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Dynamics of chloroacetanilide herbicides in various types of mesocosm wetlands

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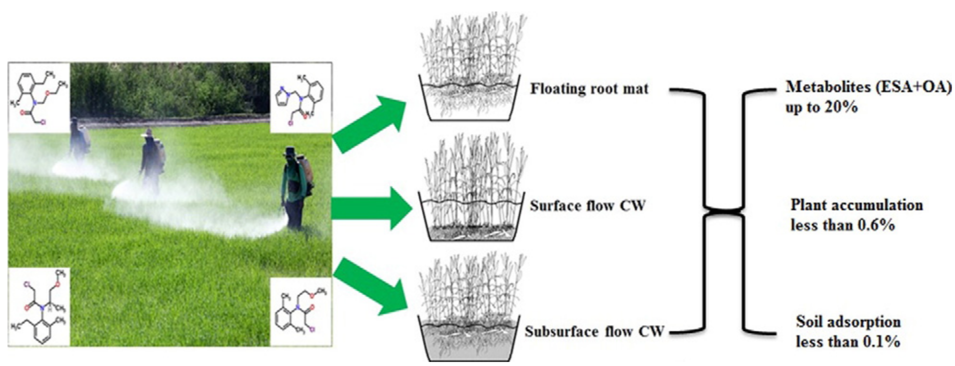
HIGHLIGHTS

- Four chloroacetanilide herbicides were studied in various constructed wetlands.
- Planted systems are effective in removing all four herbicides (>90%).
- Detected metabolites account about 20% of the mother compounds.
- Plant uptake and soil adsorption are negligible for the removal processes (<0.6%).

GRAPHICAL ABSTRACT



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ABSTRACT

Constructed wetlands (CWs) for pesticide mitigation from agricultural runoff became widespread in the last decade. However, comparison of different types of CWs at one location is missing. Therefore, site by site comparison of three different types (subsurface flow, surface flow and floating hydroponic root mat) of CWs treating four chloroacetanilide herbicides (acetochlor, s-metolachlor, metazachlor, dimethachlor) were carried out. All three planted systems are effective in removing the four herbicides with removal efficiency >92% after 9 days. The metabolites ethane sulfonic acids (ESA) and oxanilic acids (OA) of the four herbicides peaked at 9 days in the surface flow CWs with soil, but all the metabolites didn't peaked in the subsurface flow with gravel systems and the floating hydroponic root mat system after 21 days. All the detected metabolites account about 20% of the mother compounds. There is no noticeable metabolites accumulation in the control system (no plants and no substrate), which indicate no microbial degradation taken place. Plant accumulation and soil adsorption are negligible for the removal of the four herbicides, which are <0.6%. In conclude, plants can enhance the removal of chloroacetanilide herbicides in all the CWs, and the floating hydroponic root mat is the most cost-efficient alternatives for chloroacetanilide herbicides removal due to the absence of substrate.

1. Introduction

Pesticides have been used intensively in modern agriculture in order to increase crop production, as a result, they have become important

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water quality components in agricultural runoff. For crops like maize, sugar beet and sunflower, chloroacetanilide herbicides are often used to control annual grasses and broadleaved weeds. Acetochlor and s-metolachlor are substitutes of alachlor and r-metolachlor, and are among the ten most commonly used herbicides in Europe and United States (EPA, 2011). Therefore, chloroacetanilide herbicides are often detected compounds in ground and surface water, as well as their metabolites such as ethane sulfonic acids (ESA) and oxanilic acids (OA) (Baran and Gourcy, 2013; Hladik et al., 2005). Acetochlor is classified as suggestive evidence of carcinogenic potential and metolachlor is classified as possible human carcinogen (EPA, 2015). Therefore, it is crucial to improve agricultural runoff water quality.

Constructed wetlands (CWs) are engineered systems to mimic natural wetlands to enhance water treatment process using wetland plants, substrate, and the associated microbes. They have been used to treat different types of wastewater since the 1950s (Vymazal, 2011). CWs have been tested for pesticide removal in lab scale since the 1970s (Wolverton, 1975), and a number of field experimental wetlands were established to evaluate the capability of CWs for pesticide mitigation from agricultural runoff in 1988 near Oxford, Mississippi (Rodgers and Dunn, 1992). CWs have been exhibiting itself a great potential to alleviate agricultural runoff pollutants such as pesticides, and become widespread in the last decade (Vymazal and Březinová, 2015). In CWs, pesticides can be removed through physical, chemical, and biological processes, and microbial degradation, adsorption, plant uptake, photolysis, hydrolysis, and sedimentation are the main processes (Vymazal and Březinová, 2015).

Conventional CWs can be classified according to water table and water flow direction. Surface flow (George et al.) CWs are vegetated systems with open water surface, while in subsurface flow (SSF) CWs no free water is visible because the water flows through a porous medium planted with wetland plants. SSF CWs are further subdivided into horizontal flow (HF) and vertical flow (VF) systems depending on the direction of water flow through the porous soil (usually sand or gravel). Vymazal and Březinová (2015) reviewed that free water SF CWs are the most used type of wetlands for pesticides removal, but SSF CWs are less frequently used. It is not possible to judge of the effective on different variants of CWs, because direct comparative results on pesticides remove from different types of CWs are missing. Recently, a new variant of CWs which called hydroponic root mats (HRMs) system or floating treatment wetlands have attracted many interests for the treatment of different types of wastewater (Chen et al., 2016). However, there is no report on using HRMs to treat pesticides.

In the present study, the fate of four chloroacetanilide herbicides (acetochlor, s-metolachlor, metazachlor, dimethachlor) were investigated in different types of CWs, which are SF, SSF, and HRMs. Plant uptake, adsorption in soil, as well as the disappearance of parent compounds and the accumulation of their metabolites were monitored. This study provides the first site by site comparison on herbicides removal among different types of CWs, and it first tests the capacity of HRMs for the clean-up of herbicides.

2. Material and methods

2.1. Experimental setup

Six different wetland mesocosms with two replicates were set up in the campus at Czech University of Life Sciences Prague, Czech Republic. In total, 12 wetland mesocosms run in batch mode were investigated simultaneously (Fig. 1). The six wetland mesocosms are named: A-Planted SSF (gravel, 95% calcite); B-Unplanted SSF (gravel, 95% calcite); C-Planted SF (soil); D-Unplanted SF (soil); E-HRM; F-Pond. All the planted systems were planted with *Glyceria maxima*, which is a common used plant in CWs in the Czech Republic. Each mesocosms were made from a plastic container with dimension of 57 (L) × 39 (W) × 42 (H) cm. The gravel based SSF systems (A and B) were filled with 4–8 mm gravel to the height of 40 cm. The soil based SF systems (C and D) were filled with local soil to the height of 20 cm. The HRM (E) was planted with *G. maxima* without any substrate, and the pond system (F) was without substrate and plant. In each planted systems, 12 shoots of *G. maxima* with the average height of 15 cm were planted at the beginning. The addition of herbicides started after two months of plant growth, the mean height of the plants reached about 50 cm, and the number of plant doubled in all the planted systems. Each system was loaded with 6 L simulated wastewater, which potassium nitrate (KNO_3) and potassium phosphate monobasic (KH_2PO_4) were added in tap water with nitrate and phosphate concentration of 40 mg/L and 20 mg/L, respectively. Based on our survey in the agriculture runoff in the Czech Republic, the common detected and with relative high concentration herbicides are acetochlor, s-metolachlor, metazachlor, and dimethachlor, together with their concentration reported in the literature, the initial concentrations of acetochlor, s-metolachlor,

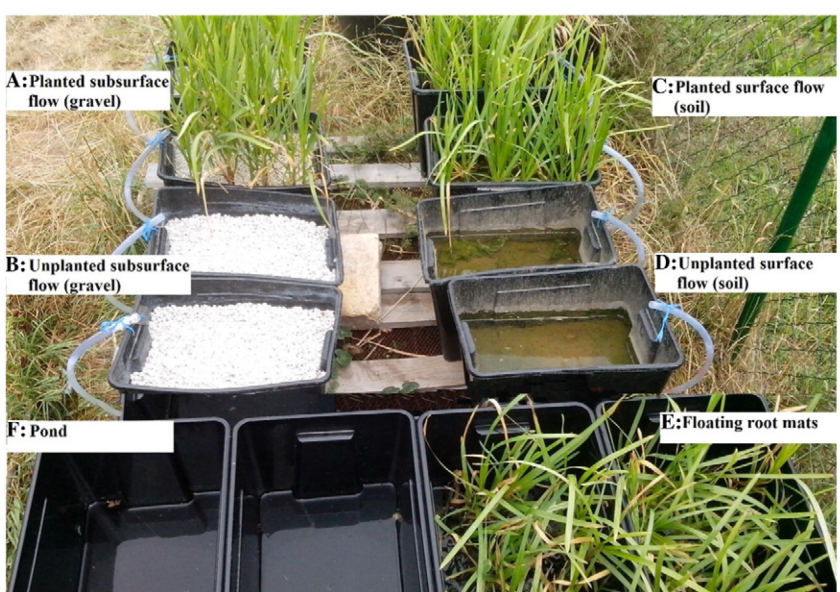

Fig. 1. Experimental setup of the mesocosm wetlands.