. Taking into account both, factors related to the physiochemical limitations associated with PAHs that restrict their intracellular and overall plant and impacts of lipophilic soil-contained components the soil-to-root-to-vegetation bioaccumulation pathway is generally not significant when assessing the risks related to exposure to PAHs through the consumption of crops grown on contaminated soils. Rather, the air-to-leaf (i.e. atmospheric deposition) and soil-to-air-to-leaf (re-volatilization) pathways dominate the contamination of terrestrial vegetation.

DEDICATION

This paper is dedicated to altruism; the underlying necessity to conduct sound scientific research to produce honest, reliable data for an ever-reliant, growing society. We exist during a truly unique period of human history and it will be the coming decades that decide our coming centuries. Obvious as it may seem, the rate of change experienced by modern day society eclipses that of nearly all of pre-industrial human history combined. There is no debate that our anthropogenic footprint is larger than ever. How we navigate the dissemination of critical information, as well as how we cooperate to identify and eliminate inaccurate or outdated assessments, will dictate the efficacy at which we continue this technological evolution into the millennia. With a little luck, and a tremendous amount of hard work and dedication, I am confident that we will finally connect the entire global network with an ideal structure that emphasizes unity through indivisible expression. It just requires us to all be on the same page.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Arthur Schwab, co-chair, Dr. Terry Gentry, and committee member Dr. Samuel Ma. This effort would have not been possible without the inspiration and support of my coordinating professor, Dr. Arthur Schwab. His input as a mentor has continuously pushed me to expand my intellect while simultaneously encouraging me to always integrate integrity and thoroughness into all of my passions.

I would also like to recognize my mother, Maureen Dermody, for the constant guidance and support that she has provided me throughout my life; and my father, James Dermody, for his work ethic and leadership. Without their wisdom, nothing I've accomplished would have been possible. I would also like to thank my wife, Stephanie Dermody, for her limitless love and patience throughout this academic journey. Together, we will show this world a thing or two!

I would also like to thank the many friends and colleagues that I have met over the years for the support and encouragement as well as the Soil and Crop Science Department's faculty and staff for making my time at Texas A&M University a great experience. Their dedication has been exuberant and their dependability a lifesaver, on more than one occasion. Lorin Harvey, Yong Wang, Frances Mutscher, Dr. Wayne Smith, Amanda Ray, Leann Hague, Dr. Frank Hons, Mark Hall, Megan Teel, Dr. Steve Hague, Dr. Katie Lewis, Dr. Joe Storlien, Ethan Diver, Russ Garretson and so many others, thank you.

NOMENCLATURE

CF(s)	Concentration Factor(s)
BCF(s)	Bioconcentration Factor(s)
Hc	Dimensionless Henry's Law Constant
K_{AW}	Air-Water Distribution Coefficient
K_{OA}	Octanol-Air Distribution Coefficient
K_{OC}	Organic Carbon Distribution Coefficient
K_{OW}	Octanol-Water Distribution Coefficient
K_d	Soil Distribution Coefficient
K_H	Henry's Law Constant
PAH(s)	Polycyclic Aromatic Hydrocarbon(s)
P_{vap}	Vapor Pressure
RCF(s)	Root Concentration Factor(s)
SCF(s)	Shoot Concentration Factor(s)
SVOC	Semi-Volatile Organic Contaminant
TSCF(s)	Transpiration Stream Concentration Factor(s)
W_S	Water Solubility

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supported by a thesis committee consisting of the committee chair, Dr. Arthur Schwab, co-chair, Dr. Terry Gentry, of the Soil and Crop Sciences Department, and committee member, Dr. Samuel Ma, of the Department of Civil Engineering of Texas A&M University.

All other work conducted for the thesis was completed by the student independently.

Funding Sources

Graduate study was supported, in part, by the David Wm. Reed Excellence Fellowship as well as through a graduate research assistantship, working for the Soil and Crop Sciences Department Texas A&M University.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Polyaromatic hydrocarbons (PAHs) are a widespread environmental contaminant and human health hazard (Agency for Toxic Substances and Disease Registry 2009). PAHs have natural and anthropogenic sources, all of which involve the burning of organic compounds such as coal and petroleum (National Research Council 1983). Being semi-volatile, PAHs are often detected in the atmosphere, but they also readily sorb onto hydrophobic/lipophilic surfaces including soil, vegetation, and particles suspended in the air (Wagrowski and Hites 1997). Vascular plants growing near sources of PAH emissions into the atmosphere can be highly contaminated. Similarly, using soil for the disposal of waste products such as coal tars or petroleum sludge can lead to concentrations exceeding 1,000 mg total PAH/kg soil (Cofield et al. 2008).

Contamination of vascular plants with PAHs is a known problem, and due to ready atmospheric transport of PAHs over long distances (Lunde and Bjorseth 1977), finding plants that contain no PAHs is nearly impossible (Edwards 1983). Concentrations generally do not exceed health advisory limits, but PAH levels in plants can be an ecological and health threat, particularly near point sources of contamination. Knowing all the mechanisms by which PAHs accumulate in plants and understanding which mechanisms are the most important is crucial to pollution prevention and minimizing the spread of PAHs through the food chain. This is particularly true with the high interest in reclaiming brownfields (De Sousa 2003).

In the 1970s, interest in cleaning up pollution sparked interest in studying PAHs in the environment (National Research Council 1983). The conclusion from many in-depth studies from the 1970s through the early 2000s that focused on PAH contamination in plants was that the predominant pathway for PAHs to accumulate in vegetation growing in soils (contaminated or uncontaminated) was aerial deposition (Grimmer and Duvel 1970; Larson et al. 1982; Bakker et al. 2000; Simonich and Hites 1994; Wagrowski and Hites 1999) and not root uptake of the PAHs followed by translocation to the stems and leaves (Gunther et al. 1967; Harms 1975; Kolar et al. 1975; Ellwardt 1979; Kampe and Leschber 1989; O'Connor et al. 1991; Preusser et al. 1993; Kipopoulou et al. 1999; Robinson et al. 2003; Tao et al. 2004; Su and Zhu 2008; Wang et al. 2014). However, beginning around 2000, much of the foundational work on PAH accumulation in plants growing in PAH-contaminated soil apparently was being contradicted by a few studies that either assumed that the soil-root-shoot pathway was predominant or claimed to demonstrate it (Fismes et al. 2002; Oleszczuk and Barak 2005; Meudec et al. 2006; Srogi 2007; Watts et al. 2008; Lu et al. 2009; Meng et al. 2011; Waqas et al. 2014). In addition to field and greenhouse studies, accumulation of PAHs by plants from hydroponic solutions was being attributed to PAH assimilated by plant roots followed by translocation to the stems and leaves through vascular tissues (e.g., Gao and Zhu 2004; Gao et al. 2012).

In light of the apparent contradictions emerging in the recent literature and the importance of understanding PAH uptake by vascular plants, a critical review is warranted. The overall objective of this review of the literature is to determine the

importance of the soil-root-shoot pathway for accumulation of PAHs in vascular plants. Sub-objectives include:

1. Thoroughly review the literature that led to the consensus that the air-to-plant pathway was the primary means for PAH accumulation in vegetation.
2. Based on the physical and chemical properties of PAHs and previous modeling studies, determine the likelihood that PAHs can be accumulated from the soil by plant roots and translocated to the plant shoots.
3. Review the recent literature that specifically addresses the soil-root-shoot pathway.

Soil versus Solution Culture

As this review of the literature progressed, results from studies involving solution culture often were different from those conducted in contaminated soils. Solution culture experiments detected significant concentrations of PAHs in stems and leaves within hours after the initiation of the experiment, and this was rarely the case for soil studies. Entire research programs have centered around PAH uptake from solution culture, and some of the resulting publications are prominent in the review. However, important differences between growing plants in soils and nutrient culture are well known. For example, plants cultivated in nutrient solutions tend to have roots with greater proliferation of finer roots, less branching, and the lack of anchor roots (Asher and Edwards 1983). The presence of soil also changes the chemistry of PAH bioavailability: the presence of soil organic matter requires that PAHs must first desorb from sites of adsorption prior to becoming available for adsorption to the roots (Ryan et al. 1988). As

shown in Figure 1, the uptake of non-ionic organic chemicals is strongly dependent on the lipophilicity of the chemical (log K_{OW}) as well as whether uptake is from soil or nutrient solution. The theoretical basis for Fig. 1 is discussed in detail in a subsequent section, but the results are given here for context. The transpiration stream concentration factor (TSCF) is the ratio of the concentration of organic chemicals (PAHs in this case) in the transpiration stream to the concentration in the aqueous phase outside the root, and the stem concentration factor is the ratio of the concentration of PAHs in the stem/leaf tissue to the concentration in the aqueous phase outside the root. Within the transpiration stream, maximum TSCF is realized for log K_{OW} 1.8 but shifts downward to log K_{OW} 1.2 (less lipophilic) in the presence of soil with 1% OM. The shift is more pronounced for the stem concentration factor (SCF); the optimum is log K_{OW} 5 for nutrient solution and log K_{OW} 1.5 for soil. For nearly all PAHs, 3.7 < log K_{OW} < 6.8, result in transpiration

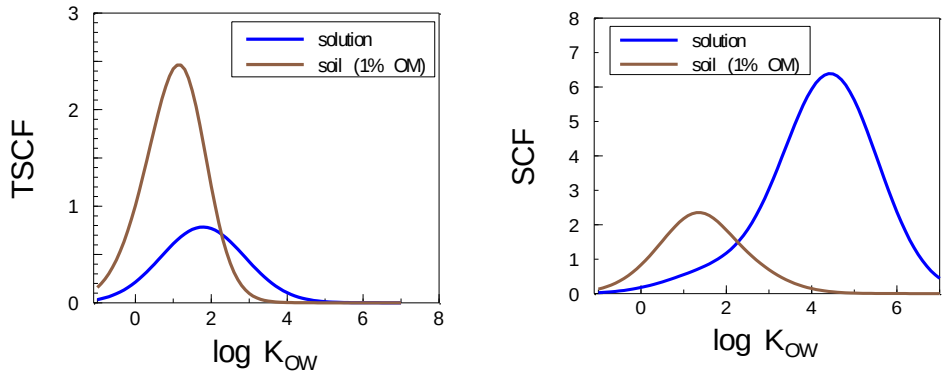

Figure 1: The impact of logK_{OW} on the transpiration stream concentration factor (TSCF) and stem concentration factor (SCF) in nutrient solution (blue) and soil with 1% organic matter (brown). Based on model calculations (Briggs et al. 1982; Ryan et al. 1988).

stream concentration factor (TSCF) and SCF approaching 0 in soil; but in nutrient solutions, the PAHs will have near-optimum log K_{OW} for SCF. From this, one can conclude that plant uptake of PAHs from nutrient solutions is very different in soil compared to nutrient solution. Therefore, we elected to focus only on those studies using contaminated soils.

Structure of the Review

The ultimate goal of this review is to assemble data that determine as definitively as possible whether or not PAHs that are assimilated by plant roots growing in contaminated soil are translocated to the shoots. The review will not discuss every scientific journal article reporting PAH concentrations in plants. Rather, it is structured to highlight experiments designed specifically to study PAH translocation or those studies that provide somewhat indirect or incomplete evidence concerning root-to-shoot translocation.

The review is structured as follows:

1) General background on PAHs including sources of contamination; chemical and physical properties of the compounds; and pathways of plant accumulation.
2) Background PAH concentrations in plants and soils
3) Aerial deposition onto plant surfaces
4) Early (pre-1990) studies of PAH accumulation in plants growing in contaminated environments
5) Modeling PAH uptake by plants: deposition from the air; root uptake from aqueous solutions; root uptake from soil

6) Direct observation of PAH movement in plant tissues

7) PAH concentrations in plant tissues growing in moderately contaminated soils

8) PAH concentrations in plant tissues growing in heavily contaminated soils

9) Summary and Conclusions

CHAPTER II

GENERAL PROPERTIES OF PAHS

PAHs in the Environment

As the human population increased over the 20th century from 1.8 billion to nearly 7 billion, industrialization and urbanization have contributed to significant increases in the concentrations of xenobiotic compounds in the environment, many of which are potentially toxic (Pepper et al. 2006). Atmospheric deposition has contributed to a fivefold increase in soil concentrations of polycyclic aromatic hydrocarbons (PAHs) near industrialized areas (Jones et al. 1989). Polycyclic aromatic hydrocarbons are semi-volatile organic contaminants (SVOCs) that are nonpolar, lipophilic, neutral molecules. They are composed of multiple benzene molecules that share sides of the rings and are arranged in linear, step, or cluster formations (Mackay et al. 1992). The smallest PAH, naphthalene, is composed of two benzene rings. The largest known PAH, coronene, contains seven benzene rings. Between them, exist hundreds of other substituted and unsubstituted PAHs, sixteen of which regulated by the U.S. EPA.

PAHs are byproducts of the incomplete combustion of carbon-based materials. Naturally occurring sources of PAHs include volcanic activity, wild fires, and synthesis by terrestrial vegetation and microorganisms (Eisler 1987). Natural PAH inputs are smaller than anthropogenic inputs, which include an array of modern industrial processes such as coke production, waste incineration, and heat and power generation. Local inputs from urbanized areas with high automobile traffic also are significant (Heit

et al. 1988). The PAH burden on the environment has been documented to vary "along the remote-rural-urban-industrial gradient" with the rural areas receiving PAH inputs that are 10 times lower than in urban areas (Bohme et al. 1999; Jones 1991; Wagrowski and Hites 1997).

Deposition of airborne particles with PAHs adsorbed to their surfaces may be the most important global contamination pathway. Soil annually receives approximately 0.7 to 1 mg/m^2 of PAH by atmospheric emissions amounting to 520 gigagrams per year worldwide (Debastani and Ivanov 1999; Dachs and Eisenreich 2000; Wilcke 2000; Zhang and Tao 2009). PAHs are typically emitted from their source directly into the atmosphere where they have the potential to traverse long distances as gases, aerosols, or adsorbed to suspended particulates. Atmospheric emissions are nearly always a mixture of PAHs and seldom a single compound (Bakker et al. 2000; Eisler 1987; McLachlan et al. 2000; Wagrowski and Hites 1997).

Soils often are a sink for emitted contaminants (Collins et al. 2013). PAHs will partition from the atmosphere onto surfaces of solids with similar physiochemical properties, such as hydrophobic moieties on the surfaces of soil organic matter or inorganic minerals. Bakker et al. (2000) suggested that this transfer occurs through particle-bound deposition for high molecular weight PAHs, while lighter molecular weight PAHs transfer via dry gaseous deposition in soils. Temperature and atmospheric pressure drive the equilibrium gradient as these compounds make contact with various surfaces (Bakker et al. 1999; Thomas et al. 1984). Jones et al. (1989) assessed soil and crop samples for PAHs dating from 1846 to 1986 and found that atmospheric deposition

is the primary pathway for PAH accumulation in affected soils. Other potential soil contamination pathways are the incorporation of PAH-contaminated sewage sludge or irrigation with contaminated wastewater (Gworek et al. 2014; Tao et al. 2004). Precipitation events remove significant quantities of PAHs from the surface of vegetation, transferring them to the underlying soil (Jouraeva et al. 2002), where they tend to be recalcitrant and persistent (Kipopoulou et al. 1999; Trapp et al. 2007).

Atmospheric PAH deposition affects vegetation more than soils (Jones et al. 1989). Simonich and Hites et al. (1995) estimated that vegetation in urban regions annually intercepted 44±18 % of emitted PAHs, accumulating on the waxy cuticle that covers the leaves. Near an oil refinery, PAHs on plants closest to the refinery were deposited as particulates, whereas gas phase deposition predominated at greater distances (Bakker et al. 2000). Leaf surface area, thickness of cuticle, presence of trichomes, quantity of stomata, leaf orientation, and lipid content affect PAH accumulation potential (Srogi 2007; Jouraeva et al. 2002; Howsam et al. 2000).

Many of the PAHs are toxic or carcinogenic to humans and animals, and surface deposition of these compounds on food crops is an important means by which PAHs enter the food chain. The ingestion of contaminated produce and other foodstuffs represents one of the most significant non-occupational pathways for exposure to PAHs by non-smokers (Skupinska et al. 2004). Determining whether plants growing in contaminated soils are capable of significant active root uptake and subsequent translocation of PAHs is important in evaluating the risks from PAH exposure (Mumtaz and George 1995, pp 245-246; Khan and Cao 2012).

In a toxicological profile, the Agency for Toxic Substances and Disease Registry identified 16 priority PAHs as important in potential exposure routes and related health effects (Mumtaz and George 1995). Many PAHs are suspected to be carcinogenic to humans and have displayed mutagenic and teratogenic characteristics in animal trials (Mumtaz and George 1995; pp 61, 67-71).

Chemical and Physical Properties of PAHs

The properties of PAHs related to their bioavailability are vapor pressure (P_{VAP}), Henry's law constant, water solubility (S_W), octanol-air partition coefficient (K_{OA}), octanol-water partition coefficient (K_{OW}), soil organic carbon-water partitioning coefficient (K_{OC}), and molecular weight (Table 1; Earl et al 2003; Odabasi et al. 2006).

Vapor pressure is a key property of PAHs because PAHs are semi-volatile and can interact with plant surfaces as a vapor in both the air-leaf and soil-root pathways. Although several relationships describe the thermodynamic behavior of multi-phase and multi-component mixtures, Raoult's law is widely applied to ideal solutions to estimate the contribution of individual components of a liquid or solid mixture to the total pressure exerted by the system (Goldfarb and Suuberg 2008):

$$P_{vap} = \sum_i x_i P_i^o \quad (1)$$

where P_{vap} is the total vapor pressure of the mixture; x_i is the mole fraction of each component; and P_i^o is the vapor pressures of the pure components. Goldfarb and Suuberg (2008) studied the application of Raoult's Law to mixtures of pure, solid PAHs and found that Raoult's Law slightly underestimated the P_{vap} of these mixtures at near ambient temperatures.

Table 1: Properties of the 16 priority pollutant PAHs. All values from Earl et al. (2003) except as noted.

Compound	M.W.	Rings	Aq. Sol.	Vapor Pressure	Henry's Law Constants (25°C)			log K_{OW}	log K_{OA} †	log K_{OC}
	g/mol		mg L^{-1}	Pa (25°C)	Pa m^3 mol^{-1}	atm m^3 mol^{-1}	Dimension-less			
Naphthalene	128.2	2	31.0	38.61	43.01	$4.24x10^{-4}$	$1.74x10^{-2}$	3.37	5.13	3.11
Acenaphthylene	152.2	3	16.1	4.14	8.40	$8.29x10^{-5}$	$3.40x10^{-3}$	4.00	6.34	3.83
Acenaphthene	154.2	3	3.8	1.52	12.17	$1.20x10^{-4}$	$4.92x10^{-3}$	3.92	6.42	3.85
Fluorene	166.2	3	1.9	0.72	7.87	$7.77x10^{-5}$	$3.18x10^{-3}$	4.18	6.90	4.14
Phenanthrene	178.2	3	1.1	0.113	3.24	$3.20x10^{-5}$	$1.31x10^{-3}$	4.57	7.68	4.36
Anthracene	178.2	3	$4.5x10^{-2}$	$7.78x10^{-2}$	3.93	$3.91x10^{-5}$	$1.6x10^{-3}$	4.54	7.71	4.47
Fluoranthene	202.6	4	0.26	$8.7x10^{-3}$	1.04	$1.02x10^{-5}$	$4.20x10^{-4}$	5.22	8.76	5.03
Pyrene	202.3	4	0.13	$1.19x10^{-2}$	0.92	$9.08x10^{-6}$	$3.72x10^{-4}$	5.18	8.80	5.02
Chrysene	228.3	4	$1.6x10^{-3}$	$1.07x10^{-4}$	$6.5x10^{-2}$	$6.41x10^{-7}$	$2.63x10^{-5}$	5.70	10.30	3.66
Benzo(a)anthracene	228.3	4	$1.1x10^{-2}$	$6.06x10^{-4}$	0.581	$5.73x10^{-6}$	$2.35x10^{-4}$	5.91	10.28	5.65
Benzo(b)fluoranthene	252.3	5	$1.5x10^{-3}$	6.6710^{-5}	0.43	$4.26x10^{-6}$	$1.75x10^{-4}$	5.80	11.34	5.74
Benzo(k)fluoranthene	252.3	5	$8.00x10^{-4}$	$4.12x10^{-6}$	$8.4x10^{-2}$	$8.27x10^{-7}$	$3.40x10^{-5}$	6.00	11.37	6.09
Benzo(a)pyrene	252.3	5	$3.8x10^{-3}$	2.1310^{-5}	$4.6x10^{-2}$	$4.54x10^{-7}$	1.8610^{-5}	6.04	11.56	6.01
Dibenzo(a,h)anthracene	278.4	5	$6.0x10^{-4}$	$9.16x10^{-8}$	$1.49x10^{-3}$	$1.47x10^{-8}$	$6.03x10^{-7}$	6.75	12.55	6.58
Indeno(1,2,3-c,d)pyrene	276.3	6	$2.2x10^{-5}$	$1.30x10^{-8}$	0.162	$1.60x10^{-6}$	$6.56x10^{-5}$	6.65	12.43	6.54
Benzo(g,h,i)perylene	276.3	6	$2.6x10^{-4}$	$2.25x10^{-5}$	$7.5x10^{-2}$	$7.40x10^{-7}$	$3.03x10^{-5}$	6.50	12.29	5.61

†Odabasi et al. (2006)

Vapor pressure may also be used in describing PAH behavior in the gas phase. The P_{vap} of PAHs cover a wide range and vapor pressure generally decreases with increasing molecular weight. For example, naphthalene is the lightest PAH (128 g mol^{-1}) with the highest P_{vap}, while benzo(a)pyrene (252.3 g mol^{-1}) has a vapor pressure 6 orders of magnitude lower. Because vapor pressure is closely tied to ambient temperature, PAH partial pressures have diurnal and seasonal variations (Simonich and Hites 1994; Komp and McLachlan 1997). At low ambient temperatures, such as during the autumn and winter, gas phase PAHs partition onto vegetation and terrain (Simonich and Hites 1994). During times of high ambient temperatures, such as during summer and spring, gas phase PAH had the tendency to re-volatilize from adsorbents and back into the atmosphere.

Henry's Law states that, at equilibrium, a fixed ratio is established between the concentration of a substance in a solution and in the gas phase (Nazaroff and Alvarez-Cohen 2001). The content in the gas phase may be expressed as partial pressure:

$$K_H = \frac{[A]}{P_A} \qquad (2)$$

where [A] is equilibrium aqueous concentration (mol m^{-3}) K_H is Henry's Law constant (atm m^3 mol^{-1}), and P_A is partial pressure (atm). Compounds with $K_H > 10^{-4}$ atm m^3 mol^{-1} tend to diffuse primarily in the vapor phase while compounds with $K_H < 10^{-6}$ atm m^3 mol^{-1} diffuse in the aqueous phase. Compounds with intermediate Henry's law constants, $10^{-6} < K_H < 10^{-4}$ atm m^3 mol^{-1}, do not exhibit a preference between and are found in both vapor and aqueous phases (Bromilow and Chamberlain 1995; Site 1997). Values of K_H

for PAHs (Table 1) range from 10^{-3} to 10^{-8} atm m^3 mol^{-1}; roughly half of the PAHs will not exhibit a preference between aqueous and gaseous diffusion. The dimensionless Henry's Law constant is sometimes preferred and is often called the air-water partitioning coefficient (K_{AW}) (eq. 5) (Ryan et al. 1988; Collins and Finnegan 2010).

The lipophilic nature of PAHs is a defining trait of these compounds, and several parameters are used to describe this property. Generally, lipophilicity is related to a compound's octanol/water partitioning coefficient (K_{OW}) which describes a compound's affinity for octanol versus water; however, the octanol-air partitioning coefficient, or K_{OA}, "has become a key parameter in the understanding of pollutant sorption to leaf structures" (Simonich and Hites 1995). The K_{OA} can be related directly to a compound's Henry's Law constant. These parameters can be measured experimentally or calculated using the following equations (Vallero 2014):

$$K_{OW} = \frac{[solute]_{octanol}}{[solute]_{water}} \quad (3)$$

$$K_{OA} = \frac{[solute]_{octanol}}{[solute]_{air}} \quad (4)$$

$$K_{AW} = \frac{[solute]_{air}}{[solute]_{water}} \quad (5)$$

$$K_{OA} = \frac{K_{OW}RT}{K_H} \quad (6)$$

in which K_H is Henry's Law constant, R is the ideal gas constant (8.21x 10^{-5} atm m^3 K^{-1} mol^{-1}), and T is temperature (K).

The partitioning of PAHs between the aqueous phase and fractions of organic carbon in soil or sediments can be predicted using the soil organic carbon-water partitioning coefficient (K_{OC}), the ratio of the mass of analyte adsorbed normalized for

the organic carbon content of the soil or sediment to the aqueous concentration (Chiou et al. 1998):

$$K_{OC} = \frac{n/f_{OC}}{[A]} \quad (7)$$

where *n* is the mass adsorbed (µg), f_{OC} is the mass fraction of organic carbon in the soil or sediment, and [A] is the equilibrium concentration of the analyte, A (µg L^{-1}). The K_{OC} for PAHs can be estimated from the compound's respective log K_{OW} (Karickhoff et al. 1979):

$$\log K_{OC} = \log K_{OW} - 0.21 \quad (8)$$

This equation originally was developed for the adsorption of PAHs and chlorinated hydrocarbons on coarse silt fractions from two sediments. The log K_{OW} for PAHs ranges from 3.3 to 6.7 (Table 1), increasing with increasing PAH molecular weight. K_{OC} also generally increases with increasing molecular weight; larger PAHs are more likely to sorb to soil constituents and become immobilized compared to the smaller, more water soluble compounds.

Pathways for Contamination of Plants by PAHs

Three predominant pathways exist that result in the deposition of PAHs on vegetation (Figure 2). Two of the pathways rely solely on the volatility of PAHs, whereas the third is a traditional mechanism for contaminants and nutrients.

Air-to-Leaf Pathway

This route of exposure includes direct deposition of gaseous PAHs and PAHs adsorbed on particulates. This is a key mechanism of PAH accumulations on vegetation in the vicinity of PAH sources and for decades was considered to be the only pathway of

significance. Air-to-leaf accumulation has been studied extensively and will be discussed in greater depth in another chapter.

Soil-to-Root/Translocation Pathway

This is the traditional pathway for root assimilation of solutes from the soil and subsequent movement to plant shoots. This mechanism has been studied extensively for organic pesticides, and the ideal properties of effective systemic herbicides are well known. As will be elaborated in subsequent sections, the chemical and physical properties of PAHs are favorable for adsorption to root surfaces but unfavorable for uptake and translocation.

Soil-to-Air-to-Leaf Pathway

The soil-to-air-to-shoot mechanism has not been studied as extensively as the air-to-leaf pathway. This pathway requires volatilization of PAHs from the soil followed by adsorption onto the leaves. Leaves are a strong sink for PAHs; therefore, once the PAHs volatilize from the soil, adsorption onto the leaves is a likely outcome.

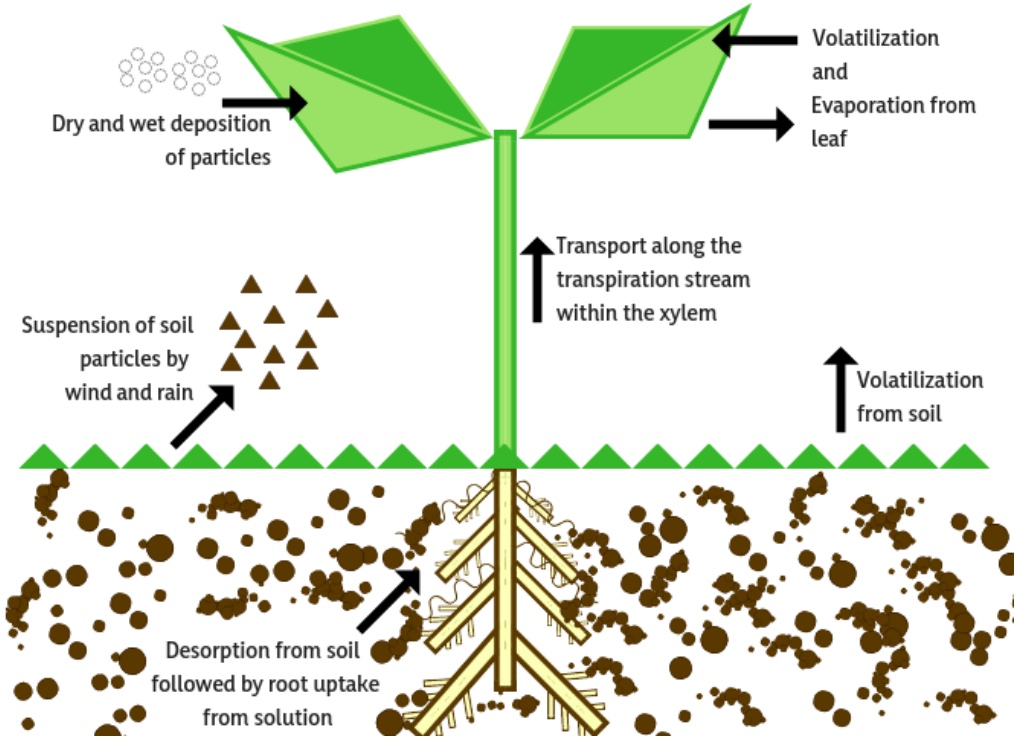

Figure 2: Overview of organic contaminant pathways in vegetation (adapted from Collins 2006)

Compounds that undergo foliar uptake may be transported within the leaf through three pathways; the symplastic, apoplastic, and transcellular pathways (North and Peterson 2011) (Figure 3). Solute transport in the symplastic pathway involves the entire network of cellular cytoplasm and organelles, such as the vacuole, that are connected by plasmodesmata or channels that enable the solute to move from cell to cell. The apoplastic pathway includes the cell walls and intercellular spaces of the leaf in which the compound never crosses any cellular membranes as it is drawn toward the vascular tissues (Wild 2006). Contrary to the symplastic pathway, at the end of the apoplasic pathway, a specialized cellular structure referred to as the "casparian strip" is

present and acts as a barrier of entry for compounds headed toward vascular tissues. The casparian strip directs all compounds into the symplastic pathway and constitutes the end of the apoplasitc uptake route (Taiz and Zeiger 2010). If the compound does not pass this barrier, it does not undergo vascular transport. The transcellular pathway involves cell-to-cell transport, combining both the apoplastic and symplastic routes where the compound enters one end of the cell and exits through the opposite end, proceeding through adjacent cells accordingly (Taiz and Zeiger 2010; Sattelmacher 2008; Raven et al. 1992, cited in Hellstrom 2004). Wild and Jones (2006) observed that the transport pathway for a given compound may be dependent upon the plant species: maize was observed to accumulate phenanthrene within the apoplast, and spinach observed to accumulate phenanthrene within the symplast.

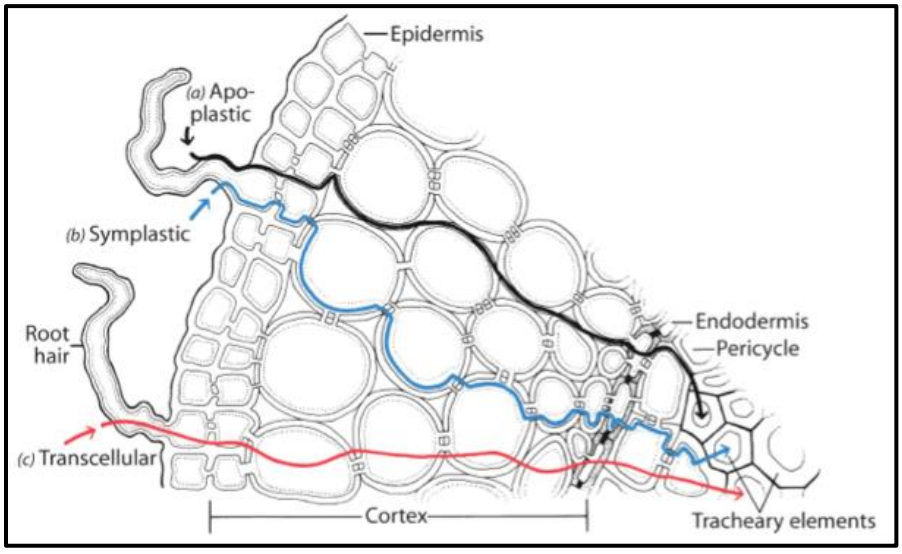

Figure 3. Pathways for the movement of water from soil into the tracheary elements - Symplastic, Apoplastic, Transcellular Transport in Plants (*Reprinted from Raven et al. 1992 cited in Hellstrom 2004; http://www.slideshare.net/mrLandi/cambridge-as-biology-plant-revision)

Physical Mechanism of Aerial Deposition onto Leaf Surfaces

The transfer of volatile compounds from the atmosphere onto the surface of the leaf is a three-step process and strongly dependent upon the "microclimate" of the leaf surface (Figure 4). A wax cuticle is usually found on the surface of the leaf, and immediately above the leaf is a laminar air boundary layer in which the airflow is parallel to the leaf surface. Wind speeds within this layer are greatly reduced compared to the bulk atmosphere but increase with distance from the leaf (Gregory 1961; Bakker et al. 1999; Wild and Jones 2006). Beyond the laminar air boundary is the turbulent "bulk" atmosphere in which transport of contaminants is by wind eddies. (Davidson 1989; Bakker et al. 1999). The first step in the process of moving a contaminant to the leaf surface is transfer of the contaminant from the turbulent atmosphere to the laminar air boundary layer. In step two, transport of gaseous compounds and particles <0.1 µm in this layer is by Brownian motion, which is far slower (up to 7 orders of magnitude slower) than convective transport in the turbulent layer (Jones 1983). The third step is the retention of the contaminant by the leaf surface. Particulates must have some physical or chemical means of retention or they will not remain on the surface; rough leaf surfaces are superior to smooth surfaces for particulate retention. For a gaseous compound, the value of K_{OA} determines its fate. For compounds with high K_{OA} (such as the PAHs), solubility in the waxy cuticle is high, and the compound is efficiently retained by the leaf (McLachlan et al. 1995). Migration into the interior of the leaf occurs slowly, and the mobility of PAHs within the intracellular spaces of plant leaves is limited (Wild and Jones 2004).

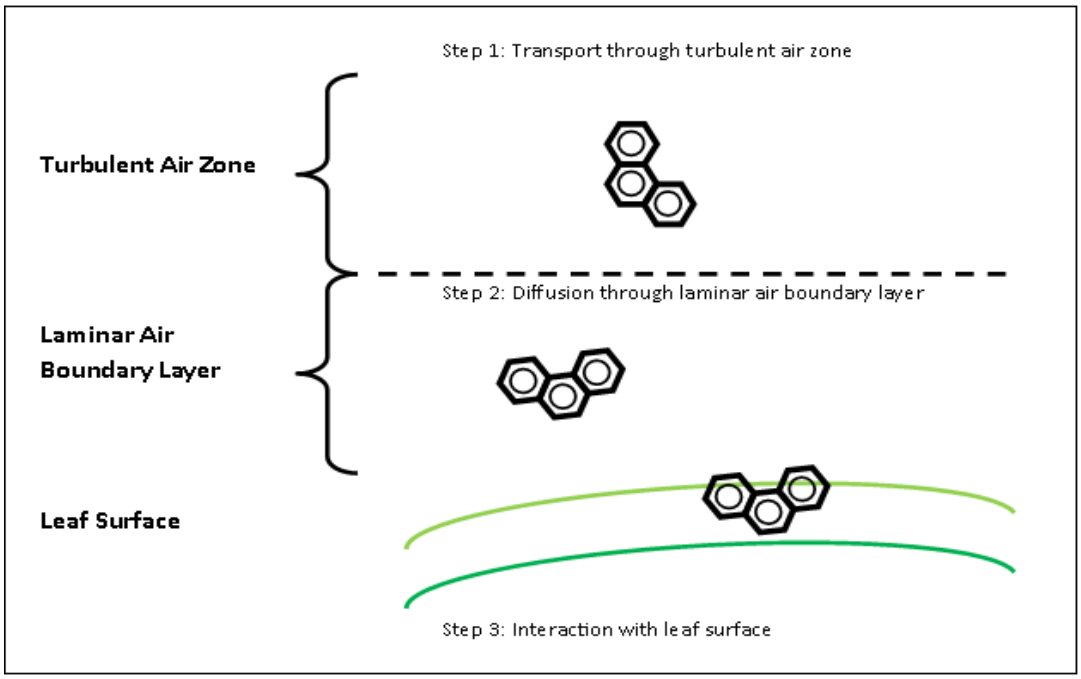

Figure 4: Air-to-leaf transfer of organic contaminants (adapted from Bakker et al. 1999)

CHAPTER III

PAHS IN THE SOIL AND PLANT ENVIRONMENTS

This chapter will compile published chemical and physical properties of PAHs that are the foundation for evaluating root uptake and translocation of PAHs in soil. Background concentrations of PAHs in plants from uncontaminated environments (i.e., far removed from known point and nonpoint sources of PAH pollution) in different settings will be reviewed, providing a baseline of contamination that one can expect regardless of the level of PAH pollution in a given soil. Aerial deposition in contaminated environments will be examined briefly to provide an understanding of plant PAH burdens when the air-to-plant contaminant pathway is the only mechanism of accumulation. Finally, modeling of PAH (and other nonionized, lipophilic compounds) will be presented with the objective of providing insight into uptake variables that must be considered in determining the likelihood that soil-to-root/translocation is significant for PAHs.

Background Concentrations in Plants and Soils

One of the earliest, published scientific studies of PAHs in vegetation (Guddal 1959) observed PAHs on the roots of *Chrysanthemum vulgare* Bernh growing in contaminated soils near a gas works plant. The roots contained 17 mg kg^{-1} total PAHs and 0.21 mg kg^{-1} anthracene. Gunther et al. (1967) measured the concentrations of anthracene found in oranges growing alongside a heavily-trafficked highway and found 5 mg kg^{-1} (all in the rind) compared to essentially undetectable quantities in oranges

grown in unpolluted areas. The authors also determined that PAHs are not mobile within the oranges; 85% of the PAHs applied to the rind volatilized or degraded rapidly, and PAHs were undetectable in the pulp of the fruit or the twigs of the trees.

Hancock et al. (1970) examined the impact of diesel train traffic on PAH content of little bluestem (*Schizachyrium scoparium* (Michx.) Nash) and post oak (*Quercus stellate* Wagenh.). Total PAH content was higher in post oak than little bluestem and higher in control areas than in the railroad right of way. Total PAH in post oak was approximately 225 μg kg^{-1} near train traffic and 275 μg kg^{-1} in control areas; 115 μg kg^{-1} in right of way for little bluestem and 150 μg kg^{-1} in control areas. The authors stated that the control plants were too remote from any source of contamination to account for the observed PAH concentrations and postulated the synthesis of PAHs by the plants.

Grimmer and Duvel (1970) measured background PAH concentrations in vascular plants grown in growth chambers under different conditions. Plants that were cultivated in chambers in which the air was filtered through particle filters and activated charcoal to remove all airborne organics and contained no measurable PAHs, with the exception of 0.1 μg kg^{-1}coronene detected in soybean. All crops grown in unfiltered air were found to contain PAHs with some concentrations reaching >4.0 μg kg^{-1}. The experiment initially was conducted not as a demonstration of aerial deposition of PAHs on higher plants but to test an emerging hypothesis that plants were synthesizing PAHs (Blumer 1961; Graf and Diehl 1966; Andelman and Suess 1970). Although the study demonstrated that PAHs were not being biosynthesized by terrestrial plants, researchers who were skeptical of long-distance transport of PAHs continued to quote the PAH-

synthesis hypothesis for another fifteen years (e.g., Suess 1976; Sims and Overcash 1983.) However, the long-range transport of PAHs from multiple sources has been demonstrated (Lunde and Bjorseth 1977; Halsall et al. 1997, 2001; Garban et al. 2002; and Friedman and Selin 2012).

Sims and Overcash (1983) summarized published background concentrations of individual PAHs in plants growing in uncontaminated areas. The highest concentrations were reported by Hancock et al. (1970) as discussed above with individual PAHs ranging from 22 to 88 μg kg^{-1}. Nearly all the concentrations reported by other authors were <1 μg kg^{-1}.

Edwards (1983) reviewed published concentrations of PAHs in soils and plants. He found that soil concentrations ranged from 1 μg kg^{-1} to 650,000 μg kg^{-1} but were typically < 1000 μg kg^{-1}. Concentrations of plants ranged as high as 12,300 μg kg^{-1} in the vicinity of a gas works facility in Norway (Guddal 1959) and 25,000 μg kg^{-1} next to a highway in California with high air pollution (Gunther et al. 1967). In a study in Switzerland far from human impacts, plant concentrations as high as 2200 μg kg^{-1} were observed (Graf and Diehl 1966). Among the 22 studies reviewed by Edwards (1983), only four reported PAH concentrations in both soil and plants. No obvious trends emerged between soil concentration and plant concentrations.

Jones et al. (1989a) analyzed PAHs in archived soil samples from the Rothamsted Research Station (Table 2). Jones et al. (1989a) analyzed soils from untreated plots sampled and archived at various intervals from 1846 to 1980. Total PAH concentrations in the soils sampled from 1846 to 1914 ranged from 300 to 370 μg kg^{-1}

but exceeded 1000 μg kg^{-1} by 1944 and increased to 1770 μg kg^{-1} by 1980. "The rates of PAH input (i,e., atmospheric deposition) clearly exceed rates of output (microbial breakdown, photooxidation, vaporization, crop offtake, and leaching) at Broadbalk. The similarities between the average annual rates of increase in the soil PAH burden and the likely average atmospheric deposition flux at Rothamsted suggest that losses via these five possible mechanisms probably effectively remove only a relatively small proportion of the total annual input" (Jones et al. 1989a).

Changes in grass and grain concentrations (Jones 1989b) were determined from samples using the same plots and time intervals as Jones et al (1989a). The concentrations of PAHs in the grain were much higher initially (623 μg kg^{-1} total PAH in grass in 1860 and 46 μg kg^{-1} in grain in 1880) than the most recent sampling (1980: 109 μg kg^{-1} total PAH in grass and 4.3 μg kg^{-1} in grain). The greatest concentrations in the grass were observed in 1880: 6859 μg kg^{-1} total PAH. The concentrations of PAHs decreased from 1880 to 1980. Total mass was 1500 μg m^{-2} in 1880 and only 37 μg m^{-2} in 1980, and this trend was consistent for the five sampling intervals during this period. The authors attribute this to improvements in air quality with time. The trend in decreased concentrations of PAHs in the grass and grain (either as concentration or total mass) bore no resemblance to the soil concentrations. The soil concentrations increased at each time interval but plant concentrations decreased; the authors concluded that the soil contributed very little to plant accumulation of PAHs.

Table 2: Rothamsted PAH soil concentrations (Jones et al. 1989).

PAH	1846	1881	1893	1914	1944	1956	1966	1980	1986
	---------- μg kg^{-1} ----------								
Phenanthrene	46	68	45	89	110	120	160	140	48
Anthracene	4.5	13	9		4	10	9	13	11
Fluoranthene	39	45	43	37	120	190	120	210	120
Pyrene	19	14	7	11	50	120	75	150	99
Benzo(a)anthracene	22	9.4	3	5.9	25	69	26	110	56
Chrysene	24	16	11	18	50	87	41	120	78
Benzo(e)pyrene	24	13	7	11	35	65	27	130	53
Benzo(a)pyrene	18	6.7		12	23	73	28	120	72
Perylene	2.2	0.86			<3	15	9	18	14
Anthanthrene	1.2	0.12				1.2		2.9	
Benzo(ghi)perylene	22	8.3		6.1		55		66	
Benzo(b)fluoranthene	18	12	9	86	35	76	30	220	58
Benzo(k)fluoranthene	17	8.4	9	6.2	35	73	30	250	58
Naphthalene	39	38		53		28		23	
Acenaphthylene	1.6	0.73				3.4		5.0	
Acenaphtene	2.0	0.9		2.0		4.2		6.0	
Fluorene	0.78					3.7		9.7	
Dibenzothiophene	6.2	6.8		6.6		11		32	
4H-cyclopenta(def)phenanthrene	14	19		4.9		15		22	
Indeno(1,2,3-cd)pyrene	23	14	5	12	31	92	29	100	63
Coronene	7.1	5.4	3	5.4	9	18	9	22	17
TOTAL	350	300	350*	370	1250*	1130	1390*	1770	1770

*Different methods were used for analyzing the PAH, and the methods did not yield the same concentrations on the same samples. Therefore, the authors "normalized" their values to make them as equivalent as possible.

Accumulation of PAHs in vegetation was measured in rural, suburban, and urban areas across the Midwestern United States (Wagrowski and Hites 1997). *Acer saccurum* was a common species to each environment. Total PAH was 220 µg kg^{-1} in maple leaves in the rural settings; 510 µg kg^{-1} in maple leaves in suburban areas; and, 1600 µg kg^{-1} in urban maple leaves, all of which was attributed to aerial deposition.

Samsoe –Petersen et al (2002) measured the concentration of PAHs in fruits and vegetables in uncontaminated control soils. Soil PAH concentration averaged 0.42 mg kg^{-1}, and concentrations in the vegetables were below detection.

Terzaghi et al. (2015) examined PAH concentrations as a function of time in tree leaves in an unpolluted environment in northern Italy. PAH concentrations varied considerably from one month to the next, and the two species studied (*Cornus mas* and *Acer pseudoplatanus*) exhibited different time trends. The concentrations in both species varied from 15 to 52 µg kg^{-1}, within the range of background concentrations found in other studies.

Aerial Deposition of PAHs onto Plants

Although the focus of this review is the accumulation of PAHs in plants from the soil through root uptake, aerial deposition is an important pathway that has the potential to account for nearly all the PAHs in vegetation under many circumstances. Aerial deposition of PAH on vascular plants has been studied for decades, and this section will review some of the key publications to provide the range of concentrations one can expect when aerial deposition is predominant or the only mechanism of accumulation.

As discussed in the previous section, Grimmer and Duvel (1970) monitored PAH accumulation in plants grown in growth chambers with ambient air and in growth chambers with the air filtered to remove all organics. Concentrations of PAHs were undetectable in those plants grown in filtered air but were each greater than 4 μg kg^{-1} for plants grown in ambient air.

Hancock et al. (1970) measured PAHs in plants growing near and 24 km away from a railroad right of way. For both sets of samples, the concentrations of the PAHs varied seasonably but ranged from 100 to 325 μg kg^{-1}. Particularly in the case of the samples far from the railroad, aerial deposition was the only likely source of the PAHs.

Larsson et al. (1982) measured PAHs in lettuce grown at various distances from a highway and from an aluminum smelter. Total PAHs nearest the highway were 89 μg kg^{-1} but declined to a relatively constant concentration of 17 to 25 μg kg^{-1} at distances of 17 to 50 m from the highway. Near the smelter (0.5 km downwind), the total PAH concentration was 922 μg kg^{-1}. At 6.5 km downwind, the PAHs declined to 160 μg kg^{-1} but were <30 μg kg^{-1} in lettuce samples taken upwind of the facility.

Larsson et al. (1985) examined directly the impact of aerial deposition of PAHs on leaf lettuce and subsequent removal by rain near a highway. One plant shelter (8 m from the highway) was constructed of transparent plastic that fully enclosed the plants, limiting particulate deposition, and may have slightly restricted vapor deposition (a small opening was constructed on the side of the roof of the shelter that faced away from the highway). A “rainout” shelter built 8 m from the highway had a transparent roof but

was otherwise fully open; this shelter allowed deposition from the air but prevented any washing action of rain. Leaf lettuce (*Lactuca sativa*) was planted in these structures as well as fully in the open at distances of 8 to 65 m from the highway. The plants sampled at 8 m from under the rainout shelter and in the open (no enclosure) had similar total PAH concentrations (49 and 46 μg kg^{-1}, respectively). The fully enclosed plants contained 23 μg kg^{-1} total PAHs. Concentrations of total PAHs steadily declined to 17 μg kg^{-1} at 65 m from the highway.

Bakker et al. (1999) examined the concentrations of PAHs in the leaves of *Plantago* spp. after short-term exposures in the field. The plants were germinated in a closed greenhouse and transferred to a greenhouse with open sides to allow full exposure to outside air. The nearest source of PAHs was a highway 800 m away. Total PAH concentrations were low (ranging from 20 to 100 μg kg^{-1}), but the impact of leaf architecture was evident. Leaves with low density of leaf hairs (*Plantago major* and *P. lanceolata*) tended to accumulate the highest total PAHs though leaves with high density of hairs (*P. media*) accumulated greater amounts of high molecular weight PAHs.

Bakker et al. (2000) examined PAH concentrations in plants and soils at varying distances from a petroleum refinery. The highest PAH concentrations in plants (8 mg kg^{-1}) and soils (≤300 mg kg^{-1}) were observed nearest the refinery, but concentrations up to 4 km away from the refinery tended to rapidly reach a consistent value (5 to 30 mg kg^{-1} for soils; 300 to 800 μg kg^{-1} for plants). The authors discussed their results and other published results in the context of aerial deposition: for soils, lighter PAHs tend to

be vapor phase only and travel greater distances, and higher molecular weight PAHs deposit closer to the source due to their association with airborne particulates. This distribution is not seen for plants, probably because the particulates are washed from plant surfaces with rainfall.

Peck and Hornbuckle (2003) measured the flow of gaseous anthracene from a growth chamber in which *Ficus benjamina* was growing. The original emphasis of the study was to provide validation for a model of the fate of gas phase anthracene introduced into an atmosphere, but some unanticipated observations were the most relevant to this review. The *Ficus benjamina* was purchased from a local florist, and when the plants were introduced into the chamber, the gaseous anthracene concentrations immediately spiked from an ambient level of ~10 ng m^{-3} to over 100 ng m^{-3}. The authors speculated that the *F. benjamina* had been contaminated at the florists due to the proximity of the store to a very busy city street. The conclusions from this study are a) PAH accumulation on the surface of plant leaves occurs readily, even in indoor environments, and b) anthracene on the surface of *F. benjamina* readily desorbed. The authors did not report the anthracene concentrations of the leaves.

In a field study of a forest and nearby clearing, PAH accumulation by leaves was measured over time and as a function of air concentrations (Terzaghi et al. 2015). Concentrations of the PAHs in the plants was found to be due to atmospheric deposition only but related to leaf area index, leaf specific area, plant species, and concentrations of PAHs in the air. Beginning from the bursting of the leaf buds, PAH concentrations in the

leaves increased steadily to a plateau concentration, the value of which was dependent upon the plant species.

Early Studies of PAH Accumulation in Plants Growing in Contaminated Soils

Harms (1975, as reported in Edwards 1983) examined the movement of ^{14}C-benzo(a)pyrene in wheat seedlings grown in solution culture and found that 0.2% of the original parent compound was found in the shoots.

Ellwardt (1976) measured uptake of PAHs from soil amended with PAH-contaminated compost. The plant tissues examined were potato tubers and stems; oat grain and straw; and rye grain and straw. Soils amended with PAH-contaminated sludge and composts showed an increase of approximately 65% in total PAHs. However, only the oat materials showed a consistent increase in PAH content, leading the authors to the conclusion that PAH uptake and translocation from the soil was far less important than atmospheric inputs.

Edwards et al. (1982) examined the uptake of ^{14}C-anthracene from soil and solution culture by soybean (*Glycine max*) using three experiments. In the first experiment, plants grown in nutrient solution were exposed for 1.6 to 119 h in aqueous solutions containing 2.94 µg ^{14}C-anthracene L^{-1}, after which dried plants were analyzed for ^{14}C. Thin layer chromatography was used as a qualitative analysis to determine if the ^{14}C was present as the parent compound. Approximately 1.5% of the original radioactivity was found in the leaves (Table 3). The total activity in the nutrient solution declined rapidly in the first 2 hours of the experiment to approximately 20% of the

original value. Activities in all plant parts reached a maximum at 22 hours and rapidly declined. The authors measured the evolution of volatiles from the nutrient solutions, and the amount of radioactivity volatilized was similar to the activity in the leaves. The second experiment was uptake of anthracene by soybean from soils spiked by pipetting an aqueous solution to the surface of the soil containing growing plants. After 4 days, the leaves contained 0.4% of the original ^{14}C activity (Table 4). The third experiment measured accumulation of anthracene by soybean from the atmosphere. Anthracene was dissolved in water contained in an open, flat dish and allowed to diffuse into the atmosphere surrounding soybean plants growing in solution culture. After three days, anthracene concentration in the leaves was 463 µg kg^{-1}, 11.8 µg kg^{-1} in the stems, and 10.2 µg kg^{-1} in the roots. The low percentages of anthracene observed to transfer from roots to leaves were similar to nearly all the observations preceding the experiments of Edwards et al. (1982).

Table 3: ^{14}C activities in various components of soybean and soil (Edwards et al 1982).

Medium	**----------^{14}C Activity (% of Total) ----------**					
	Roots	**Stems**	**Leaves**	**Volatiles**	**Medium**	**Total**
Nutrient Solution	61	5	1.3	0.8	19	87
Soil	2	2	0.4	0.6	93	98

Table 4: Anthracene concentrations and masses in various soybean components and soil as reported by Edwards et al. (1982).

Component	Dry weight	Anthracene	
		Concentration	Mass
	---- g ----	--- μg kg^{-1} ---	---- ng ----
Roots	0.25	125	31
Leaves	0.18	31	5.6
Stems	0.06	500	30
Soil	103	10	1,030
CO_2			21*
Volatiles			8.3*
Transpired			0.1*

* Edwards et al. (1982) reported the anthracene in these components as μg anthracene per g plant tissue. The masses reported here were calculated using the total plant mass (0.49 g).

Sims and Overcash (1983) reviewed several publications that focused on the fate of PAHs in soil-plant systems. Using a compilation of data from multiple studies, background soil/sediment concentrations of benzo(a)pyrene ranged from 0.010 to 8010 μg kg^{-1}, dry wt. depending on proximity to point sources. Concentrations of benzo(a)pyrene for several plant species ranged from 0.01 to 50 μg kg^{-1} (dry wt.)

depending on the plant tissues being analyzed. Leaves generally exhibited the highest concentrations while underground plant structures and fruits were observed to have the lowest concentrations. This trend suggests that PAHs are poorly transported within plants and that atmospheric deposition is the major source for detected contamination in the foliar tissues and fruits of contaminated plants.

CHAPTER IV

SOIL-TO-ROOT-TO-VEGETATION PATHWAY

When one considers the accumulation of inorganic ions or compounds in plants, root uptake followed by translocation to the shoots is the assumed pathway. Likewise, many classes of organic contaminants follow this route including triazine herbicides, systemic insecticides, and some chlorinated solvents are readily removed from the soil by plant roots and moved to the leaves and stems. However, a long list of chemicals cannot be efficiently removed from the soil, and the reason for this can be explained by strength of retention by the soil (e.g., Pb), water insolubility (PCBs), and incompatibility with root uptake mechanisms. For nonionic organic compounds, one can determine the likelihood of significant plant uptake through modeling and experimental determinations.

In this chapter, modeling will be discussed first to illustrate the theoretical considerations: a) air deposition on the surfaces of vegetation; b) PAH uptake from soil by plant roots; and c) integrated models that consider all deposition and uptake pathways. The last section will be a thorough review of the literature discussing d) direct observations of PAH movement within plant tissues; e) accumulation in leaves and stems in low- to moderately-contaminated soil; f) accumulation in leaves and stems in highly contaminated soils.

Definitions of Common Parameters

As K_{OA}, K_{OW}, and K_{OC} each have been used as a measure of chemical lability of PAHs in the vapor, aqueous, and solid phases, respectively, several parameters have been established to designate biolability. Examples are bioconentration factor (BCF), stem concentration factor (SCF), root concentration factor (RCF,), and transpiration stream concentration factor (TSCF) (Briggs et al. 1983, Trapp 2002, Collins et at 2006, Collins et al. 2009). BCFs refer to the ratio of the concentration of a chemical within the whole plant to the concentration of chemical in the surrounding medium (Burken 2003; Trapp 2000). The RCF and SCF are similar to the BCF but refer specifically to concentrations in the roots and the shoots, respectively. The TSCF is a measure of the mobility of a given compound within the transpiration stream (Bromilow and Chamberlain 1995).

$$BCF = \frac{concentration\ in\ plant\ tissue\ (\frac{mg}{kg})}{equilibrium\ conc.in\ soil/water\ (\frac{mg}{kg})} \quad (9)$$

$$RCF = \frac{concentration\ in\ root\ tissue\ (\frac{mg}{kg})}{equilibrium\ conc.in\ soil/water\ (\frac{mg}{kg})} \quad (10)$$

$$SCF = \frac{concentration\ in\ stem\ tissue\ (\frac{mg}{kg})}{equilibrium\ conc.in\ soil/water\ (\frac{mg}{kg})} \quad (11)$$

$$TSCF = \frac{concentration\ in\ transpiration\ stream\ (\frac{mg}{kg})}{equilibrium\ conc.in\ soil/water\ (\frac{mg}{kg})} \quad (12)$$

Models of Air Deposition on Vegetation Surfaces

Simonich and Hites (1994) derived a two equation model for semivolatile organic compounds (SVOC) to explain partitioning between gas phase and particle phase in the atmosphere and between the vegetation and the atmosphere. In the atmosphere, the partitioning was defined by:

$$K_p = \frac{F/TSP}{A}$$

"where K_p is the partition coefficient, F is the equilibrium concentration of the SVOC associated with atmospheric particles (ng/m^3); TSP is the total atmospheric particle concentration (pg/m^3), which is a measure of the total capacity for gas-phase sorption to particles, and A is the equilibrium gas-phase concentration of the SVOC (ng/m^3)," (Simonich and Hites 1994). A high correlation between log K_p values and vapor pressures suggests that partitioning of the SVOCs increases as vapor pressure increases. An important aspect of this equation is that K_p is termperature dependent: partitioning to atmospheric particles increases as ambient temperature increases.

The authors defined the vegetation-atmosphere coefficient as:

$$K_v = \frac{veg/lipid}{gas}$$

"where veg is the concentration of an SVOC in vegetation (ng/g of dry wt), lipid is the lipid content of the vegetation, which is a measure of the total capacity for sorption of lipophilic SVOCs to vegetation (mg/g of dry wt), and gas is the atmospheric gas-phase SVOC concentration prior to the collection of vegetation (ng/m^3). The units for K, are

m^3 of air per mg of lipid." Also, the authors calculated binding energies for the PAHs onto vegetation and found that the energy of binding increased with increasing mass of the PAH except for the highest molecular weight compounds, indeno[l,2,3-*cd*]pyrene and benzo[ghi]perylene, suggesting that the latter compounds are more strongly bound to the atmospheric dust particles than the vegetation.

McLachlan et al. (1995) conducted a field validation of a model that focused on the foliar uptake of gaseous SVOCs in ryegrass. The organic compounds in question were dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs). The model was founded on experimental measurements of equilibrium between the gas phase and adsorption of the compounds onto plant leaves; the air fugacity was known from measurement, and the plant surface fugacity was calculated. The model was developed based on a three compartment model (air, leave surface, and reservoir for organic compounds within the leaf), chemical diffusion across these boundaries, dissolution of the compounds in the lipids of the leaves, and temperature dependence from the Clausius-Claperyon equation. Partitioning between the air and the leaf was based on fugacity: fugacity of the compounds in the air was measured, and the fugacity capacity of the leaves was calculated using octanol/air partition coefficients (K_{OA}) and lipid content of the leaves. After measuring some of the coefficients and simplifying others, the model reduces to the equation:

$$\frac{dc_g}{dt} = k_{AG}a_{AS}(c_A - c_G/K_{GA})$$

Where c_G is the grass concentration on a volume basis, K_{GA} is the fresh grass/air partition coefficient (K_{GA} = 0.01 K_{OA} for a given compound), a_{AS} is the surface area of the cuticular resistance, c_A is the concentration in the air. The correspondence between the model and the field measurements were excellent, with agreement within 30% for nearly all compounds. However, the data also illustrated some important points about the importance of K_{OA} on the nature of the partitioning. The relationship between c_G/c_A and log K_{AO} was linear for values below log K_{OA} = 9 and then plateaued (Figure 5), indicating that equilibrium was not reached for compounds with high K_{OA}. The authors then identified three groups of compounds, based on these and other observations: "those that approached equilibrium with the gas phase during the period of this study (log K_{OA} < 8); those that did not approach equilibrium (8 < K_{OA} < 11); and those that did not approach equilibrium and where particle bound deposition may have been a significant pathway to the plant (K_{OA} > 11)." These delineations were used by other authors investigating aerial deposition of SOVCs, particularly PAHs.

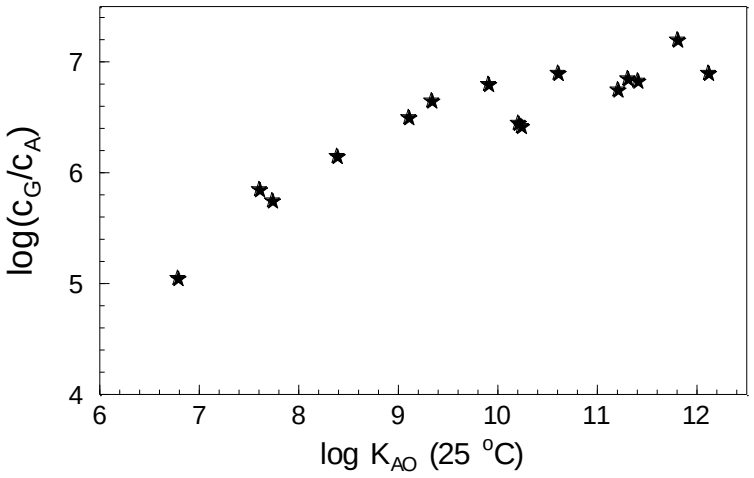

Figure 5. A plot of measured values of the ratio of the grass concentrations to the gas-phase concentrations versus logK_{OA}.

Schreiber et al. (1996) constructed and tested a simple model for the diffusion of organic compounds across the cuticular membrane of leaves. The waxy cuticle provides a barrier for loss of water through the leaf surfaces as well as a layer of protection. The model was based on the flow of a substance across the cuticle:

$$F = P \cdot A \cdot \Delta c$$

where F is steady state flow, P is the permeance, A is the exposed area, and Δc is the concentration gradient across the cuticle. The permeance P is further defined:

$$P = \frac{D \cdot K}{\Delta x}$$

"D (m^2 s^{-1}) is the diffusion coefficient of the compound within the membrane, K is the dimensionless partition coefficient of the compound between the external donor solution and the membrane and Δx (m) is the path length of diffusion

through the membrane," (Schreiber et al. 1996). Because of the nature of the diffusion across the cuticular membrane, Δx is more than just the thickness of the cuticle, representative of the tortuous path length. The authors found that passive diffusion across the waxy, lipophilic membrane (outlined above) followed the laws of passive diffusion as outlined above. Although the authors included a limited number of compounds in their study (and no PAHs), the results make clear that passive transport across the cuticle is an important process in the deposition of semi-volatile organic compounds on the surfaces of leaves.

Models for PAH Uptake by Plant Roots from Aqueous Solutions

Once in solution, PAHs will move with the transpiration-generated flow of water toward the root. If the PAH adsorbs to the root surface (RCF, Equation 10), a small concentration gradient may be generated and cause diffusion from the bulk soil toward the root (Kaliszova et al. 2010). The magnitude of the RCF is not necessarily a reflection of true "uptake" but may simply be surface adsorption, and RCF values often increase with increasing lipophilicity (Shone and Wood 1974).

Briggs et al. (1982) applied the RCF and TSCF equations generated by Shone and Wood (1974) to investigate and model the root uptake and translocation of non-ionized chemicals by barley cultivated in solution culture. ^{14}C-labeled o-methylcarbamoyloximes, a chemical belonging to a family of systemic insecticides, as well as inactive analogues of 1,1-dimethyl-3-phenylurea, compounds belonging to the herbicide family of substituted phenylureas, were used as representative compounds for

their experiment. The lipophilicity (log K_{OW}) of these compounds ranges between -0.57 and 4.6 for the insecticides and -0.12 and 3.7 for the herbicides. Their experimental design included uptake trials that lasted 24 and 48 hours, followed by destructive sampling and analysis. RCF and TSCF values were calculated and compared against the lipophilicity of the compound in order to test the application of using the lipophilicity of a given compound as an indicator to predict potential accumulation. The relationship between the RCF and log K_{OW} was very strong, with an R-value equal to 0.98. This relationship allowed the authors to conclude that two distinct mechanisms exist for accumulation of organics in roots: 1) lipophilic compounds tend to primarily adsorb to root surfaces; 2) polar compounds have far less adsorption and tend to favor uptake into the aqueous of the roots (the free space between the roots). The relationship between the TSCF and log K_{OW} did not supply the same level of accuracy.

The Briggs et al. (1982) study was expanded to calculate stem concentration factors (SCF) by exposing plant roots to radiolabeled compounds in nutrient solution and measuring the distribution of the radioactivity within various portions of the plants after the experimental period (Briggs et al. 1983). Stem concentration factors were calculated with the following equation:

$$SCF = \left[10^{(0.95 \log K_{ow} - 2.05} + 0.82\right] \cdot 0.784 \; exp\{-[(\log K_{ow} - 1.78)^2 / 2.44]\} \qquad [17]$$

Unfortunately, the compounds studied all had log Kow < 4, so application of these results to PAHs is difficult. However, extrapolation of equation 17 beyond log K_{ow} = 4 finds a SCF maximum at log K_{ow} = 4.5.

Bromilow and Chamberlain (1995) examined the underlying principles that regulate the plant uptake of chemicals. Their emphasis was mostly on pesticides, but the principles are general and apply to PAHs. For uptake of chemicals in soils by plant roots, the authors first considered vapor phase versus solution phase. The PAH with the smallest H' (dimensionless Henry's Law constant) is dibenzo(a,h)anthracene and is predicted to diffuse in the aqueous phase only. Those PAHs with $H' > 10^{-4}$ are expected to diffuse in the air phase only, and those with $10^{-4} > H' > 10^{-6}$ will diffuse in either the aqueous or air phases (Figure 6).

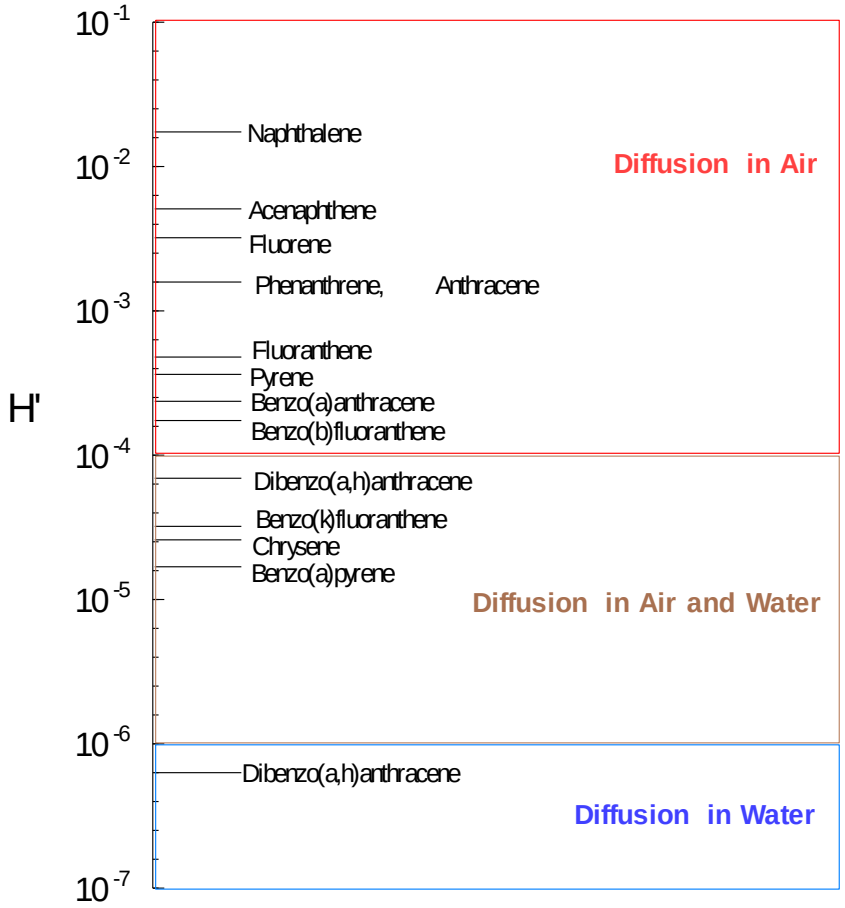

Figure 6. The relationship between Henry's Law Constant (H', dimensionless; see Table 1) and predominant medium for diffusion of PAHs. (adapted from Bromilow and Chamberlain 1995)

In the context of the TSCF, the authors stated, "To reach the vascular system and thus the shoot, compounds must cross the plasmalemma, the membrane separating the apoplast and symplast, and TSCF is thus a measure of the ability of a compound to do this. The curve shown…" (Figure 1 in this thesis) "…therefore can be taken to represent membrane permeability plotted against lipophilicity, with maximum permeation

occurring at a log K_{ow} value of approximately 1.8." (Bromilow and Chamberlain 1995). Most relevant to this was the comment, "It thus appears that, for reasons not certain, the more lipophilic compounds cross the endodermis much less efficiently than water, with compounds of log $K_{ow} > 4$ scarcely moving into the shoots at all." Among the PAHs, only naphthalene has log $K_{ow} < 4.0$, and, therefore, none of the PAHs are expected to have significant TSCFs. As discussed previously in this thesis, including the influence of organic matter shifts the optimum log K_{ow} even further from the lipophilic PAHs.

Using a pressure apparatus to accelerate collection of xylem sap from roots with the plant tops removed, the effect of log K_{ow} on TSCF was determined for a suite of pesticides (Sicbaldi et al. 1997). The authors generated a bell-shaped curve similar to that of Briggs et al. (1982) except that the maximum TSCF was observed for log K_{ow} near 3.0. The authors also measured the time required to for xylem sap concentrations to establish steady state; higher log K_{ow} values were associated with longer equilibration times. The authors explained that low lipophilic chemicals move mainly in an apoplastic pathway (Fig. 3), moving by water mass flow with minimal adsorption to membrane surfaces and rapidly attaining steady state concentrations. Highly lipophilic compounds, however, move through the plant by a symplastic pathway, moving relatively easily and relatively quickly across membrane structures once steady state is achieved. Steady state for these compounds is achieved only when all sites of interaction with all lipid or lipid-like have been saturated.

Trapp et al. (2007) examined diffusion of PAHs across thin disks of plant tissue

(carrot and potato) and compared the diffusion to a pure water system. Diffusion in these simple systems was independent of hydrophobicity of the compounds (log K_{ow}). However, the BCF values for potato grown in soil decreased linearly with log K_{ow}, illustrating the impact of hydrophobicity on total plant accumulation and the importance of considering the competing effects of soil.

Models for PAH Uptake by Plant Roots from Soils

The first step in the accumulation of PAHs by roots is the detachment from the soil and subsequent movement to the root surface. Concentrations of PAHs in the solution phase of contaminated soils will be governed by the Chiou partition coefficient (K_{OC}; Equation 7) and the fraction of organic carbon in the soil. Under nearly all circumstances, adsorption of organic chemicals by the hydrophobic surfaces in the soil, particularly soil organic matter, will result in significant decreases in solution concentrations.

Briggs (1983) discussed chemical uptake by plant roots from the solution phase, but made the following observation concerning the introduction of soil into system: "For plants grown in soil, adsorption of the chemical by the soil would make more lipophilic compounds less available for uptake by plants, and so the optimum K_{ow}, for stem accumulation would be less." A similar observation was made by Burken (2002).

Ryan et al. (1988) integrated soil properties into the absorption and translocation equations of Shone and Wood (1974) and found that plant uptake of organic pollutants was predicted to be significantly reduced compared to nutrient solutions with no soil

(Fig 7). The stem concentration factor (SCF) was used to represent the combined effects of bioavailability from the soil and translocation within the plant. The authors also investigated the impact of increasing organic matter content on the Gaussian uptake/translocation curves and is displayed in Figure 8. As soil organic matter increases, SCF values decreased and the value of log K_{OW} required for maximum SCF also decreased from log K_{ow} 2 at 0.25% OM to 0.75 at 6% OM.

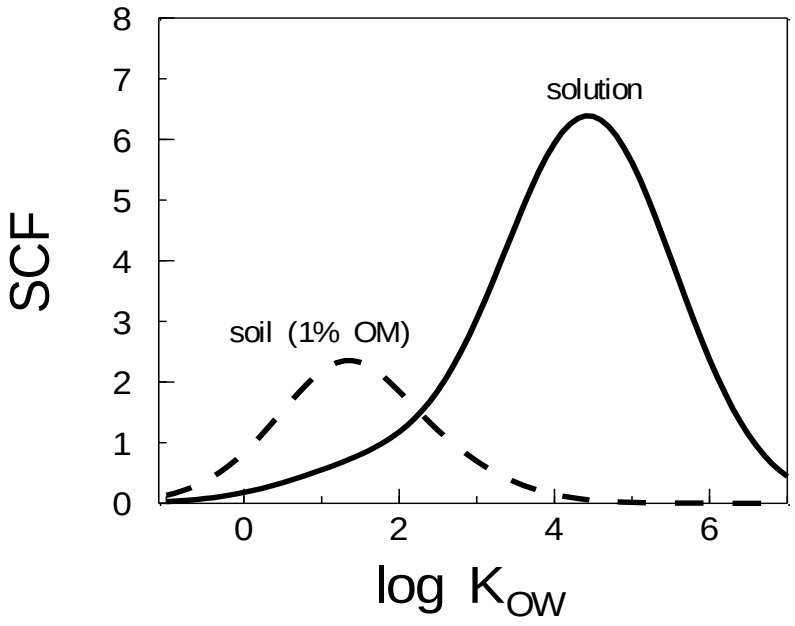

Figure 7: The relationship between logK_{OW} and stem concentration factor (SCF) for nutrient solutions and soils with 1% organic matter (adapted from Ryan 1998).

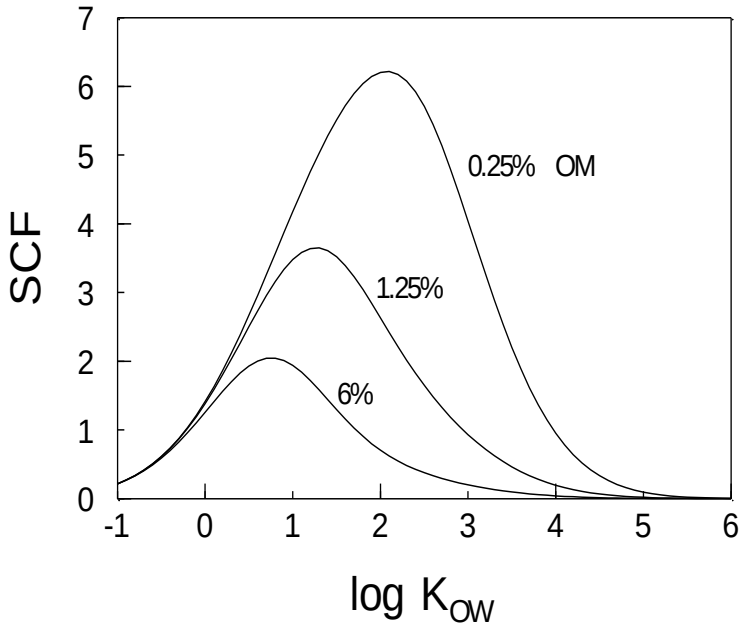

Figure 8: Impact of organic matter content in soils on the relationship between logK_{OW} and SCF. (adapted from Ryan et al. 1998)

Models for SCF and TSCF have the same general shape but vary considerably with respect to the location of the log K_{OW} required for maximum uptake. This difference is very important in the case of PAHs: for TSCF, nearly all PAHs are predicted to have limited uptake. In the case of SCF, the SCF for all PAHs in nutrient solution would be greater than every SCF for PAHs in soil. The presence of soil organic carbon shifts the SCF curves to lower log K_{OW}, excluding nearly all but naphthalene from plant uptake.

Trapp (2002) developed dynamic root uptake model specific to non-ionizing, lipophilic compounds (e.g., PAHs) and compared this to the classic equilibrium model. Underlying assumptions of the model:

1) Concentrations in root are defined by equilibrium as described by a linear root partition coefficient (K_{PW}) modified by soil bulk density and proportional to volumetric water content, volumetric lipid content, and K_{OW} of the compound.
2) Diffusion into roots is proportional to root diameter squared and inversely proportional to the diffusion coefficient. The analytical solution to the contributing equations is determined for concentration in the z-direction as a function of time (*C(z,t)*):

$$C(z,t) = C_0 erfc[\frac{z}{\sqrt{4Dt}}] \quad (13)$$

where C_0 is the constant concentration at the surface and D is the diffusion coefficient.

3) Flux into roots is based on the assumption that only the root epidermis is in diffusive exchange with the soil and that uptake is through transpiration stream flux, Q (L d^{-1}). The resulting rate equation for the mass of chemical in the roots (m_R) is:

$$\frac{dm_R}{dt} = C_S Q - C_{xylem} Q - k_m m_R \quad (14)$$

where k_m is the rate of metabolism (d^{-1}), C_S is the concentration of soil solution (mg/L), and C_{XY} is the concentration in the xylem (mg/L). Also, the model assumes that the xylem sap is in equilibrium with the root and incorporates the coefficient, K_{RW}, the partitioning of a compound between root structures and surrounding pore water.

The resulting dynamic (steady-state) model for quantifying the BCF between root core

and soil matrix, Q/K_d is:

$$BCF = \frac{C_R}{C_M} = \frac{Q/K_d}{Q/K_{RW}+kV} \quad (15)$$

In evaluating the dynamic model compared to equilibrium models, Trapp (2002) found that the dynamic model succeeded in providing more realistic estimates for the root concentrations of carrot cores for PCBs and chlorinated benzenes, while the equilibrium approach correlated well only with the peel concentrations. The same success was not observed for benzo(a)pyrene, in which the dynamic model still resulted in an overestimation of the BCF for carrot roots by a factor of 5, suggesting that high molecular weight PAHs are less labile than predicted by the dynamic model and far less than the equilibrium models.

Burken (2003), as part of a broader examination, summarized the literature concerning uptake of chemicals by plant roots and subsequent translocation to the shoots. Burken (2003) emphasized that the studies were performed on a limited basis in the absence of the competitive soil matrix. Referring to Ryan et al. (1988) and Hsu et al. (1990), the authors reiterated that maximum uptake occurs near log K_{ow} near 3 for the hydroponic systems but would be 0.5 to 1 for soil systems. This was illustrated previously in Fig. 1. The author further stated, "Sorption to the soil does not decrease the TSCF value for the uptake of a compound; sorption only decreases the aqueous concentration at the root surface," meaning the total plant concentrations will be diminished by the competition imposed by the presence of soil, but the TSCF (which is a ratio) will remain unchanged.

Integrated Models for Plant Uptake from Soil and Air

The traditional conceptual model of plant assimilation of chemicals from the soil is partitioning of the chemical from the soil solids into solution, transport to the root surface, root uptake, and translocation from root to shoot. This was the foundation for the models discussed in the previous section. Those with expertise in air pollution and atmospheric transport viewed vegetation and plant leaves as a potential sink for lipophilic, semivolatile organic compounds, and some of the modeling approaches were reviewed above. Combining these concepts is a critical step to evaluate theoretically the relative importance of gaseous/particulate deposition versus assimilation through the roots followed by transport to the shoots. Three models will be reviewed in this regard.

Paterson and Mackay (1994) developed a mass balance model for uptake of organic chemicals from the soil using a three plant-compartment model: leaves, stems, roots. The authors' stated intent was to provide a predictive tool to estimate concentrations in plant components based on known chemical and physical properties of the chemicals. Using diffusion and bulk flow as the primary transport drivers of the chemicals, the authors were comprehensive in defining pathways and included soil-root, root-stem, stem-foliage, foliage-air, air-soil, and the opposite flow in all cases (e.g., root-soil, soil-air). Their ideal plant was the soybean, and physicochemical properties were compiled to define partitioning within the soil, air, and all plant components. Paterson and Mackay (1994) did not model PAHs, but hexachlorobiphenyl (6-PCB) was their model compound and has many similar properties. The model output led the authors to

this conclusion: “The relatively high Henry's law constant and hydrophobicity of 6-PCB result in contamination of the foliage mainly by the soil-air-leaf exchange route. The rate of transfer from soil to root, stem, and foliage is slow as indicated by a long residence time in each of these compartments. The residence time of 6-PCB in the air is short, and equilibrium is rapidly reached between air and foliage after evaporation from soil.”

Trapp and Matties (1995) constructed a combined model based on differential mass-balance that ultimately provided plant concentrations of organic chemicals derived from the soil and air. The model accounted for uptake from soil, deposition from gas phase onto leaves, volatilization from leaves, transformation of the parent chemicals, and plant growth to account for potential dilution due to increased plant biomass. Root uptake from the soil was the result of partitioning from soil to solution and solution to root:

$$K_{RB=}\frac{K_{RW}}{(Q_B K_d)+\theta}$$

where K_{RB} is the partition coefficient between the root and bulk soil, K_{RW} is the partition coefficient between roots and water, Q_B is the soil bulk density, K_d is the partition coefficient between soil and water, and θ is the volumetric water content of the soil. Transpiration stream concentration factors were based on published models. Equilibrium between air and leaves was based on a simple distribution coefficient, and the diffusive flux from the leaves into the atmosphere (N_A) was given as:

$$N_A = Ag[C_A - C_L/K_{LA}]$$

where A is the leaf surface area, g is the conductance, C_A is concentration of the compound in air, C_L is the concentration in the leaf, and K_{LA} is the simple distribution coefficient between the leaf and air. The authors did not include particulate deposition as part of the model because they determined it to be insignificant. Metabolism of the compounds in the plants, photodegradation of the compounds on the surface of the leaves, and plant biomass growth all were based on first order kinetics. Trapp and Matthies (1995) concluded that the model was adequate based on limited testing with 2,3,7,8-TCDD which predicted that, for background concentration, all plant accumulations of the dioxin would be from the air, even when the TSCF was forced to 1.0.

Collins and Finnegan (2010) developed and tested a model to predict the accumulation of semi-volatile contaminants in vegetation based on all potential pathways of assimilation, including volatilization from the soil followed by leaf deposition. Their model used previously developed uptake "modules" employing soil parameters (bulk density, porosity, moisture content, organic carbon content), air parameters (velocity, mixing, diffusion rates), properties of the compounds (Henry's Law constant, K_{OC}, TSCF, K_{OW}, K_{OA}), and plant characteristics (lipid content, growth rate, contaminant uptake, surface area, transpiration stream flux) in an attempt to quantify the importance of the soil-to-air-to-leaf route of contamination relative to other pathways.

A large fraction of PAH accumulation for PAHs with 4 or more rings is predicted to be through volatilization, but the total assimilation of these larger compounds is relatively small, <10% of the naphthalane concentration (Table 5). For PAHs with log K_{OA} < 9 and log K_{AW} (dimensionless Henry's Law constant) > -3, the TSCF model predicts that root uptake and translocation may be the more important route. All PAHs with two or three rings fits these criteria. The model also predicts that 98% of the total PAH content is from naphthalene, acenaphthene, and acenaphthylene. This result also strongly suggests that for PAH plant assimilation experiments in which the sum of naphthalene, acenaphthene, and acenaphthylene is far less than 98% of the total PAH content, the source of the total PAHs in the plant will not be root uptake from the soil followed by translocation. Collins and Finnegan (2010) further predicted that PAH concentrations would need to exceed 100 mg/kg for vegetation concentrations from the soil-air pathway to exceed concentrations expected from background concentrations.

A two partition-limited model was published assuming the soil-root-shoot pathway only (Zhu and Gao 2004; Yang and Zhu 2007) and, because they did not consider the vapor phase, are mentioned here for reference only. Takaki et al (2014) updated and further refined the modeling result of Collins and Finnegan (2010) and came to the same conclusions about the importance of vapor phase transport of PAHs with more than three benzene rings.

Table 5: Predicted leaf accumulation of PAHs through volatilization from soil using the modeling results of Collins and Finnegan (2010).

Compound	Soil-to-Air-to-Leaf Accumulation		Relative Total Uptake†
	Fraction of Total	Mass Accumulated	
	-----%	-----mg m^{-3}-----	
Naphthalene	10^{-1}	10^{-3}	10^{0}
Acenaphthylene	10^{-2}	10^{-4}	10^{0}
Acenaphthene	$10^{-1.5}$	10^{-3}	$10^{0.5}$
Fluorene	10^{0}	$10^{-3.5}$	$10^{-1.5}$
Phenanthrene	10^{0}	10^{-3}	10^{-1}
Anthracene	$10^{0.5}$	10^{-3}	$10^{-1.5}$
Fluoranthene	10^{1}	10^{-3}	10^{-1}
Pyrene	10^{1}	10^{-3}	10^{-2}
Chrysene	10^{1}	$10^{-3.5}$	$10^{-2.5}$
Benzo(a)anthracene	$10^{1.5}$	$10^{-4.5}$	10^{-4}
Benzo(b)fluoranthene	$10^{1.5}$	10^{-6}	$10^{-5.5}$
Benzo(k)fluoranthene	10^{2}	$10^{-4.5}$	$10^{-4.5}$
Benzo(a)pyrene	10^{2}	$10^{-4.5}$	$10^{-4.5}$
Dibenzo(a,h)anthracene	$10^{1.5}$	10^{-5}	$10^{-4.5}$
Indeno(1,2,3-c,d)pyrene	$10^{0.5}$	10^{-6}	$10^{-4.5}$
Benzo(g,h,i)perylene	$10^{1.5}$	10^{-6}	$10^{-5.5}$

†Calculated using the Fraction of Total to convert Mass Accumulated into mass; resulting values normalized to naphthalene=1

Direct Observation of PAH Transport in Plants

Destructive analysis (i.e., plant harvesting followed by solvent extraction) is the traditional path to assessing contamination, but this type of approach does not provide insight into the existence or potential mechanisms of transport within and between plant tissues. Isolating individual plant structures to examine the physical or chemical behaviors can provide important information. For example, accumulation of PAHs deposited on the cuticular surface of leaves has been studied often (McLachlan et al. 1995; Fernandez et al. 1999; Schreiber and Reiderer 1996; Bakker et al. 2001; Srogi 2007; Jouraeva et al. 2002; Howsam et al. 2000). The data from such studies are valuable, but isolating an active biological component limits the interpretation. A more direct method of observing contaminants in plants is required in order to distinguish the specifics of such interactions.

Optical fluorescence and phosphorescence techniques have been used for decades for the direct detection of PAHs in plant tissues (Alves et al. 2017; Tan et al. 2017) as an integral part of quantification of PAHs in particulates, soils and plants (Moser-Boroumand et al. 1997; Lee et al. 2004) and in the observation of PAHs on airborne particulates (Garra et al. 2015). Confocal laser scanning microscopy has been proposed as a method for visualizing plant cuticles (Fernandez et al. 1999). Recently, a similar and less destructive technique, two-photon excitation microscopy (TPEM), has been implemented to study the behavior of select PAHs in the root- and shoot- systems of commonly used crops (Wild et al. 2004, Wild et al. 2005, Wild et al. 2006, Wild et al.

2009). TPEM is an analytical technique that "is used to visualize the locations of an organic chemical in three-dimensional images of whole living leaves [and roots], without the need for sample manipulation or modification, through the novel use of both the plant and compound autofluorescence" (Wild et al. 2004). The major advantage of TPEM is that it provides a powerful nonintrusive tool for directly observing interactions between contaminants and plant structures. This technique has a depth of penetration of 200 μm.

TPEM was used to track anthracene applied to the leaves of living maize (*Zea mays*) (Wild et al. 2004) by applying anthracene as an acetone solution directly onto the underside of the leaves and tracking anthracene movement for 96 hours. Twenty-eight different leaves and 98 locations on each respective leaf were tracked with a detection limit of ~0.1 pg. Within the first 24 hours, anthracene had penetrated the cuticle and reached the upper surface of the cell walls of the epidermis. After 48 hours, anthracene was visible in all regions of the cuticle and cell walls but was not observed in the cytoplasm. After 72 hours, anthracene had penetrated ~3 μm within the cytoplasm, increasing to ~7μm by 96 hours, moving "between ~0.2 and 0.8 μm hr^{-1}" (Wild et al. 2004). Figure 9 is a schematic diagram generated by the authors to overview these observations. Approximately 70% of the initial concentration existed outside of the cytoplasm, while ~10% was detected within the cytoplasm. These results challenged several traditional views regarding the behavior of organic contaminants within leaf tissues as well as demonstrating that the movement of anthracene within the leaf is

extremely limited. During the 96-hour study duration, anthracene was not observed to reach vascular tissue and had moved a maximum of 28 μm. Assuming this is a general observation, systemic transport of the parent compound is negligible in the air-leaf pathway.

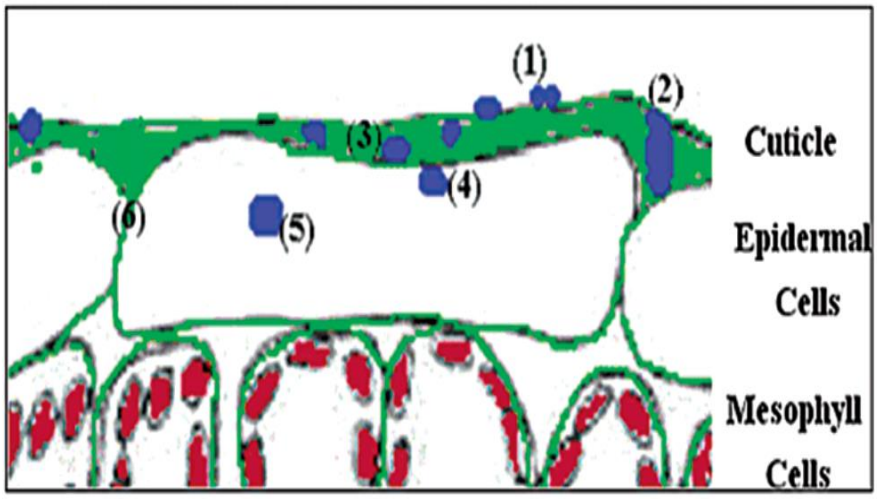

Figure 9: Schematic diagram indicating the different areas of the leaf where anthracene was found after 96 hours of exposure. Labeled areas: (1) diffuse layer of anthracene within the epicuticular wax; (2) thick anthracene diffuse bands extending from the epicuticular wax through the cuticle; (3) anthracene deposited on the external surface of epidermal cell walls; (4) deposits on internal surface of epidermal cell walls; (5) anthracene within the cytoplasm of the epidermal cells; and (6) the cuticular pegs (*Reprinted with permission from "A novel analytical approach for visualizing and tracking organic chemicals in plants" by Authors' Wild, E., Dent, J., Barber, J.L., Thomas, G.O., Jones, K.C. 2004. *Environmental Science and Technology*, 38, 4195-4199, Copyright 2004 by Dr. Kevin Jones).

Two-photon excitation microscopy (TPEM) was again used by Wild et al. (2005) to track the 56-day movement of anthracene and phenanthrene in the roots of maize (*Zea mays*) and wheat (*Triticum aestivum*) grown in a contaminated sand culture over a 56 day period (Wild et al. 2005). Seeds were germinated and transplanted to clean sand (60

g) that had been spiked with either ~42 mg phenanthrene kg^{-1} sand or ~42 mg anthracene kg^{-1} sand, applied to the sand via acetone solution. Plants were maintained with a hydroponic solution and analyzed between 1 and 56 days. This should be an ideal system for PAH uptake by roots and translocation to the shoots: 1) The TSCF model of Collins and Finnegan (2010) predicts that anthracene and phenanthrene, with log $K_{OA} < 9$ and log K_{AW} (dimensionless Henry's Law constant) > -3, uptake by the roots and translocation to the stems and leaves is far more favorable than the soil (sand)-air-leaf pathway. 2) The sand medium was devoid of organic matter and would not be subject to the lipophilic surfaces of the organic matter acting as a sink for the PAHs and restricting uptake (Ryan et al. 1988).

The authors observed no uptake of either compound in the actively growing portions of the roots (root cap, apex, divisional zones), but both compounds were observed on the outer surfaces of epidermal cells of lower-growth root surfaces and throughout the zone of elongation on much of the root surface. The compounds were observed to penetrate the cell walls at depths up to 6 μm. In the branching and root hair zones of the roots, some uptake and movement upward was observed. The compound was observed in the interior of cortex cells and some in the vacuoles. Compounds tended to cluster and/or "stream" in streaks that extended over time (up to 1500 μm). The streaming was mostly toward the shoots and traversed multiple cells, not inhibited by cell walls, becoming located within distinct regions of the root over time. Anthracene movement was about three times slower than phenanthrene. Anthracene and

phenanthrene have very similar properties (K_{OW}, K_{OA}, vapor pressure, etc.) except phenanthrene is 24 times more soluble in water. Also, both compounds moved more slowly in wheat than in maize; however, the differences were small with the exception of lateral movement of phenanthrene (1500 μm in maize vs 465 μm in wheat at 56 days). Lateral (upward) movement was greater than radial (inward) movement in both species for both compounds.

Both compounds were undetectable in the aboveground portions of both species over the entirety of the experiment. The authors estimated that approximately 50% of the streaming anthracene was degraded by day 56. Once the compounds enter the cortex, they no longer move radially, but move laterally. "Anthracene and phenanthrene are residing within the cell wall structure in solution, binding to the polysaccharide components, and moving longitudinally in the direction of least resistance through the cell walls through the apoplast. Essentially, once the compound has begun to undergo apoplastic movement within the cortex cells, we envisage it as being 'dragged' laterally by the flow of water. Here the compound may become partially bound to the cellulose microfibrals of the cell wall structure, further slowing its progress through the root." This concept represents the chromatography model of PAH movement (Figure 10).

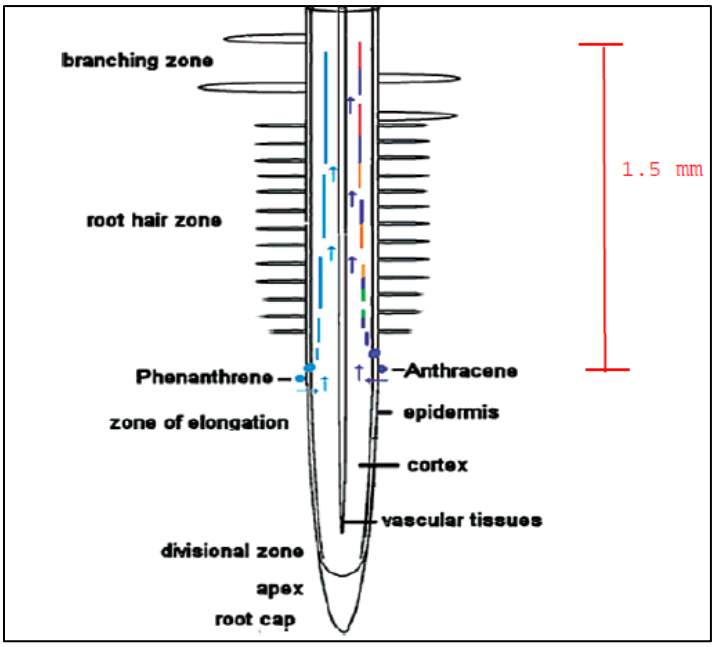

Figure 10: Schematic summarizing the movement, location, and degradation of anthracene and phenanthrene after 56 days. Note that, for convenience, anthracene is shown as entering one side of the root and phenanthrene the other. The additional colors are used to depict the metabolic conjugates of anthracene (*Reprinted with permission from "Direct observation of organic contaminant uptake, storage, and metabolism within plant roots" by Authors' Wild, E., Dent, J., Thomas, G.O., Jones, K.C. 2005. *Environmental Science and Technology*, 39, 3695-3702, Copyright 2005 by Dr. Kevin Jones).

Wild et al (2006) continued their research on PAH transport within leaf tissues. They shifted their focus to phenanthrene (due to its abundance in contaminated atmospheres), and, rather than applying the contaminant directly to the leaf, the phenanthrene was allowed to diffuse through the gas phase. Maize and spinach plants were grown hydroponically to the 2 to 3 leaf stage and then transferred to a 54 L glass chamber. The walls of the chamber had been coated with phenanthrene (dissolved in acetone and "painted" on walls). As the phenanthrene on the walls equilibrated with the

atmosphere, the resultant concentrations in the air was ~0.3 μg L^{-1} (phenanthrene concentration in the air is 1.4 L^{-1} at saturation). Typical, ambient concentrations of atmospheric phenanthrene range from extremely low (<0.1 μg L^{-1}) to as high ~1 μg L^{-1} in contaminated areas (Prevedouros et al. 2004). Plants were kept in the chamber for 1 to 12 days. Phenanthrene concentrations in the leaves after 5 days' exposure, obtained by grinding in liquid nitrogen followed by extraction with dichloromethane, ranged from 3.0 to 9.0 mg kg^{-1} for maize and 1.1 to 4.0 mg kg^{-1} for spinach, approximately 100 times higher than concentrations typically encountered in urban environments (Soceanu et al. 2014). Thus, the authors maximized the possibility of observing significant translocation within the plant tissues. Phenanthrene was traced in the leaf tissues using TPEM. Vapor phase deposition for both plant species resulted in a more diffuse distribution across the leaves, but there were important differences. In maize, the distribution of phenanthrene was fairly uniform across the cuticle; but, in spinach, phenanthrene tended to accumulate along on the cuticle at the edges of the leaf and accumulated in depressions and the stomatal wax plugs in the leaves. The authors attributed the difference in phenanthrene distribution between species to differences in leaf topography: maize has a more uniform surface, and spinach leaves contained more irregularities.

With time, the phenanthrene was observed to move to the interior of the leaves of both species but with different patterns (Wild et al. 2006). For maize, almost all accumulation and retention was external: cell walls, epidermis, cuticular wax plugs. The phenanthrene did move to the interior of the leaf, though, penetrating 100 μm into

second layer of cells in the mesophyll. For spinach, the movement was into the cytoplasm and vacuoles; there seemed to be transport from one cell to the next (over a limited range). Phenanthrene was not detected in the vascular system of spinach but was seen in the xylem of maize after 288 hours and extended toward the leaf tip. The depth of penetration to reach the xylem was 115 to 135 μm, and the extent of translocation along the xylem was 95 μm. The phenanthrene was mostly bound to the xylem wall. No phenanthrene was detected in root or stem tissues. The full partitioning of phenanthrene in the leaves of spinach and maize are illustrated in Figure 11.

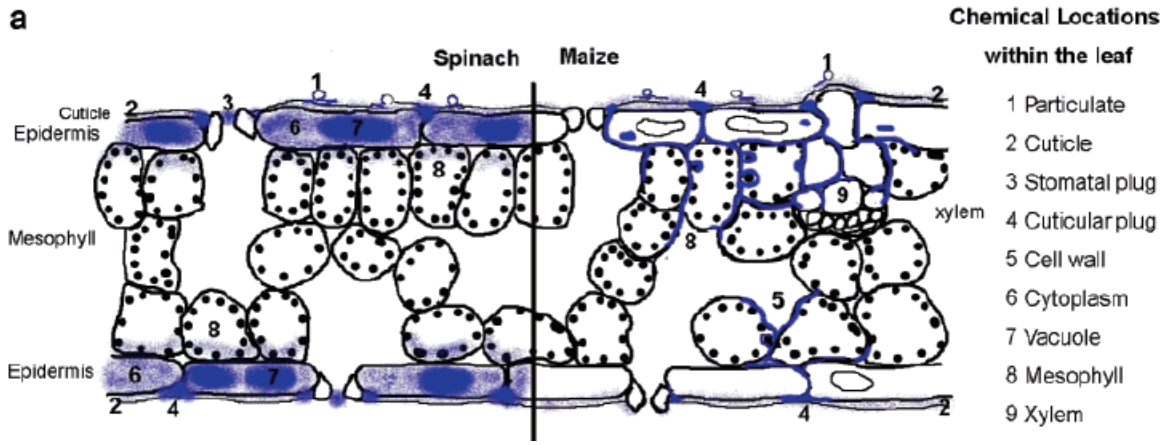

Figure 11: Schematic diagrams showing the locations where phenanthrene was visualized within leaves of spinach (left) and maize (right) after 12 days of exposure to an atmosphere contaminated with phenanthrene (*Reprinted with permission from "Visualizing the air-to-leaf transfer and within-leaf movement and distribution of phenanthrene: Further studies utilizing two-photon excitation microscopy" by Authors' Wild, E., Dent, J., Thomas, G.O., Jones, K.C. 2006. *Environmental Science and Technology*, 40, 907-916, Copyright 2006 by Dr. Kevin Jones).

An important observation from Wild et al. (2006) was that for both plant species, the general distribution of phenanthrene across the leaf surface and patterns of distribution were apparent after 24 h. By 48 hours, all cuticle reached saturation with all sites of deposition "filled up." This observation is key because some studies of PAH accumulations in plants, particularly those in hydroponics, observed a similar temporal pattern for PAH concentrations in the leaves and attributed this to the soil-root-leaf pathway. The results from Wild et al. (2006) suggest that the solution-air-leaf pathway is far more likely.

PAH Concentrations in Plants Grown in Soils with Low or Moderate PAH Contamination

This section mostly will examine published articles in which PAHs were measured in plant components with efforts taken to either account for aerial deposition or exclude it. None of the studies definitively point to a specific pathway of PAH accumulation in plants but can give important, supportive information. All studies in this section used soils with total PAHs less than 10 mg kg^{-1}.

Wild et al. (1992) studied the impact of adding to soils sewage sludge contaminated with typical concentrations of PAHs on plant uptake. The authors specifically wanted to address four key issues: 1) incomplete analyses of the plant materials; 2) artificially amending soil/sludge mixtures with PAHs rather than using the PAHs present in the sludge after sewage processing; 3) unrealistically high concentrations of PAHs in the amended soils; 4) use of radiolabeling without concurrent

analysis of the parent compounds. Although the authors insured that their experimental conditions mimicked actual field conditions as much as possible, they intentionally skewed the design to favor uptake: use of a sandy soil with low organic matter and uptake by carrots, known to have very high lipid content and most likely to act as a sink for PAHs. The original soil had a total PAH content of approximately 200 μg kg^{-1}, and the amended soils ranged from 300 to 1100 μg kg^{-1} (three rates of application). The PAH content of the foliage of the carrots remained constant over all treatments, but the core of the carrots showed a slight increase in PAH content (particularly the two- and three- ring compounds) for the first two application rates, but the third rate was statistically equivalent to the second. Principal component analysis of the PAHs showed no resemblance between the PAH profile of the carrot foliage and either soil or sludge. Predictably, PAHs in the core were similar in profile as determined by principal component analysis to the PAHs in both soil and sludge. The authors concluded that uptake of PAHs from the soil into the foliage was essentially nonexistent and minimal into the carrot core.

Kipopoulou et al. (1999) measured the PAH content of the edible portions of five species of vegetables, soil, and air from four locations during consecutive years in an urban setting in northern Greece. Soil total PAH concentrations ranged from 38 to 2244 μg kg^{-1}, representing only slight contamination. For carrot (*Daucus carota*), the exterior of the roots were peeled and only the interior was analyzed for PAHs. The vegetable concentrations followed the typical profile of concentrations: the two- and three-ring

PAHs had concentrations ranging from 0.4 to 63 μg kg^{-1}, and the higher molecular weight PAHs were at least 10 times lower in concentration or non-detectable. Principal component analysis demonstrated that the PAH profiles in the vegetables closely resembled atmospheric PAHs, not those in the soil. Uptake of PAHs into the roots was strongly correlated with K_{OW} values whereas accumulation in the leaves was strongly correlated with vapor pressures and log K_{AW} values for the PAHs. These results support that root uptake from the soil and leaf accumulation via atmospheric deposition occur simultaneously with limited, to no, transfer between root- and shoot-systems.

Banks et al. (1999) added 50 mg/kg ^{14}C-labeled benzo(a)pyrene to soil and grew tall fescue (*Festuca arundinacea*) in a chamber in which the soil was physically separated from the atmosphere. The ^{14}C was traced through the soil, plant roots, atmosphere above the soil, aboveground plant biomass, and aboveground atmosphere. Forms of ^{14}C quantified were $^{14}CO_2(g)$, leachate (all forms as an aggregate), volatile organics, and bulk ^{14}C in the shoots, roots, and soil. The parent compound was quantified in the soil but not in the plant biomass. Total mineralization of the benzo(a)pyrene (as measured by $^{14}CO_2(g)$) was 1.3% of that originally added. The roots contained an average of 0.12% of the original $^{14}CO_2(g)$, and the shoots contained 0.01%. This would represent a very low quantity of benzo(a)pyrene in the shoots if all the ^{14}C was present as benzo(a)pyrene, but, because the parent compound was not measured in plant biomass, this experiment cannot definitely determine whether or not benzo(a)pyrene is significantly translocated from root to shoot. However, a study by

Brady et al. (2003) offered confirmation for the results of Banks et al. (1999). The authors executed a simple hydroponic experiment with *Plantago lanceolate* to measure root and shoot uptake of ^{14}C-benzo(a)pyrene (determined by autoradiography). After 24 hours, 7 days, and 14 days, root uptake of the radiolabel was obvious, but the ^{14}C was not detectable in the shoots. These results support those of Lee et al. (1999) but suffer from the same limitation of not measuring the benzo(a)pyrene in the plant tissues.

Samsoe –Petersen et al (2002) investigated in the field the accumulation of PAHs in fruits and vegetables in uncontaminated control soils and soils with elevated levels of PAHs. Soil contamination ranged from 0.42 mg kg^{-1} (uncontaminated soil) to 86 mg kg^{-1} total PAHs. Concentrations in the vegetables ranged from below detection in uncontaminated soils to 3 µg kg^{-1} in lettuce in contaminated soil. Potato and carrot were examined with and without peels: PAH concentrations tended to not change with level of contamination but dropped dramatically when analyzed without peels. Fruits and berries also were analyzed. In the uncontaminated reference soil, concentrations tended to be <0.1 µg kg^{-1}; in contaminated soil, concentrations tended to be only slightly higher with maximum of 0.4 µg kg^{-1}. The authors calculated BCF values; all were <0.1, and the vast majority <0.01. Removing peels from potato and carrot decreased BCF values several fold. Authors ran correlations between plant and soil concentrations and found no significant correlation between soil and plant PAH content.

Chen et al. (2003) used radiolabeled, ^{14}C-pyrene to examine the degradation of pyrene in the roots of tall fescue (*Festuca arundinacea*) and switchgrass (*Panicum*

virgatum L.). The plants were grown in a specialized growth chamber in which the soil/roots were kept in a fully contained chamber and physically isolated from the atmosphere/shoot chamber. The movement of ^{14}C was traced throughout the 190-day experiment, measuring the label in CO_2 in the leaf chamber, CO_2 in the root chamber, shoot biomass, soil+roots, and volatile organic compounds captured in the leaf chamber. The parent compound was not measured in the plant biomass, which limits the interpretation of the results. However, the measurement of ^{14}C-labeled VOCs in the leaf chamber is revealing because previous observations of Peck and Hornbuckle (2003) and theoretical considerations (e.g., Collins and Finnegan 2010; Trapp and Matthies 1999) demonstrated that PAHs in the leaves will volatilize into the atmosphere. In the experiment of Chen et al. (2003), the total accumulation of VOCs after 190 days was <0.1% of the total biomass (compared to 30-37% in ^{14}C as CO_2 in the leaf chamber and 2-5% of the ^{14}C in the shoot biomass). Considering that 91-93% of the initial pyrene in the soil was no longer in the form of pyrene and only 30-40% of the initial ^{14}C in the soil remained in the soil after 190 days, the very small fraction of VOCs captured in the leaf chamber is an indication that pyrene was not accumulating in the upper portions of the tall fescue and switchgrass used in this experiment.

Allard et al. (2005) grew plants in a greenhouse in soil contaminated by creosote (approximately 1.4 mg total PAHs kg^{-1} soil) to determine foliar concentrations of PAHs and dissipation of PAHs in the soil. The soil concentrations were highest for the three-ring PAHs (14 to 83 mg kg^{-1}) with concentrations declining with increase number of

rings. The concentrations in the plants were 3.4 to 150 μg kg^{-1} for the three-ring compounds and again declined with increase size of the PAHs. A strong correlation between plant and soil concentrations (r^2=0.8) was exhibited, but the correlation between plant PAHs and log K_{OW} or log K_{AW} was poor. Although the concentrations in the plants are consistent with background PAH concentrations in plants in uncontaminated regions (e.g., Edwards et al 1983; Jones et al. 1989b), the strong correlation suggests that much of the plant PAH burden was from contamination of the leaves by the soil.

To investigate the impact of sewage sludge additions on crop PAH concentrations, Oleszczuk and Baran (2005) applied 30 to 600 Mg sewage sludge ha^{-1} and harvested various crops over five growing seasons. The highest rates sludge initially increased the total soil PAHs from 42 μg kg^{-1} to 932 μg kg^{-1}, but this declined to 375 by the end of the experiment. In the first year of the experiment, corn grain contained 5.8 μg kg^{-1} total PAHs with 22 μg kg^{-1} in the highest sludge rate. In year 2, barley grain in the control was 8 μg kg^{-1} and 13 μg kg^{-1} in the highest sludge treatment; in year 3 winter rape seeds in the unamended control contained 5 μg kg^{-1} total PAHs with 14 μg kg^{-1} in the highest treatment; year four had 6 μg kg^{-1} in control plot potato tubers with 25 μg kg^{-1} in the highest treatment; and, in year five, mixed cereal grains contained 7 μg kg^{-1} in the control and 12 μg kg^{-1} in the highest treatment. The distribution of the 2 + 3 ring, four-ring, and five-or-more-ring PAHs in the grains for years 2, 3, and 5 were nearly identical between the control and the amended soils (i.e. concentrations heavily dominated by the 2 and 3 ring PAHs), indicating that the source of the PAHs were the

same for the control and treated soils for those years, and the source was likely the atmosphere.

Tao et al. (2006) examined the accumulation of PAHs in the vegetative portions of cabbage at two sites with similar soil (660 μg kg^{-1} and 1.2 μg kg^{-1}) and air (10^{-15} to 10^{-11} mol m^{-3}) distribution among the 16 measured PAHs. A multilinear regression analysis revealed that the PAH concentrations in the cabbage were strongly correlated with gas phase and suspended air particulate PAHs (R^2 = 0.92). Adding soil PAH concentrations to the regression actually made the regression weaker. The authors concluded, "By comparing the two equations and the results of significant test on the regression slopes, it is concluded that the two-pathway model without soil is better for describing the PAH uptake by aerial parts of cabbage."

In a study examining plant uptake of PAHs from soils amended with sewage sludge, Li and Ma (2016) grew wheat in sandy loam field soils amended with various annual rates of sewage sludge resulting in 25 to 260 μg total PAHs kg^{-1} soil. The wheat was harvested, and PAH concentrations in roots, straw, and grain were measured. The light contamination of the soils was associated with similarly light plant contamination with concentrations of total PAHs in the plants ranging from 110 to 260 μg kg^{-1} in the straw, 81 to 95 μg kg^{-1} in the grain, and 166 to 700 μg kg^{-1} in the roots. The authors performed a logarithmic transformation on the soil and plant concentrations prior to regressing the two variables and obtained R^2 = 0.98 for the roots and 0.98 for the straw. However, the untransformed data show that concentrations in the roots were continuing

to increase with increasing soil concentrations but the straw concentrations reached a plateau.

In two separate studies concerning the relationship between adding sewage to soil and plant uptake of PAHs, Gworek et al. (2014, 2016) found that concentrations of PAHs in the plant increased with soil PAH concentration but nonlinearly with the plant concentrations approaching a maximum. Total PAH concentrations in the soil of less a maximum of 8 mg kg^{-1} resulted plant concentrations maximum concentrations of 400 μg kg^{-1} but generally less than 150 μg kg^{-1}. PAHs in the plants were 2 and 3 ring compounds with vanishingly small concentrations of the 5+ compounds. If the modeling studies discussed above are accurate, they would suggest that the 2- and 3-ring compounds were accumulating by soil-root-shoot transfer, and all others were either transferring via soil-air-leaf or not at all.

PAH Concentrations in Plants Grown in Highly Contaminated Soils

In the previous section, the maximum concentration of total PAHs in the soil were ≤100 mg kg^{-1}. In this section, all studies examine soils with total PAH concentrations >100 mg kg^{-1}. The model of Collins and Finnegan (2010) predicts that 100 mg kg^{-1} total concentrations would be necessary for the PAH content in plants arising from contaminated soils to exceed the plant concentrations generally observed from background PAHs in the atmosphere.

Fismes et al. (2002) studied the accumulation of PAHs in plants growing in highly contaminated soils from a former gasworks site. Five locations were sampled, and

total soil PAH concentrations ranged from 4 to 2500 mg PAHs kg^{-1} soil. The individual PAHs contributing to the total in the soil were those with more than three rings; the concentrations of the two- and three-ring compounds made up 10% or less of the total. Lettuce, carrot, and potato were grown, harvested, and measured for PAH accumulation in lettuce leaves and roots; potato leaves, peels, and peeled tubers; and carrot leaves and peeled carrot pulp. The total PAH concentrations in lettuce leaves ranged from 200 μg kg^{-1} in the least contaminated soil to over 2.6 mg kg^{-1} in the most contaminated soil. Potato leaf total PAH concentrations ranged from 300 μg kg^{-1} to 1.3 mg kg^{-1}, and carrot from 600 μg kg^{-1} to 2.1 mg kg^{-1}. The leaf concentrations in the most contaminated soils are unprecedentedly high, although the authors considered them to be "low." Total PAH concentrations in potato peels were somewhat elevated compared to most studies, ranging from 400 to 600 μg kg^{-1} and were completely independent of soil concentrations. The potato pulp (peeled tuber) concentrations were all less than 100 μg kg^{-1} and independent of soil concentrations. Thus, potato leaf concentrations were higher than peels and pulp in all but the lowest total soil concentrations. Carrot pulp concentrations were similar to potato pulp (75 to 100 μg kg^{-1}), an unexpected result considering the extraordinarily high concentrations in the carrot leaves, meaning that the carrot leaf concentrations were higher than the carrot pulp concentrations and potato peel concentrations for every soil concentration. The most unusual result was for the lettuce roots which ranged from 1 to 22 mg kg^{-1} over the entire soil concentration range. The distribution of the 2-, 3-, 4-, and 5 to 6-ring PAHs for the soils were nearly identical for

the lettuce roots, carrot leaves, lettuce leaves at the 2 highest soil concentrations, potato leaves, potato peels, and lettuce leaves at the highest soil concentrations. This would be consistent with contamination of these plant tissues with soil, a result supported by the observation that PAH distribution in the pulps of potato and carrot bore no resemblance to the soil concentrations and consistent with modeling results.

Meudec et al. (2006) conducted a short-term experiment in which *Salicornia fragilis* plants were transplanted into sediments contaminated with 0.2%, 2%, and 20% fuel oil. After one week, the plants were harvested and analyzed for PAHs. In the case of the soil contaminated with 0.2% fuel oil, plants were harvested once per week for six weeks and analyzed for PAHs. For the one-week experiment, the 0.2% contamination level had plants with individual PAH concentrations ranging from <20 $\mu g\ kg^{-1}$ to 1320 $\mu g\ kg^{-1}$ and a total PAH content of 3.5 $mg\ kg^{-1}$. For the 2% contamination level in sediment, the plant concentrations of individual PAHs ranged from 25 to 4200 $\mu g\ kg^{-1}$ and 15 $mg\ kg^{-1}$ total PAH. At 20% contamination in the sediment, the plant concentrations of individual PAHs ranged from 120 to 13,000 $\mu g\ kg^{-1}$ with 41 $mg\ kg^{-1}$ total PAH. Concentrations this high in plants after a single week of growth were unprecedented, but so were the soil concentrations. In the six-week experiment with the 0.2% fuel oil contaminated soil, some of the PAHs in the plants reached maximum concentrations after one week and declined; for the other PAHs, concentrations peaked after one week. The authors indicated that they sometimes observed droplets of fuel oil on the plants and, although these visibly contaminated tissues were discarded,

contamination of the plants with sediments or directly by the oil would account for the very high plant concentrations of PAHs.

Both Meudec et al. (2006) and Fismes et al. (2002) attributed the observed plant PAH concentrations to soil/sediment-root-shoot translocation. Although it is tempting to dismiss these values as the result of contamination of the leaves by the contaminant (fuel oil in the case of the Meudec et al. 2006) or by the deposition of PAH-enriched soil on the leaves, one cannot overlook the extraordinary PAH concentrations in the growth medium that could somehow change the uptake dynamics. An experiment conducted by Cofield et al. (2007) gives another perspective. Cofield et al. (2007) were working with manufactured gas plant soils that were contaminated with coal tar with high levels of PAHs. The soil was so laden with tar that it was hydrophobic and required the addition of 25% potting soil (by weight) to allow the soil to imbibe water. After amending with potting soil, the sum of the individual PAHs ranged from 2500 to 3200 mg kg^{-1} with the majority being the 4-, 5-, and 6-ring PAHs. Fescue and switchgrass were grown for 3, 9, and 12 months after which changes in soil PAH concentrations and PAH concentrations in roots and shoots were quantified. The root concentrations of both fescue and switchgrass were elevated, 39 and 42 mg kg^{-1}, respectively. As with the soil, the 2- and 3-ring compounds in the roots were the least represented with 4-, 5-, and 6-ring compounds dominating; however, the percentage of 6-ring compounds in the roots was somewhat higher than in the soil. In the shoots, the majority of the concentrations were below detection (3 μg kg^{-1}), with detectable concentrations ranging from 4 to 30 μg kg^{-1}

and total PAHs of 120 μg kg^{-1} for fescue and 10 μg kg^{-1} for switchgrass. In a similar but separate experiment with the same soil, zucchini was selected as the plant species because of its remarkable ability to assimilate p,p'-DDE, chlordane, and dioxins from soil (White et al. 2002; White et al. 2003; Hulster et al. 1994). The zucchini was grown for 3 months, after which plant concentrations were measured in roots and shoots. Root total PAH concentrations in the zucchini (14 mg kg^{-1}) were lower than for the grasses in their earlier experiment. The total PAH concentrations in the zucchini shoots (440 μg kg^{-1}) were significantly higher than in the grasses but were still far less than those observed by Fismes et al. (2002) and Meudec et al. (2006). Only phenanthrene, anthracene fluoranthene, pyrene, benzo(a)anthracene, and chrysene were detected in the shoots, indicating that the mechanism of transfer was soil-air-leaf.

Somtrakoon et al. (2014) grew *Zea mays*, *Psophocarpus tetragonolobus*, and *Cumumis sativus* for 30 days in soil spiked with 139 mg anthracene kg^{-1} soil and 96 mg fluorene kg^{-1} soil. At the end of the growth period, the PAHs were below detection limits (200 μg kg^{-1}) for both compounds in roots and shoots of all species. The construction of this experiment was ideal for assimilation of these two PAHs, and the lack of detection of the compounds in the plant shoots suggests lack of assimilation of PAHs in the plant tissue, despite the relatively high detection limits.

CHAPTER V

CONCLUSION

Polyaromatic hydrocarbons (PAHs) are a diverse family of lipophilic, semi-volatile organic compounds (SVOCs) generated from a variety of natural and industrial processes, and due to their wide distribution, toxicity, and recalcitrance in the environment, have become a growing environmental concern. PAHs are volatile enough to be ubiquitous in the atmosphere, even in remote areas with no industrial activities, and plants everywhere have measurable background PAH concentrations (Eisler 1987). In industrial and urban areas, PAH concentrations are elevated in plants resulting solely from atmospheric deposition (Wagrowski and Hites 1997).

PAHs are sparingly soluble but semi-volatile; as a result, PAHs do not conform to pathways of uptake from contaminated soils and translocation from roots to shoots observed in bioavailable organics such as pesticides. PAHs bind strongly to soil organic matter and, if, sorbed by the plant roots, partition onto lipophilic surfaces within the plant tissues (Bromilow and Chamberlain 1995, Chiou et al. 1998). Direct observation of PAH transport within plant tissues demonstrate clearly that PAHs are not mobile in roots, stems, and leaves (Wild et al. 2004, Wild et al. 2005, Wild et al. 2006).

Despite decades of research showing limited uptake from soil and restricted translocation within plant tissues, an increasing number of published studies have been attributing PAH concentrations in leaves to uptake from soil to root to shoots (Fismes et al. 2002; Goa et al. 2004; Meudec et al. 2006; Goa et al. 2006). The goal of this research

was to critically review the literature and determine as definitively as possible whether or not PAHs that are assimilated by plant roots growing in contaminated soil are translocated to the shoots.

To dissect the phenomenon of PAH uptake by plants followed by subsequent translocation in soils, insight concerning physical and chemical properties as well as the significance of every other PAH input pathway was necessary. Multiple authors have applied these chemical attributes (lipophilicity, solubility, volatility, etc.) to measure plant uptake and refine predictive models, producing thresholds that predict the likelihood that a compound may undergo plant uptake and systemic translocation. Briggs et al. (1982) observed for plants grown in solution culture maximum translocation to shoots was for compounds with $\log K_{OW} = 1.8$. Furthermore, the uptake of lipophilic compounds with $\log K_{OW} > 4.5$ was very small and to caution against accepting false-positive detections related to such lipophilic, volatile compounds coming into contact with the base of the shoot tissues. Ryan et al. (1988) adapted this model and further indicated that, for plants grown in soils, the maximum lipophilicity for translocation dropped to $\log K_{OW} = 1$. Plant uptake by transpiration is important for chemicals with a $\log K_{OW} < 2.5$ and a $\log K_{AW} < -1$ (Cousins and Mackay, 2004). Chemicals with a $\log K_{OA} > 8$ and a $\log K_{AW} < -3$ had a higher chance of being transferred along the soil-air-plant pathway than chemicals falling outside of that range (Collins and Finnegan 2010). As we take all of those considerations into account, PAHs with a $\log K_{OW} > 2.5$, a $\log K_{AW} < -3$, and a $\log K_{OA} > 8$, those with four rings or more (fluoranthene, pyrene,

benzo[a]pyrene, etc.), are unlikely to undergo plant root uptake followed by systemic translocation to higher plant parts but instead have a greater potential to re-volatilize and come into contact with above ground tissues.

Limitations to plant uptake and translocation are due to lipophilic attractions and the affinity of heavier PAHs to remain adsorbed to these surfaces, thus restricting their mobility in the soil matrix as well as within the plant tissues (Wild and Jones 1992; Kipopoulou et al. 1999; Robinson et al. 2003; Tao et al. 2004; Su and Zhu 2008; Wang et al. 2014). PAHs with four or more rings are unlikely to undergo systemic translocation after being taken up by the roots as they are too lipophilic, fluoranthene having the lowest log K_{OW} of this group (5.22), and not volatile enough to enter the transpiration gradient in the vapor phase, rather remaining attached to their adsorbed surfaces. Any concentrations of these PAHs detected in the foliar tissues of plants grown in contaminated soils is most likely due to atmospheric deposition or the re-volatilization of these compounds out of the soil where they re-deposit on above ground tissues.

Only the two and three-ringed PAHs have the potential to undergo plant uptake followed by vascular transport and distribution to higher plant tissues. However, as indicated by their physiochemical parameters, the fate of these contaminants remains ambiguous and their behavior is difficult to predict with any degree of certainty. As these compounds are highly lipophilic when compared to the optimum log K_{OW} associated with maximum uptake potential, it still seems unlikely that they will undergo systemic transport post root uptake. TPEM-visualized intracellular movement of

phenanthrene and anthracene demonstrated that neither compound moved very far within the plant with respect to the long experiment duration. When applied to the leaf (Wild et al. 2004), anthracene penetrated the epidermal cells of maize distancing ~40 um over 96 hours. When observed with respect to the roots for 56 days (Wild et al. 2005), anthracene moved a radial distance of 220 um and a lateral distance of 490 um in maize; and a radial distance of 180 um and lateral distance of 300 um in wheat. Phenanthrene moved a radial distance of 240 um and the greatest lateral distance of 1500 um in maize; and a radial distance of 200 um and lateral distance of 465 um in wheat. From these observations it seems justified to claim that systemic transport between the roots to above ground tissues, or vice versa, will not occur with 2-3 ringed PAHs. This bioaccumulation pathway is essentially not a danger when assessing the soil-to-root-to-shoot exposure pathway related to consuming contaminated foods. Coupled with the fact that these smaller PAHs do not appear to be as toxic as the larger PAHs (Skupińska et al. 2004), these compounds that are capable of traveling, to a small degree, along the transpiration gradient are not of great concern. The only exceptions to this include tubers or other edible root crops that are grown in contaminated soils, as the lipophilic surfaces on the roots can become highly contaminated, as correlated to the contamination of their growth media (Wild and Jones 1992; Trapp et al. 2007). This conclusion is supported by studies in field, greenhouse, and lab studies in which the soil contamination levels did not correlate with the detected foliar concentrations; rather the foliar concentrations were a direct result of atmospheric deposition or in-direct result of the compounds re-

volatilizing and subsequently depositing back onto the foliar tissues (Ellwardt 1979; O'Connor et al. 1991; Wild and Jones 1992; Kipopoulou et al. 1999; Cousins and Mckay 2001; Robinson et al. 2003; Tao et al. 2004; Su and Zhu 2008; Wang et al. 2014).

Those studies concluding that PAH uptake and translocation was the predominant mechanism fall into one or more of the following categories:

- Solution culture experiments often are unrepresentative of field trials, and this is particularly the case for PAHs. Eliminating the soil matrix dramatically shifts the likelihood that relatively high concentrations PAHs can diffuse to roots.
- The conclusions of several studies referred to solution culture experiments as evidence that uptake from soils was possible.
- Omitted the impact of the atmospheric deposition and/or soil-to-air-to-leaf pathway(s) without sufficiently restricting or accounting for the PAHs that came into contact with foliar tissues through wet, dry and particulate deposition that re-volatilized from below soils.

Although the PAHs do not have a favorable affinity to undergo translocation via plant uptake, it was observed in the Wild et al. 2005 that anthracene began to be metabolized after 21 days of accumulation within maize roots. By day 56, nearly half of the applied anthracene was detected as a metabolic product. The breakdown of PAHs within plant tissues and their respective biochemical fate offer another avenue of pursuit for future research efforts. Specifically, it would be of great interest to assess the breakdown of the heavier, more carcinogenic, PAHs to observe how plants

compartmentalize these byproducts so that it may be determined whether they pose any danger to toxifying the food chain. Novel techniques, such as the application of two-photon excitation microscopy, will be required to make further ground on these plant uptake analyses as this scope of observation enables the in-situ examination of these complex biochemical processes without the need for destructive sampling.

REFERENCES

Agency for Toxic Substances and Disease Registry. 2009. Toxicity of polycyclic aromatic hydrocarbons (PAHs). Centers for Disease Control and Prevention. https://www.atsdr.cdc.gov/csem/pah/docs/pah.pdf (last access July, 2018)

Ahrens, M. J., and Hickey, C. W. 2003. Extractability of polycyclic aromatic hydrocarbons in sediments. A matter of association? Australian Journal of Chemistry, 56:193-199.

Allard, A-S., Malmberg, M., Neilson, A.H., Remberger, M. 2007. Accumulation of polycyclic aromatic hydrocarbons from creosote-contaminated soil in selected plants and the oligochaete worm *Enchytraeus crypticus*. J. Environ. Sci. Health. 40:2057-2072.

Allen, R.G., Pereira, L.S., Raes, D., Smith, M. "Crop Evapotranspiration - Guidelines for Computing Crop Water Requirements - FAO Irrigation and Drainage Paper 56." FAO Corporate Document Repository. FAO, 1998. Web. 08 June 2016. http://www.fao.org/docrep/X0490E/X0490E00.htm

Alves, W.W., Manoel, E.A., Santos, S., Nunes, R.O., Dominciano, G.C., Soares, M.R. 2017. Detection of polycyclic aromatic hydrocarbons (PAHs) in Medicago sativa L. by fluorescence microscopy. Micron. 95:23-30.

Andelman, J.B., Seuss, M.H. 1970. Polynuclera aromatic hydrocarbons in the water environment. Bull. World Health Org. 43:479-508.

Asher, C.J., Edwards, D.G. Modern solution culture techniques. *In* Lauchli, A., Bieleski, R.L. (eds) *Inorganic Plant Nutrition*, Encyclopedia of Plant Physiology. 15:94-119.

Bakker, M. I., Vorenhout, M., Sum, D. T. H. M., and Kolloffel, K. 1999. Dry deposition of atmostpheric polycyclic aromatic hydrocarbons in three plantago species. Environmental Toxicology and Chemistry, 18(10):2289-2294.

Bakker, M. I., Casado, B., Koerselman, J. W., Tolls, J., and Kolloffel, C. 2000. Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery. Science of the Total Environment, 263:91-100.

Bakker, M.I., Koerselman, J.W., Tolls, J., Kolloffel, C. 2001. Localization of deposited polycyclic aromatic hydrocarbons in leaves of *Plantago*. Environ. Toxicol. Chem. 20:1112-1116.

Banks, M.K., Lee, E., Schwab, A.P. 1999. Evaluation of dissipation mechanisms for benzo[a]pyrene in the rhizosphere of tall fescue. J. Environ. Qual. 28:294-298.

Bohme, F., Welsch-Pausch, K., and McLachlan, M. S. 1999. Uptake of airbone semivolatile organic compunds in agricultral plants: Field measurements of interspecies variability. Environmental Science and Technology 33:1905-1913.

Blumer, M. 1961 Benzpyrenes in soil. Science. 134:474-475.

Brady, C.A.L., Gill, R.A., Lync, P.T. 2003. Preliminary evidence for the metabolism of benzo(a)pyrene by *Plantago lanceolata*. Environ. Chem. Health. 25:131-137.

Briggs, G.G., Bromilow, R.H., and Evans, A.A. 1982. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pestic. Sci. 13:495-504.

Briggs, G.G., Bromilow, R.H., Evans, A.A., Williams. 1983. Relationships between lipophilicity and the distribution of non-ionised chemicals in barley shoots following uptake by the roots. Pestic. Sci. 14:492-500.

Bromilow, R. H., and Chamberlain, K. 1995. Principles governing uptake and transport of chemicals *In* Trapp S, Mc Farlane JC (eds), *Plant contamination.* Lewis/CRC Press, Boca Raton, FL.

Burken, J.G. 2003. Uptake and metabolism of organic compounds: green-liver model. *In* McCutcheon, S.C. and J.L Schnoor (ed), *Phytoremediation: Transformation and Control of Contaminants* pp 199-216. Wiley Interscience, Hoboken, NJ.

Burken, J.G. and J.L. Schnoor. 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environ. Sci. Tech. 32:3379-3385.

Chen, Y-C., Banks, M.K., Schwab, A.P. 2003. Pyrene degradation in the rhizosphere of tall fescue (*Festuca arundinacea*) and switchgrass (*Panicum virgatum* L.). Environ. Sci. Technol. 37:5778-5782.

Chiou, C.T., McGroddy, S.E., and Kile, D.E. 1998. Partition chracteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ. Sci. Technol. 32:264-269.

Chiou C.T., Porter, P.E., Schmedding, D.W. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17:227-231.

Cofield, N., Schwab, A.P., Banks, M.K. 2007. Phytoremediation of polycyclic aromatic hydrocarbons in soil: part i. dissipation of target contaminants. Int. J. Phytorem. 9:355-370.

Cofield, N., M.K. Banks, A.P. Schwab. 2008. Lability of polycyclic aromatic hydrocarbons in the rhizosphere. Chemosphere. 70:1644-1652.

Collins, C.D., Finnegan, E. 2010. Modeling the plant uptake of organic chemicals, including the soil-air-plant pathway. Environ. Sci. Technol. 44:998-1003.

Collins, C., Fryer, M. and Grosso, A. 2006. Plant uptake of non-ionic organic chemicals. Environ. Sci. Technol. 40:45-52.

Collins, C.D., Mosquera-Vasquez, M. Gomez-Eyles, J.L. , Mayer, P., Gouliarmou, V., Blum, E. 2013. Is there sufficient 'sink' in current bioaccessibility determinations of organic pollutants in soils? Environ. Pollution 181:128-132.

Collins, C.D., Willey, N.J. 2009. Phylogenetic variation in the tolerance and uptake of organic contaminants. Internatl. J. Phytorem. 11:623-639.

Dachs, J., and Eisenreich, S.J. 2000. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 34:3690-3697.

Davidson C.I., Wu Y-L. 1989. Dry deposition of trace elements. *In* Pacyna J.M., Ottar B. (eds) *Control and Fate of Atmospheric Trace Metals*. NATO-ASO Series C, Mathematical and Physical Sciences/NATO, 268. Kluwer, Dordrecht, The Netherlands, pp 147–202.

Debastani, R. and Ivanov, I.N. 1999. A compilation of physical, spectroscopic, and photophysical properties of polycyclic aromatic hydrocarbons. Photochem. Photobiol. 70:10-34.

De Sousa, C.A. 2003. Turning brownfields into green space in the City of Toronto. Landscape and Urban Planning. 62:181-198.

Earl, N. Cartwright, C.D., Horrocks, S.J., Worboys, M, Swift, S., Kirton, J.A., Askan, A.U., Kelleher, H., Nancarrow, D.J. 2003. Review of the fate and transport of

selected contaminants in the soil environment. Environment Agency R&D Technical Report P5-079/TR1. Bristol, UK.

Edwards, N.T. 1983. Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment--A review. J. Environ. Qual. 4:427-441.

Edwards, N. T., Ross-Todd, B. M., and Garver, E. G. 1982. Uptake and metabolism of ^{14}C anthracene by soybean (*Glycine max*). Environmental of Experimental Botany. 22:349-357.

Eisler, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife, and invertebrates: A synoptic review. Contaminant Hazard Reviews Report 11 ; Biological Report 85(1.11). 55 pp. U.S. Department of the Interior, Fish and Wildlife Service. Laurel, MD.

Ellwardt, P.Chr. 1979. Variation in content of polycyclic aromatic hydrocarbons in soil and plants by using municipal waste composts in agriculture. *In* Proc. Symp. on Soil Organic Matter Studies, Vol. II. International Atomic Energy Agency, Vienna. pp 291-298.

Fernandez, S., S. Osorio, and A. Heredia. 1999. Monitoring and visualizing plant cuticles by confocal laser scanning microscopy. Plant Physiol. Biochem. 37:789-794

Fismes, J., Perrin-Ganier, C., Empereur-Bissonnet, P., and Morel, J. L. 2002. Soil-to-root transfer and translocation of polycyclic aromatic hydrocarbons by vegetables grown on industrial contaminated soils. J. Environ. Qual. 31:1649-1656.

Friedman, C.L., and Selin, N.E. 2012. Long-range atmospheric transport of polycyclic aromatic hydrocarbons: a global 3-D model analysis including evaluation of arctic sources. Environ. Sci. Technol. 46:9501-9510.

Gao, Y., H. Li, and S. Gong. 2012. Ascorbic acid enhances the accumulation of polycyclic aromatic hydrocarbons (PAHs) in roots of tall fescue (*Festuca arundinacea* Schreb.). PLOS One.

Gao, Y., and Ling, W. 2006. Comparison for plant uptake of phenanthrene and pyrene from soil and water. Biol. Fertil. Soils 42:387-394.

Gao, Y., and Zhu, L. 2004. Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils. Chemosphere, 55(9):1169-1178. doi:10.1016/j.chemosphere.2004.01.037

Garban, B., Blanchoud, H., Motelay-Massei, A., Chevreuil, M., Ollivon, D. 2002 Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. Atmos. Environ. 36:5395-5403.

Garra, P., Maschowski, C., Liaud, C., Dieterlen, A., Trouvé, G., Le Calvé, S., Jaffrezo, J-L., Leyssens, G., Schönnenbeck, C., Kohler, S, Gieré, R. 2015. Fluorescence microscopy analysis of particulate matter from biomass burning: Polyaromatic hydrocarbons as main contributors. Aerosol Science and Technology 49:1160-1169, DOI: 10.1080/02786826.2015.1107181

Goldfarb, J.L. and Suuberg, EM. 2008. Raoult's Law and its application to sublimation vapor pressures of mixtures of polycyclic aromatic hydrocarbons. Environ. Eng. Sci. 25:1429-1437.

Graf, W., and Diehl, H. 1966. Concerning the naturally caused normal level of carcinogenic polycyclic aromatics and its cause. Arhc. Hyg. 150:49-59.

Gregory P.H. 1961. The microbiology of the atmosphere. In Polunin N (ed), *The Microbiology of the Atmosphere*. Leonard Hill, London, UK, pp 22–27.

Grimmer, G.; Duvel, D. 1970. Cancerogene kohlenwasserstoffe in der umgebung des Menschen. Untersuchungen zur endogenen bildung von polycyclischen kohlenwasserstoffen in hoheren. Pflanzen. Z. Naturforsch. 25:1171-1175

Guddal, E. 1959. Isolation of polynuclear aromatic hydrocarbons from the roots of *Chrysanthemum vulgare* Bernh. Acta. Chern. Scand. 13:834-835.

Gunther, F. A., F. Buzzetti, and W. E. Westlake. 1967. Residue behavior of polynuclear hydrocarbons on and in oranges. Residue Rev. 17:81-104.

Gworek, B., Klimczak, K., and Kijenska, M. 2014. The relation between polyaromatic hydrocarbon concentration in sewage sludge and its uptake by plants: *Phragmites communis, Polygonum persicaria* and *Bidens tripartita*. PLoS One 9(10), e109548. doi:10.1371/journal.pone.0109548

Gworek, B., Klimczak, K., Kijenska, Gozdowski, D. 2016. Comparison of PAHs uptake by selected Monocotyledones and Dicotyledones from municipal and industrial sewage sludge. Environ. Sci. Pollut. Res. 23:19461-19470.

Hafner, W. D. Carlson, D. L. Hites, R. A. 2005. Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. Environ. Sci. Technol. 39:7374-7379.

Halsall, C.J., Barrie, L.A., Fellin, P., Muir, C.G., Billeck, B.N. , Lockhart, L., Rovinsky, F.Ya., Kononov, E. Ya., Pastukhov, B. 1997. Spatial and Temporal Variation of Polycyclic Aromatic Hydrocarbons in the Arctic Atmosphere. Environ. Sci. Technol. 31:3593-3599.

Halsall, C.J., Sweetman, A.J., Barrie, L.A., Jones, K.C. 2001. Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. Atmos. Environ. 35:255-267.

Hancock, J.L., Applegate, H.G., Dodd, J.D. 1970. Polynuclear aromatic hydrocarbons on leaves. Atmos. Environ. 4:363-370.

Harms, H. 1975. Metabolism of benzo(a)pyrene in plant cell cultures and wheat seedlings. Landbauforsch. Voelkenrode 25:83-90.

Heit, M., Tan, Y. L., and Miller, K. M. 1988. The origin and deposition history of polycyclic aromatic hydrocarbons in the Finger Lakes Region of New York. Water, Air, and Soil Pollution 37:85-110.

Hellstrom, A. 2004. Uptake of organic pollutants in plants. pp 1-40 Department of Environ. Assessment, Swedish Univ. Agricul. Sci., Upsalla, Sweden ISSN 1403-977X.

Henry, H. F., Burken, J. G., Maier, R. M., Newman, L. A., Rock, S., Schnoor, J. L., and Suk, W. A. 2013. Phytotechnologies--preventing exposures, improving public health. International Journal of Phytoremediation, 15:889-899. doi:10.1080/15226514.2012.760521.

Howsam M, Jones KC, Ineson P. 2000. PAHs associated with the leaves of three deciduous tree species. I: Concentrations and profiles. Environ Pollut 108:413–424.

Hsu, F.C., Marxmiller, R.L., Yang, A.Y.S. 1990. Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using a pressure chamber technique. Plant Physiol. 93:1573-1578.

Hulster, A., Muller, J.F., and Marschner, H. 1994. Soil-plant transfer of polychlorinated dibenzo-p-dioxins and dibenzofurans to vegetables of the cucumber family (*Curcurbitaceae*). Environ. Sci. Technol. 28:1110–1115.

Jones H.G. 1983. *Plants and Microclimate. A Quantitative Approach to Environmental Plant Physiology.* Cambridge University Press, Cambridge, UK, pp 37–59.

Jones, K. C. 1991. Contaminant trends in soils and crops. Environ. Pollut. 69:311-325.

Jones, K.C., Stratford, J.A., Waterhouse, K.S., Furlong, E.T., Giger, W., Hites, R.A., Schaffner, C., Johnston, A.E. 1989a. Increases in the polynuclear aromatic hydrocarbon content of an agricultural soil over the last century. Environ. Sci. Technol. 23:95-101.

Jones, K. C., Grimmer, G., Jacob, J., and Johnston, A. E. 1989b. Changes in the polynuclear aromatic hydrocarbon content of wheat grain and pasture grassland over the last century from one site in the U.K. Sci. Tot. Environ. 78:117-130.

Jouraeva, V.A., Johnson, D.L., Hassett, J.P., Nowak, D.J. 2002. Differences in accumulation of PAHs and metals on the leaves of Tilia x euchlora and Pyrus calleryana. Environ. Pollution. 120:331-338

Kaliszova, R., Javorska, H., Tlustos, P., Balik. J. 2010. Polycyclic aromatic hydrocarbons in the atmosphere-soil-plant system. The root uptake role and consequences. Fresenius Environ. Bull. 19:406-416.

Kapustka, L. A. 2004. Do PAHs Pose Unacceptable Ecological Risks to Terrestrial Receptors at Hazardous Waste Sites? Human Ecol. Risk Assess.: An International Journal, 10:233-243. doi:10.1080/10807030490438184

Karickhoff, S.W., Brown, D.S., and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Research 13:241-248.

Khan, S. and Cao, Q. 2012. Human health risk due to consumption of vegetables contaminated with carcinogenic polycyclic aromatic hydrocarbons. J. Soils Sediments 12:178-184.

Kolar, L., R. Ledvina, J. Ticha, and R. Hanus. 1975. Contamination of soil, agricultural crops, and vegetables by 3,4-benzpyrene in the vicinity of Ceska Budejovice. Ceskosolvenska Hygiena 20, 135.

Komp, P., and McLachlan, M.S. 1997. Influence of temperature on the plant/air partitioning of semivolatile organic compounds. Environ. Sci. Technol. 31:886-890.

Kipopoulou, A. M., Manoli, E., and Samara, C. 1999. Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area. Environmental Pollution 106:369-380.

Larsson, B and G. Sahlberg. 1982. Polycyclic aromatic hydrocarbons in lettuce. Influence of a highway and aluminum smelter. In M. Cooke, A.J. Dennis, and G.L. Fisher (eds) Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry. Sixth Battelle International Symposium. pp 417-426.

Lee, C.K., Ko, E.J., Kim, K.W., Kim, Y.J. 2004. Partial least square regression method for the detection of polycyclic aromatic hydrocarbons in the soil environment using laser-induced fluorescence spectroscopy. Water Air Soil Pollut. 158:261-275.

Li, H., Y. Ma. 2016. Field study on the uptake, accumulation, translocation and risk assessment of PAHs in a soil-wheat system with amendments of sewage sludge. Sci. Total Environ. 560-561:55-61.

Lu, L., Zhu, L. 2009. Reducing plant uptake of PAHs by cationic surfactant-enhanced soil retention. Environ. Pollut. 157:1794-1799.

Lunde, G., Bjorseth, A. 1977. Polycyclic aromatic hydrocarbons in long-range transported aerosols. Nature. 268:519-519.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Vol. 2. Polyaromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Chapter 2. Polynuclear aromatic hydrocarbons (PAHs). pp 57-367. Lewis Publishers, Chelsea, Michigan

McLachlan, M.S. 1997. A simple model to predict accumulation of PCDD/Fs in an agricultural food chain. Chemosphere 34:1263-1276.

McLachlan, M.S., Welsch-Pausch, K., and Tolls, J. 1995. Field evaluation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (rye grass). Environ. Sci. Technol. 29:1998-2004.

McLachlan, M.S., Kaupp, H., and Blumenstock, M. 2000. Retention and mobility of atmospheric particle-associated organic pollutant PCDD/Fs and PAHs in maize leaves. New Phytologist, 148:473-480.

Meng, L., Qiao, M., Arp, H.P.H. 2011. Phytoremediation efficiency of a PAH-contaminated industrial soil using ryegrass, white clover, and celery as mono- and mixed cultures. J. Soils Sediments. 11:482-490.

Meudec, A., Dussauze, J., Deslandes, E., Poupart, N. 2006. Evidence for bioaccumulation of PAHs within internal shoot tissues by a halophytic plant artificially exposed to petroleum-polluted sediments. Chemosphere 65:474-481.

Moser-Boroumand, J., Martins, J.M., Furi, P., Forrer, M., Mermoud, A., Van den Bergh, H. 1997. Development of an optical fiber fluorescence setup for in-situ PAHs detection in porous media. Application to pyranine transport in sand columns. Inter. J. Environ. Anal. Chem. 68:239-256.

Mumtaz, M., and George, J. 1995. Toxicological profile for polycyclic aromatic hydrocarbons. U.S. Government Printing Office: 1995-639-298: Agency for Toxic Substances and Disease Registry. Research Triangle Institute for US Department of Health and Human Services, 457 pp.

Nazaroff, W.W., L. Alvarez-Cohen. 2001. *Environmental Engineering Science.* John Wiley and Sons, NY. pp 95-97.

National Research Council. 1983. Polycyclic aromatic hydrocarbons: Evaluation of sources and effects. https://nepis.epa.gov/Exe/ZyPDF.cgi/9100V03I.PDF?Dockey=9100V03I.PDF (last accessed July 2018)

North, G.B., Peterson, C.A. 2011. Water flow in roots: Structural and regulatory features. *In* Holbrook, N.M., Zwieniecki (eds) *Vascular Transport in Plants*. Elsevier. New York. pp 131-156.

Odabasi, M., Eylem, C., Sofuoglu, A. 2006. Determination of octanol–air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas–particle partitioning in an urban atmosphere. Atmos. Environ. 40:6615-6625.

Oleszczuk, P., Baran, S. 2005. Influence of soil fertilization by sewage sludge on the content of polycyclic aromatic hydrocarbons (PAHs) in crops. J. Environ. Sci. Health. 40:2085-2103.

O'Connor G.A., Chaney R.L., Ryan J.A. (1991) Bioavailability to plants of sludge-borne toxic organics. In: Ware G.W. (eds) Reviews of Environmental Contamination and Toxicology. Reviews of Environmental Contamination and Toxicology, vol 121. Springer, New York, NY

Paterson, S., Mackay, D. 1994. A model of organic chemical uptake by plants from soil and the atmosphere. Environ. Sci. Technol. 28:2259-2266.

Peck, A.M., Hornbuckle, K.C. 2003. Use of a climate-controlled chamber to investigate the fate of gas-phase anthracene. Water Air Soil Pollut. 145:17-34.

Pepper, I.L., C.P. Gerba, and M.L. Brusseau. 2006. The extent of global pollution. *In* Pepper, I.L., C.P. Gerba, and M.L. Brusseau (eds), *Environmental and Pollution Science.* Academic Press, San Diego CA. pp 3-12.

Prevedouros, K.; Brorstrom-Lunden, E.; Halsall, C. J.; Jones, K. C.; Lee, R. G. M.; Sweetman, A. J. 2004. Seasonal and long-term trends in atmospheric PAH concentrations: evidence and implications. Environ. Pollut. 128:17-27.

Preusser, M., Rhohoo, H., Schwermann, J. 1993. Transfer of polycylic aromatic hydrocarbons from contaminated soil in vegetables. *In* F. Arendt (ed). Contaminated soil '93. Pp 1199-1200. Kluwer Academic Publ., Dordrecht, The Netherlands.

Reilley, K. A., Banks, M. K., Schwab, A.P. 1996. Dissipation of Polycyclic Aromatic Hydrocarbons in the Rhizosphere. J. Environ. Qual. 25:212-219

Robinson, S.L., Novak, J.T., Widdowson, M.A., Crosswell, S.V., Fetterolf, G.J. 2003. Field and laboratory evaluation of the impact of tall fescue on polyaromatic hydrocarbon degradation in an aged creosote-contaminated surface soil. J. Environ. Engg. 129(3):232-240.

Ryan, J.A., Bell, R.M., Davidson, J.M., O'Connor, G.A. 1988. Plant uptake of non-ionic organic chemicals from soils. Chemosphere. 17:2299-2323.

Samsoe-Petersen, L., Larsen, E. H., Larsen, P. B., and Bruun, P. 2002. Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. Environ. Sci. Technol. 36:3057-3063.

Schreiber, L. , Kirsch, T., and M. Riederer. 1996. Diffusion through cuticles: principles and models. *In* G. Kierstens (ed), *Plant Cuticles*, BIOS Scientific Pubs., Oxford. pp. 109-119.

Sattelmacher, B. 2008. The apoplast and its significance for plant mineral nutrition. New Phytologist 149:167-192.

Shone, M.G.T., Wood, A.V. 1974. Comparison of uptake and translocation of some organic herbicides and a systemic fungicide by barley. 1. Absorption in relation to physicochemical properties. J. Exper. Bot. 25:390-400.

Shone, M.G.T., Clarkson, D.T., Sanderson, J., Wood., A.V. 1973. A comparison of the uptake and translocation of some organic molecules and ions in higher plants. *In* Ion Transport in Plants. Academic Press. Chapter 8, 571-582.

Sicbaldi, F., Sacchi, G.A., Trevisan, M., Del Re, A. A.M. 1997. Root uptake and xylem translocation of pesticides from different chemical classes. Pestic. Sci. 50:111-119.

Simonich, S.L., and Hites, R.A. 1994. Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons. Environ. Sci. Tech. 28:939-943.

Simonich, S.L. and Hites, R.A. 1995. Organic pollutant accumulation in vegetation. Environ. Sci. Technol. 29:2905-2914.

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

Site, A. D. 1997. The vapor pressure of environmentally significant organic chemicals: A review of methods and data at ambient temperature. J. Physics Chem. Ref. Data 26:157-193.

Skupińska K, Misiewicz I, Kasprzycka-Guttman T. Polycyclic aromatic hydrocarbons: physicochemical properties, environmental appearance and impact on living organisms. Acta Pol Pharm. 2004 May-Jun; 61(3):233-40. Review. PubMed PMID: 15481250.

Smith, K. E. C.; Green, M.; Thomas, G. O.; Jones, K. C. The behavior of sewage sludge-derived PAHs on pasture. Environ. Sci. Technol. 2001. 35:2141-2150.

Soceanu, A. S. Dobrinas, G., Stanciu, V. Popescu. 2014. Polycyclic aromatic hydrocarbons in vegetables grown in urban and rural areas. Environ. Eng. Mgmt. J. 13:2311-2315.

Somtrakoon, K., Chouychai, W., Lee, L. 2014. Comparing anthracene and fluorene degradation in anthracene and fluorene-contaminated soil by single and mixed plant cultivation. Int. J. Phytorem. 16:415-428.

Srogi, K. 2007. Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ. Chem. Lett. 5:169-195.

Su, Y.H, Zhu, Y.G. 2008. Uptake of selected PAHs from contaminated soils by rice seedlings (*Oryza sativa*) and influence of rhizosphere on PAH distribution. Environ. Pollut. 155:369-365.

Suess, M.J. 1976. The environmental load and cycle of polycyclic aromatic hydrocarbons. Sci. Total Environ. 6:239-250.

Taiz, L., and Zeiger, E. 2010. *Plant Physiology*. 5th ed. Sunderland, MA: Sinauer Associates, 2010.

Takaki, K., Wade, A.J., Collins, C.D. 2014. Assessment of plant uptake models used in exposure assessment tools for soils contaminated with organic pollutants. Environ. Sci. Technol. 48:12073-12082.

Tan, H.D., Li, R.L., Zhu, Y.X., Zhang, Y. 2017. In situ quantitative and visual investigation of the retention of polycyclic aromatic hydrocarbons on the root surface of Kandelia obovata using a microscopic fluorescence spectral analysis method. Talanta 167:86-93.

Tao, S., Cui, Y. H., Xu, F. L., Li, B.G., Cao, J., Liu, W.X., Schmitt, G., Wang, X.J., Shen, W.R., Qing, B.P, and Sun, R. 2004. Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin. Science of the Total Environment, 320:11-24. doi:10.1016/s0048-9697(03)00453-4

Terzaghi, E., Zacchello, G., Scacchi, M., Raspa, G., Jones, K.C., Cerabolini, B., Di Guardo, A. 2015. Towards more ecologically realistic scenarios of plant uptake modelling for chemicals: PAHs in a small forest. Sci. Tot. Environ. 505:329-337.

Thomas, W., Ruhling, A., and Simon, H. 1984. Accumulation of airborne pollutants (PAH, chlorinated hydrocarbons, heavy metals) in various plant species and humus. Environmental Pollution, 36:295-310.

Trap, S., Matthies, M. 1995. Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environ. Sci. Technol. 29:2333-2338.

Trapp, S. 2000. Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds. Pest Management Sci. 56:767-778.

Trapp, S, Miglioranza, K.S., Mosbaek, H. 2001. Sorption of lipophilic organic compounds to wood and implications for their environmental. Environ. Sci. Technol. 35:1561-1566.

Trapp, S. 2002. Dynamic root uptake model for neutral lipophilic organics. Environmental Toxicology and Chemistry 21:203-206.

Trapp, S., Cammarano, A., Capri, E., Reichenerg, F., and Mayer, P. 2007. Diffusion of PAH in Potato and Carrot Slices and Application for a Potato Model. Environ. Sci. Technol. 41:3103-3108.

Vallero, D. 2014. *Fundamentals of Air Pollution.* Chapter 18. Air pollutant kinetics and equilibrium. pp 437-474. Academic Press, NY.

Wagrowski, D. M., and Hites, R. A. 1997. Polycyclic aromatic hydrocarbon accumulation in urban, suburban, and rural vegetation. Environ. Sci. Technol. 31:279-292.

Wang, Y.C., Qiao, M., Liu, Y.X., Arp, H.P.H., Zhu, Y.G. 2011. Comparison of polycyclic aromat hydrocarbon uptake pathways and risk assessment of vegetables from waste-water irrigated areas in northern China. J. Environ. Monitor. 13:433-439.

Waqas, M., Khan, S., Chao, C., Shamshad, I., Qamar, Z., Khan, K. 2014. Quantification of PAHs and health risk via ingestion of vegetable in Khyber Pakhtunkhwa Province, Pakistan. Sci. Tot. Environ. 497-498:448-458.

Watts, A.W., Ballestro, T.P., Gardner, K.H. 2006. Uptake of polycyclic aromatic hydrocarbons (PAHs) in salt marsh plants *Spartina alterniflora* grown in contaminated sediments. Chemosphere 62:1253-1260.

White, J.C., Mattina, M.J.I., Eitzer, B.D., and Iannucci-Berger, W. 2002. Tracking chlordane compositional and chiral profiles in soil and vegetation. Chemosphere 47:639–646.

White, J.C., Wang, X., Gent, M.P.N., Ianucci-Berger, W., Eitzer, B.D., Schultes, N.P., Arienzo, M., and Mattina, M.J.I. 2003. Subspecies-level variation in the phytoextraction of weathered p,p' -DDE by Cucurbita pepo. Environ. Sci. Technol. 37:4368–4373.

Wilcke, W. 2000. Polycyclic hydrocarbons (PAHs) in soil – A review. J. Plant Nutr. Soil Sci. 163:229-248

Wild, S.R. and Jones, K.C. 1992. Organic chemicals entering agricultural soils in sewage sludges: Screening for their potential to transfer to crop plants and livestock. Sci. Total Environ. 119:85-119.

Wild, E., Dent, J., Barber, J.L., Thomas, G.O., Jones, K.C. 2004. A novel analytical approach for visualizing and tracking organic chemicals in plants. Environ. Sci. Technol. 38:4195-4199.

Wild, E., Dent, J., Thomas, G.O., Jones, K.C. 2005. Direct observation of organic contaminant uptake, storage, and metabolism within plant roots. Environ. Sci. Technol. 39:3695-3702.

Wild, E., Dent, J., Thomas, G.O, Jones, K.C. 2006. Visualizing the air-to-leaf transfer and within-leaf movement and distribution of phenanthrene: Further studies utilizing two-photon excitation microscopy. Environ. Sci. Technol. 40:907-916.

Yang, Y., Zhu, L. 2007. Performance of the partition-limited model on predicting ryegrass uptake of polycyclic aromatic hydrocarbons. Chemosphere 67:402-409.

Zhang, Y and Tao, S. 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos. Environ. 43:812-819.

Zhu, L., Gao, Y. 2004. Prediction of phenanthrene uptake by plants with a partition-limited model. Environ. Pollut. 131:505-508.