Phosphate Replacements: Problems with the Washday Miracle

Detergents containing phosphates have been under indictment for some time as a significant cause of the eutrophication of lakes and other waterways. Phosphates are believed to contribute to the unwanted growth of algae that often choke bodies of water and that, in their decay, can exhaust the oxygen supply in the bottom waters, so that the lake becomes uninhabitable for cold water fish and less attractive for recreational use. Although many scientists are convinced that phosphates should be controlled, there is evidence that under certain circumstances the availability of other nutrients such as nitrogen or carbon limits algal growth; in these waters, phosphates may be present in such amounts that their removal from detergents would make little difference in water quality. But detergents are marketed nationally, rather than regionally, and the federal government seems to be committed to removing phosphates as soon as suitable replacements can be found. In Canada and in some local areas of the United States laws have been passed restricting the phosphate content of detergents. The detergent industry is reluctantly getting ready to shift to phosphate replacements; and within the past year products containing both new materials, such as nitrilotriacetate (NTA), and new formulations of standard ingredients, notably carbonates and silicates, have appeared on the market. Some of these products have been accompanied by advertised claims that these detergents are "nonpolluting." However, the nonphosphate products available today are far from perfect; in addition to some possibly detrimental environmental effects, there are unanswered questions about their safety and washing effectiveness.

Detergents in the Ecosystem

Most of the laundry detergents available today contain between 35 and 50 percent sodium tripolyphosphate, and sales of these products by the three largest detergent manufacturers, Procter & Gamble, Lever Brothers, and Colgate-Palmolive, account for about 80 percent of the total U.S. market. Almost 2.5 million metric tons of detergents are used in the United States annually, resulting in the release of about 1 million metric tons of phosphates into waste water, and hence into the environment, every year (*1*). Domestic waste water—in which detergents predominate, but which also contains phosphates from human wastes and industrial processes—is the largest single source of phosphates in most waterways. The relative contributions from waste water, urban storm sewer runoff, and agricultural runoff from fertilized fields and livestock feedlots vary widely from place to place and, particularly in the case of agricultural runoff, show large seasonal variations as well. It is generally agreed, however, that detergents account for about 50 percent of the phosphates in waste water and for some lower fraction of the total amount entering waterways. Near large metropolitan areas where there is little dilution of waste water, some estimates of the relative contribution from detergents run as high as 70 percent.

Algae blooms are no longer a rare occurrence in many parts of the United States. In some instances it appears that phosphorus has clearly been the limiting nutrient, implying that a reduced supply of phosphates would have reduced the amount of algal growth; in other incidents, it is simply not known what the limiting nutrient was or how much of the algal growth could have been controlled by lower concentrations of phosphates. Research into the water chemistry of nutrient cycles is intensifying, but the complexity and variability of aquatic systems tend to obscure the details of how nutrients are taken up by algae and other primary producers, then released as the algae die and are decomposed by bacteria. Comprehensive field studies have so far been carried out in relatively few bodies of water.

The relative importance of phosphorus in contributing to excess algal growth and hence to the accelerated decay of a lake seems to depend on the trophic state of the lake. Phosphorus may be limiting to algal growth in nutrient-poor or oligotrophic lakes, but it may be present in excess in nutrient-rich waters. In the Great Lakes, for example, it is estimated by Fred Lee of the University of Wisconsin—in a talk given at the recent American Chemical Society (ACS) meeting in Los Angeles—that phosphorus is the limiting nutrient in the open waters of Lakes Superior, Huron, and Michigan; he believes that in more eutrophic waters, such as Erie and Ontario, phosphorus may be no longer limiting, but could be made so by removing phosphates from waste water. But in some shallow, near-shore sections of the lakes the total input of phosphates from other sources is such, Lee believes, that the removal of phosphates from detergents or even the removal of 80 percent of the phosphates from waste water in treatment plants—as is now planned for much of the Great Lakes region—would not improve water quality substantially. In order to make phosphorus limiting in these sections, Lee thinks it will be necessary to reduce urban and rural runoff as well.

Much less is known about nitrogen inputs to waterways, although both natural and manmade sources of this nutrient appear to be abundant. The input from ammonia found in rainfall is apparently high in many areas, and fertilizers and sewage wastes contain large amounts. Some types of algae and bacteria can fix nitrogen, and although this process appears to be an insignificant source of nitrogen for lakes, it may give the nitrogen-fixing blue-green algae that usually are commonly found in blooms an advantage over other forms. Nitrogen sources are hard to control because of their diffuse nature, in contrast to many sources of phosphorus. At the ACS meeting, A. T. Prince of the Department of Energy, Mines, and Resources in Ottawa, Canada, estimated that 70 percent of the phosphates entering Lake Erie are from point sources that are potentially controllable, compared to only 40 percent of the nitrogen.

It is generally agreed, however, that nitrogen is a limiting nutrient in some lakes and in many or perhaps even most estuarine and coastal waters. John Ryther and William Dunstan of the Woods Hole Oceanographic Institute point out in a recent report that coastal waters receive the sewage of roughly half of the population of the United States, and their measurements in the New York City region indicate that nitrogen is the limiting nutrient in such waters (*2*). Hence they question the value of replacing phosphates in detergents in these regions.

Under some circumstances carbon may be the limiting nutrient, especially in extremely eutrophic, soft-water lakes, according to Pat Kerr of the Environmental Protection Agency (EPA) laboratory in Athens, Georgia. In her talk at the ACS meeting, Kerr emphasized the interdependence of algae and decomposing bacteria, which often compete for the same nutrients; typically they are linked in a daily cycle in which carbon dioxide is removed by algal growth by late afternoon and regenerated during the night by the bacteria. Because of this linkage, Kerr believes that the control of carbon may be important.

However, the circumstances in which carbon is really a limiting nutrient may be fairly restricted. For example, although Lake Erie is a highly eutrophic system, the carbon reservoir provided by dissolved bicarbonate in the lake appears to be much larger than all human inputs of carbon. Prince estimates the biological oxygen demand in the lake at about 200,000 tons per year, which is equivalent to about 75,000 tons of annual carbon input from sewage. The carbon content of the biomass in the lake is estimated to be about 1.8 million tons, clearly larger than could be supplied from the sewage source, but small compared to the 10 to 12 million tons of bicarbonate in the lake. Hence Prince believes that carbon in sewage waste is not an important nutrient in this lake. Many scientists also believe that where carbon does become limiting, further algal growth would lead to relatively little additional deterioration in water quality.

Options in Detergent Formulation

A typical household laundry detergent is made up of a builder, a surfactant, and miscellaneous ingredients such as brighteners, perfumes, antiredeposition agents, and, in some products enzymes. The builder's primary role in a detergent is as a sequestering agent which ties up calcium and magnesium ions that are present in hard water and that would otherwise interfere with the surfactant. Builders also provide in the washing solution a source of alkalinity which is necessary for effective soil removal. The surfactant acts as a wetting agent, which helps to float off dirt from fabrics. The detergent action of most current surfactants, such as the widely used linear alkylate sulfonate (LAS), is poisoned by unsequestered hardness ions. Antiredeposition agents help to keep dirt—once it is removed from the fabrics—in suspension.

Phosphates are excellent builders for detergents, except for their detrimental effects on the environment. Phosphate detergents perform well in soil removal and have a good safety record as far as the phosphate content itself, although some questions have been raised about adverse health effects from enzyme additives. Continued low level exposure to the enzymes used in detergents may cause an allergic sensitization reaction in some persons, although there is considerable disagreement at present as to the exposure level at which this reaction might occur and the frequency of its occurrence.

The search for phosphate replacements has not as yet turned up any widely accepted substitutes, despite research efforts in the detergent industry and in some independent laboratories under contract to EPA. So far replacement efforts seem to be following one of two directions. The approach favored by the large detergent manufacturers is to look for a new builder that has properties similar to phosphates. The favorite candidate for at least partial replacement of phosphates was NTA, which was increasingly used in some products last year as large quantities began to be available from suppliers.

As of 18 December, however, the industry agreed at the request of the Surgeon General to "voluntarily" suspend use of NTA pending further tests. The request was based on a report from the National Institute of Environmental Health Science (NIEHS) that NTA may have a teratogenic effect in combination with a heavy metal, such as cadmium and mercury, by increasing the transmission of these metals across the placental barrier to the fetus, thus increasing the likelihood of birth defects. NTA is normally degraded in waste treatment systems and in the environment and thereby loses its ability to combine with the metals. But NTA does not degrade in anaerobic systems such as may be found in some septic tanks. Since mercury and other heavy metals occur widely in many waterways (*Science*, 26 February, pp. 788–789), there is apparently some basis for concern.

These preliminary findings were a major setback to industry plans. Procter & Gamble, for example, estimates that it has already spent many millions of dollars in the development and testing of NTA detergents, and since December the entire industry has been examining the NIEHS experimental data and conducting its own tests. The major companies might be expected, on the basis of substantial investments, to be reluctant to move on to other phosphate replacements while there is still hope for NTA, and in fact both the large detergent manufacturers and their suppliers continue to believe that NTA is a safe material at concentrations that would occur in the environment. They expect eventually to go ahead with NTA as, at least, a partial phosphate replacement. Apart from its possible role in the mobilization of heavy metals, NTA appears to be a nontoxic material that performs well as a detergent builder. Total dependence on NTA is unlikely, however, because the material is hygroscopic and would tend to absorb moisture from the air, causing the detergent to cake.

Another potential class of new builders is the polyelectrolytes, principally derivatives of polycarboxylic acids, which appear to have good sequestering properties and good washing characteristics and are available at reasonable cost. The trouble with these compounds is that those tested so far have poor biodegradability, an essential property in the quantities that would eventually be used in detergents. Other compounds including various proteins have been suggested as builders, but their safety has not yet been determined.

A second approach toward finding a nonphosphate detergent—and the approach which seems to be advancing most rapidly at the present—involves the development of surfactants that will work without a sequestering agent. Many of the nonphosphate products on the market are of this type. Small companies—some of them entering the detergent business for the first time—produce essentially all of these products. The surfactants are combined with a builder to provide alkalinity and to improve washing performance. The nonphosphate detergents on the market have largely used precipitating builders—carbonates and silicates—so called because they usually combine with calcium ions in hard water and precipitate as an insoluble residue. The buildup of this residue on cloth and in washing machines is apparently one of the major potential disadvantages with detergents which do not use sequestering builders. Nonphosphate detergents of the type now available have also been criticized for poor cleaning performance, although presumably the individual housewife will be the ultimate judge of washing performance, and so far many of the new no-phosphate products seem to be selling well. The large variety of possible combinations of soils, fabrics, and water hardness make most laboratory washing tests—and hence most claims about washing performance—unreliable.

If small companies have the advantage of a lesser commitment to existing methods and materials so that they can be more innovative in detergent formulation, they can also be more irresponsible, and the products on the market now include instances of both. The use of precipitating builders results in more alkaline detergents. Most phosphate detergents at normal use levels—about 0.15 percent solution—have a *p*H between 9 and 10.5, whereas the nonphosphate detergents based on silicates and carbonates typically have a *p*H between 10.5 and 11. A few products have been marketed with high concentrations of metasilicates—which are highly alkaline in contrast to the more widely used liquid silicate formulations—and products based on metasilicates have been reported to have *p*H higher than 11. Above *p*H 11, alkaline substances can apparently cause gel formation in protein tissue, making it difficult to flush out any of the material that comes in contact with the eyes or is accidently swallowed. The Food and Drug Administration (FDA) is beginning to screen new detergent products for skin corrosion, eye irritation, and ingested toxicity in tests on animals. Under the Hazardous Substances Act, the FDA requires all products alkaline enough to cause tissue damage to carry a warning label indentifying the caustic substance, although with such a label even very alkaline substances can be sold. It was for violation of this labeling requirement that two detergents with high metasilicate content, Ecolo-G and Bohack, were seized last month.

Many industrial detergents are highly alkaline, but the major manufacturers have avoided such products for home use on the basis that, even with warning labels, children would inevitably come into contact with the material. Some 2000 to 3000 cases of children swallowing detergents and other cleaning products are commonly reported each year, so that the trade off between the safety hazards of highly alkaline detergents and washing efficiency, which generally improves at higher alkalinities, is substantial. By no means all the nonphosphate detergents contain metasilicates, however, even though many of them carry warning labels.

Social Options

Essentially everyone agrees that the best long-range method for controlling nutrients in waste water lies with advanced sewage-treatment systems. Phosphates are easily precipitated by the addition of metal ions such as aluminum or iron, and methods for the removal of other nutrients are under rapid development. But because of the time lag in getting public financing for comprehensive treatment systems, many scientists believe that detergent reformulation to remove or reduce phosphates is necessary in the short run. It has been argued, for example by the large detergent manufacturers, that since the elimination of phosphates from detergents would only cut the input of this nutrient in sewage by about half, there would be little to no improvement in water quality. Critics of phosphates in detergents, while admitting that this estimate is probably correct in some areas, point out that such a reduction would at least help to reduce the rate of eutrophication in the future, and more importantly, would help to keep those lakes that are now relatively free of excess algae from becoming like the western basin of Lake Erie, which is largely choked with algae every summer.

If phosphates ought to be removed from detergents, then should laws banning phosphate-containing products by a specific date be passed? The industry has argued that antiphosphate legislation will not help them come up with replacements, and it is true that replacement chemicals need careful testing, as the questions about NTA make clear. On the other hand the large companies—which would be primarily affected by such laws—have not taken the lead in developing and test marketing no-phosphate products based on new surfactants, presumably in part because of their large investments in NTA and in current processing methods. National no-phosphate laws would probably restrict the available technological options too severely, since there are probably some regions of the country where phosphate nutrients are not a critical problem, but it appears likely that more regional and local legislation will be passed.

The replacement of phosphates in detergents with other formulations does appear to involve some trade offs among environmental quality, safety, washing performance and cost. This last factor is a significant constraint, because detergents based on surfactants alone, for example, would apparently be possible if about ten times more product—at a comparable increase in cost to the consumer—were to be used per wash.

Although there is some concern over the nutrient input from replacements products containing nitrogen or carbon, it appears that the amounts of these elements that would be released into waste water from detergents would augment the input from other sources at most only slightly—about 5 percent for nitrogen, in most estimates—as compared to the 50 percent relative contribution of detergent phosphates. More alkaline detergents, in the case of products based on precipitating builders, do pose greater safety problems for home use. According to the makers of phosphate detergents, the phosphate replacements now available are inferior in washing performance, and it is not yet clear whether they will satisfy most users—is whiter than white necessary, or will simply clean do? Although there seems to be no perfect answer, it might well be that regional marketing of products tailored to a given watershed—an idea that appears to horrify the industry because of the complexities involved and the greater expenses that the lack of a national market entails—would help to minimize environmental impact of detergents until adequate waste treatment systems are available while retaining maximum flexibility for the consumer.—ALLEN L. HAMMOND

References

1. Hearings on phosphates in detergents before a subcommittee of the Committee on Government Operations of the House of Representatives, 15 and 16 December 1969 (U.S. Government Printing Office, Washington, D.C., 1969).
2. J. Ryther and W. Dunstan, *Science* **171**, 1008 (1971).