

# Potential for Plant-Based Remediation of Pesticide-Contaminated Soil and Water Using Nontarget Plants such as Trees, Shrubs, and Grasses

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Appropriate environmental management of pesticides includes their proper application, use of filter strips and riparian buffers to contain pesticides in runoff from fields, prompt cleanup of spills, and treatment processes for wastewater associated with manufacturing and equipment usage. Plants have beneficial effects in the management of pesticide-contaminated soil and water, including direct metabolism of many pesticides, stimulation of microbial activity in the root zone, extraction of contaminated water, and reduction of infiltrating contaminated water. In this work, we review the literature on nontarget plants that can grow in pesticidecontaminated soil and water, and the fate of pesticides in filter strips, riparian buffers, and vegetated remediation environments. Past research indicates that there are significant differences in the tolerance of plants to pesticides present in soil and water, and that some plants are more effective than others in the remediation of pesticide-contaminated soil and water. Thus, there is value in the identification of tolerant plants and favorable plant-based remediation technologies for management of pesticides and contaminated sites.

**Keywords** degradation, herbicides, pesticides, phytoremediation, riparian buffers, vegetation.

#### 1. INTRODUCTION

Pesticide application has become an integral part of agriculture worldwide. Often, pesticide application methods fail to apply the chemicals homogeneously to the target area. Pesticide drift outside the target area is economically wasteful and potentially hazardous for nearby nontargeted plants, animals, or other organisms. Soil, surface waters, groundwater, and sediments become contaminated with pesticides because of spills, accidents, and misapplication. Pesticides can also enter surface water via runoff or soil erosion from croplands. According to Bicki and Felsot (1994), an estimated 14,000 agrochemical facilities in the USA store, sell, mix, and/or apply pesticides. Similar facilities exist in most other countries. Pesticide-contaminated soil caused by spills, improper storage, and improper disposal of rinsates and containers is known to be a problem in the U.S. (Bicki and Felsot, 1994) and in other countries such as Kazakhstan (Nurzhanova et al., 2003). Vegetation-based treatment systems have been used successfully to remediate soil and water contaminated by pesticides and other organic pollutants (Cunningham et al., 1996; Davis et al., 2002; Shimp et al., 1993). The emphasis in this review is on potential remediation of pesticide-contaminated soil and water using nontarget plants such as trees, shrubs, and grasses.

#### 2. PLANT-BASED REMEDIATION USING NONTARGET PLANTS

Ecological problems caused by contamination of soil and water with pesticides may be solved partially by using filter strips and buffer zones of nontarget plants (Borner, 1994). Such technologies are valuable and cost-effective, exploiting the physical abilities of plants to reduce pesticide runoff and their metabolic capacity to accumulate and transform toxicants (Dobson *et al.*,

1997). Detoxification potential of higher plants, analogous to "green livers," may be effectively used as a basis to create treatment technologies to remediate contaminated environments (Hall et al., 2001; McCutcheon and Schnoor, 2003). Plant-based remediation may integrate well with conservation biology to speed the recovery of natural ecosystems from local or more widespread anthropogenic changes (Dobson et al., 1997). There are several reviews available on plant-based remediation systems (Bicki and Felsot, 1994; Cunningham et al., 1996, 1997; Davis et al., 1998, 2002; Shimp et al., 1993; Scheper and Tsao, 2003; Tsao, 2003). In general, plant-based systems are designed on the basis of known plant capabilities to stabilize or remediate contaminated soil and water. Because plants use significant quantities of water, plume control and groundwater management are benefits that should be considered in plant-based remediation. Several characteristics of plants, such as local adaptation, metabolism, uptake, and tolerance, are important factors in designing plant-based treatment systems. Plants may enhance transport of volatile compounds from the soil into the atmosphere (Davis et al., 2002; 2003). Pesticides which enter plants may be transformed into less toxic forms that may be further degraded or incorporated into plant biomass such as lignin (Hall et al., 2001; McCutcheon and Schnoor, 2003).

Plants create a favorable environment around their root-zone (in the rhizosphere) for contaminant degradation. The unique status of the rhizosphere as a treatment-zone is discussed in several research papers (Anderson et al., 1993; Cunningham et al., 1996; Curl and Truelove, 1986; Davis et al., 1998, 2003). The enhanced rate of biodegradation in the rhizosphere may be due to cometabolism and/or the larger microbial populations stimulated by root exudates, root turnover, and improved soil moisture, oxygen, and nutrient conditions. Roots also sorb pesticides onto their surfaces, and dead roots add organic matter to soil, which can enhance the sorption of pesticides onto soil humic matter where microbial transformation may occur. In the following sections, several well-established plant-based systems are discussed. We also present several possible plant-based treatment systems based on the available literature on response of nontarget plants to pesticides.

#### 2.1 Rhizosphere Systems

The rhizosphere is the zone of soil close to plant roots. The rhizosphere supports consortia of microbes capable of degrading pesticides (Anderson *et al.*, 1993). It provides habitat for a wide range of microorganisms. Bacterial numbers in the rhizosphere often exceed  $10^9$  per gram dry weight of rhizosphere soils, at least 10 to 100 times greater than in bulk soil (Erickson *et al.*, 1995). Most members of the soil biota are organotrophs, and the major source of carbon for such soil organisms is derived from plant roots and organic residues contributed during and following plant growth. Plants release nutrients such as amino acids, simple sugars, carbohydrates, and enzymes into the soil. These are potential substrates for microorganisms (Paul and Clark, 1996). Root exudates usually are low molecular weight

substances that leak from plant cells into the soil, either through the spaces between cells or directly from epidermal cell walls. Root secretions include low molecular weight compounds and high molecular weight mucilages, both of which are released as a result of growth and metabolic processes (Al-Khatib et al., 2002). Root turnover is another mechanism that adds organic carbon to the soil matrix. Both quantitative and qualitative measurements show that bacterial coverage of root surfaces usually ranges from 5 to 10%. Single bacteria often are associated with pits in root-cell walls, and clusters of bacteria are found in void spaces between cells (Paul and Clark, 1996). The rhizosphere harbors a great diversity of microorganisms. Chemicals released by plants can beneficially affect xenobiotic degradation by at least three mechanisms, including the selective enrichment of degrader organisms, enhancement of growth-linked metabolism, and the induction of cometabolism in certain microorganisms that carry degradative genes and plasmids. More information on rhizosphere effects on contaminant degradation can be found elsewhere (Davis et al., 2002, 2003; Karthikeyan and Kulakow, 2003).

Since rhizosphere systems depend on the extent (density and depth) of plant root systems, root depth plays an important role in determining the effective zone for vegetative remediation technologies. Typically, some turf grasses such as bluegrass have very shallow but dense fibrous root systems that extend less than 15 cm in depth. Other grasses such as ryegrass, tall fescue, many warm season grasses, and herbaceous species have root systems that can extend 0.5 to 2 m in depth or more. Rooting depth for woody species varies; some trees root to a depth of 3 to 5 m or more (Tsao, 2003).

Several laboratory studies were conducted to assess the impact of the rhizosphere on pesticide degradation (Anderson and Coats, 1994; Anderson et al., 1994; Hoagland et al., 1994, 1997; Kruger et al., 1997a, 1997b; Nair et al., 1993; Perkovich et al., 1995; Shann and Boyle, 1994; Zablotowicz et al., 1994, 1997). The results of the studies are summarized in Table 1. In general, the rhizosphere soil of many plant species has the potential to support degradation of various agrochemicals, mostly by stimulating microbial activity. The extent to which the rhizosphere effect is specific is poorly understood. Some plants such as legumes obviously support large populations of certain genera of microbes. These may have selective capacity to degrade certain pesticides. Plant species have been identified that release aromatic compounds either as root exudates or through root turnover. These plants may selectively stimulate microbial populations capable of degrading aromatic compounds like polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and pesticides like dichloro-diphenyl-trichloro ethane (DDT) (Leigh et al., 2002).

#### 2.2 Plant-Based Remediation Systems Using Trees

In many terrestrial ecosystems, woody stems and branches of trees provide most of the visible biomass. Roughly 95% of aboveground forest biomass is stems and branches. The large pool of biomass may act as a storage or sink compartment for agrochemicals. Meredith and Hites (1987) found PCBs in the bark of black walnut and tulip poplar trees that were exposed to a PCB-contaminated landfill, as well as in the bark of white oak (*Quercus alba*) trees 14 km away from the landfill. Pier *et al.* (2002) examined the concentration of PCBs in 1043 Arctic vascular plants, comprising 31 genera, and also their associated soils. The species were grouped as grasses, sedges/rushes, herbs, and shrubs. Bioaccumulation factors were not fixed within

Pesticide Environment Summary Reference About 15% of ring label <sup>14</sup>C was released Nair et al. (1993) Atrazine Poplar rhizosphere as CO<sub>2</sub> 2,4-D Grass rhizosphere 50% increase in mineralization compared Shann and Boyle (1994) to dicots 2,4,5-T Grass rhizosphere Doubled mineralization compared to Shann and Boyle (1994) dicots Kochia rhizosphere Greater degradation compared to Perkovich et al. (1995) Atrazine nonrhizosphere soils Atrazine, metolachlor, and Kochia rhizosphere Increased mineralization compared to Anderson et al. (1994) trifluralin nonrhizosphere soils Atrazine and metolachlor Anderson and Coats (1995) 14 Rhizosphere soils All 14 rhizosphere soils had positive effects; greatest mineralization was found in musk thistle (*Carduus nutans*)

TABLE 1

Rhizosphere systems to treat pesticide-contaminated soils and water that have been studied in the laboratory

		Tound in musk unstie (Carauus nutans)	
		and catnip (Nepeta cataria)	
		rhizosphere soils	
Parathion and diazinon	Grass rhizosphere	Increased degradation in rhizosphere soils	Hsu and Bartha (1979)
Propanil	Rice rhizosphere	Rapid dissipation in rhizosphere soil	Hoagland et al. (1994)

a single genus or species, but decreased with increasing soil concentrations. Simonich and Hites (1995a, 1995b) concluded that vegetation is a major pathway through which lipophilic organic compounds are removed from the atmosphere by sorption. Life spans of trees are longer than for many other plant communities, and hence trees experience chronic exposure to various pesticides.

Pesticides may enter a plant with water uptake, by sorption from soil water to roots, or from air to plant stems and leaves. Once absorbed, an organic chemical could be retained for long periods of time by sequestration or transformed by metabolism (Trapp *et al.*, 2001). Degradation rates and pathways of agrochemicals inside trees are not well established. Living cells (parenchyma) where pesticides may be metabolized make up to 40% of wood in some species. Dieldrin, chlorobenzenes, and DDT were found in plants after one week of application (Trapp *et al.*, 1990). Volatile compounds diffuse through the plant surface cells into the atmosphere (Zhang *et al.*, 2001) and conversely move into cells from the atmosphere depending on the concentration gradient (Meijer *et al.*, 2003a, 2003b).

Calamari et al. (1995) have shown detectable concentrations of hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB) in mango leaves and pine needles. Simonich and Hites (1997) collected 200 tree bark samples from 32 countries worldwide and analyzed them for 22 pesticides, including active ingredients and degradation products such as HCHs, HCB, dieldrin, aldrin, chlordanes, endrins, endosulfans, and DDT. The study showed that chemicals can be taken up from soil into trees, retained in the trunk, and lost through transport and/or transformation. The combination of long retention time and high potential for metabolism or sequestration of agrochemicals makes trees a common sink for many organic compounds. This property is used in plant-based remediation systems for contaminated soils and groundwater. Known transformation processes include degradation and incorporation into lignin (Castro et al., 2001; Conger and Portier, 1997; Davis et al., 2003; Hall et al., 2001; McCutcheon and Schnoor, 2003). However, potential ecological risk of pesticides stored in plant material should be considered, as lignification may be a pathway for bioaccumulation.

Deep-rooted trees may be installed in multiple rows at the leading edge of a contaminated plume with tree rows set perpendicular to the direction of groundwater flow (Ferro *et al.*, 2003). Trees will transpire groundwater at a substantial rate, depending on climatic factors and the age of the stand. Rapidly growing trees with large canopies and high transpiration rates are well suited as biological pumps. Davis *et al.* (1998) described this phenomenon of plants as "solar pumps" in remediating contaminated water. Ferro *et al.* (2003) present an overview of using trees to maintain hydraulic control.

In general, when pesticide-tolerant plants translocate pesticides from roots to leaves via xylem, injury to the plant is minimized due to one or a combination of the following: (1) dilution of pesticides in the transpiration stream and thus decreased toxicity (Sundaram, 1965); (2) loss of pesticides from transpiration

stream through stems and leaves by diffusion; (3) binding of pesticides from the transpiration stream to plant components as bound residues; and (4) placing of pesticides in or near reactive sites, thus metabolizing the pesticide to less toxic compounds (Akinyemiju et al., 1983; Burken and Schnoor, 1996, 1997, 1998; Field and Peel, 1971a, 1971b, 1972; Lund-Hoie, 1969; Schnabel and White, 2001; Wichman and Byrnes, 1975). Other reasons for tolerance may include efficient translocation and detoxifying mechanisms, presence of detoxifying enzymes or plant compound (for example, benzoxazinone), and nonaccumulating capability of toxic metabolites (which is comparable to excreting toxic materials as a natural response by mammalian systems). On the other hand, the pesticide sensitivity of plants may be related to the following: (1) assimilation of pesticides in phloem vessels, thus injuring living cells, (2) sorption and binding of pesticides to roots and other plant material to reach toxic levels, (3) lack of metabolic capability to detoxify pesticides, (4) accumulation of toxic metabolites of pesticides, and (5) poor translocation and detoxifying mechanisms (Akinyemiju et al., 1983; Dhillion et al., 1968; Hamner and Tukey, 1946; Leonard et al., 1966; Norris and Freed, 1966a, 1966b, 1996c; Pallas, 1963; Sundaram, 1965; Wichman and Byrnes, 1975).

It is well established that two systems are responsible for rapid movement of materials in plants-the xylem and the phloem (Salisbury and Ross, 1991). The xylem transport is in general upwards from roots to shoots and leaves via the transpiration stream. Phloem movement is downward from source to sink via the assimilation stream. Materials can move laterally from one of these systems into the other. Movement in and out of the xylem must take place via the apoplast, and movement up to and away from the sieve tubes of the phloem must take place via the symplast (Salisbury and Ross, 1991). The chemical might be subjected to any or all of the types of movements described above. To move upward in the xylem, the chemical must penetrate the outer cortex layers, diffuse along the apoplast across phloem zone, and finally it must enter the xylem conduits and move upward in the transpiration stream. For downward movement to occur from basal bark to roots, it must traverse the outer bark layers, it must be absorbed into living parenchyma cells, and it must move via the symplast to the phloem of inner bark and be released into the sieve tubes. The rate of downward movement of a chemical can approach the rate of assimilate movement, but it is generally retarded by retention in phloem parenchyma or by leakage from sieve tubes to the xylem vessels, leading to movement in the transpiration stream. The study by Sundaram (1965) showed that in susceptible species where there is more phloem movement, the chemical is least mobile, whereas in the tolerant ones where the chemical moves in the xylem, it is most mobile. Longitudinal and radial investigation of herbicide movement in trees indicated that the killing action in sensitive trees is due to the retention of the herbicide by the phloem, and that its failure to kill tolerant trees is due to upward movement in the transpiration stream via the xylem (Sundaram, 1965).

In the study of Leonard et al. (1966), upward movement, presumably via the xylem after stem application, was appreciable, as indicated by the accumulation of herbicides, amitrole and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in the leaves following such application. Leonard et al. (1966) concluded that absorption into living cells would be possible wherever contact with the herbicide occurs; symplastic transport then would be expected. The herbicide, 2,4,5-T essentially failed to translocate in the phloem of red maple and moved only slightly in the phloem of tolerant white ash. Failure of herbicides to translocate from leaves to roots in appreciable quantities may have been due to injury to the phloem. Herbicidal treatments did not markedly interfere with normal symplastic transport. Passage of herbicides from cell walls into the cytoplasm of living cells of red maple might have been inhibited or limited by the cell membranes. If such absorption did occur, then possibly the 2,4,5-T became trapped within the living cells (perhaps vacuoles) in a manner that prevented its transport (Leonard et al., 1966; Pallas, 1963). In the study by Lund-Hoie (1969), phloem movement of simazine was ascribed limited importance because simazine may not be able to enter the symplast from the apoplast. Consequently, the symplastic movement of simazine in spruce may take place only when simazine is applied directly to exposed phloem. Field and Peel (1971a, 1971b, 1972) studied transport and metabolism of herbicides, 2,4-dichlorophenoxyacetic acid (2,4-D), and 2,4,5-T, in tolerant willow trees. The parent compounds were converted to other unidentified compounds in 24 h.

Based on our review of responses of nontarget trees to pesticides, we can summarize reasons for either tolerance or sensitivity (for an extensive review of studies on response of nontarget trees to pesticides, see Karthikeyan *et al.*, 2003, and references cited therein). However, caution should be taken when generalizing a particular response of a species to a certain pesticide. For example, maple trees that are sensitive to simazine, a triazine herbicide, may or may not be as sensitive to atrazine, another triazine herbicide. At the same time, it may be useful to deduce information, from the previous studies that have limited information and extend our knowledge to future treatment designs. Keeping that in mind, we have summarized the responses of many trees to various pesticides in Table 2.

## 2.3 Plant-Based Remediation Systems Using Aquatic Plants

Aquatic plants have a great potential to function as *in situ* and on-site biosinks and biofilters of aquatic pollutants because of their abundance and limited mobility. These plants possess a large surface area that is covered by a lipid-rich cuticle and thus they have the potential to take up lipophilic pesticides. Sequestration of pesticides includes physical (absorption, adsorption, and partitioning), chemical (complexation reaction with cuticular and membrane components), and biological (microbial degradation and plant uptake) processes by which plants remove any anthropogenic organic compounds from air and liquid media (Garrison *et al.*, 2000; Nzengung and Jeffers,

2001). Aquatic plants can be grown in constructed wetlands to treat water/wastewater contaminated with pesticides (George *et al.*, 2003). Natural wetlands with aquatic species can also serve as treatment systems for pesticide-contaminated water and sediments.

Based on our review of responses of nontarget aquatic plants to pesticides (for an extensive review of studies of the responses of nontarget aquatic plants to pesticides, see Karthikeyan *et al.*, 2003, and references cited therein), we here have summarized the reasons for tolerance/sensitivity of aquatic plants to pesticides (Table 3). Typically, the tolerance is due to sequestration and metabolism of pesticides by various aquatic plants and the enzymes present in them. Most of the transport of pesticides occurs via rhizomes. Once moved inside the plants, pesticides are acropetally distributed from the roots primarily into the leaves and lost via diffusion if volatile.

## 2.4 Plant-Based Remediation Systems Using Crops/ Grasses/Colonizing Plant Species

## 2.4.1 Buffer Strips

Frequently, rotational crops are exposed unintentionally to herbicides applied previously to crop fields. Residues of pesticides applied to agricultural fields can enter surface waters and flow through grass filter strips in surface runoff. Both crops and native plant communities may be exposed to contaminated surface waters. Nontarget crops and grasses are affected (Obrigawitch et al., 1998). Some plants can sequester and metabolize those herbicides if they possess the capability (Hamilton, 1964; Harris and Sans, 1967; Lichtenstein, 1959, 1960; Lichtenstein and Schulz, 1960, 1965; Lichtenstein et al., 1965). Responses of various crops are summarized in Table 4. For an extensive review of studies of the response of nontarget crops to pesticides including metabolism see Karthikeyan et al. (2003) and references cited therein. In general, crop species sequester pesticides and form bound residues that are less toxic than the parent compound. For target crops the pathways are generally well documented.

Although the literature on riparian buffer strips establishes their effectiveness as nutrient and sediment filters under a range of environmental and hydrologic conditions, very little is known about their effectiveness for control of pesticide transport (Lowrance et al., 1997). Asmussen et al. (1977) found that about 70% of 2,4-D in runoff was retained in a 25 m grass waterway. Rohde et al. (1980) found that 86 to 90% of trifluralin could be retained in vegetated buffer strips. Hall et al. (1983) found that edge of field losses could be reduced by over 90% by an oat strip used as a field edge buffer. Arora et al. (1996) reported that retention of atrazine in a bromegrass strip (Bromus inermis L.) ranged from 11 to 100% in natural rainfall and runoff events. Infiltration was the key process for retention by the grass buffer for atrazine and the other two herbicides studied (metolachlor and cyanazine). In another related study, Misra et al. (1996) found higher percent retention of herbicides at higher inflow concentrations. At a nominal concentration of 100  $\mu$ g/L, 29% of the inflow atrazine was retained. At a concentration of 1000  $\mu$ g/L,

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			ntarget trees to various pesticides	
Nontarget species	Pesticide	Response	Reason for tolerance/sensitivity	Reference
Juniper (Juniperis communis)	2,4-D, 2,4,5-T	Tolerance	No apparent reason given	Hamner and Tukey (1946)
Elm ( <i>Ulmus americana</i> )	2,4-D, 2,4,5-T	Sensitive	Long uninterrupted vessels help transport of agrochemical throughout the tree; no metabolism	Hamner and Tukey (1946)
White ash (Fraxinus americana)	2,4-D, 2,4,5-T	Tolerance	Physical resistance (undefined exclusion)	Pallas (1963)
Red maple (Acer rubrum)	2,4-D, 2,4,5-T	Sensitive	Greater absorption and assimilation via phloem	Pallas (1963)
Xylopia quintasii and Ricinodendron heudeotii	2,4,5-T	Tolerance	Distributed upwards in the transpiration stream	Sundaram (1965)
Piptadeniastrum africanum and Celtis mildbraedii	2,4,5-T	Sensitive	Absorption and retention in phloem	Sundaram (1965)
Red maple (Acer rubrum)	2,4,5-T, amitrole	Sensitive	Greater absorption into living cells and translocation in the symplast	Leonard <i>et al.</i> (1966)
White ash (Fraxinus americana)	2,4,5-T, amitrole	Tolerance	Physical resistance (undefined exclusion)	Leonard <i>et al.</i> (1966)
Bigleaf maple (Acer macrophyllum)	2,4-D, 2,4,5-T	Sensitive	Poor translocation and hence accumulation of agrochemical in living cells	Norris and Freed (1966a, 1966b, 1966c)
Red pine (Pinus resinosa)	Simazine	Sensitive	Greater absorption but no metabolism	Dhillion <i>et al.</i> (1968)
Norway spruce (Picea abies)	Simazine	Tolerance	Active uptake of agrochemical and metabolism	Lund-Hoie (1969)
Willow (Salix sp.)	2,4-D, 2,4,5-T	Tolerance	Metabolism of agrochemical	Field and Peel (1971a, 1971b, 1972)
Black walnut (Juglans nigra)	Simazine	Tolerance	Uptake and metabolism of agrochemical to nontoxic metabolites	Wichman and Byrnes (1975)
Yellow poplar ( <i>Liriodendron tulipifera</i> )	Simazine	Sensitive	Uptake and metabolism of agrochemical to phytotoxic metabolites	Wichman and Byrnes (1975)
Poplar clones	Simazine	Tolerance	Active uptake and metabolism of agrochemical to nontoxic metabolites	Akinyemiju <i>et al.</i> (1983)
Poplar clones	Simazine	Sensitive	Active uptake but no metabolism	Akinyemiju <i>et al.</i> (1983)
Hybrid poplar	Atrazine	Tolerance	Active uptake and metabolism to nontoxic metabolites	Burken and Schnoor (1996, 1997, 1998)
Feltleaf willow (Salix alaxensis)	Aldrin	Tolerance	Uptake and metabolism	Schnabel and White (2001)
Balsam poplar ( <i>Populus</i> balsamifera)	Aldrin	Tolerance	Uptake and metabolism	Schnabel and White (2001)
Virginia sweetspire ( <i>Itea</i> virginica L.)	Isoxaben	Sensitive	Reduction in photosystem (II) efficiency and CO <sub>2</sub> assimulation	Baz and Fernandez (2002)
Virginia sweetspire ( <i>Itea</i> virginica L.)	Oryzalin	Tolerance	No apparent reason given	Baz and Fernandez (2002)
White willow (Salix alba L.)	Isoxaben	Sensitive	Reduction in photosystem (II) efficiency and CO <sub>2</sub> assimulation	Baz and Fernandez (2002)
White willow (Salix alba L.)	Oryzalin	Tolerance	No apparent reason given	Baz and Fernandez (2002)
Black pussywillow (S. gracilistyla)	Isoxaben	Sensitive	Reduction in photosystem (II) efficiency and CO <sub>2</sub> assimulation	Baz and Fernandez (2002)
Black pussywillow (S. gracilistyla)	Oryzalin	Sensitive	Reduction in photosystem (II) efficiency and CO <sub>2</sub> assimulation	Baz and Fernandez (2002)

 TABLE 2

 Summary of responses of nontarget trees to various pesticides

#### PLANT-BASED PESTICIDE REMEDIATION

Wilson *et al*.

Nzengung and Jeffers (2001)

(2000)

(2002)

Summary of responses of nonnarget aquatic plants to various pesticides				
Nontarget species	Pesticide	Response	Reason for tolerance/sensitivity	Reference
Canna, Pickerel weed, Iris	Oryzalin	Tolerant	No apparent reason given	Fernandez <i>et al.</i> (1999)
Parrot feather ( <i>Myriophyllum</i> <i>aquaticum</i> ), Duck weed ( <i>Spirodela oligorrhiza</i> ), and Elodea ( <i>Elodea canadensis</i> )		Tolerant	Uptake and enzymatic transformation	Gao <i>et al</i> . (2000a)
Parrot feather, Duck weed,	DDT	Tolerant	Uptake and enzymatic metabolism	Gao et al. (2000b)

Tolerant

Tolerant

Tolerant

Uptake in the transpiration stream

Uptake and metabolism by several

using glutathione-S-transferases

Uptake and conjugation to glutathione Knuteson et al.

enzymes

TABLE 3 Summary of responses of nontarget aquatic plants to various pesticides

\*Plants were older than two weeks.

gramenius) and Pickerel weed (Pontederia cordata) Parrot feather and Elodea

Parrot feather and Canna\*

Simazine

Simazine

Halogenated pesticides

and Elodea

Sweet flag (Acorus

# TABLE 4

Summary of responses of nontarget crops to various pesticides

	Summary of ies	poinses of f	ionalget crops to various pesticides	
Nontarget species	Pesticide	Response	Reason for tolerance/sensitivity	Reference
Oats (Avena sativa)	DDT and HCH	Tolerant	Accumulation and bound residue formation	Fuhremann and Lichtenstein (1978)
Soybeans (Glycine max)	Heptachlor	Tolerant	Accumulation and transformation	Nash et al. (1970)
Cotton (Gossypium hirsutum)	Heptachlor	Sensitive	High accumulation to toxic levels due to high fatty acid content	Nash et al. (1970)
Barley (Hordeum vulgare)	DDT	Tolerant	Accumulation	Mitra and Raghu (1989)
Peanut (Arachis hypogaea)	DDT	Sensitive	Lipids of plant cell solubilize and disperse agrochemical in the cytoplasm that in turn affects normal metabolism	Mitra and Raghu (1989)
Tobacco (Nicotiana tabacum)	DDT	Sensitive	High accumulation to toxic levels due to high fatty acid content	Rosa and Cheng (1973)
Maize (Zea mays)	DDT, HCH	Sensitive	No translocation in the shoots	Verma and Pillai (1991)
Dryland rice (Oryza sativa)	DDT, HCH	Sensitive	No translocation in the shoots	Verma and Pillai (1991)
Canola (Brassica napus)	Atrazine	Tolerant	Metabolism and formation of bound residues	Dupont and Khan (1993)
Cowpea (Vigna sp.)	DDT	Tolerant	Uptake and accumulation	Kiflom et al. (1999)
Carrot ( <i>Daucus carota</i> ), beets ( <i>Beta vulgaris</i> ), and potatoes ( <i>Solanum tuberosum</i> )	Chlordane	Tolerant	Translocation via transpiration stream and bioaccumulation in root tissues	Mattina <i>et al</i> . (2000)
Spinach ( <i>Spinacea oleracea</i> ), lettuce ( <i>Lactuca sativa</i> ) and dandelion ( <i>Taraxacum sp.</i> )	Chlordane	Tolerant	Translocation via transpiration stream and bioaccumulation in aerial tissues	Mattina <i>et al</i> . (2000)
Zucchini (Cucurbita sp.)	Chlordane	Tolerant	Translocation via transpiration stream and efficient bioaccumulation in edible fruit tissues	Mattina <i>et al.</i> (2000)
Ryegrass (Lolium perenne) and alfalfa (Medicago sativa)	<i>p</i> , <i>p</i> ′-DDE	Tolerant	Rhizosphere degradation	White (2000)

49% of atrazine was retained. Several grass species were utilized to create grass waterways and buffer strips to contain polluted surface waters (Angier *et al.*, 2002; Barling and Moore, 1994; Dillaha *et al.*, 1988, 1989; Dosskey, 2002; Paterson and Schnoor, 1992; Rankins *et al.*, 1999, 2001).

P. L. Barnes (unpublished data, 2003) initiated a study to investigate the effect of different rates of atrazine applied on  $C_3$  and  $C_4$  grasses that might be used in filter strips. Atrazine effect was measured by the amount of plant biomass produced. The grasses selected were  $C_3$  (typically cool season grasses that included brome grass (*Bromus secalinus* L.) and  $C_4$ (a warm season grass mixture that included big bluestem (*Andropogon gerardii* Vitman), little bluestem (*Schizachyrium scoparium* (Michx.) Nash), blue grama (*Bouteloua gracilis*), and buffalograss (*Buchloe dactyloides*). Atrazine had a pronounced effect on biomass yields of  $C_3$  grasses and limited effects on  $C_4$  grasses. The labeled rate for application of atrazine to row crops such as maize is 2.8 kg/ha, which, if applied on a  $C_3$  grass, would kill the grass but would only slightly stunt the  $C_4$  grasses, (P. L. Barnes, unpublished data, 2003).

Zhao et al. (2003) studied the use of native prairie grasses to degrade herbicides in soils. Big blue stem (Andropogon gerardii Vitman), yellow Indian grass (Sorghastrum nutans L.), and switchgrass (Panicum virgatum L.) were utilized in the study to degrade atrazine and metolachlor in soil. The mixture of grasses was planted in small trays in the greenhouse and transplanted to two herbicide-contaminated soils. Atrazine concentration in the soil was 100  $\mu$ g/g<sub>drysoil</sub> and metolachlor concentration was 25  $\mu$ g/g<sub>drysoil</sub>. The mixture of the prairie grasses significantly enhanced the degradation of atrazine in soil where indigenous atrazine-degrading microorganisms were not present. However, vegetation had no effect on increasing biodegradation of atrazine in soil that had indigenous atrazine-degrading organisms. The addition of the prairie grasses significantly reduced the concentration of metolachlor in both soils. In general, the grasses significantly decreased the amount of metolachlor, but not atrazine. This was related to the greater water solubility and lipophilicity of metolachlor. The concentration of the herbicide in soil water is a major factor influencing the direct uptake of the herbicide through plant roots (Zhao et al., 2003). These grasses can potentially be used in buffer strips to degrade atrazine- and/or metolachlor-contaminated water.

When selecting a particular species, we must consider longevity, competitiveness, tolerance to pesticides, tolerance of the filter strip to inundation, soil type, and ease of establishment (Rankins et al., 2001). Major functions of grasses in buffer strips are (1) reducing surface runoff, (2) particle sedimentation and adsorption of herbicides to plant surfaces, (3) reducing groundwater aquifer infiltration and recharge, and (4) uptake of pesticides. Most often, reduction in the amount of pesticides in surface runoff is caused by infiltration into the root zone rather than by direct uptake of pesticides (Dosskey, 2002).

Lowrance *et al.* (1997) studied the effect of a riparian forest buffer system on the transport of two herbicides, atrazine, and

alachlor. The buffer system included a grass buffer strip immediately adjacent to the field, a managed pine forest downslope from the grass buffer, and a narrow hardwood forest containing a stream channel system. They found the concentration reduction was greatest per meter of flow length in the grass buffer adjacent to the field. There was only minor transport of herbicides through the buffer system in shallow groundwater. Herbicide concentration in the riparian buffer area and at the edge-of-field was generally at or below detection limits (0.05  $\mu$ g/L).

A well-managed riparian buffer system such as the one reported by Lowrance *et al.* (1997) is a good example of the use of nontarget species to contain pesticide transport effectively. The system used nontarget grasses such as bermudagrass (*Cynodon dactylon* L. Pers.), bahiagrass (*Paspalum notatum* Flugge), and ryegrass (*Lolium perrene* L.), and nontarget trees such as slash pine (*Pinus elliottii* Engelm.), long leaf pine (*Pinus palustris* Mill.), yellow poplar (*Liriodendron tulipifera* L.), and swamp sweet gum (*Nyssa sylvatica* var. *biflora* Marsh.) to reduce atrazine and alachlor transport.

#### 2.4.2 Restoration of Contaminated Sites

The use of nontarget plants for phytoremediation of pesticides has potential for application in regions where minimal resources are available for implementing environmental remediation technologies. A detailed understanding is needed of the interactions of nontarget plants and pesticides at contaminated sites. Former pesticide storage sites are one group of pesticidecontaminated sites present in many countries. Commonly, natural plant colonization by nontarget species results in diverse plant communities growing in pesticide-contaminated soil. Plant species growing in these conditions may have some inherent level of tolerance to pesticides, although this has not been documented. Bioavailability of aged pesticide residues may also be very low. If we can understand the effect of plant growth on pesticide fate, then it may be possible to develop phytoremediation systems to address these sites. Understanding the fate of pesticides in the presence of plants will also help document the potential for bioaccumulation and risk in plants that are allowed to grow in pesticide-contaminated soils.

The Institute of Plant Physiology, Genetics, and Bioengineering of the Republic of Kazakhstan, Kansas State University, and the Technology Innovation Office of the United States Environmental Protection Agency are cooperating on research to develop phytoremediation strategies for pesticide-contaminated soils in Kazakhstan (Nurzhanova *et al.*, 2003). This applied research project is designed to identify pesticide-tolerant plant genotypes from contaminated locations. The first stage in the research has been to identify and characterize several former pesticide storage sites in Kazakhstan that are contaminated with organochlorine pesticides. Significant concentrations of the following organochlorine pesticide residues were observed: 4,4-DDE, 2,4-DDD, 4,4 DDD, 4,4 DDT,  $\alpha$ -HCH,  $\beta$ -HCH, and  $\gamma$ -HCH. Plant species surveys at these locations have identified plants representing more than 19 angiosperm families. Typically there are weedy species and relatives of crop species that have broad distribution in the northern hemisphere and ability to colonize recently disturbed soils. This is consistent with the work of Anderson and Coats (1995) and Anderson *et al.* (1994), showing enhanced remediation of herbicides in rhizosphere soils of weedy species (see also Table 1). The identified plant species will be studied for accumulation and biodegradation of the pesticides with the objective of developing practical phytotechnology systems for managing these sites.

#### 3. SUMMARY

The information regarding potential use of nontarget plants such as trees, shrubs, and grasses in remediating pesticidecontaminated soil and water was reviewed in this article. Plant survival strategies and responses can be exploited to design plant-based treatment systems. Trees can be used to contain a contaminated plume, aquatic plants can sequester pesticides, and crops and grasses can take up pesticides. Several nontarget plant species may possess inherent tolerance to various pesticides or may efficiently translocate and metabolize them to nontoxic metabolites. Field trials should be conducted to advance the knowledge of using nontarget plants in remediation of pesticidecontaminated soil and water. Before designing any plant-based pollution prevention and/or remediation system using nontarget plants, the following questions should be asked:

- 1. Is the species sensitive or tolerant to the particular pesticide?
- 2. How efficiently can the nontarget plants translocate and metabolize the pesticide?
- 3. Are any toxic metabolites formed? and
- 4. Is it cost effective to use nontarget plants for environmental management of pesticide-contaminated soil and water?

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