

**ECOLOGICAL RISK ASSESSMENT OF SURFACTANTS ASSOCIATED WITH HERBICIDE
APPLICATIONS IN RIGHTS-OF-WAY AREAS**

Hotze Wijnja, Ph.D.
Division of Crop and Pest Services
Massachusetts Department of Agricultural Resources

February, 2010

Table of Contents

1.	Introduction.....	1
2.	Background Information on Herbicide Surfactants	2
3.	Ecotoxicity of Herbicide Surfactants	3
3.1	General Overview of Ecotoxicology of Herbicide Surfactants	3
3.2	Ecotoxicological Endpoint Values for Herbicide Surfactants	5
4.	Exposure Assessment.....	6
4.1	Application rates	6
4.2	Exposure Pathway Evaluation	6
4.3	Overview of Modeling Approach for Exposure Assessment	6
4.4	Tier I Exposure Assessment.....	7
4.4.1	Screening Level Results for POEA.....	8
4.4.1.1	AgDrift model and runoff assumption	
4.4.1.2	GENEEC2 model	
4.4.2	Screening Level Results for NPE	10
4.4.2.1	AgDrift model and runoff assumption	
4.4.2.2	GENEEC2 model	
4.4.3	Screening Level Results for AE.....	11
4.4.3.1	AgDrift model and runoff assumption	
4.4.3.2	GENEEC2 model	
4.4.4	Screening Level Results for PE	12
4.4.4.1	AgDrift model and runoff assumption	
4.4.4.2	GENEEC2 model	
4.5	Tier II Refined Exposure Assessment for Soil	13
4.5.1	Introduction	
4.5.2	PRZM Model Overview	
4.5.3	PRZM Input Parameters	
4.5.4	PRZM Results for POEA	
4.6	Tier II Refined Exposure Assessment for Surface Water.....	16
4.6.1	PRZM/EXAMS Model Overview	
4.6.2	PRZM/EXAMS Input Parameters	
4.6.3	PRZM/EXAMS Results	
4.6.3.1	POEA	
4.6.3.2	NPE	
4.6.3.3	AE	
4.6.3.4	PE	
4.7	Estimation of Surfactant Concentrations in the Shore Margin	24
4.7.1	Completely Mixed Pond versus Short-Term Near-Shore Margin	
4.7.2	Near-shore margin Concentrations in a Model Pond	
4.7.3	Margin Concentration for POEA	
4.7.4	Margin Concentration for NPE	
4.7.5	Margin Concentration for AE	
4.7.6	Margin Concentration for PE	

4.8	Summary of Tier II Refined Modeling Results	30
4.8.1	Soil Concentrations	
4.8.2	Surface Water Concentrations	
5.	Toxicity Summary and Risk Characterization.....	33
5.1	Comparison of EECs with Toxicity Endpoints.....	33
5.2	Risk Characterization by Risk Quotients	35
6.	Discussion and Conclusions	36
6.1	POEA, NPE, AE, and PE Surfactant	36
6.2	Additional Surfactants and Exposures	38
6.2.1	General Comments	
6.2.2	Organosilicones	
6.2.3	Adjuvants	
6.2.4	Terrestrial Exposure related to amphibians	
7.	References.....	40
	Appendix 1 Ecotoxicity Assessment of Phosphate Ethoxylated Ester Surfactants ...	A1
	Appendix 2 PRZM Input file for PRZM Modeling.....	A14
	Appendix 3 PRZM Input file for PRZM/EXAMS Modeling.....	A16

1. INTRODUCTION

Herbicide applications are used in rights-of-way (ROW) management in Massachusetts to control vegetation in support of public safety measures. These herbicide applications are regulated according to provisions specified in rights-of-way management (333 CMR 11.00) in order to prevent unreasonable risks to human health or the environment. Specific restrictions are provided for so-called ‘sensitive areas’, including wetlands and other water resources. These restrictions include application methods, designations of no-spray and limited-spray zones, and a list of herbicide products to be used in sensitive areas.

In the evaluation process of herbicide product registrations for use in sensitive ROW areas, the Department of Environmental Protection (MassDEP) and Department of Agricultural Resources (MDAR) follow a memorandum of understanding (MOU) (333 CMR 11:04 (1)) that specifies the selection criteria for suitable herbicide products for this use. For the evaluation of possible herbicide risks, the MOU provides criteria for the active ingredients as well as for the so-called “inert” or “other” ingredients, specifically surfactants.

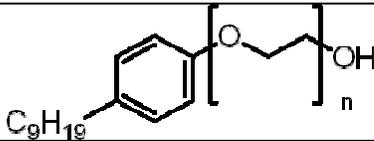
Concerns have been raised about the potential risk that surfactants in herbicide products may pose to aquatic organisms, specifically amphibians. Review of scientific literature suggests that certain types of surfactants used in herbicide formulations may have acute toxic effects at elevated exposure levels. These toxicological concerns for herbicide formulations are predominantly based on studies that determined toxicological endpoints in dose-response laboratory or mesocosm experiments. For a proper risk assessment in field situations, it needs to be evaluated whether the dose-response data translate into unreasonable risk in the field. Such a risk assessment requires an evaluation of the exposure of surfactants from herbicide applications. Subsequently, a risk assessment can be made relative to established toxicological end-points.

The following document describes a risk assessment of herbicide surfactants in ROW areas taking into account the restrictions provided in the ROW management regulations. Federal regulations allow only limited information regarding the identity and nature of the inert ingredients. Consequently, the evaluation of these ingredients relies mainly on review of the open literature on the toxicity and environmental fate. First, the ecotoxicology of herbicide surfactants will be reviewed, followed by an exposure assessment and risk characterization.

2. BACKGROUND INFORMATION ON HERBICIDE SURFACTANTS

Besides active ingredients, herbicide formulations also contain other compounds called adjuvants. Adjuvants are ingredients that modify and enhance the performance of the herbicide product by affecting functions such as solubility, absorption, penetration and translocation (Krogh et al, 2003). Among the adjuvants, surfactants generally make up the largest part of the inert ingredients. Most surfactants used with herbicides are considered non-ionic surfactants and include alcohol ethoxylates (AEs), alkylphenol ethoxylates (APEs), alkylamine ethoxylates (ANEs), silicon-based surfactants (organosilicones), and oils. Surfactants are typically present as a technical mixture containing a range of compounds in different ratios (Knowles, 1998). The nature of a surfactant is that they have an affinity for accumulation at interfaces between water and some other phase or surface. Consequently, the surface tension is affected, which in turn facilitates the emulsifying, dispersing, spreading, sticking and wetting properties of the herbicide formulation (Knowles, 1998). The hydrophilic part of a non-ionic surfactant molecule is generally formed by an ethoxylate chain, whereas the hydrophobic (or lipophilic) part is formed by an alkyl chain. Some examples are shown in Table 1. In addition to non-ionic surfactants, anionic surfactants find also applications in herbicides. The anionic phosphate ethoxylated ester (PE) will be included in this assessment. Many herbicides products already contain adjuvants as part of their formulation and can be used directly; others require additional adjuvants in the final tank-mix to further optimize performance and adjust the tank mix for specific applications.

Table 1. Molecular structures of surfactants commonly used in herbicide formulations.

SURFACTANT CLASS	EXAMPLE OF MOLECULAR STRUCTURE
Alkyl Amine Ethoxylate (ANE) (includes POEA)	$R - N \begin{cases} (CH_2CH_2O)_x H \\ (CH_2CH_2O)_y H \end{cases} \quad x+y = 15$ <p>[Polyoxyethylene (15) cocoalkylamines]</p>
Alkyl Phenol Ethoxylates (APE) Shown: Nonylphenol Ethoxylate (NPE)	
Alcohol Ethoxylates (AE) Shown: C ₁₂ AE ₈	$CH_3(CH_2)_{10}CH_2 \left[OCH_2CH_2 \right]_8 OH$
Phosphate Ethoxylated Ester (mono)	$CH_3(CH_2)_nOCH_2CH_2 (OCH_2CH_2)_mOP(O)OHO^-$

3 ECOTOXICITY OF HERBICIDE SURFACTANTS

3.1 GENERAL OVERVIEW OF ECOTOXICOLOGY OF HERBICIDE SURFACTANTS

This general overview presented here is based on several reviews on this topic in the literature and some general assessments and conclusions are summarized here. In general, surfactants and other coformulants in herbicide products could pose toxicological or environmental risk since they are applied directly onto or migrate to terrestrial or aquatic areas where they can subsequently affect biota (Blasco et al., 2003). At sufficiently high levels of exposure, surfactants are toxic to biota, especially aquatic organisms, because of their surface tension and wetting effects (Reekmans, 2003). However, at typical environmental concentrations, most surfactants are not acutely or chronically toxic to aquatic organisms (Ying, 2006).

A comprehensive review of the environmental properties, fate and toxicology of non-ionic surfactants (focused mostly on AEs, some ANEs) in pesticides concluded that these surfactants used in herbicide formulations pose no significant risk to aquatic and terrestrial organisms (Krogh et al., 2003). The relatively low rate of surfactant applications associated with pesticide products compared to other surfactant uses, and the physical and chemical properties that make them relatively immobile in terrestrial systems and their relative low persistence in the environment result in low environmental concentrations.

With the review of the ANE herbicide surfactant class, Krogh et al. (2003) did not discuss the particular ANE surfactant polyethoxylated alkylamine (POEA), which is an ingredient in commonly used glyphosate formulations. It is well documented that POEA has higher toxicity towards aquatic organisms than the active ingredient glyphosate (Giesy et al., 2000). Giesy et al. (2000) presented a comprehensive ecological assessment of glyphosate-POEA formulations and concluded that terrestrial uses pose minimal risk for potentially exposed non-target organisms, including aquatic organisms. It was also indicated that direct applications to shallow water bodies may pose a higher risk.

The toxic effects of glyphosate-POEA herbicides on aquatic organisms, specifically amphibians, has been shown in several studies (Mann and Biddwell, 1999; Perkins et al., 2000; Howe et al., 2004; Relyea, 2005abc; Braush et al., 2007). Among commonly used herbicide surfactants, the POEA-based surfactants showed the highest toxicity towards aquatic (bluegill sunfish) organisms among 19 herbicide surfactant products (Haller and Stocker, 2003). Surfactant products containing AEs and APEs showed moderate toxicity, while the organosilicones showed low toxicity.

The dramatic effects observed in Relyea's studies (Relyea, 2005abc) attracted significant media attention and were also discussed in the context of global amphibian decline. As was pointed out, however, the direct applications of the glyphosate-based herbicides containing POEA surfactant to aquatic systems, as was done in the mesocosms studies by Relyea, was in violation with label instructions (Langeveld, 2006; Thompson et al., 2006). In addition, the applied rates were 3-10 times higher than the label rates for uses in non-cropland, forestry, or agriculture. These studies have therefore limited relevance to typical field terrestrial applications. However, these studies do have value as a worst-case scenario of inadvertent overspray of a water body by aerial spraying as may occur in forest management (Thompson et al., 2006; Relyea, 2006).

While the studies on glyphosate-POEA formulations listed above highlight and confirm the known aquatic ecotoxicology of POEA surfactants (and very low toxicity of the active ingredient glyphosate itself), a comprehensive research using a tiered risk assessment of the use of glyphosate-POEA based herbicides in forest management indicated that the risk was low under typical field conditions and management (Edgington et al., 2003; Chen et al., 2003; Wojtaszek et al., 2004; Thompson et al., 2004). These conclusions are also consistent with other comprehensive risk assessments (Solomon and Thompson, 2003; Giesy et al., 2000). Addressing public concerns about herbicide applications in forest management, Tatum (2004) concludes that modern herbicides formulations used according to label instructions pose little risk to non-target wildlife.

Nevertheless, the potential ecotoxicity of POEA surfactants and their common use in ROW herbicide applications justifies an evaluation of the ecotoxicological risk in the context of the evaluation of herbicide products for registration in Massachusetts' ROW's Sensitive Area List. It should be evaluated whether spikes in environmental concentrations in ROW sensitive area waters could occur as a result of herbicide applications.

Another class of surfactants of ecotoxicological concern comprises the alkylphenol ethoxylates (APEs). This class of surfactants has received a lot of attention because of its wide use as a household, industrial, and pesticide surfactant. Its toxicological concerns are especially related to the nonylphenol ethoxylates (NPEs). The NPEs are found to be much less toxic and persistent than their degradation products nonylphenol (NP) and nonylphenoxy acetic acids (NPECs) that are formed under anaerobic conditions in wastewater treatment (Ying, 2006). It is well documented in the literature that under aerobic conditions very little NP is formed in terrestrial and aquatic systems (Jonkers et al., 2001; USDA Forest Service, 2003a; Naylor et al., 2006; Ying, 2006). Consequently, the fate of NPEs in agricultural and other land-use settings does not result in NP and therefore, its toxicological concern is much less in the context of herbicide use. It was concluded that the NPE surfactants from herbicide applications therefore pose low ecological risk (USDA Forest Service, 2003a).

The ecotoxicological concern for these POEA and NPE surfactants associated with certain herbicide applications has generated evaluations and reviews by several government agencies that are directly involved with herbicide applications, such as the USDA Forest Service and the Bureau of Land Management (Diamond and Durkin, 1997; USDA 2003a, 2003b; USDI, 2007). These evaluations generally concluded that applications according to regulations (specifically with respect to rates and avoidance of applications near surface waters and other sensitive areas) pose very low risk to aquatic and terrestrial organisms. These reports point out that the terrestrial fate of these surfactants is characterized by strong adsorption to soil particles, degradation in a timely manner and, consequently, little concern for leaching into groundwater and runoff to surface waters. In addition, the environmental concentrations caused by drift or runoff are normally well below levels of concern.

Based on the review presented above, the following types of surfactants are of most relevance for risk evaluation in this context: nonionic ANEs, AEs and APEs. The surfactant POEA (belonging to the ANEs) has been subject to many studies (see review above) and was also found to be the

most toxic among commonly used herbicide adjuvants (Haller and Stocker, 2003). Therefore, the evaluation of POEA can provide a reference point for assessing the other surfactants.

A less common type of herbicide surfactant is the class of phosphate ethoxylated esters, which appeared in a recently introduced rights-of-way herbicide formulation. Little information on environmental fate and toxicity is available for this class of surfactant. Similar surfactant compounds (such as polyoxyethylene-polyoxypropylene-phosphate, nonylphenol-ethoxylated-phosphate ester, polyethylene-glycol—nonylphenyl-ether-phosphate) were classified by EPA-OPP as inerts that will not adversely affect public health or the environment (former List 4B) based on exposures via typical pesticide use patterns (US EPA-OPP, 2004). Since this type of surfactant is part of a new formulation that replaces a current product on the Sensitive Area Materials List, the phosphate ethoxylated esters were included in this risk assessment at a later stage of this assessment.

The overview of ecological risk described above highlights the concern for potential risks or effects of surfactants to aquatic systems. Although ROW herbicide applications do not involve direct applications to aquatic systems, there could be potential indirect impact to aquatic systems by exposure through drift, runoff or leaching into water bodies from treated ROW areas.

3.2 ECOTOXICOLOGICAL ENDPOINT VALUES FOR HERBICIDE SURFACTANTS

Aquatic toxicology endpoints (e.g., LC₅₀, EC₅₀, NOEC) for several commonly used types of surfactants are available in the various review documents cited in the previous sections. The endpoint data are used in the risk characterization that is described in chapter 5. In the absence of sufficient ecotoxicity information for the phosphate ethoxylated ester surfactants, endpoint values were estimated using quantitative structure activity relationship (QSAR) modeling. More details on this analysis are described in Appendix 1.

4. EXPOSURE ASSESSMENT

4.1 HERBICIDE APPLICATION RATES

The application rates of herbicide products used in ROW vegetation management vary widely due to factors such as method of application, type of ROW area, and vegetation types. Massachusetts' ROW regulations require the use of the lowest labeled rate. Broadcast foliar applications are typical for rail road and highway applications. Utilities ROW applications typically use selective foliar application to manage specific plant species. This selective spraying pattern consequently results in lower application rates per acre compared to broadcast spraying. Cut-stump application is a more selective method focused on smaller areas and consequently results in even lower application rates per acre. For the purpose of this risk assessment, the highest rates in a broadcast foliar application as is used in a railroad scenario will be considered as part of a conservative worst-case approach.

4.2 EXPOSURE PATHWAY EVALUATION

The ROW regulations contain provisions that specifically protect aquatic systems from unreasonable adverse effects. Direct applications of herbicides on or within 10 feet from wetlands, waters over wetland, riverfront areas, and certified vernal pools are prohibited. Only limited herbicide applications (selectively by low pressure) are allowed in the zone between ten feet and 100 feet from a water body (333CMR:11.04 (4)). In addition, applications are prohibited within state-listed species habitat. The exposure pathways for herbicides to water bodies in ROW sensitive areas are therefore indirect through migration from applied areas. Off-site drift may occur when herbicides are applied and a portion of the herbicides drifts outside of the treatment area and may deposit on non-target areas such as nearby water bodies. As a worst-case scenario, a broadcast spray at typical rates in a limited-spray area will be considered. Other potential pathways are through surface runoff and leaching through the soil. Accordingly, the exposure of water bodies to surfactants from herbicides will be evaluated using these pathways.

4.3 OVERVIEW OF MODELING APPROACH FOR EXPOSURE ASSESSMENT

The exposure assessment to estimate concentrations of herbicide surfactants in aquatic systems was based on the tiered approach employed by EPA-OPP. In this approach, Tier I and Tier II computer modeling are used to generate estimated environmental concentrations and support aquatic risk assessments¹. Initially, an exposure assessment was done using a drift model combined with a runoff assumption. An overview of the various models and scenarios used in the assessment here is presented in Table 2. For a given application rate, these model approaches can be used for surfactants for formulated herbicide products as well as for surfactants added as adjuvants to a tank mix.

The results of the various exposure assessments are presented here to show the progression from a generic approach toward a more refined exposure assessment that was performed during the course of this risk assessment.

¹ Further information available at URL: <http://www.epa.gov/oppfead1/trac/science>

Table 2. Overview of models and scenarios used in the exposure assessment

Screening Level and Model	Scenario	Exposure Pathway Simulation		Fate in Water
		Spray Drift	Runoff/Leaching	
Tier I:				
AgDrift + Runoff/Leaching Assumption	Generic situation; Distance from water body; Single event	Modeled based on application method, distance and conditions	Fraction of total applied chemical is assumed to runoff/leach	Not Considered
GENEEC2	Generic highly vulnerable site; 10 ha field, 1 ha x 2 m deep pond	Modeled based on application method, condition parameters and distance from application	Single large rainfall event; removal of large fraction of applied chemical; adsorption + degradation	Degradation and adsorption to sediment; peak and multiple-day average concentrations
Tier II:				
PRZM	Site-specific soil, topography, weather, and crop (30 yrs); detailed soil profile	Application efficiency factor (total – spray drift fraction); edge-of-field	Day-to-Day simulation of hydrology and chemical transport in each soil layer	Not Applicable
PRZM/EXAMS	Site-specific as described with PRZM; 10 ha field draining into 1 ha x 2 m deep pond	Spray drift load in pond based on fraction (input) of total applied chemical; edge-of-field	Day-to-Day simulation of hydrology and chemical transport through soil and into pond	Day-to-Day simulation of concentration in pond based on influx, adsorption and degradation

4.4 TIER I EXPOSURE ASSESSMENT

The initial evaluation was performed based on the assessment of drift exposure using the AgDrift model and the assessment of a worst-case runoff scenario. Subsequently, an exposure assessment was performed using the GENERIC Estimated Exposure Concentration (GENEEC) model initially developed by Parker et al. (1995). The model was adopted by EPA’s Office of Pesticide Programs (EPA-OPP) as a first tier screening model in their evaluation of aquatic risk assessments.² This first tier model was developed based on criteria that included the simulation of a vulnerable site defined as one at which high concentration levels are expected due to conditions of pesticide application, weather, and soils known to favor transport to and persistence in surface water. The model mimics a more sophisticated PRZM/EXAMS model (see Section 4.6), but requires fewer inputs. The model is generic in that it considers a given set of conditions related to climate, soils, topography or crops. It simulates the effect of a single large (6 inch) rainfall/runoff event occurring two days after application and the impact on a “standard pond”. GENEEC2 calculates acute as well as longer-term estimated environmental

² Further information available at URL: http://www.epa.gov/oppefed1/models/water/geneec2_description.htm

concentrations in the pond water. It considers reduction in dissolved concentration due to adsorption of pesticide to soil or sediment, incorporation, degradation in soil before wash-off to a water body, direct deposition of spray drift into a water body, and degradation of a pesticide in the soil and within a water body.

4.4.1 Screening-level exposure assessment of POEA surfactants

4.4.1.1 AgDrift Model and Runoff Assumption

An exposure assessment was done based on the use of glyphosate herbicides (for example, Razor SP, Accord SP³), containing POEA surfactants. The typical application rate of POEA used in ROW areas in Massachusetts was estimated based on recommended herbicide rates as listed in yearly operational plans of various utilities and municipalities. For glyphosate herbicides products containing 41% glyphosate the typical rate is 2 qt/acre in broadcast foliar applications. It was conservatively assumed that the typical 15% v/v surfactant concentration in glyphosate-POEA herbicide formulas was 100% POEA. It can be calculated, taking into account the density of the herbicide product and the density of the surfactant, that at this herbicide rate results in a rate of 0.607 lbs/acre (0.68 kg/ha) for POEA.

The off-site drift of POEA was estimated based on the modeling results using the AgDrift model. The modeling was performed using the Tier 1 ground application model option. The results from the AgDrift model were evaluated to estimate POEA concentrations deposited at various distances from the application site. The input parameter values were selected to be representative of the ROW scenario, including low-boom ground applications, fine-medium drop size, typical application rate, distances of 10ft and 100ft from application area, and deposition downwind in a water body with dimensions of a width of 100ft and a depth of 0.5ft, considered to be representative of a vernal pool (Thompson et al., 2004). The off-site drift scenario based on a 10 ft distance can be considered a worst-case scenario in ROW area by intrusion of a normal spray application in a limited-spray zone between 10 and 100 feet away from a water body. The estimated environmental concentrations (EEC) of POEA from deposition in pond water for this scenario are 0.0038 mg/L at 10 ft and 0.0031 mg/L at 100 ft application distance.

Migration of POEA by infiltration and percolation through the soil is expected to be low based on the POEAs environmental fate characteristics. The mobility of POEA in soils is very low (Giesy et al., 2000; Wang et al., 2005), consistent with the observations of other ANEs in soils (Krogh et al., 2003). As is typical for non-ionic surfactants (Krogh et al., 2003; Ying, 2006), POEA has a very high affinity for sorption onto soil materials. The organic carbon/water partitioning coefficient (K_{OC}) for POEA is reported to be in the range of 2500-9600 L/kg, indicating a high affinity for sorption (Wang et al., 2005). POEA readily degrades in soils with an estimated soil half-life of less than a week (Wang et al., 2005).

Runoff of POEA is also expected to be low given the high affinity for sorption to soil. Although direct runoff data for POEA are not available, field observations of herbicide (formulation with POEA) runoff along highways indicated that only very small amounts of glyphosate were mobilized (Huang et al., 2004). Given that glyphosate and POEA both have similar

³ Razor SP, EPA reg. #: 222-366; Accord SP, EPA reg. #: 62719-322

environmental fate characteristics with respect to sorption affinity ($K_{OC} > 2500$ L/kg), it can be expected that POEA also has low mobility in situations with runoff. A monitoring study performed by MDAR on the glyphosate impact on waters in the proximity of railways showed that glyphosate was not traveling beyond the 10 ft buffer zone (MDAR, 2006). Although the surfactant was not determined, it is likely that POEA has a similar fate.

Nevertheless, an initial assessment considering a worst-case scenario for runoff can be considered where 1% of the applied herbicide product runs off from a 0.5-acre area near a pond of the same dimensions considered above with the drift assessment. The 1% runoff is a reasonable value considering the values used in the risk assessment by Giesy et al. (2000) and the buffer zones used in the ROW area applications. The resulting instantaneous concentration in the pond water would be 0.0091 mg/L POEA.

The total EEC value in a worst-case scenario due to drift and runoff would be 0.013 mg/L POEA. Overall, it can be concluded that the exposure of POEA surfactants from ROW herbicide application is very low. For comparison, the EEC value in Relyea’s mesocosm experiment (2005a) was estimated at 1.3 mg/L.

4.4.1.2 GENEEC2 model

Subsequently, an exposure assessment was performed with the EPA’s Tier 1 aquatic exposure GENEEC2 model⁴. This model combines the runoff and spray drift exposures to a water body from herbicide applications on a nearby field. The input parameters for this model included the application rate, number of applications per year, the soil organic carbon-water partitioning coefficient (K_{OC} : 2500-9600), aerobic soil metabolic half-life (conservatively uses 3 times the experimental value: $3 \times 5 \text{ d} = 15 \text{ d}$), ground spray option using low boom and fine-to-medium drop size, width of no-spray zones (10 and 100ft), aqueous solubility (used as upper limit for EEC; set at 100 ppm), aerobic metabolic aquatic half-life (21 d), hydrolysis half-life (set at 0), and photolysis half-life (set at 0 d). The EECs are calculated for peak as well as maximum averages over 4, 21, 60, and 90 d. Table 3 lists the peak EEC values at 10 ft and 100 ft distance for three different K_{OC} values. The values at the different K_{OC} values reflect to some extent the behavior in different soil types. A K_{OC} value of 2500 represents a sandy-loam, 6000 a silt-loam, and 9600 a clay-loam soil. The model-generated concentrations were multiplied by a factor of 2.67 based on modifications of the “standard pond” dimensions and land-to-water ratio to make it more representative of a vernal pool scenario in a rights-of-way situation. The use of this multiplication factor is described in more detail with the description of the PRZM-EXAMS model in section 4.6.2.

Table 3. Peak estimated environmental concentration (EEC) of POEA as a function of distance and soil K_{OC} value calculated with the GENEEC2 model. See text for input parameters.

K _{OC} VALUE	EEC (MG/L)	
	10 ft No-Spray Zone	100 ft No-Spray Zone
2500	0.016	0.015
6000	0.010	0.0097
9600	0.0083	0.0080

⁴ EPA OPP-EFED water models URL: <http://www.epa.gov/oppefed1/models/water/index.htm#geneec2>

Comparison of the GENEEC2 model results with the initial assessment data indicates similar EEC values. As the initial analysis indicated, the contribution due to drift is relatively small compared to the contribution of runoff. The GENEEC2 modeling results also indicate the dominance of runoff. The relatively small difference between the results of 10 ft and 100ft no-spray zone is consistent with low drift exposure and dominance of runoff. Comparison of the modeling results at different K_{OC} values indicates the importance of sorption to the overall exposure.

4.4.2 Screening Level Exposure Assessment of NPE surfactant

4.4.2.1 AgDrift and Runoff Assumption

This evaluation will focus on the NPE, which is the more common type of APE used in herbicide formulations and is also of most toxicological concern within the APEs. There are several commercial NPE surfactants available for use as adjuvants in herbicide formulations (Bakke, 2002). The most common NPE used in pesticide formulation is a mixture that has, as a majority, 8-10 ethoxylate groups attached (NPE8-10). In contrast to POEAs, NPEs are typically blended with other surfactants such as AEs and organosilicones.

The same conservative application rate of 0.607 lb/acre as described with the POEA surfactant will be adapted here for NPE. Drift exposure was evaluated using a conservative assumption that the surfactant was composed only of NPE in the herbicide formulation (15 % v/v). Given the input parameter values, the AgDrift model-generated EEC values of NPE in pond water for this scenario are 0.0038 mg/L at 10 ft and 0.0031 mg/L at 100 ft distance.

The runoff and leaching into the soil can be qualitatively evaluated based on the sorption characteristics. NPE surfactants have a very high affinity for sorption to soils and sediments. Soil/sediment-to-water partitioning coefficients (K_D) for NPE8-10 are approximately 500 L/kg (Ying, 2006). The groundwater regulatory standard for immobility in soils is a $K_D > 20$ L/kg (333 CMR 12, section 2). Consequently, it can be expected that NPE surfactants exhibit low mobility upon application in terrestrial systems. With the same assumptions as described for POEA above, an initial assessment considering a worst-case runoff scenario would result in the same pond water concentration of 0.0091 mg/L NPE. The total EEC value in a worst-case scenario due to drift and runoff would be 0.013 mg/L NPE, indicating a low exposure of NPE surfactants from ROW herbicide application.

4.4.2.2 GENEEC2 model

The GENEEC2 model-generated peak EEC values for NPE are shown in Table 4. The EECs calculated with a K_D value of 500 represent situation based on the typical value for soil-water partitioning. The EECs calculated with a K_D value of 100 represent a situation with soils exhibiting a lower affinity for NPE sorption.

Table 4. Peak EEC values for NPE as a function of distance and K_D value calculated with GENEEC2 model. ¹

K_D VALUE	EEC (MG/L)	
	10 ft No-Spray Zone	100 ft No-Spray Zone
100	0.0088	0.0084
500	0.0060	0.0058

¹Input for aerobic metabolic soil and aquatic half-life was conservatively set at 25 d.

The GENEEC2 model-generated EEC values are slightly lower than the results of the initial assessment. This may be the result of NPE's relative high K_D values that were part of the model simulations, causing lower runoff and leaching due to higher retention in soils.

4.4.3 Screening Level Exposure Assessment of AE surfactant

4.4.3.1 AgDrift Model and Runoff Assumption

For the off-site drift analysis for AEs, the same assumptions were made as described with the assessment of drift for NPE and POEA. It was conservatively assumed that a formulation contained 100% AEs as a surfactant at a 15% v/v concentration. The EEC values for AEs in water for the pond scenario are 0.0038 mg/L at 10 ft and 0.0031 mg/L at 100 ft distance.

The surface runoff and transport through soils of AEs from the treated area is again characterized by low mobility due to high affinity for sorption to soil materials. The partitioning constant values for AEs range from 40 to 3500 L/kg (Krogh et al., 2003; Ying, 2006), indicating that these compounds are generally immobile in soils and sediments. Exposure of AEs to nearby water bodies through these pathways is therefore expected to be low. As described above for POEA and NPE, an initial assessment considering a worst-case runoff scenario could result in a pond water concentration of 0.0091 mg/L AE. The total EEC value in a worst-case scenario due to drift and runoff would be 0.013 mg/L AE, indicating low exposure of AE surfactants.

4.4.3.2 GENEEC2 model

The GENEEC2 model-generated peak EEC values for AEs are shown in Table 5. The range of K_D values used here represents a variety of different AEs that can potentially be present in formulations. It also represents variability in sorption affinity of soils.

The GENEEC2 model EEC values calculated with the low K_D are similar to values of the initial assessment. The lower EEC values calculated with the high K_D indicated the importance of sorption to soil in the fate of AEs.

Table 5. Peak EEC values for AE calculated as a function of distance and soil K_D value calculated with GENEEC2 model. ¹

K_D VALUE	EEC (MG/L)	
	10 ft No-Spray Zone	100 ft No-Spray Zone
40	0.0124	0.0120
3500	0.0034	0.0033

¹Input for aerobic metabolic soil and aquatic half-life was conservatively set at 10 d.

4.4.4 Screening Level Exposure Assessment of PE surfactant

4.4.4.1 AgDrift Model and Runoff Assumption

Using the same assumptions as described with the previous surfactants, the simple off-site drift and runoff evaluation results in the EEC values for PEs in pond water of 0.0038 mg/L at 10 ft and 0.0031 mg/L at 100 ft distance. An initial assessment considering a worst-case runoff scenario could result in a pond water concentration of 0.0091 mg/L PE. The total EEC value in a worst-case scenario due to drift and runoff would be 0.013 mg/L PE.

The partitioning constant values for a PE surfactant were estimated based on the value for anionic surfactants as reported by Ying (2006). An average K_{OC} value of 600 was used here. It is known that anionic surfactants have somewhat higher mobility (lower partitioning coefficients, K_{OC}) compared to non-ionic surfactants (Ying, 2006). Given that PE surfactants are relatively biodegradable (Wasow, 1996), the soil half-life value was assumed to be 10 d. These parameter values together with application and scenario parameters as described previously were used to estimate peak EEC values, which are shown in Table 6. The range of K_{OC} values used here represents a variability in sorption affinity of PEs as well as the variability in sorption characteristics of soils.

4.4.4.2 GENEEC2 model

The GENEEC2 model-generated EEC values calculated with the low K_{OC} are somewhat higher to the values of the initial assessment. This is consistent with the somewhat higher mobility of PEs. The lower EEC values calculated with the high K_D indicated the importance of sorption to soil in the fate of PEs.

Table 6. Peak EEC values for PE as a function of distance and soil K_{OC} value calculated with the GENEEC2 model. See text for input parameters.

K_{OC} VALUE	EEC (MG/L)	
	10 ft No-Spray Zone	100 ft No-Spray Zone
200	0.0222	0.0219
600	0.0152	0.0149
1000	0.0114	0.0112

4.5 TIER II REFINED EXPOSURE ASSESSMENT FOR SOIL

4.5.1 Introduction

The refined exposure assessment was performed with the use of the more sophisticated PRZM-EXAMS model. This model combines a field scale leaching and runoff model with a water model and requires site-specific soil, topography, weather, and vegetation input. Since the behavior and fate of surfactants in soil is a critical factor in the aquatic exposure, the behavior and fate of the POEA simulated by the PRZM model will be described first. Subsequently, the aquatic exposure will be described considering a whole-pond scenario and a near-shore margin scenario (section 4.7).

4.5.2 PRZM model overview

The Pesticide Root Zone Model (PRZM)⁵ is a one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone. The model consists of hydrologic (flow) and chemical transport components to simulate runoff, erosion, plant uptake, leaching, decay, foliar wash off, and volatilization. Pesticide transport and fate processes include advection, dispersion, molecular diffusion, and soil sorption. The model simulations include soil temperature effects, volatilization and vapor phase transport in soils, irrigation simulation.

Predictions can be made for daily, monthly or annual output. PRZM allows the user to perform dynamic simulations considering pulse loads, predicting peak events, and estimating time-varying emission or concentration profiles in layered soils.

PRZM3 is a standard model to be used in environmental risk and exposure assessments by the U.S. EPA and is included in the FIFRA list of recommended regulatory models for USA Pesticide Registration.

4.5.3 PRZM input parameters

The input for PRZM model includes hydrology and erosion parameters, crop characteristics including emergence and harvest dates, pesticide properties and application rates, soil characteristics, and meteorological data.

For the purpose of the risk assessment in the MDAR Rights-of-Way (ROW) scenario, an existing scenario (described in Section 4.6.2 below) for the Texas Barton Spring Segment Rights-of-Way scenario was modified with respect to the soil input parameters, and the meteorological data set for Boston was used for climate input.

As a first approach, the soil selected for the MA ROW scenario model simulations was the Massachusetts State soil: Paxton fine sandy loam. The Paxton soils occur on about 400,000 acres in the state and consist of well drained loamy soils formed in acid subglacial till. The horizons

⁵ URL address: <http://www.epa.gov/oppefed1/models/water/index.htm#przm>

and parameters as defined in the model input are listed in Table 7. The PRZM input file is included in Appendix 2.

The “crop” data were defined to be representative of vegetation in a ROW area. Pesticide (in this case, POEA surfactant) application was once a year on June 10 at a rate of 0.68 kg surfactant per ha (0.607 lb/acre). This rate is representative for herbicide applications in a rail road scenario.

Table 7. Soil input parameters for the Paxton soil as used in the PRZM and PRZM-EXAMS model simulations.

Horizon	Thickness (cm)	Bulk Density (g/cm ³)	Field Capacity water content (cm/cm)	Wilting pt. Water content (cm/cm)	Organic carbon (%)
1	0-12	1.51	0.28	0.16	1.0
2	12-23	1.55	0.28	0.16	0.75
3	24-46	1.55	0.25	0.15	0.40

The input values for the chemical and physical parameter of the surfactants is listed in Table 8. Hydrolysis and photolysis was not simulated (values were set to zero).

Table 8. Surfactant physical and chemical parameter values used in PRZM and PRZM-EXAMS modeling

Surfactant	Sorption constant		Soil Aerobic half-life (d)	Aquatic aerobic half-life (d)
	K _{OC}	K _D		
POEA	2500-9600		15	21
NPE		100-500	15	21
AE		40-3500	10	15
PE	200-1000		15	21

4.5.4 PRZM modeling results for POEA

Some examples of options for output data are shown below. The simulated total POEA soil concentration in the various horizons of a soil in a ROW management area with an annual herbicide application rate of 0.68 kg/ha POEA is shown in Fig. 1 for 1980-1990. The data indicate an annual peak concentration ranging from approximately 250-325 ppb in the top horizon. Note that the POEA surfactant was only present in the top horizon of the profile, indicating very low mobility within the soil profile.

The PRZM output includes an annual mass balance of the applied pesticide and specifies the fractions in the various environmental compartments. Figure 2 shows the mass balance fractions for POEA. These data indicate that the majority (>98%) of the applied POEA decays in the soil. Loss due to runoff and erosion ranges between 0.1 and 1.2%. The results show no leaching below the root zone and core depth, and negligible residual total concentrations in the soil profile.

POEA Surfactant Concentration in Soil Horizons

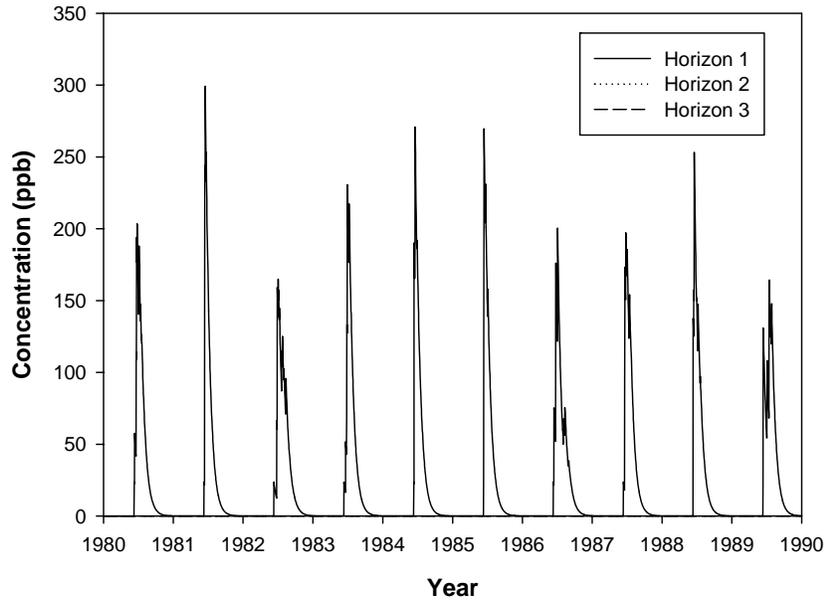


Fig. 1. PRZM model-generated total soil concentrations ($\mu\text{g}/\text{kg}$) in various horizons for 1981 - 1990.

Mass Balance of POEA Surfactant in Soil

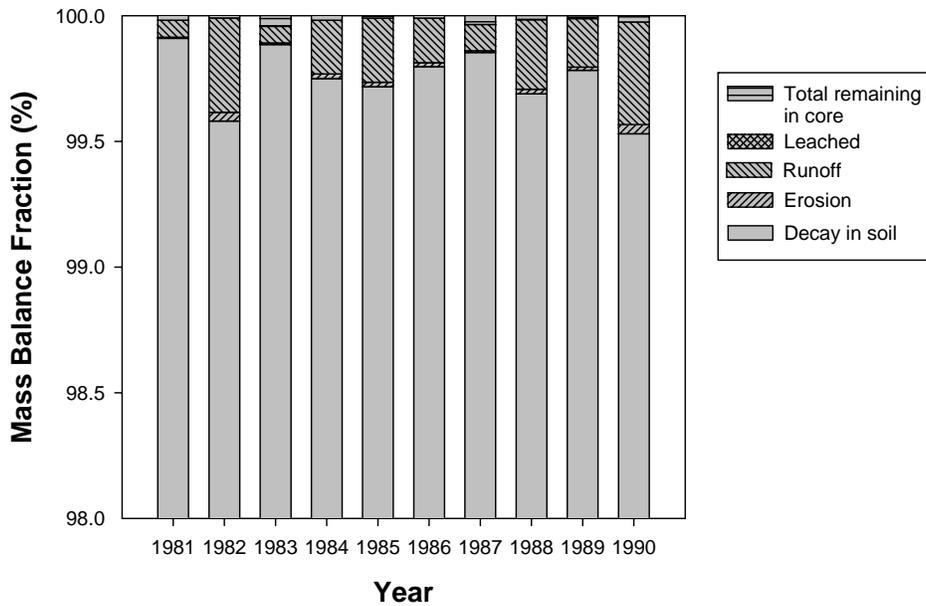


Fig. 2. The mass balance fractions for the annual POEA application of 0.68 kg/ha for 1981-1990. Note that the results indicate that the major fraction dissipated through decay in the soil.

4.6 TIER II REFINED EXPOSURE ASSESSMENT FOR SURFACE WATER

4.6.1 PRZM-EXAMS model overview

EPA's OPP currently uses the PRZM-EXAMS shell⁶ for a refined (Tier II) estimation of pesticide concentrations in surface waters for drinking water and aquatic exposure assessments. The field-scale runoff/leaching PRZM model is linked with the surface water EXAMS model (Exposure Analysis Modeling System) to estimate pesticide concentrations in surface water. EXAMS' core is a set of process modules that link fundamental chemical properties to the limnological parameters that control the kinetics of fate and transport in aquatic systems.

The standard PRZM-EXAMS runoff modeling scenario is based on a 10 ha field draining into a 1 ha by 2 meter deep water body. Each PRZM modeling scenario represents a unique combination of climatic conditions (*e.g.*, rainfall), crop specific management practices, soil specific properties, site specific hydrology, and pesticide specific application and dissipation processes. Each PRZM simulation is conducted for multiple years to provide a probabilistic exposure characterization for a single site.

Daily edge-of-field loadings of pesticides dissolved in runoff waters and sorbed to entrained sediment, as predicted by PRZM, are discharged into a standard small water body simulated by the EXAMS model. The model does not consider buffer zones. The physicochemical properties of the small water body are characteristic of a farm pond in Georgia. Since EXAMS is a steady-state model, the farm-pond volume is maintained at a constant volume (20,000 m³). Therefore, the water body is a closed-system with no outflow. It is assumed the inflow from runoff is exactly balanced by evaporative losses. The EXAMS model accounts for volatilization, sorption, hydrolysis, biodegradation, and photolysis of the pesticide.

Multiple-year pesticide concentrations in the water column are extracted from the simulation as the annual daily peak, maximum annual 96-hour average, maximum annual 21-day average, maximum annual 60-day average, and annual average. The upper 10th percentile concentrations (except annual average) are used to compare against ecotoxicological and human health levels of concern (LOC).

4.6.2 PRZM-EXAMS Input

Various standard crop scenarios and meteorological data sets are available for the PRZM-EXAMS model version 5.0 (PE5) to perform standard assessments. For the purpose of the risk assessment in the MA ROW scenario, the Texas Barton Spring Segment Rights-of-Way scenario was modified with respect to the soil input parameters, and the meteorological data set for Boston was selected.

As a first approach, the soil selected for MA ROW model simulations was the Massachusetts State soil: the Paxton fine sandy loam. The Paxton soils occur on about 400,000 acres in the state and consist of well drained loamy soils formed in acid subglacial till. The horizons and

⁶ URL address: <http://www.epa.gov/oppefed1/models/water/index.htm#przmexamshell>

parameters as defined in the model input are listed in Table 7 (see section 4.5.3). The PRZM-EXAMS input file is included in Appendix 3.

The “crop” data were defined to be representative of vegetation in a ROW area. The surfactant application rate was 0.68 kg/ha once a year on June 10 with 99% application efficiency and 1% drift. The model simulates for the 1960-1990 time period; the data for the 1980-1990 decade are displayed in this evaluation. Spray drift deposition is assumed to be 1% of the application rate. No buffer zones are considered in the PRZM-EXAMS scenarios. The input values for physical-chemical parameters of the surfactants is listed in Table 8 (section 4.5.3).

For the purpose of the application in ROW scenarios, the model-generated concentrations were modified to make them more representative of the shallow pond in a ROW scenario. The model-generated concentrations were corrected by a factor of 2.67, thereby making it more conservative. This factor was derived from a decrease in depth (compared to the standard depth of 2 m) and a decrease in land area-to-water area ratio (compared to the standard 10-to-1 ratio). The factor of 2.67 represents combinations of depth and area ratio such as 0.15 m and 2:1, 0.25 m and 3:1, and 0.30 m and 4:1. This trend is consistent with small shallow pools that are associated with lower land-to-water area ratios. This factor also represents modifications to field-size-to-volume ratios that were proposed for an aquatic refined risk assessment model (US EPA, 2004). A concern addressed with the proposed modifications in the field-size-to-volume ratios was that the standard pond scenario may not represent smaller volume surface waters. The modification used here of, for example, 0.25 m and 3:1 land-water area ratio represents an increased drainage area-volume capacity ratio of 12 m²/m³ compared to a value of 5 m²/m³ for the standard pond scenario.

4.6.3 PRZM-EXAMS results

4.6.3.1 PRZM-EXAMS modeling results for POEA surfactant

The chemically specific input parameter values for POEA were an application rate of 0.68 kg/ha, soil half-life of 15 d, aquatic half-life 21 d. The simulation was for the scenario with the highest leaching/runoff potential with a K_{OC} of 2500. The output includes the peak and various time-interval average concentrations in the pond water for the simulated decade. The data in Fig. 3 show that the peak concentrations reach up to 2.5 ppb, but time-interval averaged data indicate that POEA readily decrease due to various dissipation processes.

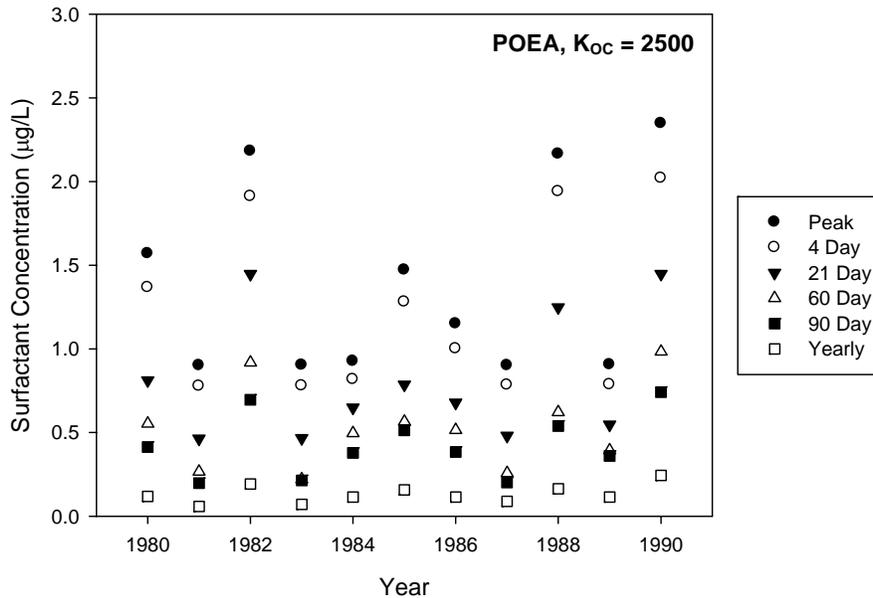


Fig. 3. POEA surfactant estimated environmental concentrations (EEC) in pond water at peak and various time-interval averaged values during the simulated years 1980-1990. Simulations were done with the most conservative (lowest) value of 2500 for K_{oc} .

4.6.3.2 PRZM/EXAMS modeling results for NPE surfactant

The EEC values for a NPE surfactant were simulated using the same scenario parameter values as listed above with the POEA surfactant, except for the characteristic K_D values for NPE surfactant. The first simulation shown in Fig. 4A was performed with a K_D value of 500 mL/g. The second simulation shown in Fig. 4B was performed with a K_D value of 100 mL/g, representing a situation with more leaching potential.

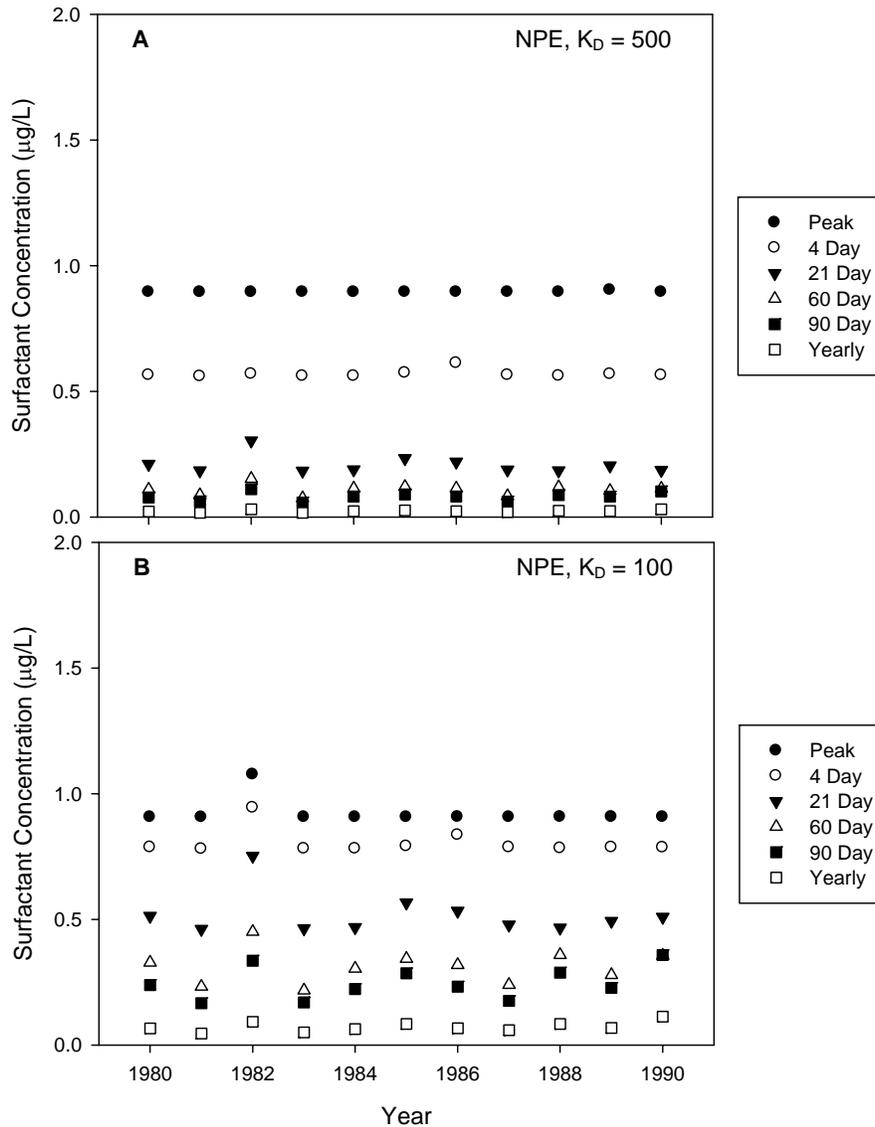


Fig. 4A and B. PRZM/EXAMS generated estimated environmental concentrations (EEC) for NPE surfactant in pond water at peak and various time-interval averaged values during the simulated years 1980-1990. Data were simulated with a K_D value of 500 mL/g (A) and a K_D value of 100 mL/g

The simulated data indicate that peak values in situations with typical K_D values generally do not exceed 1 ppb. The data in Fig. 4B also indicate that the trend in EEC values shows more variation in a situation with higher leaching potential, presumably due to the higher susceptibility to hydrology effects such as precipitation.

4.6.3.3 PRZM/EXAMS modeling results for AE surfactant

The EEC values for an AE surfactant were simulated using the same scenario parameter values as listed above with the POEA and NPE surfactant, except for the characteristic K_D values for AE surfactant. The first simulation shown in Fig. 5A was performed with a K_D value of 3500 mL/g, the second simulation shown in Fig. 5B was performed with a medium K_D value of 1000 mL/g, and the third simulation shown in Fig. 5C was performed with a low K_D value of 40 mL/g representing a situation with lower sorption affinity and more leaching potential.

The simulated data in Fig. 5A and 5B indicate that peak values for AE in situations with high or medium K_D values do not exceed 1 ppb. In situations with higher leaching potential (Fig. 5C), the EEC values reach up to approximately 1.7 ppb. The data in Fig. 5C also indicate that the trend in EEC values shows more variation in a situation with higher leaching potential, presumably due to the higher susceptibility to hydrological effects such as precipitation.

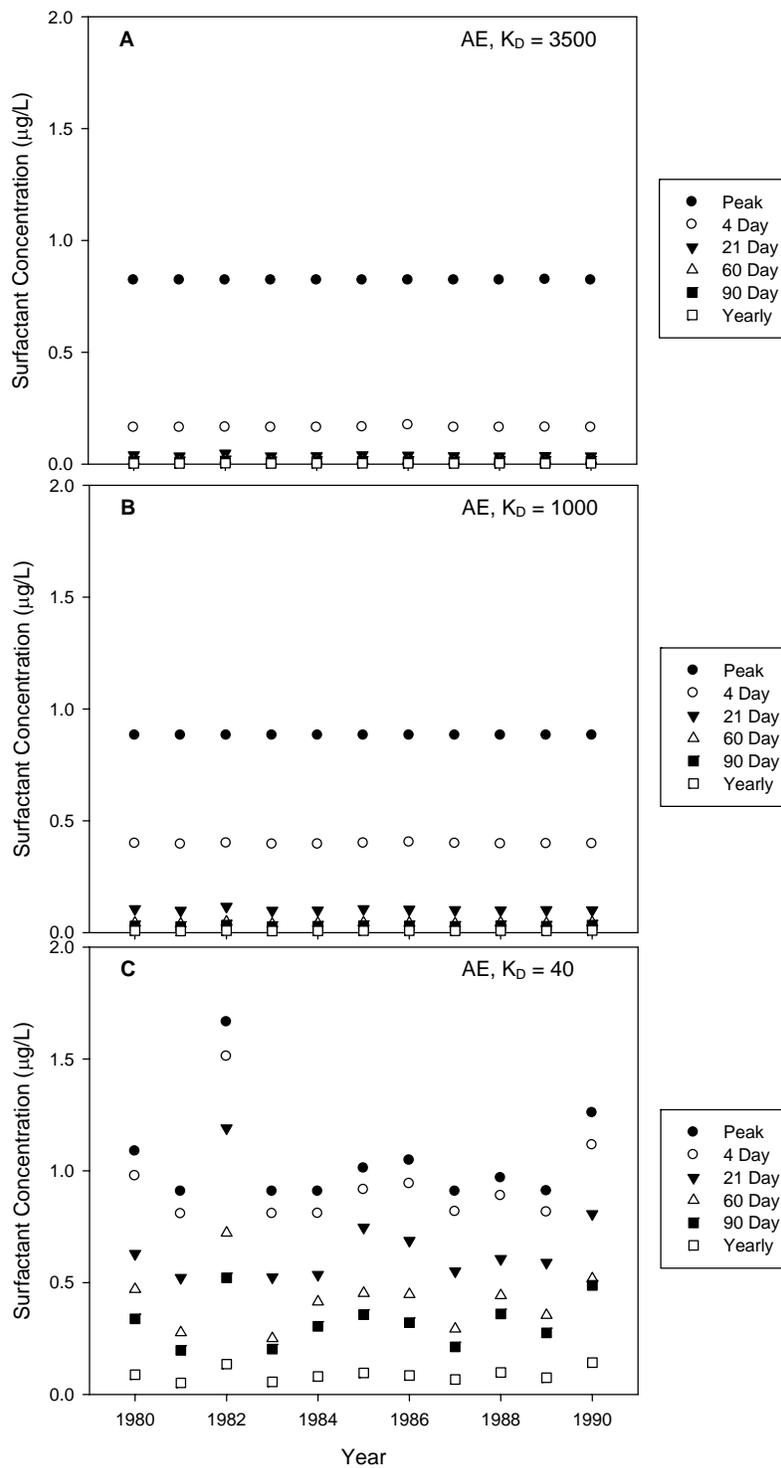


Fig. 5. PRZM/EXAMS generated estimated environmental concentrations (EEC) for AE surfactant in pond water at peak and various time-interval averaged values during the simulated years 1980-1990. Data were simulated with a K_D value of 3500 mL/g (A), K_D of 1000 (B) and a K_D of 40 (C).

4.6.3.3 PRZM/EXAMS modeling results for Phosphate Ester (PE) surfactant

The EEC values for PE surfactants were simulated using the same scenario parameter values as described with the surfactants in the main document, except for the soil-water partitioning constant, in this case K_{OC} , values for PE surfactant. The K_{OC} values for PE surfactants were estimated based on literature values for anionic surfactants reported by Ying (2006).

The results of the simulations are shown in Fig. 6A,B and C with organic carbon-water partitioning coefficients of K_{OC} value of 600 mL/g (Fig. 6B), a low K_{OC} value of 200 mL/g (Fig. 5C), and with a high K_{OC} value of 1000 mL/g (Fig. 6A) representing a situation with higher sorption affinity and lower leaching potential.

The simulated data in Fig. 6A and 6B (next page) indicate that peak values for PE concentrations in pond water in situations with high or medium K_{OC} values do not exceed 6 ppb. In situations with higher leaching potential (Fig. 6C, next page), the EEC values reach up to approximately 9 ppb. The data in Fig. 6C also indicate that the trend in EEC values shows more variation in a situation with higher leaching potential, presumably due to the higher susceptibility to hydrological effects such as precipitation.

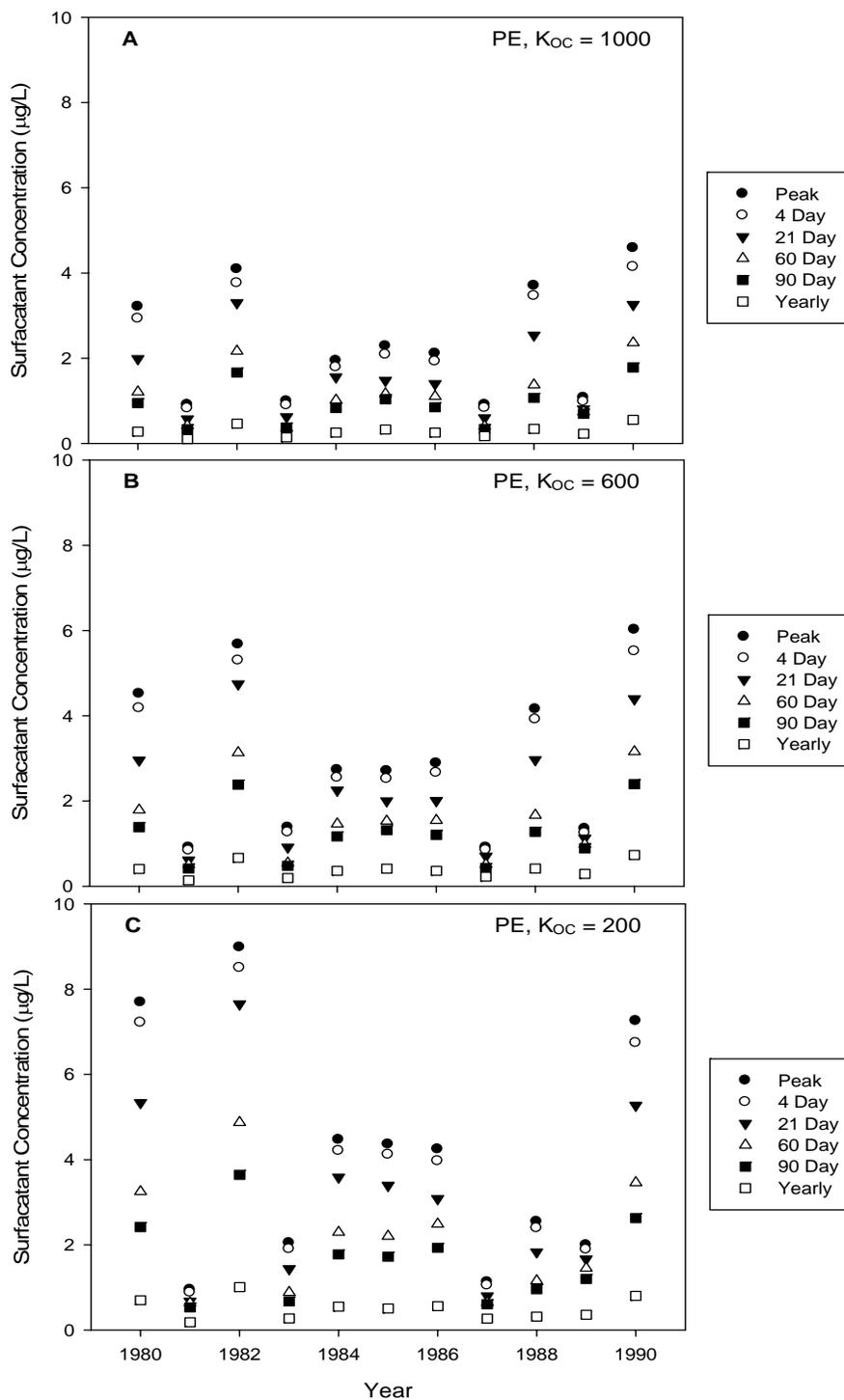


Fig. 6 PRZM/EXAMS generated estimated environmental concentrations (EEC) for PE surfactant in pond water at peak and various time-interval averaged values during the simulated years 1980-1990. Data were simulated with a low K_{OC} of 1000 mL/g (A), a K_{OC} of 600 mL/g (B), and a K_{OC} of 200

4.7 ESTIMATION OF SURFACTANT CONCENTRATION IN THE SHORE MARGINS

4.7.1 Completely mixed pond versus short-term near-shore accumulation

The PRZM-EXAMS model assumes instantaneous mixing and dilution upon runoff exposure of chemicals in a water body. It does not consider the potential for higher short-term concentrations in the areas of a pond that initially receive the pesticide components runoff such as the shallow near-shore areas of a pond. It is possible that concentrations immediately following the exposure of runoff and drift will initially be higher in the near-shore margins of the pond than the model simulates based on instantaneous distribution throughout the pond. The current version of the model does not allow for adjustments of dilution to account for this effect. Guidance on estimation of this effect is currently not available from EPA-EFED. In order to include an evaluation of this initial near-shore accumulation effect in this current assessment, an estimation of margin concentrations will be made considering a model pond. The PRZM-EXAMS generated results as presented in section 4.6.3 above will be adjusted accordingly to represent this near-shore margin effect.

4.7.2 Near-shore Margin Concentrations in a Model Pond

Even though large variability in near-shore margin concentrations can be expected in a pond upon receiving pesticide runoff due to variability in dimensions and other system characteristics, it is worthwhile to evaluate a margin-exposure scenario in a model pond. Such an evaluation can provide an estimation of the potential surfactant concentrations that could occur in such a situation and thereby provide a basis for a further refined aquatic risk assessment.

For the purpose of the evaluation of the margin effects in a small pond scenario, a shallow pond was considered with the following dimensions (adapted from Solomon and Thompson, 2003): a circular pond (cylindric cross section) with a surface area of 0.1 ha, 18 m radius, an average depth of 0.38 m (1.5 ft), with near-shore depth of 0.25 m. Different margin sizes were considered since runoff under heavy rainfall conditions is expected to impact a wider margin compared to runoff under light rainfall conditions. Therefore margin sizes of 0.6, 1.0, and 2.0 m were considered. Margin concentration factors were calculated based on the water volumes in the margin and the total pond volume. Essentially this procedure represents the instantaneous mixing and dilution of runoff exposure in the water volume of the pond margin. The concentration factors for the three margin sizes are listed in the table below.

Margin Size (m)	Margin Concentration Factor
0.6	22.9
1.0	14.0
2.0	7.2

Based on these initial concentration factor values for a model pond, the following factors were applied in the approach to estimate the margin concentrations from the pond water estimates derived in section 2.3.

Runoff Scenario	Margin Concentration Factor
High runoff (heavy rainfall during 3 weeks following the application)	7
Medium runoff (medium rainfall)	15
Low runoff (low rainfall)	25

Note that a low value for concentration factor is associated with high runoff due to the larger margin size impacted by runoff, resulting in a larger margin volume and consequently a lower concentration factor. High rainfall also results in more dilution due to higher water levels. Subsequently, the margin concentration factors were estimated based on evaluation of the rainfall data for each year during the month of June following the simulated application on June 10. The concentration factors for each year during the 1980-1990 decade are summarized in the table below.

Year	Margin Concentration Factor
1980	15
1981	15
1982	7
1983	25
1984	15
1985	10
1986	7
1987	15
1988	20
1989	7
1990	10

Subsequently, the margin concentrations estimates were determined by multiplying the simulated environmental concentrations for the whole pond scenario as presented in Section 3.5.2.3 by the margin concentration factor. Since the elevated margin concentrations are expected to exist for a relatively short time, only the peak and 96 h estimates were considered here. The data for the various surfactants are presented below.

4.7.3 PRZM-EXAMS modeling results

4.7.3.1 Margin concentrations for POEA surfactant

The following graphs show for each surfactant the margin concentration estimates compared with the whole-pond concentration estimates from section 2.3. The results for POEA are shown in Fig. 7. The highest peak concentration in the margin is 43 ppb.

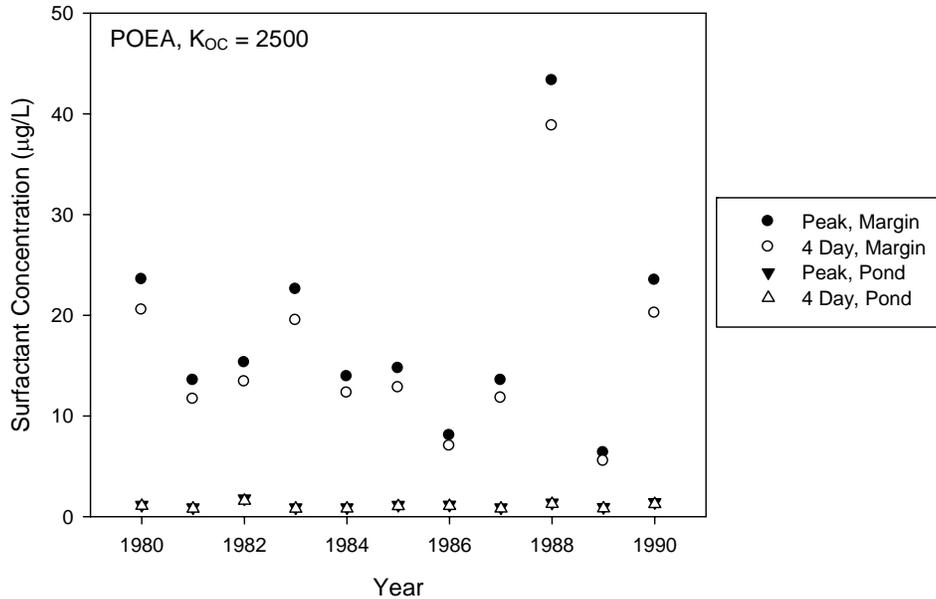


Fig. 7. Margin concentrations of POEA surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a K_{OC} value of 2500 mL/g.

4.7.3.2 Margin concentrations for NPE surfactant

The results for NPE are shown in Fig. 8 (see next page). The highest peak concentration in the margin is approximately 23 ppb.

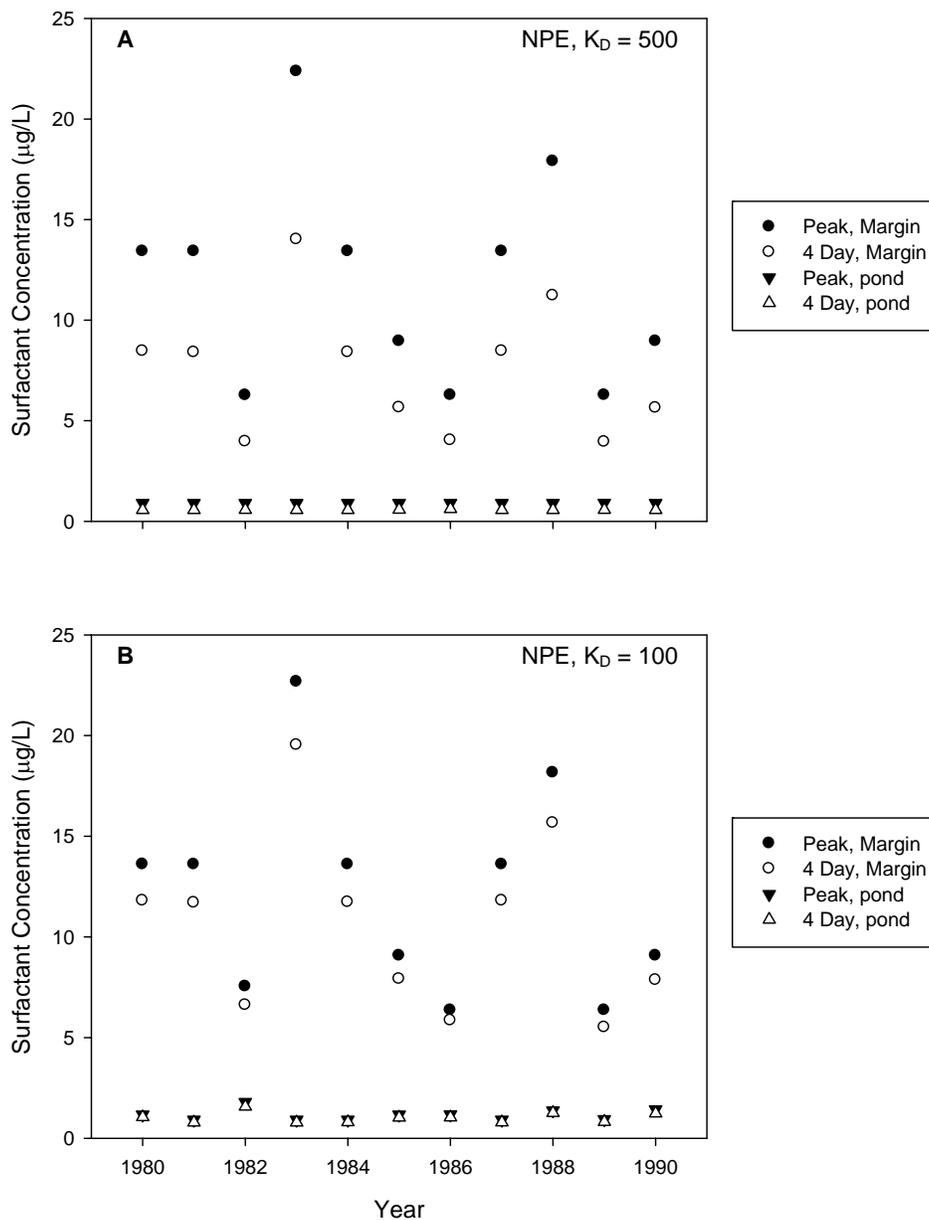


Fig. 8. Margin concentrations of NPE surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a K_D value of 500 mL/g (A) and a K_D value of 100 mL/g.

4.7.3.3 Margin concentrations for AE surfactant

The results for AE are shown in Fig. 9 (see next page). The highest peak concentration in the margin is approximately 23 ppb.

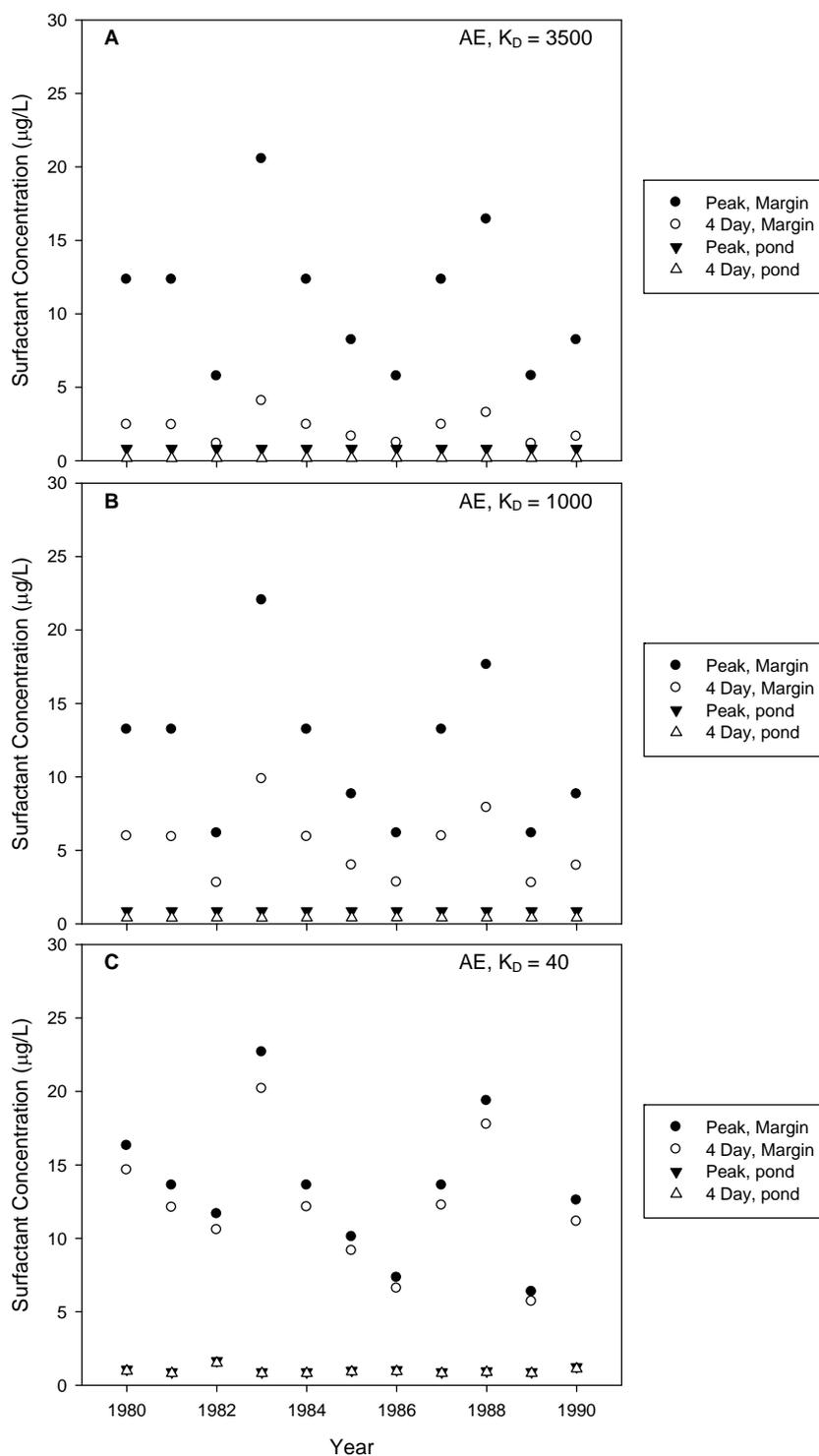


Fig. 9. Margin concentrations of AE surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a K_D value of 3500 mL/g (A), a K_D value of 1000 (B) and a K_D value of 40 (C).

4.7.3.4 Margin concentrations for PE surfactant

Figures 10A, B and C below show the simulated data for the phosphate ester surfactant. The highest peak concentration in the margin is 115 ppb simulated with a K_D of 200.

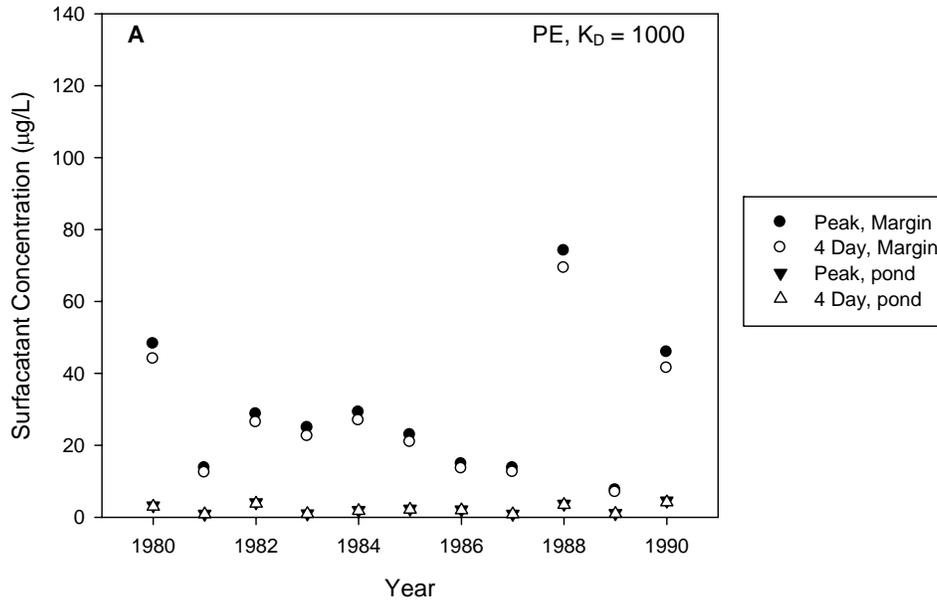


Fig. 10A. Margin concentrations of PE surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a low K_{OC} value of 1000 mL/g.

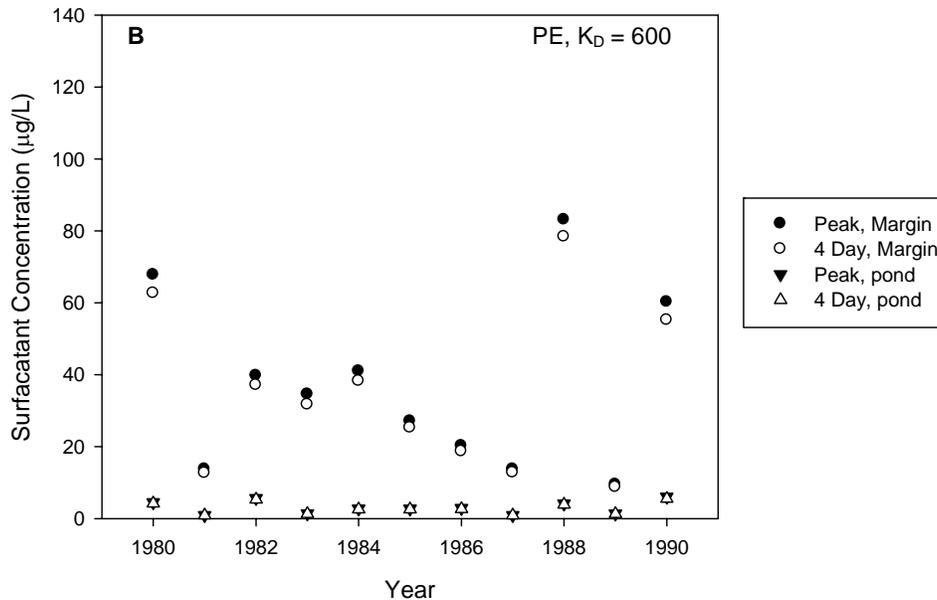


Fig. 10B. Margin concentrations of PE surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a low K_{OC} value of 600 mL/g.

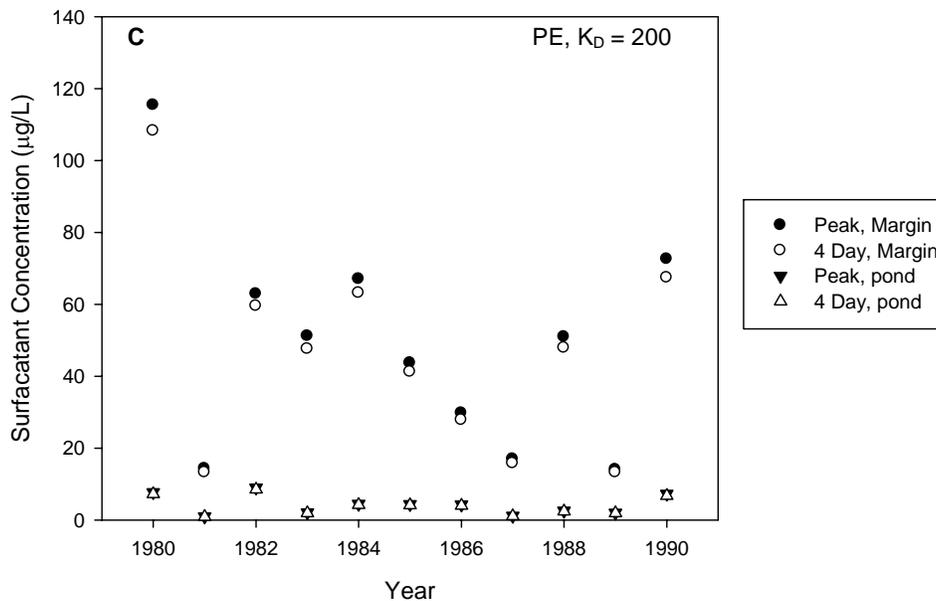


Fig. 10C. Margin concentrations of PE surfactant compared with the completely mixed pond concentrations based on PRZM/EXAMS generated estimated environmental concentrations (EEC) for surfactant in pond water at peak and 96 h time-interval averaged values during the simulated years 1980-1990. Data were simulated with a low K_{OC} value of 200 mL/g.

4.8 SUMMARY AND DISCUSSION OF REFINED MODELING DATA

4.8.1 Soil Concentrations (PRZM-generated)

The simulated POEA surfactant concentrations in a typical Massachusetts soil resulting from a typical ROW herbicide application indicated:

- The surfactant is only present in the top soil horizon (0-12 cm depth) with an annual peak concentration ranging from 150-300 ppb.
- The majority of the applied surfactant (>98%) decays in the soil. Run-off loss is in the range of 0.1 – 1.2%.

It can be expected that the other surfactants considered here (i.e., NPE, AE, PE) have a similar soil distribution and dissipation pattern based on similarity in environmental fate characteristics.

4.8.2 Surface Water Concentrations based on PRZM/EXAMS-estimates

The simulated maximum 1-in-10-year peak surfactant concentrations in pond water resulting from typical ROW herbicide applications are summarized in the Table 9 below. The phosphate ester (PE) surfactant shows the highest concentrations, which is to be expected given the lower sorption affinity of this surfactant compared to the POEA, NPE and AE surfactants. It is important to point out that these estimates are not based on the consideration of buffer zones. Consequently, the estimated environmental concentrations are very conservative values for the Massachusetts ROW management scenario, where regulations include buffer zones as described earlier. Actual real-world concentrations, therefore, are not expected to reach these levels with normal labeled use and adherence to setback distances around aquatic systems in or near ROW areas. Also note that margin concentrations are only relevant for acute risk since mixing and dilution processes will cause a decline in the temporarily elevated margin levels.

Table 9. Estimated maximum 1-in-10 year peak aqueous concentrations of surfactants in completely mixed whole pond and near-shore margins

Surfactant	K _D	K _{OC}	Whole Pond Concentration (µg/L)	Margin Concentration (µg/L)
POEA		2500	2.4	43
NPE	100		1.1	23
	500		0.9	22
AE	40		1.7	23
	1000		0.93	22
	3500		0.82	20
PE		200	9.0	115
		600	6.0	83
		1000	4.6	74

Upon review by an experienced PRZM-EXAMS modeler and review by US EPA Office of Pesticide Programs, it was suggested that a refinement of the model simulations was possible. The previously described modeling approach used a *post-simulation* correction factor for water body dimensions (depth) and land-to-water area ratio. A refined approach could encompass an adjustment of model input values for the water body dimensions and parameter for field area.

These options for refinement were evaluated. Using a 0.25 m depth instead of the standard 2 m depth resulted in a higher simulated pond water concentration. For example, with POEA the simulated concentration in a 0.25 m deep pond was 5.73 ppb compared to 6.91 ppb calculated based on simulated concentration in a 2 m deep standard pond and a factor proportional to the volume decrease associated with the change in depth from 2 m to 0.25 m. This indicates that the simulated concentration in shallow pond was about 17% lower than value determined with a post-simulation correction factor. This may be attributed to a higher sorption of surfactant in a shallower pond. Note that the concentrations stated above are predicted concentration for the whole pond scenario.

Adding the adjustment of the land-to-water area ratio from the standard 10-to-1 to, for example, 3.33-to-1 ratio, to the depth adjustment described above resulted in a decrease of the simulated pond water concentration. In order to show the effect of lower land-water area ratios, it was necessary to lower the drift input in the model. Again using POEA as an example, the simulated concentration was 1.92 ppb compared to 2.11 ppb calculated with the post-simulation correction factor, corresponding to a 9% decrease.

Overall, the refined approach indicates that slightly lower predicted concentrations would be generated. For this assessment, it was decided to adhere to a conservative approach and keep the previously described analysis and data as the basis for the risk assessment.

5. TOXICITY SUMMARY AND RISK CHARACTERIZATION

5.1 COMPARISON OF ENVIRONMENTAL CONCENTRATIONS WITH TOXICITY ENDPOINTS.

A quantitative estimate of the risks from can be made by comparing the estimated environmental concentration from the exposure assessment with toxicity data obtained from the review documents cited in section 3 and additional sources in the open literature. Very little information is available on the ecotoxicological endpoints for PE surfactants. Estimates of the toxicity endpoints considered here were obtained using the using the OECD-QSAR Application Toolbox (see Appendix 1). The refined exposure assessment data generated with PRZM/EXAMS (section 4.8) were used for the estimated environmental concentrations in this risk characterization.

The comparison is graphically displayed by a comparison of the EEC values, generated with PRZM-EXAMS and summarized in section 4.8, with acute LC_{50} and EC_{50} data for various aquatic organisms. Figures 11 - 13 show that both the whole-pond and the margin EEC values for POEA, NPE and AE surfactants are all below the most sensitive acute toxicological endpoints.

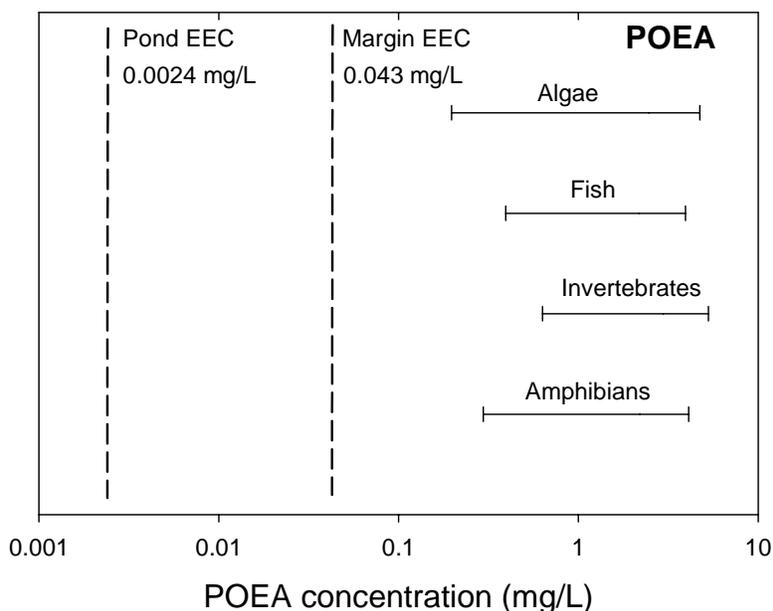


Fig. 11. Comparison of the estimated environmental concentration (EEC) in pond and margin of POEA surfactant (dashed lines) with ranges of LC_{50} / EC_{50} acute toxicity endpoints for various freshwater organisms. Graph was adapted from Thompson et al. (2004) and is also based on data from Edginton et al, 2004. The EEC values were generated with PRZM-EXAMS (see section 4.8.2). The LC_{50} for POEA were estimated from of glyphosate acid equivalent concentration data used in Thompson et al. (2004), formulation composition, and comparison of the toxicity data for glyphosate-POEA in Solomon and Thompson (2003) (p.302). Other toxicity data for POEA fall within the range indicated here (Giesy et al., 2000; Haller and Stocker, 2003; Howe et al., 2004).

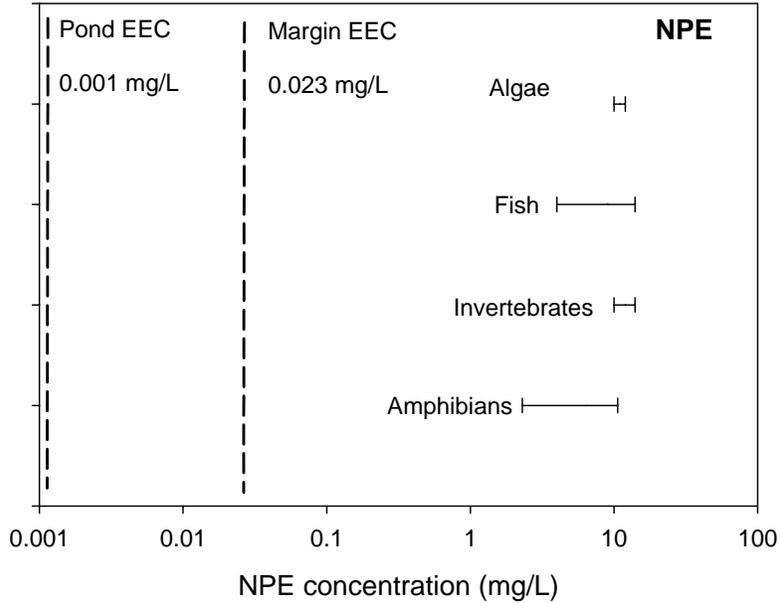


Fig. 12. Comparison of the estimated environmental concentration (EEC) of NPE surfactant (dashed lines) with ranges of LC_{50}/EC_{50} toxicity endpoints for various freshwater organisms. The EEC values were generated with PRZM-EXAMS (see section 4.8.2). The toxicity data are from USDA Forest Service, 2003a; Trumbo, 2005; and Mann and Bidwell, 2001.

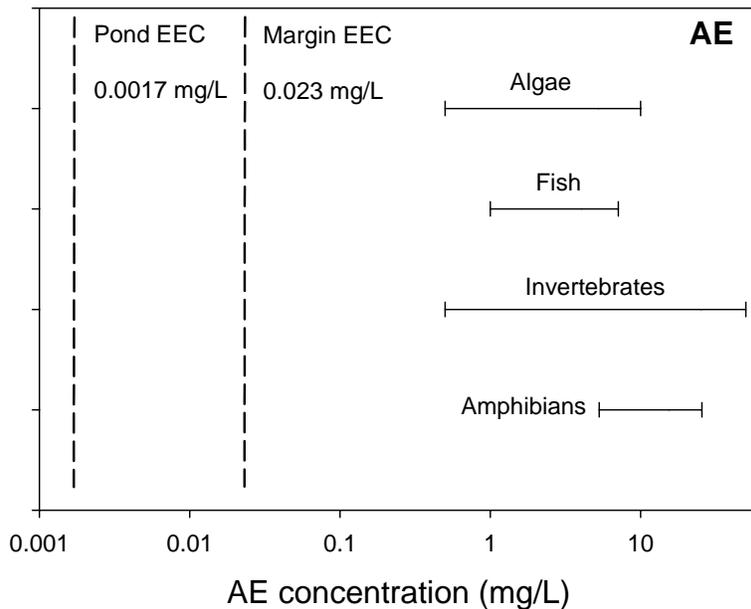


Fig. 13. Comparison of the estimated environmental concentration (EEC) of AE surfactant (dashed line) with LC_{50}/EC_{50} toxicity values for various freshwater organisms. The EEC values were generated with PRZM-EXAMS (see section 4.8.2). The toxicity data are from Krogh et al. (2003), Ying (2006), and Mann and Bidwell (2001).

5.2 RISK CHARACTERIZATION BY RISK QUOTIENT

The potential risks can also be expressed in terms of risk quotients (RQs). US EPA uses a deterministic approach or the quotient method to compare toxicity to environmental exposure. In this deterministic approach, a risk quotient (RQ) is calculated by dividing a point estimate of exposure by a point estimate of effects (US EPA, 2008). This ratio is a simple, screening-level estimate that identifies high- or low-risk situations. The RQ values listed in the Table 9 below were calculated by dividing the EEC value by the lowest acute toxicity endpoint. The highest RQ values were found for POEA, consistent with the established toxicity data reviewed in section 3 and the relatively high EEC values for this surfactant (section 4.8.2).

Table 9. Acute toxicity risk quotients (RQ) for various fresh water organisms. The risk quotients are based on the most conservative EEC value (whole pond and margin) and the most sensitive toxicological endpoint.

Surfactant	Organism	RQ Whole Pond	RQ Margin
POEA	Amphibians	0.0080	0.15
	Invertebrates	0.0038	0.07
	Fish	0.0060	0.11
NPE	Amphibians	0.0008	0.010
	Invertebrates	0.0002	0.002
	Fish	0.0005	0.006
	Algae	0.0002	0.002
AE	Amphibians	0.0001	0.007
	Invertebrates	0.0050	0.070
	Fish	0.0020	0.035
	Algae	0.0046	0.070
PE	Amphibians	0.0001	0.0002
	Invertebrates	0.0013	0.016
	Fish	0.0001	0.0012
	Algae	0.0002	0.0021

In order to indicate the potential risk to non-target organisms and the need to consider regulatory action, the RQs are compared to Levels of Concern (LOCs). The US EPA-established LOC value for acute high risk for aquatic animals is 0.5. None of the RQ values exceed the LOC for general risk indicating low risk situations. Only endangered species (0.05) LOCs are slightly exceeded with POEA and AE surfactants in the margin scenario. Such a risk indication, however, is addressed in the ROW regulations by provisions that prohibit applications within endangered species habitat. In addition, the assumptions in this risk assessment are conservative. Specifically, buffer zones are not considered in the PRZM/EXAMS model simulations. The provisions for no-spray and limited spray zones provide mitigation for any slight risk indicated here.

6. DISCUSSION AND CONCLUSIONS

6.1 POEA, NPE, AE and PE Surfactants

Laboratory and mesocosm studies have shown that certain surfactants associated with herbicides products that are applied in ROW vegetation management may have the potential to cause acute ecotoxicological effects to aquatic organisms. However, the analysis for the alkyl ethoxylated surfactants presented here indicates that the exposure levels of surfactants in sensitive areas of ROW are very low when applied according to label instructions and state ROW management regulations. The risk assessment described here indicates that, even in the worst-case scenarios, the use of these surfactants in herbicide formulations poses minimal risks to aquatic organisms.

The risk assessment described here represents a scenario with the highest application rate such as along railways. Other application scenarios such as power line and highway corridors generally use lower application rates and, consequently, would result in lower exposures and risk.

The POEA surfactant is known to have the highest toxicity and its risk assessment can provide a reference for other herbicide surfactants. The risk assessment for POEA surfactants indicates that its use does not pose significant acute risks to aquatic organisms. The minimal risks associated with POEA surfactant implies therefore that the other surfactants pose even less acute risk. This is indicated by the lower RQ values for the AEs, NPEs, and PEs determined in this assessment.

Acute risks are of most concern since the concentrations of surfactants are expected to decrease rapidly due to their environmental fate characteristics that result in low persistence in water as has been shown in fate studies (Wang et al., 2005) and the general observation of very low environmental concentrations (Krogh et al., 2003; Ying et al., 2006). Insignificant chronic risk is also indicated, for example, by comparison of the 60-day average EEC of up to 1 µg/L for POEA (section 4.6.3.1, Fig. 3) with a no-observed effect concentration (NOEC) value of 100 µg/L for POEA (Giesy et al., 2000).

The conclusions of this risk assessment are consistent with the several other risk evaluations in the context of forest and land management as reviewed earlier in this document (Section 3). The minimal risk assessed in this evaluation is largely the consequence of low exposure of aquatic systems to herbicide products applied in ROW areas.

Additional protection from exposure to herbicides and associated surfactants is provided by no-spray and limited-spray zones as mandated by ROW management regulation. The importance of such protective buffer zones is highlighted by a recent study on the occurrence of various herbicides in vernal pools and streams as a result of vegetation management in national parks and wildlife refuges (Battaglin et al., 2008). The data indicated that contamination of vernal pools with herbicides, including glyphosate, is more likely if application occurs directly *adjacent* to these aquatic systems. As a result of such practices, herbicides were detected occasionally in the pools and streams, albeit at concentrations that were generally not exceeding the freshwater aquatic life standards. The study was performed at sites with high likelihood of detection of herbicides in order to provide baseline information about the exposure of sensitive areas to herbicide use in the management of national parks and wildlife refuges. The use of buffer zones for herbicide applications as required in MA-ROW management will minimize and likely

prevent such exposure under normal use scenarios as was indicated by a glyphosate monitoring study (MDAR, 2006). Bureau of Land Management (US Dept. of Interior, 2007) points out that, from a land-management perspective, the size of the buffer zone may be the single most controllable variable (other than equipment and tank mix) that has a substantial impact on ecological risk.

Comparison of the simulated model results with monitoring data is not possible due to lack of such data for the surfactants considered here. However, the monitoring data on glyphosate in waters along railways (MDAR, 2006) provide an opportunity to do such a comparison of model results with monitoring data. A PRZM-EXAMS simulation using the ROW scenario as developed for the surfactant simulations in section 4.6, the application rate as used in the study, and conservative input values for the environmental fate characteristics of glyphosate showed simulated concentrations (whole pond) in the range of 0.9-1.6 ppb. Comparison with the monitoring data, that did not show detections above the limit of 1.1 ppb, indicates that the model simulations are conservative.

With respect to NPE, the concern with the occurrence of in the NPE surfactants is largely driven by findings of estrogenic effects in fish and other aquatic organisms, although these effects are mainly caused by the nonylphenol (NP) degradate (Ying, 2006). As pointed out earlier, under aerobic conditions very little NP is formed in terrestrial and aquatic systems. The threshold for estrogenic effects is generally above the threshold for other effects (USDA, 2003a); hence protective levels of NPE exposure would encompass any concerns for estrogenic effects. The USDA-Forest Service uses a protective level of 1 mg/L NPE9 for fish and 10 mg/L for aquatic invertebrates. The worst-case scenario in ROW situation estimated here is a NPE level of 0.023 mg/L. It is important to note that sorption and biodegradation mitigate the potential risks from these surfactants (Krogh et al., 2003).

With respect to PE surfactants, only the monoester of this surfactant molecule was considered in this analysis. The possible contribution of the diester version of this ester that may be present in the formulation is not expected to contribute significantly to the aquatic toxicity. Although the diester will be intrinsically more toxic, it is not expected to express its intrinsic toxicity in a mixture with the monoester because of solubility and aggregation cut-offs (Roberts, 2008; pers. comm.). Another aspect of the phosphate esters is the type of alkoxy groups. In addition to ethoxy groups, the product information indicates that the parent alcohol surfactant may also contain propoxy groups in its hydrophilic part of the surfactant molecule. It has been shown that the presence of propoxy groups in place of ethoxy groups does not affect the molar toxicity on the same parent alcohol (Roberts et al., 2007). Therefore, surfactant molecules containing the propoxy groups as part of the ethoxylated chain were not evaluated here.

In conclusion, this risk assessment indicates that the use of herbicides containing POEA, NPE, AE, or PE surfactants in ROW sensitive areas managed according to the ROW regulations and adherence to protective buffer-zones and rate restrictions appear to provide adequate protection for sensitive aquatic systems. This is consistent with the mandate to protect and prevent unreasonable risk to these sensitive areas associated with ROW.

6.2 DISCUSSION OF ADDITIONAL SURFACTANTS AND EXPOSURES

6.2.1 General Comments

The risk assessment presented above focused on several different types of alkyl ethoxylated surfactants. As a first approach, these surfactants were selected based on priority for evaluation given their current use in herbicide products for rights-of-way areas. While the selected types of surfactants are expected to represent a significant part of the surfactants used in ROW herbicide applications, some additional types will be discussed briefly below. A more thorough risk assessment was not conducted at this time due to the limited information and data that is readily available for these surfactants. While the initial assessments described below indicate low risks, a more detailed risk assessment is desirable in order to meet the same levels of thoroughness and confidence in risk assessments as with the alkyl ethoxylated surfactants described above. The intention is to do a more thorough assessment for these surfactants in the near future once a more detailed database has been established.

6.2.2 Organosilicones surfactants

Organosilicones as surfactants are increasingly more used in herbicide formulations because of their superior spreading ability. Some studies have indicated that these surfactants have lower acute aquatic toxicity than some of the ethoxylated surfactants (Haller and Stocker, 2003; Stark and Walthall, 2003). The exposure levels from off-site drift for these surfactants would be similar as with the screening-level assessment (Section 4.4) based on the assumption of the same surfactant concentration in the product. Exposure through runoff and transport through soil is again typical for surfactants with high affinity for sorption and rapid degradation (Stevens, 1993) resulting in low mobility and low exposure. Therefore, the same total EEC value in a worst-case scenario due to drift and runoff of 0.013 mg/L can be considered here. Acute LC₅₀ values for *Daphnia pulex* exposed to organosilicone adjuvants were approximately 23 mg/L (Stark and Walthall, 2003). Chronic exposure studies indicated the extinction (i.e., negative population growth) occurred after exposure to 18 to 28 mg/L. Haller and Stocker (2003) reported LC₅₀ (96 h) to juvenile sunfish (*Lepomis macrochirus*) of 18.1-29.7 mg/L for organosilicones. Compared to the levels of 0.013 mg/L as determined in the screening-level assessment, organosilicones are not expected to pose significant acute and chronic risk with typical ROW herbicide applications.

6.2.3 Surfactants used as adjuvants

Some herbicide formulations require the addition of a surfactant as an adjuvant in the tank mix prior to application. For example, the adjuvant Induce® is commonly used in ROW areas at 0.25-.50% concentration in the tank mix (Jeff Taylor, pers. comm.). Induce® is non-ionic adjuvant consisting of a blend of AE, APE, fatty acid and organosilicone surfactants (Helena Chemical Company, 2005). A 25 gal/acre application rate equates to a typical surfactant rate of 0.625 lbs/acre, which is similar to the surfactant rates considered above. The same screening-level assessments as described above would then result in the same worst-case scenario EEC values.

Comparison of the EECs for the Induce® adjuvant with the toxicity endpoints to juvenile sun fish (*Lepomis macrochirus*) reported by Haller and Stocker (2003) indicates that these

surfactants pose a lower aquatic risk than POEA. In that study, the POEA surfactants showed a LC₅₀ of 1.6-2.9 mg/L compared to a LC₅₀ of 9.0 mg/L for the Induce® surfactant.

6.2.3 Terrestrial exposure related to amphibians

Although the aquatic ecotoxicological impacts are of most concern due to the inherently higher sensitivity of aquatic organisms to surfactants, the potential impact on amphibians in terrestrial settings is also a relevant exposure scenario. A worst-case scenario assuming no foliar interception was simulated in laboratory experiments using juvenile frogs and toads located in plastic tubs that were directly sprayed with a glyphosate-POEA herbicide at a rate of 1 kg a.i./ha (Relyea, 2005c). Although the substantial mortality in this experiment raised concerns, the author pointed out that these data had limited representative value for real-world situations. More natural field studies were needed to better assess the risk of this herbicide to juvenile and adult amphibians in natural terrestrial settings.

Considering the situation in ROW areas, typically not a prime amphibian habitat, the most likely scenario in this case is the presence of amphibians in the no-spray area or limited-spray area in the vicinity of a water body. Considering the method of selective spraying in the limited spray-areas and the expected high foliar interception and relatively low application rate associated with such spraying, applications will result in low exposure to amphibians present in these areas. As an example, assuming a rate of 1 kg a.i./ha glyphosate herbicide and 80% foliar interception, the potential exposure could be 0.20 kg a.i./ha.

Considering the terrestrial exposure scenario, a proper risk assessment is not possible due to the lack of sufficient exposure and toxicity data. A study on the toxicity of technical glyphosate on terrestrial vertebrates showed, as expected, very low toxicity for amphibians based on LD₅₀ endpoint value (McComb et al., 2008). However, no such data are available for POEA containing formulations. The terrestrial exposure of 0.20 kg a.i./ha estimated above is more than six times lower than the exposure level used in lab experiments conducted by Relyea (2005c).

7. REFERENCES

- Bakke, D. 2002. Analysis of issues surrounding the use of spray adjuvants with herbicides. Pacific Northwest regional invasive plant environmental impact statement. USDA Forest Service. URL: [www.fs.fed.us/r6/invasiveplant-eis/Region-6-Inv-Plant-Toolbox/Surfactants/surfactants%20bull%](http://www.fs.fed.us/r6/invasiveplant-eis/Region-6-Inv-Plant-Toolbox/Surfactants/surfactants%20bull%20)
- Battaglin, W.A. et al., 2008. The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005-2006. *Environ. Monit. Assess* (Online First, Aug. 2008).
- Blasco, J., M. Hampel, I. Moreno-Garrido. 2003. Toxicity of surfactants (p. 827-862). In: T.P. Knepper, D. Barcelo, P. de Voogt (Eds.), *Analysis and Fate of Surfactants in the aquatic environment*. Wilson & Wilson's comprehensive analytical chemistry, Vol. 40, Elsevier.
- Boeije, G.M. et al., 2006. Ecotoxicity quantitative structure-activity relationships for alcohol ethoxylate mixtures based on substance-specific toxicity predictions. *Ecotoxicol. Environ. Saf.* 64:75-84.
- Chen, C.Y. et al., 2003. Multiple stress effects of Vision herbicide, pH, and food on zooplankton and larval amphibian species from forest wetlands. *Environ. Cont. Toxicol.* 23:823-842.
- Diamond, G.L. and Durkin, P.R., 1997. Effects of surfactants on the toxicity of glyphosate, with specific reference to Rodeo. Prepared under USDA Contract No. 53-3187-5-12. URL: <http://www.fs.fed.us/foresthealth/pesticide/pdfs/Surfactants.pdf>
- Edgington, A.N. 2004. Comparative effects of pH and Vision® herbicide on two life stages of four anuran amphibian species. *Environ. Cont. Toxicol.* 23:815-822.
- Giesy J.P. et al., 2000. Ecotoxicological risk assessment for Roundup herbicide. *Rev. Contam. Toxicol.* 167: 35-120.
- Haller, W.T. and R.K. Stocker. 2003. Toxicity of 19 adjuvants to juvenile *Lepomis macrochirus* (bluegill sunfish). *Environ. Toxicolog. Chem.* 22:615-619.
- Helena Chemical Company, 2005. Induce® adjuvant label and MSDS. URL: <http://www.helenachemical.com/products/Pages/specialtyLabels.aspx>
- Howe, C.M. et al., 2004. Toxicity of glyphosate-based pesticides to four North American frog species. *Environ. Toxicolog. Chem.* 23:1928-1938.
- Jonkers, N. et al., 2001. Aerobic biodegradation studies of nonylphenol ethoxylates in river water using liquid chromatography-electrospray tandem mass spectrometry. *Environ. Sci. Technol.* 35:335-340.

- Knowles, D.A. 1998. Formulations of agrochemicals. (p.41-79) *In*: D.A. Knowles (Ed.), Chemistry and technology of agrochemical formulations. Kluwer Academic Publishers.
- Krogh, K.A. et al., 2003. Environmental properties and effects of nonionic surfactant adjuvants in pesticides: a review. *Chemosphere* 50:871-901.
- Mann, R.M. and J.R. Bidwell. 1999. Toxicity of glyphosate formulations to four species of southwestern Australian frogs. *Environ. Toxicolog. Chem.* 36:193-199.
- Mann, R.M. and J.R. Bidwell. 2001. The acute toxicity of agricultural surfactants to tadpoles of four Australian and two exotic frogs. *Environ. Poll.* 114:195-205.
- McComb, B.C. 2008. Acute toxic hazard evaluations of glyphosate herbicide on terrestrial vertebrates of the Oregon coast. *Environ. Sci. Pollut. Res. Int.* 15:266-272.
- MDAR, 2006. Surface water monitoring of glyphosate used in rail road rights-of-way vegetation management. Massachusetts Department of Agricultural Resources.
- Naylor, C.G. et al., 2006. Biodegradation of ¹⁴C ring-labeled nonylphenol ethoxylate. *Arch. Environ. Cont. Toxicol.* 51:11-20.
- Parker, R.D. et al., 1995. GENEEC: A Screening Model for Pesticide Environmental Exposure Assessment.,in Proceedings of the International Exposure Symposium on Water Quality Modeling; American Society of Agricultural Engineers, pp. 485-490; Orlando, Florida.
- Perkins P.J., et al. 2000. Toxicity of glyphosate and triclopyr using the frog embryo teratogenesis assay-Xenopus. *Environ Toxicol Chem.* 19: 940-945.
- Reekmans, S. 1998. Novel surfactants and adjuvants for agrochemicals. (p.179-226) *In*: D.A. Knowles (Ed.), Chemistry and technology of agrochemical formulations. Kluwer Academic Publishers.
- Relyea, R.A. 2005a. The impact of insecticides and herbicides on the biodiversity and productivity of aquatic communities. *Ecological Applications* 15:618-627.
- Relyea, R.A. 2005b. The lethal impacts of Roundup and predatory stress on six species of North American tadpoles. *Arch. Environ. Cont. Toxicol.* 48:351-357.
- Relyea, R.A. 2005c. The lethal impact of Roundup® on aquatic and terrestrial amphibians. *Ecological Applications* 15:1118-1124.
- Relyea, 2006. The impact of insecticides and herbicides on the biodiversity and productivity of aquatic communities. Response. *Ecological Applications* 16:2022-2027.
- Roberts, J.F., S.J. Marshall, and D.W. Roberts. 2007. Aquatic toxicity of ethoxylated and propoxylated alcohols to *Daphnia magna*. *Environ. Tox. Chem.* 26:68-72.

Solomon, K.R., and D.G. Thompson. 2003. Ecological risk assessment for aquatic organisms from over-water uses of glyphosate. *J. Toxicol. Environ. Health* 6:289-324.

Stark, J.D. and W.K. Walthall, 2003. Agricultural adjuvants acute mortality and effect on population growth rate of *Daphnia Pulex* after chronic exposure. *Environ Toxicol Chem.* 22: 3056-3061.

Stevens, P.J.G. 1993. Organosilicone surfactants as adjuvants for agrochemicals. *Pest. Sci.* 38:103-122.

Tatum, V.L. 2004. Toxicity, transport and fate of forest herbicides. *Wildlife Soc. Bull.* 32:1042-1048.

Thompson, D.G. et al., 2004. Chemical and biomonitoring to assess potential acute effects of Vision herbicide on native amphibian larvae in forest wetlands. *Environ. Tox. Chem.* 23:843-849.

Thompson, D.G. et al., 2006. The impact of insecticides and herbicides on the biodiversity and productivity of aquatic communities. *Ecological Applications* 16:2022-2027.

Trumbo, J. 2005. An assessment of the hazard of a mixture of the herbicide Rodeo and the non-ionic surfactant R-11 to aquatic invertebrates and larval amphibians. *CA Fish and Game* 91:38-46.

Tsui, M.T.K., and L.M. Chu, 2003. Aquatic toxicity of glyphosate-based formulations: comparison between different organisms and the effects of environmental factors. *Chemosphere* 52:1189-1197.

US Dept. of Interior, Bureau of Land Management, 2007. Final Vegetation Treatments Using Herbicides Programmatic Environmental Impact Statement, Vol. 2, Appendix D. Evaluation of risks from degradates, polyoxyethyleneamine (POEA) and R-11, and endocrine disrupting chemicals. Washington, D.C. URL: http://www.blm.gov/wo/st/en/prog/more/veg_eis.html

USDA Forest Service, 2003A. Human and Ecological Risk Assessment of Nonylphenol Polyethoxylate-based (NPE) Surfactants in Forest Service Herbicide Applications. Pacific Southwest Region. URL: www.fs.fed.us/r6/invasiveplant-eis/Risk-Assessments/NPE-Surfactant_RA_final.pdf

USDA Forest Service, 2003B. Glyphosate – Human Health and Ecological Risk Assessment Final Report. URL: www.fs.fed.us/foresthealth/pesticide/pdfs/04a03_glyphosate.pdf

US EPA, 2004. A Discussion with the FIFRA Scientific Advisory Panel Regarding the Terrestrial and Aquatic Level II Refined Risk Assessment Models (Version 2.0) - IV. The Aquatic Level II Refined Risk Assessment Model (Version 2.0). Accessed at: http://www.epa.gov/oppefed1/ecorisk/fifrasap/rra_chap_four.htm#IVB2

US EPA-OPP, 2004. List of pesticide inert ingredients. Accessed at:
http://www.epa.gov/opprd001/inerts/inerts_list4Bcas.pdf

US EPA, 2008. Technical Overview of Ecological Risk Assessment. Available at:
http://www.epa.gov/oppefed1/ecorisk_ders/toera_risk.htm

Wang, N. et al., 2005. Influence of sediment on the fate and toxicity of a polyethoxylated tallowamine surfactant system (MON 0181) in aquatic microcosms. *Chemosphere* 59: 545-551.

Wasow, G.W. 1996. Phosphorus-containing anionic surfactants. *In Anionic Surfactants: Organic Chemistry*. Ed. H.W. Stache. CRC Press.

Wojtaszek, B.F et al., 2004. Effects of Vision® herbicide on mortality, avoidance response, and growth of amphibian larvae in two forest wetlands. *Environ. Cont. Toxicol.* 23:832-842.

Ying, G.G. 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environ. Int.* 32:417-431.

Appendix 1

ECOTOXICITY ASSESSMENT OF PHOSPHATE ETHOXYLATED ESTER SURFACTANTS

1.1. Introduction

Phosphate ethoxylated esters are a less commonly used as herbicide surfactant, but appeared in a recently introduced rights-of-way herbicide formulation that was submitted for addition to the Massachusetts Rights-of-Way Sensitive Area Materials List. Little information on environmental fate and toxicity is available for this type of surfactant. Since this type of surfactant is part of a new formulation that replaces a current product on the Sensitive Area Materials List, the phosphate ethoxylated esters were included in this surfactant risk assessment. In order to do a risk characterization, toxicity endpoint data are needed. Since these data were not available in the open literature, toxicity endpoint values were estimated using an analysis based on the comparison with the endpoints of similarly structured compounds. The estimation of the desired toxicity endpoints for risk characterization is described below. The estimated toxicity endpoints are used to determine risk quotients in Section 5.2 in the main document.

1.2. General Information on Phosphate Ethoxylated Ester Surfactants

Some of the attractive properties of phosphate ethoxylated esters compared to the ethoxylated alcohol parent surfactants are stability in neutral and alkaline conditions, good solubility in saline water, electrolyte tolerance in hard water, ability to disperse lime soaps. Phosphate esters possess excellent skin compatibility and are used as emulsifiers in cosmetics. Other applications include the use as emulsifier and detergent in textile in textile and agricultural chemicals (Cross, 1998). Depending on the pH, the phosphate ester has a more or less anionic character; i.e., increasingly more anionic with increase in pH.

Regarding ecological properties, a distinct feature is the biodegradability. The ester bond is easy biodegradable. Upon splitting of the ester bond, the resulting alcohol ethoxylates are degraded following their characteristic mechanism (Wasow, 1996). Very little data are available on the ecotoxicity of phosphate ester surfactants. With respect the sorption characteristics, it is known that anionic surfactants have somewhat lower partitioning coefficients (K_D) compared to non-ionic surfactants (Ying, 2006). Consequently, anionic surfactants exhibit a somewhat higher mobility in terrestrial and aquatic systems.

The general structure of a phosphate ethoxylated ester (monoester) is:



1.3 Phosphate Ester Surfactant Product Information

The product information for specific phosphate ester surfactant (BASF, 2009A) indicates it is a surfactant product consisting of complex phosphate ester surfactants. Phosphate ester surfactants are formed through a phosphating process of non-ionic surfactants, giving the surfactant an anionic nature that results in increased stability and solubility in alkaline and hard-water systems.

The phosphate ester surfactant can be used as a hydrotrope, which are compounds with a high hydrophile-lipophile-balance (HLB) value. This relative high HLB value of PE surfactants is achieved with high ethoxylation degree and anionic character. Typical ethoxylation degrees are in the 50-70% range (Wasow, 1996). For example, a C₁₂ alkyl chain with 6 moles EO represents a surfactant molecule with 50% ethoxylation degree. This proper ethoxylation degree is considered with selection of structures to be evaluated for this assessment. The product information indicates an alkyl chain length with a range of C₁₀-C₁₆.

2. Ecotoxicological Endpoint Identification

2.1. Available Information

Very little information is available on the ecotoxicological endpoints for this surfactant product. The MSDS (BASF, 2009B) provides only information on estimated acute toxicology endpoint for *Daphnia magna* or 1-10 mg/L (LC₅₀, 48 h), which was derived from comparison with products of a similar structure and composition.

In order to obtain additional information on ecotoxicology for this compound and fill data gaps in the ecotoxicity profile, several toxicity endpoints were estimated using the OECD-QSAR Application Toolbox (OECD, 2009).

2.2. Estimation of Aquatic Toxicological Endpoints for Phosphate Ester Surfactants using the OECD-QSAR Application Toolbox

2.2.1. The OECD-QSAR Application Toolbox

The Organization for Economic Cooperation and Development (OECD) Quantitative Structure-Activity Relationships [(Q)SARs] Project has resulted in the release of OECD-QSAR Application Toolbox in 2008. This toolbox includes methods for estimating properties of a chemical from its molecular structure.

The Toolbox is a software application intended to be used by governments, chemical industry and other stakeholders in filling gaps in (eco)toxicity data needed for assessing the hazards of chemicals. The Toolbox incorporates information and tools from various sources into a logical workflow. Crucial to this workflow is grouping chemicals into chemical categories.

A chemical category is a group of chemicals whose physicochemical and human health and/or environmental toxicological properties and/or environmental fate properties are likely to be similar or follow a regular pattern as a result of structural similarity. Category approach, not every chemical needs to be tested for every endpoint. Rather, the overall data for that category must prove adequate to support a hazard assessment. The overall data set must allow the estimation of the hazard for the untested endpoints. Data gap filing can be done using read-across from one tested chemical to an untested chemical, trend analysis, or QSAR equations.

The Toolbox allows a user to systematically group chemicals according to the presence or potency of a particular effect for all members of the category. The Toolbox is able to quickly

evaluate all members of a category for common toxicological behavior or consistent trends among results related to regulatory endpoints.

The Toolbox estimates missing values by: (1) Read-Across, that extrapolates for an untested chemical from tested chemicals within a category; (2) Trend Analysis, that estimates for an untested chemical from a "trend" (increasing, decreasing or constant) in effect within a category; or (3) (Q)SAR Models that estimate missing values from a statistical model for a category.

2.2.2. Estimation of toxicity of individual surfactant homologues

The procedure followed for the estimation of toxicity endpoints for phosphate ester surfactants for this risk assessment was: (1) drawing the structure of a phosphate ester surfactant homologue (considering a straight alkyl chain), (2) categorization according to the class of US EPA anionic surfactants, (3) applying trend analysis within the selected category (contained 918 compounds) to fill data gaps, and (4) subcategorization by chemical elements P,C and O. Endpoints for following organisms were estimated: crustaceans (*Daphnia magna*) LC₅₀, 48 h; fish (*Pimephales promeales*), LC₅₀, 96 h; amphibians (*Xenopus laevis*), EC₅₀, 96 h; algae (*Selenastrum capricornutum*), EC₅₀, 96 h.

Tables 1 through 4 list the results from a number of surfactant homologues in the C₁₂-C₁₆ range with an ethoxylation range of 5 to 9 moles. Examples of the trend analysis results can be found in the supplemental information and data section at the end of this appendix.

Table 1. Estimated LC₅₀, 48 h. endpoint data (mg/L) for **crustaceans** (*Daphnia magna*)

Alkyl chain length	NUMBER OF ETHOXYLATE GROUPS				
	5	6	7	8	9
12	9.75	16.8	29.9	48.3	84
13		7.6	13	17	22
14		3.6	6.3	11.4	18
15		1.6	2.9	4.5	8.0
16		0.73	1.2	2.1	3.4

Table 2. Estimated LC₅₀, 96 h. endpoint data (mg/L) for **fish** (*Pimephales promeales*)

Alkyl chain length	NUMBER OF ETHOXYLATE GROUPS				
	5	6	7	8	9
12	19	157	235	334	472
13		99	141	209	294
14		65	92	130	183
15		40.4	55	78	110
16		25	34	48	68

Table 3. Estimated EC₅₀, 96 h. endpoint data (mg/L) for **amphibians** (*Xenopus laevis*)

Alkyl chain length	NUMBER OF ETHOXYLATE GROUPS				
	5	6	7	8	9
12	96	156	263	417	659
13		80	128	213	336
14		43	68	108	171
15		22	33	52	83.7
16		11.3	17	27	43

Table 4. Estimated EC₅₀, 96 h. endpoint data (mg/L) for **algae** (*Selenastrum capricornutum*)

Alkyl chain length	NUMBER OF ETHOXYLATE GROUPS				
	5	6	7	8	9
12	54	71	92.7	117	148
13		54	68	89.9	113
14		43	55	69	86.3
15		32.9	40	51	64.1
16		25.3	31	39	49

The data in Table 1 are consistent with the information provided on the MSDS document for the phosphate ester surfactant, which lists an estimated ecotoxicology LC₅₀ value for invertebrates of 1 – 10 mg/L. The MSDS does not list any endpoint information for other aquatic organisms.

The trend in toxicological endpoint value as a function of alkyl chain length and ethoxylation degree is graphically represented in Figures 1-4. The general trend is that the toxicity increases with increasing alkyl chain length and decreasing ethoxylation degree.

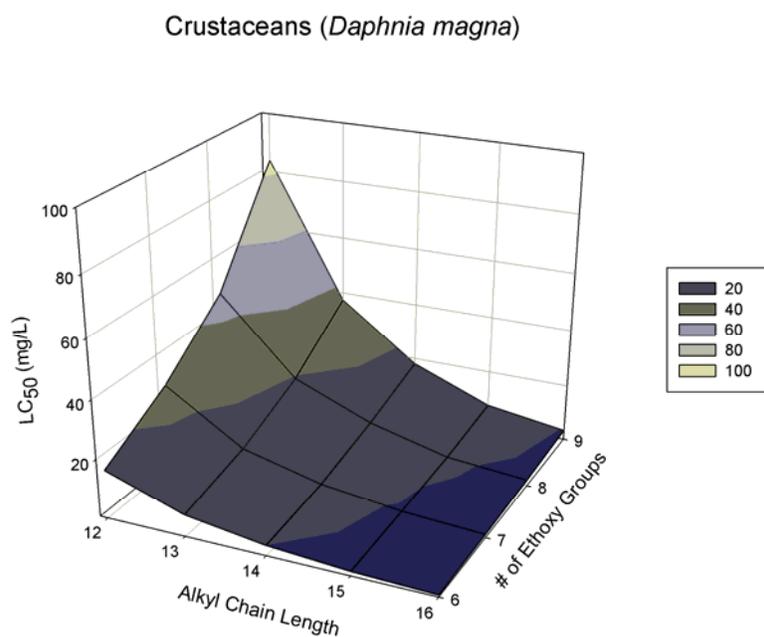


Fig. 1. The toxicity of phosphate ethoxylated ester to **crustaceans** (*Daphnia magna*) as a function of the compound's alkyl chain length and number of ethoxylated groups. The LC₅₀, 48 h. endpoint values were estimated using the OECD-QSAR Toolbox.

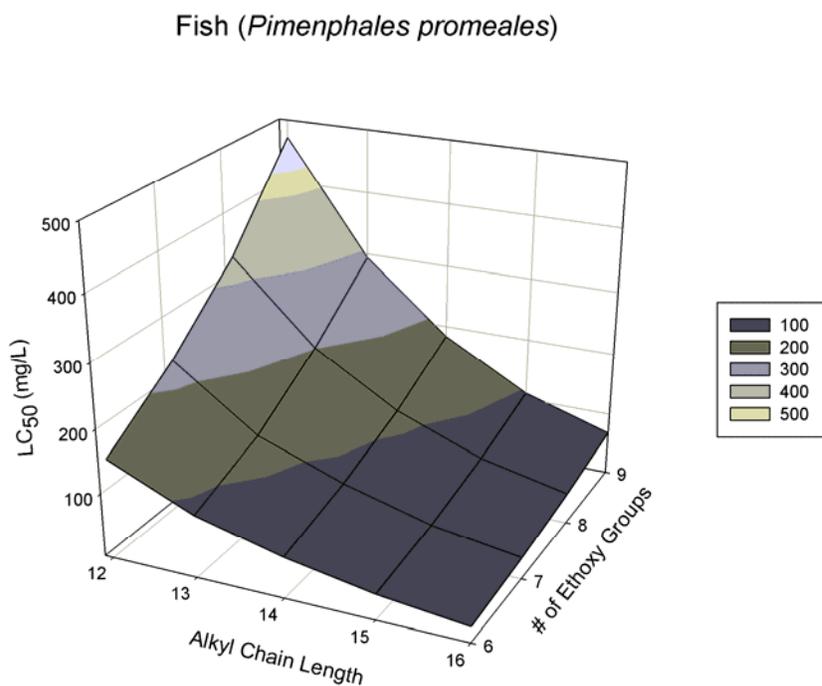


Fig. 2. The toxicity of phosphate ethoxylated ester to **fish** (*Pimenphales promeales*) as a function of the compound's alkyl chain length and number of ethoxylated groups. The LC₅₀, 96 h. endpoint values were estimated using the OECD-QSAR Toolbox.

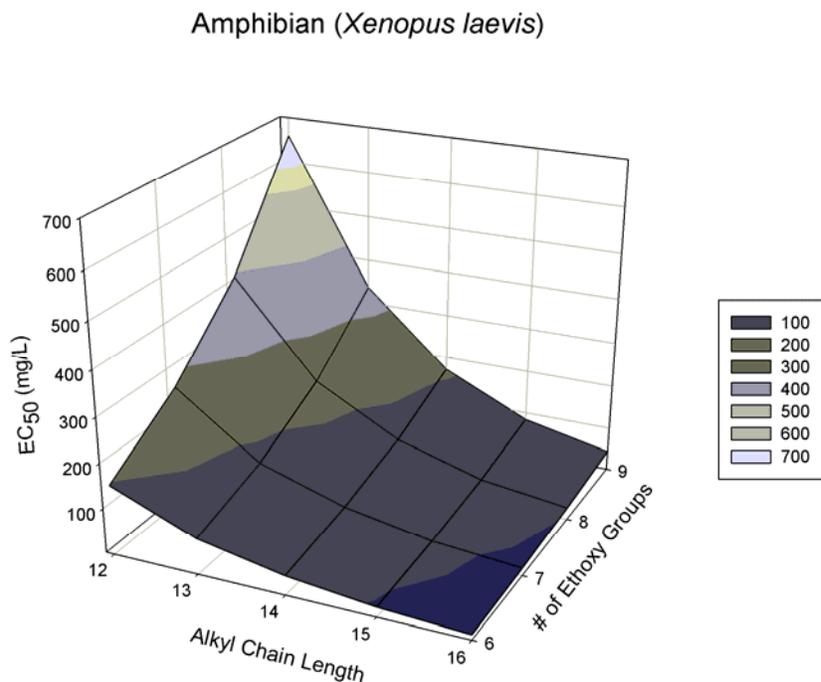


Fig. 3. The toxicity of phosphate ethoxylated ester to **amphibians** (*Xenopus laevis*) as a function of the compound's alkyl chain length and number of ethoxylated groups. The LC₅₀, 96 h. endpoint values were estimated using the OECD-QSAR Toolbox.

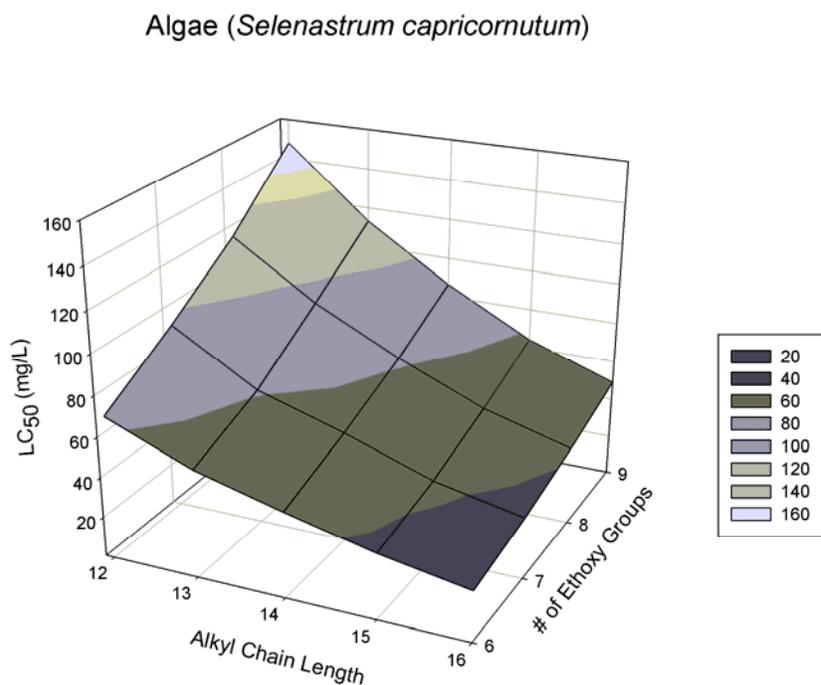


Fig. 4. The toxicity of phosphate ethoxylated ester to **algae** (*Selenastrum capricornutum*) as a function of the compound's alkyl chain length and number of ethoxylated groups. The EC₅₀, 96 h. endpoint values were estimated using the OECD-QSAR Toolbox.

2.3. Determination of the Overall Toxicity for the Phosphate Ester Surfactant

Based on the endpoint values of the various individual surfactant homologues listed in tables 1-4, an overall toxicity endpoint value can be estimated for the product formulation. Based on additivity, each homologue will contribute to the overall toxicity in proportion to its fraction in the whole product. The product information does not provide data on the fractions of the various surfactant homologues. An estimation can be made based on properties of the phosphate ester surfactant product. Considering the typical ethoxylation degree of a phosphate ester of 50 to 70% (see surfactant information), a conservative value of 50% ethoxylation criterion was used for the selection of homologues to be considered in the determination of the overall toxicology. The six selected homologues are listed in Table 5 with their assumed fractions in the whole product. For the estimation of fractions it was assumed that the medium-sized C₁₄ homologue in the C₁₂-C₁₆ range is dominant, with smaller fractions of the smaller and larger homologues in the given range.

Table 5 Phosphate ester homologues used in the determination of the whole product toxicology and their estimated fraction in the whole surfactant product.

<i>Surfactant Homologue</i>	<i>Fraction (%) of whole product</i>
C ₁₂ EO ₆	10
C ₁₃ EO ₆₋₇	20
C ₁₄ EO ₇	40
C ₁₅ EO ₇₋₈	20
C ₁₆ EO ₈	10

The overall surfactant toxicity endpoint values were estimated by determining the sum of the fractional toxicities of each individual homologue:

$$\text{Overall Toxicity} = \sum f_x \times \text{Tox}_x$$

Where f_x is the fraction of homologue x and Tox_x is the endpoint value for homologue x .

The estimated overall toxicological endpoints are listed in Table 6.

Table 6 Estimated overall toxicity endpoint values for phosphate ester surfactant

<i>Aquatic Species</i>	<i>Toxicological endpoint (mg/L)</i>
Crustaceans (<i>Daphnia magna</i>), LC ₅₀ , 48 h	7.2
Fish (<i>Pimephales promeales</i>), LC ₅₀ , 96 h	95
Amphibians, (<i>Xenopus leavis</i>), EC ₅₀ , 48 h	75
Algae (<i>Selenastrum capricornutum</i>), EC ₅₀ , 48 h	54

2.4. Discussion

Considering the relatively low application rates of herbicide surfactants and the toxicity endpoint values estimated above, which are in general higher than some other major herbicide surfactants, it can be expected that risks to aquatic organisms are low. This is consistent with conclusions made by EPA-OPP about the risk of related surfactant compounds. Similar surfactant compounds (such as polyoxyethylene-polyoxypropylene-phosphate, nonylphenol-ethoxylated-

phosphate ester, polyethylene-glycol—nonylphenyl-ether-phosphate) were classified by EPA-OPP as pesticide inerts that, given the use pattern, will not adversely affect public health or the environment (former List 4B) (US EPA-OPP, 2004).

As pointed out in the discussion (section 6.1), only the monoester of this surfactant molecule was considered in this analysis. The possible contribution of the diester version of this ester that may be present in the formulation is not expected to contribute significantly to the aquatic toxicity. Although the diester will be intrinsically more toxic, it is not expected to express its intrinsic toxicity in a mixture with the monoester because of solubility and aggregation cut-offs (Roberts, 2008; pers. comm.). Another aspect of the phosphate esters is the type of alkoxy groups. In addition to ethoxy groups, the product information indicates that the parent alcohol surfactant may also contain propoxy groups in its hydrophilic part of the surfactant molecule. It has been shown that the presence of propoxy groups in place of ethoxy groups does not affect the molar toxicity on the same parent alcohol (Roberts et al., 2007). Therefore, surfactant molecules containing the propoxy groups as part of the ethoxylated chain were not evaluated here.

3. References

- BASF, 2009A. Klearfac AA 270 Product information, accessed on 2/19/2009 at URL:
http://www2.basf.us/performancechemical/pdfs/Klearfac_AA270.pdf
- BASF, 2009B. Klearfac AA 270 MSDS accessed on 2/19/2009 at URL:
http://worldaccount.basf.com/wa/NAFTA~en_US/Catalog/ChemicalsNAFTA/doc4/BASF/PRD/30085577/.pdf?title=&asset_type=msds/pdf&language=EN&validArea=US&urn=urn:documentum:ProductBase_EU:09007af880093dc8.pdf
- Cross, J. 1998. Anionic surfactants-An introduction. *In* Anionic surfactants, Analytical Chemistry. *Ed.* J. Cross. CRC Press.
- OECD, 2009. OECD (Q)SAR Application Toolbox; accessed at
http://www.oecd.org/document/23/0,3343,en_2649_34379_33957015_1_1_1_1,00.html
- Roberts, J.F., S.J. Marshall, and D.W. Roberts. 2007. Aquatic toxicity of ethoxylated and propoxylated alcohols to *Daphnia magna*. *Environ. Tox. Chem.* 26:68-72.
- Roberts, D.W. 2008. Personal communication.
- US EPA-OPP, 2004. List of pesticide inert ingredients. Accessed at:
http://www.epa.gov/opprd001/inerts/inerts_list4Bcas.pdf
- Wasow, G.W. 1996. Phosphorus-containing anionic surfactants. *In* Anionic Surfactants: Organic Chemistry. *Ed.* H.W. Stache. CRC Press.
- Ying, G.G. 2006. Fate, behavior and effects of surfactants and their degradation products in the environment. *Environ. Int.* 32:417-431.

Supplementary Data and Information to the Toxicity Endpoint Estimation Using the OECD-QSAR Application Toolbox

The supplemental information included here provides some examples of results that were generated by the OECD QSAR Toolbox for estimation of aquatic toxicity endpoints for phosphate ester surfactant.

The procedure followed for the estimation of toxicity endpoints for the various homologues of phosphate ester surfactants in this assessment was:

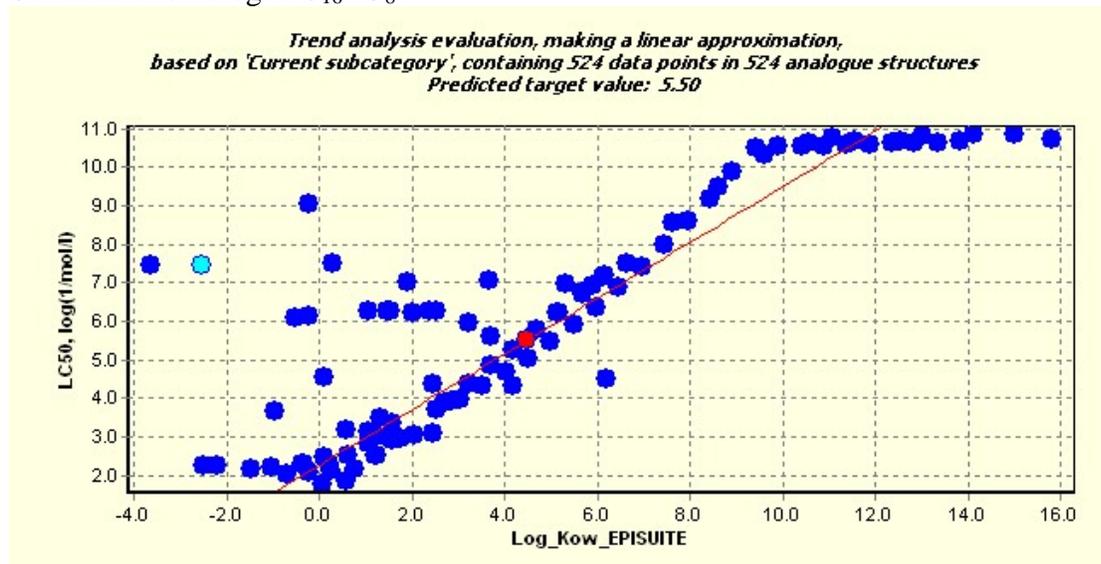
- (1) drawing the structure of a phosphate ester surfactant homologue. The structures considered here were contained a straight alkyl chain;
- (2) categorization according to the class of US EPA anionic surfactants (which contained 918 compounds);
- (3) selecting an endpoint of interest. Endpoints for following organisms were estimated: crustaceans (*Daphnia magna*) LC₅₀, 48 h; fish (*Pimephales promelas*), LC₅₀, 96 h; amphibians (*Xenopus laevis*), EC₅₀, 96 h; algae (*Selenastrum capricornutum*), EC₅₀, 96 h;
- (4) applying the option of trend analysis within the selected category to fill data gaps;
- (5) within the results obtained, subcategorization by chemical elements P,C and O was performed if sufficient data were available. This was the case for the results with crustaceans, fish, and algae. The results for amphibians contained a small dataset that was not sufficient to be subjected to further subcategorization;

The examples below illustrate the results that were obtained. The results are shown for the C₁₆EO₈ homologue and the C₁₂EO₈. The C₁₆EO₈ homologue is an example of a homologue with toxicity endpoint values at the lower end of the range of values obtained, the other homologue has endpoint values at the higher end of the range. In addition to the trend analysis graph showing the estimated value along with the data points used in the analysis, the regression and statistics on goodness of fit are provided.

The following pages show the trend analysis data for the four selected aquatic toxicity endpoints.

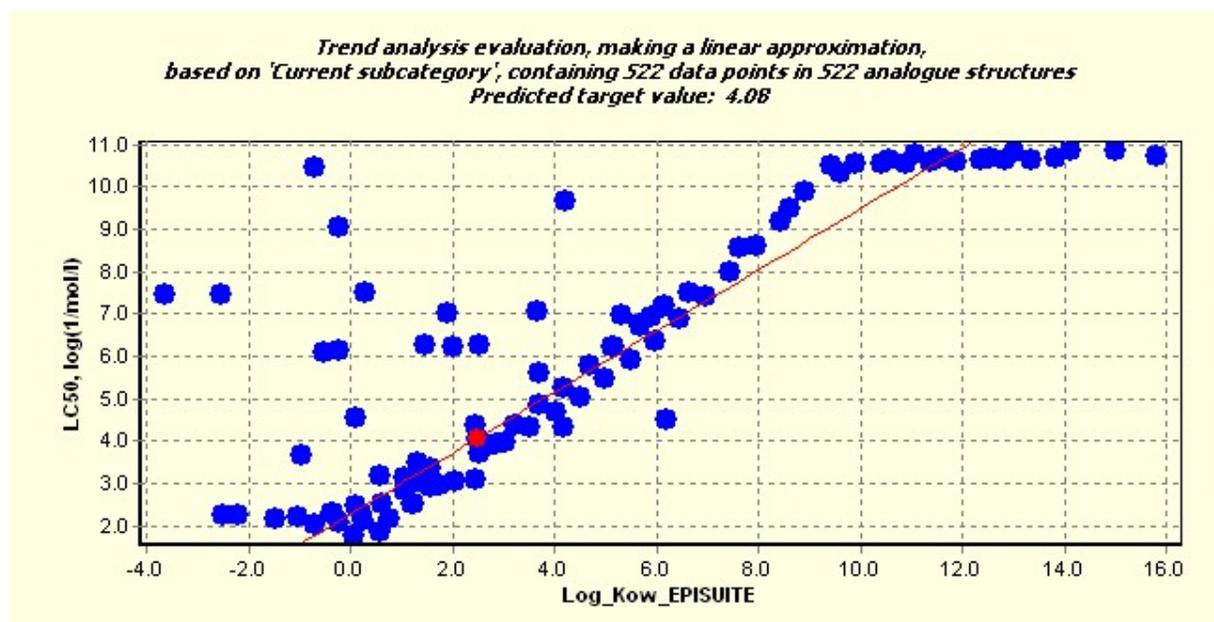
Trend-analysis data for crustaceans (*Daphnia magna*):

Surfactant homologue C₁₆EO₈:



- $2.27 + 0.723 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.842, s = 1.11$

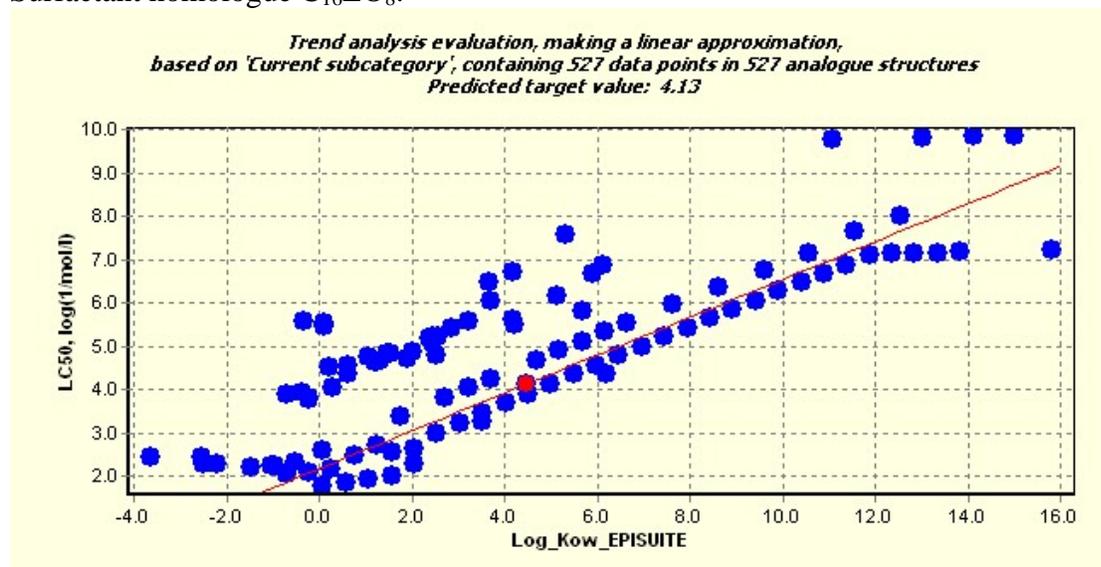
Surfactant homologue C₁₂EO₈:



- $2.28 + 0.720 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.838, s = 1.13$

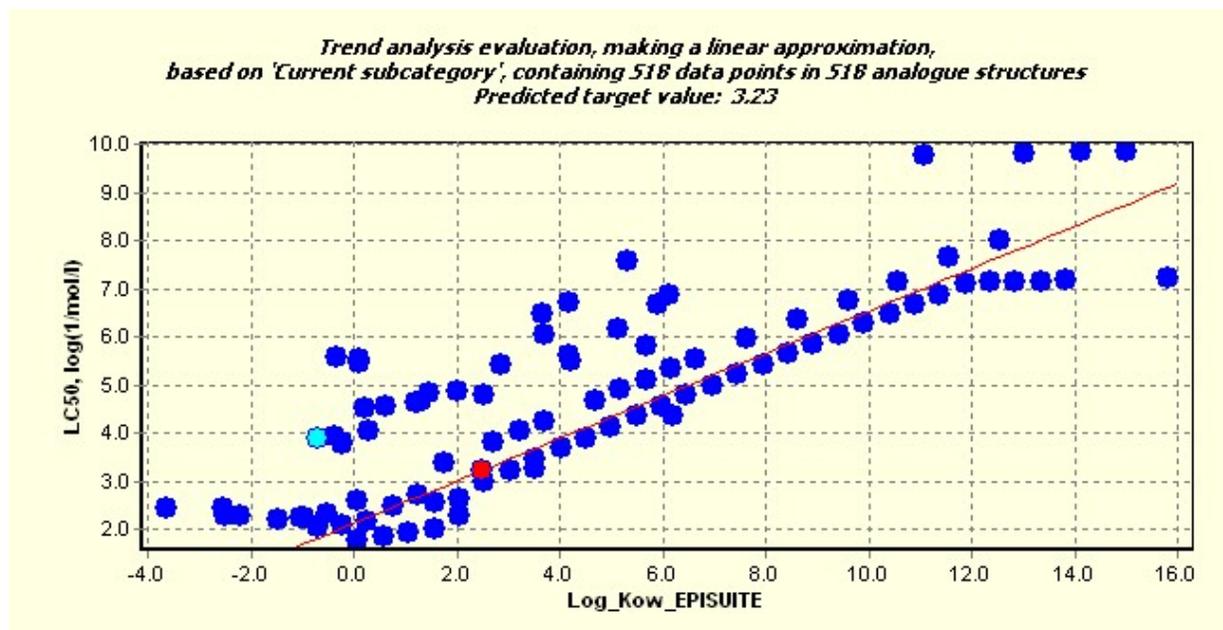
Trend analysis data for fish (*Pimenphales promeales*):

Surfactant homologue C₁₆EO₈:



- $2.18 + 0.437 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.829, s = 0.714$

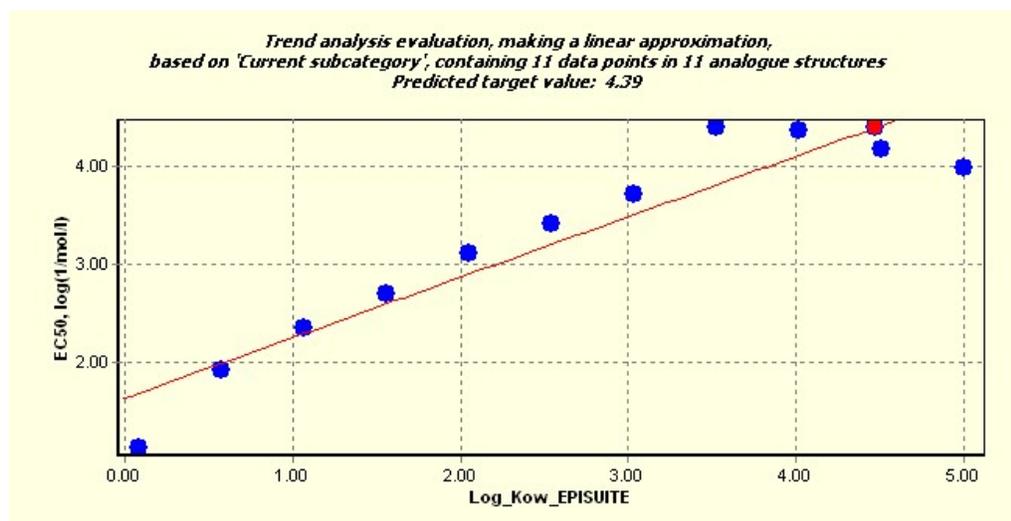
Surfactant homologue C₁₂EO₈:



- $2.13 + 0.441 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.829, s = 0.715$

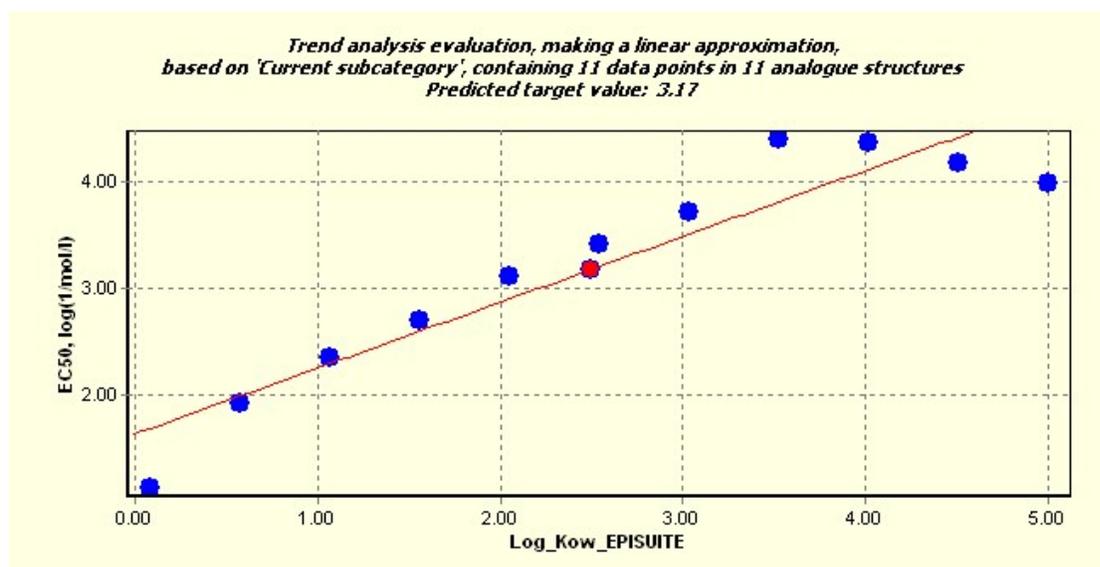
Trend analysis for amphibians (*Xenopus laevis*):

Surfactant homologue C₁₆EO₈:



- $1.64 + 0.615 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.873, s = 0.383$

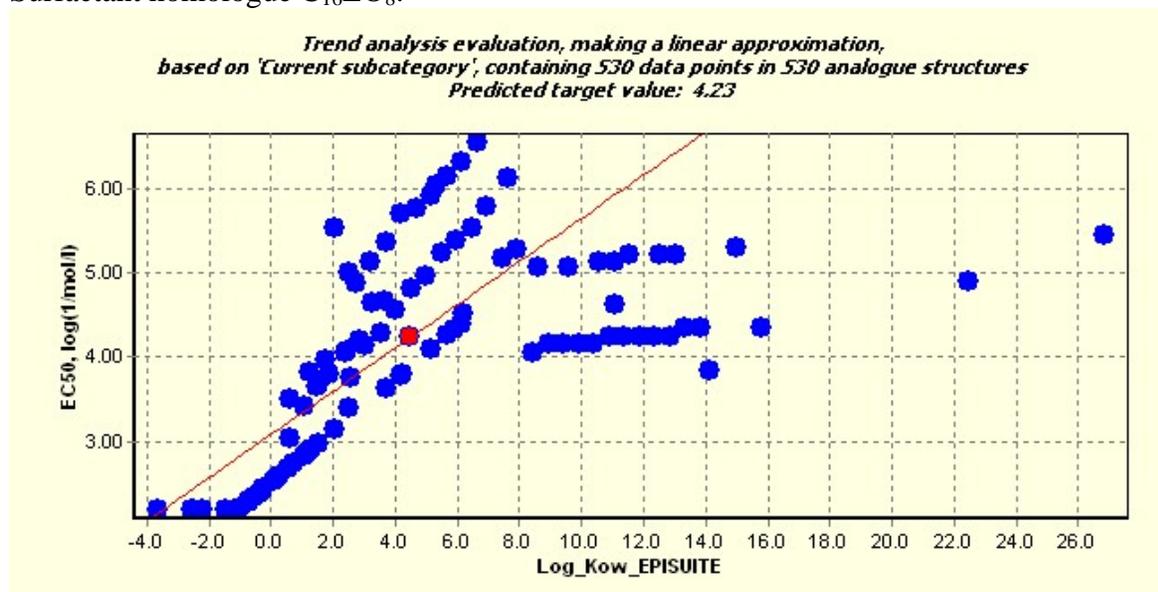
Surfactant homologue C₁₂EO₈:



- $1.64 + 0.615 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.873, s = 0.383$

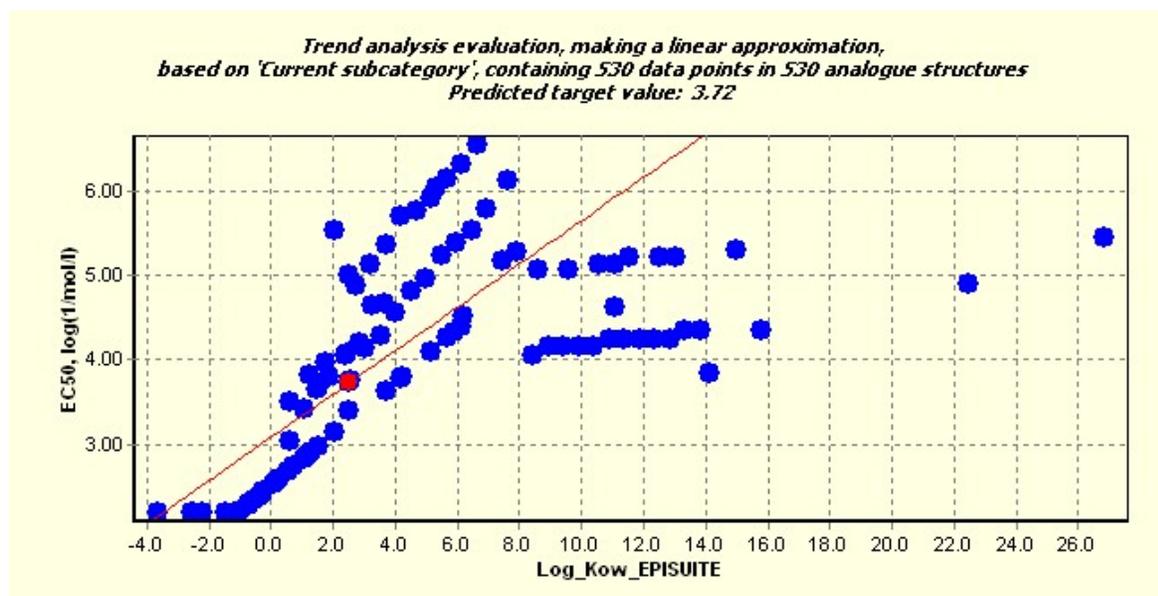
Trend analysis for algae (*Selenastrum capricornutum*):

Surfactant homologue C₁₆EO₈:



- $3.08 + 0.256 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.558, s = 0.86$

Surfactant homologue C₁₂EO₈:



- $3.08 + 0.256 * \text{Log_Kow_EPISUITE}$
- $R^2 = 0.558, s = 0.86$

Appendix 2

PRZM Input file for PRZM Modeling

```
"MA Right-Of-Way based State Paxton soil"
*** Record 3:
  0.69   0.36       0       25       1       3
*** Record 6 -- ERFLAG
  4
*** Record 7:
  0.37   1.34       1       10               4       6   356.8
*** Record 8
  1
*** Record 9
  1   0.2       31       97       3  90  90  90       0   122
*** Record 9a-e
  1   24
0103 1603 0104 1604 0105 1605 0106 1606 0107 1607 0108 1608 0109 1609 0110 1610
.004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004
.110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110
  90  90  90  90  90  90  90  90  90  90  90  90  90  90  90  90
0111 1611 0112 1612 0101 1601 0102 1602
.004 .004 .004 .004 .004 .004 .004 .004
.110 .110 .110 .110 .110 .110 .110 .110
  90  90  90  90  90  90  90  90
*** Record 10 -- NCPDS, the number of cropping periods
  30
*** Record 11
  010361 150661 151161       1
  010362 150662 151162       1
  010363 150663 151163       1
  010364 150664 151164       1
  010365 150665 151165       1
  010366 150666 151166       1
  010367 150667 151167       1
  010368 150668 151168       1
  010369 150669 151169       1
  010370 150670 151170       1
  010371 150671 151171       1
  010372 150672 151172       1
  010373 150673 151173       1
  010374 150674 151174       1
  010375 150675 151175       1
  010376 150676 151176       1
  010377 150677 151177       1
  010378 150678 151178       1
  010379 150679 151179       1
  010380 150680 151180       1
  010381 150681 151181       1
  010382 150682 151182       1
  010383 150683 151183       1
  010384 150684 151184       1
  010385 150685 151185       1
  010386 150686 151186       1
  010387 150687 151187       1
  010388 150688 151188       1
  010389 150689 151189       1
  010390 150690 151190       1
*** Record 12 -- PTITLE
POEA - 1 applications @ 0.68 kg/ha
*** Record 13
```

30 1 0 0

*** Record 15 -- PSTNAM

POEA

*** Record 16

100661	0	2	0.0	0.68	.99	.01
100662	0	2	0.0	0.68	.99	.01
100663	0	2	0.0	0.68	.99	.01
100664	0	2	0.0	0.68	.99	.01
100665	0	2	0.0	0.68	.99	.01
100666	0	2	0.0	0.68	.99	.01
100667	0	2	0.0	0.68	.99	.01

Records for yrs 68 - 84 not printed

100685	0	2	0.0	0.68	.99	.01
100686	0	2	0.0	0.68	.99	.01
100687	0	2	0.0	0.68	.99	.01
100688	0	2	0.0	0.68	.99	.01
100689	0	2	0.0	0.68	.99	.01
100690	0	2	0.0	0.68	.99	.01

*** Record 17

0 3 0

*** Record 18

0 0 0.5

*** Record 19 -- STITLE

"Brackett-Rock outcrop complex, 12 to 60 percent slopes (MapUnit), Brackett (Component), Hydrologic Group C"

*** Record 20

46 0 0 1 0 0 0 0 0 0

*** Record 26

0 0 0

*** Record 30

4 2500

*** Record 33

3

1 12 1.51 0.28 0 0 0

0.04621 0.04621 0

0.1 0.28 0.164 1.85 0

2 11 1.55 0.28 0 0 0

0.04621 0.04621 0

1 0.28 0.164 0.75 0

3 23 1.55 0.252 0 0 0

0.04621 0.04621 0

1 0.252 0.145 0.4 0

***Record 40

0

WATR YEAR 10 PEST YEAR 10 CONC YEAR 10 1

1

1 -----

10 YEAR

PRCP TSER 0 0

RUNF TCUM 0 0

INFL TCUM 1 1

TCON1 TAVE 1 120 1.0E3

TCON1 TAVE 121 132 1.0E3

TCON1 TAVE 133 154 1.0E3

ESLS TCUM 0 0 1.0E3

RFLX TCUM 0 0 1.0E5

EFLX TCUM 0 0 1.0E5

RZFX TCUM 0 0 1.0E5

Appendix 3

PRZM INPUTS.XLS - PRZM Data Inputs for Massachusetts Right-of-Way Scenario

PRZM Record #	Variable Name	Value	Parameter Name and Guidance	Source Comments
1	TITLE MA_ROWPA		Title of input file	
2	HTITLE		"MA Right-Of-Way based State Paxton soil, Metfile w14739 (Boston, MA); Scenario adapted from Texas Right-Of-Way in the Barton Springs Segment of the Edwards Aquifer, Hays and Travis Counties, TX. "	
3	PFAC	0.69	Pan factor (dimensionless)	
	SFAC	0.36	Snowmelt factor (cm/C)	
	IPEIND	0	Pan factor flag - 0 = pan data read from meteorology file	
	ANETD	25	Min. depth from which evaporation is extracted during fallow period (cm); 10 cm = soil with limited drainage	
	INICRP	1	"Flag for initial crop if simulation date is before emergence date (see Record 10); 1 = yes, 2 = no"	
	ISCOND	3	"Surface condition of initial crop if INICRP = 1; 1 = fallow, 2 = cropping, 3 = residue"	
6	ERFLAG	4	"Flag to calculate erosion; 0 = none, 2 = MUSLE, 3 = MUST, 4 = MUSS; note that a value of 1 is meaningless; MUSS selected by EPA and industry as most appropriate."	
7			"Only needed if ERFLAG = 2,3, or 4 (Record 6)"	
	USLEK	0.37	Universal soil loss equation (K) of soil erodibility	
	USLELS	1.34	Universal soil loss equation (LS) length-slope topographic factor	
	USLEP	1	Universal soil loss equation (P) practice factor	
	AFIELD	10	Area of field or plot (ha); EPA default is 10	
	IREG	4	Location of NRCS 24-hour hyetograph/Soil Conservation Service rainfall distribution region	
	SLP	6	Land slope (%)	
	HL	356	"Hydraulic length (m); for a circular 10 ha field emptying into a 1 ha pond (when linked to EXAMS), default HL = 354 m"	
8	NDC	1	Number of different crops in simulation (1 to 5) Right-of-way (grass)	
9			(repeat this record NDC times)	
	ICNCN	1	Crop number	
	CINTCP	0.2	Maximum interception storage of crop (cm)	
	AMXDR	31	Maximum rooting depth of crop (cm)	
	COVMAX	97	Maximum areal coverage of canopy (%)	
	ICNAH	3	"Surface condition of crop after harvest date (see Record 11); 1 = fallow, 2 = cropping, 3 = residue"	
	CN(x3)	85	"Runoff curve numbers of antecedent moisture condition for fallow, cropping, and residue (three values); note that runoff and leaching are very sensitive to these factors."	
		85		
		85		
	WFMAX	0	"Maximum dry weight of crop at full canopy (kg/m2), required if CAM = 3 (Record 16) else set to 0.0"	
	HTMAX	122	Maximum canopy height (cm) at maturation date (Record 11)	
	RECORD9A		1 24 Crop Number and Number of RUSLE Dates	
	RECORD9B		0103 1603 0104 1604 0105 1605 0106 1606 0107 1607 0108 1608 0109 1609 0110 1610 RUSLE Dates	
	RECORD9C		.004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 .004 USLEK	
	RECORD9D		.110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110 .110	

```

      .110 .110 .110      Mannings N
RECORD9E      85  85  85  85  85  85  85  85  85  85  85  85  85
      85  85  85 Curve Number
RECORD9B      0111 1611 0112 1612 0101 1601 0102 1602      RUSLE Dates
RECORD9C      .004 .004 .004 .004 .004 .004 .004 .004 USLEC
RECORD9D      .110 .110 .110 .110 .110 .110 .110 .110 Mannings N
RECORD9E      85  85  85  85  85  85  85  85 Curve Number

10  NCPDS  30      Number of cropping periods (sum of NDC for all cropping dates in
      Record 11)

11  (Repeat this record NCPDS times)
      Right-of-way (grass)
EMD  1      Integer day of crop emergence
EMM  3      Integer month of crop emergence
IYREM 61     Integer year of crop emergence
MAD  15     Integer day of crop maturation
MAM  6      Integer month of crop maturation
IYRMAT 61    Integer year of crop maturation
HAD  15     Integer day of crop harvest
HAM  11     Integer month of crop harvest
IYRHAR 61    Integer year of crop harvest
INCROP 1     Crop number associated with NDC (Record 8)

19  STITLE  ), "Paxton fine sandy loam"

20  CORED  46     Total depth of soil core (cm); must be sum of all horizon
      thicknesses in Record 33 and at least as deep as the root depth in
      Record 9
BDFLAG 0      "Bulk density flag; 0 = bulk density known and entered in Record
      33, 1 = mineral value entered"
THFLAG 0      "Field capacity and wilting point flag; 0 = water contents are
      entered, 1 = calculated by model."
KDFLAG 0      "Soil adsorption coefficient; 0 = Kd entered in Record 37,
      1 = calculated by model."
HSWZT 0      "Drainage flag; 0 = free draining, 1 = restricted (should be set
      to zero)"
MOC  0      "Method of characteristics flag; 1 = yes, 0 = no; this flag is
      used for the leaching program and PRZM is not recommended as a
      leaching model by the EPA at this time."
IRFLAG 0      "Irrigation flag; 0 = no irrigation, 1 = year round, 2 = during
      cropping period only."
ITFLAG 0      "Soil temperature simulation flag; 1 = yes, 0 = no (must = 1 if
      nitrogen is being simulated)"
IDFLAG 0      "Thermal conductivity and heat capacity flag; 1 = yes, 0 = no."
BIOFLG 0      "Biodegradation flag; 1 = yes, 0 = no; this flag is used when
      transformation occurs only by the microbial pathway and requires
      knowledge of microbe population characteristics"

33  NHORIZ  3     Number of horizons

Horizon 1:
34  "(Repeat Records 34, 36, and 37 for each horizon)"
      HORIZN 1     Horizon number
      THKNS 12     Thickness of horizon (cm)
      BD  1.51     Bulk density if BDFLAG = 0 or mineral density if BDFLAG = 1
      (Record 20) (g/cm3)
      THETO 0.28   "Initial soil water content in horizon (cm3/cm3); if site-specific
      value not known, use field capacity"
      AD  0        "Soil drainage parameter if HSWZT = 1 (Record 20), else set to 0.0
      (day-1); note that the # of compartments (= DPN/THKNS) is needed
      To determine AD"
      DISP  0      Pesticide hydrodynamic solute dispersion coefficient for each

```

NCHEM; should be set to zero unless field data are available for calibration

ADL 0 Lateral soil drainage parameter if HSWZT = 1 (Record 20) (should be set to zero)

37 DPN 0.1 Thickness of compartments in horizon (cm)

THEFC 0.28 Field capacity in horizon (cm³/cm³)

THEWP 0.164 Wilting point in horizon (cm³/cm³)

OC 1.00 Organic carbon in horizon (%)

Horizon 2:

34 "(Repeat Records 34, 36, and 37 for each horizon)"

HORIZN 2 Horizon number

THKNS 11 Thickness of horizon (cm)

BD 1.55 Bulk density if BDFLAG = 0 or mineral density if BDFLAG = 1 (Record 20)(g/cm³)

THETO 0.28 "Initial soil water content in horizon (cm³/cm³); if site-specific value not known, use field capacity"

AD 0 "Soil drainage parameter if HSWZT = 1 (Record 20), else set to 0.0 (day-1); note that the # of compartments (= DPN/THKNS) is needed To determine AD"

DISP 0 Pesticide hydrodynamic solute dispersion coefficient for each NCHEM; should be set to zero unless field data are available for calibration

ADL 0 Lateral soil drainage parameter if HSWZT = 1 (Record 20) (should be set to zero)

37 DPN 1 Thickness of compartments in horizon (cm)

THEFC 0.28 Field capacity in horizon (cm³/cm³)

THEWP 0.164 Wilting point in horizon (cm³/cm³)

OC 0.75 Organic carbon in horizon (%)

Horizon 3:

34 "(Repeat Records 34, 36, and 37 for each horizon)"

HORIZN 3 Horizon number

THKNS 23 Thickness of horizon (cm)

BD 1.55 Bulk density if BDFLAG = 0 or mineral density if BDFLAG = 1 (Record 20) (g/cm³)

THETO 0.252 "Initial soil water content in horizon (cm³/cm³); if site-specific value not known, use field capacity"

AD 0 "Soil drainage parameter if HSWZT = 1 (Record 20), else set to 0.0 (day-1); note that the # of compartments (= DPN/THKNS) is needed To determine AD"

DISP 0 Pesticide hydrodynamic solute dispersion coefficient for each NCHEM; should be set to zero unless field data are available for calibration

ADL 0 Lateral soil drainage parameter if HSWZT = 1 (Record 20) (should be set to zero)

37 DPN 1 Thickness of compartments in horizon (cm)

THEFC 0.252 Field capacity in horizon (cm³/cm³)

THEWP 0.145 Wilting point in horizon (cm³/cm³)

OC 0.40 Organic carbon in horizon (%)

40 ILP 0 "Flag for initial pesticide levels before simulation start date; 1 = yes, 0 = no"

CFLAG 0 "Conversion flag for initial pesticide levels; 0 = mg/kg, 1 = kg/ha, blank if ILP = 0"