Carbonate and Phosphate Detergent Builders: Their Impact on the Environment[1]

E. JUNGERMANN and **H.C. SILBERMAN**, Armour-Dial, Inc., Chicago, Illinois 60608

ABSTRACT

The impact of detergent builders on the environment is critically examined by review of the literature, material balance calculations, wastewater treatment experiments and aquatic toxicity studies. The experiments were designed to assess the influence of alkalinity and carbonates on various sewage treatment processes. Carbonate detergent builders were found to have no detrimental effect on sewage treatment. There was no indication that carbonate detergents are more toxic to fish than phosphate detergents.

INTRODUCTION

The impact of detergent builders on health and the environment has received a great deal of attention in recent years. Interest has focused on making the builders environmentally acceptable, avoiding risks to humans in intended use of the detergent, and preserving aquatic life. This paper stresses those facets which have to do with ecological soundness and aquatic safety. In other words it examines the role of a detergent builder after the homemaker has done her laundry and the wash water goes down the drain.

ENVIRONMENTAL EFFECTS OF PHOSPHATES

As early as 1953, it was reported by Ohle that phosphates must be regarded as the initial factor in the development of eutrophic conditions (1). Since then researchers have shown that overabundance of nutrients causes eutrophication and that phosphorus is in many instances the nutrient which can be most effectively controlled (2-6). Many have reported that reduction of phosphorus from influent waters is the only method available for controlling the rate of eutrophication (8-12).

Detergent sources account for ca. 50-70% of the phosphorus in city wastes. The increased usage of synthetic detergents, coupled with increasing phosphate content of these detergents, has been reflected in an increase in raw sewage phosphorus from 6 mg/liter P in 1960 to 10 mg/liter P in 1970 for a typical city (13,14).

Total phosphorus concentrations in the western basin of Lake Erie show increases from 14 μg/liter in 1942 to 33 μg/liter in 1958, 36 μg/liter in 1959 and 40 μg/liter in 1967-68 (7). Analyses indicate a greater increase in phosphorus than in any other chemical. Similar increases in phosphorus have been observed in other lakes in various parts of the world and correspond with the increasing use of phosphate-rich detergents since the 1940's (13-16).

Phosphates along with other nutrients promote the growth of algae (17). As the algae grow the phosphate content of lake water goes down significantly, although other nutrients are still available. This is an indication that phosphate is a limiting nutrient. Because of stratification in a lake, the phosphate content in the upper water layer can be significantly depleted. As the algae die they fall to the bottom of the lake where they start decaying. It is this decay which depletes the lake of its oxygen, causing septic conditions. As a consequence laws restricting the amounts of phosphates that can be discharged into lakes and streams have been passed (11,18).

It has been stated that phosphates are not removed in an ordinary sewage treatment, and that therefore one had to add special precipitating agents for reducing the phosphate content of sewage effluents to admissible levels. However a normal sewage treatment does remove phosphates from sewage (19-21). For instance the City of Chicago sewage treatment plants remove 35-72% of the phosphates entering the treatment plants through conventional secondary sewage treatment (13). Additional removal of phosphates from sewage would be costly. It has been estimated, for example, that reducing the phosphate content of Chicago sewage to meet the 0.1 mg/liter standard would increase the annual cost of treatment from the present 10-14 million dollars to 27 million dollars (22).

ENVIRONMENTAL EFFECTS OF CARBONATES

Prior to the widespread use of phosphates in detergents, carbonates were commonly used in combination with soap in household laundry products. Until the 1930's homemakers relied on soap flakes and powders. Because the minerals in "hard" water caused a soap-and-dirt scum, many homemakers used washing soda (sodium carbonate) in their wash to deactivate the minerals and make the water "soft." Washing soda has been and is being used in many cleaning formulations, especially in institutional laundry detergents (23-25).

The impact of carbonates on the environment has also been studied (26). Kuentzel claimed that carbon is always the limiting nutrient and the cause of most of the trouble (27). While it is possible that carbon could sometimes be growth rate limiting to the algal mass, this would be in systems where other nutrients are in considerable excess such as in sewage or in lakes that are already eutrophic; it could also occur in lakes of very low alkalinity or in extremely hard water lakes (28). However in most waters the carbon supply from inorganic sources in the water or from the daily increments from the atmosphere or from

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TABLE I

Formulation of Reference and Nonphosphate Detergents

Ingredients	Detergent, % Phosphate	Detergent, % Carbonate
Sodium carbonate	—	67
Sodium tripolyphosphate	50	—
Sodium silicate solids	7	7
Surfactants	17	12
Sodium sulfate	20	—
CMC, optical brighteners, etc.	1	3
Moisture	5	11

TABLE II

Carbon Balance of Detergents, % Carbon

Ingredient	Detergent Phosphate	Detergent Carbonate
Anionic surfactant	15.3	—
Nonionic surfactant	—	7.6
Sodium carbonate	0.3	7.6
Total	15.6	15.2

TABLE III

Sodium Balance in Detergents, % Na

Ingredient	Detergent Phosphate	Carbonate
Sodium Tripolyphosphate	15.6	—
Sodium silicate solids	2.1	2.8
Sodium sulfate	6.4	—
Sodium carbonate	1.2	29.0
Total	25.3	31.8

TABLE IV

Average Increment Added During Water Use, mg/liter

Ion	Without detergents	With phosphate detergents	With carbonate detergents
Na^+	55	70	74
PO_4^{---}	10	33	10

TABLE V

Conditions During Sewage Treatment

Detergent	pH	Alkalinity, mg/liter as $CaCO_3$
I. Aerobic (secondary treatment)		
Phosphate	8.5	350
Carbonate	8.5	380
II. Anaerobic (septic tank)		
Phosphate	7.2	530
Carbonate	7.2	530

TABLE VI

Median Tolerance Limits of Surfactants to Fishes

Surfactant	TL_{50}, 96 hr, mg/liter
C_{12} Linear alkylbenzene sulfonate[a]	3.0
C_{14} Linear alkylbenzene sulfonate[a]	0.6
Linear ethoxylated alcohol[b]	1.1

[a]Bluegill fingerlings, pH 6.5-7.7, 21-25 C (46).
[b]Fathead minnows, pH 7.2, 18 C.

bacterial degradation is adequate to make carbon nonlimiting (29-32).

Numerous phosphate and nonphosphate heavy duty laundry detergents are commercially available (33). One representative composition of each class was chosen for calculations and laboratory investigations (Table I). The carbon balance of the high foaming phosphate detergent was compared to the carbon balance of a controlled suds nonphosphate household laundry product. The products have approximately the same carbon content (Table II). The reason for this similarity in carbon content is the lower surfactant requirement for the carbonate detergent as compared to a phosphate detergent (34). The circumstance that the carbon in a phosphate detergent is organically bound and has to be biodegraded, while the carbon in a carbonate detergent is already biodegraded, means less of a load for the secondary treatment plant microorganisms.

In a sewage treatment plant with activated sludge, organic-bound carbon is transformed into inorganic carbonate and carbon dioxide. Some carbon is also used by microorganisms to form sludge, and another portion of organic carbon remains organic carbon in the effluent. Of the 100% raw sewage carbon entering the sewage treatment plant, ca. 19% goes into primary sludge and skimmings; 32.5% is used to produce secondary sludge; 14% enters the atmosphere as CO_2; 28% becomes dissolved carbonates and broken-down organic compounds; and 6.5% is unaccounted for (35).

TABLE VII

Fish Bioassays[a]

Detergent	TL_{50}, 96 hr, mg/liter
Phosphate detergent I	6.5
Phosphate detergent II[b]	26.7
Phosphate detergent III	7.8
Carbonate detergent	6.9

[a]Conducted at 18 C with fathead minnows at pH = 7.1.
[b]Formulation of Table I.

TABLE VIII

Static Fish Bioassays[a]

Components of carbonate detergent	TL_{50}, 96 hr, mg/liter
Carbonate	267.0
Silicate	1740.0
Surfactant	1.1
Carbonate detergent minus surfactant	625.0
Whole carbonate detergent	6.9

[a]Minnows, 18 C, pH = 7.1.

TABLE IX

Dynamic Fish Bioassays: Comparative Lethal Toxicity of Carbonate Detergent to Three Species of Fishes[a]

Species	Temperature, C	TL_{50}, 168 hr, mg/liter
Trout	13	5.9
Bluegill	18	14.9
Minnow	18	14.0

[a]pH = 7.1, hardness - 35 mg/liter.

A balance similar to that of carbon was calculated for sodium. Sodium is provided by phosphates and silicates as well as by carbonate (Table III). The sodium content of the nonphosphate detergent is slightly higher than the sodium content of a typical phosphate detergent. Table IV illustrates that, when compared with the total sum of sodium from all sources, the difference in sodium is small whether a phosphate or a nonphosphate detergent is used. Table IV shows the amount of sodium ion taken up by household drinking water as it is used in a home. The figures indicate the loading due to all household uses except laundering, the loading due to all household wastes when a carbonate detergent is used and the loading from all household wastes when a carbonate detergent is used (15,36,37). The sodium increase in domestic sewage due to detergents was calculated by taking into account the accepted figure of 60 mg/liter detergent as contribution to domestic sewage (38).

The calculation also indicates that the increment in sodium ion due to carbonate detergent use is 19 mg/liter vs. 15 mg/liter when a phosphate detergent is used. The increment of 4 mg/liter contributed by this carbonate type detergent is small when compared to the 55 mg/liter of sodium ions contributed by sources other than detergents such as human waste and kitchen waste (39). It is also small when compared to the increase in sodium ions which would be caused by precipitation of phosphates with sodium aluminate during a tertiary sewage treatment. Such treatment, as well as others recommended for the removal of phosphates from municipal sewage, results in an increase of pH or the increase of minerals in sewage treatment effluents, or both (40-42). For comparison purposes Table IV also shows differences in the contribution of phosphate to domestic sewage calculated for the two types of detergents.

Neither pH nor alkalinity of sewage treatment effluents is essentially changed through treatment of sewage containing either of the two types of detergents; the pH of waste water in the various stages of its purification depends greatly upon the carbon dioxide produced during biological oxidation. Other factors which change pH and alkalinity during sewage treatment regardless of the type of detergent used are the buffering capacity of sewage and aeration. The latter increases the pH about half a unit because carbon dioxide is stripped from the sewage during this process (43). The similarity in sewage treatability for both types of detergents was confirmed by experiments conducted at the University of Wisconsin (unpublished). Bench-type units were run for 2 months, simulating sewage treatment by both the activated sludge process and by the septic tank process. There was no significant difference in pH or alkalinity between runs with either a phosphate or a carbonate detergent (Table V).

Changes toward increased alkalinity of the buffered sewage system were found to either not interfere or to have a beneficial effect in the primary skimming stage and in the settlement of sludge in the secondary stage (44). Furthermore fixed carbon dioxide in general is of considerable importance in detoxifying various salts of heavy metals. Sodium carbonate precipitates such compounds from sewage, thereby preventing these heavy metals from interfering with secondary treatment operations.

AQUATIC TOXICITY

Because of differences in the chemical composition of the surfactants and because of differences in the formulation between phosphate and nonphosphate detergents, there could be differences in fish toxicity. The aquatic toxicity of phosphate detergents was compared to the aquatic toxicity of carbonate detergents using standard experimental procedures. This work was conducted at an independent laboratory (Bionomics, Inc., Wareham, Mass. 02571) specializing in fish bioassays.

Surfactants are known to be relatively lethal to fish when tested by standard bioassay methods (45,46). The susceptibility of the fish to the chemical tested was measured in terms of the median tolerance limit (TL_{50}), the nominal concentration of the chemical in water which causes 50% response (death) under the test conditions during a specified time interval. The toxicity of the chemicals tested was evaluated under static bioassay conditions for a minimum period of 96 hr, and was expressed as the 96 hr TL_{50}. For the nonionic surfactant used in the nonphosphate detergent, this TL_{50} was 1.1 mg/liter for the fathead minnow *(Pimephales promelas)* at 18 C, pH 7.1, and 35 mg/liter total hardness (Table VI). These figures apply to surfactants which have not yet been biodegraded by sewage treatment. The nonionic and the anionic surfactants in both types of detergents are readily biodegraded and lose their toxicity to fish.

The toxicity to fish of three leading commercial phosphate laundry detergents was compared to the toxicity of a nonphosphate detergent (Table VII). The carbonate detergent is seen to occupy an intermediate position with regard to toxicity. Again, because of biodegradation of the surfactant, such toxicity figures will not exist in field conditions. Additional bioassays did also indicate that the aquatic toxicity of a detergent is clearly due to the surfactant which is biodegradable (Table VIII). An important consideration when evaluating the potential effect of a pollutant is the range in susceptibility that a variety of species may exhibit to that toxicant (47). To study this comparative toxicity of the nonphosphate detergent, dynamic bioassays were conducted with three species of fish (Table IX). The toxicity under dynamic bioassay conditions is expressed as the incipient TL_{50} which is defined as the concentration in water which causes 50% response (mortality) under the test conditions with no additional mortality during the final 48 hr of exposure. The figures in Table IX indicate no great variation in susceptibility of the species and are in line with the variations to other chemicals (48). The results confirm that the nonphosphate detergent is per se no more toxic to fish than phosphate detergents.

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