



Project Summary

Higher Plant Accumulation of Organic Pollutants from Soils

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This work determines the effect of higher plants on sites polluted by organic chemicals and discusses the potential use of plants as an *in situ* cleanup treatment.

In situ cleanup systems have many advantages when compared with other cleanup techniques. These systems treat polluted soils, without excavating the bulk of the polluted material, by detoxifying, neutralizing, degrading, immobilizing, or otherwise rendering harmless the contaminants where they are found.

The first steps in developing an *in situ* plant cleanup system for organically polluted soils are to (1) determine the technical feasibility and cost effectiveness of the method, (2) determine the availability of suitable plant species or varieties, (3) determine whether the site possesses optimal soil conditions, (4) conduct greenhouse scale confirmatory uptake tests, and (5) confirm that the plant materials that have extracted the contaminants can be disposed of in an environmentally safe manner and that the plant mass and harvesting mechanics are realistically manageable.

This work is based primarily on literature review but also includes greenhouse experiments and field testwork. It is concerned with the behavior of organic pollutants in the plant-soil environment, plant uptake and accumulation of organic pollutants, and variation in uptake by different plant species in different conditions.

The literature review involved keyword searches into suitable databases (including Water Resources Abstracts, Biosis Previews, Chemical and Biological Abstracts, Agricola, and Phytotox) and review of over 750 scientific publications for information. Within this report greater emphasis has been placed on the few reports where sufficient details concerning experimental methods to make comparisons is provided.

The greenhouse experiments investigate the actual extent of plant uptake of pollutants from soils under known environmental conditions. The field testwork quantifies natural effects.

The full report is not concerned with foodchain effects where the plant may accumulate pollutants, and animals feeding on the plant may receive high doses of the pollutant for subsequent effect. Nor does this report address effects of the pollutant on the plant itself. As will be seen, these effects result from interactions between pollutant concentrations and a variety of environmental effects.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The full report is concerned with the behavior of organic compounds in soils and the potential use of higher plants as an *in situ* cleanup technique to clean up these polluted soils. For polluted soils, *in situ* cleanup systems have many advantages over other cleanup techniques. These systems encompass methods of treating polluted soils, without excavating the bulk of the polluted material, by detoxifying, neutralizing, degrading, immobilizing, or otherwise rendering harmless, contaminants where they are found. As the polluted materials are not excavated, the workforce is not exposed and pollutants do not migrate from the site during excavation.

The first steps in developing an *in situ* plant cleanup system for organic polluted soils are to:

1. determine whether vegetative extraction from the contaminated soil has a high probability of being the most tech-



nically and cost-effective approach at the specific site, realizing that this approach will require a substantial time period and intensive agronomic management over that time;

2. determine whether suitable plant species (or varieties within a species) are available to accomplish the desired contaminant extraction;
3. determine whether the site possesses, or can be readily modified to possess, soil conditions that will support optimal growth of the selected plant materials;
4. conduct greenhouse-scale confirmatory uptake tests; and
5. confirm that the plant materials that have extracted soil contaminants can be adequately disposed of in an environmentally safe manner and that the plant mass and harvesting mechanics are realistically manageable.

No limits have been placed on the methods of soil cleanup by plants. It could be that the plant accumulates the pollutant for subsequent disposal, or that the plant degrades the pollutant, or that microbes attached to the plant root degrade the pollutant.

Using plants to clean up organic polluted soils, which may prove suitable in a number of different pollutant situations, could be most useful for soils contaminated by organic chemicals to shallow depths, i.e., less than 2 meters. The maximum depth that plant roots normally penetrate the soil is 2 meters. Such surface situations are commonly encountered from spills or leaks when the source of the contamination is at or near the soil surface. It also occurs on many former dumping sites.

Using the ability of plants to accumulate pollutants and then metabolizing them to simple units would essentially be inexpensive to establish and maintain. It could, therefore, prove extremely useful when vast volumes of soil and sediment materials are polluted but not to an immediately hazardous extent. These materials may be polluted by dust blow or by surface erosion resulting from adjacent contaminated sites.

The ability of plants to remove and accumulate compounds from the soil is an essential function of the plant. Plants remove great amounts of applied nitrogen and phosphorus while they grow and thereby protect the groundwater from these nutrients. Plants may also be able to extract excessive levels of some micro-elements from polluted sites and thereby rehabilitate the site for more normal crops.

The full report, based on literature review, greenhouse experiments, and field testwork, is concerned with:

1. the behavior of organic pollutants in the plant-soil environment;
2. plant uptake of organic pollutants from the soil; and

3. variation in the extent of plant uptake by different plant species in different conditions.

Literature Review

Behavior of Pollutants in the Plant-Soil

The study of organic chemicals in the soil environment has been limited to agricultural chemicals (e.g., insecticides, pesticides, and herbicides) and specific compounds that cause a problem or persist in the soil for long periods (e.g., PCBs, PBBs). This has possibly occurred because of the complexity of reactions, the large number of compounds, and the cost associated with their analysis.

Many transformations and processes affect an organic chemical when it is in the soil environment. The sum of these determine both the compound's environmental impact and its life. Soil and environmental factors such as pH, cation exchange capacity, organic matter, clay content, and water content all affect the rate and degree of these transformations. In a given situation (soil and environmental conditions), however, these transformations are dependent upon the physical and chemical properties of the compound and therefore vary between compounds.

The greatest influences on the potential for all nonionic organic chemicals to affect a plant are the relationships and interactions between their vapor, liquid, and adsorbed phases in the soil, and their soil degradation rates. These processes determine not only the form of the compound that is available to affect the plant but also the speed at which the compound moves or spreads through the soil to achieve its effect. The importance of each of these processes will be discussed separately.

The concentration of all organic compounds in the soil decreases with time as long as no further additions occur. This decrease results from interactions between the compound and a number of physical, biological, and chemical parameters acting in the soil that either remove the compound from the soil or alter its original state.

Extensive research investigated the equilibrium between the pollutant sorbed to the soil and that in solution in the soil water. This is often expressed as an adsorption isotherm, that, at low concentrations, approximates a straight line, giving rise to the equation

$$C_s = K_d (C_l)$$

where C_s is the adsorbed concentration (g/kg soil), C_l is the solution concentration (g/m³ soil solution), and K_d (m³/kg) is the slope of the adsorption isotherm of the distribution coefficient. This immediately assumes complete reversibility, or an equilibrium between these

phases, that may not strictly occur for some chemicals.

Where the clay content of soils and sediments is relatively low, pollutant adsorption occurs primarily on the organic fraction of the soil. The degree of adsorption of the non-ionic pollutant is then dependent on the organic carbon content of the soil or the sediment. Variation between materials, which exhibit a wide range of physicochemical properties, can then be reduced by defining an organic carbon distribution coefficient

$$K_{oc} = \frac{K_d}{f_{oc}}$$

where K_d is again the slope of the adsorption isotherm in m³/kg, and f_{oc} is the organic carbon fraction in the soil or sediment. This equation ultimately assumes that all organic matter behaves in the same manner.

Where the adsorption value of a particular pollutant in a particular soil is not available or has not been measured, a good correlation has been found between the organic carbon distribution coefficient, K_{oc} , above and the *n*-octanol/water partition coefficient, K_{ow} , of the chemical. The K_{ow} is defined as the ratio of the chemical concentration in octanol to that in water, when an aqueous solution of the chemical is mixed with octanol and then allowed to separate.

The relationship between K_{oc} and K_{ow} with different groups of environmentally active chemicals and varying soil types has been investigated with many authors reporting equations similar to

$$\log K_{oc} = 0.524 \log K_{ow} + 0.62$$

This equation illustrates that as adsorption of the pollutant to the soil increases, and thus soil solution concentration of the pollutant decreases, $\log K_{ow}$ increases.

To have the greatest effect upon a plant, the organic compound must stay within the vicinity of the plant root and not be quickly leached away by mass flow.

The vapor partitioning of a compound in the soil is important because the speed at which a vapor spreads through the soil in the vapor phase is considerably greater than that in the solution phase. Even for chemicals with relatively low vapor densities, this transport route has been shown to be significant.

The relationship between the compartmentalization of the compound between the soil solution and the air spaces in the soil is often described by Henry's Law and the extent of partitioning is described by Henry's Constant.

Those chemicals having a high vapor pressure, and thus a relatively high Henry's Constant, will easily move from the soil solution

into the soil air, will be quickly lost from the soil and the immediate vicinity of the plant root, and will have a low overall effect within the soil. They may subsequently be taken up into the plant leaf from this vapor phase; this is discussed later.

There have been no all-embracing studies to determine the Henry's Constant above which volatilization plays an important role in the transport of the compound in the environment. It is not possible, therefore, to select a Constant above which transport in the soil will occur primarily by the vapor phase.

The effect of the vapor phase is strongly influenced by the amount of water in the soil; limitations in soil water mean limited partition from the soil water to the soil air and on the density or pore space of the soil itself.

Plant Uptake of Organic Pollutants

Uptake of chemicals from the soil into plants can be both a complex process involving compound-specific or active processes and/or a passive process in which the chemical accompanies the transpiration water through the plant. When the former occurs, then a rigorous relationship between the degree of uptake and the physicochemical parameters of the chemical cannot be expected although some general trends may be evident. When uptake into the plant is a passive process, then relationships should exist.

It is generally accepted that a chemical in the soil enters a plant through four pathways:

1. root uptake into the conduction channels and subsequent translocation by the transpiration stream;
2. uptake from vapor in the surrounding air;
3. uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it; and/or
4. uptake and transport in oil cells found in oil-containing plants like carrots and cress.

The amount of a pollutant found in a plant growing in organic polluted soil will therefore be the sum total of each of these transport routes. Their respective importance depends on the nature of the pollutant and the soil and the environmental conditions during which plant exposure occurs. Although the latter two uptake routes may be significant in a local context, they are not generally widespread and can be discounted as major routes of plant contamination. Because most reported instances of plant uptake of soil-borne organic compounds make no attempt to distinguish the extent of the first two uptake routes, the relative importance of each, under different environmental conditions and for different pollutants, cannot be assessed.

To describe the relationship between herbicide transport and water uptake into plants,

the Transpiration Stream Concentration Factor (TSCF) has been proposed as

$$\text{TSCF} = \frac{\mu\text{g herbicide in shoots per ml water transpired}}{\mu\text{g herbicide per ml uptake solution}}$$

In turn, it has been proposed that the uptake of a chemical into a plant root could be described by the Root Concentration Factor (RCF), defined as

$$\text{RCF} = \frac{\text{concentration in root}}{\text{concentration in external solution}}$$

and the analogous Stem Concentration Factor (SCF) as

$$\text{SCF} = \frac{\text{concentration in stem}}{\text{concentration in external solution}}$$

Although the concentration factor concept is useful in describing the relative concentration in a particular plant part, it has many limitations. These arise because the concentration of organic chemicals, both within the soil and within the plant, do not remain constant but change with time. The concentration of any organic chemical in the soil, or in nutrient solution, may be depleted by plant uptake or degradation; the concentration of an organic chemical in a plant will also be reduced with time both by degradation within the plant and by the plant increasing its mass and thus effectively diluting the chemical.

Research in the early 1980s with herbicides related both the RCF and the TSCF to the already defined K_{ow} of the different groups of herbicides under test. TSCF shows a bell-shaped dependence on K_{ow} with a broad maximum around a K_{ow} of 1.8. The RCF increases with increasing K_{ow} and decreases to a limiting value of less than unity for polar compounds. The explanation for this is that at K_{ow} values below 1.8, translocation is limited by the root concentration of the herbicide. At values above 1.8, translocation is limited by the rate of release of the sorbed lipophilic chemical from the plant root into the transpiration stream. All the TSCF in this investigation were, like earlier reports, below unity, indicating that the chemicals under test moved passively into the shoot with the transpiration stream and were not taken up against a concentration gradient.

In another experiment with more lipophilic chemicals, the sorption of chemicals by macerated roots was shown to be very close to the RCF above, but (in contrast to the RCF) the sorption continued to fall sharply as the lipophilicity decreased. There was a linear relationship between the concentration factor of the macerated roots and K_{ow} , shown as

$$\log \text{RCF (macerated root)} = 0.77 \log K_{ow} - 1.52$$

This relationship suggests that sorption of chemical by roots is the same whether the root is living or dead; the sorption process of chemicals to the root is therefore likely to be a partitioning event.

In conclusion, if degradation of the chemical does not occur within the plant and plant root uptake and translocation of pollutants from the soil is a passive process, then plant uptake can be described as a series of consecutive partitions between the soil solids and the soil water, the soil water and the plant roots, and then the plant roots and the transpiration stream, and the plant roots and the plant leaves.

Pollutants with a highest log K_{ow} value, for example dioxin (6.14), PCBs (4.12-6.11), some of the phthalate esters (those with values above 5.2), and the polycyclic aromatic hydrocarbons (4.07-7.66), are those most likely to be accumulated by or in the root and not be translocated out of it. Those chemicals with a lower K_{ow} (those that are lipophobic and water soluble) are likely to be translocated within the plant and may reach significant concentrations within the plant leaves.

It also seems likely that for some of the more volatile herbicides at least diffusion in the vapor phase and subsequent uptake by the shoot may be an important route of chemical entry into the plant. Two processes precede the penetration of chemicals in the soil into leaf tissue by the air. The first process concerns volatilization of the chemical from the soil. The volatilization depends on the vapor pressure of the compound in the soil pores and it varies according to ambient temperatures, the water solubility of the compound, and the adsorption capacity and physical properties of the soil. The second process involves deposition from the air onto the leaf surface. As this deposition proceeds, the vapor pressure of the chemical is decreased and more volatilization occurs.

Variations in Pollutant Uptake by Different Plant Species

A further variable affecting plant uptake of soil-borne organic pollutants is the type of plant being exposed to the pollutant. No systematic examination has been made of plant responses to organic chemicals in soil, although it does appear that, as with plant uptake of soil-borne heavy metals, there is variation in uptake both between species and within the same species on an individual level.

Some of these experimental variables were investigated in a series of greenhouse studies and in a field assessment.

Greenhouse Studies

The greenhouse investigations consisted of adding pure chemical to a soil to produce a contaminated soil. Plants were then grown in

this soil and their accumulation of the pollutant was assessed. Although environmental conditions in a greenhouse are normally very different from those outside the greenhouse, the greenhouse trials produced some very interesting results.

In trials with hexachlorobenzene (HCB), the plant root concentration of the pollutant was, in many cases, greater than that occurring in the soil; this showed that pollutant accumulation had occurred. This accumulation occurred to a greater extent with least organic matter fraction within the soil medium, and it occurred increasingly with increasing time. In one experiment, 33% of the soil-borne pollutant was accumulated from the soil to the roots of radish within 67 days of seed sowing. Between plant species, the ability to accumulate soil-borne pollutants varied.

This suggests that further work could identify species with great affinity for cleanup.

Field Assessment

The field trial consisted of collecting plants actually growing on polluted soil at a polluted site and then comparing the root and plant leaf concentrations with those found in the soil surrounding the root. The results from a dioxin (TCDD) polluted site near St. Louis, MO, again showed that plant roots accumulate soil-borne pollutants with high log K_{ow} to concentrations many times those found in the soil. Plant-leaf concentrations of most collected plants were not detectable; however, all three replicates of one species showed high plant-leaf concentrations of TCDD and this requires further investigation.

Recommendations

This investigation of the behavior of organic pollutants in soils and the accumulation of these pollutants by plants has highlighted the potential for using plants to degrade these pollutants, either directly or through microbes attached to the plant root. Further investigation into these areas is merited and the probability of achieving a plant cleanup system for polluted soils remains high.

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The complete report, entitled "Higher Plant Accumulation of Organic Pollutants from Soils," (Order No. PB92-209 378/AS; Cost: \$26.00, subject to change) will be available only from:

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