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REVIEW

Evaluating Pesticide Degradation in the Environment: Blind Spots and Emerging Opportunities

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The benefits of global pesticide use come at the cost of their widespread occurrence in the environment. An array of abiotic and biotic transformations effectively removes pesticides from the environment, but may give rise to potentially hazardous transformation products. Despite a large body of pesticide degradation data from regulatory testing and decades of pesticide research, it remains difficult to anticipate the extent and pathways of pesticide degradation under specific field conditions. Here, we review the major scientific challenges in doing so and discuss emerging opportunities to identify pesticide degradation processes in the field.

An estimated 1 to 2.5 million tons of active pesticide ingredients are used annually, mainly in agriculture (*1*, *2*). Since the discovery of certain synthetic organochlorine compounds as insecticides in the 1940s, a large number of chemical pesticide classes with different uses and modes of action have been developed and brought to market (Table 1). Despite different chemical structures and target organisms [i.e., 40% used as herbicides, followed by insecticides and fungicides (*2*)], pesticides have in common that they are applied extensively over large areas in agriculture and urban settings. Their use therefore represents an important source of diffuse chemical pollution that is difficult to control.

In principle, pesticides are only registered for use if they are demonstrated not to persist in the environment considerably beyond their intended period of use (i.e., soil half-lives in the range of a few days to weeks). Nonetheless, residues of many pesticides are found ubiquitously in the natural environment in ng/liter to low µg/liter concentrations. For instance, surveys of groundwater and raw drinking water in industrialized countries typically detect 10 to 20 substances in recurrent findings above 0.1 µg/liter, the maximal accepted drinking water concentration for pesticides in many countries (Table 1) (*3*, *4*). An even more striking indication of widespread pesticide persistence is that about half of the detected substances have long been phased out of use, and another 10 to 20% are stable transformation products. Pesticide contamination is not limited to groundwater, as transport from groundwater may lead to a low-level, yet continuous presence of pesticides in surface waters (*5*). Current-use pesticides have further been detected in high-altitude regions, demonstrating sufficient persistence to carry them over hundreds of kilometers in the atmosphere (*6*). To protect natural and human food resources such as plants, aquatic biota, and drinking water, it is therefore important to understand what controls pesticides' environmental fate, and particularly their degradation—being the only process that actually clears pesticides from the environment.

Degradation of pesticides involves both biotic transformation processes—mediated by microorganisms or plants—and abiotic processes such as chemical and photochemical reactions. What transformation processes a given pesticide undergoes is determined by its structural affinity to specific types of transformation, and the environmental conditions it is exposed to as a result of its distribution and transport behavior (Fig. 1). For instance, redox gradients in soils, sediments, or aquifers often determine which biotic and/or abiotic transformations can occur. Similarly, photochemical transformations are restricted to compartments exposed to sunlight—e.g., the topmost meter(s) of lakes or rivers, the surfaces of plants, or submillimeter layers of soil. Although atmospheric phototransformation may also strongly affect the chemical nature and transport potential of pesticides, this topic has been treated elsewhere (*7*) and will not be covered here.

For pesticides as a strictly regulated category of substances, a large body of information is available from regulatory testing for market authorization. This includes data from laboratory-based tests on aqueous hydrolysis, photolysis in water and air, biodegradability in soils and water-sediment systems under aerobic and anaerobic conditions, and fate in soil lysimeters. The drawback of these rather phenomenological studies is that they provide little insight into how individual transformation processes contribute to observed bulk degradation. Therefore, they do not support a mechanistic understanding of how specific environmental conditions (i.e., the presence of certain reactants) affect pesticide transformation. Regulatory studies further fail to cover less frequently encountered environmental conditions such as those present in strongly sulfidic environments (e.g., estuaries, prairie potholes) or in different types of water treatment units, nor are they able to highlight transformations at low residual pesticide concentrations at which biodegradation may not take place. Thus, although chemists can generally predict intrinsic reactivity of a pesticide from its molecular structure, their ability to quantitatively predict or interpret degradation under actual field conditions is still limited.

In the following, we will present current understanding, but also prevalent knowledge gaps for pesticide transformation in the terrestrial and aquatic environment. Specifically, given the mentioned shortcomings of most available data, we will address the major challenges in extrapolating from laboratory to field conditions and discuss emerging methods to address these challenges.

The Dominating Role of Microorganisms

Biodegradation is generally recognized as the mass balance–wise most important route of pesticide degradation. Whereas plants, animals, and fungi (Eukaryota) typically transform pesticides for detoxification or through fortuitous metabolism by broad-spectrum enzymes, bacteria (Prokaryota) more commonly metabolize them for assimilation as essential nutrients and energy. This dichotomy is likely due to a wider range of sensitive targets in Eukaryota. For example, the organophosphate esters that interfere with nerve signal transmission in insects do not affect microbial processes and may therefore serve as sources of carbon and phosphorus for microorganisms if they harbor enzymes capable of hydrolyzing phosphotriesters. Bacteria are further more likely to contain such enzymes because of their well-documented propensity for rapid evolution of new enzymes and metabolic pathways that are strongly selected for when they supply one or more essential nutrients for the cell (*8*). In addition, facile horizontal transfer of biodegradation genes is known to occur within microbial populations, and this has been observed to spread newly evolved biodegradation pathways globally (*9*).

Some pesticide transformation reactions, particularly substitutions, can proceed both biotically and abiotically, but typically higher rates are observed for enzyme-catalyzed reactions. For example, the hydrolytic dechlorination of atrazine to hydroxyatrazine in soil had previously been attributed to abiotic processes, but later studies identified atrazine-dechlorinating enzymes in bacteria that produced hydroxyatrazine with a second-order rate constant of 10^5 M^{-1} s^{-1} (*10*) (Fig. 1D). A comparison of these rates with rates of abiotic atrazine dechlorination and the presence of detectable levels of the gene encoding

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those enzymes in most soils surveyed make it highly likely that biotic atrazine degradation dominates in the environment. In cases where biotic and abiotic reactions may both contribute to observed biotransformation, the ability to evaluate their respective contribution is critical to enable extrapolation to structurally similar compounds or to other environmental conditions. In other cases, enzymes have been shown to facilitate reactions that have no counterpart in abiotic chemistry, as with the herbicide glyphosate. Glyphosate contains a C-P bond that is stable to light, reflux in strong acid or base, and other abiotic conditions. Yet, microbes that cleave the C-P bond are now known to be fairly widespread in the environment, and some of those systems can

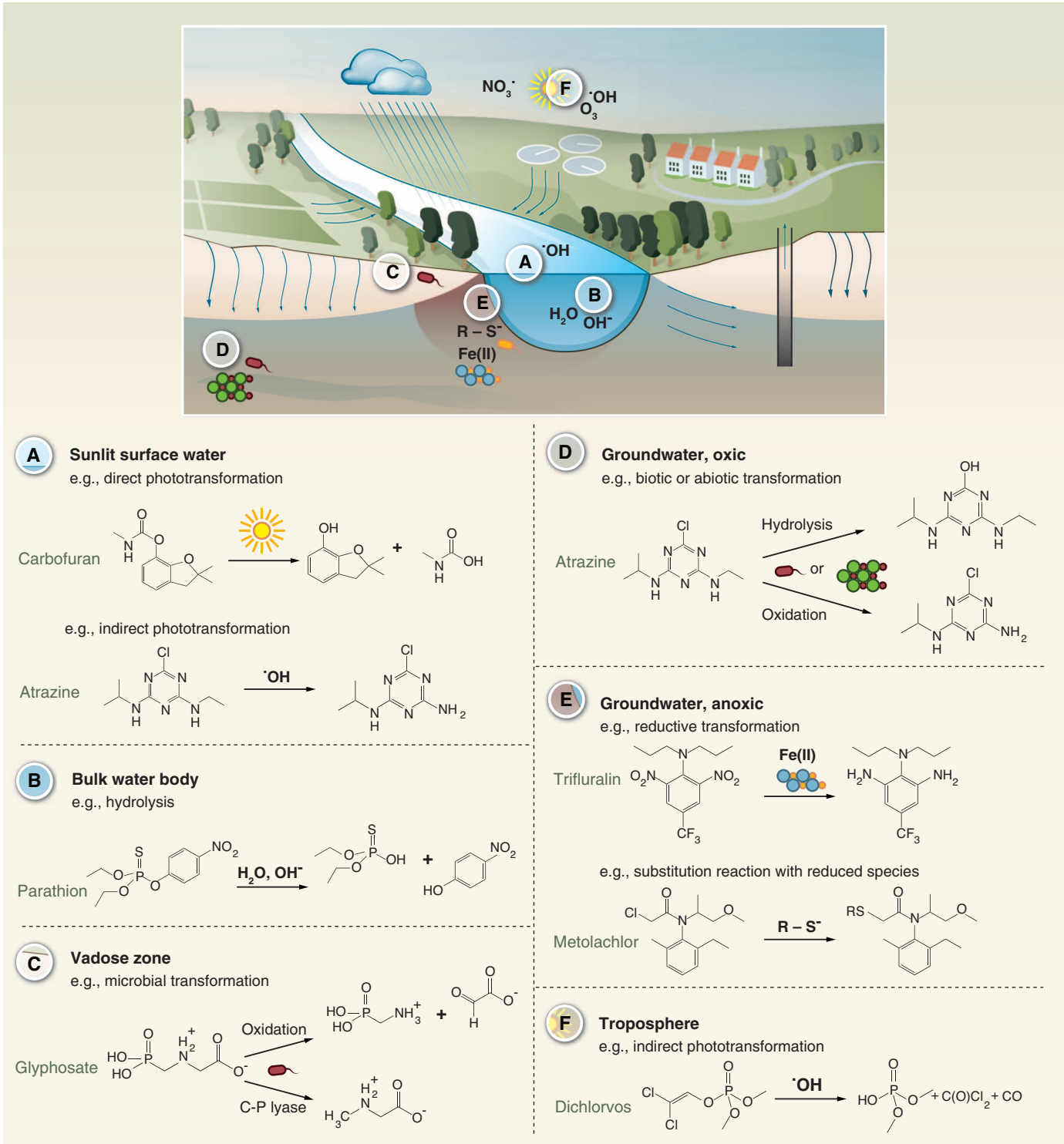
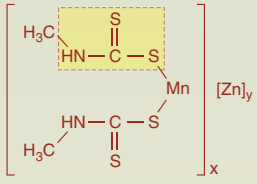
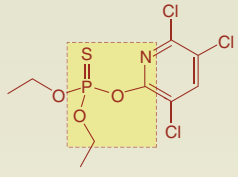
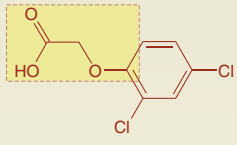
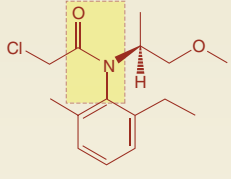
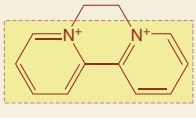
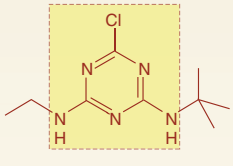
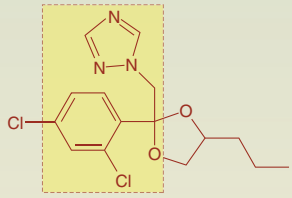
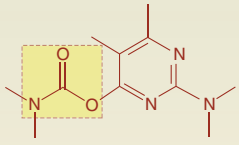
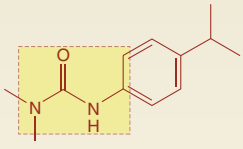
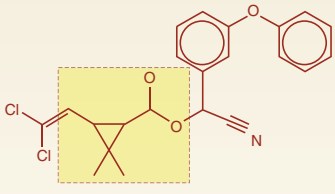


Fig. 1. Overview of pesticide degradation in the environment. (Upper) Main compartments and reaction partners for pesticide degradation. (Lower) Examples of relevant reactions in each compartment, including example reactions for important pesticide representatives [i.e., (**A**) carbofuran (direct phototransformation), atrazine (indirect phototransformation), (**B**) parathion, (**C**) glyphosate, (**D**) atrazine, (**E**) trifluralin (reductive transformation), metolachlor (substitution reaction), (**F**) dichlorvos].

Table 1. Main environmental degradation routes and environmental occurrence in secondary compartments for top 10 pesticide classes. Values are based on amounts used relative to total global pesticide consumption in 2009/2010 (*1*). AMPA, aminomethylphosphonic acid; DEA, desethylatrazine; NDMA, *N*-nitrosodimethylamin.

Pesticide class	Major representative active substance and structural motif	Major use category	Percent of global pesticide use	Main environmental degradation route	Environmental occurrence in secondary compartments (remote regions surface water, groundwater, etc.)
Dithiocarbamates	 Mancozeb	Fungicides	7.1	Acid-catalyzed hydrolysis; formation of potential NDMA precursors (*49*)	Rarely observed
Organophosphates	 Chlorpyrifos	Insecticides	6.7	Microbial transformation (oxidation and hydrolysis)	Glyphosate and AMPA frequently detected in groundwater (*3*, *50*); chlorpyrifos, diazinon, disulfuton detected in rainwater and remote lake waters (*6*, *51*)
Phenoxy alkanoic acids	 2,4-D	Herbicides	4.7	Microbial transformation (oxidative dealkylation and aromatic ring cleavage)	Parent compounds frequently detected in groundwater (*3*, *52*)
Amides	 S-Metolachlor	Herbicides	4.2	Microbial transformation (hydrolysis and glutathione coupling)	Chloroacetanilides and their transformation products oxanilic (OXA) and ethanesulfonic acid (ESA) frequently detected in groundwater (*4*); metolachlor and alachlor detected in remote lake waters (*6*, *51*)
Bipyridyls	 Diquat	Herbicides	3.2	Only very slowly biotransformed due to strong sorption to soil matrix	Rarely observed; mainly sorbed to sediments and soils
Triazines	 Terbuthylazine	Herbicides	2.3	Microbial transformation (oxidative dealkylation and hydrolysis)	Parent compounds and hydroxy- and dealkylated transformation products frequently detected in groundwater (significantly beyond phase-out period); atrazine and DEA detected in remote lake waters (*6*, *51*)

Triazoles, diazoles	 Propiconazole	Fungicides	2.0	Slow microbial transformation (oxidation); photo-transformation of specific representatives	Flutriafol detected in remote lake waters (*51*)
Carbamates	 Pirimicarb	Insecticides/ herbicides	2.0	Ready microbial or base-catalyzed transformation (hydrolysis of ester bond); photo-transformation of specific representatives	Rarely observed
Urea derivatives	 Isoproturon	Herbicides	1.7	Microbial transformation (oxidative dealkylation and hydrolysis)	Parent compounds frequently detected in groundwater (*3*)
Pyrethroids	 Cypermethrin	Insecticides	1.3	Microbial transformation (hydrolysis, oxidation); photo-transformation (direct and indirect)	Rarely observed; mainly sorbed to sediments and soils

metabolize glyphosate (Fig. 1C). The difficult nature of the reaction is underscored by the observation that C-P lyase, the enzyme system catalyzing C-P bond cleavage, is encoded by a 14-gene operon (*11*).

Given that biotic processes are often dominant and prokaryotes typically degrade pesticides completely, one may ask why transformation products of biotic processes are observed at all. This is sometimes attributed to "cometabolism," but the term itself does not provide insight into the numerous reasons why biotransformation products may accumulate. In atrazine metabolism, for example, many bacteria produce hydroxyatrazine and further metabolize it to carbon dioxide and ammonia. However, both whole cell (*12*) and purified enzyme studies (*13*) indicate that the enzyme producing hydroxyatrazine acts faster than the enzyme consuming it, so a substantial steady-state level of hydroxyatrazine accumulates. Therefore, the hydroxyatrazine that is observed in soil fate studies is not an end product of metabolism, but a metabolic intermediate that nonetheless can accumulate to substantial levels. In other situations (e.g., in wastewater treatment), microorganisms mostly grow on other, more readily assimilable carbon substrates, whereas pesticides present at trace concentrations are transformed through fortuitous metabolism, producing potentially recalcitrant intermediates.

An even more puzzling question is why pesticides are observed to persist over decades in groundwater although bacteria are in principle abundant and a potential for microbial pesticide degradation can therefore be detected even in groundwater (*14*). This paradox is closely related to the question of threshold concentrations [i.e., pesticide concentrations below which microbial degradation appears to stall (*15*)] in low-nutrient environments such as groundwater. As yet, very little is known about pesticide biodegradation under such conditions. Most prominently, methods have been lacking to follow biodegradation in groundwater over the relevant long time scales and to isolate relevant degraders from such environments.

Under Which Conditions Can Abiotic Pesticide Transformation Become Important?

In surface waters, phototransformation can substantially contribute to pesticide transformation (*5*, *16*). Environmental photochemistry distinguishes between direct and indirect photolysis/phototransformation: "direct" meaning that photons are absorbed by the contaminant itself, and "indirect" denoting that reactive species are formed through photon absorption by other water constituents. Because the electronic absorption spectrum of most pesticides shows little overlap with the spectrum of terrestrial sunlight, only a few pesticides are affected by direct phototransformation (*17*) (e.g., trifluralin, a dinitroaniline derivative, which absorbs sunlight even in the visible spectral region). By contrast, indirect phototransformation processes are more likely, because various photochemically active light absorbers are present in surface waters. The most prominent among these absorbers is dissolved natural organic matter (DOM), which is the precursor of excited triplet states, singlet (molecular) oxygen, superoxide radical anions, and other DOM-derived radicals. Nitrate and nitrite ions are additional active absorbers that produce hydroxyl radicals under irradiation. Indirect phototransformation of a given pesticide can be considered as the result of parallel reactions

with all these reactive species (*18*). To assess the transformation rate of a pesticide in the environment, one therefore has to know the concentrations of all relevant reactive species, together with their corresponding second-order rate constants for this pesticide. For hydroxyl radical and singlet oxygen, a comprehensive compilation of experimentally determined rate constants for organic compounds is available (*19*). In the absence of such rate constants, quantitative structure-activity relationships (QSARs) may allow their estimation for a specific pesticide from its chemical structure (*20*).

The relevance of non–sunlight-mediated chemical ("dark abiotic") transformations can differ greatly between pesticides. Textbook reactions can directly be predicted for some compounds based on the presence of functional groups. For example, abiotic hydrolysis in aqueous solution is well established for organophosphates (Fig. 1B), carboxylic acid esters, carbamates, carbonates, some halides (methyl bromide, propargyl), and many more. By contrast, compounds lacking suitable reactive groups, are frequently recalcitrant to chemical transformation. For rates to compete with biodegradation, specific conditions such as high pH or low-redox environments may be required, combined with in situ formation of suitable abiotic catalysts [e.g., (poly)sulfides, surface-bound Fe(II), MnO_2]. The latter is actually often mediated by microorganisms, which blurs the strict distinction between abiotic and biotic transformations. Nonetheless, some chemical transformations may only be recognized when investigated under the respective relevant conditions. Examples are clay-catalyzed triazine hydrolysis (Fig. 1D) (*21*), chloroacetanilide (*22*) and nitroaromatics transformation (*23*) in sulfidic environments (Fig. 1E), or glyphosate oxidation by MnO_2 (*24*). Chemical reactions may also prevail in compartments such as groundwater or lake hypolimnions, which have hydraulic retention times on the order of years and where biomass densities are lower due to almost complete removal of assimilable organic carbon.

What Methods Are Available to Assess and Predict Pesticide Degradation in Nature?

Available strategies to directly identify transformation of pesticides in nature either rely on the detection of parent compound disappearance, detection of transformation products, or evidence of an intrinsic transformation potential in a given environment. Many of the existing methods, however, are only sensibly applicable on the micro- or mesocosm scale (Fig. 2). For instance, the common strategy of monitoring parent pesticide concentrations by gas chromatography–mass spectrometry (GC-MS) or liquid chromatography–tandem mass spectrometry (LC-MS/MS) does not allow distinguishing transformation from other processes such as dilution or sorption unless combined with stringent mass balance modeling of the environmental system in question. Although the use of ^{14}C-labeled pesticides does enable mass balances, investigations with radioactively labeled substrates cannot be conducted in the field.

Detection of transformation products may provide evidence of degradation in the field. This approach is straightforward if products are known and standards are available (target analysis), and becomes more challenging otherwise (suspect or nontarget analysis). Here, the availability of high-resolution mass spectrometry has facilitated not only the development of multicomponent analytical methods for several hundred target

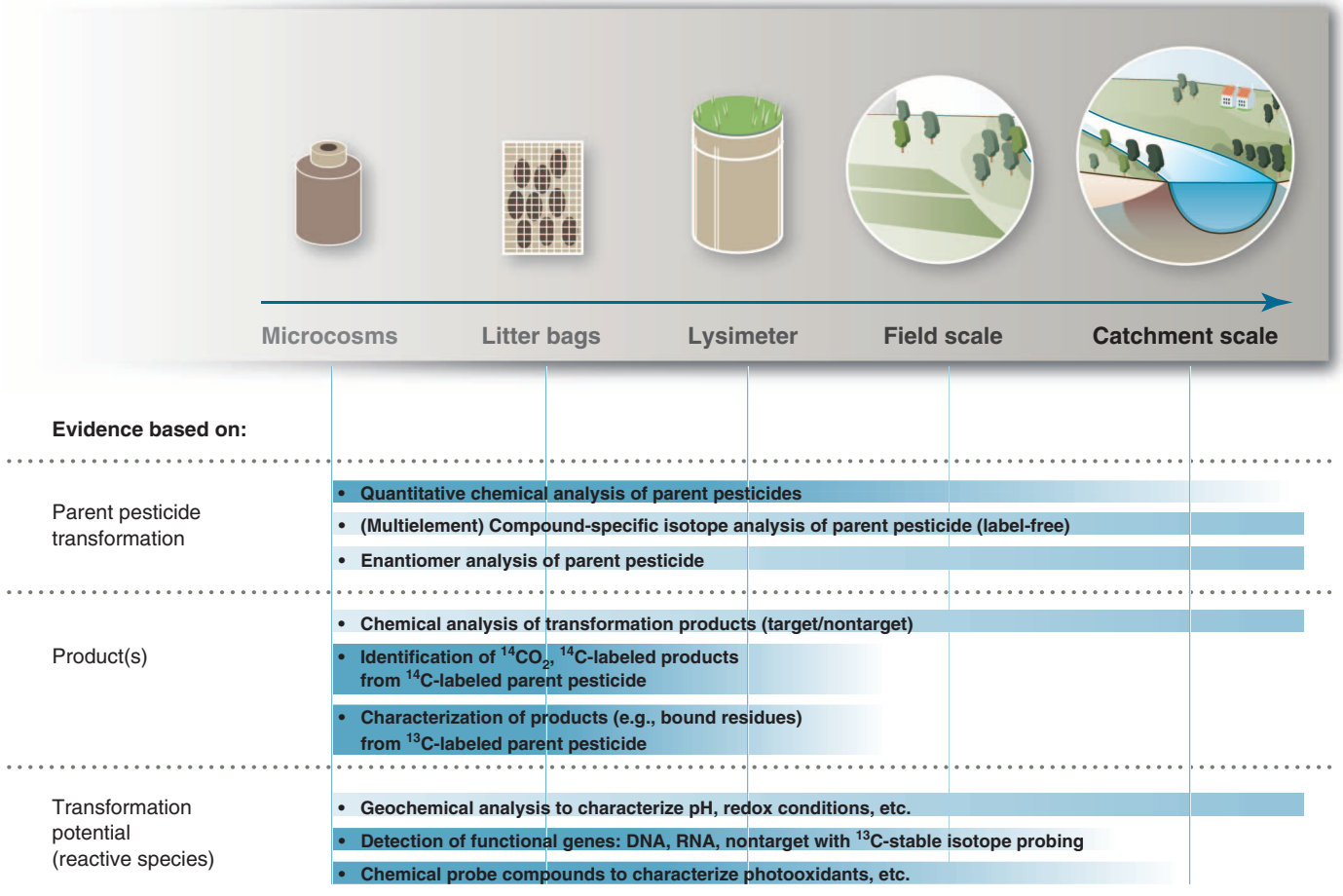


Fig. 2. Available analytical approaches to identify pesticide transformation in natural environments. For each approach, shading indicates the spatial scales at which it can best be applied.

analytes, as was recently done for 150 pesticide transformation products (*25*), but also the screening for suspected transformation products. Particularly in combination with models that predict likely transformation product structures, this latter option allows a more comprehensive assessment of the presence of pesticide transformation products in the environment, independent of the outcome from degradation studies carried out under specific conditions (*26*).

Compound-specific isotope analysis may provide yet a complementary line of evidence because it can detect degradation even if no metabolites are found and has the potential to cover sufficiently long time scales to study transformation in groundwater. Degradation-related information is derived from analysis of isotope ratios (e.g., $^{13}C/^{12}C$, $^{15}N/^{14}N$) of the parent pesticide in the absence of any label (natural isotopic abundance). Because kinetic isotope effects typically favor transformation of light isotopes (e.g., ^{12}C), heavy isotopes (^{13}C) become enriched in the remaining pesticide. Increasing $^{13}C/^{12}C$ isotope ratios in a parent compound thus provide direct evidence of its degradation. Therefore, if repeated pesticide analyses in groundwater over time—or spatially resolved measurements in combination with groundwater dating—show increasing $^{13}C/^{12}C$ isotope ratios in a parent pesticide, this provides direct evidence of its degradation, even if the pesticide was released long in the past. As demonstrated for the pesticide atrazine (*27*), even different transformation pathways can be elucidated provided that isotope effects of multiple elements are analyzed. In such a case, transformation mechanisms are identifiable from plots of $^{13}C/^{12}C$ versus $^{15}N/^{14}N$ parent compound data, reflecting different underlying carbon- and nitrogen-isotope effects. A challenge of the approach is the currently relatively high amount of substance needed for gas chromatography–isotope ratio mass spectrometry (GC-IRMS) or LC-IRMS analysis (100 ng to 1 μg), which, for instance, requires extraction of 10 liters of groundwater at pesticide concentrations of 100 ng/liter (*28*). For the special case of chiral pesticides, enantiomer analysis may provide yet another line of evidence based on a similar principle: enrichment of enantiomers (rather than isotopes) as a result of stereoselective biotransformation (*29*). Strongest insights can be expected when both approaches are combined in the field (*30*).

Methods detecting an intrinsic transformation potential are generally suited for field-scale investigations. Geochemical analysis of pH, redox potential, dissolved ions, and so forth is routinely applied to detect conditions that are conducive to certain biotic and abiotic pesticide transformations (Fig. 1). Chemical probe compounds are an elegant way to characterize the occurrence of abiotic reactive species in natural systems, but their use to estimate transformation rates in the field may be challenging. A first problem area is given when the reactive species are defined as a category and not as a single, well-defined chemical species. This is, for instance, the case with indirect photochemical reactions in surface waters, where excited triplet states of the DOM are formed as a manifold displaying a wide range of reactivities. 2,4,6-Trimethylphenol (TMP) has been used as a probe compound to measure DOM excited triplet states capable of undergoing oxidation reactions (*31*). Depending on the ability of the target pesticide to be transformed by such reactions, it will "feel" more or less triplet states than determined by TMP. Thus, the development of methods using additional probe compounds that better match target pesticide reactivity is essential to improve transformation rate predictions. A second critical question concerns the selectivity of probe compounds to detect individual reactive species when a mixture of reactive species is present. In general, a probe compound will react with more reactive species than with the one it is mainly intended for. To overcome these limitations, methods relying on the combined use of selective probe compounds and scavengers or quenchers appear most promising (*32*). An illustrative case from recent research is *N*,*N*-dimethylaniline. Used as probe compound for the carbonate radical (*33*), it also reacts very quickly with DOM excited triplet states, and its oxidation is partly hampered by DOM (*34*). Consequently, more selective and suitable probe compounds to detect carbonate radicals are urgently needed

To demonstrate a biotransformation potential in soil and sediment samples, nontarget analysis of degraders by stable isotope probing (SIP), where the use of ^{13}C-labeled parent pesticides facilitates ^{13}C labeling, isolation, and subsequent amplification of degrader DNA, is increasingly used (*35*). A complementary, potentially more quantitative, emerging technique is to directly study the potential of a community for pesticide biodegradation through enumeration of the biodegradative gene(s) via quantitative polymerase chain reaction (QPCR), high-throughput gene sequencing, or use of functional gene microarrays, as all of these methodologies have become easily accessible. A prerequisite for gene-based approaches, however, is that the involved genes are known and can be clearly attributed to a given transformation reaction. For instance, the *atzD* gene encoding cyanuric acid hydrolase has been found to correlate with atrazine biodegradation in the surface layers of an agricultural soil (*36*), consistent with the knowledge that AtzD cleaves the *s*-triazine ring during the course of bacterial atrazine metabolism. AtzD met the requirement of being unambiguously identifiable and hence quantifiable, as it belongs to a small protein family that largely consists of biodegradative enzymes. However, this situation is rare. Most pesticide biodegradative proteins studied to date are members of very large protein superfamilies, with as many as 600,000 individual members, the vast majority of which have different functions than the target enzyme. Another factor confounding gene-based approaches is that biodegradative functions can arise independently in evolution, such that genes with completely different sequences may catalyze the same reaction. It is well known that organophosphate esterases that differ markedly in their protein fold and mechanism can nonetheless act on the same organophosphate pesticide (*37*). This likely explains why PCR amplification failed to detect a target gene encoding an organophosphate esterase in soils containing bacteria that were later shown to express organophosphate esterase activity (*38*).

In the future, the broad-based applicability of gene-based methods for demonstrating biodegradation will be improved by new developments in bioinformatics that seek to better assign biological function to proteins when only their sequence is known (*39*). Moreover, it is also advisable to couple sequence-based methods with other independent methods whenever possible. If certain genes are implicated by nucleic acid–based methods, one can potentially use computational tools or protein functional databases to infer possible transformation products of a pesticide and then use sensitive mass spectrometric methods to identify the products as discussed above.

Are Transformation Products an Issue of Concern?

Even though their original effect is typically lowered (*40*), pesticide transformation products may still be highly relevant. First, certain transformations leave the active moiety intact—for instance, oxidation of thioethers to sulfones and sulfoxides (*41*). Mixtures of parent compound and transformation products may therefore have additive effects (*42*). Second, (eco-)toxicologically more potent structures may be generated. For instance, a recent debate centers on phenolic degradates of such diverse chemical classes as pyrethroids and aryloxyphenoxypropionic herbicides and whether they can act on estrogen receptors (*43*, *44*). Such transformation products with a potential for endocrine disruption or other chronic effects should receive particular attention because they are often smaller and more polar than their respective parent compounds. This increases their potential to reach drinking water resources such as groundwater and surface waters, where polar transformation products are found at fairly constant concentrations throughout the year (*5*). Pesticide transformation products in drinking water resources may also cause unexpected new problems such as the recently discovered formation of carcinogenic *N*-nitroso-dimethylamine from dimethylsulfamide, a microbial transformation product of the fungicides tolylfluanide and dichlofluanide, during drinking water treatment with ozone (*45*).

The issue of transformation product formation is specifically addressed in major regulatory frameworks. In Europe, for instance, "nonrelevant"

metabolites are distinguished from metabolites that are "relevant for groundwater resources" or even "ecotoxicologically relevant" (*46*). Ecotoxicologically relevant metabolites are those that pose a comparable or higher risk to soil or aquatic biota than the parent compound, and are therefore subject to the same level of risk assessment. Metabolites relevant for groundwater are those likely to reach groundwater in concentrations above 0.1 μg/liter and to display the same toxicity as the parent compound (target toxicity or severe other toxicity such as genotoxicity, reproductive toxicity, or carcinogenicity). Despite these regulatory provisions, however, it remains unclear how complete our current understanding of the occurrence and effects of pesticide transformation products really is. The past has shown that findings of particularly prevalent or toxicologically relevant transformation products typically emerged only 20 to 30 years after their market introduction. Examples are the detection of chloridazon transformation products (first marketed in 1964) in surface and groundwater (*47*), or the above-mentioned formation of carcinogenic *N*-nitroso-dimethylamine from tolylfluanid (first marketed in 1971). That these substances have been overlooked for so long may partially be attributable to limited analytical capabilities in the past. However, it also seems that the distinction between relevant and nonrelevant metabolites may have resulted in mobile and persistent transformation products receiving little attention because they were generally not considered toxicologically relevant.

A more complete picture of pesticide transformation products in environmental resources is expected to emerge over the next years thanks to advances in mass spectrometry as outlined above. This will confront society with questions on how to deal with the occurrence of certain transformation products in water resources, and on how to weigh human and environmental health against the benefits of the respective pesticides. Specifically, the decision to tolerate up to 10 μg/liter of "nonrelevant" metabolites in groundwater and drinking water is politically highly contentious in Europe. Some consider the higher limit acceptable as no imminent health risk can be proven, whereas others regard it as a fundamental deviation from the precautionary principle (*48*).

Outlook

As global pesticide use can be anticipated to continue to increase, the question of what residual pesticide concentrations are environmentally and socially acceptable will remain important. The new pesticide legislation in Europe puts more emphasis on hazard assessment, source control measures, and substitution. Substitution, however, also bears risks when substituting a well-investigated pesticide with one whose actual environmental fate is yet to be explored. Therefore, it is imminently important for scientist to improve their ability to predict the long-term fate, and in particular degradation, of pesticides in the environment beyond what is known from regulatory testing.

Future research in that field should particularly address the blind spots with respect to pesticide degradation at low concentrations and in low-nutrient situations encountered in groundwater, lake hypolimnions, or seawater. The development of such a system-oriented understanding of natural pesticide attenuation will require innovative tools for characterizing the transformation potential in those environments such as using combinations of advanced analytical approaches (e.g., compound-specific isotope analysis, enantiomer analysis, and mass spectrometry–based screening for transformation products). Also, developments in bioinformatics to assign biological functions to proteins on the basis of their sequences alone, in combination with inferring and screening for potential transformation products, are expected to play a crucial role. With these and other innovative tools at hand, questions on the extent of biodegradation at low pesticide concentrations, the underlying limitations ("bottlenecks of degradation") at such threshold concentrations, and the relative importance of biodegradation versus chemical processes in low-nutrient situations will become increasingly addressable.

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