DISPERSION OF KAOLINITE BY DISSOLVED ORGANIC FROM DOUGLAS-FIR ROOTS[1]

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The organic constituents of water extracts from Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco var. *menziesii*) roots that cause kaolinite dispersion were investigated. The dissolved organic matter was fractionated according to molecular size and chemical characteristics into acids, neutrals, and bases of the hydrophilic and hydrophobic groups. The dominant fraction causing dispersion included the hydrophobic acids and organics with molecular sizes greater than 10^4 nominal molecular weight. Partial oxidation of the dissolved organic matter increased its carboxylic acid content and dispersion potential. Organic acids promoting kaolinite dispersion included aliphatic and aromatic carboxylic acids. The dispersing ability of a carboxylic acid was related to its charge and charge density. Kaolinite has a pH-dependent surface charge; specific adsorption of carboxyl groups makes the clay more negative and promotes dispersion. Polycarboxylic acids appear to play the major role in kaolinite dispersion by dissolved organic matter in forests.

Key words: Fulvic acid, specific adsorption, carboxylic acid, fractionation

[Dispersion de la kaolinite par la matiere organique dissoute des racines de sapin de Douglas.]

Titre abrégé: Dispersion de la kaolinite par la matière organique.

Les éléments organiques des extraits aqueux de racines de sapin de Douglas (*Pseudotsuga menziesii* [Mirb.] Franco var. *menziesii*) qui entraînent la dispersion de la kaolinite ont fait l'objet de recherches. La matière organique dissoute a été fractionnée d'après sa taille moléculaire et ses propriétés chimiques en acides, en corps neutres et en bases à groupements hydrophiles et hydrophobes. La fraction dominante qui entraîne la dispersion comprend les acides et la matière organique hydrophobes dont les molécules dépassent le poids moléculaire nominal de 10^4. Une oxydation partielle de la matière organique dissoute augmente la concentration d'acide carboxylique et la capacité de dispersion. Les acides organiques qui favorisent la dispersion de la kaolinite comprennent les acides carboxyliques aromatiques et aliphatiques. Le pouvoir dispersif des acides carboxyliques dépend de la charge et de la densité de charge de ces derniers. La charge superficielle de la kaolinite dépend du pH; l'adsorption spécifique des groupements carboxylis rendent l'argile plus négative ce qui en facilite la dispersion. Les acides polycarboxyliques semblent jouer le rôle principal dans la dispersion de la matière organique dissoute dans le sol forestier.

Mots clés: Acide fulvique, adsorption spécifique, acide carboxylique, fractionnement

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Dissolved organic matter — a common constituent of natural water — is generated as organic matter decomposes (Hu et al. 1972). Dissolved organics leached from the leaves of some trees can effectively deflocculate kaolinite (Bloomfield 1954). Kaolinite has a variable surface charge. It can adsorb anions (i.e. specific adsorption) that will change its charge (Hingston et al. 1967) and thereby influence its flocculation-dispersion state.

Dispersion can regulate a soil's erodibility and promote soil development. Dispersed kaolinite has been associated with turbid and extremely turbid streams from a mountainous watershed in Oregon (Youngberg et al. 1975). Dispersion or deflocculation not only influences surface erosion, but is also associated with subsurface erosion (soil piping or suffusion), which can be a precursor to landsliding on steep slopes (Durgin 1984). Dispersed kaolinite can be carried by water moving through the soil. Bloomfield (1954) used this process to help explain the formation of podzols with their clay-leached "A" horizon. Jenny and Smith (1935) explained claypan formation as a result of dispersed clay being flocculated or being attracted to sesquioxides. Claypans did not develop if humus leachates were applied to the clay. Apparently the fulvic acid attached to the clay, dispersed it, and kept it in suspension as the water moved through the soil.

While it is well established that sodium promotes clay dispersion, it remains unclear which organic constituents have dispersion potential. Bloomfield (1954) concluded that polyphenols were the major contributors to kaolinite deflocculation but recommended that his work be repeated more rigorously. Since then, new organic fractionation techniques have been developed. Leenheer and Huffman (1976) developed a procedure that emphasizes the hydrophilic-hydrophobic nature of organic molecules.

This paper reports a study of a strong disperser of kaolinite: water-soluble organic constituents of Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco var. *menziesii*). Leachate of Douglas-fir root was fractionated and tested for dispersion potential, and the functional groups most responsible for kaolinite dispersion were identified.

MATERIALS AND METHODS

Live Douglas-fir roots less than 10 mm in diameter were collected at random from the Lower Trinity District of the Six Rivers National Forest of northwestern California. The roots were washed with water and ground in a laboratory mill then sieved through a 355-µm soil sieve and combined into a composite sample. The composite sample can not show the variance occurring between different Douglas-firs. Therefore, the variance of the replicates are more a reflection of different lab conditions than of different field conditions.

The dissolved organic matter was prepared by placing 2 g of Douglas-fir root powder in a bottle with 100 mL of reagent grade water. The bottle was shaken for 6 h at 180 rpm, and filtered through a prefilter and a 0.45-µm membrane filter. The dissolved organic matter was stored at 4°C and used as soon as possible after extraction.

Size Fractionation

Size fractionation was done by pressure filtering a 15-mL, aliquot of root leachate through Millipore ultrafilters of 10^3, 10^4, or 10^5 nominal molecular weights (NMW). Aliquots were also filtered through Amicon 3×10^4 and 3×10^5 NMW ultrafilters. Nitrogen was used to provide pressure for the filter cells in order to minimize sample oxidation. Each 15-ml, aliquot was diluted to 80 mL, reduced by filtration to about 15 mL, diluted again, and refiltered. This rinsing procedure helped sieve most of the appropriate material through the filter. The diluted filtrate was then reduced to its original volume by rotary evaporation. The final six size fractions were: $<10^3$, $<10^4$, $<3 \times 10^4$, $<10^5$, $<3 \times 10^5$ NMW and the unsieved leachate. Amounts of organic carbon in each size class were estimated with an infrared carbon analyzer.

Each size fraction was tested for its ability to disperse kaolinite. One-half milliliter of leachate was added to 49.5 mL of reagent grade water. This solution was then added to 1 g of ceramic grade Georgia kaolinite and shaken in a 25 ×

200-mm test tube. The suspension settled for 2 h before the top 20 mL were pipetted off. This suspension was placed in a beaker, oven-dried, cooled, and weighed. Each sample and a water blank were replicated four times.

Chemical Fractionation

We used a modification of the Leenheer and Huffman (1976) fractionation procedure for water-soluble organic matter. Their basic approach was to separate out various organic constituents of natural waters on the basis of molecular polarity and charge. A macroreticular resin was used to absorb nonpolar or slightly polar compounds, namely the hydrophobic fractions. The hydrophilic compounds were adsorbed on either a cation or anion exchange resin. By elution of the columns with appropriate solvents, the organic matter was further separated into both hydrophobic and hydrophilic acid, neutral, and base fractions.

The size fractionation showed that the less than 10^3 NMW fraction of root leachate did not effectively disperse kaolinite. Since salts and light organics in this fraction tended to load the resin columns, they were removed by ultrafiltration through a 10^3 membrane. The remaining organic carbon concentration in the leachate (10^3 NMW to 0.45 µm) was determined and referred to as the whole root leachate. This value was later used to estimate recovery rates of organic carbon in the fractionation procedures.

The whole root leachate was diluted by adding water to 50 ml, of leachate to form 1 L. The leachate was then fractionated by the Leenheer and Huffman technique with the following modifications: first, the XAD column did not include XAD-2. Removal of the small organics before fractionation eliminated the need for XAD-2 and its ommission increased the recovery of organics from the leachate. Second, the 0.1 M base, used to elute the hydrophobic acid fraction, was changed to 0.05 M to keep base catalyzed oxidation of polyphenols to a minimum. This procedure was later revised so that a highly diluted solution of 0.0025 M (pH 11.4) was used. Third, we eliminated the methanol elution through the XAD-8 column since no organic carbon was found in this fraction during preliminary testing.

The pH of each eluted sample was adjusted to 7.0. The sample was then desalted through a 10^3 ultrafilter until the conductivity of the effluent was less than 10 µmhos/cm and the pH had stabilized. This method prevented the salts, produced during the neutralization process, from interfering with the kaolinite dispersion tests. The fractions were reduced to the original 50-mL volumes by the 10^3 ultrafilter cell.

The hydrophobic and hydrophilic acids, neutrals and bases, and a water blank were tested for kaolinite dispersion activity and total organic content. The dispersion test was similar to the one used for the size fractionation.

Carboxylic Acids

The root leachate was oxidized by slowly bubbling air through it for a week. The carboxylic acid content was determined in the unoxidized and oxidized root leachate by the decarboxylation method of Schnitzer and Gupta (1965). Rate of kaolinite dispersion was measured by mixing 2 g of kaolinite in water with 2 mL of root leachate. This amount is equivalent to 2% of dry root per unit weight of clay. A paired *t*-test with seven replications was used to analyze the carboxyl contents and the dispersion capacities of the root leachates.

Potassium carboxylates were tested for their kaolinite dispersion activity. The potassium concentration was held constant at 0.002 M and the molarity of carboxylates varied from that according to its charge. These solutions were each mixed with 2 g of kaolinite and the dispersion measured as in other parts of the study. Each prepared solution was replicated four times, and each solution was made up three times. The values were corrected for a water blank and the weight of potassium carboxylate in 20 mL of solution.

Hydroxybenzoic acids were also tested for dispersion potentials. Their concentration was 0.002 M and the solution's pH was raised to 6.0 by addition of KOH. Dispersion tests were conducted similar to the tests for potassium carboxylates. The weight of hydroxybenzoic acid in 20 mL was subtracted from the results.

RESULTS AND DISCUSSION

Although 75% of the organic matter had a nominal molecular weight of less than 10^4 (Fig. 1), those size fractions accounted for only 6% of the dispersion (Fig. 2). Conversely, the largest 10% of the size fractions ($>3 \times 10^4$ NMW) accounted for about 30% of the dispersion, suggesting that larger polymers are responsible for most organic-induced dispersion.

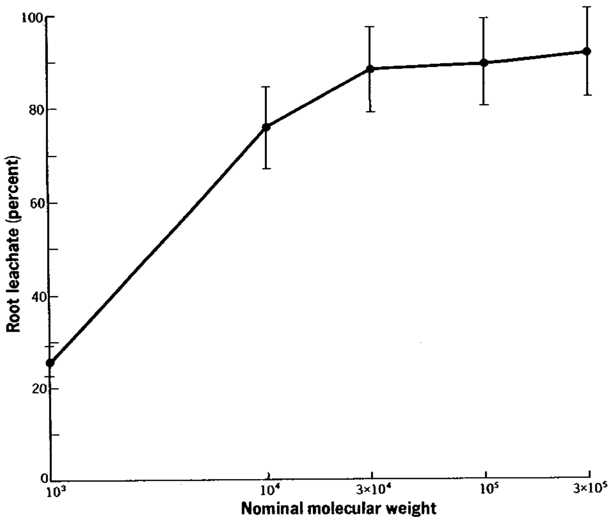

Fig. 1. Cumulative graph indicating quantity of specific sizes of dissolved organic matter as a percentage of organic matter in the whole root leachate.

An organic polymer is expected to have a higher dispersion potential if it has more functional groups and, therefore, more negative charges. A polyvalent anion can not only satisfy any positive charge on the kaolinite edge, but can provide an excess of negative charges that promotes dispersion. For example, polyphosphates become more effective at deflocculating kaolinite as their molecular weight increases up to a polymer of four phosphates at which level their effectiveness evens out (Michaels 1958).

The hydrophobic acid fraction was most abundant and had the greatest dispersing

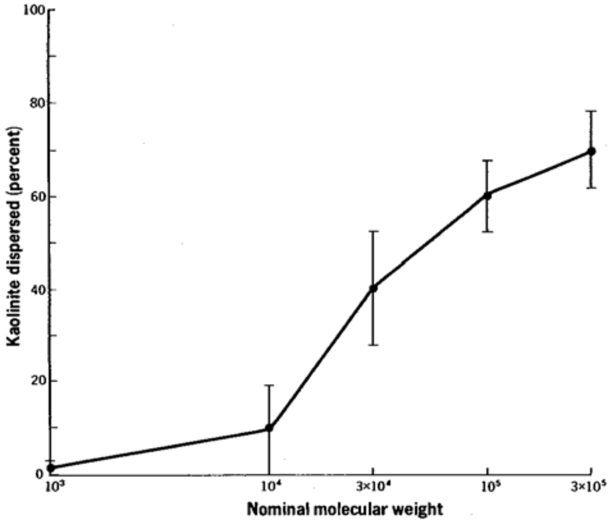

Fig. 2. Cumulative graph of kaolinite dispersion by organic matter size fractions compared to the whole root leachate.

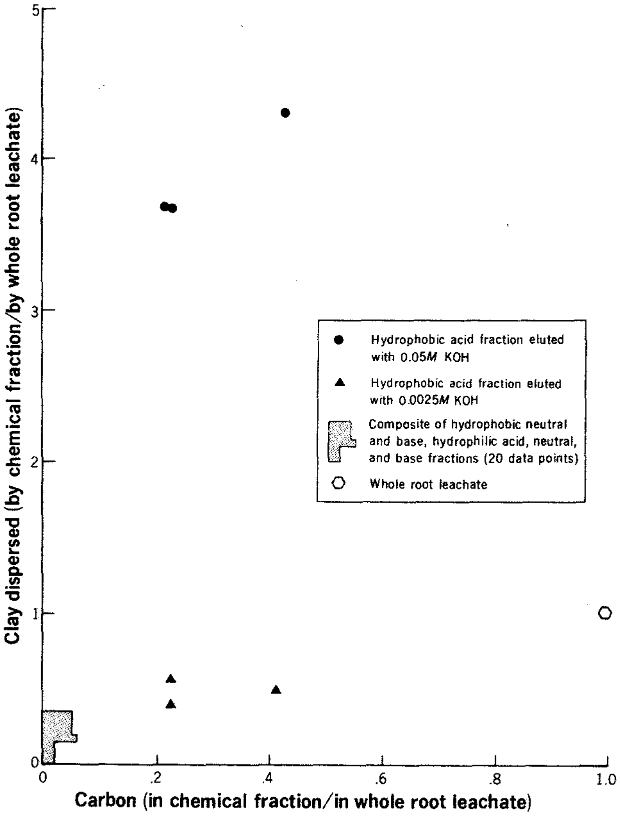

Fig. 3. Dispersion of kaolinite by the whole root leachate as compared to its chemical fractions. The hydrophobic acid fractions were obtained by elution with two concentrations of base.

potential (Fig. 3). The other organic fractions had minor influence and tended to overlap. Composed of molecules that are partially hydrophobic and partially hydrophilic, the hydrophobic acid fraction is actually amphophilic. The hydrophilic portion is anionic and polar, thus keeping the molecule water-soluble while the hydrophobic portion is nonpolar. The hydrophilic and hydrophobic bases on the other hand are organic cations and are ineffective in dispersing kaolinite. The hydrophobic acid fraction is composed primarily of polyphenols and polycarboxylic acids.

Phenols are decomposition products of lignin that have been metabolized by fungi (Nord 1964). Microorganisms oxidize the phenols and polyphenols by splitting their benzene rings to form carboxylic acids, such as succinic and acetic acid (Dagley 1967). These acids can then enter the tricarboxylic acid cycle and supply energy to microorganisms as they are oxidized through a series of carboxylic acids.

Two unexpected results were that the total organic carbon of the fractions averaged only 39% of the whole root leachate, and that the hydrophobic acids eluted from the column with 0.05 M KOH had dispersion capacities four times greater than the whole root leachate. In contrast, when the hydrophobic acid fractions were leached with dilute KOH (0.0025 M), they had less dispersion potential than the whole root leachate.

Gjessing (1971) found that the pH of dissolved organic matter was a critical factor and when he raised the pH above 8, the color changed and the size of the organic molecules increased. The root leachate less than 10^3 NMW was colorless while the whole root leachate in our study was yellow. The fractionation procedure with 0.05 M KOH changed the color of the hydrophobic acids to a dark brown. These acids never returned completely to their original color, even at their original pH. Only the hydrophobic acids were colored and their color changes were indicative of a shift in molecular structure. The color of organics in naturally occurring surface water has been attributed to carboxylic acids (Lamar and Goerlitz 1966). Therefore, the additional color with high pH suggested the possibility of carboxylic acid formation. In any case, these newly formed colored organic molecules showed a high capacity for dispersion.

Oxidation appears to be the key in explaining what happened to the hydrophobic acids during fractionation. Raising the pH of an organic solution above 7 catalyzes the oxidation of phenols (Mihailovic and Cekovic 1971). Oxidation allows polymerization of the phenols but also can split the organic molecules apart, thereby creating lower molecular weight particles (Swift 1976). Oxidation of organic matter by alkali produces more carboxyl and carbonyl groups (Swift and Posner 1972). These functional groups are classed in the hydrophobic acid fraction — the fraction having the greatest dispersion potential and one clearly modified by oxidation. Therefore, oxidation helps to explain the loss of dissolved organic carbon during the fractionation process. The losses included organics (1) left on the columns, (2) attached to the 10^3 filter, (3) filtered through the 10^3 filter after oxidative splitting, and (4) held by the 0.22-mm filter following oxidative polymerization.

The explanation of how the hydrophobic acid fraction can be four times more dispersive than the whole root leachate is also related to oxidation. However, the explanation requires a close examination of the dispersion mechanism.

The companion paper (Durgin and Vogelsang 1984) shows that some inorganic anions are specifically adsorbed and produce dispersion. Similarly, some organic anions are held specifically by replacing the hydroxyl ions on the A1(OH) surfaces of kaolinite, while others are held loosely within the diffuse double layer of the clay.

Flocculated kaolinite commonly occurs as the positively charged edges of the clay attach to the negative faces to form a card-house-type structure (Schofield and Samson 1954). If organic anions are specifically adsorbed, they become potential determining ions. They can offset the positive charge at the absorption site, provide surplus negative charge, and promote dispersion. If the anions are held nonspecifically, they are only expected to neutralize the positive charge at their exchange sites.

A weak monobasic acid undergoes its greatest specific adsorption at the pH of its dissociation constant (pKa) (Hingston et al. 1972). Carboxylic acids have dissociation constants in a pH range (4-6) that is common under forest conditions. In contrast, phenols have a pKa in the range of pH 10. Although carboxylic acid is a weak acid, it is several orders of nagnitude stronger than the phenols and, under forest conditions, it is more apt to dissociate and attach to clay than are phenols.

Various potassium carboxylates were tested for their ability to disperse kaolinite (Fig. 4). Charge and dispersion capacity appear to be correlated. The monovalent organic anions do not have sufficient charge to effectively replace the hydroxyl ion. If replacements occur they have little influence on the negative charge or kaolinite dispersion. By contrast, the divalent carboxylates are effective. And citrate, a trivalent anion, has the greatest dispersion potential. The same pattern occurs with dispersion of kaolinite by polyphosphates of differing valence.

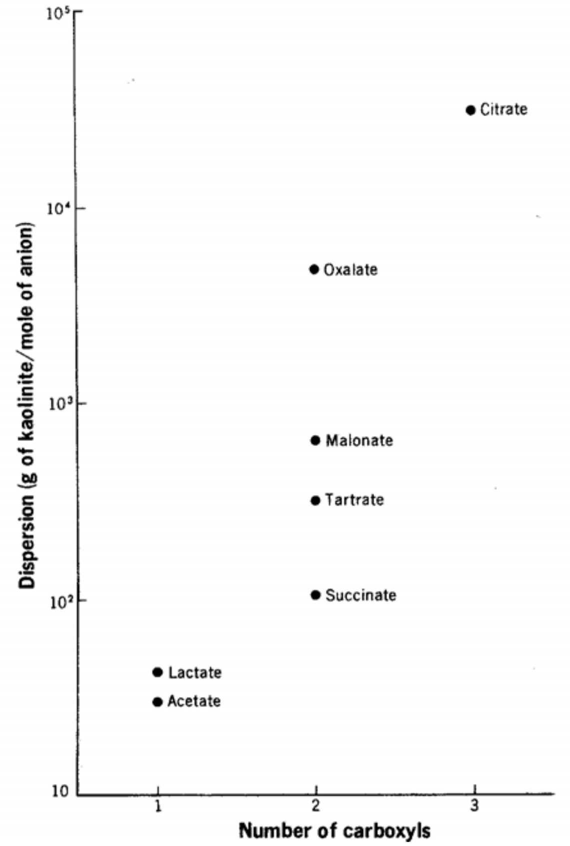

Fig. 4. Dispersion potential of potassium carboxylates according to the number of carboxyl groups. Data are based on solutions containing 0.002 M potassium.

Specific adsorption of carboxylates is related to kaolinite dispersion. Citrate and oxalate undergo specific adsorption and had the highest dispersion potentials; acetate, succinate, and lactate are nonspecifically adsorbed (Nagarajah et al. 1970) and had the lowest potentials.

Oxalate is the divalent carboxylate with the highest dispersion potential (Fig. 5). Oxalate consists simply of two carboxyl groups and, therefore, has the greatest charge density of any of the dicarboxylic acids. As the carboxylic acids are spaced farther apart they lose their dispersion potential.

The dissolved organic matter in forest soils and streams contains aromatic hydroxy carboxylic acids (Dawson et al. 1981). Consequently, some hydroxybenzoic acids were tested for their dispersion potentials (Fig. 6). The results suggest that the hydroxyl group acts like the carboxyl group in that dispersion potential is greater as the number of adjacent hydroxyls increases. However, hydroxyl groups are much less effective than carboxylate groups in promoting dispersion. The hydroxybenzoic acids were oxidized by letting them sit for 1 wk. Gallic acid underwent the most notable changes. Unoxidized gallic acid was colorless but when oxidized it became yellow and had significantly ($\alpha = 0.05$)

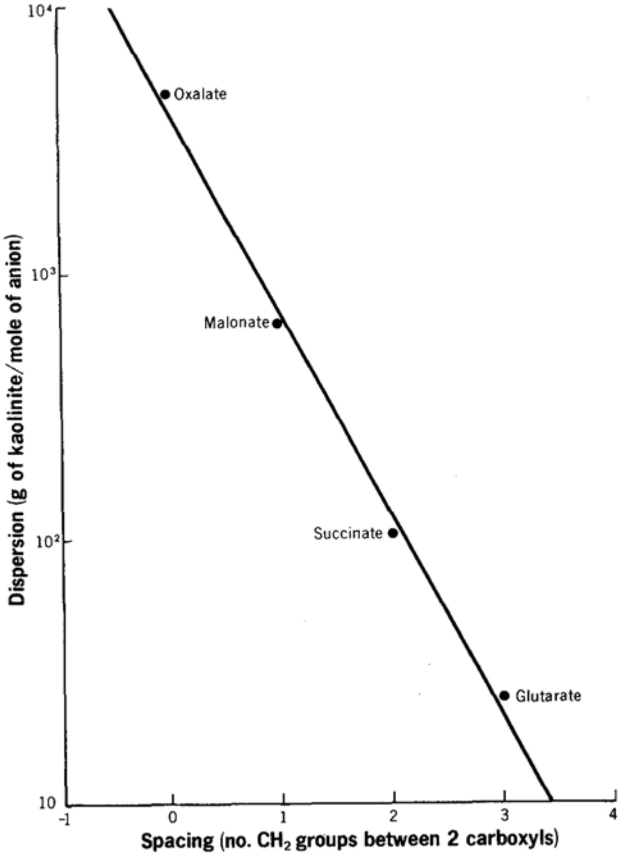

Fig. 5. Dispersion potential of dicarboxylates in relation to the charge density of the anion. Data are based on solutions containing 0.002 M potassium.

more dispersion potential. These hydroxybenzoic acids are precursors of acids with more carboxyl groups (Dagley 1967).

We oxidized the root leachate and with a paired *t*-test found that the carboxylic acid content was significantly greater in the oxidized leachate (12 meq COOH/g organic matter). The oxidized root leachate was also significantly more effective at dispersing kaolinite than the unoxidized leachate. The oxidized leachate had 2.6 times more carboxylic acid and had 2.8 times greater dispersion potentials than the unoxidized leachate.

Therefore, the apparent explanation of why the hydrophobic acid fraction, oxidized by 0.05 M KOH, had four times more dispersion potential than the whole root leachate is that polycarboxylic acids were produced that were more effective at dispersing kaolinite than the original phenols and polyphenols.

Bloomfield (1957) suggested that polyphenols are responsible for kaolinite dispersion. Others have reported that phenolics, specifically tannic acid, are effective in dispersing clay (van Olphen 1977). However, phenolics are not as water-soluble as carboxylic acids, nor do they dissociate and produce anions as easily under the pH conditions of forests. Therefore, it is more likely that the carboxyl group and polycarboxylic acids in particular are the dominant contributors to kaolinite disper-

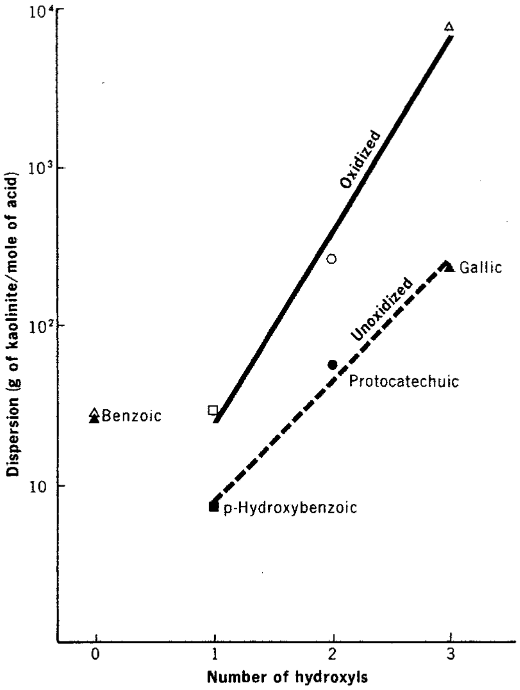

Fig. 6. Relationship of kaolinite dispersion to the number of hydroxyl groups on oxidized and unoxidized hydroxybenzoic acids. Data are based on 0.002 M solutions.

sion under natural conditions. Hydroxyl groups may act in coordination with carboxyls in promoting dispersion,

An apparent contradiction is that while polycarboxylic acids enhance kaolinite dispersion, they are also used as soil conditioners to produce aggregates (Harris et al. 1966). The explanation may be that the size of the polyanion determines its influence. If the polyanion is no longer than the edge of the clay, it can make the particle negative and produce dispersion. However, if the polycarboxylic acid is longer than the clay's edge, it will attach to the edges of other clay particles and bind them all together.

Carboxylic acids are common in forested areas and occur as a major component of throughfall (Hoffman et al. 1980). The water-soluble organic matter leached from fresh needle litter consists predominantly of phenols (Blaschke 1979). However, several types of fungus, particularly "white rot" fungus, are able to decompose forest litter and produce oxalic acid as well as other carboxylic acids (Blaschke 1979). Calcium oxalate is a fungal decomposition product that has been identified in the litter of a wide variety of forests (Graustein et al. 1977).

Below the soil surface, live tree roots exude aliphatic carboxylic acids — a major component of root exudate (Smith 1976). Trees also have a considerable turnover of roots that grow, decay, and release dissolved organic matter including aromatic hydroxy carboxylic acids. Therefore, the growing forest continually releases carboxylic acids to the soil that promote chemical and physicochemical erosion (Durgin 1983). Clearcutting a forested watershed can decrease the amount of dissolved organic matter draining through the subsurface (Meyer and Tate 1983).

CONCLUSIONS

This study shows that dissolved organic matter from Douglas-fir roots can disperse kaolinite. The organic molecules responsible are predominantly the larger sizes (> 10^4 NMW). The hydrophobic acid fraction has the greatest dispersion potential, particularly after oxidation. Substances responsible for kaolinite dispersion include some aromatic and aliphatic carboxylic acids including those with hydroxy groups. The carboxyl group is the most effective functional group promoting dispersion. Polycarboxylic acids have more negative charges than carboxylic acids and, consequently, more dispersion potential. Dicarboxylates with higher charge densities are more effective at producing dispersion. Polycarboxylic acids are common organic constituents of forest soils and are an important influence on their dispersion and aggregation. They are, therefore a key factor in determining soil erodibility at the surface and in the subsurface.

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