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Contribution of Humic Substances to the Cation Exchange Capacity of Different Marine Sediments*

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Introduction

Although the composition and properties of humic substances associated with marine sediments have been subjects of study for the past few years, there are only isolated instances of a detailed study. Very little is known about the properties of humic substances and the nature of the association of organic matter with the inorganic substrate. In view of the important role played by soil humic substances in the mineral nutrition of plants and various other pedologic processes, the cation exchange properties of these substances have received considerable attention of the soil scientists (Broadbent and Bradford; 1952, Schnitzer 1965, and Yuan et al 1967). It is now well recognized that the clay minerals and the silt fraction ($<20\mu$) carry a net negative charge arising essentially by isomorphous substitution, ionization of hydroxyl groups and broken bonds around the edges of silica-alumina units. Due to this charge these inorganic constituents also participate in cation exchange reaction. Several detailed studies have been carried out on the clay minerals of the soils and their relative role in exchange reactions (Toth 1967; Yuan et al 1967; Wiklander 1967; and Grim 1968). Because of the presence of carboxyl, phenolic hydroxyl and other functional groups in varying quantities, the humic substances of marine origin can also participate in such exchange reactions, thereby influencing the movement and accumulation of various metals in the bottom sediments. Marine geologists and geochemists have not paid due attention to the cation exchange capacity of sediments and hence the literature is almost devoid of pertinent references. In the investigation reported here an attempt is made to characterize the cation exchange capacity of humic substances in relation to the inorganic constituents with which they are intimately associated in the zone of sedimentation.

The term organic matter as used here is analogous to humic substances. Humic acid consists of a group of compounds extracted from the soil or sediments by means of an alkaline solution, and then precipitated upon acidification (Kononova 1966). The term "cation exchange" can be defined as an interchange between a cation in solution and another cation on the surface of any surface-active material such as clays or organic colloids.

Experimental Procedure

Description of the Samples:

The sediment samples included in this study for extraction of humic substances were collected at various locations and from contrasting marine environments. The lagoon sample and sample 68-2-1-1 were collected from Musquodoboit Harbour, Nova Scotia, Canada and Cariaco trench off the east coast of Venezuela respectively and represent a reducing environment whereas samples 68-2-2-1, KC 1244A and KC 1245 come from the normal, well-oxygenated environment of Cariaco and Scotian Shelf areas. The details of collection site, textural make-up, and organic carbon content of all the samples are given in Table 1.

Extraction and Purification of Humic Acids:

The humic acid was extracted from the sediments as outlined by Rashid and King (1969). The procedure, in brief, consists of extracting the humic acid from CO_3-free sediment with 0.5 N sodium hydroxide solution. The extract is passed over Rexyn 101 exchange resin in the hydrogen form to remove sodium and other metal cations present in the extract. The purified extract is then acidified by HCl to a pH of 3 to precipitate the humic acid. The precipitate is collected, washed, dialyzed against distilled water for several days, redissolved in 0.5 N NaOH solution and passed over the resin column several times. Finally it is freeze-dried.

Destruction of Organic Matter in the Sediments:

To determine the cation exchange capacity of the inorganic constituents, the organic

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Table 1 - Description of the Sediment Samples used in Cation Exchange Study.

Sample No. Collection Site and the Environment	Latitude	Longitude	Depth in Meters	Distance from the shoreline in Km.	Organic Carbon %	Textural Analyses		
						Sand %	Silt %	Clay %
Lagoon Musquodoboit Harbour Reducing	44°41.5'N	63°02.3'	2	1/2	13.3	2.89	43.47	53.64
68-2-1-1 Cariaco Trench Reducing	10°31'N	64°32.9'W	1390.8	33.8	1.41	31.14	41.58	27.28
68-2-2-1 Cariaco- Beyond the sill of the trench Normal	11°62.2'N	64°32.1'W	808.3	35.4	2.37	39.57	36.96	23.47
1244A Cow pen - Scotian Shelf Normal	44°18.5'N	60°20'W	198	75.6	4.97	47.66	24.85	27.49
1245 Scotian Shelf Normal	44°18.2'N	61°22.8'W	192	-	5.98	0.0	71.93	28.07

matter remaining in the sediments after extraction of humic acids, was destroyed with 30% H_2O_2; this treatment was continued until frothing stopped. The sediments were then washed and freeze dried. To test whether oxidation of the organic matter was complete, organic carbon was determined in each sample.

Cation Exchange Capacity Measurements:

The cation exchange capacity of the sediments was determined according to the method of USDA (1954). Exchangeable sites in about 4-5 g of sediment were first saturated with sodium using a 1.0 N solution of sodium acetate. This was done by shaking the samples for about four hours, with sodium acetate solution, and then centrifuging. The excess sodium acetate solution was removed by repeated washing with 95% ethanol. The absorbed sodium was displaced from the exchange sites by 1.0 N ammonium acetate solution at pH 7.0, and the concentration of sodium was determined by means of an atomic absorption spectrophotometer.

The cation exchange capacity of the humic acids was determined by ammonium acetate solution as suggested by Schnitzer (1965). In some studies the ammonium acetate solution was replaced with calcium acetate solution, but no appreciable difference in the results was noticed.

Results and Discussions

The values of the cation exchange capacity of the undisturbed sediments, H_2O_2 - treated sediments and the humic acid fractions isolated from these sediments are presented in Table 2. The cation exchange capacity of the various sediments varies from a low of 25.3 to a high of 88.6 meq/100 g, the highest being the lagoon sample which has relatively high organic carbon and clay contents. In the H_2O_2 - treated samples, in which the organic matter was completely destroyed, a drastic reduction in the cation exchange capacity was noticed in the lagoon sample, as well as samples 68-2-2-1 and 68-2-1-1, but the amount of reduction was comparatively low in samples KC 1244A and KC 1245. The cation exchange capacity of the mineral fraction varies from 12.9 to 26.4 meq/100 g, which represents 19.5 to 77.3% of the original cation exchange capacity of the untreated sediments.

Table 2- The Cation Exchange Capacity of Different Untreated (CO_3-free) Sediments, H_2O_2-Treated Sediments and Humic Acids Associated with the Sediments.

Cation exchange capacity or percent C. E. C.	Lagoon	66-2-1-1	68-2-2-1	K. C. 1244A	K. C. 1245	Average
1. Untreated (CO_3-free) sediments in meq/100g	88. 6	25. 3	27. 7	29. 5	36. 5	41. 5
2. H_2O_2-treated sediments "	17. 3	14. 1	12. 9	22. 8	26. 4	18. 7
3. Organic matter by 'difference' "	71. 3	11. 2	14. 8	6. 7	10. 1	22. 8
4. Percent C. E. C. due to organic matter	80. 5	44. 3	53. 4	22. 7	27. 7	45. 7
5. Percent C. E. C. due to clay content	19. 5	55. 7	46. 6	77. 3	72. 3	54. 3
6. C. E. C. of purified humic acids (in meq/100g)	375. 0	250. 0	290. 0	303. 0	287. 0	301
7. C. E. C. of organic matter recalculated on the basis of carbon content and C. E. C. values in line 6	85. 0	20. 4	25. 4	25. 6	29. 2	37. 1
8. Percent contribution of organic matter (line 7) to the total C. E. C. (line 1).	95. 9	80. 6	91. 5	86. 7	79. 9	86. 9
9. Difference between line 4 and 8.	14. 4	36. 3	38. 1	64. 0	52. 2	41. 2
10. Recalculated C. E. C. of the sediments on the basis of line 2 and 7 (in meq/100g)	102. 3	34. 5	38. 3	48. 4	55. 6	55. 8
11. Contribution in C. E. C. by each gram of clay in meq	0. 32	0. 51	0. 55	0. 83	0. 94	0. 634

The difference between the cation exchange capacity of undisturbed and H_2O_2 - treated sediments can be considered equivalent to the exchange capacity of the organic matter. The data in Table 2 shows that the organic fraction contributes 44. 3, 53. 4 and 80. 5% in samples 68-2-1-1, 68-2-2-1 and lagoon whereas in samples KC 1244A and KC 1245 only 22. 7 and 27. 7% of the cation exchange capacity originated from organic fraction. Thus, the overall average of the contribution of the humic acid fraction to the total cation exchange capacity of the sediment is 22. 8 meq/100 g, or about 46% of the total exchange capacity. It must, however, be remembered that the cation exchange capacity of the organic fraction is by no means as clear cut as it is in the clay mineral fraction because of its ability to form complexes with inorganic constituents. Therefore, a reliable estimate of the contribution of the organic fraction to the total exchange capacity cannot be determined by 'difference'method. Schnitzer (1965) has pointed out that the method based on 'difference' measures only one-fifth of the cation exchange capacity of the soils that might be due to the organic matter, because the exchange sites in such a medium can be blocked by iron and aluminum or hydrous oxides of these elements. Silicon and its compounds can also react with the exchange sites. It is, therefore, necessary to determine the cation exchange capacity of the organic matter by other means also.

To obtain a realistic idea about the contribution of organic matter to the exchange capacity of the total sediment, it is desirable to isolate and purify the organic fraction first, and then determine its exchange capacity. The values of the cation exchange capacity of the humic acid fractions as determined by an ammonium acetate solution at pH 7. 0 are reported in Table 2, line 6. These values range from 250-375 meq/100gof humic acid, with an average of about 300 meq/100 g. Based on these findings and the amount of organic carbon present in the sediments, it is possible to recalculate the data to estimate the 'potential' capacity of the organic fraction of the sediments. The re-calculated values which represent the 'potential' capacity of organic matter are presented in line 7 of Table 2. The values in line 8 represent the percentage contribution of the potential cation exchange capacity of the organic fraction to the total exchange capacity of the undisturbed sediments as reported in line 1. A comparison between the 'potential' cation exchange capacity of organic matter and that obtained by 'difference' indicates an increase of 2-4 times in the cation exchange capacity values of some of the samples. In sample KC 1244A, for example, the contribution of organic matter as estimated by 'difference method was 6. 7 meq/100 g, whereas on the basis of its potentiality the same organic fraction appears to contribute 25. 6 meq/100 g. Similarly, in sediment samples KC 1245 the increase in cation exchange capacity value is almost three-fold. Such increases are noticeable in the other samples also. On the basis of data recalculated to show the potential exchange capacity of organic matter, it is evident that the contribution of this fraction ranges from about 80-96% with an overall average of 87%, which is almost double the value obtained by 'difference' method. If the potential cation exchange capacity of the organic fraction is taken into account along with the contribution of inorganic constituents as shown in line 2, the entire range of cation exchange capacity of the sediments changes from 25. 3-88. 6 meq/100 g to 34. 5-102. 3 meq/100 g of sediments.

Functional Groups of Organic Matter Participating in the Exchange Reactions:

The cation exchange capacity of the organic matter originates mainly due to the exchangeable hydrogen present on carboxyl and phenolic hydroxyl groups (Broadbent and Bradford; 1952, Kyuma and Kawaguchi; 1964 and Kononova; 1966). The role of other groups has not been clearly defined yet although enolic hydroxyl groups and the hydrogen attached to the nitrogen in heterocyclic compounds may also be important in such reactions. The participation of the hydrogen of carboxyl and phenolic hydroxyl groups depends upon the condition of the medium. The higher the reaction (pH) of the medium the greater will be the participation of hydrogen in the exchange reactions (Kononova 1966).

On the basis of their investigations concerning the functional groups responsible for cation exchange capacity of organic matter Broadbent and Bradford (1952) have reported that the carboxyl groups alone do not furnish the exchangeable hydrogen, although more than half the average exchange capacity, in their studies, was found to arise from this group. They have postulated that the rest of the cation exchange capacity is probably due to phenolic and enolic hydroxyl groups and other sources. It is of significant interest to mention here that the marine humic substances are conspicuously low in phenolic hydroxyl content as shown by Rashid and King (1970). These authors reported that the acidic characteristics of humic substances of marine origin are mainly due to carboxyl groups in contrast to soil humic acids where phenolic hydroxyl groups also play a prominent role.

Terrigeneous humic matter has long been known to contain a high phenolic hydroxyl content consistent with its aromatic structure; marine organic matter on the other hand, is essentially aliphatic in character and possesses a high carboxyl content. In view of the inherent low concentrations of phenolic hydroxyl groups no attempt was made to ascertain the role of phenolic hydroxyl group in relation to carboxyl groups. Besides low concentrations of phenolic hydroxyl groups, other factors of the marine environment, especially the pH in the zone of sedimentation, may not be very favourable for effective participation of these groups in exchange reactions. Kononova (1966) expressed the view that the cation exchange capacity determined at a pH of 7. 0 is due to exchangeable hydrogens of carboxyl groups only. In her opinion hydrogens of the phenolic groups become active in an alkaline medium only. The pH values of the interstitial waters squeezed from several samples of recent oceanic sediments collected from several areas have been reported by Siever et al (1965). According to these authors values range from 7. 00 to 7. 85 with most of the values clustering in the range of 7. 2-7. 7. Under these conditions of pH, the phenolic hydroxyl groups may not assume much importance in cation exchange phenomena.

Marine geologists have not paid due attention to the phenomenon of cation exchange capacity of sediments or the organic constituents associated with them, and hence the references on this subject are scant. McAllister (1964) has reported cation exchange capacity values of marine sediments collected from West Mississippi Delta area. According to him the values range from 55. 1 to 62. 4 meq/100 g of sediments where the organic matter was left intact and 54. 7 to 64. 2 meq/100 g for sediments without organic matter. The values reported by him are generally higher than the values noted in our study. It is, however, difficult to comprehend the higher cation exchange capacity of sediments where the organic matter is destroyed as compared to sediments with organic matter left intact. With the removal of organic constituents, we have noted a drastic reduction in cation exchange capacity of the sediments, the proportion being as high as 80% in some cases. In the absence of additional information in the iterature on cation exchange capacity of marine sediments or their organic constituents, it is probably worthwhile to examine information on similar properties of soils and their humic substances.

Wiklander (1967) reported that the cation exchange capacity of the soil minerals may range, depending on the clay content, from a few to 50 or 60 meq/100 g whereas for organic soils it may exceed 200 meq/100 g. According to his report, the cation exchange capacities of a chernozem soil, a Holland soil and a California soil are 56. 1, 38. 3 and 20. 3 meq/100 g respectively. Wen (1961) reported a range of 3 to 13 meq/100 g for some tropical soils. The cation exchange capacity of separated organic matter depends on the source of humic acid as well as the stage of its decomposition. According to Kononova (1966) the cation exchange capacity of the humic acids extracted from chernozems, podzol and dark chestnut soils is 474. 5, 345. 2 and 383. 3 meq/100 g respectively. Wiklander (1967) reported a range of 250-450 meq/100 g whereas Wen (1961) reported 272. 8 and 355. 5 meq/100 g for the humic acids extracted from red earth and laterite soils respectively. According to Vil'k (1962) a mountain soil humic acid has a cation exchange capacity of 216 meq/100 g.

It is apparent from these data that the exchange capacity of the humic acids varies with the soil type. It is generally high in well developed soils like chernozems and chestnuts and low in podzol soils. In many respects the cation exchange capacity of the humic acids associated with marine sediments is similar to podzol humic acids as both are characterized by a low degree of humification.

In the soils literature there are reports indicating the relative contribution of humic substances to the overall cation exchange capacity. Yuan et al (1967), for example, reported that the contribution of the organic fraction to the total cation exchange capacity ranged from 66. 4 to 96. 5% although the corresponding clay fraction's contribution ranged from 33. 6 to as low as 3. 5%. They also stated that each gram of organic matter contributed from 1. 38 to 3. 97 meq of cation exchange capacity while each gram of clay contributes from 0. 19 to 1. 29 meq. Peech and Young (1948) reported approximately 2 meq cation exchange capacity for each percent of organic matter, while Helling et al (1964) stated that organic matter accounts for 40. 8% of the cation exchange capacity as determined at pH 7. 0. Schnitzer (1965) reported that about 70% of the exchange capacity of a Podzol soil is due to organic matter and that its potential capacity is several times greater than the measured one. In many respects the data in Table 2 are in agreement with the reports of the soil scientists.

In marine sediments the contribution of clay minerals to the cation exchange capacity ranged from 0. 32 to 0. 95 meq per gram. The values are particularly high in samples KC 1244A and KC 1245. Complete chemical and mineralogical analyses of the sediments were not carried out as this was not the purpose of the study, but it is sufficient to mention that illite, chlorite and montmorillonite are found in abundance in modern sediments of all oceans (Mackenzie and Garrels, 1966). In cation exchange reactions the various clays and their relative abundance are important factors. A small change, for example, in the percentage of montmorillonite makes considerable difference in the total cation exchange capacity while relative large changes in illite and chlorite do not seriously affect the results. The relatively high cation exchange capacity of the inorganic constituents of samples KC 1244A and 1245 may be due to higher content of montmorillonite or some amorphous substances of silica and alumina which possess a high cation exchange capacity.

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