



Using compound-specific isotope analysis to assess the degradation of chloroacetanilide herbicides in lab-scale wetlands



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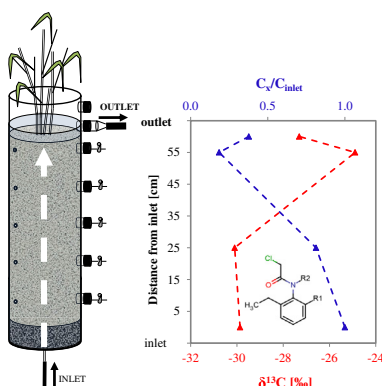
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HIGHLIGHTS

- A novel CSIA method for chloroacetanilide herbicides in water samples was developed.
- Transport of alachlor, acetochlor and metolachlor was studied in lab-scale wetlands.
- Moderate removal of acetochlor and alachlor was observed, and metolachlor persisted.
- Significant carbon isotope enrichment revealed biodegradation of chloroacetanilides.
- CSIA enables assessing the biodegradation of chloroacetanilides in the environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Compound-specific isotope analysis (CSIA) is a promising tool to study the environmental fate of a wide range of contaminants including pesticides. In this study, a novel CSIA method was developed to analyse the stable carbon isotope signatures of widely used chloroacetanilide herbicides. The developed method was applied in combination with herbicide concentration and hydrochemical analyses to investigate *in situ* biodegradation of metolachlor, acetochlor and alachlor during their transport in lab-scale wetlands. Two distinct redox zones were identified in the wetlands. Oxidic conditions prevailed close to the inlet of the four wetlands (oxygen concentration of $212 \pm 24 \mu\text{M}$), and anoxic conditions (oxygen concentrations of $28 \pm 41 \mu\text{M}$) prevailed towards the outlet, where dissipation of herbicides mainly occurred. Removal of acetochlor and alachlor from inlet to outlet of wetlands was 56% and 51%, whereas metolachlor was more persistent (23% of load dissipation). CSIA of chloroacetanilides at the inlet and outlet of the wetlands revealed carbon isotope fractionation of alachlor ($\epsilon_{\text{bulk}} = -2.0 \pm 0.3\text{‰}$) and acetochlor ($\epsilon_{\text{bulk}} = -3.4 \pm 0.5\text{‰}$), indicating that biodegradation contributes to the dissipation of both herbicides. This study is a first step towards the application of CSIA to evaluate the transport and degradation of chloroacetanilide herbicides in the environment.

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1. Introduction

Chloroacetanilide herbicides are used to control annual grasses and broad-leaved weeds on a variety of crops including maize, sugar beet and sunflower. Metolachlor-S and acetochlor are among the ten most commonly used herbicides in the European Union and the United States (EPA, 2011). Alachlor and racemic

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metolachlor were commonly used in the 1990s (EPA, 1999), until the introduction of metolachlor enriched in the active S isomer in 1996, and banning the use of alachlor in 2006 in the European Union. The extensive use of chloroacetanilide herbicides is reflected in their frequent detection in ground and surface waters, and the concomitant detection of their ionic and neutral degradation products (Steele et al., 2008; Hladik et al., 2005). However, the processes governing transport and biodegradation of chloroacetanilides from agricultural land, passing through reactive zones of the landscape, such as wetlands or ground-surface water interfaces, before they reach other ecosystems, remain poorly understood.

Wetland systems can intercept upward flow of pesticide-contaminated water from shallow aquifers during groundwater discharge (Alewell et al., 2008), and influence key ecosystem services, such as water quality improvement. Several biotic (e.g. biotransformation, plant uptake) and abiotic (e.g. adsorption, volatilisation, and photolysis) processes control the transport of organic contaminants in wetlands (Imfeld et al., 2009). Transport of pesticides in wetlands has been mostly evaluated based on assessment of pesticide concentrations and removal efficiencies (Stehle et al., 2011). However, such approach provides no distinction between destructive and non-destructive contaminant attenuation processes, which may lead to inaccurate estimations of the remediation potential of wetland systems. Few studies focused on degradation processes in wetlands through examining the relation between functional genes and observed degradation (Bers et al., 2012), or using microcosms (Runes et al., 2001) and mineralisation experiments to assess degradation kinetics and pathways (Gebremariam and Beutel, 2010). While these studies provide information about the potential of pesticide biodegradation in complex environmental systems, they offer no direct evidence of *in situ* biodegradation processes.

Compound-specific stable isotope analysis (CSIA) provides a valuable tool for the assessment of contaminant transport and fate in the environment (Thullner et al., 2012). CSIA relies on the enrichment of the heavy isotope of an element in the unreacted fraction of a compound during the degradation process. This isotope enrichment occurs due to slight differences in activation energies required to break bonds involving heavy vs. light isotopes (Hofstetter and Berg, 2011). Consequently, the isotopic composition of the contaminants can provide insights about key degradation pathways occurring *in situ*, and in some cases enables measuring the extent of biodegradation (Elsner, 2010). During the last decade, CSIA has been increasingly applied to study several groups of contaminants, most notably chlorinated ethenes (Imfeld et al., 2008), petroleum hydrocarbons (Richnow et al., 2003), and alkanes (Bouchard et al., 2008). Recently, CSIA methods have been developed for a handful of pesticides: lindane (Badea et al., 2009), isoproturon (Penning et al., 2010), atrazine (Meyer et al., 2008), 2,6-dichlorobenzamide (BAM) (Reinnicke et al., 2012), a metabolite of dichlobenil and phenoxy-acid herbicides (Maier et al., 2013). However, CSIA methods have not yet been reported for the evaluation of pesticide biodegradation in complex and dynamic environmental systems.

The aim of this study was to explore the applicability of CSIA as a tool to assess the biodegradation of chloroacetanilide herbicides in wetland systems. A gas chromatography combustion isotope ratio mass spectrometry (GC–C–IRMS) method was developed for stable carbon isotope analysis of chloroacetanilide herbicides in environmental aqueous samples. The novel method was applied to assess the *in situ* biodegradation of metolachlor, acetochlor and alachlor during transport in vertical-flow lab-scale wetlands, designed to study the upward discharge of pesticide-contaminated water into environments at groundwater/surface-water interfaces. In addition, hydrogeochemical development of the systems was monitored to determine prevailing biogeochemical processes.

2. Materials and methods

2.1. Chemicals

Physico-chemical properties of metolachlor, alachlor and acetochlor are listed in Table 1. Chloroacetanilides (metolachlor (racemic), alachlor, acetochlor; Pestanal[®], analytical grade purity: 97.2, 96.8 and 99.2 respectively) and solvents (dichloromethane and ethyl acetate; HPLC grade purity >99.9%) were purchased from Sigma–Aldrich (St. Louis, USA). Alachlor-*d*₁₃ and metolachlor-*d*₆ were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock and standard solutions of chloroacetanilides were prepared in dichloromethane and were stored at –20 °C.

2.2. Chloroacetanilide extraction from water samples and quantification

Solid-phase extraction (SPE) of 10 mL lab-scale wetland water samples was carried out using SolEx C18 cartridges (Dionex[®], CA, USA) packed with 100 mg irregular silica particles. The extraction procedure was adapted from USA EPA method 525.2 using an AutoTrace 280 SPE system (Dionex[®], CA, USA). The procedure of chloroacetanilide extraction and quantification is described in Supplementary Material.

2.3. Carbon isotope analysis

The carbon isotope composition of alachlor, acetochlor and metolachlor was analysed using a GC–C–IRMS system consisting of a gas chromatograph (Agilent 6890) coupled via a GC/C III interface to an isotope ratio mass spectrometer (Finnigan MAT 252, Thermo Fisher Scientific). The oxidation furnace of the GC/C III interface containing (Pt,Ni,CuO) was set to a temperature of 980 °C. A BPX5 column (60 m × 0.32 mm, 0.5 µm film thickness, SGE, Ringwood, Australia) was used for chromatographic separation, with helium as the carrier gas at a flow rate of 2.0 mL min^{–1}. The column was held at 50 °C for 5 min, heated at a rate of 20 °C min^{–1} to 150 °C, then up to 250 °C at 5 °C min^{–1}, then heated at 20 °C min^{–1} to 300 °C and held for 1 min, and finally heated at 20 °C min^{–1} to 320 °C, where it was held for 5 min. Samples (4 µL volume) were injected into a split/splitless injector operated in splitless mode and held at 280 °C. A chloroacetanilide standard with known isotopic composition was measured every nine injections to control the quality of the measurements.

Reference carbon isotope composition values of standards of alachlor, acetochlor and metolachlor were obtained using an elemental analyser-isotopic ratio mass spectrometer (EA–IRMS, eurovector, Milan, Italy) coupled via a conflo III (open split, Thermo Fisher Scientific, Bremen, Germany) to a MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific). The reproducibility of triplicate measurements was ≤0.2‰ (1σ). The δ¹³C values were calibrated using a two-point calibration against the V-PDB standard.

2.4. Lab-scale wetlands characteristics and set-up

The wetlands consisted of four borosilicate glass columns (inner diameter: 15 cm, height: 65 cm), filled with 5 cm of gravel (Ø 1–2 mm) and 52 cm of sand (Ø 0.40–0.63 mm) and planted with *Phragmites australis* (Cav.) (Supplementary Material, Fig. S1). Physical properties and chemical characteristics of the sand and gravel have been described elsewhere (Durst et al., 2013). The wetlands were kept in an air conditioned room at 20 °C ± 0.5 °C, and exposed daily to light from a LED lamp (Greenpower LED lamp, Philips[®], Eindhoven, The Netherlands) for 8 h. All tubing and stoppers in

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