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CONTAMINATION ATTENUATION INDICES FOR SANDY SOILS: TOOLS FOR INFORMATION TRANSFER

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ABSTRACT

The inherent characteristics of sandy soils--rapid permeability, low organic matter and clay content, limit their ability to degrade and attenuate movement of contaminants. In areas with shallow aquifers overlain by sandy soils, the risk of contamination is generally considered great. Nevertheless, well monitoring data and column studies have shown differences in rates and amounts of atrazine leakage beneath seemingly similar sandy soils. Intrinsic differences among these soils may explain the differences in transport rates. The objective of the study was to characterize the major chemical properties of the mineral and organic components of five sandy soils (representing a broad range of the variation found in the State) and relate them to adsorption of atrazine.

The estimates of the secondary crystalline Fe-oxides and noncrystalline Fe- and Al-oxides did not significantly correlate with the adsorption coefficients (K_d) of atrazine. No significant correlation resulted between the clay content, silt content and pH, and the K_ds. The amount of organic carbon (% OC) was the most important constituent in terms of atrazine adsorption, the correlation coefficient (r) was 0.95. When the correlation was done by horizon, r increased to 0.98 for the A horizons, and decreased to 0.85 for the B horizons. Physical properties that affect rate and pathways of water movement differ among the soils examined. We postulate from data obtained in this and allied studies, that sandy soils with very uniform grain size and no morphological evidence of hydrological discontinuities are associated with rapid transport of water and probably less potential for contaminant adsorption than those with more heterogeneous particle size distributions.

INTRODUCTION

Sandy soils in Wisconsin cover approximately 20% of the State or 7 million acres (Hole, 1976). The inherent characteristics of sandy soils--rapid permeability, low organic matter and clay content--limit their ability to attenuate movement and degradation of contaminants.

The pattern of contamination in sand-groundwater systems of Wisconsin is highly variable. Atrazine, the most widely-used pesticide in Wisconsin, has been detected with the largest frequency beneath the sandy soils of the Lower Wisconsin River Valley (LWRV) (as summarized by Wollenhaupt et al., 1990). Yet, aquifers beneath characteristically similar sandy soils elsewhere, with similar agricultural practices, such as the Central Sands Region of Wisconsin do not have the high frequency and degree of contamination (Wollenhaupt et al, 1990). Column

studies by Fermanich et al. (1990) have shown that solute transport rates of atrazine are greater in a Sparta soil from the LWRV than in a Plainfield soil from the Central Sands area of Wisconsin. Their study indicates that intrinsic differences among these soils may explain the difference in transport rates. Such properties include organic matter, crystalline clays, oxide coatings and clays, and mineralogy.

Both the Sparta and Plainfield soils are mapped in the LWRV and in the Central Sands. Differences in inherent soil properties may exist between these two regions, which are not accounted for in soil survey information. Small differences in sandy soil properties (e.g., clay, % OC) can have a profound effect on the chemical/physical properties related to the mobility of organic-chemicals. Soil survey information is not structured for providing detailed interpretations of the potential for contaminant migration to the groundwater. Soil properties that influence contaminant behavior need to be identified, so that interpretations/leaching potentials can be developed.

Many studies have shown a strong relationship between the adsorption of atrazine and the amount of soil organic matter (Weber et al., 1969; Dunigan and McIntosh, 1971; Hamaker and Thompson, 1972; Kanazawa, 1989; Raman and Narayana, 1989). However, this relationship is not simple, because the chemical and physical nature of organic matter varies between soils (Talbert and Fletchall, 1965; Valverde-Garcia et al., 1989). When the organic matter content is small, the mineral or organo-mineral phases become more important (Stevenson, 1972). The mineral and organic-mineral phases may be especially significant in sandy soils, where the organic matter content is usually very low, relative to finer-textured soils. Pure iron oxides alone have shown very little, if any, interaction with atrazine (Borggaard and Striebig, 1988), but when in association with other components of the soil, an interaction may occur (Huang et al., 1984). Imogolite and allophane, common in volcanic soils, have recently been found in Spodosols and Spodosol-like soils (Yoshinaga et al., 1984; Kodama and Wang, 1989). Imogolite and allophane are suspected to be in Wisconsin soils (Hole, 1976), but have never been identified. The role of these aluminosilicate clays on contaminant adsorption is poorly defined. There are inconsistencies in the literature in relating the different mineral components of the soil and adsorption of atrazine. Mineralogical analysis of Wisconsin's sandy soils is very limited. Madison and Lee (1965) determined some of the mineralogical characteristics of sandy soil from across different regions of the state. Li et al. (1983) did a mineralogical analysis of the Omega loamy sand (very fine sand, fine silt, and clay fractions) with respect to buffer potential and acid precipitation. Whittig and Jackson (1956) studied the clay mineralogy of the Omega loamy sand. In summary, there is no comprehensive information available on the properties, abundance, and distribution of minerals in

Wisconsin's sandy soils.

The objectives of this study are: 1) To characterize the major chemical properties of the mineral and organic components for a diverse range of sandy soils; 2) To determine the adsorption coefficient (K_d) for atrazine by horizon and correlate (with the data obtained in objective 1); 3) To identify soil morphological features that may be used as an index of, or proxy for, chemical characteristics that correlate well with K_d's; 4) To characterize some physical/morphological properties that influence hydrology.

MATERIALS AND METHODS

Soils

Five sandy soils were selected for this study (Fig. 1): (1) Sparta sand (sandy, mixed, mesic Entic Hapludolls) from the Lower Wisconsin River Valley; (2) Plainfield sand (mixed, mesic Typic Udipsamments) from the Central Sands area; (3) Tarr sand (mesic, uncoated Typic Quartzipsamments) from the Black River Valley; (4) Shawano sand (mixed, frigid Typic Udipsamments) from Shawano County; (5) Rousseau fine sand (sandy, mixed, frigid Entic Haplorthods) from Marrinette County (see Tables 1-5, for soil descriptions).

The soils were chosen to represent a broad range of differences in morphology, mineralogy, origin of organic matter, and particle size. The Sparta and the Tarr soils represent the darker and thicker (Mollic) surface horizons developed under prairie vegetation. Sparta and the Tarr soils differ in their mineralogy. The Plainfield, Shawano, and Rousseau represent soils formed under forest vegetation, which have a shallower surface horizon and more developed subsurface horizons. The Plainfield soil differs from the Shawano soil in particle size, land history (cropped vs. uncropped), and mineralogy. The Rousseau soil represents the most developed of the sands, having an albic and a spodic diagnostic subsurface horizon. All soils are well drained, with the exception of the Rousseau, which is moderately well drained.

The soils were also chosen based on their geomorphic/geologic settings. The Sparta and Tarr soils are in river valleys formed in glacial outwash sands. These deposits are fairly uniform (particle size) with depth. The Plainfield soil is in a glacial-lake plain (Glacial Lake Wisconsin) and formed in acid glacial outwash sands. This glacial lake is stratified with Pleistocene deposits. The Rousseau and Shawano soils are in smaller glacial-lake plains and formed in glacio-lucustrine deposits. Both of these areas have been reworked by wind, and sand dunes are present. These materials are stratified underneath the aolian deposits. In Wisconsin, soils formed in stratified materials tend to have a more diverse mineralogy than those formed in uniform deposits.

Methods

Soil samples were taken from each horizon, air dried (in the greenhouse) and passed through a 2-mm sieve. The following analyses were determined on all samples: pH (1:1), organic matter (Walkley Black), and cation exchange capacity (0.1 M barium chloride).

Characterization of Mineralogy

Samples from each horizon, of each soil, were pretreated to remove the organic matter (hydrogen peroxide) and free iron oxides (citrate-bicarbonate-dithionite) (Kunze and Dixon, 1986). The sand was separated from the silt and clay by wet sieving (53 μm sieve). The sand was then dried at 105°C, and dry-sieved into coarse, medium, fine, and very fine sand fractions and weighed. Heavy and light minerals were separated by the use of a heavy liquid, sodium-polytungstate, at specific gravities of 2.96 and 2.74 (Whitton and Churchman, 1987). At a specific gravity less than 2.74, the quartz and feldspars were isolated. A staining method to quantitatively determine feldspars and quartz was used (Reeder and McAllister, 1957). In the heavy mineral fraction (sp. gr. > 2.96), a magnet was used to isolate the magnetic minerals. Mineralogy of the sand fractions was determined optically with a petrographic microscope. The Scanning Electron Microscope with Energy Dispersive X-ray Spectrum (SEM-EDS) and reference samples were also used to aid in mineral identification. Grain counts were done with an image analysis system.

The silt fraction was separated from the clay fraction by gravity sedimentation (Whitton and Churchman, 1987) and weighed. The silt fraction was also separated into heavy and light fractions using sodium-polytungstate as outlined previously. Identification and quantification were the same as for the sand. Mineralogical analysis of the clay fraction was determined semi-quantitatively by X-ray diffraction, by peak area integration. Total elemental digestions (Lim and Jackson, 1982) of the different fractions was also run as needed to aid in mineral identification.

Characterization of the Coatings

The organic portion of the coating was sequentially extracted to determine percent of fulvic acids (FA), humic acids (HA), and humin (Rice and MacCarthy, 1989; Schnitzer and Schuppli, 1989). The A horizons containing significant amounts of organic matter was fractionated into HA, FA, and humin. The B horizons were fractionated into FA and HA. The resultant organic fractions were estimated as a weight percent. For the oxide portion of the coating, selective dissolution of Fe and Al using 0.1 M pyrophosphate (pH 10), 0.2 M acid-oxalate (pH 3) and dithionite-citrate (Blakemore et al., 1987) was used to quantify Fe- and Al-humus complexes, allophane and imogolite, ferrihydrite and secondary crystalline Fe (geothite, hematite). Iron, Al,

Si, and Mn concentrations in the extractions were determined using an inductively-coupled plasma emission (ICP) spectrophotometer.

Atrazine Adsorption Coefficients

Adsorption coefficients were determined for each horizon, of each soil. One-tenth of part per million of C-14 labeled atrazine in 0.01 M $CaCl_2$ solution was used (Kanazawa, 1989). A 1:1 ratio of C-14 labeled atrazine to weight of soil was used (2 g of soil in 2 mL 0.1 ppm atrazine). The samples were shaken for 24 h and then centrifuged at 2000 rpms for 30 min. One-half a milliliter of the solution was added to 10 mL of scintillation cocktail and counted on a liquid scintillation counter.

RESULTS AND DISCUSSION

There are differences in some of the chemical/physical properties of the sands that might affect the fate and transport of organic chemicals (tables 6-10). Based on differences in percent organic carbon, adsorption would be expected to differ because atrazine adsorption is known to positively correlate with the amount of organic carbon, which will be discussed in later sections. pH can have an effect on adsorption by creating adsorption sites on pH-dependent constituents (Green and Corey, 1971) and by affecting the solubility of atrazine (Oades, 1989). On variable-charged components (Fe-oxide surfaces, Fe and Al amorphous materials, edges of clays, organic constituents), increasing the pH increases the negative surface charge for adsorption. Since the pKa of atrazine is 1.7, at higher pHs, the amount of protonated species would be very small. For this reason, adsorption via electrostatic attraction would not be significant. The field descriptions and particle size data provide important empirical information about soil attributes that might affect water movement among the five soils. The hydrological properties of these sands greatly affects the fate and transport of organic chemicals. Textural discontinuities (stratified materials) with depth disrupts water flow because of the change in amount and size of connective pore spaces. Uniform materials have faster water flows. The textures of the Tarr and Sparta soils are fairly uniform with depth, and the sand coarseness increases with depth. By increasing the size of sand grains, the size of pores created by the sand grains also increases. The clay and silt content decrease with depth, so there is less finer materials filling these sand pore spaces. Given this scenario, water flow should increase with depth. The Shawano and Plainfield soils are texturally stratified with depth, causing impeded, slowed or horizontally directed water flow. Evidence of impeded and slowed water is depicted in their morphology by presence of mottles. Impeded water flow may be expected to increase the contact time between atrazine and potential adsorption surfaces and thus reduce contaminant leakage to the groundwater.

Secondary Oxide Coatings and Clays

The three most commonly used dissolution techniques for estimating the various Fe fractions are sodium pyrophosphate, acid-oxalate, and citrate-bicarbonate-dithionite (CBD) techniques. Sodium pyrophosphate-extractable Fe (Fe_d) is a dissolution via a solubilization or peptization mechanism (Jeanroy and Guillet, 1981), where the adsorption of pyrophosphate onto soil particles increases the negative charge of the particles and thereby increases their solubility in water (Borggaard, 1988). Amorphous colloids or gels of metal organic complexes are dispersed at the same time (Beckett, 1989). The acid-oxalate extractable Fe (Fe_o) extracts the noncrystalline and poorly ordered oxides by complexation at pH 3 (Borggaard, 1988). The stability constant for trisoxalate Fe^{3+} (Sillen and Martell, 1964) clearly demonstrates the stability of this complex compared to Fe-oxides at pH 3. Oxalate is a strong ligand and also dissolves Fe in organic complexes (Borggaard, 1988), and disperses organic matter (Beckett, 1989). The CBD technique, dithionite extractable Fe (Fe_d), uses dithionite, a strong reductant, to reduce Fe^{3+} in the most insoluble Fe oxides (geothite, hematite) to Fe^{2+}, a more soluble form (Borggaard, 1988). Also Fe from water soluble, exchangeable, and organically-bound phases is extracted.

The Fe_d extracted the largest amounts of Fe. The Fe_o was next, with the Fe_p extracting the least amount of Fe. This trend was evident in all soils (Fig. 2-6). The B horizons contained the largest amounts of extractable Fe, with lesser amounts in the A horizons and sharply dropping off in the C horizons. The Plainfield Bw4 had the largest amount of Fe_d followed by the Rousseau Bt.

Crystalline Fe-oxides can be estimated by subtracting the Fe_o from the Fe_d. This gives a fair estimate of the pedogenic crystalline Fe-oxide content (Borggaard, 1988). The Plainfield Bw4 horizon contained the largest amount of estimated crystalline Fe (4000 mg Fe kg^{-1}) followed by the Shawano Bw1 and Rousseau Bt at about 1500 mg Fe kg^{-1}). The smallest crystalline Fe-oxide contents were in the Sparta soil (750 mg Fe kg^{-1}). The degree of crystallinity and kind of pedogenic Fe-oxides, in subsoil accumulations, are a function of the weathering regime (climate, vegetation, drainage), parent materials (type and amount of Fe-bearing minerals), and age under which it is forming. The older soils, which do not always have a more developed soil, usually contain the largest amounts of pedogenic crystalline Fe-oxides, because with time, the noncrystalline Fe-oxides crystallize. The major inhibiting materials of crystallization are organic matter, silicate, and phosphate (Schwertmann, 1985). The Rousseau soil, which is the most developed, does not contain the most crystalline-Fe. The Plainfield Bw4 contained almost three times as much crystalline-Fe than the Rousseau soil, which could be explained by differences in 1) amount and type of Fe-bearing minerals in the parent materials, 2) pH of the parent materials and,

3) difference in age, 4) hydrology.

The organic matter content of the soils examined in this study is small, thus the inhibiting effect of humic substances on Fe-oxide crystallization would be small. The soils are dominated by sand (greater than 90%), which through weathering (mainly of feldspars) releases Si, which can be a major inhibiting factor in Fe-oxide crystallization (Schwertmann, 1985). The Fe_o/Fe_d ratio decreases as the crystalline-Fe-oxide amounts increase. The ratio Fe_o/Fe_d was plotted against the Si_o content of the B horizons only. The correlation coefficient (r) was 0.84 (n=10). However, no significant correlation was found between organic matter and the Fe_o/Fe_d ratio (B horizons only).

The amorphous or noncrystalline Fe-oxide contents can be estimated by subtracting the Fe_p from the Fe_o. In general, the estimated crystalline Fe-oxide contents were larger than the estimated noncrystalline Fe-oxide contents, except for the Rousseau soil, which had a larger noncrystalline Fe-oxide content. Dithionite does extract some of the Fe from primary Fe-oxide (magnetite) (Walker, 1983), which are present in all of these sands. This may explain the higher estimates of crystalline Fe-oxides.

The largest estimate of noncrystalline Fe-oxides was in the Rousseau soil (2400 mg Fe kg^{-1}). The next largest was in the Shawano, then the Plainfield and the Sparta and Tarr sand with the least (250 mg Fe kg^{-1}). The trends are what would be expected; the soils with greatest influence from podzolization contained the largest amounts of noncrystalline Fe-oxides. The Rousseau soil shows the most distinctive differentiation among horizons and the Sparta and Tarr soils the least.

The Na-pyrophosphate-extractable Fe extracts Fe complexed with organic matter. The largest Fe_p was in the Shawano A horizon, which contains the largest organic matter content. In the other soils the trend follows that Fe_p increases in the B horizons and gradually decreases to negligible amounts in the C horizons. The Fe_p of the B horizons are roughly the same for all soils (500 mg Fe kg^{-1}), except the Plainfield Bs having half as much Fe_p. The low Fe_p of the Plainfield soil could be due to the loss of unstable organic matter when the pre-settlement pine vegetation community was converted to cropland. The Fe_os are larger than the Fe_p in all cases, and the amounts of Fe_o and Fe_p tends to increase in the B horizons and then decrease. Both the Fe_o and Fe_p follow the same pattern with depth.

Dithionite does not selectively dissolve any Al-oxide mineral phase, so Al_d values do not indicate any Al-oxide phase. Silica in the acid-oxalate comes from the dissolution of allophane, imogolite, and ferrihydrite. Experimental evidence suggests that acid oxalate is an effective reagent for dissolving allophane and imogolite (Parfitt, 1990).

An estimate of the noncrystalline Al-oxides (allophane, imogolite) can be done by subtracting

the Al_p from the Al_o. The largest estimates of noncrystalline Al-oxides were in the Rousseau Bt (4500 mg Al kg^{-1}). The Shawano soil had the next highest estimates of 1100 mg Al Kg^{-1}. The Sparta and Plainfield soils had about the same estimates of noncrystalline Al-oxides (500 mg Al kg^{-1}), with the Tarr soil having the least (250 mg Al kg^{-1}).

In comparison with the noncrystalline Fe-oxide estimates, the amounts of noncrystalline Al-oxides were about the same as for the Fe, except for the Rousseau soil. The Al in the Bt horizon of the Rousseau was 2000 mg kg^{-1} higher than the Fe content. This is below the E horizon (albic) in which comparatively more weathering of the minerals has occurred. Aluminum is less mobile than Fe and will accumulate below the elluviation zone (Podzolisation). The Al_p is greater than the Fe_p in the Sparta, Tarr and Rousseau soils, and about the same as in the Plainfield and Shawano soils (Fig. 6-10).

Based on quantity, the Si_o indicates,, the presence of allophane and/or imogolite (Parfitt, 1990). The distribution of Si, in the five soils, increases with depth to the lower B horizons, and then decreases in the Cs (Fig. 11-15). The Plainfield soil has a fairly random distribution of Si_o because of the stratification, which disrupts water flow and affects drainage. The Rousseau Bt has about five times more Si_o than the other four soils. Based on literature values for Si contents, where allophane has been identified in soils, the Si_o comes within the range of these values. It is suggested that allophane might be present in the Rousseau soil, but further analysis is needed.

The Mn_o and Mn_d is mostly Mn that was occluded or substituted in the Fe and Al oxides. Manganese is weakly associated with organic matter (Gambrell and Patrick, 1982). The amount of Mn is comparatively small and decreases rapidly with depth.

Organic Matter Fractions

Organic matter from the five soils was separated into FA and HA. Only the organic matter in the A horizons was further separated to isolate the humin fraction.

The Sparta HAs decreased with depth and was present in small amounts in the C horizon. The Plainfield soil contained the same amount of HAs in the A horizon as the Sparta, but had lesser amounts with depth, and contained no HAs in the BC or C horizons. The Plainfield soil contained almost twice as much organic matter in the A horizon than the Sparta soil, giving larger amounts of FAs, which decrease with depth. FA's were present in all horizons of all soils. The Sparta soil is a Mollisol (prairie) and the Plainfield soil is an Alfisol (forest). The profile distribution of HA/FA is what would be expected for these soils. The humus of Histosols and grassland soils (Mollisols) have larger amounts of humic acid than that of forest soils (Alfisols, Spodosols, and Ultisols), and

the latter have correspondingly larger amounts of fulvic acids (Stevenson and Vance, 1989). Novak and Smeck (1991) compared HAs and FAs from an Alfisol (forest soil) and a Mollisol (prairie soil) from Ohio. Their data suggest Mollisol HAs to contain more aromatic and carboxylic acids, and Alfisol HAs to contain more phenolic-OH groups and lignin and lignin-like products. Only minimal differences were noted between the FAs of the Mollisol and Alfisol.

Mineralogy

Sand and Silt

The heavy fraction (sg > 2.97) ranges from 0.1% in the Tarr soil to 3.3% in the Rousseau soil (Fig. 16-20). In the Sparta and Tarr soils, there are larger amounts of heavy minerals at the surface that decrease with depth and then change abruptly at textural discontinuities.

The silt fraction of all soils contained a larger percent of heavy minerals than the sand fraction. The percent of heavy minerals of the sand fraction remained fairly consistent with depth, showing little change due to pedogenic weathering. The percent heavy minerals of the silt fraction varied with depth, usually showing increases in the B horizons and slight decreases in the C horizons (where there is no textural discontinuity). Mineral composition of the heavy fraction consists of mostly amphiboles, pyroxenes, garnet, and magnetite.

Mineral composition of the light sand fraction (sg < 2.74) consists of quartz, K-feldspars and plagioclase in order of decreasing abundance when present. The Tarr sand fraction consists of greater than 99% quartz. Quartz dominates about 70 to 85% of the sand fraction in the other soils. The Sparta and Plainfield sands contain about the same percentages of minerals. The Shawano and Rousseau sand fractions have higher amounts of feldspars, with the Shawano sand fraction having the largest feldspar content.

The mineral composition of the silt fraction, in all soils, is similar to the sand fraction except there are higher feldspar percentages.

Clays

The clays of the Sparta, Tarr, Plainfield, and Shawano soils are dominated by vermiculite and chlorite, with small amounts of illite. Smectite is present in tiny amounts in a few of the horizons in the Plainfield soil and all of the horizons of the Sparta soil. It is suggested that the smectite content was inherited and is part of the parent material or was deposited by aolian sources. The Tarr and Shawano soils contain no smectite.

The Rousseau soil has significant changes with depth in its clay mineralogy that can be explained by pedogenic processes. In the E horizon, smectite is the dominant clay mineral. It is suggested that the smectite weathered from the Fe-chlorites, which are unstable at pHs less than 6

under severe leaching and oxidizing conditions (Borchardt, 1989). The Bt (below E) is almost completely composed of chlorite/kaolinite and vermiculite. The Bw (below Bt) is of the same composition as the Bt, with some smectite present.

Quartz was present in all horizons, and feldspars were present in lesser amounts in some horizons of all soils

Atrazine Adsorption Coefficients

The adsorption coefficient for Atrazine (K_d) was determined on each horizon of all five soils (Tables 11-15). The largest K_d's were in the A horizons and then decreased with depth. The largest K_d was in the Shawano A horizon (4.69), which is over four times that of the next highest K_d, the Plainfield Ap horizon (1.03). The Sparta A horizon had the lowest surface K_d (0.64). The K_d of the Rousseau organic layer was not determined.

Since organic matter is the major constituent of soil that sorbs atrazine, the K_ds were normalized for differences in organic matter content. This is done by dividing the K_d by the percent organic carbon. The K_{oc}s varied from 1.19 to 2.56 for the A horizons, and from 0.40 to 15.50 for the subsurface horizons. This indicates that organic matter, especially in the subsurface horizons, is not the only contributing factor in the sorption of atrazine. When the organic matter content is low, the mineral or organic-mineral phases become important (Stevenson, 1972).

The correlation coefficient (r) between the K_ds and organic matter content was 0.95. Similar correlations were also obtained by Weber et al. (1970), Dunigan and McIntosh (1971), Hamaker and Thompson (1972), Kanazawa (1989), Raman and Narayana (1989). When just the A horizons were correlated, r increased to 0.98. The organic matter content in the B horizons were correlated against the K_ds, r decreased to 0.84. When the C horizons were correlated against the K_ds, no significant correlation resulted. No significant correlation resulted among the K_ds and clay content, silt content and pH, even when the A, B, and C horizons were correlated separately. It is suggested that an individual clay mineral species (e.g., smectite) might correlate. Correlation coefficients were also determined between the oxide coatings and K_ds. There was no significant correlation between the K_ds and the estimates of crystalline Fe-oxides and noncrystalline Fe- and Al-oxides even when the A, B, and C horizons were correlated separately.

CONCLUSIONS

The estimates of crystalline Fe-oxides were the largest component of the oxide coatings and clays. The amounts of noncrystalline Fe- and Al-oxides were about the same. The Rousseau Bt

contained the largest amounts of Al_o and Si_o , indicating the presence of allophane. Neither the crystalline nor the noncrystalline Fe- and Al-oxide estimates significantly correlated with the K_ds. The clay minerals that are dominant in these sands are chlorite and vermiculite. No significant correlation resulted between the clay content and K_ds, but an individual clay species might correlate. Percent organic carbon is the most important constituent in these sands for atrazine adsorption. The %OC was positively correlated to Atrazine adsorption (0.95). When the correlation was done by horizon, r increased to 0.98 for the A horizons, and decreased to 0.85 for the B horizons. No correlation resulted for the C horizons. Based on the wide range of K_{oc}s obtained, especially in the subsurface horizons, some of the mineral and/or organic-mineral phases are providing adsorption sites for atrazine. There could also be differences in the chemical properties of the organic matter (e.g., different FA/HA ratios) between soils and with depth. The Sparta soil had the least restricting soil for water flow and contained the lowest surface K_d.

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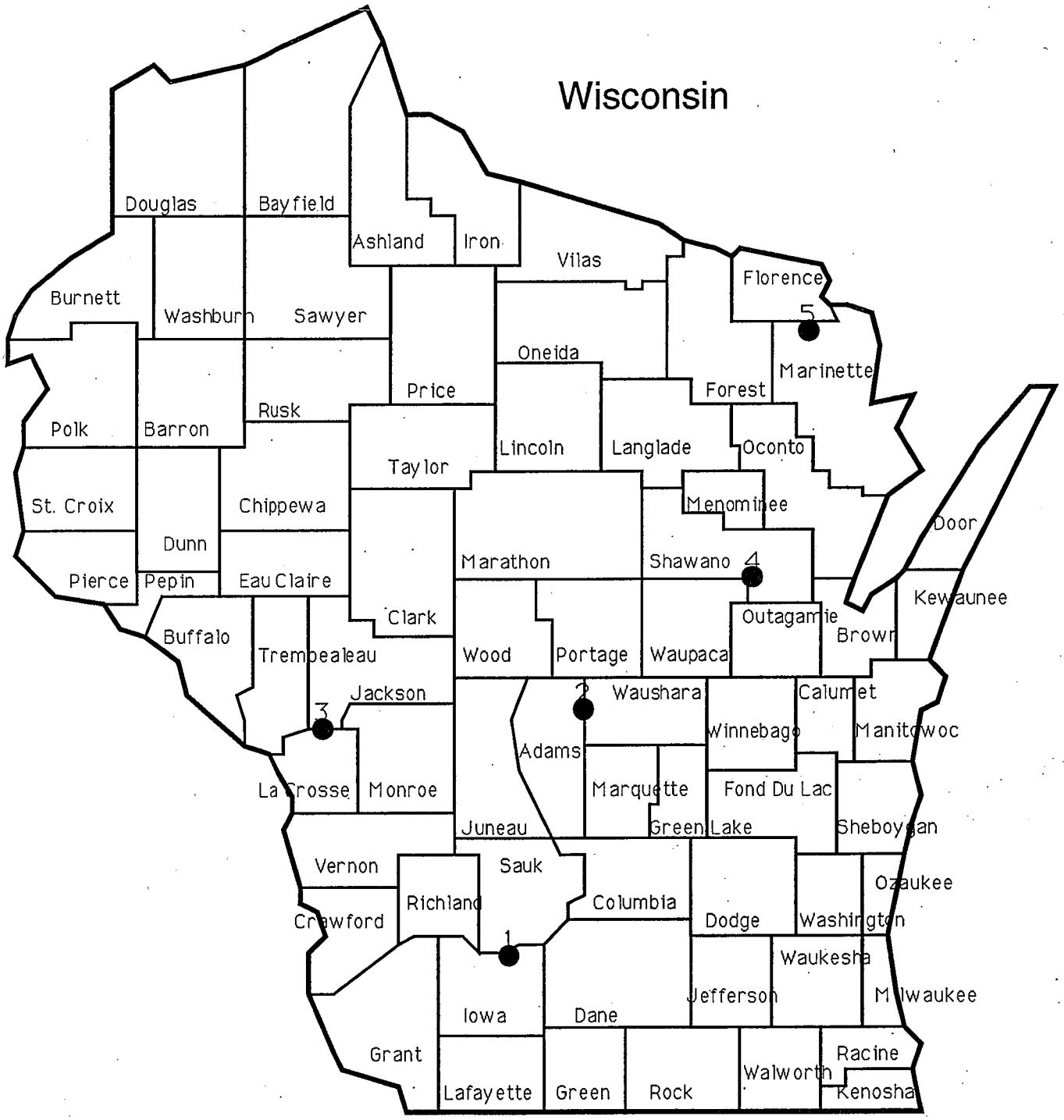


Figure 1. State of Wisconsin showing location of sampling sites: (1) Sparta; (2) Plainfield; (3) Tarr; (4) Shawano; (5) Rousseau.

Table 1. Profile description of a Sparta sand (Sandy, mixed, mesic Entic Hapludoll). This soil formed from sandy glacial outwash deposits on stream terraces, located in a cultivated field, in the Lower Wisconsin River Valley near Arena (about 1,300 ft. north and 1,100 ft. east of the southwest corner of Section 9, T.8N, R.5E).

Horizon	Depth (cm)	Description
Ap	0-23	Very dark brown (10YR 2/2) sand; weak medium subangular blocky parting to weak very fine granular structure; very friable; slightly acid (pH 6.4); abrupt smooth boundary.
A	23-33	Very dark brown (10YR 2/2) sand; weak medium subangular blocky structure; very friable; moderately acid (pH 6.0); clear wavy boundary.
AB	33-43	Dark brown (7.5YR 3/2) sand; weak medium and coarse subangular blocky structure; very friable; strongly acid (pH 5.4); clear wavy boundary.
Bw1	43-54	Strong brown (7.5YR 4/6) sand; weak medium and coarse subangular blocky structure; very friable; less than 1% gravel; strongly acid (pH 5.5); clear wavy boundary.
Bw2	54-66	Dark yellowish brown (10YR 4/6) sand; single grain; loose; less than 1% gravel; strongly acid (pH 5.3); clear wavy boundary.
BC	66-84	Yellowish brown (10YR 5/6) sand; single grain; loose; less than 1% gravel; moderately acid (pH 5.6); gradual wavy boundary.
CB	84-135	Brownish yellow (10YR 6/6) and light yellowish brown (10YR 6.4) sand; few fine and medium prominent strong brown (7.5YR 5/8) mottles; single grain; loose; less than 1% gravel; moderately acid (pH 5.7); gradual wavy boundary.
C	135-160	Pale brown (10YR 6/3) and very pale brown (10YR 7/3) sand; few fine and medium prominent strong brown (7.5YR 5/6) mottles; single grain; loose; about 3% gravel; moderately acid (pH 5.8); gradual wavy boundary.

Table 2. Profile description of a Tarr sand (Mesic, uncoated Typic Quartzipsamment). This soil formed from sandy glacial outwash deposits on a high stream terraces, located in a cultivated field, in the Black River Valley in Jackson county (S.E.1/4,

Horizon	Depth (cm)	Description
Ap	0-19	Very dark grayish brown (10YR 3/2) sand; weak coarse blocky parting and weak medium subangular blocky clods; very friable; moderately acid (pH 6.0); abrupt smooth boundary.
A	19-32	Very dark grayish brown (10YR 3/2) sand; weak medium and coarse blocky structure; very friable; slightly acid (pH 6.3); clear smooth boundary.
AB	32-43	Dark brown (10YR 3/3) sand; weak coarse blocky structure; very friable; slightly acid (pH 6.1); clear wavy boundary.
Bw1	43-63	Dark yellowish brown (10YR 3/4) sand; weak coarse blocky structure; very friable; moderately acid (pH 5.7); clear wavy boundary.
Bw2	63-87	Yellowish brown (10YR 5/6) sand; single grain; loose; moderately acid (pH 5.7); clear wavy boundary.
BC	87-109	Yellow (10YR 7/6) and 15% very pale brown (10YR 7/4) sand; few fine and medium prominent yellow (10YR 7/8) mottles; single grain; loose; moderately acid (pH 5.7); gradual wavy boundary.
C	109-155	White (10YR 8/2) and 30% very pale brown (10YR 7/4) sand; few fine and medium prominent yellow (10YR 7/8) mottles; single grain; loose; moderately acid (pH 5.6).

Table 3. Profile description of a Plainfield sand (Mixed, mesic Typic Udipsamment). This soil formed from sandy glacial outwash deposits on outwash lake plains, located in a cultivated field, in Waushara county on the Hancock Experiment

Horizon	Depth (cm)	Description
Ap	0-28	Very dark grayish brown (10YR 3/2) coarse sand; weak coarse blocky parting to weak medium subangular blocky clods; very friable; less than 1% gravel; slightly acid (pH 6.4); abrupt smooth boundary.
Bw1	28-40	Brown/dark brown (7.5YR 4/2) coarse sand/loamy coarse sand; weak coarse and medium subangular blocky structure; very friable; about 8% gravel; moderately acid (pH 5.6); clear smooth boundary.
Bw2	40-60	Strong brown (7.5YR 4/6) coarse sand; weak medium and coarse subangular blocky structure; very friable; about 7% gravel; strongly acid (pH 5.4); clear smooth boundary.
Bw3	60-87	Strong brown (7.5YR 5/6) coarse sand; weak coarse blocky structure; very friable; about 2% gravel; slightly acid (pH 6.2); clear smooth boundary.
Bw4	87-101	Brown/dark brown (7.5YR 4/4) coarse sand/loamy coarse sand; weak medium and coarse subangular blocky structure; very friable; about 10% gravel; strongly acid (pH 5.5); clear smooth boundary.
Bw5	101-124	Strong brown (7.5YR 5/6) sand; common medium and large prominent strong brown (7.5YR 5/8) mottles; weak prismatic structure; very friable; about 2% gravel; moderately acid (pH 5.8); abrupt wavy boundary.
BC	124-127	Yellow (10YR 7/6) coarse sand; single grain; loose; about 9% gravel; moderately acid (pH 6.0); abrupt wavy boundary.
C1	127-162	Very pale brown (10YR 7/4) coarse sand; common medium and large prominent yellowish red (5YR 5/8) mottles; single grain; loose; about 7% gravel; strongly acid (pH 5.5); abrupt wavy boundary.
C2	162-165	Very pale brown (10YR 7/3) coarse sand; common medium

		prominent yellowish red (5YR 5/8) mottles; single grain; loose; about 14% gravel; moderately acid (pH 5.6); abrupt wavy boundary.
C3	165+	Very pale brown (10YR 7/3) sand; few fine and medium prominent brownish yellow (10YR 6/6) mottles; single grain; loose; about 3% gravel; very strongly acid (pH 4.6).

Table 4. Profile description of a Shawano sand (Mixed, frigid Typic Udipsamment). This soil formed from sandy glacial outwash deposits on glacial lake plains, located in a forest (red and white Pine; some Oak), in Shawano county (N.W.1/4, N.E.1/4, Section 34, T.26N, R.15E).

Horizon	Depth (cm)	Description
A	0-13	Black (10YR 3/1) sand; weak fine and medium granular structure; very friable; slightly acid (pH 6.2); clear smooth boundary.
Bw1	13-34	Strong brown (7.5YR 4/6) sand; weak medium subangular blocky structure; very friable; strongly acid (pH 5.5); gradual smooth boundary.
Bw2	34-66	Strong brown (7.5YR 5/6) sand; weak coarse blocky parting to medium subangular blocky structure; very friable; moderately acid (pH 5.8); gradual smooth boundary.
Bw3	66-92	Strong brown (7.5YR 4/6) fine sand; weak medium and coarse subangular blocky structure; very friable; moderately acid (pH 5.6); clear smooth boundary.
E	92-113	Yellowish brown (10YR 5/6) fine sand; weak medium and coarse subangular blocky structure; very friable; moderately acid (pH 5.6); abrupt smooth boundary.
B'w	113-124	Strong brown (7.5YR 5/6) coarse sand; weak medium subangular blocky structure; very friable; less than 1% gravel; moderately acid (pH 5.6); clear smooth boundary.
C1	124-158	Yellowish brown (10YR 6/4) coarse sand; single grain; loose; about 2% gravel; moderately acid (pH 5.8); abrupt smooth boundary.
C2	158-180	Yellowish brown (10YR 5/4) loamy fine sand/fine sandy loam; massive; friable; contains yellowish red (5YR 4/6) lamellae 4mm thick; moderately acid (pH 5.7).

Table 5. Profile description of a Rousseau fine sand (Sandy, mixed, frigid Entic Haplorthod). This soil formed from sandy glacial outwash deposits in a glacial lake basin, located in a forest (Birch, Maple, Balsum Furr), in Marinette county (S.W.1/4, S.W.1/4, Section 2, T.37N, R.18E).

Horizon	Depth (cm)	Description
O	0-4	Black (10YR 2/1) fine sand; moderate fine granular structure; very friable; very strongly acid (pH 4.5); abrupt smooth boundary.
E	4-21	Light brownish gray (10YR 6/2) fine sand; weak medium subangular blocky structure; very friable; very strongly acid (pH 4.8); abrupt smooth boundary.
Bt	21-47	Strong brown (7.5YR 4/6) loamy fine sand; many fine, medium and large prominent yellowish red (5YR 5/8) mottles; weak medium subagular blocky structure; very friable; moderately acid (pH 5.6); gradual wavy boundary.
Bs1	47-76	(5R 4/8) fine sand; common fine and medium prominent yellowish red (5YR 5/8) and many large prominent (2.5YR 4/8) mottles; weak medium and coarse blocky structure; very friable; moderately acid (pH 5.9); gradual wavy boundary.
Bs2	76-102	Reddish brown (5YR 5/4) fine sand; many medium and large prominent yellowish red (5YR 5/8) mottles; weak coarse blocky structure; very friable; moderately acid (pH 5.7); gradual wavy boundary.
BC	102-138	Yellowish red (5YR 4/6) fine sand; many medium and large prominent reddish brown (5YR 5/3) and strong brown (7.5YR 5/6) mottles; massive; very friable; slightly acid (pH 6.1); gradual wavy boundary.
C	138+	loamy fine sand; massive; friable; slightly acid (pH 6.4).

Table 6. Soil properties of a Sparta Sand.

Horizon	Depth (cm)	pH (1:1)	O.C. (%)	CEC[1]	Particle Size sand <----- % ---->	silt	clay	>2mm (%)
Ap	0-23	6.4	0.35	3	95.7	2.7	1.6	0.0
A	23-33	6.0	0.33	2	96.2	2.2	1.6	0.0
AB	33-43	5.4	0.31	<1	96.2	2.3	1.5	0.0
Bw1	43-54	5.5	0.31	<1	96.5	2.5	1.0	0.1
Bw2	54-66	5.3	0.09	<1	96.9	2.0	1.2	0.6
BC	66-84	5.6	0.11	<1	99.0	0.4	0.6	0.4
CB	84-135	5.7	0.05	<1	99.7	0.1	0.2	0.1
C	135-160	5.8	0.02	<1	99.7	0.1	0.2	2.9

1 meq/100g soil

Table 7. Soil properties of a Plainfield Coarse Sand.

Horizon	Depth (cm)	pH (1:1)	O.C. (%)	CEC[1]	Particle Size sand <----- % ---->	silt	clay	>2mm (%)
Ap	0-28	6.4	0.62		87.7	8.2	4.1	0.3
Bw1	28-40	5.6	0.12		86.8	8.3	4.9	8.1
Bw2	40-60	5.4	0.10		90.8	5.4	3.7	7.4
Bw3	60-87	6.2	0.05		93.3	4.0	2.7	2.0
Bw4	87-101	5.5	0.07		88.9	5.4	5.8	9.9
Bw5	101-124	5.8	0.02		97.3	1.1	1.6	2.1
BC	124-127	6.0	0.01					8.6
C1	127-162	5.5	0.01		98.7	0.5	0.5	6.6
C2	162-165	5.6	0.02					
C3	165+	4.6	0.02		99.2	0.3	0.5	2.6

1 meq/100g soil

Table 8. Soil properties of a Tarr Sand.

Horizon	Depth (cm)	pH (1:1)	O.C. (%)	CEC[1]	Particle Size sand	silt	clay	>2mm (%)
					<----- % ---->			
Ap	0-19	6.0	0.50		91.7	4.4	3.9	0.0
A	19-32	6.3	0.37		89.7	5.3	5.0	0.0
AB	32-43	6.1	0.31		91.4	4.6	4.0	0.0
Bw1	43-63	5.7	0.31		92.4	3.7	4.0	0.0
Bw2	63-87	5.7	0.09		97.7	1.0	1.4	0.0
BC	87-109	5.7	0.11		98.9	0.4	0.7	0.0
C	109-155	5.6	0.02		98.4	0.7	0.9	0.0

1 meq/100g soil

Table 9. Soil properties of a Shawano Sand.

Horizon	Depth (cm)	pH (1:1)	O.C. (%)	CEC[1]	Particle Size sand	silt	clay	>2mm (%)
					<----- % ---->			
Ap	0-13	6.2	1.83		89.8	5.7	4.5	0.0
Bw1	13-34	5.5	0.31		90.3	5.2	4.6	0.0
Bw2	34-66	5.8	0.22		91.7	4.6	3.7	0.0
Bw3	66-92	5.6	0.11		97.0	2.9	0.1	T
E	92-113	5.6	0.05		97.2	1.5	1.3	T
Bw'	113-124	5.6	0.05		97.3	1.7	1.0	0.4
C1	124-158	5.8	0.03		98.6	1.0	0.4	2.4
C2	158-180	5.7	0.07		72.3	24.6	3.1	0.0

1 meq/100g soil

Table 10. Soil properties of a Rouseau Fine Sand.

Horizon	Depth	pH	O.C.	CEC[1]	Particle Size sand	silt	clay	>2mm
	(cm)	(1:1)	(%)		<----- % ---->			(%)
O	0-4	4.5						0.0
E	4-21	4.8	0.31		87.0	11.3	1.7	0.0
Bt	21-47	5.6	0.37		82.0	6.4	11.6	0.0
Bw1	47-76	5.9	0.15		93.7	3.6	2.7	0.0
Bw2	76-102	5.7	0.08		91.4	7.8	0.8	0.0
BC	102-138	6.1	0.05		97.4	2.1	0.5	0.0
C	138+	6.4	0.04		72.7	26.4	0.9	0.0

1 meq/100g soil

Table 11. Atrazine Adsorption Coefficients of a Sparta Sand.

Horizon	Depth (cm)	K_d	K_{oc}
Ap	0-23	0.64	1.83
A	23-33	0.61	1.85
AB	33-43	0.57	1.84
Bw1	43-54	0.38	1.23
Bw2	54-66	0.12	1.33
BC	66-84	0.10	0.91
CB	84-135	0.08	1.60
C	135-160	0.025	1.25

Table 12. Atrazine Adsorption Coefficients of a Plainfield Coarse Sand.

Horizon	Depth (cm)	K_d	K_{oc}
Ap	0-28	1.03	1.66
Bw1	28-40	0.16	1.33
Bw2	40-60	0.16	1.60
Bw3	60-87	0.07	1.40
Bw4	87-101	0.16	2.29
Bw5	101-124	0.07	3.50
BC	124-127	0.11	11.00
C1	127-162	0.10	10.00
C2	162-165	0.31	15.50
C3	165+	0.09	4.50

Table 13. Atrazine Adsorption Coefficients of a Tarr Sand.

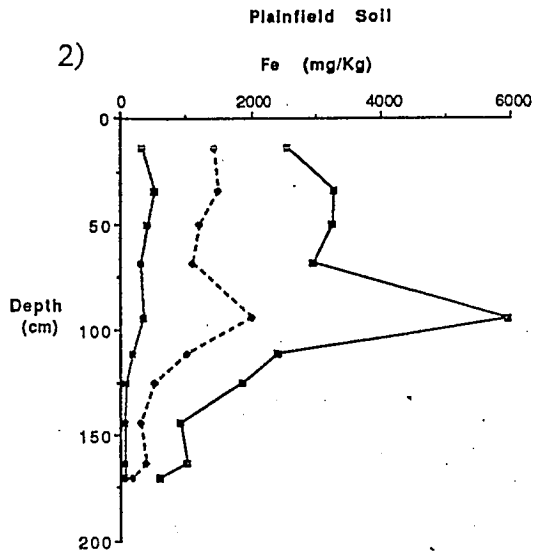
Horizon	Depth (cm)	K_d	K_{oc}
Ap	0-19	0.89	1.78
A	19-32	0.47	1.27
AB	32-43	0.37	1.19
Bw1	43-63	0.33	1.06
Bw2	63-87	0.18	2.00
BC	87-109	0.13	1.18
C	109-155	0.27	13.50
deep C		0.22	

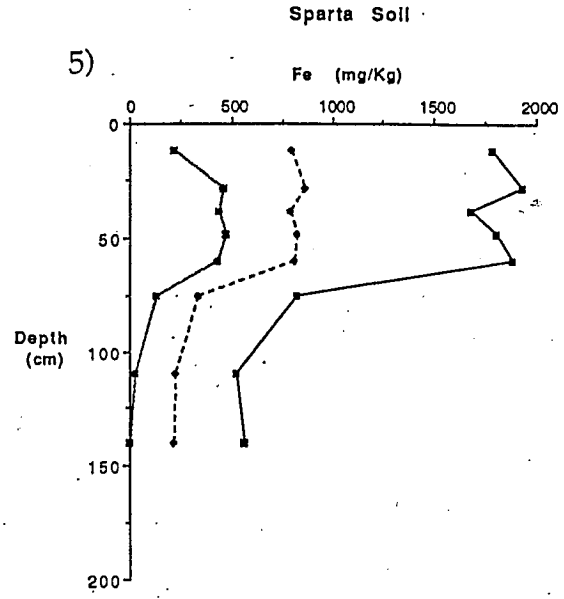
Table 14. Atrazine Adsorption Coefficients of a Shawano Sand.

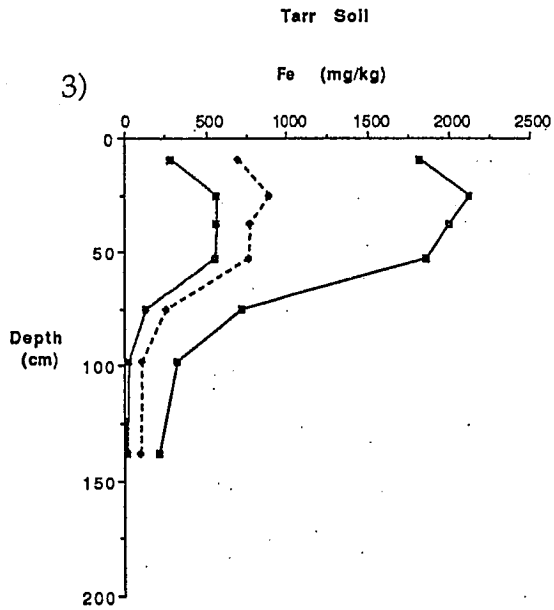
Horizon	Depth (cm)	K_d	K_{oc}
Ap	0-13	4.69	2.56
Bw1	13-34	0.41	1.32
Bw2	34-66	0.28	1.27
Bw3	66-92	0.20	1.82
E	92-113	0.14	2.80
Bw'	113-124	0.15	3.00
C1	124-158	0.09	3.00
C2	158-180	0.18	2.57

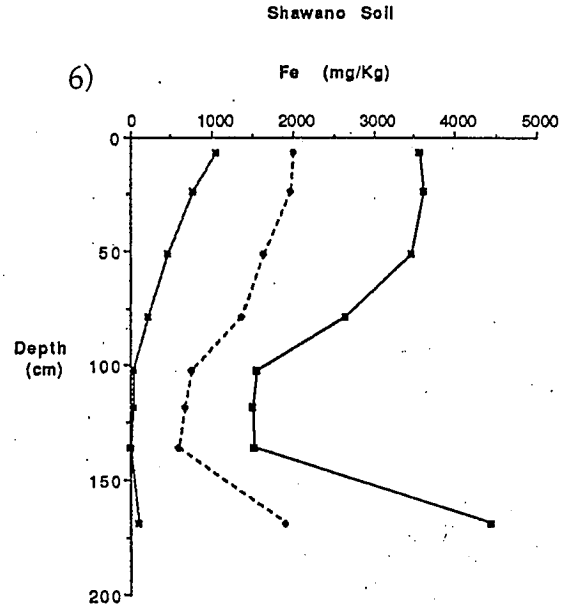
Table 15. Atrazine Adsorption Coefficients of a Rousseau Fine Sand.

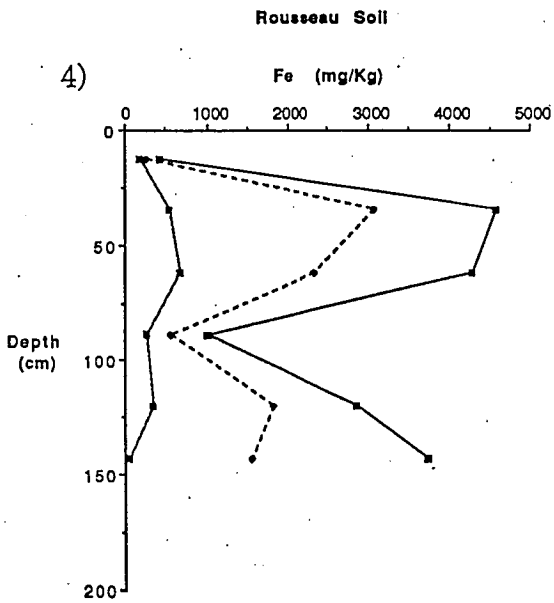
Horizon	Depth (cm)	K_d	K_{oc}
O	0-4		
E	4-21	0.44	1.41
Bt	21-47	0.27	0.73
Bw1	47-76	0.06	0.40
Bw2	76-102	0.06	0.75
BC	102-138	0.06	1.20
C	138+	0.13	3.25



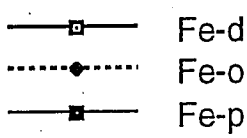


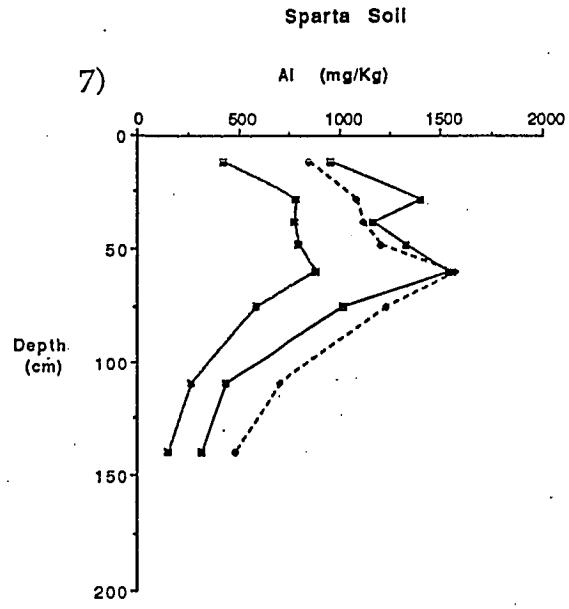


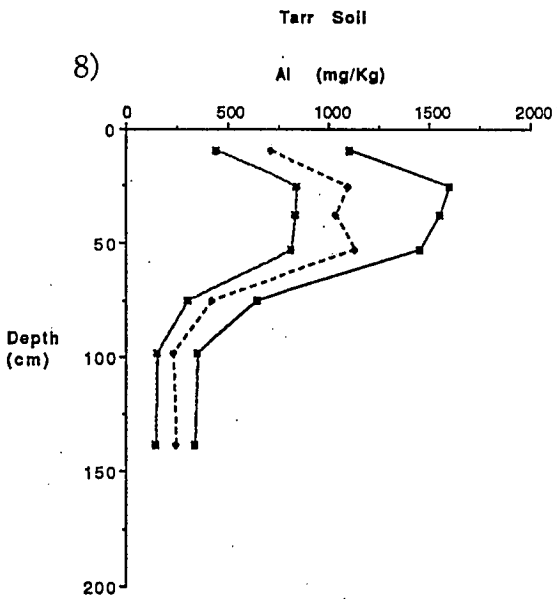


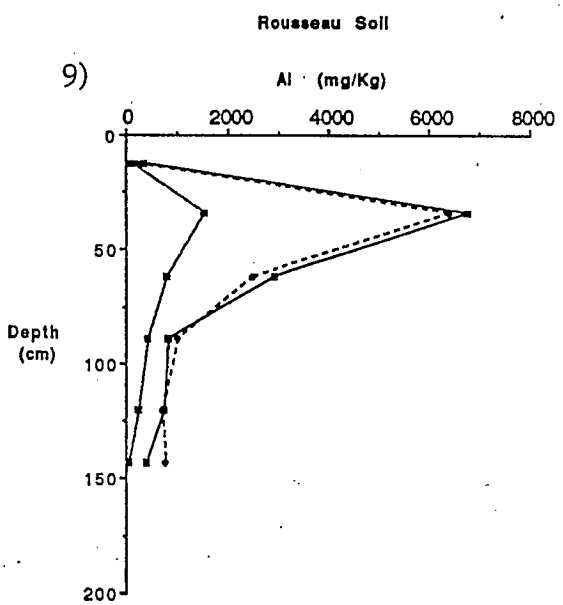


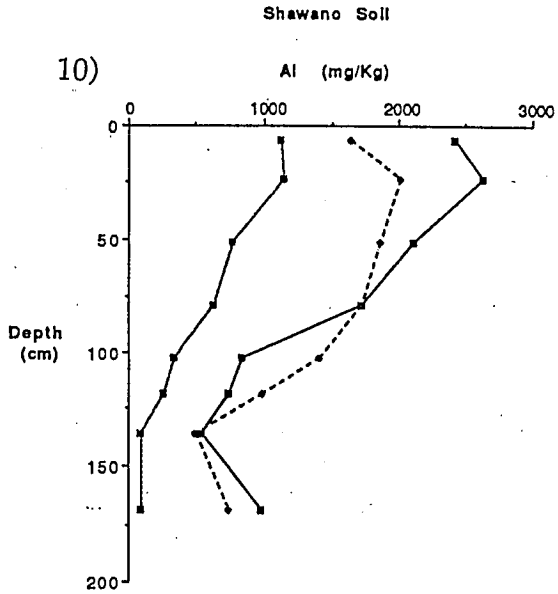
Figures 2-6. Selective dissolution of secondary Fe-oxides.

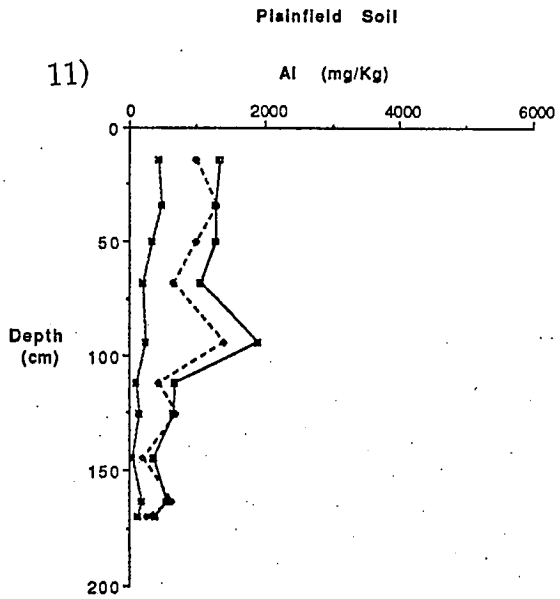




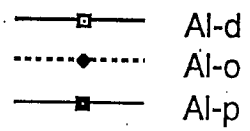








Figures 7-11. Selective dissolution of secondary Al-oxides.



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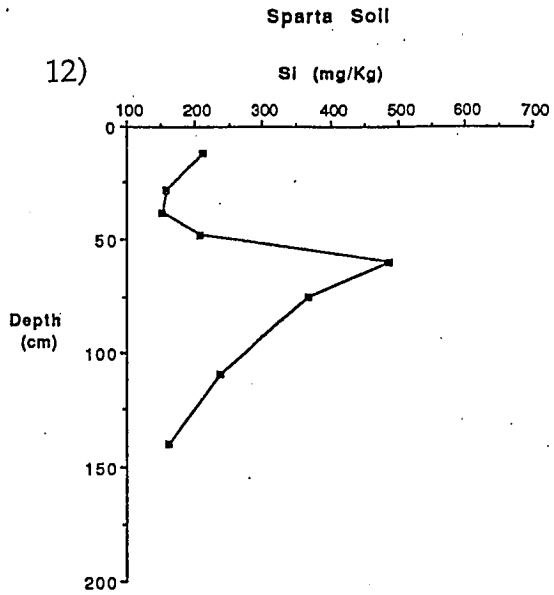

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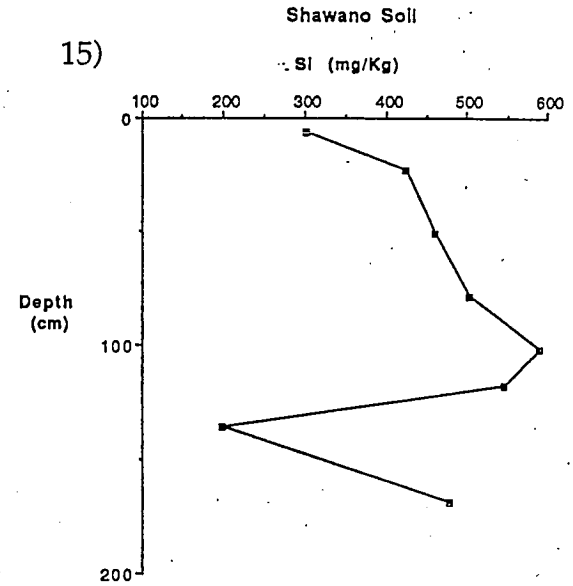

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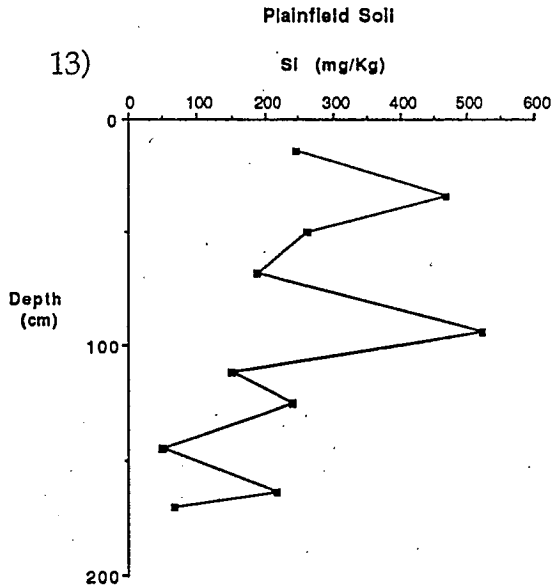

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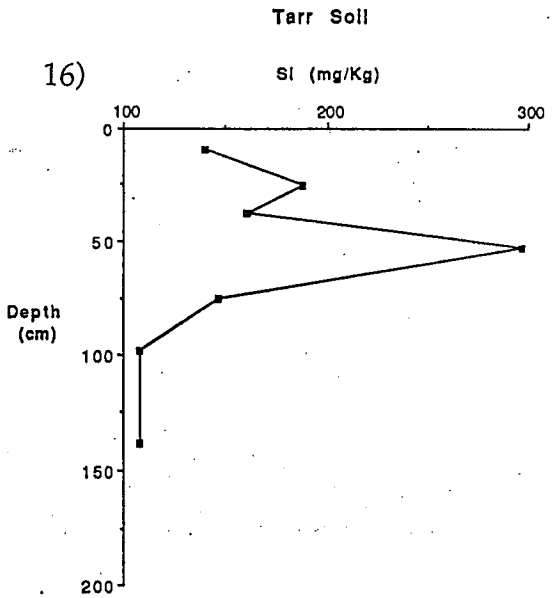

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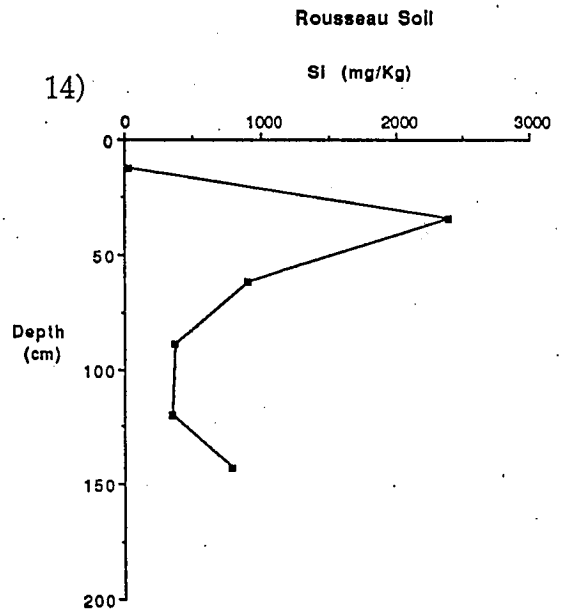
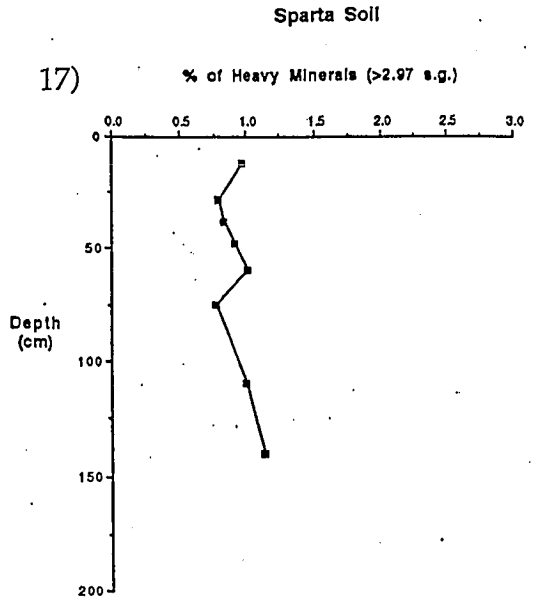


Figures 12-16. Acid-oxalate extractable silica.

17)



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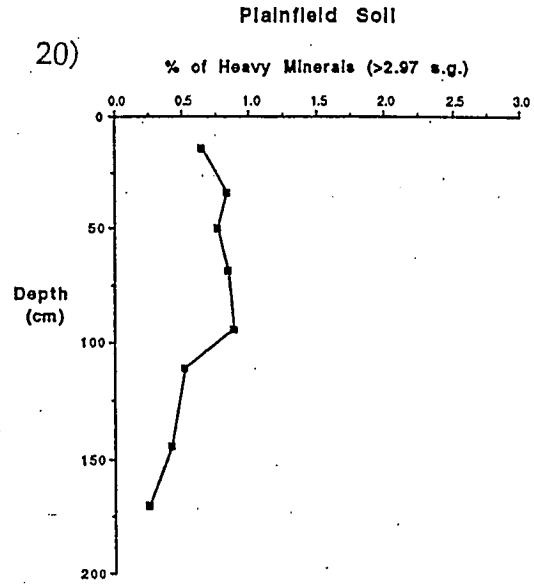

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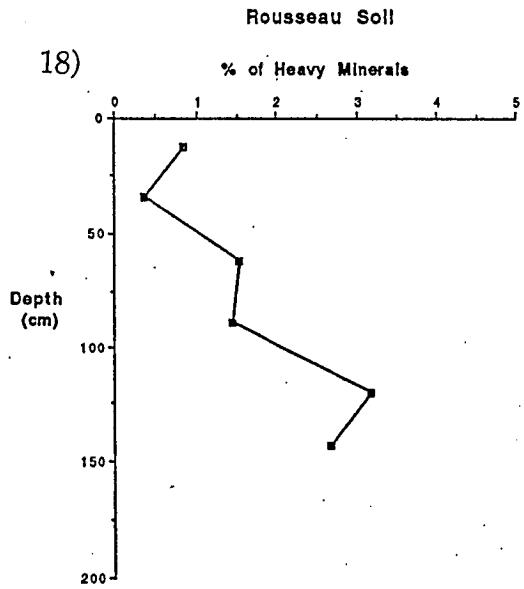

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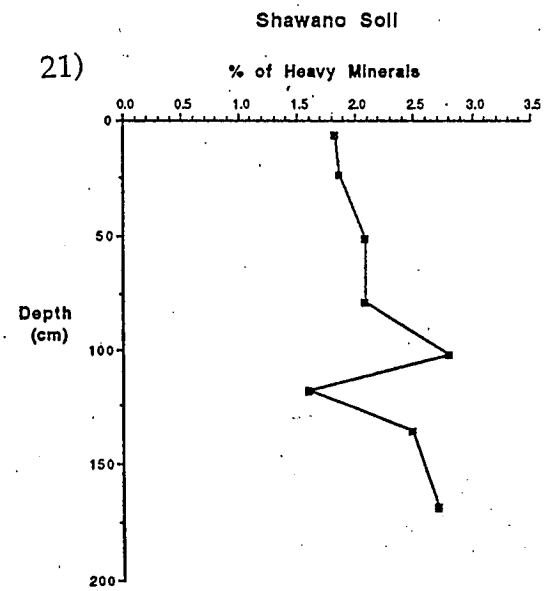

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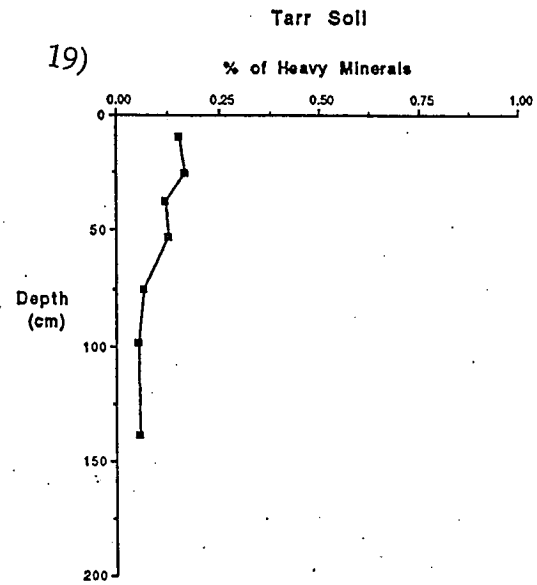

Figures 17-21. Percent heavy minerals (s.g. >2.96) of soil.