PLANT-ENHANCED REMEDIATION OF GLYCOL-BASED AIRCRAFT DEICING FLUIDS

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ABSTRACT: To ensure passenger safety during flight operations, the Federal Aviation Administration demands the use of glycol-based aircraft deicing fluids (ADFs) at airports. However, from the deicing process a significant amount of ADF runoff enters storm-water collection systems and/or finds its way to soil and ground-water ecosystems. The environmental impact of the ADF mixture is a combination of the extremely high biological oxygen demand from glycols and the toxicity to bacteria, aquatic organisms, and plants of the corrosion inhibitor tolyltriazole. The present paper discusses some alternatives that have been proposed to manage ADF waste and the need for an environmental management technology able to deal with both kinds of contaminants. Phytoremediation has been explored because a rhizosphere effect improves the efficiency of land treatment for many substances and only fungi and vegetation have been reported to be able to degrade the corrosion inhibitor (Wu et al. 1998). Below a toxic threshold of about 100 mg of methyl benzotriazole/L in the aqueous phase, plants can degrade approximately about 2 mg of methyl benzotriazole/(g dry root · day). Some of the advantages, difficulties, and conditions to apply the technology are outlined.

INTRODUCTION

Deicing Process at Airports

Human safety is an overriding concern at airports, and the Federal Aviation Administration (FAA) requires the use of deicing chemicals [only ethylene glycol- (EG-) or propylene glycol- (PG-) based aircraft deicing fluids (ADFs) are certified] to ensure passenger safety during winter operations. Aircraft deicing (with Type I ADF) entails removing ice and snow from wings and fuselages to keep these surfaces clean until the aircraft is safely in the air; anti-icing (with Type II ADF) may be performed after deicing to prevent further snow or ice accumulation during taxiing and takeoff (Mericas and Wagoner 1994). Type I ADF consists of glycol, water, corrosion inhibitor, and some other additives such as surfactants. Type II ADF is essentially type I ADF that contains synthetic polymers, allowing it to adhere to aircraft surfaces for extended lengths of time. A significant portion of ADF runs off the aircraft, where it can enter storm drains and nearby surface or ground water, causing potential damage (Bausmith and Neufeld 1999). Several innovative methods have been proposed to minimize the volume of deicing fluid (i.e., hot air or hot water, wing blankets, electrically heated wing panels, and brooms), but none of them has been shown to be as effective as the glycol-based ADFs (Mericas and Wagoner 1994).

Deicing is necessary even in areas not prone to snow and ice. Some airplanes have supercooled fuel that after landing causes ice to form on the top of the wings, and even at an airport located in a warm climate, deicing would be necessary if there were a long deplaning layover and drizzly moist weather (Backer et al. 1994). In such situations a plant-based bioremediation is particularly appealing.

It has been estimated that at least 42×10^6 L of ADF were used at the 20 largest airports in North America during the 1992–1993 deicing season, and its use is expected to increase (Mericas and Wagoner 1994). The discharge of untreated ADF wastes to surface water and storm-water collection systems is of both regulatory and practical concerns. A variety of problems have been attributed to ADF-laden waste streams in publicly owned treatment works, and municipalities are often reluctant to accept untreated ADF waste as influent to their treatment systems. Therefore, deicing fluid runoff poses a significant threat to the environment, and increasingly stringent regulations are pressuring airport officials to examine alternative methods for managing ADF waste (Bausmith and Neufeld 1999).

Environmental Impact of ADFs

While actual compositions of ADFs are proprietary, when diluted for use they are approximately as follows: propylene glycol, 20–30%; tolyltriazole, 0.05–0.2%; surfactants and viscosity enhancers, 1–2%; other additives, 1–2%; water, 65–80%. Some properties of the main components in the ADF are shown in Table 1 (USEPA 1977; Howard and Meylan 1998). The environmental impact of two main toxic components of the formulation is discussed next.

PG provides freezing-point depression to the ADF mixture. Its principal impact is a very high oxygen demand [approximately 1.6 g O_2/g PG degraded (Shieh et al.

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TABLE 1. Relevant Properties of ADF Components of Concern

Characteristic	PG	MBz
Boiling point (°C at 101 kPa)	188.2	>300
Freezing point (°C at 101 kPa)	−59	76–87
Vapor pressure (mm Hg at 20°C)	0.08	0.03
Solubility in water (g/L at 25°C)	Soluble	29.7
Specific gravity	1.05	1.24 (solid)
Theoretical oxygen demand (mg O_2/mg)	1.68	1.56
Log octanol-water partition coefficient (log K_{ow})	−0.92	1.44[a]
Henry's law constant (Pa m^3/mol) at 25°C	1.3×10^{-3}	3.2×10^{-2}

[a]Value reported for 1-H-benzotriazole is 1.44 while for MBz the log K_{ow} estimated using heptanol is 1.81 (USEPA 1977).

1998)]. The ADF volume required to deice a typical large jet (approximately 4,000 L) has a 5-day carbonaceous biological oxygen demand ($CBOD_5$) equivalent to the domestic wastewater generated by 5,000 people/day (Mericas and Wagoner 1994) (concentration lethal to half of the organisms in the defined time period).

PG as such is not toxic to aquatic species. For instance, the 48-h LC_{50} of PG is about 15 g/L for *Ceriodaphnia dubia* (water flea) (Cornell et al. 2000). Batch studies demonstrated that at an initial concentration of 10 g/L of PG there is minimal bacterial degradation of PG, probably due to oxygen limitation (McGahey and Bower 1992). The high BOD is the major concern with PG. In rivers, at levels not greater than 0.5 g/L and at winter temperatures (<8°C), monoethylene glycol may be degraded partially or completely within 7 days, while degradation is minimal for di- and triethylene glycol. For small mammals, it has been recommended that the maximum concentration of glycols in water supplies should be <1 mg/L (Evans and David 1974) because EG is highly toxic, in contrast to PG.

Methyl benzotriazole (MBz), usually a mixture of isomers known collectively as tolyltriazole, is added to ADF to reduce the flammability hazard created from the corrosion reaction that occurs when glycol solutions come into contact with metal components carrying direct current. The MBz is a weak organic acid (pKa = 8.8) that complexes strongly with some metals (Cornell et al. 2000). In benzotriazole (Bz) chemistry, stability is a key concept, giving them utility in many beneficial applications but leading to undesirable persistence under environmental conditions; MBz does not oxidize or hydrolyze and is not photoreactive (USEPA 1977). Furthermore, there is no evidence of biodegradation of Bz by bacteria (Rollinson and Callely 1986). MBz is stable to high temperature and dissipates absorbed ultraviolet (λ_{max} around 275 nm) as heat. The low vapor pressure of triazoles (about 4 to 5 Pa) ensures little loss of these contaminants into the atmosphere; however, because of their appreciable water solubility, they can potentially migrate to ground water. A retardation factor of about 2 in soil with an organic matter content of 1% indicates that triazoles are weakly sorbed to soil (the writers' unpublished observations). Their structural similarity to naturally occurring substances [e.g., adenine, guanine, and indole (Fig. 1)] suggests that they could inhibit the production of proteins, enzymes, and RNA in mammalian systems and affect the central nervous and endocrine systems as well (USEPA 1977). The similarity of triazoles to natural plant growth regulators can cause damage to the root system (Klingensmith 1961). Although the evidence is not strong, they have been identified as possible carcinogenic substances [National Cancer Institute (NCI) 1978].

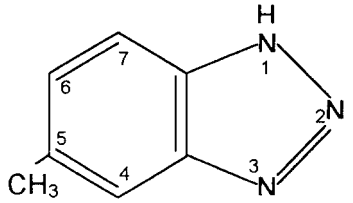

FIG. 1. Chemical Structure of 5-Methyl-1-H-Benzotriazole

Recent Microtox studies and tests with fathead minnow (*Pimephales promelas*) and water flea (*Ceriodaphnia dubia*) have shown that tolyltriazole is a major component of ADFs responsible for toxicity (Cancilla et al. 1997). Its toxicity is manifested in at least two forms: acute toxicity and a decrease in the ability of soil microorganisms to degrade PG (Cornell et al. 2000). There have been reports of tolyltriazole at concentrations of about 0.2 g/L (Cancilla et al. 1998) in a perched-water table-monitoring well at an international airport. This is sufficient to decrease PG biodegradation rates in the subsurface and cause toxicity to aquatic organisms as the 48-h LC_{50} for *Ceriodaphnia dubia* is about 0.1 g/L (Cornell et al. 2000).

The majority of Bz production goes into anticorrosion applications. These include the protection of copper-containing parts by inclusion of Bz in automobile antifreeze solutions, in recirculating water systems such as power plant and commercial air-conditioning systems, and in coatings for the protection of copper alloys in architectural and decorative applications. Their use may have markedly increased since the 1977 estimate of 28,000 tons/year (USEPA 1977), because aircraft deicers have increased in use and more vehicles are on the road. Recently the 1-hydroxy derivative is being considered as an alternative laccase mediator in biopulping for paper production, a process from which enormous amounts of a by-product, Bz, might be discharged to the environment (Call and Mucke 1997). There is no openly published environmental impact report on this application.

Alternative Methods for Remediation of ADF-Contamination

Strategies to control environmental impact of deicing vary from airport to airport, depending on terminal and airfield configuration, air traffic loads and schedules, available sanitary treatment capacity, receiving streams' assimilative capacity, and feasibility of new construction (Mericas and Wagoner 1994). The most critical issues are (1) how to collect the contaminated runoff; (2) how to

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dispose of the collected waste; and (3) how to ensure that flight operations would not be restricted. The most common design concept is to keep contaminated storm water separate from clean storm-water runoff to minimize detention and treatment volume (Backer et al. 1994). Some alternatives are described below.

Glycol can be recycled with membrane technology and distillation and sold for industrial use. Recycling may be cost-effective only when the concentration of glycol in the runoff is above 15%. It is required that EG and PG stay separated during the recycling operations at all times (Backer et al. 1994). Glycol recovery may be applicable for only the largest airports in the United States (Bausmith and Neufeld 1999).

On-site active treatments have been proposed. Jank et al. (1973) studied the optimum loading conditions for treatment of a combination of ADF and airport wastewater through an activated sludge treatment system. They worked at temperatures below 10°C at laboratory scale and found that the system would produce an effluent having a BOD <20 mg/L and suspended solids <25 mg/L at a loading of 0.15 kg BOD [1/(kg mixed liquor suspended solids·day)]. However, they pointed out that the growth of filamentous microorganisms and the resulting bulking sludge condition may lead to serious operational problems in full-scale plants. In a more recent study by Safferman et al. (1998), it was demonstrated that a batch-loaded aerobic fluidized bed reactor has the potential to treat storm water containing EG, at least at the bench scale. They noted that the system would have the advantage of a low level of suspended solids thus mitigating the need for final clarification and sludge handling, and it would have low maintenance requirements. However, real costs were not considered, and there was no discussion of other operational aspects such as recirculation, pumping, and noncontinuous loading.

Studies carried out by Kraft et al. (1998) in Norway for Oslo's new airport, investigated the degradation of glycol-based ADF by using filters filled with nutrient-enriched sandy soil from the airport area. They explored two cases, one under saturated conditions using a trench, and the other one under unsaturated conditions in columns. They found that under the mostly aerobic conditions in columns, glycol and acetate were totally degraded in medium and coarse sand at a glycol load concentration from 0.14 to 1.2 g/L [1.1 to 18.3 g PG/(m^2 day)] for a total experimentation time of 28 weeks at 6°C. At the same time, their saturated-horizontal trench provoked anaerobic degradation of the glycol with the subsequent production of mercaptan gas from sulfate.

For other researchers, on-site dryland or wetland treatment is a more favored approach, given that airports necessarily cover a significant area of land (Revitt et al. 1997; Roseth et al. 1998). Several studies have demonstrated the feasibility of land bioremediation of glycols. Microorganisms are capable of growing and metabolizing organic compounds at low temperatures as long as water continues to exist as liquid (Wang et al. 1997), and the degradation of glycols has not been an exception. Variations in the results depend on the source and acclimation of the microorganisms (Kleka et al. 1993).

In 1974, Evans and David showed that at low concentrations (0.5 g/L) EG derivatives could be degraded in rivers even at low temperatures. McGahey and Bower (1992) verified in simulated subsurface environments (batch microcosms) that, at levels <1 g/L of EG, biotransformation had a first-order kinetic rate constant of 1.01/day. Lowering the temperature from 25 to 10°C for a given soil retarded the degradation rate by a factor of 2.44, but at each temperature >99% removal was achieved in <7 days. Similarly, Klecka et al. (1993) demonstrated the biodegradability of glycol in soil microcosms at concentrations ranging from 0.3 to 5 g/L. They indicated that the kinetics of glycol biodegradation in soil was zero order with initial rates independent of the substrate concentration at levels above 0.1 g/L. The average zero-order rates were in the range of 19.7–27.0 mg/(kg soil·day) at 8°C and 66.3–93.3 mg/(kg of soil·day) for soil samples incubated at 25°C. These biodegradation rates were reduced to between 2.3 and 4.4 mg/(kg of soil·day) in soils at −2°C.

Rice et al. (1997) went one step further and evaluated the effect of rhizosphere soils in the biodegradation of EG. Their findings confirmed microbial degradation of EG by soil bacteria. They concluded that the bacteria present in rhizosphere soils enhanced the mineralization rate of EG in the soil, probably as a result of greater microbial biomass and activity generally found in rhizosphere soils. Even at temperatures as low as −10°C, microorganisms were able to survive and mineralize the EG, and they suggest that the presence of EG contamination in soil may have reduced the freezing point of the water within the soil, thus allowing the microorganisms (psychrophilic bacteria) to continue their degradative activity.

More recently, Bausmith et al. (1999) performed soil pan studies at moderate temperatures to demonstrate that the land treatment of PG-based ADF under controlled conditions is potentially an effective means of remediation for ADF solutions. Degradation of PG to acceptable levels (10–17 mg/kg soil) was observed in soils receiving ADF solutions of 5, 10, and 20% by weight, with corresponding initial PG concentrations of 7, 14, and 28 g/kg. The degradation kinetics was first order, with rate constants between 0.07 and 0.30/day. The highest rates were seen with sludge amendment, lime amendment, and soil aeration (tilling). Degradation of the PG inputs took from 6 to 30 days for about 80% completion.

Even though biodegradation of PG has been extensively studied, most researchers have not considered the toxicity to soil bacteria of the corrosion inhibitor (tolyltriazole) as an interfering factor. Pillard et al. (1995) and, more recently, Cornell et al. (1999) have stressed that tolyltriazole significantly reduces cell growth rates and yields for PG soil biodegradation, and they indicated that the tolyltri-

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azole is the most toxic component of the ADF mixture. If ADF runoff contamination is to be remediated by land treatment, it is evident that sooner or later the concentration of MBz might build up in the soil, or a significant amount might leach to ground water or both, depending on precipitation, soil physical properties (i.e., cation exchange capacity), and soil organic matter content. Unless MBz can be documented to be degradable or environmentally benign, its disposal is a problem requiring attention.

This study investigated the fate of MBz in plant-based remediation for use in situ at airports (Castro et al. 2000a,b), while soil bacteria under appropriate conditions achieve the degradation of PG. In previous studies triazole biodegradation was first reported, which may be achieved by the metabolic action of the enzyme lignin peroxidase (Wu et al. 1998). However, the fungal culture conditions under which lignin peroxidase is produced are fairly specific (Aust et al. 1997), which may make it difficult to develop a feasible on-site treatment with the fungus. Higher plants strengthen their cell walls by lignification, which is probably a free-radical catalyzed polymerization of methoxylated aromatic alcohols with laccase and lignin peroxidases as the catalysts (Buchanan et al. 2000). This suggests that Bz may be reactive in plants where lignin is being synthesized.

It is well documented that 1-hydroxybenzotriazole reacts with laccase and peroxidase (Call and Mucke 1997). Little is known about the mode of toxicity of Bz in plants. They have some similarity to natural plant growth regulators such as auxin and cytokinin (Klingensmith 1961; USEPA 1977). They are also effective metal chelators, which is the basis of their anticorrosion properties. Graham (1986) proposed that copper chelation could result in male sterility in wheat treated with Bz. Damage to the root system seems to be the main effect observed here (Castro et al. 2000a,b), suggesting interference with root lignification or nutrient uptake. The efforts here are directed toward finding appropriate conditions for the use of vegetation to remediate glycol-based ADF, focusing on the corrosion inhibitor, which has been shown by Cornell et al. to be the most toxic constituent of ADF and which is not degradable by any known bacterial process (Rollinson and Callely 1986). Many species of plants maintain significant root growth and activity whenever the ground surrounding these roots is unfrozen, so that metabolic processes including peroxidase activity must continue. Efficiency of triazole removal at low temperatures is not known.

EXPERIMENTAL STUDIES

Materials and Methods

Pure Bz, 1-hydroxybenzotriazole and 5-MBz were purchased from Aldrich/Sigma Chemical Co., St. Louis, Mo. Tolyltriazole (mixed isomers of 4-MBz and 5-MBz) was a gift of Mark Hernandez, University of Colorado. The compounds were kept as aqueous stock solutions (2 g/L) for later dilution to treat plants and as calibration standards for chromatography. Stored solutions appeared to be stable for at least 2 years. Deicing fluid was obtained from the local airport in the diluted-as-applied form. The 1999 sample contains 22% (volume/volume) PG and about 1 g/L tolyltriazole.

For separation and quantification of Bz, detection at 275 nm was used with liquid chromatography on a Hamilton PRP-1 column (Hamilton Co., Reno, Nev.), with methanol (50–70%) + water as eluent at a flow rate of 1.0 mL/min. Phenolic exudates from plants elute at a shorter time than the tolyltriazole, and so the methanol level was adjusted to optimize resolution of compounds of interest in each experiment. Appropriate standards were run each day of analysis.

Monitoring of PG was done indirectly by measuring depletion of sodium periodate (absorbance decrease at 260 nm) by PG oxidation. Adaptation for flow injection analysis work included reaction of 65°C and acid conditions (pH between 4 and 5) to improve the sensitivity. The mobile phase was a solution of 0.1 mM sodium *p*-periodate, in sodium hydroxide (0.05 M), boric acid (0.1 M), and acetic acid (10 mL/L). Samples were injected and mixed with the mobile phase using a high-pressure liquid chromatography pump and loop injector. Reaction was in high-density polyethylene tubing for 4 min at 65°C. The system allowed detection of solutions below 1 mM (~0.1 g/L) at about 30 samples/h with a flow rate of 1.0 mL/min.

Several plants were selected for the study. Tall fescue grass (*Festuca arundinacea* K-31 cultivar) is a very common grass used at airports and represents a perennial monocot with an extensive fibrous root system. Cattails (*Typha latifolia*) represent a rapidly growing perennial monocot characteristic of wetlands and freshwater marshes. They were tried for experimentation with glycol solutions because of their capability to transfer oxygen from the leaves to the roots and their tolerance of saturated substrates (Wang et al. 1997). Alfalfa (*Medicago sativa*) develops an extensive root system, and, as a legume, it helps restore nitrogen consumed by bacteria during the degradation of glycols. Sunflowers (*Helianthus annuus*) are rapidly growing dicots that produce woody stems in a short season, thus guaranteeing the production of peroxidase for the lignification process. Sunflowers are relatively easy to grow and handle for determining required parameters; therefore, they were widely used during the study, as a model system for investigating the degradation process.

Plants were cultured in different media: aqueous solution (hydroponics), pure fine vermiculite, silty sand topsoil, or a mixture of this soil with vermiculite (volumetric ratio of 1:2). Pure vermiculite has a higher cation exchange capacity than regular soil; therefore, availability of ionic compounds (nutrients and contaminants) is higher. The soil (with approximately 10% silt, 88% sand,

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2% clay, and 1% organic matter) was obtained from a site near a closed landfill on a river floodplain and has been extensively used for previous studies by the writers. Plants were grown in plastic containers, plastic columns, and/or large channels. For the plants grown in vermiculite or the soil/vermiculite mixture, three kinds of plastic containers were used: 600 mL (~10 cm diameter, 12 cm high), 800 mL (~7 cm diameter, 22 cm high) and 1,500 mL (~10.5 cm diameter, 22 cm high). The plants were started from seeds and were used at different stages of their growth. For example, sunflower seeds were planted in moist vermiculite for 10 days, and then the seedlings were transplanted to different containers (with either vermiculite or a soil/vermiculite mixture) to apply some specific treatment. When the first two main leaves were 4 cm long, the plants were watered with the corresponding solution. Lighting was done with regular 40-W fluorescent light bulbs (about 10 4-ft tubes/m^2) at 25°C, with either 24:0 or 12:12 light:dark cycle. The solutions of triazole, PG, and ADF were prepared in nutrient solution, based on Hoagland's formulation [standard Hoagland's solution contains KNO_3 (404 mg/L), KH_2PO_4 (109 mg/L), $MgSO_4 \cdot H_2O$ (394 mg/L), $Ca(NO_3)_2 \cdot 4H_2O$ (1,476 mg/L), $FeSO_4 \cdot 7H_2O$ (6 mg/L), ethylenediaminetetraacetic acid Na_2 (8 mg/L), H_3BO_3 (3 mg/L), $MnCl_2 \cdot 4H_2O$ (2 mg/L), $ZnSO_4 \cdot 7H_2O$ (0.2 mg/L), $CuSO_4 \cdot 5H_2O$ (0.2 mg/L), and $H_2MoO_4 \cdot H_2O$ (0.2 mg/L)]; if not specified, the concentration was 1/4 of the standard. Details for particular experiments are given below.

RESULTS

Sorption of Triazoles to Organic Matter

Given their organic nature, triazoles are sorbed to the culture media in which plants are grown. For the concentration ranges tested (50–200 mg/L), sorption factors were measured as the decrease in concentration of a sample taken from the soil water in equilibrium with the soil after the solution passed the soil several times. The ratio of output to input concentrations gave the following results: for vermiculite, it was 0.81 (only 0.19 was sorbed) and the mixture of vermiculite and topsoil gave a ratio of approximately 0.56 (0.44 sorbed); and for silty sand topsoil rich in roots, the ratio was 0.46 (0.54 was sorbed). These results show clearly that the effective concentration of MBz in the aqueous phase of the culture medium depends greatly on the organic matter content. Tolyltriazole gave similar results to the sorption values of MBz. Bz, having a methyl group, was less hydrophobic and showed a lower sorption (in the soil/vermiculite mixture, 0.34 was sorbed).

MBz is also passively sorbed to the roots of plants. Dry soybean roots (1.0 g) were placed in contact with different volumes and concentrations of MBz. The concentration decrease was measured after 24 h giving a ratio that varied from 0.70 to 0.85 (0.15 to 0.30 was sorbed). A soil rich in roots is expected to increase the fraction of MBz sorbed.

TABLE 2. Biomass Production and Triazole Loss for Fescue Grass Treated with MBz and Bz Solutions

Compound	Concentration fed (mg/L)	Biomass Produced Relative to Control[a] After 20 doses (%)	Biomass Produced Relative to Control[a] After 20 more doses (%)	Triazole Loss[b] (mg)	Triazole Loss[b] (%)
MBz	50	35.8	17.3	23.7	49.8
	100	44.3	5.1	17.6	18.9
	150	43.8	1.4	3.2	2.4
Bz	50	46.2	26.4	39.2	78.3
	100	31.3	3.6	33.9	36.5
	150	27.7	0.6	33.5	24.8

[a]Control produced an average of 6.5 g of fresh material/pot in 40 days; each pot with an area of about 80 cm^2 would correspond to about 600 g/($m^2 \cdot$ month) in good field conditions.
[b]Triazole removal from solution after 40 doses (50 days).

Tolerance of Grass to MBz

Fescue grass seedlings were transplanted to vermiculite (10/600 mL container having 400 mL of water and 140 g of vermiculite) and treated with either MBz or Bz in 1/4 strength Hoagland's solution on a 12:12 light:dark cycle. At a concentration of 50 mg/L they grew nearly normally, while those treated at 100 mg/L were stunted. For more mature fescue grass, watered with solutions of triazoles for about 50 days, the biomass production (as percentage in weight of leaves produced with respect to a healthy untreated control) and the disappearance of triazole from the medium (measured as the loss of the compound with respect to the material introduced) were recorded (Table 2). The leaves were trimmed after the first 20 doses of 25 mL/day and then again after 20 more doses. The aqueous phase was analyzed after a total of 40 doses. A concentration >50 mg/L of either MBz or Bz was toxic, and they were lethal at a concentration of 150 mg/L. For concentrations below 50 mg/L the plants grew somewhat less vigorously than untreated controls, but could be maintained for long periods with no cumulative toxicity. Bz was somewhat less toxic than MBz. Later studies showed that toxicity is less if higher nutrient levels are used (see below).

Several extraction methods were investigated for the recovery of the triazole from the stems and leaves of the plants. Solvents including water, methanol, ethanol, and acetone in different sequences, extraction times, and temperatures (as high as 96°C) were tried unsuccessfully. Even with 1 M NaOH or 1 M HCl solutions at low and high temperatures there was no recovery. This leads one to think that the triazole is being bonded and/or transformed within the plants, resulting in a nonextractable form of the compound, maybe as part of the plant structure.

Tolerance of Sunflower to MBz

Observations with Wild Sunflowers

After about 2 months of growth outside, wild sunflowers were transferred to the laboratory and maintained in

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aqueous solutions (usually distilled water) containing different concentrations of triazoles. Fresh solution was added based on consumption such that solution volume remained constant. In general, the rate of water consumption per gram of initial fresh plant material decreased with time of triazole treatment. This effect was larger when the triazole concentration was >100 mg/L. It was possible to observe gradual damage of the roots, which first turned brown, followed by little new root growth. The plants apparently accumulated triazole and transformation products within their structure (up to about 3.0–5.0 mg of triazole incorporated per gram of fresh initial plant material over a period of about 35 days). The accounting of triazole was done by measuring the concentration of the solution in the container at different times and comparing this with the concentration expected in this solution based on the amount added. Triazole extraction methods similar to those done for the fescue grass were also unsuccessfully attempted for stems and leaves of sunflowers, even at these high levels of expected accumulation. Either the triazoles were degraded in solution or they were incorporated and fixed to plant biomass.

Observations With Plants Grown From Seeds

Low Level of Nutrients. In a 1-month treatment, sunflower seedlings (3 plants/800 mL container) grew in the soil/vermiculite mixture almost normally (as high as the controls) when watered with 25 mg/L MBz in 1/4 strength Hoagland's solution. The leaves, however, turned yellow and brown and were less vigorous than the controls, with the effect more pronounced in the bottom leaves. The top leaves were nearly normal, and the plants (at least two out of three) flowered about 5 days before the controls did. These effects were more evident at 50 mg/L. At a concentration of 100 mg/L the plants were 20% shorter than the controls and produced small precocious flowers. The leaves and roots also showed much more damage than at 25 mg/L.

High Level of Nutrients. To improve plant growth conditions during treatment with the triazole, an extra supply of nutrients was added to the soil/vermiculite mixture. Ten-day-old sunflower seedlings (2 seedlings/800-mL container) were watered with solutions containing the triazole at 100, 200, and 300 mg/L in nutrient solution at 1/4, 1, 3, and 10 times the concentration recommended by Hoagland. Control plants received the same range of nutrient concentration without any triazole. Fig. 2 shows the dry biomass produced for different triazole treatments with different nutrient levels during the 30-day period. As mentioned above, the effective aqueous concentration of triazole is reduced as much as one-half by sorption to organic matter in the soil. It is clear that the plants can tolerate the lowest level of triazole (100 mg/L) at all levels of nutrients. Increasing the nutrient level above the standard concentration has a negative effect possibly because of the high level of nitrogen. A separate study showed than an N level greater than 700 ppm (i.e., 3× Hoagland's

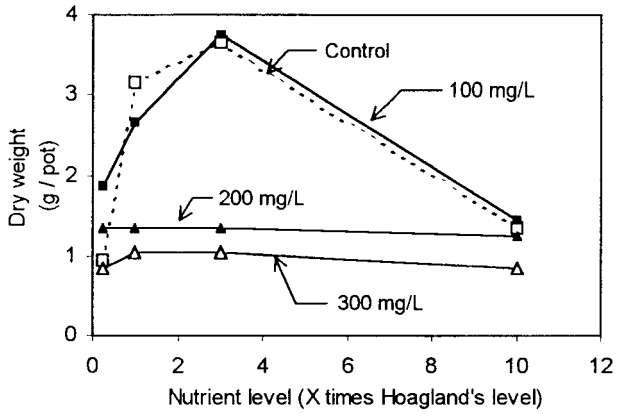

FIG. 2. Effect of Nutrient Amendments on Biomass Produced (Dry Weight of Plant Material) by Sunflowers Grown from Seed in 30-Day Treatment in Soil with Different MBz Levels

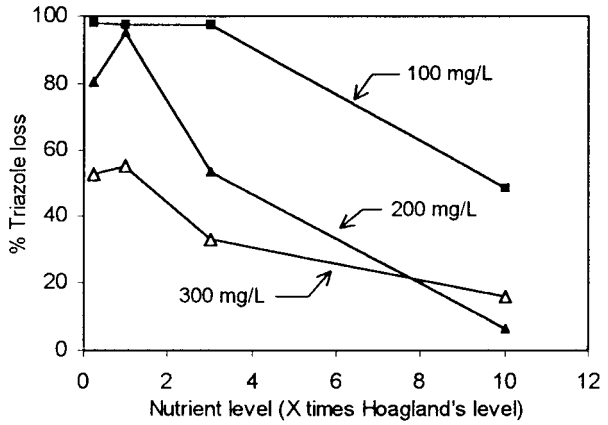

FIG. 3. Effect of Nutrient Amendments on Percentage of MBz Loss from Soil Solution in 30-Day Treatment of Sunflower Grown from Seed at Different MBz Levels

solution) is toxic to the plants. For concentrations of MBz equal to or >200 mg/L the nutrient effect on tolerance is not appreciable. With respect to the triazole disappearance (Fig. 3) increasing the nutrient level has a positive effect up to about 1× the level recommended by Hoagland for all triazole treatments.

High Level of Borate. Josten and Kutschera (1999) reported that borate is an essential element for formation of new (adventitious) roots on sunflower seedlings. Because root formation appeared to be the first inhibited process in triazole-treated plants, the effect of increased borate on the triazole inhibition of plant growth was tested. Plants (4 plants/1,500-mL container) were grown for 20 days in soil/vermiculite and watered with a fixed amount of 1/4 strength Hoagland's solution per day, containing supplementary borate at two different levels (3× and 9× the control rate of 1/4 strength Hoagland's solution) and varied levels of triazoles (100 and 200 mg/L).

Supplemental borate at 3/4 and 9/4 times the standard Hoagland's solution rate showed no significant difference from the lowest level (1/4 Hoagland's solution), indicating that borate did not have a marked effect on the triazole toxicity. Indeed, after 20 days of treatment, the plants ex-

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posed to the highest level of triazole and no extra level of borate looked better than those with the highest level of triazole and extra borate, but still not as good as the controls. There was no observable difference between the plants treated with MBz and tolyltriazole at similar concentrations. Although the different isomeric MBz may affect bacterial processes differently (Cornell et al. 2000), no difference was observed for plants.

High Level of Micronutrients. A different way to look at the problem is by considering the metal-binding capacity of the triazole. Although required by plants in very small amounts, metals such as Zn, Mo, Cu, and Mn (also called trace elements or micronutrients) are essential for the plant development. Triazole toxicity could be the result of a chelating process that prevents metal utilization by the plant. Therefore, soil was enriched by using Hoagland's nutrient solution plus an extra supply of the micronutrients at three different levels: 1×, 3×, and 10× the concentration of the micronutrients in the original Hoagland's formula. No extra borate was added since it already showed no improvement.

Pairs of sunflower seedlings were transplanted to 120 g of pure vermiculite with 470 mL of aqueous phase in 600 mL containers and were treated with MBz solutions at 100 and 200 mg/L prepared in the modified Hoagland's solutions. Plants were watered every day until the desired concentration was achieved. The plants with higher micronutrients were able to tolerate more MBz, and so they were kept at that level (maintaining volume with water) for 7 days and then watered with the solution until the predicted soil MBz-solution level was doubled. Results are shown in Figs. 4 and 5. There was not a dramatic effect of micronutrients on biomass production with no triazole present. The plant tolerance to MBz was increased somehow by higher micronutrient levels. While their final weights were very comparable, more MBz disappeared at the higher levels of micronutrients.

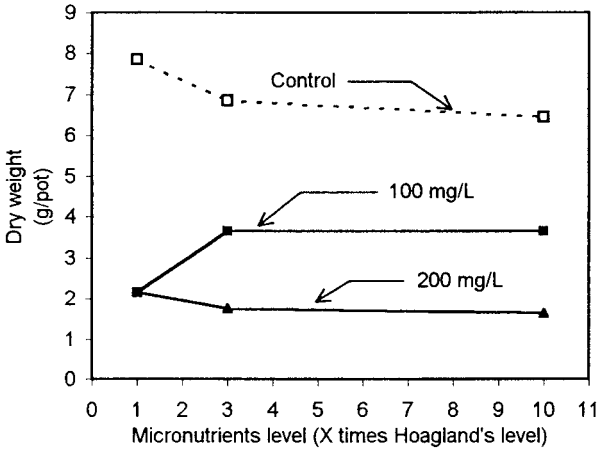

FIG. 4. Effect of Micronutrient Amendments on Biomass Produced (Dry Weight of Plant Material) by Sunflowers Grown from Seed in a 30-Day Treatment in Vermiculite with Different MBz Levels

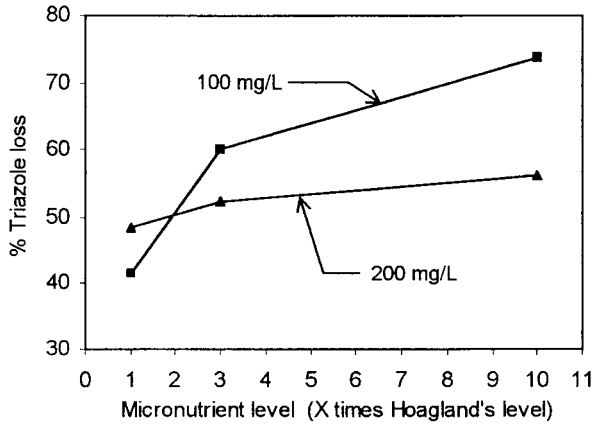

FIG. 5. Effect of Micronutrient Amendments on Percentage of MBz Loss from Solution in 30-Day Treatment of Sunflower Grown from Seed in Vermiculite at Different MBz Levels

In an attempt to determine which one of the metals was responsible for this small improvement of the capacity of the plant to incorporate the MBz, a new experiment was designed with Hoagland's solution at the recommended level (1×) but omitting (0×) or supplementing (10×) the specific compound that contains each of the metals: $MnCl_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ (0.2 mg/L), and $H_2MoO_4 \cdot H_2O$ (0.2 mg/L). Iron ($FeSO_4 \cdot 7H_2O$), which is normally added in higher amounts as the ethylenediaminetetraacetic acid complex, was also varied.

Pairs of 10-day-old sunflower seedlings were transplanted to pure vermiculite in 600 mL containers and treated with 150 mg/L of MBz prepared in the modified Hoagland's solutions. Plants were watered every day to maintain a constant weight for a month. The plants were then harvested, and fresh and dried weights of the above ground material were recorded, as well as the concentration of MBz remaining in the aqueous phase of the vermiculite.

The results of all treatments were close to each other showing that the triazole toxicity is not a simple problem controlled by one nutrient (Table 3). There was not a single component that revealed a significant improvement in plant tolerance and ability to consume MBz; the manga-

TABLE 3. Effect of Individual Micronutrients on MBz Tolerance and Degradation Capability[a]

Nutrient	Level	Control dry weight (g)	MBz-treated dry weight (g)	Treated-to-control dry weight ratio	MBz loss (%)
All five	0×	1.9	0.5	0.26	48
	1×	1.9	0.7	0.37	54
	10×	2.5	0.6	0.24	67
Mn	0×	1.9	0.7	0.37	48
	10×	2.8	1.2	0.43	52
Zn	0×	1.5	0.4	0.27	45
	10×	2.5	0.7	0.27	52
Cu	0×	1.8	0.7	0.36	59
	10×	2.5	0.9	0.36	58
Mo	0×	1.7	0.8	0.39	42
	10×	2.3	0.9	0.42	54
Fe	0×	2.3	0.6	0.27	45
	10×	2.0	0.6	0.30	52

[a]Sunflowers grown in vermiculite treated 30 days with nutrient solutions containing 150 mg/L of MBz; nutrient levels relative to those specified by Hoagland's solution (see Materials and Methods section).

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nese- and molybdenum-amended solutions showed a slight increment on the resistance (greater dry weight ratio), but none of them showed a greater percentage of MBz loss than the plant treated with the combination of all of them.

Hydroponics Studies with Sunflowers. A hydroponics study was done with sunflowers in an effort to determine the kinetics of the MBz disappearance. Pairs of ten-day-old sunflower seedlings were placed in brown glass bottles containing 500 mL of Hoagland's nutrient solution. The plants were held by an open cell polyurethane foam assuring that only the roots were in contact with the water phase. The water level was maintained constant by adding fresh water every other day. A total of 22 plants were kept under a 12-h light system for 25 days after which their fresh weight was obtained. The plants were divided into two groups: 10 small plants with fresh weights between 12 and 18 g with a solution volume of 300 mL (total biomass to aqueous phase ratio of 0.04–0.06 g/mL) and 10 large plants with fresh weight between 20 and 28 g with a solution volume of 500 mL (total biomass to aqueous phase ratio of 0.04–0.056 g/mL). Two extreme plants, with fresh weights of 10 and 32 g were used as control plants. MBz was added at two concentration levels (50 and 100 mg/L) in 1× Hoagland's nutrient solution. Water uptake was recorded every day by measuring the amount of water required to maintain the volume at the corresponding level. Samples of 1 mL were taken every other day follow the MBz concentration decrease by high-pressure liquid chromatography analysis. The disappearance of MBz because of plant-enzymatic activity was obtained by subtracting the amount of MBz lost via water uptake from the total mass of MBz that disappeared. The average remaining MBz concentration in the solution for five large and five small plants was plotted versus the elapsed time (Fig. 6). To estimate the rate at which the plants degraded the MBz, the final concentration for each time interval was subtracted from the initial concentration and the difference was divided by the interval time. This number [in mg/(L·day)] multiplied by the volume of the solution and

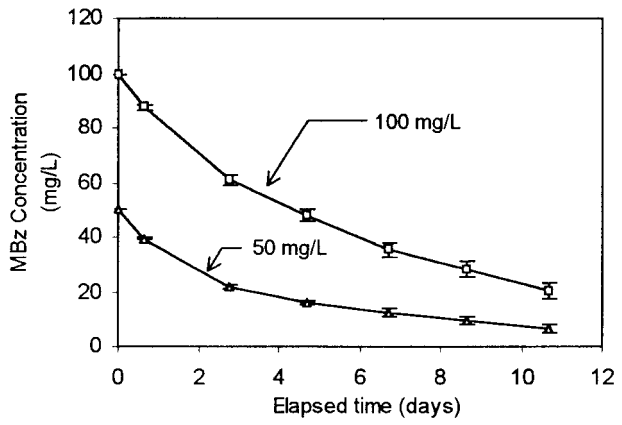

FIG. 6. Remaining Concentration of MBz in Hydroponic Treatment of Sunflower Mature Plants with 1× Hoagland's Solution at Different MBz Levels

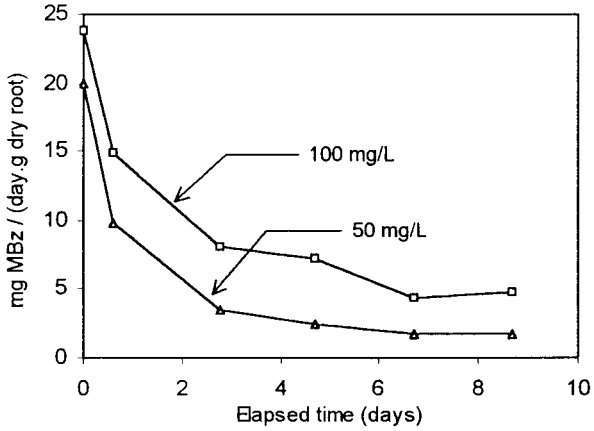

FIG. 7. MBz Loss Over Time for Hydroponic Treatment of Sunflower Mature Plants with 1× Hoagland's Solution at Different MBz Levels

divided by the final dry weight of the roots gave a rate per unit mass [in mg/(g dry root day)] (Fig. 7). Plants can tolerate a concentration of 50 mg/L and degrade the MBz in about 10 days. A safe value for the estimated rate from Fig. 7 could be 2.0 mg MBz/(g dry root·day), based on these results.

Tolerance of Sunflower to Glycol

Even though glycol biodegradation in soil is possible under certain conditions (Haines and Alexander 1975; Cox 1978; Klecka et al. 1993; Bausmith and Neufeld 1999), plants might be sensitive to processes or conditions resulting from it, because of the high BOD of the glycols. Plants in normal growing conditions with water contents that range from field capacity to lower limits of extractable soil water are subjected to oxygen concentrations not far from that of free air. When the soil environment changes from aerobic to anaerobic as the oxygen is removed from the soil, the physiological processes within the plant are affected (Wang et al. 1997). Therefore, the effect of the glycol on the plants had to be tested to evaluate the suitability of a phytoremediation alternative for ADFs.

Sunflowers at about 10 days of age, grown from seeds in the soil/vermiculite mixture were treated in 800-mL containers with ADF solutions at concentrations of 1.0, 2.0, and 4.0% of ADF (2.3, 4.6, and 9.2 g/L of glycol) in 1/4 strength Hoagland's solution. Watering was from the top with a daily dose of about 50 mL depending on the excess of runoff observed. After a period of 24 days, the plants treated with 4% of ADF had died, while the ones treated with 1% survived, although with limited growth and some leaf-edge damage typical of an osmotic stress effect. Aqueous extracts from leaves were analyzed, and PG was found at concentrations from 1.56 to 2.34 mM for the 1 and 2% ADF input solutions, respectively.

Therefore, the conditions of the experiment were changed to try to achieve aerobic degradation of the glycol prior to its contact to the plant roots. A mixture of

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culture soil was prepared by combining fresh soil with about 10% previously used soil as inoculum. This time the watering was done from the bottom, hopefully allowing enough time for the soil/plant system to take up the solution (with ADF doses reduced to 0.5, 1, and 2%) and for oxygen to diffuse in. The result was poor plant growth, but not leaf-edge burn, probably because of intense bacterial activity that consumed nutrients required by the plant.

Under similar conditions in another experiment, plants (3 plants/800-mL container, 900 g of soil + 250 mL of aqueous phase) were watered from the bottom with solutions of PG, EG, antifreeze, or ADF at a concentration of 2 g/L of glycol in standard 1× Hoagland's solution or Hoagland's solution + 10× potassium phosphate. With the higher level of phosphate, the plants grew in PG, EG, or antifreeze with no particular damage. The ADF-treated plants (equivalent to 2 g/L of glycol and 8 mg/L of triazole) showed some leaf burn with or without additional phosphate, while the standard phosphate-treated ones also consumed less water than the others.

Plants were treated in 800-mL containers (3 plants/container) with ADF solutions at different levels. Those treated with 5.0 g/L of glycol (~20 mg/L of triazole) showed poor growth but survived, while plants treated with 10 g/L of glycol and 40 mg/L of triazole showed acute toxicity with just 3 days of treatment, perhaps because the triazole level at this concentration inhibits the glycol degradation and affects the bacterial populations and root development. The surfactants in the deicer formulation may be an additional contributing factor in the toxicity of ADF to plants.

In general, it was observed that with enough nutrients in the soil and watering from the bottom, sunflower plants could safely tolerate a glycol input rate of about 150 mg of glycol/(kg of dry soil·day).

Tolerance of Other Plant Species to Glycol

Cattails, tall fescue grass, and alfalfa cultivars were also grown under different conditions to observe a general response to glycol contamination of soil.

Several tall fescue grass plants were transplanted from vermiculite, where they had been grown from the seeds for at least 2 months, to four glass cylinders, 40 cm deep and 15 cm in diameter, filled with the silty sand topsoil. The water content of this system was approximately 2 L. For about 19 weeks (135 days) with continuous light, the grass plants were top-watered approximately every 4–6 days depending on the level of runoff from the column. Three columns received at each watering 600 mL of the glycol solutions using EG, PG, or aircraft deicing fluid at a level varying from 2 to 3 g/L; one column was a water control. Any runoff was recycled to the top of the column so that there was no loss of material except through plant harvest. After the first 85 days, 1× Hoagland's fertilizer was added to all the columns along with the glycol solution at each watering for about 21 times. Every 20 to 25 days the plants were ''mowed'' to obtain the net harvestable biomass production for each column. From the observation of the plants, it was clear that glycol was affecting their health. Part of their leaves turned yellow with some of the tips brown; some of the leaves did not expand as much as the control, and their water uptake was about 20% less. Their biomass production started to decrease, and it did not seem to be caused by nutrient deficiency. Biomass produced in grams per liter of water was less than or equal to 0.9 for the PG and ADF treatments, while it was 1.2 for the control during April and May. In June and July the ADF ratio fell to 0.8 and PG stayed constant. Plants were able to recover after giving them just water, showing that in fact the glycol was affecting the plants. At the same time, there was no measurable accumulation of MBz in the cylinder treated with deicer (a methanol extract showed <5 mg/L) despite the application of about 210 mg of MBz. A sample from the soil was spiked, and the result gave a sorption to soil factor of about 3. Posterior extraction with methanol showed a reasonable recovery.

Aquatic plants such as cattails transfer oxygen to the roots. It could be favorable to have a system for degradation of ADF in which the plants are able to supply some of the oxygen required for the glycol degradation. From three to five 1-month-old cattails were replanted in each 600-mL container containing 100 g of vermiculite, 100 g of glycol-acclimated soil (previously used in sunflowers experiments), and 400 mL as the aqueous phase. Under these conditions, there was some oversaturation of the solid phase, flooding the system (20–40 mL of runoff collected in a secondary container and recycled every day) for attaining an optimal growth of this particular wetland plant. The plants were top-watered with glycol-contaminated solutions by supplying about 50 mL/day to replace the water consumed by the plant. Solutions of PG, EG, and antifreeze, the composition of which was found to be about 99% EG, were tried in different containers at two levels of glycol as input (3 and 6 g/L). The solutions were prepared in 1× Hoagland's solutions, except one of the lower level of glycol, which was amended with extra phosphate (KH_2PO_4, 10 times higher than the normal level). During a month, with a continuous light, a total of 1.5 L of the glycol solutions were added to the plants without any particular damage even at the higher concentrations. If no glycol were degraded, the total amount of solution added would give a concentration of 7.5 and 15 g/L in the water phase, and some kind of plant stress would have been evident. Although analysis of the glycol concentration was not done, it was clear that most of it could have been degraded and that the cattails were able to tolerate the environment at this input rate. Experiments with higher concentrations are in progress.

To evaluate whether a legume such as alfalfa (*Medicago sativa*) was able to tolerate a soil contaminated with glycol, a large chamber with 25-mm-thick slate walls used in previous biodegradation experiments was chosen (Na-

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rayanan 1994), but a drip irrigation system was adapted this time. The chamber was 52.5 cm wide, 95 cm long, and 35 cm deep, divided axially into two equal halves. Each half was further divided by a 78-cm-long wall to give a U-shaped channel with a width of 10 cm. There were holes 5 cm from the bottom at one end of each channel. The chamber construction and schematic details can be found elsewhere (Narayanan 1994). The channels were filled with sandy soil and a total of 36 alfalfa plants (nine plants in each row) were grown at 10-cm spacing. The channels were subirrigated using four subsurface drip tubes along with one at the end. Each drip system consisted of two 50-mL syringes connected with a Y-tube and tubing to a glass tube inserted into the soil about 20 cm. The reservoirs were refilled every day with the solution of glycols at concentrations that varied from 1.8 to 2.4 g/L and volumes varying from 3 to 5 L/($m^2 \cdot$day). The water input was controlled so that the water table was always >25 cm below the soil surface. The system apparently allowed enough time for the bacteria to degrade the glycol before reaching the roots, or alfalfa is glycol-resistant, since no particular effect was detected on plant growth and health. For a time of adaptation, the input consisted of solutions of pure EG and PG in water. Then diluted antifreeze (99% EG) and ADF (20% PG) were substituted for EG and PG at the higher rate of 2.4 g/L of glycol. After 3 months, biomass production is still excellent, as good as the production in past years by the untreated system. A water supply through a drip irrigation system might be necessary to assure glycol aerobic degradation, and the use of legumes might assure the supply of nitrogen for the glycol-degrading bacteria.

Possible Design of Plant-Enhanced ADF Bioremediation

Vegetation plays two crucial roles in the bioremediation of ADF runoff from airports: first, a rhizosphere effect might increase the rate of bacterial glycol degradation, even at low temperatures; and second, through root surface enzymes, plants seem to phytodegrade the corrosion inhibitor (MBz), which is a potential toxic contaminant that reduces the capability of bacteria to degrade the glycol. Optimal plants would be those that can tolerate climatic conditions at the specific site, that can tolerate low oxygen environments, and that possibly have their own nitrogen supply. Depending on the available area and facility for construction and/or land farming activities, a dryland or wetland system could be implemented around a particular airport. In England, wetlands are already in use for treatment of airport wastes (Revitt et al. 1997), although there is some expressed concern about wetlands attracting waterfowl in this country. Many airports are located in the vicinity of natural wetlands.

To give a rough idea of the area required, a general calculation might look as follows:

- ADF composition (Manhattan's airport, Kans.) is 200 g glycol/L and 0.7 g MBz/L.
- Assumed amount of soil available for treatment per square meter of soil area is 100–300 kg/m^2. The depth will vary depending on oxygen limitation, but conservatively is from 6 to 20 cm.
- Glycol biodegradation rate at 6°C in rhizosphere soil (Kraft et al. 1998) is 18.3 mg glycol/(kg of soil·day).
- Glycol that can be biodegraded (6°C) is 1.83–5.49 g glycol/($m^2 \cdot$day).
- The land requirement for biodegradation at 6°C per kilogram of glycol per month is 6–18 m^2/kg of glycol.

Mercias and Wagoner (1994) reported that an estimated amount of 42×10^6 of ADF were used at the 20 largest airports in North America during one deicing season and approximately 4,000 L of ADF were required per jet. Thus, assuming a 4-month deicing season, an airport deices about 100 airplanes/month (400,000 L of ADF/month). If the final dilution of the ADF runoff is about 200 g of PG/L (20% glycol), then approximately 80 tons of PG/month are discharged at airports. The land requirement for 100 deiced jet airplanes per month (at 6°C) is 48–144 ha.

Modern airports do have recovery systems and designated areas for airplane deicing and detention ponds or tanks for runoff (Backer et al. 1994). If, for example, 3/4 of the ADF runoff load is recovered and treated, the land area required for its biodegradation would be correspondingly reduced. If runoff is held in detention ponds, the average demand is the cumulative demand distributed over the time taken to fill the pond. Thus, deicing 100 jets on 1 day may still be considered as a monthly impact if deicing occurs only on a few days per winter season. Design of systems must consider both peak and average loads.

Associated with the glycol input for 100 planes, there is an MBz input; for the same amount of deicer released, assuming its content is 0.7 mg MBz/L, the MBz input will be 288 kg MBz/month. Based on the observations here, a plant can degrade about 60 mg MBz/(g fresh root·month) at room temperature of 22°C. Hence

- Reported typical mass of fresh roots per square meter of soil area for degradation (Gregory 1994) is 50–100 g root/m^2.
- The amount of MBz that the plants can handle is 3,000–6,000 mg MBz/$m^2 \cdot$month.
- Planted land requirement for MBz from 100 planes worth of ADF runoff phytodegradation (at 22°C) is 4.8–9.6 ha.

Therefore, the area required for the biodegradation of the glycol should be enough for the plants to degrade the MBz. At lower temperatures, as long as the ambient temperature around the roots is above the threshold freezing temperature specific for that plant and the water stays liquid, the enzymatic activity of the plant continues. At the

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same time, some adaptations may occur within the plant in the presence of glycol to tolerate freezing conditions. This, however, still needs experimental demonstration. Degradation rates at low temperature have not been measured. For typical chemical reactions the rate at 6°C would be about 1/4 of that at 22°C so that the capacity of the system would match that for glycol degradation.

CONCLUSIONS

In spite of the possibility to treat wastewater streams contaminated with ADF runoff by land treatment systems, it is still necessary to consider the interference of the corrosion inhibitor of the mixture (tolyltriazole) in the bacterial activity. The toxicity, physical, and chemical properties of the tolyltriazole need to be accounted for in the bioremediation design and to prevent contamination of soil and ground-water systems.

From this research, it has been found that several species of plants are able to tolerate MBz (at a concentration of 50 mg/L in the aqueous phase the plants grow without much damage) and degrade it [at a rate of approximately 2 mg MBz/(g dry root·day) at 22°C], when the soil is enriched with nutrients. The complex interactions between plants and MBz make it difficult to find a possible mechanism of MBz phytotoxicity; it might have to do with metal chelation and/or through mimicking a plant growth regulator. There was no difference between tolyltriazole and pure 5-MBz in our studies.

Phytoremediation in this case might become an active and possibly economical improvement for the in situ bioremediation of ADF runoff contamination. However, the toxic effect of high PG on plants (mainly the alteration of the leaf osmotic equilibrium) causes plant weakness and inhibits the triazole immobilization in plants. To assure the survival of the plants, a rapid aerobic degradation of the glycol has to be achieved by bacteria. In the field, probably a drip irrigation system could be adopted in a dryland design, or a wetland system could be adapted to manage the high BOD of the glycol.

Even at low temperatures, glycol can be degraded; during winter operations the selection of plants that can tolerate the low temperatures is crucial. Some plants are able to maintain significant root growth and activity whenever the ground surrounding these roots is unfrozen, so that metabolic processes including peroxidase activity must continue. It is still necessary to determine efficiency of triazole removal at low temperatures.

On the other hand, it might be possible to store the ADF runoff collected through storm-water collection systems until the conditions for the plant growth are appropriate. At Denver, the runoff is collected in detention ponds and stored in large below-ground tanks for later controlled discharge (Backer et al. 1994).

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