DEVELOPMENT OF TMDL GOALS FOR CONTROL OF ORGANOPHOSPHATE PESTICIDE-CAUSED AQUATIC LIFE TOXICITY IN URBAN STORMWATER RUNOFF¹

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ABSTRACT

Urban stormwater runoff in several municipalities in California has been found to be toxic to *Ceriodaphnia dubia*. This toxicity is due to residential use of the organophosphate (OP) pesticides, diazinon and chlorpyrifos, for termite, ant, lawn and garden pest control. This toxicity has caused regulatory agencies to list the receiving waters for the urban stormwater runoff as 303(d) "impaired" waterbodies. This listing requires that a TMDL be developed to control the concentrations of diazinon and chlorpyrifos so that they do not cause aquatic life toxicity in the runoff waters. This paper provides guidance on an approach that can be used to develop an appropriate TMDL goal to control aquatic life toxicity due to the OP pesticides used in residential areas. While the paper focuses on residential use of these pesticides, many of the same issues and approaches are applicable to runoff from agricultural areas where the pesticides are used.

KEYWORDS

Toxicity, pesticides, TMDL, urban stormwater runoff.

INTRODUCTION

The authors and their colleagues have recently completed a three-year study of aquatic life toxicity in stormwater runoff in the Upper Newport Bay, Orange County, CA watershed. Lee and Taylor (1999) have presented the results of this study. This study has found that stormwater runoff in this predominantly urban watershed contains from 5 to 20 units (TUa) of *Ceriodaphnia dubia* and *Mysidopsis bahia* acute toxicity. *Ceriodaphnia* and *Mysidopsis* are standard US EPA testorganisms used for evaluating the potential toxicity of NPDES-permitted wastewater discharges and stormwater runoff. Both organisms are zooplankton that are representative of aquatic organisms that are used as larval fish food in fresh and marine waters. The Orange County study involved conducting over 140 toxicity tests and associated chemical measurements. These tests show that all stormwater runoff in the Upper Newport Bay watershed contains sufficient diazinon and chlorpyrifos, two organophosphate (OP) pesticides, to cause part of the toxicity found in the stormwater runoff. Over 100,000 pounds of diazinon and chlorpyrifos are used in Orange County each year on residential properties for termite,

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ant and lawn and garden pest control. Only about 5 pounds of the total amount applied per year is responsible for the aquatic life toxicity found in this study.

The Orange County study results are similar to urban stormwater runoff studies conducted in the San Francisco Bay area, Stockton, Sacramento, Los Angeles, San Diego, CA, and Fort Worth, TX, in that this runoff is acutely toxic to *Ceriodaphnia dubia*. Further, the USGS (Larson, *et al.*, 1999) has recently released a report covering the national pesticide monitoring program which shows that there are sufficient concentrations of diazinon and chlorpyrifos in urban streams located in several areas of the US to be toxic to *Ceriodaphnia*. It is now clear that the aquatic life toxicity problem associated with the use of OP pesticides on residential properties is a largely unrecognized national problem that needs attention.

This toxicity has caused several of the California Regional Water Quality Control Boards to list urban streams as 303(d) "impaired" waterbodies for which TMDLs must be developed to control the OP pesticide-caused aquatic life toxicity. This paper focuses on the issues that need to be considered in developing technically valid, cost-effective TMDL goals for appropriately managing the toxicity due to OP pesticides in urban stormwater runoff.

REGULATORY ISSUES

The regulation of OP pesticide-caused aquatic life toxicity in urban stormwater runoff is complicated by several factors. Lee, *et al.* (2000) have reviewed these issues, one of the most important of which is that the OP pesticides, while highly toxic to *Ceriodaphnia* and *Mysidopsis*, are not toxic to many other types of zooplankton and are nontoxic to fish and algae at the concentrations being found in urban stormwater runoff. An issue that immediately arises from this situation is whether killing *Ceriodaphnia*-type zooplankton in the short-term toxic pulses associated with stormwater runoff events is significantly detrimental to the beneficial uses of the receiving waters for the stormwater runoff. There are some advocates for the continued use of OP pesticides on residential properties who assert that the OP pesticide toxicity is highly selective to certain types of organisms which are not essential components of the aquatic food web that lead to desirable forms of aquatic life such as edible fish and shellfish.

Another complicating factor in regulating the OP pesticide-caused aquatic life toxicity is the different regulatory approaches that are used for controlling pesticide impacts on non-target organisms versus the control of toxicity to aquatic life by non-pesticides. The Clean Water Act as being implemented by the US EPA requires the control of toxics discharged in toxic amounts. If the OP pesticide-caused aquatic life toxicity were due to heavy metals in urban stormwater runoff, they would have to be controlled under Clean Water Act requirements. However, pesticides are regulated by the US EPA Office of Pesticide Programs (OPP). The US EPA OPP Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) regulations allow toxicity to non-target organisms provided that this toxicity is not significantly adverse to the beneficial uses of the waterbody. FIFRA definitions include:

"x) Protect health and the environment.--The terms 'protect health and the environment' and 'protection of health and the environment' mean protection against any unreasonable adverse effects on the environment."

"(bb) Unreasonable Adverse Effects on the Environment.--The term 'unreasonable adverse effects on the environment' means (1) any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide, or $(2) \dots$ "

The US EPA OPP FIFRA regulations allow other factors (such as economics and social) than impairment of beneficial uses to determine whether a pesticide's registration or re-registration should be limited by adverse impacts to non-target organisms. The US EPA OPP FIFRA regulations point to the need to have a much better understanding of the role of specific types of zooplankton in influencing beneficial uses of waterbodies. Basically the question becomes one of whether the numbers, types, and characteristics of aquatic life present in receiving waters for urban stormwater runoff containing OP pesticide-caused aquatic life toxicity are being significantly adversely impacted by this toxicity.

It is important to note that OP pesticide-caused aquatic life toxicity in urban stormwater runoff is not a new problem. It has been occurring for 10 to 15 years. It was not until toxicity tests were conducted on urban stormwater runoff that this problem began to be identified. Another important issue is that under current pesticide regulations, restricting the use of OP pesticides will result in the use of other pesticides that may have at least the same or even greater adverse impacts to the beneficial uses of waterbodies as diazinon and chlorpyrifos. The current pesticide regulatory approach does not require adequate evaluation of potential toxicity to aquatic life in stormwater runoff as part of pesticide registration.

This paper summarizes these issues and presents recommended approaches for developing TMDL goals for the control of aquatic life toxicity in urban stormwater runoff that will protect the designated beneficial uses of receiving waters for urban stormwater runoff without unnecessarily restricting the use of OP pesticides for residential termite and ant control.

SUGGESTED APPROACH FOR TMDL GOAL DEVELOPMENT

Stormwater Runoff Monitoring Program

The first step in developing an appropriate TMDL goal and its implementation to control aquatic life toxicity in urban stormwater runoff is to establish a monitoring program that will define whether stormwater runoff and dry weather flow in urban streams and the receiving waters for the runoff are toxic to *Ceriodaphnia dubia*. The overall approach that should be used is the Evaluation Monitoring approach described by Jones-Lee and Lee (1998). This approach focuses on finding potential water quality use impairments in the receiving waters for the stormwater runoff. Where such use impairment potentially exists, the cause of the use impairment is determined and its significance is assessed. If it is determined to be significant to impairment of beneficial uses, then the constituents responsible are determined and their sources are defined through forensic studies.

Basically, rather than measuring potentially toxic constituents, such as copper, in urban stormwater runoff and then trying to extrapolate the chemical concentration results to toxicity in the receiving waters for the runoff, toxicity is measured directly and its cause is determined through toxicity investigation evaluation procedures (TIEs). Evaluation Monitoring is a far more reliable, technically valid, cost-effective approach for developing water quality management programs for urban stormwater runoff than the traditional, conventional monitoring approach in which a suite of chemical parameters are measured and the results are compared to worst case- based US EPA water quality criteria/state standards based on these criteria.

It was through the use of toxicity measurements on urban stormwater runoff that it was found that the heavy metals that exceed US EPA water quality criteria in the urban street and highway stormwater runoff, such as copper, lead, and zinc, were in nontoxic forms. It was also determined through this approach that the OP pesticides, diazinon and chlorpyrifos, were responsible for aquatic life toxicity in urban stormwater runoff. These issues have been reviewed by Lee and Taylor (1999).

Lee (1999) has provided guidance on the characteristics of the stormwater runoff monitoring program that is designed to assess the magnitude of aquatic life toxicity, the cause of the toxicity, and the sources of the constituents responsible. This program focuses on using *Ceriodaphnia dubia*, fathead minnow larvae (*Pimephales promelas*), and *Selenastrum capricornutum* (algae) as the three test species using the US EPA standard testing protocol (Lewis, *et al.*, 1994). For marine waters, the US EPA 1994 testing procedures are used with *Mysidopsis bahia* or other marine organisms as a test organism.

In addition to measuring the toxicity to these organisms, toxicity measurements should be conducted on a dilution series of those samples of stormwater runoff and dry weather flow that show significant toxicity to the test organisms within a day or two. The dilution series testing should be designed to assess the magnitude of the toxicity (TUa) in the sample. For the samples which are toxic to *Ceriodaphnia*, the dilution series should be tested with and without PBO (piperonyl butoxide). The addition of PBO to a sample can remove the OP pesticide-caused toxicity and, therefore, if the toxicity of the sample is either eliminated or significantly reduced upon PBO addition, this is an indication that the toxicity was due to OP pesticides.

If toxicity is found, then chemical measurements on the samples should be conducted to determine the potential cause of the toxicity. The ELISA (enzyme linked immuno sorbent assay) procedures are highly specific for each of the OP pesticides. Further, the ELISA testing should be backed up by some dual column GC or GC-MS procedures. Further information on the use of these procedures is available from Lee (1999).

Toxicity Impact Evaluation

One of the most important components of developing an appropriate TMDL goal for control of OP pesticide-caused aquatic life toxicity is an evaluation of the potential water quality-beneficial use impacts of the toxic pulses of OP pesticide-caused aquatic life toxicity. The finding of toxicity in urban stormwater runoff should not be assumed to be significantly detrimental to the beneficial uses of the receiving waters for the runoff. The conditions of the US EPA standard toxicity text using *Ceriodaphnia*, fathead minnow larvae, and *Selenastrum*, can lead to laboratory- based toxicity in urban streams is rapidly lost through dilution in the receiving waters for the stream discharges. This situation appears to be occurring in Sacramento, California. It is essential, as part of a TMDL goal development program for OP pesticide-caused aquatic life toxicity, to determine if aquatic life in receiving waters for the stream discharge experience sufficient toxicity for a sufficient period of time to be toxic.

Further, it is important to assess whether toxicity in the urban stream as well as in the receiving waters to organisms with a sensitivity to OP pesticides, like *Ceriodaphnia*, is adverse to higher trophic level organisms that depend on zooplankton as food. Novartis (1997) has developed a probabilistic ecological risk assessment (PERA) which shows that *Ceriodaphnia* is one of the most sensitive organisms known to OP pesticide toxicity. Novartis claims that killing zooplankton with an OP pesticide sensitivity, like *Ceriodaphnia*, will not be adverse to the beneficial uses of the ecosystem since there are other sources of larval or small fish food that are available that are not impacted by OP pesticide-caused toxicity. However, Lee and Jones-Lee (1999) have pointed out that the single

chemical PERA used by Novartis may not be valid since the ecological role of the *Ceriodaphnia*-like organisms that are killed by OP pesticides in stormwater runoff is not known. It could be that the zooplankton that are sensitive to OP pesticide toxicity are essential components of the food for important higher trophic level organisms. The loss of their food through OP pesticide caused toxicity could be detrimental to the beneficial uses of the waterbody. Another problem with the single chemical PERA approach is that is does not consider additive and/or synergistic effects of other pesticides or chemicals which together could be adverse to the beneficial uses of a waterbody.

As discussed by Lee and Jones-Lee (1999), a substantial site-specific research program is needed to substantiate that the PERA approach is a valid approach for protecting the beneficial uses of waterbodies that experience toxic pulses of OP pesticide-caused toxicity. Recently, Strauss (2000) of the US EPA Region IX has indicated that the PERA approach is not an acceptable approach for establishing a TMDL goal for OP pesticide-caused aquatic life toxicity. Strauss has indicated that the TMDL goal should be a chemical concentration that is based on the approach that the US EPA uses to develop a water quality criterion.

Since many urban streams have been converted to stormwater conveyance structures (often concretelined) with severely limited aquatic life habitat, the elimination of OP pesticide toxicity will, in many cases, likely have little or no impact on the aquatic life-related beneficial uses of the urban stream. In conducting the studies for establishing the TMDL goal, it is important to determine if toxicity in an urban stream persists for a sufficient period of time in the stream and in the receiving waters for the stream discharge to be toxic to stream and/or receiving water zooplankton with OP pesticide toxicity sensitivity similar to *Ceriodaphnia*. Often the period of time that zooplankton can be exposed to toxic conditions in an urban streamassociated with a stormwater runoff event is on the order of a few hours, i.e. the time it takes for a zooplankton present in the headwaters of the stream to be carried from this location to the point where the stream mixes with nontoxic downstream waters. The results of a fourday toxicity test where the toxicity is only manifested on the third or fourth day, have limited applicability to properly assessing significant urban stormwater runoff-associated toxicity.

Urban stormwater runoff that enters marine waters creates a special situation for evaluating the impact of OP pesticide-caused aquatic life toxicity. The studies conducted by Lee and Taylor (1999) involve assessing the presence and impacts of OP pesticide-caused aquatic life toxicity in Upper Newport Bay, Orange County, CA. Based on a now four-year study of stormwater runoff they have found that all stormwater runoff to Upper Newport Bay is highly toxic to *Ceriodaphnia* and *Mysidopsis* with typically 10 to 20 TUa. This toxicity is to *Ceriodaphnia* due to a combination of diazinon (LC₅₀ of 450 ng/L) and chlorpyrifos (LC₅₀ of 80 ng/L) as well as unknown constituents. This toxicity is typically manifested within 24 hours, where all *Ceriodaphnia* or *Mysidopsis* in the undiluted samples of stormwater runoff in the Upper Newport Bay watershed is not toxic to *Mysidopsis* (LC₅₀ of 4,500 ng/L). The toxicity found is due to chlorpyrifos (LC₅₀ of 35 ng/L) and some yet unidentified toxic constituents present in the runoff waters.

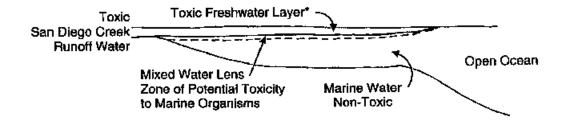
Upper Newport Bay is a marine bay with a typical salinity of 30 ppt. The stormwater runoff to the bay is freshwater. Therefore, under most conditions, the stormwater runoff forms a freshwater lens on the underlying marine waters. Studies (Lee and Taylor, 1999) on the persistence of the OP pesticide-caused aquatic life toxicity in Upper Newport Bay show that it is present only in a relatively thin layer of freshwater stormwater runoff that has mixed to a limited extent with the marine waters of the bay. Bay waters which have a salinity greater than about 5 ppt are nontoxic since the toxic freshwater has been diluted sufficiently to eliminate the toxicity to *Mysidopsis*.

Any freshwater organisms carried into the bay in the stormwater runoff will be killed by the salinity of the bay. Further, the impact of the toxicity to freshwater organisms in the tributary streams is

restricted to a few hours of exposure during a stormwater runoff event since this is the maximum transport time from the tributary stream's headwaters to the bay. No toxicity has been found in the tributary streams during non-runoff events. Therefore, the focus of evaluating the impact of the OP pesticide-caused aquatic life toxicity should be on its impact to marine zooplankton and other marine organisms.

Lee, *et al.* (2000) have reviewed the conditions that need to be considered in reliably evaluating the OP pesticide-caused aquatic life toxicity in urban stormwater runoff to marine waters. They point out that in order for the OP pesticide-caused aquatic life toxicity in the stormwater runoff to Upper Newport Bay to be significantly adverse to the beneficial uses of the Bay, a marine zooplankton must migrate from the 30 ppt marine waters into the freshwater/marine water lens that has sufficient toxicity to kill the zooplankton in the period of time that this toxicity persists in the Bay. The stormwater runoff potential toxicity situation is shown in Figure 1. The studies of Lee and Taylor (1999) have shown that the toxic concentrations persist for a day or two in the upper part of the Bay within the freshwater/marine water lens. Upper Newport Bay is a tidal bay with a maximum 10-foot tidal range. This tidal action rapidly mixes any freshwater inputs to the Bay.

Figure 1



Not only must the marine zooplankton that migrate into the toxic freshwater/marine water lens be killed by the OP pesticide toxicity, but the loss of these zooplankton must represent an essential component of the food of marine organisms that are key components of the beneficial uses of the Bay. While this is possible, it appears to be unlikely. Studies need to be done to determine if marine zooplankton migrate into the freshwater/marine water lens during a runoff event and are exposed to toxic conditions within the lens water. If organisms of this type are found, then the ecological significance of these organisms to the Bay's beneficial uses needs to be evaluated.

Water Quality Criteria/Standards as TMDL Goals

The current US EPA approach for establishing TMDL goals is to control the constituent that causes the 303(d) listing of the waterbody as being an "impaired" waterbody. Typically, the 303(d) listing arises out of an exceedance of a worst case-based water quality standard. While the US EPA (1987) published a water quality criterion for chlorpyrifos, the Agency did not require that this criterion be adopted by the states as a standard since chlorpyrifos is not considered a "toxic" pollutant.

While the US EPA has been developing the water quality criterion for diazinon for many years, it still has not developed a criterion. An Agency contractor has developed a proposed acute criterion, however, there are problems in developing the chronic criterion. The California Department of Fish and Game, however, using US EPA criteria development approaches, has developed recommended water quality criteria for diazinon and chlorpyrifos. Siepmann and Finlayson (2000) have recently

completed an updated evaluation of the recommended water quality criteria of diazinon and chlorpyrifos. They recommend a freshwater diazinon acute criterion (CMC) of 80 ng/L and a chronic criterion (CCC) of 50 ng/L. No saltwater criteria were recommended for diazinon. They recommend a freshwater chlorpyrifos CMC of 20 ng/L and a CCC of 14 ng/L. The corresponding recommended chlorpyrifos saltwater CMC was 20 ng/L and CCC was 9 ng/L. They also indicate that the diazinon and chlorpyrifos toxicities are additive.

Implementation of these criteria as worst case water quality standards which are not to be exceeded by any amount more than once in three years would likely mean that neither diazinon nor chlorpyrifos could be used on residential properties where there is any possibility of runoff from the property that has either OP pesticide in the runoff waters.

Straus (2000) has indicated these criteria would be acceptable TMDL goals to the US EPA Region IX. However these criteria can readily over-regulate the use of OP pesticides dependent on how the criteria are applied. The application of these criteria to diazinon and chlorpyrifos concentrations at the point where the stormwater runoff enters the receiving waters on a worst case basis would effectively ban the use of these pesticides for many of the current homeowners' external outside uses. They may also under-regulate aquatic life toxicity if the criteria are applied as chemical concentrations without adequate aquatic life toxicity testing to be sure that toxicity is controlled to the degree needed to protect beneficial uses.

SUGGESTED APPROACH FOR IMPLEMENTING A PHASE I TMDL GOAL FOR URBAN STORMWATER RUNOFF

In Orange County, California, about 100,000 lbs/yr (ai) of diazinon (25,000 lbs/yr) and chlorpyrifos (75,000 lbs/yr) are used by commercial applicators for residential structural purposes (termite and ant control). In addition, approximately the same amount that is purchased in the local hardware/garden store is projected to be used by the public on residential properties. The total amount of diazinon and chlorpyrifos that is needed to cause the toxicity found in stormwater runoff as it enters Upper Newport Bay is about 5 lbs/yr. It is evident that most of the diazinon and chlorpyrifos used on residential properties is not contributing to the stormwater runoff toxicity problem.

There are two types of OP pesticide uses on residential properties. The typical structural use, which is often injected into the foundations of the structures below the ground surface, probably does not contribute significantly to the OP pesticide-caused aquatic life toxicity. It is likely that the primary source of the diazinon and chlorpyrifos that causes the toxicity in urban stormwater runoff is due to the application of these pesticides above ground near structures and for lawn and garden pest control.

Studies are needed to determine how OP pesticides, and for that matter other pesticides used for various purposes on residential properties, contribute to stormwater runoff toxicity. Thus far the authors have been unable to obtain funding from either governmental agencies or pesticide manufacturers to conduct the needed studies to determine how the use of OP pesticides on residential properties leads to toxic stormwater runoff from the properties.

It is suggested that it may be possible to continue to use the OP pesticides for below ground structural pest control (termites and ants) and greatly reduce, if not eliminate, the OP pesticide aquatic life toxicity associated with stormwater runoff from residential areas. An appropriate Phase I OP pesticide control program could involve restricting the use of OP pesticides for lawn and garden pest control as well as for aboveground near-structure applications where runoff waters could carry the pesticides from the residential properties to the nearby water courses. The implementation of this approach would require restrictions on the sale of the OP pesticides to the public. Such restrictions

would have to be implemented through changing the registration governing the use of these pesticides at the federal or state level. Efforts are underway in California by municipal stormwater management agencies who face compliance with TMDLs designed to control OP pesticide-caused aquatic life toxicity in stormwater runoff to have the California Department of Pesticide Regulation change the registration of OP pesticides to restrict their use on residential properties to reduce aquatic life toxicity in stormwater runoff from these properties.

Restricting the Sales/Use of OP Pesticides on Residential Properties

Recently the US EPA has announced that it will restrict the residential use of chlorpyrifos by the public under the Food Quality Protection Act because of its potential cumulative toxicity to humans. This restriction could potentially result in a significant reduction of the OP pesticide aquatic life toxicity that is found in the Upper Newport Bay watershed stormwater runoff. Placing similar restrictions on the public sales of diazinon for residential lawn and garden use, while still allowing the use of diazinon for below ground structural control of termites and ants, could be an effective approach for implementing a Phase I TMDL OP pesticide aquatic life toxicity control program. If the restrictions on the sale of chlorpyrifos and diazinon for residential lawn and garden use do not control aquatic life toxicity in stormwater runoff, then a Phase II TMDL implementation program involving greater restrictions on the use of OP pesticides (diazinon and chlorpyrifos) would be needed.

Evaluation of the Impact of Alternate Pesticide Use

At this time there are other OP pesticides, such as propetamphos, that are used on residential properties. Several thousand lbs/yr (ai) of propetamphos are used by commercial applicators on residential properties in Orange County. Propetamphos is not measured in the conventional dual column GC scans using US EPA procedures. It could be a contributor to the unknown-caused toxicity that is found in Upper Newport Bay stormwater runoff. Also, and likely of greater concern, is the use of pyrethroid pesticides on residential properties. Through the late 1990's, approximately 25,000 lbs/yr (ai) of four pyrethroid pesticides (permethrin, cypermethrin, fenvalerate and bifenthrin) were used in Orange County. The pyrethroid pesticides are as toxic, if not more toxic, to some zooplankton as the OP pesticides. Further, the pyrethroid pesticides are beginning to be sold over-the-counter in substantial amounts for residential properties is now, or could in the future with increased use as the OP pesticides are phased out, be a cause of aquatic life toxicity in stormwater runoff.

Any appropriately developed TMDL for the control of OP pesticide-caused aquatic life toxicity must include funding to conduct appropriate studies to determine the aquatic life impacts of the alternative pesticides that are used as replacements for the OPs. Without this approach, the benefits of controlling the aquatic life toxicity in urban stormwater runoff associated with restricting the use of the OP pesticides may not occur. A key component of any TMDL program for control of OP pesticide-caused aquatic life toxicity should be an evaluation of the anticipated improvement of the beneficial uses of the receiving waters for the urban stormwater runoff.

CONCLUSIONS

The OP pesticides diazinon and chlorpyrifos are useful products for controlling pests on residential properties. They are, however, causing substantial toxicity in urban stormwater runoff and in some receiving waters for this runoff. The current degree of understanding of their impacts on beneficial uses is poorly understood. It is possible that, through appropriately conducted studies, they can continue to be used for some purposes on residential properties. The development of an appropriate TMDL goal to control OP pesticide-caused aquatic life toxicity in urban stormwater runoff will require a substantial study/evaluation program to determine for the waterbodies receiving the urban

runoff the beneficial use impairments that are likely occurring. The funding of these studies should be provided by pesticide manufacturers, formulators and users. Failure to provide adequate funding to demonstrate that the OP pesticides diazinon and chlorpyrifos can be used on residential properties without significant adverse impacts on the beneficial uses of receiving waters for the urban stormwater runoff will likely require restricting their use in residential settings.

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