Terbufos Ecotox

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

OFFICE OF PREVENTION,
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

DATE: October 1, 1998

TO: Angel Chiri, CRM
Special Review and Reregistration Division

FROM: David Farrar, Statistician, EFED task leader for terbufos David Farrar
Jim Breithaupt, Fate and Exposure scientists. James Breithaupt
Environmental Risk Branch II
Environmental Fate and Effects Division (7507C)

THROUGH: Betsy Grim, Acting Branch Chief Betsy Grim 10-1-98
EFED/ERB II

RE: **Terbufos**: Responses to American Cyanamid Co. comments on the 1996 RED draft.

DP BARCODE: D225276,D227482,D248246,D248249

EFED has reviewed comments submitted by American Cyanamid Co. (ACC) in response to the 1996 EFED draft RED chapter. Documents submitted were "An Analysis of the Environmental Fate of Terbufos: A Response to EPA on the Preliminary Science Chapters of the RED" prepared by American Cyanamid, and "Ecological Risk Assessment for COUNTER® Systemic Insecticide-Nematicide" prepared by Ecological Planning and Toxicology, Inc.

On 7/28/98 EFED provided SRRD with a list of items from these documents which would be addressed. Attached are our responses for each item. As we have mentioned, a number of EFED scientists wrote responses in 1996 dealing with particular areas. This communication serves to integrate the material developed by EFED in 1996 and relate that material to the points identified in our 7/98 memo.

Regarding ecological risk (aquatic and terrestrial), we conclude that the EFED and ACC risk assessments are similar. For aquatic risk the major exception has to do with the ecological significance of farm pond size bodies of water. EFED believes that farm ponds and bodies of water similar in size to farm ponds (e.g., prairie potholes, small shallow lakes bordering rivers) are ecologically significant. These provide cover and food for waterfowl, shorebirds, snakes, turtles, amphibians and various mammals, in addition to aquatic organisms.

Regarding the terrestrial risk, EFED is not in complete agreement with all the assumptions in the material submitted by the registrant but we have come to similar conclusions. In particular as stated in our chapter "... while these studies have consistently documented acute hazard and shown an indication of potential chronic problems from the use of the 15G formulation, the extent of the effects appears to be limited to a relatively small number of species." Based on the properties of the granules it is possible that the 20G formulation is more attractive as grit than the 15G formulation; however, there is no information to confirm that one formulation or the other is actually more attractive.

In the RED chapter, EFED had expressed concerns about water quality issues for parent terbufos and the metabolites terbufos sulfone and terbufos sulfoxide. Based on the information available to us at this time, including the information from the documents submitted by the registrant (reviewed here), we do not have major concerns for water quality for *parent* terbufos. However, EFED still has major concerns about the potential of terbufos sulfone and terbufos sulfoxide to reach surface and ground water.

With regard to fate properties of terbufos, the registrant cites different values for parent terbufos for water solubility, vapor pressure, hydrolysis, and aerobic soil metabolism. Both the water solubility (15 ppm for EFED and 5 ppm for the registrant) and vapor pressure values (2.6×10^{-4} for EFED versus 3.16×10^{-4} torr for the registrant) are similar, and EFED will update its data base to use the new water solubility and vapor pressure information. However, these differences do not have any effect on our previous conclusions about the environmental fate and effects of terbufos. The differences in half-lives from hydrolysis and aerobic soil metabolism depend on the method of calculation, and EFED will continue to use the values reported in the current RED chapter.

Additional recommendations. The EFED recommends ***surface water monitoring studies based on approved protocols.*** It will be important to monitor for terbufos sulfone and terbufos sulfoxide in addition to parent terbufos. We recommend distinct monitoring designs for drinking water and aquatic effects, with the studies for aquatic effects focusing on relatively shallow water bodies.

cc Betsy Grim Jean Holmes Dennis MacLane
Denise Keehner Ed Fite

X 2 attachments

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Attachment: **Responses to registrant comments on the 1996 EFED draft RED chapter.**

The EFED has received two documents for review:

(1) An Analysis of the Environmental Fate of Terbufos: A Response to EPA on the Preliminary Science Chapters of the RED" prepared by ACC 4/18/96 (the "ACC Fate Analysis.") Cover memo J. Wrubel (Am. Cyanamid) to A. Farrell (USEPA), 4/29/96.

(2) "Ecological Risk Assessment for COUNTER® Systemic Insecticide-Nematicide" prepared by Ecological Planning and Toxicology, Inc. (The "EPT Report"), 3/14/96, with cover memo 4/3/96 J.Wrubel to A. Farrell.

Issues related to EFEDs aquatic risk assessment.

Our responses to ecological risk issues make substantial use of responses developed in 1996 by EEB (4/16/96; author Dennis MacLane).

- The EPT report states that the most sensitive tested invertebrate is *Daphnia* (LC50=0.2 ppb) and that: "The most sensitive species of aquatic invertebrates may experience a local reduction, but the total invertebrate biomass may not be reduced because of tolerant invertebrate species so that the food base for fish is unaffected."

The RED document may be modified to include additional toxicity data which support that, in fact, Terbufos is highly toxic to most aquatic organisms. In addition to the low values of 0.3 ppb for *Daphnia* (crustacea) and 0.2 ppb for mysid (crustacea), a volume of ecotoxicity results by Meyer and Ellersieck (USFWS) reports values of 0.2 ppb for *Gammarus* (crustacea) and 1.4 ppb for *Chironomus* (insecta). These values have not been incorporated in the RED although EFED does view data from that source as acceptable. Finally, the comment focuses on biomass, whereas species composition can also be ecologically significant. In the incidents, Terbufos killed fish, snakes, and crayfish.

- The EPT report states (Section 6.2.1, p. 56) that USEPA has relied on a deterministic exposure model that does not address variability in exposure. Aquatic incidents are said to be related to unusual combinations of circumstances promoting runoff, including slope, soil condition, and weather.

No changes to the EFED chapter are suggested: As indicated on page 45 of the EPT report, the registrant is talking about results obtained with the GENEEC model. The current assessment is based on the Tier II procedure using PRZM and EXAMS. The Tier II approach takes into account slope and soil properties by assuming a "reasonable worst case" scenario. Variation in meteorological conditions is accounted for by use of time series of actual meteorological measurements. The meteorological data are used probabilistically in that the concentrations used in risk assessment are values exceeded with an estimated frequency of once per 10 years.

- The rebuttals point out that exposure estimates based on a "farm pond" scenario are not necessarily appropriate for addressing impacts on larger bodies of water such as rivers and lakes.

In accordance with current EFED practice the RED chapter has been revised to include a 'risk characterization' section. That section includes discussion of variation among kinds of aquatic habitat. The degree of dilution is the most obvious factor determining the vulnerability of a given kind of water body. As indicated in the revised chapter, exposure for some kinds of surface water bodies may be similar or higher than exposure of farm ponds as assessed using the current model.

Relatively high-exposure situations may have as much or more ecological significance as farm ponds. A scenario similar to a farm pond may be appropriate or under-protective for prairie potholes (common in some agricultural areas) or seasonal pools, which are important habitat for some species.

Terbufos can cause fish mortality in ponds larger than the one acre pond used in EFED's exposure scenario. In one incident the pond was 4 to 5 acres of surface with an average depth of 5 to 6 feet.

- The EPT report suggests (Section 6.2.3, p. 59) that farm ponds are artificially stocked with game species and have limited significance in maintaining the genetic diversity of populations of native species.

No changes to the EFED chapter are suggested. The comment applies specifically to fish or other exploited species. In addition to these species farm ponds are likely to be significant as habitat for naturally-occurring vertebrates including amphibians, snakes, turtles, birds, and mammals. Many of these will migrate overland between farm ponds and other aquatic habitat so that farm ponds contribute to wildlife populations for natural water bodies. Regarding the fish, we are concerned to some degree about impacts on fish that have been stocked.

- The rebuttals point out that farm ponds may be frequently disturbed by human activities.

No changes are suggested for the EFED chapter: The EFED does not regard the presence of stressors other than pesticides as uniformly supporting lesser (or greater) concern for pesticide effects. Presence of other stressors could sometimes be associated with elevated sensitivity to pesticides.

- When compared to the 85th percentile of STORET values, the EEC's are below the level of concern (pages 48 and 55).

No changes of the EFED chapter are suggested: Frequencies based from STORET are not reliable for quantitative exposure assessment without careful evaluation of the circumstances of the measurements, if it all. STORET values may be particularly deficient for evaluation of acute risk, because (as noted by the registrant) acute exposures of concern may occur in a narrow window in space and time. STORET measurements will not necessarily be targeted to regions where a pesticide is used. If untargeted STORET values exceed levels toxic to aquatic life, such exposure levels may be widespread.

- The EPT report provides a variety of comments on the fish kill incidents for terbufos.

No changes of the EFED chapter are suggested: The registrant does not appear to disagree with EFED's interpretation of specific incidents, but rather focuses on generic issues such as the difficulty of establishing causality and the environmental conditions where incidents occur. We agree that fish kills often result from factors other than pesticide exposure including eutrophication, turbidity, and ammonia poisoning, and we agree that fish kill incidents are particularly likely after heavy rains. The EFED continues to believe that the record of incidents for Terbufos indicates that aquatic impacts are widespread.

Issues related to EFEDs assessment of risk to birds and terrestrial wildlife.

- The ACC document points to a lack of reported terrestrial incidents for terbufos.

The frequency of reported incidents does not provide a reliable indication of actual wildlife mortality caused by a pesticide because we expect that pesticide related mortality will often not be noticed, not attributed to the pesticide, or not reported. Also, as stated in the 1996 EEB response, "Of more relevance, field studies designed to detect mortality find mortality."

Since the rebuttal documents were submitted there has been a particularly severe incident involving mortality to Swainson's hawk in Texas. As indicated in our most recent RED draft chapter, EFED tentatively concurs with the registrant that this incident occurred under a combination of circumstances that is probably unusual; however, if similar incidents occur then that tentative conclusion should be revisited. Also, we have one additional avian incident record that has not been shown to have resulted from misuse.

- The registrant relies to some degree on terrestrial field studies reportedly conducted by Knapton and Mineau, which have not been submitted for review by the Agency.

As we indicated in our 7/28/98 memo, we have not seen these studies. Based on subsequent communications with SRRD (particularly 8/20/98) it is our understanding that this study has never been submitted for review in the Agency.

- "Viewing all the field studies as a whole the evidence suggests that the birds at greatest risk ... may be ground-feeding insectivores and omnivores such as robins, particularly in wet years" (p. 33). Noting an apparent difference in mortality for such species in two years, Tank et al. speculate that higher mortality in one year may be due to relatively wet conditions that drove earthworms to the surface (p. 28). On that basis the cover level concludes that "The reduction in robin survival was related to extreme rainfall conditions that brought robins to the corn fields to feed on soil invertebrates, such as earthworms, that were at or near the soil surface because of soil saturation." Evaluation of data from the Breeding Bird Survey is said to show no population declines for such species.

The EEB response written in 1996 concurred that there was evidence from field studies that a minority of species would be affected by the 15G formulation. Other parts of the argument (e.g., the relation of high robin mortality to high rainfall) are based on very limited information. Supposing that there is some relationship between rainfall and pesticide-related mortality of robins and other ground feeding species, the registrant has not established that conditions wet enough to cause significant mortality are so rare as to be of limited concern.

The registrant argues that population data shows no declines for those species they consider to be at most risk (robins and other ground feeding species). EFED does not regard the absence of negative trends in the population data considered by the registrant as establishing no concerns. In particular, a local population reduction caused by a pesticide may not be reflected in the population trend information for a larger region.

- The EPT analysis includes a discussion of the properties of terbufos granules as these properties may affect attractiveness to birds, arguing (p. 10) that: "The clay granules used for COUNTER 15G® may not be viewed by birds as an adequate source of grit. The inert material used for COUNTER CR® is rather soft and does not look or feel like silica particles and also may not be viewed by birds as adequate for grit."

Besides pointing to properties of granules that *might* affect attractiveness to birds as grit, no information has been submitted supporting that one formulation or the other is actually more attractive. Additionally, birds may be exposed by routes other than consumption of granules for grit. As noted in the 1996 EEB response "Field studies show birds can be killed and intoxicated by applications of terbufos. Also, they show mammals can be affected. Therefore, birds and mammals have been exposed even if by a route other than being mistaken for dietary grit." Also: "The breakdown of the granule may add to the risk in contaminating food by allowing inadvertent distribution of the terbufos onto [soil organisms]."

The risk characterization in the EFED chapter can be revised to include additional material on the properties of terbufos granules, with particular reference to how those properties may affect attractiveness as grit.

- The EPT analysis presents extensive discussion of the risk from ingestion of invertebrate prey items, concluding that exposure concentrations would not usually be lethal.

Estimation of terrestrial exposure is subject to considerable uncertainty. EFED's review of field studies for terbufos has concluded that they demonstrate avian mortality.

- The EPT analysis comments (Section 4.1.2) on uncertainties associated with the use of LD50/ft2.

The issues raised are generic and not specific to terbufos. Exposure of terrestrial animals may occur through multiple pathways. Information is generally not available to quantify the individual pathways or their combined effect.

- The ACC argues (p. 14) that the available evidence does not indicate soil concentrations higher in turn-row areas, where granules may be spilled.

The specific high exposure associated with turn row areas would more likely be from granules on the surface rather than from the soil. If there is a trail of exposed granules in a turn row area and the soil samples do not happen to be collected under the trail, it is not clear that the elevated exposure would be detected.

Miscellaneous issues related to environmental fate and transport and water quality.

- The registrant argues (in the ACC Fate Analysis) that formation of the sufloxide and sulfone in soil is not a 1:1:1 process, but conservatively 1:1/2:1/4. These ratios appear to be based on peak concentrations observed in aerobic soil metabolism studies (see p. 14), i.e., for each degradate the concentration rises to a peak and then declines, with the peak concentration of the sulfoxide about 50% of the initial concentration of parent and the peak concentration of sulfone being about 25% of parent.

The EFED concurs that in at least some studies formaldehyde and carbon dioxide are important degradates. The EFED agrees that in aerobic soil metabolism studies maximum degradate were observed at 50% and 25% of the initial concentration of parent. The EFED will review the wording in the current RED chapter with regard to consistency with these observations.

The EFED has not calculated EECs for terbufos metabolites in surface water. The observations that the concentrations of the sulfone and sulfoxide did not reach the initial concentration of parent terbufos is useful information but it is not clear how EECs would be affected without doing the model runs. Observations related to peak concentrations do not take into account the fact that the degradates are more persistent and mobile that parent terbufos. Consequences of higher persistence include greater availability for runoff and greater persistence in the receiving body of water.

- "Contrary to what was presented in the draft science chapters, the predominant terbufos metabolites found in laboratory studies were carbon dioxide and formaldehyde" (p. 4)

The registrant is correct in saying that the predominant terbufos degradates are carbon dioxide and formaldehye <u>in some studies.</u> In the hydrolysis study, terbufos sulfoxide was only a minor degradate, and no terbufos sulfone was observed. Also, in the aerobic soil metabolism study, EFED noted that terbufos sulfoxide and sulfone were observed at maximum concentrations of approximately 50 and 25% of applied terbufos. However, EFED notes that in aerobic soil, the pathway of degradation goes through the sulfoxide and sulfone metabolites to carbon dioxide. As mentioned previously, the sulfoxide and sulfone metabolites are relatively persistent.

- The registrant argues that terbufos degrades more rapidly than the RED chapter indicates.

Differences in the half-life values for hydrolysis and aerobic soil metabolism result from different calculations applied to the same data. EFED will continue to use the values reported in the current RED chapter. For hydrolysis, the registrant used the same data set as EFED (MRID 00087694) but calculated a half life of 3 days (versus a value 15 days calculated by EFED). The registrant appears to be referring to the DT_{50}, which is the observed time of 50% degradation, whereas EFED used linear regression through all the sampling intervals.

For aerobic soil metabolism, EFED reported a value of 27 days, while the registrant reports values of 7-10 days (MRID 00156853). The differences in method of half-life calculation was the reason for the different half-lives. EFED notes that to calculate half-lives of 7, 10, and 27 days using simple linear regression, the 0-30 day, 0-60 day, and 0-180 day sampling intervals must be used in the regression model, respectively. The r^2 values for these calculated half-lives are 0.95, 0.99, and 0.72, respectively. EFED also notes that the 30-day interval took into account only the steep part of the decline curve, and the 60-day interval only took into account 1 interval where degradation appeared to slow down. The effect of only selecting intervals where the rate of degradation is rapid leads to a short calculated half-life, and ignores other data points that are meaningful. However, EFED notes that the DT_{50} (observed half-life) for parent terbufos was 4-7 days in the aerobic soil metabolism study. This would indicate that the sulfoxide and sulfone degradates are primarily the active ingredient(s) during a growing season.

The registrant also cites a complete sediment:water system aquatic half-life of 0.2-6.8 days that the Agency has not seen to date. EFED normally uses information on aquatic metabolism in surface and ground water models.

- The registrant cites Goolsby and Battaglin (1995) as demonstrating that terbufos is one of the least frequently detected pesticides in surface water (see particularly page 25). In particular they say that terbufos has not been detected in the NAWQA unit with the White, Missouri, and Ohio rivers.

As of our most recent review of the USGS NAWQA data, there have been 17 detections of parent terbufos in surface water at concentrations ranging from 0.01 ppb to 0.56 ppb. (This includes a single detection in the Albermarle-Pamlico study unit with an estimated value of 0.01 ppb, awaiting QA/QC confirmation.) Parent terbufos has now been detected twice in the White river (at concentrations of 0.013 ppb and 0.16 ppb). The information from NAWQA data in the RED chapter will be updated. We expect that if terbufos sulfone and terbufos sulfoxide had been looked for in the NAWQA studies, those metabolites would have been found more frequently than parent terbufos.

The comparative information displayed by the registrant does appear to suggest terbufos is not among the most frequently detected pesticides. However, the most frequently detected pesticides were herbicides with relatively high volume use. If SRRD believes that a comparative analysis like this will be important, we should do comparisons using the most recent data. Also, it may be desirable to include information on the relative volume of use.

- The registrant asserts that ground water detections reported in the EFED chapter have been discounted.

Based on information submitted by the registrant, EFED now considers ground water detections of parent terbufos in Iowa to be uncertain; however, EFED still considers the detections in Indiana and in the NAWQA database to be valid.

EPA's Pesticide in Ground Water Data Base documents 4,224 samples in twelve states tested for terbufos residues in ground water. Four states reported detections in a total of 11 wells. Iowa had seven of the eleven reported detections which came from five municipal well systems (public drinking water supply systems). Thirteen Iowa wells were sampled for terbufos sulfone and no residues were detected.

The registrant has disputed the detections of terbufos in Iowa municipal wells and provided a memorandum from Susan Wayland of EPA to William A. Stellar of Cyanamid dated 1/10/89, concluding that the findings were either not confirmed or were attributed to point sources. The registrant provided a copy of the report from which these high detections were taken. In the report, the detections of up to 11 ppb in Iowa were questioned by the study authors themselves, who believe that the lab misidentified terbufos in the 1985 Little Souix study (Kelly, Iowa Department of Natural Resources, attached as 9/18/98 fax from registrant). The problem with the detections may be related to the EPA contract lab methodology or to a short-term spike that may have occurred from unusually heavy rains immediately following application of terbufos. Upon consideration of the additional information provided by the registrant concerning the detections of terbufos in Iowa, EFED cannot draw any conclusions from the data. EFED does not expect measurable levels of parent terbufos in ground water from application in most years.

The two detections exceeding the HA of 0.9 ug/L were located in Indiana. The first detection, and highest in the U.S., was from a spring in Indiana with 20 ppb, and the second was from a domestic well with 12 ppb. Little additional information was available concerning the detections.

According to the USGS NAWQA database, there have been 3 detections of parent terbufos in ground water from a total of 3,333 samples. These were two confirmed detections of 0.008 ug/L and one estimated detection (0.012 ug/L). The detection limits of the analytical method ranged from 0.013-0.02 ug/L.

- The registrant says that none of three restricted use triggers (detection, mobility, and persistence) would be met for parent terbufos, while for t. sulfone and t. sulfoxide mobility and persistence triggers would be exceeded only based on laboratory measurements (p. 24).

With the implementation of FQPA, EFED is no longer evaluating pesticides using the mobility and persistence triggers for ground water as used in the draft of the 1994 terbufos RED. There is still a concern about potential mobility and persistence of the degradates under certain conditions. However, there is not sufficient evidence at this time to require a ground water label advisory or a ground water study. Current information on detection is reviewed above.

- The EPT report cites (p. 48) runoff studies for granular pesticides (Wauchope, 1978) and terbufos specifically (Felsot, 1990) as indicating that only a small percentage of the pesticide applied will tend to be lost in runoff.

It is necessary to place field measurements of percentage runoff in perspective by considering frequency, representativeness of the studies, and toxicological information. For assessment of acute aquatic risk, the EFED is concerned with occasional events involving high runoff. Therefore we use probabilistic calculations to account for the frequency of runoff events exceeding a given magnitude, for a 'reasonable worst-case' site. We do not consider these procedures overly protective in light of the available field information (generated by Wauchope and others). The only papers by Felsot reviewed in the RED chapters were published before 1990.

CYANAMID

American Cyanamid Co. Agricultural Research Division, P.O. Box 400, Princeton, NJ 08543-0400

FAX

Date: 9/18/98

Number of pages including cover sheet: 24

To

JIM BREITHAUPT

OPP/EFED

Re: TERBUFOS

Phone: 703-305-5925

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CC:

From: U.S. Plant Federal Registrations

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✓	[✓ Wrubel, John]	(609)716-2378

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REMARKS: ☐ Urgent ☑ For your review ☐ Reply ASAP ☐ Please comment

Good Morning Jim,

As per your telephone request, please find following:

1) Nov. 25, 1986 letter from AmCy to EPA

2) Iowa drinking water report referenced in the above letter.

Please note pages 6 and 16-17 in the report.

Have a good weekend.

Regards, John

CYANAMID

ATTACHMENT II

American Cyanamid Company
Agricultural Research Division
P.O. Box 400
Princeton, NJ 08540
(609) 799-0400

November 25, 1986

Dr. Gerald F. Kotas
Environmental Protection Agency
WH550
401 M Street, S.W.
Washington, DC 20460

Re: COUNTER(R) systemic
insecticide-nematicide
Terbufos: Aqueous Hydrolysis
and Photolysis; Soil Metabolism

Dear Dr. Kotas:

As we discussed via telephone on the referenced topics, reports enclosed are as follows:

> CL 92,100 COUNTER(R) Insecticide: Metabolism Studies of ^{14}C-Labeled CL 92,100 in Hydrolytic and Photolytic Environments.
>
> COUNTER(R) Insecticide, terbufos (CL 92,100): Water Photolysis

These reports demonstrate that only traces of terbufos sulfoxide (CL 94,301) and terbufos sulfone (CL 94,320) are formed as photolytic/hydrolytic products and that terbufos in water is primarily degraded to small nontoxic fragments, e.g. to formaldehyde (65-70% of the total).

I have also enclosed a copy of the Environmental Fate and Exposure Assessment Review conducted in conjunction with the Terbufos Registration Standard.

As you will note in the last paragraph on page 3, the reviewer concluded "The potential for terbufos to contaminate groundwater is low because terbufos degrades rapidly in soil and its residues are immobile."

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CYANAMID

Dr. Gerald F. Kotas
COUNTER(R) Insecticide

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November 25, 1986

I have also included the most recent report from the state of Iowa because a previous report from that state had reported finding terbufos in the 1985 Little Sioux study (Kelley and Drustrup, 1986). The enclosed report states on page 6, "However, terbufos was not detected and there is reason to believe that the lab misidentified terbufos in the 1985 Little Sioux study (Kelley and Drustrup, 1986)". In addition, Wisconsin has assayed approximately 1000 groundwater samples and has never detected terbufos.

I have also enclosed a literature article titled "Insecticidal Activity and Persistence of Terbufos, Terbufos Sulfoxide and Terbufos Sulfone in Soil" by R. A. Chapman and C. R. Harris. In this study terbufos was applied to two soil types at 3.4 kg a.i./Hectare which is three times the recommended label rate. The conversion to terbufos sulfoxide and sulfone and their rates of degradation in the two soil types are shown on page 539.

American Cyanamid Company does not believe there is any potential for terbufos to leach into groundwater and further we see no need for additional monitoring.

If you require any further data feel free to contact me at your convenience.

Very truly yours,

William A. Steller

William A. Steller, Manager
U.S. Regulatory Affairs

/sd
Enc.

PESTICIDES IN IOWA'S DRINKING WATER

Richard D. Kelley

Iowa Department of Natural Resources
Henry A. Wallace Bldg.
Des Moines, Ia. 50319
October 1986

ABSTRACT

The collective and cooperative work of resource agencies in Iowa over the last five years has shown that many commonly used pesticides are leaching through the soil and into ground water. The most commonly used pesticides are now routinely detected in the state's primary source of drinking water. Recent investigations suggest that over 25 percent of the state's population is now exposed to pesticides through consumption of their drinking water. Although concentrations of the various compounds are relatively low, usually less than 2 ug/l, total pesticide concentrations have been known to exceed 60 ug/l. The implications to human health from ingestion of pesticides at these concentrations are not clear.

Public water supply systems rely heavily upon ground water for their source of water in Iowa. However, many of these supplies must obtain their water from aquifers which represent very sensitive hydrogeologic settings. In sum, 33% of all water supply wells sampled in various environments have exhibited pesticide residues. In some geographic regions over 50 percent of all public water supply wells are experiencing problems. And, recent studies have shown that the best treatment techniques are unable to remove pesticides from the source water.

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Introduction

Pesticides (herbicides and insecticides) have become an integral part of today's farming operations. Iowa's farmers treat over 97 percent of the state's corn and bean acreage each year (Wintersteen and Hartzler, 1986). The use of these chemicals appears to have prevented the catastrophic loss of crops to pests. However, this chemical use has also resulted in the appearance of some pesticides in the state's primary sources of drinking water.

In recent years there has been a concerted effort by researchers in Iowa to better understand pesticide contamination of both surface and ground water. The detection of pesticides in surface streams has always been anticipated because of the strong affinity many of these compounds have to be absorbed by organic matter, clay particles and/or colloids. However, unless soils could directly enter ground water systems it was generally believed that pesticides, especially those which were not persistent, would not be found in ground water. We now know that infiltration is the primary pathway by which pesticides move into ground water. And, we now find that many pesticide, regardless of persistance or affinity for absorption, can move by infiltration into the ground water.

Pesticides are being found in ground water more extensively than anticipated, albeit in low concentrations. Much of the research in Iowa, and hence much of the attention to this problem, has been focused on northeast Iowa, particularly in the Big Spring Basin. Such contamination, however, is clearly occurring throughout Iowa and the corn belt. Currently, this contamination is primarily found in relatively shallow aquifers, but this may only be a function of time. Few long-term data exist, but Iowa studies suggest that pesticide residues in ground water are likely increasing, perhaps analogous to the rise in nitrates of a decade ago.

As with all non-point source pollution the scope of the problem is large. And, because exposure to commonly used pesticides calls into question issues of public health, considerable public attention and concern are focused on the problem.

Analytical Protocol

The University Hygienic Laboratory (UHL) is Iowa's state laboratory. Outside of a few special projects, all pesticide analyses in Iowa are conducted by UHL. The procedures outlined in this section apply to all pesticide analyses, including both research projects, as described by George Hallberg in this conference, and the monitoring of public water supplies.

All field samples were collected in one-liter glass jars with teflon lids. Samples were chilled, as needed, and generally returned to the lab within 48 hours. Standard EPA methods were used for extraction. All multi-residue analyses were performed using gas chromatography, with different polarity columns, with additional periodic confirmation by GC/MS.

Nearly all of the pesticide analyses reported here were preformed by UHL. The exceptions being the samples from the Little Sioux River SOC Survey (Kelley and Wnuk, 1986), which were analyzed by the U.S. EPA, and some splits of samples analyzed by U.S. EPA and industrial laboratories. A few particular details about the UHL procedures are outlined below (Kelley et al.,1986). Prior to 1986 all sample were analyzed by gas chromatography using a split injection system with dual capillary columns and electron capture detection. The two capillary columns used were a DB-5 and a DB-1701. Each sample with a potential positive was also analyzed with packed columns, using a nitrogen-phosphorous detector.

All of the pesticides, except atrazine, were quantitated using the electron capture detector. Atrazine, because of its poor electron capture response, was quantitated using the nitrogen-phosphorous detector.

Beginning in 1986 samples were analyzed by gas chromatography using a spit injection and two capillary columns with two nitrogen-phosphorous detectors.

Of the most widely-used pesticides in Iowa, most can be adequately detected using these multi-residue scans. Four commonly used pesticides require separate extractions and analyses; the benzoics (chloramben and dicamba) and phenoxy (2,4-D) herbicides require an acid treatment; the thiocarbonate (butylate) also required seperate treatment prior to 1986. Separate one liter samples were taken for analyses of these four pesticides (chloramben, dicamba, 2,4-D and butylate). Prior to 1986 all analyses also included results for various chlorinated hydrocarbon pesticides and related products (e.g., aldrin, DDT,DDE, etc.).

Concurrently, with the field samples, routine calibration analyses are conducted using standards for alachlor, atrazine, carbofuran, cyanazine, fonofos, metolachlor, metribuzin, pendimethalin, trifluralin, and others as needed. All the analyses reported in this paper include the major-use pesticides, the chlorinated hydrocarbon pesticides and other related modern pesticides. A lesser number of samples were processed for the phenoxy and benzoic herbicides in some of the research projects -- all samples from public water supplies and SOC surveys include these, but only about 5 percent of the total samples from the research projects at Big Spring and Floyd/Mitchell counties include these analytes. Butylate was only analyzed for in the Little

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Sioux River SOC Survey and the Treatment Effectiveness Survey and in <5 percent of the research project samples. No analyses were performed for metabolites, or breakdown products, of these pesticides prior to 1986.

As noted, all of the basic data reported here, were verified and quantitated from at least four different column-GC analyses. Detections that can not be quantitated are reported as less than detection. For that reason the words detectable and measurable are used interchangeably in this paper. In addition to reference standards, natural well water samples were spiked with atrazine, cyanazine, alachlor, metolachlor, and metribuzin, and routinely analyzed to monitor recoveries. Blank samples of organic free water are also analyzed to ensure the absence of interfering compounds which could be incorrectly identified as pesticides.

Spiked samples from 1985 gave the following average percent recoveries (and standard deviations): atrazine, 91(9.4); alachlor, 85(12); cyanazine, 79 (18); metolachlor, 97 (5.2); and metribuzin, 88 (11). "Blind" duplicates of field samples were also submitted to the lab on about 10 percent of the samples. These replications show coefficients of variation of: 3% for concentrations <2 ug/l; <5% for concentrations between 2 and 10 ug/l; and, about 5% above 10 ug/l. In addition, unreplicated positives, at or near detection limits have occurred in <2% of the samples.

Pesticide Use

Over 70 million pounds of active ingredient are applied to Iowa's landscape annually (Gianessi, 1986). Table 1 shows the primary pesticides applied to Iowa row crops, as determined from the 1985 pesticide use survey. The compounds listed in Table 1 account for 90 percent of the herbicides and insecticides used in Iowa.

Public Water Supplies

There are 2,161 public water supplies in the State of Iowa. Eight hundred twelve of these supplies are municipal systems and another 35 are rural water systems. Only 58 of the state's water supplies rely upon surface streams for their source of water. Ground water is the primary source of water for public water supply systems and the sole source for private supplies (about 140,000). Approximately, 1,750,000 people or 65 percent of the state's population are served by ground water systems.

Iowa has a number of bedrock aquifers that produce high quality water in large quanity. These bedrock systems approach the surface in the eastern half of the state.

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Table 1. Major pesticides applied to Iowa cropland. Listed in alphabetical order. (Wintersteen and Hartzler, 1986)

HERBICIDES

Common Name (Typical Trade Name)

alachlor (Lasso)
atrazine (AAtrex)
bentazon (Basagran)
butylate (Sutan+)
chloramben (Amiben)
cyanazine (Bladex)
dicamba (Banvel)
EPTC + safening add. (Eradicane)
metolachlor (Dual)
metribuzin (Lexone/Sencor)
trifluralin (Treflan)
2,4-D

INSECTICIDES

carbofuran (Furadan)
chlorpyrifos (Lorsban)
ethoprop (Mocap)
fonofos (Dyfonate)
permethrin (Ambush)
phorate (Thimet)
terbufos (Counter)

In much of western Iowa, bedrock aquifers are deeply buried by clay-rich glacial till, and/or have naturally high total dissolved solids concentrations. Therefore, bedrock aquifers in western Iowa are not utilized as drinking water sources to the degree they are in other parts of the state. Alluvial sand and gravel deposits, located along major stream valleys in western Iowa, offer large quantities of water with good natural quality, coupled with inexpensive drilling and well construction costs. These alluvial aquifers are widely used by municipalities, rural water districts, and individual rural residents.

Monitoring Public Water Supplies

Pesticides were first detected in shallow alluvial ground water systems and public water supplies in Iowa in 1974 (Richard et al.,1975). Researchers from Iowa State University looked at the occurrence of atrazine, DDE and dieldrin in surface streams, shallow ground water and the finished water of several large cities in Iowa. Atrazine, DDE and dieldrin were found in most of the water samples tested and, of the three, the concentrations of atrazine were the highest. Further, the water treatment processes used by the supplies monitored were shown to be ineffective at reducing or eliminating these pesticides from the water, including treatment with activated carbon.

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Aside from the research of the Iowa Geological Survey in northeastern Iowa, drinking water supplies in Iowa were not monitored for commonly used pesticides again until the mid-1980's (Hallberg and Hoyer,1982; Hallberg et al.,1983; Hallberg et al.,1984). In 1984, based on the findings of the Geological Survey, the Iowa Department of Water, Air and Waste Management (now the Department of Natural Resources; DNR) decided to include pesticide analyses as part of a synthetic organic monitoring survey of public water supplies in Iowa (Kelley,1985). This was to be the first of two surveys of public water supplies in the state to determine the extent of ground water contamination from 64 synthetic organic compounds, including 35 commonly used pesticides (no analysis was made for butylate). These became known as the SOC surveys.

The 1984/85 SOC survey found measurable concentrations of one or more pesticides in 40 percent of the wells monitored (Table 2). The most frequently detected compounds were pesticides. The findings of the 1984/85 survey tended to support the findings of earlier researchers. The results indicated that atrazine was likely to be found year round; shallow ground water was the most susceptible to contamination (there was an inverse relationship between well depth and the presence of a pesticide); and, that pesticides present in a public water supply's source were not likely to be removed by standard treatment processes -- including activated carbon filters.

In the spring of 1985 a second survey of public water supplies was conducted (analytes for this study were the same as the first SOC survey, but included butylate). This survey focused on municipal systems in the Little Sioux River valley of northwestern Iowa (Figure 1). The findings of this survey mirrored the 1984/85 survey. However, the data suggested that shallow ground water systems may be affected, at least for short periods of time, by any pesticide, even those compounds with rapid decay rates. Terbufos, which is believed to decay rapidly, was reported in a number of wells in the survey (Kelley and Wnuk,1986).

The detection of terbufos in the Little Sioux SOC survey was of concern to both the state and the manufacturer, American Cyanamid. Working with American Cyanamid and with the assistance of the U.S. EPA, expanded monitoring efforts were begun in the basin by DNR in the spring of 1986. With one exception, all of the wells monitored were found to have pesticide residues present. Further, every sample collected, with one exception, was found to have pesticides present, including the pre-plant samples collected in mid-April (Table 3). However, terbufos was not detected and there is reason to believe that the lab misidentified terbufos in the 1985 Little Sioux study (Kelley and Drustrup, 1986). The detection of terbufos is discussed later in this paper.

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Table 2. Summary of frequency and range of concentrations. 1984/85 and Little Sioux SOC surveys of public water supplies.

PESTICIDES	# OF SUPPLIES CONTAMINATED	# OF WELLS CONTAMINATED	RANGE ug/l LOW	HIGH
atrazine	17	27	0.1	13.0
cyanazine	8	9	0.1	1.4
alachlor	4	5	0.09	11.0
metolachlor	4	6	0.32	7.8
metribuzin	4	6	0.29	1.1
fonofos	3	3	0.11	0.9
terbufos**	5	7	0.3	7.3
sulprofos**	1	2	1.3	1.4

Multiple residues were detected in 13 wells.

** Confirmation poor, refer to text for further discussion.

The U.S. Geological Survey (USGS) and UHL have systematically monitored public water supplies in Iowa for several years. Currently, the USGS/UHL data includes 203 wells from 80 public water supplies. The wells that are monitored represent a variety of hydrogeological settings. Table 4 summarizes the data from the USGS/UHL monitoring program. Tables 5,6 and 7 summarize these data by various hydrogeologic settings.

It is evident from the USGS/UHL data that there is a relationship between the depth of the well and the detection of pesticides. The data also illustrates the general coexistence of nitrate and pesticides, although, in some settings pesticides occur without nitrate. Researchers at the USGS and Iowa Geological Survey have made similar observations regarding the relationship between well depth and pesticides, as well as denitrification in some settings (Thompson et al., 1986; DeTroy, 1986; Libra et al., 1984; Hallberg, personal correspondence).

As noted, monitoring of public water supplies has suggested the inability of standard treatment practices t remove common pesticides. In 1986, in an effort to better assess water supply treatment effectiveness, the DNR monitored 34 of the state's 58 surface water supplies. All 34 supplies collected finished water samples and 14 of the supplies collected intake water samples as well. In cases where the supply sampled both intake and finished water, collection of the finished water sample was delayed to account for retention time in the treatment process.

Table 3. 1986 Little Sioux River Study
Maximum concentrations

PESTICIDES	MAXIMUM VALUE ug/l
atrazine	10.0
cyanazine	2.8
metolachlor	8.7
alachlor	.39
metribuzin	3.7
carbofuran	1.2
dicamba	.12

Surface water supplies where chosen because they represent the most effective and sophisticated treatment systems in the state. Treatments ranged from simple rapid sand filtration to granular activated carbon filtration.

Thirty one of the 34 supplies monitored had detectable residues of pesticides in the finished water (Table 6). Further, 28 of the supplies had multiple residues. The pesticides detected (and the number of positive samples) included: atrazine (45), cyanazine (38), metolachlor (33), alachlor (29), carbofuran (15), metribuzin (5), 2,4-D (4), dicamba (2), butylate (1), trifluralin (1). All 10 pesticides, for which positive values were reported, were detected in finished water samples. And, in only one case was a substantial reduction in concentration observed after treatment (ie. atrazine fell from 21 ug/l to 6 ug/l). The treatment technique employed in this case was addition of powdered activated carbon. Concentrations decreased slightly (typically, .2 ug/l) in 35 observations, and increased (typically, 1 ug/l) in 14 observations(Wnuk,1986).

The data from the treatment effectiveness study strongly suggest that pesticides entering the treatment plants are in soluble fraction and not attached to soils. Removal of sediment failed to substantially reduce the pesticide concentrations. More importantly, the data clearly shows that regardless of the treatment technique employed, public water supplies can not effectively remove pesticides from their source water.

Geographic Distribution

Although much of the research, and thus much of the attention to the problem of pesticides in ground water, has been focused in northeast Iowa, in terms of areal extent the problem is widespread. Clearly the collective data of Iowa's resource agencies show that contamination is occurring throughout the state and probably across the corn belt.

Table 4. Summary data from USGS/UHL Public Water Supply monitoring 1982 - 1985

Total Wells Sampled (N)	# of Detections	% of Detections	Multiple Residues # (%all)	% of Detections Multiple Residues
203	39	19%	9 (4%)	23%

PESTICIDE	% DETECTION	MEAN VALUE ug/l	RANGE OF VALUES LOW (ug/l)	HIGH
alachlor	10	0.80	0.16	2.30
atrazine	90	0.40	0.12	2.10
chloramben	3	1.70	1.70	
cyanazine	13	0.46	0.11	1.60
dicamba	8	0.91	0.07	2.30
metolachlor	8	0.37	0.10	0.71
metribuzin	8	0.21	0.13	0.36
trifluralin	3	0.05	0.05	

Detections constitute 24% of all wells less than 150 feet deep.

Table 5. Summary of pesticide data -- Alluvial Aquifer Wells USGS/UHL 1982 - 1985.

Total Wells Sampled (N)	# of Detections	% Wells Positive	Multiple Residues # (% all)	% of Detections Multi-Residues
91	24	26%	(7%)	25%

ALLUVIAL WELLS WITH POSITIVE RESIDUES (Detections, March -- December)

Mean Well Depth(ft)	Range of Depth(ft)	Mean,s.d. NO3 (mg/l)	Range NO3 (mg/l)
40	16 - 90	20 , 22	<0.5 - 98
ALLUVIAL WELLS WITH NO DETECTIONS			
58	28 - 190	13 , 18	<0.5 - 63

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Table 6. Summary of pesticide data -- Pleistocene Aquifer Wells USGS/UHL 1982 - 1985.

Total Wells Sampled (N)	# of Detections	% Wells Positive	Multiple Residues # (% all)	% of Detections Multi-Residues
70	7	10%	1 (1.4%)	14%

PLEISTOCENE WELLS WITH POSITIVE RESIDUES (Detections, May -- December)

Mean Well Depth(ft)	Range of Depth(ft)	Mean,s.d. NO3 (mg/l)	Range NO3 (mg/l)
56	36 - 105	17 , 12	2.4 - 39
PLEISTOCENE WELLS WITH NO DETECTIONS			
128	28 - 485	6 , 12	<0.5 - 45

Table 7. Summary of pesticide data -- Bedrock Aquifer Wells USGS/UHL 1982 - 1985.

Total Wells Sampled (N)	# of Detections	% Wells Positive	Multiple Residues # (% all)	% of Detections Multi-Residues
42	8	19%	2 (5%)	25%
Carbonate Bedrock Aquifer Wells				
32	8	25%	2 (6%)	25%

CARBONATE WELLS WITH POSITIVE RESIDUES

Mean Well Depth(ft)	Range of Depth(ft)	Mean,s.d. NO3 (mg/l)	Range NO3 (mg/l)
96	54 - 140	34 , 25	0.5 - 54
CARBONATE WELLS WITH NO DETECTIONS			
286	60 -2120	9.5,13.5	<0.5 - 38
SANDSTONE WELLS WITH NO DETECTIONS			
454	60 -1538	3.2,5.4	<0.5 - 16

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Figure 1 shows the locations where pesticides have been detected in Iowa's ground water (exlusive of the detailed studies in the Big Spring basin and Floyd-Mitchell counties).

On a statewide basis a total of 356 wells have now been sampled (Table 9). Two hundred ninty eight of these wells are public water supply wells. One hundred seventeen (33%) of the monitored wells; eighty (27%) of the public water supply wells have been found to have measurable pesticide residues present. Three hundred thirty four samples have been collected from public water supplies since 1982. Of these samples, 34 percent, or 113 samples, have had measurable concentrations of pesticides present. Twenty one percent of these samples were detections of multiple resedues.

Table 8. 1986 Surface Water Supply Monitoring
Maximum concentrations.

	MAXIMUM CONCENTRATIONS ug/1	
PESTICIDES	INTAKE	DISTRIBUTION
atrazine	26.0	24.0
cyanazine	20.0	17.0
metolachlor	10.0	21.0
alachlor	9.3	8.8
trifluralin		.13
2,4-D	.3	.15
carbofuran	17.0	14.0
dicamba	1.2	1.4
butylate		.27
metribuzin	.89	.31

Geological Distribution

A direct relationship exists between well depth and the appearance of pesticides in ground water. This relationship is evident in both, the data from individual research projects and the data from public water supplies. Clearly, shallow wells, less than 50 feet in depth are more susceptible to contamination from the leaching of land applied chemicals. However, as noted earlier the movement of these compounds to deeper formations may be only a matter time.

Table 10 summarizes the collective data of individual research and public water supplies (exclusive of 1986) by hydrogeologic setting. While 62 percent of wells finished into shallow bedrock and 39 percent of alluvial wells were found to have pesticides present, only 14 percent of the wells finished in pleistocene aquifers were experiencing problems. Of wells finished in deep formations only 4 percent of the wells and 9 percent of the samples were found

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Table 9. Summary of Collective Monitoring Data.

TOTAL WELLS N	# WELLS POS (%)	TOTAL SAMPLES N	# POS N(%)	# MULTI RESIDUES	% DETECTS WITH MULTI RESIDUES
356	117 (33%)	548	211(39%)	44	21%

Table 10. Summary of Collective Data by Hydrogeologic Setting.

TOTAL WELLS N	# WELLS POS (%)	TOTAL SAMPLES N	# POS N(%)	# MULTI RESIDUES	% DETECTS WITH MULTI RESIDUES
		ALLUVIAL AQUIFERS			
148	58 (39%)	181	76(42%)	21	28%
		PLEISTOCENE AQUIFERS			
90	13 (14%)	92	15(16%)	3	20%
		SHALLOW BEDROCK ans KARST			
71	44 (62%)	211	114(54%)	20	9%
		DEEP BEDROCK			
47	2 (4%)	64	6(9%)	0	--
Big Spring Ground Water					
--	--	256	249(97%)	63	25%

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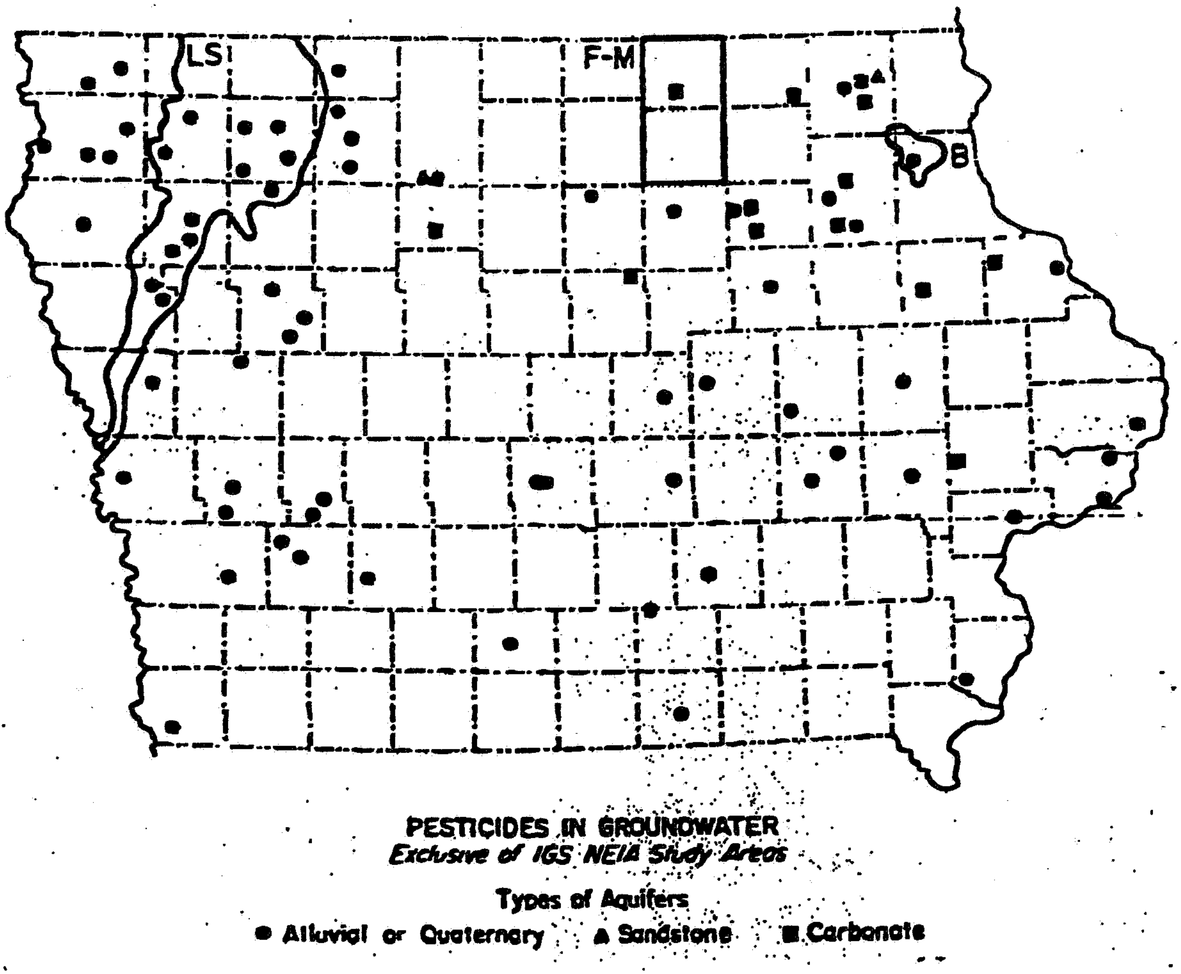
to have pesticides (and these are thought to be related to local problems).

The work conducted on municipal wells along the Little Sioux River suggests that in certain hydrogeologic settings the problem may be more acute for public water supplies than the collective data indicates. Eighty-eight percent of the municipal wells finished in the alluvium along the Little Sioux River had measurable residues of pesticides present. One possible reason for the large number of shallow municipal wells experiencing problems may be their tendency to disrupt the stratification of contaminants that appears to be occurring within the alluvial system. Certainly, the preliminary data from the work conducted in 1986 in northwestern Iowa suggests that this is happening (Thompson, C. personal correspondence, Kelley and Drustrup, 1986).

Figure 1. Pesticides In Ground Water. Locations where pesticides have been detected in ground water, exclusive of IGS studies in NE Iowa.



Distribution of Contaminants

In total, 10 herbicides and 3 insecticides have been detected in ground water in the limited sampling conducted to date (13 herbicides have been detected in the finished water of public water supplies, inclusive of surface systems). These constitute the most widely used pesticides in Iowa. On a yearly basis, periods or peaks occur with regard to the number of compounds that are likely to be detected. These peaks generally take place in conjuction with late snow melt and rainfall in late March and early April; the early summer rains of June and July; and, during the period of fall recharge in October and November. These peaks are evident in the summary of months in which various compounds were detected, listed on Table 11. Multiple pesticide residues have been detected in individual wells throughout the year, but multiple residue occurrences peak in June and July. As noted though, in various locations nearly all the herbicides have been detected in winter or spring samples prior to new applications. This all suggests that many of the herbicides are persisting in the subsoil and hence are present to be leached by the water moving through the soil during winter or spring recharge.

In general, the typical concentration at which any one of these compounds is detected is low, usually less than 2 ug/l. Although, the maxima for the most widely used herbicides may range as high as 15 to 20 ug/l. Those pesticides that have been detected very infrequently tend to degrade very quickly (e.g., 2,4-D) or have strong affinities for absorption. Atrazine is by far the most commonly detected pesticide and it is also the herbicide that has had the greatest use across the state, for the longest period of time (Table 12).

Table 11. Month In Which Pesticide Was Detected.

Compound												
2,4-D*			X									
sulprofos**					X							
terbufos**					X							
chloramben*							X					
trifluralin						X	X					
dicamba*			X			X	X					
fonofos				X		X	X	X				
metolachlor			X	X	X	X	X				X	
alachlor			X	X	X	X	X	X	X	X	X	
cyanazine			X	X	X	X	X	X	X	X	X	
metrobuzin			X	X	X	X	X	X	X	X	X	X
atrazine	X	X	X	X	X	X	X	X	X	X	X	X
Month	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC

(* see text; ** confirmation poor see text)

Table 12. Summary of All Pesticide Data.

PESTICIDE	TYPICAL VALUE(ug/l)	MAXIMUM VALUE(ug/l)	% OF DETECTIONS
alachlor	1.5	16.6	15%
atrazine	.6	13.0	72%
chloramben*	---	1.7	<1%
cyanazine	0.7	13.0	13%
dicamba*	0.8	2.3	2%
metolachlor	0.6	9.0	9%
metribuzin	0.8	4.4	10%
trifluralin	0.1	0.2	1%
2,4-D*	---	0.2	<1%
fonofos	0.4	0.2	2%
sulprofos**	1.3	1.4	<1%
terbufos**	5.4	12.0	5%

* Analyzed by different methods, thus N not the same as for other herbicides.

** Only detected in one study, confirmation poor.

Table 13. Pesticide and nitrate concentration from 10 case studies in vicinity of ag-chemical Dealership (Hallberg,1986). ND=not detected.

PESTICIDE	MAXIMUM CONCENTRATIONS POOLS OR SOILS(ug/)	 WELLS OR SEEPS(ug/l)	LOCAL BACKGROUND(ug/l)
atrazine	70,000	600.0	ND-1.6
alachlor	270,000	580.0	ND-1.3
cyanazine	225,000	36.0	ND-0.3
metolachlor	270,000	250.0	ND-0.8
metribuzin	52,000	28.0	ND-0.2
trifluralin	1,000+	0.2	ND
carbofuran	1,000+	ND	ND
fonofo	1,000+	1.3	ND-0.3
FUMIGANTS			
EDB	(10	1.0	ND
1,2-DCE	to	2.0	ND
Carbon Tet	100)	66.0	ND
Chloroform		4.0	<1.0
NITRATE (mg/L)		20-117	4-9

The detection of two insecticides merits some discussion. The insecticide sulprofos is not registered for use in the state of Iowa. Yet, it was detected in two public water supply wells in northwestern Iowa. This represents the only incident of its detection in the state. Likewise, the detection of terbufos in seven public water supply wells in western Iowa marks the only detection to date of this compound. Unlike sulprofos however, terbufos is registered and widely used in Iowa.

While terbufos is persistent in soil (up to 23 weeks), it is believed to decay rapidly once in solution in water. Thus, the appearance of terbufos in ground water was surprising to both the state and manufacturer. At the time of its detection it was suggested that it may reflect a rather fortuitous combination of climatic conditions and sample collection prior to the passage of a sufficient period of time to allow for decay. In 1985, 60 percent of the corn in the study area was planted in a seven day period prior to sampling (rootworm insecticides are commonly applied at the time of planting). Over two inches of rain fell in the study area during the three days sampling occurred. Therefore, the detection of terbufos may have been attributable to heavy rainfall and macropore flow at the time of application (and monitoring). Certainly, if that is true, then it strongly suggests that shallow ground water systems respond almost immediately to local climatic events. Indeed, a detection of metribuzin in the Iowa River Study was associated with a similar set of circumstances; first time application and an early summer rainfall/recharge event (DeTroy,1986). Such occurrences suggest that the movement of some pesticides into and through shallow ground water systems may be rapid, sporadic and highly dependent upon local weather events.

Unfortunately, as noted earlier, UHL did not provide analytical support on the Little Sioux SOC survey. The EPA contract lab clearly demonstrated its ability to correctly identify spiked samples of terbufos, however, the lab procedure for confirmation on the samples submitted for analyses was very poor. Thus, the possibility arose that the lab had errorred in identifying terbufos.

In 1986, American Cyanamid asked DNR if the state would work with them on a monitoring project along the Little Sioux River in an effort to identify their product in ground water. At the same time, the U.S. EPA also provided support for the monitoring of public water supplies in the study area. Municipal wells were monitored from mid-April through the end of July. Samples were collected about every ten days and submitted to UHL for analyses. Splits of the first, second and fourth rounds of samples were submitted to American Cyanamid's lab in Princeton, New Jersey. As noted earlier, pesticides were detected in every sample, from every well, with one exception. However, no terbufos, or its breakdown product sulfone, were found. Unfortunately, climatic, cropping and land management practices (20% of the land was out of production in 1986) were not the same in 1985 and 1986. At this point, it is not clear if terbufos was correctly identified in the 1985 survey. However, given the unstable nature of the compound when in solution and the fact that it has not been detected elsewhere in Iowa, it seems probable that the EPA contract lab did error in its identification of terbufos in the 1985 study. The 1986 study suggest that under the rather typical conditions, where planting is conducted over a period of several weeks and rainfalls are not intense, terbufos will not move to the ground water.

Local Problem Areas

As noted earlier, observed concentrations are generally low. Certainly, these concentrations are below those one might expect (and have been observed) from the spillage or improper disposal of these compounds. The potential health effects from low concentrations of pesticides leaching from farm fields to sources of drinking water are unclear. However, situations are arising that are much more serious, and have caused the closing of both public and private water supply wells. These situations have all occurred in the immediate vicinity of local farm chemical dealerships. Table 13 summarizes data from 10 such case studies where ground water contamination has been found. It should be pointed out that these situations have turned up inadvertently (from routine monitoring of public water supplies, for example). These were not cases where anyone was clearly suspected of negligence or improper handling of any chemicals.

The pesticide concentrations found in pools of water or the soils in loading, handling and equipment rinsing areas are relatively high. In these areas the chemical concentrations in the local ground water have increased 10-fold for nitrate (NO3) and 100 times for pesticides, over the background concentrations of the area. Also, other pesticides and chemicals, which have not been routinely detected elsewhere, are leaching to ground water around these sites; e.g. -- EDB and carbon tetrachloride. Grain fumigants from these sites have been suggested as a possible factor in the relatively frequent detection of trihalomethanes in Iowa's ground water.

Public Health

Pesticide concentrations, which are being routinely detected in Iowa's ground water, are below acute toxicity levels and generally below levels assumed to contribute to long-term, chronic problems such as cancer and immunosuppression. However, chronic toxicity and carcinogenicity are legitimate concerns considering the low concentrations presently found in ground water and the potential for long-term and widespread exposure to the public.

Work conducted in Sweden has found the formation of human soft tissue sarcomas to be linked to exposure to 2,4-D and 2,4,5-TP (Hardell and Sandstrom,1979). Recent work at the University of Iowa has indicated that the post World War II population of Iowa farmers has a higher incidence of certain cancers than other farm populations or the state as a whole (Burmeister et al.,1983). This coincides with major changes in agricultural practices, among which was the development of agriculture's heavy use of pesticides. This work is supported by related studies in Nebraska and Illinois which offer similar findings (Blair and Thomas, 1979., Bueschinq, D., 1986).

Beyond concerns over cancers which may result from direct exposure, there are also many uncertainties involved with the combinations of pesticides and their metabolites that occur in relation to other environmental factors. For example, pesticides in ground water nearly always appear in conjunction with high nitrates. With triazine herbicides the possibility exists for combination with N-compounds to form nitrosamines, most of which are carcinogenic or mutagenic, The implications of the coexistence of these chemicals in drinking water with microbial pathogens and with other man-made compounds or metals are unknown. The potential widespread, but unforeseen, exposure of the public to pesticides through drinking water (in combination with other routes) and the possible synergistic interactions with other contaminants, may necessitate a wholesale reevaluation of risk assessment. Certainly, if we continue to weigh the risk to public health against the economic benefit of the compound then, at the very least, we must begin to recognize that there is an economic benefit to health as well. The long-term cost of treatments associated with adverse public health may very easily out weigh any short-term monetary gain from putting the public at risk.

Because we are just beginning to find pesticides in Iowa's ground water ,and, cancers and other chronic disorders may require 20 years or more to manifest themselves; the impact to human health (and resulting economic cost associated with those illnesses) from exposure to low concentrations of one or more pesticides and/or break down products remains to be seen. We do know however, from the limited sampling to date of a little more than 60 public water supplies with pesticide residuals in their source water (as well as the finished water for some), that we are possibly placing at risk approximately 785,000 people, or 27 percent or the state's population. And, about 20 percent of these are likely to have been exposed to multiple pesticide exposures.

Discussion

Although modern agriculture has relied upon heavy pesticide usage in the past 30 years, it has only been within the last five years that research has begun to systematically monitor for pesticides in ground water. Only recently have

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low concentrations of pesticides been detected in Iowa's shallow ground water. And, although pesticide registration requires detailed and extensive toxicity data, there is still a great deal that is not known about how pesticides behave in the environment and the threat they may pose to human health. Ongoing research projects, as well as numerous proposed projects, should provide much of the information we currently need. However, there are a great many questions to be answered. Besides questions concerning the implications to human health from long term exposure to low concentrations of one or more pesticides or their break down products, there are numerous questions regarding the fate of pesticides in the environment and the economic and social implications of both continued use and changes in use.

The collective data of research and public water supply monitoring provides a definition of the problem between land application of pesticides and ground water quality. We are now at a point where we must question the wisdom in continuing to use the same arguments that led us into this situation to justify continuation of present practices. As long as the current generation of pesticides are applied to land under our current set of agricultural practices, within the vagaries of climatic conditions, losses to the environment will continue.

Ground water quality problems related to agriculture will only be resolved through a holistic approach to agricultural management and research. We must couple our standard concerns for soil conservation and surface water quality with the need to protect ground water. And, an emphasis will have to be placed on the development and production of new, environmentally safe, approaches to pest control. Resolving the problem is going to require the concerted efforts of every segment of society.

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