

Petition No. 3F1357
Reg. No. 6308-29
Co. name: Ansul Co.

10-21-74

I. INTRODUCTION

- A. Other names: MSMA, Ansar 529H.C.
- B. Type: herbicide
- C. Physical-Chemical properties see review for PP 9F0794 (2/17/69)
- D. Crops involved. Sugarcane (Louisiana)
- E. Other reviews pp 9F0794 (also see reviews for DSMA and Cacodylic acid)

II. DIRECTIONS FOR USE

Use as a directed application for plant sugarcane or as a directed or topical application to stubble sugarcane for post-emergent control of weeds and grasses. Apply at rate 1/3 to 2/3 gallons/acre of acre actually sprayed.

Mix 4 to 6 3/4 pints in 40 to 60 gallons of water per acre. Do not apply any surfactant to spray solution. Apply in a band 24-36" for adequate coverage of the row.

Johnson grass and raoul grass:

Apply first in spring (mid April) when grass is about 14" tall. Retreat when regrowth is 14" tall (3-4 weeks later). Do not exceed 2 applications per year, nor apply after June 1.

Precautions

Temporary damage to sugarcane foliage may occur after second application. Do not exceed 2 applications per year, nor apply after June 1.

III. DISCUSSION OF DATA

The following discussion utilizing information from these submissions: Ansar 529 H.C., PP #3F1357 (10-11-73 and following), PP 9F0794 (1-29-69) Reg #6308-29 (2-16-71), Reg #6308-18 (5-10-71) and Bolls-Eye 6308-91 (3-23-73). The chemicals for which pertinent information is available are MAA, MSMA, DSMA and cacodylic acid. Information not derived from studies using monosodium methanearsonate (MSMA) will be so designated.

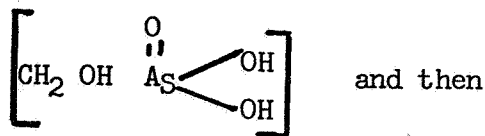
- A. Leaching studies. Studies with DSMA (#5, pp9F0794) indicated that clay minerals had a high affinity for arsenicals and that DSMA is found mostly in the top 6" (especially the top inch) of a clay loam soil. Studies with MAA, MSMA and DSMA indicated that after 4 years of surface applications the greatest concentrations of arsenic were found in the top 5 cm of Chesterfield sandy loam (9F0794, #27).

Studies discussed below indicate that the decomposition products of MSMA are CO₂ and sodium arsenate. The arsenate binds to clay minerals in a manner similar to phosphate, the chemical which arsenate most closely resembles in biological systems. The differences are that the binding is not as tight for arsenate and that the association is with the aluminum fractions rather than the iron ones as with phosphates. (#27, 9FO794) The similarities of phosphate and arsenate behavior in soil environments were discussed in #26, 9FO794 where the amount of clay minerals and especially the iron content of soils determined much of the ability to fix arsenate. This study concluded that arsenate could build up to phytotoxic levels in soil after repeated applications depending upon the availability of Fe or AL sites in the various soils.

B. Degradation

I. Aerobic Microbial degradation of MSMA releases CO₂ as evidence and leaves sodium arsenate as the two degradation products. Degradation is aerobic and slow (#22, 9FO794). Release of ¹⁴C as evidence of decomposition shows that without additional carbon sources, the process results in less than 6% of the label being detectable as evolved from soil in 30 days while additional carbon permits release of 15% of the labelled materials in the same time from the same soil, (Norfolk loamy sand, #5 9FO794). Using pure culture techniques, four microorganisms were found to degrade 3.20% of MSMA in 11 days. A fungus released 3% of the ¹⁴C as CO₂ while a "standard" bacterium released 20%. Two other bacteria both actinomycetes, degraded 9 and 13% in 11 days.

II. Anaerobic: An article indicated that organic arsine could be produced from cacodylic acid by penicillia and bacilli. Arsenious oxide gave rise to trimethyl arsine when incubated with Penicillium brevicaulis. Similar gases are produced from sodium methylarsonate (MSMA) and cacodylic acid. The proposed pathway from arsenate is the single carbon transfer of formaldehyde group to condense with arsenious acid giving hydroxymethylarsenic acid



MAA which ultimately would condense with other single carbon groups to form cacodylate. This could lead to (CH₃)₃ AsO which is reduced to trimethyl arsine, a gas. (#8, reg. #6308-18). Another report (p 11, 6308-91) referred to a study which indicates that dimethyl arsine can be formed in a similar manner. Isensee et. al. (see below) pointed out that dimethylarsine and dimethyl mercury are similar in structure.

III. Conclusions: "Degradation" of MSMA is apparently accomplished by microbial action by two distinct pathways. In one case the products are carbon dioxide and the toxic sodium arsenate. In the other case, the products are relatively unstable organic arsines, also toxic. The aerobic process provides a product which is liable to remain fixed undegraded in soil for some time (as long as oxidising conditions prevail) while the anaerobic process produces a mobile, unstable chemical which is liable to convert to arsenate if reducing conditions do not prevail. In sterile soil the compound MSMA does not appear to significantly degrade. Dissipation rates to 2 half-lives were not provided. Methods which identified metabolic products unambiguously were not used. Persistence studies under anaerobic conditions were not presented.

C. Bioaccumulation:

While MSMA will, with time, degrade to CO₂ and sodium arsenate, the arsenate will be fixed in the soil. A study done with Cacodylic acid and MSMA revealed that arsenic did not build up significantly after five annual applications of product on soils in Texas. Applying 6 lb/A/yr MSMA the following as residues were found

	ave As (ppm) in Soil				
	1968	1969	1970	1971	1972
MSMA	7.1	7.7	9.1	11.5	6.6
Check	7.5	6.2	8.2	9.1	6.4

Assuming 1 lb/acre (6" depth=2x10⁶ lb) 2 quads 0.5 ppm, then 7.5 ppm total as were added (12" depth). The additional 7.5 ppm was not found to occur after 5 yrs. (compared with the control). The loss of arsenate was assumed to be as a result of volatilization after microbial conversion of the arsenicals applied to gaseous forms (arsines?). It was assumed that leaching was not a factor due to the adsorptive capacity of the soils and the low rainfall at the fields.

If this study is assumed to be typical of conditions to be encountered with use of Ansar 529 H.C. then the likelihood of this material is reaching sensitive aquatic systems is low. However, this submission involves use in Louisiana where conditions are quite different. The heavy soils and high rainfall might produce soil atmosphere conditions such that bound arsenate could be mobilized. Runoff is also a possible source of movement of bound arsenate to aquatic systems. In any aquatic system, arsenate would probably find its way to lake or river bottom sediments. Under situations of stagnation, reducing conditions are likely to exist and the conversion of arsenate to methylarsines is possible (C.F. #6308-91 pp 11-49). Isensee et.al. (J. Env. Qual, 1972, "Distribution of Alkyl Arsenicals in a Model Ecosystem". (cited by Sandberg in Reg. 6308-91. p. 31) Showed the following accumulations in their model system.

	Algae	Snails	Daphnia	Fish
Dimethyl arsine (O ₂)	1605	446	2175	19
Cacodylic acid	1635	419	1558	21
Dimethyl arsine (N ₂)	1248	299	736	49

No data for fish accumulation was supplied with this submission though a study involving crayfish and catfish (in a water - algae - snail-crawfish - catfish model system) was reported to be in progress (6308-91, p. 28). It would seem that the opportunity for arsenate to find its way into aquatic ecosystems as a result of application of MSMA is not remote under the conditions likely to be encountered under this proposed use. It is unknown whether a hazard to the aquatic environment would result from this potential contamination. The review of arsenic contamination of aquatic environments (6308-91, p 80) was not enlightening since no data was presented.

- D. Rotational crops: Toxicity to rice, corn, soybeans, oats and cotton were reported following application of 50 ppmw DSMA to Bosket silt loam. Rice was inhibited 75%. Five ppmw produced some inhibition of rice. One might not be able to tell background levels from levels found in rotated crops.
- E. Metabolism in plants: When applied to leaves. (Sackerl, 1968, thesis- with pp #9FO794) Uptake and absorption by the grass was greater than with cotton. The MAA is apparently bound in both plants. The MAA is associated with both organic acids and amino acids (probably histidine). A mode of action involving a MAA metabolite histidine analogue was proposed. Amino acids were found to build up in the grass compared with the cotton, suggesting protein synthesis inhibition in the target plant. The MAA metabolite was not detected in cotton extracts, but was found in the affected johnson grass. Thus nonsensitive plants may not be inhibited as a result of limited uptake or due to complexing of the MAA taken up with cellular components other than critical amino acids.
- F. Effects on Microorganisms: A study (reg. #6308-18, study #8) utilized a variety of arsenicals in an attempt to determine levels at which total inhibition (no growth) would occur with 4 species; Bacillus mycoides, Aerobacter aerogenes, Penicillium expansum and Aspergillus niger. All are soil microorganisms. of the products tested, MAA and DSMA were among the least toxic (no inhibition at 2000 ppm) only B. mycoides was at all sensitive (at 1400 ppm).

IV. CONCLUSIONS:

There are two items for which evidence bearing on the environmental safety of this product is inconclusive. One is related to the persistence of Ansar 529 H.C. proper and its metabolite sodium arsenate. The other deals with potential hazard to aquatic ecosystems.

Though evidence exists that arsenic does not build up in W. Texas soil plots after MSMA treatment, the relevance of this study to Southern Louisiana sugar cane fields is questionable. Both climate and soil type in the two locations are quite different. The evidence from other soil, and from pure culture microorganism studies under optimal conditions, indicate a slowly degrading product.

Loss by volatilization as a result of methyl arsine formation would seem to be unlikely in aerobic light soils, but possible in soils where low oxygen tension can occur. Indeed, mobilization as a result of water logging, may well occur when the sugarcane fields are in undated during tropical storms, a common Louisiana occurrence.

The last item relates to the problem of possible contamination of aquatic ecosystems. Phosphates are known to be liberated from water logged soils, as in rice paddy culture. Arsenates behave in many fashions similar to phosphates. Mobilization of soluble arsenates, or alkyl arsines formed during anaerobic metabolism by soil microorganisms is a possibility that should be investigated. Runoff could also move arsenic, though in a bound form in silt.

Once in a bottom silt, river or lake, the methyl arsines can be expected to form during stagnation. Their accumulation has been suggested in model ecosystem studies. Therefore, standard fish and crayfish accumulation studies would be helpful.

V. RECOMMENDATIONS: Object registration

Additional Studies are required:

1. Aerobic soil studies are needed. See enclosure. (Note Ms. Critchlow please enclose pp V16 - V22)
2. Anaerobic soil studies. See enclosure (Note: Mrs. Critchlow please enclose p V22)
3. Field persistence study under actual use conditions. See enclosure (Ms. Critchlow please enclose pp V24 - V26)
4. Bound residue study. See enclosure (Ms. Critchlow please enclose pp V22-V24).
5. Runoff study. See enclosure. (Ms. Critchlow please enclose pp V-32-33).
6. Fish residue studies. Submit result of catfish and crayfish studies reported underway in 1973, (Report in Reg: 6308-91, p.28) or new studies according to enclosure pp V-37-V38)
7. If proof cannot be supplied that sugarcane is not rotated, then data pertaining to rotational crops uptake and translocation of residues is needed.

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