The Impact of Biodegradable Surfactants on Water Quality

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Abstract

The purpose of this paper is to review some of the recent contributions of the detergent industry to the national effort for cleaner water. Probably the single most important achievement to date has been the industry's voluntary conversion from the use of alkyl benzene sulfonate (ABS) to linear alkylate sulfonate (LAS) and other biodegradable surfactants. This changeover was completed in mid-1965 at a cost that has been estimated to exceed $150,000,000.

Since LAS was the surfactant of primary interest, the bulk of the pre- and postconversion research, in terms of water-pollution control, has been with that material. This paper concerns itself mainly with the over-all impact of the conversion to LAS on water quality. Data from pilot and full-scale sewage-treatment plants throughout the country are included, which clearly demonstrate the effectiveness of the conversion in terms of significantly lower surfactant residue levels.

In June 1965 the detergent industry completed its voluntary conversion from the use of alkyl benzene sulfonate (ABS) to linear alkylate sulfonate (LAS) and other more readily biodegradable surfactants. It has been estimated that the cost of this program exceeded $150,000,000 (1).

Because LAS use in detergents far exceeded that of other surface-active agents, the bulk of the pre- and postconversion water quality research has been with that material. The full significance of the change-over as a contribution to the national effort for cleaner water and the findings of this research are discussed in this paper.

Prior to the change-over, extensive field studies had been conducted by detergent manufacturers and raw-material suppliers, by The Soap and Detergent Association, and by government and university research laboratories. These studies covered a wide range of waste-treatment systems, and the research was designed to give information on the performance of LAS as it underwent treatment. Since these studies have been widely reviewed in the literature, it is unnecessary to describe them in detail. However the major findings of these studies have been summarized in Table I.

As can be seen, LAS performance was evaluated in activated sludge systems (both conventional and extended aeration), in trickling filters, and in oxidation ponds or lagoons. In all cases, LAS removal in these systems was most satisfactory and demonstrated the fact that, after undergoing adequate waste treatment, LAS residues would not contribute to the deterioration of water quality.

Other work carried out at the same time indicated that, even in the primitive septic tank-soil adsorption systems which serve many individual homes in the United States, LAS removal in the order of 97% could be expected if the systems were properly designed (7).

The most recent controlled field study was that conducted by the National Sanitation Foundation at Ann Arbor, Mich. A report on this research was released in September 1966, which discussed the basic performance characteristics of extended aeration package sewage-treatment plants of varying design (8).

A portion of the study included an evaluation of LAS removal under the various test conditions. The plants were operated under a variety of flow and climatic conditions, as shown in Table II.

The plants under test ranged in capacity from 5,000 to 16,000 gallons per day. Influent MBAS[1]

[1] Methylene blue active substances—a commonly used method of reporting ABS/LAS levels.

TABLE I
Summary of Principal Field Test Results
(Not All Data from All Studies Are Shown Below)

Location	Process	Material in use	Detention time in hrs (where applicable)	Mixed liquor suspended solids mg/liter (where applicable)	% Removal		
					ABS/LAS	Suspended solids	BOD
Manassas AFS Va. (2)	Conventional activated sludge	ABS	6–16	3090	54	67	89
Manassas AFS Va.	Conventional activated sludge	LAS	6–16	3510	85	75	91
Woodbridge Va. (3)	Extended aeration	ABS	47	.....	58–61	.....	85–91
Woodbridge Va.	Extended aeration	LAS	47	.....	97.7	.....	94.6
Kettle Moraine Wis. (4)	Extended aeration	ABS	34.5	8430	90.7	91.1	96.0
Kettle Moraine Wis.	Extended aeration	LAS	28.6	3937	96.5	93.6	96.0
Kettle Moraine Wis.	Extended aeration	LAS	34.0	3413	51.3	.....	46.0[a]
Kettle Moraine Wis.	Extended aeration	ABS	39.0	2578	68.3	38.3	84.0
Columbus Ohio (5)	Extended aeration	ABS	12.8	1820	32.8	.....	75.1
Columbus Ohio	Extended aeration	LAS	13.4	1560	70.2	.....	71.6
Columbus Ohio	Extended aeration	LAS	24.3	2180	93.5	.....	73.6
Columbus Ohio	Extended aeration	ABS	18.5	1560	42.0	.....	69.8
New Lisbon New Jersey (6)	Trickling filter	LAS	.....	.....	75.5	.....	79.5
New Lisbon New Jersey	Trickling filter	LAS	.....	.....	80.0	.....	83.0
Richmond Calif. (7)	Oxidation pond (standard rate)	ABS	30 Days	.....	<40.0	.....	.....
Richmond Calif.	Oxidation pond (standard rate)	LAS	30 Days	.....	93.1	.....	.....

[a] Plant operated to simulate poor removal conditions.

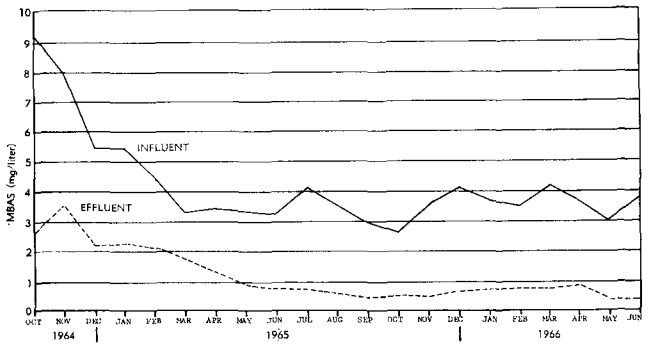

FIG. 1. Influent and effluent MBAS levels at Columbus, O., October 1964 to June 1966 (9).

values varied between 5.0 and 6.8 mg/liter, and effluent levels for the different test conditions fell between 0.8 and 1.2 mg/liter. In all cases, average effluent values were close to, or below, the incipient foaming level of 1.0 mg/liter.

Of more immediate and practical importance however have been the findings on LAS performance under actual conditions of use at full-scale sewage-treatment plants throughout the country.

Many data of this type have been compiled by The Soap and Detergent Association although the largest share of collected data was contributed by sewage-treatment plant operators, university researchers, and pollution-control agencies. The plants for which the most extensive data are available are those at Columbus, Ohio; the City of Los Angeles, California (Hyperion); Milwaukee, Wisconsin; Los Angeles County, California (Whittier Narrows); and Livermore, California. The results obtained at these locations are best summarized by reference to Fig. 1 through 5. With the exception of the Livermore plant, all plants employed the activated sludge process or variation thereof.

Sample collection and analyses began at one Columbus plant in October 1964, well before the conversion to LAS was completed. This plant handles a flow of approximately 45 million gallons per day and has an aeration detention time of approximately 6 hours. Effluent MBAS values at the beginning of the monitoring program were about 3 mg/liter and fell steadily until they reached a level well below 1 mg/liter in August of 1965. They remained at approximately 0.5 mg/liter until the conclusion of the study in early 1966 (Fig. 1).

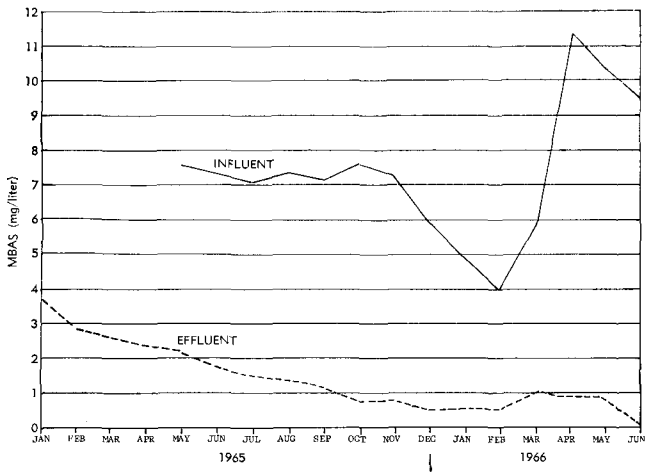

FIG. 2. Influent and effluent MBAS levels at the Hyperion (Los Angeles, Calif.) sewage-treatment plant, January 1965 to July 1966 (13).

TABLE II
Summary of Results, National Sanitation Foundation Package Plant Study (8)

Number of plants under test	Flow condition	Climatic condition	% Removal MBAS	% Removal BOD
10	Steady state[a] full load	Fall-winter	76	90
4	Steady state[a] full load	Spring-summer	84	92
4	Steady state[b] half-load	Spring-summer	82	92
4	Subdivision[c] full load	Spring-summer	87	90
4	Subdivision[d] half-load	Spring-summer	85	95
4	School[e] full load	Spring-summer	82	82
4	School[f] half-load	Spring-summer	85	90

[a] Uniform flow over 24-hr period at full design capacity.
[b] Uniform flow over 24-hr period at one-half design capacity.
[c] Varied flow over 24-hr period to simulate typical subdivision flow pattern at full design capacity.
[d] Varied flow over 24-hr period to simulate typical subdivision flow pattern at one-half design capacity.
[e] Total daily flow applied at uniform rate over 8-hr period at full design capacity.
[f] Total daily flow applied at uniform rate over 8-hr period at one-half design capacity.

In terms of percentage removal, MBAS removal increased from between 60% and 70% at the beginning of the study to about 90% at the end. BOD removals were in the 90%–95% range throughout (9).

The behavior of influent MBAS levels throughout the course of the study deserves mention. From an initial, high concentration of over 9 mg/liter in October 1964, influent values fell steadily until early 1965 when they stabilized at between 3 and 4 mg/liter. They remained at this level for the rest of the study.

At first this was attributed to dilution. However, when BOD-MBAS ratios were examined, a steady increase was noted, indicating that the effect was not attributable to dilution alone. As far as could be ascertained, no other external factors were involved. Thus it appeared, at least circumstantially, that some removal or degradation of the LAS was occurring in the sewers prior to reaching the treatment plant (10). This same effect was also seen, to a lesser extent, at Milwaukee.

This had also been observed in both Germany and Great Britain. Husmann (11) had reported that LAS removal in sewers leading to treatment plants in Germany was as high as 24%. A similar reduction had also been noted at the Luton treatment plant in Great Britain (12). Further studies are reportedly under way in Europe to obtain additional information on this subject.

The Hyperion sewage treatment plant, which serves a portion of the City of Los Angeles, handles a waste flow of approximately 100 million gallons per day in its activated sludge plant. The plant generally achieves a BOD removal in the order of 95%. As can be seen in Fig. 2, effluent MBAS values have dropped from about 4 mg/liter in January 1965 to below 1 mg/liter by October of that year. Percentage removal of MBAS increased from about 70% to slightly more than 90% (13).

Data are available for two treatment plants serving the City of Milwaukee. The two plants handle a combined flow of from 150 to 200 million gallons per day. These plants are unique in that the incoming wastewater does not undergo primary sedimentation but is passed through fine screens instead. Both plants (East and West) demonstrated highly effective LAS removal (Fig. 3). Effluents from the East and West

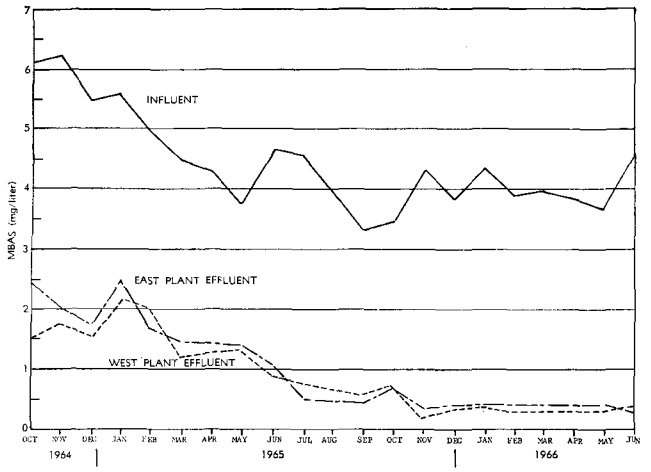

FIG. 3. Influent and effluent MBAS levels at East and West sewage-treatment plants, Milwaukee, Wis., October 1964 to July 1966 (14).

plants dropped from about 2.5 and 1.5 mg/liter MBAS respectively to under 0.5 mg/liter during the period of the study (October 1965 to July 1966). Over-all removal of MBAS was 90% or better during the last six months of the study. BOD removal during this period was consistently in the 95% range. There was, as was previously noted, a drop in the influent MBAS values observed at this site also (14).

Results from the Whittier Narrows Water Reclamation plant, operated by the county sanitation districts of Los Angeles County, are summarized in Fig. 4. This plant employs the step-aeration modification of the conventional activated sludge process and handled a flow of 15 million gallons per day during the monitoring period.

At this site there was a steady reduction in effluent MBAS levels from about 4 mg/liter in January 1965 to approximately 0.5 mg/liter in January 1966. Effluent MBAS values remained essentially constant thereafter. During the study period MBAS removal increased from 50% to 60% to better than 90%. BOD removal approximated 95% throughout the study period (15).

The Livermore sewage treatment plant was monitored by staff members of the University of California's Sanitary Engineering Research Laboratory. This study was of particular interest since foaming problems had occurred in the past at the treatment plant's receiving stream (Alameda Creek).

The plant handled a hydraulic loading of some 2.5 million gallons per day throughout the monitoring period. The treatment system itself consists of solids grinding, pre-aeration, and primary sedimentation (1.5 hours). This is followed by treatment in a 110-foot diameter, 4.25-foot deep, trickling filter loaded at a rate of 2.84 pounds of BOD per cubic yard per day. This, in turn, is followed by a secondary sedimentation unit with a nominal two-hour detention time. After chlorination, the effluent is discharged to a 18.5-acre oxidation lagoon with a theoretical detention time of 15 days.

When sampling began in March 1965, pond effluent MBAS values approximated 8 mg/liter. By October of 1965, MBAS levels (Fig. 5) dropped to 2 mg/liter and have remained at that value or lower ever since (16).

Few additional definitive data are available on LAS performance in trickling or biofiltration plants. This

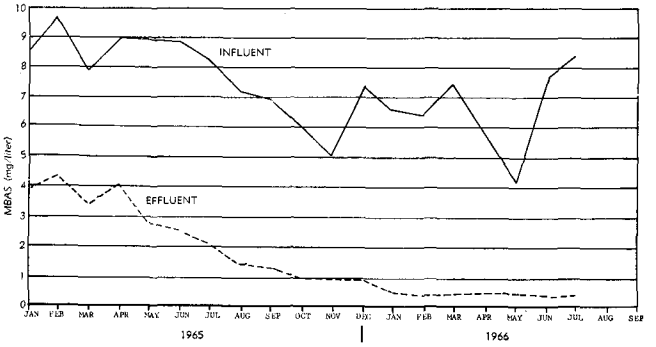

FIG. 4. Influent and effluent MBAS levels at the Whittier Narrows water reclamation plant (Los Angeles County, California), January 1965 to July 1966 (15).

probably results from the fact that these plants generally serve smaller communities, which often do not have the manpower or facilities needed to conduct a meaningful monitoring program. This, coupled with the fact that great variations exist in filter design and operation (e.g., bed depth, recirculation rate, etc.), makes effective performance comparisons particularly difficult even when data are available. Klein and McGauhey concluded however that, based on their observations, MBAS-removal efficiency in high-rate trickling filters has doubled since the conversion to LAS but that it has not reached the over-all efficiency anticipated in laboratory studies. This, they felt, could have resulted from the peculiar design of the filters investigated or from the slower acclimatization of the filters to LAS. This latter fact had been noted by them in earlier plant studies (16).

Information on changes in MBAS levels in rivers and streams is also somewhat limited. This probably results from two factors; first, even when ABS was in use, MBAS levels in streams were extremely low, often less than 0.1 mg/liter and second, it is particularly difficult to measure significant changes at these low concentrations because of the inherent limitations of the methylene blue test method. However there is solid evidence that changes are occurring and that MBAS levels have dropped significantly.

Klein and McGauhey have reported on their studies on Alameda Creek in California. This work began in December 1965 after the conversion to LAS was complete and sufficient time had elapsed to minimize the effect of residual amounts of ABS still present in the stream. Samples were collected during periods

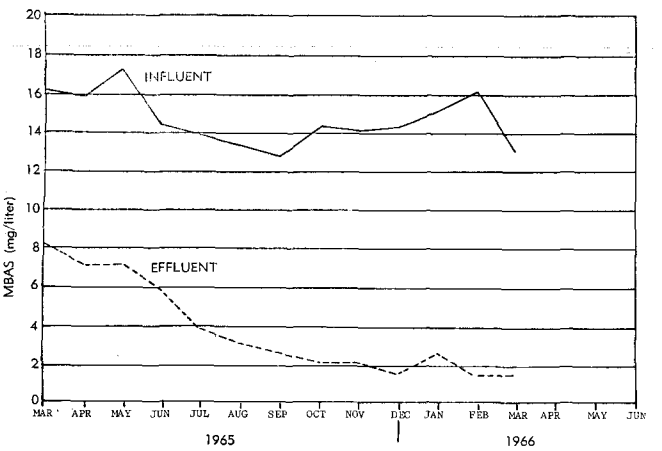

FIG. 5. Influent and effluent MBAS levels at the Livermore, Calif., sewage treatment plant, March 1965 to March 1966 (16).

of dry and rainy weather. Combining all data, MBAS concentrations varied between 0.1 and 0.26 mg/liter, well below the incipient foaming level. They also reported that there was virtually no foaming tendency in the waters of the creek, which was not the case prior to the conversion to LAS (16).

Another recently published report described studies conducted on the Illinois River at Peoria by the Illinois State Water Survey (17). This research is of particular interest since at one time the Illinois River was described as "the largest river in the country that currently contains more than 0.5 ppm ABS" (18).

The river is formed by the juncture of the Kankakee and Des Plaines rivers at a point some 54 miles downstream from Lake Michigan and receives the flow of the Chicago Sanitary and Ship Canal. This flow consists largely of treated sewage-plant effluent, industrial effluent, and storm run-off from the greater Chicago area. The average time of river flow from Chicago to Peoria is 12.5 days, and the total distance travelled is approximately 154 miles. MBAS monitoring began at Peoria in September 1959. During the period from 1959 through 1965 the average MBAS concentration in the river was 0.56 mg/liter, with a range in monthly averages of from 0.42 to 0.87 mg/liter. However in the 12-month sampling after conversion to LAS was complete (July 1965 to June 1966), these values dropped to an average of 0.22 mg/liter with a range of from 0.13 to 0.30 mg/liter.

In order to minimize the effect of variations in flow, the actual weight of MBAS transported by the river was also calculated. During the period 1959–1965 the average yearly load in tons/day varied between 13 and 20.6 whereas the comparable value for the 1965–1966 "post-conversion" period was 9.0 tons/day. Thus, both in concentration and in total pounds of MBAS, a marked reduction has been noted in the Illinois Waterway at Peoria.

Although no comprehensive analysis has been made of the extensive data collected by the Federal Water Pollution Control Administration on MBAS levels in rivers and streams throughout the country, a general review of this information indicates that levels have dropped. This, coupled with the fact that reported foam incidents in natural waters have decreased, would indicate that MBAS levels have reached a point where they are no longer of practical concern to pollution-abatement authorities. The exception, of course, would be those areas where raw or partially treated sewage is introduced to a water course.

A similar conclusion could be drawn regarding the current situation in ground waters. Relatively few reports of foaming well waters find their way into the technical literature or the public press at this time. This is, of course, in marked contrast to the situation that existed as recently as two years ago.

By every visual, scientific, and socio-economic yardstick the conversion to LAS has resulted in a marked reduction in the presence of MBAS in sewage-treatment-plant effluents and in natural ground and surface waters.

Certain parallels can also be drawn from developments in Europe, principally Great Britain and West Germany.

In West Germany conversion to biodegradable detergents (containing surfactants meeting an 80% degradability standard by the approved test method) was made mandatory by a federal regulation, effective in October 1964. In Great Britain, as in the United States, the conversion to more biodegradable surfactants was voluntary and took effect during the Fall of 1965.

Results so far reported from both countries have been most encouraging. Husmann (11) has reported that, in 1955, the MBAS level in effluents of sewage-treatment plants of the Emschergenossenschaft and of the Lippengenossenschaft averaged 1.1 mg/liter. In the period 1962–1964, when "hard" surfactants were in common use, this level had risen to 5.4 mg/liter. However by 1966 the level had dropped back to 1.2 mg/liter. He reported that the efficiency of MBAS removal in sewage-treatment plants during the comparable periods had also risen from 25% to 75%, not including degradation in sewers.

As far as levels in streams are concerned, the total weight of detergents in the Ruhr River has reportedly been reduced from 3,060 to 955 pounds per day after the conversion to LAS. Husmann noted however that only by the construction of additional biological treatment plants would the full benefit of the conversion be realized in Germany.

In Great Britain a similar pattern developed. Levels of MBAS in natural waters have diminished, in some cases dramatically. As an example, in the River Thames at Laleham, where MBAS levels had ranged from 0.22 to 0.42 mg/liter during the period 1954–1965, they dropped to 0.06 mg/liter in the first six months of 1966. A similar picture was observed on the River Lee at New Gauge, where levels had varied between 0.21 and 0.53 mg/liter during the 1954–1965 period and diminished to 0.07 mg/liter in 1966 (19).

At Luton, England, where an extensive pre-conversion field study had been carried out, recent sampling indicated a marked reduction in MBAS levels in the effluent of the sewage-treatment plant (12).

As in the United States, one could summarize the European experience by stating that, where adequate sewage-treatment facilities exist, LAS will meet the aesthetic objectives of water quality without recourse to special treatment.

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