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Derivation of South African water quality guidelines for Roundup® using species sensitivity distribution

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ABSTRACT

Glyphosate-based herbicides are among the leading products used in South Africa to control weeds and invading alien plant species. Although these herbicides ultimately find their way into aquatic ecosystems, South Africa has no water quality guideline based on indigenous species to protect the country's aquatic biota against these biocides. In this study, South African water quality guidelines (SAWQGs) for Roundup® based on species sensitivity distribution (SSD) using indigenous aquatic biota were developed. Short-term and long-term toxicity tests were conducted with eight different aquatic species belonging to five different taxonomic groups. Static non-renewal experimental methods were employed for short-term lethal tests (≤4 days), and static renewal for long-term sublethal tests (≥4 days ≤21 days). LC50 values for animal exposure and EC50 values for algae were calculated using probit analysis and linear regression of transformed herbicide concentration as natural logarithm data against percentage growth inhibition, respectively. No effect concentration (NEC) was determined based on the dynamic energy budget model, using survival data. The LC50, EC50 and NEC values were used to develop species sensitivity distribution (SSD) concentrations for Roundup®. Based on the SSD concentrations, the short-term and long-term SAWQGs for Roundup® were derived as 0.250 (0.106–0.589) mg/L, and 0.002 (0.000–0.021) mg/L, respectively. These WQGs may be useful in protecting South African aquatic life against transient or long-term exposure to glyphosate-based chemicals as part of integrated water resources management.

1. Introduction

Globally, herbicides are the leading group of pesticide in terms of annual production, total acreage usage, and total value from sale (Pérez et al., 2011). Over the past decades, public awareness of the worldwide increase in the use of herbicides and their adverse effects on aquatic ecosystems has been growing (Pérez et al., 2011). Herbicides may reach water bodies directly by overhead spray of aquatic weeds, or indirectly through processes such as agricultural runoff, spray drift and leaching. Potential problems associated with herbicide-use include injury to non-target vegetation, injury to crops, residue in soil or water, toxicity to non-target organisms, and concerns for human health and safety (Radosevich et al., 2007). Herbicides can decrease environmental water quality and ecosystem functioning by, for example, reducing species diversity, changing community structure, modifying food chains, altering patterns of energy flow and nutrient recycling, and reducing resilience of ecosystems (Pérez et al., 2011).

Glyphosate-based herbicides are among the leading products used in South Africa to control weeds and invading alien plant species. Although these herbicides ultimately find their way in aquatic ecosystems, South Africa has no water quality guideline based on indigenous species to protect the country's aquatic biota against these biocides. Although literature on glyphosate research in South African is scarce, glyphosate has been found since the 1990s in high concentrations in the Hex River Valley, an agriculturally intensive grape-farming area in the Western Cape Province of the country (Maharaj, 2005; Dalvie et al., 2011). In recent years, the use of glyphosate-based herbicides has increased tremendously in South Africa because of their promotion by both private and public organisations including the manufacturers, Working for Water (WfW) program (an initiative by the National Department of Water Affairs for the control of aquatic alien plant species), and commercial farmers (DWAF, 1996; Maharaj, 2005; Dalvie et al., 2011). However, there is no South African water quality guideline that can be used to measure the effects of glyphosate-based herbicides on water resources (DWAF, 1996). Other reasons why it is necessary to derive water quality guidelines for glyphosate-based herbicides for the protection of aquatic life include: (1) the fact that it has been detected in surface waters long after being used to kill aquatic weeds even though it is regarded as having a

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low potential for contaminating surface waters due to its perceived rapid dissipation and strong adsorption to soils and sediments (Glusczak et al., 2007); (2) there is a growing concern among aquatic ecotoxicologists regarding its potential impact on the environment due to increased cultivation of genetically modified glyphosate-resistant (GMG-R) crops and consequent increase in herbicide use (Kolpin et al., 2006); (3) its mode of action was designed to affect only plants (Stenersen, 2004), but various studies have reported adverse impact on non-target animals, which warrants scientific interest and study (Giesy et al., 2000; Tsui and Chu, 2003; El-Shebly and El-Kady, 2008). Roundup® was selected as a representative of glyphosate-based herbicides by the virtue of it being the most popular and widely used herbicide in South Africa and most parts of the world (Bold, 2007; Romero et al., 2011). It is composed of isopropylamine (IPA) salt of glyphosate as the active ingredient; the surfactant polyoxyethylene amine (POEA); and water. Roundup® readily dissolves in water because of the IPA salt form of glyphosate that it contains.

The exposure of non-target aquatic organisms to glyphosate formulations because of its high water solubility and the extensive use of glyphosate-based herbicides in the environment, especially in shallow water systems, have attracted public concerns in recent years (Tsui and Chu, 2003). Surfactants, which act as wetting and dispersing agents in herbicides, have also been implicated as adding to the toxicity of the active ingredients, and in some cases, have been even more toxic than the active ingredient alone (Radosevich et al., 2007). The surfactant polyoxyethylene amine (POEA) is thought to be responsible for the relatively high toxicity of Roundup® to several freshwater invertebrates and fishes, although isopropylamine (IPA) salt of glyphosate also contributes its share (Giesy et al., 2000; Tsui and Chu, 2003; CCME, 2012). Technical grade glyphosate is slightly to very slightly toxic to aquatic invertebrates, with reported LC50 values of greater than 55 mg/L and a 21-day NOEC value of 100 mg/L. Conversely, formulations of glyphosate are moderately to very slightly toxic to aquatic invertebrates with 2-day EC50 values of 5.3–5600 mg/L and 21-day MATC values of 1.4–4.9 mg/L reported (WHO, 1994). The LC50 values also determine which glyphosate formulation can be applied in aquatic systems. For example, Touchdown 4-LC® and Bronco® have low LC50s for aquatic species ($<$ 13 mg/L), and are not registered for aquatic use in the USA, while Rodeo® has relatively high LC50s ($>$ 900 mg/L) for aquatic species and is permitted for use in aquatic systems. In the same manner, Roundup® is not registered for use in aquatic systems in the USA because its 96-h LC50 for *Daphnia* is 25.5 mg/L, while that of glyphosate alone is 962 mg/L (Tu et al., 2001). However, Roundup® and other glyphosate-based herbicides are commonly used in South Africa to control both aquatic and terrestrial weeds, even though there is no local water quality guideline to indicate the effects of such herbicides on non-target organisms. In this study, Roundup® was used as a test chemical to derive South African water quality guidelines (SAWQGs) for glyphosate formulated herbicides- based on species sensitivity distribution (SSD) using indigenous aquatic biota. Roundup® was selected as a representative of glyphosate-based herbicides by the virtue of it being the most popular and widely used herbicide in South Africa and most parts of the world (Bold, 2007; Romero et al., 2011).

Water quality guidelines (WQGs) are perceived as environmentally safe levels (ESLs) or protective concentrations (PCs) that would provide adequate protection to aquatic life (ANZECC and ARMCANZ, 2000; Warne, 2001). Trigger value (TV) is another term similar in meaning to the ESL or the PC. Trigger values indicate risk of impact if ESLs or PCs are exceeded. Exceeding such values will normally result in (i.e. “trigger”) some form of management action, which may include further investigation, remediation and/or implementation of strategies (Warne et al., 2004). Thus, a WQG can be defined as environmentally safe and protective concentration as well as a reference tool for initiating management activities aimed to provide adequate protection to aquatic life. Trigger values may be derived using a species sensitivity distribution (SSD) in preference to assessment factor (AF) approach. Using AF to determine the TV involves dividing the most sensitive toxicity value by an assessment factor (usually 10, 100 or 1000), whereas the use of SSD approach involves fitting a statistical distribution to toxicity data of a number of species in order to estimate the concentration that should protect any chosen percentage of species (Warne et al., 2004). Although the SSD is the preferred approach, the AF method is used where data is constrained (ANZECC and ARMCANZ, 2000; USEPA, 2005; Warne et al., 2004; CCME, 2007).

There are three grades of hierarchical TVs, namely high reliability (HR), moderate reliability (MR) and low reliability (LR). The LR TV is further divided into interim (LR (interim) TV) and environmental concern level (LR (ECL) TV), depending on the quality of data. Warne et al. (2004) suggested that derivation of HR TV should always be the target if there is adequate and suitable toxicity data. However, if data to derive HR TV are inadequate, then the hierarchy is descended until the available data meet the minimum requirements for a particular grade of TV (Warne et al., 2004). The data requirements for using the SSD approach in determining trigger values to protect South African aquatic species are presented in Tables 1 and 2 (Warne et al., 2004). In the current study, eight South African aquatic organisms belonging to five different taxonomic groups were used to derive a HR TV for protecting aquatic life from Roundup® exposure.

Species sensitivity distributions (SSDs) are not only useful for comparing the sensitivities of different taxonomic groups of organisms to environmental toxicants, but are also used in ecological risk assessments for the formulation of water quality guidelines (Hose, 2005). Globally, species sensitivity distributions (SSDs) are used to generate WQGs to protect aquatic life (Zajdlik et al., 2009; Feng et al., 2013). The aim of SSDs is to determine the concentration of a toxicant that is protective of most species (usually 95 percent) in the environment (Hose, 2005; Feng et al., 2013). Hence in this study, SSD was applied to determine the concentrations of glyphosate that is protective of most South African aquatic species and the eventual formulation of water quality guidelines based on these concentrations. Construction of SSDs is done by fitting a cumulative distribution function to a plot of species toxicity data against rank assigned percentiles (Wheeler et al., 2002). From the cumulative distribution, the concentration that is protective of 95 percent species (PC95) value is extrapolated (Hose, 2005). The PC95 is often referred to as HC5 (hazardous concentration 5 percent) and it is the same as the TV (trigger value) used in this study. The HC5 has been used to set

Table 1
Minimum data required by the statistical distribution approach for the three grades of trigger values (after Warne et al., 2004).

Level of trigger value	Minimum data requirement
High reliability	Requires chronic NOEC toxicity data for at least five species that belong to at least four different taxonomic groups
Moderate reliability	Requires acute toxicity data (i.e. LC50 or EC50) for at least five species that belong to at least four taxonomic groups
Low reliability (interim) for non-polar chemicals only	Requires nineteen estimates of chronic toxicity derived by QSARs