

Topic 2.6

Release of pesticides into the environment and initial concentrations in soil, water, and plants*

K. D. Racke

Dow AgroSciences, 9330 Zionsville Road, Bldg. 308, Indianapolis, IN 46268, USA

Abstract: Considerable information exists as to the initial concentrations of pesticide residues to be expected in soils, plants, and water. Empirical or theoretical models have been developed for incorporating this data into exposure assessments for humans as well as terrestrial and aquatic wildlife. In addition, monitoring data exists for many older products, especially with respect to typical concentrations observed in food commodities for human consumption and in surface and ground waters. Estimated and observed concentrations of pesticides in these matrices have been routinely employed for more than 30 years in assessing the potential impacts of pesticides on a variety of biologically relevant endpoints. The same data will also prove useful for exposure assessments of endocrine active substances. There are some additional research needs, however. First, further research and development is needed to ensure that estimation and monitoring methods for pesticide concentrations in soil, water, and food are applicable and utilized for all important and relevant cultural, agronomic, and environmental conditions. This is especially true with respect to developing countries and tropical climates, which are often disproportionately ignored in favor of developing countries and temperate climates. Second, methodologies for collection of monitoring data and generation of modeled estimates for pesticide residues in soil, water, and food need to be carefully designed with the requirements of higher-tier, probabilistic exposure assessments in view. Although worst-case, point estimates or analyses may be useful for screening-level assessments, advanced assessments targeted at addressing the likelihood of biologically relevant exposures are urgently required by scientists and regulatory authorities for reaching sound risk assessment and management decisions.

INTRODUCTION

Pesticides are chemicals used to manage pest organisms in both agricultural and nonagricultural situations. By definition, a pesticide is a “substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood, wood products or animal feedstuffs, or which may be administered to animals for the control of insects, mites/spider mites or other pests in or on their bodies” [1]. Although most attention for pesticides is generally directed at the active ingredients they contain (i.e., pesticidal), formulated pesticide products also contain a variety of so-called “inert ingredients” (i.e., nonpesticidal) intended to assist with such properties as handling, stability, de-

*Report from a SCOPE/IUPAC project: Implication of Endocrine Active Substances for Human and Wildlife (J. Miyamoto and J. Burger, editors). Other reports are published in this issue, *Pure Appl. Chem.* **75**, 1617–2615 (2003).

livery, application, and crop safety. Although abundant information is widely available on the use, properties, and behavior of active ingredients, the content and identity of inert ingredients is generally considered proprietary, trade secret information. Therefore, the primary focus of this paper will be on pesticidal active ingredients.

Government authorities involved in regulating the human safety aspects of chemical exposures are in the early stages of developing testing and evaluation criteria for endocrine active substances (EASs). Major programs are currently being developed in a number of regions including Europe [2], Japan [3], and the United States [4,5]. Pesticide products are some of the most widely tested chemicals with respect to toxicological hazard evaluation (e.g., multigeneration, developmental, and reproductive toxicology testing) and human health risk assessment (e.g., dietary, occupational). The exceptions to this rule are natural products and biochemicals (e.g., azadirachtin, rotenone, pyrethrum), for which some regulatory authorities have granted authorizations in the absence of availability of the same level of extensive testing. Although the popular literature and the Internet are replete with listings of pesticides and other chemicals “known” or “suspected” of causing endocrine disruption (many lists are merely compilations or modifications of earlier lists), uniform criteria for classifying products with respect to endocrine activity and the human or wildlife health risks they may pose have yet to be developed by regulatory authorities. The class of pesticides which contains several of the more widely recognized EASs is the chlorinated hydrocarbons (e.g., DDT), of which the most highly persistent members are in the process of being phased out by most national authorities. Regulatory authorities are in the early stages of developing testing and evaluation processes for endocrine-disrupting pesticides, and in some cases, prioritized listings of pesticides are being developed for purposes of screening and review [2,5].

Rather than narrow discussion to any one or two particular groups of pesticides, the focus of this paper will be on a review of general principles and considerations related to the environmental release of pesticides. Particular emphasis will be placed on crop protection products, for which both human and environmental risk assessment considerations are highly relevant. A general introduction of the major types and classes of pesticide products will be followed by discussion of sources of environmental entry. Summary information on initial concentrations of pesticides in environmental matrices will be presented, including residues that may be present in soil, water, target crops, and harvested food commodities. Finally, research needs related to availability of reliable estimates of pesticide environmental exposure levels and their appropriate use via the risk assessment paradigm will be presented.

PESTICIDES AND ROUTES OF ENVIRONMENTAL ENTRY

Pesticide classes and trends

Major types of pesticides include herbicides, insecticides, fungicides, and biocides (e.g., bactericides, algicides, slimicides). The number of existing active ingredients currently employed as pesticides is quite large (approx. 1000), and the great majority have been subject to extensive toxicological and environmental testing as part of government registration processes. Examples of major classes of existing products include organophosphate, pyrethroid, and neonicotinoid insecticides, phenoxy, dinitroaniline, and sulfonamide herbicides, and dithiocarbamate and strobilurin fungicides.

There has been a general trend during the past 30–40 years toward introduction of products with lower application rates, decreased environmental persistence, and reduced nontarget organism toxicity. For example, whereas the average use rate for chlorinated hydrocarbon insecticides was estimated at 3 kg/ha, more recently introduced pyrethroid or neonicotinoid insecticides may be applied at 0.01 to 0.1 kg/ha [6]. Similar trends exist also for herbicides and fungicides, which for many crop uses had shifted from kg/ha in the 1950s to g/ha by the 1990s. As an example of this trend, Table 1 lists major classes of insecticide products along with their period of significant introductions and typical field use rates. Some of the trend toward lower-use rate and reduced impact products has been driven by more

stringent testing criteria and increasing regulatory hurdles for new products. The U.S. EPA reduced risk pesticide program, which since the early 1990s has provided fast-track evaluation and approval for products demonstrating lower potential human and environmental impacts than currently available alternatives, is a different type of initiative nurturing this trend [7].

Table 1 Periods of major insecticide product introductions and typical use rates (adapted from [6]).

| Insecticide class | Major introductions | Typical use rate (kg/ha) |
|-------------------------|---------------------|--------------------------|
| Arsenical | 1890–1940 | 4.00–60.00 |
| Chlorinated hydrocarbon | 1939–1956 | 1.00–4.00 |
| Organophosphorus | 1946–1986 | 0.50–2.00 |
| Carbamate | 1957–1984 | 0.50–2.00 |
| Pyrethroid | 1973–1992 | 0.01–0.20 |
| Benzoylurea | 1972–2002 | 0.01–0.05 |
| Neonicotinoid | 1990–2001+ | 0.01–0.10 |
| Phenylpyrazole | 1992–2001+ | 0.10–0.15 |

In contrast to active ingredients, the pool of inert formulation components is significantly larger (>2500), and there have been relatively fewer and less detailed toxicological or environmental studies generated. Examples of classes of inert formulation components include carrier solvents, emulsifiers, antifoamers, and preservatives [8]. Some inert ingredients, such as alkyl phenol ethoxylates, have been implicated as potential EASs [4]. As opposed to active ingredients, which may comprise from <0.1 to 50 % or more of the pesticide product on a wt/wt basis, inert ingredients generally form the bulk of formulated product. As with active ingredients, industrial development efforts and regulatory trends have been aimed toward introduction of less hazardous (e.g., low flammability) and more environmentally benign inert ingredients [9].

Sources of environmental entry

Pesticides are employed for pest management programs in both agricultural and nonagricultural settings. Agricultural pest management relies most heavily upon herbicides, with significant use of insecticides and fungicides in certain cropping situations. Row crop situations in particular (cereals, cotton, maize, soybean, rice) account for the bulk of pesticide applications on a yearly basis, with fruit and vegetable crops also important avenues for pesticide use. Summaries of world agricultural pesticide use by type of pesticide and crop group are listed in Table 2.

Table 2 World pesticide usage by class and crop (adapted from [10,11]).

| World pesticide use by type | | World pesticide use by crop | |
|-----------------------------|-----------------------|-----------------------------|--------|
| Herbicides | 10.2×10^5 MT | Fruits and vegetables | 25.0 % |
| Insecticides | 6.7×10^5 MT | Cereals | 15.6 % |
| Fungicides | 2.5×10^5 MT | Maize | 14.2 % |
| Other | 6.5×10^5 MT | Soybeans | 10.9 % |
| | | Rice | 8.8 % |
| | | Cotton | 7.9 % |

Intentional placement of pesticides into agricultural environments occurs by a variety of application methods including air and ground boom spraying. The highest initial concentrations of pesticides are generally present in plant foliage, soil, and water to which direct applications are made. Relatively

few pesticide applications are made directly and exclusively to the target pest, and most application methods rely on application of enough pesticide to the environment so that exposure to the pest species reaches efficacious levels. Estimates for some scenarios indicate that less than 0.1 % of applied materials ever do so [12]. A recent and more precisely targeted method of pesticide application involves the use of transgenic crop plants, which have been engineered so as to synthesize insecticidal active ingredients or proteins within their tissues [13].

Unintentional entry of pesticides into the agricultural environment is associated with transport and offtarget deposition during or following application. For example, during spray application drift of airborne particles and/or volatilized pesticide to adjacent areas may occur. A literature survey revealed median offsite deposition of aerially applied pesticide at 30, 60, and 120 meters of 5, 2, and 0.8 % of the material, respectively [14]. Recent testing by the industry Spray Drift Task Force has confirmed levels of offsite drift from aerial and ground application equipment may be significant without appropriate management practices [15]. In addition, moving water may transport pesticides from treated areas to ground water via leaching or surface water via run-off [16]. The magnitude of transport to water may be fairly limited, but detection of trace quantities is made fairly routinely. It has been estimated that less than 0.5 % of applied pesticide may be lost from treated areas via surface run-off; losses of persistent chlorinated hydrocarbon pesticides, however, may be nearly twice this level [16]. Finally, inadvertent entry of pesticides into the environment may occur via accidental spills onto soil or into water bodies or via contamination associated with improper waste handling and disposal.

Nonagricultural use of pesticides may also represent significant sources of entry to the environment [17]. In the urban environment, significant pesticide uses include applications for turf and ornamental pests and for termite control. Aquatic weed management in lakes and recreational waters may involve direct application of herbicides to surface waters. Vector control programs rely in part on pesticide application to both surface waters and terrestrial environments to control insect larvae and adults, respectively, which may transmit diseases. Nonagricultural use of pesticides in the United States, for example, has been estimated to account for approximately 25 % of pesticide use by volume [10].

PESTICIDE CONCENTRATIONS IN THE ENVIRONMENT

Uses and sources of information

Major uses of data related to pesticide concentrations in environmental matrices include conduct of risk assessment, regulatory evaluation for product approval or reapproval, and regulatory compliance evaluation. The risk assessment process underlies most uses of this data, and it involves an evaluation of the likelihood of an adverse effect in an individual or population in light of known properties of hazard (effects) and estimated or actual exposure (magnitude, frequency, duration). Generally, the risk assessment process involves comparing some biological endpoint (e.g., NOEL, NOEC, NOAEL) with individual values or distributions of data related to pesticide concentration or intake. These evaluations can be focused on acute, short-term, or chronic biological endpoints, and thus different types of exposure value may need to be available.

For new pesticide products, environmental concentrations and potential exposures are most commonly estimated from laboratory and highly controlled field studies by use of empirical or mechanistic models. These data are generated by pesticide manufacturers and affiliated laboratories, and submitted to regulatory authorities for purposes of new product evaluation and approval. For existing pesticide products, in addition to modeled estimates there may be actual monitoring data available for various environmental matrices. Such monitoring data may be generated by manufacturers as well as by universities and government institutes. Routine environmental monitoring data is most widely available for human foods. Data on pesticide concentrations in raw surface and groundwater are also becoming more widely available, although monitoring of finished drinking water is still relatively difficult to obtain. Comprehensive data on pesticide residues in soils, sediments, and biota are not generally available. On

a geographic basis, plentiful and reliable monitoring data is available only in some of the more highly developed countries of North America (e.g., U.S.), Europe (e.g., UK, Germany), and the Pacific (e.g., Australia, Japan). The bulk of the world's human population lives in countries in which monitoring data is sparse, unreliable, and/or nonexistent.

It should be pointed out that estimates or measurements of pesticide concentrations in environmental matrices are useful for a wide variety of human and ecological risk assessment processes and are not restricted with respect to endpoints of concern. Thus, the duration of exposure associated with a potential effect of interest (e.g., acute, short-term, chronic) is far more important than the type of effect (e.g., neurological damage, cancer, reproductive impairment, endocrine disruption) with respect to discrimination of environmental concentration data.

Pesticide concentrations in soil

Significant agricultural soil concentrations may result from either direct application to soil or drift and wash-off from foliar application. Depending on the rate employed, direct soil application may result in initial residues of less than 0.05 mg/kg to more than 10 mg/kg [18]. A common assumption for initial pesticide concentration in surficial (0–15 cm) soil is that it is approximately one-half that of the application rate (note: assumes 0.4 ha of 0–15 cm soil with a bulk density of 1.5 g/ml has a weight of 908 000 kg). For example, application of 1 kg (active ingredient) per hectare would result in approximately 0.5 mg/kg of initial pesticide concentration. A summary evaluation of initial soil pesticide concentrations from 184 field studies reported that measured concentrations averaged 74.9 % of the theoretical and were highly variable (SD = 43.2 %) [18]. Selected results are also summarized in Fig. 1. It should also be noted that a high level of variability is often observed in pesticide soil concentration even within a single agricultural field.

Some nonagricultural pesticide use scenarios may result in significantly higher initial pesticide concentrations. For example, soil drench barriers for termite protection around houses and other wooden structures may require initial deposit of 500 mg/kg or more [19,20]. Soil pesticide concentrations resulting from accidental spills or waste contamination are often very much higher than those concentrations resulting from intentional use, with deposits of 1000 mg/kg or higher not uncommon [21].

Pesticide concentrations in soil for risk assessment purposes are most often drawn from empirical estimates or limited numbers of field studies. Since most contemporary pesticides dissipate from the soil relatively quickly through various degradative or transport processes, initial soil concentrations may

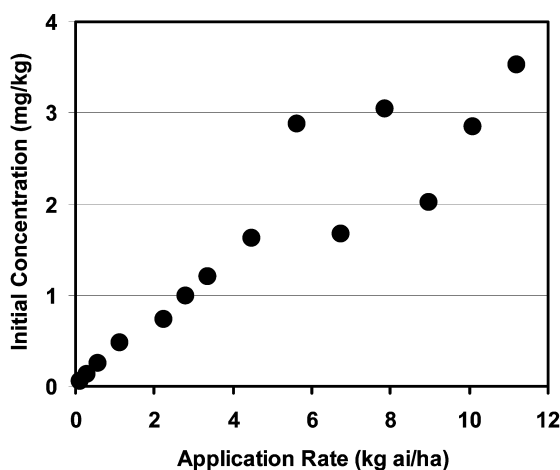


Fig. 1 Initial pesticide concentrations in 0–15 cm soil (adapted from [18]).

not be extremely useful for exposure evaluations. The most direct use may be for evaluation of effects to soil-dwelling arthropods or annelids. Indirectly, soil concentrations are often employed in a number of models that estimate crop plant uptake and run-off or leaching mobility with water. These models are most useful when the dissipation rate of pesticide is considered. Problems with respect to information on pesticide concentrations in soil include a high degree of spatial and temporal variability, accurate prediction of dissipation rate in light of variable environmental conditions, lack of routine monitoring data for most soils, and near total lack of pesticide residue data from tropical soils [22].

Pesticide concentrations in water

Surface water concentrations of pesticides are highest for those use patterns associated with direct application to water bodies such as for aquatic weed control or insect larvae management. For example, initial herbicide concentrations of 0.2 to 3 mg/l are generally targeted for aquatic weed control [23]. Indirect or unintentional entry of pesticides into water generally results in much lower concentrations, in the range of 0.001–0.01 mg/l or lower [24]. Such entry may occur due to accidental overspray or off-target spray drift, or to surface run-off or leaching transport from a treated agricultural field.

Regarding offtarget drift of pesticide spray and deposition on nearby surface waters, initial concentrations are most commonly estimated from empirical or theoretical models. For example, spray drift tables of deposition with increasing distance from the edge of a treated field have been assembled based on experimental observations [25,26]. Example results of using such an approach to predict initial pesticide concentrations in water are presented in Table 3. Various spray drift models are also employed to predict surface water deposition and initial concentration under various application scenarios (e.g., ground boom, airblast sprayer, aerial application) and under different environmental conditions [14]. A key challenge for this type of estimation is the extreme variability in observed deposition of pesticide spray based on factors related to geography (e.g., size of field in relation to water body, distance of water from treated field), environmental conditions (e.g., wind direction, windspeed, humidity), and application parameters (e.g., sprayer type, nozzle type, formulation viscosity, spray boom height).

Table 3 Predicted offtarget spray drift as percent of applied and initial concentrations in water at the 95th percentile (assumes 1 kg ai/ha application rate and 1 m water depth) (adapted from [25,26]).

| Distance from edge of field (m) | Vineyard | | Orchard | | Vegetable | |
|---------------------------------|-----------|--------------|----------|-------------|-----------|--------------|
| 5 | 1.6–5.0 % | 1.6–5.0 µg/l | 10–20 % | 10–20 µg/l | 0.6–5 % | 0.6–5 µg/l |
| 10 | 0.4–1.5 % | 0.4–1.5 µg/l | 4.5–11 % | 4.5–11 µg/l | 0.4–1.5 % | 0.4–1.5 µg/l |
| 20 | 0.1–0.4 % | 0.1–0.4 µg/l | 1.5–4 % | 1.5–4 µg/l | 0.1–0.4 % | 0.1–0.4 µg/l |
| 30 | 0.1–0.2 % | 0.1–0.2 µg/l | 0.6–2 % | 0.6–2 µg/l | 0.1–0.2 % | 0.1–0.2 µg/l |

Surface or ground water pesticide concentrations may be measured experimentally in lysimeter or field studies. For groundwater concentration estimates, lysimeter studies in which small soil monoliths (0.5–2 m diameter) are maintained under actual or simulated environmental conditions have been employed. Prospective field monitoring studies, in which groundwater is sampled from within the soil profile or from well stations placed at various depths have also been commonly employed. For surface water evaluations, small plot (0.1–1 ha) or watershed-scale, site-specific studies have been used to measure pesticide concentrations in run-off water and sediments. These experimental approaches are useful for generating realistic data under a small set of experimental conditions, but are highly costly and cannot easily cover the range of environmental, geographic, and climatic variables present on a landscape-scale over time. For these reasons, theoretical surface run-off or groundwater leaching models are commonly employed to provide estimates of initial pesticide concentrations [27,28], and probabilistic approaches can accommodate the variability inherent for key input parameters.

In addition to site-specific field studies or modeling, large-scale surface or groundwater monitoring has been employed to a limited extent for assessing the concentrations and frequency of pesticide detections. For example, the National Water Quality Assessment Program (NAWQA) has been ongoing in the United States for the past 10 years and has involved analysis of thousands of samples across both agricultural and urban streams and groundwaters for a large number of pesticides and metabolites [29,30]. Some summary data is presented in Table 4 with respect to frequency of detection and 95th percentile water concentrations of some representative herbicides and insecticides. In general, these results indicate that the greatest frequency and highest concentrations are observed for several widely used, highly water-soluble, and loosely sorbed herbicides.

Table 4 USGS National stream and groundwater monitoring results for several common pesticides (1992–1998) (adapted from [29,30]).

| Pesticide | Detection limit (mg/l) | Stream residue frequency | 95 th Percentile stream conc. (mg/l) | Groundwater residue frequency | 95 th Percentile groundwater conc. (mg/l) |
|-----------|------------------------|--------------------------|---|-------------------------------|--|
| HERB-1 | 0.002 | 39.0 | 0.21 | 2.8 | 0.50 |
| HERB-2 | 0.001 | 85.0 | 3.51 | 44.0 | 3.00 |
| HERB-3 | 0.005 | 59.0 | 0.22 | 12.0 | 1.30 |
| HERB-4 | 0.15 | 15.0 | 0.37 | 0.6 | 4.54 |
| CHL-1 | 0.006 | 5.5 | 0.00 | 3.6 | 0.00 |
| CHL-2 | 0.001 | 5.5 | 0.00 | 1.1 | 0.05 |
| CHL-3 | 0.004 | 0.6 | <0.004 | 0.0 | <0.004 |
| OP-1 | 0.004 | 17.0 | 0.02 | 0.9 | 0.02 |
| OP-1 | 0.002 | 15.0 | 0.02 | 0.5 | 0.07 |
| OP-2 | 0.005 | 6.0 | 0.01 | 0.3 | 0.00 |
| OP-3 | 0.001 | 1.9 | <0.001 | 0.4 | 0.18 |
| CB-1 | 0.003 | 9.2 | 0.01 | 0.4 | 0.02 |
| CB-2 | 0.003 | 12.0 | 0.06 | 1.6 | 1.30 |
| CB-3 | 0.017 | 1.2 | <0.017 | 0.1 | 0.00 |
| PYR | 0.005 | 0.3 | <0.005 | 0.0 | 0.00 |

*CHL = chlorinated hydrocarbon; OP = organophosphorus; CB = carbamate; PYR = pyrethroid; OTH = other

Problems with respect to usefulness of monitoring information on pesticide concentrations in water include a high degree of spatial and temporal variability, lack of availability of results for newly introduced pesticides, extremely high cost, and limited availability of data on a geographic basis.

Pesticide concentrations in target plants

Following many types of agricultural and urban (e.g., turfgrass) pesticide applications, plant foliage (crop or weed) often contains the highest initial concentration of pesticide residues among various environmental matrices. Depending on such factors as plant type and growth stage, application method, spray volume, and formulation characteristics, agricultural crops may intercept from 10 % to more than 80 % of the applied active ingredient [31,32]. For purposes of environmental modeling assessments, a set of harmonized foliar interception factors by crop and growth stage has been suggested, and some examples are listed in Table 5.

With respect to initial concentrations of pesticides in various plant components, in addition to percent foliar interception the application rate of the pesticide (kg ai/ha) is extremely important. Measurements indicate that, regardless of active ingredient, initial concentrations in plant components scale directly with application rate [33]. Initial concentrations of pesticides, assuming a 1 kg ai/ha ap-

plication rate, may range from 1.5–7 mg/kg in fruit to 35–125 mg/kg in leaves. Based on a large series of field trials conducted with various insecticides, herbicides, and fungicides, an empirical distribution for maximum and typical initial concentrations in various plant components was developed during the early 1970s. The so-called Hoerger–Kenaga nomogram, with some slight modification, has been routinely employed by some regulatory authorities for wildlife exposure and risk assessments [33,34]. A summary of estimated mean and maximum pesticide concentrations in various types of plant components upon initial application is found in Table 6.

Table 5 Examples of harmonized foliar interception factors for various crops and stages (adapted from [32]).

| Crop | Growth phase % | Foliar interception |
|---------------|------------------------------|---------------------|
| Beans | Flowering | 70 % |
| Cabbage | Flowering | 90 % |
| Cereals | Tillering | 50 % |
| Onions | Flowering | 40 % |
| Pasture grass | All stages | 40 % |
| Pome fruit | Bloom/leaf development | 40 % |
| Rice | Flowering, fruit development | 70 % |
| Stone fruit | Dormant | 20 % |
| Stone fruit | Bloom/leaf development | 40 % |
| Stone fruit | Full foliage | 80 % |
| Vines | Leaf development | 30 % |
| Vines | Inflorescence emergence | 50 % |
| Vines | Flowering/fruitletting | 80 % |
| Vines | Senescence | 60 % |

Table 6 Estimated mean and maximum pesticide concentration on crop groups immediately following application of 1 kg ai/ha (adapted from [33,34]).

| Plant Category | Estimated mean concentration (mg/kg) | Field data mean \pm SD (mg/kg) | Estimated maximum concentration (mg/kg) | Estimated maximum concentration (mg/kg) |
|---------------------|--------------------------------------|----------------------------------|---|---|
| Short-range grass | 112 | 76 \pm 54 | 214 | 214 |
| Long grass | 82 | 32 \pm 36 | 98 | 98 |
| Leaves, leafy crops | 31 | 31 \pm 40 | 112 | 112 |
| Forage legumes | 30 | 40 \pm 51 | 52 | 121 |
| Pods and seeds | 3 | 4 \pm 5 | 11 | 11 |
| Fruits | 1 | 5 \pm 9 | 6 | 13 |

Of critical importance from an environmental exposure standpoint are considerations related to dissipation of pesticide residues from plant parts due to such factors as degradation, volatilization, or wash-off. Many semivolatile or photolabile pesticides display dissipation half-lives of several hours to several days from exposed, foliar surfaces. For example, although Hoerger and Kenaga estimated typical initial concentrations of pesticide of 1.5–30 mg/kg, by six weeks after application these typical concentrations had decreased to <0.2 to 5 mg/kg [33].

Pesticide concentrations in harvested food commodities

Although generic estimates of pesticide residues in crop plants and weeds are often sufficient for assessment of wildlife exposure and risk, human dietary risk assessments have often relied upon more robust, product-specific residue data. Results of controlled field trials, in which maximum application rate/frequency and minimum preharvest intervals are employed, are relied upon by most regulatory authorities as well as the Codex Alimentarius Commission to establish maximum residue limits (MRLs) for pesticides in various agricultural commodities. For example, Table 7 lists established or proposed MRLs for a variety of insecticide products on selected food commodities [35].

Table 7 Examples of established or proposed Codex MRLs (mg/kg) for members of various insecticide classes (adapted from [35]).

| Compound class* | First JMPR** | Apple | Cabbage | Grape | Orange | Potato | Tomato | Wheat |
|-----------------|--------------|-------|---------|-------|--------|--------|--------|-------|
| CHL-1 | 1965 | 1 | 1 | 1 | 0.5 | 0.2 | 0.5 | 0.2 |
| CHL-2 | 1968 | | | 5 | 5 | | | |
| OP-1 | 1965 | 2 | | | | 0.05 | 1 | |
| OP-2 | 1965 | 0.3 | 2 | | | 0.01 | 0.5 | |
| OP-3 | 1965 | 1 | 2 | 1 | 2 | 0.05 | 2 | 0.2 |
| OP-4 | 1965 | 2 | 8 | 8 | 4 | | 3 | 0.5 |
| OP-5 | 1972 | 1 | 1 | 1 | 1 | 0.05 | 0.5 | 0.5 |
| OP-6 | 1974 | 2 | 2 | | 2 | 0.05 | 1 | 5 |
| CB-1 | 1965 | 5 | 5 | 5 | 7 | 0.2 | 5 | 2 |
| CB-2 | 1975 | 2 | 5 | 5 | 1 | 0.1 | 1 | 0.5 |
| CB-3 | 1979 | | | 0.2 | 0.2 | | | 0.02 |
| CB-4 | 1980 | 2 | | | 5 | 0.1 | 2 | |
| PYR-1 | 1979 | 2 | 3 | | | | 1 | 2 |
| PYR-2 | 1979 | 2 | 5 | 2 | | 0.05 | 1 | 2 |
| PYR-3 | 1980 | 0.1 | | 0.05 | 0.05 | 0.01 | 0.2 | 1 |
| PYR-4 | 1992 | | | | 0.05 | 0.05 | | 0.5 |
| OTH-1 | 1981 | 1 | 1 | 1 | 1 | | 1 | |
| OTH-2 | 1992 | 0.02 | | | 0.01 | 0.01 | 0.02 | |
| OTH-3 | 1996 | 1 | 5 | 2 | 2 | | 1 | |
| OTH-4 | 2000 | | 0.02 | | | 0.02 | | 0.002 |
| OTH-5 | 2001 | 0.1 | 2 | | 0.3 | 0.01 | 0.3 | |

*CHL = chlorinated hydrocarbon; OP = organophosphorus; CB = carbamate; PYR = pyrethroid; OTH = other

**1st evaluation by the FAO/WHO Joint Meeting on Pesticide Residues (JMPR)

Considerable monitoring of pesticide residues in foodstuffs also occurs through farmgate and market basket surveys [36–39]. Such monitoring data provide more realistic estimates for risk assessment purposes of the likely residues in the human diet. Examination of such data indicates that in many cases observed pesticide residue levels in consumed food are one to several orders of magnitude below maximum residue limits. As an example, α -endosulfan was detected in 43.7 % of cucumbers (322 out of 737 samples) in a U.S. survey, but the range of concentrations was 0.007–0.15 mg/kg as compared with an MRL of 2 mg/kg [37]. Even these values may be somewhat overpredictive of human consumption since research indicates that processing and cooking of foods may result in further decreases in residues due to dissipation or degradation [40]. Human dietary assessment methodologies for both chronic (lifetime) and acute (single-day) exposures have been well developed at the national and international level to make use of available residue trial and monitoring data [36,40].

DISCUSSION

Conclusions

Considerable information exists as to the initial concentrations of pesticide residues to be expected in soils, plants, and water. Empirical or theoretical models have been developed for incorporating this data into exposure assessments for humans as well as terrestrial and aquatic wildlife. In addition, monitoring data exists for many older products, especially with respect to typical concentrations observed in food commodities for human consumption and in surface and ground waters. Estimated and observed concentrations of pesticides in these matrices have been routinely employed for more than 30 years in assessing the potential impacts of pesticides on a variety of biologically relevant endpoints. The same data will also prove useful for exposure assessments of endocrine-disrupting substances.

There are some noteworthy problems, however, with the use of existing information on pesticide residues for exposure assessment purposes. One problem involves a lack of sufficient data for evaluation of all important and relevant cultural, agronomic, and environmental conditions. For example, whereas several of the countries with highly developed economies and agricultural systems (e.g., Australia, Japan, UK, USA) have plentiful data and calibrated models with respect to pesticide concentrations in key environmental matrices, many developing countries lack even the most rudimentary information or applicable models. Another problem involves the large degree of spatial variability that exists with respect to environmental concentrations of pesticides. Not only are concentrations of a given pesticide often orders of magnitude different depending on which soils or plants or waters are assayed, but even within a single field or a single fruit tree residue levels can vary dramatically. Finally, the temporal distribution of pesticide residues presents unique challenges for both monitoring and modeling evaluations. The concentration of a given pesticide should be viewed as a moving target, with factors related to transport and degradation ensuring that concentrations are in a constant state of flux. Although point estimates in time (e.g., initial concentrations) may provide suitable information for a tier I, screening level exposure evaluation, they are inadequate for the higher-tier (e.g., probabilistic) assessments that are necessary to answer questions related to the likelihood of an organism being exposed to a concentration of concern.

Research needs

- Recommendation 1: Further research and development is needed to ensure that estimation and monitoring methods for pesticide concentrations in soil, water, and food are applicable and utilized for all important and relevant cultural, agronomic, and environmental conditions. This is especially true with respect to developing countries and tropical climates, which are often disproportionately ignored in favor of developed countries and temperate climates.
- Recommendation 2: Methodologies for collection of monitoring data and generation of modeled estimates for pesticide residues in soil, water, and food need to be carefully designed with the requirements of higher-tier, probabilistic exposure assessments in view. Although worst-case, point estimates or analyses may be useful for screening-level assessments, advanced assessments targeted at addressing the *likelihood* of biologically relevant exposures are urgently required by scientists and regulatory authorities for reaching sound risk assessment and risk management decisions.

REFERENCES

1. P. T. Holland. *Pure Appl. Chem.* **68**, 1167–1193 (1996).
2. European Community. *Communication from the Commission to the Council and the European Parliament on the Implementation of the Community Strategy for Endocrine Disrupters*. p. 262, Brussels, Belgium (2001).
3. Japan Ministry of Health, Labor, and Welfare. *The Interim Risk Assessment Report by Review Committee Meeting of MHLW Regarding Hazards to Human Health of Endocrine Disrupting Chemicals*, Office of Chemical Safety, Pharmaceutical and Food Safety Bureau, Tokyo, Japan (2002).
4. U.S. National Research Council. *Hormonally Active Agents in the Environment*, National Academy of Sciences, National Academy Press, Washington, DC (1999).
5. U.S. Environmental Protection Agency. *U.S. Federal Register*, **67**, 79611–79629 (2002).
6. J. E. Casida and G. B. Quistad. *Ann. Rev. Entomol.* **43**, 1–16 (1998).
7. K. D. Racke. In *Chemistry of Crop Protection*, G. Voss and G. Ramos (Eds.), pp. 322–333, Wiley-VCH, Weinheim (2003).
8. U. S. Environmental Protection Agency. *List of Pesticide Product Inert Ingredients*. Washington, DC (1995).
9. T. S. Woods. In *Pesticide Chemistry and Bioscience: The Food-Environment Challenge*, G. T. Brooks and T. R. Roberts (Eds.), pp. 120–133, Royal Society of Chemistry, London (1999).
10. A. L. Aspelin and A. H. Grube. *Pesticides Industry Sales and Usage: 1996 and 1997 Market Estimates*, U.S. Environmental Protection Agency, 733-R-99-001, Washington, DC (1999).
11. Wood-Mackenzie. *Crop-Pesticide Sector Report* (1999).
12. D. Pimental and L. Levitan. *BioScience* **36**, 86–91 (1986).
13. A. D. Hammock, A. B. Inceoglu, W. Rajendra, J. R. Fuxa, N. Chejanovsky, D. Jarvis, T. N. Hanzlink. In *Pesticide Chemistry and Bioscience: The Food-Environment Challenge*, G. T. Brooks and T. R. Roberts (Eds.), pp. 73–99, Royal Society of Chemistry, London (1999).
14. S. L. Bird. In: *Agrochemical Environmental Fate: State of the Art*, M. L. Leng, E. M. K. Leovey, P. L. Zubkoff (Eds.). pp. 195–207, CRC/Lewis Press, Boca Raton, FL (1995).
15. Spray Drift Task Force. *A Summary of Aerial Application Studies*, Macon, Missouri (1997).
16. R. D. Wauchope. *J. Environ. Qual.* **7**, 459–472 (1978).
17. K. D. Racke. *Pesticides in Urban Environments: Fate and Significance*. American Chemical Society, Symposium Series No. 421, Washington, DC (1993).
18. R. S. McAllister. *Field Dissipation Studies: Zero-Time Recovery*, National Agricultural Chemicals Association, CL94-315.RSM, Washington, DC (1994).
19. K. D. Racke, D. D. Fontaine, R. N. Lubinski, J. R. Miller. *Pestic. Sci.* **42**, 43–51 (1994).
20. S. Baskaran, R. S. Kookana, R. Naidu. *Pestic. Sci.* **55**, 1222–1228 (1999).
21. A. S. Felsot, K. D. Racke, D. J. Hamilton. *Rev. Environ. Contam. Toxicol.* **177**, 123–200 (2003).
22. K. D. Racke, M. W. Skidmore, D. J. Hamilton, J. B. Unsworth, J. Miyamoto, S. Z. Cohen. *Pure Appl. Chem.* **69**, 1349–1371 (1997).
23. M. A. Ross and C. A. Lembi. *Applied Weed Science*, Macmillan, New York (1985).
24. R. D. Wauchope, D. B. Baker, K. Balu, H. Nelson. *Pesticides in Surface and Ground Water*, Council for Agricultural Science and Technology, Issue Paper No. 2, Ames, IA (1994).
25. H. J. Holterman, H. A. J. Porskamp, J. F. M. Huijsmans. *Modelling Spray Drift from Boom Sprayers*, Institute of Agricultural and Environmental Engineering (IMAG-DLO). Wageningen, The Netherlands (1994).
26. H. Ganzelmeier et al. *Studies on the spray drift of plant protection products*. Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft, Berlin, p. 305 (1995).
27. S. Z. Cohen, R. D. Wauchope, A. W. Klein, C. V. Eadsforth, R. Graney. *Pure Appl. Chem.* **67**, 2109–2148 (1995).

28. P. Adriaanse, R. Allen, V. Gouy, J. Hollis, J. Hosang, N. Jarvis, T. Jarvis, M. Klein, R. Layton, J. Linders, H. Schafer, L. Smeets, D. Yon. *Surface Water Models and EU Registration of Plant Protection Products: Final Report of the Work of the Regulatory Modelling Working Group on Surface Water Models of FOCUS*. 6476-VI-96 (1996).
29. A. W. Kolpin. *Pesticides in Ground Water: Summary Statistics, Results of the National Water Quality Assessment Program (NAWQA) 1992–1998*, U.S. Geological Survey, Washington, DC (2001).
30. J. Larson. *Pesticides in Streams: Summary Statistics, Results of the National Water Quality Assessment Program (NAWQA) 1992–1998*, U.S. Geological Survey, Washington, DC (2001).
31. J. A. R. Bates. *Pure Appl. Chem.* **62**, 337–350 (1990).
32. J. Linders, H. Mensink, G. Stephenson, D. Wauchope, K. Racke. *Pure Appl. Chem.* **72**, 2199–2218 (2000).
33. F. Hoerger, E. E. Kenaga. In *Environmental Quality and Safety: Chemistry, Toxicology, and Technology*, F. Coulston and F. Kort (Eds.), pp. 9–28, Georg Thieme, Stuttgart (1972).
34. S. Fletcher, J. E. Nellessen, T. G. Pflieger. *Environ. Toxicol. Chem.* **13**, 1383–1391 (1994).
35. Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, Codex Committee on Pesticide Residues, Document CX/PR 02/6, Rome, Italy (2002).
36. D. J. Hamilton, P. T. Holland, B. Ohlin, W. J. Murray, A. Ambrus, G. C. De Baptista, J. Kovacicová. *Pure Appl. Chem.* **69**, 1373–1410 (1997).
37. U.S. Department of Agriculture. *Pesticide Data Program: Annual Summary Calendar Year 2000*, USDA Agricultural Marketing Service, Washington DC (2002).
38. European Commission. *Monitoring of Pesticide Residues in Products of Plant Origin in the European Union, Norway, Iceland, and Liechtenstein: 2000 Report*, Health & Consumer Protection Directorate-General, SANCO/687/02 (2002).
39. Australia New Zealand Food Authority. *The Australian Market Basket Survey 1996*, Melbourne (1998).
40. D. Hamilton, A. Ambrus, R. Dieterle, A. Felsot, C. Harris, B. Petersen, K. Racke, S. Wong, R. Gonzalez, K. Tanaka, M. Earl, G. Roberts, R. Bhula. *Pest Manag. Sci.* (2003). In press.