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Chemical Properties of the Arid Soil Organic Fraction

The organic fraction of soils of the humid and subhumid regions of the world is known to exert an influence on soil transformations which far exceeds what might be deduced from its proportion by weight. The soil organic matter contributes substantially to soil sorption of nutrient elements (Wiklander, 1964), pesticides (Armstrong *et al.*, 1967; Wildung *et al.*, 1968a) and radionuclides (Mortensen and Marcusiu, 1963; Nishita *et al.*, 1956). Furthermore, the soil microflora are often directly involved in transformations of these materials (Alexander, 1961; Crafts, 1961; Stevenson, 1965). However, information regarding the mechanisms and extent of the participation of the soil organic fraction and the soil microflora in these phenomena is far from complete, particularly in arid climates.

The lack of information regarding the chemical properties of the arid soil organic fraction is presumably due to the inherent low concentrations of organic matter in these soils. However, in arid soils low in clay minerals, the organic fraction, due to its high charge density, may assume, in addition to its functions in the flow of energy and cyclization of C and N, an important role in exchange reactions which govern the fate of inorganic and organic ions in soil. With increased dependence upon arid lands by a growing world population, an integrated approach must be taken to elucidate the role of soil in the arid land ecosystem. In 1967, the United States Atomic Energy Commission set aside 210 square km of the Hanford Reservation at Richland, Washington, as an arid land ecology (ALE) reserve. This arid shrub-steppe region has been relatively undisturbed for over 25 years and present access is strictly controlled. Over a distance of approximately 13 km the elevation increases up a north-facing slope from about 155 m on the basal plains to more than 1060 m along the crests of what are known as the Rattlesnake Hills, thus providing a unique area for the study of the arid land ecosystem, including the biochemistry of the arid soil organic fraction, over a broad altitudinal range.

As the first phase in a continuing program to determine the role of the soil in the flow of energy, the cyclization of nutrients, and the behavior of soil-deposited pollutants within the arid land ecosystems on the ALE reserve, this study was designed to (1) develop and evaluate methodology for the chemical characterization and study of arid soils, (2) characterize intact arid soils representing several plant-soil associations over a broad altitudinal range as to physicochemical properties, and (3) isolate and characterize chemically arid soil humic colloids as to elemental composition and Sr ion exchange capacity.

Materials and Methods

In order to evaluate possible changes in the chemical properties of the soil organic fraction as influenced by changes in ambient temperature and moisture, soil humic acids were isolated from surface (0-8 cm) soils sampled in the fall along a 13-km altitudinal transect from 155 to 1060 m elevation. The sampling sites on the ALE Reserve were selected on the basis of their altitude, vegetation and surface-soil characteristics. The principal characteristics of the sampling sites are described in Table 1.

The primary influences of altitude on soil organic matter deposition and transformations may be expected to arise from differences in vegetation, temperature, and moisture. *Artemisia tridentata* (Big sagebrush) is the principal overstory shrub species throughout the altitudinal sampling range (155 to 1060m) whereas the grass understory consists primarily of *Bromus tectorum* at the lower elevations (< 180m), *Poa secunda* at approximately 180 to 270m, and *Agropyron spicatum* at elevations above 270m (Table 1).

The soils (Table 1) at the lower elevation (Burbank 1s, Ephrata 1) developed in sand overlying gravelly river deposits. At the higher elevations (Warden sl, Ritzville sil, and Licksillet 1) the parent material was primarily aeolian silt (Hajek, 1966). The pH of the untreated soils was measured by the glass electrode method on a thin aqueous paste equilibrated 30 minutes. Particle-size composition was determined by centrifugation techniques according to the method of Jackson (1956).

Soil humic acids, high-charge density extractives of the soil organic matter, were isolated from soils after (1) treatment (3 times) of soil samples (3-5 kg) with HCl (0.1N) at a 3/2 HCl/soil ratio to remove carbonates and undecomposed plant fragments by flotation, and (2) pre-extraction with a 1/1 benzene/ethanol mixture for eight hours in a Soxhlet apparatus to remove fats, waxes, resins, and tannins which might contaminate the humic acid. The benzene/ethanol mixture was saved for elemental analysis. Humic acids were isolated from the residue by NaOH dissolution as described by Wildung *et al.* (1965).

The initial crude humic acid preparations were purified by three repeated dissolutions and precipitations and finally dialyzed against distilled H₂O to remove excess salts. Purified humic acids were chemically characterized as to elemental composition (C, H, and N) and pH dependent cation (Sr) exchange capacity (CEC), a relative measurement of the affinity of the organic functional groups for cations in solution.

The C, H, and ash contents of intact soils and soil humic colloids were measured as described by Wildung *et al.* (1970), whereas N was determined by the Dumas method as described by Welcher (1966).

The CEC of soils and soil humic acids were measured by a modification of the method described by Okazaki *et al.* (1962). Air-dry soil samples (4.000 to 6.000 g), of known moisture contents, were cation saturated at pH 4.0 and pH 7.0 using a buffer solution containing Sr(OAc)₂ (0.8N) and SrCl₂ (0.2N) spiked with ⁸⁵Sr (10,000 dpm/ml) and adjusted to the appropriate pH with dilute HCl or Sr(OH)₂. Cation saturation involved equilibration of the soil by mechanical shaking (3 hrs) with the buffer solution (30 ml) in tared 50-ml centrifuge tubes. Following initial equilibration, centrifugation, and decantation of the supernatant buffer solution, the samples were re-equilibrated (20 min) with a fresh increment (30 ml) of Sr buffer solution. The short equilibrations were repeated an additional five times. Following

TABLE 1. Description of arid land soils.

Classification	Vegetative understory	Elevation	pH	Contents* of				CEC at pH 7.0
				Organic carbon	Sand (> 50 μ)	Silt (50 to 2 μ)	Clay (< 2 μ)	
		M			%			meq/100g
Typic Torripsamment	<i>Bromus</i>	155	<i>Burbank ls</i> 6.9	0.46	76.8	16.8	6.4	11.2
Andic Mollic Camborthid	<i>Bromus</i>	155	<i>Ephrata l</i> 7.4	0.43	44.2	47.1	8.7	16.1
Andic Mollic Camborthid	<i>Poa</i>	190	<i>Warden cl</i> 7.0	0.52	55.5	34.1	10.4	18.1
Andic Aridic Haplustoll	<i>Agropyron</i>	445	<i>Ritzville sil</i> 6.2	0.66	23.3	64.1	12.6	22.5
Lithic Haplustoll	<i>Agropyron</i>	940	<i>Licksillet l</i> 6.2	3.62	42.6	41.1	16.3	40.3

* Percent organic carbon based on total soil, other values on total minerals.

Sr saturation, the samples were equilibrated during 20-min shaking periods a total of six times with diluted buffer solution (0.1N) to reduce the concentration of salts retained by the sample as buffer solution. After final centrifugation the tube and its contents were weighed accurately. Total Sr was displaced from the sample and the buffer solution it retained by 6 (20 min) extractions with N Mg(OAc)₂ adjusted to pH 5.0 with HOAc. The Sr concentrations in a fresh increment of the 0.1N buffer solution and in the combined Mg(OAc)₂ extracts (containing total Sr) were calculated from measurement of ⁸⁵Sr specific activity. The quantity of buffer solution retained by the sample after the final equilibration was determined gravimetrically. A knowledge of the quantity of wash solution retained by the sample and the concentration of Sr in the wash solution (soluble Sr) allowed calculation of exchangeable Sr by subtraction of soluble Sr from total Sr.

The CEC of soil humic acids (0.0250 to 0.0500g) were determined in a similar manner except saturating, washing, and displacing solutions were decreased to 10 ml and plastic 50-ml centrifuge tubes were employed. The plastic centrifuge tubes were lighter in weight than the glass tubes, thereby minimizing weighing errors.

Results and Discussion

The principal objectives of this investigation were to (1) characterize physicochemically representative soils of the ALE Reserve and (2) define the chemical nature of the arid soil organic fraction to provide insight into its role in arid soil chemical transformations.

Intact soils were characterized as to contents of C, alcohol-benzene soluble components, humic acids, and CEC. Isolated humic acids were characterized as to contents of C, H, N, and ash and as to pH-dependent CEC.

Established techniques for the characterization of the soil organic fraction proved generally applicable to the arid soil system when sample size was increased to provide sufficient materials for adequate analytical resolution and precision.

Chemical Properties of Intact Soils

The C content of the intact soils showed an overall increase with increased elevation (Table 1) likely reflecting increased soil organic matter contents as a result of (1) increased plant understory biomass and soil deposition of organic matter with increased rainfall and (2) decreased soil organic matter degradation rate with decreased mean ambient temperature (Rickard, 1968; Hinds and Thorp, 1969). The increased soil C content with higher elevation may also reflect a larger quantity of aromatic substances, resistant to microbial decomposition, deposited on the soil as lignin in associated grass tissues. Previous investigations (Wildung *et al.*, 1968b) have shown that the lignin content of mature *Bromus*, *Poa*, and *Agropyron* tissue amounted to 2.7, 3.6, and 4.5 percent, respectively. Assuming total biomass deposited on the soil by the individual grasses was equivalent, the quantity of lignin reaching the soil in the form of grass tissue should be proportional to the lignin content of the grass tissues and therefore increase upslope.

The soil clay contents ranged from 6.4 to 16.3 percent and also increased upslope (Table 1). Cation exchange capacities (Table 1) of the Burbank, Ephrata, Warden, Ritzville, and Licksillet soils at pH 7.0 were 11.2, 16.1, 18.1, 22.5, and 40.3 meq/100g, respectively, thereby increasing with increased soil clay and organic C content. The

observed increase in CEC resulted from increased surface area and solid-phase coulombic charge associated with higher concentrations of colloidal mineral and organic matter.

Chemical Properties of Soil Humic Colloids

The C removed from soil as humic colloids or accessory (alcohol/benzene soluble) components ranged from 4.0 to 16.5 and 1.7 to 7.8 percent, respectively (Wildung *et al.*, 1968b). On a total weight basis, yields of NaOH and alcohol/benzene soluble materials from soils were less than 0.5 percent and therefore comparisons of the yields of soil extractives would be tenuous. Yields of humic components were substantially increased by removal of CO₂-C prior to extraction. The C, H, and N contents of isolated soil humic colloids were quite similar and ranged from 54.3 to 58.1, 5.7 to 6.2, and 4.8 to 5.8 percent, respectively (Table 2). These data are comparable with values reported by previous investigators (Kononova, 1966; Wildung *et al.*, 1970) for humic components from a wide variety of mineral soils developed under different climatic conditions.

Although elemental compositions of the humic colloids were similar, the Warden sl and Ritzville sil humic acids exhibited significantly higher C and N contents and lower C/N ratios than either the Burbank or Ephrata humic colloids, whereas the Lickskillet humic colloid gave intermediate values (Table 2). The H contents were quite similar with the maximum difference occurring between the Warden (6.2% H) and Lickskillet (5.7% H) samples. The C/H ratios were also similar ranging from 9.1 (Burbank ls) to 9.9 (Lickskillet l).

Cation exchange capacities of soil humic colloids (Table 2) at pH 4.0 and 7.0 ranged from 76 to 196 and 190 to 270 meq/100g, respectively. Thus, the CEC of soil humic acids were markedly pH-dependent, substantiating previous evidence that the CEC of humic acids arises from the negative charge present on the conjugate base of an organic acid after ionization of H. The CEC of the Warden humic acid amounted to over twice that of either the Burbank or Ephrata humic acids at pH 4.0. The Ritzville and Lickskillet were intermediate between the Warden and the Burbank and Ephrata humic acids at the low pH. At pH 7.0, the Warden and Burbank samples gave the highest CEC; the Ritzville and Lickskillet humic acids exhibited the lowest values and the Ephrata occupied an intermediate position.

The comparatively high CEC of the Warden humic acid, particularly at pH 4.0, may reflect the high CEC of the associated plant lignin, *Poa* at 7.0 (Wildung *et al.*,

TABLE 2. Elemental composition and cation exchange capacity of soil humic acids.

Soil humic acids	Ash	Contents of			Ratio of		CEC	
		C	H	N	C/N	C/H	pH 4.0	pH 7.0
	%	% of dry, ash-free sample					 meq/100g	
Burbank ls	1.9	54.3	6.0	4.8	11.4	9.1	93	270
Ephrata l	12.4	55.6	5.8	4.9	11.3	9.6	76	232
Warden sl	1.6	58.1	6.2	5.6	10.3	9.3	196	260
Ritzville sil	2.9	57.8	6.1	5.8	9.9	9.4	132	190
Lickskillet l	1.2	56.6	5.7	5.3	10.8	9.9	117	200

1968b). It may be speculated that the *Poa* lignin contains a larger number of acidic groups ionizing near pH 7.0 than the other lignins, and during soil decomposition these groups are strengthened, resulting in a humic acid comparatively higher in CEC at pH 4.0.

The present investigations have formed a basis for future study of the flow of energy and the influence of the organic fraction on the behavior of organic and inorganic ions in arid soils. Immediate future investigations will be oriented toward (1) elucidation of the factors affecting the rate of decomposition of untreated native plant tissue in arid soils, and (2) isolation of native organo-clay complexes and determination of their role in ion retention.

Summary

As part of a continuing program to determine the role of soil in the flow of energy and cyclization of nutrients within an arid land ecosystem, these investigations were designed as an initial phase in the elucidation of the chemical and biological properties of the soils on the Arid Land Ecological Reserve at Hanford, Washington. Representative arid land soils were characterized as to pH, contents of organic C, sand, silt, clay, and cation (Sr) exchange capacity (CEC). Soil humic acids, amorphous, high molecular weight, and high-charge density organic colloids were isolated from representative soils and compared chemically as to elemental composition and pH-dependent CEC.

Techniques established for isolation and characterization of soil humic colloids from soils in humid and subhumid regions of the world generally performed well when applied to arid soils provided initial soil sample size was increased to allow adequate analytical resolution and precision.

The C and clay contents of untreated soils ranged from 0.43 to 3.6 percent and from 6.4 to 16.3 percent, respectively, and increased with sample site elevation. The increase in organic C content upslope apparently reflects (1) increased plant understory biomass and soil deposition of organic matter with increased rainfall, (2) decreased soil organic matter degradation rate with decreased mean ambient temperature, and (3) increased grass lignin content.

The soil CEC increased with increased C and clay contents as a result of increased surface area and solid phase coulombic charge associated with higher concentrations of colloidal mineral and organic matter.

The yield of soil humic colloids, based on the C content of the intact soil, ranged from 4.6 to 16.6 percent. The CEC of soil humic colloids were markedly pH dependent ranging from 76 to 196 meq/100g at pH 4.0 to 190 to 270 meq/100g at pH 7.0, indicating the presence of a number of acidic functional groups capable of bonding the index cation, Sr.

Elemental composition and CEC of the arid soil humic acids were similar to analogous isolates from humid regions. The chemical properties of arid soil humic acids were quite uniform regardless of changes in altitude or vegetative type.

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