

Ecological Effects of Evaporation Retardation Monolayers on Reservoirs

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The impoundment of water in man-made lakes may cause beneficial or harmful ecological effects. One of the major environmental problems created by the impoundment of water in reservoirs is increased evaporation losses.

Different methods have been applied to prevent excessive evaporation losses. These included efficient site location, windbreaks, control of plants and seepage, floating covers of reflective materials, and the application of monomolecular films on the surface of the impounded water. The chemical-filming method has been applied widely and still holds promise for use in effective evaporation control. *Parker and Barsom* [1970] have pointed out that naturally occurring surface microlayers are also formed by organic materials in runoff or caused by the introduction of man-made substances or pollutants into aquatic ecosystems. Some of the major problems encountered with using chemical monolayers have been the method of application [*Dressler*, 1964] and the resultant changes in water quality. Reports made on the use of monolayers [*Symons et al.*, 1966] have indicated a need for further study and evaluation of theoretical, laboratory, and field applications of natural or induced monolayers.

This paper describes research that was carried out to evaluate the ecological effects of a continuous antievaporation film of hexadecanol and octadecanol and to solve an applied pollution problem resulting in part from an alcohol

monolayer formed from organics discharged in lead-milling and zinc-milling waste waters and causing undesirable ecological changes.

EFFECTS OF CONTINUOUS MONOLAYERS

Many different combinations of evaporation reduction chemicals have been applied to reservoirs and lakes in an attempt to suppress evaporation and conserve stored water. One of the more common chemicals used for forming antievaporation films has been a blend of hexadecanol and octadecanol. These long-chain alcohols form a monomolecular film on the water surface that is self healing at wind speeds of up to 12.9 km/hr and is seemingly capable of reducing water evaporation by 30-50% under ideal conditions [*Gilby and Heymann*, 1948]. An additional benefit in the use of a hexadecanol and octadecanol monolayer has been that it could be biodegraded by the bacteria in the water. On the basis of ease of assimilation these compounds also received clearance from the U.S. Public Health Service [*Ludzack and Ettinger*, 1957].

However, research has indicated that a continuous monolayer can change or indirectly alter some of the ecological characteristics in treated aquatic environments. Initial evaluations of the effects of continuous monolayers were carried out in experimental aquatic ecosystems in laboratories at Texas A&M University with simulated field conditions and adjustable light banks to provide light energy at the water sur-

face. Lights were automatically controlled to give 12-hour photoperiods (8:00 A.M. to 8:00 P.M.), and the air and water temperature of the experimental ecosystem were maintained at a constant $22^{\circ} \pm 2^{\circ}\text{C}$. Water and algae from three local ponds were used to inoculate experimental ecosystems during the summer of 1966.

Half of the experimental systems were filmed with a 1:1 mixture of hexadecanol and octadecanol that was maintained as a continuous monolayer for 30-day experimental periods. A film material dose rate of $56.05 \text{ mg/m}^2/\text{day}$ of treated water surface was used following the recommendations of *Meinke and Waldrip [1964]*. Water quality and biological population measurements were evaluated during each experimental testing period.

A Gilson differential respirometer was used to evaluate the effects of oxygen diffusion through the monolayer. At 20°C the hexadecanol and octadecanol film reduced the oxygen diffusion rate by approximately 10–15%. This test indicated that efficient monolayers can affect the kinetics of reaeration and cause oxygen deficiencies in small reservoirs. Similar adverse effects have been reported by *Amad [1968]*.

The data collected for 30-day replicate tests indicated that the number of bacteria increased in aquatic systems treated with the continuous monolayer of alcohol. A lag growth period was observed for about 7 days after which the bacteria in the monolayer-treated systems progressed into a log growth period compared with the plateau or stationary growth period of bacteria in the control systems. A similar bacterial increase due to the biological oxidation of hexadecanol has also been noted by other investigators [*Wixson, 1970*]. A significant bacterial growth was observed in all experimental systems treated with a continuous antievaporation film of hexadecanol and octadecanol.

Phytoplankton population studies indicated that certain algal growths were altered by the application of a continuous monolayer. The green algae *Chlorella* in the monolayer-treated systems was inhibited during the first 15 days but increased during the rest of the time in contrast to the declining algal populations in the controls. The biodegradation of the monolayer by bacteria seemed to add nutrients that could be used effectively by some species of algae for growth.

The increased algal growth in monolayer-treated systems could be beneficial in recreational

areas, where increased phytoplankton growth would furnish food for the aquatic biota. However, the same features could be most undesirable in municipal and industrial water, where an uncontrolled prolific algal growth or 'bloom' might cause water quality and filter-clogging problems.

The application of a continuous film decreased water surface tension, which caused some filamentous algae and water plants to sink rather than to float at the water surface. Reduction of the surface tension can present problems by introducing increased amounts of normally floating plants into the hypolimnion. The film can also interfere with aquatic organisms that normally use the water surface during their life cycle.

EXPERIMENTAL CONCLUSIONS

The application of continuous hexadecanol and octadecanol films increased the growth of bacteria and certain algae (Figure 1). The monolayer can also alter the oxygen content and interfere with aquatic biota that are dependent on the water surface tension during some phase of their life cycle. Water quality studies should be conducted to determine whether a reservoir has acceptable bacterial and algal populations combined with good water quality and high dissolved oxygen prior to the application of antievaporation films. The addition of a floating nutrient source at the water-air interface of a reservoir can contribute to the rapid growth of bacteria and algae, which can further alter the lotic ecosystem in man-made reservoirs.

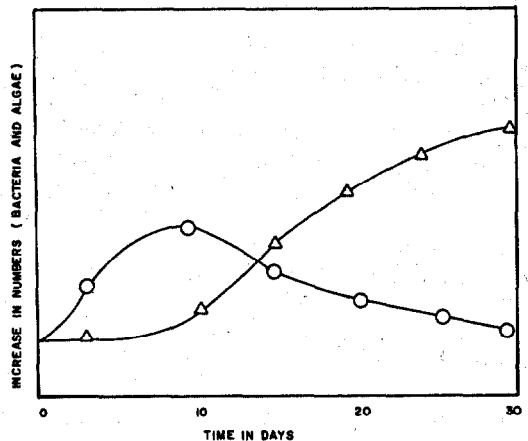


Fig. 1. Schematic comparison of bacterial and algal growth in control (open circles) and monolayer-treated (open triangles) ecosystems.

MINING POLLUTION AND MONOLAYERS

In 1955, improved mineral exploration led to the discovery of new lead deposits in the rolling forests of southeastern Missouri. By 1962 this rich belt of lead-zinc ore was found to extend for approximately 57.9 km almost due south from Viburnum, Missouri. The name given to this discovery was the Viburnum trend or 'New Lead belt.'

Geologically, the lead ore was found to be disseminated throughout the Cambrian Bonneterre formation, and, since it is a good aquifer, most mines constantly employ extensive pumping to prevent flooding. Part of the pumped mine water is used as process water for the milling procedure, chemical reagents being added during the flotation circuit to separate the lead, zinc, and copper minerals from the finely ground rock or gangue. The final discharge of mining and milling waste waters containing decomposed organic milling reagents and suspended rock material has caused undesirable water quality changes.

The pollution problem manifested itself as an unusual bacterial-algal growth that trapped large amounts of dolomite rock flour and coated the stream bottom, the result being the killing off of most of the other biota of the stream.

A research project was carried out to study the cause and effect of the mining pollution and make practical applied recommendations toward solving the existing problems and preventing future stream and reservoir pollution by the lead-zinc industry [Wixson, 1970].

EFFECTS OF MINING AND MILLING WASTE WATERS

Fletcher Mine, operated by the St. Joe Minerals Corporation, provided feed rates and samples of the chemical reagents used at their facility for separating and concentrating lead, zinc, and copper by the flotation process. Typical reagents employed were sodium isopropyl xanthate (collector), isopropyl ethyldithiocarbamate (collector), mixed alcohols (6-9 carbons) (frothers), zinc sulfate ($ZnSO_4$) (zinc depressant), sodium cyanide (NaCN) (zinc depressant), copper sulfate ($CuSO_4 \cdot 5H_2O$) (zinc activant), sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) (lead depressant), sulfur dioxide (SO_2) (lead depressant), and starch (lead depressant). This information assisted in the development of research techniques for detecting specific decomposition products that could cause pollution problems. At

the Fletcher Mine, underground water was pumped to the surface at a rate of 1.89×10^4 to 2.65×10^4 l/min. Flotation reagents were added to the part of this water (6.05×10^3 l/min) used for the milling process. The final effluent from the lead, zinc, and copper thickeners was then combined with the rest of the underground water and discharged into three sedimentation lagoons constructed in series. The water from the lagoons passed over a spillway, and the final discharge was approximately 3 times the volume of the receiving stream.

Decomposition products of the reagents used in the flotation process were found to form a surface monomolecular film in the settling lagoons. The film was not detained sufficiently for biological degradation but was drawn rapidly across the lagoon surface owing to the spillway discharge arrangement. Once this organic material reached the quiescent stream sections, it contributed to the prolific growth of bacteria and large bottom-coating mats of the blue green algae *Oscillatoria*. Decomposition products from the sodium isopropyl xanthate (collector) were found to act as nutrients for the accelerated growth of stream bacteria. Assimilation of similar alcohol monolayers by bacteria in water has been reported by other investigators [Chang *et al.*, 1962; Silvey, 1960]. Biochemical oxygen demand and chemical oxygen demand determinations were difficult owing to the concentration of organics in the monolayer at the water surface.

A spectrophotometric determination was used to measure the concentration and decomposition rate of sodium isopropyl xanthate. Optical absorbance was measured at 303 nm to evaluate the effects of time and frothing reagents on xanthates (Figure 2). Temperature increases were found to accelerate the decomposition rate of xanthates used in the milling process [Wixson *et al.*, 1969].

No deterioration in stream water quality was found for alkalinity, hardness, pH, or dissolved oxygen. However, mine water was found to contain a higher fluoride concentration (1 ppm) than the normal surface stream water (0.15 ppm). The fluoride concentration was one method used to detect mine waste water in the New Lead belt.

The responses of different biotic organisms to changes in their aquatic environments were evaluated by population studies correlated with analytical determinations of heavy metals and organic compounds. Confirmatory photomicrographs were taken for the comparison of

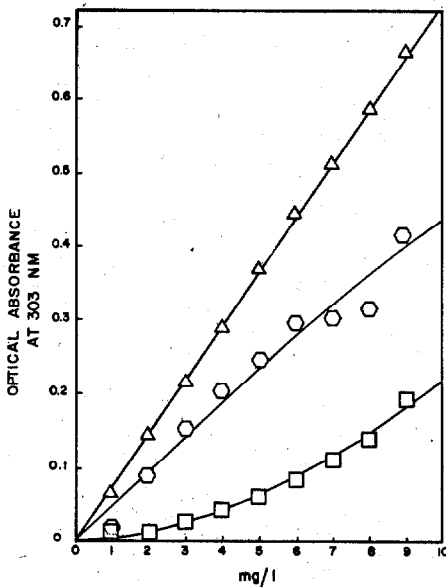


Fig. 2. Spectrophotometric determination for the concentration of sodium isopropyl xanthate. The open triangles represent the standard solution, the open hexagons represent the standard solution treated with frother 71, and the open squares represent the standard solution after 1 week of decomposition.

diatoms and filamentous and nonfilamentous algae in polluted and unpolluted streams.

A biological examination of water samples indicated that the three diatom genera *Synedra*, *Navicula*, and *Cymbella* could be used as biological indicators of mining pollution in the New Lead belt. A composite evaluation indicated that *Synedra* and *Navicula* were tolerant of mining pollution, *Synedra* becoming the dominant population close to the pollution source. *Cymbella* was normally found in control streams but almost disappeared in polluted streams. Immediately below the point where the mine waste water entered the stream the blue green algae *Oscillatoria* was found to cause pollution problems with large matlike growths that covered the stream bottom and destroyed the other benthic life.

APPLIED RECOMMENDATIONS

On the basis of knowledge gained through this study the following recommendations have been made and applied to assist in stream pollution abatement in the New Lead belt of southeastern Missouri: (1) that mine discharge water be separated from the milling waste water and mill

effluent be recycled through the flotation process and (2) that all settling lagoons be modified for the biological treatment of monolayers or other remaining nutrients prior to the discharge of treated water into receiving streams. Streams in the New Lead belt must be protected, since most of them drain into Clearwater Lake in southeastern Missouri.

The determination of which organic or inorganic compounds, individually or mixed, form monolayers that can alter water quality and ecological systems has contributed valuable applied information toward protecting other streams, rivers, and reservoirs from lead-mining and zinc-mining pollution. This knowledge has now been applied to the development of waste treatment methods to control the monolayer problem and prevent future pollution problems.

The practical use of evaporation retardation monolayers on reservoirs has yet to be determined. More efficient antievaporation films may be used effectively on reservoirs if specific water quality and impoundment ecosystems are known. Induced or artificial monolayers that cause pollution problems can also be evaluated by their effects on water quality and aquatic ecosystems. Effective treatment can then be instigated by using all possible analytical methods. All aspects being considered, further applied studies are needed to use the promising aspects of monolayer evaporation control to conserve needed water resources in reservoirs.

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REFERENCES

- Amad, M. T., Predicting dissolved oxygen concentrations in a lake covered with evaporation suppressant, *J. Water Pollut. Contr. Fed.*, 40, 423, 1968.
- Chang, S. L., M. A. McClanahan, and P. W. Kabler, Effect of bacterial decomposition of hexadecanol and octadecanol in monolayer films on the suppression of evaporation loss of water, in *Retardation of Evaporation of Monolayers: Transport Processes*, edited by V. K. LaMer, 119 pp., Academic, New York, 1962.
- Dressler, R. G., The suspension process for reservoir evaporation control, *Ind. Chem. Eng.*, 56, 36, 1964.
- Gilby, A. R., and E. Heymann, The rate of evaporation of water through duplex films, *Aust. J. Sci. Res.*, 1, 197, 1948.

- Ludzack, F. J., and M. B. Ettinger, Biological oxidation of hexadecanol under laboratory conditions, *J. Amer. Water Works Ass.*, 49, 849, 1957.
- Meinke, W. W., and W. J. Waldrip, Research on evaporation retardation in small reservoirs, 1958-63, *Tex. Water Comm. Bull.*, 6401, 1964.
- Parker, B., and G. Barsom, Biological and chemical significance of surface microlayers in aquatic ecosystems, *BioScience*, 20, 87, 1970.
- Silvey, J. K. G., Physical, chemical and biological effects of hexadecanol on Lake Hefner, 1958, *J. Amer. Water Works Ass.*, 52, 791, 1960.
- Symons, J. M., S. R. Weible, and G. G. Robeck, Influence of impoundments on water quality, U.S. Dep. of Health, Ed., and Welfare, Cincinnati, Ohio, 1966.
- Wixson, B. G., Water quality protection in streams in mining districts, in *Developments in Water Quality Research*, edited by H. I. Shuval, pp. 199-209, Ann Arbor-Humphrey Science Publishers, Ann Arbor, Mich., 1970.
- Wixson, B. G., E. A. Bolter, N. H. Tibbs, and A. R. Handler, Pollution from mines in the New Lead belt of southeastern Missouri, *Proceedings of the 24th Purdue Industrial Waste Conference*, pp. 632-643, Purdue University, Lafayette, Ind., 1969.