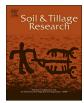Contents lists available at ScienceDirect

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Herbicides degradation kinetics in soil under different herbigation systems at field scale

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ABSTRACT

Application of pesticides in agriculture is one of the main sources of soil and water contamination. Herbicides used by herbigation increases the possibility of water and soil contamination by these toxins. Thus, knowledge on degradation of herbicides in soil for selecting more efficient management strategies is necessary. The objective of this study was to quantitatively describe herbicides degradation in soil under different herbigation and conventional spraying systems in actual field conditions. Consequently, Metribuzin was applied to soil by herbigation and conventional spraying via four methods. The degradation kinetics of herbicide was determined by soil sampling of four layers over a period of 70 days. Results indicated that the herbicide degradation kinetics depends on application method and studying scale. Based on these results, at each of soil layer, degradation rate remained constant due to no changes in soil physical and chemical properties and soil moisture conditions during the experiment. In these conditions, degradation trends followed a single first order kinetics model. However, herbicide degradation kinetics at entire soil profile was different depending on application method. Once the herbicide was applied via the first irrigation, large portion of herbicide was leached out to the second, third and fourth soil layers. Owing to roughly similar clay, organic matter, moisture content along with microbial activity and population in these three layers, the degradation rate was constant, during the experiment, and degradation trend followed the single first order kinetics model. However, in other application methods, the degradation rate was inconstant as a result of remaining a large portion of herbicide in the first soil layer, as well as different soil physical, chemical and biological properties of this layer compared to other layers. This contributed to a deviation from first order kinetics. The degradation kinetics was described much better by bi-exponential model.

1. Introduction

Several hazardous materials are imposed to our environment daily as results of human activities (Davari et al., 2015a,b; Eskandari et al., 2015, 2016). In last few decades, many natural resources have been contaminated by organic and inorganic wastes due to widely different activities such as industrial emissions, application of sewage sludge and waste disposals (Asadi Kapourchal et al., 2009; Eskandari et al., 2012; Farrokhian Firouzi et al., 2015). Contamination of soil and water resources by organic and inorganic pollutants is one of the most important agricultural and environmental challenges in the world (Babaeian et al., 2016; Jafarnejadi et al., 2011, 2013; Khodaverdiloo and Homaee, 2008). Among organic contaminants, oil derivatives and pesticides are the most common organic pollutants in the soil (Mohammadi et al., 2018; Nouri et al., 2014; ElSayed and Prasher, 2013). Herbicides, which are increasingly used to control weeds, are the most important and widely used chemicals. Due to increased

environmental pollution caused by their consumption, many studies have been carried out to determine fate and transport of these materials in the soil (Arabi et al., 2017; Mutua et al., 2016).

Progressive new technology used for agricultural input applications, such as herbigation, has been pretty advantageous owing to enhancement of weed control and crop production, no time limits, no soil compaction and being cost-saving. However, beside such merits, considerable apprehension has been raised upon application of herbigation due to its strong potential for soil and water contamination (Eberlean et al., 2000; Bielinski et al., 2008; Koumanov et al., 2009; Nalayini et al., 2013).

Some researchers believe that herbigation has more potential for further soil and water resources contamination upon more herbicide application along with consumption of large volume of water (Esua and Rumeny, 1995; Viera et al., 2003; Goodman, 2004; Nalayini et al., 2013). Thus, employing more efficient management strategies for herbigation is necessary to reduce environmental contamination. This

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requires the knowledge on fate and transport process of herbicides in soil as well as quantification of these processes. Chemical and biological degradation are the main processes affecting herbicide fate in soil (Pot et al., 2011; Mutua et al., 2016). Soil pH, temperature, moisture, and organic matter content are the most important factors influencing the chemical and biological degradation of herbicides (Khoury et al., 2006; Lagat et al., 2011). Several kinetics models are available for quantitative description of herbicides degradation. Recently, FOCUS work group have introduced several more practical models including Single first order kinetics, bi-phasic kinetics and Lag-phase models (FOCUS, 2011). These are recommended as the first step to derive regulatory endpoints such as Half-life for parent compounds and metabolites in soil or water-sediment studies (FOCUS, 2011). Half-life is a major indicator of herbicide dissipation in natural environments. This parameter is commonly used to manage herbicide application and irrigation programs (FOCUS, 2011).

In most previous studies, a first-order kinetics model has been used and the reported results indicate that this model can accurately describe the herbicide degradation in soil (Khoury et al., 2006; Lopez-Pineiro et al., 2013). However, in majority of these studies the herbicide degradation in soil has been studied in a conventional spraying method (Villaverde et al., 2008; Pot et al., 2011; Lopez-Pineiro et al., 2013). Studies on herbicide degradation used by herbigation in soil have been limited due to the need for certain facilities and equipments (Kazemi et al., 2009; Koumanov et al., 2009). Indeed, in herbigation, due to the changes in moisture conditions of soil layers and changes in herbicides availability in soil solution, degradation kinetics may be described better by some other kinetics models.

Some published results have shown that changing in temperature and moisture conditions, soil microbial activity, herbicides availability in soil solution, and soil heterogeneity lead to a deviation from the first order kinetics and transform it into bi-phasic kinetics and Lag-phase models (Robert et al., 2010). This study was aimed to i) quantitatively investigate herbicide degradation in soil used by herbigation and conventional spraying methods and ii) determine the best kinetics model describing herbicide degradation in each application methods to reduce the hazardous influences of herbicides on soil and groundwater resources.

2. Materials and methods

The designated field experiments were conducted in an agricultural site, located at the 27° 41′ 33″ N, 54° 20′ 12″ E, in a semi-arid region with means annual precipitation, air temperature and evaporation of 198.8 mm, 23 °C and 1200 mm, respectively. The experimental field plots did not receive any herbicides for at least 5 years. The experiments included four treatments each with three replicates in 2.5 × 2.5 m plots. A 2-m buffer between plots was established. The layout levees were covered by plastic sheets. The plots were also planted, so that flood irrigation was done uniformly. Prior to this study, some samples from 0 to 20, 20–40, 40–60 and 60–80 cm soil increments were taken and their physical and chemical properties including particle size distribution, calcium carbonate equivalent (CCE), cation exchange capacity (CEC), and organic carbon (OC) were measured, using hydrometery, titration, ammonium acetate, and Walkley–Black methods, respectively.

A commercial form of Metribuzin with 75% purity was applied at a rate of 0.75 kg ha^{-1}. Treatments included conventional spraying without delay in initial irrigation (CS1), conventional spraying with initial 24 h irrigation delay (CS2), herbigation via the first irrigation (HRB1) and herbigation via the second irrigation (HRB2). In herbigation treatments, herbicide was diluted in water and uniformly sprayed through sprayer inside the plots when the water level was about 8 cm. Conventional spraying was performed along with the first herbigation by using a sprayer. The CS1 plots received irrigation water immediately after chemical application and the CS2 plots were irrigated after a 24 h

delay. After application of herbicide to the soil, irrigations were done every 7–10 days based on the usual irrigation regimes in this region under wheat cultivation.

Soil sampling was performed after each irrigation when soil moisture in surface layer had reached to field capacity (FC). Samples were taken from 0 to 20, 20–40, 40–60 and 60–80 cm depths on seven selected dates including 10 (T_1), 20 (T_2), 30 (T_3), 40 (T_4), 50 (T_5), 60 (T_6) and 70 (T_7) days after chemical application. To avoid degradation, samples were transported to the laboratory instantly, air dried at a dark roomed within a period of 24 h, passed through a 2 mm sieve, and stored at -80 °C until laboratory analyses.

Before chemical extraction, samples were allowed to equilibrate to room temperature. Extraction of Metribuzin from soil was performed using the method developed by Fenoll et al (2009). Then Metribuzin concentrations were measured in the extracted solutions by GC using an Agilent gas chromatograph, model 7890 A, equipped with a 63 Ni electron-capture detector and fitted with HP-5 column [30 m (length) × 320 μm (i.d.) with 0.25 μm film thickness]. The temperature was programmed as follows: 60 °C (2 min) ramped up to 140 °C at 10 °C min^{-1} then to 270 °C at 5 °C min^{-1}. The temperature was then held at 270 °C for 4 min. The carrier gas pressure was set at 40 kPa for 2 min then increased to 64 kPa at 3 kPa min^{-1} and continued to ramp at 1.5 kPa min^{-1} to 103 kPa which was maintained for 4 min. The total run time was 8 min.

For quantitative description of herbicide degradation processes in soil, several kinetics models, such as single first-order kinetics, bi-phasic kinetics and Lag-phase model were used as described by FOCUS work group (FOCUS, 2011). These were recommended for use as a first step to derive regulatory endpoints for parent compounds and metabolites in soil or water-sediment studies. Also, the endpoints like mean half-life (DT_{50}) and time required for degradation of 90% herbicide (DT_{90}) values were calculated by the equation suggested by FOCUS.

Single first-order kinetics (SFO) is a simple exponential equation with only two parameters (Eq (1)). It was assumed that the proportion of herbicide molecules was relatively smaller compared to those of degrading microorganisms and their enzymes. As a result, the rate of the change in herbicide concentration at any time would be directly proportional to the actual concentration remaining in the system. The SFO equation and its derived endpoints can be written as:

$$C = C_0 e^{-Kt} \tag{1}$$

$$DT_{50} = \frac{ln2}{k} \tag{2}$$

$$DT_{90} = \frac{ln10}{k} \tag{3}$$

where C is herbicide concentration at time t, C_0 is herbicide concentration at time t_0, t is time and K is the degradation rate constant.

The SFO kinetics cannot always describe the degradation process. A fast initial decrease in herbicide concentrations is often followed by a slower decline. This is usually referred to as a bi-phasic pattern of herbicide degradation. There are several possible reasons for this phenomenon. Some researchers hypothesized that only the fraction of the herbicide in soil solution is available for degradation and the available fraction often decreases with time due to slow sorption and diffusion processes. This may decrease the herbicide degradation rate at next stages of the experiment. Moreover, in field conditions, seasonal changes in temperature and/or moisture can affect the degradation rate and cause deviations from first-order kinetics (e.g., degradation rate may decrease in winter due to lower temperatures, however, it may decrease in summer due to drier conditions) (FOCUS, 2011).

Soil is a spatially variable medium. Gustafson and Holden hypothesized that the degradation rate will also be variable throughout the soil. They divided the soil into a large number of unconnected subcompartments, each with a different first-order degradation rate constant. The distribution of these rate coefficients was described by a