

facilitated by not going above the 2 pound concentrate level. It should be noted here that this oil-soluble, water-emulsifiable diamine acts like an ester at extremely cold temperatures, merely becoming very viscous. It does not crystallize as do the water-soluble amines. Since it will be recommended for spraying only during the growing season, this should not prove to be much of a problem.

Volatility comparisons made at Boyce Thompson Institute using the procedure officially approved by the A.O.A.C. showed the oleoyl 1,3 propylene diamine salts of 2,4-D and 2,4,5-T to be in a class safer than the standard low-volatile esters being used commercially today. To detect smaller volatility differences, the plants were held for an additional seven days, after which leaf modification readings were recorded. Our oil-soluble, water-emulsifiable amine salts of 2,4-D and 2,4,5-T showed no leaf modifications, while some of the low volatile 2,4-D formulations showed a degree of leaf modification indicating some minor volatility during this seven-day period.

A point worth mentioning at this time is that the oleoyl 1,3 propylene diamines do not possess the characteristic odor associated with the water-soluble amines. Any undesirable odor would be one emanating from the solvents used. The addition of an appropriate solvent also lacking an undesirable odor would produce a finished formulation with still another advantage over the water-soluble amines.

Brush control trials conducted on a limited scale show these formulations to be equal to the low-volatile esters in effectiveness. In crops, recent work indicates that certain resistant weeds can be controlled using the Dacamines. At the present time, the use of these amines on brush and crops is recommended at rates of application equal to those of the low-volatile esters being used in your area.

In summary, the oleoyl 1,3 propylene diamine salts of 2,4-D and 2,4,5-T has several advantages which are as follows:

1. Oil soluble amines act somewhat like an ester but have the non-volatile features of regular amines. Effectiveness of esters, safety of amines.

2. Oil soluble amines can be used later in the growing season than the other amine salts because 5 or 10 gallons of oil can be added to the spray solution. This is important in brush control.

3. In cold weather, they do not salt out like the ordinary water-soluble amines. They merely become more viscous (similar to esters).

4. Indications are that the Dacamines will control certain weeds which have been resistant to 2,4-D and 2,4,5-T.

Preliminary, but extensive, trials with our field personnel has yielded mainly observational data which, while giving an indication, is still qualitative in nature. We should like to obtain more quantitative data during the 1962 growing season and would welcome the opportunity of working with anyone involved in research in weed and brush control.

Some Effects Of 2,4-D On Drinking Water Quality*

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Water purveyors are concerned about the general effect of aquatic herbicides on the chemical quality of drinking water supplies. In particular, tastes and odors are important since these are the qualities by which the consumer judges water potability and palatability. Since, to the consumer, any off-taste or off-odor suggests that the water is unfit for human consumption, the purveyor is sensitive to any potential source of taste and odor in his water supply.

Ester derivatives of 2,4-dichlorophenoxyacetic acid (2,4-D) have proven to be successful aquatic herbicides. Since this compound is a phenoxy derivative, there is concern as to the occurrence of 2,4-dichlorophenol (2,4-DCP) as a formulation impurity or as a product of chemical or biological degradation of 2,4-D in surface waters. At concentrations less than 8 ug/1

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or 2 ug/1, respectively, chlorinated phenols impart objectionable "medicinal" tastes and odors to water¹.

Data presented herein indicate: (a) the concentrations of 2,4-DCP in various commercial liquid and granular forms of 2,4-D; (b) the release, occurrence, and persistence of 2,4-DCP from four granular forms of 2,4-D in laboratory carboy studies; and (c) a field observation on the effect of 2,4-D on lake water quality.

Experimental Procedures: The field study was reported previously¹.

In the laboratory, 1 and 3 mg/1 of 2,4-D acid or ester equivalents was added, respectively, to 15 or 18 liters of tap or lake water; the treated water was stored in 5-gallon carboys at room temperature and maintained aerobically.

Threshold odor levels were made in accordance with "Standard Methods"². The 2,4-DCP was determined by a 4-aminoantipyrine colorimetric procedure³, the 2,4-D by a colorimetric method using chromotropic acid⁴.

Threshold dilution values were calculated according to the data of Burttschell¹. These values represent the dilution required by odor-free water for the odor or taste to be just detectable according to the "Standard Methods" test². A value of 1 or less means that no dilution is indicated; values greater than 1 indicate that dilution is required.

Experimental Results: Several liquid and granular formulations of 2,4-D were analyzed for 2,4-DCP. These data are reported as ug 2,4-DCP per gram of formulation (Table I). Liquid forms showed higher amounts of the phenol impurity, (70 to 4500 ug/gram), than did the granular forms (200 to 960 ug/gram). Using these figures to calculate the concentrations of 2,4-DCP that would result from the application of 100 pounds of 2,4-D per one million gallons of water (3.1 acre-foot), the amounts of phenol ranged from 8.4 to 539.3 ug/1. Subsequently threshold taste and odor dilution values for 2,4-DCP were calculated. In general, all formulations indicated high dilution values and, therefore, would presumably impart typical chlorophenolic tastes and odors to water.

TABLE I

Type of formulation	2,4-Dichlorophenol Impurity in Formulations of 2,4-D		Dilution values	
	% Ester	2,4-DCP per gram of formulation ug	2,4-DCP ug/1 (a)	Threshold Taste Odor (b)
Liquid				
Iso-octyl ester	98.3	1250	149.8	18.7 74.8
Iso-propyl ester	98.5	4500	539.3	67.4 270.0
Iso-propyl ester	47.0	1500	179.8	22.5 90.0
Butyl	98.9	1000	119.8	15.0 60.0
Butyl	39.0	70	8.4	1.05 4.2
Iso-octyl	69.0	3250	389.5	48.7 195.0
Granular				
Butoxyethanol		560	67.1	8.4 33.6
Propylene Glycol				
Butyl Ether		200	24.0	3.0 12.0
Iso-octyl-A	30.15	960	115.0	14.4 57.6
Iso-octyl-B		650	77.9	9.7 38.8

(a) concentration at the rate of 100 lbs. of formulation applied per 1 million gallons of water (3.1 acre-foot).

(b) according to Burttschell et al (ref 1.).

Table II shows the release and persistence of 2,4-DCP from two granular forms of 2,4-D added to a natural lake water. Subsequently, these systems were analyzed for 2,4-DCP over a period of 218 days. Maximum concentrations of 14.7 and 20.7 ug/1 of the phenol were observed after 148 and 218 days. Values of 9.5 and 16.7 ug/1 after 7 days of storage indicated that phenol was released rather quickly. A high degree of persistence was indicated also by the levels of the chlorinated phenol that remained after 218 days of storage. Threshold dilution values show that very low, almost insignificant, taste levels were present, whereas the persistence of odor levels was significant.

Table III shows the release, occurrence, and persistence of 2,4-DCP from two iso-octyl esters of 2,4-D added to tap water that was seeded with settled sewage. These systems were stored for 59 days in an effort to show the influence of bacterial seeding on the persistence of the chlorinated phenol. In general, these systems exhibited lower levels of 2,4-DCP and threshold

TABLE II

Release and Persistence of 2,4-Dichlorophenol From Two Granular Forms of 2,4-D in a Natural Surface Water (a)

Time Days	Butoxy Ethanol Ester (b) 2,4-DCP (d) Threshold Dilution (e)			Propylene Glycol Butyl Ether Ester (c) 2,4-DCP (d) Threshold Dilution (e)		
	ug/1	Taste	Odor	ug/1	Taste	Odor
0	2.8(f)	1.0	1.4	1.0(f)	1.0	1.0
7	9.5	1.2	4.8	16.7	2.1	8.4
14	10.3	1.3	5.2	3.5	1.0	1.8
21	11.9	1.5	6.0	14.1	1.8	7.2
28	10.3	1.3	5.2	14.5	1.8	7.2
88	9.7	1.2	4.8	7.8	1.0	3.8
148	14.7	1.8	7.2	9.2	1.2	4.8
218	8.7	1.08	4.32	20.7	2.6	10.4

- (a) Laboratory carboy studies, 18 liters, room temperature.
- (b) Added as 1 mg/1 as the ester equivalent of 2,4-D.
- (c) Added as 1 mg/1 as the 2,4-D acid equivalent.
- (d) Corrected for interferences and volume depletion.
- (e) Calculated according to Burttschell (ref 1).
- (f) Amount of 2,4-DCP added from the impurity in the formulation.

TABLE III

Release and Persistence of 2,4-Dichlorophenol From Two Granular Forms of 2,4-D in Seeded Tap Water (a)

Time	Iso-octyl Ester — A (b) 2,4-DCP (c) Threshold Dilution (d)			Iso-octyl Ester — B (b) 2,4-DCP (c) Threshold Dilution (d)		
	ug/1	Taste	Odor	ug/1	Taste	Odor
0	14.4(e)	1.8	7.2	9.75(e)	1.2	4.9
1 hr.	0.0	0.0	0.0	0.0	0.0	0.0
2 days	9.1	1.1	4.4	5.6	1.0	2.8
7 days	6.3	1.0	3.2	3.9	1.0	1.95
9 days	11.6	1.5	5.8	8.9	1.1	4.4
11 days	9.0	1.1	4.4	2.2	1.0	1.1
19 days	13.8	1.7	6.8	13.8	1.7	6.8
24 days	4.2	1.0	2.1	13.5	1.7	6.8
31 days	4.7	1.0	2.4	10.6	1.3	5.2
59 days	0.0	0.0	0.0	0.0	0.0	0.0

- (a) Laboratory carboy studies — 15 liters seeded with 5 ml settled sewage.
- (b) Added as 3 mg/1 as the acid equivalent of 2,4-D.
- (c) Corrected for volume depletion and interferences.
- (d) Calculated according to Burttschell (ref 1).
- (e) Amount of 2,4-DCP added from the impurity in the formulation.

TABLE IV

Occurrences and Persistence of 2,4-D and 2,4-Dichlorophenol in a Natural Lake Water (a)

Time	Average of Four Sampling Areas			Observed	
	2,4-D (b)	2,4-DCP (c)	Threshold Dilution Levels for 2,4-DCP		
	ug/1	ug/1	Taste Calculated	Odor Calculated	
Before	8.0	00.0 (4.4) (f)	0.0	0.0	2 (d)
1 hour	38.5	1.0	0.1	0.5	2
2 days	45.0	3.0	0.4	1.5	2
13 days	49.5	2.0	0.3	1.0	2
22 days	30.8	0.5	0.06	0.3	2
27 days	25.8	2.0	0.3	1.0	2
48 days	25.8	0.0	0.0	0.0	2
55 days	20.0	11.3	1.4	5.7	2
70 days	24.5	10.5	1.3	5.3	2
132 days	13.0	13.0	1.6	6.5	(e)

- (a) Field observations previously reported⁴.
- (b) 2,4-D applied to the concentration of 1.34 mg/1 in the lake.
- (c) Corrected for interfering phenol, C₆H₅OH.
- (d) Qualitatively identified as "musty".
- (e) No "chlorophenolic" taste or odor were observed qualitatively.
- (f) Impurity in the formulation.

dilution values, and for a considerably shorter period of time, than did the systems shown in Table II.

Table IV shows the occurrence and persistence of 2,4-D and 2,4-DCP up to 132 days from a field observation⁴. The maximum concentration of 2,4-D, 49.5 ug/1, was observed 13 days after herbicide treatment which, thereupon, decreased to 13 ug/1 after 132 days. The 2,4-DCP exhibited the same pattern of occurrence and persistence as 2,4-D, but at lesser concentrations. There appeared to be a secondary release of the phenol after 55 days. (Figures of 18.7 and 37.5 ug/1 of 2,4-DCP were observed between 70 and 132 days. These data were not verified by subsequent analysis and, therefore, were not considered valid.) Threshold taste and odor dilution values for 2,4-DCP are presented as well as an observed odor value.

Discussion: 2,4-dichlorophenol is a significant factor affecting the taste and odor quality of drinking water supplies. That this phenol can occur in waters subject to aquatic plant control by 2,4-D is seen in Table I. Ten commercial formulations of 2,4-D contained enough of the phenolic impurity so that a several-fold dilution of the water would be required to bring the tastes and odors to acceptable levels. For example, a 38.8-fold dilution is required to lower the 77.9 ug/1 concentration of 2,4-DCP impurity from one of the iso-octyl esters to the just barely detectable odor concentration of 2.0 ug/1. Another way of expressing this effect is that the odor level is intensified 38.8 times.

Since liquid formulations of 2,4-D contain higher amounts of the chlorinated phenol than the granular forms, the threshold taste and odor dilution values are higher consequently. This is in addition to the effect of the aromatic carriers (kerosene or fuel oil) for 2,4-D on the taste and odor quality previously reported⁴.

Subsequent laboratory studies showed that 2,4-DCP is released from 1 mg/1 dosages of 2,4-D to raise the odor levels of a natural surface water significantly. Moreover this phenol persists for a considerable period of time, as seen by the 218-day period in one of the systems. Qualitative data (not shown here) also indicated that, for the same period of time, the 2,4-D persisted in concentrations greater than 200 ug/1.

One of the reasons for the persistence of 2,4-DCP in natural surface water may be the lack of an adequate microbiological population to degrade these compounds. The phenol persisted at generally lower concentrations and for a shorter time in tap water seeded with sewage than in natural water (Table III). Tastes and odors were reduced to acceptable levels within 59 days in the seeded systems, whereas after 218 days in the natural water systems, considerable taste and odor was evident.

The field study indicated that concentrations of 10 to 13 ug/1 of 2,4-DCP did not raise the threshold odor level greater than 2, but the calculated value indicated an increase of 6.5. This apparent discrepancy may be well within the error of the phenol and odor procedures.

The field study that showed the persistence of 2,4-DCP in a natural surface water for a long period of time substantiates, to some extent, the findings of the laboratory study. There was some question in the field study about the release of this phenol as an intermediate biological degradation product of 2,4-D. Some evidence of this release was reported in previous carboy studies⁴ and from soil studies⁷, but the work reported here sheds new light on the question. The data in Table II, which shows levels of 2,4-DCP higher than that contributed by the impurity in the original formulation, suggest that 2,4-D is slowly decomposed to the 2,4-DCP throughout the 218-day storage. Although this is quite possible since levels of 2,4-D ranging from 200 to 1000 ug/1 persisted during this period, Tables III and IV, on the other hand, suggest that any 2,4-DCP present in a surface water would be there primarily as an impurity from the formulation. These data indicate that 2,4-DCP decomposes at about the same rate as 2,4-D.

Summary and Conclusions: Ten liquid and granular formulations of 2,4-D were analyzed for 2,4-dichlorophenol. Concentrations of this phenol ranged from 70 to 4500 ug per gram of formulation, and the liquid forms generally contained the higher phenol concentrations. Subsequent calculations indicated that levels of 2,4-DCP that ranged from 8.4 to 539.3 ug/1 would result in lakes dosed at the rate of 100 lbs. of formulation per one million gallons of water. In surface water these levels of the chlorinated phenol would produce significant threshold dilution values for tastes and odor.

Four granular forms of 2,4-D were placed in carboys containing tap water seeded with settled sewage and a natural

surface water. Subsequent release, occurrence, and persistence of 2,4-DCP were observed. The seeded tap water systems indicated lower levels of the phenol for shorter periods of time than did the natural surface water systems. A field observation substantiated the seeded tap water system.

The following conclusions are made:

1. Commercial formulations of 2,4-D contain 2,4-dichlorophenol as an impurity. Liquid formulations contain more of the phenol than the granular forms.

2. The 2,4-dichlorophenol persists at concentrations high enough to affect odor levels of a natural surface water for at least 218 days as observed in the laboratory.

3. The persistence of 2,4-dichlorophenol in water was decreased to acceptable odor levels within 59 days by addition of a sewage seed as observed in the laboratory.

4. As observed in field and laboratory, threshold taste dilution values were not significantly affected by the 2,4-dichlorophenol impurities in 1 and 3 mg/1 dosages of 2,4-D.

5. As observed in the laboratory, threshold odor dilution values were significantly increased by the 2,4-dichlorophenol impurities in 1 and 3 mg/1 dosages of 2,4-D.

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Effects Of Water Pollution On Aquatic Vegetation

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In the past few years there has been a great increase in aquatic weed control activities in Florida. Involved in this are several state and federal agencies, each with its own particular need. Frequently, one agency in its activities fails to consider the needs or problems of other agencies. It is through such a society as this that mutual understanding can be brought about.

Recent publications dealing with the biological aspects of stream pollution have referred almost exclusively to the animal life in streams. A notable exception is the work of Fjordingstad (1950). Even this excellent publication is confined to the algae. A survey of the literature covering biological aspects of stream pollution reveals little information regarding the larger aquatic plants.

The following remarks are based on personal experience only. There is no experimental evidence supporting this, with one or two exceptions.

For the sake of this discussion the effects of pollution on aquatic vegetation will be divided into two groups — non-lethal and lethal.

NON-LETHAL EFFECTS

The most significant problem in this category is that of the fertilizing effect of domestic sewage, certain industrial wastes, commercial fertilizers and the like. Here are available not only compounds of nitrogen, phosphorus and potassium but, in the case of domestic sewage and certain industrial wastes, trace elements and growth promoting substances such as vitamin B-12.

The water hyacinth shows the effects of such discharge as does no other higher aquatic plant. Mats of hyacinths in which the individual plants were thirty inches high, with little devel-

opment of the root system, have been found in areas of enrichment with domestic sewage. When the receiving waters are not covered by mats of floating aquatic vegetation a rich bloom of unicellular algae usually develops. If this effect is produced in a lake there may be extensive kills of fish, production of offensive odors by the algae, an increase in production of blind mosquitoes or any combination of these manifestations.

Less clearly defined effects have been observed with regard to Bermuda-grass, alligator-weed, pickerel-weed, Salvinia and duckweed. The use of biological ponds for the removal of nutrients from domestic sewage and certain industrial wastes is being studied by the Florida State Board of Health at the present time.

Certain other effects which are more difficult to evaluate have been noted. The increased use of synthetic detergents in recent years and the fact that these detergents cannot be broken down by biological methods combine to produce extensive foaming if sufficient agitation occurs in the receiving stream. Where this foam covers growths of hyacinths there is a possibility than an inhibitory action affects plant growth. Frequently hyacinths thus affected are only three or four inches high and generally have a chlorotic appearance.

LETHAL EFFECTS

The most widely known and intentionally used lethal effects on aquatic vegetation are obtained with heavy metal ions, especially salts of copper and arsenic. Many of these heavy metals are toxic enough to kill virtually all plant and animal life in the receiving waters.

Petroleum products in general and heavy oils in particular are especially damaging to floating and emergent vegetation.

Kraft pulp mill effluent with its high hydrogen sulfide content will destroy not only vegetation in the stream but frequently trees along the edge of the stream.

Recently much publicity has been given to the deleterious effects of fluorides in connection with air pollution. Liquid wastes from one processing plant completely sterilized a section of a small river, with the exception of a single species of algae. The first visible effect of the waste in the stream in question was the rapid disappearance of a lush growth of Vallisneria.

Heat as a pollutant has only recently begun to receive the attention it deserves. An excellent study of the cooling water discharge from a generating plant and its effects on the Delaware River is approaching completion and should be available shortly. Preliminary information indicates that Elodea, Potamogeton and blue-green algae will tolerate water temperatures of slightly over 100°F. for at least brief periods.

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Submersed Weed Control With Aqualin* Herbicide

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July 9, 1962

In June, 1960, Southern Mill Creek Products Company, Inc., became a licensed applicator of the Aqualin herbicide process by Shell Chemical Company. There have been numerous studies and reports on Aqualin herbicide (active ingredient: acrolein) since it was first reported by van Overbeck, et al². We have evaluated the performance of Aqualin herbicide both on an experimental and commercial basis. Our main interest, of course, is in commercial applications.

There are basically two methods of applying Aqualin herbicide (1) flowing water, in which the Aqualin herbicide is added to the water at one or more points and is carried through the canal by the current, and (2) static water such as ponds, lakes and non-flowing canals. In static water, the Aqualin herbicide must be distributed throughout the body of water by moving the equipment.

In Florida, nearly all of our underwater weed control work has been in ponds, lakes and static ditches. We have not treated

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