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Phytoremediation of Atrazine

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Atrazine is a herbicide used by farmers worldwide since 1959 (Solomon et al. 1995). Atrazine interferes with photosynthesis (photophosphorylation) in many annual broadleaf plants and grasses, while *Zea mays* (corn), *Sorghum bicolor* (sorghum), *Saccharum officinarum* (sugarcane), and a few other crops (Solomon et al. 1995) are tolerant of the chemical's effects at recommended application concentrations. After application, atrazine continues to control sprouting weeds for 5-6 weeks (Ballantine et al. 1998), allowing the desired crop to become well established without competition for moisture, nutrients and sunlight. Atrazine is much less expensive than comparable herbicides.

Atrazine residue and spills are not only toxic to plants where applied or spilled, but can runoff or leach into streams and rivers, potentially interfering with photosynthesis of aquatic plants which in turn could affect the food and shelter requirements of aquatic animals. Atrazine spills occur at agrochemical dealer sites where the chemicals are mixed and distributed, and occasionally at farms where the chemicals are delivered and loaded into dispersal equipment.

Herbicide remediation techniques typically involve excavation of the contaminated soil for land application at half the legal rate allowed for the particular chemical, or above ground, lined 'biopiles' with soil amendments and aeration to assist mineralization of the chemical. Occasionally landfarming or landfilling may be used. The U.S.Department of Agriculture inspects commercial facilities and tests soils for toxic levels of agrochemicals. When contamination is found, the dealer will usually hire a consultant to conduct a full investigation and oversee remediation efforts. The Department of Agriculture will provide technical support for cleanup. Dealers can apply for financial assistance for the cleanup from the Agricultural Chemical Response and Reimbursement Account (ACRRA), which is primarily funded by a portion of licensing fees paid by commercial dealers, and a surcharge on chemicals sold. Farmers are required to report their own spills, and when properly reported they will also receive technical support from the Department of Agriculture for cleanup, and may also apply for financial support from ACCRA (Cathy Villas-Horns 1999).

More recently, phytoremediation technology is becoming a popular issue for cleanup of toxic spills. Phytoremediation uses carefully selected plants to assist with mineralization and uptake of contaminants in soil and water. Phytoremediation has had limited success for many chemicals, but it does show some promise for remediation of atrazine spills. One of the challenges using phytoremediation for herbicides is choosing plants that will tolerate, and hopefully, metabolize the contaminant.

The objective of any remediation of soil or water contamination is to either remove the contaminant, or render it harmless. Phytoremediation has the potential to accomplish both, and as an in situ process, is much less expensive than strategies involving the removal, transport, and treatment and/or disposal of contaminated soil. Planting costs are relatively inexpensive, and monitoring costs are comparable to those of other remediation alternatives (Schnoor et al. 1995).

The purpose of this paper is to discuss how phytoremediation works, review lab and field studies of this relatively new technology, and discuss how it might be applied to restoration and reclamation projects.

Site Stabilization

The first concern when dealing with a toxic spill is the on-site stabilization of the contaminant. Stabilization is best achieved by stabilizing the soil itself to prevent runoff into streams, leaching into groundwater, or even wind erosion that could result in contamination of a broad area and inhalation by humans and wildlife. Plants are effective for site stabilization because their root systems hold the soil in place and the above ground structure helps to reduce wind erosion. Atrazine is moderately water soluble, and therefore can be a very mobile herbicide, increasing the likelihood that the chemical will find its way into streams and ground water through surface runoff or leaching. In water, atrazine is more resistant than in soil to microbial attack because of chemical structure differences (Solomon et al. 1995). Therefore, site stabilization with plants is an important preventive measure to keep the chemical from reaching bodies of water. Atrazine adsorbs or binds to organic matter in the soil, so a higher percentage of organic material provided by plants will reduce the runoff or leaching into water.

Reducing Soil Atrazine Levels: Evidence From Laboratory Studies

After site stabilization, the next step in remediation is to remove the toxin from the soil or water, or otherwise render it harmless. Organic compounds including atrazine are typically biodegraded or mineralized into components, such as carbon dioxide, water, inorganic ions and molecules, and possibly cellular material (Eweis et al. 1998). Tests using poplar trees show that part of the atrazine residue becomes a part of the plant leaves, stems and roots (Burken & Schnoor, 1996).

Soils with high organic matter, oxygen and moisture have better mineralization rates of atrazine (Nair & Schnoor 1994). Many plants transfer oxygen through their roots and into the rhizosphere, the soil around the roots, which aids aerobic mineralization. Roots excrete compounds, including enzymes, amino acids, sugars, and carbohydrates, (Burken and Schnoor 1996) that provide nutrients for soil microorganisms, particularly symbiotic mycorrhizal fungi. Increased microbial activity in the rhizosphere helps to mineralize toxins and degrade organic pollutants (Schnoor et al. 1995).

Burken and Schnoor (1996) conducted lab experiments evaluating the effectiveness of using poplar trees to help mineralize and take up atrazine from soil. Poplar trees have shown some success removing atrazine and other contaminants from soil, both in the lab and in the field. *Populus deltoides nigra DN34* (poplar trees) are fast growing, hardy, long lived, and tolerant of organics, such as atrazine, making them suitable for phytoremediation studies. They are also easy to start from cuttings, and can be harvested and will grow again from the root system. (Schnoor et al. 1995)

Burken & Schnoor (1996) compared atrazine uptake and mineralization rates in soils with different amounts of organic carbon. They used silty loam soil with a fraction of organic matter of 25%, and sandy soil with 0.1% organic matter. The organic matter is believed to affect the rate at which atrazine adsorbs, or binds to the soil, rendering it immobile. Each soil type was placed in multiple reactor flasks, and the flasks were sealed with a stopper. Cuttings of *Populus deltoides nigra DN34* (Imperial Carolina hybrid poplar trees) were inserted through holes in the stopper, then sealed with silicon to separate the roots from the leaves.

Burken and Schnoor used carbon-14 isotope label with the atrazine to track the source of carbon in the plant structure and in the vapor from around the soil. The carbon-14 labeled atrazine was applied to the soil at about three times the normal field application rate. Controls were set up with no atrazine, or no trees. Soil moisture was monitored, and light and humidity were carefully controlled to maintain uniformity throughout all bioreactors. Air flow was controlled through the soil compartments of each bioreactor so that the gases exiting each reactor were collected in carbon dioxide traps to measure the level of carbon-14 label in the gases around the soil, indicating the rate of mineralization. At various times the plants were harvested and both plant material and soil were analyzed for detection of the carbon-14 label.

After just 9 days the poplars growing in sand appeared to have taken up 93-94% of the carbon-14 labeled atrazine. The trees showed no visible detrimental effects (phytotoxicity) from the atrazine, when compared with trees growing in control bioreactors not treated with atrazine. The trees growing in the silty loam soil showed a much slower rate of uptake and took up a much lower proportion of the carbon 14 labeled atrazine, ranging from 20% in 22 days to 29.2% in 80 days. The soils were then tested to determine how much of the atrazine was still mobile, or available for uptake (or runoff/leaching if in the field). They used water to extract the atrazine that was still bioavailable, and found that the mobility of the atrazine remaining in the soil decreased with time. In the silty loam soil, only 36% was mobile after 22 days, suggesting that the trees took a much greater proportion of the bioavailable atrazine; that which had not adsorbed to the organic matter in the soil. Burken and Schnoor surmised that since the silty loam soil has more organic matter than the sandy soil, more of the carbon-14 atrazine adsorbed to the soil and was not available for plant uptake.

The leaves, stems and roots of the trees were analyzed separately in Burken and Schnoor's study. The bulk of the carbon-14 atrazine taken up by the plants accumulated in the leaves of the trees, regardless of the soil type and number of days, suggesting it moves through the roots and stems quickly. Burken & Schnoor assumed that since high levels of carbon-14 in plants were not accompanied by visible signs of stress, the atrazine had been detoxified. This assumption remains to be adequately studied (Burken & Schnoor 1996).

The levels of carbon-14 labeled carbon dioxide in the gasses from the soil chambers showed a greater percentage of the carbon-14 transpired (mineralized) from the bioreactors containing plants in silty loam than the unplanted silty loam or the sand, possibly due to higher microbial activity stimulated by the plants. With time, the unplanted silty loam bioreactors exceeded the planted bioreactors in carbon-14 mineralization, very likely due to the uptake of the bioavailable atrazine in the plants.

Burken and Schnoor (1996) also set up microcosm studies, using the same two soil types in the same bioreactor setup but without plants, to determine levels of mineralization in soil. Root exudates taken from tree cuttings grown in washed sand were added to some of the bioreactors.

Dried and pulverized root matter from poplar cuttings grown separately was added to other bioreactors. All bioreactors were treated with the carbon-14 labeled atrazine and stored in darkness. Gasses were periodically withdrawn and analyzed for carbon-14 labeled carbon dioxide to determine mineralization rates. Burken and Schnoor (1996) showed that adding root exudates and organic material from poplar tree roots to the soil in the bioreactors increased the mineralization of atrazine in both sand and silty loam. In the soil with higher organic matter, more of the atrazine bound to the soil, thus less was bioavailable for plant uptake. The bound portion of the atrazine was considered to be harmless.

E. L. Kruger et al. (1997) conducted experiments using soils from agrochemical dealer sites in the midwestern United States (Iowa, Illinois, Nebraska) that have been repeatedly contaminated with atrazine and other agrochemicals over time. They conducted lab experiments similar to the microcosm studies by Burken & Schnoor (1996). Soil samples from sites without vegetation were taken to a laboratory, along with rhizosphere soil from *Kochia scorpa* plants from the same dealer sites. The highest atrazine mineralization rates were site-specific. Rhizosphere soils showed a somewhat higher rate of mineralization than non-rhizosphere soils in 36 days, but little difference was detected after 63 days. Some soils developed atrazine mineralization characteristics, while others did not. They tried to inoculate the non-mineralizing soils with the mineralizing soils, with little success. The researchers surmised that mineralization rates were highly influenced by soil conditions, such as pH and salinity.

Field Trials

The Environmental Protection Agency's Technology Innovation Office has offered the private sector partnerships to use new phytoremediation technologies in the field (Kling 1996). Researchers are hesitant, however, to commit to large projects, concerned that the wrong choice of plant could result in failure (Kling 1996). Phytoremediation is still a relatively new technology. Much research is still needed, particularly in the field, before using plants can become a viable remediation strategy on a broad scale. While field tests for some contaminants have shown favorable results, little information is currently available for field trials of atrazine. In Amana, Iowa, poplar trees planted along a small creek to control agricultural runoff (nonpoint source pollution) showed 10-20% of the applied atrazine was taken up by the plants (Schnoor 1995).

Limitations To Atrazine Uptake Effectiveness

At Utah State University, B.J. Orchard et al. (1999) have been conducting similar lab experiments, also using tree cuttings of *Populus deltoides x nigra DN34* , but using a different organic compound, trichloroethylene (TCE) and improved testing techniques. They are reviewing the ability to measure actual effects of the various plant processes, and have found a large variation in test results. The Utah State University study showed less plant uptake and transpiration through the leaves than comparative studies, possibly due to improved testing methods, specifically a more complete root-shoot separation than that used by Burken and Schnoor (1996) and other studies evaluated.

A common misconception about the use of plants to remove soil toxins is that the plants 'pump' the chemical out of the soil. Plant uptake of TCE and atrazine is a passive process, as indicated by past estimates of the transpiration stream concentration factors (TSCF) which are all less than one. Values greater than 1 would have suggested a pump or concentration mechanism. As a passive process, water is required to transport the chemical through the plant. Moderately hydrophobic pollutants are best transpired through plants. Uptake is affected by the chemical properties of the compound, environmental conditions, and plant species characteristics (Burken & Schnoor, 1996).

Bruce Bugbee, a professor at Utah State University participating in the studies, believes that phytoremediation has been overrated in general; that plants cannot do as much as people would like to believe. However atrazine does appear to be an exception, for it has been shown to work even after the chemical has been in the soil for some time and has had time to adsorb to the organic carbon in the soil. Corn takes up and degrades atrazine in the plant, and poplar trees show success as well.

Phytoremediation does have many limitations. Performance of phytoremediation is difficult to predict, and lab tests are difficult to scale up to field application. Actual contaminated sites are typically contaminated with multiple chemicals, complicating efforts including the choice of plants that will tolerate and/or metabolize all the toxins. Microbes that assist with mineralization are sensitive to many conditions which will likely vary from site to site, including soil temperature, pH and salinity. The contaminants must be near the root zone of the plants to benefit from plant processes (McIntyre & Lewis 1997), therefore the cleanup will be limited to shallow contamination of less than five meters (Schnoor 1995). Phytoremediation is time-consuming, requiring patience while the plant grows and metabolizes the toxins (Elweis et al. 1998). In northern latitudes with long winters, mineralization will cease during part of the year, further slowing the progress. Phytoremediation would not be a good choice if there was an immediate risk to humans or the environment, (McIntyre & Lewis 1997), such as a large spill adjacent to a stream or drinking water supply.

Conclusion

In reclamation or restoration projects, phytoremediation has many potential uses. Many wetland and prairie restorations will be located in areas where they will be surrounded by agricultural fields. Herbicide tolerant plants, such as the *Populus deltoides nigra DN34* , may be helpful for defending the boarders of the project from herbicide drift during spraying, or from atrazine treated soils carried by wind and water. Phytoremediation can be helpful as a riparian buffer zone to protect a stream restoration from adjacent farm fields.

Phytoremediation has the potential to be a cost-effective alternative for remediation of soils contaminated with atrazine. As an in situ process, the soil does not have to be excavated and transported for other remediation processes. Phytoremediation focuses on detoxifying the pollutant, rather than simply moving it to another site. Less disturbance of the contaminated soil means the toxin is less likely to be blown or washed away. While practical application of phytoremediation appears to be limited, research of the technology continues.

References

Ballantine, L.G., J.E. McFarland, and D. S. Hackett. 1998. Triazine Herbicides: Risk Assessment. American Chemical Society. Washington D.C.

Burken, J.G. And J. L. Schnoor. 1996. Phytoremediation: plant uptake of atrazine and role of root exudates. Journal of Environmental Engineering (ASCE) 122: 958-963.

Bugbee, Bruce G., Professor in Plants, Soils and Biometeorology Department, Utah State University. Personal conversation, October 22, 1999.

Chard, J. and B. Bugbee. Phytoremediation poster. <http://www.usu.edu/~cpl/phytorem. html.> Utah State University. 1999.

Cunningham, S.D. And D.W. Ow. 1996. Promises and prospects of phytoremediation. Plant Physiology 110: 715-719.

Eweis, J.B., S.J. Ergas, D.P.Y. Chang, and E.D. Schroeder. 1998. Bioremediation Principles. WCB/McGraw Hill. United States of America.

Galatawitsch, Susan. 1999. Lecture notes from Restoration and Reclamation Ecology. University of Minnesota. St. Paul, MN. Fall Semester.

Kling, J. 1996. Phytoremediation of organics moving rapidly into field trials. Environmental Science & Technology, 31: 129A.

Kruger, E.L., J.C. Anhalt, D. Sorenson, B. Nelson, A.L. Chouhy, T.A. Anderson, and J.R. Coats, 1997. Chapter 4: Atrazine Degradation in Pesticide-Contaminated Soils: Phytoremediation Potential in Kruger, E.L., T.A. Anderson and Joel R. Coats, Phytoremediation of Soil and Water Contaminants. American Chemical Society. Washington, D.C.

McIntyre, T. And Lewis, G.M.. 1997. The Advancement of Phytoremediation as an Innovative Environmental Technology for Stabilization, Remediation, or Restoration of Contaminated Sites in Canada: A Discussion Paper. Journal of Soil Contamination, 6(3): 227-241.

Nair, D. R., and Schnoor, J. L. (1994). Effect of soil conditions on model parameters and atrazine mineralization rates. Water Research, 28(5): 1199-1205.

Nair, D. R., J. G. Burken, L. A. Lucht, and J. L. Schnoor. (1993). Mineralization and Uptake of Triazine Pesticide in Soil-Plant Systems. Journal of Environmental Engineering, ASCE, 119(5): 842-584.

Orchard, B.J., Doucette, W.J., Chard, J.K. And Bugbee, B. Uptake of Trichloroethylene by Hybrid Poplar Trees Grown Hydroponically in Flow-Through Plant Growth Chambers. 1999. In Press.

Pereira, W.E. and F.D. Hostetter. 1993. Nonpoint Source Contamination of the Mississippi River and its Tributaries by Herbicides. Environmental Science & Technology, 27(8), 1542-1551.

Schnoor, J. L., L.A. Licht, S.C. McCutcheon, N.L. Wolf, and L.H. Carreira. 1995. Phytoremediation of organic and nutrient contaminants. Environmental Science & Technology, 29(7): 318A-323A.

Schnoor, J. L.1992. Fate of Pesticides and Chemicals in the Environment. John Wiley & Sons, Inc. New York.

Schnoor, J. L. 1996. Environmental Modeling, Fate and Transport of Pollutants in Water, Air, and Soil. John Wiley & Sons, Inc. New York.

Solomon, K. R., D. B. Baker, R. P. Richards, K. R. Dixon, S.J. Kaline,T.W. LaPoint, R.J. Kendall, C.P. Weisskopf, J.M. Giddings, J.P. Giesey, L.W. Hall, Jr., and W.M. Williams. 1996. Ecological Risk Assessment of Atrazine in North American Surface Waters. Environmental Toxicology and Chemistry, 15(1): 31-76.

Villas-Horns, C., Senior Hydrologist, Minnesota Department of Agriculture, St. Paul, MN. Personal conversation, December 1, 1999.