APPROACHES TO THE PROBLEM ON PESTICIDE RESIDUES IN CROPS AND SOILS IN JAPAN

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ABSTRACT

Pesticide residues adversely affect human health and the natural environment. In Japan, several pesticides were detected to exceed Maximum Residue Level (MRL) of foods. Its current pesticide registration system requires performing a set of acute toxicity examinations in three aquatic organisms. Persistent Organic Pollutants (POPs), most of which are “past pesticides,” have now become a global issue. The objective of this paper is to provide basic knowledge on pesticide exposure and what are the approaches used to deal with residue issues in Japan. Each pesticide has its own physicochemical/biochemical properties and management purposes, including target diseases/insects/weeds and target crop. The characters of each target pest and crop are also largely diverse. In addition there are a lot of pesticide formulation and application methods. Thus, various routes exist in pesticide exposure to crop and soil. First is the direct exposure of crop to pesticides, which includes the application of target/applicable crop and drift to non-target crop. The second is indirect exposure of non-target plants via variety of routes. Soil, water and air or their combinations are major media for pesticide behavior. Pesticides intentionally or accidentally applied pollute soil in arable land. It persists in soil by several kinds of intermolecular interactions. “Aging” is an important idea to deal with pesticide persistence in soil. The bioavailability and/or the extractability from bound residues are getting more difficult with time. It largely affects length of persistence of pesticides in soil. Pesticides largely move with water in soil to ground water and on soil to surface water. Dissolved organic matter and suspended solid should be taken into account on pesticide contamination in water. POPs high bioaccumulation, and long distance transport have long persistence in the environment. Methyl bromide had been used intensively worldwide. These were transported to the atmosphere causing problems both to human and the environment. There are a lot of approaches to the problem on pesticide residues in crop and soils. In the viewpoint of air pollution, the risk of spray drift is assessed in EU and USA by computer simulation models. However, it is very difficult to introduce them in Japan due to the limitation of buffer zone. Therefore, application methods and drift guards as alternatives prevent spray drift, which fits small-scale farming. In addition, vapor drift, which has two states (gas and/or particle-adsorption), also have very important issues to be considered. Multimedia model for global behavior of organic chemicals were based on “fugacity capacity” developed just recently in Japan. There are three types of on-site remediation methods in soil. Those were phytoremediation, bioremediation, and chemical remediation. Grafting method can be used in cucumber/pumpkin combination in phytoremediation of drifts. Bioremediation is effective for on-site remediation of pesticides and POPs. The practically effective bacterial consortia, which degrade triazines, were found in our institute. Chemical remediation is useful with single or in combination with the above remediation methods. Computer simulation models for pesticide behavior in paddy-river system were developed in Japan and in Europe. In diatom, good correlation was observed in the 50% effective concentration (EC50) values of dimethametryn between the native colonies and the cumulative values of isolated single species. Large difference in susceptibility was observed between the upper and middle reaches of stream. Crop residue is not simple, due to the following reasons, 1) many exposure ways to existing pesticides, 2) pesticide transport to edible parts depend upon crop and pesticide combination, and 3) pesticides are metabolized not only in soil but also in crop. Pesticide registration in minor crops is a social problem in Japan. There are more than 200 crops, which could not be categorized in 11 minor
INTRODUCTION

The import/export of agricultural products qualitatively and quantitatively had been increasing in recent years, due to international food diversification. On May 29, 2006 in Japan, the Ministry of Health Labour and Welfare introduced the “Positive List System” for agricultural chemicals (pesticides, feed additives and veterinary drugs) in order to improve food safety.

Paracelsus (1493-1541) mentioned: “All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy. The dose makes the poison.” It means that risk by chemicals cannot be determined by either hazard properties (toxicity) or the amount of exposure. They must be combined for risk assessment.

Pesticide residues adversely affect human health and the natural environment (Baker et al. 1994, Freemark and Boutin, 1994, Clark and Ohkawa 2003). For issues concerning human health, several pesticides were detected to exceed Maximum Residue Level (MRL) in imported vegetables such as spinach, mushroom and shellfish including Corbicula japonica Prime (brackish-water clam) in brackish-water region in Japan in recent years. Social problems arose on dermal/skin exposure of organophosphorus pesticide to children and persons with chemical sensitivity. In case of natural environment, Japan’s current pesticide registration system requires performing a set of acute toxicity examinations in three organisms — fish, water fleas, and green algae (Nyholm and Källqvist 1989) — to assess the ecotoxicity of a pesticide in inland water ecosystem, based on the OECD guideline (Campbell 1999). However, they live in lakes and marshes, not in rivers directly linked from paddy fields. No chronic and/or ecological study was required for pesticide registration (Newman et al. 2006).

In addition, POPs are now considered as global issues (Barra et al. 2004). Future POPs are proposed, and will be approved in POPROC in a few years time. Some pesticides are included such as chlordecone, hexachlorocyclohexane (lindane, ã-HCH), endosulfan, as well as current POPs.

The objective of this paper is to provide basic knowledge on pesticide exposure and how to approach the residue issues in Japan. Pesticides here refer to synthetic organic pesticides. Biological pesticides such as microbe-origin pesticides are not included.

PESTICIDE EXPOSURE

Each pesticide has its own physicochemical/biochemical properties and management purposes, including target diseases/insects/weeds and target crop. The characters of each target pest and crop are largely diverse. There are a lot of pesticide formulation and application methods. As a result, various routes exist in pesticide exposure to crop and soils (Fig. 1).

First, there are two types of direct exposure when pesticide with dilution water is sprayed. One is to apply target/applicable crop, and the other is “spray drift” of sprayed pesticide from target crop to non-target crop. What is a “drift”? There are spray drift and vapor drift. Spray drift occurs at spraying, and is composed by preliminary droplet, which directly occur from spray nozzle, and secondary droplet, which occur after hitting/bounding to crop and soils at application. Vapor drift also occurs from crop and soils. The driving force is the vapor pressure of pesticide. Pesticides are lost in the atmosphere with gas and/or particle-adsorption state for long period, depending on pesticides, soils and the meteorology.
Second, non-target plants, including crops, are indirectly exposed to pesticide via a variety of routes. Soil, water and air are major media for pesticide behavior, and are sometimes combined (Jury et al. 1987, Ferenc 2001). Most distinctive phenomena of organic pesticide behavior are metabolism and degradation. Pesticides change their structures biotically (Wolt et al. 2001) and abiotically in the environment (Choudhry 1985; Katagi 2002; Katagi 2004; Kobara et al. 2002; Kobara et al. 2003).

**Via Soil**

Pesticides that are intentionally or accidentally applied pollute soils in arable land and persist in soil by several kinds of intermolecular interactions, such as van der Waals-London, hydrophobic bond and ligand or ion exchange (Kovacs 1986). “Aging” is an important idea to deal with pesticide persistence in soil. The bioavailability and/or the extractability from bound residues are getting more difficult with time (Kovacs 1986). It largely affects length of persistence of pesticides in soil.

Pesticides equilibrate between solid (soil) and liquid (water) phase, by adsorption to soil and desorption from soil. Pesticides in soil were carried over to succeeding crop, when they have long duration of activity or the cropping interval was short. Especially in greenhouse were soil fumigant is applied in many cases, plastic film largely cut UV, and rotation of vegetables is very short. Consequently, risk of phytotoxicity and pesticide residue in crop will increase.

Pesticides move in soil via water. However, soil particles with pesticides also move in the soil by cultivation, on the soil surface by excess water, and in the air by wind. They cannot be neglected environmental contamination of pesticides.

**Via Water**

Pesticides largely move with water in soil to ground water and on soil to surface water. The movement in soil is leaching and percolation (penetration). Leaked water to ground water is used for irrigation or drinking water (Honeycutt and Schabacker 1994), and percolated water came to the next field. The movement on soil is runoff and drainage, which are also used as water flow (Figs. 1 and 2). About half of Japanese arable land is paddy field, which directly link to river via drainage canal. These contaminated water cause phytotoxicity to crop or bring excess crop residue, and adversely affect human health.
Dissolved organic matter and suspended solid should be taken into account on pesticide contamination, since they are very mobile and most of pesticides with hydrophobic moiety strongly adsorb to them (Krop et al. 2001).

**Via Air**

Twelve compounds are currently listed as POPs at Stockholm Convention (May 17, 2004), and nine of them are pesticides, such as mirex, drins (aldrin, dieldrin, endrin), toxaphene, DDT, chlordane, heptachlor, hexachlorobenzene. Dioxins are their byproducts. They have hazard (highly toxic) and exposure (long persistence in the environment, high bioaccumulation, long distance transport) characteristics. Results were found in the polar region. POPs are monitored all over the world (Hebert and Miller, 2004). Passive and active air sampler is introduced to correct them other than collecting precipitation. Passive air sampler is fit for covering number of sampling sites in wide areas. Active air sampler is fit for relatively precise and detailed experiment to clarify trend of pesticide transfer.
from soil to the atmosphere. Jaward et al. (2005a/2005b) monitored POPs and the related compounds in Asian region (Fig. 3). There are significant difference in amount and kinds of POPs among countries.

Methyl bromide as soil fumigant had been intensively used in the world but it causes ozone layer depletion. Global efforts are required to repair the world’s protective ozone layer. Methyl bromide was then banned starting in 2005. Many researchers has studied the environmental fate (Yates et al. 2003). Kobara (Kobara 2005, Kobara et al. 2001) estimated atmospheric concentrations of methyl bromide alternatives in the Kanto area by AIST-ADMER (Atmospheric Dispersion Model for Exposure and Risk Assessment) developed by National Institute of Advanced Industrial Science and Technology.

Other studies on pesticide exposure are also conducted in silage corn, (Uegaki et al. 2004), spinach (Eun et al. 2001) and domestic animals (Gurge et al. 2004, Gurge et al. 2005).

**APPROACHES TO PESTICIDE RESIDUE**

There are a lot of approaches to the problem of pesticide residues in crop and soils. The following approaches are arranged for risk assessment and risk management (mitigation) including some example in our institute, the National Institute for Agro-Environmental Sciences (NIAES), Japan.

**Air Pollution**

**Spray drift**

Risk assessment of spray drift is more advanced in EU and USA in comparison to Japan. Computer simulation model were used to predict the spray drift in aerial and ground spray. These simulation models are used to elucidate the buffer zone to the neighboring crop and residential area. Physical characteristics of spray droplet, spraying apparatus and meteorological parameters are input to these simulation models, but active ingredient and formulation of pesticides are not considered.


In Japan it is very difficult to place the buffer zone. Therefore, spray drift were prevented by application method and drift guard. Drift less nozzle, air curtain in boom spray, inter-row application, and electrostatic spray deposition (ESD) technique were developed and practically used in some cases. Small pore size net and crop such as sorghum are used as drift guards by surrounding target field.

Attention should be made on small droplet size particularly those smaller than fine particulate matter (PM2.5). PM2.5 is very small, has droplets in the air (size is less than 2.5 m in width) and able to go deeply into the lungs. Long-term exposure to PM2.5 is associated with increased chronic bronchitis, reduced lung function and increased mortality from lung cancer and heart disease. People with breathing and heart problems, children and the elderly may be particularly sensitive to PM2.5.

Kobara designed and developed the detection apparatus for fine droplet size in spraying pesticides. Spray pressure and temperature showed positive relation to number of droplets (Fig. 4).

**Vapor drift**

As mentioned before, vapor drift transfer from crop and soils to the atmosphere with gas and/or particle-adsorption state. Balance between gas and particle is greatly different among pesticides (herbicides). Pendimethalin and trifluralin were in gas state. Alachlor and metolachlor were in particle state. Thiobencarb was detected in both states.

Several types of Multimedia Model (MMM) for global behavior of organic chemicals, such as pesticides and POPs, were developed in the world (Mackay 2001). Kobara and Nishimori are recently developing MMM for pesticides and POPs (Kobara et al. 2005; Kobara et al. 2006; and Nishimori et al. 2006). Most of MMM are fugacity model, which is closely related to the principle of pressure. The differentiations of this model in comparison to the conventional models are as follows:

- Target chemicals are expanded to polar and ion chemicals.
- Temperature is included as a parameter, this largely affect half-life and movement.
- Application method of pesticides is considered.
Nine media are considered, including paddy field, rice growth and salt concentration in the oceans. Relative assessment

Quantitative Structure-Activity and Structure- Property Relationship (QSAR/QSPR) secure accuracy of parameters.

The target status is Level IV, non-equilibrium and non-stationary. Kobara et al. (1999) developed the plastic film to prevent methyl bromide emission to the atmosphere. The film is composed of gas-barrier layer, TiO2 photocatalytic layer and support layer (Fig. 5). Then, Methyl bromide was dramatically reduced with this film without any vapor.

Soil Residue

Dioxin concentrations were analyzed in preserved arable land. Soils were periodically collected from 1960 to 2002. Its concentration increased in the 1960s till 1970s and eventually decreased. The results of principal component analysis and chemical mass balance based on functional relationship analysis indicated that dioxin concentrations were increased due to the herbicide use. The examples are pentachlorophenol (PCP) and chlornitrofen (CNP), which included dioxin as impurities (Fig. 6). The half-lives of dioxins in the paddy soils were estimated to be 10 to 20 years and the dissipation trends are “hockey-stick” curve, i.e.
quick reduction in the first 10 years, and slow reduction in the later years (Seike and Otani, 2004; Seike et al. 2005; and Seike et al. 2007). Therefore, Monitored Natural Attenuation (MNA) is difficult to be introduced in POPs contaminated soils.

Enantiomeric ratio of chiral pesticides is effective in analyzing the environmental behavior (Hegeman et al. 2002). Since physicochemical and/or biological properties are different among optical isomers. Thus, contamination source can be assumed by analyzing enantiomeric ratio in soils among different depth and sites.

There are three types of on-site remediation methods; 1) phytoremediation by using plants, 2) bioremediation by using microbe and 3) chemical remediation. The uptake of drins were particularly high in Cucurbita genera, and no other crops can absorb them by roots (Otani et al. 2006; and Otani et al. 2007). Otani and Seike (2006)
examined the effect of grafting by pumpkin as rootstock on drins (dieldrin and endrin) uptake from soil into cucumber plants. The results indicated that drin concentrations in the grafted plants were influenced mainly by rootstock varieties (Fig. 7, Otani and Seike 2006). This remediation method can be applied not only to drins but also to other POPs (dioxins and heptachlor).

Bioremediation is effective for on-site remediation of pesticides and POPs. Takagi et al. found the bacteria, which degraded triazine herbicides. They produced bacterial consortia that would completely degrade methylthio- and chloro-triazines. Then they constructed a charcoal material containing these consortia (Fig. 8). Consequently, triazine contamination of the subsoil, river water, and groundwater could be minimized (Fujii et al. 2006; Harada et al. 2006; and Iwasaki et al. 2006). This idea can be applied to the other pesticides including POPs.

Chemical remediation is useful in single or in combination with the above remediation methods. However, details are not mentioned here.

**Water Contamination**

Computer simulation models for pesticide behavior in paddy-river system were developed in Japan. They were PADDY (Inao and Kitamura 1999; Inao et al. 2001; Inao et al. 2003), PCPF (Tournebize et al. 2006; Vu et al. 2006; Watanabe and Takagi, 2000a/2000b; Watanabe et al. 2006), and RICEWQ (Williams et al. 1996) in Europe. They were useful tools to prevent pesticide contamination in drainage canal and river. PADDY model accurately simulated the pesticide behavior in paddy field (Fig. 9, Inao and Kitamura 1999). It will enable the prediction of the required water holding periods to avoid excess amount of pesticide runoff from the paddy outlet. They are now developing the model, which can simulate not only parent ingredient but also the metabolites and the optical isomers. Watanabe et al. also improved their model in order to simulate the required foot path height by using originally developed compact lysimeter.

In the viewpoint of ecotoxicology, Ishihara et al. developed an easy detection method of herbicide susceptibility of native colonies of diatoms. These are the dominant producer organisms in rivers of Japan. Diatom growth was measured by absorbance of chlorophyll a, and growth inhibition was calculated between 24 and 96 h after application of the herbicide.

A good correlation was observed in the 50% effective concentration (EC50) values of dimethametryn between the native colonies and
the cumulative values of isolated single species (Fig. 10). Large difference in susceptibility was observed between upper and middle reaches of stream, where paddy fields either exist or not in nearby fields.

**Crop Residue**

Approaches for crop residue problem were complicated. The reasons are first there are many different ways of pesticide exposure as mentioned above. For example, cucumber absorbs dioxins via soil while other plants are exposed in a different way. Gramineous plants were contaminated due to high concentration of dioxin in the atmosphere and its isomer profile (Fig. 11, Uegaki et al. 2005; and Uegaki et al. 2006).

Second, pesticide transport to the edible parts depends upon crop and pesticide combination. Even though certain amounts of pesticides were absorbed from roots, almost no residues were detected in seeds when there is a strong barrier between roots and shoots.

Third reason was because pesticides were metabolized not only in soil but also in

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**Fig. 9.** Comparison between calculated and measured molinate concentration in (a) paddy water and (b) soil.

Source: Inao and Kitamura, 1999

Note: (a) calculated (Solid line) and measured (●) value, (b) calculated (Solid line = 0-2 cm, broken line = 2-4 cm) and measured (● = 0-2 cm, △ = 2-4 cm)

**Fig. 10.** Comparison of acute toxicity of dimethametryn to native diatom colonies in upper and middle reaches of streams.

Source: NIAES Annual Report 2006
crop. Metabolism depends upon crop and pesticide combination as well as transportation. Pesticides were metabolized in plants in two major steps, the first phase reactions and second phase reactions, including mammals. The first phase reactions are oxidation, reduction and hydrolysis by P450, esterase and so forth. The second phase reactions are composed of several types of conjugations by glutathione-S-transferase (GST) and so forth. Some pesticide combinations antagonistically inhibit these enzymatic activities, such as piperonyl butioxide (PBO) against P450, and organochlorines or carbamates against GST or esterase.

Pesticide registration in minor crops is a social problem in Japan. There are more than 400 minor crops in Japan, although it was only 0.9% of total diet. It is difficult to register each pesticide to each minor crop. The conduct of crop residue trials is time and labor consuming and the pesticide companies cannot afford the registration costs. About 120 minor crops were categorized to 11 groups in order to make the registration efficient. It was required that for each pesticide residue trial it should be with two crops. However, there are more than 200 minor crops, which could not be categorized in these 11 groups. In trying to estimate pesticide residue by harvesting crops based on initially attached pesticide to the crop, a good correlation was observed in pesticide residues among tested minor crops within the family level (Fig. 12).

- **Cucurbitaceae**: cucumber, *Momordica charantia* L. (“Nigauri”), zucchini
- **Umbelliferae (“Seri”)**: 15 crops, such as celery, parsley
- **Lamiaceae (“Shiso”)**: 17 crops, such as perilla, basil, rosemary etc.
- **Minor gramineae**: foxtail millet, barnyard grass and millet (*Panicum miliaceum* L.)

**FUTURE PROSPECTS**

The 11th IUPAC International Congress of Pesticide Chemistry was held in August 6-11 at Kobe, Japan (Ohkawa *et al.* 2007). Here are several hints and approaches which maybe used as reference for future prospects.

Integrated risk assessment to human and natural ecosystem is the most remarkable issue
There are many interactions not only in living things but also in the environment such as genetically, biochemically, biologically, physiologically and chemically. They negatively and positively affect human and environment. These interactions are too complex to clarify. The idea of grouping chemicals based on their properties is rising now (Fig. 13).

Ecological risk assessment in arid and semiarid ecosystem will come soon for pesticide registration (Markwiese et al. 2001). This ecosystem is called “upland” against paddy field and/or inland water. OECD had recently set several test guidelines for acute toxicity of living things in upland. However, upland conditions varied more than paddy or inland water, due to the change of soil moisture and wide range of living things inhabiting there (birds in the sky and earthworm in the soil). Therefore risk assessment is quite difficult to perform for the ecosystems with upland condition.

Ecological risk assessment on long-term effect is also important to clearly understand the adverse effect of pesticides to the ecosystem (Newman et al. 2006). Recovery is the most important key word, and the test guideline should be newly developed to compensate conventional acute toxicity tests. Another important keyword is time. It means that each living thing has their own life cycle and sensitivity to pesticides are largely different among ages. Pesticides temporally (not continuously) contaminate the environment. Therefore, timing between their life cycles and pesticide contamination will affect the intensity of adverse effect to the population. They enable to reduce safety factors for the ecological risk assessment.

Cost benefit analysis should also be done. The relationship between lasting effect and persistence of pesticides in soil had been studied in the past (Rajagopal 1984). Furthermore, pesticides are essential tools in agriculture. However, they have their own “pros (merit)” and “cons (demerit)”, for biology, ecology and economy. Therefore, these points should be taken into consideration to understand and assess the pesticide use.

Approaches to the problem on pesticide residues in crop and soils are very complex it
involves piles of research for issues to be tackled. A single researcher or one country cannot address these issues. Thus, further cooperation among countries and individuals by exchanging information and technology is needed to solve them effectively.

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