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Occurrence of commonly used pesticides in personal air samples and their associated health risk among paddy farmers

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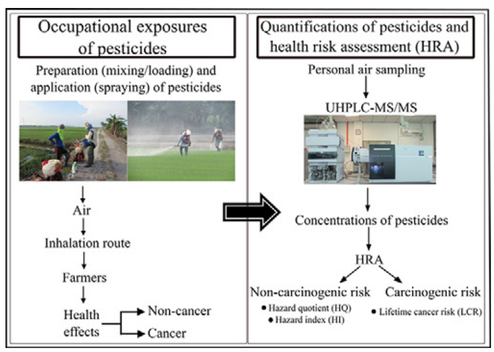
HIGHLIGHTS

- 8.4% of paddy farmers used proper PPE while 91.6% of them did not wear proper PPE.
- First time, 12 of target pesticides were investigated in personal air samples.
- Personal air sample was collected using XAD-2 resin and analyzed using UHPLC-MS/MS.
- Maximum concentration detected in personal air sample was 462.5 ng m^{-3} (fipronil).
- No significant chronic non-carcinogenic and carcinogenic health risks reported

GRAPHICAL ABSTRACT



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ABSTRACT

Tanjung Karang, Selangor, is widely known for its paddy cultivation activity and hosts the third largest paddy field in Malaysia. Pesticides contamination in agriculture fields has become an unavoidable problem, as pesticides are used to increase paddy productivity and reduce plant disease. Human exposure to agrichemicals is common and could results in both acute and chronic health effects, such as acute and chronic neurotoxicity. This study aims to determine the concentrations of commonly used pesticides (azoxystrobin, buprofezin, chlorantraniliprole, difenoconazole, fipronil, imidacloprid, isoprothiolane, pretilachlor, propiconazole, pymetrozine, tebuconazole, tricyclazole, and trifloxystrobin) in personal air samples and their associated health risks among paddy farmers. Eighty-three farmers from Tangjung Karang, Selangor were involved in this study. A solid sorbent tube was attached to the farmer's breathing zone with a clip, and an air pump was fastened to the belt to collect personal air samples. Pesticides collected in the XAD-2 resin were extracted with acetone, centrifuged, concentrated via nitrogen blowdown and reconstituted with 1 mL of 3:1 ultrapure water/HPLC-grade methanol solution. The extract was analyzed using ultra-high-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). The target compounds were detected with a maximum concentration reaching up to 462.5 ng m^{-3} (fipronil). The hazard quotient (HQ) was less than 1 and the hazard index (HI) value was 3.86×10^{-3}, indicating that the risk of pesticides related diseases was not significant. The lifetime cancer risk (LCR) for pymetrozine was at an acceptable level (LCR < 10^{-6}) with 4.10×10^{-8}. The results reported in this study can be beneficial in terms of risk management within the agricultural community.

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1. Introduction

Rice is a staple food in many parts of Asia with Malaysians averagely consuming two and half plates of rice per day (Norimah et al., 2008). As a primary source of food in Malaysia, the paddy and rice industry has been given special attention by the government and is considered an important sector of the economy (Ramli et al., 2012). In an effort to increase rice production, the use of pesticides have become relatively prevalent and act as a crucial tool to increase in land productivity, minimize crop damage, and to ensure that the quantity and quality of agricultural products can be protected. Despite the numerous benefits that could come from the usage of pesticides, the risk of environmental contamination and effects to human health remains a major concern. These chemicals can enter the environment via various routes, such as spraying activities, soil seepage and water contamination. Moreover, the persistent nature and high toxicity of these pesticides can be detrimental to public health when exposed (Kim et al., 2016), either through consumption, dermal contact or inhalation.

The acute effects of exposure to pesticides are skin and eye irritation, headaches, nausea and dizziness while chronic effects are asthma, diabetes, and cancer (Kim et al., 2016). Besides that, Van Maele-Fabry et al. (2010) suggested that diseases such as cancer, hormone disruption, asthma, allergies, and hypersensitivity have been linked with exposure to pesticides. For example, Lerro et al. (2016) demonstrated an increase in the risk of lung cancer among users of herbicides and product mixtures compared to non-users. Meanwhile, Hernandez et al. (2011) and Amaral (2014) reported that the exposure of pesticide may contribute to the exacerbation of asthma through inflammation, irritation, immunosuppression, or endocrine disruption. The data collected from European Union (EU) showed that some pesticides are listed as suspected endocrine disrupting compounds, thus increasing the health concern regarding the endocrine-disrupting potential of pesticides (EU, 2016). Based on a study by Kjeldsen et al. (2013), the results showed that currently used pesticides in Denmark (terbuthylazine, bitertanol, propiconazole, prothioconazole, mancozeb, cypermethrin and malathion) had potential to disrupt the endocrine homeostasis by interfering with sex steroid hormone receptors and aromatase enzyme activity.

A major group of workers who are constantly handling pesticides are farmers, and according to Jaipieam et al. (2009), they are exposed to pesticide residues via direct and indirect inhalation during the preparation (mixing and loading) and application (spraying) of pesticides. Upon inhalation, pesticides are absorbed through the lung surface, and the harmful chemicals then penetrate into the blood stream and are circulated to the rest of the body (Jaipieam et al., 2009). The lack of awareness among farmers regarding safety protocol while handling pesticides, may lead to chronic health effects after long term exposure, such as cancer, neurobehavioral changes, liver abnormalities, kidney dysfunction and parkinson's disease (Kim et al., 2016). The risk of exposure further increases with the absences of personal protective equipment (PPE) and poor personal hygiene (Baharuddin et al., 2011). Based on a review by Mamane et al. (2015), 12 out of 15 cross-sectional studies linked occupational pesticides exposure with respiratory diseases or symptoms such as chronic wheeze, cough, dyspnea, chest tightness and breathlessness. Besides that, frequent exposure of more than twice a month was shown to result in a higher prevalence of respiratory symptoms according to Faria et al. (2005).

To date, there have been many studies focusing on pesticide exposure in ambient air (Batterman et al., 2008; Coscollà et al., 2014a, 2014b, 2013, 2011, 2010, 2009; Lin et al., 2015; López et al., 2017, 2016; Yang et al., 2008; Yusà et al., 2014, 2009; Zhao et al., 2015). However, there are not many studies on the concentration of pesticides in personal air samples. Among the few on were reports on the concentrations of imidacloprid (Choi et al., 2013), chlorpyrifos, dicrotophos, profenofos (Jaipieam et al., 2009), 2,4-D, paraquat (Baharuddin et al., 2011), atrazine (Lozier et al., 2013), penconazole (Tsakirakis et al., 2014) and amitraz (Aghasil et al., 2010). These papers however, were specific case studies in Korea, Thailand, Honduras, Greece, Iran and there have been limited case studies in Malaysia regarding this issue. On top of that, 12 out of 13 target compounds investigated in this present study have never been reported in personal air samples before this.

Although the common routes for pesticide exposures are through dermal and inhalation, in this study, only inhalation exposure was investigated. This is because a majority of the paddy farmers in the observation area used proper PPE against dermal exposure but went without proper protection for inhalation exposure. Malaysian standard code of recommended practice (MS 479:2012) as developed by the Department of Standards Malaysia and SIRIM Berhad was referred to ensure the farmers had adequate dermal and inhalation protection (DOS, 2012). A quantitative measure of the risk of a chemical exposure could be generated via the health risk assessment (HRA) (Williams and Burson, 1985). Currently, no studies have reported the assessment of chronic carcinogenic and non-carcinogenic health risk based on occupational exposure of pesticides in personal air samples.

This study aims to quantify the concentration of the commonly used pesticides in personal air samples and assess their potential health risk to the paddy farmers. The target compounds in this study were selected based on interviews with the farmers. The interview was conducted six months before the collection of personal air samples in order to identify the commonly used pesticides among the paddy farmers in the study area. The most applied pesticides were selected as the target compounds in this study. The final list of target compounds contained a total of 13 compounds, which were azoxystrobin, buprofezin, chlorantraniliprole, difenoconazole, fipronil, imidacloprid, isoprothiolane, pretilachlor, propiconazole, pymetrozine, tebuconazole, tricyclazole and trifloxystrobin. Detailed information on the individual target compounds including International Union of Pure and Applied Chemistry (IUPAC) names, type, class, Chemical Abstracts Service (CAS) number, molecular formula, molecular structure, molecular weight, vapor pressure and LogP are available in Supplementary material at the Elsevier publisher website (Table S1).

2. Materials and methods

2.1. Chemicals and standards

Reference standards of azoxystrobin (98.5%), buprofezin (99.0%), chlorantraniliprole (99.5%), difenoconazole (98.7%), fipronil (99.0%), imidacloprid (99.0%), isoprothiolane (97.2%), propiconazole (99.0%), pymetrozine (99.0%), tricyclazole (99.0%) and trifloxystrobin (99.0%) were purchased from Dr. Ehrenstorfer (Germany). Pretilachlor (98.7%) and tebuconazole (99.3%) were purchased from Sigma-Aldrich (Germany). The internal standards (IS) diuron-d_6 (99.9%) and imidacloprid-d_4 (99.9%) were purchased from Sigma-Aldrich (Germany). Stock standard solutions (1000 mg L^{-1}) were prepared monthly by dissolving the standards in methanol. Working standard solutions (10 mg L^{-1}) were prepared from the stock standard solutions weekly. HPLC-grade methanol and HPLC-grade acetone were purchased from Fisher Scientific (UK).

2.2. Sampling and site characterization

Tanjung Karang, Kuala Selangor, is known as a “rice bowl” village with sweeping paddy fields. This study was conducted in *Kampung* Sawah Sempadan (2304 ha) (Fig. 1), a rice farming village where most of the communities in the area are involved in rice farming and exposed to pesticides. A cross-sectional study was carried out in *Kampung* Sawah Sempadan. The sample size for this study was calculated based on the formula adapted from Lemeshow et al. (1990). Based on the calculation, the minimum number of respondents was 66 respondents. The sample size was increased 20% by considering non-response and missing data. The final sample size was 83 respondents. The study was conducted among 83 paddy farmers who were directly involved in pesticides spraying activity. The inclusion recruitment criteria were (i) farmers who directly handled pesticides (preparation and spraying) in the