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Impact of dry-wet and freeze-thaw events on pesticide mineralizing populations and their activity in wetland ecosystems: A microcosm study

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HIGHLIGHTS

- Mineralization of the herbicides IPU and MCPA in wetlands was simulated in microcosms.
- Dry-wet and especially freeze-thaw events negatively affected the mineralization of IPU and MCPA under flooded conditions.
- IPU/MCPA mineralizing cells increased after the imposed changes implying that cell decay is not responsible for the effects.
- Prior exposure of the wetland community to the herbicides counteracted the effect of freeze-thaw events.

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ABSTRACT

Riparian wetlands are proposed to mitigate diffuse pollution of surface water by pesticides in agricultural landscapes. Wetland ecosystems though are highly dynamic environments and seasonal disturbances such as freezing and drying can affect microbial population sizes in the sediment and their functionality including pesticide biodegradation, which has hardly been studied. This study examined the effect of artificially induced dry-wet or freeze-thaw events on the mineralization of the pesticides isoproturon (IPU) and 2-methoxy-4-chlorophenoxy acetic acid (MCPA) in wetland microcosms, either without or with prior enrichment of IPU/MCPA degrading populations. Without prior enrichment, mineralization of IPU and MCPA was significantly reduced after exposure to especially freeze-thaw events, as evidenced by lower mineralization rates and longer lag times compared to non-exposed microcosms. However, herbicide mineralization kinetics correlated poorly with cell numbers of herbicide mineralizers as estimated by a most probable number (MPN) approach and the number of IPU and MCPA mineralizers was unexpectedly higher in freeze-thaw and dry-wet cycle exposed setups compared to the control setups. This suggested that the observed effects of season-bound disturbances were due to other mechanisms than decay of pesticide mineralizers. In addition, in systems in which the growth of pesticide mineralizing bacteria was stimulated by amendment of IPU and MCPA, exposure to a freeze-thaw or dry-wet event only marginally affected the herbicide mineralization kinetics. Our results show that season bound environmental disturbances can affect pesticide mineralization kinetics in wetlands but that this effect can depend on the history of pesticide applications.

1. Introduction

Herbicides have been used intensively since the 1940s mainly to increase the efficiency of agricultural production. 3-(4-isopropylphenyl)-1,1-dimethylurea (isoproturon) (IPU), a phenyl urea herbicide inhibiting photosynthesis, and 2-methoxy-4-chlorophenoxy acetic acid (MCPA), a synthetic plant hormone

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that causes uncoordinated plant growth, are currently among the most used herbicides worldwide (Eurostat, 2007). Processes such as run-off, spray drift, leaching and erosion however result in diffuse contamination of groundwater and surface water. The fate of herbicides in the environment largely depends on microbial degradation (Alexander, 1981; Cox et al., 1996). Specialized bacteria that use IPU (Hussain et al., 2010) or MCPA (Baelum et al., 2006) as a source of carbon for growth were identified in soil and other environments and largely contribute to IPU or MCPA removal in the environment. Proliferation of IPU/MCPA mineralizing microorganisms as a consequence of selective pressure due to repeated herbicide exposure has been reported various times (Piutti et al., 2002; Sørensen and Aamand, 2003).

Wetlands are at the interface between terrestrial and aquatic habitats and are defined by a temporary or permanent inundation, hydric soils with reducing conditions in the deeper layers and the presence of macrophytes, i.e., aquatic vegetation (Dušek et al., 2008). They are increasingly recognized and restored as critical zones for flood control, biodiversity, food supply and water purification. In agricultural landscapes, wetlands are also restored with the aim of improving surface water quality by acting as buffer zones for mitigating pollution of surface water bodies due to run-off from adjacent agricultural fields (Gregoire et al., 2009; Gumiero et al., 2013; Moreno et al., 2007). Previously the focus was on the removal of nitrate and phosphate but recently also removal of pesticides is addressed (Agudelo et al., 2010; Borges et al., 2009; Matamoros and Salvadó, 2012; Passeport et al., 2010; Reichenberger et al., 2007). Although less studied compared to soil ecosystems, microbial degradation appears to play an important role in pesticide removal in wetland ecosystems (Anderson et al., 2002; Bois et al., 2011; Karpuzcu et al., 2013; Larsen et al., 2001; Muñoz-Leoz et al., 2009; Weaver et al., 2004). In temperate climates, wetlands are typically highly dynamic ecosystems depending on seasonal weather conditions that include drying in summer and freezing in winter (Dušek et al., 2008). Dry-wet and freeze-thaw cycles were shown to affect microbial community structure, biomass and microbial activity in soil. Drying (Borken and Matzner, 2009) as well as freezing (Morley et al., 1983; Soulides and Allison, 1961) were reported to result in cell death of non-adaptive organisms and a concomitant decrease in microbial biomass in soils, while rewetting (Birch, 1958; Unger et al., 2010; Xiang et al., 2008) as well as thawing (Lipson et al., 2000; Schimel and Clein, 1996; Skogland et al., 1988) generally result in an increase of microbial activity in soils, which is explained by an increase in easily accessible substrates including substrates that originate from dead cells due to desiccation or freezing (Franzluebbers et al., 2000; Unger et al., 2010; Xiang et al., 2008). In streambed sediments, dry-wet cycles decreased the numbers of microbial gene copies and altered the composition of the microbial community (Conrad et al., 2013; Marxsen et al., 2010). As a consequence, dry-wet and freeze-thaw cycles might also affect important microbial ecosystem services relating to carbon and nutrient fluxes, as already shown for nitrification (Sharma et al., 2006), degradation of petroleum hydrocarbons (Eriksson et al., 2001) and sulfate reduction (Sawicka et al., 2010), and hence might also affect pesticide biodegradation. Several reports indicate that this is indeed the case. Drying or reducing the moisture content of soil either improved or reduced the mineralization of pesticides (Issa and Wood, 2005; Shelton and Parkin, 1991) while dry-wet cycles usually reduced pesticide mineralization in soils (Gebremariam and Beutel, 2010; Mercadier et al., 1996; Pesaro et al., 2004). On the other hand, Sniegowski et al. (2011) found that despite the decreased mineralization of herbicides due to drying alone, pesticide mineralization improved after a dry-wet cycle in microcosms that simulated on farm biopurification systems that treat pesticide polluted wastewater. A few studies have explored the impact of freeze-thaw cycles on the mineralization of pesticides in soil and effects were always negligible (Pesaro, 2003; Stenrød et al., 2005). To our knowledge, neither the effect of dry-wet nor that of freeze-thaw cycles on herbicide mineralization has been addressed in wetland sediments so far. Since the microbial mineralization of pesticides is overall strongly related to redox conditions, with faster and more efficient mineralization in oxic environments (Larsen and Aamand, 2001; Tuxen et al., 2006), pesticide mineralization likely occurs in the water phase and the top few mm of a wetland's sediment, which are also the most prone to drying and freezing. Plausible changes in pesticide degrading population sizes as a consequence of dry-wet and freeze-thaw cycles will affect overall pesticide degrading activity and hence the functionality of the wetland for mitigating pesticide pollution of adjacent surface water bodies.

The objective of this study was to measure the effect of dry-wet and freeze-thaw cycles on the mineralization of the herbicides IPU and MCPA in wetlands. To that end, dedicated wetland microcosms were subjected to dry-wet and freeze-thaw cycles, without and with prior exposure to the pesticide. Prior exposure to the pesticide was done to simulate a situation where a proliferation of pesticide degrading bacteria had occurred prior to the dry-wet or freeze-thaw cycles. We hypothesized that the effect of dry-wet or freeze-thaw cycles on herbicide degradation in wetlands would primarily be related to changes in the number of herbicide mineralizing bacterial cells in the sediment. Therefore, we estimated the number of herbicide mineralizing cells by the most probable number approach described by Johnsen et al. (2009).

2. Materials and methods

2.1. Microcosm setup

Wetland microcosm experiments were performed in Erlenmeyer flasks equipped with a side-arm reservoir containing 800 μL of 0.5 M NaOH to trap $^{14}CO_2$ produced from mineralization of added ^{14}C-labeled pesticides (Supporting information S1). The Erlenmeyer flasks were filled with 60 g moist soil and 40 mL of artificial surface water at pH 7, resulting in a sediment layer of approximately 2 cm and an overlying water layer of approximately 1 cm. The gravimetric moisture content of the sediment layer was 1.2 g water g^{-1} dry soil. The composition of the artificial surface water was based on the chemical composition of water from the Turfputten, a peat wetland in Belgium, and the Rourbron spring, a Belgian freshwater spring located in a peat moor (see Supporting information S2 for composition). The sediment originated from a recently (2009) restored riparian wetland located in Sint-Truiden, Belgium (50°50′16.55″N, 5°13′33.40″E). This riparian wetland is fed by a brook (Melsterbeek) which contains average concentrations of IPU and MCPA of 131 ng L^{-1} and 360 ng L^{-1} (measured between 2004 and 2010), with maximal concentrations of 2.7 μg L^{-1} and 5.3 μg L^{-1} (VMM, 2012). Wetland sediment was sampled from the top 10 cm using a spade in January 2012. At the moment of sampling, the air temperature was around 7 °C and the water table was 20 cm below the soil surface. The gravimetric moisture content (θ_g) of the sampled sediment was 0.53 g g^{-1} dry soil. The sediment contained on average 11% sand, 59% silt and 30% clay, 0.5% N and 6.3% C. The pH measured in 0.01 M $CaCl_2$ was 7.4. After sampling, sediment samples were stored at 4 °C for 28 weeks before the start of the experiments. The mineralization of IPU and MCPA was assessed in wetland microcosms in two parallel experiments. In a first experiment, mineralization of MCPA or IPU was assayed after a series of seasonal disturbances. In a second experiment, growth of herbicide