The Detergents and Water Quality Standards

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Abstract

The residual surfactants in watercourses as a result of detergent use have made the public more aware of water pollution. This awareness has accelerated the Federal water pollution control program especially in the research area.

Research at two new Public Health Service laboratories will define the effects of specific materials on specific water uses. All of the detergents in common use will be studied. These research findings coupled with the comprehensive drainage basin studies will permit management decisions on the limiting concn of materials in water.

Another phase of research which concerns the PHS is the development of new methods to remove more materials from waste waters. The active participation and cooperation of industry is needed in this endeavor in order to arrive at water quality standards which are readily attainable. The detergents could well be an indicator of efficiency in removing organic materials from waste waters.

We salute the brilliant chemists who developed detergents. We salute the petrochemical industry for achieving production efficiency enabling detergents to compete with other cleaning materials. Finally, we salute the merchandisers who placed on the market these better cleaners at lower cost. Together these people have inadvertently accomplished in a very few years what many of us could *never* have done. They have made the public aware of water pollution. The suds on our waters have cried out. People believe what they see! This has resulted in an amazing amount of verbal froth—perhaps more than the froth on our rivers. When legislative restrictions are proposed in the Congress of the United States for one particular compound out of thousands, I would say that compound is recognized.

We all realize, of course, that the advent of the "soft" detergents will not decrease the suds problem *unless* effective waste treatment takes place. The onus, then, for suds on rivers will revert to the taxpayers for not providing a treatment system to remove them.

The sudsing properties of some well water supplies have also created a lot of commotion. The septic tank and tile drainage field have become very suspect as a satisfactory disposal system. Foam on water accelerated the Federal water polllution control program especially in the research area. Truly, the detergents have made an impact!

Before we discuss this business of setting water quality standards, let's have a definition of standards: There can be two kinds of standards. One is scientific; the other is administrative. The scientific standards are established by research on the effects of specific materials on specific water uses. The administrative standards are established by authority as rules for the measure of water quality related to water use.

Without some well-defined limiting concn of materials, we cannot answer the question of "why" and "how much" pollution control is necessary. The answers to those questions must be based on scientific fact. Water pollution is a river basin problem. The water resource must be managed on a river basin and watershed basis. It is inconceivable that water quality can be managed without specifying water quality objectives.

It could be said that we have always had rules for the measure of water quality. Not too many years ago these rules were largely based on sensory perception.

If a river looked bad or smelled bad you needed abatement. The amount of abatement was that which removed the obvious and eliminated the odors. The detergents made some watercourses look bad.

Dead fish indicated the need for abatement. The amount of abatement was that which avoided dead fish.

As early as 1914, the Public Health Service established standards for drinking water for interstate carriers. These standards have been revised in 1925, 1942, 1946 and 1962. The original purpose of the standards was to provide the traveling public with safe, palatable water; now they are used by all vendors of public water supplies. Bacteriological quality, turbidity, color, odor and taste are considered of prime importance for public acceptance of drinking water. The 1964 Standards also limited ABS content to 0.5 parts/million. This does not imply that concn above that create health hazards but only that foam should not occur at 0.5 ppm or lower and that concn above that might indicate excessive sewage contamination.

Such things as turbidity, color, odor and taste may not be important at all to some other water uses such as industrial cooling or irrigation. Here, we run head-on into specific water use and the quality necessary for those uses.

Establishing concn limits of various substances for the control of water pollution is not a simple task. The fundamental steps may be simply depicted:

Comprehensive Study
+
Research Findings
↓
Management Decisions
↓
Limiting Concn

Congress has authorized the Secretary of the Department of Health, Education and Welfare, in Public Law 660, Sec. 2, "to make joint investigations with any such agencies of the condition of any waters in any State or States and of the discharges of any sewage, industrial wastes, or substances which may adversely affect such waters." This language supports a previous authorization for Comprehensive River Basin Planning for water pollution control.

Now, the Comprehensive Basis Projects are planned and operated to accomplish these things among others: 1) Identify present water uses and sources of pollution; 2) Project future water uses and sources of pollution; 3); Determine consequences of various levels of pollutants (i.e., effects on use); 4) Determine the costs to control pollutants to various levels; and 5) Determine the benefits of controlling pollutants to various levels. Upon completion of these studies, the people of the basin should be in a position to make a management decision based on political, economic and sociological factors. The question for decision is: "What water uses in each reach of the Basin must be protected and what uses can be made of the water within these protection requirements?"

Having made this decision, the concn limits which will accomplish these objectives can be established.

With regard to research, the role of the Federal Government was assigned by Congress to the Secretary of Health, Education and Welfare by this wording in P. L. 660: "The Secretary shall develop and demonstrate, under varied conditions . . . improved methods and procedures to identify and measure the effects of pollutants on water uses . . ."

The 1962 Committee on Appropriations included funds for the construction of two water quality standards research laboratories—one for fresh water, one for salt water. The justification for these laboratories in the exact Committee report language was:

"Experts throughout the Nation are demanding realistic water quality standards. This need is confirmed by the alarming number of fish kills, the increasing difficulties in purifying municipal water supplies, and by the increasing incidence of offensive taste and odors and unsightly discoloration found in both our streams and our household drinking water. The committee recommends that such standards of water quality for all uses—the protection of aquatic life and wildlife, industrial, agricultural, recreational and other uses—be developed. We need to known with much greater precision the water quality requirements for the various water uses. Only when the water pollution control administrator is armed with this knowledge can we expect to fully safeguard water users, design the kinds of treatment facilities that will meet these standards effectively and economically, and understand the changes that are deteriorating water resources.

"High in the need to develop water quality standards is that of determining the requirements for aquatic life, both fresh water and marine. The Nation's fishery resource is dwindling steadily and, aside from the loss of this commercial and recreational resource which we cannot afford, there is a danger signal. If fish cannot live in the water we use to drink and process our food, something is wrong and we need to take immediate steps to find the cause. Our fishery resource can well serve as the 'canary in the mine.' "

Contracts have been let and these laboratories should be operational by mid-1966. The fresh water laboratory is at Duluth, Minn., while the salt water laboratory is at Narragansett, R.I. The laboratories will each be staffed with 50–75 scientific and technical people. The disciplines required cover the biological, microbiological and chemical fields as well as engineering. These people working as a team will apply the most up-to-date techniques available to determine the effects of various materials on the several water uses. Each of the laboratories will have about 21,000 ft^2 of working space.

The research tasks then, are fairly well defined and facilities are being built to accommodate the required disciplines. Research will establish the effects of pollutants on various water uses.

Let's take a specific example—one with which we are all familiar—phenol. We are to set a standard on phenol for propagation of fish. We may find something like this evolve:

Conc mg/liter	Impairment of use
0.5	none
1.0	Causes odor in flesh
5.0	Chronic toxicity plus odor
10.0	Acute toxicity plus odor

The phenol standard then would be 0.5 mg/liter for fish propagation. The standard for dichlorophenols might well be 0.005 mg/liter or 5 μg/liter since this is the concn below which no odor is accumulated in the fish flesh.

Now our rapid tests for phenol do not tell us which phenols are present, so to be safe the phenol standards assume that only the dichlorophenols are present although this is not stated. For many years our aquatic biologists have been telling us that we must examine the whole ecology of a watercourse in order to truly evaluate the impact of materials discharged to water. A case in point is the recent research finding that $\frac{1}{16}$ of the 96-hr median tolerance limit of zinc and copper completely eliminated all reproduction of fathead minnows. The test fish appeared completely normal. The matter of water quality standards can become very complex. The synergistic or antagonistic action of materials compounds the complexity.

The 600 million lb/year detergents from households alone represent some 7% of the organic matter carried by domestic sewerage systems. If not removed by treatment processes, the detergents would represent 7% of the total solids added by water use and then discharged to streams.

This 7% makes the detergents an important segment of the total problem. Other materials may have higher pollution potential and generate greater professional concern than detergents, but the public recognizes the one and not the others.

The two water quality standards laboratories will study all of the detergents in common use to define their effects on water use and will establish maximum permissible concentrations.

Another phase of research with which we are most concerned is the development of new methods to remove more materials from waste waters so that repeated water re-use can be practised efficiently and safely. In a single use of water by a municipality ca. 500–800 ppm of materials are added. The best sewage treatment processes we have will remove 40–60% leaving ca. a 300–400 ppm increase in total solids. We are concerned, then, not only with the small fraction due to detergents but to the whole—suspended and dissolved, organic and inorganic. The detergents could well be an indicator of efficiency in removing organic materials.

We need the active participation and cooperation of industry in developing the field-evaluating these new methods.

The Federal Government, then, is aiding the local jurisdictions through research and comprehensive basin projects to arive at soundly-based, equitable and attainable water quality objectives.

There exists today a joint committee on pollution abatement progress criteria. This Committee is made up of representatives of the State and Interstate Water Pollution Control Administrators, the Conference of State Sanitary Engineers and the Public Health Service. The charge of this Committee is: to recommend criteria for use in measuring water pollution and progress, or lack of progress, in abating pollution. Such criteria are to be: 1) based on information now available or readily obtainable; 2) expressed in terms that will be understood by laymen and professionals alike; and 3) expressed in such terms as will have fairly universal acceptance. It will be most interesting to learn what this Committee recommends based on present facts. It will be even more interesting to observe the changes in these recommendations as more facts and better analytical techniques are developed.

Out of all this interest in the matter of water quality standards for water pollution control should come a more enlightened use of the Nation's waters. Once we can clearly understand *why* abatement in necessary, the *how* is more energetically sought, and the *cost* is more palatable.

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Measurement of Biodegradability

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Introduction

FOR THE PAST TEN YEARS OR SO, it has been common practice to use the nickname "ABS" for tetrapropylene derived alkyl benzene sulfonate. If the same ABS nickname were used now for straight-chain alkyl benzene sulfonate, it would add chaos to the confusion. Since straight-chain alkyl benzene sulfonates are in fact "linear alkylate sulfonates," the Research Committee of the Soap and Detergent Assoc. has adopted the abbreviation "LAS" for the commercial replacement of the present workhorse of the detergent industry "ABS." These technical nicknames will be used in this discussion.

Biodegradability is key to this new development and its measurement is an essential part of the program. In this review of the subject of the "Measurement of Biodegradability," the approach will be that of technical people involved broadly in the water pollution abatement program rather than that of the biochemist who has the extremely important responsibility of developing appropriate methodology.

The discussion will: 1) Define biodegradability; 2) review test procedures with broad brush strokes, including the test which has been adopted in the German Regulations; 3) review some of the research in depth which had established the biodegradability of LAS even before the methods used in such research had been described in publications; 4) discuss biodegradability as one of the characteristics which fits into the picture of over-all detergent performance, and 5) conclude by briefly pointing out the contribution of LAS to the water pollution abatement program.

Definition of Biodegradability of Surfactants

Biodegradability is the susceptibility of a surfactant to the common processes by which organic matter in waste water is decomposed by bacterial action. A pure chemical is either biodegradable or not, but the rate of breakdown varies among such pure chemicals. In mixtures of pure chemicals, rate of degradation and completeness both must be considered. Degradation, to a point where there is a loss of surface-activity, removes "detergent" properties. Breakdown to carbon dioxide and water represents the theoretical maximum. A realistic goal for the disappearance of surfactants in any given treatment system would be to match, substantially in a quantitative manner, the disappearance of the usual waste organic matter in sewage or surface streams, or natural organic matter in surface streams.

Biodegradability cannot be an absolute value like mol wt, but like the boiling point, it depends on the conditions under which the determination is made. For example, in sterile water there is no degradation of even "completely biodegradable" substances. In a similar manner, in a ground water suitable for drinking purposes, degradation does not occur. Even in some waste treatment systems such as cesspools, septic tanks and primary sewage treatment plants, there is little or no destruction of mildly resistant organic matter, including tetrapropylene benzene sulfonate, although some breakdown of readily degradable substances does occur. In activated sludge treatment, the amount of the destruction of organic matter will vary, as does the disappearance of ABS which probably averages around 50%. In river waters like the Ohio, over a period of 30 days or so, as much as 75% of ABS and better than 95% of LAS is degraded.

Analytical Procedures for Biodegradability

No matter how you approach the problem, it is not easy to measure biodegradability. Ludzack and Ettinger (1) emphasize that bench scale tests should approach treatment plant conditions as closely as possible. This is particularly true of a method to be used for regulatory purposes, as in Germany. Because of the nature of regulatory processes, a method for this purpose must have extremely good reliability and precision. Also, if the regulatory agency is to do a good job, it must be able to make an adequate number of determinations without too great an expense to the public. For quality control purposes, inexpensive methods should be found from which results are obtained as quickly as possible.

For research purposes, the river die-away procedure is extremely useful and as basic as it sounds. Its use was reported by Hammerton (2) in England, and by Sawyer in this country (3). It has been used extensively as a research tool for the measurement of biodegradability of anionics and non-ionics (4–10).

The details of the river die-away and other methods as used in our laboratories, which have been reported by Weaver (10), are as follows:

River Die-Away. A liter of freshly-sampled Ohio River water, seeded to a concn of 20 ppm of the test substance, is added to a new 0.5-gal mason jar equipped with a screw cap. A magnetic bar is placed in the jar and after stirring for one min a sample is drawn off for immediate surfactant analysis. After sampling, the top is screwed tightly on the jar, which is placed under quiescent conditions at normal room