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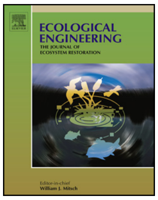

Treatment of agricultural equipment rinsing water containing a fungicide in pilot-scale horizontal subsurface flow constructed wetlands

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ABSTRACT

Boscalid is a carboxamide fungicide, developed as an alternative reagent to classic fungicides, which acts against several ascomycetous fungal species. The use of boscalid is continuously on the rise due to its unique mode of action and low toxicity to mammals and birds. However, boscalid can be transported from the application sites and contaminate the environment. Recent studies have reported detection of boscalid in air, precipitation, streams and groundwater samples. Moreover, boscalid was the fourth most frequently encountered pesticide residue in food according to the latest European Union report. Thus, the aim of this study was to explore the efficiency of two pilot-scale horizontal subsurface flow (HSF) constructed wetlands (CWs) to remove boscalid from rinsing water produced during the cleaning of pesticide spraying equipment. The two CWs were planted with common reeds (*Phragnites australis*). One contained fine gravel (code name FG-R) and the other cobbles (CO-R). Both CWs were loaded daily with water containing boscalid at concentrations similar to those usually detected in rinsing water near sites where pesticide mixing, loading and washing takes place. The results showed that the removal in both systems ranged from 49 to 100%. In the first two months, the removal ranged from 75–94% and 95–100% for CO-R and FG-R, respectively. From April up to the next February, the mean removal was 76.3% and 72.4% for FG-R and CO-R, respectively. It seems that HSF CWs are efficient systems in treating boscalid-polluted agricultural equipment rinsing water in agricultural areas. Therefore, their construction and use near sites where pesticide mixing, loading and washing takes place is recommended.

1. Introduction

Pesticides are mainly used in agriculture as weed, insect and fungi control agents, and represent essential tools in pest management (Birkett and Lester, 2003). However, their intensive, inconsiderate and improper use and application leads to adverse impacts on the environment and the ecosystems, and is in part responsible for global environmental pollution (Vallée et al., 2014). Impacts include those on humans, either direct or through food intake, and those on the environment, such as surface and ground water contamination, soil and air contamination, effect on soil fertility through impact on beneficial soil microorganisms, and contamination of non-target vegetation and non-target organisms (Aktar et al., 2009).

In particular, contamination of surface and ground waters by pesticides is a widespread and a worldwide pollution problem (Aktar et al., 2009; Reilly et al., 2012; Smalling et al., 2013a; Vryzas et al., 2012), originating from diffuse (non-point) or point sources in the agricultural environment (Reichenberger et al., 2007; Spanoghe et al., 2004). Agricultural runoff and soil erosion, leaching, subsurface drainage and spray drift water constitute significant forms of non-point source pollution (Locke et al., 2011; Papadopoulos et al., 2012), while point source pollution includes activities, such as mixing and loading of pesticides, spray equipment filling and washing, defective equipment leaks, improper handling of tank

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mix leftovers, incorrect storage of boxes, accidents, and pesticide waste disposal operations (Reichenberger et al., 2007).

The presence of pesticides in surface and groundwater bodies has been documented in Europe more than 40 years ago, and since then numerous reports have been published (Cerejeira et al., 2003; Hildebrandt et al., 2008). The concentrations of pesticides have been documented as high, often exceeding the permissible limit of 0.1 μg/L for potable water established by the EU Drinking Water Directive (EC, 1998). During the last decade, pesticide monitoring studies have also been conducted in Greece; the herbicides prometryn, fluometuron, terbuthylazine and metolachlor, and the fungicides metalaxyl, boscalid are among the most frequently detected in surface and ground water bodies (Papadopoulou-Mourkidou et al., 2004; Konstantinou et al., 2006; Kalogridi et al., 2014; Papadakis et al., 2015).

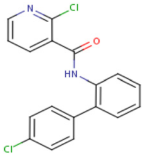
There have also been several management practices proposed worldwide in order to reduce or/and remove pesticide entry into surface and ground waters. These include: pesticide type alteration, changes in irrigation practices and application methods, runoff treatment through vegetated buffer zones, riparian vegetation growing, and use of vegetated treatment systems such as vegetated ditches and constructed wetlands (Schulz, 2004; Reichenberger et al., 2007; Vymazal and Březinová, 2015).

Constructed wetlands (CWs) constitute an effective, practical, low-cost option for treatment of various types of wastewater and runoff such as municipal, agricultural, and industrial (Gkika et al., 2014; Tsihrintzis et al., 2007; Tsihrintzis and Gikas, 2010). CWs can also be used for nutrients (e.g., N, P) and pesticides removal from both non-point and point sources. The efficiency of CW systems is mainly related to the physicochemical properties of each contaminant. Generally, pollutant removal occurs through physical, chemical and biological processes, which include microbial breakdown of pollutants, plant uptake, retention, settling, adsorption, etc. (Gikas and Tsihrintzis, 2010; Kadlec and Wallace, 2009; Stefanakis and Tsihrintzis, 2012; Vymazal and Březinová, 2015). At present, CWs constitute a very popular and innovative mitigation strategy, which is gaining recognition and acceptance (Rose et al., 2006). However, in the literature there is only a small number of studies regarding the use of these systems in mitigating pesticide contamination (e.g., O'Geen et al., 2010; Vymazal and Březinová, 2015). According to Gregoire et al. (2008), among research reports on CWs, 65% dealt with the fate of the nutrients (nitrogen and/or phosphorus), 13% dealt with dairy operations at farm scale, 18% engaged with the fate of heavy metals, and only 4% dealt with the fate of pesticides.

In recent years, one of the most abundantly used fungicides in the Mediterranean countries is boscalid. This compound has high application rates and widespread use, and therefore, increased runoff risk and residual concentrations within the water bodies. According to Reilly et al. (2012), boscalid is the most frequently detected fungicide with concentrations in surface water that reach 0.1 μg/L and potential to leach to ground water. Boscalid is a fungicide with maximum residue levels (MRLs) in food products in EU up to 30 mg/kg (EU, 2015). Moreover, the most frequently detected pesticide in food monitored in the European Union during 2014 was boscalid, with 6823 determinations and a detection rate of 10.61% (EFSA, 2016). Although boscalid is considered moderately to highly toxic to aquatic invertebrates (Elskus, 2014), it has been found in fish and crabs which could absorb the fungicide directly from the environment or through their food (Smalling et al., 2013a). In addition, considerable effect of boscalid on macro-invertebrate leaf decomposition has recently been observed (Elskus et al., 2016), suggesting long-term risk to aquatic ecosystems, and impact on trophic transfer and nutrient cycling (Vu et al., 2016).

Various remediation strategies based on photocatalytic degradation, biodegradation, phytoremediation, and biochar have been recently proposed for boscalid and other pesticide removal from aquatic systems (Lagunas-Allue et al., 2010; Mukherjee et al., 2016; Taha et al., 2016; Vallée et al., 2016). These methods have been proved effective; however, they may be costly for farmers and difficult to apply. Therefore, low-cost, low-maintenance, easy-to-use and technologically-effective solutions are sought. CWs, as mentioned before, offer such opportunities. The use of CWs is expected to be an efficient technique to remediate polluted water by systemic pesticides such as boscalid. Systematicity (uptake and translocation) of pesticides within plant tissues is influenced by various factors. Physicochemical properties of a pesticide and interaction with soil, plant microbiome, water, and chemicals surrounding the rhizosphere determine the behavior of pesticides within the plant (uptake, translocation, action, detoxification and excretion).

Table 1
Physicochemical properties and characteristics of boscalid (Vallée et al., 2014; PPDB, 2012).

Parameter	Value
Formula	$C_{18}H_{12}Cl_2N_2O$
Substance group	Carboxamide
Structure	
Molar mass (g/mol)	343.21
Water solubility at 20 °C (mg/L)	4.6
Partition coefficient Log K_{ow}	2.96
Vapour pressure at 25 °C (mPa)	7.20×10^{-4}
Sorption coefficient K_{oc} (L/kg)	809 (750–1200)
Half-life at 20 °C (days)	246 (27–372)
Soil degradation $DT_{50,field}$ [a]	118

[a] Half-life for field studies.

The objective of this study is to evaluate the performance of constructed wetlands as an efficient and low-cost technology for boscalid treatment, ultimately aiming to the reduction of boscalid concentrations reaching surface and ground waters. Specifically, the study aims at the investigation of the efficiency of pilot-scale horizontal subsurface flow constructed wetlands (HSF CWs) in the removal of boscalid originating from point and non-point sources in the agricultural environment. In the literature, there is a lack of research regarding the treatment of water contaminated with boscalid with the use of natural systems, such as horizontal subsurface flow constructed wetlands.

2. Materials and methods

2.1. Physicochemical characteristics of boscalid

Boscalid (CAS name: 2-chloro-N-(4′-chloro(1,1′-biphenyl)-2-yl)-3-pyridine carboxamide) is a systemic carboxamide fungicide developed as an alternative reagent to classic fungicides. It acts against a broad range of fungal pathogens, including *Botrytis* spp., *Alternaria* spp. and *Sclerotinia* spp. Boscalid is used on a wide range of crops including fruits, vegetables and ornamentals. The physicochemical characteristics of boscalid are summarized in Table 1 (Vallée et al., 2014; PPDB, 2012). The fate of a pesticide in the environment is mainly affected by its physicochemical properties. Water solubility determines the ability of a pesticide to be transported through the water cycle, the partition coefficient (Log K_{ow}) is a useful indicator of the behavior of a pesticide in the environment and its bioaccumulation and biomagnification capacity, and the sorption coefficient in the organic carbon of soil (K_{oc}) is a crucial factor that controls the leaching and runoff of the pesticide in the