Preparation and Evaluation of Controlled-Release Formulations of 2,6-Dichlorobenzonitrile

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The herbicide dichlobenil (2,6-dichlorobenzonitrile) was incorporated in alginate- and carboxymethylcellulose (CMC)-based granules to obtain controlled-release (CR) properties. The effects of the addition of kaolin, an inexpensive filler, on release rate and granule yield were studied. Yield was increased more than 13-fold by the addition of 20% kaolin to the formulation. Release profiles were constructed for the release of dichlobenil from conventional (23-day release) and CR granules (>150-day release for some) into a reconstituted fresh water (pH 8). Barium-gelled alginate products gave slower release than calcium gelled, and the release from granules containing kaolin decreased as the kaolin concentration increased. An alginate product evaluated in a flowing-water apparatus containing hydrilla [*Hydrilla verticillata* (L.f.) Royle] propagules prevented regrowth during a 6-week test. Applied to container-grown ornamental plants in a 12-week test involving weedy grasses, alginate and CMC CR granules outperformed the conventional type in only a few cases. Because soil adsorption significantly narrowed the differences in release of free dichlobenil into soil leachate from conventional and CR formulations, the latter should be more effective in sandy or poorly adsorbent soils.

Dichlobenil (2,6-dichlorobenzonitrile) is a broad-spectrum herbicide that is effective for terrestrial and aquatic weed control. The pure compound has a water solubility of 18 ppmw at 20 °C and a relatively high vapor pressure (1.5 × 10⁻² mmHg at 50 °C) (Weed Science Society of America, 1983). Because of its volatility and risk of phytotoxicity in soil, together with the increased residence time that is generally sought for aquatic use, dichlorobenil is a good candidate for controlled-release (CR) formulations (Schacht et al., 1980; Steward, 1980; Steward et al., 1982).

Alginate gels have been used as matrices for the controlled release of chemical herbicides (Barrett, 1978; Barrett and Logan, 1982; Barrett and Murphy, 1982; Connick, 1983) including dichlobenil (Connick, 1982). A sustained release of fungus spores from mycoherbicides incorporated in alginate granules has been reported by Walker and Connick (1983). The use of an aqueous system at ambient temperature plus ease of incorporation of bioactive materials makes the alginate gel process for granule production useful for studying a variety of controlled-release applications. Like sodium alginate, aqueous solutions of sodium carboxymethylcellulose (CMC) can be gelled by certain metal cations (Fuji Photo Film Co., 1971), and the same basic process can be used with either polymer to make herbicide-containing granules that are biodegradable.

In this study we evaluated the effect on release rate and other properties caused by incorporating kaolin, an inexpensive filler, in the formulations. We also determined and compared the dichlobenil release characteristics of alginate and CMC granules in soil and water under laboratory conditions and relate the findings to aquatic and terrestrial weed bioassay results. Finally, we sought a better understanding of the adsorptive properties of soil on the release of dichlobenil from conventional and controlled-release formulations into water.

EXPERIMENTAL SECTION

The dichlobenil-containing products Casoron W-50 wettable powder (50% a.i.), Casoron G-10 granules (10% a.i.) used in aquatic weed control, and Casoron G-4 granules (4% a.i.) used for weed control in woody ornamentals were obtained from T H Agriculture and Nutrition Co. The sodium alginate was Keltex (Kelco Co.), an industrial-grade algin in granular form. The CMC was Cellulose Gum Type 7M (Hercules, Inc.), a medium viscosity polymer with a 0.7 degree of substitution. Kaolin, RC-32 grade (89% of particles are smaller than 2 μm), was obtained from Thiele Kaolin Co. in dry and slurry (70% clay solids) forms. Deionized water and reagent- or HPLC-grade chemicals were used. Percentages are expressed as weight percent or percent weight per volume.

The amount of dichlobenil in the alginate and CMC granules was calculated from the average of duplicate percent N analyses after a blank correction. Metal analysis was by atomic absorption, and microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Granule Preparation. *Alginate Process.* Formulations contained 0.5% or 1.0% by weight of sodium alginate, 0–20% kaolin solids (from the 70% kaolin slurry), and 0.3–4.0% Casoron W-50 (0.15–2.0% dichlobenil) made up in water (refer to Table I). To a mixture of water and kaolin were added the Casoron W-50 and sodium alginate while stirring with a propeller-type stirrer. The mixture was stirred about 45 min or until all of the sodium alginate had dissolved. The pH of these moderately viscous formulations was 6.4–6.8.

By use of the apparatus described by Connick (1982), which is assembled from common laboratory glassware and is useful for small-scale processing, the mixture was added dropwise over a 5-min period to a 300-mL gellant bath of 0.25 M CaCl₂ or 0.25 M BaCl₂·2H₂O. In the 5-min period, about 92 g of formulation for samples 1, 2, and 7 and about 53 g for samples 3–6 had been added. A 1-min additional residence time in the gellant was allowed before filtering through a 600-mL coarse-frit Büchner funnel to isolate the gel beads that had formed when droplets of formulation contacted the gellant solution. This batchwise method was continued until the desired amount of formulation had been processed. The gellant solution was recovered from

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Table I. Alginate and CMC Granules Containing Dichlobenil

sample	formulation					product								
	Na alg. or CMC, %	kaolin solids, %	dichlo-benil,[a] %	metal gellant	wt processed, g	dry wt, g	concn factor[b]	yield[c]	a.i., %[d]	alg. or CMC,[e] %	kaolin,[e] %	metal[f] gellant, %	size,[g] sieve no.	granule av wt, mg
alginate														
1	1.0	0	0.15	Ca	1541	30.7	50.2	2.0	6.8	50.2	0	9.6	14-25	0.7
2	1.0	0	0.15	Ba	1395	34.3	40.7	2.5	6.0	40.7	0	28.9	14-20	0.8
3	1.0	10	1.00	Ca	1620	233.6	6.9	14.4	6.7	6.9	69	2.1	12-14	4.1
4	1.0	10	1.00	Ba	1659	245.1	6.8	14.8	6.5	6.8	68	5.7	10-14	5.0
5	1.0	20	2.00	Ca	1420	375.5	3.8	26.4	7.0	3.8	76	1.4	8-12	8.9
6	1.0	20	2.00	Ba	1350	362.8	3.7	26.9	7.1	3.7	74	4.0	8-12	8.5
7	0.5	20	2.00	Ca	1591	423.0	3.8	26.6	7.2	1.9	76	1.4	10-12	8.7
carboxy-methyl-cellulose														
8	1.0	0	0.16	Al	1617	30.2	53.5	1.9	7.2	53.5	0		12-18	
9	2.0	0	0.16	Al	1493	45.2	33.0	3.0	5.0	66.0	0		16-20	1.0
10	1.0	10	1.00	Al	1576	215.4	7.3	13.7	7.4	7.3	73		12-14	4.8
11	2.0	10	1.00	Al	1451	213.0	6.8	14.7	7.4	13.6	68		12-14	5.0
12	1.0	20	2.00	Al	741	195.1	3.8	26.3	6.5	3.8	76		10-12	8.0

[a] Using Casoron W-50 (50% a.i.) wettable powder. [b] Concentration factor = weight of formulation processed/weight of dry product. [c] Weight of dry product × 100/weight of formulation processed. [d] Calculated from % N analyses (average of two) less blank. [e] Approximated: concentration factor × formulation concentration. [f] By atomic adsorption. [g] Held on screen sizes (U.S. standard sieve numbers) listed; blended; discarded others.

the filter funnel and was reused once before being discarded.

The gel beads were placed in a jar, and after 1 day, the water that had collected due to gel syneresis was discarded and the beads were spread on aluminum foil to air-dry for 3–5 days. Drying was facilitated by the use of a fan to circulate the air and by the periodic redistribution of the beads on the foil. Rolling the beads occasionally with the hand as they dried reduced aggregation. Dried beads (granules) were sieved and minor fractions were discarded after weighing. An apparatus suitable for large-scale production of granules has been described by Walker and Connick (1983).

CMC Process. Formulations contained 1% or 2% by weight of CMC, 0–20% kaolin (dry), and 0.32–4.00% Casoron W-50 (0.16–2.00% dichlobenil) made up in water (refer to Table I). The same apparatus and the same process that were used to make the alginate granules were used to make the CMC granules except that the gellant solution was 0.125 M $Al_2(SO_4)_3 \cdot 18H_2O$, adjusted to pH 3.0–3.2 with 50% NaOH. Kaolin in powdered form was used because the slurry gelled the CMC mixture. The pH of these moderately viscous formulations was 5–7. Unlike alginate beads, the freshly prepared CMC gel beads were fragile until dry.

HPLC Analytical Procedures. Dichlobenil was determined in aqueous samples in the static tests by the direct, reverse-phase method of Connick and Simoneaux (1982) using a C_{18} column, 50% CH_3CN–50% H_2O mobile phase, and ultraviolet (UV) detection at 280 nm. In the flowing-water apparatus, chromatographic conditions using a C_{18} column were 50% CH_3CN–49% H_2O–1% HOAc mobile-phase at 2.1 mL/min, (2,4-dichlorophenoxy)acetic acid internal standard, and UV detection at 238 nm. Soil leachates were analyzed for dichlobenil and 2,6-dichlorobenzamide, without prior extraction or concentration, by the method of Connick and Bradow (1984) using a radial compression C_{18} column, 50% CH_3CN–50% H_2O mobile phase, and UV detection at 205 nm.

Aquatic Experiments. *Static Tests To Determine Release Profiles.* Dichlobenil-containing alginate and CMC granules (Table I, samples 1–12) and Casoron G-10 were added to 1 L of a reconstituted fresh water (RFW) in 1-L Erlenmeyer screw-cap flasks. RFW is a hard water

(pH 8) prepared (Marking and Dawson, 1973) by adding 192 mg of $NaHCO_3$, 120 mg of $CaSO_4 \cdot 2H_2O$, 120 mg of $MgSO_4$ and 8 mg of KCl to 1 L of deionized water. Samples were run in duplicate and the results were averaged. Each flask mouth was covered with aluminum foil pierced to permit, after cap removal, sampling with a disposable Pasteur-type pipet. This arrangement minimized loss of dichlobenil vapors. Samples were weighed to 0.1 mg such that a total of 12.1–12.7 mg (ppm) of dichlobenil was available for release in each flask. Flasks were shaken once each week and before each sampling. Aliquots of about 1 mL were removed for determination of dichlobenil by HPLC after which unused sample portions were returned to the flasks. The temperature for the duration of the experiment was 24 ± 3 °C. At the conclusion of the study, granules were removed from each flask and extracted (3 × 100 mL) with 50% CH_3CN–50% H_2O at 60 °C for 7 h. Extracts were analyzed to determine the amount of dichlobenil that had remained incorporated in the granules. Release data were normalized at 100% based on the highest amount of dichlobenil released plus the amount extracted, if any, at the end of the experiment. Total recovery of dichlobenil from all the samples averaged 99.7%.

Flowing-Water Apparatus and Bioassay of Hydrilla Propagules. Natural pond water was continuously pumped from a 10-gal reservoir aquarium into 19-L glass culture jars by using two multichannel pumps. Jars with plants and soil contained 17.8 L of water or 18.9 L without plants and soil. The soil was a mixture of 10% (v/v) composted cattle manure added to 90% sandy loam (60% sand, 26% silt, 14% clay). Water flow was adjusted so that one complete exchange occurred once every 24 h. Alginate-based sample 6 (Table I) was added to the jars at various treatment levels. Dichlobenil concentration in the jars was determined at 1, 3, 4, and 6 weeks posttreatment by reverse-phase HPLC. A control with plants, but without dichlobenil, was included, and no interfering peaks were observed for the duration of the experiment.

Hydrilla [*Hydrilla verticillata* (L.f.) Royle] regrowth from tubers and rootstock was investigated under different dichlobenil concentrations provided by the alginate controlled-release granules. Tubers were pregerminated in distilled water. Four uniformly germinating tubers 3–6 cm

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long were planted in each of three 250-mL beakers. Three beakers were placed in each glass culture jar, and there were four replicates per treatment level. The temperature was maintained at 28 ± 2 °C. Light conditions were 14-h days of 150 μEinsteins m^{-2} s^{-1} from a combination of fluorescent and incandescent lamps. Rootstock was handled in a similar manner. Hydrilla apical plant sections were established in 250-mL beakers for 2 months before use. The above-ground vegetation was clipped, and regrowth was observed under different treatment levels of dichlobenil. The experiments were terminated at 6 weeks posttreatment, at which time the plants were removed and regrowth was measured.

Terrestrial Experiments. *Soil Leachate Tests.* Alginate and CMC controlled-released granules (Table I, samples 5 and 12) and Casoron G-4 granules were placed in soil and watered on a regular schedule, and the leachates were analyzed for dichlobenil and 2,6-dichlorobenzamide, its degradation product in soil (Verloop, 1972). One of the soils used was a pine bark mixture (PBM), pH 4, consisting of 80% (v/v) crushed pine bark, 10% sandy loam, and 10% sand. The other soil was purified (washed and ignited) sand, pH 6.1.

The individual soils were added to a depth of 3.0 cm in 150-mL Büchner-type filter funnels (65-mm diameter) with coarse glass frits. The funnels were inserted through one-hole rubber stoppers into 250-mL filter flasks. Deionized water (pH 6.8) was added to soil capacity, and then 200 mL more was added, filtered, and discarded. Each sample of dichlobenil-containing granules was incorporated in the top 1 cm of soil. The dichlobenil was applied at 2.6 times the normally recommended rate of 6 lb/acre of a.i. (5.9 mg of a.i./funnel), which corresponded to an average of 83.4 mg of alginate granules (9 each), 91.3 mg of CMC granules (11 each), and 147.8 mg of Casoron G-4 under the test conditions. The funnels were covered lightly with aluminum foil to reduce the loss of dichlobenil vapors. The experiments were done in duplicate at a temperature of 24 ± 3 °C. Controls were run simultaneously and consisted of the soils without herbicides.

Each Tuesday and Friday, 90 mL of deionized water was added to each funnel and allowed to filter overnight by gravity. Application of vacuum was occasionally needed to complete the PBM filtration. The leachate (filtrate) was transferred to a 100-mL volumetric flask and diluted to the mark. The sand leachates were analyzed directly, but the cloudy PBM leachates were centrifuged 20 min at 1100 g (average) before HPLC analysis. Periodic analysis of the leachates from the PBM and sand controls showed no interfering peaks in the chromatograms. The twice-weekly watering and leachate analysis was changed at 84 days to a biweekly schedule until the experiment was terminated at 210 days. The soils were then extracted with acetonitrile at room temperature to remove any remaining dichlobenil and 2,6-dichlorobenzamide. An average of 86% dichlobenil equiv was accounted for; the remainder was presumed lost by volatilization.

Soil Adsorption Coefficients. To a 125-mL Erlenmeyer flask was added 4.0 g of air-dried PBM and 50.0 mL of a 2.0 ppm (w/v) dichlobenil and 2,6-dichlorobenamide solution. After 24 h on a wrist-action shaker at 25 °C, the aqueous phase was analyzed for each compound by HPLC. The adsorption coefficient, K, is expressed as the ratio of μg/g compound on the soil to mg/mL in the water. A 20.0 g-portion of sand was treated the same way. Adsorption coefficients were also determined for the PBM and sand that were used as controls in the soil leachate experiment. Results are reported as the average of two determinations.
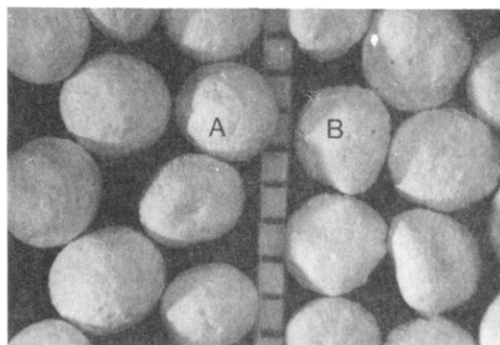

Figure 1. Alginate (A) and CMC (B) granules (Table I, samples 5 and 12) containing dichlobenil shown with a millimeter scale.

Application of Granules to Container-Grown Plants. Two plants each per replication, four replications, of gold coast juniper (*Juniperus chinensis* "Gold Coast") and dwarf burford holly (*Ilex cornuta* "Dwarf Burford") were potted in 1-gal plastic nursery containers by using the PBM soil described above. Each cubic yard of the soil mixture was fertilized with 8 lb of dolomite lime, 8 lb of Osmocote (18–6–12), 3 lb of superphosphate (20%), and 2 oz of Peters 503 trace elements. All containers were overseeded with a mixture of common purslane (*Portulaca oleracea*), broadleaf signalgrass (*Brachiaria platyphylla*), goosegrass (*Eleusine indica*), and large crabgrass (*Digitaria sanguinalis*) and then cultivated lightly to incorporate the weed seeds before herbicide application. On May 24, 1982, at Hammond, LA, alginate and CMC controlled-release (Table I, samples 3, 5, 10, and 12) and conventional granules (Casoron G-4) were hand-shaken from a small paper bag onto the four containers of each replication placed in a marked-off 3 ft × 3 ft area. Application rates were 6 and 10 lb/acre dichlobenil and a mixed rate of 6 lb of a.i. of CR granules plus 4 lb of a.i. of G-4. The 29 in. of rain was supplemented by overhead irrigation, as needed (almost daily in the hot summer months). Weed control ratings were taken at 4, 7, and 12 weeks.

RESULTS AND DISCUSSION

Granule preparation with sodium alginate formulations was carried out using calcium and barium ions from their chloride salts as gellants in order to further study gellant-related differences in release rates (Connick, 1982). CMC solutions were gelled by aluminum ions from solutions of $Al_2(SO_4)_3$. The CMC gel beads that formed were brittle and fragile, unlike the relatively tough alginate gel beads. However, drying transformed the CMC gel beads into hard granules very similar to the alginate granules (Figure 1). The granules made by the gel process have dichlobenil incorporated uniformly throughout an alginate or a CMC matrix. This is different from the usual encapsulation that produces a distinct wall around a core containing the active material.

The addition of kaolin to the alginate and CMC formulations led to larger and heavier granules that were more spherical and dried with less aggregation. It is evident from the data in Table I that the inexpensive kaolin effectively increased granule yields and reduced the amount of the more expensive gums in the final products. For example, sample 1, which was formulated without kaolin, contained an estimated 50.2% alginate while sample 5, which was made with 20% kaolin in the initial mixture, contained only about 3.8% alginate. Product yield was increased from 2.0% to 26.4%. Weight loss during drying concentrates the ingredients in the granules by an amount that is proportional to the water loss. In order for samples
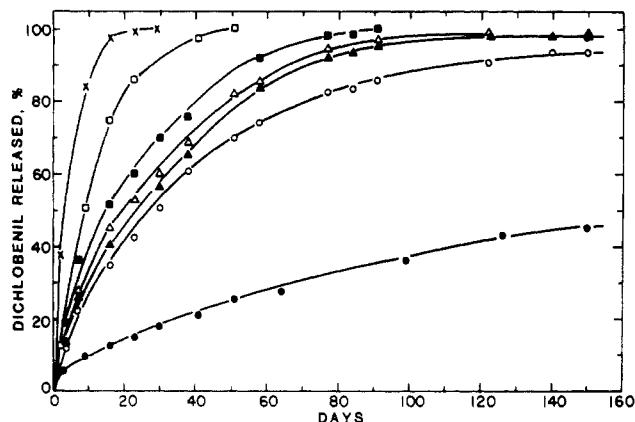
Figure 2. Dichlobenil release profiles of a conventional and alginate CR granules in a reconstituted fresh water. Samples numbers refer to Table I, and percentages refer to the initial formulation and not to the final product. (×) Casoron G-10, conventional; (□) sample 1, 0% kaolin, Ca; (■) sample 3, 10% kaolin, Ca; (△) sample 5, 20% kaolin, Ca; (▲) sample 4, 10% kaolin, Ba; (○) sample 6, 20% kaolin, Ba; (●) sample 2, 0% kaolin, Ba.

Figure 3. Dichlobenil release profiles of CMC CR granules in a reconstituted fresh water. Sample numbers refer to Table I, and percentages refer to the initial formulation and not to the final product. (□) sample 11, 2% CMC, 10% kaolin; (△) sample 10, 1% CMC, 10% kaolin; (▲) sample 9, 2% CMC, 0% kaolin; (○) sample 12, 1% CMC, 20% kaolin; (●) sample 8, 1% CMC, 0% kaolin. See Figure 2 for the release profile of conventional granules.

to contain 5–8% a.i., a reasonable compromise for aquatic and terrestrial application, the amount of dichlobenil added to the formulations varied and was determined by preliminary experiments. The calcium and barium content of the alginate samples mainly reflected their atomic weight and not their reactivity differences. Aluminum pickup by CMC from the gellant solution was not determined because aluminum was already present in kaolin.

Aquatic Experiments: Static. Dichlobenil release profiles that were obtained with alginate samples 1–6 and the commercial 10% a.i. granules placed in RFW, an artificial pond water, are shown in Figure 2. The commercial granules released essentially all the dichlobenil by 23 days. The Ca^{2+}-gelled alginate granules released in the order 0% kaolin (51 days) > 10% kaolin (91 days) > 20% kaolin (122 days). Sample 7, not shown in the figure, which was made with 20% kaolin and 0.5% sodium alginate, released at about the same rate as its 1% sodium alginate counterpart (sample 5), showing that the sodium alginate concentration is not a significant factor at these levels. Because the viscosity increase makes processing very difficult, 20% kaolin is near the maximum that can be used with 1% of a medium-viscosity sodium alginate.

The Ba^{2+}-gelled alginate granules gave slower release of dichlobenil than the Ca^{2+}-gelled granules, with and without kaolin filler, under the test conditions. The order of release was 10% kaolin (122 days) > 20% kaolin (>150 days) >> 0% kaolin (>>150 days). Release from the alginate granules is nonlinear; a high initial release rate diminishes with time. However, sample 2 (Ba^{2+} gelled, 0% kaolin) approximates a linear or zero-order release throughout the 150-day duration of the experiment. A linear or constant release is often considered the most desirable type, but this may not necessarily be the case for all weed control problems. For some situations a "burst" of herbicide release soon after application may be more effective.

Release profiles obtained with the CMC granules (samples 8–12) are shown in Figure 3. They are nonlinear and show a high initial release that slows with time. Granules made from 1% CMC formulations gave the same relative order to dichlobenil release that was observed with the alginate–Ba^{2+} samples: 10% kaolin (51 days) > 20% kaolin 57 days) >> 0% kaolin (101 days). When 2% CMC was used, this order was also followed, but release rates were faster than for the 1% CMC samples. Formulations
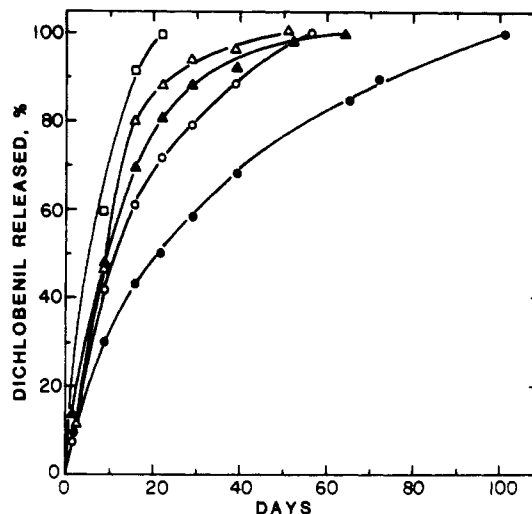
containing 1% CMC–20% kaolin and 2% CMC–10% kaolin are near the maximum viscosity for processing through the laboratory apparatus.

It is fortunate and desirable that, for alginate and CMC granules containing kaolin, the sustained release becomes longer as the kaolin concentration is increased. Kaolin-filled alginate–Ca^{2+} or –Ba^{2+} granules gave slower release than the CMC–Al^{3+} samples, but even the latter gave slower release than the commercial granules. Any comparison of release profiles is an approximation because differences in size and shape of granules can affect release properties. Dichlobenil release from alginate granules occurs mainly by a diffusion or leaching mechanism. All the alginate granules were intact at the conclusion of the experiment. For the CMC granules there is, in addition to leaching, a disintegration of the kaolin-filled granules in RFW that increases release rates. Inorganic fillers other than kaolin, as well as organic fillers, should be considered for alginate and CMC granules and may give different release profiles.

Aquatic Bioassay Experiments: Dynamic. Aquatic weed control using controlled-release herbicide formulations will probably be accomplished most effectively by using the CR material to prevent regrowth of the target weed after applying a conventional formulation to get an initial kill. Alginate-based sample 6, which gave an average release of 0.45 mg of dichlobenil (g of granules)$^{-1}$ day^{-1} over the 150-day static experiment, was chosen for evaluation in the flowing-water apparatus because it was a good compromise between slow release and a practical formulation. Sample 2 had given the slowest and most linear release profile but, without kaolin filler, was much less practical. Table II shows that, with plants present, treatment rates were 1.58–15.79 mg/L dichlobenil available for release into the system. Without plants, the rate was 14.88 mg/L.

Prior experience had shown that a 0.05 ppm dichlobenil concentration is near the threshold level to prevent regrowth of hydrilla from propagules. The measured dichlobenil concentrations at 6 weeks showed that treatment A was well below the threshold, B only slightly below, and C and D were above this level. However, even A main-

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Table II. Release of Dichlobenil from Alginate Granules in Flowing Natural Water

treatment	dichlobenil[a] available, mg/L	wt of granules, g	dichlobenil concn, mg/L[b] at weeks posttreatment[c]				dichlobenil released from granules, mg/g at weeks posttreatment			
			1	3	4	6	1	3	4	6
with plants										
A	1.58	0.3973	0.07 ± 0.00	0.04 ± 0.01	0.03 ± 0.01	0.01 ± 0.00	3.14 ± 0.00	1.79 ± 0.45	1.34 ± 0.45	0.45 ± 0.00
B	3.96	0.9911	0.16 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.04 ± 0.02	2.87 ± 0.18	2.16 ± 0.18	1.44 ± 0.18	0.72 ± 0.36
C	7.91	1.9837	0.32 ± 0.05	0.22 ± 0.02	0.22 ± 0.08	0.06 ± 0.01	2.87 ± 0.45	1.97 ± 0.18	1.97 ± 0.72	0.54 ± 0.09
D	15.79	3.9582	0.52 ± 0.10	0.41 ± 0.01	0.21 ± 0.01	0.11 ± 0.01	2.34 ± 0.45	1.84 ± 0.05	0.95 ± 0.05	0.49 ± 0.05
without plants										
E	14.88	3.9608	0.39 ± 0.11	0.34 ± 0.02	0.23 ± 0.03	0.13 ± 0.08	1.86 ± 0.52	1.62 ± 0.10	1.10 ± 0.14	0.62 ± 0.38

[a] Sample 6, Table I; 7.1% dichlobenil. [b] Means of four replicates ± standard deviation. [c] Sampled on days 7, 21, etc.

Table III. Effect of Dichlobenil Released from Alginate Granules on Hydrilla Regrowth from Tubers and Rootstock after 6 Weeks in Flowing Water

dichlobenil treatment[a]	regrowth from tubers[b]			regrowth from rootstock[b]		
	shoot length, cm	shoot weight, g	root weight, g	shoot length, cm	shoot weight, g	root weight, g
A	18 b[b]	0.20 b	0.024 b	17 b	0.176 b	0.036 b
B	5 c	0.06 c	0.004 c	5 c	0.156 b	0.024 c
C	4 c	0.03 c	0.003 c	4 c	0.129 b	0.030 bc
D	5 c	0.04 c	0.002 c	6 c	0.178 b	0.034 bc
control[c]	50 a	1.44 a	0.188 a	38 a	0.440 a	0.087 a

[a] Refer to Table II. [b] Values in a column followed by the same letter are not significantly different at $P = 0.05$ as determined by the Waller–Duncan Test (Waller and Duncan, 1969). Each value is the mean of four replicates. [c] Plant control without dichlobenil.

tained an effective concentration for 1–3 weeks. In the jars without plants, release was slower than treatment D until week 4 when the values became nearly the same.

Two types of hydrilla regrowth, from tubers and from rootstock, were studied at different concentrations of dichlobenil in the flowing water. The data of Table III for regrowth from tubers measured at the conclusion of the 6-week test show that treatment A (1.58 mg/L available) reduced substantially but did not prevent regrowth. All the higher treatment levels were almost equally effective in preventing regrowth from tubers. These findings are consistent with the dichlobenil concentration data of Table II and the 0.05-ppm threshold concentration. With rootstock, there was some increase in shoot length in treatment A, but the shoot and root weight data are about the same for all treatment levels and show that regrowth from these propagules was substantially reduced compared with the control. It is evident that the alginate–dichlobenil granules can effectively prevent regrowth of hydrilla over an extended time period.

Soil Adsorption and Leachate Tests. The sand and pine bark mixture soils were tested for their ability to adsorb dichlobenil and its amide degradation product when both are present together in water in competition for adsorption sites. The adsorption coefficients, K (Table IV), showed that dichlobenil was strongly adsorbed on PBM, not only when the soil was in its initial state but also after it had been leached with water periodically over a 210-day period. This indicates that the soil components responsible for the adsorption were not removed to any great extent by leaching and/or degradation over this time. The 2,6-dichlorobenzamide was adsorbed by PBM less than dichlobenil by more than an order of magnitude. Although dichlobenil had a greater affinity for pure sand, neither compound was appreciably adsorbed by it. Verloop (1972) and Rolland and Frissel (1975) reported that K values for dichlobenil and the amide, respectively, were linear over

Table IV. Adsorption Coefficients of Dichlobenil and 2,6-Dichlorobenzamide When Present Together in Water[a]

soil	K[b]	
	dichlobenil	2,6-dichloro-benzamide
PBM (fresh)	148	11
PBM (leached)[c]	130	10
sand (fresh)	0.13	0.05
sand (leached)[c]	0.12	0.05

[a] Determined at 25 °C by using a 2-ppm solution of dichlobenil and 2,6-dichlorobenzamide in water. [b] $K = \mu g/g$ on soil/$\mu g/mL$ in water. [c] Leached with water twice per week over a 210-day period.
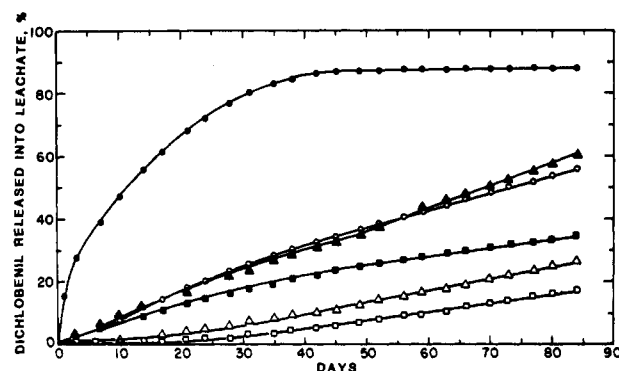

Figure 4. Dichlobenil in soil leachate: release profiles of conventional and alginate and CMC CR granules (Table I, samples 5 and 12). (●) Casoron G-4 in sand; (▲) CMC in sand; (O) alginate in sand; (■) Casoron G-4 in PBM; (△) CMC in PBM; (□) alginate in PBM.

a wide range of initial concentrations.

The dichlobenil release profiles constructed from leachate analyses of soils containing alginate, CMC, and conventional granules (4% a.i.) are shown in Figure 4. In sand, the conventional granules rapidly released dichlobenil into the leachate for 49 days, after which there was no significant increase. This is in striking contrast to the much slower and almost linear release from the alginate and CMC granules in sand.

The PBM soil exerts a pronounced effect on the leachate release profile of the conventional granules. Instead of the rapid release noted in sand, there was a slow linear release in PBM out to the 84-day conclusion of the test. The alginate CR granules released slower than the CMC granules and both released slower, as expected, than the conventional granules. However, it is very important to note that the magnitude of the difference in release of dichlobenil into the leachate between the standard and CR granules in PBM was much less than it was in sand. Because of the strong adsorption of dichlobenil on PBM, there is a double control over its release as a free compound into water. First it is released from the granules, and then
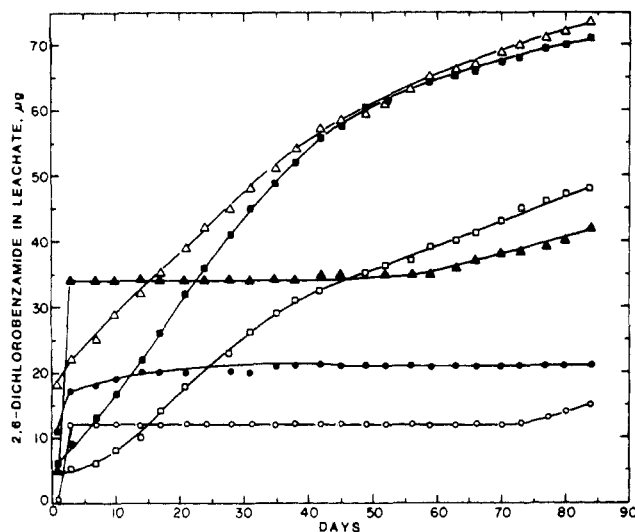
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Figure 5. 2,6-Dichlorobenzamide in soil leachate: release profiles of conventional and alginate and CMC CR granules (Table I, samples 5 and 12). (●) Casoron G-4 in sand; (▲) CMC in sand; (○) alginate in sand; (■) Casoron G-4 in PBM; (△) CMC in PBM; (□) alginate in PBM.

it must be released from the PBM soil. The net effect is one of a leveling of release rates between different types of formulations. Because of this, controlled release does not seem to be as useful or desirable in a soil that strongly adsorbs the herbicide, as it might be in a sandy soil.

Release profiles for 2,6-dichlorobenzamide in soil leachate are shown in Figure 5. It was determined in separate experiments in water that the total amount of amide released from each of the samples in sand was present initially in the granules. It originated as a trace impurity in the conventional granules and in two different lots of the wettable powder formulation used to make the alginate and CMC granules. In the PBM soil environment, the amide was released, as well as formed continuously, from dichlobenil. However, the total amount of amide involved was very small and, under the experimental conditions, did not significantly affect the dichlobenil concentrations.

Alginate granules were found to be intact in both soils at the conclusion of the leachate experiment. Most of the CMC granules had partially disintegrated by this time.

Weed Control in Container-Grown Plants. The weed control data on grasses reported in Table V are mainly for goosegrass and large crabgrass because broadleaf signalgrass germination was poorer than expected. The broad-leafed weed, common purslane, did not germinate enough to be rated accurately.

Granules were applied at 6 and 10 lb/acre a.i. and in a 10 lb/acre combined treatment consisting of CR granules at 6 lb and conventional granules at 4 lb. The combination treatment was applied to see if the conventional granules would provide a faster release to prevent initial weed establishement and if the CR granules would give long-term control. Because it had the lowest percent a.i., the G-4 conventional granules had the best coverage on the soil. At the 6-lb rate, G-4 gave the best weed control throughout the test. This may be due to its faster release and the greater amount of a.i. available at any given time. At 10 lb, G-4 was best through 7 weeks but weed control suddenly dropped at 12 weeks below that of CMC sample 12, which maintained its effectiveness throughout. The combination treatment was better at 12 weeks for alginate sample 3 and CMC sample 10 than for G-4 at 10 lb. Lack of incorporation of granules in the soil, which is not commercially practical in container-grown plants, and high

Table V. Weed Control by Alginate, CMC, and Conventional Granules Applied to Container-Grown Ornamental Plants

sample[a]	kaolin,[b] %	appl. rate, a.i., lb/acre	weed control[c] at weeks		
			4	7	12
alginate CR granules					
3	10	6	7.75	8.50	6.50
3	10	10	7.75	7.75	5.25
3 + G-4[d]	10	6 + 4	9.25	8.50	8.50
5	20	6	6.25	5.75	4.50
5	20	10	8.00	7.75	7.00
5 + G-4	20	6 + 4	10.00	9.50	6.50
CMC CR granules					
10	10	6	7.50	6.75	4.75
10	10	10	7.75	7.50	6.75
10 + G-4	10	6 + 4	9.50	9.25	8.50
12	20	6	6.50	7.00	7.00
12	20	10	8.75	9.00	9.00
12 + G-4	20	6 + 4	9.25	9.00	7.75
conventional granules					
G-4		6	9.00	9.00	8.25
G-4		10	10.00	9.75	7.75
untreated check			4.00	2.50	6.00

[a] Refer to Table I. [b] Present in original formulation, not final product. [c] Weed control of grasses, average of four replications: 10 = complete control; 0 = no control. [d] A combined treatment including Casoron G-4 at 4 lb/acre a.i.

temperatures decreased the effectiveness of the volatile dichlobenil. Entrapment in alginate and CMC matrices reduces, but does not stop, the rate of dichlobenil loss by volatilization. The lack of a clear advantage in weed control for the CR materials, especially at 12 weeks, demonstrates also the leveling effect of the adsorptive PBM soil on the different dichlobenil formulations as discussed in the leachate experiments.

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