

results. The westward flow between stations 90–91 is slightly more intense and deep-reaching than that of the *Ob*.

The *Discovery* and *William Scoresby* profiles suggest that currents in the southern Drake Passage are slightly more active than those found by the *Ob*, though the directions are similar. This may represent a seasonal change, since the *Ob* section was taken in early winter and the *Discovery* and *William Scoresby* sections were taken under summer conditions. The *Eltanin* 90–91 station pair which represents summer conditions agrees more closely with the *Discovery* 646–647 stations pairs. Table 1 indicates a more active summer circulation. Yeskin finds the maximum transport occurring during March and April (10).

The geostrophic results indicate that the velocity field of the Drake Passage may be considered to have two parts: a northern part (north of 59°S) with moderate easterly currents extending to the bottom, and a southern part with lower velocities and westerly currents between 59° and 60°S.

The total volume transport determined from the *Ob* profile is 218×10^6 m³/sec. This large value results from the generally deep-reaching effects of the axis of the circumpolar current. More than one half of this immense transport is accomplished between *Ob* stations 466 and 467, which are slightly over 80 km apart. It appears that more water passes between approximately 56° and 57°S in the Drake Passage than is carried by the Gulf Stream.

The flow south of 55°S is somewhat dependent on the quantity of water flowing through the Drake Passage (11). The circumpolar current, after transversing the Drake Passage, turns northward to enter the Atlantic Ocean to the west of South Georgia. The water of the eastern and southern Scotia Sea, though at the same latitude as the Drake Passage, is derived from the Weddell Sea. The line separating the waters from the Weddell Sea and Pacific Ocean is called the Bellingshausen Front. It is well defined throughout the deep and bottom water and is situated in a zone of instability in the surface water (8). No doubt the positioning of the Bellingshausen Front and the northward penetration of the Weddell water are dependent on the Drake Passage transport.

The results of this study are consistent with the qualitative understanding of the flow through the Drake Passage gained in earlier descriptive

studies (4, 8). This consistence supports the validity of these findings. Direct current measurements would be needed in the Drake Passage to further test these results. Since transient motion is significant in the Antarctic Ocean (8), these measurements must be made over a time interval long enough to determine the geostrophic component.

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Amazon River: Environmental Factors That Control Its Dissolved and Suspended Load

Abstract. *Analytical results of sampling during both wet and dry seasons along the Amazon River, at its mouth, and from 16 tributaries reveal that the physical weathering dominant in the Andean mountainous environment controls both the overall composition of the suspended solids discharged by the Amazon and the amount of dissolved salts and suspended solids discharged.*

The purpose of this study was to determine the factors that control erosion in the Amazon River system. The amount and composition of suspended solids and the amount of dissolved salts carried by this system are evaluated. Analysis of the composition of the dissolved salts will be reported upon completion.

The Amazon River basin was selected as the area for the present study because (i) the influence of man on its properties is negligible; (ii) the effects

of local natural anomalies are minimized by the large area of the drainage basin; and (iii) the series of 16 large tributaries that drain the Amazon's wide range of geologic and climatic source areas make possible the sampling of the material before it is mixed with the materials from other tributaries, thereby permitting the testing of the hypothesized controlling factors.

Periodic (monthly to semiannual) sampling of the suspended solids, bottom sediments, and water, and the measurement of salinity, temperature, and pH were accomplished throughout the seasonal cycle in these 16 tributaries (accounting for more than 90 percent of tributary discharge into the Amazon River) and along the Amazon. The *in situ* conductivities were taken as a measure of the concentration of dissolved salts.

Suspended solids were removed from each of 74 samples of water (20 liters each) in the field, mainly by pressure molecular filtration (size of pores, 0.45 μ), and the material was stored in a small amount of river water with Hutter's (1) volatile organic preservative (a mixture of *o*-chlorobenzene, *n*-butyl chloride, and 1,2-dichloroethane) to prevent decay by microbes and alteration of the distribution of the particles according to size.

Fifty samples of the suspended material were analyzed by x-ray diffraction for mineral composition after separation, by size, into fractions (< 2 μ , 2 to 20 μ , and > 20 μ) and removal of organic material and iron oxide coatings, according to procedures published elsewhere (2). Analytical results were considered in connection with the environmental factors of geology, elevation, climate, and vegetation. As the possible controlling factors, nine parameters related to these four environmental factors were measured for each tributary basin from appropriate maps and data: (i) areal percentage of "calcic" rocks (limestone, dolomite, and volcanic rocks other than rhyolite); (ii) areal percentage of igneous and metamorphic rocks (mainly Precambrian shield areas of acid- to intermediate-type rocks); (iii) areal percentage of continental sedimentary rocks; (iv) areal percentage of marine sedimentary rocks, excluding "calcic" rocks; (v) areal percentage of "calcic" rocks in the upper third of each tributary basin; (vi) mean elevation (using 13 elevation intervals) above the mouth (base level) of the tributary; (vii) mean tem-

perature for the months of minimum and of maximum temperature and the mean annual temperature; (viii) mean precipitation for the months of minimum and of maximum precipitation and the mean annual precipitation; and (ix) areal percentage of broadleaf evergreen vegetation (high values representing dense jungle and low values representing grasslands or shrubs, or both). Analytical results and measured values of the environmental parameter data are compiled separately (3), as are the results of the multiple regression and correlation analyses of the data (3).

The salinity distribution of the Amazon River and its tributaries (Fig. 1) shows the dilution of the contribution of higher-salinity (ranging from about 250 to 85 parts per million) tributaries from mountainous environments by the tributaries with lower salinity (ranging from about 50 to 4 ppm) from tropical environments as they join the Amazon's eastward flow to the ocean.

A plot of the salinity versus the elevation of each tributary shows a strong overall covariance for the wet and dry seasons. Of the nine parameters studied, elevation was the overall dominant factor controlling salinity (accounting for 85 percent of the variability of salinity), the other parameters being of far less importance.

Calculations were made of the total weight of dissolved salts eroded from each tributary per year, on the basis of both measured conductivities and calculated discharges (3). The calculation of tributary discharges was made by subdivision of measured discharges of both the upper Amazon (above the Rio Negro) and the lower Amazon (excluding the Negro and Tapajós for which separate discharge estimates are available) (4). The basis for subdivision of the discharges was the mean value for annual precipitation obtained for each tributary basin (3) and the assumption of equal runoff factors with-

in each portion, upper and lower, of the Amazon basin. These calculations of the load of salts clearly indicate the dominant contributions of the Andean environment. Total dissolved salts eroded from the mountainous environment were computed by combining the estimated amounts of dissolved salts eroded from the mountainous headwaters of the Marañón, Ucayali, Napo, Içá, Japurá, and Madeira rivers. On this basis about 85 percent of the total dissolved salts discharged by the Amazon is supplied from the 12 percent of the total area of the basin, comprising the mountainous-type environment.

A discharge-weighted mean salinity of 36 ppm was calculated for the Amazon from the salinity data I obtained for the mouth of the Amazon (3) and from discharge data for this river (4). On this basis, a provisional discharge-weighted mean salinity of 114 ppm was calculated for the river water of the world. This value is lower

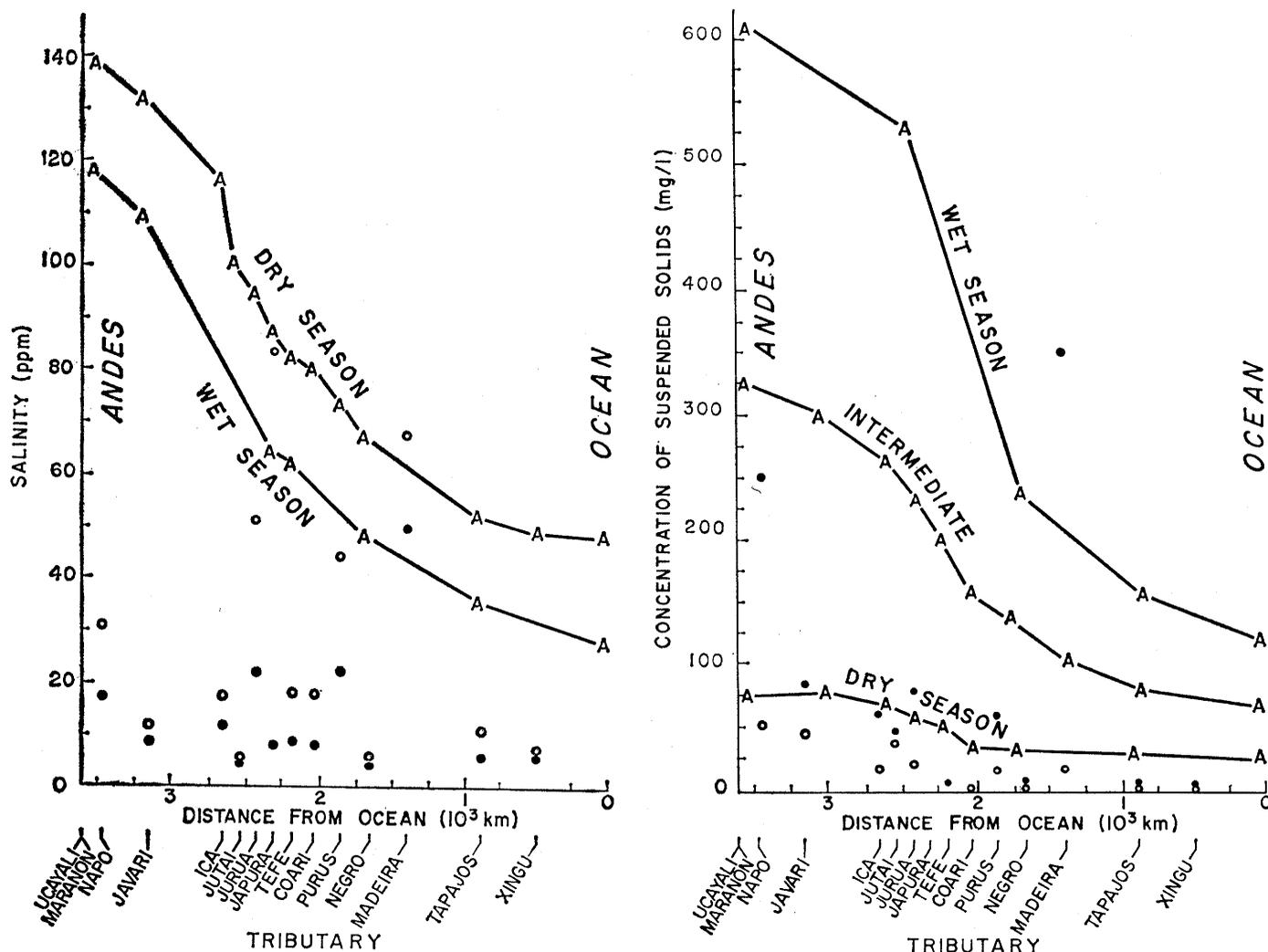


Fig. 1 (left). Variation of salinity of Amazon River and its tributaries. A, Concentrations of main stream of Amazon. Open circles, concentrations in dry seasons; closed circles, concentrations in wet seasons of indicated tributaries. Fig. 2 (right). Variation of suspended solids of Amazon River and its tributaries. A, Concentrations of main stream of Amazon. Open circles, concentrations in dry seasons; closed circles, concentrations in wet seasons of indicated tributaries.

Table 1. Sediment load-weighted mean mineralogic composition by size of fractions of solid material transported by six tributaries from tropical environments, five tributaries from mountainous environments, and from the Amazon River at its mouth in weight percent (see 6).

Fraction	Minerals (%)						
	Quartz	Plagio- clase	K- feldspar	Kao- linite	Mica	Montmo- rillonite	Chlorite
<i>Tributaries from tropical environment</i>							
< 2 μ	6	0	0	88	5	< 1	< 1
2 to 20 μ	48	5	9	26	13	0	< 1
<i>Tributaries from mountainous environment</i>							
< 2 μ	8	0	0	29	30	29	3
2 to 20 μ	42	8	6	13	26	0	5
<i>Amazon at its mouth</i>							
< 2 μ	7	0	0	31	33	27	2
2 to 20 μ	40	7	7	14	27	0	5

than the 120 ppm mean salinity calculated by Livingstone (5).

Concentrations of the suspended solids in the Amazon River and its tributaries (Fig. 2) show the dilution of the waters with high concentrations from mountainous environments by the dilute rivers from tropical environments. The bed load, or that material carried within 50 cm of bottom, contributes only a small portion of the total solid material carried, with bed-load transportation for the mixed and mountainous tributaries estimated at 2 to 3 percent and 5 to 10 percent, respectively, of total sediment transported. Concentration of these solids was controlled mainly by elevation and, to a lesser extent, by precipitation. The range of the concentration of suspended solids of each tributary was controlled by elevation; variations within each range, however, were due to seasonal variations in precipitation.

Annual rates of erosion of suspended solids of the tributaries, based on both the above calculated discharges and the measured concentrations (3), indicate the dominant contributions of the Andean environment. The total suspended solids eroded from the mountainous environment were estimated by combining the estimated amounts of suspended solids eroded from the mountainous headwaters of the Marañon, Ucayali, Napo, Içá, Japurá, and Madeira rivers. On this basis about 80 percent of the total suspended solids discharged by the Amazon is supplied from the 12 percent of the total area of the basin comprising the mountainous-type environment.

Mean diameter (ranging from 1 to 13 μ) of the particles of the material transported showed a positive covari-

ance with elevation. Distribution of particles according to size also varied with the elevation of each tributary basin; these particles ranged from coarse sand (1 mm) to fine clay (< 0.1 μ) for the mountainous tributaries and from coarse clay (2 μ) to fine clay (< 0.1 μ) for low-elevation tributaries.

Composition of the fractions (< 2 μ and those from 2 to 20 μ) of the solid material discharged from mountainous and tropical tributaries and by the Amazon at its mouth is given in Table 1. Composition of the clay mineral suite discharged by the Amazon into the ocean strongly resembles that of the clay mineral suite from mountainous tributaries and, it will be noted, is radically different from the composition of the clay mineral suite from tropical tributaries. Among the minor constituents identified, gibbsite, though barely detectable in the samples of suspended solids of the discharge of the Amazon, was identified by its characteristics 4.85 Å peak in some of the samples from 12 of the 16 tributaries.

Composition of the 2- to 20- μ fraction of the solid material discharged by tributaries from the mountainous environments and that discharged by the Amazon into the ocean is also remarkably similar. Compositional averages for the fraction > 20 μ are not included in Table 1 because analytical results indicated that many of the rivers either did not transport material of this size or transported so little that results of mineralogic analysis are not applicable to this discussion.

Rivers from the tropical environments contain the highest percentage of clay minerals and are far richer in kaolinite (up to 94 percent of the < 2- μ fraction) than tributaries from

the mountainous environments. However, the facts that mountainous rivers have transport rates for minerals more than 100 times those of tropical rivers, and that the overall composition distribution of minerals discharged into the ocean differs only slightly from that of material eroded by tributaries from the mountainous environments are accounted for by the much higher concentrations of suspended solids in the waters from these mountainous environments.

Of the nine environmental parameters, elevation was the most significant in controlling the greatest number of concentrational and compositional parameters of the Amazon River system. Elevation determined, to a great extent, the concentrations of dissolved salts and suspended solids, the particle size, and concentrations of many of the various minerals of the suspended solids. The other factors proved dominant for only a few of the minerals of the suspended solids.

Control of the dissolved and suspended loads of the Amazon River system by physical weathering dominant in the Andean environment is indicated by the following observations: (i) the overall composition of the suspended solids discharged by the Amazon differs only slightly from that of the suspended solids eroded from the mountainous environment; and (ii) about 85 percent of the total amount of dissolved salts and suspended solids discharged is eroded from the 12 percent of the total area of the Amazon basin comprising the Andean-type environment.

Since the sediments carried by the Amazon River obviously do not indicate the existence of the immense area of the basin's tropical rain forest (probably one of the largest in geologic history), it is important to use caution in paleoenvironmental studies of sediments and sedimentary rocks in order not to overlook similar circumstances that may have occurred in the geologic past.

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- Japurá; and, for the Amazon at its mouth, sampling locations in the main channel off Macapá, Brazil, above the influence of sea water.
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Coordination Polymers of Osmium: The Nature of Osmium Black

Abstract. *The design of cytochemical reagents that yield osmiophilic products from which an osmium black may be derived on exposure to osmium tetroxide has resulted in new methods described previously for the ultrastructural demonstration of enzyme activity and functional groups of macromolecules with the electron microscope. Attempts to determine the nature of the osmium black end products have been frustrated by their insolubility. The preparation of water-soluble analogs and their characterization as polymers suggest that the insoluble osmium blacks are coordination polymers. This is consonant with the unusually favorable properties of osmium black in electron microscopy. Although polymers of osmium have frequently been postulated as the end products of reaction of osmium tetroxide with tissue constituents or with other organic compounds, this is the first example of their characterization.*

Osmium tetroxide has become an important reagent for the electron microscopy of biological material. According to the old literature, osmium black is finely divided osmium metal which is formed by the reduction of osmium tetroxide (OsO_4) in solution (1). However, other investigators believed that reduction of osmium tetroxide by the unsaturated lipid components of tissue yielded black, hydrated $\text{OsO}_2 \cdot n\text{H}_2\text{O}$ (2). More recent work (3) indicates that cyclic osmate esters, first postulated by Criegee (4), are probably the major reaction products and that some $\text{OsO}_2 \cdot n\text{H}_2\text{O}$ is formed as a by-product. However, there is no evidence to substantiate its presence.

The osmium blacks which are used in the ultrastructural chemical demonstration of enzymes and functional groups with the electron microscope (5) are amorphous; they are generally insoluble in tissue constituents, in the organic solvents used for dehydrating tissue, and in the acrylic and epoxy monomers used in the preparation of ultrathin sections required for electron microscopy.

In the course of our study of the reactivity of osmiophilic reagents and their end products with OsO_4 , it became apparent that the osmium blacks were not a single, uniform substance, but vary in properties, depending upon the sulfur-containing organic reductant.

Several of these osmium blacks were

prepared (6) by reaction of OsO_4 with thiosemicarbazide, thiocarbohydrazide, thiophenol, *p*-chlorothiophenol, and 2-naphthalenethiol. Conductivity measurements on these samples ruled out the presence of significant amounts of osmium metal. Infrared and elemental analyses confirmed that these materials were not hydrated OsO_2 but rather coordination compounds of osmium with organic sulfur ligands.

The compound formed by reaction of OsO_4 with *p*-chlorothiophenol had considerable solubility in pyridine. Nuclear magnetic resonance examination 5 kc up- and downfield from pyridine showed no proton peaks. Since the presence of hydrogen had been confirmed by infrared and elemental analyses, we suspected that this particular osmium black did not truly dissolve in pyridine but formed a colloidal suspension. This was affirmed by the high viscosity of the solutions. These results, in conjunction with the demonstrated ability of organic sulfur ligands to bridge osmium to osmium as well as to other metals (7) led us to suppose that the osmium blacks are coordination polymers of osmium.

Determinations of molecular weight could not be performed by colligative methods on the existing samples of osmium blacks, owing to their extreme insolubility. Attempts to obtain products which would be more soluble in organic solvents by using ligands with

a greater carbon-hydrogen content were unsuccessful. However, it proved possible to form a water-soluble osmium black by using a hydrophilic ligand. To a solution of 3-mercapto-1,2-propanediol (8) (86 mg, 0.0008 mole) in 25 ml of water, 10 ml of 2 percent OsO_4 solution (0.0008 mole) was added by drops, with stirring, at room temperature. During the addition, the solution changed from brown to black. The addition of acetone caused the separation of a very fine dark brown precipitate which coalesced into larger particles after brief digestion on a steam bath. The mixture was then cooled in an ice bath, whereupon the precipitate settled out. It was collected by suction filtration, washed with acetone, and allowed to dry in air. The product was a dark brown amorphous powder (67 mg). It was readily soluble in water and changed from brown to black on heating to 300°C, but did not melt. This product is probably the tetramer $[\text{Os}(\text{SCH}_2\text{CHOHCH}_2\text{OH})_4]_4$. The analyses (9) were: calculated for the monomer $\text{C}_{12}\text{H}_{28}\text{O}_8\text{S}_4\text{Os}$: C, 23.3; H, 4.6; O, 20.7; S, 20.7; Os, 30.7; found: C, 23.1; H, 4.6; O, 20.9; S, 19.7; Os, 30.5. The material gives a vapor-pressure osmometric molecular weight of 2555 in water (calculated, 2475).

By repeating the preparation but dissolving the 3-mercapto-1,2-propanediol in 5 ml of water instead of 25 ml, a blacker product (about 200 mg) was obtained. This has essentially the same properties, and gave the same elemental analyses. However, it showed an osmometric molecular weight of 3040, in fairly good agreement with the calculated molecular weight of 3093 for the pentamer $[\text{Os}(\text{SCH}_2\text{CHOHCH}_2\text{OH})_4]_5$.

A relationship between the more soluble and less soluble osmium blacks and the importance of bridging in polymer formation can be demonstrated by treating an aqueous solution of the pentamer with excess OsO_4 ; a black precipitate is obtained which is insoluble in water or organic solvents, which presumably indicates further polymerization.

The infrared spectrum of the tetramer or pentamer is similar to that of 3-mercapto-1,2-propanediol except that the SH stretching absorption at 2540 cm^{-1} has disappeared and the CH_2 deformation peak (10) of 3-mercapto-1,2-propanediol is broadened and shifted to 875 cm^{-1} from 864 cm^{-1} . Evidence that this is not due to an Os—O stretching mode is provided by the fact that the same shift and broad-