or around surface waters may result in contamination of water supplies for various municipalities. Some of those cities in Florida which could be affected by weed control operations on nearby watersheds would be Tampa, Arcadia, West Palm Beach, Bradenton, and Melbourne, to mention but a few.

One of the effects of such chemicals, perhaps modified into other substances by treatment processes, for instance alum coagulation, may be the production of very unpleasant tastes and odors. These may be intensified by treatment with chlorine, which may chlorinate the molecule. The case with phenol in amounts greater than 0.001 mg/1 is well known among the water works profession; chlorine intensifies the odor of phenol in water very strongly, and it reacts similarly with many organic compounds.

To show the diversity of chemical types among the various herbicides, the following list, by no means exhaustive, is offered for your consideration: "CMU" is 3-para chloro phenol dimethyl urea, a phenol derivative of urea, chlorinated.

"2,4D" is 2,4 dichloro phenoxy acetic acid, a phenol derivative of acetic acid, chlorinated.

"dichlone" is 2,3 dichloronaphthoquinone, a chlorinated naphthoquinone, derived from napthalene.

copper sulfate ("bluestone") is an inorganic compound, used primarily as an algicide.

sodium arsenite (no common name) is also an inorganic compound, but used for submerged weeds (some are algae).

"PMA" is phenyl mercuric acetate, a phenol derivative containing complexed mercury (no ions).

aminotriazole is an alicyclic nitrogenous organic compound (no chlorine).

potassium cyanate is another inorganic compound, not closely related to cyanide in spite of similar name.

"Ferbam" is ferric dimethyl dithio carbamate, a thiourea derivative, usually an algicide.

The effects of the various herbicidal chemicals on the human physiology are largely unknown. Although in the dosages employed for weed control they may not be "poisonous" or result in the death of those drinking the water; they may on the other hand possibly interfere with enzyme action of one kind or another, or affect the central nervous system adversely, or perhaps produce other unpredictable and undesirable effects. Just feeding handfuls of any of the pesticides to laboratory animals and demonstrating a high L.D./50, does not prove them safe for man at low levels of intake.

Some house plants, notably hibiscus, altheas, hollyhocks and in general, the malvaceae, are sensitive to truly minute quantities of 2,4D. When a plane in Texas several years ago sprayed a field with this material and cotton was destroyed many miles away, it was calculated that no plant could have received more than microgram amounts of the weed killer, yet the entire crop was lost. It is possible for whole towns to be defoliated by the herbicides carried in the water supply, if care is not exercised to keep them out of that supply.

The detection and quantitative estimation of these exotic substances by the carbon chloroform extractables procedures is cumbersome, time-consuming and subject to errors and interferences. It would add a considerable burden to the operational load already imposed on those employed in treating surface water. This test consists of passing large measured volumes of pre-filtered or pre-strained water through beds of activated carbon, a typical volume being 1000 gallons, and, after drying, the extraction of the carbon material with chloroform, evaporation of the chloroform and the direct weighing of the chloroform — extracted residue. A suitable correction factor gives parts per million or parts per billion, depending on the quantity of material present.

There is a rough analogy here with bacteriological testing in that this indicates to a greater or less degree contamination by all exotic organic material. But carbon has a much greater affinity for some organic pollutants than for others. Chloroform, for instance, is not taken up during the extraction because its one carbon atom is modified in its effects by the presence of three big, inorganic chlorine atoms (plus one hydrogen). Carbon dioxide, with one carbon atom and two oxygen atoms, is considered inorganic by most chemists, it has so little in common with most other carbon compounds. So you see, the carbon chloroform extractables test, which is at present our most reliable procedure, is at best limited in its precision and accuracy.

Removal by treatment: Alum coagulation, because of the affinity of the aluminum hydroxide floc for organic materials, doubtless would remove a percentage but not all of suspended as well as dissolved organic herbicides. The arsenic-containing ones might not be stopped at all, but likely would pass through into the effluent. Nearly all arsenic compounds are soluble when we consider the parts per million range. The detective stories, as well as actual case histories, are full of chronic arsenic poisoning by accumulation of sublethal doses of this cumulative poison.

Activated carbon is credited with removal, more or less complete, of organic matter dissolved in water and responsible for natural tastes and odors. This holds good for most hydroxylated organic derivatives, even though some are highly complex. However, as noted above, when chlorine and some other elements enter the molecule, carbon has less affinity for the substance. We, therefore, should not depend on activated carbon to remove the typical herbicide, which contains, as a rule, chlorine and perhaps nitrogen and phosphorus or sulphur as well.

Breakpoint chlorination. While many organic substances can be "burned out' by breakpoint chlorination — and I'll spare you the details of the process because of limited time — not by any means all of them can be removed in this manner. Some which contain nitrogen (i.e. the triazines) will form highly stable complexes with active chlorine, and cannot be "burned out" at any reasonable dosage. So we cannot look to breakpoint chlorination with any degree of certainty for removal of herbicides.

In short, the herbicides in general may be considered as undesirable additives for potable water. The processes available in the best operated water treatment plants for surface water cannot be depended on to remove all kinds or all amounts of these chemicals. Let us, therefore, take pains to prevent their reaching potable water sources, and keep weed control sprays, as well as other pesticides, off our watersheds insofar as possible, understanding all the while that small local applications may be found necessary in isolated instances.

Dacamine: Oleoyl 1,3 Propylene Diamine Salts Of 2,4-D and 2,4,5-T

(An Oil-Soluble, Water-Emulsifiable Amine Salt of 2,4-D and 2,4,5-T)

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Water-soluble amine salts of 2,4-D and 2,4,5-T have been used for many years in brush control work because of their non-volatile nature. They have been recognized as being less effective than the oil-soluble, water-emulsifiable ester formulations. The erratic effectiveness of these amines has been partly attributed to the cutin and cutin waxes on the leaf surface, which are relatively impervious to penetration by the water-soluble amine sprays.

With the above facts in mind, it becomes obvious that the "ideal" product would combine both the advantages of esters and amines. In order to test the practicality of this hypothesis, several oil-soluble, water-emulsifiable amines were produced, screened, and field tested.

Initial laboratory studies were set up to test a series of long chain oil-soluble amines. Most of these amines were of a viscous nature, some very viscous. Preliminary screening results pointed to the use of the Duomeens. Since the physical handling of these materials would be of great significance, the oleoyl trimethylene diamine (Armour's trademark name is Duomeen-O) was selected. Another reason for the use of a diamine is that it contains two reactive sites and, therefore, one part of diamine will react and combine with 2 parts of 2,4-D acid.

At the present time the above-mentioned salts of 2,4-D and 2,4,5-T are being formulated as 2 pound concentrates; that is, 2 pounds acid equivalent per gallon of 2,4-D; 2,4,5-T; and 1 pound acid equivalent per gallon each of 2,4-D and 2,4,5-T (2 pounds total). There was no chemical reason for the production of the 2 pound concentrate since chemically they could be made up to contain approximately 4 pounds acid equivalent per gallon. However, due to the viscosity of this 4 pound material, especially at low temperatures (about 10 degrees Farenheit,) it was felt the handling of this material would be 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 eminating 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/l or 2 ug/l, respectively, chlorinated phenols impart objectionable "medicinal" tastes and odors to water[1].

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 previously[4].

In the laboratory, 1 and 3 mg/l 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[5]". The 2-4-DCP was determined by a 4-aminoantipyrine colorimetric procedure[2], the 2,4-D by a colorimetric method using chromotropic acid[3].

Threshold dilution values were calculated according to the data of Burttschell[1]. These values represent the dilution required by odor-free water for the odor or taste to be just detectable according to the "Standard Methods" test[5]. 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-feet), the amounts of phenol ranged from 8.4 to 539.3 ug/l. 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

2,4-Dichlorophenol Impurity in Formulations of 2,4-D

Type of formulation	2,4-DCP per gram of formulation		2,4-DCP ug/l (a)	Dilution values	
	% Ester	ug		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-feet).

(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/l of the phenol were observed after 148 and 218 days. Values of 9.5 and 16.7 ug/l 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

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