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Whole body dosimetry and risk assessment of agricultural operator exposure to the fungicide kresoxim-methyl in apple orchards

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ABSTRACT

This study examined dermal and inhalation exposure of agricultural operators to kresoxim-methyl during pesticide mixing/loading and speed sprayer application (10 replicates, each of 3000 L of spray suspension) in an apple orchard and performed risk assessment. For the whole body dosimetry (WBD) exposure protocol, outer clothing, inner clothing, gauze, and nitrile gloves were examined to measure dermal exposure. In contrast, an IOM (institute of occupational medicine) sampler with a glass fiber filter was used to measure inhalation exposure. Analytical method accuracy in the exposure matrices was evaluated by a field recovery study. The dermal and inhalation exposure amounts for mixing/loading were 9.7 mg [0.002% of the total mixed/loaded active ingredient (a.i.)] and 1.2 µg (1.7×10^{-6}% of the total mixed/loaded a.i.), respectively. The body parts more exposed were the forearms (35.5%), chest & stomach (30.2%), and hands (17.9%). During application, the dermal and inhalation exposure amounts were 66.5 mg (0.009% of the total applied a.i) and 34.8 µg ($4.6 \times 10^{-5\%}$ of the total applied a.i.), respectively. The shins (18.5%) and chest & stomach (16.0%) were exposed to higher proportion of pesticide, followed by the thighs (15.8%) and back (14.7%). Comparing the exposure pattern as assessed by the WBD method in the present study with the patch method as in our previous study, the ADE (actual dermal exposure) as measured by the WBD method was 25 times less than that measured by the patch method. The daily exposure amounts of ADE and AIE (actual inhalation exposure) for mixing/loading were 711.8 µg/day and 4.3 µg/day, respectively, whereas the amounts of ADE and AIE for application were 1825.8 µg/day and 116.1 µg/day. In risk assessment of the mixing/loading and application scenarios, the AOEL (acceptable operator exposure level) of kresoxim-methyl was used as the reference dose to show that the RI (risk index) was much lower than 1, indicating that agricultural operators are at low risk of exposure to kresoxim-methyl.

1. Introduction

Pesticides are used to control harmful insects, diseases, and weeds in agriculture fields; however, the safety of agricultural workers with regard to pesticide exposure is a major concern (Ramos et al., 2010). Agricultural workers are particularly susceptible because they are exposed to pesticides during mixing/loading, spraying, crop harvesting, and other field-based activities. It is necessary to measure the occupational exposure of agricultural workers to pesticides since they must be protected from pesticide exposure. In particular, exposure measurement in each agricultural worker's particular situation is critical for accurate pesticide exposure and risk assessment, since these can differ according to the specific agricultural environment and scenario. The most important factors that affect pesticide exposure are pesticide formulation, packaging type, spraying technique, amount sprayed, working time, type of agricultural activity, and climatic conditions.

During agricultural activities, dermal absorption and inhalation are the major routes by which workers are exposed to pesticides (Choi et al., 2006). For dermal exposure, body, hand, and head exposure are generally measured; however, the patch method (An et al., 2014a; Aprea et al., 2016; Choi and Kim, 2014; Choi et al., 2013, 2006; Kim et al., 2012b, 2013, 2015; Moon et al., 2013; Nuyttens et al., 2009; Zhao et al., 2015) is traditionally used for dermal exposure, and whole body dosimetry (WBD) (An et al., 2014b; Atabila et al., 2017; Cao et al.,

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2015; Gao et al., 2014; Hughes et al., 2008; Nuyttens et al., 2009; Ramos et al., 2010; Thouvenin et al., 2017; Tsakirakis et al., 2014) has also been used with the outer and inner clothing (Atabila et al., 2017; Thouvenin et al., 2017; Tsakirakis et al., 2014). Hand exposure is very important because of the high percentage of dermal exposure (Nuyttens et al., 2009). Conventionally, hand exposure is measured using gloves (Aprea et al., 2016; Atabila et al., 2017; Cao et al., 2015; Kim et al., 2015; Thouvenin et al., 2017; Zhao et al., 2015) or by washing bare hands (Durham and Wolfe, 1962). The head is only responsible for a small portion of the total dermal exposure, but it is nevertheless important because of the placement of the eyes, nose, and mouth – all of which are critical exposure routes. Head exposure is generally measured using patches on a cap or hood (An et al., 2014a; Aprea et al., 2016), wearing a cotton mask (Choi and Kim, 2014; Choi et al., 2013; Kim et al., 2012b, 2013, 2015; Moon et al., 2013; Zhao et al., 2015), or by the face/neck wiping method (Atabila et al., 2017; Thouvenin et al., 2017).

While the proportion of inhalation exposure is relatively small compared to that of dermal exposure (about 1%), inhalation exposure is still very important because 100% of all inhaled chemicals are assumed to be absorbed by the body (Choi et al., 2013, 2006; Kim et al., 2012a; Machado-Neto, 2001; Moon et al., 2013). To measure inhalation exposure, a large glass fiber filter (Kim et al., 2013, 2015; Moon et al., 2013; Zhao et al., 2015) and a solid adsorbent such as XAD-2 resin (An et al., 2014a, 2014b; Cao et al., 2015; Choi and Kim, 2014; Gao et al., 2014; Kim et al., 2013, 2015; Moon et al., 2013; Tsakirakis et al., 2014; Zhao et al., 2015) connected to a personal air pump are conventionally used. In recent studies, an IOM (Institute of Occupational Medicine) sampler equipped with a small glass fiber filter has been used (Aprea et al., 2016).

Apples are one of the most highly consumed fruits in Korea and worldwide. One report found that 64.9% of all farmers usually use speed sprayers rather than power sprayers for application of pesticides in apple orchards in Korea (Hong et al., 2007). Kresoxim-methyl is a strobilurin fungicide that is used of apple fields in Korea for the control of powdery mildew (*Podosphaera leucotricha*) and scab (*Venturia* spp.) in apples, pears, mandarin, grapes, tomatoes, and various vegetables (Knight et al., 1997). The mammalian toxicity of kresoxim-methyl is low, with an acute oral LD_{50} in rat > 5000 mg/kg; moreover, the no observed effect level (NOEL) is 146 mg/kg daily (Tomlin, 2009).

The present study was conducted to evaluate the exposure of apple orchard farmers to kresoxim-methyl using WBD and IOM sampler. The pesticide was dispensed using a speed sprayer with the pesticide in a water-dispersible granule formulation, and exposure was assessed following the global and harmonized trend of exposure measurement. To assess dermal exposure by the WBD exposure protocol, the exposure amounts to the whole body (outer clothing and inner clothing), gloves, hands, and head (face/neck wipes) were measured and pesticide distribution on the body was investigated. Especially cloth penetration rates, which are rarely available from experimental data, were calculated. An IOM sampler was successfully utilized for inhalation exposure. Dermal exposure patterns and cloth penetration rates obtained by the present WBD method during application was compared with those by patch method, which was conducted in same place and was reported already (Kim et al., 2015). Based on these results, risk assessment was carried out using the acceptable operator exposure level (AOEL) of kresoxim-methyl and the exposure amount. For this study, method validation for instrumental analysis, recovery from various dermal and inhalation exposure matrices were conducted and reported (Lee et al., 2017).

2. Materials and methods

2.1. Chemicals and reagents

A kresoxim-methyl water-dispersible granule formulation (Haevichi, WG, 50%, Sungbo Chemical, Seoul, Republic of Korea) was purchased through a local dealer. Analytical standards of kresoxim-methyl (purity, 96.1%) and formic acid (purity, 99.7%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All high-performance liquid chromatography (HPLC) grade solvents were purchased from Fisher Scientific (Seoul, Republic of Korea). Aerosol-OT detergent was from a local company (Jaekyu Chemical, Seoul, Republic of Korea).

2.2. Exposure matrices

Outer clothing made of cotton/polyester (35/65) and 100% cotton inner clothing were obtained from Uniseven and TRY (Republic of Korea) for WBD. Gauze (10 × 10 cm, Kukjae, Republic of Korea) and nitrile gloves (Kukjae, Republic of Korea) were used for head and hand exposure measurement, respectively. An air pump (GilAir-3, Sensidyne, Clearwater, FL, USA) and an IOM (institution of occupational medicine) sampler (SKC, Eighty Four, PA, USA) equipped with a glass fiber filter (25 mm, SKC, Eighty Four, PA, USA) were used for inhalation exposure measurement. A solid sorbent tube (ORBO 609 Amberlite XAD-2 400/200 mg, Supelco, Bellefonte, PA) was used in the breakthrough test.

2.3. Field trials and exposure matrix sampling

All field studies were conducted in an apple orchard which is located in Kyungbuk province, and all workers wore outer clothing, inner clothing, and nitrile gloves when mixing/loading or applying (driving and spraying) the pesticide. The IOM sampler with the glass fiber filter was attached using clips within the breathing zone of the worker, and a personal air pump was fastened to the belt which located on waist of workers. The air flow rate was 2 L/min. A worker prepared the pesticide suspension for approximately 30 min by mixing it in a Haevichi WG 50% (1500 g) instrument with 3000 L of water. Next, ten workers (height: 162–181 cm) sprayed the solution with driving a speed sprayer (Model TLD ASS-555, Asia Motors, Daegu, Republic of Korea) for 63–93 min over 3 ha. Ten replicates of each scenario (i.e., mixing/loading or application) were carried out. Their activities were monitored and recorded on work sheet, on pictures and on video. The farmers are very experienced person of 5–30 years farming careers. They did not show any unusual or characteristic behaviors during spraying and the working behavioral characteristics were similar with each replicates. Pictures of mixing/loading and application are provided in supplementary materials (Fig. S1). The temperature, relative humidity, and wind speed were monitored every 30 min using a Pocket Weather Tracker (Kestrel 4500, Nielsen-Kellerman, Boothwyn, PA) during mixing/loading and application (Table S1).

After mixing/loading or application, the gloves and hands were washed with 1000 mL of 0.01% aerosol OT-75 detergent solution, and the face and neck were wiped with 2 pieces of gauze moistened with 4 mL of the same detergent solution. The outer and inner clothing were carefully removed from the workers and cut into 11 pieces [left/right upper arm, forearm, thigh, shin, front (chest & stomach), back, and pelvis/hip]. The glass fiber filter was collected from the IOM sampler. Each exposure sample was wrapped with aluminum foil, contained in a zip-lock bag, and placed in an ice box for transportation. Samples were stored at −18 °C until analysis.

2.4. Extraction and analysis of exposure matrices

Kresoxim-methyl was extracted from the inner clothing, outer clothing, gauze, and glass fiber filter using 200, 500, 100, and 10 mL of acetonitrile, respectively. Kresoxim-methyl residue on outer clothing was determined by HPLC-DAD (Agilent 1100 series, Agilent Technologies Inc., Santa Clara, CA, USA) with a Luna C18 column (5 μm particle size, 4.6 × 250 mm, Phenomenex, Torrance, CA, USA) using acetonitrile and water as the mobile phase. Kresoxim-methyl residues on other samples (inner clothing, gauze, glass fiber filter and wash