

Current United States Department of Agriculture – Agricultural Research Service research on understanding agrochemical fate and transport to prevent and mitigate adverse environmental impacts^{†‡}

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Abstract: Environmentally and economically viable agriculture requires a variety of cultivation practices and pest management options as no one system will be appropriate for every situation. Agrochemicals are some of the many pest control tools used in an integrated approach to pest management. They are applied with the intent of maximizing efficacy while minimizing off-site movement; however, their judicious use demands a practical knowledge of their fate and effects in agricultural and natural ecosystems. Agrochemical distribution into environmental compartments is influenced by the physical and chemical properties of the agrochemical and environmental conditions, ie soil type and structure, and meteorological conditions. Agricultural Research Service (ARS) researchers working in the area of agrochemical fate have focused on accurately describing those processes that govern the transport, degradation and bioavailability of these chemicals under conditions reflecting actual agronomic practices. Results from ARS research concerning the environmental fate and effects of agrochemicals have led to the development of science-based management practices that will protect vulnerable areas of the ecosystem. The new challenge is to identify these vulnerable areas and the temporal and spatial variations prior to use of the chemical by predicting how it will behave in environmental matrices, and using that information, predict its transport and transformation within an air- or watershed. With the development of better predictive tools and GIS (Geographic Information System)-based modeling, the risks of agricultural management systems can be assessed at the watershed and basin levels, and management strategies can be identified that minimize negative environmental impacts.

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1 INTRODUCTION

Environmentally and economically viable agriculture requires a variety of cultivation practices and pest-management options as no one system will be appropriate for every situation. Agrochemicals are some of the many pest-control tools in an integrated approach to pest management. They are applied with the intent of maximizing efficacy while minimizing off-site movement; however, their judicious use demands a practical knowledge of their fate and effects in agricultural

and natural ecosystems. Agrochemical distribution into environmental compartments is influenced by the physical and chemical properties of the agrochemical and environmental conditions, ie soil type and structure, and meteorological conditions. ARS researchers working in the area of agrochemical fate have focused on accurately describing those processes that govern the transport, degradation and bioavailability of these chemicals under conditions reflecting actual agronomic practices. This information will be used

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to assess risks to wildlife and water quality, and it will be used to focus further mitigation efforts. Ultimately, results of ARS research will be used in the development of improved management strategies that not only reduce erosion and nutrient losses, but increase the effectiveness of agrochemicals, thus reducing overall pesticide usage.

2 MOLECULAR PROCESSES

2.1 Sorption

The degree and extent of availability of an agrochemical in the aqueous phase versus that which is bound to soil particles can influence its performance, resistance to degradation, and surface and sub-surface transport. Agrochemicals can have several possible sorption mechanisms due to the different physical and chemical properties of both the sorbate and the sorbent, such as functional groups, acid–base character, polarity and polarizability, charge distribution, water solubility, hydrophobicity, configuration and conformation. Strong physical and/or chemical affinity for a sorbate would render the compound less available for biodegradation and transformation.¹

2.1.1 Soil properties

The soil's capacity for the sorption of most agrochemicals increases with increasing organic carbon content.^{2,3} The nature of soil organic matter is distinctive to the environment in which it occurs, yet its structure remains elusive. Newer technologies are being utilized to define the quality and quantity of the humic substances. Nuclear magnetic resonance (NMR) and various multi-dimensional techniques have improved functional group assignments.⁴ Understanding the moieties of humic materials and their relationships to agrochemicals will provide insight to the overall fate of those chemicals.

For agrochemicals that contain a pH-dependent functional group, soil pH can affect sorption. Increased irreversible sorption of the insecticide imidacloprid was observed with decreasing soil pH, although organic carbon content was still the most important component affecting sorption.^{5,6} Sorption of the post-emergence herbicide acifluorfen, which contains a carboxylic acid moiety, increased with increasing soil carbon content, cation exchange capacity, and soil acidity (decreasing pH).⁷ At low pH more of the herbicide imazethapyr, an amphoteric compound (both acidic and basic moieties are present), was sorbed to soil than at high pH, but it was readily desorbed. This carryover was observed to cause injury to the subsequent crops of canola and sugarbeet.⁸ Soil moisture levels will also influence sorption, and in general, increased sorption is observed with increasing soil moisture content for the less polar agrochemicals.^{9,10}

2.1.2 Agrochemical structure

The type of chemical interactions are also determined by the structure of the agrochemical. Data obtained in

a series of NMR studies of metolachlor with organic matter surrogates suggested that acetamide pesticides can form weak hydrophobic interactions with some organic matter functionalities and more specific, stronger interactions with others. The non-aromatic sites were involved in forming specific interactions initially with the polar groups such as those of cellulose, chitin, and collagen while more non-specific interactions were formed with lignin.^{11–13} FT-IR study of the interaction of a series of chloroacetanilides with clays and/or humic substances indicated the possible formation of hydrogen bonds and charge-transfer complexes. Spatial arrangement of the side-chains affected the relative sorption and thus the reactivity of the functional groups to participate in these interactions.¹⁴

2.2 Transformation processes

Numerous studies exist that examine agrochemical fate in soil and water. Indigenous microbial communities are responsible for most of the transformations, although abiotic processes do occur. These reactions, such as hydrolytic or transition metal-mediated reactions, are dependent on the pesticide moieties and the chemistries of the soil components. The ability of organisms to metabolize agrochemicals is influenced by the availability of the agrochemical to the organism which, as discussed above, is in large part a function of the amount and structure of the organic matter, oxygen availability (which can be a function of) the degree of water saturation. Indigenous soil and water-borne micro-organisms that degrade agrochemicals can prevent agrochemical carryover to next growing season, leaching into the groundwater and volatilization into the atmosphere. Scientists often only measure the degradation rate of a pesticide without considering the products formed. An understanding of the chemical mechanisms involved in pesticide degradation is needed to evaluate the risk associated with wildlife exposure to degradation products.

2.2.1 Nucleophilic substitution and hydrolysis

Enhanced abiotic and biotic degradation of soil fumigants has been observed in soils to which organic amendments have been applied.¹⁵ Many soil fumigants that possess halogenated alkyl groups can undergo abiotic degradation via nucleophilic reaction. This reaction mechanism likely occurs in unamended soil (with nucleophilic groups on soil organic matter acting as the nucleophile) and is accelerated in soil treated with nucleophilic compounds such as thiosulfate compounds. Ammonium thiosulfate, a sulfur-type fertilizer, can rapidly transform certain fumigants into water-soluble products and reduce fumigant atmospheric emissions.¹⁶

Atrazine is readily dechlorinated via chemical, biological or photolytic hydrolysis, giving rise to hydroxyatrazine. Sorption to organic matter and pH extremes can enhance hydrolysis.¹⁷ The primary pathway for atrazine hydrolysis is biological.

Hydroxylated atrazine degradation products, which include hydroxyatrazine, N^4 -ethyl-2-hydroxy-1,3,5-triazine-4,6-diamine (OEAT), and N^4 -isopropyl-2-hydroxy-1,3,5-triazine-4,6-diamine (OIAT), were found to account for 60% of the total atrazine load in northern Missouri streams.^{18,19}

Degradation of agrochemicals can occur readily even in sterile soils. The resultant compounds can be adsorbed more strongly to soil than the parent as was observed with bentazone. Bentazone, with a pK_a of 3.2, is poorly sorbed except in very acidic soils. Abiotic degradation of bentazone results in several products including 2-aminobenzoic acid which readily sorbs to soils.²⁰

2.2.2 Isomerization

The applied isomeric ratio ($7\alpha:3\beta$) of the insecticide endosulfan is not conserved while cycling within various environmental compartments; α is the overwhelmingly predominant form in air while more β is seen in rain. Furthermore, isomerization of β -endosulfan to α -was noted in the volatilization of β -endosulfan from water which led to the re-examination of the structure of each of the isomers.²¹ The α -isomer was established unequivocally by X-ray crystallography as asymmetric, and additional investigations revealed a eutectic concentration of *ca* 63% α and 37% β .²² Computational chemistry demonstrated that the isomerization mechanism involved induction of asymmetry that is associated with changes in the sulfite conformation of the symmetrical β form. The structural and isomeric conversion data combined with the measured Henry's Law Constants ($\alpha:2.7 \times 10^{-3}$; $\beta:3.6 \times 10^{-4}$) and subcooled liquid water solubilities ($\alpha:3.7 \text{ mg litre}^{-1}$; $\beta:21 \text{ mg litre}^{-1}$) provided an explanation for the observed isomeric compartmentalization. That is, very little of the β -isomer would be expected to be in the air and that which is volatilized is readily removed by water droplets. Furthermore, the β -isomer would be much more prevalent in the soil and in runoff.²³

2.2.3 Photolysis

Environmental photolysis can proceed either by direct photolysis or by indirect photolysis whereby another matrix component absorbs the solar light energy and then interacts with the agrochemical causing decomposition via energy transfer (sensitization), direct electron transfer or other free radical processes. Photolytic degradation can occur in the atmosphere, in aqueous systems, within the first millimeter of soil, or on foliar surfaces. Dissolved organic matter, NO_3^- and other compounds can serve as sensitizers or precursors for the production of singlet oxygen, peroxy radicals, H_2O_2 and OH radicals. Alternatively, dissolved organic matter can alter the rate of agrochemical degradation by absorbing the available light energy. Several processes are involved in atrazine degradation in aqueous systems. Photo-initiated hydroxy radical processes were reported to be much faster than direct photolysis,

and the ratio of these processes was a function of the type of dissolved organic matter.^{24,25} Hydroxy radical processes formed dealkylated [2-chloro- N^4 -isopropyl-1,3,5-triazine-2,6-diamine (CIAT) and 2-chloro- N^4 -ethyl-1,3,5-triazine-2,6-diamine (CEAT)] or oxidized alkyl CDIT (N -(4-chloro-6-isopropylamino-1,3,5-triazin-2-yl) acetamide), and CDET (N -(4-chloro-6-ethylamino-1,3,5-triazin-2-yl) acetamide) products, whereas direct photolysis afforded hydroxylated atrazine degradation products.²⁴ The contribution of direct photolysis to the environmental fate of atrazine is relatively insignificant.^{17,24}

3 ENVIRONMENTAL PROCESSES

The chemical and physical properties of an agrochemical determine its fate and transportability; although hydrology, climate, formulation, application methods and land use (cropping practices) are also very important. Subsequent to application, agrochemicals can sorb to the soil matrix and the foliar surfaces of the crop, leach into groundwater, be transported to surface water bodies, and/or volatilize to the atmosphere and be deposited on unintended targets. Some best-management practices have been developed primarily to control nutrient and soil losses, but these practices may increase pesticide losses to surface or groundwater.²⁶ A number of the most commonly used best-management practices have been examined to determine their effectiveness at mitigating pesticide loss.

3.1 Sampling and detection methods

Environmental sample collection techniques have improved over the last 10 years to provide higher resolution datasets for in-depth analysis of processes affecting release of agrochemicals to surface waters, ground waters and the atmosphere. Passive air sampling methods, ie solid phase micro-extraction, are being developed to improve the resolution and accuracy of agrochemical volatilization flux measurements.²⁷ Automated rain sample collectors equipped with on-line rainwater extraction equipment have provided event-based information on agrochemical loadings from wet deposition while minimizing degradation during sampling.²⁸

More rapid, facile technologies with increasing lower detection limits are being developed. In addition, multi-residue methods for agrochemical determinations and their degradation products are quite useful.²⁹ The extraction efficiency of agrochemicals from soil has been improved considerably over Soxhlet or shake-extraction methods with the introduction of accelerated solvent extraction (ASE). By applying elevated temperature and pressure, ASE uses markedly less solvent and requires a much shorter processing time.³⁰ ASE can also be used as a fast alternative to batch equilibration systems.³¹ Sonication followed by GC analysis was found to be as effective as traditional

Soxhlet extraction but required much less time and solvent for analyzing multiple residues in sediment and on plant material.³² Recent advances in LC/MS techniques have facilitated the analysis of the newer, more water-soluble pest-management chemical classes.³³

3.2 Transport to groundwater

Occurrence and concentration of agrochemicals within the soil profile and in groundwater have been related directly to soil characteristics that control water movement through soil. For instance, atrazine concentrations in water moving through the soil column were found to have a positive correlation with silt content and an inverse correlation with soil organic matter in the upper soil layers.³⁴ The latter relationship is likely due to an increase in available adsorption sites, which decreases the rate of transport through the soil column. However, no correlation was found between atrazine concentration and soil organic matter in deeper soil layers. Water capacity was correlated strongly to atrazine concentration in the deepest layer.³⁴ Other studies have shown that atrazine movement is governed not only by interaction with the soil column but also as a result of macropore formation, which by-pass most of the soil matrix.³⁵

As atrazine is transported through the soil profile, microbial degradation can occur, producing two major dealkylated products, CIAT and CEAT. Thus, the ratio of CIAT to atrazine in receiving groundwaters can be used as a means to determine the retention time of atrazine in the soil column. A CIAT/atrazine ratio value of >1 would indicate significant soil–water interaction, whereas a CIAT/atrazine ratio of $\ll 1$ would indicate little or no interaction with the soil matrix such as in a tile drainage system.³⁶

3.2.1 Influence of management practice on fate and transport to groundwater

The sorption and degradation of agrochemicals can also be influenced by tillage practices. In no-till managed fields, organic matter increases in the upper soil layers which will adsorb greater quantities of agrochemicals; however, if the substrate is tightly bound, it becomes unavailable to microorganisms, and less degradation is observed.³⁷ This low mineralization under no-tillage may also indicate a poor adaptability of native microbial populations due to lower substrate availability.³⁸ High levels of cover crop residue can suppress weed emergence, but can also intercept pre-emergence herbicides and potentially reduce their effectiveness, as was observed in a comparison study of no-till corn plots with and without a hairy vetch cover crop. Pre-emergent herbicide concentrations were low enough in all treatments that grassweed numbers exceeded threshold levels; in the presence of high crop residue levels, full-season weed control was not available.³⁹ Furthermore, atrazine and metolachlor losses from the first runoff event subsequent to application were

slightly higher from no-till corn plots than from no-till corn field plots with hairy vetch cover crop residue.⁴⁰

Under conservation tillage, herbicide concentrations in sub-surface drainage are often higher due to increased infiltration, but herbicide losses in runoff are often lower. Temporal variability in herbicide concentrations in sub-surface drainage is substantial between and within growing seasons and is primarily driven by precipitation trends. Management practices such as banding, that decrease the overall amount of herbicide used, and those that decrease runoff while increasing soil retention will decrease the risk to sub-surface drainage and improve surface water quality.^{41,42} Spatial variability of observed herbicide concentrations in soil one week after application was shown to be a function of organic matter content and cation exchange capacity and was inversely related to pH. By coupling all of this information with weed growth patterns, effective variable-rate herbicide application can be implemented.⁴³ Finally, the use of starch-encapsulated formulations for several herbicides reduces leaching during the first part of the growing season. For atrazine, however, the overall degradation rate decreased, which led to greater leaching in the latter part of the year. Thus, the soil type, climate, hydrology and subsequent crops need to be considered when using controlled-release formulation products.^{44–46}

3.2.2 Interaction of surface water and groundwater

Some geological conditions are conducive to exchange between surface (river and stream) water and groundwater. Alluvial aquifers are unconfined, unconsolidated sand and gravel deposits and are found throughout the Midwest USA. These aquifers are generally near the surface and are easily contaminated by agrochemicals present in surface waters. If a relatively lower hydraulic head exists in the aquifer, there is the potential for vertical stream leakage to groundwater.⁴⁷ In other cases where the groundwater is very near the soil surface, the water can exfiltrate and become a primary source for agrochemical contamination in streams.⁴⁸

3.3 Runoff

Runoff and erosion from agriculture have been identified as major contributors to water quality degradation, although runoff losses typically account for only 1–6% of applied agrochemicals.⁴⁹ However, runoff losses are dependent on the slope of the field, management practices, presence or absence of sub-surface drains and the intensity and timing of rainfall after application.⁵⁰ For example, sub-surface drains were found to decrease runoff volume and soil loss from the fields by increasing soil infiltration of rainwater. Agrochemicals with low water solubilities were typically found on the soil particles while those with higher solubilities were in the aqueous phase.⁵¹

3.3.1 *Runoff to estuarine systems*

Agricultural runoff is also an important agrochemical source to estuarine systems. In many cases, estuaries receive loadings from runoff occurring miles upstream in freshwater regions of a watershed. An intensive study was conducted to determine the loads of currently used agrochemicals to the Chesapeake Bay estuary from the Susquehanna River. This river provides 90% of the fresh water flow to the upper half of the Chesapeake Bay, and much of its watershed is agricultural. Water samples were collected at the mouth of the river every 9 days for 13 months. The major components proved to be atrazine, its transformation product CIAT, and metolachlor, with maximum concentration values and loads occurring in early spring. Increasing loads of pesticide transformation products relative to the parent pesticide were observed through the growing season and into the fall. Large winter storms also caused large pulses of pesticides to enter the estuary. Using measurements from this study and from other researchers, it was discovered that annual atrazine and metolachlor loads to the Chesapeake Bay could be predicted accurately from annual water discharge through the dam at the mouth of the Susquehanna River.⁵²

Additional studies of other smaller tributaries of the Chesapeake Bay have been carried out in the Patuxent and Choptank River watersheds.^{53,54} As cropping in the region is dominated by corn and soybean production, pre-emergent herbicides such as atrazine, metolachlor and alachlor were observed in the highest concentrations. Overall, pesticide concentrations in the Patuxent River were highest in the upper watershed and decreased with distance down the river. While tidal dilution was an important removal mechanism, degradation appeared to be a major factor leading to the decrease in atrazine concentrations down the river. Overall, triazine herbicides appeared to move quickly into the river and persisted longer in surface waters compared with the acetanilide herbicides.⁵³

In a more detailed study of the Patuxent River estuary, simultaneous concentration measurements from multiple locations along the salinity gradient of the estuary throughout one growing season were used in a physical transport box model to elucidate sources and estimate residence time and persistence of pesticides in the estuary.⁵⁵ The estimated half-life of atrazine in the turbid, shallow upper estuary was 20 days, but was much longer (100 days) in the deeper lower estuary. Although most (93%) atrazine entered the estuary upstream via the river, simulations suggested additional inputs directly to the lower estuary. The total atrazine load to the estuary from April 5 to July 15, 1996 was 71 kg with 48% loss by degradation and 31% exported to the Chesapeake Bay. Atrazine persistence in the estuary was directly related to river flows into the estuary. Low flows were expected to increase atrazine residence time in the upper estuary and increase degradation losses.⁵⁵

3.3.2 *Runoff from plastic mulch*

Current vegetable production systems utilize polyethylene (plastic) mulch and require multiple applications of agrochemicals. During rain events, runoff from vegetable production is enhanced because 50–75% of the field is covered with an impermeable surface. The plastic covering increases the volume and velocity of water moving across the surface of the field and causes severe erosion of bare soil between the raised plant beds. A comparison study of runoff from tomato plots cultivated using polyethylene mulch or a hairy vetch residue mulch indicated that two to four times more water and at least three times as much soil came from plots with polyethylene mulch versus plots with hairy vetch residue.⁵⁶ Greater loads of copper hydroxide, a fungicide which is used prophylactically on many vegetable crops, were measured in the particulate phase than in the dissolved phase of runoff from both mulch treatments, with the particulate phase accounting for more than 80% of the copper loads.⁵⁷ Total agrochemical loads were approximately an order of magnitude greater from polyethylene than from hairy vetch mulch plots, due to greater concentrations and larger runoff volumes. The increased runoff volume, soil loss and off-site loading of agrochemicals measured in runoff from the polyethylene mulch suggests that this management practice is less sustainable and may have a greater negative impact on the environment.^{56,57}

3.4 Volatilization and deposition

Environmental parameters influence agrochemical atmospheric dispersion and local, regional and long-range transport processes. These compounds can bind to dusts or exist in the vapor phase and can rise high into the atmosphere and be deposited far from the point of application risking contamination of sensitive ecosystems and potentially becoming a health concern. Atmospheric transport is largely controlled by partitioning coefficients between air–water and air–soil. Studies have been conducted to measure the air–water distribution coefficients, Henry's Law constants (HLC), for a series of agrochemicals over a range of temperatures and salinity.⁵⁸ These HLC measurements are extremely useful in modeling agrochemical behavior over a range of environmental conditions.^{28,59,60}

Cultivation practices can influence agrochemical losses to the atmosphere. In a study comparing volatilization of metolachlor from broadcast versus banded application, a greater than threefold cumulative metolachlor loss (22% versus 6%) was observed from the broadcast fields.⁶¹ The greatest losses occurred in the first 12-h period after application. Residue cover and timing of subsequent precipitation events, both of which affect the drying rate at the soil surface, also affected volatilization; the closer a precipitation event occurred after agrochemical application, the higher and more extended were the volatilization rates of the chemical.⁶⁴

In a study of pesticide volatilization rates from bare soil, Rice *et al*⁶² found that a significant portion of the pesticide loss from the top 8 cm of soil was due to volatilization, ranging from 7.5% of total losses for atrazine to 34.5% of total losses for α -endosulfan. Of those compounds included in the study, the order of volatile flux losses were trifluralin > α -endosulfan > chlorpyrifos > metolachlor > atrazine > β -endosulfan. Even though heavy rains occurred from the first to third day after treatment, the majority of the volatile losses took place within 4 days of treatment.⁶² These results support the need to establish generalized methods to gauge critical factors impacting conditions that prevail during the earliest periods after spray application.

3.4.1 Fumigants

A substantial body of work exists concerning volatilization of fumigants whose physical properties, especially on vapor pressures which are orders of magnitude higher than those of most herbicides, making them very efficacious but also challenging to control.⁶³ Use of high-density polyethylene, impermeable tarps, water, soil amendments and deep injection have all been examined as methods to control the unintended release of fumigants to the atmosphere. Injection depth and water management were found to be most important in controlling 1,3-dichloropropene volatilization.^{64–66} Results further indicated that for chloropicrin and methyl bromide, application rates can be reduced substantially when using virtually impermeable films (VIFs) or deep injection, because the fumigant is held in the soil at a higher concentration for a longer period of time due to decreased rates of volatilization.^{67–71}

3.4.2 Atmospheric transport and deposition to estuarine systems

A pioneering study of agrochemical atmospheric deposition to the Wye River estuary within the Chesapeake Bay watershed estimated that atmospheric deposition could contribute up to 30% of the atrazine loadings to the Bay's two major tributaries, the Potomac and Susquehanna Rivers.⁷² More recently, agrochemical concentrations in air and rain were measured in the Patuxent River watershed, another tributary of the Chesapeake Bay, and compared with estimated pesticide use patterns in the watershed.⁶⁰ Of the sixteen agrochemicals studied, chlorothalonil had the highest maximum concentration in air. Maximum wet deposition flux measurements were highest for methyl parathion, malathion, metolachlor and atrazine. Air–water gas exchange fluxes were calculated for chlorpyrifos and metolachlor and indicated that the major equilibration transfer direction for chlorpyrifos was from water to air while for metolachlor the direction was from air into surface waters.⁶⁰

More recently, an intensive study of wet deposition fluxes and air concentrations of pesticides has

been carried out in the Choptank River watershed.²⁸ Chlorothalonil, metolachlor, atrazine, simazine, endosulfan and chlorpyrifos were frequently detected in the air and rain, with maximal concentrations occurring during the period when local or regional crops were planted. The wet deposition load to the watershed was estimated at 150(\pm 16), 61(\pm 7), and 51(\pm 6) kg year⁻¹ for chlorothalonil, metolachlor and atrazine, respectively. The high wet deposition load compared to the estimated annual usage for chlorothalonil (13%) and endosulfan (14–90%) suggests an atmospheric source from outside the watershed. Net air–water gas exchange fluxes for metolachlor varied from $-44(\pm 19)$ to $9.3(\pm 4.1)$ ng m⁻²d⁻¹ with negative values indicating net deposition. Wet deposition accounted for 3–20% of the total metolachlor mass in the River and was a more important source to the river than gas exchange. Estimates of herbicides flux measured in this project were likely low as the location was distant from significant agricultural activity, and actual rates may be significantly higher in areas closer to pesticide application.²⁸

3.4.3 Atmospheric transport and deposition to alpine ecosystems

Agricultural activity in California's Central Valley has been suggested to be a significant source of agrochemicals currently being deposited in the Sierra Nevada mountain range. A theory has been presented which suggests that agrochemicals applied to this area of intensive agriculture may be volatilized by high temperatures in the valley, transported through the atmosphere, and finally deposited in cooler, higher elevations of the Sierra Nevada Mountains.⁷³ Residue analyses showed that highest levels of contaminants found in surface water and dry particulate samples in the mountains were those of agrochemicals applied in the valley during heavy use periods in summer.⁷⁴ Agrochemical residues have been detected in tissues of adult Pacific treefrogs (*Hyla regilla*) collected in the Sierra Nevadas. Acetylcholinesterase activity (a bioassay reflecting agrochemical exposure to organophosphates or carbamate pesticides) was significantly inhibited in tadpoles of *H regilla* in regions where ranid frogs have experienced the worst declines. Because treefrog tadpoles share the same habitat as larval ranids, inhibition of cholinesterase strongly suggests that carbamate or organophosphate agrochemicals may be adversely affecting amphibians inhabiting these wetlands.⁷⁵

3.4.4 Long-range transport

Persistent agrochemicals, such as the organochlorine insecticides, have been found in the polar regions, areas quite remote from their application sites. Hexachlorocyclohexane isomers (HCHs), for instance, have been detected over the Arctic waters as well as the Sea of Japan. Much information about organochlorine processing in the atmosphere on a global scale has been derived from extensive studies

on the occurrence of HCHs in Arctic regions.^{76,77} Of the currently used agrochemicals, chlorpyrifos, chlorothalonil, metolachlor, terbufos, atrazine and trifluralin have also been observed in the Arctic marine ecosystems. Trace quantities were measured in the surface water and surface microlayer while slightly higher levels were found in ice and in fog. The elevated agrochemical levels in the fog suggests that this medium was readily exchanging with the other compartments, especially ice and surface microlayer, thus acting to redistribute these materials over this region. This is probably a very important cycling and transport process because fog occurs frequently over this area.^{78,79}

4 MITIGATING AGRICULTURAL POLLUTION BEYOND THE FIELDS

4.1 Farm ponds and constructed wetlands

Understanding agrochemical dissipation and runoff losses from agricultural systems is important to ensure minimal exposure to native fauna in nearby enclosed ponds and for establishing guidelines for total maximum daily loads (TMDLs) of commonly used agrochemicals. Farm ponds and constructed wetlands can receive high levels of pesticide when runoff events closely follow pesticide applications; however, impact on the aquatic life can be marginalized if the pesticide is rapidly degraded. Studies were conducted to follow dissipation processes of agrochemicals and exposure effects on larval amphibians in model laboratory and outdoor pond systems.⁸⁰ Several applied concentrations of the herbicides atrazine and metolachlor and the insecticide chlorpyrifos were examined. No appreciable losses were apparent for either herbicide when applied at high concentrations in the aquaria treatment; however, at lower concentrations, some herbicide loss was observed, with concomitant formation of corresponding degradation products. Chlorpyrifos disappeared rapidly from both systems due to what appeared to be rapid initial volatile loss. Thus, exposure to the most toxic of the three compounds examined was minimal.⁸⁰ Additional studies have determined the length of travel distance that is necessary to mitigate pesticide-laden runoff waters.^{81,82}

4.2 Riparian systems

Riparian buffers (forested corridors along stream channels) along rivers and streams are important landscape components of the agricultural ecosystem for protecting ground and surface water quality. First-order riparian wetlands are reported to be especially effective at groundwater remediation. Small first-order streams are the primary lines of defense for protecting surface water bodies from pollutant loadings. Riparian systems have been shown to be helpful in mitigating non-point source pollution and have been recommended as an essential part of best management practices (BMPs). Under the National Conservation Buffer Initiative, USDA and

partners have set a goal of establishing 2 million miles of buffers along rivers and streams in the USA. Among the important site-specific information that can significantly influence the ability of a riparian area to attenuate water pollution are topography, soil permeability, depth to water table, vegetation, prevalence of preferential (bypass) flow and amounts of upland nutrient inputs.^{83–86}

Leaching can transport applied agrochemicals into underground aquifers which may serve as storage sites and regions for degradation. An extended period of rainfall can mobilize the storage cells, adding them to the upland loads and accelerating their delivery to the riparian buffer region (Gish T, pers comm, 2002). Agrochemical transport and transformation were examined within a forested buffer system. As expected, transformation/loss rate was found to be temperature dependent and was influenced by organic carbon abundance. Sorption is presumably a major process in agrochemical mitigation.^{87,88}

Water flow through riparian systems can vary widely. The highest average agrochemical loads were observed near the stream head in a riparian system with a first-order stream.⁴⁸

Preferential flow was often the dominant process for stream flow generation near the stream head. Zones of active groundwater emergence onto the surface displayed elevated concentrations of nitrate throughout the soil profile and in the exfiltrating water, while inactive areas (where there was no visible upwelling) showed rapid attenuation of nitrate with decreasing depths. Atrazine degradation products appeared to penetrate more readily through the most active upwelling zones, and a correlation was found between zones of high nitrate and high atrazine metabolite levels. Atrazine:CIAT ratios indicated that the stream flow was dominated by groundwater and that much of the groundwater may have reached the stream by preferential flow.⁴⁸

5 CONCLUSIONS

Responsible use of soil, air and water resources in the production of food, feed and fiber requires that impacts on environmental and human health be minimized and that natural ecosystems and the biodiversity which they support be preserved. Results from ARS research concerning the environmental fate and effects of agrochemicals has led to the development of science-based management practices that will protect vulnerable areas of the ecosystem. The new challenge is to identify vulnerable areas and their temporal and spatial variabilities prior to use of the chemical. The resulting information should be used to predict the fate of particular agrochemicals within the air- or watershed. With the development of better predictive tools and GIS (Geographic Information System) based-modeling, the risks of agricultural management systems can be assessed at the watershed

and basin levels, and management strategies can be identified that minimize negative environmental impacts.

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