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CHEMICAL CHARACTERIZATION OF BOTTOM SEDIMENTS

D. G. Ballinger and G. D. McKee

Characterization of bottom deposits is an important factor in the study of water quality in that it yields valuable information about the source of settleable material, the effect of the sediments on the quality of the overlying water, and the biological systems that will predominate.

Bottom deposits are the result of the settling of suspended material from the overlying water. In a flowing stream, reduced velocity in some reaches permits the accumulation of solids on the stream bed in localized areas, whereas in lakes and reservoirs the sediment is more uniformly distributed.

In rivers the predominant source of bottom sediments is land runoff. Impoundments and estuaries are often characterized by heavy siltation from tributary streams. In fertile lakes and swamps, the sediment may be largely composed of decaying vegetation, i.e., humus. Polluted streams often contain large beds of organic deposits from wastewater. These sludge beds generally occur downstream from points of discharge of raw wastewater or effluent from primary treatment plants. Industrial wastes from paper mills, textile plants, gravel, lumbering, and mining operations may contain large amounts of suspended solids (SS) that form deposits in the receiving stream.

Influence on Water Quality

While bottom deposits were derived from the overlying water, these sediments may continue to have a significant effect on the water quality. Decomposing organic materials exert an oxygen demand,[1,2] release nutrients during periods of flush-out or turnover,[3] and contribute hydrogen sulfide and methane to the water.

The nature of bottom substrates determines the type of organisms in the benthos.[4] A shifting sand bed offers a poor habitat, while rich organic ooze is often teeming with macroscopic and microscopic life.

Identification or characterization of bottom deposits is generally based on sensory criteria. Color, odor, texture, or even proximity to an outfall are often used to distinguish wastewater sludge from natural sediments. "Standard Methods"[5] offers little assistance in securing uniformity of identification or description. In the use of appearance, "(there are) no standard methods being recommended for describing these characteristics." For color, "there are no recommended terms for recording the color of the sample." In the case of odor, "(there are) no standard terms for defining odors." Aquatic biologists are reluctant to define a deposit as "sludge" unless certain characteristic living forms are present. It is obvious that the experience and judgment of the observer influences his identification of a deposit. There seems to be no standard definition or classification, and therefore disagreement may exist

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concerning the source, nature, and significance of a bottom sediment at a particular site.

Efforts toward the chemical characterization of sediments have been largely restricted to nutrient studies. Juday *et al.*[6] analyzed bottom deposits in Wisconsin lakes for phosphorus, organic carbon, and organic nitrogen. Sawyer[7] studied muds in the Madison, Wis., lakes to determine "their significance as contributors of nitrogen and phosphorus to waters above them." McGauhey *et al.*[8] determined moisture, Kjeldahl nitrogen, and total carbon in Lake Tahoe sediments as part of a study on proposed waste disposal methods. Bottom sediments in Green Lake, Seattle, Wash., were analyzed for total phosphorus, total nitrogen, and volatile solids (VS) by Sylvester and Anderson.[3] Wrobel[9] determined total nitrogen and organic carbon in muds in a study of the interdependence of bottom and water in ponds.

The use of chemical analyses as a means of bottom sediment classification has been proposed by Lenhard *et al.*[10] Using methods derived from soil analysis, these authors classified bottom sediments according to their physical, chemical, and biochemical characteristics. The pollution of the Apies River near Pretoria, South Africa, was studied by means of sediment chemical characteristics.

As suggested by the studies cited above, chemical analysis of bottom deposits offers an additional tool for the investigation of pollution. The methods and classification systems proposed in this paper are the result of 2 yr of examination of bottom sediments from a variety of waters in the U. S. Using analytical procedures currently available in most water pollution laboratories, data on the chemical nature of sediments was obtained, and such data led to conclusions as to the source of deposits and their probable effect on water quality.

In terms of pollutional sources and effects, the most important characteristic of bottom deposits is the organic matter. The concentration of organic carbon and organic nitrogen depend on the composition of the material originally suspended in the water and govern the extent of oxygen demand and nutrient contribution.

Organic carbon in soils has long been determined by wet oxidation. In 1914, Ames and Gaither proposed an acid dichromate digestion.[11] The procedure was modified by Schollenberger[12] in 1927, by Clark and Ogg[13] in 1942, and by Allison[14] in 1960. The wet oxidation method was applied to the determination of organic carbon in marine muds by El Wakeel and Riley.[15] Because of the routine application of the dichromate chemical oxygen demand (COD) procedure to industrial wastes, that technique was adapted to the determination of organic carbon in the studies described here.

Organic nitrogen is traditionally measured by the Kjeldahl method. In this investigation a micro-Kjeldahl apparatus was used and the procedure modified to eliminate ammonia.

Sample Preparation

Sediment samples were collected by dredge, restricting the sample to the upper 2 in. (5.1 cm) of deposit, with care to include the mud-water interface material. Core samples were removed intact and segmented later. In the laboratory the excess water was removed by decanting or filtration, and the sediment spread in evaporating dishes. After drying in a vacuum oven at 50°C overnight, the samples were pulverized in a ball mill or mortar and pestle and returned to the oven for an additional hour. After cooling in a desiccator, the dried powder was transferred to vials and stored until analyzed.

The following procedure is recommended for determining the contents of the samples.

TABLE I.—Bottom Sediment Composition and Type

Typical Sediments	Organic Carbon (%)	Organic Nitrogen (%)	Type
Sand, silt, clay, loam	0.4– 2.1	0.02–0.10	I
Old stable sludge, peat, organic debris	2.0– 5.0	0.10–0.20	I
Paper mill wastes	6 –15	0.10–0.30	II
Packinghouse wastes	2.8– 4.3	0.30–0.50	III
Fresh sludge, decaying algae, wastewater solids	5 –40	0.70–5.0	IV

Determination of Organic Carbon

Reagents and Apparatus

Use reagents and apparatus identical to those used for the determination of COD, as shown in "Standard Methods."[5]

Procedure

Accurately weigh approximately 100 mg of the dried sediment and transfer to the boiling flask. Add 50 ml distilled water and proceed with the addition of reagents, refluxing for 1 hr, and titrating, as in COD determination.

Calculation

Percent Organic Carbon

$$= \frac{(a - b) \times N \times 8 \times 100}{2.67 \times \text{mg sample}}$$

where

a = milliliters ferrous ammonium sulfate used for blank,
b = milliliters ferrous ammonium sulfate used for sample,
N = normality of ferrous ammonium sulfate.*

Determination of Organic Nitrogen

Reagents and Apparatus

Use any standard or micro-Kjeldahl apparatus and associated reagents.

Procedure

Accurately weigh approximately 100 mg of the dried sediment and transfer to the digestion flask. Add the necessary amount of distilled water and pH 7.4 buffer. Boil for 20 min on digestion rack. Cool and proceed as in usual Kjeldahl determination.

Calculation

Percent Organic Nitrogen

$$= \frac{\text{mg nitrogen found} \times 100}{\text{mg sample}}$$

Using the analytical procedures described, more than 200 bottom sediment samples from rivers, lakes, and estuaries were examined. Based on the range of values obtained, the sediments were arbitrarily divided into four general classes. A summary of the analytical results and the classifications assigned are shown in Table I.

To aid in classifying deposits by means of carbon and nitrogen values, a grid system, shown in Figure 1, was developed. The division lines at 5 percent organic carbon and 0.20 percent organic nitrogen were chosen as the best approximation of the distinction between sediment types, even though all deposits did not fit neatly into one of the four classes.

Organic Sediment Index

While the classification shown in Figure 1 is useful in predicting the pollutional significance of the sediment, a single index of relative organic concentration is desirable. Initially, the ratio of organic carbon to organic nitrogen was considered, but this value gave poor correlation with either source or significance because deposits may be either actively decomposing or rela-

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* The factor 2.67 is derived from the oxidation of molecular carbon to CO_2. It is recognized that not all carbon reacts as molecular carbon and that oxidation to CO_2 is not always complete. Thus the percent organic carbon, while reasonably correct, is relative rather than absolute.

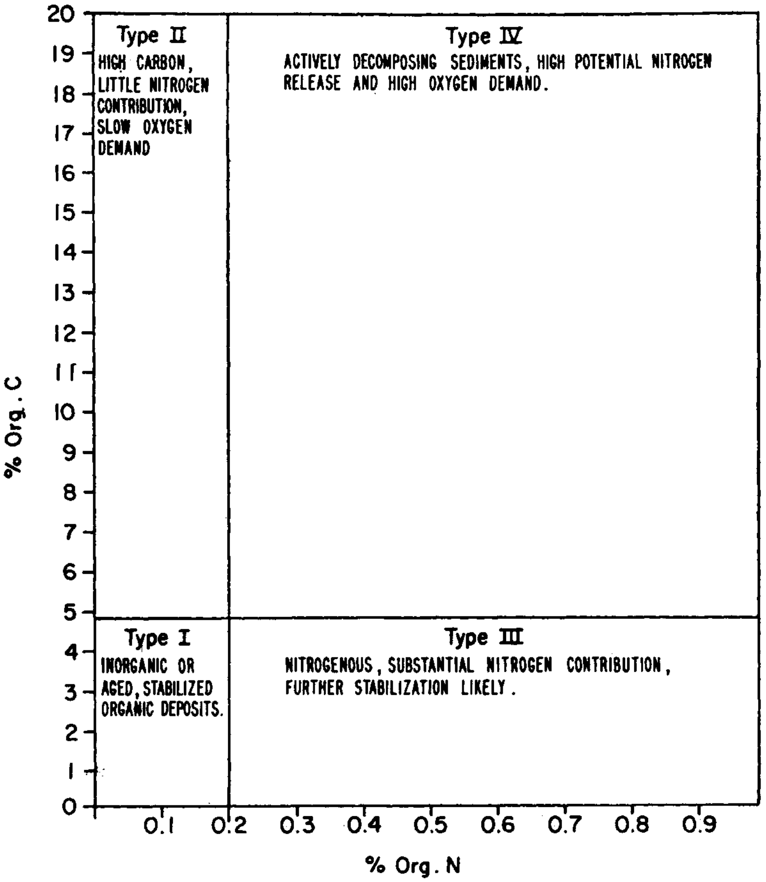

FIGURE 1.—Bottom sediment classification.

tively stable, yet have the same ratio of carbon to nitrogen. Because both carbon and nitrogen are required for decomposition, an expression incorporating the magnitude of both elements seemed necessary. Accordingly, the product of the percent organic carbon and percent organic nitrogen was calculated. An excellent correlation with sediment source was obtained. This product, termed the "Organic Sediment Index" (OSI) is

TABLE II.—Analysis of Bottom Sediments, Red River (N. D. and Minn.) and Kanawha River (W. Va.)

Sampling Station	River Mile		Organic Carbon (%)		Organic Nitrogen (%)		Organic Sediment Index		Sediment Type	
	Red River	Kanawha River	Red River	Kanawha River	Red River	Kanawha River	Red River	Kanawha River	Red River	Kanawha River
No. 1	462	71.2	1.6	1.8	0.14	0.04	0.22	0.06	I	I
No. 2	445	67.9	3.1	3.8	0.31	0.05	0.96	0.19	III	I
No. 3	441	54.3	4.3	8.6	0.39	0.30	1.67	2.58	III	IV
No. 4	436	43.0	2.4	5.9	0.22	0.2	0.53	1.18	III	II–IV
No. 5	426	31.3	1.9	5.8	0.21	0.1	0.40	0.58	III	II
No. 6	416		1.1		0.11		0.12		I	

Note: Miles × 1.61 = km.

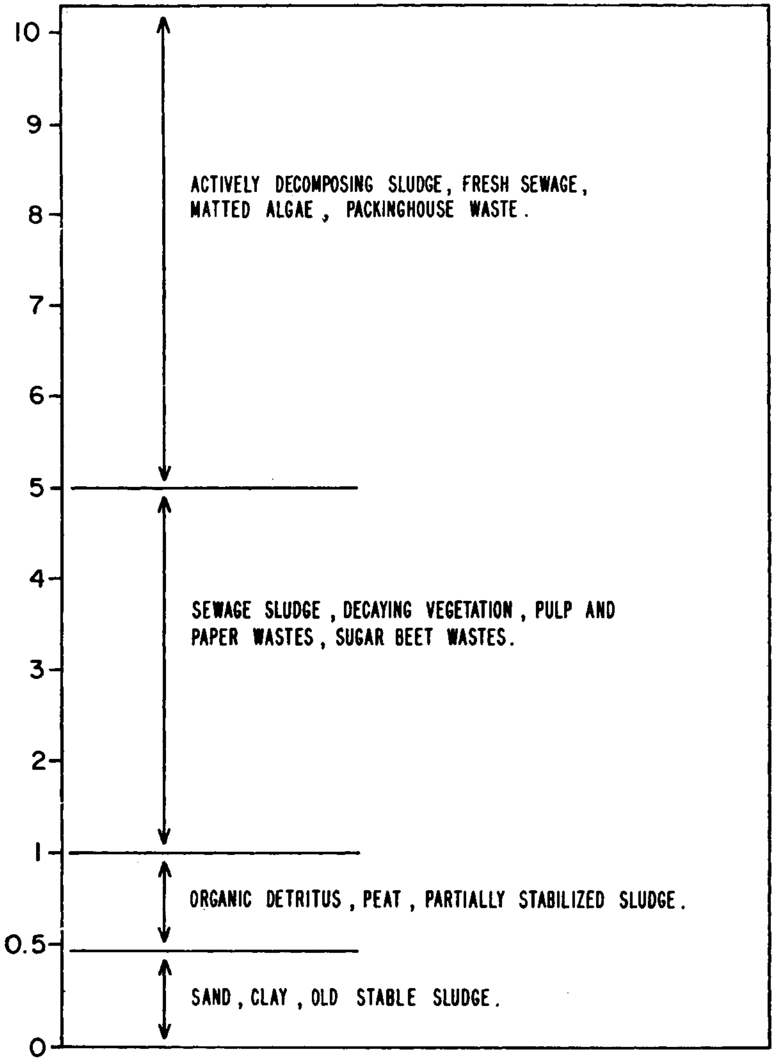

FIGURE 2.—Organic sediment index for typical bottom deposits.

correlated with the sediment material in Figure 2.

Examples of the use of the OSI are illustrated in Figure 3. The results of analyses of bottom sediments collected from the Red River of the North in the vicinity of Fargo, N. D., and the Kanawha River upstream and downstream from Charleston, W. Va., are tabulated in Table II.

In Figure 3, the sediment at the Red River control station (Mile 462) gave an OSI value of 0.22 for a Type I deposit. The influence of the Moorehead, N. D., wastewater treatment plant is shown by an increase to 0.96 for the OSI; the sediment was Type III. Below the Fargo, N. D., plant, the sediment index rose to 1.67, then steadily decreased at downstream stations until at Mile 416, a Type I deposit was found, with OSI = 0.12.

In the Kanawha River (Figure 3), the index for the control station (Mile 71.2) was 0.06. A very slight increase to 0.19 was found above Marmet Dam. The organic deposits from the waste treatment plants at Charleston and South Charleston, W. Va., are dramatically evident in the OSI increase to

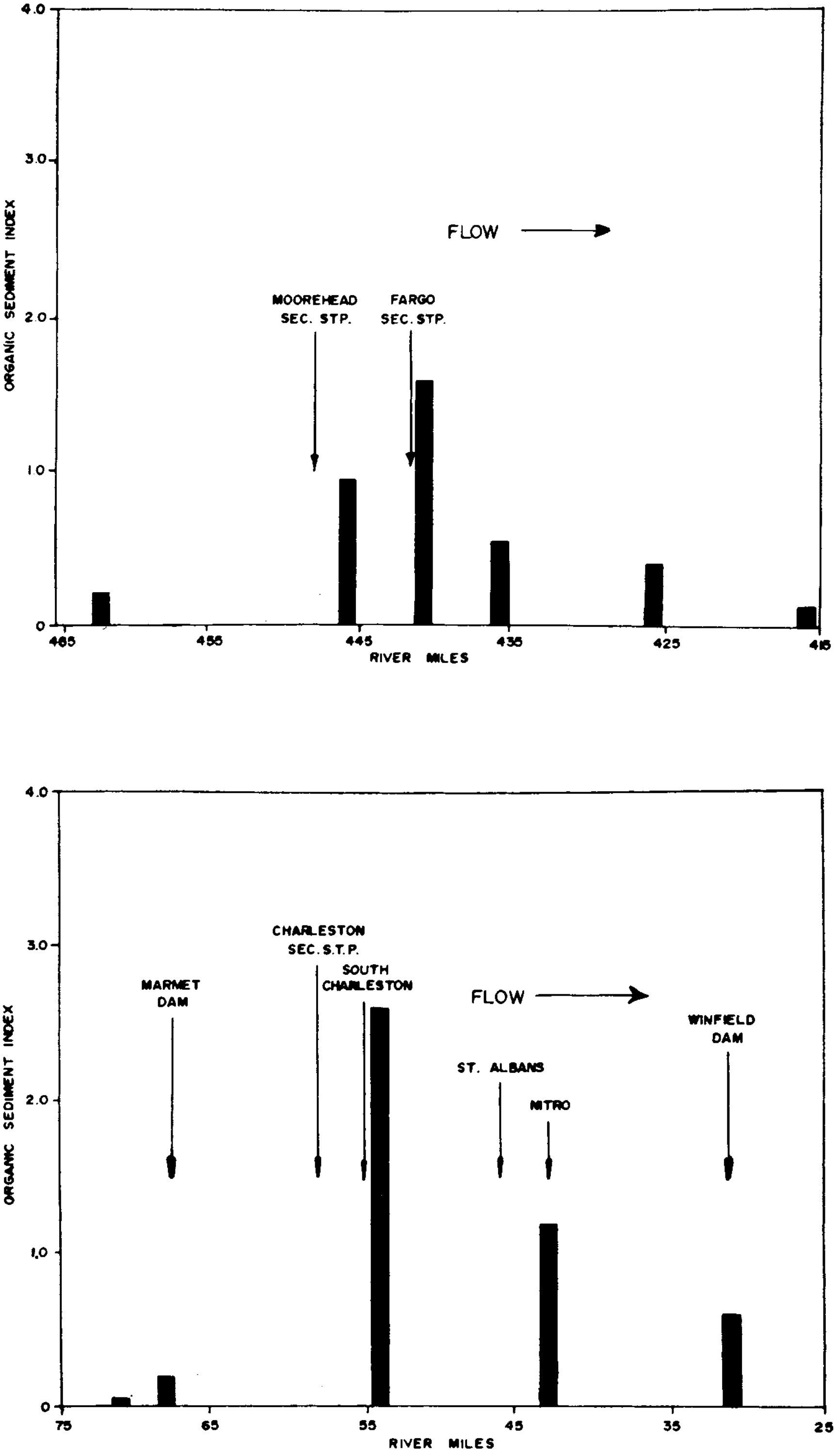

FIGURE 3.—Organic sediment profile—Red, Kanawha, and Mississippi rivers.

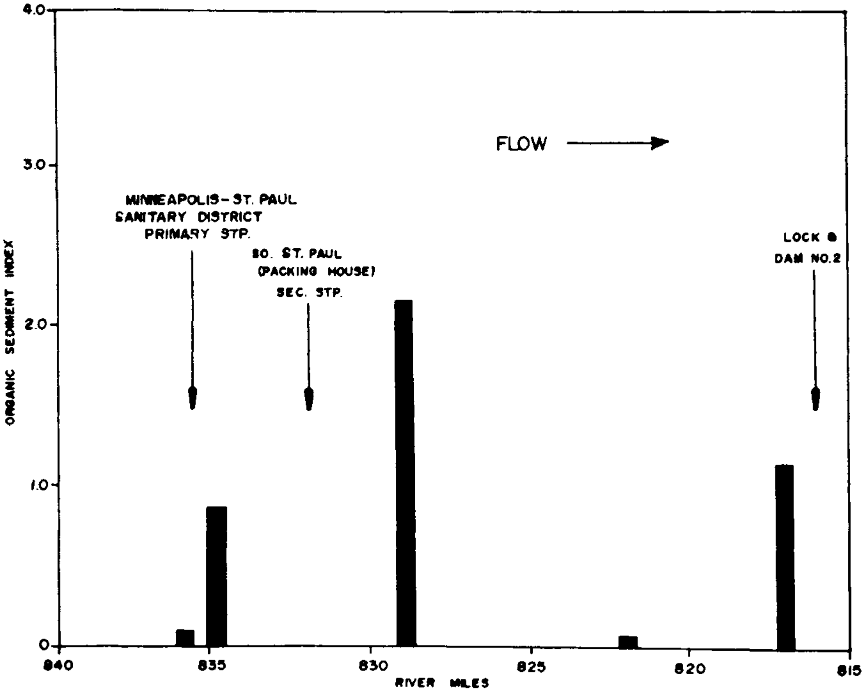

FIGURE 3.—*Continued.*

2.58. The general decrease in the organic nature of the deposits to Winfield Dam (Station 5) is largely the result of dentrification of the sediments, although some reduction in carbon content also occurred. The sediment classifications were Type I upstream and Type IV for the major sludge deposits, with a transition to Type II at the downstream station.

The sensitivity of the sediment index to stream flow and channeling is evident in Figure 3. The OSI profile for the Mississippi River above and below Minneapolis-St. Paul is shown in Figure 3, derived from the data in Table III.

The sand bottom at Mile 836.5 yielded a very low OSI (0.09). Sludges from both the Minneapolis-St. Paul and South St. Paul treatment plants are evident, with the presence of packinghouse wastes increasing the sediment index sharply. Cursory examination shows a dramatic reduction in organic sediment in 7 miles (11.3 km) of stream flow, and a third source of sludge near Mile 820. Examination of stream characteristics, however, discloses changes

TABLE III.—Mississippi River

Sampling Station	River Mile	Organic Carbon (%)	Organic Nitrogen (%)	Organic Sediment Index	Sediment Type
No. 1	836.5	0.9	0.1	0.09	I
No. 2	835.0	4.2	0.2	0.84	I–III
No. 3	829.7	4.3	0.5	2.15	III
No. 4	822.5	0.4	0.1	0.04	I
No. 5	817.6	2.8	0.4	1.12	III

Note: Miles × 1.61 = km.

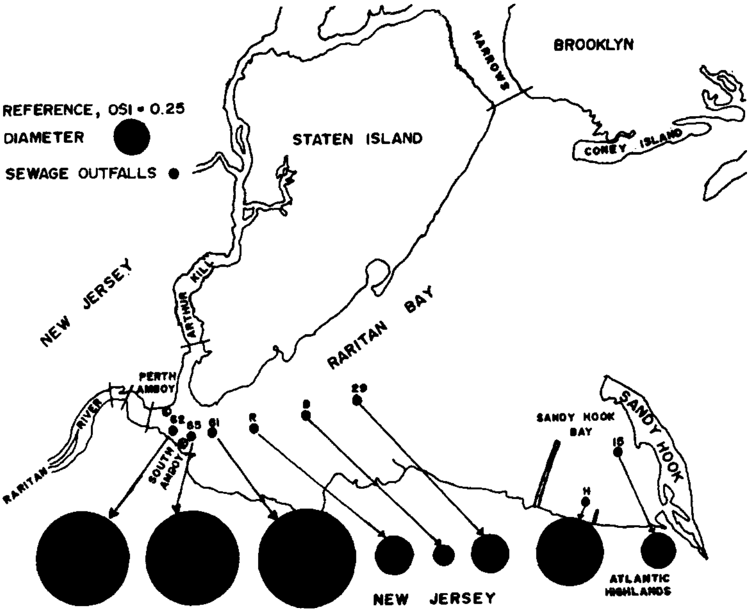

FIGURE 4.—Organic sediment index, Raritan Bay (N. J.)

in velocity in the stretch between Mile 825 and Mile 817. The solids remain in suspension until reduced velocities in the wide pool above Lock and Dam No. 2 result in organic deposits at Mile 817.6 having an index of 1.12. The sand bottom at Stations 1 and 4 are Type I, while the deposits from the treatment plant are Type III.

Estuary Sediments

The sediment classification and OSI have been found useful in characterizing bottom deposits in estuarine waters as well as rivers. In Raritan Bay (N. J.) samples were collected on a transect from the mouth of the Raritan River toward the center of the bay, as shown in Figure 4. Two wastewater outfalls in the western end of the bay as well as the location of two additional bottom sampling stations in Sandy Hook Bay are indicated on the map. The respective OSI values are indicated by circles of proportional area. Carbon and nitrogen

TABLE IV.—Bottom Sediment Data, Raritan Bay (N. J.) and Charleston Harbor (S. C.)

Raritan Bay					Charleston Harbor				
Sampling Station	Organic Carbon (%)	Organic Nitrogen (%)	Organic Sediment Index	Sediment Type	Sampling Station	Organic Carbon (%)	Organic Nitrogen (%)	Organic Sediment Index	Sediment Type
62	5.3	0.10	0.53	II	27	1.5	0.01	0.015	I
65	5.0	0.11	0.55	II	26	4.8	0.29	1.39	III
R	4.6	0.06	0.28	I	24	13.8	0.29	4.00	IV
B	3.9	0.04	0.16	I	23	4.5	0.17	0.76	I
29	4.9	0.06	0.29	I	22	6.3	0.40	2.52	IV
H	5.3	0.08	0.42	II	21	5.4	0.31	1.67	IV
15	4.5	0.05	0.22	I	14	3.63	0.21	0.76	I
					11	4.6	0.42	1.93	III
					7	4.0	0.33	1.32	III
					13	3.3	0.32	1.06	III

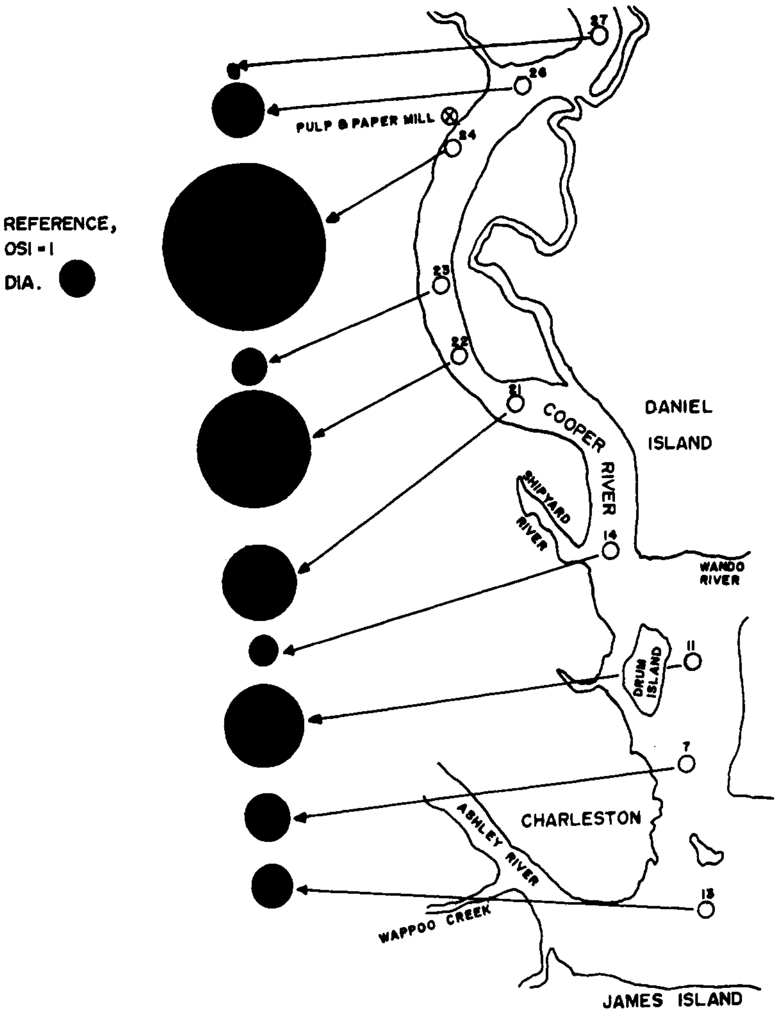

FIGURE 5.—Organic sediment index, Cooper River, Charleston, S. C.

values, with type classifications, are shown in Table IV. Sediments near the mouth of the Raritan River (Stations 62, 65, and 61) clearly show Type II sludge deposits, while samples nearer the center of the bay are Type I. In Sandy Hook Bay, Station 15 has a low sediment index while the index at Station H is significantly higher, suggesting organic solids contribution from Atlantic Highlands.

A study of bottom sediments in the Cooper River, Charleston, S. C., shows additional evidence of the sensitivity of the OSI to physical conditions in the estuary. In Figure 5 the sampling stations and OSI values are shown. Organic carbon and organic nitrogen values are shown in Table IV.

The control, Station 27, is upstream from the principal sources of pollution and shows a very low index. A pulp mill discharges solids between Stations 26 and 24. Tidal influences carry some of the solids upstream to Station 26, but the major deposits occur immediately downstream from the outfall (Station 24). The sediments there contained nearly 14 percent organic carbon. The OSI decreased steadily downstream, but anomalous results appear at Stations 23 and 14. Investi-

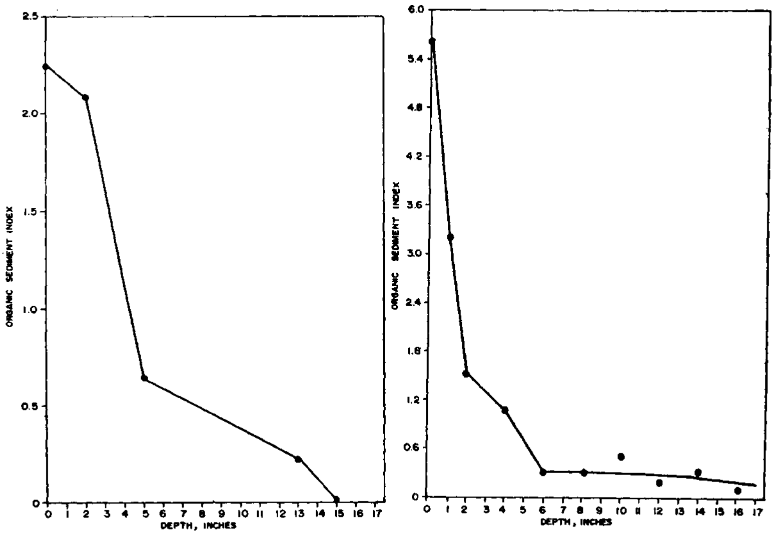

FIGURE 6.—Lake Sebasticook sediment core (right), Waterville Reservoir core (left).

gation disclosed that the navigation channel in the Cooper River is continually dredged. Station 23 is located near a dock where deep-draft tankers are berthed, while Station 14 is in the center of the channel. Recent dredging in these reaches has removed most of the organic sediment, leaving silt having an index less than 1.0, while the index for the adjacent stations is much higher.

Sediment Cores

The techniques for characterizing sediments were also used to examine core samples from the bottom of eutrophic lakes. During a study of Lake Sebasticook (Me.) reported by Mackenthun,[16] an 18 in. (46 cm) core was removed from the bottom sediment in the deepest part of the lake. The sample was segmented into 10 separate portions and the OSI determined for each segment. The OSI values are plotted in Figure 6 as a function of depth below the mud-water interface. The material near the interface is unstable, but the sediments become rapidly stabilized in the first 6 in. (15 cm) of the core with little difference in sediment index in the lower 12 in. (30 cm).

A similar core was obtained from Waterville Lake, an impoundment on the Pigeon River in eastern Tennessee. In this sediment (Figure 6), the first 5 in. (15 cm) are relatively uniform, with a gradual reduction in OSI to a very low value for the bottom segment.

It is probable that the change in chemical composition within a core represents differences in the nature of the original material deposited. Thus, in the Sebasticook core, the upper 6 in. (30 cm) of sediment have been deposited since the lake became eutrophic, while the lower section represents the sedimentation of an earlier oligotrophic period. This assumption is strengthened by biological evidence of eutrophication. The number of diatom particles in the upper 2 in. (5.1 cm) of the core was 326 mil/g, while only 2.7 mil/g was found in the 12-in. (30-cm) segment. A similar correlation was not possible on the Waterville sample because waste load rather than eutrophication was involved.

Although the OSI of core segments seems to indicate the nature of settleable material deposited in a given time period, a technique of accurate dating of sediments or a knowledge of sedimentation rate is essential to an adequate interpretation of core sediment indexes.

Discussion

Using standard laboratory procedures for COD and Kjeldahl nitrogen, a system for the chemical characterization of bottom sediments was developed. In most water pollution control programs, the sediment analyses may be added to the laboratory work load without difficulty, while the sample collection can be made a routine part of biological stream studies.

The parameters selected are directly related to the source of bottom deposits. Wastewater sludge contains high concentrations of organic carbon and organic nitrogen; packinghouse wastes are proportionally higher in organic nitrogen, while, conversely, paper and wood fibers are high in organic carbon; silt from gravel washing and mine tailings are lower in both organic carbon and organic nitrogen. Values for these chemical constituents have been shown to correlate well with known sources, permitting the classification of deposits into four general types.

In addition to the type of classification, the relationship of combined organic carbon–organic nitrogen to active decomposition led to the development of the OSI, which may be considered a measure of the oxygen demand and nutrient resource of the sediment.

The system as described does not in any way constitute a complete chemical analysis of the sediment but, as shown in the data presented, yields an excellent correlation to the field observations of source locations and flow characteristics of the waterways studied. In addition, the OSI accurately reflects local conditions such as the transport of solids to the pool on the Mississippi, the concentration of sludge deposits near river mouths in Raritan Bay, and the effect of dredging in Charleston Harbor.

The studies reported here are strong circumstantial evidence of the usefulness of the OSI. Further work should be done on identification of Type III wastes, on the relationship of *in situ* oxygen demand to OSI, on leaching experiments to establish nutrient release from high nitrogen sediments, and on the correlation of the index with biological populations.

Summary

The characterization of bottom sediments, while an important consideration in water pollution studies, depends on subjective observation of color, odor, texture, and stream location. Through the use of routine COD and Kjeldahl nitrogen tests, a system of sediment analysis has been developed to yield objective information that may be specifically correlated to source of deposit and probable influence on overlying water. Laboratory examination of more than 200 sediment samples from a variety of streams, lakes, and estuaries was used to classify bottom deposits into four general types on the basis of percentages of organic carbon and nitrogen. The product of the percentages was used as an index of the organic nature of the sediment. The correlation of OSI with stream loading and flow characteristics was demonstrated.

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