Appendix H

Toxicity Control Options for Organophosphate Insecticides

Organophosphate insecticides, including diazinon, chlorpyrifos, malathion, and chlorfenvinphos, have been found to cause effluent toxicity at POTWs throughout the United States (Norberg-King et al., 1989; Amato et al., 1992; USEPA, 1987; Botts et al., 1992; Fillmore et al., 1990). A case study of the occurrence of organophosphate insecticide toxicity at POTWs in the San Francisco Bay area is presented in Appendix F. Although procedures are available for identifying organophosphate toxicants, less is known about how to control organophosphate insecticides in POTW effluents. This section describes approaches for organophosphate toxicity control that have been successfully implemented at POTWs. Information is also presented on ongoing research into POTW operational improvements that may reduce effluent concentrations of organophosphate toxicants.

A review of the literature suggests that two approaches may be successful in reducing organophosphate compounds at POTWs:

- Public education to limit the discharge of organophosphate compounds to the POTW.
- POTW modifications, particularly involving enhancements to the biological treatment and chlorine disinfection processes.

The latter approach has been the subject of a research study being funded by the two principal manufacturers of organophosphate compounds in North America: Novartis Crop Protection, Inc., and Makhteshim-Agan of North America, Inc.

Public Education Approach

Organophosphate insecticides are used widely for pest control by homeowners, restaurants, veterinarians, and other commercial businesses. These sources are not readily controlled by pretreatment program regulations. Alternative efforts to minimize the use or disposal of organophosphate insecticides must have broad appeal to the public at large.

Organophosphate insecticide control measures that have been considered by POTW staff include public outreach and education programs and approaches to restrict the use of organophosphate compound applications. Efforts to ban or restrict the use of organophosphate insecticides have not been successful, largely because of concern about legal issues and the difficulty in controlling the sale of organophosphate compounds outside of the community.

Restrictions on Organophosphate Insecticide Use

In 1990, the City of Largo, Florida, evaluated the feasibility of banning the use of diazinon and other organophosphate insecticides (malathion and chlorfenvinphos) to control effluent toxicity (C. Kubula, personal communication, City of Largo, Florida, 1992). It was determined that a diazinon ban would likely increase the use of other, equally toxic, insecticides. For example, Dursban®, a likely alternative insecticide, contains chlorpyrifos, which has been found to be more toxic than diazinon. Also, restrictions on diazinon use would apply only to new supplies, not to insecticides already in stock at stores. The City of Largo estimated that the stockpiled diazinon would last for more than a year. An effective control program would also require the cooperation of neighboring communities in limiting the purchase of diazinon outside of the community. In addition, the local banning of federally approved insecticides would be controversial. It was anticipated that insecticide manufacturers and distributors would challenge the City's authority to implement such controls. Based on this analysis, the City of Largo determined that banning diazinon would not be a practical control option.

Public Education Campaigns

Based on the impracticality of insecticide bans, the City of Largo elected to pursue a public awareness approach to control diazinon toxicity. The City of Greenville, Texas, also implemented a public education program in 1990 (City of Greenville, 1991). The first year of the program focused on determining significant users of the insecticide and developing educational materials. The following years have involved distributing the materials and conducting other informational activities.

The City of Greenville initially identified nine groups of diazinon users: pest control businesses, lawn care businesses, veterinarians, animal shelters, janitorial services, apartment complexes, restaurants, hotels, and retail stores (City of Greenville, 1991). The residential population also was added as a target user group. The City service area was divided into sections, and a telephone survey was conducted. Information was gathered on diazinon use, including existing supplies and application and waste disposal practices, and business owners and homeowners were notified of the importance of controlling diazinon wastes. The program involved the following public education activities:

- Brochures and handouts
- Pest control fact sheets describing integrated pest management methods, which focused on minimizing insecticide usage
- Mass mailings
- Newspaper articles
- Public service announcements
- Occasional talk shows on local radio stations
- Biweekly presentations to schools and business groups
- A telephone information line.

The City of Greenville also enacted an ordinance to encourage environmentally sound use of insecticides. The ordinance requires retail vendors, pest control services, and apartment managers to distribute educational material to customers and to periodically report insecticide applications to the City.

The results of the Greenville education campaign are encouraging. Beginning in December 1993, the treatment plant effluent was not toxic to *C. dubia* for 3 consecutive months. The public awareness effort is continuing and the City will monitor its effect on toxicity reduction.

The City of Largo initiated a public education campaign in 1992. An information brochure was prepared and distributed in 1993. Effluent toxicity decreased; however, it was not known if the reduction is related to the public education program. A strong emphasis has not been placed on the program because the City has opted for a land irrigation treatment system in lieu of continued effluent discharge.

As noted in Appendix A of this manual, diazinon and its toxic metabolite diazoxon were tentatively identified as effluent toxicants at the City of Lawton POTW. The City decided to implement a public awareness program in 1993 to control the discharge of insecticides to the POTW (Engineering Science, 1993). Information on the proper use and disposal of insecticides was printed in newspaper articles and on monthly water bills. An electronic message sign with insecticide information also was located at major intersections. Since August 1993, the POTW effluent has met the toxicity permit limit (NOEC >96% effluent) with the exception of 2 months in 1994 and several months in 1995 (as of September 1997). Although diazinon was not confirmed as an effluent toxicant, the City's ongoing insecticide control effort appears to have been successful in achieving compliance with the chronic toxicity limit.

POTW Operational Improvements

Diazinon Treatment

In 1992, Novartis Crop Protection, Inc., in cooperation with Makhteshim-Agan of North America, Inc., initiated a study on diazinon and its relationship to effluent toxicity at POTWs (Novartis, 1997). A principal objective of the study was to determine the treatability of diazinon and assess its fate in POTWs. Research on this subject included a survey of POTWs in which organophosphate insecticide toxicity was observed and bench-scale treatability tests were conducted to evaluate diazinon removal by various treatment methods and operating conditions.

Two types of POTW biological treatment processes were investigated in the Novartis study: fixed film (trickling filter and RBC) and activated sludge. Influent and effluent concentrations at several POTWs in the southwestern United States were compared to determine removals of diazinon and chlorpyrifos.

Overall, the data indicated that diazinon reduction could be achieved in conventional POTW treatment processes. A statistical analysis of the data showed that the fixed film process had a significantly lower percent removal (p=0.95) for diazinon than the activated sludge process or a combined fixed film/ activated sludge process. A similar trend was observed for chlorpyrifos, although no significant differences were found between the process types.

Bench-scale treatability testing was conducted to further evaluate the fate of diazinon in typical POTW processes. These tests considered the effect of design and operating conditions for biological treatment processes on diazinon removal and effluent toxicity. Additional tests were performed to investigate the effect of physical/chemical processes, including chemical precipitation, chlorination/dechlorination, and post aeration on diazinon concentrations and toxicity.

As shown in Figure H-1, a correlation was found to exist between diazinon removal and sludge retention time (SRT), HRT, and MLSS concentration in activated sludge treatment tests. The primary removal mechanism in the activated sludge tests was adsorption onto the biological solids. These results suggest that diazinon removal may be improved by increasing the SRT, HRT, and/or MLSS concentration of the treatment process.

Auxiliary process studies provided additional information on treatment of diazinon (Novartis, 1997). Chemical precipitation using ferric chloride and polymer only slightly reduced diazinon levels. No major change in diazinon concentrations was observed whether the coagulants were added to primary wastewater or secondary treated wastewater prior to clarification. Chlorination treatment was effective in reducing diazinon from secondary clarifier effluent; however, chronic toxicity was unchanged. Qualitative results suggest that the chlorine oxidized diazinon to diazoxon, a by-product that exhibits similar toxic effects as diazinon. Post aeration of secondary clarifier effluent also reduced diazinon levels; however, once again, chronic toxicity was not significantly changed. Again, it was assumed that diazinon was oxidized to diazoxon.

Additional tests evaluated the fate of diazinon in POTWs (Novartis, 1997). Anecdotal evidence from other studies (Fillmore et al., 1990) and the treatability studies suggested that adsorption onto solids was the dominant removal mechanism. Therefore, the tests focused on partitioning of diazinon and chlorpyrifos onto primary and mixed liquor solids. These tests showed that about 30% of the diazinon and 85 to 90% of the chlorpyrifos present in POTW primary influent samples is adsorbed onto primary influent solids. Mixed liquor adsorption results revealed that approximately 65 to 75% of the diazinon added to the mixed liquor adsorbed onto the biomass. Diazinon adsorption was greater for a 30-day SRT biomass than for a 15-day biomass. Chlorpyrifos strongly adsorbed to the biomass; 100% was removed.

Summary

Studies have shown that organophosphate compounds can be effectively controlled through public education (City of Greenville, 1991; Engineering Science, Inc., 1993) . This effort may vary from the distribution of educational materials to the enactment of ordinances that require strict accounting of insecticide use. The studies conducted to date indicate that characterization of the sources of organophosphate compounds is key to the development of a successful toxicity control program.

Recent information shows that relatively simple enhancements to POTWs may help to reduce organophosphate compounds. Factors affecting diazinon and chlorpyrifos removal include the SRT, HRT, and MLSS concentrations in activated sludge processes, chlorination/dechlorination, and post aeration. Further studies are in progress to better define the operating conditions that will promote organophosphate compound removal (D. Tierney, personal communication, Novartis Crop Protection, Inc., 1997).

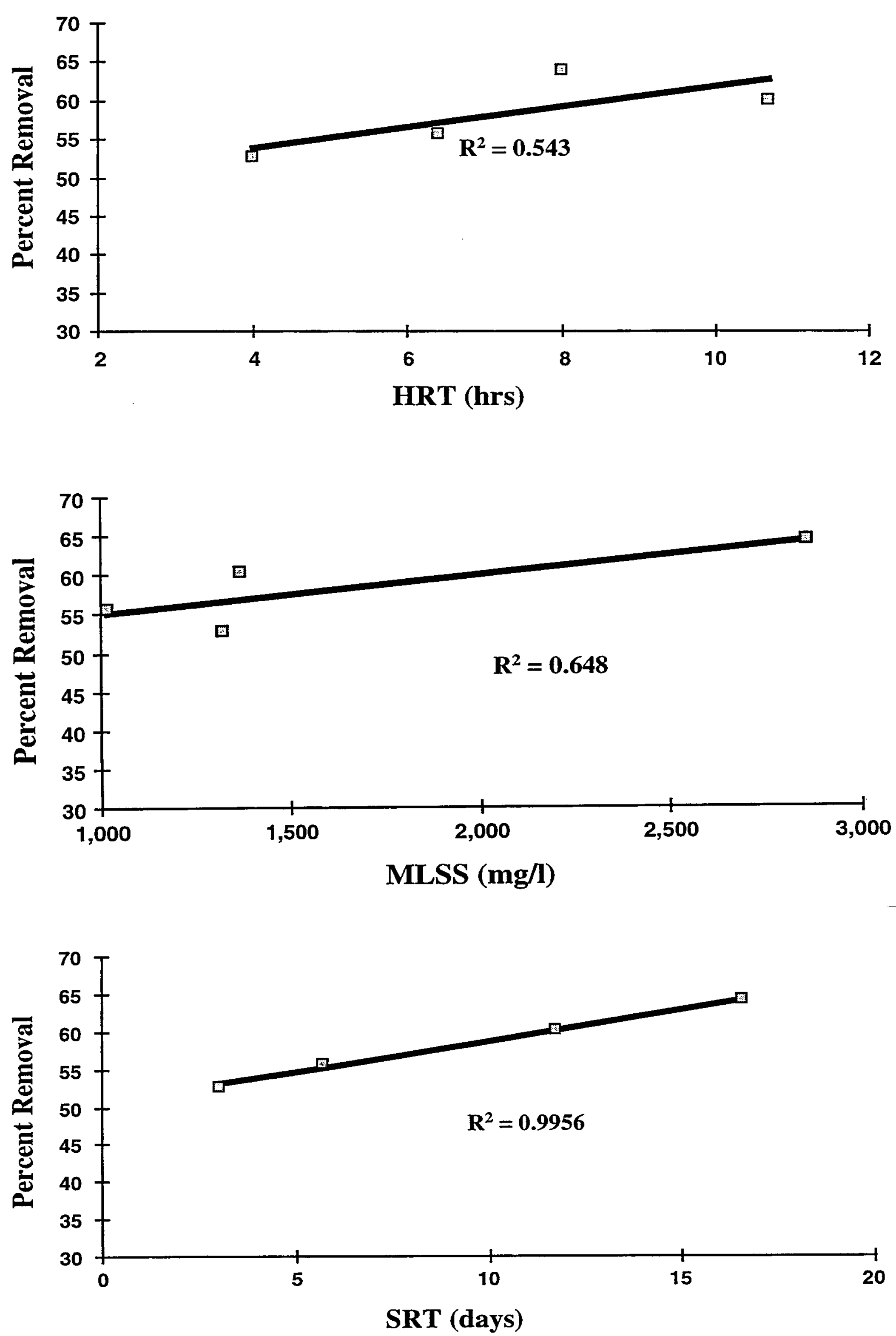

Figure H-1. Diazinon removal as a function of SRT, HRT, and MLSS concentration (reprinted with the permission of Novartis Crop Protection, Inc.) (Source: Novartis, 1997).

References

Amato, J.R., D.I. Mount, E.J. Durhan, M.L. Lukasewycz, G.T. Ankley, and E.D. Robert. 1992. An Example of the Identification of Diazinon as a Primary Toxicant in an Effluent. *Environ. Toxicol. Chem*. 11: 209-16.

Botts, J.A., T.L. Morris, J.E. Rumbo, and C.H. Victoria-Rueda. 1992. Case Histories - Municipalities. *Toxicity Reduction: Evaluation and Control*. D.L. Ford, ed. Lancaster, PA: Technomic Publishing Co.

City of Greenville. 1991. *TRE Phase B Final Report*. City of Greenville, North Carolina.

Engineering-Science, Inc. 1991. *Toxicity Reduction Evaluation Phase I Report*. Submitted to the City of Lawton, Oklahoma, September 1991. Parsons Engineering Science, Inc., Fairfax, Virginia.

Engineering-Science, Inc. 1992. *Toxicity Reduction Evaluation: Toxicant Identification and Confirmation*. Submitted to the City of Lawton, Oklahoma, Parsons Engineering Science, Inc., Fairfax, Virginia.

Engineering-Science, Inc. 1993. *Review of Diazinon Control Options*. Submitted to the City of Lawton, Oklahoma, April 1993. Parsons Engineering Science, Inc., Fairfax, Virginia.

Fillmore, L.B., T.L. Morris, T.L. Champlin, M.C. Welch, and J.A. Botts. Draft 1990. *Toxicity Reduction Evaluation at the City of Fayetteville Cross Creek Wastewater Treatment Plant.* Draft Report. USEPA Risk Reduction Engineering Laboratory, Cincinnati, Ohio.

Norberg-King, T.J., M. Lukasewycz, and J. Jensen. 1989. *Results of Diazinon Levels in POTW Effluents in the United States*, Technical Report 14-89. USEPA, National Effluent Toxicity Assessment Center, Duluth, Minnesota.

Novartis Crop Protection, Inc., and Makhteshim-Agan of North America, Inc. 1997. *Investigation of Diazinon Occurrence, Toxicity, and Treatability in Southern United States Publicly Owned Treatment Works.* Technical Report 3-7, Environmental Affairs Department, Greensboro, North Carolina.

USEPA. 1987. *Toxicity Identification Evaluation of the Largo, Florida POTW Effluent.* J.R. Amato, D.I. Mount, M. Lukasewycz, E. Durham, and E. Robert. National Effluent Toxicity Assessment Center, Duluth, Minnesota.

USEPA. 1989a. *Methods for Aquatic Toxicity Identification Evaluations: Phase II: Toxicity Identification Procedures*. EPA/600/3-88/035. Office of Research and Development, Duluth, Minnesota.

USEPA. 1989b. *Methods for Aquatic Toxicity Identification Evaluations, Phase III*. EPA/600/3-88/036. Toxicity Confirmation Procedures. Office of Research and Development, Duluth, Minnesota.

USEPA. 1992. *Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I*. EPA/600/6-91-005F. National Effluent Toxicity Assessment Center, Duluth, Minnesota

USEPA. 1993a. *Methods for Aquatic Toxicity Identification Evaluations: Phase II Toxicity Identification Procedures for Samples Exhibiting Acute and Chronic Toxicity*. EPA/600/R-92-080. National Effluent Toxicity Assessment Center, Duluth, Minnesota.

USEPA. 1993b. *Methods for Aquatic Toxicity Identification Evaluations: Phase III Toxicity Confirmation Procedures for Samples Exhibiting Acute and Chronic Toxicity*. EPA/600/R-92-081. National Effluent Toxicity Assessment Center, Duluth, Minnesota.