EXCHANGEABLE MANGANESE IN RIVER AND OCEAN MUDS.*

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ABSTRACT. Manganese in an exchangeable form has been found in river and ocean muds. This exchangeable manganese is coexistent with dissolved manganese in the waters in direct contact with the muds. As the amount of total manganese in the muds increases the amount of exchangeable manganese decreases. A high content of total manganese in sediments is caused by accumulation of one or more insoluble hydrated manganese dioxide minerals of unknown constitution.

An increase of exchangeable manganese and a decrease of insoluble oxides of manganese in sediments are promoted by reducing conditions that arise through the decomposition of organic matter, and conversely, a decrease of exchangeable manganese and an increase of insoluble oxides are favored by oxidizing conditions that generally prevail in the absence of decomposing organic matter.

INTRODUCTION.

AT the request of A. C. Spencer of the U. S. Geological Survey an investigation of the exchangeable cations that are present in river muds was recently undertaken in the Survey's Chemical Laboratory. This was part of a preliminary study by Doctor Spencer of the exchange reactions that the suspended matter of rivers undergoes when it is discharged into the sea. The chemistry of cationic exchange in materials closely related to river muds, namely, clays, soils, and soil colloids, has been actively investigated by soil chemists for many years, and the writings of Kelley[1] and Jenny[2] may be consulted for summaries of the modern literature.

The exchange of cations by river muds on entering the sea represents an adjustment to the change in environment from fresh river water to ocean brine, and it has been found that in the course of this adjustment the muds liberate calcium and manganese and take up in exchange sodium, magnesium, and potassium from sea water. The quantities of the several elements involved in this reaction of the muds are appreciable when compared with the amounts reaching the sea in the dissolved state. The problem in its broadest aspect will be discussed by Doctor Spencer and the writer in another paper.

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[1] Kelley, W. P., Dore, W. H., and Brown, S. M.: Soil Sci. 31, 25, 1931.

[2] Jenny, Hans: Jour. Phys. Chem. 36, 2217, 1932.

This report will deal only with a constituent of river and ocean muds that was not thought of at the beginning of the study but was found in every sample examined, namely, exchangeable manganese.

The river muds might be expected to contain some exchangeable manganese in view of its universal occurrence in soils.[3] Furthermore, owing to their submerged condition, the muds are likely to encounter reducing environments rich in dissolved manganese, like those examined by Robinson,[4] and this would tend to increase their exchangeable manganese content.

Curiously enough, the fundamentals of manganese exchange have not yet been formally established. No exchange isotherms with clays or permutites which would make comparisons with other cations possible seem to have been determined. However, the experiments of Prince and Toth,[5] in which soils treated with a manganous chloride solution were subjected to electrodialysis or to leaching with one normal ammonium acetate and one-twentieth normal hydrochloric acid, show that the presence of exchangeable manganese can be demonstrated by the methods of displacement in current use by soil chemists. The effect of calcium and magnesium carbonates on the water-soluble manganese of soils has been studied by Mann,[6] who found a rapid decrease of the soluble manganese with increasing quantity of the carbonates. It may be inferred from this that the existence of exchangeable manganese, which is concomitant with the water-soluble manganese, tends to be disfavored by a high percentage of carbonates in sediments. Prince and Toth have shown that dilute solutions of calcium hydroxide readily reduce the amount of exchangeable manganese in soils.

MATERIALS STUDIED AND ANALYTICAL METHODS.

Muds from five rivers, the Colorado, Mississippi, Ohio, Potomac, and the Monocacy, a tributary of the Potomac, were available for study.

The Colorado River sample was collected by C. S. Howard of the Water Resources Branch of the U. S. Geological Survey, from the bottom of Lake Mead at Boulder Canyon, which is about one hundred miles from the point where the river enters

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[3] Slater, C. S., and Byers, H. G.: U. S. Dept. Agr. Tech. Bull. 461, 1934.

[4] Robinson, W. O.: Soil Sci. 30, 197, 1930.

[5] Prince, A. L., and Toth, S. J.: Soil. Sci. 46, 83, 1938.

[6] Mann, H. B.: Soil Sci. 30, 117, 1930.

the Lake. Over 90 per cent of it had a particle size less than twenty microns.

The Mississippi River sample represents the suspended matter that was in the river at New Orleans during the height of the 1938 spring flood, and was collected by A. A. Hirsch of the New Orleans Sewerage and Water Board.

The Ohio River mud was that found deposited on the banks near Mound City, Illinois, by G. R. Mansfield of the U. S. Geological Survey, after the great flood of January, 1937. Seventy-four per cent of it consisted of materials with particle size less than twenty microns.

The Potomac River sample was from a deposit in a shallow portion of the Dalecarlia Reservoir near Washington, D. C., and contained much coarse matter.

The material from the Monocacy River was collected near its mouth by A. C. Spencer. It was very fine in texture and occurred as a dry deposit on the banks.

The Colorado, the Mississippi, and the Potomac muds arrived in the laboratory, bottled in contact with their respective river water. They were filtered off on Buchner funnels, partly dried on the steam bath, pulverized, screened through a 200-mesh sieve, and allowed to dry under room conditions. The Ohio and the Monocacy samples were merely passed through the 200-mesh sieve and allowed to dry under room conditions.

In addition to the five river muds, the well-known composite samples of red deep-sea clay, of terrigenous blue mud, and of the deltaic deposit of the Mississippi River that have been studied by Clarke and Steiger[7] were examined. A partial mechanical analysis of the red clay and the blue mud composites by Robinson and Fry of the Bureau of Chemistry and Soils is on record,[8] as follows:

	Red clay	Blue mud
Colloids	63.3	66.5
Noncolloids	16	22
$CaCO_3$*	8.8	9.2

* Determined by George Steiger.

A small sample of red clay (No. 73), collected from the Pacific Ocean by a *Carnegie* expedition and submitted to the

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[7] Clarke, F. W.: Proc. Roy. Soc. Edinburgh 27, 167 and 269, 1906-07.
Clarke, F. W., and Steiger, G.: Jour. Washington Acad. Sci. 4, 59, 1914.

[8] Wells, R. C.: U. S. Geol. Survey Bull. 878, 71, 1937.

Chemical Laboratory for dehydration studies, was also available for study.

The following characteristics were first noted for the nine samples:

Sample	Loss of wt. at 160°C per cent	CO_2 from carbonates per cent	Organic matter per cent	H_2O_2 reaction
Colorado	7.45	3.20	1.31	slow
Mississippi	8.12	none	2.57	slow
Ohio	3.76	none	2.94	slow
Potomac	3.40	none	2.99	slow
Monocacy	3.46	none	3.36	fast
Red clay	4.89	3.52	.82	violent
Pac. red clay	3.06	....	.70*	fast
Blue mud	5.18	4.05**	2.38**	slow
Mississippi delta	2.47	1.28	.86	slow

* Analysis by R. Revelle.
** Analysis by George Steiger.

The carbon dioxide of the inorganic carbonates was determined gravimetrically, and ferrous chloride was added to the 1:10 hydrochloric acid that was employed, to reduce the breaking down of the organic matter. The chromic acid oxidation method, arranged for a gravimetric procedure, gave the carbon dioxide of both the carbonates and organic matter. That of the organic matter was obtained by difference and the organic matter calculated by using the conventional factor 0.47. An acidified silver sulphate solution was present in the train to fix the hydrochloric acid formed from the sea salts. The reaction of a sample towards 15 per cent hydrogen peroxide, as was demonstrated by Robinson,[9] is a rough measure of the manganese dioxide content.

The method for determining exchangeable manganese was similar to the one used by Robinson. A gram sample was allowed to stand overnight in 75 ml. of neutral normal ammonium acetate and then leached on a paper filter with further portions of the ammonium acetate solution until 250 ml. of the leachate was obtained. This was evaporated on the steam bath with 5 ml. of hydrochloric acid, the ammonium salts and the dissolved organic matter were decomposed by evaporating with nitric acid followed by sulphuric acid to fumes, and manganese determined colorimetrically by the well-known periodate

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[9] Robinson, W. O.: Soil Sci. 27, 335, 1927.

method. A blank was also run with negative results. The residue on the filter was ignited, decomposed with a mixture of nitric and hydrofluoric acids, fumed with sulphuric acid, and its manganese also determined colorimetrically. The sum of the manganese in the ammonium acetate leach and in the residue is reported as total manganese. Duplicate determinations were made on some samples and they indicate the precision obtained.

The analytical results are calculated on the basis of carbonate-free samples dried at 160° C. However, the analyses themselves were always made on unheated samples as the work of Kelley and McGeorge[10] on Hawaiian soils has revealed the effect of heating on the solubility of soil manganese. The reference temperature of 160° C., which was suggested by P. G. Nutting of the Geological Survey's Chemical Laboratory, is such that the muds are entirely free of their absorbed water and therefore independent of the moisture that causes their weight to vary considerably with the changes in humidity. Some of the organic matter may be decomposed at this temperature, however. With the three composite samples, the occluded sea salts were also deducted on the basis of Steiger's analyses. In calculating out the carbonate found in some of the samples, the assumption was made that it was solely calcite. Some detrital dolomite was found in the Colorado River mud by F. C. Calkins of the Geological Survey. As rhodochrosite interferes with the determination of exchangeable manganese, the samples were examined for it under the microscope but none was found.

Correns[11] has made an extensive study of the total manganese content of the bottom muds collected by the *Meteor* expedition to the South Atlantic, and his average values for samples from the deep sea (depths$>$200 meters) and the shallow sea (depths$<$200 meters) are included in the table of results for comparison. Likewise, the average manganese content of American soils as given by Byers, Anderson and Bradfield[12] is included.

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[10] Kelley, W. P., and McGeorge, W.: Hawaii Agr. Exp. Sta. Bull. 30, 1913.

[11] Correns, C. W.: Deutsche Atlantische Expedition 1925-1927, Band 3, Teil 3, Lieferung 2, 219-233, 1937.

[12] Byers, H. G., Anderson, M. S., and Bradfield, R.: U. S. Dept. Agr. Yearbook for 1938, p. 917.

Total and exchangeable manganese of river and ocean muds. Per cent of sample free of carbonates and soluble salts, weight at 160° C.

Sample	Total MnO per cent		Exchangeable MnO per cent	
Colorado	0.080		0.044	
Mississippi	.105	.115	.052	.061
Ohio	.179	.172	.024	.029
Potomac	.149		.039	.044
Monocacy	.220		.020	
Red clay	1.02		.012	
Pacific red clay	.370		.014	
Blue mud	.144		.032	
Mississippi delta	.074		.029	
Meteor deep-sea	.381*			
Meteor shallow-sea	.035*			
Average American soil	.14**			

* Weight at 105° C; contains sea salts.
** Weight at 110° C.

Although the number of samples examined is too small for the results to serve as a basis for final generalizations, certain trends are apparent. The average total manganese content of the five river muds is 0.147 per cent, which is close to the average figure for the American soils and for the composite blue mud sample. It is much lower than the amount in the composite sample of red clay and the *Meteor* deep-sea material, but higher than the average amount in the *Meteor* shallow-sea material. For an extended discussion of the distribution of manganese, the reader is referred to Correns' paper and to Vernadsky's book on geochemistry.[13] As noted by Correns, both the samples of the *Meteor* expedition and the composites of red clay and blue mud demonstrate that manganese accumulates in the sediments of the deeper seas, but the MnO contents of the shallow- and deep-sea samples of the *Meteor* expedition are notably lower than those of the corresponding composites. The higher manganese content of the Pacific muds, which are included in the composite samples, may account for the discrepancy in part.

The Monocacy mud and the two samples of red clay, of the materials examined, contain the largest amounts of total manganese and they react most vigorously with hydrogen peroxide. This relationship agrees with what has been found in

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[13] Vernadsky, W. J.: Geochemie, pp. 61-80, Leipzig, 1930.

soils and directly indicates that a high percentage of total manganese is due to an accumulation of one or more insoluble manganese dioxide minerals. The constitution of these hydrated oxides of manganese is unknown, though many chemical analyses have been made. For convenience these hydrated oxides will be referred to simply as manganese dioxide. In a recent X-ray study of a black manganese nodule from the Mid-Pacific, Merwin and Posnjak[14] arrived at the interesting result that the manganese mineral of these nodules is distinct from any of the other known higher oxides and hydrous oxides of manganese.

The waters in contact with the samples from the Colorado, Mississippi, and Potomac rivers were found to contain 1.8, 0.47, and 6.8 parts of Mn per million respectively. This gives the order of magnitude of the concentration of dissolved manganese that is in equilibrium with the river muds. The quantities fall within the range of concentration for river waters in general as given by Hewett,[15] though they probably are higher than the quantities that usually prevail in the three particular rivers.

The average exchangeable manganese content of the river muds is equivalent to 1.1 milliequivalents per 100 grams. This quantity is of the same order of magnitude as that of the exchangeable alkalies, sodium and potassium that are present in the river muds.

In view of the fact that the concentration of dissolved manganese in sea water is only around 20 parts per billion[16] the presence of as much exchangeable manganese in the blue mud as in the river muds is at first surprising. Sea water having a pH of around 8 and containing dissolved oxygen rapidly removes dissolved manganese to an exceedingly low concentration by precipitating it as manganese dioxide. The explanation lies in the fact that the solution in contact with the blue muds is different from normal sea water, and contains far more dissolved manganese. Murray and Irvine[17] have reported an average of 6 parts per million in the waters in direct contact with the coastal muds of Scotland. The reducing action of

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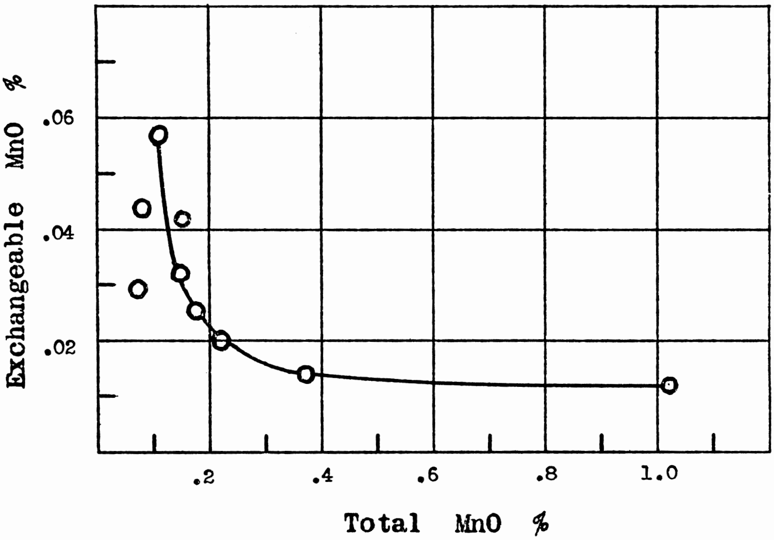
[14] Merwin, H. E., and Posnjak, E.: This Journal 35-A, 182, 1938.

[15] Hewett, D. F.: in W. H. Twenhofel's Treatise on Sedimentation, 2nd ed., p. 563, 1932.

[16] Thompson, T. G., and Wilson, T. L.: Jour. Am. Chem. Soc. 57, 233, 1935.

[17] Murray, J., and Irvine, R.: Trans. Roy. Soc. Edinburgh 37, 721, 1894.

decomposing organic matter renders the manganese dioxide particles in the muds soluble and enhances the manganese content of the mud waters. Murray and Irvine, however, failed to recognize the possibility of dissolved manganese becoming fixed in the mud in exchangeable form. They interpreted the manganese extracted from the coastal muds by dilute acetic acid as being derived from a hypothetical manganese carbonate, whereas it most likely was exchangeable manganese that had been displaced by the hydrogen ion of the acid.



Relation between exchangeable and total manganese in river and ocean muds.

The amount of exchangeable manganese in the muds decreases as the total manganese increases. This relation is most clearly revealed in the above graph.

As Robinson (1927) has shown that manganese dioxide in soils is concentrated in the silt fraction and the exchangeable manganese is found largely in the clay fraction, a possible explanation of the relationship found in the muds that first suggests itself is a fractionation which has brought about differences in the mechanical composition of the samples. However, no correlation between the manganese content of the muds and their mechanical composition is apparent.

The results clearly show that conditions that favor the accumulation of manganese dioxide in sediments disfavor the existence of exchangeable manganese, and conversely conditions that increase exchangeable manganese reduce the manganese dioxide content. The relationship seems best explained by the theory of Murray and Irvine, which stresses the action of decomposing organic matter in dissolving the manganese dioxide of the sediments. This action, by changing the element from an inert state into a mobile and potentially mobile condition of dissolved and exchangeable divalent cations, promotes the escape of manganese from the muds and thereby tends to lower the total manganese content. Murray and Irvine state,

> "The chemical processes in operation tend to favour its (manganese dioxide) accumulation towards the surface of marine deposits and in those areas on the ocean floor where there is relatively small amount of decomposing organic matter in the deposits at the bottom."

As postulated by them, the red clay of the ocean deeps is notably poorer in organic matter than the blue muds closer to land or the river muds.

The same relation between content of organic matter and solubility of manganese was noted by Robinson (1930) in his study of submerged soils. Samples low in organic matter showed no appreciable solubility of their manganese upon submergence. Without organic matter to work on, bacteria could not bring about the intensely reducing conditions noted in the other samples. In accounting for the accumulation of radium in sediments of the deeper parts of the ocean, Piggot[18] also attached great importance to the reducing action of decomposing organic matter and to the oxidizing condition that prevails in absence of decomposing organic matter.

Important as this factor of reducing and oxidizing conditions is in directing the general distribution of manganese in river and ocean muds, its influence is often obscured by other factors that locally affect the distribution of the element. For the discussion of these the reader is referred to Correns' detailed work on the manganese content of the South Atlantic sediments.

ACKNOWLEDGMENTS.

The writer expresses his sincere thanks to those who collected the river muds, and to R. C. Wells who critically read the man-

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[18] Piggot, C. S.: This Journal 25, 229, 1933.

uscript of this report. Grateful acknowledgment is also made of valuable informal discussions with A. C. Spencer and with W. O. Robinson, of the Bureau of Chemistry and Soils.

APPENDIX.

The solubilities of manganese minerals in ammonium acetate.

The solubilities in neutral normal ammonium acetate of some of the manganese minerals that may occur in sediments are of interest here in that the manganese dissolved from them may be confused with exchanged manganese. Determinations were made on samples that were finely ground and washed with water. The amounts dissolved are given below in terms of milligrams of MnO per 250 ml. in order to facilitate comparison with the amounts of exchangeable manganese found above in the muds. The colorimetric method, as employed, would detect about 5 x 10^{-8} gram MnO.

Solubilities of manganese minerals[19] in neutral normal ammonium acetate at 25° C.

	Milligrams of MnO per 250 ml.
Rhodochrosite	6.8
Deep-sea nodule	.49
Wad	.13
Psilomelane	.05
MnO_2, C. P.	none

These figures indicate the relative solubilities of the several minerals, but cannot be used directly to calculate a correction for dissolved manganese because the full solubilities are not realized in the leaching method for determining the exchangeable cations. It may be inferred, however, that rhodochrosite would interfere in the determination of exchangeable manganese.

The amount of manganese dissolved from the deep-sea nodule is equivalent to 0.049 per cent MnO on a gram sample of a sediment. To learn whether this amount of dissolved manganese would appear in the leaching method, 10 mg. of the

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[19] The sample of rhodochrosite available had the composition, $MnCO_3$ 62.6, $FeCO_3$ 31.8, $MgCO_3$ .9, $CaCO_3$ 2.2, insoluble 2.4 per cent.

The manganese nodule was dredged from the South Pacific Ocean by the Agassiz-Albatross expedition, specimen No. 76,672. Kindly furnished by Dr. W. F. Foshag of the U. S. National Museum.

For analyses of the psilomelane and the wad, see Wells, R. C., U. S. Geol. Survey Bull. 878, pp. 92 and 93 respectively.

finely ground and washed material of the nodule was thoroughly mixed into one-gram samples of the composite red clay and the Monocacy mud, which were then leached with 250 ml. of ammonium acetate and the leachate analyzed as in the regular determination of exchangeable manganese. The amounts in the leachate were 0.008 and 0.025 per cent MnO of the samples. These are the same, within experimental error, as the exchangeable manganese, namely, 0.012 and 0.020 per cent MnO for the red clay composite and the Monocacy mud respectively. Therefore, manganese nodules of this kind do not dissolve sufficiently in the leaching method to alter the figure for exchangeable manganese, and the same may be concluded for the other less soluble oxides of manganese listed above.

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