

contributor to river fluoride. This agrees with Carpenter's (1969) conclusion that the rate of fluoride removal by oceanic sedimentation processes is insufficient to account for the majority of this element discharged to the World Ocean by rivers.

The importance of nonmarine sources to the fluoride content of atmospheric precipitation may be gauged by comparing estimates of the maximum rates of fluoride availability from anthropogenic activity (4×10^8 kg yr⁻¹), volcanism (1×10^9 kg yr⁻¹), and airborne terrigenous dust (5×10^8 kg yr⁻¹) with the estimated rate of global precipitation of fluoride in rain and snow (1.2×10^{10} kg yr⁻¹) (Bewers and Haysom 1974). Not only is fluoride from nonmarine sources inadequate to greatly influence the composition of atmospheric precipitation on a global scale, but anthropogenic fluoride superpositions on natural levels are unlikely to be detectable in polar ice or lake sediments, even if the latter were unmodified by postdepositional changes.

In conclusion, Kilham and Hecky's paper provides valuable and well interpreted geochemical data from the African continent. Considerably more evidence is required, however, to support their contention that weathering dominates atmo-

spheric recycling of oceanic fluoride on a global scale.

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Transparency-chlorophyll relations

Recent papers by Bannister (1974a, b) in this journal have developed equations for phytoplankton production which are more satisfying theoretically than previous ones in the literature and which I regard as a major contribution to the subject. However, as the author points out, there are problems in applying the equations to a natural situation. One difficulty is that total light absorption must be partitioned into k_c , the extinction coefficient for phytoplankton pigments, and k_w , the extinction due to the water itself and to dissolved and particulate substances. This presupposed

that k_c is relatively constant, and one must then measure total absorption and determine k_w by difference.

Bannister (1974b) postulated a value of 0.016 for k_c ; the extinction coefficient for phytoplankton is then $0.016C$, where C is the concentration of chlorophyll a . In deriving this value he quoted various literature sources, and among them was a paper that I wrote some years ago (Riley 1956) in which a statistical analysis of the relations between the extinction coefficient K and chlorophyll C yielded the equation

$$K = 0.04 + 0.054C^{0.75} + 0.0088C.$$

As Bannister says (p. 18) “. . . the combined extinction coefficient $K (= k_c C + k_w)$ is consistent with values of k_c between 0.020 (at high chlorophyll concentration) and 0.060 (at low concentration); the latter high value is unreasonably large.” His statement is correct as far as it goes, but I think that this rather odd old equation may be pertinent to the present problem and therefore deserves further comment.

The analysis was based on open ocean observations in the western North Atlantic with a range of chlorophyll concentrations of about 0.02–20 mg C m⁻³. It assumed that the absorption coefficient of pure seawater is about 0.04 in the visible range and that the remainder of the variability could be ascribed to chlorophyll or perhaps to a combination of chlorophyll and other substances related to it.

To be sure, the analysis was based on old data, obtained by methods that are now obsolete. There was no distinction between true chlorophyll and phaeo-pigments, and most of the extinction coefficients were converted Secchi disk readings. Nevertheless, the data fit the postulated curve with a considerable degree of precision through a chlorophyll variation of three orders of magnitude.

An equation with this degree of empirical validity cannot be dismissed lightly, although the reasons for its peculiar form were not obvious at the time and still are not entirely clear. However, later work suggests that nonliving particulate organic matter may be a major factor. Riley et al. (1964) examined a series of samples of surface water from the tropical and subtropical Atlantic Ocean, making cell counts and estimates of the quantity of organic aggregates. There was a significant positive correlation between the two; however, the regression equation had a low slope and a relatively large constant. Cell numbers varied about tenfold (300–2,500 cells liter⁻¹), and the corresponding variation in the number of nonliving particles was only about fivefold (8–40 × 10³ liter⁻¹). Moreover, comparison with highly productive

temperate waters where cell counts are very much higher indicates a further reduction in the slope of the regression, for particle counts are never more than about four times the maximum value cited above. The reason for this appears to be that much of the nonliving particulate matter is cell wall material and other refractory remains. It persists for a long time and is found in the deep sea as well as in the surface layer. Algal growth adds a little fresh material to the “background” concentration, and the number of particles increases but not as fast as the cell count goes up.

Data of this sort cannot be applied directly to the problem of transparency-chlorophyll relations, but an analogy can be demonstrated. First let us assume for purposes of discussion that Bannister's figure for k_c is correct. This is debatable, but I find no reason to suspect serious error. If we subtract $k_c C$ from my equation the remainder of the chlorophyll-related terms will be $0.054C^2 - 0.0072C$, and I propose that this largely represents nonliving organic matter of planktonic origin. For convenience we will call it k_{wc} . It is analogous to Bannister's k_w except that the latter can include silt and substances of nonplanktonic origin.

Now within normal limits of chlorophyll variation the relations between $k_c C$ and k_{wc} are similar to the variations in cell counts and particle numbers described above. Consider a tenfold variation in chlorophyll of 0.1–1 mg C m⁻³, which includes a major fraction of oceanic observations. The calculated range of k_{wc} is 0.011–0.047. The variation is smaller than that of chlorophyll; at the lower level k_{wc} is 6.9 times as large as $k_c C$, and at the upper limit it is only 2.9. A further increase in chlorophyll to 20 mg m⁻³ will include most of the diatom flowerings in the open sea. At that level $k_c C = 0.32$, which is slightly larger than the calculated value of 0.25 for k_{wc} , and the latter has increased by a factor of only slightly more than five.

The equation has only empirical significance and should not be extrapolated very

far beyond the limits for which it was intended. At the lower limit it extrapolates to the origin, which is almost certainly incorrect. As chlorophyll increases k_{wc} reaches a maximum at $C = 125$ and then decreases, becoming negative at very high concentrations, an obviously unacceptable result.

However, despite theoretical flaws, the equation as a whole has statistical validity beyond the limits for which it was originally intended. As I reported earlier (Riley 1956), data by Conover (1954) on red tides in Long Island Sound also fit the curve. Her largest value, 314 mg C m^{-3} , gives a calculated K of 5.3, as compared with an observed value of 5.5. Incidentally the computed k_c is 0.0167, which is close to Bannister's constant, or alternatively, the results would be satisfied if k_c is 0.016, and k_{wc} levels off at about 0.45.

Practical application of Bannister's production equation to a particular body of water ordinarily would require measurements of light, chlorophyll, and extinction coefficients. However, its use in theoretical models poses more difficult requirements. These commonly involve a system of interrelated equations for nutrients, phytoplankton and zooplankton, and the results require simultaneous solution of the equations. Transparency is in part a biological variable and logically can be included in

the system if a suitable equation can be found for relating phytoplankton and transparency. I used my 1956 equation in one such model (Riley 1965), and although the problem needs to be re-examined with a new and better set of data, I think I have demonstrated a possibility of applying the same principles to modern models.

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Reply to comment by G. A. Riley

As discussed in my paper on production equations (Bannister 1974a), the extinction coefficient k_w must include the contributions of pure water, components such as inorganic silts and pigments and also organic materials not originating directly or indirectly from phytoplankton, and components such as zooplankton, their feces, algal cell walls, and pheophytins, all of which are, broadly speaking, algal derivatives. Dr. Riley suggests that, at any instant, k_{wc} , the contribution to the total

extinction made by algal derivatives, might be an essentially constant function of the concentration C ($\text{mg Chl } a \text{ m}^{-3}$) of the phytoplankton existing at that instant. He also suggests that this function, $k_{wc} = f(C)$, might be generally applicable to any mixed layer.

I cannot help resolve the question of whether there is a single general function, or, if there is, whether the expression that Riley derives from his empirical equation for the total extinction K is the function