Reports

Use of Chemicals To Control Shellfish Predators

Abstract. Many enemies of such bivalves as oysters and clams can be controlled by the use of heavy oils, such as orthodichlorobenzene. These oils are mixed with dry sand, or other inert carriers, to anchor them in place on shellfish beds. Effects of the treatment may be increased by incorporating other chemicals in heavy oils. The treated sand can be used to surround the shellfish beds, thus preventing the entrance of the enemies, or it may be spread over the infested areas, killing the enemies and, under certain conditions, stopping their larvae from reinvading the beds. Snails, starfish, and, in some instances, crabs can be controlled in this manner.

The need for controlling enemies of mollusks has been obvious ever since people began to harvest them for food (*1*). In this report we describe the principle of a new, simple, but effective chemical method which may help solve the problem, although, because it is still in the experimental stage, it is too early to recommend its commercial application.

The method is devised to prevent boring gastropods, starfish, crabs, and other enemies of bivalves from invading shellfish beds, and also to render these beds unsuitable for their existence. To prevent invasion, beds are surrounded with "barriers" or "belts" of sand or some other inert carrier treated with chemicals which either stop, repel, or kill predators. Clearing an area of predators and preventing setting of their larvae can be accomplished by spreading chemically treated sand over the bottom.

While testing numerous compounds on marine invertebrates, we found that heavy chlorinated oils, such as trichloroethylene, orthodichlorobenzene, paradichlorobenzene, trichlorobenzene, and tetrachlorobenzene will repel, stop, cause swelling in, or even kill boring gastropods, such as oyster drills, *Urosalpinx cinerea* and *Eupleura caudata*, and those of the genera *Polinices, Busycon, Thais*, and others. We realize the serious danger that may be created by indiscriminate use of chemicals, but fortunately the oils that we have selected are insoluble or only slightly soluble in water and, therefore, they should not pose a pollution problem.

Although barriers of heavy oils and sand stopped gastropods, their efficiency was increased by incorporating some other compounds in the oils. One of these is Sevin (1-naphthyl-N-methylcarbamate), an insecticide which is relatively nontoxic to mammals but is highly toxic to gastropods and to crabs, another important enemy of shellfish. Still another enemy, the starfish *Asterias forbesi*, can be stopped by barriers consisting of sand, heavy oils, and certain compounds, such as 2-chloro-1-nitropropane. Eventually, several formulas were developed that can stop the movements of boring gastropods, starfish, and under certain conditions, crabs. One such mixture was orthodichlorobenzene containing 2-chloro-1-nitropropane and Sevin (*2*).

There are many conditions that determine the effectiveness of our methods. In barriers, the width, the proportion of sand, the oils and other chemicals, and the concentrations of these chemicals per unit of surface are of importance. The general condition of the bottom, silting, and the velocity of currents should also be considered. We may give, nevertheless, some illustrations of the effectiveness of certain formulas. In one of our experiments a barrier only 8 in. wide, composed of sand and orthodichlorobenzene, remained effective against drills from 1 February 1959 through March 1960. During this time not a single drill crossed the barrier, although new groups of ten drills were placed in the experimental trough every 2 weeks.

Virtually no starfish crossed barriers only 3 feet wide composed of sand, orthodichlorobenzene, and 2-chloro-1-nitropropane or similar mixtures. In nature, because starfish may be helped to move along the bottom by currents, barriers should be considerably wider.

All the heavy oils tested caused extreme swelling in gastropods. Affected in this way they were unable to move, and some soon died. The first sign of distress shown by starfish upon coming in contact with barriers was usually a curling of the tips of their rays. Disintegration of the lower surfaces soon began, and casting of the rays sometimes followed.

Affected crabs first lost equilibrium and later went into convulsions. However, orthodichlorobenzene alone usually does not seriously affect crabs. To stop them, other chemicals, principally insecticides, should be added to the oils. Thus, narrow barriers composed of sand and orthodichlorobenzene are relatively safe for crabs and can be used to control gastropods in areas where crabs are commercially important.

Spreading chemically treated sand over oyster beds is another method for controlling shellfish enemies. This method may kill most oyster drills on the infested bottoms. Field experiments to test this method further are now in progress. The same method may kill ready-to-metamorphose larvae of starfish, certain gastropods, and crabs and worms, which, being pelagic, can float over the barriers. Adult and recently set starfish can be attacked by spreading treated sand over beds. Sand grains will imbed in the membrane covering the starfish's body and cause its decomposition.

Because certain gastropods, such as the clam-killing snail *Polinices*, are able to move under several inches of bottom soil, they may not be stopped by the above-described methods. However, by injecting into the bottom soil plugs of treated sand, or oil alone, it may be possible to create an effective, three-dimensional barrier.

Since the principle of our method is rather simple, it may have other applications. For example, it might be possible to control *Dermocystidium*, a widespread fungus disease of southern oysters, by incorporating water-soluble fungicides in the oils and surrounding oyster beds with belts of these mixtures or spreading them over entire areas where diseased oysters are found.

Spreading chemically treated sand over oyster-growing bottoms may eliminate the mud shrimp *Upogebia* and the predaceous flatworm *Stylochus*. Moreover, variations of the basic method could be tried to reduce the population of fresh-water snails such as *Oxytrema*, intermediate hosts of para-

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Type manuscripts double-spaced and submit one ribbon copy and one carbon copy.

Limit the report proper to the equivalent of 1200 words. This space includes that occupied by illustrative material as well as by the references and notes.

Limit illustrative material to *one* 2-column figure (that is, a figure whose width equals two columns of text) or to *one* 2-column table or to *two* 1-column illustrations, which may consist of two figures or two tables or one of each.

For further details see "Suggestions to Contributors" [*Science* **125**, 16 (1957)].

sites causing numerous diseases in fish. Finally, the method may be helpful in the control of schistosomiasis by destroying snails which act as intermediate hosts of human schistosomes.

We believe that we have now the basic principles of a method by means of which the age-old problem of protecting shellfish beds from predators can be solved. We realize, nevertheless, that our studies represent only the first steps toward achieving full control of these enemies and that many secondary problems have to be solved before the method can be recommended for general use. For example, it will be necessary to determine the effects of the chemicals on aquatic communities in general and ascertain if some of the substances used accumulate in the body tissues of mollusks, such as oysters, rendering them undesirable or dangerous as food (*3*).

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References and Notes

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2. V. L. Loosanoff, C. L. MacKenzie, Jr., L. W. Shearer, *Proc. Natl. Shellfisheries Assoc. 1959*, in press.
3. We wish to thank John F. LesVeaux of the Niagara Chemical Division, Food Machinery and Chemical Corporation, for providing numerous samples of chemical compounds for our "screening" studies.

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Sulfur Dioxide Sensitized Photochemical Oxidation of Hydrocarbons

Abstract. Near-ultraviolet sunlight is absorbed by sulfur dioxide to produce electronically excited molecules, which react with *n*-butane in the presence of wet or dry air to produce an aerosol and eventually a liquid precipitate. The product is a heavily oxidized, sulfur-containing, organic strong acid. The possible role of these reactions in photochemical air pollution is discussed.

The photodissociation of sulfur dioxide to SO and O occurs only at wavelengths below 2100 A; at longer wavelengths an electronically excited molecule is produced (*1*), which is chemically much more active than ordinary sulfur dioxide. Irradiation of pure sulfur dioxide with a wavelength of 3130 A produces sulfur and sulfur trioxide, with a quantum yield of about 10^{-2} (*2*). At similar wavelengths, sulfur dioxide and oxygen yield only sulfur trioxide, again with a quantum yield of about 10^{-2} (*2*). Gaseous solutions of sulfur dioxide and hydrocarbons, saturated or unsaturated, react photochemically with sulfur dioxide with a quantum yield of about 10^{-2} to produce sulfinic acids, RSO_2H (*3*).

This more or less constant quantum yield for a wide variety of reactions, plus spectroscopic considerations, leads to the following interpretation: In about 99 percent of the cases sulfur dioxide absorbs near-ultraviolet radiation to form an excited singlet electronic state, which deactivates itself by fluorescence in about 10^{-8} sec. In about 1 percent of the cases a conversion to an excited triplet state occurs, for which fluorescence to the ground state is a forbidden process. The excited triplet state may survive for as long as 10^{-3} sec and thus may undergo up to 10^{6} collisions at ordinary pressures; however, if any of these collisions is with sulfur dioxide, or with oxygen, or with a hydrocarbon, reaction may occur. This study concerns itself with a preliminary survey of reactions of photoexcited sulfur dioxide molecules with oxygen and *n*-butane.

Two-liter Pyrex flasks were equipped with a small, easily sealed glass tube on the top and, on the bottom, with a closed-end glass tube which could be shielded from sunlight. The flask was filled with known amounts of sulfur dioxide, *n*-butane, and air, and it was sealed off. The flasks were placed in sunlight for various periods of time, from 2 minutes to 3 weeks. The bulbs were occasionally removed to a dark room and examined for aerosol by means of a Tyndall beam of light, and the nature of the liquid which settled out on the walls and into the bottom tubes was noted. Eventually these bottom tubes were broken off, and chemical, gas-phase chromatographic, or spectroscopic studies were made of the liquid product.

The qualitative nature of the fog formation and liquid formation is given in Table 1. Whereas light fogs were formed with sulfur dioxide and butane or with sulfur dioxide and air, heavy fogs were formed only when all three components, sulfur dioxide, butane, and air, were present. No fog or liquid precipitate formed when the mixtures were kept in the dark, even after 6 months. The liquid which settled out at first was colorless (butane and sulfur dioxide, alone) or light yellow (with air), but where the liquid was struck by sunlight it turned dark brown. The half time for settling out of fog from the 2-liter flasks was about 2 hours.

Table 1. Formation of aerosol and liquid precipitate upon irradiation of sulfur dioxide and other substances in sunlight.

Partial pressure initially present (mm-Hg)			Aerosol formed	Liquid product formed
SO_2	*n*-butane	Air (dry)		
20	0	0	None	None
20	20	0	Light	Clear liquid
20	0	400	Light	None
0	20	400	None	None
20	20	400	Heavy	Yellow liquid
20	20	400	None in dark in 6 mo	None in dark in 6 mo
50	50	400 (dry)	Heavy within 2 min	At first yellow, later clear (all O_2 consumed)
50	50	400 (wet)	Heavy within 2 min	

The liquid products were sent through a gas-phase chromatography column at 115°C, packed with firebrick coated with *p*-tolyl cresyl phosphate. The products from a flask originally filled with sulfur dioxide, *n*-butane, and dry air at partial pressures of 20, 20, and 400 mm-Hg, respectively, showed eight major peaks and other broad minor ones; two were identified as dissolved sulfur dioxide and butane; the other peaks were not identified. Water was absent and sulfur trioxide was absent. The product from 20 mm of sulfur dioxide and 20 mm of butane showed 11 major peaks, including the two reactants. Aside from the reactants and two other, minor peaks, the products from the reaction without air and with air were all different.

The liquid products were pumped free of reactants and dissolved in alcohol, and the ultraviolet spectrum was taken. The liquid products absorb near-ultraviolet radiation much more strongly than the parent reactants; this spectrum lacks completely the vibrational structure shown by sulfur dioxide.

The liquid product was soluble in ethyl alcohol or in acetone to give a clear solution, and it was insoluble (at least in part) in carbon tetra-