



Potential application of immunoassays for simple, rapid and quantitative detections of phytoavailable neonicotinoid insecticides in cropland soils

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ABSTRACT

This study evaluated the applicability of commercially available kit-based enzyme-linked immunosorbent assay (ELISA) to simple, quick, and quantitative detection for three water-extractable (phytoavailable) neonicotinoid insecticides: dinotefuran, clothianidin, and imidacloprid in soils. ELISA showed excellent analytical sensitivity for determination, but with cross-reaction to structurally related neonicotinoid analogues, which might produce false positives. To analyze insecticides in soil samples of diverse physicochemical properties, they were extracted with water. The aqueous soil extracts were assayed directly with ELISA. No matrix interference was observed without additional dilution with water. Recovery experiments for the insecticides from aqueous soil extracts spiked at 2–10 ng/mL showed good accuracy (72–126%) and precision (< 16%). Kit-based ELISAs were used to estimate soil–water distribution coefficients (K_d). Values estimated using this method showed positive correlation between organic carbon contents in soil and those for evaluated insecticides. Results indicate that the evaluated kit-based ELISA has applicability for simple, quick, and reliable detection of phytoavailable insecticides in soils and for estimating K_d values in soil.

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1. Introduction

The agricultural system in Japan characteristically uses small-scale, multi-item production to utilize limited expanses of cropland effectively. Because pest and fungus control methods differ among crops in such an agricultural system, stable production and supply of agricultural products are maintained using a wide variety of pesticides.

Conditions for the use of a pesticide are defined in detail so that the post-harvest residue concentration in agricultural products does not exceed the maximum residue limits (MRLs). However, situations such as suspension of shipments or voluntary recalls of agricultural products because of “accidental residue” have occurred despite widespread compliance with the conditions. One factor is

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readily apparent: pesticides used during prior cultivation of crops persist in soil even after harvesting, with the result that successive crops absorb the pesticides (Motoki et al., 2015). If concentrations in agricultural products by the accidental residue exceed the MRL, then previously legislated measures must be taken, dealing a devastating economic blow to production areas. Accordingly, to alleviate risks of accidental residues in crops, it seems extremely important to ascertain residue concentrations of pesticides in soil at the time of planting succeeding crops.

Most of the pesticides in soil including the pesticides that are adsorbed strongly onto organic carbon can be extracted using organic solvents such as acetone or acetonitrile. However, Sugiyama et al. (1990) and Sugiyama and Kobayashi (1993) presented knowledge supporting that all pesticides extracted with these organic solvents do not contribute to the described previously accidental residue. Specifically, a significant correlation was found between the concentrations of phytoavailable herbicides and the weed-growth-suppressing action effects of extracting herbicides that are available to plants (which can be absorbed through roots) with water rather than organic solvents such as acetone. Consequently, they suggested that the herbicide concentrations where weeds or crops are available should be determined originally when evaluating the concentrations in soil from the viewpoint of the persistence of the herbicidal effects and the avoidance of

phytotoxicity. Such knowledge is fundamentally important to reduce the risks posed by pesticide residues in soil. Based on reports by Sugiyama et al. (1990), Sugiyama and Kobayashi (1993), Motoki et al. (2015) and Sakai et al. (2009), high correlation can be found between the concentrations of water-extractable or 50% (v/v) methanol-extractable pesticides and pesticide concentrations in crops.

Therefore, we conducted this study with the aim of establishing a simple and quick analytical method to detect phytoavailable pesticide residues in soil before planting of crops to prevent the risks posed by pesticide residue in crops and to contribute to the safety of agricultural products. Chromatographic techniques such as high-performance chromatography (HPLC) and gas chromatography that are superior in terms of their analytical precision and sensitivity have been used exclusively for analyses of pesticide residues in soils. However, troublesome sample preparation before chromatographic determination is generally necessary. Therefore, they are unsuitable for analytical methods for immediate assessment of the propriety of planting of crops at a site. However, enzyme-linked immunosorbent assay (ELISA) method can save labor and obviate complicated procedures because of its high specificity (high selectivity) to a certain pesticide (Jourdan et al., 1996; Aga and Thurman, 1997). Furthermore, because the method can accommodate many samples simultaneously, its applicability as an analytical method for simple and quick inspection of pesticide residues in agricultural products before shipment has been proposed (Watanabe, 2011). Most ELISAs developed for detection of pesticide residues in soil samples are intended to ascertain the total residue concentrations with extraction using organic solvents (Le et al., 2003; Chuang et al., 2006; Liu et al., 2011; Li et al., 2013; Cui et al., 2014).

Rapid assessment of sites for planting of crops is possible by application of ELISA method, which has the previously described advantages over the chromatographic methods for analysis of phytoavailable pesticide in soil extracted with water. For this study, concentrations of three neonicotinoid insecticides (dinotefuran, clothianidin and imidacloprid), were determined using commercially available kit-based ELISAs selected for pesticides that are often used and which can be applied directly to soil. The present work was conducted to evaluate (1) the fundamental analytical performance of the kit-based ELISAs, (2) the potential matrix interference from soil samples, and (3) the analytical reliability of using target insecticide-spiked aqueous soil extract samples for analysis by ELISA for simple and quick quantitative determination method for phytoavailable insecticides in soil samples. Finally, the soil–water distribution coefficient (K_d), which is a parameter of the initial assessment of the accidental risk posed by pesticide residues in crops was also estimated using the kit-based ELISA we evaluated.

2. Material and methods

2.1. Chemicals and materials

Pesticide-grade dinotefuran, clothianidin, imidacloprid, and other neonicotinoid analogues (acetamiprid, nitenpyram, thiacloprid, and thiamethoxam) for cross-reactivity studies with purities of > 98% were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and Kanto Chemical Co. Inc. (Tokyo, Japan). The respective kit-based ELISAs (SmartAssay Series, <http://www.horiba.com/us/en/analysis-based-on/immunochemistry/immunoassay/>) for dinotefuran, clothianidin, and imidacloprid were supplied by Horiba Ltd. (Kyoto, Japan). HPLC-grade and pesticide residue analysis-grade organic solvents were acquired from Wako Pure Chemical Industries Ltd. HPLC-grade water was produced

using a Milli-Q water purification system (Millipore Corp., Bedford, MA).

Chem Elut SPE cartridges (20 mL capacity) packed with diatomaceous earth material and ENVI-Carb-II/PSA SPE cartridges packed with 500 mg of graphitized carbon black and 500 mg of primary secondary amine were obtained from Agilent Technologies Inc. (Santa Clara, CA) and Supelco (Bellefonte, PA).

Stock solutions of each analyte (1 mg/mL) were prepared in acetonitrile for ELISA and HPLC analyses. They were kept at 4 °C when not in use. Working standard solutions of various concentrations were prepared every time by appropriate dilutions of stock aliquots in water for ELISA analysis and water/acetonitrile (75:25, v/v) for HPLC analysis. Then they were used for the construction of the calibration curves for both methods. Other working standard solutions for recovery and sorption experiments were also prepared in water.

2.2. Soil samples

Twenty-one Japanese cropland soils having various physico-chemical characteristics were used (Table 1). Soil samples were air-dried and were passed through a 2.0-mm sieve. The organic carbon (OC) contents were determined using dry combustion method with a CN coder (MT-700; Yanaco Analytical Systems Inc., Kyoto, Japan). The particle size distribution was analyzed using the pipette method with a pipette apparatus (DIK-2020; Daiki Rika Kogyo Co. Ltd., Saitama, Japan). The soil texture was determined according to standards developed by the International Society of Soil Science (Editorial Board of “A Glossary of Pesticide”, 2009). Soils were classified according to the criteria adopted by the Cultivated Soil Classification Committee (1995).

2.3. Extraction of soil samples

Water (25 mL) was added to 5 g of each air-dried soil sample. The sample mixtures were vigorously shaken for 48 h at room temperature (between from about 20 °C and 25 °C) (pre-equilibration for 24 h and equilibration for 24 h). After equilibration, the sample mixtures were centrifuged using a low-speed centrifuge (LC-100; Tomy Seiko Co. Ltd., Tokyo, Japan) at 3500 rpm for 30 min. An aliquot of the supernatant (aqueous soil extract) was determined directly with ELISA or was cleaned up for HPLC analysis.

2.4. Pre-treatment before ELISA analysis

If necessary, each aqueous soil extract was diluted approximately with water before ELISA analysis.

2.5. Pre-treatment before HPLC analysis

Each aqueous soil extract (15 mL) was applied to a Chem Elut SPE cartridge. After being left to stand for 10 min, the cartridge was washed with 50 mL of *n*-hexane. Then the retained insecticides were eluted with 100 mL of dichloromethane. The eluate was concentrated to about 0.5 mL. Then the residue was reconstituted with 2 mL of acetonitrile. The solution was applied to an ENVI-Carb-II/PSA SPE cartridge preconditioned with 4 mL of acetonitrile. The retained insecticides were eluted with 8 mL of acetonitrile. The eluate was concentrated to about 0.5 mL and was then evaporated to dryness by a gentle nitrogen stream at 50 °C (dry thermos unit, DTU-2C; Taitec Corp., Saitama, Japan). The residue was reconstituted in 150 µL of water/acetonitrile (75:25, v/v) and syringe-filtered using a 0.45 µm PVDF filter (Merck Millipore Ltd., Tullagreen, Carrigtwohill Cork, Ireland) into an autosampler vial.

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