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To: Bob Taylor
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Registration Division (TS-767)

Carolyn K. Offutt

From: Carolyn K. Offutt, Chief
Environmental Processes and Guidelines Section
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of...

Reg./File # : 352-475
Chemical Name: Cyanazine
Type Product : H
Product Name : Bladex
Company Name : Dupont
Purpose : Review of ground water monitoring study

Action Code: 605 EAB #(s) : 70243
Date Received: 2/9/87 TAIS Code: 102
Date Completed: 4/2/87 Total Reviewing Time: 2
Monitoring study requested: x
Monitoring study voluntarily:

Deferrals to: Ecological Effects Branch
 Residue Chemistry Branch
 Toxicology Branch

REVIEW OF GROUND WATER MONITORING STUDY

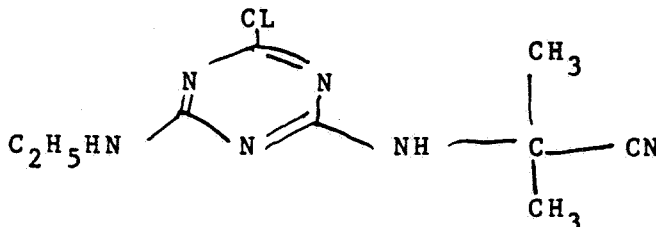
1. CHEMICAL:

Chemical name: 2-((4-chloro-6-ethylamino-1,3,5-triazin-2-yl)amino)-2-methylpropionitrile

Common name: Cyanazine

Trade name: Bladex

Structure:



2. TEST MATERIAL:

Not applicable

3. STUDY/ACTION TYPE:

Review of ground water monitoring study submitted by Dupont as part of Cyanazine Registration Standard.

4. STUDY IDENTIFICATION:

Title: Groundwater Monitoring Studies for Cyanazine and SD20258 in Four Counties.

Authors: D.R. Hoagland
Roy F. Weston, Inc.

Report No: RIR-22-017-87 (9/3/86 completed)

Submitted by: E.I. du Pont de Nemours & Co. (Inc.)
Attn.: Mrs. Billie Lynn Rash
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Issue Date: 1/9/87

Accession No: 400487-01

5. REVIEWED BY:

Matthew N. Lorber, Agricultural Engineer Matthew Lorber Date 6/23/87
Environmental Processes and Guidelines Section/EAB/HED

6. APPROVED BY:

Carolyn K. Offutt, Chief Carolyn Offutt Date 6/23/87
Environmental Processes and Guidelines Section/EAB/HED

7. CONCLUSIONS:

The study was conducted under an approved protocol, and did not deviate from the original study design. However, the approved protocol was not specific concerning the criteria for well selection: that they must be tapping the uppermost portion of affected aquifers, that they must be within a certain distance from fields known to be treated with cyanazine, that they must be downgradient from use sites, and so on. Rather, the protocol was general in content, only stating that the intention was to monitor ground water in impacted areas (see Discussion section). Subsequently, information supplied on the wells chosen indicate that the majority of them were not what could be termed "impacted" by cyanazine use. As a result, none of the 200 wells sampled twice (for 400 samples) had any cyanazine or degradate SD 20258 residues.

8. RECOMMENDATIONS:

Accept the study as meeting the requirements for a groundwater monitoring study as specified in the 1/3/85 Cyanazine Registration Standard on the condition that the registrant submit detailed well information for each well tested. This detailed information was not supplied with this report. Information requested for each well includes: depth of well, depth of water table in the vicinity of the well, proximity of well to a treated and/or corn field, and ground water gradient with respect to the well and the treated field (is the well upgradient or downgradient from the treated field). In addition to this raw data, it would be helpful if the registrant could summarize it, qualitatively and quantitatively. Retain the submitted study for future reference.

9. BACKGROUND:

A ground water monitoring study was required by the Cyanazine Registration Standard dated 1/3/85. A draft proposal entitled, "Groundwater Monitoring Program for the Reregistration of Bladex Herbicide" was prepared by Roy F. Weston and submitted to the Agency sometime in mid-1985 (no date was on the proposal, and no formal Agency review was done). Members of Shell Oil Company met with EAB representatives on 10/17/85 to discuss this proposal. Shell responded to EAB's comments made in that meeting in a letter from E.L. Hobson to R. Taylor dated 11/22/85. According to S. Cohen (personnal communication), the revisions to Roy F. Weston's protocol were accepted and S. Cohen requested that EAB's acceptance be documented by Shell in a letter to the Agency. This was accomplished in a letter from E.L. Hobson to R. Taylor dated 3/14/86 which detailed the status of studies required by the cyanazine Registration Standard including the ground water study: "A program and completion date has been

agreed with Exposure Assessment Branch and will be reported by November 20, 1986." The ^{12/85} final protocol was submitted on January 2, 1986, although it was not formally reviewed. Sampling began, as proposed in the 11/22/85 letter, in March of 1986.

10. DISCUSSION

As outlined in the accepted protocol (accepted with revisions specified in the 11/22/85 letter), two study areas consisting of two counties each were examined. In the hydrogeologically sensitive East Coast, Sussex County, Delaware, and Worcester County, Maryland, were sampled. In the moderately vulnerable Midwest study area, Champaign County, Illinois, and Jones County, Iowa, were studied. Approximately one hundred wells were sampled twice in each area, resulting in a total of four hundred samples, all of which showed no residues for cyanazine. The number of wells selected in each county was roughly proportional to the land area in each county. Specifically, a total of 70 wells were sampled in Sussex County in the March 1986 sampling period, 69 of which were resampled in the June/July 1986 sampling period. In Worcester County, 32 wells were sampled in each sampling period. In Jones County, 32 wells were sampled in the March sampling period, and 31 wells were resampled in the June/July sampling period. In Champaign County, 69 counties were sampled in the March period, and 68 were resampled in the June/July period. ←

The results of this study highlight the need for detailed ground water guidelines for large scale retrospective studies. Although the "objectives" specified in the study proposal would meet the Agency's needs, information supplied on the final wells selected (and critical information that was not supplied, but is requested of the registrant) would indicate that the study was fated not to find cyanazine residues. Each critical point will be discussed individually:

Well Depth vs. Ground Water Depth:

The approved protocol, included as Appendix C of the final report, stated, "The objective of the proposed program is to determine the occurrence of cyanazine in the first encountered potable groundwaters." and, "...it is groundwater, rather than existing well population, which is being characterized with respect to cyanazine occurrence." If that is the case, one would hope that the depth of a significant portion of wells should roughly correspond to the depth of groundwater. It has been shown that it is primarily the upper portion of surficial aquifers that is affected by leaching pesticides - that dilution and degradation result in dissipation of residues in deeper portions of the impacted surficial ground waters. Therefore, a study testing the impact of cyanazine use on the "first encountered potable aquifers" would not be complete if a significant portion of the tested wells were missing the "impacted" portion of that aquifer.

In Sussex County, the ground water is described as, "The water-table ranges from the surface to a depth of about 25 feet." The well information supplied indicates that 47 of the 70 wells in that county were greater than 50 feet deep. No further information on well depth is available, so it is not clear how deep the 23 wells less than 50 feet were. In Worcester County, the ground water is described as, "Depth to groundwater is shallow, with seasonal high water-tables ranging from the surface to a depth of 5 feet." In this county, 19 of the 31 wells were greater than 50 feet, and information on the 12 wells less than 50 feet was also unavailable. In Jones County, apparently there were no substantial surficial aquifers to tap: "The areal distribution of surficial aquifers in Jones County is depicted in Figure 5. These aquifers include alluvial and buried channel sands, glacial drift and Silurian Dolomite. The first three of these are unconsolidated quaternary deposits not commonly accessed for water supply. Based on logs from water wells within Jones County, approximately 97 percent of these wells tap the Silurian Dolomite, which underlies the quaternary deposits throughout the county." In Jones County, only 2 of 32 wells were less than 50 feet with 21 wells greater than 100 feet. A similar situation exists in Champaign County, Illinois: "...Municipal and domestic groundwater supplies are most commonly obtained from the glacial drift units, with the lower unit accounting for most of the County's water supply. Shallower drift units are not extensively utilized, though local sand and gravel aquifers of sufficient thickness occur at various locations within the county." In Champaign County, only 12 of the 69 wells are less than 50 feet, with 36 wells being greater than 100 feet.

Since depths of wells tested with respect to depth of first encountered potable aquifers were not specified, it would appear that the wells chosen for sampling were in deeper portions of the surficial aquifer. This can be verified once the registrant supplies detailed well logs, as requested in the "Recommendations" section of this data review. For the two Midwest Counties, it would appear from the descriptions supplied that there was not a great deal of potable surficial aquifer. Subsequently, the wells in these counties were probably tapping invulnerable confined aquifers.

Objective to Sample "Impacted" Wells

The protocol states that, "Areas within counties where cyanazine has been used within the past five years will be identified during county characterization. Should this information be unavailable, areas where corn has been grown within the five-year period will be used instead." The final report reiterates this objective another way by stating, "Wells were within one-quarter mile of a field in which corn had been grown within the past five years." Finally, in regard to hydrogeologic characterization, the protocol states, "Hydrogeology and geologic

data will be examined in order to ascertain depth to groundwater, groundwater flow direction, and aquifer properties". (note: it was based on these claims that the additional detailed information for each well is now being sought.) With this type of verbiage, one would hope that a significant proportion of chosen wells would be near fields with known past usage of cyanazine, and that the wells are downgradient of these treated fields. Locations of specific wells with respect to the ground water gradient and treated fields were not supplied and are being requested of the registrant. In terms of being in the proximity of known usage, the following information was ascertained: in 46 of 70 wells in Sussex County, the well owner responded "No &/or don't know" when asked if Bladex was used on the associated corn field (wherever it was); in Worcester County, 24 of 32 responded similarly; in Jones County, only 6 of 32 responded similarly; and in Champaign County, 46 of 69 responded similarly. In summary, in 60% of all wells tested, either cyanazine was not used or usage was unknown in the associated corn field. In the hydrogeologically vulnerable eastern counties, this percentage is higher at 69%.

Based on analysis of these two trends, depth of wells and the objective to sample impacted wells, it is clearly seen that it is possible to design a retrospective study that meets an acceptable protocol and yet will, by nature of the selected wells, not show any residues. Specifically, the design called for blocking off each county with discrete land areas (1-mile square sections), identifying the qualifying wells in these areas (wells tapping impacted ground waters within a quarter mile of a corn field), and then randomly selecting one from each blocked area. It is possible that the registrant purposively selected wells at this point to insure that residues would not be present (i.e., upgradient instead of downgradient from a treated field, deeper portion instead of shallow portion of impacted ground water, etc.). If the registrant did so, then this study would be deemed unacceptable and the registrant should be required to conduct a second monitoring study. Analysis of submitted detailed well records requested in this review should more clearly determine whether selected wells met the stated objectives of the study.

More than likely, however, the registrants were in fact selecting randomly from a set of qualified drinking water wells. As stated in their protocol, "...every reasonable effort will be made to eliminate purposeful bias in individual well selection, while providing confidence that the sampled well is completed in the first encountered aquifer...Available logs for wells in each section will be reviewed and a list of wells completed in the first

encountered aquifer prepared." It is likely that wells with available logs were more recently (within the past 20 years) put in, and that they were completed to deeper portions of the first encountered aquifer to insure a steady supply of water. Even if there were some wells completed to shallower portions of impacted aquifers, they would likely be in the minority and a random selection might miss them entirely, or, as in the case of this study, only a very small number of them would be selected (see earlier discussion on number of wells less than 50 ft).

The results of this study point out some important considerations for future studies of this nature:

- 1) Most existing wells used for drinking water extract from portions deep in aquifers which are somewhat invulnerable to leaching pesticides, particularly pesticides that are not "heavily" leaching pesticides. Available data on cyanazine indicates that it is a moderate leacher.
- 2) If the objective of EPA-required retrospective monitoring studies is to determine whether pesticide use has "impacted" potable ground water, then a random, statistical design will most likely not target "impacted" wells. Rather, there should be a purposive selection of wells to include only wells with the following characteristics:
 - a) verified use in associated fields should probably be higher than the 30-40% range of this study.
 - b) candidate wells should include USGS observation wells, irrigation wells, and even wells specifically put in for purposes of the study.
 - c) wells should largely be tapping the upper portions of surficial aquifers, in the downgradient direction