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Date Out EFB: APR 3 1979

To: Product Manager Costillo (32)
TS-767

Through: Dr. Gunter Zweig, Chief
Environmental Fate Branch

From: Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 10182-19

Chemical: poly(hexamethylene biguanide hydrochloride)

Type Product: Algacide

Product Name: Baquacil

Company Name: ICI

Submission Purpose: Resubmission with data. Swimming pool use

ZBB Code: Sec. 3

Date in: 11/20/78

Date Completed: 3/29/79

Deferrals To:

☐ Ecological Effects Branch

☐ Residue Chemistry Branch

☐ Toxicology Branch

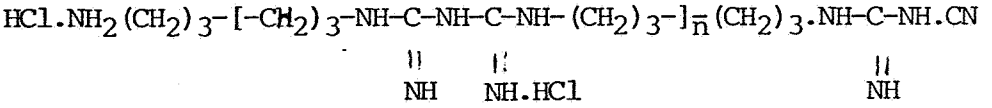
1.0 Introduction

1.1 New Chemical

1.2 Poly(hexamethylene biguanide hydrochloride)
liquid formulation
20% active ingredient

1.3 Other names PHMB, polyhexamethylene biguanide, Vantocil IB, Baquacil SB, Cosmoquil CQ

1.4 Structure



1.5 Physical and Chemical properties

Color colorless

Molecular Formula:

$C_8H_{18}N_5Cl(C_8H_{18}N_5Cl)_n$ (n average 4.5 to 6.5)

Molecular Weight $(219.7)_n$

Total solids 19-21% at 105°C

pH 5.0 - 5.5

Mol. weight 1,000-1400

Biguanide content 0.90

UV ratio (10nm cell) 1.2 - 1.6
237/222 nm

1.6 For use in swimming pools

2.0 Directions for Use

To control microorganisms in pool water, adjust pH to 7.0 - 8.0 and add Baquacil at 50 ppm level (10 ppm active). Frequency of additional doses of Baquacil will depend on pool load and organic debris.

To overwinter pool: adjust the Baquacil level to 50 ppm and top it up every several months as indicated.

2.1 Disposal

In case of leak or spill, soak up with absorbent, such as sand, earth or sawdust and shovel into waste container. Remove waste to chemical waste area and dispose of in accordance with local pollution regulations. (Any unused material should be returned to manufacturer.)

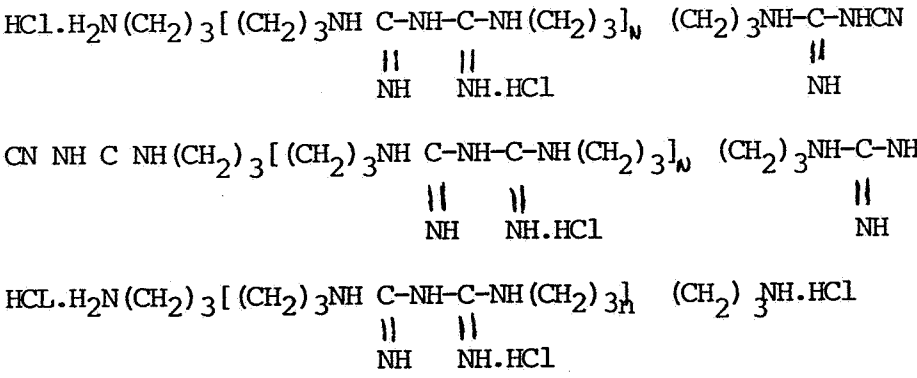
Do not reuse empty container. Triple rinse residue from empty container and add to dilution mixture for swimming pool. Dispose of container in sanitary landfill.

3.0 Discussion of Data

The following Environmental Chemistry data has been submitted. Acc. # 234289 Vol. 6 of 7 Section C Appendix nos. C-24 to C-27.

Appendix C-24	Sewage Treatment Studies	Page 937
Appendix C-25	Adsorption to Soil and Leaching	Page 968
Appendix C-26	Degradation in Soil	Page 1027
Appendix C-27	Photodegradation in Water	Page 1055

Note: PHMB is a mixture of three different molecules



This chemcial does contain trace metals and are listed below:

1. Iron 4 ppm
2. Lead 1 ppm
3. Chromium 6 ppm
4. Zinc 320 ppm
5. Mercury less than 0.05 ppm
6. Arsenic less than 0.05 ppm
7. Cadmium less than 0.05 ppm

3.1 Physico-chemical
Hydrolysis

3.1.1 No hydrolysis study was submitted per se in this submission. From Vol. 6 of 7 Acc. # 234259 Tab C-27 Report No. TMJ 1163B entitled, Preliminary study of the photodegradation in water, a pertinent set of data was found. ^{14}C-Baquacil (adiponitrile group) was placed into deionized water at pH values of 5,7, and 9. Samples were kept in the dark and incubated at room temperature for 20 days. Samples were taken at 0, 1, 4, 14 and 20 days and analyzed for Baquacil. Results indicated that after 20 days a 9% reduction occurred at pH 9, a 16% reduction occurred at pH 5 and a 22% reduction occurred at pH 7. By using regression analysis, corresponding half-lives can be calcualted for pH 5, 7, and 9 and are 32, 28, and 59 days respectively. Since at 20 days between 10-22% degreation occurred, the identity of the potential degradates should be identified (EFB can estimate two potential hydrolysis products: 1. hexamethylene diamine 2. reaction with cyano end group to give guanyl urea.

Conclusions

Since the amount of chemical degradated in water was greater than 10% of applied material, and is important to aquatic treatment, this data can not substitute for a hydrolysis study and one will have to be submitted to determine the fate of this chemical in the environment.

3.1.2 Physico-chemical
Photolysis (in aqueous solution)

Acc. # 234289 Vol. 6 of 7 Section C Appendix No. C-27 page 1055. Preliminary study of the photodegradation in water of Baquacil. J.P Leahey, R.E. Griggs, H.E. Hughes. Report No. TMJ-1163B.

3.1.3 Materials

^{14}C-Baquacil (labeled in the hexamethylene diamine hydrochloride moiety) and non-labeled Baquacil was placed in solutions of deionized water at 10.4 ug/g and then adjusted to different pHs by the addition of HCl and/or NaOH. The solutions were placed into crystallizing dishes and covered with polythene that was perforated. The dishes were stored in glasshouses and exposed to artificial light (flourescen and/or mercury lamp) and natural sunlight. Controls were kept in the dark. Supplemental studies were carried out with river water adjusted to pH values of 7.0 - 8.0 and exposed

to artificial (flourescent) and natural sunlight. Controls were kept in the dark. The degradation of Baquacil was further monitored by the addition of Baquacil to tap water and exposed to mercury vapor lamp filetered through pyrex glass.

3.1.4 Methods

The concentration of Baquacil was determined by spectrophotometry and LCS. Solutions that showed degradation were chromatographed on silica gel TLC plates.

3.1.5 Results

Concentration of Baquacil in the solutions kept in artificial light. (Flourescent light.)

p^H of solution	Concentration of Baquacil in solution (ug/g) after: 0	2 months	4 months	% loss of Baquacil
pH_5	10.4	10.6	10.1	2.9%
pH7	10.4	10.0	9.6	7.8%
pH_9	10.4	10.4	9.4	9.0%
pH7 dark	10.4	9.7	9.7	5.9%

Sample	Conditions	Concentration of Baquacil (ug/g) after: 0 Day	4 Days	14 Days	20 Days
Deionised water at pH 5	Sunlight	10.7	10.1	9.5	7.1
pH 7	Sunlight	10.7	10.7	8.4	7.7
pH 9	Sunlight	10.7	9.3	8.3	7.6
River water at: pH 8	Sunlight	10.7	4.1	3.1	0.0
pH 7.5	Sunlight	10.7	6.3	5.2	2.4
pH 7.0	Sunlight	10.7	4.9	3.6	1.8
Deionised water at pH 5	Dark	10.7	10.7	10.7	8.9
pH 7	Dark	10.7	10.7	10.7	8.4
pH 9	Dark	10.7	10.0	10.4	9.7
River water at: pH 8	Dark	10.7	6.1	7.1	5.1
pH 7.5	Dark	10.7	8.7	9.1	8.7
pH 7.0	Dark	10.7	7.1	7.1	5.3

Degradation of Baquacil by a medium pressure mercry lamp filtered through pyrex glass.

Time	Concentration of Baquacil ug/g
0	10.4
2.5 hrs	7.9
5 hrs	6.6
100 hrs	0.7

3.1.6 Conclusions

Solutions of Baquacil (in deionized water) subjected to sunlight showed a loss of activity with time and at pH 5,23% was lost after 20 days; at pH 7, 28% was lost after 20 days and at pH 9, 29% was lost after 20 days. The controls kept in the dark (pH 7) lost 5.9%.

Baquacil did not photodegrade rapidly as indicated by the data, although what effect the glass storage containers and polythene covering on the plates had can not be determined. The reaction in the dark indicates either binding to the glass (loss of activity) or hydrolysis or both are occurring.

No photodegradation occurred after 60 days of exposed Baquacil to artificial light (flourescent). After 4 mos. 6.9% was degraded at pH 5, after 4 mos. 7.8% at pH 7 and 9.0% at pH 9. The same deficiencies mentioned above apply to this part of the study.

Solutions exposed to mercury pressure lamp (filtered throught pyrex) were degraded in 5 hrs. from 10.4 to 6.6 ug/g and to 0.7 ug/g in 100 hrs. (pH unknown).

Solutions exposed to natural sunlight in tap water for 20 days degraded from 10.4 ug/g to 4.4 ug/g (pH unknown).

River water at pH exposed to sunlight degraded by 83% after 20 days, at pH 7, 76% and at pH 8, 100%. In the dark at pH 5, 5.3% degraded, at pH 7, 8.7% and at pH9, 5.1%. This indicates organic matter acceleration of the photoreaction is occurring.

Author claims microbial attack, however, the rate of degradation in deionized water (in the dark) is the same or less than river water (kept in the dark), which indicates hydrolysis and not microbial action. This is further substantiated by the activated sludge study in which little degradation occurred by the sludge micoorganisms.

The comparision of flourescent vs. mercury lamp degradation indicates that UV light is in part responsible for the photoreaction. The artificial light spectrum had wavelenghts of light below 280 nm (8.3%). The comparision of artificial light vs natural light indicates a gap on the 600-700 nm range for the artificial source.

TLC analysis indicates that Baquacil degrades to a compound still polymeric in nature (modification of the biguanide group--no eosin colour reaction). Hexamethylene diamine is not indicated to occur. Photoproducts were only tentatively identified.

This study does not fulfill the data requirement and can not be used to support the proposed use until the discrepancies mentioned above are resolved.

3.1.7 Metabolism
Aerobic Soil

Acc. # 234289 Vol. 6 of 7. Section C. Appendix No. C-26 page 1027. Preliminary laboratory studies of the degradation of ^{14}C-Baquacil in Soil. I.R. Hill, J.H. Willis Report No. TMJ 1165B.

3.1.8 Materials

^{14}C-Baquacil was applied to sandy loam [p^H 7.0], sandy loam [p^H 6.6], and loam soils. Soils were incubated both aerobically and one soil was tested anaerobically [by waterlogging] in an enclosed system for up to 52 weeks.

3.1.9 Methods

Soils were extracted with methanol and acetone by refluxing for 6 hrs.. One part of the soil was further extracted with HCl. Soils were also extracted with NaOh and refluxed for 6 hrs., or with H_2SO_4 refluxing for 6 hrs., or by tetrapyrophosphate and either shaking at room temperature for 16 hrs. or by ultrasonication for 10 mins.. Isotopic exchange was also carried out with one soil. Soils were kept at 40% of water holding capacity for the aerobic portion. Air was passed over the soil and bubbled through a trapping solution consisting H_2SO_4, 2-methoxyethanol and ethanolamine in succession.

3.2.0 Results/Conclusions

After one year's incubation in sandy loam [p^H 7.0], sandy loam [p^H 6.6], and loam soils treated at 1, 10, and 100 kg/ha, 10-13%, 10-14%, and 15-20% of the applied activity was recovered in the ethanolamine traps. Less than 0.1 % was recovered in the methoxyethanol and H_2SO_4 traps. The activity was not characterized, the author claims $^{14}CO_2$, but this does not seem to be totally accurate based on other study data-- our estimate is that it may be in part parent material volatilizing from the surface of the soil.

Author claims that Fig. 2 is the anaerobic incubation data, however, the title of fig. does not lend to this. This will not need clarrification since anaerobic soil metabolism is not a data requirement for this use.

Of the extration procedures, methanol, acetone and HCl did not recover (extract) a large amount of activity, with only 3% extracted. Soidum pyrophosphate extracted 10% of the activity and soidum pyrophosphate plus ultrasonication extracted 30% of the activity. NaOH extraction extracted 40% of the applied activity. H_2SO_4 extracted up to 73% of the activity from the soil. The NaOH and H_2SO_4 were used at 1.0 and 5.0M respectively,

which would solubilize the organic matter. The results indicate that over 50% of the material is being bound to the soil (unless the activity is being released and re-adsorbed during alkaline extraction).

Isotopic exchange with saturation of the soil with 6 parts Baquacil and 10 parts soil resulted in 33 and 40% of the activity being released from the soil during HCl and methanol:Water extraction. This indicates that 30-40% of the activity bound may be present as a polymeric biguanide.

No attempt was made to characterize the extracts as to potential metabolites. The temp on incubation was not given . The compound appears to be stable to soil degradation and/or the compound adsorbs rapidly enough as to make it unavailable for degradative processes to occur.

This study, although deficient, is required for a swimming pool use, and therefore the deficiencies do need to be addressed, since some pools may be drained to soil.

Soil	mechanical analysis (%) sand	silt	clay	organic matter (%)	pH	CE C (m. equiv. /100g)	Moisture holding capacity (%)	Soil classification
Peartree 7	57	24	19	6.3	7.0	19.0	81.3	sandy loam
Frensham	73	20	7	1.9	6.6	5.0	41.8	sandy loam
Gore	38	48	14	10.3	7.5	29.0	98.7	loam

Soil	Baquacil application rate (Kg. a.i/ha)	Weeks incubation	Radioactivity as % of that applied to the soil: radioactivity evolved and "trapped" in ethanolamine	radioactivity recovered from soil (by combustion)	Total radioactivity recovered from soil and 'trapping' solutions
Peartree 7	10	0	0	104	104
	10	16	8	87	95
Frensham	10	0	0	87	87
	10	16	9	86	95
Gore	10	0	0	97	97
	10	16	12	81	93
Gore	100	16	10	88	98

3.2.1 Metabolism

Activated sludge

Acc. # 234289 Vol. 6 of 7. Section C. Appendix C-24 page 937. Vantocil IB and Sewage Treatment. Report BL/B/1649.

3.2.2 Materials and Methods

A. Semicontinous Activated Sludge
A labeled sample of Vantocil IB was diluted with unlabeled Vantocil IB such that the solution contained approximately 0.6 6uCi activity and 3 mg of Vantocil Ib. The experiment was carried out at 20^0C in a modified procedure of Brixham. The system operated was a fill and draw activated sludge system with daily additions of settled sewage (3 l; mean BOD_5 77mg/l) to the unit along with 5cc (15 mg; 3uCi) of labeled Vantocil IB. $^{14}CO_2$ was trapped in ethanolamine/methanol contained in Drechsel bottles. The activity in the 3 l of settled effluent which is the portion discharged prior to the addition of sewage feed was also monitored. Activated sludge obtained from a local sewage works was added as a suspension in one litre of settled sewage at the start of the experiment which was run for 25 days.

B. Continuous Activated Sludge
Eight porous units containing activated sludge were fed for an initial 6 day period on either settled sewage or synthetic sewage which were the feeds to which the two sets of activated sludge were accustomed. The sludge had a volume of 3 l and the rate of feed was 0.5 l/hr. and a retention time of 6 hr.. The test was carried out at 20^0C. At the end of the initial period the units were fed 0, 10, and 40mg/l respectively of Vantocil IB. The experiment was carried out 41 days.

C. Activated Sludge Respiration Rate Test
Activated sludge was mixed with a specified excess of biodegradable material and immediately transferred to a closed cell equiped with a magnetic stirrer and an oxygen electrode, by which the rate of fall of oxygen concentration was measured. Levels of Vantocil IB from 0 to 480 mg/l were added and monitored.

D. Total solids, TOC, pH, BOD_5 (water) and BOD_5 (glutamic acid), and suspended solids were monitored.

E. Adsorption of Vantocil by Activated Sludge
A sample of activated sludge from a nearby sewage works treating sewage was washed by centrifugation and addition of water. Samples were added to cylinders (glass) and sludge was added at rate from 1 - 35 mg dry weight. Water was added to make the total volume 99ml with one cyclinder receiving no sludge sample. Vantocil IB (3 mg) was added to the cylinders and stopped. The cylinders were shaken for 24 hrs. and allowed to settle and a portion counted for activity. The remainder was filtered, the filtrate discarded and The filter ; and solids added to 3 ml of proprietory sample solubilizer and allowed to digest for 10 days. An additional 10ml of proprietory liquid was added and a further 8 day incubation period was maintained to allow any chemiluminescence to die away and the sample counted by LSC with Freundlich isotherms est.

F. Effect of Vantocil on Sludge Digestion
A sample of sludge was taken from the digesters of a sewage works, and a sample of feed sludge was taken at the same time. Both sludges were sieved through a coarse sieve, mixed (2:1 digested sludge to feed), solids level measured and portion of the batch were added to two units and Vantocil IB (250mg and 56mg) added with water. The digesters were monitored for gas evolution and incubated at 36^0C. Controls were used in all experiments.

3.2.3 Results

Vantocil IB-Effect on Sludge Digestion

Experiment	% expected Gas Production
Control	100%
Control	102%
Vantocil IB 250 mg	95%
Vantocil IB 56 mg	97.5%
Pentachlorophenol 141 mg	10%

Vantocil IB - Effect on the
Respiration Rate of Activated Slduge

Vantocil Concentration mg/l	Respiration Rate mg O_2/g.S.S/hr	% Inhibition	Suspended Solids in Cell (mg/l)
0	42.6	-	2000
48	36	15	2000
160	34	20	2000
320	31	27	2000
480	29	32	2000
0	17.8	-	1570
200	17.8	0	1570
300	17.8	0	1570
0	31.3	-	1044
200	24.6	21	1044
300	26.9	13.5	1044
Pentachlorophenol Concentration			
0	17.8	-	1570
1	17.1	4	1570
5	14.0	21	1570
10	10.8	39	1570
100	3.5	80	1570
300	0	100	1570

Vantocil IB. Effect on Performance
of Units A-D Treating Settled Sewage

	Vantocil IB (mg/l)	Total Organic Carbon			5 Day Biological Oxygen Demand		
		Feed	Effluent (Mean Levels: mg/l)	% Removal	Feed	Effluent (Mean Levels: mg/l)	% Removal
Unit A	0	51	14.4	72	74	9.1	88
Unit B	10	45	12.3	73	72	6.6	91
Unit C	20	46	9.7	79	78	9.1	88
Unit D	40	44	16	63	63	10.5	83

Vantocil IB Activated Sludge Adsorption Experiment

Dry Wt. of Activated Sludge (mg)	Activity in Supernatant (uCi)	Activity in Sludge	Total Activity uCi)	% Recovery
0	0.72	0	0.72	100
35.1	0.11	0.11	0.29	40.3
27.3	0.09	0.22	0.31	43
19.5	0.12	0.11	0.23	31.9
11.7	0.15	0.27	0.42	58.3
3.9	0.29	0.29	0.58	80.5
1.9	0.43	0.15	0.58	80.5

Vantocil IB Activated Sludge Adsorption Experiment

Dry Wt. of Activated Sludge (mg)	Activity in Supernatant	Activity in Sludge	Total Activity (uCi)	% Recovery
0.95	0.54	0.06	0.60	83.3

Vantocil IB Adsorption on Activated Sludge:
Results of Table 7 in
Freundlich equation form

Wt. Sludge (m) (mg)	Residual Activity (c) %	Activity Adsorbed (x) (%)	$\frac{x}{m}$
35.1	15.3	84.7	2.41
27.3	12.5	87.5	3.21
19.5	16.7	83.3	4.27
11.7	20.8	79.2	6.77
3.9	40.3	59.7	15.31
1.9	59.7	40.3	21.21
0.95	75	25	26.32

C^{14} Labelled Vantocil IB-Fill and Draw Activated Sludge Experiment
Effluent and Ethanolamine Activities

Day	Effluent Activity (uCi)	Ethanolamine Activity uCi)
1	0.4	0.11
5	0.51	0.21
10	1.56	0.18
11	1.59	0.18
12	0.82	0.21
13	0.90	0.26
14	0.58	0.29
15	0.72	0.25
16	0.43	0.36
17	0.53	0.14
18	0.67	0.20
19	0.82	0.24
20	0.81	0.33
21	0.80	0.31
22	0.72	0.26
23	0.78	0.35
24	0.76	0.24[2]
25	0.95[1]	0.24[2]
Totals[3]	19.17	6.08
Overall Mean	0.77	0.24
Mean Days 9-23	0.84	0.26

Note
1 Calculated on 4 l. of effluent as opposed to 3 l. for rest of effluent results
2 Estimates based on mean of days 1-23
3 Total Activity added as Vantocil IB 82.9uCi. Data from 2,3,4,6,7,8 and 9 days has been sumbitted.

-14 cont.

C^{14} Labelled Vantocil-Fill and Draw Activated Sludge Experiment
Sludge Analysis

Sludge Wet Weight (grams)	Total Activity (uCi)
0.0830	41.6
0.1108	40.8
0.1187	39.1
0.1166	38.4
Mean	40.0

3.24 Conclusions

Results from the semi-continuous activated sludge experiment indicate that approximately 6.1 uCi (7%) of the total activity added was collected in the ethanolamine traps, with no significant amount degraded over the latter part of the experiment. This indicates that the compound is resistent to microbial attack. The activity present in the effluent (bio-elimination) was 19.3Ci (77%) with a slight increase in the effluent levels (over 25 days - or 10%/day/recovered activity) over the latter part of the experiment (9-23 days). The sludge results indicate a total activity of 40uCi (48%). A total of 65.3uCi was recovered and gives a overall recovery of 79% (7% CO_2, 23% aqueous effluent, 48% in sludge), of a total 82.9uCi input of Vantocil IB. A estimate of the low recovery is the calculation in the sludge. Other data indicates that as the weight of the sludge increased the recovery decreased.

Results from continously fed activated sludge units did show a slight increase in TOC for the Vantocil IB treated units, although the results are not considered significant enough to indicate inhibition to the system. BOD values for control vs treated are significant with influent and effluent values for the 40mg/l Vantocil IB treatment. The values are 11-15% higher in difference with the control. The ratio of TOD:BOD does not indicates this with a value of 0.5, which is normal. A plausable explanation is that the BOD does not show inhibition as the author states but rather shows that the compound is not very biodegradable and thus the higher BOD values for treated units. From graphs one and two which show pH changes, a clear indication of a change occurs from (pH 5.5-6.0) to (p7.5 - 8.0) for the 40 mg/l concentration and possibly for the 20mg/l concentration. The drastic rise in pH indicates that deterioration in nitrification of the system and BOD removal efficiency. Nitrification was not monitored with this study, and at concentrations of 40 mg/l of Vantocil the BOD removal efficiency may be decreased, although this can not be substantiated from the data. The data indicates that the solids production (from graphs 3 and 4) is reduced for the 40 mg/l concentration, indicating that the conversion of BOD to sludge solids is depressed at this level.

Data from the respiration studies indicate that there can be from 0 - 32% inhibition depending on the sludge and the suspended solids content.

Data from the BOD_5 tests indicate that the Vantocil IB is resistant to microbial attack or that the chemical is toxic to the microorganisms.

Data from anaerobic sludge digenstion indicates that at concentrations form 56- 250 mg/l of Vantocil IB no inhibition occurs in the gas production from the anaerobic sludge digestor.

Data from the adsorption (graph 5) tests indicates that the Vantocil IB is readily adsorbed to the sludge and in high amounts. At 10% residual Vantocil IB the sludge removed 2.65% of Vantocil IB/mg of sludge. This can be expressed as 90/2.65 mg of sludge/100 ml are required to reduce the concentration of a 3 mg/100 ml solution of Vantocil to 0.3 mg/100 ml. The concentration of suspended soils has a great impact on the amount adsorbed and at 35.1 mg 84% is adsorbed while at 0.95 mg only 25% is adsorbed.

This is an acceptable activated sludge study and fulfills the data requirement. It can be used to support any proposed use of Baquacil, where this data is required.

Note: Since this chemical does have trace metals contained in it (see section 3.0) it can be assumed that some of these metals will be discharged into the receiving aquatic environment.

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3.2.5 Mobility
Leaching

Acc. # 234289 Vol. 6 of 7. Section C. Appendix C-25 page 982. Adsorption and leaching in soil. Report # D81161A.

3.2.6 Materials and Methods

The mobility of parent Baquacil was determined by thick-layer chromatography. Distilled water, ^{14}C-Baquacil, plus soil samples of Fresham, Pear tree [p^H6], Pear tree [p^H 8], and Gore were mixed together and the water allowed to evaporate. A 5 mm thick layer of the ground soil (non treated) was placed on a TLC plate, which was supported at an angle of 5^o to the horizontal. A cloth wick was attached to the upper end of the plate. A 1 cm band of treated soil was removed from the top of the plate and replaced with the Baquacil treated soil. The chromatograms were developed by dipping the wick into 0.01M $CaCl_2$. The $CaCl_2$ was taken up by the wick in 3-7 days depending on the soil type and the leachate was collected from the chromatograms. After the chromatograms had been run, the soil was split into segments, air dired, ground, and samples combusted to determine activity. The leachates collected were analyzed by scintillation counting. Atrazine was chosen as a control.

The mobility of potential degradative products of Baquacil was obtained by colum leaching studies. ^{14}C-Baquacil was incubated with the soils used in the TLC method for one month aerobically, with the Pear tree soil [p^H 7]incubated under anaerobic conditions inclusive. ^{14}C-Baquacil was added to the top of the columns at a rate equivalent to 9.0 kg/ha. Activity in the leachate as well as activity in segments of 5cmm deep were analyzed by scintillation counting. Temperature of incubation was 18^oC.

3.2.6.1 Results

Properties of soils

Name	*	Gore	Frensham	Pear Tree pH6	Pear Tree pH8	Whiskers
Type		Calcareous clay loam	Coarse sand	Coarse sandy loam	Loam	Coarse sandy loam
Sample reference numbers		1/23/A and 1/37/B	1/27/A and 1/40/B	1/15/A and 1/50/B	1/19/A	1/8/E
Coarse sand (200-2000u)%	1	6.7	59.3	41.8	27.8	38.5
Fine sand (20-200u) %	1	41.4	23.0	23.5	27.0	26.2
Silt (2 - 20u)%	1	17.4	8.1	14.5	19.5	13.9
Clay (2u) %	1	34.5	9.6	20.2	25.7	21.4
Organic matter %	2	9.9	2.0	4.9	6.8	6.1
pH	3	7.4	6.7	6.2	7.7	6.3
Cation Exchange capacity (meg/ 100g)	6	35.2	6.5	13.0	18.0	19.8
Available phosphorus (ug/g)	7	40	50	50	100	40
Available potassium (ug/g)	8	180	50	480	750	180
Available magnesium (ug/g)	8	140	<20	180	240	240

3.2.7 Conclusions

The mobility of the parent ^{14}C-Baquacil determined by thick-layer chromatography indicated very low mobility in calcereuous clay loam, coarse sand, coarse sandy loam and loam soils. In these soils about 90-95% of the activity remained in the top 5 cm of the soil that had been leached with an equivalent 32 cm of rain. Atrazine, the control, leached 10-20 cm. Recoveries were 82-117%, indicating some volatilization had occurred during incubation time.

The mobility of Baquacil degradates incubated in calcareous clay loam, coarse sand, and coarse sandy loam soils for 4 weeks under aerobic conditions and anaerobic conditions was determined by soil column and thick-layer chromatography. The 35 cm long columns were leached with equivalent 68 cm rain over a 60 day period at 4 kg/ha. About 90-95% of the activity remained in the top 5 cm of the columns and none was detected in the leachate. The thick-layer chromatograms indicated greater than 90% of the parent and potential degradates remained in the top 2 cm as eluted with an equivalent 50 cm of rain. The control, Atrazine, leached 15-25 cm.

No difference in the columns incubated under aerobic vs. anaerobic conditions.

This is an acceptable leaching study and can be used to support proposed uses were this data is required.

3.2.8 Mobility
Adsorption

Acc. # 234289 Vol. 6 of 7. Section C. Appendix C-25 page 982. Adsorption and leaching in soil. Report D81161A

3.2.9 Materials and Methods

Samples of soil classified as sandy loam [p^H 6.6] [pH 8.0], coarse sand, calcareous clay loam, and sandy loam, were equilibrated with ^{14}C-Baquacil (both labeled and non-labeled mixture) and 0.01M $CaCl_2$. The soil suspensions were shaken for 16 hrs., centrifuged, and the supernatant counted by a scintillation unit. [redacted]. This procedure was conducted for a period of seven days. Adsorption was presented as K_d values were k_d = ug/adsorbed/g soil / ug/ml equilibrium solution.

3.3.0 Results

Leaching of ^{14}C labeled Baquacil plus its degradation products by 67.5 (1380 ml) 0.01 M $CaCl_2$ in four different soil columns, incubated under aerobic or anaerobic conditions.

Soil Segment CM	Soil Type/ Conditions of Incubation 1. Pear tree aerobic	2. Pear tree anaerobic	3. Gore aerobic	4. Fresham aerobic
	a) expressed % of total applied			
0-5	0.36	0.09	81.16	109.45
5-10	82.08	80.95	0.17	6.17
15-20	0.51	1.00	0.04	0.12
25-30	0.09	0.61	0.00	0.04
Leachate	0.05	0.11	0.07	0.07
Total	83.27	83.86	82.17	117.42

a) numbers do not add up to totals for not all data (10-15, 20-25, 30-25 cm) were included, however they have been submitted.

~~TABLE 8~~. Adsorption of Baquacil on Pear Tree (pH_6) soil

Initial concentration Baquacil in solution (ug/ml)	Equilibration time (days)							
	Conc. Baquacil in Equilibrium Solution (ug/ml)	% of Baquacil remaining in Equilibrium solution	Baquacil Adsorbed on Soil ug/g)	K_D	Conc. Baquacil in Equilibrium solution (ug/g)	% of Baquacil remaining in Equilibrium solution	Baquacil Adsorbed on Soil (ug/g)	K_D
4.3	0.10	2.30	84.0	851	0.05	0.98	85.0	1,824
24.3	0.61	2.35	474	772	0.29	1.08	480	1,644
100	2.77	2.77	1,945	703	1.79	1.62	1,963	1,096
500	17.9	3.57	9,643	540	12.3	2.22	9,747	792
1,000	42.8	4.28	19,144	447	35.6	3.22	19,277	541
2,000	746	37.3	25,083	33.6	670	31.2	26,539	39.6

Adsorption of Baquacil on Pear Tree (pH 8) Soil

Initial concentration Baquacil in solution (ug/ml)	Equilibration time (days)							
	Conc. Baquacil in Equilibrium Solution (ug/ml)	% of Baquacil remaining in Equilibrium solution	Baquacil Adsorbed on Soil (ug/g)	K_D	Conc. Baquacil in Equilibrium Solution (ug/ml)	% of Baquacil remaining in Equilibrium solution	Baquacil Adsorbed on Soil (ug/g)	K_D
4.3	0.10	2.22	84.1	880	0.12	2.49	83.7	705
24.3	0.67	2.75	473	707	0.68	2.51	473	699
100	3.06	3.06	1,939	633	2.86	2.58	1,943	680
500	17.5	3.50	9,650	552	18.2	3.40	9,305	512
1,000	37.2	3.72	19,255	517	37.9	3.43	19.241	507
2,000	127	6.37	37,454	294	133	6.04	37,354	280
4,000	2,284	57.1	34,331	15.0	2,368	56.5	32,818	13.9

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Adsorption of Baquacil on Gore Soil

Initial concentration Baquacil in solution (ug/ml)	Equilibration time (days)							
	Conc. Baquacil in Equilibrium solution (ug/g)	% of Baquacil remaining in Equilibrium solution	Baquacil Adsorbed on Soil (ug/g)	K_D	Conc. Baquacil in Equilibrium solution (ug/ml)	% of Baquacil remaining in Equilibrium ug/g)	Baquacil Adsorbed on Soil (ug/g)	K_D
4.3	0.10	2.43	83.9	803	0.13	2.78	83.4	629
24.3	0.79	3.25	470	595	0.84	3.13	469	557
100	3.14	3.14	1,937	612	4.13	3.73	1,919	464
500	17.6	3.52	9,648	548				
1,000	37.8	37.8	19,244	509	47.3	4.27	19,069	403
2,000	94.3	4.71	38.115	404	51.2	4.63	37,900	371
4,000	1,310	32.8	53,792	41.1	1,139	26.5	57,036	50.1

3.3.1 Conclusions

Baquacil is rapidly adsorbed to all soils tested and equilibrium was reached between 1-4 days. The amount adsorbed by sandy loam [pH 6.6[, sandy loam [pH 8.0], calcareous clay loam, and coarse sand was 25,000; 34,331; 51,000; 6,970; ug/g respectively. Adsorption K_d values were (maximal) 851, 880, 803, and 540 respectively (after one day). Adsorption values are related to percent orgainc matter. K_d values increased over time of incubation and at 7 days were (maximal) 1824, 705, 629,and 816. The notable exception was calcareous clay loam which decreased with time.

No corresponding desorption values were reported. Since the leaching study showed that Baquacil and its degradates do not leach, the desorption values for this particular use do not need to be submitted. The soil metabolism study as well as the activated sludge also indicated high adsorption and strongly bound, as indicated by the difficulty in extraction.

This study is acceptable and can be used to support proposed uses were this data is required.

3.3.7 Ancillary

Rat metabolism

A dosage of 100 mg/kg ^{14}C-Baquacil resulted in around 90-95% of the activity excreted in the faeces within five days; c. 6% in the urine, 0.6% in the bile and c. 0.2% in the expired air. Only c. 20% of the material could be extracted from the faeces and showed a chromatographic profile similiar to Baquacil. Chromatorgraphy of the urine indicated that it consisted of highly mobile components. Chromatogrphy of the Baquacil itself indicated up to 10 components of which some are mobile and some are immobile.

A dietary exposure of 100 ppm of Baqucil (radio labeled) found tissue distribution in fat (1.2 ppm/ depuration half-life of four weeks),liver (0.8 ppm), kidney (0.1 ppm), and none detected in the brain.

Identification of components in the urine indicate that two oligomers of Baquacil with two cyanoguanidine end groups plus 3,3'-dicyano-1,1 -hexamethylene diguanide and 1-(6-aminohexyl) -3-cyanoguanidine.

Indications are that the faecal polymer-related material is not metabolized by the gut microorganisms.

This study is an ancillary study and was reviewed as such, with intent to understand the fate in the environment more fully, with potential deficiencies not addressed.

4.0 Environmental Fate Profile/General Conclusions

4.1 Hydrolysis

No hydrolysis study submitted per se with this submission. Samples of Baquacil placed into deionized water at pH 5,7, and 9 that were kept in the dark at room temperature (controls for photolysis experiment) indicate that after 20 days 8% hydrolysis occurred at pH 9,16% at pH 5, and 22% at PH 7.0. Regression analysis indicate that corresponding half-lives are calcualted as 32, 28 and 59 days respectively. No attempt was made to identify the hydrolysis products and a material balance was not submitted. EFB speculates that hexamethylene diamine and reaction of the end group (cyano) to give guanyl urea may be potential hydrolysis products. It can be assumed that indoor swimming (principal use area) have temperatures above STP and the hydrolysis reaction may increase. This combined with swimming pools (and aquatic systems being the principal reaction sites) lends that a hydrolysis study is needed and the data above submitted can not be used to substitute for a hydrolysis study. This study does not fulfill the data requirement and can not be used to support proposed uses of Baquacil, where this data is required.

4.2 Photolysis

Solutions of Baquacil (in deionized water) subject to sunlight showed a loss of activity with time; at pH 5, 23% was lost after 20 days; at pH 7.0, 28% was lost; and at pH 9.0, 29% was lost. Controls (pH 7.0) kept in the dark lost 5.9%. No photo-degradation occurred after 60 days of exposed Baqacil to artificial light (flourescent). Solutions exposed to mercury pressure lamp (filtered through pyrex) were degradated in 5 hrs. from 10.4 to 6.6 ug/g and to 0.7 ug/g in 100 hrs. River water containing Baquacil 10.7 ug/g (pH 5.0) was degraded by 83% after 20 days; 76% at pH 7.0, and 100% at pH 8.0. Controls dept in the dark degraded 5.3 - 8.7%. Author claims microbial degradation is important, however, the rate of degradation in deionized water (in the dark) is the same or less than river water (kept in the dark), which indicates hydrolysis and not microbial attack. This is further substantiated by the activated sludge and soil metabolism studies. Photoproducts were not

identified, although the ~~compounds~~ photoproduct is still polymeric in nature (modification of biguanide group?-- based on no eosin color reaction). Hexamethylene diamine is not indicated to occur. Light spectrums submitted indicate UV is partially responsible for the photodegradation, although a gap from the 600 - 700 nm range occurs from the artificial source. The crystallising dishes (were Baquacil solution were placed) were covered with polythene and stored in glasshouses during exposure. What effect this may have is unknown and will have to clarified before it can be used to support proposed uses of Baquacil.

4.3 Soil metabolism

After one year only 10-20% of the activity was recovered in etholamine traps for sandy loam (p^H 7.0), sandy loam (p^H 6.6), and loam soild treated with 1, 10, and 100 kg/ha. Over 50% is bound and of the 50%, 33-40% appears to be polymeric in nature. No attempt was made to identify the extractable metabolites and it was assumed that the activity in the etholamine traps was $^{14}CO_2$. Table referenced as to anaerobic soil degradation did not appear to be anaerobic degradation data (by title). The temperature of incubation was not given. Anaerobic soil degradation was not a data requirement outline in the 10/17/73 meeting between ICI and EFB and the deficiencies will not have to be addressed for this use, but may for future uses that require this data. Clarification of above points needs to be resolved before this data can be used to support this proposed use.

4.4 Activated sludge metabolism

Results indicate that Baquacil is resistent to microbial attack and that at concentrations of 40 mg/l and higher the sludge process is affected such that respiration is inhibited, p^H changes to basic nature (5.5-6.0 to 7.5-8.0) which lends to nitrification inhibition, and suspended solids accumulation. From 10-23% of the material may be discharged into the receiving aquatic environment, (over 25 days) or 1% per day depending on the concentrations of suspended solids (based on adsorption isotherms submitted). No effect is observed on anaerobic sludge digestion from 56-250 mg/l concentrations of Baquacil. This is an acceptable activated sludge metabolism study and can be used to suport proposed uses of Baquacil.

4.5 Leaching

The mobility of parent Baquacil determined by TLC analysis indicated very low mobility in calcareuous clay loam, coarse sand coarse sandy loam and loam soils. In these soils 90-95% of the parent material remained in the top 5 cm of the soil. Some volatilization appears to have occurred during incubation. Soils columns incubated aerobically or anaerobically for four months resulted in 90-95% of the material remaining in the top 5 cm of the soil column. No activity was detected in the leachate. This is an acceptable leaching study and fulfill the data requirement and can be used to support proposed uses of Baquacil.

4.6 Adsorption

Baquacil adsorbs to sandy loam (p^H 6.6), sandy loam (p^H 8.0), calcareuous clay loam and coarse sand readily, with equilibrium reached in 1-4 days. Adsorption values at day one were 851, 880, 803, and 540 respectively. These values increased with time and at day seven were 1824, 705, 629, and 816, with a notable exception calcareuous clay loam which decreased with time. No corresponding desorption values were reported. The leaching study, soil metabolism, and activated sludge stuy lend to the fact that Baquacil is strongly adsorbed and desorption would not be rapid. The meeting of 10/17/73, did not indicate that adsorption was a requirement for this use. It has been used to support the registration of this chemical (in that sense is acceptable for this use) and if other uses are proposed that have this requirement, desortion values may be required.

4.7 Ancillary (rat metabolism)

Dosages of 100 ppm Baquacil resulted in c. 90-95% of the compound excreted in the faeces, c. 6% in the urine, 0.6% in the bile and 0.2% in the expired air. Only 20% of the material could be extracted from the faeces and chromatographed similar to Baquacil itself. Dietary exposure resulted in residues in fat (depuration half-life of 4 weeks) of 1.2 ppm, liver (0.8 ppm), kidney (0.1 ppm), and none in the brain. Identification of components in the urine indicate that two oligomers of Baquacil with two cyanoguanidine end groups plus 3,3'-dicyano-1, 1-hexamethylene diguanide and 1-(6-aminohexyl)-

3-cyanoguanidine. Indications are that the faecal polymer-related material is not metabolized by the gut microorganisms.

Note: chromatography of this chemical indicated that there were at least 10 components of Baquacil and that some are mobile and some are immobile. The mobile ones apparently are excreted in the urine and it may be plausable that the immobile ~~are~~ components-fractions are the adsorbed components in soil, activated sludge, etc., with the mobile ones being discharged, desorbed, or extracted from soil or activated sludge.

This is an ancillary study and was reviewed in that context.

4.8 From the meeting of 10/17/73, the following data requirements were outlined:

1. Soil TLC
2. Activated sludge
3. Hydrolysis at pH 5, 7, and 9
4. Photodegradation
5. Data on mixtures--microbial degradation in water of mixture vs. separate chemicals.
   1. identify, if any, reaction products and quantify.

5.0 Recommendations

5.1 The fate of this chemcial in the environment has not been discerned.

5.2 The following study is required for this use and was not submitted with this submission (data gap).
1. Hydrolysis

5.3 The following studies submitted have deficiencies and/or require clarification.
1. Soil metabolism Acc. #234289 Vol. 6 of 7. Section C. Appendix No. C-26 page 1027. Preliminary laboratory studies of the degradation of ^{14}C-Baquacil in soil.
   a) degradates/metabolites extracted will have to be identified.
   b) temperature of the study was not given.
   c) Fig. 2 is claimed to be anaerobic degradation data, however, the title does not indicate this (i.e. is the table correctly indentified). Anaerobic soil degradation is not a requirement for this use and this comment is for the applicants own information.
   d) these deficiencies/clarifications do not have to be addressed if the applicant attaches a statement to the label such as, Do not discharge into lakes, streams, or ponds.
2. Photolys[is] Acc. #234289 Vol. 6 of 7. Section C. Appendix No. C-27 page 1055. Preliminary study of the photodegradation in water of Baquacil.
   a) degradative products greater than 10% of applied material will have to be identified.
   b) material balance will have to be submitted.
   c) what effect does the polythene covering on crystallising dishes have on the photodegradation of Baquacil.
   d) what effect to photolysis does storing the samples in glass houses have (other than simulate indoor pool conditions) to outdoor treated pools.
   e) degradation rates for deionized water (kept in the dark), are less or the same as river water (kept in the dark), which indicates hydrolysis and not microbial attack when compared to photodegradation of Baquacil in river water. Could this photodegradation be mitigated by organic matter in the water?

f) these deficiencies/clarifications do not have to be addressed if the applicant attaches a statement to the label such as, Do not discharge into lakes, streams, or ponds. These deficiencies/clarifications will have to be addressed if Toxicology Branch requires photodegradation studies (see section 5.4).

3. Adsorption Acc. # 234289 Vol. 6 of 7. Section C. Appendix C-25 page 928. Adsorption and leaching in soil.
   a) corresponding desorption values were not submitted.
   b) do not have to be submitted if EEB does not need this information.

5.4 PM Note

According to current "What to do now with the reader's guide to the guidelines" of March 15, 1979, for swimming pool uses the data required by Toxicology Branch are classified as:
1. Photodegradation
2. Hydrolysis
3. Volatility

Co-ordinate with Toxicology Branch as to the need for photolysis and volatility data, if they concur, then section 5.2 has volatility as an additional data gap, and section 5.3 [2. Photolysis a) - e)] will have to be addressed.

5.5 EEB Note

1. Over a 25 day period 10-25% of the parent or polymeric degradate (very similar to parent) [about 1% discharge per day] may be discharge into the aquatic environment from the activated sludge process. Defer additional data requirements.
2. Baquacil is adsorbed readily to soil with equilibrium reached in 1-4 days. No corresponding desorption values were submitted. Defer the need for desorption from soil per comment 1.
3. Baquacil contains trace amounts of metals (see section 3.0 for listing) and some of these (how much can not be determined) may be discharged from a sewage treatment system receiving Baquacil. Defer the significance of this.

5.6 PM Note

Co-ordinate with EEB on desorption/adsorption data requirement (section 5.5(2.) and 5.3(3.).

5.7 PM Note

The following questions from EFB need to be asked of the applicant.

1. Baquacil is a mixture of 3 different chemicals; are all three subject to the same rate of degradation in water, soil, and photolysis in water.

Robert. Robert F. Carsel 4/3/79
~~Ronald~~ F. Carsel
Environment Fate Branch
Review Section One