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S-metolachlor herbicide removal in pilot-scale horizontal subsurface flow constructed wetlands

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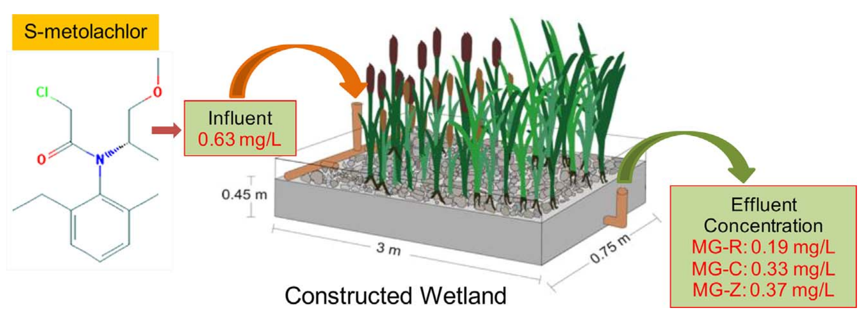
HIGHLIGHTS

- Horizontal subsurface flow (HSF) constructed wetlands (CWs) systems are used to remove S-metolachlor.
- Microbial biodegradation and plant uptake were the main processes of herbicide removal.
- *Phragmites australis* (common reed) showed the highest removal capacity (68.9%).
- Higher S-metolachlor concentrations were detected in the roots of *Phragmites australis*.
- The hydraulic residence time (HRT) of 6 days was adequate for S-metolachlor removal.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to explore the efficiency of three horizontal subsurface flow (HSF) constructed wetlands (CWs) to remove S-metolachlor from contaminated water. The three CWs, with code names MG-R, MG-C and MG-Z, all contained medium gravel as porous media. MG-R and MG-C were planted with *Phragmites australis* and *Typha latifolia*, respectively, and MG-Z was left unplanted and used as control unit to study the effect of vegetation. The CWs units in this experiment operated continuously for one year but they were mature systems operating in various experiments for more than fourteen years. The results showed that the mean percent S-metolachlor removal values were 68.9%, 47.8% and 40.8% for MG-R, MG-C and MG-Z units, respectively. The vegetation (*Phragmites australis*) and the hydraulic residence time were found as the most important parameters affecting the CW capacity in herbicide removal. The current data suggest that HSF CWs are an efficient and low-cost technology in treating S-metolachlor-contaminated surface runoff in agricultural areas.

1. Introduction

Pesticides are essential tools and have become an integral part in modern farming, used to control a wide range of weeds, insects and fungi. Their use results in increased crop yields, with most crops receiving at least one and usually more applications (e.g., 10–15 applications per year are normal for some vegetables and fruits). However, their effects are undesirable when they leave the agricultural fields and

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enter in rivers and streams, creating point and non-point source pollution, and resulting in contamination of surface and groundwater. The negative impacts of pesticides also extend to soil and air contamination [1,2]. Filling and washing of spray equipment, pesticide waste disposal operation, improper storage of packages, agricultural runoff, spray drift, leaching and atmospheric deposition constitute the main sources of pollution [3]. Pesticide concentrations in surface water and groundwater exceeding the permissible limit of 0.1 μg/L for potable water set by EU Drinking Water Directive [4] have been measured in Europe [5,6,7,8] and in the USA [9,10].

S-metolachlor is one of the most well-known and frequently used herbicides in Europe and the USA. In 2008, between 13.6 and 15.9 million kg of S-metolachlor were applied annually in the USA, ranking it as the 4th most applied pesticide [11]. S-metolachlor is a chloroacetanilide herbicide, which acts as an inhibitor of very long chain fatty acid formation, and is extensively used as pre-emergence herbicide for the control of grasses and some broad-leaved weeds in a wide range of crops, such as corn, sugar beets, cotton, tomato, potato, tobacco, soybean and sunflower [12,13]. According to Zemolin et al. [14], S-metolachlor shows moderate to long persistence in soil and moderate persistence in water bodies. Therefore, it has the potential to contaminate surface and groundwater. Indeed, it is one of the five most commonly encountered compounds in European freshwaters [6,15,16] with concentrations 0.33–3.00 μg/L in Spanish surface waters [16] and 0.16–3.68 μg/L in Arno river, Italy [17]. The presence of S-metolachlor has also been measured in French surface waters at concentrations ranging between 0.9 and 1.5 μg/L [18]. Furthermore, metolachlor was constantly detected in Erythropotamos river, Evros Prefecture, North Greece, with highest concentrations detected during the month of pesticide application [19].

Regarding the effect of S-metolachlor on microorganisms, Joly et al. [20] and Elias and Bernot [21] reported the impact of the herbicide on the activity and structure of soil microbial community, and on aquatic microbial community. Furthermore, the toxic effects of S-metolachlor on non-target organisms, such as phytoplankton and mammals, have been reported in the literature [22,23]. In addition, the US Environmental Protection Agency (USEPA) and the World Health Organization (WHO) consider as a serious problem the fact that pesticide use residue may remain in food [24]. Therefore, the development of technologies for the treatment of water contaminated with herbicides or other pesticides consist a high priority.

Among the most commonly used techniques for preventing and mitigating the entry of pesticides into water bodies are riparian buffer zones, planted ditches, and constructed wetlands [3,25]. Constructed wetlands (CWs) are an efficient and low-cost option for treatment of municipal wastewater and contaminated surface runoff, removing nutrients, heavy metals and pesticides. Systems comprise basins with soils or porous media, where plants (e.g., *Phragmites australis*, *Typha latifolia*) with specific known ability to accumulate or remove pollutants are planted [1,26,27]. The efficiency of CWs is related to the physicochemical properties of each contaminant. In the wetland environment, pesticide removal occurs through physical, chemical and biological processes such as retention, settling, adsorption, plant uptake, microbial breakdown [28,29].

In the literature, there are studies regarding the removal of pesticides from surface runoff using CWs. In most cases, free-water surface (FWS) CWs are used, whereas the use of horizontal subsurface flow (HSF) CWs is more limited [1,30,31]. Furthermore, there is lack of research regarding the treatment of water contaminated with S-metolachlor by using HSF CWs. The aim of this study is to evaluate the efficiency of constructed wetlands in reduction of S-metolachlor concentrations in water, in order to minimize the amount of this herbicide entering in water bodies through surface runoff and leachate. For this purpose, three pilot-scale mature HSF CWs were used for the treatment of water contaminated with S-metolachlor originating from sources like spraying equipment rinsing sites, and agricultural runoff. The experimental period lasted one year, so seasonal effects were fully assessed (e.g., temperature and seasonal variation). Two of the CW units were planted with different plants and one unit was left unplanted; with this set-up, the comparison of the removal capacity of the two plant species and the evaluation of the contribution of plant presence were possible. Furthermore, the effect of hydraulic residence time (HRT) was evaluated.

2. Materials and methods

2.1. Physicochemical characteristics of S-metolachlor

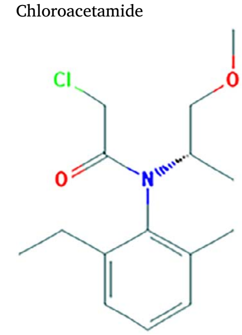
S-metolachlor (GAS name: (2-chloro-N-(2-ethyl-6-methylphenyl)-N-((1S)-2-methoxy-1-methylethyl) acetamide) is the stereoisomer of metolachlor (2-chloro-N-(6-ethyl-o-tolyl)-N-((1RS)-2-methoxy-1-methylethyl) acetamide). It is a nonionic compound and belongs to the chloroacetanilide family of herbicides. The commercial composition of S-metolachlor contains 88% S-enantiomer and the rest is the R-enantiomer, while the metolachlor is a 1:1 mixture of the (S)- and (R)-stereoisomers. Biologically active is only the S-enantiomer [32], which is widely used for grass and broadleaf weed control as it is absorbed through roots and shoots. The R-enantiomer has been studied over the past years, however, data in the scientific literature about the S-enantiomer is limited [33,34,35].

The fate of the pesticides in the environment and their distribution among the various elements of the environment (i.e., water, soil, and plants) is a complex process, affected by the physicochemical properties of pesticides such as solubility in water, octanol-water partition coefficient (K_{ow}), the soil adsorption coefficient normalized with the organic matter content in the soil (K_{oc}), vapor pressure and half-life. The physicochemical characteristics of S-metolachlor are presented in Table 1. Based on them, S-metolachlor is relatively highly soluble in water (480.0 mg/L), and it is considered moderately hydrophobic and highly bio-accumulating as its $LogK_{ow}$ is 3.05 [36].

2.2. System configuration and operation

The experiment of the current study was conducted in the open space of the laboratory of Ecological Engineering and Technology,

Table 1
Physicochemical properties and characteristics of S-metolachlor [36].

Parameter	Value
Formula	$C_{15}H_{22}ClNO_2$
Substance group	Chloroacetamide
Structure	
Molecular weight (g/mol)	283.79
Water solubility at 20 °C (mg/L)	480.0
Octanol-water partition coefficient (at pH 7, 20 °C) $LogK_{ow}$	3.05
Vapour pressure at 25 °C (mPa)	3.70 (low volatility)
Sorption coefficient K_{oc} (L/kg)	200
Half-life at 20 °C (days)	246 (27–372)
Soil degradation $DT_{50,field}$[1] (days)	21.0

[1] Half-life for field studies.