

UNITED STATES  
ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

APR 19 1979

Attached please find the environmental fate review of:

Reg./File No.: 10182-RO

Chemical: poly(hexamethylene biguanide hydrochloride)

Type Product: Algaecide

Product Name: Baguacil

Company Name: ICI

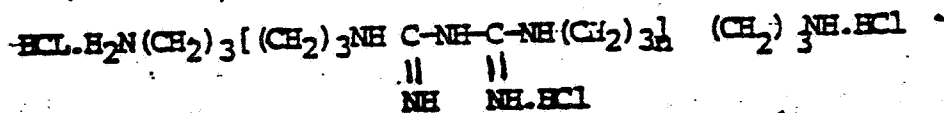
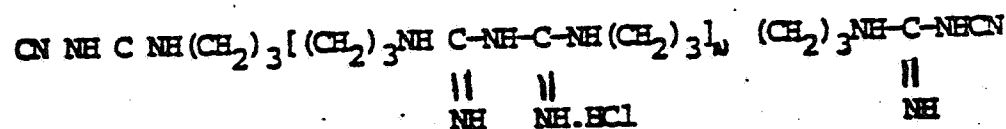
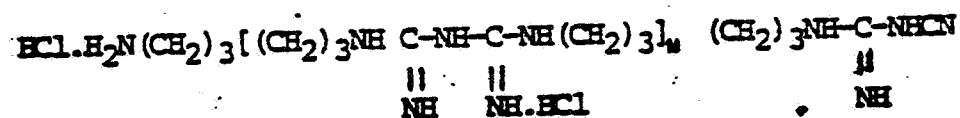
Submission Purpose: Resubmission with data. Swimming pool use

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: PEMB is a mixture of three different molecules



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

## Environmental Fate Profile/General Conclusions

### Hydrolysis Physico-chemical

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. 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 3% hydrolysis occurred at pH 9, 16% at pH 5, and 22% at pH 7.0. Regression analysis indicate that corresponding half-lives are calculated 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.

### Conclusions

Since the <sup>amount of</sup> chemical degraded 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.

### 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.

## 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 pH 9, 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 microorganisms.

The comparison 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 comparison 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.

Metabolism  
Aerobic Soil

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

Results/Conclusions

After one year's incubation in sandy loam [ $\text{pH}$  7.0], sandy loam [ $\text{pH}$  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  $\text{H}_2\text{SO}_4$  traps. The activity was not characterized, the author claims  $^{14}\text{CO}_2$ , 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 clarification since anaerobic soil metabolism is not a data requirement for this use.

Of the extraction procedures, methanol, acetone and HCl did not recover (extract) a large amount of activity, with only 3% extracted. Sodium pyrophosphate extracted 10% of the activity and sodium pyrophosphate plus ultrasonication extracted 30% of the activity. NaOH extraction extracted 40% of the applied activity.  $\text{H}_2\text{SO}_4$  extracted up to 73% of the activity from the soil. The NaOH and  $\text{H}_2\text{SO}_4$  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 of 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.

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.

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.

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 resistant 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<sub>2</sub>, 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 continuously 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 plausible 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 (pH 7.5 - 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 <sup>effluent</sup> ~~sludge~~ 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<sub>5</sub> tests indicate that the Vantocil IB is resistant to microbial attack or that the chemical is toxic to the microorganisms.

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

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 solids 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.

#### trace metals

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

Mobility  
Leaching

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

Conclusions

The mobility of the parent  $^{14}\text{C}$ -Baquacil determined by thick-layer chromatography indicated very low mobility in calcareous 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 where this data is required.

Mobility  
Adsorption

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

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, desorption values may be required.

## 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 organic 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 where this data is required.

## Ancillary

### Rat metabolism

A dosage of 100 mg/kg <sup>14</sup>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 similar to Baquacil. Chromatography of the urine indicated that it consisted of highly mobile components. Chromatography 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 Baquacil (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-aminoethyl)-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.

8



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 plausible that the immobile 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.

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.

## Recommendations

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

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

### 1. Hydrolysis

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  $^{14}\text{C}$ -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. Photolysis 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 <sup>will have</sup> 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

Questions you may have concerning this environmental fate review should be addressed to either Dr. Gunter Zweig or Robert J. Carsel of the Environmental Fate Branch, Telephone 557-7377

Sincerely,

*A. E. Castillo*  
for A. E. Castillo  
Product Manager (32)  
Disinfectants Branch  
Registration Division (TS-767)

(Any changes to this review must be coordinated with the product manager)

4/19/79 CSD