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Ecotoxicity of Surfactants toward Terrestrial Plants: An Overview

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INTRODUCTION

Surfactants are massively used in domestic cleaning detergents and diverse industrial processes because of their effectiveness in cleaning dirt and also greasy materials. Therefore, high concentrations of surfactants can be found in sewage sludge (Ying, 2006). This situation leads to the development of huge number of studies on toxicity of surfactants. However, the previous studies were mainly focused on the aquatic environment rather than terrestrial (Ying, 2006; Ivankovic and Hrenovic, 2010). As a consequence, there is limited information on ecotoxicity of surfactant towards terrestrial organisms, especially terrestrial plants compared to aquatic organisms.

Nowadays, significant amounts of surfactants were detected at terrestrial area mainly due to application of pesticide and through the sewage sludge that was applied as fertiliser on agricultural lands as reported by other researchers (Ivankovic and Hrenovic, 2010). Surfactants are present in most pesticide formulations as they solubilise, bind granules and disperse, and emulsify the active ingredients (Asok and Jisha, 2012). In general, a pesticide formulation includes two main components, namely active ingredient and inert ingredient. Active ingredient refers to the chemicals accountable for the desired effects, which is capable of preventing, repelling, destroying or mitigating pests. Meanwhile, inert ingredient is characterised by inactive chemicals without pesticidal action (Abhilash and Singh, 2009). Applications of modern pesticide using spray tanks can often successfully achieve high efficacy for targeted pests (Green and Beestman, 2007). However, non-target plants from adjacent area may be unintentionally exposed *via* spray-drift and surface water (Karthikeyan *et al*., 2003). Therefore, the terrestrial ecosystem has become a large sink for the pesticides, including surfactants in them. This has caused concern to public, instead of due to the active ingredients in pesticide, where the information is already known and documented (Carpenter *et al*., 2013), it is because of surfactants can alter the soil physical properties, and long-run exposure to surfactants that may cause water and soil pollution. Every year, about 230 000 t of surfactants are used in pesticide, with a formulation normally contain 1%-10% of one or more surfactants (Edser, 2007).

According to a review article by Ying (2006), the toxicity data of surfactant on terrestrial plants were limited, old and scattered, and they were mainly measured for petroleum-derived synthetic surfactants, *i.e.* linear alkylbenzene sulphonate (LAS). In the late 1980s and early 1990s, Unilever (1987) and Mieure *et al.* (1990) reported that the EC_{50} (concentration that results in an undesirable change of 50% in the test endpoint being measured relative to the control) of LAS towards sorghum (*Sorghum bicolour*), sunflower (*Helianthuus annuus*) and mung bean (*Phaseolus aureus*) within 21 days was determined as 167, 289, and 316 mg kg^{-1}, respectively. The authors studied the effect of different concentrations, *i.e.* 1, 10, 100 and 1000 mg kg^{-1} of LAS in potting soil toward sorghum, sunflower and mung bean using OECD 208, Terrestrial Plant Growth Test method. The highest no observed effect concentration (NOEC) reported was 100 mg kg^{-1} LAS for all three species tested. In 1989, Figge and Schöbert conducted an extensive study on LAS effects towards bush beans, grass, radish and potato using a plant metabolism box. The field NOEC values were estimated to be 16 mg kg^{-1} for bush beans, grass and radish, and 27 mg kg^{-1} for potatoes. A few years later, Gǜnther and Pestemer (1992) performed a series of toxicity tests with LAS on oat (*Avena sativa*), turnip (*Brassica rapa*) and mustard (*Sinapis alba*) in sandy loam at different concentrations and measured the fresh weight of shoots after 14 days exposure. Estimated EC_5 and EC_{50} values of LAS were as follows, Oat: 50 and 300 mg kg^{-1}; Turnip: 90 and 200 mg kg^{-1}; Mustard: 200 and 300 mg kg^{-1}. In a field experiment, Litz *et al*. (1987) observed a short-term acute physiological damage of

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LAS, *i.e.* chlorosis and necrosis, on ryegrass using an application rate of 500 kg ha^{-1}, but no reduction in yield was found after harvest (*Table 1*). From these previous reports, more new data on various types of surfactants are needed for toxicity assessment on terrestrial plants. Lack of data or study on the ecotoxicity of surfactants in this environmental compartment may cause important toxicity outcomes remain unknown (Mullin *et al*., 2016) and maintaining environment sustainability become more challenging (Ying, 2006; Ivankovic and Hrenovic, 2010).

Through literature survey, no ecotoxicity studies of surfactants toward terrestrial plants have been conducted in Malaysia. There were a number of studies performed on toxicants such as organic mulches, palm oil mill effluent (POME), heavy metal, *etc*. towards different aquatic plants, *e.g. Azolla pinnata*, *Lemna minor* and *Eleusine indica*, using conventional and ASTM methods (Radziah, 1996; Dilipkumar *et al.,* 2015; Azlin *et al.,* 2017). Hence, the development of facility to study the terrestrial plants' ecotoxicity is crucial and the assessment of surfactant toxicity towards terrestrial plants is relevant and necessary.

USE OF SURFACTANTS IN AGROCHEMICAL

According to De *et al.* (2014), based on statistics, the worldwide consumption of pesticides is about 2 million tonnes per year, of which 25% is consumed in the USA, 45% is used in Europe and 30% is used in other countries of the world (*Figure 1*). Malaysia is highly dependent on herbicides, which contributed for 83% of the total pesticide usage in 2014 (Dilipkumar *et al*., 2017), with the aim of controlling weed in the oil palm plantation and other crops in Malaysia (Ismail *et al.*, 2010). This proves that enormous benefits have been obtained from the use of pesticides, especially in the agriculture sector, where pesticides help increase world food production by reducing losses from disease, weeds and insect pest (Michael, 2009). In short, pesticides are very indispensable and absolutely necessary (Mitra and Raghu, 1998).

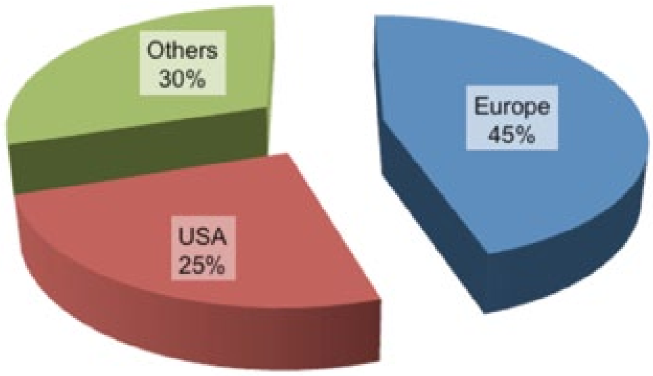
All pesticide formulations require the use of surfactants, which is not only essential for its preparation and maintenance of long-term physical stability, but also to intensify biological performance of the pesticide (Castro *et al*. 2013). Surfactants

TABLE 1. TOXICITY DATA OF LAS TOWARDS TERRESTRIAL PLANT

Species	Test condition	Endpoint	References
Bush beans, radish, grasses	Field tests in sludge amended clay soil	Yield and growth NOEC – 76 days, 27 mg kg^{-1}	Figge and Schöbert (1989)
Potatoes	Field, sandy loam	Yield and growth NOEC – 106 days, 16 mg kg^{-1}	
Ryegrass	Field, two soil	Yield NOEC 500 kg ha^{-1}, with necrosis and chlorosis observed	Litz *et al*. (1987)
Sorghum	Lab, potting compost	Growth EC_{50} – 21 days, 167 mg kg^{-1}	Unilever (1987); Mieure *et al.* (1990)
Sunflower		Growth EC_{50} – 21 days, 289 mg kg^{-1}	
Mung bean		Growth EC_{50} – 21 days, 316 mg kg^{-1}	
Oat	Lab, sandy loam	Growth EC_{5} – 14 days, 50 mg kg^{-1}	Gǜnther and Pestemer (1992)
		Growth EC_{50} – 14 days, 300 mg kg^{-1}	
Turnip		Growth EC_{5} – 14 days, 90 mg kg^{-1}	
		Growth EC_{50} – 14 days, 200 mg kg^{-1}	
Mustard		Growth EC_{5} – 14 days, 200 mg kg^{-1}	
		Growth EC_{50} – 14 days, 300 mg kg^{-1}	

Source: Ying (2006).

Note: NOEC (no observed effect concentration) – the highest concentration of the test substance at which no effect was observed.
ECX – concentration that results in an undesirable change or alteration of x% in the test endpoint being measured relative to the control.



Source: De *et al*. (2014).

Figure 1. Worldwide consumption of pesticides.

are used as wetting agents or spreader that physically alters the surface tension of a spray droplet to improve pesticide coverage over an area, such as a leaf surface (Herzfeld and Sargent, 2011). Surfactants are also normally added into the formulations to elevate the effectiveness of pesticides by improving the ability of the active ingredients to penetrate or protect the target species (Mullin *et al*., 2016). Most surfactants used in pesticide formulation are considered to be non-toxic and inert (Norris, 1982), or toxic that has no effect on overall growth, or their growth is inhibited as concentration increases (Bhat *et al*., 1992). However, according to Fishel (2014), surfactants are also capable of causing phytotoxicity or injury in plants. Therefore, although surfactant or mixed surfactants used are important, the effects of surfactants are inconsistent and unpredictable. On that account, manufactures should be aware of the type of surfactants and formulation components used in their product, while regulatory agency should periodically monitor and evaluate the risk and toxicity of pesticides and their formulation components, not only to users, but also to other non-target animals and plants. Hence, it is important for users to select the agrochemical product based on the ingredient used.

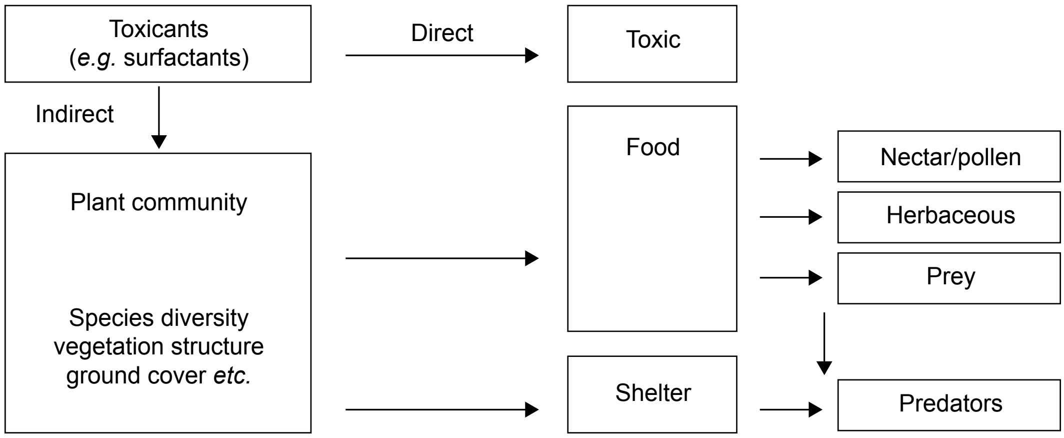
THE IMPORTANCE OF SURFACTANTS' ECOTOXICITY ASSESSMENT TOWARDS TERRESTRIAL PLANTS

Terrestrial plants are exposed to surfactant in many ways. They may be exposed to non-target effects from various sources, including pesticide application (Obrigawitch *et al.*, 1998; Mitra and Raghu, 1998; Boutin *et al.*, 2000; Karthikeyan *et al.*, 2003) and fate of surfactant (Ying, 2006; Srivasta *et al.*, 2012).

Exposure of plant species to surfactant, especially of high concentration, may cause changes in survival, health, vegetative growth, reproduction or plant death, which subsequently resulted in ecological impacts. This is because, plants produce oxygen and they are essential in the process of nutrient cycling and sediment stabilisation (Benenati, 1990). Besides, they provide food, shelter and nesting habitats for small invertebrates such as insects (Breeze *et al., 1999)* (*Figure 2*). Therefore, ecotoxicity assessment of surfactants towards plants should be performed in order to preserve the big diversity of plants and prevent extinction of the local species.

The toxic effect of surfactants can be assessed or measured by their direct or indirect effects on the terrestrial plants. The effects consist of a variety of indications or symptoms, including changes of plant vegetative growth, plant death and reduced fitness due to alteration of productive capability (Altman, 1993). However, individual plant usually responds differently to the same dose of toxic surfactants. Therefore, a population-level measure of toxicity is typically used, which relates the probabilities of a result for a given individual in a population (USEPA, 1994). For terrestrial plant ecotoxicity assessment, an appropriate statistical analysis is used to obtain the effective concentration, EC_x, for the parameter(s) of interest. EC_x is concentration that results in an undesirable change or alteration of x% in the test endpoint being measured relative to the control. For example, a 50% or 5% reduction in seedling growth, or an increase in visual symptom would constitute an EC_{50} and EC_5, respectively. Also, the non-observed effect concentration (NOEC) can be calculated in ecotoxicity study. NOEC is the highest concentration of the test substance (*e.g.* surfactants) at which no effect is observed. In the ecotoxicity assessment, the concentration corresponding to the NOEC has no statistically significant effect ($p<0.05$) within a given exposure period when compared to the control (OECD, 2006).

According to Versonnen *et al.* (2014), the standard toxicity assessment towards terrestrial plants under Registration, Evaluation, Authorisation and Restriction of Chemicals (REACh) regulation follows a different approach and requires concurrent testing on several species, using the same test conditions and adapted to each species, if needed. However, only 26.2% of the studies reported the test methods they used as guidance in performing the studies. For the rest 73.8% of the cases, the



Source: Breeze *et al*. (1999).

Figure 2. Potential ecological effects of surfactants on invertebrates.

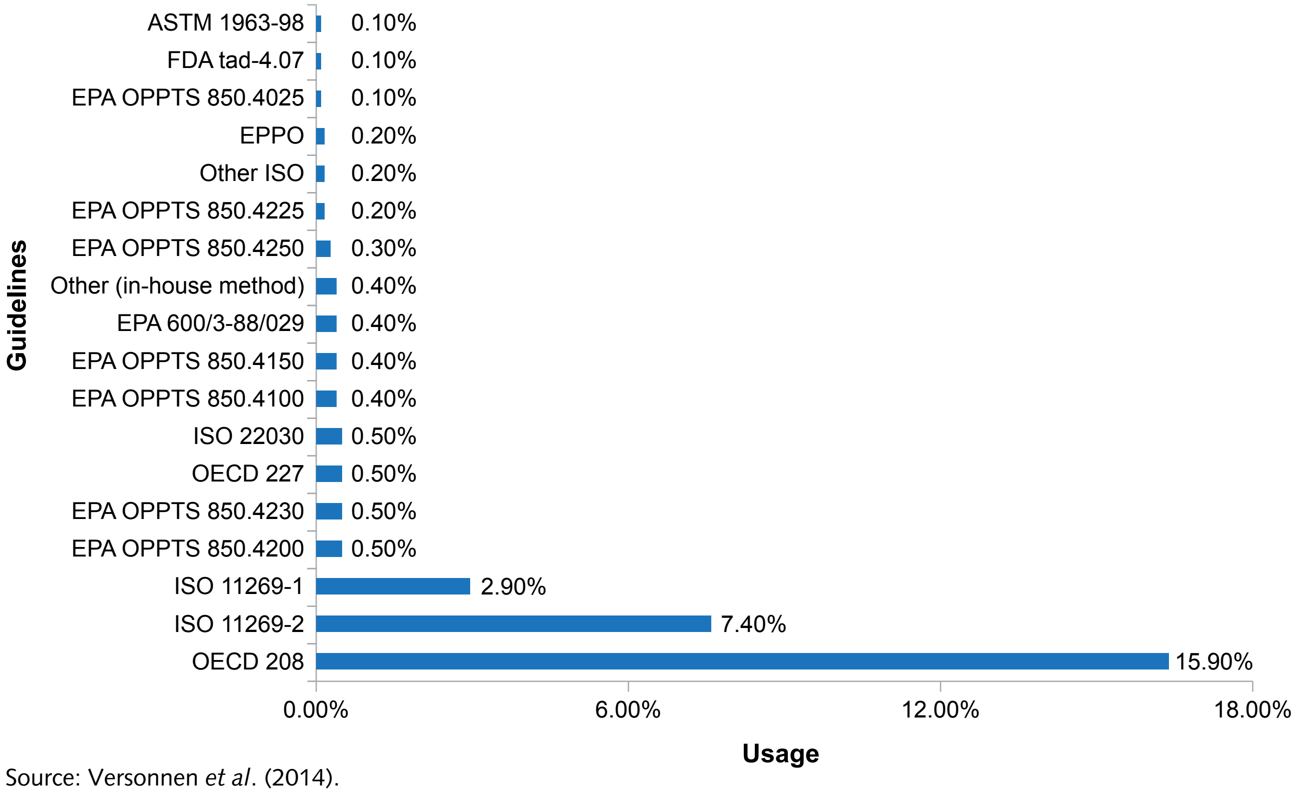
test methods were not proclaimed and the suitability of these studies can only be evaluated in a more comprehensive assessment. In assessment that reported the method used, the tests were mostly conducted according to universal recognised guidelines. Among these, the OECD test guideline 208: Plant seedling emergence and growth test, ISO standard 11269-2: Plant emergence and early growth test and the ISO standard 11269-1: Plant root growth inhibition test was the most commonly used methods with 15.9%, 7.4% and 2.9% cases reported, respectively (*Figure 3*).

The relevancy of terrestrial plant assessment has been recognised in the regulatory context of EU chemical regulations since the 1980s (Smeets, 1981). However, the sensitivity of plant species to toxicants (*e.g.* surfactants) can be significantly varied with environmental conditions such as organic matter, pH, temperature, alkalinity, hardness and toxicant interactions (Wang, 1987). For this reasons, limited number of studies on plant ecotoxicity have been performed in the past (Pallet *et al.*, 2007; Strandberg *et al.*, 2012). Besides, the previous studies were mostly focusing on rare forest species, which produced seed only once in its lifetime. This plant was purposely studied for its sustainability and to find solutions to protect it from extinction (Kigel, 1995; Tobe *et al*., 2005). Since this is an era where toxicity studies of overall ecosystem become very important, more studies on terrestrial plant ecotoxicity are being explored. As supported by Wang and Freemark (1995), among the terrestrial organisms, plants have several advantages over the others. For example, plant seeds can be obtained in bulk, most can be kept for a year or more, maintenance cost is almost zero and the test can be set up quickly when needed. Hence, ecotoxicity assessment towards terrestrial plants can be considered a low cost and rapid test, thus, deemed as crucial and necessary.

DEVELOPMENT OF FACILITY FOR TERRESTRIAL PLANT TOXICITY STUDY IN MPOB

Ecotoxicity effects from surfactants interference may affect the plants' physiology process, including the plants' wellness and health, as well as vegetative growth and development. Among the examples of toxic symptoms are failures of germination, distortion of leaves or growing points, burning of tips or leaves, chlorosis, stunted growth and in severe cases fall of leaf, wilting, necrosis and death of plant (*Figure 4*). Plants growing in surfactant-polluted environments will suffer from high concentration of toxic surfactants. They may be wiped out or abundantly decreased, and may experience local extinction (Boutin *et al.*, 2000).

Therefore, ecotoxicity assessments toward terrestrial plants have become more important as a result of the growing environmental concern. This situation has prompted the researchers to perform studies involving various plant species, and different types of toxicants (including surfactant), in order to obtain more ecotoxicity data on plant species. Since Malaysian economy depends much on agriculture and commodity crops, it is important for Malaysia to have expertise in ecotoxicity assessment field in order to ensure environmental sustainability. Thus, Malaysian Palm Oil Board (MPOB) has taken the initiative to develop ecotoxicological studies facilities for terrestrial plant. Besides ecotoxicity assessment, the development of the facility is expected to provide more information on the toxicity of surfactants on terrestrial plants, and indirectly encourage manufacturers to select efficient vegetable-based



Source: Versonnen *et al*. (2014).

Figure 3. Distribution of the test guidelines reported for terrestrial plants assessments.

Figure 4. Necrosis in (a) tomato and (b) corn.

surfactants with lower impact towards the environment.

CONCLUSION

Ecotoxicity assessment of surfactant towards terrestrial plants must be warranted, although not routinely practiced in the environmental assessment of toxic chemicals or toxicants. Besides, more researches are needed to determine the plant toxicity level of the targeted surfactants or other toxicants. Many areas related to plant ecotoxicity also need to be investigated. This information can contribute in finding the tolerance limit of certain surfactants or other toxicants to terrestrial plants and thus a comprehensive database of terrestrial plants ecotoxicity can be developed. This is because the findings will indirectly provide important information for improving environmental monitoring, risk assessment and protection towards terrestrial plants for current and future generation.

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