# REPORT

on the review of

"TECHNOLOGY TRANSFER FOR THE

PESTICIDES CHEMICAL INDUSTRY"

by the

ENVIRONMENTAL ENGINEERING COMMITTEE

SCIENCE ADVISORY BOARD

U. S. ENVIRONMENTAL PROTECTION AGENCY

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## BACKGROUND

Effluent limitations guidelines for the pesticide chemicals category, as required under the Clean Water Act, were proposed on November 30, 1982. The proposed guidelines cover 137 pesticide active ingredients classified as non-conventional pollutants. When EPA proposed the guidelines, data were not available for treatability under the technology-based standard-setting approach required by the Clean Water Act.

In order to develop the requirements for pesticide compounds for which data did not exist or where "treatment performance was considered inadequate," the concept of technology transfer was applied.

In this context, "technology transfer" is based on the assumption that both "type" of treatment technology and the "level" of effluent quality or level of reduction in effluent amount can be established for a compound by judicious comparison with "type" and "level" experience with other compounds of similar physical and chemical properties. The approach taken groups pesticide compounds by priority pollutant matrix to arrive at subcategories. In each subcategory, the least-treatable compound is identified, then the effluent guidelines and standards are set for the entire subcategory on the basis of the known or predicted "type" and "level" of technology.

The Environmental Engineering Committee (EEC) of the Science Advisory Board was asked to review the methodology and assumptions used in the transfer of "type" and "levels" of technology.

The EEC formed a subcommittee consisting of Dr. J. William Haun (Chairman), Mr. Richard Conway, Dr. Raymond Loehr, Dr. Charles O'Melia, and Mr. George Green to carry out the review. The Subcommittee was assisted by Dr. Richard G. Luthy, Consultant to the SAB, Dr. George Baughman of EPA's Athens Environmental Research Laboratory, Dr. William Mabey, SRI International, and members of EPA's regulatory staff.

GENERAL COMMENTS

The paucity of data was further aggravated in this review by the claims of confidentiality asserted by the industry in many reports of the performance of treatment systems. In view of the time constraints, the Agency stated that it could not provide declassification of data that might have been helpful in a quantitative review. These data gaps are of particular significance in the application of the methodology to the identification of the "least-treatable" compound in a subcategory.

In a similar vein, all treatment process trains considered in the methodology were limited to combinations of only two processes, selected from the four of primary interest: carbon adsorption, hydrolysis, chemical oxidation, or biological oxidation. Other combinations may exist which would alter the conclusions, but there is no information which would justify reaching beyond the submitted data.

As a result of the constraints, this review must be characterized as essentially qualitative in nature. In a few instances, as Dr. Luthy's report points out, quantitative information is available to increase confidence in the judgments made. However, this review is essentially a qualitative assessment of the reasonable validity of the methodology and assumptions. The Committee feels that the burden is on the discharger to provide quantitative information where that qualitative assessment is called into question.

FINDINGS

1. The data available to the Committee are scanty and fragmentary.
2. The technology transfer approach is basically sound as a starting point and can provide a logical means to initially predict the behavior of related pesticides in treatment systems.
3. In a qualitative sense, the methodology and assumptions involved in the technology transfer approach are reasonable and can be tested in a limited way against available results.
4. Application of technology transfer to quantitative prediction of treatability of pesticide compounds is subject to large uncertainties. Such application cannot be scientifically supported. At best, these estimates of treatability are a weak substitute for actual treatment data. These limitations particularly apply to the selection of least-treatable compounds.

RECOMMENDATIONS

1. Treatability research in real wastewater systems needs to be emphasized. A few valid experiments would accomplish much to allow better evaluation of the quantitative capabilities of treatment technologies.
2. The EEC observes that the Effluent Guidelines Division (EGD) does not always know of the existence of data within the

EPA itself which might be useful in its work. A more systematic approach to improved communication within EPA is needed.

3. The Committee feels that the burden is on the discharger to provide quantitative information where the qualitative assessment is called into question.

4. The Agency should review the general issue of confidentiality of data. Procedures to shorten the time period for declassification should be developed in order to make data available for use in the scientific review process in a timely fashion. Regulated industries should balance the competitive benefits of claims of confidentiality against enhanced operation of the scientific review. No guidelines are suggested, only that the benefits to a more open process should be evaluated in the light of the fact that the burden of proof is on the discharger.

5. A computer-aided literature search should be conducted to seek new, pertinent information on the more difficult-to-treat pesticides. The search should cover both treatability and physical-chemical properties.

6. EPA has not used correlations based upon physical-chemical properties, such as solubility and vapor pressure, of pesticides as one way of estimating treatability. It is recommended that this be done.

APPENDIX A

# REVIEW OF THE EPA PROTOCOL FOR TECHNOLOGY TRANSFER FOR THE PESTICIDE CHEMICALS INDUSTRY

Report to the
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Science Advisory Board
Environmental Engineering Committee

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June 24, 1983

## Introduction

The purpose of this report is to review the appropriateness of the procedures employed to establish effluent limits and standards for non-conventional pollutants for the pesticides chemical industry. The report focuses on an evaluation of the procedures employed to establish limits and standards for pesticides for which full-scale operating data were not generally available. The procedures employed by the EPA to achieve this objective have been termed "technology transfer."

## Discussion

The EPA has identified 137 pesticides as non-conventional pollutants. These pesticides are comprised of 27 classes of pesticide compounds, where class refers to a listing of pesticides on the basis of parent compound or principal functional group. Examples of classes of pesticides are carbamates, amides, and metallo-organics.

Effluent regulations for non-conventional pesticides are required by law to be promulgated on the basis of subcategories. Subcategories have nothing whatsoever to do with class of pesticide. Subcategories are established on the basis of priority pollutant matrix in which the non-conventional pesticides are found. Thus, a wastewater from a particular subcategory may contain several pesticides from various classes.

The EPA has indentified thirteen subcategories for purposes of regulating non-conventional pesticides. Furthermore, within each subcategory the EPA has proposed two types of regulations. One type of regulation is referred to as indirect discharge. Indirect discharge means that the wastewater is discharged for subsequent treatment prior to release to a watercourse. Typically this may refer to discharge to a municipal sewage treatment works. Hence the purpose of the indirect discharge regulation is to establish pretreatment guidelines. The terminology "effluent standard" is applied to pretreatment guidelines.

The other type of regulation promulgated by the EPA is that for direct discharge. Direct discharge means that the wastewater is discharged to a watercourse. The terminology "effluent limit" is applied to direct discharge guidelines.

It is important to recognize that the EPA must operate within a special legal constraint when establishing effluent limits and standards. The legal constraint dictates that all non-conventional pesticides within any subcategory must be regulated at the same standard or limit. In other words, no matter how many or what classes of non-conventional pesticides are found in any particular subcategory, all pesticides within the subcategory must be regulated at the same level, i.e. pound of pesticide discharged per pound of pesticide produced. This approach for establishing effluent levels can be viewed as based on treatment technololgy, rather than based on effects to the environment.

A question now arises: If all non-conventional pesticides within a subcategory must be regulated at the same level, what should be that level? The answer to the question is that effluent levels will be promulgated on the basis of best available treatment technology. Hence, if best available treatment technology is applied to a particular pesticide in a particular subcategory, one may estimate an effluent achievable. This effluent achievable can be expressed as lb/1000 lbs. The process can be repeated for each pesticide in the subcategory, and a listing may be made in order of least treatable compound to most treatable compound. The most treatable compound will have a small numerical value of lb/1000 lbs, while the least treatable compound will have largest value of lb/1000 lbs. Since the EPA is required by law to mandate that all pesticides within a given subcategory be treated to the same level, the level to which all pesticides must be treated in that subcategory will be goverened by that value of lb/1000 lbs identified for the least treatable compound.

An important phrase in the above paragraph is "estimate an achievable effluent". The procedures which have been used in this process can be summarized as follows:

1. The EPA reviewed a large body of information. This included data from full-scale operating facilities as well as that from pilot plant and bench scale tests. Some information was available from prior field sampling for purposes of priority pollutant screening. Some data were supplied by industry. Much of the available full-scale and pilot scale data were proprietary, and the EPA maintained confidentiality in its reports.

2. The EPA reviewed available treatment data in comparison to a target level of treatment of 0.00129 lb/1000 lbs. This level served as a benchmark from which to judge the quality of available treatment data. The value of 0.00129 lb/1000 lbs had been established previously in BPT standards for both priority and non-priority pollutant pesticides. There was an exceptionally large data base from which this value was derived. It was judged to be an acceptable and reasonable treatment objective.

3. Available treatment data for non-conventional pesticides were compared to

the 0.00129 lb/1000 lbs standard. If a pesticide in a particular treatment process could be reduced to less than 0.00129 lb/1000 lbs, then it was decided that no additional treatment was economically achievable, and 0.00129 lb/1000 lbs became the treatment standard or limit. None of the least treatable pesticides were within this limit.

4. If removal performance for a particular pesticide in a treatment process gave a value higher than 0.00129 lb/1000 lbs, then the design and operation of the treatment process were evaluated. If it were judged that the design and operating criteria for the treatment plant were adequate, then the higher value was accepted. If the design and operating criteria were judged to be inadequate, then the treatment performance data were rejected, and the results were not used in establishing achievable effluent criteria for purposes of identifying the least treatable compound.

It happened that for the majority of the indentified least treatable compounds, full-scale operating data were not available. Therefore, for purposes of identifying the least treatable compound in each subcategory, it was necessary to make inferences from other sources of information such as pilot-scale or laboratory-scale tests. Some of this information was available for tests with actual wastewater; in other cases only clean water, or synthetic wastewater, test data were available. In a few instances no test data were available for the identified least treatable compound. In these cases it was necessary to make inferences regarding behavior of the compound during treatment on the basis of physical and chemical properties of the compound in relation to another compound for which there was treatment data. Since these evaluative activities required a combination of subjective and objective analysis, it was asked of the Science Advisory Board to review the procedures employed by the EPA and to comment on the adequacy and validity of the methodology for technology transfer and the reasonableness of the value for achievable effluent.

## Approach

In preliminary review of documents supplied by the EPA, it became apparent that it was not feasible, or adequate, to assess the procedures involved in technology transfer on the basis of general, programatic descriptions. It was judged necessary to evaluate particular information on the non-conventional pesticides, and to make an independent evaluation of the procedures on a case-by-case basis. It was recognized that this would become a large, cumbersome task to perform for all 137 non-conventional pesticides. Therefore, it was suggested that the review focus on those pesticides which had been identified as least treatable pesticides. It is appropriate that a review assess the criteria developed for establishing effluent achievable levels for the least treatable pesticides, since these pesticides establish the treatment levels for all pesticides within a given subcategory.

There are thirteen subcategories, and each subcategory may have an indirect discharge standard and a direct discharge limit. Hence, it is possible that twentysix non-conventional pesticides could be categorized as least treatable pesticides. However, the list of thirteen subcategories is reduced to six subcategories when certain subcategories are eliminated from evaluation owing to considerations such as no wastewater being generated, or no non-conventional pesticides being regulated, or the manufacturing process consisting of re-packaging. In addition, for two of the remaining six categories it happened that the least treatable pesticide for indirect discharge was the same as for direct discharge. This process of elimination reduced the total number of pesticides to ten compounds which were to be evaluated for methodology employed in technology transfer.

In review of the EPA documents it is apparent that four types of treatment technologies are invloved in technology transfer. These are: granular activated carbon adsorption, chemical oxidation, hydrolysis, and biological oxidation. For this reason the evaluation of technology transfer is limited to these four treatment technologies. A manufacturer is not restricted to use of any of these four treatment technologies for satisfying proposed effluent regulations. Rather, a manufacturer is required to achieve the effluent quality which is predicted to be attainable by use of one or more unit operations under consideration in technology transfer.

The following discussion reviews the methodology employed for technology transfer for the ten least treatable non-conventional pesticides. The pesticides are discussed in no particular order other than to discuss first those compounds for which the data base is strongest, based on full-scale data with actual process wastewater.

## Review

Fensulfothion (Subcategory 5, Direct Discharge)

This is a phosphorothioate pesticide which is treated by hydrolysis (pH = 10-12, temp >50°C, time = 2.5 hours) at full-scale to a level of 1 mg/l (0.00167/1000 lbs.). The plant at which this pesticide is produced declares a proprietary percent removal through biological treatment, although large dilution in final effluent precluded verification because of analytical detection limit. Therefore, removal during biological treatment could not be estimated reliably, and the direct discharge limit was set at the pretreatment level of 0.00167 lb/1000 lbs.

A review of this approach suggests that there is no difficulty with accepting the proposed treatment level, although an assumed nominal value for per cent removal during biological treatment could have been imposed.

Profluralin (Subcategory 2, Direct Discharge)

Profluralin is a nitro pesticide that is treated at one manufacturing facility by biological oxidation to a level of less than 1.62 mg/l (<1.05 lb/1000 lbs.). This was judged to be an unacceptable pesticide removal system. The effluent limit proposed for profluralin was based on transfer of activated carbon adsorption technology for the pesticide trifluralin.

Trifluralin is treated at full-scale by granular activated carbon adsorption to achieve 0.13 lb/1000 lbs. The wastewater at this plant contains other pesticides and priority pollutants from three pesticide manufacturing processes. The treatment level for profluralin was taken to be 0.13 lb/1000 lbs.

The treatment level proposed for profluralin is judged to be reasonable because:

1. Both the profluralin and trifluralin process wastewaters are reported to contain similar priority pollutants, although it is noted that no information was provided on the level of priority pollutants and other contaminants in these wastewaters.

2. Profluralin and trifluralin have similar molecular weights (347.3 and 335.5 respectively) and both have water solubilities less than 1 mg/l.

3. Profluralin and trifluralin have similar chemical structures. Both have a parent molecule comprised of 2-6-dinitro-4-trifluoromethyl-aniline. The only difference is the substitution of one of two propyl groups on the trifluralin aniline-nitrogen for a cyclopropylmethyl group. This change is likely to have minimal effect on the adsorptive properties of profluralin compared to trifluralin.

Propazine (Subcategory 10, Indirect and Direct Discharge)

Propazine is a triazine pesticide with a water solubility of 5 mg/l and molecular weight of 229.7. It is manufactured at two plants. One plant in this subcategory removes propazine by activated carbon treatment, but the conditions under which the plant are operated were judged by the EPA to be less severe than those recommended in BAT regulations or those employed in other systems in the industry. The other plant in this subcategory has a biological oxidation system, and the removal efficiency for propazine across the biox system was used for estimating direct discharge levels following pretreatment.

Removal of triazine presticides is accomplished at full-scale at two plants by means of hydrolysis, and at three plants by means of granular activated carbon adsorption. This information was employed for establishing effluent standards for propazine.

Atrazine, another triazine pesticide, is removed at full-scale at a plant not in this subcategory to a level of less than 1 mg/l by granular activated carbon adsorption. This plant treats comingled wastewater from other triazine manufacturing processes. Another plant, also not in this subcategory, removes the related pesticide cyanazine at full-scale to less than 1 mg/l by hydrolysis. These data were used to predict removal to a level of 1 mg/l for propazine using treatment by either activated carbon adsorption or hydrolysis.

It is noted that the half-life of cyanazine is 30 hours at pH = 1.5 and 25°C, while that for atrazine is 80 hours at pH = 1.0 and 25°C. The structural similarity of atrazine and propazine suggests that propazine may also undergo slower hydrolysis than cyanazine. Nonetheless, by analogy with atrazine, it would appear that hydrolysis of propazine may be feasible by operating at elevated temperature and extremes of pH. For example the half-life of atrazine is reported to be reduced from 80 hours at 25°C and pH = 1, to 3.3 hours at pH = 0.5 and 40°C. These considerations indicate that technology transfer for hydrolysis of propazine is reasonable if a treatment system is designed with flexibility to control pH and to maintain elevated temperatures.

The technology transfer for the case of activated carbon adsorption is reasonable, based on consideration of solubility and chemical structure. The only difference in structure between atrazine and propazine is that propazine contains a propyl substitution in a location where atrazine contains an ethyl substitution. This reduces the solubility of proprazine to 5 mg/l from 30 mg/l for atrazine. The structural change should have no detrimental effect on adsorption characteristics. In fact, it should tend to enhance adsorption.

One of the plants that produces propazine treats its effluent by granular activated carbon adsorption. The operating characteristics of this plant are compared below with the plant treating atrazine and with EPA proposed design criteria:

| | Contact time, min. | Flow, gpm/ft$^2$ |
|---|---|---|
| Propazine (full-scale) | 18 | 5.6 |
| Atrazine (full-scale) | 19 | 3.6 |
| EPA Design | 600 | 0.5 |

This comparison suggests that the design criteria will be adequate to reduce propazine to 1 mg/l.

In conclusion, it appears that appropriate application of hydrolysis or activated carbon treatment technology can justify the proposed indirect discharge standard for propazine. The direct discharge limit for propazine is justifiable based on full-scale biological oxidation experience.

Alachlor (Subcategory 2 - Indirect Discharge)

This is an amide type pesticide (MW=269.8, solubility = 240 mg/l) manufactured at two plants. One plant uses gravity separation prior to discharge to a POTW, the other plant uses biological oxidation to achieve 10.3 mg/l (0.5566 lb/1000 lbs). Treatment levels at both of these facilities were judged unsatisfactory.

The treatment level for alachlor was established by transferring activated carbon treatment technology. The compound used for the technology transfer was propachlor, another amide type pesticide but with somewhat lower molecular weight (MW = 211.7) and higher water solubility (700 mg/l) than alachlor.

Propachlor is treated by activated carbon adsorption at full-scale at a third plant. This wastewater contains propachlor, some reaction products, and other priority pollutants. The percentage removal of propachlor at this plant was reported to be greater than that observed in laboratory activated carbon adsorption studies conducted by A.D. Little. The A.D. Little study used synthetic water and found 99.8 percent removal. The lower percentage removal for propachlor observed in the A.D. Little study was used to compute effluent standard for alachlor.

It is noted that both alachlor and propachlor are acetanilide-structurally based pesticides. Alachlor has two ethyl groups on the aromatic ring while propachlor does not. Also, alachlor has different functionality branching from the nitrogen, i.e.

methoxy rather than isopropyl. These differences in structure result in lower solubility for alachlor as compared to propachlor. The structural differences are not judged to be sufficient to result in detrimental adsorption characteristics for alachlor as compared to propachlor, in fact, lower solubility for alachlor suggests a tendency towards enhanced adsorption properties.

The effluent standard proposed by the EPA appears reasonable in view of no additional information, as well as in consideration of the structural similarity of alachlor and propachlor and lower solubility of alachlor compared to propachlor and in consideration of the success with treating propachlor successfully at full scale.

Maneb (Subcategory 3, Direct Discharge)

Maneb is a metallo-organic pesticide manufactured at two plants. One plant previously employed a metal separation or chemical precipitation process, along with biological oxidation prior to direct discharge. However, removal efficiencies in this system are not available.

The direct discharge limit was based on treatment studies performed by Research Triangle Institute. Granular activated carbon adsorption studies were performed on actual wastewaters from two manufacturers. Presumably these samples were from the two plants that manfacture maneb. Both wastewaters could be treated to less than 0.15 mg/l. This was achieved even after 88 bed volumes for one of the wastewaters. These results were judged to be attained under operating conditions (i.e. contact time and flow loading) that were no more restrictive than EPA recommended criteria; and thus a pretreatment level of 0.15 mg/l was recommended.

The same Research Triangle Institute study showed fifty percent reduction of maneb in biological treatment of combined wastewater from several metallo-organic manufacturing processes. The biological oxidation studies were performed with raw wastewater diluted one to ten with municipal wastewater. It is noted that the biological oxidation studies were not performed on pesticide wastewater pretreated by granular activated carbon adsorption. However, it is believed that had the raw pesticide wastewater been pretreated by granular activated carbon adsorption, the pesticide loading to the biological oxidation facility would have been less than that obtained by 1:10 dilution. In this respect, the removals obtained by biological oxidation in the Research Triangle Institute studies represent a conservative estimate of pesticide removal that might be obtained with less concentrated influent. The only reservation in this argument is that municipal wastewater provides a suitable environment for growth and maintenance of microorganisms, thus caution is required in selecting design and operating criteria for biological treatment of pesticide effluents from the Research Triangle Institute investigations.

In summary the above results provide reasonable basis from which to establish effluent standard and limit for maneb in absence of any full-scale data.

Ziram (Subcategory 3, Indirect Discharge)

Ziram is a metallo-organic pesticide manufactured at two plants. One plant treats its process wastewater by evaporation/crystallization with 0.23 mg/l (0.0213 lb/1000 lbs) in condensate prior to discharge to a POTW. The other plant uses biological oxidation followed by granular carbon adsorption; however no performance data were available from this facility.

The treatment level for ziram was established at 0.15 mg/l for granular activated carbon treatment by technology transfer with the compound maneb. This was justified by the following arguments:

1. Ziram and maneb are metallo-organic dithiocarbamate pesticides. Maneb is a straight chain molecule comprised of repeating sequences of a parent functional compound containing manganese. Ziram contains zinc in the form of a dithiocarbamate; its molecular weight is 305.8. It is noted that no information on the true molecular weight of maneb was provided, apparently because this pesticide is comprised of a repeating series of a parent compound.

2. The solubility of ziram in water is 65 mg/l, while that for maneb is 100 mg/l. It is reasoned that although no information was provided on the true molecular weight of maneb, the similarity of water solubilities sugests a similarity in physical characteristics between ziram and maneb.

3. The lower solubility of ziram as compared to maneb, and the similarity in chemical functional groups between ziram and maneb, suggests no adverse effects with respect to granular activated carbon adsorption properties for ziram in comparison to maneb.

4. The Research Triangle Institute study showed that maneb can be removed successfully from actual process wastewater by granular activated carbon adsorption. In view of the similarity in functionality and solubility, it is assumed that ziram can also be removed successfuly by granular activated carbon treatment. Furthermore, the EPA proposes substantially longer contact times than that employed in the Research Triangle Institute study.

Although no data are available from which to judge raw waste loadings and wastewater matrix effects for ziram production as compared to maneb production, this does not necessarily detract from the logic of the argument, since these differences can be accomodated to a certain extent by designing on the basis of lb of carbon per lb of pollutant in lieu of lb of carbon per gallon of wastewater.

In view of the above arguments, it appears that the indirect discharge standard for ziram is reasonable given available information. However, it is recognized that difference in structure between ziram and maneb introduces a degree of uncertainty in the evaluation.

Niacide (Subcategory 1, Indirect Discharge)

Niacide is a metallo-organic pesticide manufactured at one plant only. Wastewater at this plant is treated by evaporation and crystallization prior to discharge of condensate to a POTW. No data are available on treatment performance. Niacide is a manganous dimethylthiocarbamate, it is similar to ziram except manganese replaces zinc, also niacide has three dimethylthiocarbamate groups rather than two groups as for ziram.

The treatment level for niacide was establisbed at 0.15 mg/l for granular activated carbon treatment by technology transfer with the compound maneb. This was justified by the following arguments:

1. Both niacide and maneb are metallo-organic dithiocarbamate pesticides. However, maneb is a straight chain molecule comprised of repeating sequences of a parent functional compound containing manganese, while niacide contains maganese as single dithiocarbamate molecule with molecular weight 414.3. No information was provided on the true molecular weight of maneb.

2. The solubility of niacide in water is the same as that for maneb at 100 mg/l. This suggests that difference in physical structure between niacide and maneb does not result in different solubilities.

3. Similar water solubilities and similar functional groups suggest no adverse effects with respect to granular activated carbon adsorption for niacide as in comparison to maneb.

4. The Research Triangle Institute study showed that maneb can be removed successfully from actual process wastewaters by granular activated carbon adsorption. In view of the similarity in functionality and solubility, it is assumed that niacide can also be removed successfully by granular activated carbon treatment. Furthermore, the EPA proposes substantially longer contact times than that employed in the Research Triangle Institute study.

No data are available from which to compare raw waste loadings or wastewater matrix effects for niacide production as compared to maneb production. However, this does not necessarily detract from the logic of the above argument since design can be based on lb carbon per lb of pollutant in lieu of lb of carbon per gallon of wastewater.

In view of the above arguments, it appears that the indirect discharge standard for niacide is reasonable given available information. However, it is recognized that difference in structure between niacide and maneb introduces a degree of uncertainty in the evaluation.

Zineb (Subcategory 5, Indirect Discharge)

Zineb is a metallo-organic pesticide manufactured at only one plant. Wastewater at this plant is treated by evaporation and crystallization with effluent levels of 0.35 mg/l in evaporation condensate. Zineb is structurally similar to maneb and, both are comprised of repeating sequences of ethylenebisdithiocarbamate. The only difference between these pesticides is that the molecular sequences are joined by manganese in the case of maneb and zinc in the case of zineb.

The treatment level for zineb was established at 0.15 mg/l for granular activated carbon adsorption by technology transfer with the compound maneb. This was justified by the following arguments:

1. Maneb and zineb are structurally similar, straight chain, ethylenebisdithiocarbomates.

2. The solubility of zineb in water is 10 mg/l, while that for maneb is 100 mg/l.

3. The lower solubility of zineb compared to maneb, and the similarity in structure and in chemical functional groups suggest no adverse adsorption characteristics with respect to granular activated carbon treatment for zineb in comparison with maneb.

4. The Research Triangle Institute laboratory study with maneb, using actual process wastewater, showed that maneb could be reduced to less than 0.15 mg/l by granular activated carbon treatment. Given the similarity in structure and functionality between maneb and zineb, and the lower solubility of zineb compared to maneb, it is assumed that zineb can be removed successfully by activated carbon treatment. Furthermore, the EPA proposes longer contact times for granular activated carbon treatment than that employed in the Research Triangle Institute study.

In view of the above arguments, it appears that the indirect discharge standard for zineb is reasonable given available information. It is recognized that raw waste loadings and wastewater matrix effects are assumed to be similar for zineb-containing wastewater and maneb-containing wastewater. To a certain extent differences between loadings and matrix effects can be accomodated by designing on the basis of lb of carbon per lb of pollutant, rather than lb of carbon per gallon of wastewater.

Terbacil (Subcategory 1, Direct Discharge)

Terbacil is an uracil pesticide which is manufactured at one plant. This plant also manufactures another uracil pesticide, bromacil. Presently this plant employs chemical oxidation with chlorine, followed by biological oxidation, for destruction of bromacil and terbacil. Both pesticide process effluents at this plant are comingled prior to treatment. The removal efficiency for terbacil during chemical oxidation or biological oxidation is not available. However, data are available for removal of bromacil in this process. The treatment standard for terbacil was established by assuming similar removal efficiency during chemical oxidation and biological oxidation for terbacil as observed for bromacil. Hydrolysis is alluded to as an alternate pretreatment technology for chemical oxidation.

The arguments were justified by the following:

1. Terbacil and bromacil are structurally similar. The only differences are that terbacil contains chloride in the 5-position and tert-butyl in the 3-position, while bromacil contains bromide in the 5-position and sec-butyl in the 3-position

2. The hydrolysis reaction for terbacil and bromacil is reported to occur most readily at the carbonyl groups on the pesticide, and that difference in halogen specie the 5-position should not effect the rate of hydrolysis.

3. The EPA proposed design shows treatment by chemical oxidation at a residence time of twenty-four hours rather than the eight hours employed at the production facility. The longer residence time provides a measure of conservatism in treatment of terbacil by chemical oxidation.

4. Wastewater matrix effects do not seem to be an issue for biological oxidation because the treatment data available for bromacil were from the only full-scale process producing terbacil and bromacil.

The above discussion indicates that the EPA is considering either hydrolysis or chemical oxidation as appropriate treatment technologies. With regard to hydrolysis, one study in the literature states that "complete structural change of bromacil" can be achieved with addition of sulfuric acid. While no specific data are available, treatment by hydrolysis appears to be a viable treatment alternative.

The plant that produces bromacil has treatment data to assess percentage removal of bromacil by chlorination; these data were used to predict that a chlorination process can be used to remove bromacil to a pretreatment level of 0.14 mg/l (0.149 lb/1000 lbs). These test data are available for chemical oxidation of comingled bromacil and terbacil effluents.

No information is provided on the chemical reactions accompanying chlorination of bromacil or terbacil, although it would appear that the minor difference in chemical structure probably has small effect on reactivity with respect to chlorination.

Wastewater matrix effects are likely to play a minor role for hydrolytic treatment of terbacil. For the case of pretreatment by chlorination, wastewater matrix effects for combined terbacil and bromacil effluent should be manifested as an increase in chlorine demand; presumably this is already accomodated in the present full-scale treatment process.

The removal of terbacil across biological oxidation was taken as being similar to that obtained at full-scale for bromacil (i.e. 82.5%). While this assumption may be perceived as rational, it is unsubstantiated. The assumption needs to be substantiated by documentation of the mechanisms responsible for biological decomposition of uracil and uracil presticides. Alternatively, a nominal value of 50% removal during biological oxidation could be assumed. This removal efficiency would be consistent with other instances in which an estimate of removal during biological treatment was required in the absence of data.

In summary, it appears that the pretreatment standard for terbacil is justifiable, while the discharge limit is not as readily justified, although a nominal value may be assumed.

Fluometuron (Subcategory 4, Direct and Indirect Discharge)

Fluometuron is an urea pesticide manufactured by one plant. Treatment data are not available for this pesticide. The pretreatment level was based on literature data for enzymatic hydrolysis and previously promulgated BPT regulations for two similarly structured urea pesticides, diuron and linuron. The pretreatment level was established at a factor of two greater than the BPT standards, owing to an assumed

50% removal via biological oxidation; the discharge limit for fluometuron was established at the same level as for diuron and linuron (0.00129 lb/1000 lbs.). This approach was justified according to the following:

1. Enzymatic hydrolysis, has been reported in two studies to be effective in removing urea pesticides, although no data are available for fluometuron.
2. The BPT level of 0.00129 lb/1000 lbs has been established for two related pesticides, linuron and diuron.

Enzymatic hydrolysis, or the more common alkaline hydrolysis seems a reasonable approach for destruction of fluometuron and related other urea pesticides. The reactive group for these pesticides is the urea functionality, not ring-bound chloride (as for diuron or linuron) or trifluoromethyl group (as for fluometuron). Hydrolysis cleaves the nitrogen-carbon bond closest to the aromatic ring.

It should be appreciated that enzymatic hydrolysis is not a commercial treatment process for destruction of fluometuron. Also, there is only general information in the literature on alkaline hydrolysis of fluometuron. There is no reference to original research.

It is recognized that no full-scale or other wastewater test data are available from which to judge hydrolytic treatment of fluometuron. However, the established standards are reasonable in view of information on the chemistry of hydrolysis reactions and in consideration of previously promulgated standards for related urea pesticides. Furthermore, it should be recognized that wastewater matrix effects probably have minimal impact on treatment by alkaline hydrolysis.

## Summary

The preceeding discussion has provided a review of the procedures employed for evaluation of the methodology of technology transfer. This review has focused on a list of ten least treatable non-conventional pesticide compounds.

The evaluation was performed on a compound-by-compound basis. It is apparent that available data are fragmentary and scanty, and that in most cases the evaluation relies on qualitative assessment of the problem. Futhermore, a general observation is that in most instances various assumptions and inferences were required in order to establish an effluent standard or limit for the least treatable compounds. Nonetheless, as reviewed here, all the assumptions and inferences that were required in order to establish effluent standards and limits are generally reasonable given available information. Thus, it is recommended that the proposed effluent standards and limits be accepted, with the possible exception of minor changes as indicated in the preceeding discussion.

The following comments are suggestions for activities that may be undertaken in order to obtain a higher degree of confidence in the recommended standards and limits. These suggestions are not intended to detract from the general conclusion summarized above.

The best way to strengthen the data base for effluent standards and limits is to conduct treatment studies with actual process wastewaters. The treatment studies need not be extensive, since only a small number of least treatable pesticides are of principal concern.

It is recognized that the information used to establish effluent standards and limits was obtained from readily available sources, and that this information was supposedly current at the time the development document was prepared. However, approximately three years have lapsed since the development document was prepared, and it is suggested that a computer-aided literature search be initiated in order to determine if any new, pertinent information is available for the ten least treatable pesticides. The search would be used to seek new data regarding physical or chemical properties, or behavior during wastewater treatment. This would help to ensure that all current, relevant information was employed in establishing effluent guidelines for the various subcategories of non-conventional pesticides. It would also serve to identify any literature sources that may have been overlooked previously.

It is appreciated that several approaches can be used to obtain correlations in order to estimate treatability of organic pollutants. These approaches typically make use of physical and chemical properties such as Henry's Law coefficient, octanol-water partition coefficient, dissociation constant, and water solubility. These types of correlations were not employed by the EPA to estimate treatability of the non-conventional pesticides. It is suggested that these correlations are potentially useful for the problem under consideration, and that an effort should be made in order to apply these approaches for estimating treatability of non-conventional pesticides. It is recognized that it is not known if sufficient data are available to attempt correlations in order to estimate treatability characteritics; furthermore, it is not certain whether this approach would provide a greater degree of confidence in the proposed standards and limits. Nonetheless, the Effluent Guidelines Division has been working on problems of this type for several years with respect to treatability of organic priority pollutants, and it is suggested that the issue of theoretical treatability of non-conventional pesticides would be worthy of study. It is understood that this type of exercise runs the risk of making one estimate in order to make a second estimate, and that it is preferred to make predictions on treatability from full-scale or other treatment data with actual wastewater. Nonetheless, it is worthwhile to attempt an analysis of this type in order to become more quantitative in estimating treatability of pesticides. The approach can be useful for identifying questionable or anolamous data. This, in turn, suggests areas for additional research investigations.

It is important for the EPA to attempt application of new skills and methodologies to the problem of treatability of pollutants. This will advance the state-of-the-art, while ensuring that effluent guidelines have a strong, rigorous scientific basis.

## Conclusion

This report has reviewed the procedures and methodologies employed for technology transfer for ten least treatable, non-conventional pesticide compounds. It has been found that the available data base is fragmentary and scanty, and that in most cases only qualitative interpretations can be made. The available data are generally insufficient for reliable design of a non-conventional pesticide removal system. Further, the review has shown that various assumptions and inferences were required in order to establish effluent standards and limits for most of these compounds. Nonetheless, a case-by-case analysis has shown that, in general, the approach was reasonable given available information. It is suggested that the data base may be strengthened by conducting treatability studies with actual wastewaters, as well as by executing a computer-aided literature search. It is also suggested that future work be directed towards theoretical prediction of treatability through use of correlations with physical and chemical data.