



Evaluation of transfer rates of multiple pesticides from green tea into infusion using water as pressurized liquid extraction solvent and ultra-performance liquid chromatography tandem mass spectrometry



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ABSTRACT

Pesticide residues could be transferred from tea into its infusion and by-products, and subsequently consumed by humans. Extra extraction conditions may induce more pesticide leaching into the infusion and by-products of tea and cause greater damage to humans. The aim of this study is to evaluate the infusion of multiple pesticides from green tea into hot water via pressurized liquid extraction. The results showed that pesticides in spiked samples generally have higher leaching (0.8–45.0%) than those in the positive samples. There was a marked rise of transfer rates when water solubility increased from 20 mg L⁻¹ to 450 mg L⁻¹ and LogKow decreased from 6 to 4. All pesticides had more leaching into hot water using pressurized liquid extraction than traditional tea brewing. This study helps in risk assessment of pesticide residues and in the formulation of maximum residue levels (MRLs) in tea and its by-products.

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1. Introduction

Tea is the most popular and widely consumed beverage in the world after water because of its benefits to health, such as antioxidant capacity, weight management, cognitive performance, mental relaxation, and neuroprotection (Pinto, 2013). Active components of tea such as tea polyphenols, tea polysaccharide, theanine, and caffeine, are consumed by humans by tea brewing. Brewing procedure varies depending on tea types. Generally, 2–3 g of green tea or black tea is brewed with 100–150 mL of boiled water for 5–6 min twice or thrice (ISO, 1990). For dark tea and various oolong tea, infusion time may be prolonged to 20–30 min at 100 °C, with tea/water ratio increased to 20 g/500 mL. During brewing, pesticide residues in tea leaves are transferred into the infusion and consumed by human (El-Aty et al., 2014). Moreover, various pathways of pesticide residues affect humans through consumption of tea by-products, such as bottled ready-to-drink tea (Wang, Cheng, Zhou, & Cheng, 2013), tea nutraceutical products (Martínez-Domínguez, Nieto-García, Romero-González, & Frenich, 2015), and instant tea (Zhu, Hu, Yao, Shen, & Yue, 2015). Tea by-products are generally made from tea extracted by boiling water

with additional conditions, such as a complex manufacturing processing (Alasalvar et al., 2013; Kraujalytė, Pelvan, & Alasalvar, 2016), high pressure (Jacques, Dariva, Oliveira, & Caramão, 2008), and ultrasound-assisted extraction (Both, Chemat, & Strube, 2014). Therefore, the study on the transfer rate of pesticides from tea to infusion and tea by-products helps in risk assessment and formulation of maximum residue levels of pesticide residues in tea.

Regarding traditional tea brewing methods, the transfer rates of several kinds of pesticides, such as pyrethroids, organophosphorus, organochlorine, neonicotinoids, carbamates, and benzoylurea, have been reported (Chen et al., 2015; El-Aty et al., 2014; Wang, Cheung, & Leung, 2014). Transfer rate of pesticides from tea to infusion in brewing depended on their physicochemical properties, including water solubility, partition coefficient (logKow), and vapor pressure (Chen & Wan, 1998; Pérez-parada et al., 2010). Neonicotinoids, carbamates, and other pesticides with high water solubility and low partition coefficient have increased leaching capacity into infusion. Transfer rates of the pesticides with water solubility higher than 500 mg L⁻¹ and logKow lower than 1.0, such as thiamethoxam, methomyl, carbendazim, imidacloprid, acetamiprid, dimethoate, and acephate, are higher than 60% (Hou et al., 2013; Pan et al., 2015; Wang et al., 2014). Pyrethroids and organochlorine pesticides with extra low water solubility and high LogKow hardly leached into tea infusion, and their transfer rates are lower than 6% or are equal to 0 (Chen et al., 2015). Transfer

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rates of most organophosphorus pesticides fall within the range of 5–40%, between neonicotinoids & carbamates, and pyrethroids & organochlorine pesticides (Ozbey & Uygun, 2007). Tea brewing method plays an important role in the pesticide transfer rate. The proportion of pesticides leached from tea into infusion shows a positive relationship with brewing time (Chen et al., 2014; Jaggi, Sood, Kummar, Ravindranath, & Shanker, 2001). Transfer rate of chlorpyrifos under the brewing times of 2, 5, and 10 min were 4%, 6.7%, and 10.9%, respectively (Jaggi et al., 2001). When the infusion time was prolonged to 30 min, transfer rates of difenoconazole and azoxystrobin increased to 19.0–58.1% and 38.1–71.2%, respectively, compared with when the infusion interval was 5 min (Xue et al., 2014). In addition, continuous boiling and increased brewing times could result in more pesticides leaching into the tea infusion (Chen et al., 2015; Jaggi et al., 2001). Many kinds of tea by-products are made from tea extracts using water as the extraction solvent and under additional conditions, which could result in more pesticide residues being transferred into tea extracts and eventually adsorbed by humans. Therefore, it is necessary to understand transfer rates of pesticide residues from tea to infusion during traditional brewing and extra preparation for tea infusion. To our best knowledge, transfer rates of pesticides from tea into infusion under extra extraction conditions have not been reported, although several kinds of pesticides with their transfer rates have been reported for the traditional tea brewing methods.

Pressurized liquid extraction (PLE) is an extraction technique that has been developed and used successfully in the extraction of pesticides (Schäfer et al., 2008), polycyclic aromatic hydrocarbon, and polychlorinated biphenyls (Richter, Jones, Ezzel, & Porter, 1996) from solid or semisolid substances. PLE could improve the penetration of solvents into analyzed samples, thereby obtaining higher extraction efficiencies and consuming less solvent and labor time because PLE uses extraction solvents at high pressure levels and at temperatures above the boiling point (Björklund, Nilsson, & Bøwadt, 2000). Besides organic solvents, water was also used as an extraction solvent to obtain higher extraction efficiencies of endogenous or exogenous compounds from plant or animal materials (Kronholm, Hartonen, & Riekkola, 2007). Based on the PLE performance and application, it could be an alternative to various traditional tea brewing methods and extra extraction methods for tea by-products. PLE can be used to investigate and obtain the maximum transfer rates of pesticides from tea into hot water.

Although the transfer rates from tea into infusion via traditional brewing methods of more than 20 pesticides have been revealed, a number of pesticides with unknown transfer rates still exist. Investigation of transfer rates of various pesticides from tea into infusion using traditional brewing methods is difficult and time consuming because transfer rates depend on different tea types and brewing methods. The aim of this study is to investigate transfer rates of multi-residues of pesticides from tea into infusion with water as PLE solvent using ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS). The influence of key PLE parameters (e.g., temperature, pressure, static time, and running cycles) on transfer rates of pesticides from tea into infusion was investigated. This study helps in the risk assessment of pesticide residues and formulation of maximum residue levels (MRLs) in tea and tea by-products.

2. Materials and methods

2.1. Reagents and materials

Solvents and reagents such as methanol, dichloromethane and acetonitrile, toluene, NaCl, anhydrous Na₂SO₄, HPLC-grade water,

and PSA/GCB SPE columns were used in a previous study (Chen et al., 2015). Diatomaceous earth (Zhejiang Medicine, China) was baked for 3 h at 650 °C before use. Certified pesticide standards and triphenyl phosphate (TPP) were purchased from Sigma-Aldrich (Steinheim, Germany).

Green tea samples were collected from Chinese supermarkets, monopoly stores, and wholesale markets. Sixteen green tea samples were used in this study. Organic, pesticide-free green tea residue was selected as blank samples for preparation of matched calibration standard solutions and spiked samples.

In this study, blank green tea samples spiked with 76 pesticides at 80 µg kg⁻¹ and 16 green tea samples were used to investigate transfer rates of pesticides from tea into infusion. Ground organic tea powder (2 g) was introduced into 34 mL PLE cell and mixed with standard solution (200 µL) to achieve a spiked level of 80 µg kg⁻¹. Spiked samples were strenuously vibrated by hand and then let stand for overnight (about 18–20 h). These spiked samples were used to study the transfer rates of multiple pesticides from tea into infusion using water as PLE solvent.

2.2. PLE extraction

Homogenized tea sample (2 g) and diatomaceous earth (5 g) were blended and introduced into a 34 mL PLE cell with a filter paper in the bottom. Internal standard triphenyl phosphate (IS TPP) surrogate standard solution was mixed with the tea samples prior to dichloromethane extraction, but not water extraction. HPLC-grade water (5 mL) was added into PLE cell prior to extraction using dichloromethane. Extraction was performed with dichloromethane (or water for preparation of tea infusion) at 100 °C and 2000 psi for 5 min, followed by static extraction for 5 min. The cell was flushed with 20% volume for 60 s. Running cycles were set up twice for each sample. All the collected extractions went through the following clean-up procedure.

2.3. Clean up

Clean up of the dichloromethane extraction was same as in our previous study (Chen et al., 2015). Extractions were filtered briefly through 3 g Na₂SO₄ and concentrated to dryness using a rotary evaporator (Buchi, Switzerland) at 40 °C and dissolved with 2 mL of acetonitrile, and then added into GCB/PSA SPE column, which was conditioned with 5 mL of acetonitrile/toluene (3:1, v/v) before use. Target pesticides were eluted from the SPE column with 25 mL acetonitrile/toluene (3:1, v/v). Elutes were evaporated into dryness using a rotary evaporator at 40 °C and dissolved in 2 mL of methanol/water (1:1, v/v) for UPLC-MS/MS analysis.

Tea infusion was diluted with water until 100 mL and mixed with TPP surrogate standard solution and 5 g of NaCl. Infusion was cleaned up by liquid-liquid extraction with 100 mL of dichloromethane twice. Dichloromethane was evaporated into dryness and dissolved in 2 mL of methanol/water (1:1, v/v) for UPLC-MS/MS analysis.

2.4. Preparation of standard solutions

Individual pesticide stock solution at 1000 mg L⁻¹ (200 mg L⁻¹ for carbendazim) and internal standard triphenyl phosphate (IS TPP) at 1000 mg L⁻¹ were prepared with methanol. Intermediate mixed standard solutions at 40 mg L⁻¹ and IS TPP solution at 20 mg L⁻¹ were prepared by diluting stock standard solutions with methanol. All stock solutions and intermediate solutions were stored in the dark at –18 °C.

Liquid (2 mL) obtained from blank samples with the proposed treatment was dried by evaporation. Solvent standard mixtures (2 mL; containing IS TPP at 40 µg L⁻¹) with concentrations ranging

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