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Chemical Characterization of Pond Sediments

Although water pollution is now a subject of considerable interest and concern among the scientific community, relatively little is known of the effect of bottom sediments on the behavior of the various chemical forms of pollutants in the aquatic environment. A major obstacle to the development of an understanding of these complex systems has been the lack of suitable methodology for elucidation of the chemical characteristics of the sediments.

As part of a continuing program to characterize the terrestrial and aquatic components of the arid land ecology reserve on the Hanford Project operated by the United States Atomic Energy Commission at Richland, Washington, this investigation was initiated to determine (a) the chemical composition and particle size distribution of the sediments and (b) the chemical composition of the sediment interstitial water in an impoundment at the Rattlesnake Springs ecology site. Inherent in this objective was the evaluation of present methods of soil analysis for use in sediment investigations.

It is anticipated that the information gathered in this investigation will form a basis for future studies of the genesis of pond sediments and the mechanisms of nutrient sorption and release from sedimented and suspended particulates.

Materials and Methods

The following chemical and physical characteristics of the sediment were determined: (a) exchangeable cations, (b) soluble cations (solution cations in equilibrium with exchangeable cations), (c) cation exchange capacity, (d) particle size distribution, (e) content of organic carbon, and (f) sediment humate content, elementary composition (C, H and N), and humate cation exchange capacity.

Sediments were removed from several locations (Table 1) in the pond using a glass tube to which suction was applied. Samples were stored at 4°C and all analyses were conducted on the moist sample. The sediments were separated from the associated water by gravity filtration through filter paper, and the sediment and water analyzed for exchangeable and soluble cations, respectively.

Cations (Ca, Mg, Na and K), either displaced from the sediment exchange sites with NH_4 (pH 7.0, $\text{N NH}_4\text{OAc}$) or soluble in the associated water, were analyzed directly. The Ca and Mg were resolved by EDTA titration (American Public Health Association, 1965) whereas Na and K were determined by flame photometry. Exchangeable Al was determined as described by McLean (1965). Exchangeable NH_4 was estimated by colorimetric measurement (American Public Health Association,

1965) of NH_4 displaced from the sediment exchange (1N KCl). The sediment pH was measured by glass electrode pH meter on a thin pond water paste equilibrated 30 minutes.

In the determination of the sediment cation exchange capacity (CEC) the exchange sites were saturated with Sr [pH 7.0, 0.1N $\text{Sr}(\text{NO}_3)_2$ spiked with ^{85}Sr] by column leaching. Following saturation the column was allowed to drain and the total retained Sr was determined by measurement of ^{85}Sr γ activity. That portion of total Sr retained unadsorbed in the saturating solution (soluble Sr) was estimated by gravimetric techniques (Frylinger and Thomas, 1955). The exchangeable Sr was taken as the difference between total and soluble Sr. This method proved particularly useful since it eliminated errors due to hydrolysis of exchangeable cations and dispersion of soil colloids normally associated with methods which employ water-washing to remove excess saturating solution. Preliminary attempts to avoid the dispersion problem by use of an alcohol- or acetone-water mixture met with little success due to dissolution of the sediment organic matter.

Particle size distribution was determined by the method of Jackson (1956) and involved separation of Na-saturated minerals by centrifugation after removal of carbonates (pH 5.0, N NaOAC) and organic matter (20% H_2O_2).

Microcombustion techniques (Wildung *et al.*, 1968) were employed for determination of C and H contents. Samples of known moisture content and containing 10-50 mg of C were heated at 800-1000°C over CuO wire. Evolved H_2O was trapped in anhydrous granular Anhydrite [$\text{Mg}(\text{ClO}_4)_2$]. The CO_2 was trapped in granular Ascarite (NaOH-treated asbestos). The C, H and Ash contents were measured gravimetrically.

Sediment humates, isolated using NaOH (5%) extraction (Wildung *et al.*, 1965) were characterized as to elementary composition and CEC as described by Wildung *et al.*, (1968).

TABLE 1. Description of sampling sites within the Rattlesnake Springs pond.

Sample Number	Depth of		location
	sediment (cm)	water (m)	
1	0-7.5	1.5	3 m behind dam in eddy current
2	0-7.5	1.5	9 m behind dam in eddy current
3	0-7.5	1.0	18 m behind dam in eddy current
4	0-7.5	1.2	Pond head at stream influent

Results and Discussions

This investigation was designed as a preliminary study of (a) the chemical characteristics of the pond sediments of the arid land ecology reserve and (b) the application of the techniques of soil chemical analysis to the aquatic system. It was hypothesized that soils and pond sediments would have several features in common. For example, the parent mineral material of sediments should be similar to the surrounding soils. Furthermore, the production of organic matter in both cases is regulated by the supply of energy in the form of reduced compounds of C and by the supply of available nutrients. However, it is obvious that major differences also exist. For example, pond sediments and soils differ in that pond sediments are (a) normally left relatively un-

disturbed by man and (b) permanently waterlogged with the O₂ supply severely limited (Mortimer, 1949).

Evaluation of Analytical Techniques. Techniques of soil analyses proved quite applicable to sediment systems. Preliminary analyses showed that exchangeable Ca and Mg values exceed the determined CEC of the respective pond sediments, a phenomenon characteristic of calcareous soils. The pH 7.0, N NH₄OAc extractant normally employed in the determination of exchangeable cations will partially dissolve the carbonates of Ca and Mg and thus is not suitable as an extractant in soils or sediments containing significant quantities of these minerals. The sediments apparently contained sufficient quantities of Ca and Mg carbonates to preclude analysis of exchangeable Ca and Mg by this method. An alternative method would involve determination of the amount of carbonate in the sediment prior to and after NH₄OAc extraction and appropriate correction for dissolved carbonate. However, in these preliminary investigations no attempt was made to determine exchangeable Ca and Mg.

TABLE 2. Distribution on Na and K between the solid phase and interstitial water of pond sediments.

Sample Number	Soluble		Exchangeable	
	Na	K	Na	K
	meq/l		meq/100g	
1	0.69	0.18	0.27	0.73
2	0.68	0.18	0.37	1.34
3	0.70	0.17	0.31	1.02
4	0.64	0.15	0.38	1.06

Cation Distribution. The distribution of Na and K between the solid and associated liquid phases is shown in Table 2. Soluble Na and K ranges from 0.64 to 0.70 and 0.15 to 0.18 meq/l, respectively. The concentration of soluble Ca and Mg (not shown) ranged from 1.7 to 2.0 and from 0.9 to 1.0 meq/l respectively. Thus, in the case of these ions, the composition of the water associated with the sediment is relatively constant.

As might be expected, a broader range in the content of exchangeable Na and K was observed. Exchangeable Na and K ranged from 0.27 to 0.38 and 0.73 to 1.34 meq/100g, respectively. The order of concentration was therefore soluble Na > K and exchangeable K > Na. The higher concentration of soluble Na compared to K is in accordance with the fact that K is bound more tightly than Na to organic and inorganic exchange sites. Furthermore, K may be fixed within the interlayers of certain expanding clay minerals, thereby increasing the ratio of Na to K in the interstitial water. The lower concentration of exchangeable Na may therefore be explained on the basis of (a) the larger hydrated radius of Na in relation to K resulting in decreased bond strength between Na and the sediment, and (b) the lack of any mechanisms for interlayer retention of Na as occurs in the case of K.

An inverse relationship between soluble and exchangeable Na was apparent; i.e., in increase in exchangeable Na, relative to the other sediment samples, was accompanied by a corresponding decrease in soluble Na. This was not apparent in the case of K.

Exchangeable NH₄ was not detected in significant quantities. No exchangeable Al could be detected. Assuming the measured sediment pH of 7.2 was an accurate reflection of the pH of the interstitial water, the mineral form of Al should be stable, resulting in little soluble Al on the sediment exchange sites.

The CEC of the pond sediment 1, 2, 3, and 4 were 25.0, 24.5, 18.3, and 27.0 meq/g, respectively. The sum of exchangeable Na, K and NH_4 amounted to less than 10% of the CEC at pH 7.0. The relatively high concentrations of Ca and Mg in the associated water indicate that the remainder of the exchange sites must be occupied largely by Ca and Mg. However, the difficulties in determination of exchangeable Ca and Mg in the presence of their carbonates precludes an accurate determination of their contribution to the neutralization of sediment charge.

Particle Size Distribution. The distribution of particles within the mineral fraction of the sediments is illustrated by sediment 4 which contained 65.9% sand ($> 50\mu$), 20.9% silt (50 to 2μ), and 13.2% clay ($< 2\mu$). Thus, the textural class of the sediment, based on the classification scheme commonly used for soils (Miller *et al.*, 1958), corresponds to a sandy loam. This classification also corresponds to that of the Warden soil which surrounds the Rattlesnake Springs pond.

Sediment Organic Fraction. The C content of sediment samples 1, 2, 3, and 4 were 4.5, 5.7, 2.9, and 5.7%, respectively. Thus, the C content of the sediment samples ranges from approximately four to eight times higher than the surrounding soils which average 0.8% C (Wildung *et al.*, 1968), suggesting that either considerably more organic matter is deposited in the sediments or the rate of organic matter decomposition is less in sediments relative to the rate of deposition. Both factors may be important. The lower C content of sediment 3 in relation to the other samples is reflected in a lower CEC (18.3 meq/100g vs 24.5 to 27.0 meq/100g), indicating the high charge density of the sediment organic fraction and its importance in ion exchange reactions. The reduction in CEC amounted to approximately 3 meq/100g for a corresponding decrease of 1% C, suggesting a sediment organic matter charge density approximating that of the soil organic fraction. A humate isolated from sediment 4 and representing 4.7% of the total C, contained 44.8% C, 5.8% H, and 6.7% N. Thus, the sediment isolate contains considerably less C, approximately the same H, and more N than soil humates and plant lignins isolated from the surrounding soils and plants using the same techniques (Wildung *et al.*, 1968).

The low C/H ratio (7.7) in comparison to the plant lignins (av. 9.7) and soil humates (av. 9.5) is indicative of a higher degree of H saturation, and, consequently, the sediment humate may be less aromatic in character than would be expected if the major sources of organic matter were soils and partially decomposed terrestrial plant tissue.

The sediment humate CEC amounted to 93.1 and 478 meq/100g at pH 4.0 and 7.0, respectively. Thus, the sediment humate CEC exhibits pH dependency as does the soil humate (Wildung *et al.*, 1968), suggesting the presence of acidic functional groups. The sediment humate CEC approximates that of the soil humates over the same pH range, indicating that the acidic groups of the soil and sediment isolates may be similar in number and acidic strength.

Summary

The physiochemical properties of pond sediments and associated interstitial waters were determined using analytical techniques commonly employed in soil science. Techniques of soil analyses gave reproducible results without apparent interference when applied to sediment systems, simplifying future investigations of particulate behavior in the aquatic environment.

The Na and K contents of interstitial waters were quite constant between sediment samples ranging from 0.64 to 0.70 and 0.15 to 0.18 meq/l, respectively. Exchangeable Na and K ranged from 0.27 to 0.38 and 0.73 to 1.34 meq/100g, respectively. The higher concentration of Na in the interstitial water and lower concentration on the exchange may be largely attributable to (a) the lower bond strength between Na and the sediment and (b) mineral interlayer selectivity for K. The CEC of pond sediments ranged from 18.3 to 27.0 meq/100g. A representative sediment sample contained 68.9% sand, 20.9% silt, and 13.2% clay. The organic C contents ranged from 2.90 to 5.73%. Sediment humates contained less C, approximately the same H and more N than soil humates and plant lignins. The sediment humate exhibited a pH dependent CEC similar in magnitude to the soil humates. Thus, the CEC of sediment humates may arise from acidic functional groups similar to the soil humates in number and acidic strength. Measurements of (a) intact sediment CEC in relation to C content and (b) pH dependent sediment humate CEC indicate that the charge density of the intact sediment organic fraction may be approximately that of the soil organic fraction.

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