

# Nitrogen, Phosphorus, and Eutrophication in the Coastal Marine Environment

**Abstract.** *The distribution of inorganic nitrogen and phosphorus and bioassay experiments both show that nitrogen is the critical limiting factor to algal growth and eutrophication in coastal marine waters. About twice the amount of phosphate as can be used by the algae is normally present. This surplus results from the low nitrogen to phosphorus ratio in terrigenous contributions, including human waste, and from the fact that phosphorus regenerates more quickly than ammonia from decomposing organic matter. Removal of phosphate from detergents is therefore not likely to slow the eutrophication of coastal marine waters, and its replacement with nitrogen-containing nitrilotriacetic acid may worsen the situation.*

The photosynthetic production of organic matter by unicellular algae (phytoplankton) in the surface layers of the sea is accompanied by, is indeed made possible by, the assimilation of inorganic nutrients from the surrounding water. Most of these substances are present at concentrations greatly in excess of the plants' needs, but some, like nitrogen and phosphorus, occur at no more than micromolar levels and may be utilized almost to the point of exhaustion by the algae. It is, in fact, the availability of these nutrients that most frequently controls and limits the rate of organic production in the sea.

Harvey (1) was among the first to point out that phytoplankton growth caused the simultaneous depletion of both nitrate and phosphate from the ambient seawater. Much has since been written about the interesting coincidence that these elements are present in seawater in very nearly the same proportions as they occur in the plankton (2-4). For example, Redfield (3) reported atomic ratios of available nitrogen to phosphorus of 15 : 1 in seawater, depletion of nitrogen and phosphorus in the ratio of 15 : 1 during phytoplankton growth, and ratios of 16 : 1 for laboratory analyses of phyto-

plankton. This relationship may have resulted from adaptation of the organisms to the environment in which they live, but Redfield suggested a mechanism, the microbial fixation of elementary nitrogen, which could regulate the level of fixed nitrogen in the sea relative to phosphorus to the same ratio as these elements occur in the plankton. In other words, any deficiency of nitrogen could be made up by nitrogen fixation.

Such a process could, in times past, have adjusted the oceanic ratio of nitrogen to phosphorus to its present value, and it may be important in regulating the level or balance of nutrients in the ocean as a whole and over geological time. It is certainly not effective locally or in the short run. As analytical methods have improved and as the subject has been studied more intensively, it has become increasingly clear that the concept of a fixed nitrogen to phosphorus ratio of approximately 15 : 1, either in the plankton or in the water in which it has grown, has little if any validity.

As early as 1949 Ketchum and Redfield (5) showed that deficiencies of either element in culture mediums may drastically alter their ratios in the algae. They reported (5) nitrogen to

phosphorus ratios by atoms in cultures of *Chlorella pyrenoidosa* of 5.6 : 1 for normal cells, 30.9 : 1 for phosphorus-deficient cells, and 2.9 : 1 for nitrogen-deficient cells. A number of subsequent studies of both algal cultures (6, 7) and oceanic particulate matter (8, 9) have reported highly variable ratios of nitrogen to phosphorus. These ratios are somewhat difficult to interpret in oceanic particulate matter, since living algae may comprise a very small fraction of the total particulate organic matter collected by the usual sampling methods, and the origin and nature of the remaining material are largely unknown. On the other hand, the chemical composition of algae grown in the usual culture mediums may differ significantly from that of naturally occurring organisms. Despite these uncertainties, the following generalizations may be made: (i) ratios of nitrogen to phosphorus from less than 3 : 1 to over 30 : 1 (by atoms) may occur in unicellular marine algae; (ii) the ratio varies according to the kind of algae grown and the availability of both nutrients; and (iii) although there is no indication of any "normal" or "optimum" nitrogen to phosphorus ratio in algae, values between 5 : 1 and 15 : 1 are most commonly encountered and an average ratio of 10 : 1 is therefore a reasonable working value.

In seawater, a 15 : 1 atomic ratio may be typical of the ocean as a whole. But since 98 percent of its volume lies below the depth of photosynthesis and plant growth, such mean values have little relevance to the present discussion. If one considers only the remaining 2 percent of the ocean's volume, the so-called euphotic layer, high ratios approaching 15 : 1 occur only at the few times and places where relatively deep water is mixed or upwelled into the euphotic layer (9). Over the greater part of the sea surface, the

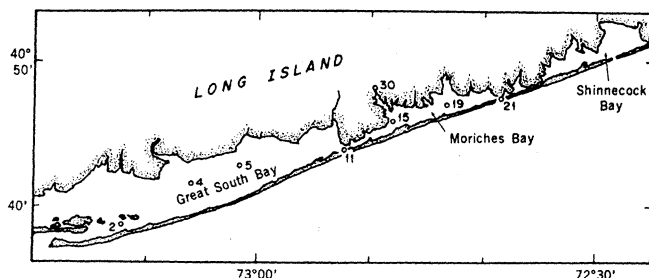
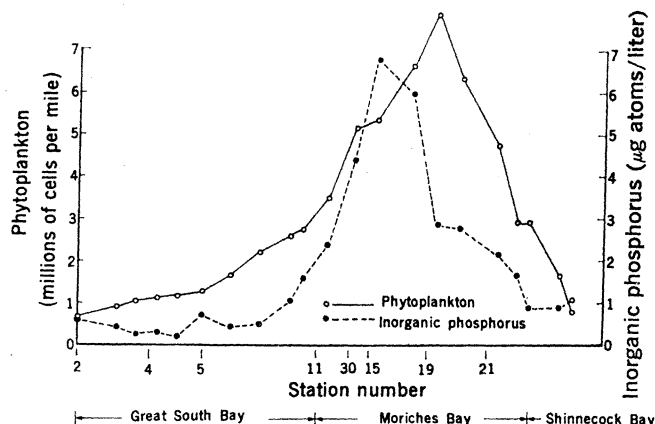


Fig. 1. The distribution of phytoplankton and inorganic phosphorus in Great South Bay, Moriches Bay, and Shinnecock Bay, Long Island, in the summer of 1952. Station numbers on the map (above) correspond to station numbers on the abscissa of the figure (right).



two elements appear to bear no constancy in their interrelationship (5, 9–12).

Detailed examination of the nutrient data from the sea surface reveals that, as the two elements are utilized, nitrogen compounds become depleted more rapidly and more completely than does phosphate. This is particularly true when only nitrate-nitrogen is considered. Both Vaccaro (9) and Thomas (13) have pointed out, however, that ammonia may often be quantitatively a more important nitrogen source than is nitrate in surface ocean waters, particularly when nitrogen levels in general become reduced through plant growth. But even when all known forms of available nitrogen are considered together, they are often found to be reduced to levels that are undetectable in the euphotic layer. In this event, almost invariably a significant amount of phosphate remains in solution. There is, in short, an excess of phosphate, small but persistent and apparently ubiquitous, in the surface water of the ocean, relative to the amount of nitrogen available to phytoplankton nutrition. This is true in both the Atlantic (9, 10, 12) and Pacific oceans (11, 13, 14). Thus, the ratio of nitrogen to phosphorus in surface seawater may range from 15 : 1, where subeuphotic water has recently been mixed or upwelled to the surface, to essentially zero when all detectable nitrogen has been assimilated. Since most of the surface waters of the ocean are nutrient deficient most of the time, nitrogen to phosphorus ratios appreciably less than 15 : 1 are the common rule.

A puzzling question remains to be answered. If the ultimate source of nutrients is deep ocean water containing nitrate and phosphate at an atomic ratio of 15 : 1 and if the average phytoplankton cell contains these elements at a ratio of about 10 : 1, why is it that nitrogen compounds are exhausted first from the water and that a surplus of phosphate is left behind? How can nitrogen rather than phosphorus be the limiting factor? Before turning to this question, we will present two examples of nitrogen as a limiting factor to phytoplankton growth.

*Long Island bays.* Great South Bay and Moriches Bay are contiguous and connected embayments on the south shore of Long Island, New York, formed by the barrier beach that extends along much of the East Coast of the United States. They are shallow, averaging 1 to 2 m in depth, have a hard sandy bottom, and traditionally

Table 1. Regeneration of nitrogen and phosphorus accompanying the decomposition of mixed plankton [after Vaccaro (18)]. Excess phosphorus (last column) was calculated on the assumption that all nitrogen was assimilated as produced and that phosphorus was assimilated at a nitrogen to phosphorus ratio of 10 : 1.

Days	NH <sub>3</sub> + NO <sub>3</sub> + NO <sub>2</sub> (μg atoms N/ liter)	PO <sub>4</sub> (μg atoms P/ liter)	N : P (by atoms)	Excess P (μg atoms P/ liter)
0	0.00	0.80	0.0	0.80
7	0.86	0.79	1.1	0.70
17	2.81	0.84	3.3	0.56
30	3.08	1.05	2.8	0.74
48	3.86	0.98	3.9	0.59
87	4.14	1.04	4.1	0.63

have supported a productive fishery of oysters and hard clams. Introduction and growth of the Long Island duckling industry, centered along the tributary streams of Moriches Bay, resulted in the organic pollution of the two bays and the subsequent development of dense algal blooms in the bay waters, to the detriment of the shellfisheries.

As a result of studies by the Woods Hole Oceanographic Institution during the period 1950–55, the ecology of the region and the etiology of its plankton blooms were described in some detail (15). The situation has since changed, but certain of the unpublished results of the study are especially pertinent to this discussion and will be reviewed here.

During the period of dense phytoplankton blooms, the peak in the abundance of phytoplankton occurred in Moriches Bay in the region nearest the tributaries, where most of the duck farms were located. The algal populations decreased on either side of this peak in a manner that suggested dilu-

tion from tidal exchange via Great South Bay to the west and Shinnecock Bay to the east (Fig. 1). Further study suggested that growth of the phytoplankton was actually confined to the tributaries themselves and that the algae in the bays represented a nongrowing population that was able to persist for long periods of time, during which they became distributed in much the same way that a conservative oceanographic property (for instance, freshwater) would behave.

Roughly coincident with the distribution of the phytoplankton was that of phosphate, which reached a maximum concentration of 7.0 μmole per liter in eastern Moriches Bay and fell to levels of about 0.25 μmole per liter at the eastern and western ends of the region (Fig. 1). Phosphate, in fact, was used throughout the study as the most convenient and diagnostic index of pollution from the duck farms.

Analyses were also made for nitrogen compounds, including nitrate, nitrite, ammonia, and uric acid (uric acid is the nitrogenous excretory product of ducks). Except in the tributaries that were in direct receipt of the effluent from the duck farms, no trace of nitrogen in any of the above forms was found throughout the region studied. It was tentatively concluded that growth of the phytoplankton was nitrogen-limited and that the algae quickly assimilated nitrogen in whatever form it left the duck farms, exhausting the element from the water well up in the tributaries before it could reach the bay.

To confirm this theory, water samples were collected from a series of stations (Nos. 2, 4, 5, 11, 15, 30, 19, and 21) in Great South Bay and Moriches Bay and in the Forge River, one of the tributaries of Moriches Bay on which several duck farms were located. These station locations are indicated by number in Fig. 1. The water samples were Millipore-filtered, and each was then separated into three 50-ml portions. The first of these served as a control while the other two received separately NH<sub>4</sub>Cl and Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O at concentrations of 100 and 10 μmole per liter, respectively. All flasks received an inoculum of *Nannochloris atomus*, the small green alga that was the dominant species in the blooms. The cultures were then incubated for 1 week at 20°C and approximately 11,000 lu/m<sup>2</sup> of illumination, after which the cells were counted (Fig. 2).

The algae in the unenriched controls increased in number by roughly

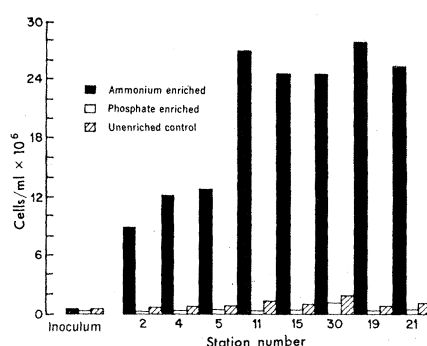


Fig. 2. Growth of *Nannochloris atomus* in unenriched, ammonium-enriched, and phosphate-enriched water collected from Great South Bay and Moriches Bay at the station locations indicated by number in Fig. 1.

two- to fourfold, the best growth occurring in the water collected from within (station 30) or near (stations 11 and 15) the Forge River. No growth occurred in any of the samples enriched with phosphate, with the exception of that taken from the Forge River (station 30), in which the cell count increased about threefold. In fact, the addition of phosphate seemed to inhibit the growth of the algae relative to that observed in the unenriched controls. In contrast, all the water samples to which ammonia-nitrogen were added supported a heavy growth of *Nannochloris*, resulting in cell counts an order of magnitude greater than were attained in the control cultures. About twice as many cells were produced in the samples from Moriches Bay as were produced in samples from Great South

Bay, which suggests that some other nutrient became limiting in the latter series. One might surmise, from the distribution of phosphate in the two bays (Fig. 1), that phosphorus was the secondary limiting factor in Great South Bay, but this possibility was not investigated. There can be little doubt, however, that nitrogen, not phosphorus, was the primary limiting factor to algal growth throughout the region.

**New York bight and the eastern seaboard.** In September 1969, an oceanographic cruise (R.V. *Atlantis II*, cruise 52) was undertaken along the continental shelf of the eastern United States between Cape Cod and Cape Hatteras. The primary objective of the cruise was to study the effects of pollution of various kinds from the population centers of the East Coast upon the

productivity and cycles of organic matter in the contiguous coastal waters. To obtain input data, samples were collected inside the New York bight, at the locations where sewage sludge and dredging spoils from New York City are routinely dumped, as well as from up the Raritan and Hudson rivers.

Of the 52 stations occupied during the cruise, 16 will be discussed here. These stations constitute three sections originating in New York Harbor, one extending eastward along the continental shelf south of Long Island and the New England coast, one extending southeasterly along the axis of Hudson Canyon and terminating at the edge of Gulf Stream, and one running southerly along the coast of New Jersey to the mouth of Delaware Bay (Fig. 3A). The nearshore nontidal currents of the region are predominantly to the south (Fig. 3B), so that pollution emanating from New York Harbor would be expected to spread in that direction roughly along the axis of section 3. Section 1 and the inshore stations of section 2 might be considered as typical of unpolluted or moderately polluted coastal waters, whereas the two distal stations of section 2 (1513 and 1547) should be oceanic in character.

At the inshore end of the three sections, station 1507 was located in heavily polluted Raritan Bay. The water at that location was a bright apple-green in color and contained nearly a pure culture of a small green alga identified in an earlier study of the area by McCarthy (16) as *Didymocystis* sp. Karshikov. Stations 1505 and 1504 are the respective dumping sites for dredging spoils and sewage sludge for the city of New York.

The distribution of total particulate organic carbon at the surface are shown for the three sections in Fig. 4. The measurements were made by the method of Menzel and Vaccaro (17). It is clear from the two sets of measurements that living algal cells made up only a small fraction of the particulate organic content of the water. On the basis of either criteria, one can see that the high content of particulate organic matter characteristic of the New York bight extends seaward for less than 80 km to the east and southeast, whereas evidence of pollution occurs at least 240 km to the south (section 3), along the New Jersey coast to Delaware Bay, presumably the direction of flow of the water flushed out of the bight.

The distribution of inorganic nitro-

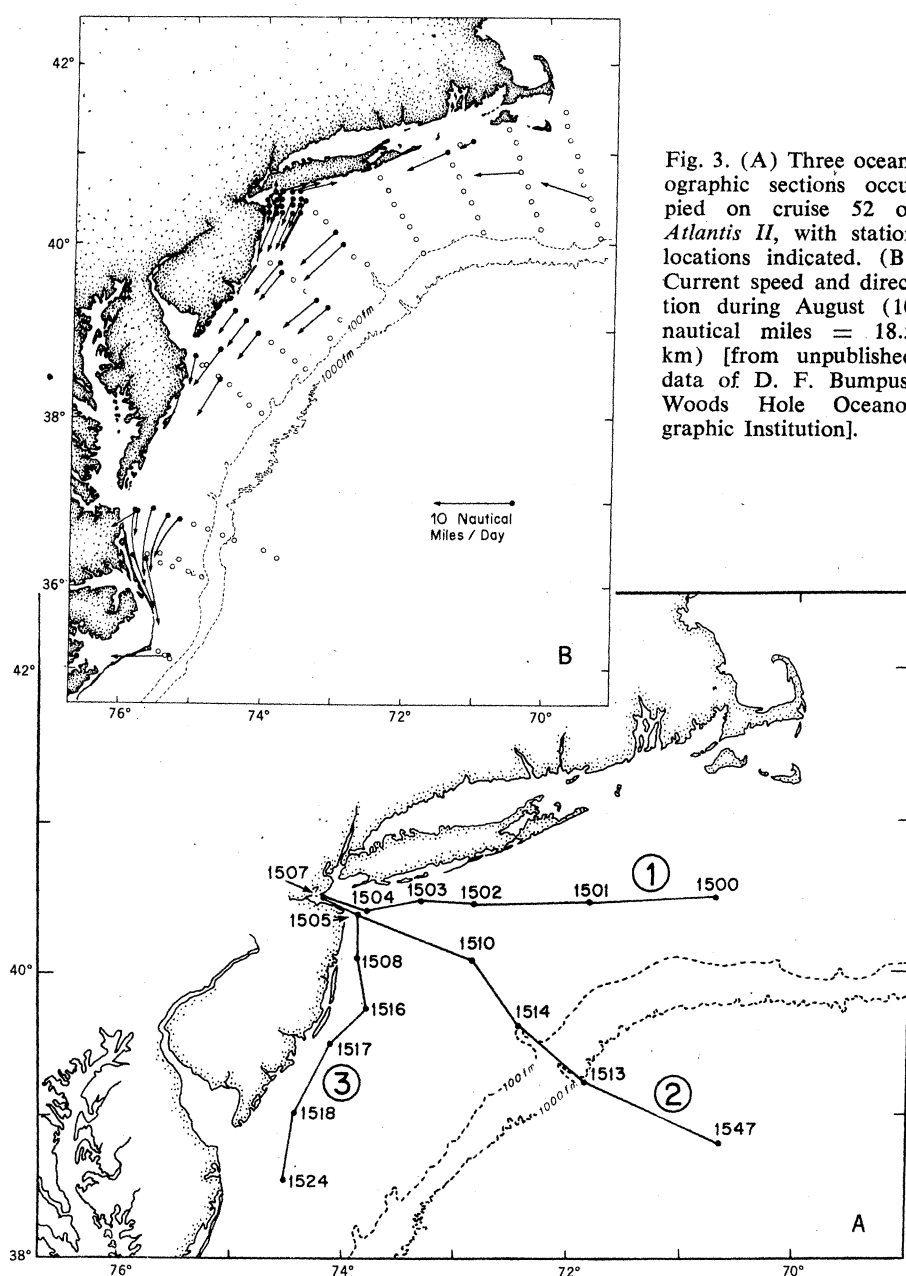


Fig. 3. (A) Three oceanographic sections occupied on cruise 52 of *Atlantis II*, with station locations indicated. (B) Current speed and direction during August (10 nautical miles = 18.5 km) [from unpublished data of D. F. Bumpus, Woods Hole Oceanographic Institution].

gen, as combined nitrate, nitrite, and ammonia, in the surface water of the three sections is shown in Fig. 5. If one considers that the two terminal stations of section 2 (1513 and 1547) are oceanic in character, it is clear that the level of inorganic nitrogen immediately outside New York Harbor, even at the two dumping sites, are as low as, if not lower than, those found in the open sea and that such low values are, in fact, characteristic of the entire continental shelf. Phosphate (Fig. 6), however, presents a quite different picture. Its surface concentrations throughout the shelf area and particularly in the water south of the New York bight are appreciably higher than those observed at the two oceanic stations. As in the Great South Bay–Moriches Bay situation, the available nitrogen from the center of high pollution within the New York bight seems to be utilized by microorganisms as quickly as it becomes available, but there is a surplus of phosphate, which is carried seaward and is distributed throughout the continental shelf.

Experiments similar to those described above were carried out with surface water collected from the 16 stations of sections 1 to 3. This water was Millipore-filtered immediately after its collection and was stored frozen in polycarbonate bottles until used. In the laboratory, the water from each station was divided into three portions, as in the experiments described earlier; one served as a control, one received 10  $\mu$ mole of sodium phosphate, and one received 100  $\mu$ mole of ammonium chloride. In this instance, the mediums were inoculated with the common coastal diatom *Skeletonema costatum*, the cells of which had been washed and nutrient-starved in sterile, unenriched Sargasso Sea water for 2 days prior to their use. Growth of the cultures at 20°C and 11,000  $\text{lu}/\text{m}^2$  of illumination proceeded for 5 days; the results are shown in Fig. 7.

As in the earlier experiment, there was some growth in most of the unenriched controls, and this varied from station to station. Growth in the samples enriched with phosphate was no better and, in several cases, not so good as growth in the control cultures. In contrast, and again as in the bay experiments, heavy growth of *Skeletonema* occurred in most of the samples enriched with ammonia; in several cases growth was ten times or more the growth in the controls and phosphate-enriched samples.

Variability of the growth in the  $\text{NH}_4$ -

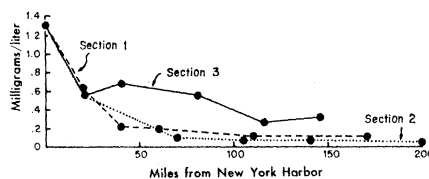


Fig. 4. The distribution of particulate organic carbon along the three sections shown in Fig. 3 (50 miles = 80 km).

enriched samples from station to station again reflects the differential development of secondary nutrient deficiencies, perhaps of phosphate but possibly of one or more other nutrients. This would be expected to occur first in the more offshore stations (see Fig. 6), and such an explanation is consistent with the experimental results. Currently unexplained, however, is the poor growth in the ammonia-enriched samples from stations 1507 and 1505 (two of the heavily polluted stations from within the New York bight), particularly at station 1505, where the best growth occurred in the unenriched and phosphate-enriched series. With the exception of the anomalous results from those two stations, the generalization can be made, consistent with the nutrient distribution picture, that also in these waters nitrogen, not phosphorus, is the primary limiting factor to algal growth.

**Sources and mechanisms.** To return to the question of why and how nitrogen can limit the growth of phytoplankton when the amount of phosphorus

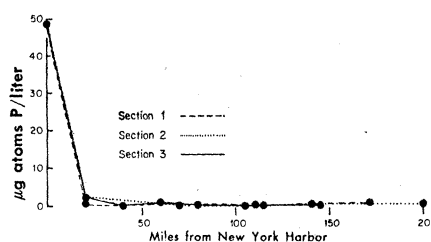


Fig. 5. The distribution of inorganic nitrogen ( $\text{NO}_2 + \text{NO}_3 + \text{NH}_4$ ) along the three sections shown in Fig. 3 (50 miles = 80 km).

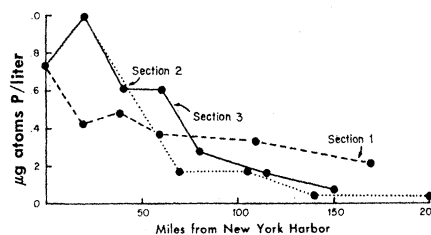


Fig. 6. The distribution of phosphate along the three sections shown in Fig. 3 (50 miles = 80 km).

relative to nitrogen in the plants is greater than it is in seawater, there are probably two explanations. One explanation applies to the ocean in general; the other, to coastal waters and estuaries specifically.

Seasonally or aperiodically, as a result of surface cooling, wind mixing, or other processes leading to vertical instability, the surface layers of the ocean are recharged with nutrients from subeuphotic depths. This mechanism, important though it is as the ultimate source of enrichment of the open sea, probably occurs infrequently. Most of the time, in the thermally stratified, nutrient-impovertished surface waters of the open ocean, organic production is maintained largely through recycling. The supply of nutrients by vertical transport from beneath the thermocline is relatively insignificant. Under these circumstances plant production is limited by the rate of regeneration of the nutrient that is mineralized most slowly. Table 1 lists the relative rates of mineralization of inorganic nitrogen compounds and of phosphate from a mixed plankton tow (18). The excess phosphate left in the water is also shown; the amount was calculated on the assumption that all the nitrogen is assimilated as quickly as it is formed and that phosphate is used at a ratio of one atom of phosphorus for each ten atoms of nitrogen assimilated (see above). Even if nitrogen and phosphorus were assimilated at a ratio of 5 : 1, an appreciable amount of phosphate would still be left unassimilated. This mechanism is probably responsible for the small but persistent supply of dissolved phosphate observed in surface waters throughout most of the open ocean environment.

The situation is quite different in coastal waters and estuaries. Here the surplus of phosphate may be quite large, as we have seen, and its source is unquestionably the land.

In Great South Bay and Moriches Bay it was pointed out that phosphate could be used as a tracer of the pollution originating from the duck farms located on the tributaries to Moriches Bay. Nitrogen and phosphorus are contained in duck feces in the ratio of 3.3 : 1 by atoms. Total nitrogen and phosphorus analyses of dissolved and suspended matter in the tributaries and in Moriches Bay itself gave nitrogen to phosphorus ratios of 2.3 : 1 to 4.4 : 1, consistent with the presumed origin of this material. About half of the total phosphorus was present as dissolved, inorganic phosphate, with the re-

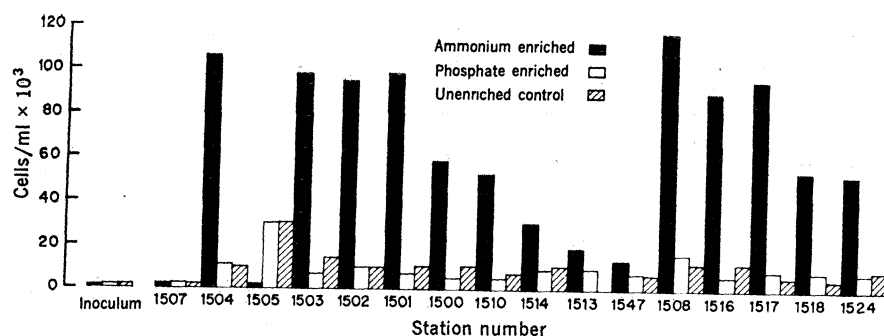


Fig. 7. Growth of *Skeletonema costatum* in unenriched, ammonium-enriched, and phosphate-enriched water from the New York bight collected from the stations shown in Fig. 3.

mainder being tied up in the algae and other particulate matter. All the nitrogen occurred in the latter form. As mentioned earlier, no inorganic nitrogen in any form and no uric acid could be detected anywhere in the water (15).

According to the above data, the ratio of nitrogen to phosphorus in the plankton would be about 6.6 : 1. The population of algae in the area consisted of an almost pure culture of two species of green algae, which were identified at the time as *Nannochloris atomus* and *Stichococcus* sp. The green algae (Chlorophyceae) are characterized by a low nitrogen to phosphorus ratio (5, 6). This fact was believed to be partly responsible for their presence in the bay waters, though other factors such as low salinity and high temperature were also shown to be important selective mechanisms (15).

In the New York bight and the contiguous coastal waters, a high level of phosphate was again measured (Fig. 6). From its distributional pattern there can be little doubt that this material originated in New York Harbor and its tributaries. In Raritan Bay, as mentioned, the phytoplankton consisted almost exclusively of a small green alga, owing presumably to a combination of ecological conditions similar to those that obtained in Great South Bay and Moriches Bay. In the New York bight and the waters farther offshore, conditions more typical of the marine environment prevailed, and the plankton flora consisted of a mixture of diatoms, flagellates, and other forms (19). What is the origin of the surplus phosphate in this case?

From data provided by Pearson *et al.* (20) one can calculate that the nitrogen to phosphorus ratio by atoms in domestic wastes that have been subjected to primary sewage treatment is 5.8 : 1. In wastes that have undergone secondary treatment, the ratio, accord-

ing to Weinberger *et al.* (21), is 5.4 : 1. On the assumption that the ~4 billion kl per day of domestic wastes entering the New York bight from the New York-New Jersey megalopolis have been subjected to something intermediate between primary and secondary treatment, some 90 metric tons of nitrogen and 36 metric tons of phosphorus are discharged into these waters each day. If the phytoplankton that inhabit the area assimilate nitrogen and phosphorus in the ratio of 10 : 1 by atoms (4.5 : 1 by weight), nearly half the phosphate entering the system is in excess of the amount that can be used by the plants.

**Eutrophication.** As we have seen, phosphate is a convenient index or tracer of organic pollution. Its analysis by conventional colorimetric techniques is quick, accurate, and highly sensitive and is far easier than analysis of other chemical nutrients. Furthermore, it persists when other products of organic decomposition, such as nitrogenous compounds, have disappeared from solution. Thus, domestic wastes can be tracked longer and farther from their source of input by looking at the distribution and concentration of phosphate than by using almost any other criteria. From this fact, it is a short and easy step to the conclusion that phosphate is the causative agent of algal growth, eutrophication, and the other adverse effects associated with organic pollution. In the sea, such is far from true.

There is the possibility, alluded to briefly above, that blue-green algae, and possibly other microorganisms capable of fixing atmospheric nitrogen, may by this process bring enough nitrogen into the biological cycle to balance the surplus of phosphate. Filamentous blue-green algae are common in freshwater lakes, and their ability to fix nitrogen is well demonstrated (22). For this reason, or simply because of a high

natural ratio of nitrogen to phosphorus, there is probably, as Edmondson (23) suggests, "A large class of lakes in which phosphorus is the dominating element," a hypothesis that he has well documented for Lake Washington. As Edmondson has also shown, however, such is true only in the relatively unpolluted condition. During the period when Lake Washington received sewage effluent, phosphate was present in excess quantities relative to the available nitrogen.

In the open tropical ocean, there are also filamentous blue-green algae, of the genus *Trichodesmium*, that are capable of fixing nitrogen, though the process is so slow and inefficient as to be almost undetectable (24). In the more eutrophic coastal waters and estuaries, such algae are almost unknown, and nitrogen fixation has not been demonstrated. Here, as we have shown, it is unquestionably nitrogen that limits and controls algal growth and eutrophication.

Much of the phosphate in domestic waste has its origin in detergents. The fraction of the land-derived phosphate in our coastal waters that can be attributed to this source is difficult to assess but has been estimated to be 25 to 50 percent of the total (25). The total land-derived phosphate also includes human excreta, agricultural runoff, industrial wastes, and other material, all of which vary greatly from place to place. As shown earlier, the nitrogen to phosphorus ratio in domestic waste is slightly higher than 5 : 1 by atoms. Even if as much as half of the phosphate in sewage came from detergents and if all of the phosphate from this source could be eliminated by its complete replacement with other compounds, which is a most unlikely possibility (26), the amounts of nitrogen and phosphorus entering the environment would still be in the atomic ratio of 10 : 1, and no reduction of algal growth or eutrophication could be expected.

If, in fact, the phosphate in detergents is replaced with nitrilotriacetic acid (NTA), as is the current trend in the industry (26), the net effect could be an acceleration and enhancement of the eutrophication process. In sewage treatment (and presumably in nature, if more slowly), NTA undergoes biodegradation and probably yields glycine and glycolic acid as intermediate decomposition products (27). These compounds may be used directly as a nitrogen source by at least some species of unicellular algae (15), or they may

be deaminated to ammonia, which is universally available to phytoplankton.

Coastal waters already receive the sewage of roughly half the population of the United States. To replace a portion of the phosphate in this sewage with a nitrogenous compound and to then discharge it into an environment in which eutrophication is nitrogen-limited may be simply adding fuel to the fire.

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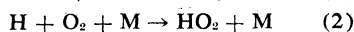
## Carbon Monoxide: Its Role in Photochemical Smog Formation

**Abstract.** *The photochemistry of trace amounts of isobutene and oxides of nitrogen in an atmosphere of air was studied both in the presence and in the absence of small amounts of carbon monoxide. Carbon monoxide accelerates the reaction as measured by nitric oxide oxidation or ozone formation. This finding has relevance to photochemical smog formation.*

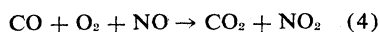
Until recently, the reactivity of carbon monoxide in polluted atmospheres has been all but ignored. Leighton (1) noted that the reaction of CO with O, H, or O<sub>3</sub> was demonstrably too slow to be significant. He did not discuss the reaction of CO with OH because, prior to 1966, the activation energy for that reaction was believed to be at least 7 kcal/mole (2), which would give a negligible reaction rate constant of approximately  $10^5 M^{-1} \text{ sec}^{-1}$  at atmospheric temperature. More recently, it has been demonstrated that the reaction of CO with OH (see reaction 1 below) has an activation energy of approximately 1 kcal/mole and that the rate constant at 25°C is  $8 \times 10^7 M^{-1} \text{ sec}^{-1}$  (2), thus making this reaction of possible significance in the atmosphere.

Recently Heicklen *et al.* proposed a mechanism to explain the previously

unaccountably rapid rate of conversion of NO to NO<sub>2</sub> in polluted atmospheres (3). The mechanism involves three parallel chain reactions, each with OH as the chain carrier. Two chain reactions involve OH attack on hydrocarbons; the third involves the reaction of OH with CO and consists of the following steps (where M represents O<sub>2</sub> or N<sub>2</sub>):



The net reaction from these three steps is



Experimental evidence is presented here for the effect of CO on the oxidation of NO in polluted atmospheres.

Experiments were performed in a 7.68-m<sup>3</sup>, Teflon-lined, constant-tem-

perature, stirred smog chamber (4). In each experiment approximately 3 parts per million (ppm) of isobutene, 1.5 ppm of NO or NO<sub>2</sub>, and varying amounts of CO were mixed with an atmosphere of pure air and irradiated with light approximating the intensity and spectral characteristics of sunlight. Figures 1 and 2 show some of the results. A mixture consisting of NO, isobutene, carbon monoxide, and air was chosen for study because, in many ways, it simulates the chemical reactivity of a dilute mixture of automobile exhaust and air. The concentrations of hydrocarbon, NO, and CO used in these experiments are about an order of magnitude higher than those found in polluted atmospheres, but they are in roughly the correct proportions. High pollutant concentrations and the relatively high volume-to-surface ratio (V/S = 0.227 m) of the smog chamber helped to minimize the importance of wall reactions; identical results were obtained when the walls were newly cleaned or when they were well seasoned by numerous experiments.

As may be seen in Figs. 1 and 2, continuous measurements were made of the concentrations of O<sub>3</sub> [by means of an oxidant meter (Mast Development) with the use of Bufalini's method (5)], NO<sub>2</sub> (Saltzman reagent), NO + NO<sub>2</sub> (dichromate oxidation and Saltzman reagent), CO (infrared absorption), and isobutene (gas chromatography). Formaldehyde, peroxyacetyl nitrate (PAN), acetone, methyl nitrate, isobutene oxide, total hydrocarbon, and total oxidant were also monitored; for simplicity, these species have been omitted from the graphs since the effect of CO on their concentration was what would have been predicted from the altered O<sub>3</sub> concentration.

The air used in these experiments was purified by methods described elsewhere (4). Chemically pure grade isobutene, NO, and NO<sub>2</sub> were used without further purification. Carbon monoxide was purified by passage through a packed column cooled to liquid nitrogen temperatures to remove iron carbonyl, which is present in CO taken from conventional steel cylinders. In our CO samples the Fe(CO)<sub>5</sub> concentration was 0.15 percent. The purification procedure employed is effective only if carried out carefully, in which case it removes more than 99 percent of the iron carbonyl present. One of the experiments shown in Fig. 1 was performed with CO generated in a glass system by the reaction of H<sub>2</sub>SO<sub>4</sub> with