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Isolation and Size Fractionation of Microparticulate Matter Suspended in the Columbia River

Particulate matter sedimented in natural waters is known to exert a direct influence on solution concentration of radionuclides (Garder and Skulberg, 1964) and pesticides (Lotse *et al.*, 1968), and the importance of the role of suspended particulate matter in the sorption of pesticides from water has been recently demonstrated (Pfister *et al.*, 1969). However, relatively little attention has been directed toward determination of the influence of suspended particulate subdivision on ion sorption from solution particularly in the clay size range (less than 2μ) although total surface activity generally increases markedly with reduced mean particle diameter (Farrar and Coleman, 1967).

In order to evaluate the influence of suspended particle size on the behavior of radionuclides and pesticides in the Columbia River, a centrifugation technique was devised which allowed size fractionation of suspended particulate matter in the micron and submicron size ranges in quantities sufficient for further studies of isolated fractions but without harsh chemical treatment which might alter the properties of the individual components. The isolation method, designed for waters of low suspended sediment concentration, should be particularly applicable to surface waters of the Northwest.

Materials and Methods

Suspended particulate materials were isolated from samples (200 liter) of Columbia River water taken off-shore approximately five miles upstream from the U.S. Atomic Energy Commission Hanford reactors near Richland, Washington.

Particulate materials greater than 53μ in diameter were removed from subsamples of river water by siphoning the water through a 53μ stainless steel sieve. Particulates in the sieve effluent water were concentrated by continuous flow centrifugation of the water in a Sharples Laboratory Super Centrifuge (Model T-1) equipped with a No. 1-H standard clarifier rotor lined with cellulose acetate membrane and operated at maximum speed (23,000 rpm) which exerted a force of 13,200 *g*. Under these conditions, the flow rate through the centrifuge amounted to 60 ml/min, and the turbidity of the supernatant solution as measured on a Hach Model 1860 Laboratory Turbidimeter was reduced to a level approximating that of distilled water. Assuming a particle specific gravity of 1.52 or greater (Jackson, 1956), centrifugation under these conditions will sediment medium-fine clay with a limiting particle diameter of 0.07 micron.

At the completion of centrifugation, sediment was transferred from the liner to a volumetric flask using a small quantity (less than 5 ml) of a neutral sodium chloride solution (1.5M) to facilitate dispersion, and the resulting suspension taken to appropriate volume.

Particulate matter isolated from the raw river water and redispersed as described above was fractionated according to equivalent spherical diameter by centrifugation techniques. The quantity of material in each size fraction was determined gravimetrically after collection on a filter of appropriate limiting particle diameter.

Centrifugation parameters were designed to meet the requirements of Stoke's law for viscous flow about a falling spherical body, and centrifugation time intervals were calculated using the Svedberg and Nichol's integrated form of Stoke's law (Jackson, 1956) as follows:

$$t_{\min} = \frac{63 \times 10^8 \eta \log_{10} R/s}{(N_m)^2 (D_\mu)^A (\Delta s)}$$

in which t_{\min} was the time of centrifugation (min), η , the viscosity (poises) at centrifuge temperature; R and S, the radii (cm) of rotation for the sediment and the surface of the suspension, respectively; N_m , the centrifugation speed (rpm); D_μ , the desired particle diameter (μ) and Δs , the difference in specific gravity of the solvated particle and the suspension liquid. For clay particles less than 2μ , s was taken as 2.50 and for particles greater than 2μ , s was assumed to equal 2.65 (Jackson, 1956).

A Lourdes Model A-2 Beta-Fuge, an automatic refrigerated centrifuge equipped with a No. 1100 Density Gradient Rotor and centrifugation tubes (250 ml) of the polypropylene type, was employed in the separation of particles suspended in the concentrated solution. Time intervals and centrifugation speeds required for particle size fractionation were calculated from the above equation.

After centrifugation of an aliquot of the concentrated suspension at the designated speed for the required time interval, the supernatant liquid, containing particles of diameter equal to or less than the calculated limiting diameter, was removed under vacuum using a narrow glass tube with an upturned tip and collected in a vacuum trap. The remaining sediment was resuspended in a dilute solution of sodium chloride. Centrifugation and resuspension was repeated ten times or until the measured turbidity of the supernatant liquid approximated that of distilled water. The supernates were composited for each size fraction and stored under refrigeration at 4° C for future analyses. The above procedure was repeated at centrifugation parameters appropriate to the removal of the desired size fractions. The sediment remaining after completion of centrifugation was taken as the fraction containing the largest particle diameter.

The dilute size fraction suspensions were concentrated for further characterization by addition of sufficient solid calcium chloride to result in a 0.1M solution to flocculate the suspensions followed by centrifugation until the supernatant turbidity approximated distilled water. After dilution to volume, the concentrated suspensions were stored at 4° C.

The concentration of solids in the size-fractionated suspensions was determined by filtration, under vacuum pressures up to 70 cm Hg, of a known volume of suspension through a dry (60° C) pre-weighed filter disc of appropriate pore size, and gravimetric determination of the dry (60° C) retained solids. The filters, both membrane

and microfiber matric types, were preconditioned by leaching with distilled water (200 ml) to constant weight. Calculation of the mean concentration of fractionated suspended matter in the concentrated suspensions included sediment concentration values obtained by evaporation of known volumes of the size-fractionated suspensions to dryness (60° C) in pre-weighed glass ampules. These were evacuated and flame-sealed before gravimetric measurement of the residues (Kittrick, 1970).

Results and Discussion

The centrifugation method described allowed isolation and reproducible size fractionation of particulate matter in sufficient concentrations for further studies of ion sorption and release. Variation in mean concentration of the fractionated suspended matter was less than 2 percent for both of the filter media employed. However, use of the fiber matric filter significantly reduced filtration time in the submicron size ranges due to increased flow rate. Turbidity values of the filtered effluent solution did not exceed those of distilled water, indicating the number of particles in each fraction having diameters less than the lower limiting diameter were insignificant. The size fractions may have contained particles with diameters greater than the upper limiting diameter, *e.g.*, algal cells and organo-mineral complexes, if these materials had a lower specific gravity than the clay minerals used as a basis for calculation of the centrifugation time. Filtration through filters of pore diameters equivalent to the calculated upper limiting particle diameter or measurement of the average specific gravity of particulate matter in isolated size fractions may be employed as necessary to assure precise definition of particle size.

Application of the procedures to size fractionation of small quantities (0.1g) of ZnS particles (less than 2 μ to greater than 44 μ in diameter) of known specific gravity (3.97) resulted in mean recovery of 99.7 percent of ZnS.

The determined particle size distribution of particulate matter suspended in the Columbia River after the spring freshet is outlined in Table 1. Mean recovery of

TABLE 1. Particle size distribution of particulate matter isolated from Columbia River water after the spring freshet.

Equivalent spherical diameter (μ)	Particle size distribution	
	Concentration (mg/liter)	Fraction of total (%)
<0.2	2.6	7.5
0.5 to 0.2	5.3	15.3
2.0 to 0.5	13.0	37.5
5.3 to 2.0	12.4	35.8
Total	34.7	96.1

total solids in the several size fractions amounted to over 95 percent. The importance of investigations to determine the influence of clay-size particulate matter on ion behavior in surface waters was emphasized by the results of these investigations which indicated that of the particulate matter less than 53 μ in diameter suspended in the river during the spring, 60 percent was less than 2.0 μ in diameter or of clay size, and as much as 22 percent of the total suspended matter was in the less-than-0.5 μ fraction. Materials in these size ranges may be expected to exhibit high surface areas and, if of terrestrial origin, high charge densities relative to particles larger in diameter.

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