PESTICIDE MOBILITY IN SOIL AND COMMERCIAL GRADE HUMIC MATERIAL AMENDED SOIL

By

LÁSZLÓ PINTÉR

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A practicum submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfilment of the requirements of the degree of Master of Natural Resources Management.

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ABSTRACT

The study investigated the potential of applying humic materials to remediate pesticide contamination from agricultural soil. The kinetics of atrazine sorption have been studied under laboratory circumstances in slurries of whole agricultural soil from Southern Manitoba and soil amended with commercial humic materials extracted from leonardite coal. Two commercially prepared leonardite products, Humex (GeoResources, Inc., Williston, ND) and Black Hills Lig (Black Hills Liginite, Inc., Glenrock, WY) were examined in the tests. Concentration changes of atrazine free in solution, atrazine reversibly sorbed, and irreversibly sorbed atrazine were monitored over time using an HPLC-microfiltration technique. The rate of reversible sorption was measured for soil, leonardite extract amended soil, and leonardite extract alone.

Humex was found to decrease reversible sorption but significantly increase irreversible sorption of atrazine by an agricultural soil. The concentration of atrazine free in solution was also lower in the soil amended with Humex. Black Hills Lig was shown to significantly decrease the concentration of free atrazine, increase the irreversible and slightly the reversible sorption of atrazine. The magnitude of these effects was specific for the type and concentration of leonardite extracts used.

Because of their impact on atrazine sorption, and irreversible sorption in particular, commercial leonardite extracts could play a role in remediation where atrazine contamination of soil has occurred. Because of economic and technical considerations, the use of commercial humic materials in pesticide contamination abatement is most promising in the case of ex-situ or in-situ decontamination from point source pollution. In the case of non-point source pollution, commercial humic materials might also be applied under specific circumstances in the construction of filter strips to prevent pesticide contaminants in base flow from reaching open bodies of water. The low cost and the effectiveness of the amendment procedure indicated in these test warrant a pilot study to demonstrate the success ot the technique under field conditions.

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LIST OF ABBREVIATIONS

At	-	Atrazine
AtOH	-	Hydroxyatrazine
CEC	-	Cation Exchange Capacity
DEA	-	Des-Ethyl-Atrazine
DIA	-	Des-Isopropyl-Atrazine
DOM	-	Dissolved Organic Matter
FA	-	Fulvic Acid
HA	-	Humic Acid
HPLC-MF	-	High Pressure Liquid Chromatography-Microfiltration
K_d	-	Distribution Coefficient
NPOC	-	Non-Polar Organic Compound
SOM	-	Soil Organic Matter

1. INTRODUCTION

1.1. PROBLEM STATEMENT

Pesticide contamination of the biosphere became an environmental concern early in the 1960s and is not expected to diminish in importance in the coming decades. Overall, there are two principal reasons that indicate this problem is going to stay with society for some time to come. The ***first*** reason is related to the dependency of highly productive but also 'externality-intensive' agricultural practices on pesticide application. The ***second*** reason relates to the significant buffering capacities of terrestrial and aquatic ecosystems for toxic substances in regard to pesticide residues. This buffering capacity ensures that by the time pollution problems are measured and recognized subsequent policy actions do not ***readily*** lower immediate risk because of already high contaminant accumulations in the system (Hallberg, 1986; Hallberg, 1989; Leistra and Boesten, 1989; Stigliani and Salomons, 1993). These statements are particularly valid for pollution from non-point sources.

Preemptive and mitigatory propositions regarding pesticide pollution abatement must satisfy both biophysical, as well as applicable regulatory / economic criteria. One of the preconditions of determining the impact and optimum level of mitigatory or preemptive measures is a rigorous knowledge of pesticide behaviour in ecosystems, in the context of the particular measure. Exact chemical / biophysical data are also required by computer simulation models that are being developed and used to project the fate of pesticides in terrestrial, as well as aquatic ecosystems

(Mill, 1980; Aller et al., 1985; Alexander et al., 1986; Varshney et al., 1993; Wagenet and Hutson, 1989; Carsel et al., 1985).

The particular procedure that is the subject of this investigation involves the amendment of soil with commercially available humic materials, and its impact on the persistence of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine], an *s*-triazine herbicide extensively used on corn, sorghum, and rangeland in the temperate climatic zones of North America and Europe. Humic material amendment of contaminated soil is expected to result in decreased atrazine availability in the soil. This decrease results from increased sorption of pesticide residues.

Traditionally, measurement of pesticide sorption have relied on the measurement of apparent rate constants, associated only with free pesticide residues in the liquid phase. This approach has been shown to give imprecise sorption equilibrium constants and high data scatter. Such data are inappropriate for the accurate predictive calculation of pesticide sorption. The chemical kinetics and the underlying analytical chemistry necessary to obtain true equilibrium constants have been described by Gamble and co-workers (Gamble and Khan, 1985; Gamble et al., 1986a; Gamble et al., 1986b; Gamble and Khan, 1988; Gamble and Khan, 1990). Analytical methodology is available that permits the contiguous monitoring of all chemical species of the pesticide, i.e., atrazine in free, reversibly sorbed, and irreversibly sorbed states. Precise chemical data allow a more reliable assessment of the potential use c^Xxmercial humic materials may have in the remediation of pesticide contaminated soils.

1.2. RESEARCH OBJECTIVES

The primary purpose of this study was to measure and demonstrate the effectiveness of commercial humic material as a soil amendment in the remediation of pesticide contamination. The study examined the effect such soil amendments have on the kinetics of pesticide sorption.

Specific objectives were:

a/ to study the sorption of atrazine in agricultural soil as a function of commercial grade humic material amendment;

b/ to monitor changes in the molarity of atrazine chemical species with time in the model soil, in the presence and absence of the humic material amendment;

c/ to measure the atrazine specific sorption capacity of the test soil and humic materials, and compare sorption equilibria of soil and humic material amended soil;

d/ to provide, on the basis of experimental results obtained, a preliminary assessment of the potential use of commercial humic materials in pesticide pollution abatement and soil remediation.

1.3. LIMITATIONS

a/ The humic materials, soil, and pesticide used in these experiments are only representatives of their respective heterogeneous classes. Considering the remarkable diversity of these categories of substances, caution should be exercised in interpreting the results for situations involving materials of different character.

b/ These experiments provide stoichiometrically detailed information on pesticide interaction with soil and humic materials. The dynamics of pesticide sorption and desorption was monitored over time for three kinetic species, atrazine in solution, reversibly sorbed, as well as irreversibly sorbed. Kinetics and equilibria derived fromj this study may provide insight into pesticide mobility in a three dimensional, heterogeneous hydrogeologic system over time in that the stoichiometry of pesticide interaction has been studied. Climatic and seasonal effects are other variables which must be addressed in other studies.

a/ Humic substances are known to influence a number of parameters related to organic chemical behaviour in the soil, including, but not restricted to pH, microbial metabolism, or solubility characteristics and bioavailability of organic compounds. This study is restricted to the measurement of the aggregate impact of these factors, as influenced by humic material amendment, in terms of sorption capacity phenomena.

2. LITERATURE REVIEW

The amount of research that has been done on various aspects of pesticide/soil interactions is voluminous. The following review of related literature is centred around, but can not be strictly limited to the reactions of pesticides, especially the herbicide atrazine, and soil components, particularly humic materials. There are two reasons for a wider scope.

First, the justification for scientific interest in pesticide contamination lies in the fact that trace level residues have been reported from hydrogeologic media, mainly in intensively farmed areas. Data on the health effects of long term low level exposures likely to be associated with this type of pollution are scant (Hallberg, 1986; Wasserman, 1991), and techniques to satisfactorily remediate contaminated soil or aquifers are either too costly or currently unavailable. This study of atrazine was intended to prove helpful to evaluate the practical practical applications commercial humic materials might have in pesticide pollution control.

Second, the behaviour of pesticides in an agricultural soil is a phenomenon of numerous variables, where pesticide sorption on humic materials is important, but it is not the ***sole*** factor determining contamination risk. Because of the inherent complexity of the phenomena, mention of other processes through which humic materials may also impact pesticide behaviour is appropriate, e.g., their impact on plant and microbial metabolism.

2.1. FACTORS AFFECTING PESTICIDE MOVEMENT AND DEGRADATION IN TERRESTRIAL ECOSYSTEMS

Behaviour of pesticides in the soil is a multivariate phenomenon. The soil itself is a heterogenous system in both chemical, physical, and biological terms. On the other hand, the variety of organic chemicals used in agroecosystems is also very large, and their reactions in the three dimensional structure of soil are ultimately defined by their particular molecular structure and characteristics. Adding seasonal / climatic variations and the consideration of the time factor presents a picture of remarkable complexity.

Weber and Miller (1989) identifies the following transport processes of pesticides in the soil environment:

"1. Absorption, exudation, and retention by crops and crop residues;

2. Runoff movement in either a dissolved or sorbed state;

3. Sorption and desorption to organic matter, clays and mineral surfaces;

4. Vapour phase diffusion; and,

5. Hydrodynamic transport, including advection and dispersion as soluble constituents of the aqueous phase."

While the above processes coexist and dynamically interact in a given system, their relative weights are not equal. Sorption phenomena have been shown to play a key role in the environmental fate of a number of pesticides, including atrazine (Talbert and Fletchall, 1965;

Li and Felbeck, 1972; Khan, 1972; Weber, 1993). The definition of sorption for the present purposes is taken from Hassett and Banwart (1989): "***sorption*** is the term used to describe adsorption and/or absorption when an independent determination of the nature of the process, that is, whether it is adsorption or absorption, is not possible." The importance of soil organic matter (SOM) in pesticide sorption phenomena has been widely acknowledged (Stevenson, 1982).

2.2 HUMIC SUBSTANCES

Humic substances or humus (used interchangeably) "refer to organic material in the environment that results from the decomposition of ***plant and animal residues***[1], but that does not fall into any of the discrete classes of compounds such as protein, polysaccharides, polynucleotides, and so on" (MacCarthy and Rice, 1991).

Humic substances or humus are viewed as the most active soil components influencing the fate of pesticides and pesticide residues primarily through sorption reactions (Weber and Miller, 1989; Stevenson, 1982). Contrary to most other natural polymers such as proteins or nucleic acids, humic substances are composed of a relatively high number of discrete and uniform monomer classes (Fig. 1).

[1] Instead of "plant and animal residues" the broader term of biological residues recommended; italics added.

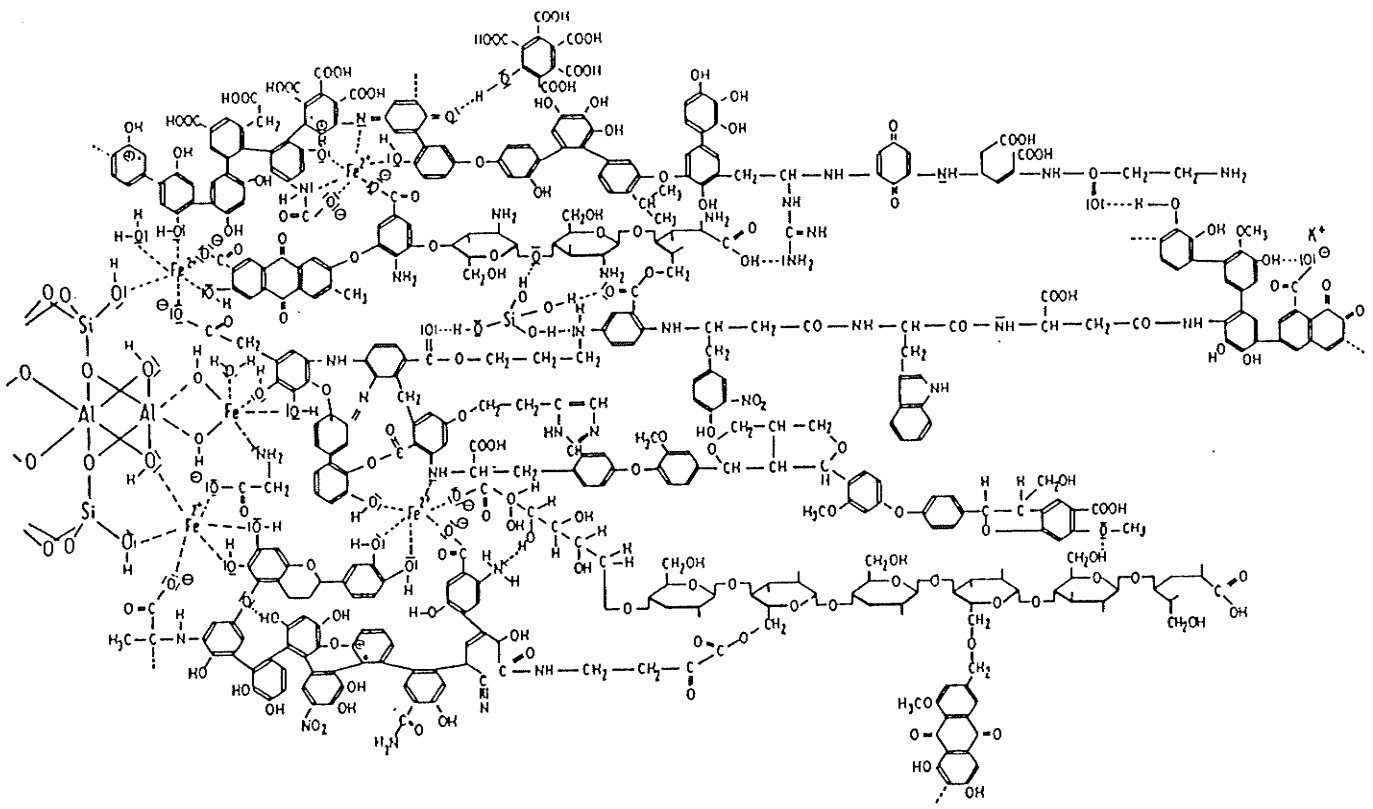

Figure 1: A theoretical HA molecule structure (Kleinhempel, 1970).

Fractionation studies have failed to identify humic material classes with accurately reproducible, deterministic structures. Owing to the practically infinite number of building blocks available for the synthesis of humic substances, their size- and molecular structure-classes are continuous, but their characteristics can be interpreted and classified in statistical terms. This exceptional variability is emphasized by some as a key to understand the fundamental role humic substances

play in stabilizing geochemical processes in the lithosphere. This role is further emphasized by the longevity of humic materials in soils: while many other organic chemicals are able to perform the tasks humic materials are able to perform (such as sorption, nutrient supply, waterholding capacity, etc.), they are readily decomposed, either by physical, chemical or biological forces. By withstanding decomposition, humic substances provide a basis for continuity in soil ecosystem processes (MacCarthy and Rice, 1990; MacCarthy et al., 1990)

Within the category of humic substances, fulvic acids (FA) and humic acids (HA) exhibit the largest sorptive capacity (Stevenson, 1982; Karickhoff, 1984; Perdue and Wolfe, 1982; Somasundaram et al., 1991). Both humic and fulvic acid extracts contain various amounts of associated organic molecules, most significantly amino acids, carbohydrates, fatty acids and alkanes. These molecules are believed to be either physically adsorbed or chemically bonded to humic materials (Stevenson, 1982). Humin is the third generally acknowledged class of humic substances. Besides HA, FA and humin, several subclasses of humic materials have been identified. The validity of the other classes is, however, subject to scientific debate (Figure 2).

Humic substances are separated and operationally classified on the basis of their pH-dependent solubilities, but differences between classes extend to other parameters, such as molecular weight, functional group content, bioactivity or colour. HAs are the alkali soluble, acid insoluble part of SOM with molecular weights up to 300,000. While they are insoluble in water at low pH, their Na^+ salts are fully water soluble. FAs are soluble in water at both low and high pH, with molecular weights up to 2,000 daltons. HA and FA molecules are composed of

both aliphatic and aromatic subunits, with a variety of functional groups.

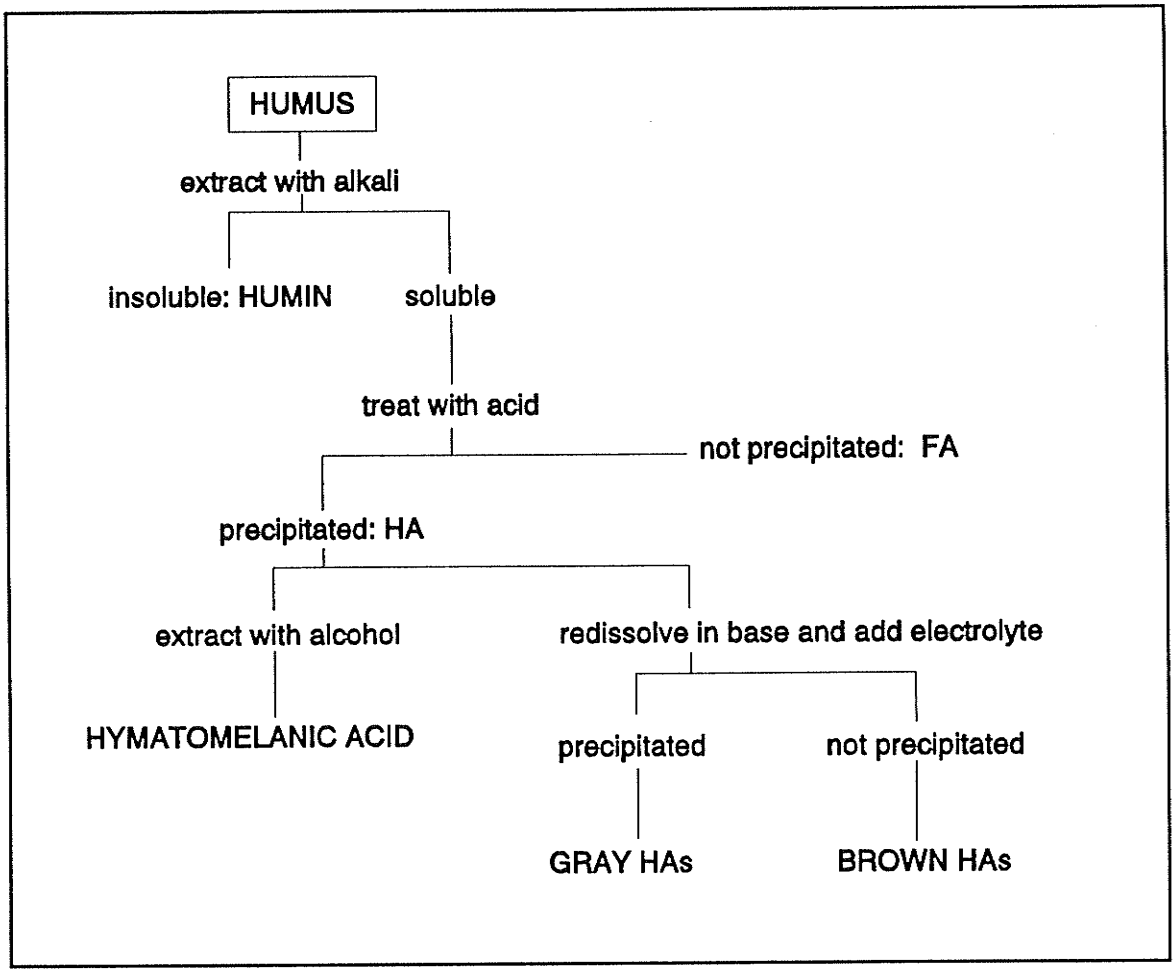

Figure 2: Fractionation of humic substances (after Stevenson, 1982).

Due to the dissociation of H^+ ions between pH 5-7 mainly from carboxylic groups, humic acids possess an overall weak negative charge, giving humic acid molecules significant cation exchange capacity [CEC] (Stevenson, 1982; Chen and Stevenson, 1986). In summary, HAs and FAs behave as carboxylic type cation exchangers exhibiting pH dependent solubilities. Besides carboxylic groups HAs and FAs may carry a large variety of functional groups. Large

functional group densities enable humic substances to form complexes with inorganic or organic compounds, including most pesticide molecules (Stevenson, 1982).

Some further complexities arise from the consideration of the variability of pesticide molecules and the variability within classes of functional groups:

(a) Because of different pesticide molecular structures, it is improbable that different pesticides use exactly the same set of binding sites on a given humic acid molecule. The binding capacity of a particular humic acid (θ_c) is likely to be substrate specific (Gamble et al., 1980; Gamble and Langford, 1988).

(b) Due to differences in the three dimensional steric environment of functional groups, there are differences between weak acid dissociation constants (pK_A) even within the category of one type of functional group (e.g., carboxylic). The presence of multiple titration endpoints, based on functional group heterogeneity, has been shown experimentally (Gamble and Khan, 1992). The implications for atrazine sorption are discussed in Chapter 2.5.

Major types of interactions between humic materials and pesticides involve ion exchange, charge transfer mechanisms between electron-poor groups of HAs and electron-rich groups of the pesticide molecule, van der Waals' forces, hydrogen bonding, and coordination complexes (Stevenson, 1982). According to Bollag and Myers (1992) and Bollag (1992), biologically or abiotically catalyzed oxidative coupling of pesticides to humic substances is also an important reaction, potentially leading to the inactivation of xenobiotics during humification.

Fulvic acids are water soluble, however, HA migration in soil is very slow because of their apolar, insoluble character. Polar HA salts, e.g., potassium humate, are however water soluble and able to migrate in the soil. Humic acid salts have been shown to increase the mobility of non-polar organic compounds [NPOC] (Chiou et al., 1986; Wershaw, 1986, etc.), and Abdul et al. (1990) have suggested that humic materials could be used for the removal of NPOCs from hydrogeologic systems.

2.3. HUMIC MATERIALS IN CROP PRODUCTION

The effect of humic substances on plant physiology has been studied and recognized. Positive correlations have been found between soil or foliar application of a variety of humic material extracts and some physiological parameters of plant growth, such as root formation, nutrient uptake and total biomass (Duplessis and MacKenzie, 1983; Vaughan and Malcolm, 1985; Lobartini et al., 1992; Govindasmy and Chandrasekaran, 1992; Piccolo et al., 1992). According to Chen and Aviad (1990) humic material extracts enhance root length and secondary root formation, and to a smaller extent shoot development. The growth promoting effect is proportional to humic material quantities added; only extreme high concentrations elicit a negative growth response. The mechanism of this beneficial effect is not understood in full, but humic materials are believed to enhance plant growth in several ways. Most importantly, macronutrient uptake is improved, and plant growth is influenced through a hormone-like activity of particular fractions of humic materials that are small enough to permeate cell membranes. While the economic feasibility of direct soil application is still subject to

discussion, humic material based foliar sprays have been proven economic under some specific circumstances. Such foliar sprays, containing chelated macro and/or micronutrients are used primarily in regions where soil organic matter contents are low, and nutrient, e.g., iron, deficiencies are frequent. The marketing base of humic materials for agricultural uses is particularly well developed in, e.g., Spain, Italy and Israel.

Gray and Wallace (1957) has also demonstrated a relationship between bacterial numbers and SOM, and humic materials may potentially influence plant physiology, as well as soil parameters through their impact on microbial activity as well.

While humic material content of agricultural soils is usually well under 5%, some fossil deposits, primarily peats and lignites may contain as much as 30 to 60% (Stevenson, 1986). The chemical properties of humic materials are known to vary with the source from which they have been extracted. Significant differences exist in molecular size, functional group content, carbon/oxygen content, and total acidity, features which determine reactivity and behaviour of the molecule (Lobartini and Tan, 1988; Lobartini et al., 1992; Piccolo et al., 1992). Experiments aimed at various aspects of pesticide / humic material interactions have most often used either soil and natural water origin, or laboratory grade humic substances; however, as noted above, commercially available humic substances are either lignite or leonardite in origin, or to a smaller extent relics of alluvial Bh horizons of Spodosols (Kopint Datorg, 1991; Lobartini et al., 1992).

Industrial grade humic materials are extracted from fossil deposits, and used, among other applications, in crop production, as a fertilizer additive (Burdick, 1965; REDA, 1986; Chen and Aviad, 1990; Lobartini et al., 1992). The product for field application may be either raw lignite or leonardite with high humic material content, or more frequently, base treated, purified HA. Foliar sprays containing HA chelated micronutrients are applied primarily in intensive production systems, under conditions of nutrient deficiency. Referring to the previously mentioned complexity and heterogeneity of humic materials, expecting commercial humic material products to be 'pure' from the analytical chemistry point of view is unrealistic. Purity should be understood only in the statistical sense, and interpreted in close correlation with whether or not it affects the practical utility of the product.

Although there is a concern regarding the economic feasibility of the general field applicability of humic substances, due to product heterogeneity and dissimilarities between soil and fossil origin and the quantity to be applied (Stevenson, 1979), recent studies do not readily confirm these assumptions (Vaughan and Malcolm, 1985; Chen and Aviad,^Xx990; Lobartini et al., 1992; Piccolo et al., 1992). Fossil origin humic substances, being relatively cheap and environmentally safe soil amendments, seem to have their place in specific crop production technologies.

2.4. ATRAZINE CHEMISTRY

Atrazine is the most widely used selective pre- and post-emergence *s*-triazine herbicide for the control of broadleaf and grassy weeds in corn, sorghum, and rangeland. It is also used for nonselective vegetation control in noncrop land. Atrazine is marketed under a number of brand names, such as Aatrex, Gesaprim, and Accent. Major physical and chemical properties of the compound are shown in Table 1.

Table 1: Physical and chemical properties of atrazine (Trotter et al., 1990; WSSA, 1989)

Chemical formula:	$C_8H_{14}ClN_5$
Molecular weight:	215.7
Physical state:	White, crystalline.
Melting point:	173-175 °C
Vapour pressure:	3 x 10-7 mm Hg at 20 °C
Water solubility:	33 mg/L at 27 °C
Elemental analysis:	C, 44.55%; H, 6.54%; Cl, 16.44%; N, 32.47%
LD_{50}(acute oral toxicity for rats):	3,800 mg/kg
pK_a value at 20 °C:	1.64

The molecular structure and major degradation pathways of atrazine are shown on Figure 3. Atrazine undergoes hydrolysis in acidic soil during which the chlorine is replaced by a hydroxyl group (Armstrong et al., 1967; Skipper et al., 1978). Hydroxyatrazine (AtOH) is not active as a herbicide. Atrazine hydrolysis has been seen as a primarily chemical phenomenon, catalyzed either by hydrogen ions or unionized carboxyl groups associated predominantly with soil organic matter (Gamble and Khan, 1985). Microbial hydrolysis has been also reported, but its significance under usual field conditions is probably secondary (Kaufman and Kearney, 1970; Mandelbaum et al., 1993).

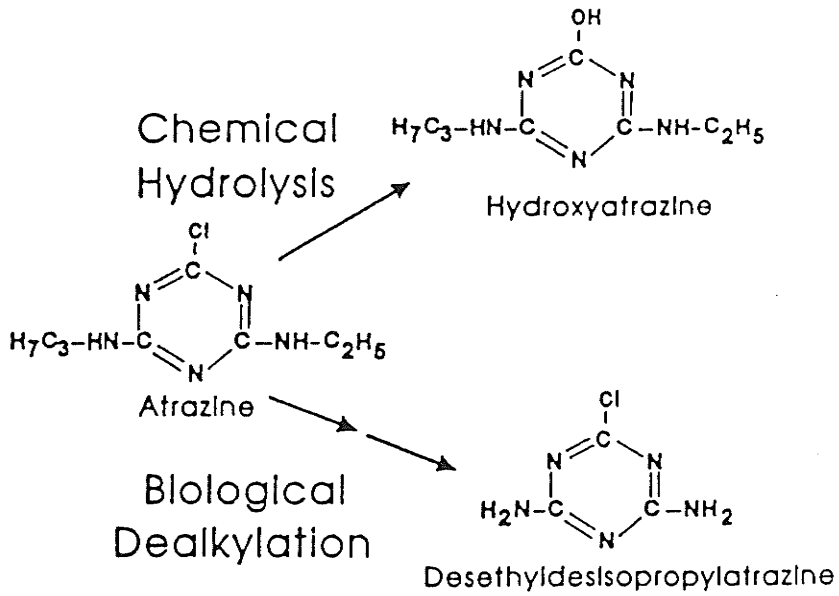

Figure 3: Molecular structure and degradation pathways of atrazine.

An alternative decomposition pathway is dealkylation at the ring carbon in the 4 or 6 position, producing either des-ethyl-atrazine (DEA) or des-isopropyl-atrazine (DIA). Both DEA and DIA are phytotoxic. Dealkylation is predominantly a microbial process, with preferential utilization of the isopropyl side chain under aerobic conditions (Behki and Khan, 1986). Reduction of microbial degradation has been reported under denitrifying conditions, with important implications for atrazine transformation under anoxic conditions that exist in deeper soil depths (Nair and Schnoor, 1992). Decomposition by ring cleavage is also possible, but its importance is insignificant as compared to other pathways (Skipper and Volk, 1972).

Based on a review of five studies in the literature, Nash (1980) has estimated the half life of atrazine in soil between 47-110 days, with an average of 74 days. Accuracy of these estimates highly depend upon the actual soil and climatic conditions, but also on the ability of accurate sampling to account for material mass balance at the field level.

2.5. ATRAZINE CONTAMINATION OF SOIL AND GROUNDWATER: PATHWAYS AND EMPIRICAL DATA

Pesticide contamination of terrestrial and aquatic ecosystems may occur through either diffuse non-point pollution or pollution from point-sources. Pollution from ***non-point sources*** is associated with standard operating practices (SOPs), overuse, and poor handling routines inclusive (Hallberg, 1989). Non-point pollution generally entails lower contamination levels affecting very large areas. Pollution from ***point-sources*** is associated with spills and other

concentrated discharges. The affected area is usually smaller, but the local concentration of the released contaminant is high. In particular cases, where point source pollution is frequent, it may be valid to talk about ***quasi-point source*** pollution because of overlap between contaminated areas.

The distinction between the two major types of pathways, viz. point-source and non-point source pollution, is important for practical purposes including the amendment of soil under investigation in this project. The policy choice for handling point-source contamination, if the risk is perceived as unacceptably high, is treatment, containment, or landfilling. In the United States, for instance, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or, as commonly known, the Superfund program, has been initiated to handle these situations (e.g., US EPA, 1987; Gupta et al., 1993). These procedures are by definition reactive, in the sense that they deal with the situation after the contamination has occurred. Handling the issue of non-point source pollution, on the other hand, necessitates proactive action, as in-situ cleanup of large tracts of soil or aquifers is generally uneconomical with techniques currently available. Non-point source pollution abatement requires techniques that are integrated in technological, ecological and economic sense into agricultural practices, and usually require multidisciplinary effort (e.g., Weinberg, 1990; Gassman, 1993; Hatfield, 1993).

There is no general agreeme^Xx as to what is an acceptable level of atrazine in drinking water. Some of the available international guidelines are summarized in Table 2.

Table 2: International guidelines for atrazine in drinking water.

WHO[a]	2 μg/L
US EPA[b]	3 μg/L
EC[c,d]	0.1 μg/L

[a] WHO (1987)

[b] Thurman et al. (1991)

[c] Council of the European Communities (1980)

[d] Atrazine was banned in Germany in 1991 (Gassman, 1993).

Table 3: Recommended Canadian Water Quality Guidelines for atrazine (Trotter et al., 1990).

Uses	Guidelines
Raw water for drinking water supply	60 μg/L
Freshwater aquatic life	2 μg/L
Agricultural uses	
Livestock watering	60 μg/L (interim)
Irrigation	10 μg/L (interim)
Recreational water quality/aesthetics	no recommended guideline
Industrial water supplies	no recommended guideline

Canadian Water Quality Guidelines for atrazine were published in 1990 and are summarized in Table 3.

There are two reasons why agreement on safe levels of pesticides (or for this case, atrazine) is difficult. First, health effects of chronic, long term exposure are not known with adequate certainty. Secondly, knowledge on the environmental fate and behaviour of most compounds, including atrazine, is inadequate to conduct accurate risk assessments.

Atrazine and atrazine residues have been detected by monitoring programs in soil and groundwater in a large number of cases, both in North America and Europe. One of the earliest comprehensive regional studies was conducted by the Pollution from Land Use Activities Reference Group (PLUARG), established jointly by the United States and Canada under the Great Lakes Water Quality Agreement. They indicated a correlation between atrazine area load and primarily corn, soybean and vegetable production. Atrazine and atrazine residues have been measured at 0.1-1.2 μg/L concentrations in all the 11 monitored watersheds (Coote et al., 1982). Monitoring studies conducted in the humid zones of the United States during the 1980s have been summarized by Hallberg (1989). Regarding atrazine, he notes that this compound has been the most frequently detected pesticide in groundwater samples in the Midwest. The typical level of atrazine in groundwater samples from 4 Midwestern states plus Maryland were estimated at 0.3-3.0 μg/L (Cohen et al., 1986). Thurman et al. (1991) found atrazine residues exceeding EPA promulgated maximum contaminant level (PMCLs) in 52% of the samples taken in 12 Midwestern states.

The pattern of surface and groundwater contamination in many European countries shows a similar pattern to those in North America. In a comprehensive review by Leistra and Boesten (1989), *s*-triazine herbicides, primarily atrazine were the most frequently detected pesticides in Germany, Italy, France and Denmark.

Besides empirical measurements, several computer models have been developed to forecast pesticide behaviour and estimate the associated environmental risk. One of the recent models, PESTFADE, has been developed to take benefit of the detailed stoichiometric information obtained from HPLC-microfiltration measurements, such as the ones used in the current study (Clemente, 1991; Clemente et al., 1993). Another model, DRASTIC had been prepared in the United States to determine the potential and rate of groundwater contamination by pesticides through simulation (Alexander et al., 1986; Aller et al., 1985). Using the same simulation technique combined with available monitoring data, Lee and Nielsen (1987) identified 1,437 counties in the mainland USA, where pesticide contamination of groundwater can be expected. They concluded that contamination of groundwater with pesticides and fertilizers combined can affect 53.8 million people in the continental U.S. In a separate analysis, 4,123 of 10,942 surface water samples, and 343 of 3,208 ground water samples contained residues of atrazine (STORET, 1988). Several other models are in use by different government agencies, but their detailed discussion is out of the context of this project.

One particular observation in regard to pesticide fate modelling is, however, appropriate to quote. Further data on the physical processes involved in groundwater pesticide contamination

is necessary to support preventive or remedial actions with high social cost (Lee and Nielsen, 1987). This view is supported by Villeneuve et al. (1988), who found, that the use of deterministic hydrology models for forecasting pesticide behaviour increases the importance of physical parameters, such as sorption and degradation kinetic data and rate constants. According to their sensitivity analysis, 15 to 24% errors of these parameters can modify final predictions with up to 100 %, and produce a false under or overstatement of pesticide contamination risk.

2.6. ATRAZINE SORPTION BY HUMIC SUBSTANCES

The ability of humic substances to catalyze the degradation of atrazine through sorption has been extensively studied. During the last three decades, the motives of study and the methods, however, have changed. Li and Felbeck (1972), for instance, studied atrazine / HA interactions, because HAs were held responsible for accelerated bioactivity loss of atrazine in cases where SOM content was high. With the emergence of pollution problems, attention shifted towards the need for understanding the underlying mechanisms of soil contamination.

In the practical sense, our purpose was to describe and evaluate the differences between humic acid amended and unamended control soil with respect to the pesticide contamination risk. Risk of pesticide pollution in soil is expected to be higher with higher quantities of mobile pesticide molecules. Pesticide mobility, however, does not only imply that at a given point in time, pesticide molecules are actually free in solution. When atrazine is introduced into a suspension of organic soil or HA, sorption onto specific binding sites starts to take place from t_0. As noted

before, not all organic molecules use the same sort of binding sites, and, in turn, not all the binding sites used by a particular organic molecule are the same. Some of the binding sites hold atrazine molecules lightly, and even a weak extractant, such as methanol or water, will cause the pesticide molecule to desorb and go into solution again, which creates increased contamination risk. Stronger interactions between binding sites and the pesticide are also possible, and more strongly sorbed molecules will not desorb with a weak or even stronger extractant.

The kinetic model describing the interactions of soil organic matter and organic compounds has been pioneered by Gamble and co-workers and published in a series of papers on the subject (Gamble, 1972; Gamble and Khan, 1990; Gamble and Khan, 1988; Gamble and Ismaily, 1992; Wang et al., 1992; Gilchrist et al., 1993). In the most general form, the equilibrium between pesticide and HA molecules in a system can be written as follows:

$$At_{(aq)} + HA_0 \overset{K_1}{\rightleftarrows} At\ HA_{(LS)} \qquad (1)$$

where $At_{(aq)}$ is the amount of atrazine in solution, HA_0 is the number of unoccupied binding sites available for atrazine sorption, and $At\ HA_{(LS)}$ designates bound atrazine. K_1 is the weighted average equilibrium constant representing that binding sites are expected to have a wide range of affinities towards HAs.

The number of sites available for reversible sorption can be described by the following simple equation:

$$\theta_C = \theta_L + \theta_0 \qquad (2)$$

where θ_C is defined as the labile surface sorption capacity, representing the total number of binding sites available for atrazine sorption. At any given point of time, some of these sites will hold sorbed atrazine molecules (θ_L = [$AtHA_{LS}$] = labile sorbed), and some will be left empty (θ_0 = [HA_0]). θ_L has been traditionally used to calculate the distribution coefficient K_D for slurries of pesticide and organic soil:

$$K_D = \frac{\theta_L}{M_{At}} \tag{3}$$

where M_{At} represents the molarity of atrazine in the solution. K_D is intended to describe the adsorbability of a given pesticide to a particular soil. It is, however, only an empirical constant. The correct meaning of K_D can be calculated using equation (3), and the true rate constant K_1 as noted in equation (1), and calculated using the law of mass action:

$$K1 = \frac{[AtHA_{LS}]}{[At_{aq}][HA_0]} \quad \text{or} \quad K_1 = \frac{\theta_L}{M_{At}\,\theta_0} \tag{4}$$

where M_{At} is atrazine molarity in the solution, θ_L represents the moles of atrazine sorbed per g of soil, and θ_0 is the moles of carboxylic groups not occupied by sorbed molecules, per g of soil. Applied to the case of atrazine sorption specifically, the weighted average equilibrium constant for atrazine and humic acid is:

$$\bar{K}_1 = \frac{[HA_{At}]}{[M_{At}]\,[HA_0]} \tag{5}$$

Thus,

$$\bar{K}_D = K_1\,(\theta_C - \theta_L) \tag{6}$$

Sorption of organic molecules on surface binding sites is a second order phenomenon depending

on both the concentration of the organic molecules and the concentration of the adsorbent. When the adsorbent is in vast excess, only the concentration of the organic molecule is important and the kinetics becomes essentially first order. Once atrazine molecules are sorbed on HA surfaces, they may either desorb or diffuse into the interior of the HA molecule (θ_D = diffusion into intraparticle or HA intramolecular space). Another source of θ_D may be pesticide that becomes bound to HA with covalent binding or another mechanisms making it unextractable by the method used. The differential rate law gives the relationship between sorption and desorption:

$$- \frac{dM_{At}}{dt} = k_1 M_{At} \theta_0 - k_{-1} \theta_L \qquad (7)$$

where k_1 is a second order rate constant for sorption, and k_{-1} is a first order rate constant for desorption. There are two observations that simplify equation (7). First, in systems where the number of binding sites is large, the constant for sorption will show pseudo-first order instead of second order character. Secondly, the rate of desorption has been shown to be fundamentally lower than sorption. Thus, equation (7) is simplified to:

$$- \frac{dM_{At}}{dt} = k_1 M_{At} \theta_0 \qquad (8)$$

$k_1\theta_0$ has been written as k_2, a pseudo-first order rate constant for labile sorption. Hence,

$$- \frac{dM_{At}}{dt} = k_2 M_{At} \qquad (9)$$

The analytical chemistry necessary to measure the substrate specific reversible sorption capacity of a pesticide molecule (θ_C), the amount of atrazine that is free in solution at any given point of

time $(M_{A\ell})_i$, as well as the compounded measurement of $(M_{A\ell})_i + \theta_L$ is available. θ_D can be readily calculated as material balance loss:

$$\theta_D = M_{At0} - [(M_{A\ell})_i + \theta_L] \quad (10)$$

The possibility of irreversible sorption either through chemical or bio-enzymatic catalysis has been indicated for a number of compounds (Martin et al., 1979; Cheng et al., 1983; Schneuert et al., 1991; Bollag and Myers, 1992). According to Smith (1981), the amount of organic chemical that can be recovered from soil is expected to decrease over time. As noted by Cheng et al. (1983) in regard to cathecol / HA interactions, decreased availability for microbial degradation was one of the results of increased sorption. Whether this phenomenon is disadvantageous or not from the pesticide's availability as a pollutant point of view, depends on whether the increase is due to reversible or irreversible sorption. The environmental risk associated with θ_D is expected to be significantly lower than it is with θ_L or $(M_{A\ell})_i$. Thus, even if the rate at which a pesticide is microbiologically degraded is lower as a consequence of sorption to soil organic matter, the level of environmental risk may not change significantly, if the sorption counteracting microbial decomposition is ***irreversible***.

3. MATERIALS AND METHODS

3.1. MATERIALS

(a) Humic substances

Humic substances were obtained from two commercial sources (Table 4). Bulk HA was stored at room temperature under dry conditions. HA samples withdrawn from the containers for testing were air dried, sieved with a $<38\mu m$ mesh size screen, and stored at 4 °C.

Table 4: Commercial humic materials tested.

Manufacturer	Product	Source
GeoResources, Inc. Williston, ND	Humex	Leonardite
Black Hills Lignite, Inc. Glenrock, WY	Black Hills Lig	Leonardite

(b) Soil

The soil used in the experiments was Miniota sand collected in the Shilo region of southwestern Manitoba. The soil was air dried, randomly mixed, sieved with a $<38\mu$m mesh size screen, and stored at 4 °C. Typical parameters of Miniota Loamy coarse Sand from the A horizon of a well-drained association is shown in Table 5.

Table 5: Representative analytical parameters of a Miniota Loamy Coarse Sand (from Ehrlich et al., 1957).

Depth (cm)	0 - 8
Moisture Equivalent	11.7
Organic Carbon	1.91
Nitrogen	0.15
C/N Ratio	12.7
Percent CO_3	0.0
pH	7.1

(c) Reagents

Exactly 0.01078 g of analytical grade atrazine (Riedel-de Häen, purity 98%) was measured into

a volumetric flask, and 150 mL HPLC grade water was added. The solution was stirred for 72 h on a magnetic stirrer until atrazine was completely dissolved. The flask was filled to the mark with HPLC grade water to obtain 250 mL stock solution (2×10^{-4} M), and stored at 4°C. HPLC analyses employed 10^{-4} M standards, obtained by diluting the stock solution.

The mobile phase (1:3 water/methanol) was prepared in 1 liter lots, and stirred magnetically for 2 h prior to introduction into the instrument.

(d) Experimental samples

Soil + HA sample combinations for kinetic tests are summarized in Table 6. Soil and HA were calculated for a total dry weight of 0.5000 g per combination. HPLC grade water (10 mL) was added to soil / HA samples, and they were hydrated for 48 h on a vertical shaker. Following hydration, atrazine from the stock solution was added, to adjust atrazine molarity to 1.000×10^{-4} in the test samples.

Soil / HA sample combination for sorption capacity measurements are listed in Table 7. Aggregate weight of soil / HA was again 0.5 g/combination. Following hydration as described for kinetic tests, the suspension was adjusted with HPLC grade water to 25 mL.

Table 6: Soil / HA combinations for kinetic tests.

	SOIL	HA AMENDMENT	HA TYPE	INITIAL ATRAZINE (M)
1.	100 (%)	0 (%)	-	10^{-4}
2.	99.5	0.5	Humex	10^{-4}
3.	99.0	1.0	Humex	10^{-4}
4.	100	0	-	10^{-4}
5.	99.5	0.5	Black Hills Lig	10^{-4}
6.	99.0	1.0	Black Hills Lig	10^{-4}

Table 7: Soil / HA combinations for sorption capacity tests.

	SOIL	HUMIC ACID AMENDMENT	HA TYPE
1.	100 (%)	0 (%)	-
2.	99	1	Black Hills Lig
3.	99	1	Humex
4.	0	100	Humex
5.	0	100	Black Hills Lig

3.2. EQUIPMENT

(a) pH meter

A Perkin-Elmer 05669-20 digital pH meter equipped with a combination glass electrode was used for pH measurements.

(b) Test vessels

Experimental samples for both chemical kinetic runs and sorption capacity measurements were prepared in 50 ml Pyrex 8422 screw cap cylinders. A Teflon coated stir bar was used on a magnetic stirring base to mix the suspension. Test vessels were placed in double walled glass jackets connected to a thermostate controlled water bath to keep slurry temperature constant at 25 °C.

(c) HPLC

A schematic representation of the HPLC system is shown on Figure 4. The HPLC system used for the measurements of atrazine included a Rheodyne 7125 injector with a 20 μL injection loop (1. on Fig. 4), a Waters Associates 6000A solvent delivery system, a Waters 490 programmable multiwavelength UV detector (10.), and a Fisher Recordall Series 5000 paper chart recorder. A first guard column (3.) with Whatman 4102-010 packing, two 15 μm inline microfilters (2. and 4.), three 0.2 μm stainless steel frits (5., 6., and 7.), and a cartridge type C-18 guard column (8.) were used to protect the main C-18 column (9.; Bondapak C-18, Waters Associates) from soil particles. Slurry microfiltration was done using a 0.22 μm size MSI Cameo Nylon

66 type disposable microfilter.

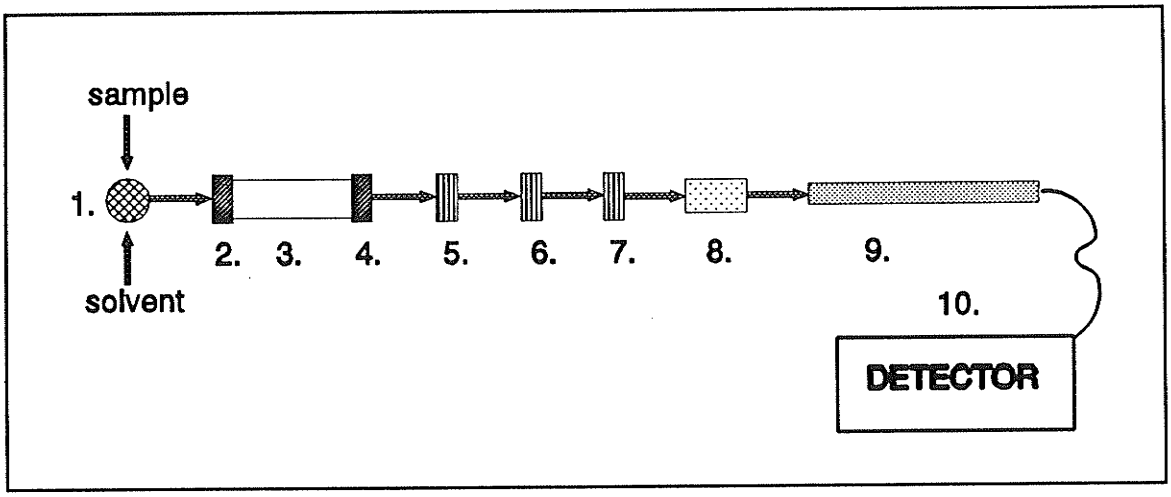

Figure 4: Setup of HPLC instrument (explanation in text).

HPLC analytical conditions are summarized in Table 8.

Table 8: HPLC conditions for atrazine measurement.

detector wavelength	245 nm
a.u.f.s.	0.02
pressure	0.8 - 1.8 MPa
flow rate	1 mL min^{-1}
chart speed	0.5 cm min^{-1}

Retention time (t_R) for atrazine was ca. 7.0 min. Considering the 1 mL min^{-1} flow rate the soil / extractant ratio was 2.5 g L^{-1}. The volume of solvent available to extract atrazine from 1 g of soil (v_m) was calculated as:

$$v_m = \frac{Ut_R}{W_A} \tag{9}$$

where U is the flow rate, t_R is the retention time of atrazine, and W_A is the weight of the injected aliquot. This gives 17.5 L g^{-1} extractant for the 7.0 min retention time as calculated. As Gamble and Khan (1990) noted, the appearance of sharp and symmetrical peaks indicates that elution time (t_E) is significantly smaller than t_R; thus, the method can be reliably used for atrazine detection. Wang (1989) has shown that precision of estimation with the current method at 1.000×10^{-5} M atrazine is better than 1.5%.

3.3. PROCEDURES

(a) Kinetic measurements

Analysis of slurry and filtrate samples started immediately after atrazine stock solution has been added to the soil / HA samples. As noted before, test samples were kept in suspension by a magnetic stirrer, and at 25 °C constant temperature. Before every set of measurements, an undiluted sample of atrazine stock solution was injected into the instrument in order to decrease data scatter because of atrazine specific binding capacity of the HPLC system. Every sample injection was bracketed by the injection of a 10^{-4} M atrazine standard.

Approximately 0.1 mL slurry was withdrawn from the test vessel with a syringe, and by overfilling the 20 μL injection loop, it was injected directly into the HPLC instrument. The particles > 0.2 μm were trapped by the inline microfilters, but the solvent eluted the labile sorbed atrazine (θ_L) molecules from the surface of trapped particles, so these molecules were measured together with the unsorbed, free atrazine (M_{Aii}) in solution.

Prior to the second sample injection, the slurry sample was filtered through the MSI disposable filter to obtain sufficient filtrate to fill the injection loop. Soil particles > 0.45μm were trapped by the filter; thus, the injected filtrate was assumed to contain only atrazine molecules free in solution (M_{Aii}).

(b) Sorption capacity measurements

Sorption capacity measurements involved the daily addition of 140 μL 10^{-4} M atrazine stock solution to each combination, and the regular monitoring of pesticide species in the suspension. Analysis of pesticide species in the slurry and filtrate was undertaken as described above for kinetic measurements.

(c) Data analysis

HPLC peak height values were introduced into a LOTUS 123, Version 2.0 spreadsheet file that calculated atrazine measurements in slurry and filtrate samples and plotted them against time. Regression analysis was undertaken using the F-Curve package to obtain 1-5 order polynomial equations and corresponding regression lines, as well as standard deviations for regression

equation constants. The dynamics of some of the sorption kinetics phenomena has been such that none of the other available packages gave adequate fit for the primary data set. Using F-Curve two or in some cases three equations were necessary to correctly fit parts of the particular data. These polynomials were used to create the single best fit curve describing the sorption phenomenon. Three kinetic species, atrazine in solution, or reversibly as well as irreversibly sorbed atrazine were plotted against time on a single graph, as illustrated on Figure 3.

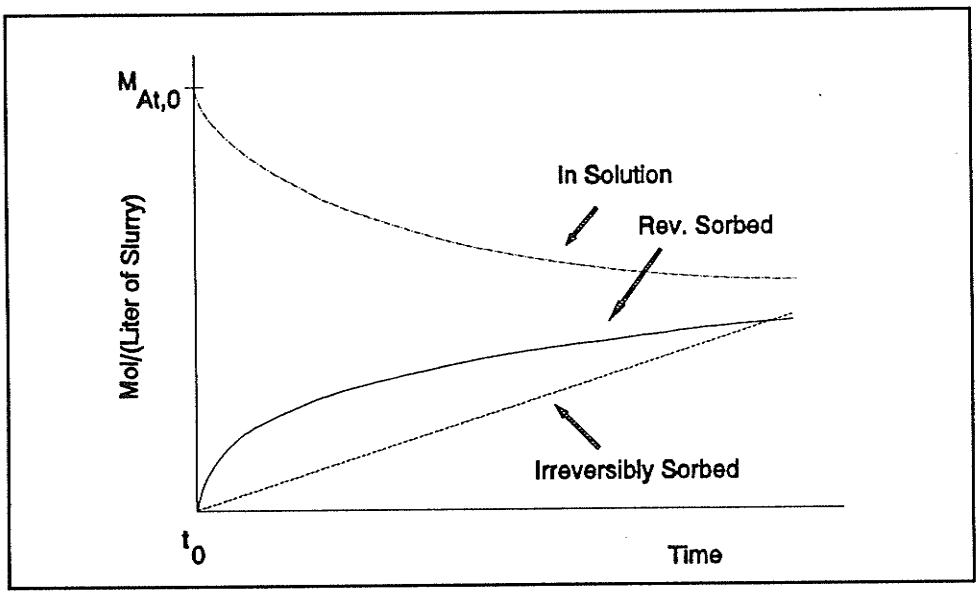

Figure 5: Representation of three kinetic species, free in solution, reversibly as well as irreversibly sorbed over time.

Note, that the curve representing atrazine measurements in the slurry is not shown, because it represents not one, but the sum of *two* chemical species, θ_L and M_{At}.

4. RESULTS

3.1. KINETIC MEASUREMENTS

Chemical species of atrazine, as measured in kinetic experiments involving Miniota sand, as well as HA amended Miniota sand, are shown on Figures 10-14 in the Appendix. Each graph displays three chemical species of atrazine, characteristic of the given soil / HA combination:

(a) atrazine in solution (M_{At});

(b) reversibly sorbed atrazine (θ_L);

(c) irreversibly sorbed atrazine (θ_D).

M_{At} is measured directly in the filtrate, while ($M_{At}+\theta_L$) values are measured directly in the slurry. As noted earlier, ($M_{At}+\theta_L$) is an intermediate value, thus it is not shown on the graphs, but used in the calculation of θ_L and θ_D.

At t_0, when the experiment begins, and atrazine is added to the suspension, all atrazine molecules are, by definition, in solution. Thus, the Y-axis intercept for M_{At0} is the initial atrazine concentration (1.00×10^{-4} M), and zero for θ_L and θ_D. Actual measurements of initial free atrazine practically never gave exactly 1.00×10^{-4}M concentration, and the Y-axis intercept of the regression line was usually above 1.00×10^{-4}. Repeated tests found, that the deviation was not caused by experimental error, imprecise measurement or atrazine contamination of the Miniota soil used in the tests. In terms of these measurements, the UV absorbance of atrazine is higher when measured in a heterogeneous soil slurry. The fact that further increasing humic

material concentration increased absorbance values, suggests that association of atrazine with humic materials may play a role in shifting atrazine spectral values. The regression line was 'anchored' at 1.00 x 10^{-4}M on the Y-axis based on the proof that there were no atrazine residues detected in the sample prior to the test, as analyzed by HPLC, and the amount of atrazine put in the solution was known. Similarly, regression lines of labile sorbed and irreversibly sorbed atrazine were anchored at the zero intercept.

Free atrazine concentration in the control sample decreases at a high rate for ca. 3 days, then the rate of change levels out, and the regression line becomes quasi-linear. The initial rapid drop in free atrazine concentration is paralleled by a high rate of increase in θ_L, that starts to level out at around 2.5 x 10^{-5} M/L of slurry, showing the characteristics of a typical Langmuir isotherm. The existence of an initial high sorption rate and a subsequent rate which is significantly lower may indicate that there are two classes of binding sites, with different sorption kinetics. Irreversible sorption (θ_D), in agreement with the theory, is described by a linear plot, with no saturation reached during the experimental period. These results correspond with the findings of Gamble and Khan (1990) obtained for the case of atrazine and Typic Mesosol peat from Quebec. Reversible sorption capacities (θ_C) and $\bar{K}_1$ equilibrium constants are shown in Table 9.

Table 9: Reversible atrazine sorption capacity and equilibrium constants of Miniota soil and humic material amended Miniota soil.

Soil	θ_L (moles/g)	$\bar{K}_1$
Miniota Sand	1.47×10^{-6}	4.83×10^{2}
Miniota + 1% GEO HA	0.93×10^{-6}	4.71×10^{2}
Miniota + 0.5% GEO HA	1.28×10^{-6}	5.74×10^{2}
Miniota + 1% BHL HA	1.67×10^{-6}	7.17×10^{2}
Miniota + 0.5% BHL HA	1.73×10^{-6}	6.44×10^{2}

(a) GEO HA amended soil

The dynamics of free atrazine concentration in the GEO HA amended suspension is similar to the case with Miniota soil (Fig. 11 and 12). The sorption appears to change character at ca. 3 days and 8×10^{-5} M, when the initial rate of sharp concentration decrease moderates. The reversibly sorbed and irreversibly sorbed chemical species curves changed compared to what has been observed for Miniota soil with no amendment. The rate of change is related to the amount of GEO HA added.

Figures 15-17 show a plot of respective species curves for the control as well as GEO HA amended soils. Due to HA amendment there is a drop in free atrazine in the solution as shown on Figure 15. The difference in the case of the 1% amendment at the end of the 40 day testing

period is in the order of 0.7 x 10^{-5} M. The change is more significant in the case of reversibly sorbed atrazine (Fig. 16), and the impact of HA is manifested by a drop in reversibly sorbed pesticide concentration. The initial rate of reversible sorption is already different, compared to the control, from the start of the test. The rate of increase in reversibly sorbed atrazine drops significantly, especially in the case of the 1% HA amendment. By the end of the 42 day experimental period, the amount of decrease in reversibly sorbed atrazine for the 1% case is in the order of 45%.

Curves of irreversibly sorbed atrazine are plotted on Figure 17. No saturation limit is reached* ^^ y of the cases, as the slope of the curves remains positive. This is in agreement with comparable data in the literature (Gamble and Khan, 1990). The rate of irreversible pesticide sorption increases significantly with the amount of HA added to the soil. The difference in irreversible sorption rates is detected from the beginning of the experiment. By the end of the tests, the 1% GEO HA amended soil exhibits an approximately fourfold increase in irreversibly sorbed atrazine in comparison with the control. The measurements indicate that the increase of irreversibly sorbed atrazine in the case of GEO HA amendment is accompanied by a drop in both reversibly sorbed and free atrazine levels in the slurry.

(b) BHL HA amended soil

Chemical species in the BHL HA amended slurries are shown on Fig. 13 and 14. Comparing atrazine kinetics to the control on Fig. 10 shows that the kinetic ***character*** of chemical species is similar after BHL HA amendment. In correlation with theory, reversible sorption shows

second order kinetics, while irreversible sorption is quasi-first order. The inflexion point in free atrazine and irreversible sorption is seen at day 3 of the test runs. In the case of BHL HA there was a plateau associated with reversible sorption, which indicates saturation of surface coverage sites, i.e., a limit of surface sorption capacity. Reversible sorption capacity and associated kinetic rate constants are given in Table 9.

Respective chemical species from the control as well as the BHL HA amended combinations are plotted on Figures 18-20. Amendment with BHL HA decreases the amount of free atrazine in the suspension. The decrease is more noticeable than it was in the case of GEO HA amendment in the initial phase of the test period (inflexion point at 6.7 x 10-5 M for 1% BHL HA), but following the initial drop, the decrease of free atrazine is small, and differences between the effects of GEO HA and BHL HA level out at 40 days (4.8×10^{-5}M).

The increase in reversible sorption was marked in the first 3 days. Due to the initial increase in θ_L, reversible sorption capacity of amended slurries remained higher than that of the control until about the 30 day mark. This effect is characteristic of BHL HA, and was not observed in the case of GEO HA amendment. The reversible sorption capacity (θ_C), as shown by the quasi-horizontal section of the post-inflexion plateau of the curves has been calculated as 10^{-5} M g^{-1} (Fig. 16).

Figure 20 illustrates the effect on irreversible sorption for BHL HA (θ_D). The curves show inherently first order kinetics. BHL HA amendment also leads to an increase of irreversible

sorption, the magnitude of which is in the range of 80% at 40 days for the 1% amendment. Contrary to what has been ^Xxserved for GEO HA, increasing the amount of BHL HA amendment from 0.5% to 1% is not reflected in a comparable increase of irreversible sorption. The increase of irreversible sorption was paralleled by a decrease in free atrazine in the solution, and in the initial phase of the experiment by an increase in reversible sorption.

3.2. SORPTION CAPACITY MEASUREMENTS

Reversible sorption capacity measurement of soil and HA amended soil for atrazine was undertaken in order to confirm saturation values obtained during kinetic tests. Reversible sorption capacity, θ_C, has already been obtained from the kinetic runs, as given in Table 9, simply because the arbitrarily chosen level of atrazine at t_0 was significantly more than sufficient to saturate the sites available for reversible sorption, i.e., $\theta_C << M_{At0}$. This allowed reversible sorption curves to reach a plateau after three days following the start of tests. Results of individual site saturation experiments are given on Figures 21-25 in Appendix 2. Results of labile sorption saturation experiments are summarized on Figure 6 below.

By the end of a 75 day experimental period total aggregate atrazine concentration in the slurry increased to 45 μM. At 45 μM total atrazine concentration neither of the curves reach a plateau, which indicates that reversible sorption capacity has not been reached. Comparing curve endpoints of Miniota soil as well as 1% GEO and BHL humic material amended with θ_L values in Table 9 it becomes clear that total atrazine concentration is below saturation concentration.

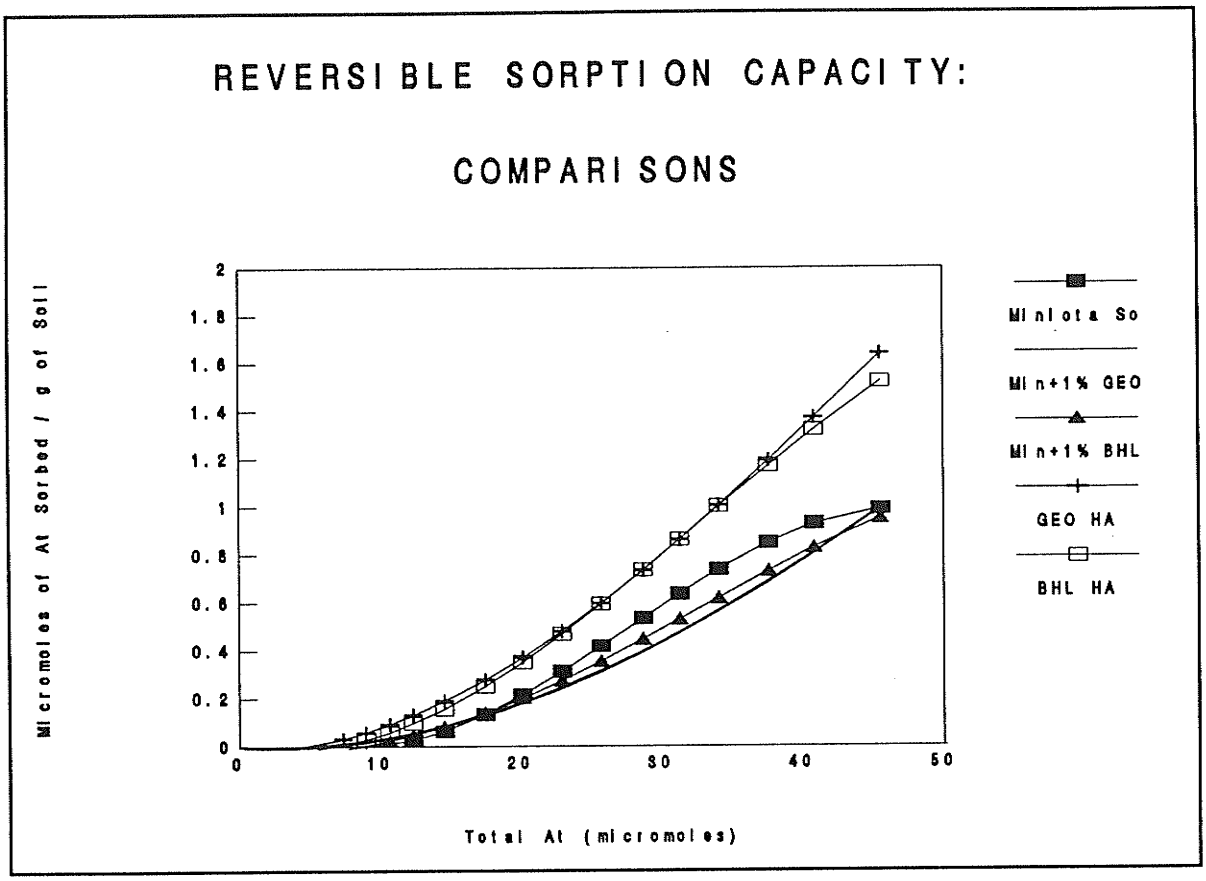

Figure 6: Kinetics of reversible atrazine sorption in Miniota soil, humic material amended soil, and humic material amendment (ticks are for line identification).

This is also true for the tested GEO and BHL HA. Interestingly, reversible sorption equilibria of both BHL and GEO HAs with no soil added are above humic material amended soil and the control soil. Although experimental results from the current tests are sufficient to describe the kinetics of reversible sorption, further tests would be necessary to clarify the ***mechanism*** beyond this phenomenon.

5. DISCUSSION

The experimental section of this project have undertaken the monitoring of atrazine chemical species under laboratory conditions with whole soil and humic material amendment. Based on the test results, the following general conclusions can be drawn:

a./ HA amendment decreased the amount of free atrazine (M_{At}) in the suspension. This result was characteristic of each HA used in the tests, in terms of magnitude of the effect. Increasing the amount of HA amendment from 0.5% to 1.0% resulted in a further small drop in free atrazine concentration in both cases.

b./ The impact on reversibly sorbed atrazine (θ_L) is characteristic of the type of HA applied. HA amendment has been shown to decrease the amount of reversibly sorbed atrazine in the case of GEO HA. Reversible atrazine sorption was initially increased in the BHL HA amended soil above control values. These observations are supported by calculated reversible sorption capacities.

c./ Both HA amendments have significantly increased the amount of irreversibly sorbed atrazine (θ_D) in the suspension. The effect is HA specific in the sense, that the GEO HA produced a significantly higher increase in irreversible sorption than the BHL HA. It is also a function of HA concentration.

Amendment of soil with SOM has been found by other authors to increase pesticide sorption capacity. Barriuso et al. (1992) studied the impact of several types of dissolved organic matter (DOM) on the adsorption of several herbicides, and concluded that adsorption of less soluble pesticides, including atrazine was increased. They found, that a tannic acid amendment resulted in increased sorption, but decreased desorption for atrazine and carbetamide. Irreversible sorption has been reported for a number of other pesticides and SOM (Schneuert et al., 1991; Martin et al., 1979; Cheng et al., 1983; Bollag and Myers, 1992).

Although for predictive purposes the availability of reversible sorption capacities and kinetic rate constants is critical, for the purposes of practical application describing irreversible sorption effects is even more important. Increased irreversible sorption due to HA amendment is of environmental importance, because potential consequences may include decreased toxicity of a given pesticide in the soil or water. Referring to Crank (1975), Gamble et al. (1994) notes that "steady state labile surface sorption drives the retarded intraparticle diffusion into a semi-infinite sink". In terms of the present experiments and comparable literature data, irreversible sorption capacity had not been reached, the rate of irreversible sorption remained positive and quasi-linear (Gamble and Khan, 1990; Gilchrist et al., 1993; Gamble et al., 1994). What has been demonstrated is higher ***rates*** of irreversible sorption for humic material amended soil. Whether higher initial rates will lead to actually higher irreversible sorption capacity should be found out in experiments where irreversible sorption rates approach zero. The demonstration of increased rates of irreversible sorption alone, however, permits the contemplation of practical applicability humic materials may have under circumstances where atrazine contamination of hydrogeological systems is a matter of concern.

There have been a number of recommendations regarding the function of humic substances in the detoxification of polluted sites. Bollag and Myers (1992) and Bollag (1992) suggest, that detoxification is possible by enzymatically coupling contaminants to humic materials. Organic pollutants oxidatively coupled to HAs are suggested to 'lose' their contaminant character, and become an integrated, inseparable part of the HA complex. Upon measuring the retention of hydrophobic organic compounds, Khan and Schnitzer (1972) commented as follows: "Since toxic pollutants can be held very tightly by humic substances, it is likely, that their concentrations in soils and sediments are often underestimated. On the other hand, humic substances may adsorb toxic pollutants in such a manner as to make them unavailable to plants and animals, so that the problem is less serious than one would expect it to be." This apparent duality of HA behaviour in relation to pollutant behaviour may be seen as a hindrance to meaningful predictions. As discussed in Chapter 2, however, this apparent duality, or rather, multiplicity of potential outcomes can be explained in significant detail by exact stoichiometry. It is true, that the stoichiometry is specific of the given HA-contaminant relationship. However, there are situations, where the nature of a contamination problem is very specific, and there is likely to be place for highly specific solutions. The need for site specific remediation objectives is also recognized by Canadian legislative authorities:

"In order to remediate a contaminated site effectively, site-specific objectives must be established with due regard for a number of factors including existing site quality, current and proposed uses, socioeconomic and technological factors, and physical factors that may affect the impact of a contaminant on the environment or human health."

(CCME, 1991)

Commercial humic materials used at the rates indicated are relatively cost effective, and environmentally safe soil amendments. Average market prices for 1994 for the kinds of HA products used in this project are in the range of C$100-130/ton, based on quantity and method of shipment. The feasibility of decontamination procedures should be assessed by comparing the effectiveness of using HAs as a decontamination medium, versus the effectiveness of available alternative methods.

Cast in the environmental economic framework of pollution control, some policy implications, data requirements, and practical complexities of deciding the optimum amount of humic material required for remediation or pollution prevention could be elucidated. For a very simplified scenario, the marginal analysis to determine the optimal level of humic material amendment requires the marginal control cost (MC_C) function for the particular technique of humic material application, and the marginal damage cost (MC_D) arising from pesticide damage be equal (e.g., Pearce and Turner, Ch. 5), as illustrated on Figure 7.

In order to obtain the MC_C function for the cleanup or prevention technique, it is not sufficient to know only the marginal change in the unit price of the humic material applied. As noted by Gamble and Khan (1992), atrazine sorption is directly related to internal variables, and reliance on humic material quantities simply causes unnecessary data scatter. Internal variables to be used in this case are related to the broader policy objectives of pollution control. Presuming that these objectives require pollutants be irreversibly removed from the system, the potential of the humic materials to increase irreversible sorption rates and capacities is of primary importance.

The

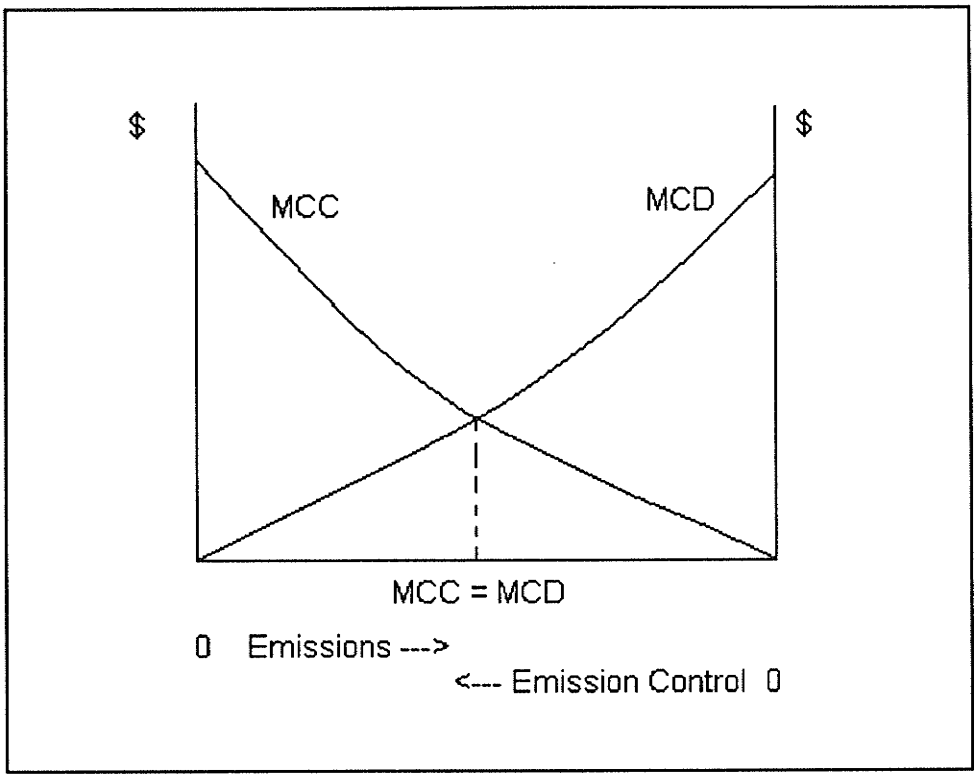

Figure 7: The principle for allocating the optimum amount of pollution control.

specificity of humic material / soil / pesticide interactions requires case-specific knowledge of irreversible as well as reversible sorption enhancing parameters. Considering a real-life agricultural field scenario, the slope of the cost function of humic material application would be also influenced by other non-pesticide related effects of humic materials, such as effect on yields or soil nutrient retention capacities.

The determination of the MC_D function would involve the determination of damage caused by increasing rates of pesticide contamination under the given circumstances. The application of standards seems to be the most frequently applied pollution abatement criterion (Table 2 and 3).

Even though standards do not necessarily lead to optimum allocation of pollution control or prevention, their application seems reasonable given the difficulties associated with expressing pesticide externalities in monetary terms (Pimentel et al., 1991; Pimentel et al., 1992).

Based on the results obtained in HPLC-MF tests, technological alternatives can be contemplated for the use of humic materials in tackling pesticide contamination risk. Such scenarios could be used to direct future research towards field experiment and technology-oriented development work.

The framework for the evaluation of pesticide pollution control alternatives is given on Figure 8.

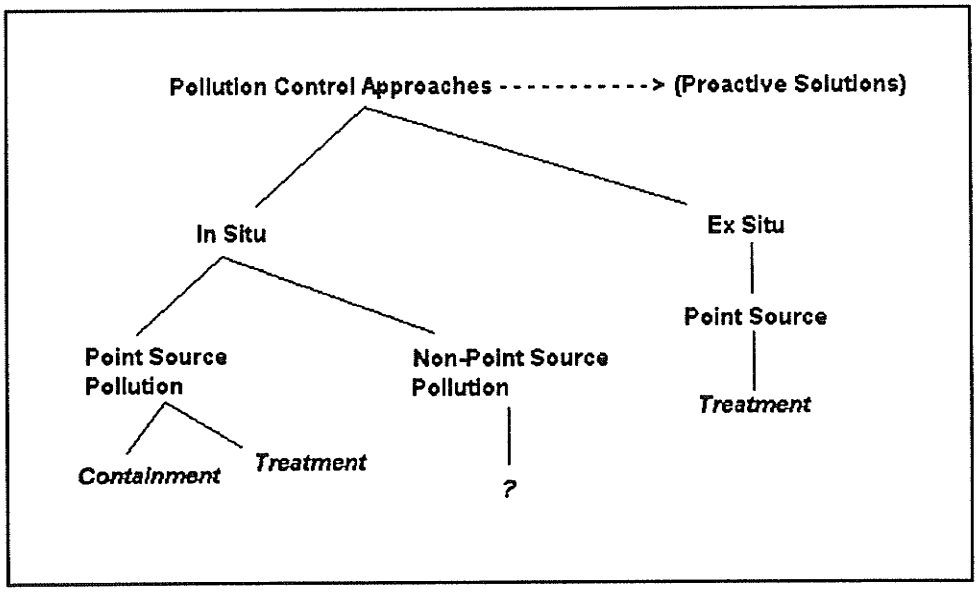

Figure 8: Framework for the evaluation of pollution control alternatives using humic materials.

In the case of point source pollution reactive pesticide pollution control technologies involve either containment, or treatment of the contaminated soil. Pesticide degradation rates may be promoted in specific cases through amending the soil with external humic material. As noted earlier, key parameters of the interacting soil, humic material as well as pesticide should be obtained prior to field scale treatment.

Humic acids migrate very slowly in the soil. Thus, if humic material amendment is simply spread on the surface, the pesticide sorption enhancing effect is limited to the upper few centimeters of the topsoil. In case the amendment is tilled in, the effect extends to the depth of tilling. Humic material amendment is not expected to significantly affect the sorption and persistence of pesticide residues below the tilled layer. Ex situ treatment may allow mixing the soil with humic substances, followed by containment until pesticide levels fall below acceptable standard values.

Pesticide from point as well as non-point sources should be prevented from leaching into groundwater or surface water supplies. In the case of point source pollution the problem is limited to a small area, non-point source pollution, however, affects extensive areas. Wu et al. (1983) found that percolation to base flow and dissolution in surface overland flow are important transport mechanisms. Paterson and Schnoor (1992) tested the capacity of riparian poplar tree buffer strips in intercepting pesticide contaminated runoff or percolating subsurface flow, thus protecting surface water supplies. Under conditions, where contaminated subsurface flow or runoff is draining into surface water bodies, humic material filled filter strips may be applied

to retain and concentrate pesticide (Figure 9).

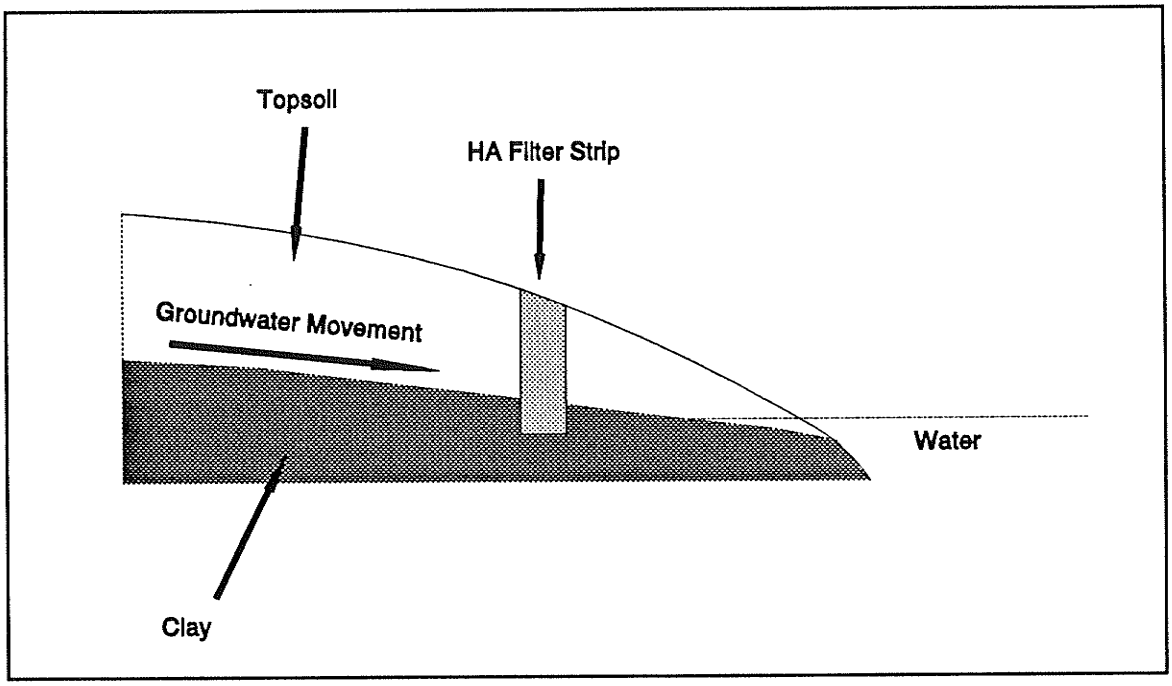

Figure 9: Conditions for the application of humic material filter strip to prevent pesticide leaching to open water bodies.

The application of humic materials in decontamination or pollution prevention technologies requires a number of basic assumptions be investigated under given field circumstances.

(a) Atrazine measured as being 'irreversibly sorbed' by HPLC-MF, the method used in the current study, should be confirmed as such by other methods, used in official confirmatory testing of pesticide residues. In Manitoba provincial government agencies do not maintain

pesticide testing laboratories. One of the major institutions involved in testing soil for pesticide residues is the Environmental Sciences Center in Winnipeg. The method used by the Environmental Sciences Center for atrazine residues involves mehtylene chloride extraction followed by gas chromatography-nitrogen phosphorus detector (GC-NPD) analysis.

(b) The pesticide measured by this method as irreversibly sorbed is to be shown as unavailable for plant uptake.

(c) Irreversibly sorbed pesticide is unlikely to desorb and migrate to groundwater.

A combination of laboratory and field experiments would be required, first to characterize soil / humic material / pesticide interactions in the laboratory, and field trials to test whether laboratory predictions can be validated under conditions where topographic, climatic as well as vegetation factors come into effect.

6. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1. SUMMARY

The effect of commercial grade humic material amendments has been tested on the sorption characteristics of atrazine, a herbicide causing groundwater contamination in the temperate zones of North America and Europe. The tests involved soil amendment with 1% and 0.5% humic material and monitoring the kinetics of atrazine chemical species over time using HPLC-microfiltration technique. Atrazine in solution (M_{At}) was measured in the microfiltrate of the soil slurry, and direct injection of the slurry provided values for the atrazine in solution plus labile sorbed state ($M_{At} + \theta_L$). Kinetically slow intraparticle diffusion (θ_D) was calculated from initial atrazine levels ($M_{At,0}$) and slurry atrazine concentrations: $\theta_D = M_{At0} - [(M_{At})_i + \theta_L]$

Both humic materials were found to decrease free atrazine concentration in the slurry, although the rates of decrease were different. Reversible sorption was decreased by GEO HA, but increased by BHL HA, as demonstrated by kinetic rate lines and calculated labile sorption capacities. Irreversible sorption was significantly increased by GEO HA, and to a lesser extent by BHL HA. The increase of irreversible sorption is of environmental importance, because it means that the rate at which atrazine becomes undetectable in the system is higher in the presence of humic material amendment. Considering that humic materials are not pure but highly variable from the analytical chemistry point of view, these differences in mode of action are not unexpected. Reversible sorption rates exhibited second order, and irreversible rates

quasi-first order kinetics, in accordance with literature data.

Based on the current test results, commercial humic materials are expected to play a role in pesticide contamination abatement. The present tests demonstrate possible effects for the case of atrazine and Miniota soil only, but comparable effects can be anticipated for some other pesticides and soils as well. Especially soils whose innate organic matter content is low should react to humic material amendment with increased pesticide sorption capacity. The concept of site specific solutions for site specific contamination problems is known and accepted by legislative authorities and the environmental remediation industry.

The economic condition for choosing the optimum amount of pollution control is interpreted for the case of humic material amendment, and irreversible sorption capacities are identified as critically important in the determination of the marginal control cost function. The currently used method did not yield irreversible sorption capacities; neither are such capacities known from the literature. Increased ***rates*** of irreversible sorption were, however, observed for humic material amended soil, which suggests potentially higher irreversible sorption capacities as well.

Because of the demonstrated effect of increasing irreversible atrazine sorption, the tested humic materials may play a role in both soil remediation and containment of pesticide polluted soil. Remediation involves either in situ or ex situ treatment techniques. Main parameters that should be considered in field application include solubility as well as polarity of the pesticide and humic material, soil pH, climatic and topographic conditions, and vegetation effects. For situations

where point-source or non-point source pollution is reaching open water bodies at tile drains, the applicability of humic materials in constructing filter strips should be investigated.

As noted in the literature review section, commercial humic material products may affect plant physiology, soil structure and microbial activity as well. Therefore, it is important, that impacts of humic material amendment on pollution abatement be considered ***in conjunction with*** effects on other environmentally and economically important components of the system. Judgements about the utility of humic materials in pesticide pollution control should be based on their cumulative impact on the given field situation.

6.2. CONCLUSIONS AND RECOMMENDATIONS

Based on the investigations undertaken, recommendations apply on one hand to the strategy of application-oriented further research, and on the other hand w the methodology used in this experiment.

1. Enhancement of irreversible sorption was the effect of the highest practical importance humic material amendment caused under the given test conditions. A procedure for the measurement of irreversible sorption capacity should be developed, that would clearly point out the highest expected irreversible loss of pesticide in the soil owing to humic material amendment. Irreversible sorption equilibria through intraparticle diffusion take very long time to achieve, and currently available methods are impracticable to determine such equilibria.

2. Atrazine or other test pesticide measured with the HPLC-MF method as irreversibly sorbed following humic material amendment, should be also confirmed as such by applicable extraction methods used in laboratories of regulatory authorities.

3. While some of the parameters relevant for pesticide remediation, such as sorption by whole soil, pH, temperature effects, organic matter content can be modelled under laboratory conditions, consideration of others, e.g., climatic or topographic effects demand field experiments. For the purposes of *ex situ* remediation in a closed system, laboratory scale models may provide sufficient information. For *in situ* containment or remediation, however, laboratory experiments should be used in parallel with field studies.

4. In case when humic materials are applied to an agricultural field with the purpose of alleviating pesticide contamination, experiments should be designed where positive yield effects are also evaluated. If positive yield effects can be also demonstrated, the marginal control cost function of humic material application in the context of pesticide contamination abatement decreases, that makes the technology more competitive. In order to examine yield effects separately, experimental design would require holding all conditions - including pesticide application - constant and studying yields at appropriately selected humic material amendment quantities.

5. The applicability of humic material filter strips preventing pesticide contamination of water bodies, as suggested in Section 5. should be tested. The applicability of the buffer zone

technique for other cases, such as hazardous waste (pesticide) storage facilities should be also investigated.

6.3. RECOMMENDATIONS FOR THE USER OF HPLC-MF

The following are observations that apply to some technical difficulties encountered in relation to the test methodology used during the current experiment, and are intended to help future investigators design similar experiments.

1. HPLC-MF is a technique that involves the injection of whole soil into the HPLC instrument. Because of the buildup of soil on frits, above-normal pressure is a frequent phenomenon. Injecting soil slurries, that have been mixed over an extended period of time causes the frits clog up faster. Designing reversible sorption capacity experiments should, therefore, pay attention to reaching reversible sorption capacity prior to clogging problems become too frequent.

2. The addition of humic materials in the current tests lead to the partial masking of atrazine peaks at 245 nm and a.u.f.s. = 0.02. This effect could have been decreased without significant loss of sensitivity if total amount of soil+HA in the test vessel was decreased from 0.5 g / 25 mL to e.g. 0.25 g / 25 mL.

3. Although the combination of Lotus 123 and the F-Curve package allowed very flexible

data analysis, the procedure requires a sequence of 5 files to obtain a fitted curve for a raw data set. The use of newer, more userfriendly packages is encouraged, that would make the data analysis more expedient.

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APPENDIX

APPENDIX 1: Chemical Species of Atrazine

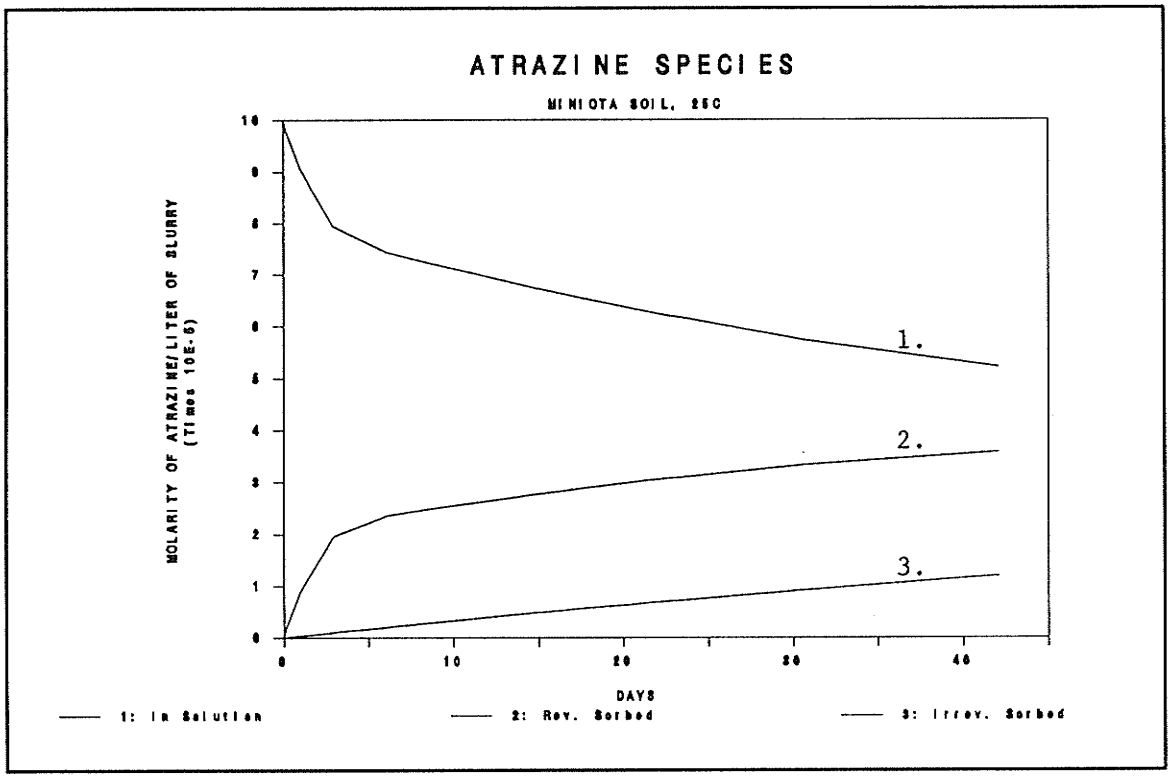

Figure 10: Chemical species of Atrazine in Miniota Sand.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
In Solution (filtrate)	0-2.9	a = 9.9440E-05	4.9842E-06
		b = -8.6021E-06	2.9689E-06
		c = 1.0032E-06	4.9403E-07
		d = -5.0575E-08	3.2077E-08
		e = 1.0899E-09	8.8488E-10
		f = -8.4123E-12	8.6983E-12
	2.9-42	a = 8.5466E-05	2.5346E-06
		b = -9.3039E-07	3.1761E-07
		c = 4.2897E-09	7.9051E-07
In Solution + Reversibly Sorbed (slurry)	0-42	a = 1.0887E-04	1.9260E-06
		b = -3.2743E-07	2.4673E-07
		c = 2.9377E-09	6.4196E-09

Constants apply to polynomial equations, corresponding to the fitted curve: $y = a + bx + cx^2 + dx^3 + \ldots$

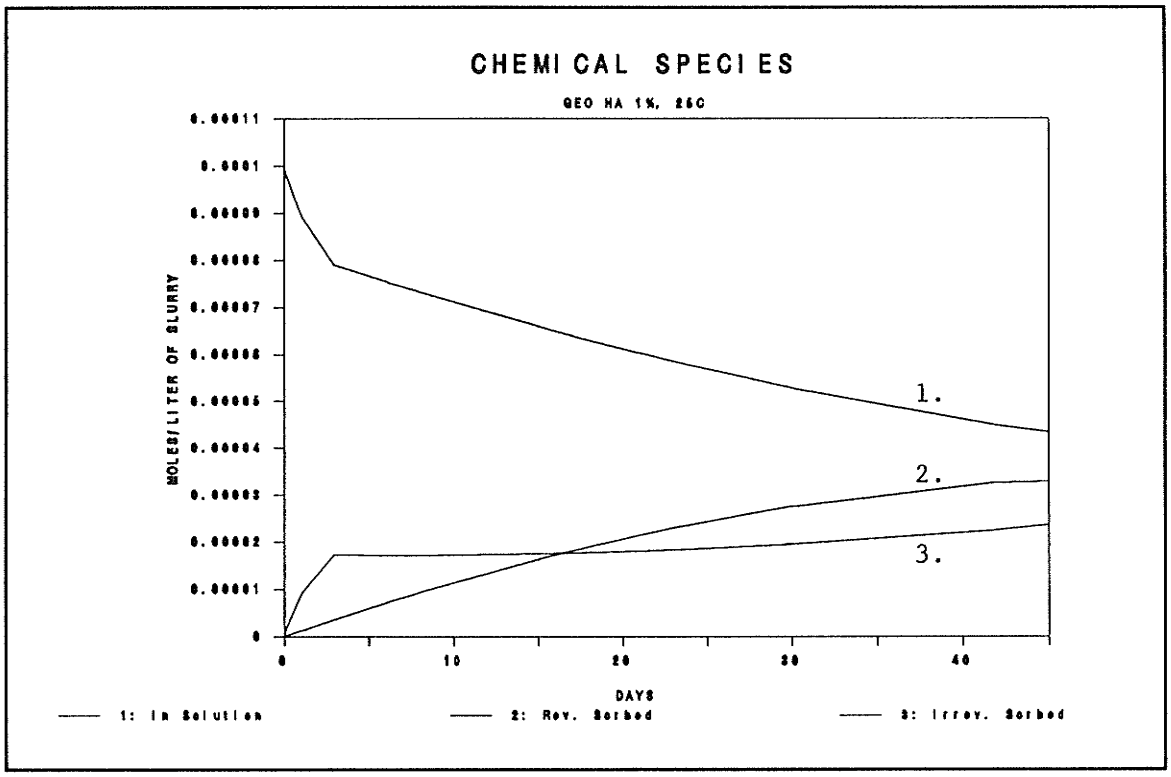

Figure 11: Chemical species of Atrazine in Miniota Sand amended with 1% GEO HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
In Solution (filtrate)	0-2.9	a = 9.9457E-05	5.2565E-06
		b = -1.0801E-05	2.9877E-06
		c = 1.2736E-06	4.9429E-07
		d = -6.5707E-08	3.2254E-08
		e = 1.4837E-09	8.9481E-10
		f = -1.2238E-11	8.8372E-12
	2.9-42	a = 8.2580E-05	3.3256E-06
		b = -1.2204-06	4.2868E-07
		c = 7.6682E-09	1.0620E-08
In Solution + Reversibly Sorbed (slurry)	0-42	a = 1.1118E-04	2.0030E-06
		b = -1.2744E-06	2.5837E-07
		c = 1.1849E-08	6.4041E-09

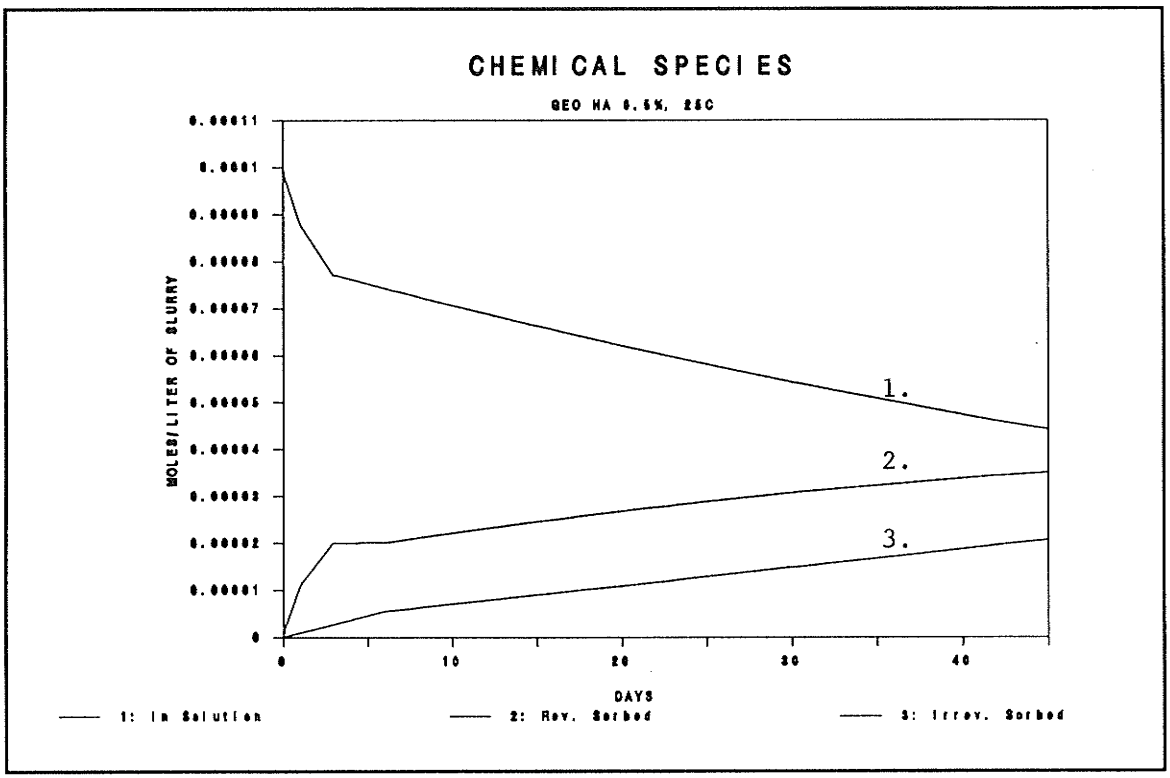

Figure 12: Chemical species of Atrazine in Miniota Sand amended with 0.5% GEO HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
In Solution (filtrate)	0-2.9	a = 9.9292E-05	7.4808E-06
		b = -1.2622E-05	4.2552E-06
		c = 1.6541E-06	7.0393E-07
		d = -9.2504E-08	4.5907E-08
		e = 2.2647E-09	1.2729E-09
		f = -2.0245E-11	1.2564E-11
	2.9-42	a = 8.0018E-05	4.5777E-06
		b = -9.6594-07	5.8923E-07
		c = 3.7489E-09	1.4587E-08
In Solution + Reversibly Sorbed (slurry)	0-42	a = 1.1336E-04	1.7622E-06
		b = -9.7889E-07	2.3058E-07
		c = 1.5036E-08	5.6643E-09
	2.9-42	a = 1.1020E-04	1.4916E-06
		b = -3.8978E-07	7.1815E-08

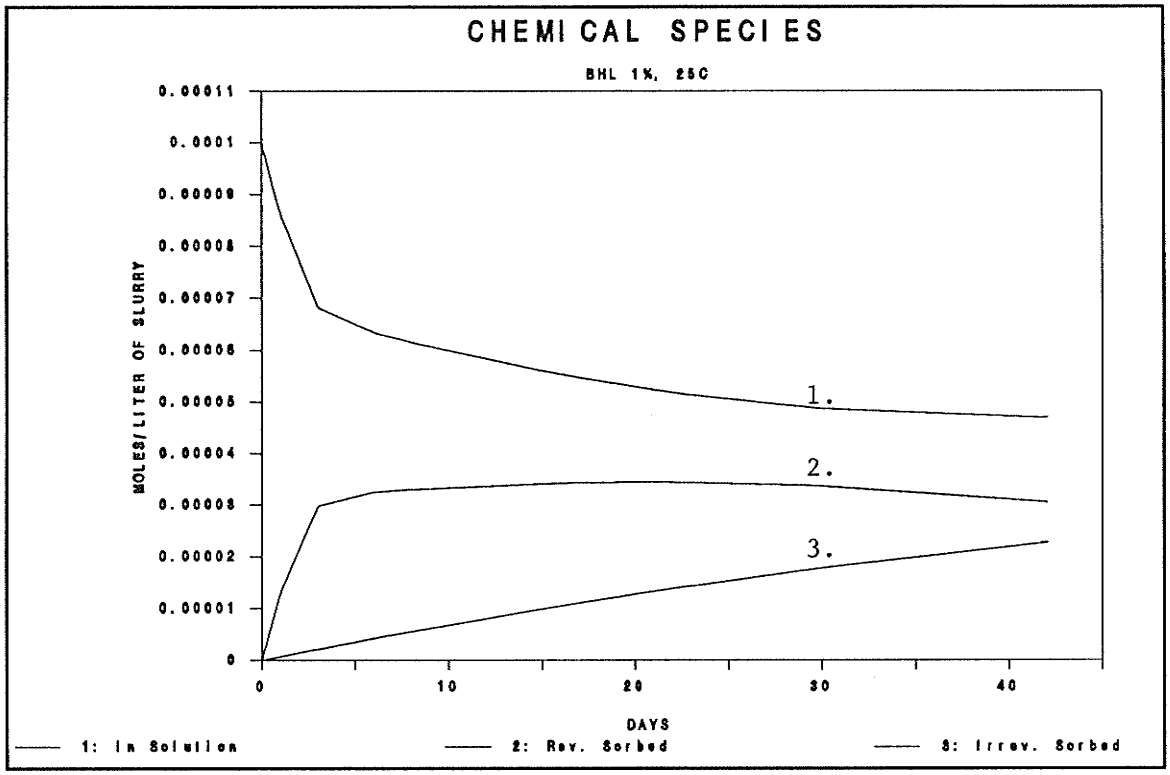

Figure 13: Chemical species of Atrazine in Miniota Sand amended with 1% BHL HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
In Solution (filtrate)	0-5.9	a = 1.0004E-04	6.5552E-06
		b = -1.5365E-05	3.8677E-06
		c = 1.8892E-06	6.5721E-07
		d = -1.0208E-07	4.3597E-08
		e = 2.4618E-09	1.2251E-09
		f = -2.1804E-11	1.2248E-11
	5.9-42	a = 6.9396E-05	3.2339E-06
		b = -1.0918E-06	4.1284E-07
		c = 1.3298E-08	1.0371E-08
In Solution + Reversibly Sorbed (slurry)	0-42	a = 1.1541E-04	1.9597E-06
		b = -7.2570E-07	2.6177E-07
		c = 4.4772E-09	6.7944E-09

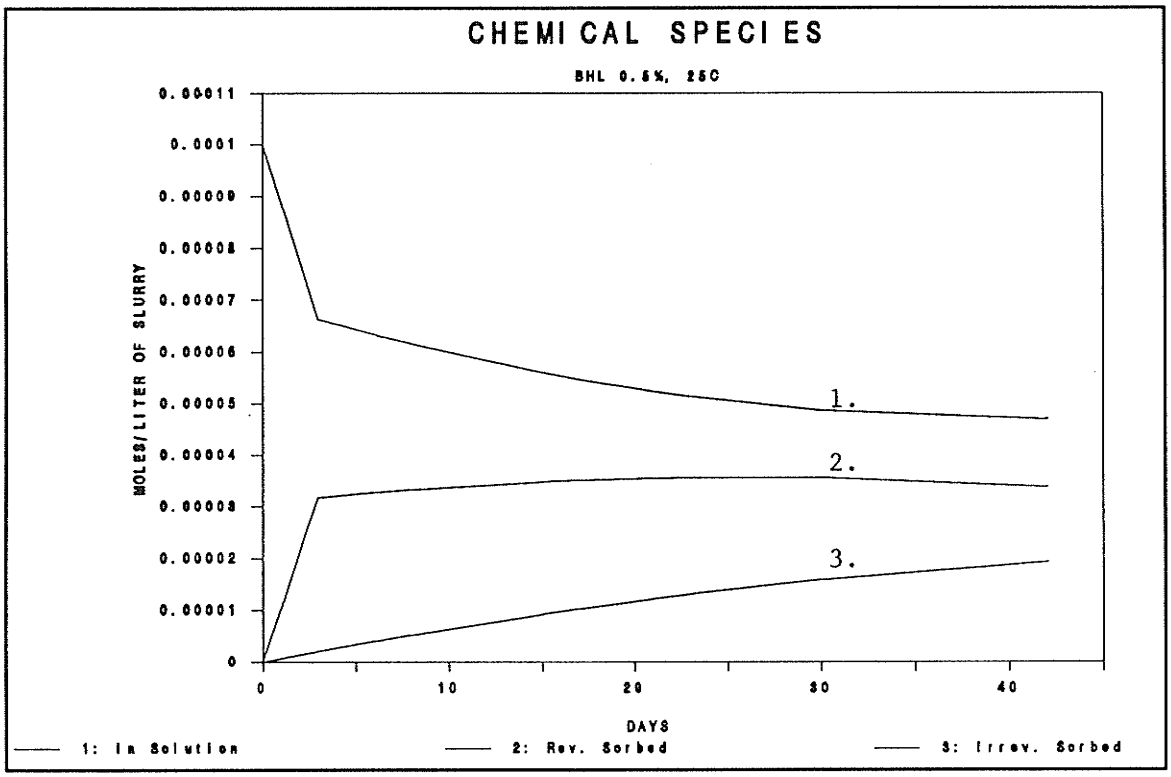

Figure 14: Chemical species of Atrazine in Miniota Sand amended with 0.5% BHL HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
In Solution (filtrate)	0-1.1	a = 9.9866E-05	4.3974E-06
		b = -1.2128E-05	1.7816E-06
		c = 9.5722E-07	1.9147E-07
		d = -2.9563E-08	7.3736E-09
		e = 3.1216E-10	9.2179E-11
	1.1-42	a = 6.9396E-05	3.2339E-06
		b = -1.0918E-06	4.1284E-07
		c = 1.3298E-08	1.0371E-08
In Solution + Reversibly Sorbed (slurry)	0-42	a = 1.0924E-04	1.6757E-06
		b = -7.0239E-07	2.2377E-07
		c = 5.7749E-09	5.8044E-09

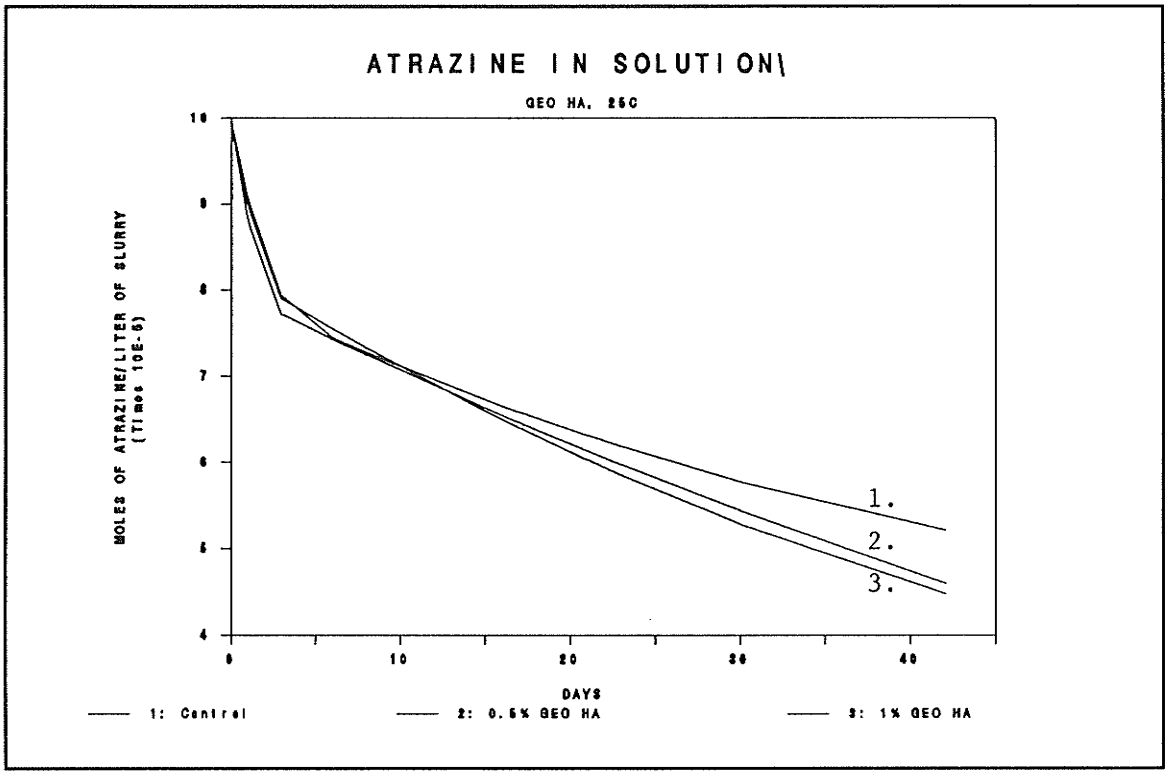

Figure 15: Impact of GEO HA (1 and 0.5%) amendment on kinetics of Atrazine in solution (M_{Al}).

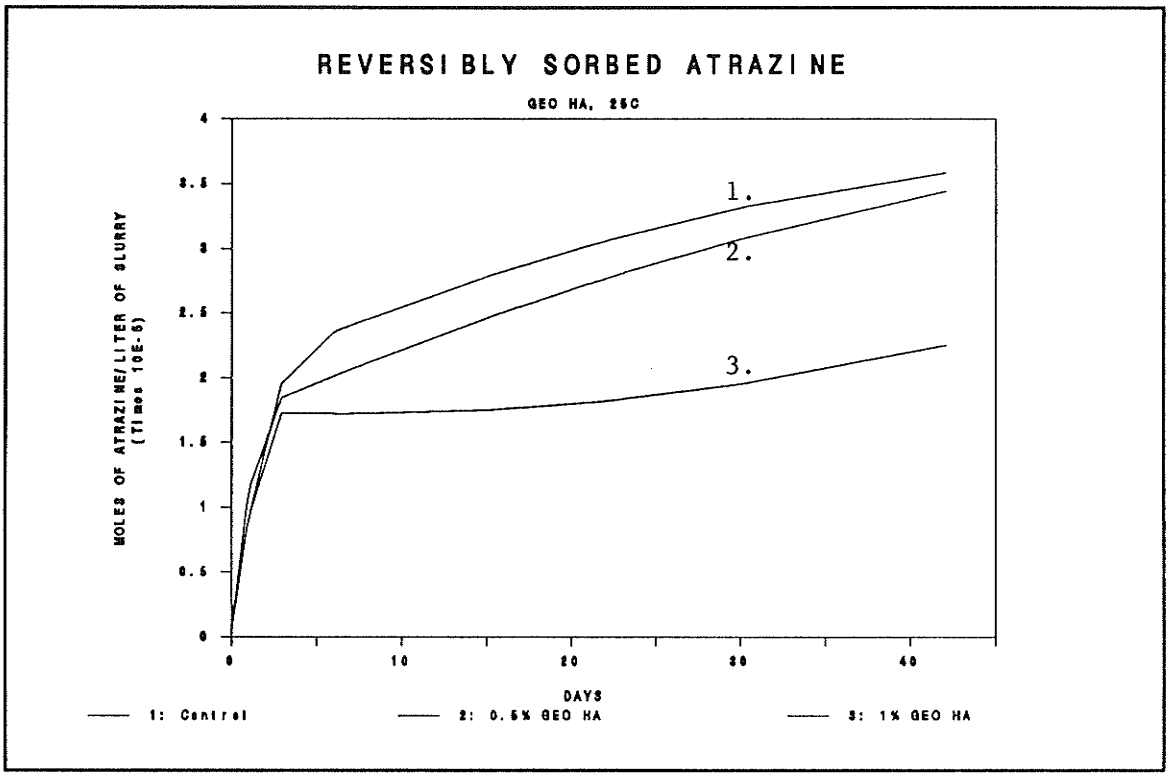

Figure 16: Impact of GEO HA (1 and 0.5%) amendment on kinetics of reversibly sorbed Atrazine (θ_L).

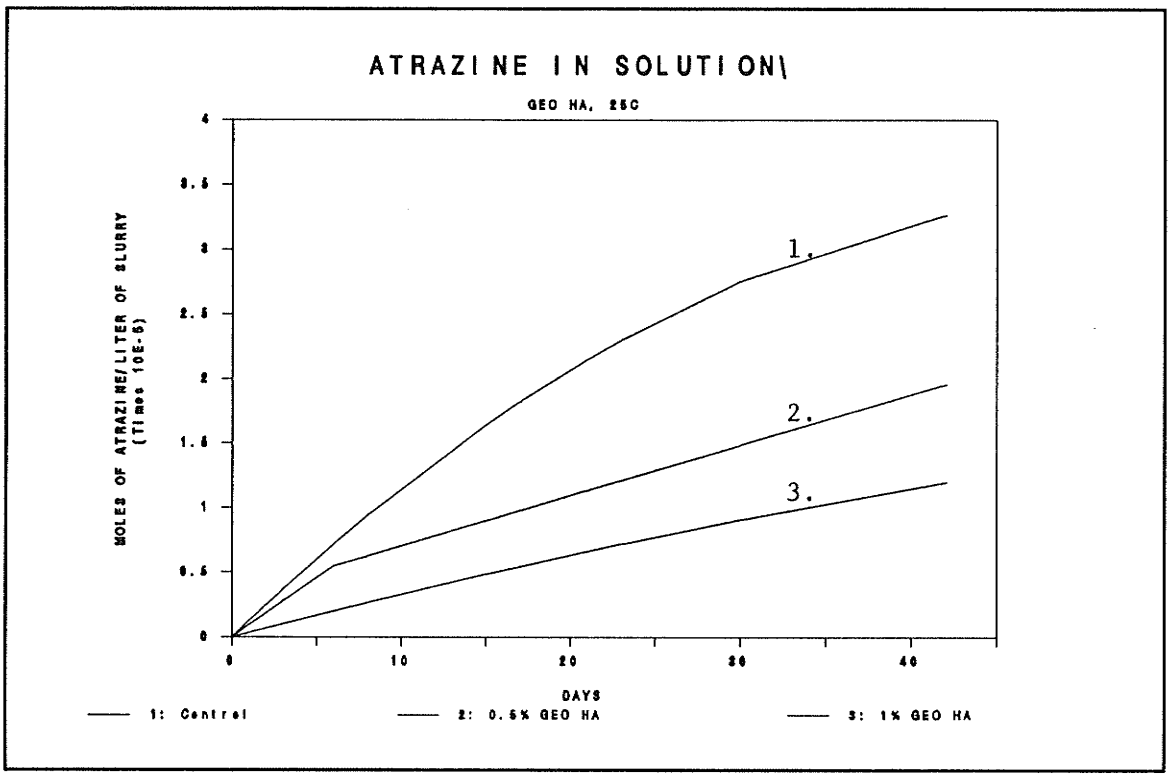

Figure 17: Impact of GEO HA (1 and 0.5%) amendment on kinetics of irreversibly sorbed Atrazine (θ_D).

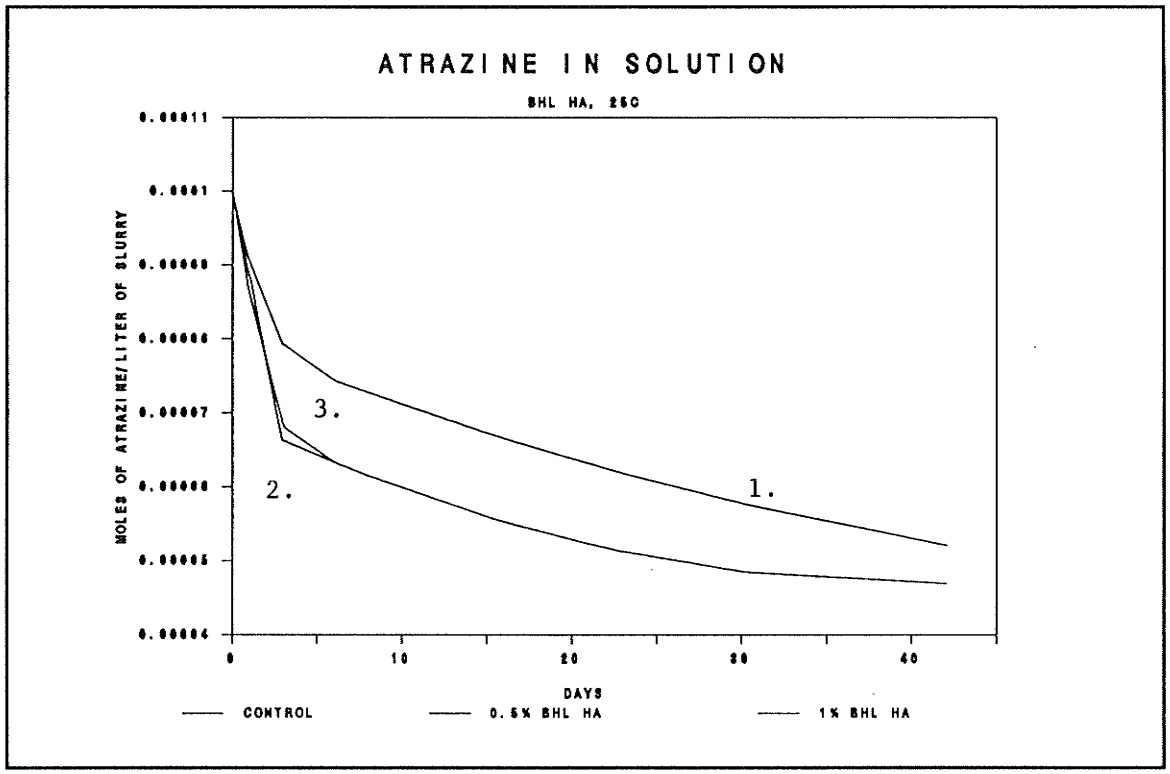

Figure 18: Impact of BHL HA (1 and 0.5%) amendment on kinetics of Atrazine in solution (M_{Al}).

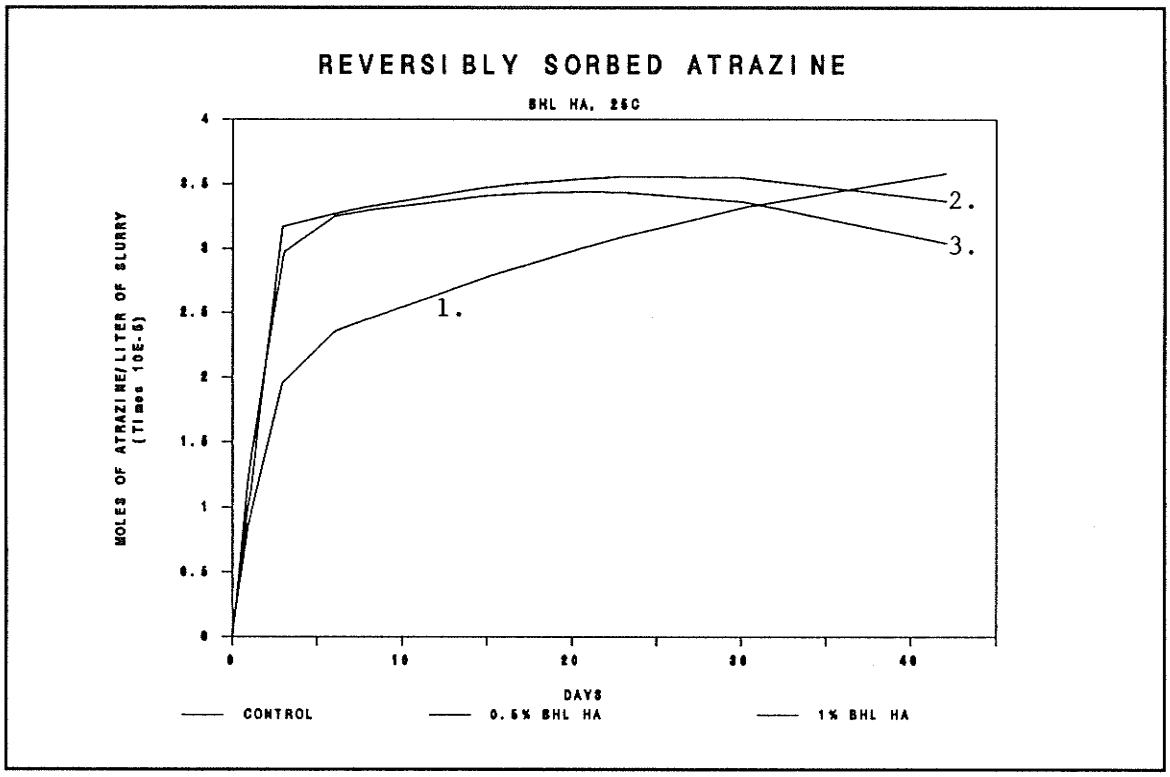

Figure 19: Impact of BHL HA (1 and 0.5%) amendment on kinetics of reversibly sorbed Atrazine (θ_L).

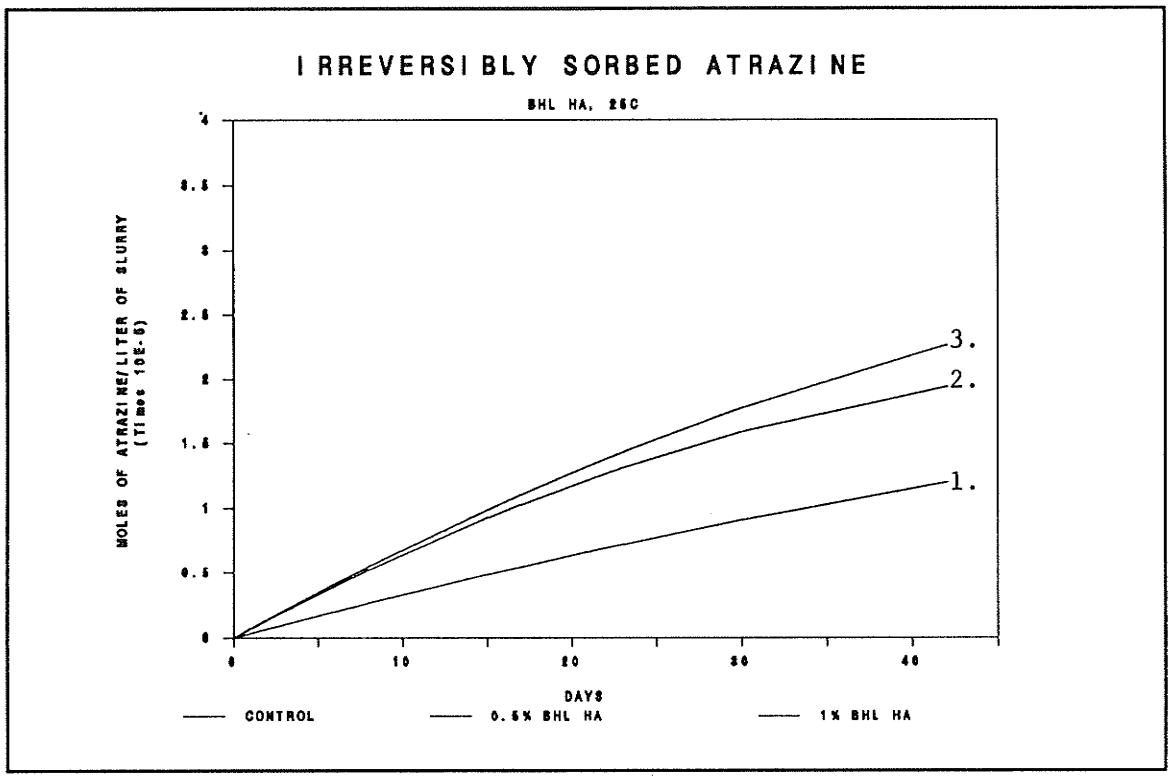

Figure 20: Impact of BHL HA (1 and 0.5%) amendment on kinetics of irreversibly sorbed Atrazine (θ_D).

APPENDIX 2: Sorption Capacity Measurements

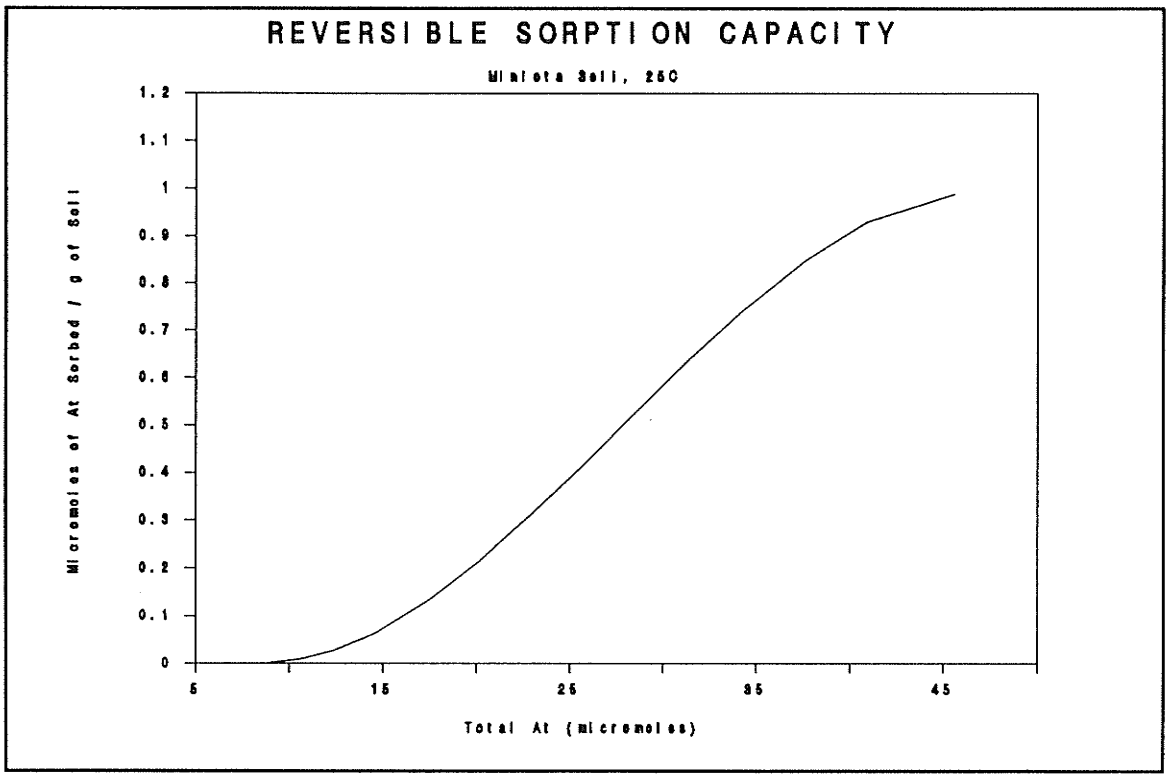

Figure 21: Surface sorption capacity of Miniota soil.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
Reversibly Sorbed	0-45	a = 1.8609E-01	6.6273E-02
		b = -4.4699E-02	1.2058E-02
		c = 3.0225E-03	5.7667E-04
		d = -3.6315E-05	7.6224E-06

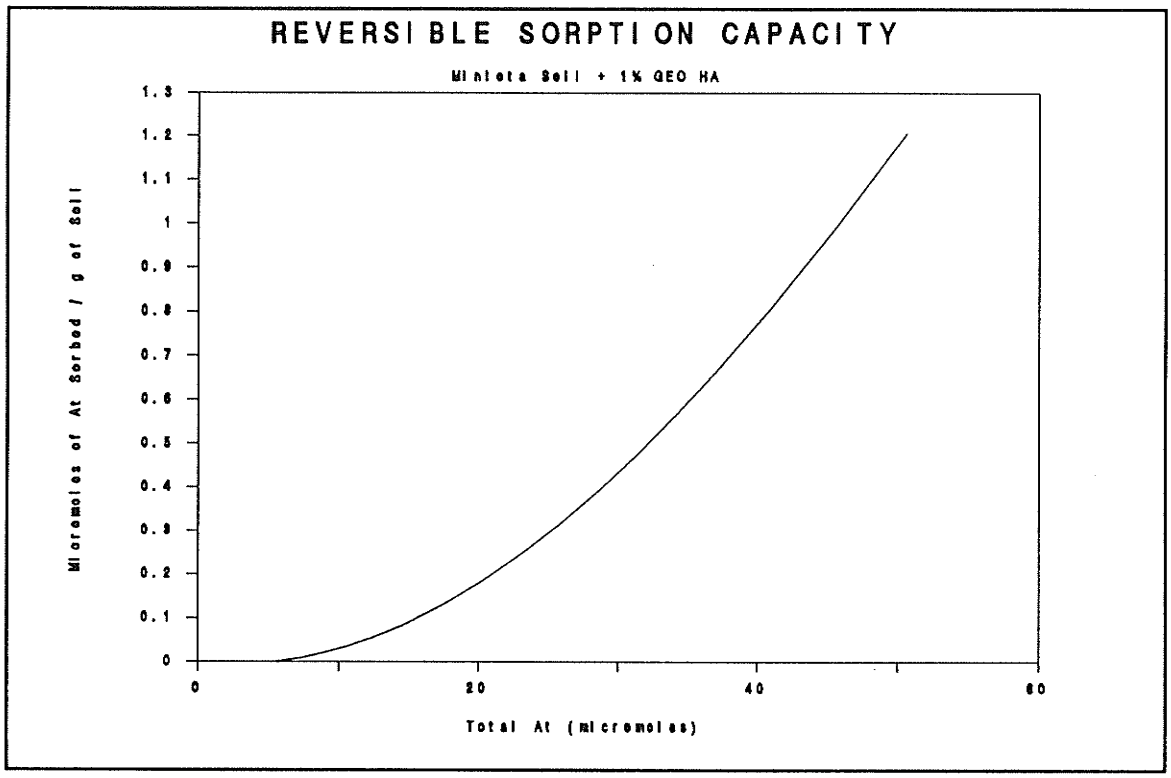

Figure 22: Surface sorption capacity of Miniota soil amended with 1 % GEO HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
Reversibly Sorbed	0-45	a = -4.3926E-04	6.8623E-02
		b = -3.7651E-03	1.2492E-02
		c = 6.9698E-04	5.9786E-04
		d = -2.9823E-06	7.9065E-06

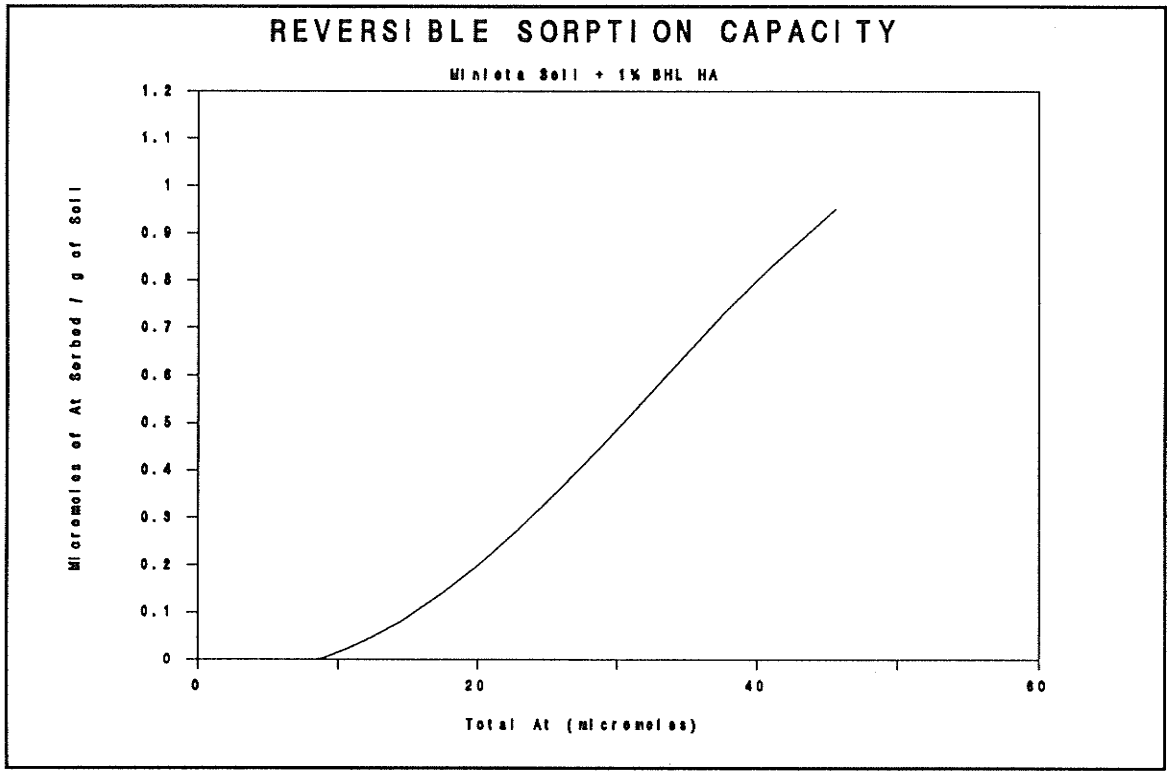

Figure 23: Surface sorption capacity of Miniota soil amended with 1 % BHL HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
Reversibly Sorbed	0-45	a = -2.2125E-02	9.0565E-02
		b = -4.5303E-03	2.7163E-02
		c = 8.3070E-04	2.3601E-03
		d = -2.7558E-08	7.2948E-07
		e = -1.2567E-07	7.2665E-07

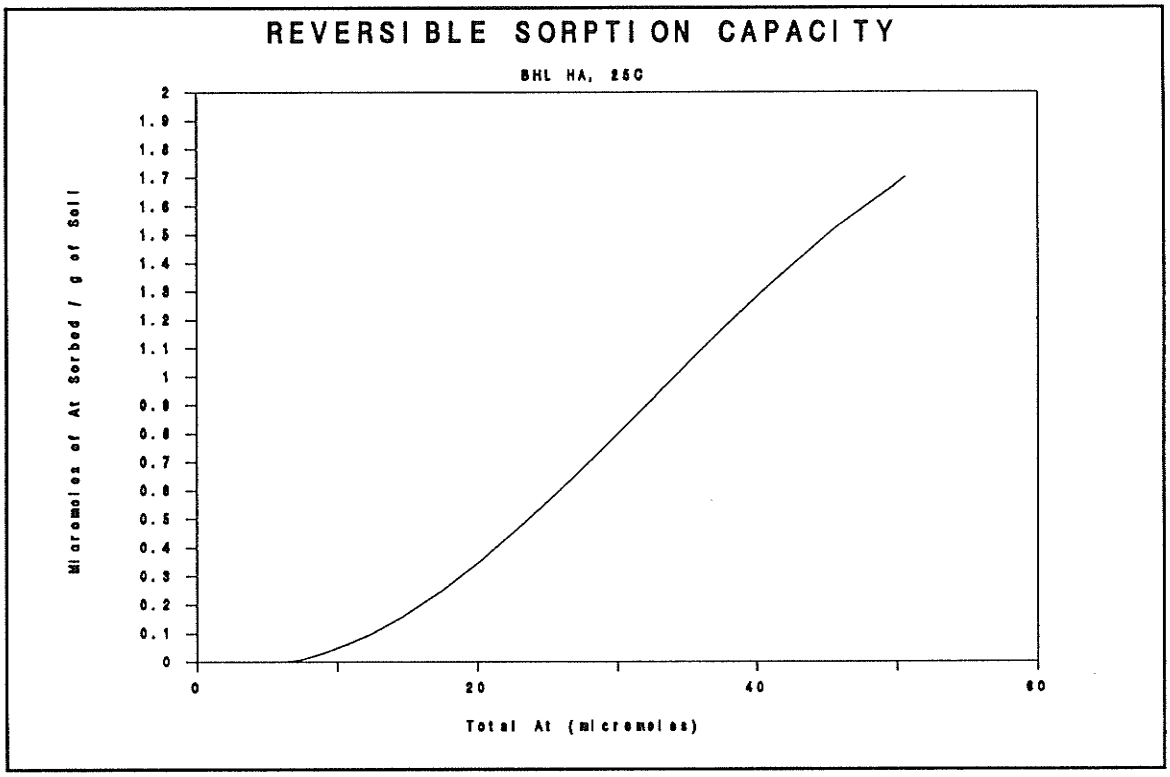

Figure 24: Surface sorption capacity of GEO HA.

Constants and Standard Deviations

Chemical Species	X-Range	Constant	SD
Reversibly Sorbed	0-45	a = -2.2125E-02	9.0565E-02
		b = -4.5303E-03	2.7163E-02
		c = 8.3070E-04	2.3601E-03
		d = -2.7558E-08	7.2948E-07
		e = -1.2567E-07	7.2665E-07

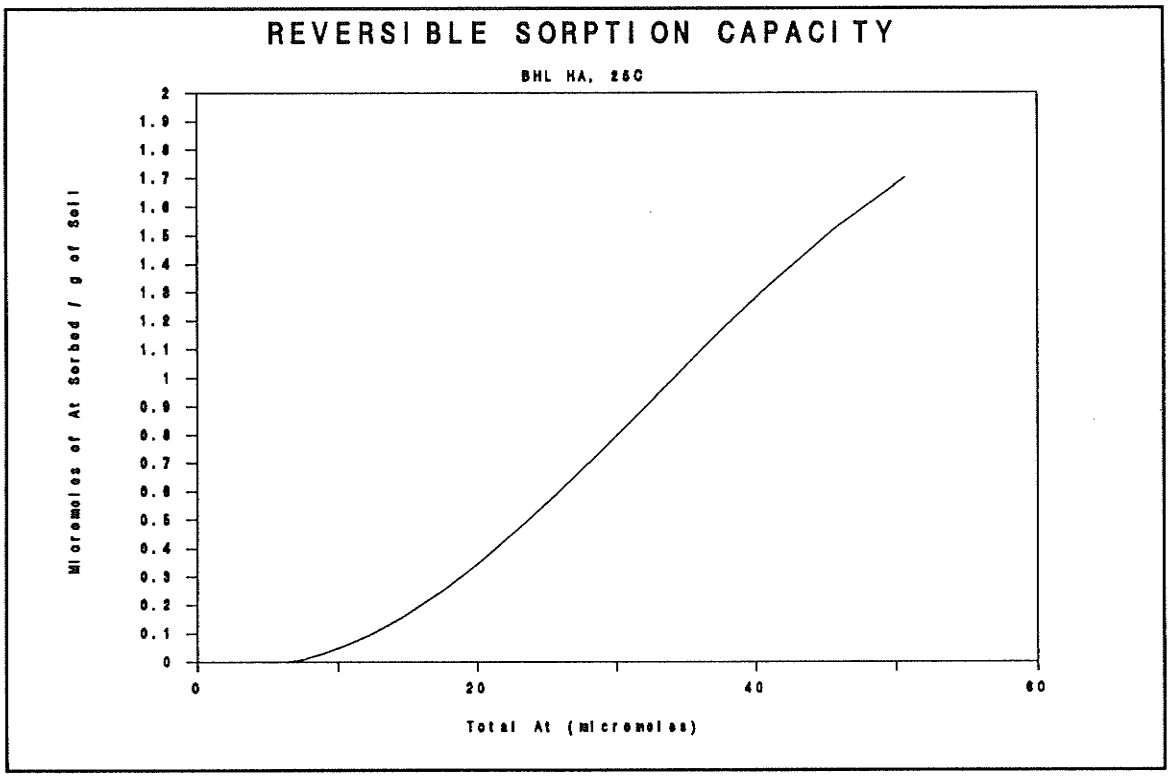

Figure 25: Surface sorption capacity of BHL HA.

Chemical Species	X-Range	Constant	SD
Reversibly Sorbed	0-45	a = 1.5850E-02	1.3142E-01
		b = -1.4377E-02	2.4434E-02
		c = 1.9389E-03	1.1754E-03
		d = -1.9708E-05	1.5553E-05

APPENDIX 3: Calculation of Atrazine Molarities

a. Atrazine Molarities in Slurry: In Solution (M_{At}) + Reversibly Sorbed (θ_L)

$$\theta_L + M_{At} = \frac{2 * s_{At} * p_s}{s1 * s2}$$

where s_{At} = concentration of atrazine standard (M)
p_s = atrazine peak height in slurry (cm)
s1 = peak height of standard injection 1 (cm)
s2 = peak height of standard injection 2 (cm)

b. Atrazine Molarities in Filtrate: In Solution (M_{At})

$$M_{At} = \frac{2 * s_{At} * p_f}{s1 * s2}$$

where s_{At} = concentration of atrazine standard (M)
p_f = atrazine peak height in filtrate (cm)
s1 = peak height of standard injection 1 (cm)
s2 = peak height of standard injection 2 (cm)

APPENDIX 4: Raw Numerical Data from HPLC-MF Experiments

ATRAZINE SORPTION IN MINIOTA CLAY - CONTROL (SLURRY)
FILE: CTGSLUR.DAT

DAYS	AT/L SLURRY
-9.027778E-03	1.113074E-04
1.063194	1.082251E-04
1.900694	1.141593E-04
3.005556	1.178073E-04
4.002083	1.015873E-04
4.819445	1.185548E-04
6.813889	9.932432E-05
7.829306	1.063908E-04
9.872222	1.059578E-04
11.81319	1.082076E-04
13.88819	1.080501E-04
16.09028	1.059022E-04
18.04236	1.027778E-04
19.91458	1.005272E-04
22.78056	1.049631E-04
23.81667	1.002747E-04
26.94028	1.059122E-04
28.96736	1.003534E-04
32.87292	1.046693E-04
35.80278	9.890909E-05
38.78542	9.950576E-05

ATRAZINE SORPTION IN MINIOTA CLAY - GEO CONTROL (FILTRATE)
FILE: CTRL.DAT

DAYS	AT/L SLURRY
1.77991E-12	8.833922E-05
1.070833	7.792208E-05
1.906944	8.00885E-05
3.013889	8.273749E-05
4.827778	8.280015E-05
6.825695	7.567568E-05
7.833333	7.351311E-05
9.883333	7.239819E-05
11.82222	7.287449E-05
13.93333	7.799642E-05
16.10069	7.082631E-05
18.05069	7.152778E-05
19.9243	6.643234E-05
22.7895	7.042254E-05
23.8430	6.730769E-05
26.9479	6.528835E-05
28.9763	6.254417E-05
32.8819	4.747082E-05
35.8145	4.909091E-05
38.7937	5.864909E-05
40.8597	4.983498E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 1% GEO HA (SLURRY)
FILE: G3SLUR.DAT

DAYS	AT/L SLURRY
1.634248E-13	1.107143E-04
1.072917	1.066667E-04
1.9125	1.140878E-04
3.017361	1.074523E-04
4.027083	1.059246E-04
4.847917	1.101056E-04
6.836805	1.027778E-04
7.836111	9.72549E-05
9.889584	1.00738E-04
11.82847	9.059475E-05
14.12431	9.615385E-05
16.09931	9.571428E-05
18.05139	9.411765E-05
19.92639	8.741259E-05
22.7993	8.88535E-05
23.85625	8.628763E-05
26.95278	8.892989E-05
28.97778	8.55615E-05
32.88403	8.863198E-05
35.81597	7.655677E-05
38.79514	7.086093E-05
40.87083	8.434505E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 1% GEO HA (FILTRATE)
FILE: G3FILT.DAT

DAYS	AT/L OF SLURRY (M)
6.944444E-03	7.892857E-05
1.079861	7.859649E-05
1.923611	7.667436E-05
3.061111	6.811352E-05
4.036111	7.109515E-05
4.85625	7.579185E-05
6.845139	7.743056E-05
7.844444	6.901961E-05
9.898611	6.863468E-05
11.83681	6.224067E-05
14.16319	6.888112E-05
16.1118	6.714286E-05
18.05972	6.851211E-05
19.93472	5.874126E-05
22.80764	6.11465E-05
23.86458	6.053512E-05
26.96111	5.904059E-05
28.98611	5.632799E-05
32.89305	5.279384E-05
35.825	4.249084E-05
38.80347	4.403973E-05
40.87917	4.664537E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 0.5% GEO HA (SLURRY)
FILE: G4SLUR.DAT

DAYS	AT/L SLURRY
2.263079E-12	1.117438E-04
1.074306	1.100719E-04
1.922917	1.168591E-04
3.070139	1.123377E-04
4.032639	1.132216E-04
4.853472	0.000106
7.023611	1.070326E-04
7.841667	1.028791E-04
9.891666	1.058394E-04
11.84097	9.992987E-05
14.14653	9.769911E-05
16.10903	1.057592E-04
18.05694	1.078571E-04
19.93611	0.00010
22.80486	9.659443E-05
23.8625	9.409836E-05
26.98542	8.419118E-05
28.98403	9.946524E-05
32.89028	1.020561E-04
35.85139	9.525617E-05
38.8	9.786536E-05
40.87639	9.756888E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 0.5% GEO HA (FILTRATE)
FILE: G4FILT.DAT

DAYS	AT/L SLURRY
6.944444E-03	7.900356E-05
1.08125	6.834533E-05
1.93333	7.806005E-05
3.08263	6.818182E-05
4.04097	6.256983E-05
4.87847	7.309487E-05
7.03263	7.204117E-05
7.85	7.754318E-05
9.899305	7.372263E-05
11.85	5.539972E-05
14.1636	6.265486E-05
16.11736	7.678883E-05
18.06528	6.142857E-05
19.94444	6.486486E-05
22.81389	6.346749E-05
23.87222	5.868853E-05
26.99444	6.360294E-05
28.99236	5.418895E-05
32.89028	5.383178E-05
35.83333	5.047438E-05
38.80972	4.597701E-05
40.89097	4.376013E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 1% BHL HA (SLURRY)
FILE: B3SLUR.DAT

DAYS	AT/L SLURRY
-3.073097E-12	1.212121E-04
0.9694445	1.113079E-04
2.027083	1.085973E-04
2.991667	1.16996E-04
4.185417	1.148362E-04
5.025	1.121043E-04
7.113889	1.081967E-04
9.121528	7.968254E-05
11.18125	1.011364E-04
14.1875	1.082927E-04
18.06528	1.103448E-04
19.98056	9.954198E-05
22.06667	0.00010
23.86319	1.04878E-04
26.23958	9.683098E-05
27.99792	9.52862E-05
30.19514	9.702277E-05
32.22847	9.963235E-05
34.06736	0.00010
37.18681	9.378531E-05
40.02847	9.113924E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 1% BHL HA (FILTRATE)
FILE: B3FILT.DAT

DAYS	AT/L SLURRY
8.333334E-03	9.250399E-05
1.19375	6.967818E-05
2.036111	6.606335E-05
3.000695	6.640316E-05
4.167361	7.475915E-05
5.033333	6.405959E-05
7.122917	6.065574E-05
9.129167	4.698413E-05
11.19306	5.454545E-05
14.19722	5.821138E-05
18.14028	6.394985E-05
19.9868	4.854962E-05
22.0757	4.948097E-05
23.87083	5.888502E-05
26.23333	4.964789E-05
28.00486	5.016835E-05
30.20417	4.378284E-05
32.23542	0.00005
34.07292	4.43686E-05
37.19236	5.235405E-05
40.0368	4.367089E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 0.5% BHL HA (SLURRY)
FILE: B4SLUR.DAT

DAYS	AT/L SLURRY
3.232969E-12	1.114007E-04
1.179861	1.085383E-04
2.022917	1.055556E-04
2.989583	1.126214E-04
4.193056	1.080769E-04
5.022222	1.02693E-04
7.114583	1.003322E-04
9.118055	8.878505E-05
11.18056	9.816594E-05
14.18681	9.818182E-05
18.12153	1.027778E-04
20.15208	1.002011E-04
22.07847	9.787234E-05
23.85833	9.478992E-05
26.2368	9.646643E-05
27.99167	9.066214E-05
30.19236	9.340278E-05
32.22292	9.680851E-05
34.06111	8.721311E-05
37.18889	9.504587E-05
40.02639	8.772455E-05

ATRAZINE SORPTION IN MINIOTA CLAY AND 0.5% BHL HA (FILTRATE)
FILE: B4FILT.DAT

DAYS	AT/L SLURRY
9.027778E-03	8.729642E-05
1.188194	7.901592E-05
2.029861	6.697531E-05
2.997917	6.951456E-05
4.201389	6.615384E-05
5.030556	6.355475E-05
7.123611	5.348837E-05
9.128472	4.485981E-05
11.19028	4.978166E-05
14.19583	5.39394E-05
18.13611	5.62963E-05
20.16042	4.825737E-05
22.09653	5.640074E-05
23.89305	5.07563E-05
26.24514	5.441696E-05
27.99931	5.195246E-05
30.19931	4.930556E-05
32.23056	5.319149E-05
34.06805	5.016393E-05
37.19653	5.504587E-05
40.04375	4.94012E-05

REVERSIBLE ATRAZINE SORPTION IN MINIOTA SOIL
FILE: MINSORP.DAT

DAYS	AT/L SLURRY
-1.629417E-12	0.00000
1.843333	2.457002E-02
3.456445	0.00000
5.598834	-0.1521739
7.390833	-3.527337E-02
8.974	1.841621E-02
10.66683	-1.956947E-02
12.35508	0.0907441
14.57672	0.1489758
17.49144	0.1234568
20.15533	0.1717557
22.97011	0.3639847
25.76078	0.4008016
28.74822	0.6508875
31.38256	0.4341317
34.15805	0.7956989
37.67151	0.7647059
40.88311	0.9343936
45.57311	1.142857
40.60261	0.8866995

REVERSIBLE ATRAZINE SORPTION IN MINIOTA SOIL + 1% GEO HA
FILE: MINGSORP.DAT

DAYS	AT/L SLURRY
-1.177796E-12	0.00000
1.774889	0.00000
3.475889	-4.158004E-02
7.391222	-5.434782E-02
8.973611	0.00000
10.66683	0.04000
12.35033	1.814882E-02
14.58061	5.639098E-02
17.49144	0.1992032
20.16506	0.1698113
22.96856	0.1848429
25.75805	0.305499
28.74667	0.54000
31.38411	0.4265403
34.15572	0.683112
37.67361	0.6013746
40.91111	0.5872194
45.56844	1.386139
50.5995	1.163311

REVERSIBLE ATRAZINE SORPTION IN MINIOTA SOIL + 1% BHL HA
FILE: MINBSORP.DAT

DAYS	AT/L SLURRY
-7.241851E-13	0.000000
1.806389	-4.587156E-02
3.474333	-2.083333E-02
7.392	-3.846154E-02
8.974389	-1.915709E-02
10.66722	5.964215E-02
12.34956	0.0358423
14.58256	7.220217E-02
17.49261	0.160000
20.17478	0.2111324
22.96856	0.2083333
25.75572	0.4025424
28.74744	0.7027027
31.38839	0.3044872
34.15533	0.6533575
37.67205	0.535117
40.915	0.9345794
45.56417	1.047619
50.60144	0.5830904

REVERSIBLE ATRAZINE SORPTION IN GEO HA
FILE: GEOSORP.DAT

DAYS	AT/L SLURRY
1.267324E-12	0.00000
1.805222	0.00000
3.472778	0.041841
5.604278	-5.221932E-02
7.392	0.00000
8.974	0.00000
10.66761	3.952569E-02
12.41956	0.1642036
14.581	0.1462523
17.49183	0.2750491
20.16039	0.5692599
22.94056	0.3846154
25.753	0.6779661
28.74394	0.8709176
31.38605	0.790378
34.15222	1.092279
37.66895	0.866426
40.91383	1.173228
45.56533	2.109705
50.59639	1.781609

REVERSIBLE ATRAZINE SORPTION IN BHL HA
FILE: BHLSORP.DAT

DAYS	AT/L SLURRY
0.00000	0.00000
1.799778	0.1470588
3.476278	0.00000
5.598444	-0.1435407
8.968945	-3.558719E-02
10.6645	0.00000
12.41489	3.527337E-02
14.57633	0.1937985
17.48833	0.4008016
20.16583	0.4051565
22.967	0.4562738
25.746	0.4848485
28.73656	0.8978328
31.45605	0.7804878
34.14522	0.9060403
37.66233	1.237113
40.90761	1.657251
45.55639	1.00000
50.58706	1.904762