Tracking the fate of pesticides

If the fate of plant protection and pest control agents in the environment is to be reliably assessed, knowledge of the substances concerned is not in itself sufficient – it is also essential to understand the underlying biogeochemical processes. Using highly sensitive measurement techniques and sophisticated analytical tools, it is now becoming possible to track pesticide degradation more effectively.

Fig. 1: Worldwide, around two million tonnes of agricultural pesticides are used per year. Their fate in the environment remains poorly understood.

Each year, about two million tonnes of pesticides are used on agricultural land, and smaller amounts are also applied in urban settings. Both types of areas are significant sources of diffuse inputs of chemicals to the environment. The widespread use of pesticides is once again a matter of growing concern. It is suspected that neonicotinoid insecticides are contributing to the decline of bee colonies worldwide, and Eawag investigations indicate that these substances are also harmful to aquatic organisms [1]. In addition, recent studies have demonstrated that regional biodiversity is markedly lower in aquatic ecosystems exposed to higher levels of pesticides [2].

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Persistent gaps in scientific understanding

Against this background, attention is increasingly being focused on the evaluation of pesticide degradation in the environment; for example, an article on this topic was included in the recent special issue of Science devoted to "smarter pest control" [3]. Particularly striking is the fact that numerous pesticide residues occur very widely in the environment – at concentrations in the micro- to nanogram per litre range – even though degradation is evaluated in various laboratory and controlled field tests before new substances are approved by regulatory authorities. Thus, groundwater quality monitoring programmes in Switzerland and Germany typically reveal the presence of 10 to 20 active ingredients in concentrations exceeding 0.1 micrograms per litre – the maximum acceptable level specified in many countries for pesticides in drinking water. The fact that around half of the substances in question are no longer used – and that 10 to 20 per cent occur as transformation products – provides clear evidence of the persistence of certain pesticides.

Why does our understanding of pesticide degradation remain limited despite at least 30 years of research efforts? There would appear to be two main reasons: firstly, the degradation studies required for pesticide registration are essentially descriptive. With only rudimentary information available on experimental conditions, it is almost impossible to understand how degradation is affected by various environmental factors. In addition, as has been shown by basic research – which has investigated the degradation of individual substances such as the herbicide atrazine in great detail – the interaction of these factors is highly complex. However, studies of this kind which are sufficiently detailed to elucidate the interaction of the various processes are resource-intensive and cannot be carried out for all pesticides. Consequently, quantitative prediction of degradation under real-world environmental conditions remains extremely challenging.

Difficulties of gathering field data

To meet these challenges, Eawag is pursuing a twofold approach: firstly, within the departments of Environmental Chemistry and Water Resources & Drinking Water, we are investigating the underlying processes and developing predictive models. Secondly, we are elaborating new analytical strategies for studying degradation processes directly in the field.

In order to gain a better understanding of degradation processes under environmental conditions, good-quality field data are indispensable. But various difficulties are involved in tracking pesticide degradation in the field: because of the low concentrations, there is a need for appropriate enrichment techniques and highly sensitive analytical methods to allow the substances to be detected at all. Even sampling – e.g. the collection of sufficient quantities of soil water – can be logistically and methodologically challenging. And even if these difficulties have been overcome, the fact remains that the disappearance of a substance in the environment is often attributable to a combination of processes, such as dilution, sorption and degradation. To read out the extent of degradation from such data generally requires precise modelling, based on

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the processes involved in the system under investigation. This in turn calls for considerable additional efforts and information on quantities applied and input pathways.

Fig. 2: Gathering field data is essential to improve our understanding of pesticide degradation.

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Transformation products: indicators of degradation

For the interpretation of field data, it would therefore be useful to have further qualitative or quantitative evidence concerning degradation processes. Accordingly, this is one of the main lines of inquiry in our research. For example, the detection of transformation products is an important indicator of degradation and, at best, permits conclusions as to its extent. Knowledge of the chemical structure of transformation products indicates whether they are stable or toxicologically relevant. In recent years, thanks to extremely sensitive high-resolution mass spectrometry (HRMS) and the development of appropriate methods of data analysis, there have been dramatic improvements in our ability to detect transformation products in the environment. In the establishment of analytical methods, Eawag researchers have played a pioneering role [4].

Using HRMS, multicomponent analytical methods can be developed for hundreds of expected transformation products [5]. In addition, with this approach, it is even possible to screen for potential transformation products in the environmental matrix if analytical reference standards are not readily available [6]. In particular, HRMS combined with computer-aided prediction provides a fuller picture of the presence of transformation products in the environment than individual studies of degradation under specific conditions [7].

Further valuable evidence of degradation processes can be obtained from compound-specific isotope analysis, as illustrated in detail by an article in a recent edition of Eawag News [8]. Spatial or temporal changes in isotope ratios not only indicate that contaminants are being degraded – they also provide information on degradation pathways, especially if the isotope ratios of several elements (such as carbon, nitrogen and hydrogen) are observed simultaneously [9].

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Fig. 3: Transformation products can be detected using high-resolution mass spectrometry.

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Ultimately, it can be assumed that, in a given field situation, the most robust results can be obtained using a combination of these various analytical methods.

Molecular probes used to visualize reactions

To detect a degradation process in a complex environmental situation, it can also be useful to look for other substances participating in the reaction, rather than studying the degraded substance itself. Accordingly, various efforts have been made to use parameters such as redox potential, pH or specific indicators (e.g. reduced iron or hydrogen) to predict the transformation potential of the substances concerned vis-à-vis pesticides or other contaminants. It has become apparent, however, that measurement of such reactants only permits precise predictions if the transformation process is sufficiently well understood. Only then is it possible to determine the reactants that are relevant in a particular environmental compartment or under specific conditions.

A number of examples from Eawag's research demonstrate how degradation processes can be detected with the aid of other reactants involved. In the area of photochemistry, for instance, scientists are studying how sunlight can bring about transformation processes in various types of aquatic systems. Absorption of sunlight can cause molecules to enter an excited state, in which electrons are elevated to a higher energy level (triplet state). The release of this energy can induce chemical transformation processes in other substances – e.g. in pesticides. This is called indirect phototransformation.

It is known that dissolved organic matter can promote indirect phototransformation in surface waters [10]. Molecular probes such as 2,4,6-trimethylphenol are therefore used as indicators reacting to the presence of organic matter in an excited triplet state. The challenge is to identify suitable molecular probes which – in terms of reactivity – should if possible be representative for a variety of pesticides, but which at the same time should ideally respond selectively to reactants or transformation processes of just one kind in the environment. In the identification of suitable molecular probes and the development of selective measurement methods, Eawag researchers are making important contributions.

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Iron-bearing clay minerals redox-active over a wide range

A different approach is adopted by Eawag researchers for the assessment of redox reactions typically occurring on the surfaces of reduced iron-bearing minerals, such as iron oxides or clay minerals. As well as contributing to the degradation of organic contaminants, such electron transfer reactions can also alter mobility and toxicity in inorganic substances (e.g. metals). Although the redox potentials of total environmental systems are standardly measured, we still do not know the reduction potentials of the individual mineral phases therein. This is partly due to the fact that the properties of many minerals and of organic matter vary according to the redox potential.

Using new electrochemical methods, we have now managed to measure the reduction potentials of iron in clay minerals. It is thus possible for the first time to make general predictions concerning the extent of electron transfer between contaminants and complex environmental phases [11, 12, 13]. This knowledge is important not only for the evaluation of pesticide degradation, but also for redox reactions of clay minerals used in the permanent storage of radionuclides. Most surprising was the finding that iron-bearing clay minerals are active over an enormous range of redox potentials and can thus participate in many reactions involving contaminants (Fig. 4).

Using enzymes to reconstruct biodegradation

Similar approaches are being pursued in order to determine the role played by biological degradation processes. Here, however, the reactants in question are not inorganic phases or chemical species, but enzymes which can catalyse the transformation of a pesticide. These come from microorganisms involved in the decomposition of the contaminant. Using sophisticated methods, it is possible to detect such enzymes, or genes coding for them. It was thus shown, for example, that the degradation of the herbicide atrazine in various soils is associated with
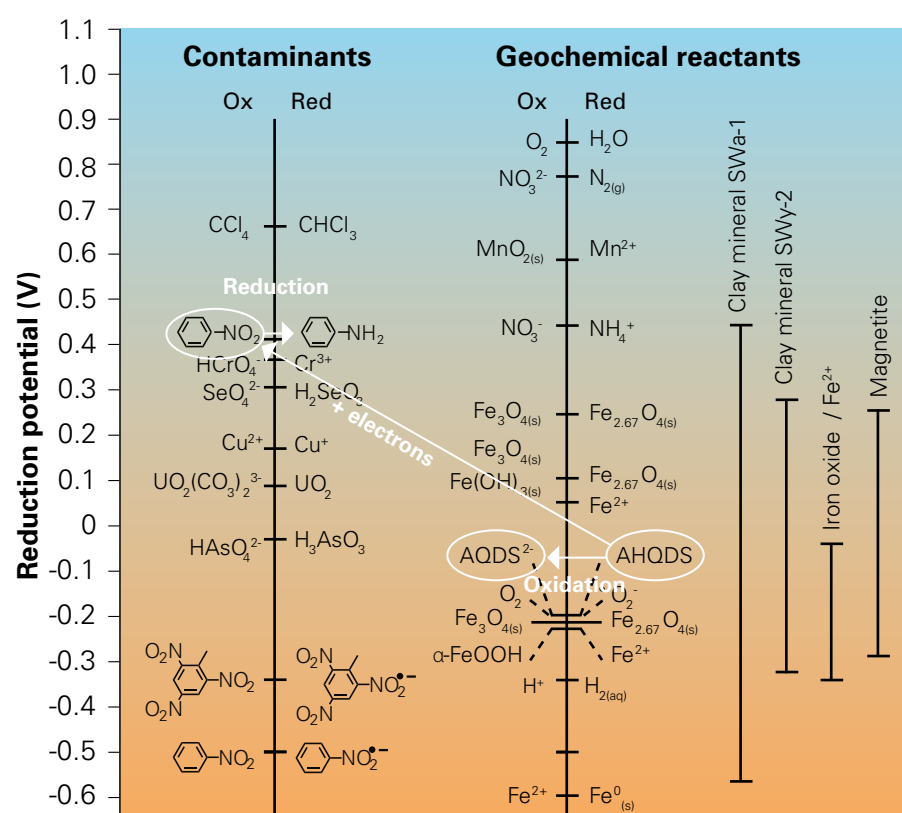

Fig. 4: Reduction potentials of important contaminants and reactants occurring in the environment. Contaminants are reduced if their reduction potential is higher than that of the reactants (see example), and oxidized if it is lower. While many reactants show precise reduction potentials, the iron-bearing minerals can react over wide potential ranges.

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the presence of a gene known as atzD. This gene codes for an enzyme which catalyses the hydrolytic breakdown of the triazine ring of atrazine. Eawag scientists have now also detected similar patterns in activated sludge from wastewater treatment plants. They found that expression of the archaeal amoA gene correlates with the transformation rate for the herbicide isoproturon (Fig. 5), and that inhibition of the associated enzyme ammonia monooxygenase leads to a marked reduction in the transformation of isoproturon [14]. In the future, this approach comparing transformation rates and gene expression patterns is also to be used to identify those enzymes in a naturally occurring microbial community which are involved in the degradation of particular chemical structures.

As is apparent from the above examples, the evaluation of pesticide degradation not only requires knowledge of the pesticides themselves but also depends on a fundamental understanding of the processes occurring in the environment, and of the reactants typically involved – microbes, redox-active minerals, enzymes, etc. Progress made on these fronts should make it possible to move gradually away from case-specific towards more generally valid evaluation concepts.
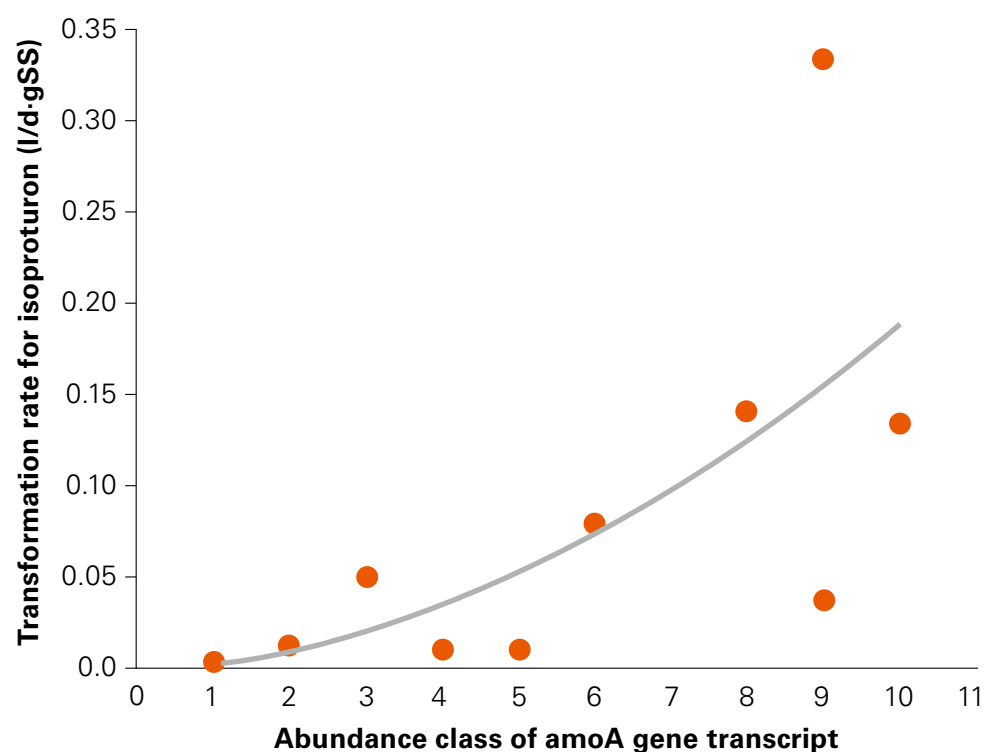

Fig. 5: Correlation observed between the transformation rate for the herbicide isoproturon and the abundance of the archaeal amoA gene transcript among ten different activated sludge communities from diverse municipal and industrial wastewater treatment plants. The transformation rate is given in litres per day per gram of suspended solids.

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