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ENVIRONMENTAL FATE OF IMAZAPYR AND IMAZAPIC HERBICIDES IN PADDY SOIL AND WATER AND ITS POTENTIAL HEALTH RISK VIA *Anabas testudineus* CONSUMPTION

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ABSTRACT

Mixtures of imazapyr and imazapic herbicides are used to control weedy rice problem in Malaysian rice cultivation area. These two herbicides share the same characteristics which are high mobility, phyto-toxicity and persistency in soil, thus could pose problems to the environment and human health. Since there is limited information regarding the concentration and behaviour of imazapyr and imazapic herbicides in Malaysian paddy soil and water, this study was conducted: (i) to develop and optimize the extraction and detection method of imazapyr and imazapic in water, soil and fish tissue samples using HPLC-UV; (ii) to determine the concentration and distribution pattern of these herbicides for 120 days in paddy soil and water, and estimate their leaching potential capacity using GUS index; (iii) to evaluate their adsorption and desorption capability in soils; (iv) to evaluate their abiotic degradation in water and soil; and (v) to examine their level in *Anabas testudineus*, and estimate their potential health risk amongst farmers. Several extraction techniques including SPE, SLE and LLE were tested to extract imazapyr and imazapic in spiked water, soil and fish tissue samples. The extracts were then quantified using the optimized HPLC-UV. Collections of samples were carried out at Sawah Sempadan, Tanjung Karang, Selangor. Surface water and soil were sampled for 120 days, whereas *A. testudineus* were sampled just after rice harvesting period together with public survey. Adsorption-desorption and abiotic degradation of imazapyr and imazapic were investigated under controlled laboratory conditions using the standard protocols by USEPA. Results showed that SPE technique was able to successfully extract imazapyr and imazapic from spiked water and fish tissue, whereas SLE technique was suitable for fortified soil samples with the recoveries ranging from 80% to 130%. These methods were then used to extract and determine the level of imazapyr and imazapic in the subsequent studies. Analysis of water samples showed that there were no traces of imazapyr and imazapic residues after 120 days from their single application. However, their leftovers were still detected at three different soil depths with half-lives between 24 to 186 days. The GUS index showed that imazapyr and imazapic are leacher herbicides (>2.8), with capability to be mobile and leach further into deep soil. Adsorption-desorption study proved that imazapyr and imazapic were strongly adsorbed into soil containing higher clay, CEC and organic content ($p<0.05$). However, these two herbicides were also shown to have reversible sorption thus promoting abiotic degradation processes. Degradation studies of imazapyr and imazapic in aqueous solutions and soil found that hydrolytic activity for both herbicides was low, while photolytic results showed that these herbicides degraded faster in solutions compared to soil (>90%). For the potential health studies, hazard index (HI) and hazard quotient (HQ) was less than 1, indicating that ingestion of imidazolinone-contaminated *A. testudineus* in six months period poses a low potential health risk. In conclusion, sorption and photodegradation of imazapyr and imazapic were greatly affecting the behaviour of these herbicides in water and soil. Hence, the results from this study can provide a fundamental scientific evidence and information regarding the concentration and behaviour of imazapyr and imazapic herbicides in Malaysian paddy soil and water. The optimized extraction and detection methods obtained in this study can be used by other researchers and regulatory agencies for routine monitoring of these herbicides in the environment.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

For decades, pesticides have become an important component of worldwide agriculture systems which allows significant incremental in crop yield and food production (Carvalho, 2017). Notwithstanding, their pattern of usage has increased in parallel with population growth in order to meet the demand for food production (Carvalho, 2017; Demoliner et al., 2010; Gerónimo et al., 2014). Approximately 30% of the global pesticide consumer market is dominated by developing countries, where annual pesticide usage in Malaysia is more than 200,000 tonnes that comprising for more than 50,000 tonnes of active compounds (Caldas, Zanella & Primel, 2011; Food and Agriculture Organization, 2005; Sabere, Zakaria & Ismail, 2013).

In general, pesticides are chemical compounds that are used to kill pests including insects, rodents, fungi and unwanted plants (World Health Organization [WHO], 2018). Application of pesticides in agricultural and plantation sectors is an effort to reduce yield losses and maintain high quality of crop production by preventing or control the pests, diseases, weeds and other plant pathogens (Caldas et al., 2011; Fuad et al., 2012). Pesticides can be classified either according to the functional group in their molecular structures, for example inorganic, organochlorine, organophosphate, or their biological activity towards target species such as herbicides, insecticide and fungicide (Fuad et al., 2012; Sabere et al., 2013). Normally, pesticide product contains one or more active ingredients formulated with other compounds (Sebere et al., 2013). Despite the advantages of using pesticide, it also can cause harm to the environment and public health due to repeated application, overuse and improper use of the chemicals (Caldas et al., 2011; Fuad et al., 2012). The adverse effects of certain pesticides towards non-target organism such as aquatic life and human have become known due to their acute and chronic toxicity (Nakano et al., 2004).

Regardless of this issue, herbicides are the most preferable pesticide used in agricultural site, followed by insecticides and fungicides (Sebere et al., 2013). Herbicides are applied to the agricultural area in order to manage weedy problems,