

ATTACHMENT 1:

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

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Executive Summary

Introduction

Herbicides applied as part of vegetation management in rights-of-way (ROW) areas in Massachusetts are regulated according to provisions specified in rights-of-way management (333 CMR 11.00). Specific use restrictions, such as no-spray and limited-spray zones and a selection of approved herbicide products, are provided for so-called ‘sensitive areas’, including wetlands and other water resources. With the evaluation of herbicide products for use in these sensitive 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. 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. The risk assessment described herein was conducted in order to assess whether the use of herbicides in ROW areas according to regulations will result in unreasonable risks to non-target aquatic organisms from exposure to surfactants. This risk assessment was based on an aquatic exposure assessment and a subsequent comparison of the estimated environmental concentrations with toxicological endpoint values for potential non-target aquatic organisms.

Surfactants in Herbicide Formulations

Besides active ingredients, herbicide formulations also contain other compounds generally referred to as “inert” or “other” ingredients. Among the “inert” or “other” ingredients in herbicide formulations are substances that enhance the performance of the active ingredient(s). Surfactants generally make up the largest part of the supporting ingredients. In some cases, additional surfactants are required as adjuvants in the final tank-mix to further optimize performance and adjust the tank mix for specific applications. Most surfactants used with herbicides are non-ionic surfactants and include alcohol ethoxylates (AEs), alkylphenol ethoxylates (APEs), alkylamine ethoxylates (ANEs), silicon-based surfactants (organosilicones), and oils. Anionic surfactants, such as phosphate ethoxylated esters (PE), find also applications in herbicide products. Surfactants facilitate the emulsifying, dispersing, spreading, sticking and wetting properties of the herbicide formulation. Information on the “other” ingredients is generally protected by trade secrets. Consequently, the evaluation of these ingredients relies mainly on review of the open literature on the toxicity and environmental fate.

Comprehensive reviews of the environmental properties, fate and toxicology of non-ionic surfactants in herbicides concluded that these substances pose no significant risk to aquatic and terrestrial organisms. The surfactant POEA (polyethoxylated alkylamine belonging to the ANEs), an ingredient in glyphosate formulations, has been subject to many studies. Laboratory studies indicated that the POEA surfactants have the highest aquatic toxicity among commonly used herbicide surfactants. Field studies, however, have generally indicated low risk to aquatic

organisms, which may be attributed to the relatively low rate of surfactant applications associated with herbicides, their low persistence, and relative immobility in the environment.

Based on their use in ROW herbicides and availability of data, the nonionic ANEs, AEs and APEs, and the anionic PE surfactants were selected for consideration in this risk assessment

Herbicide Applications In ROW

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. An exposure assessment was conducted to estimate the environmental concentrations in adjacent surface water through analysis and modeling of these environmental fate processes.

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. As part of a conservative worst-case approach, this assessment considered a broadcast foliar application rate of 0.68 kg/ha, which representative of what is used in a railroad scenario. In addition, it was assumed that the surfactant in a herbicide formulation was only of one type (i.e., no surfactant blends) and present at a 15% v/v concentration in the formulation. Additional input parameters, such as environmental fate, soil and vegetation characteristics, for the models employed were either based on available data or professional judgment.

Exposure Assessments

Various exposure assessments were performed to show the progression from a generic screening-level approach toward a more refined exposure assessment of environmental concentrations in surface waters. The final risk assessment was based on the refined exposure estimates. Initially, a simple screening-level exposure assessment was conducted using AgDrift model simulations combined with a assumption for runoff. This screening-level assessment resulted in estimated environment concentrations (EEC) of 0.013 mg/L of surfactant. Subsequently, EPA's GENERIC Estimated Exposure Concentration (GENEEC) model was employed. This screening-level model is based on a generic vulnerable site representing conditions that favor transport to and persistence in surface water. The GENEEC model simulations resulted in EECs (highest values) of 0.016 mg/L for POEA, 0.0088 mg/L for NPE, 0.012 mg/L for AE, and 0.022 mg/L for the PE surfactant.

The refined Tier II exposure assessment was performed with the use of the more sophisticated PRZM-EXAMS model. This model links a field scale leaching and runoff PRZM model (Pesticide Root Zone Model) with the surface water EXAMS model (Exposure Analysis Modeling System) to estimate pesticide concentrations in surface water. This model requires site-specific soil, topography, weather, and vegetation input.

To illustrate the behavior of surfactants in soil, the POEA surfactant was simulated by the root zone model PRZM. A model scenario representative of a ROW application area in Massachusetts was developed. The surfactant application rate was 0.68 kg/ha once a year on June 10 with 99% application efficiency and 1% drift. The simulation results 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.

The environmental concentrations in an adjacent pond were simulated with the PRZM-EXAMS model. The ROW scenario that was developed for the PRZM model was also applied here. The simulations yield multiple-year pesticide concentrations in the water column. The upper 10th percentile concentrations (1-in-10 year highest peak and 4-day concentration) were used in the subsequent risk assessment. For the purpose of the application in ROW scenarios, the model-generated concentrations for a standard-size scenario (10-ha field draining into a 1-ha by 2-meter deep pond) were modified to make them more representative of the shallow pond in a ROW scenario, thereby making it more conservative. Furthermore, the potential for higher short-term concentrations in the shallow near-shore areas of a pond was considered. These margin concentrations were estimated by applying a shore-margin concentration factor to the previously estimated whole-pond values.

The summarized refined assessment data show that the 1-in-10 year peak concentrations of surfactants (whole pond and margin, respectively) were 2.4 and 43 µg/L for POEA, 1.1 and 23 µg/L for NPE, 1.7 and 23 µg/L for AE, and 9.0 and 115 µg/L for PE. As expected, the refined EECs are lower than the screening-level EECs listed above. It is important to point out that these estimates are not based on the consideration of buffer zones. Consequently, even these refined EECs can be considered conservative values.

Risk Characterization

A risk characterization was made by comparing the EECs from the refined Tier 2 exposure assessment results with acute toxicity endpoints for various aquatic organisms, such as invertebrates, fish, amphibian and algae. Aquatic toxicology endpoints (e.g., LC₅₀, EC₅₀) for most of the surfactants were available in the open literature. In the absence of sufficient ecotoxicity data for the PE surfactants, endpoints were estimated based on a comparison with the endpoints of similarly structured compounds using the OECD-QSAR Application Toolbox. The comparison of EECs with toxicological endpoints indicates that both the whole-pond and the margin EECs for POEA, NPE and AE surfactants are all below the most sensitive acute toxicological endpoints.

The potential risks were also expressed in terms of risk quotients (RQs) as is commonly employed by US EPA. The RQ values for surfactant exposures were determined by dividing the EEC value with the lowest acute toxicity endpoint. This ratio is a screening-level estimate that identifies high- or low-risk situations. The RQ values were in the range of 0.0001 to 0.0080 for the whole-pond scenario and in the range of 0.0002 to 0.15 for the margin scenario. The highest RQ values were found for POEA, consistent with the established toxicity profile of this surfactant.

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 approach or 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.

Discussion and Conclusions

The analysis for the alkyl ethoxylated surfactants described 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 indicates that even in a scenario with the highest application rate such as along railways and without the consideration of buffer zones, the use of these surfactants in herbicide formulations poses minimal risks to aquatic organisms. Other application scenarios such as power line and highway corridors generally use lower application rates and, consequently, would result in lower exposures and risk. While there is always uncertainty associated with model simulations, the margins of exposure (toxicity endpoint/exposure level) are generally of such a level that it is unlikely that significant adverse effects will occur with these applications. Additional protection is provided by no-spray and limited-spray zones as mandated by ROW management regulation.

The trend in risk of surfactants as indicated by the RQ values is consistent with the established toxicity data that show POEA surfactant associated with the highest aquatic toxicity. This risk assessment considered the acute risks, which are of most concern given that the concentrations of surfactants are expected to decrease rapidly due to their low persistence in water. With regard to chronic risk, the simulated exposure data is also indicated a very low risk. With respect to concerns related to estrogenic effects of the NPE surfactant, it was concluded that this risk is not significant given that the simulated concentrations are below established protective levels.

The conclusions of this risk assessment are consistent with the several other risk evaluations that were made in the context of forest and land management. The minimal risk assessed in this evaluation may be attributed to the low exposure of aquatic systems to herbicide products applied in ROW areas. The use of buffer zones for herbicide applications as required in MA-ROW management will minimize and likely prevent such exposure in normal use scenarios as was indicated by a glyphosate monitoring study conducted by MDAR in 2006. Comparison of PRZM-EXAMS simulation for the active ingredient glyphosate with the monitoring data also indicated that the model simulations are conservative.

The types of surfactants considered in this assessment are expected to represent a significant part of the surfactants used in ROW herbicide applications. The class of organosilicones surfactants was not included due to the limited information and data available for this type of surfactant. An initial assessment indicates low risks compared to POEA. The intention is to do a more thorough assessment for this type of surfactants once a more detailed database has been established.

In conclusion, this risk assessment indicates that the use of herbicides containing alkyl ethoxylated surfactants POEA, NPE, AE, and PE 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.