The Physical Chemistry of Pesticides in Soil and Water

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Abstract: Soils are the ultimate examples of physically and chemically irregular mixtures. They are also dynamic. Early investigators consequently did not understand the physical chemistry of pesticides in soil and water. By taking shortcuts instead of trying to understand the physical chemistry, they measured the wrong variables, used the wrong units, calculated the wrong parameters, and totally ignored chemical stoichiometry. Theoretical concepts for the physical chemistry of pesticides in soil have been published during the last quarter century. They are experimentally supported. Yet, chemically incorrect descriptions persist in the literature to this day. That has serious environmental and economic consequences. In particular, government regulators make legally binding pesticide decisions based on computer predictions that are wrong by 1 to 3 orders of magnitude. This needs the attention of scientists, governments, and multinational corporations.
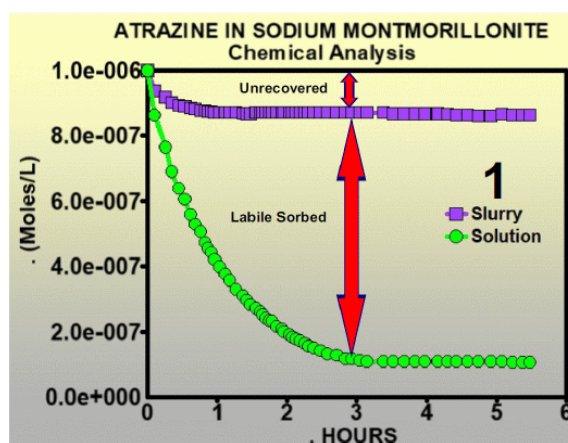
1. Introduction

A soil is the ultimate example of physically and chemically irregular mixtures. They are also dynamic. This has to be taken into account for the chemical kinetics and mechanisms of pesticides in soil and water at the molecular level. The scientific challenge is the adaptation to complicated dynamic mixtures, and the physical chemistry that is more readily understood for monomeric pure reagents. The engineering challenge is the use of this physical chemistry for the prediction and control of pesticides in soil and water under field conditions. A better understanding of the physical chemistry of soils can improve the control of pesticides under field conditions. The chemically incorrect concepts and parameters that government regulators still use for agricultural pesticides should be replaced. Section 4 and the references that it cites describe such examples.
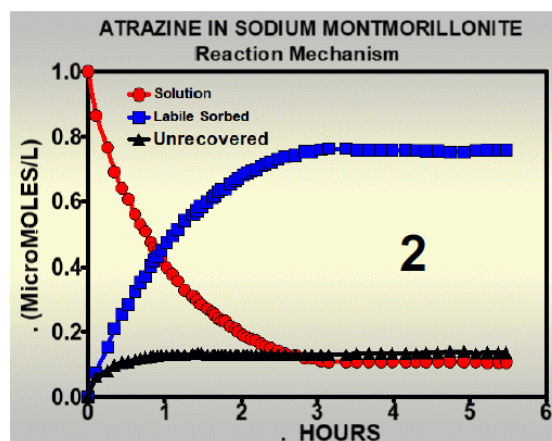
2. What Has Been Done

Proof of concept has been published for the experimentally supported theory that reveals the kinetics and mechanisms of pesticides in soil and water [1–9]. For a soil immersed in a pesticide solution, the starting point was the answer to a critical question. How many (Moles/g) of pesticide were reversibly sorbed at the solution—solid interface? Until that is answered, the chemical stoichiometry remains unknown. Historically, the science of chemistry was founded on the stoichiometry of molecular level reactions and processes. Without it, there is no valid description of kinetics and mechanisms. A simple extraction of a pesticide from a soil and water mixture recovers the total of two labile fractions. One is the dissolved fraction and the other is the labile sorbed fraction. How much of this total is in each fraction? The (Moles/g) of labile sorbed pesticide could possibly not have been measured using this method [1]. Solution concentrations can be measured after the removal of the solids. Microfilters and centrifuging have both been used for this. However, the fractions not found in a solution can

include a total of those that are labile sorbed, physically trapped, chemically reacted, and evaporated. The (Moles/g) of labile sorbed pesticide is again unknown. Any attempts to research the kinetics and mechanisms in this way would not produce the quality expected of modern chemistry [1].

This problem was solved by adding a new HPLC (High Pressure Liquid Chromatography) method to the analytical chemistry methods already available [1,6,7]. In brief, a sample consisted of soil slurried in a pesticide solution. Aliquots of the whole slurry were injected into an HPLC. After the chromatographic peaks had been recorded, the solids were flushed out of the instrument. That produced the slurry curve in Figure 1. After solids removal by microfilters, solution injections gave the solution curve in Figure 1. Simple subtractions indicated by the arrows produced the three curves for fractions in Figure 2. These are the dissolved, labile sorbed, and unrecovered fractions.
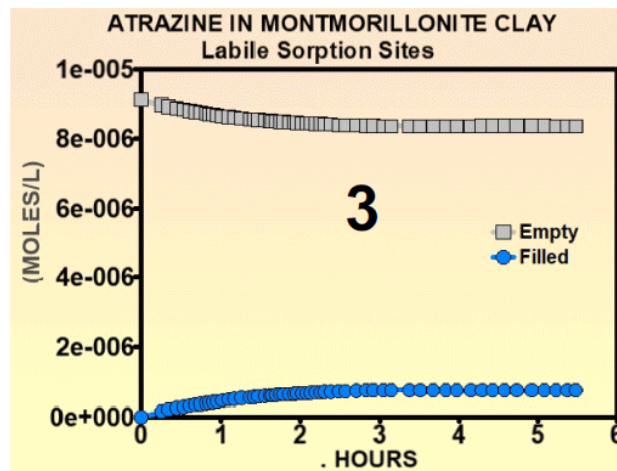

Figure 1. Chemical analysis of sodium montmorillonite suspension in an aqueous solution of atrazine. Initial concentration, 1.0×10^{-6} M. 4.0 (g/L) of montmorillonite 25.0 °C. The indicated subtractions produced the kinetics curves in Figure 2.
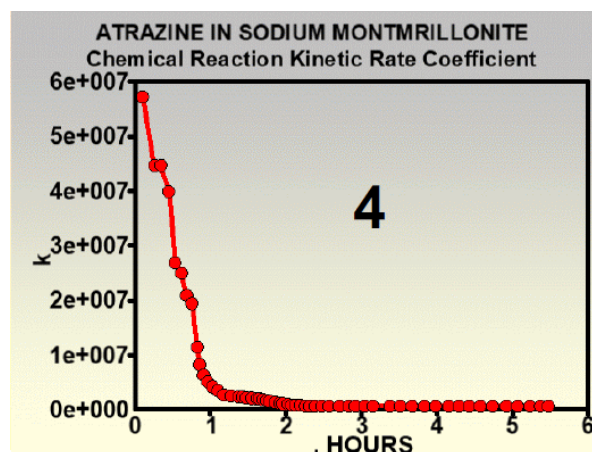

Figure 2. Atrazine in a suspension of sodium montmorillonite 25.0 °C. Kinetics curves for sorption and chemical reaction, produced by the subtraction indicated in Figure 1.

Additional analyses can resolve the total loss fraction into intraparticle diffused, evaporated, and reaction product fractions. At this stage, the reaction mechanisms have all been separately determined. Stoichiometry is next. Reactants and products include dissolved pesticide, empty sorption sites, and filled sorption sites. Figure 3 shows the (Moles/g) of empty and filled labile sorption sites [1,6]. The (Moles/g) of empty and filled labile sorption sites as well as separate time-dependent mechanism curves are now available. Experimentally based kinetics and mechanism calculations can

begin. As anticipated from Langford's research [3,10,11], time-dependent kinetic rate coefficients result. Figure 4 provides an example of this [12].

Figure 3. Atrazine in a suspension of sodium montmorillonite 25.0 °C. Empty and filled sorption sites with solution concentration define the stoichiometry.

Figure 4. Atrazine in a suspension of sodium montmorillonite 25.0 °C. Chemical reaction. First order kinetic rate coefficient.

With predictive spreadsheet models created this way, chemistry support for multidisciplinary research can be seriously considered. This includes environmental toxicology and integrated hydrology—chemistry models. Government regulatory agencies can then use more realistic technology for legally binding decisions. This clearly shows the dependence of practical technology on pure science. Shortcuts do not work.

3. What Must Be Done Next

The progress reported here has only scratched the surface. For this research to match the standards set by other important areas of science and technology, a comprehensive research and development program is needed. Table 1 lists eight projects for the program, and there might be more.

Table 1. New Research Projects Required for Pesticides in Soil and Water

#1	Analytical chemical methods for slurry and solution curves: improved and automated.
#2	The (Moles/g) of labile sorption sites: effects of pesticide chemical structure and soil materials
#3	Kinetic rate coefficients: effects of pesticide chemical structure and soil materials
#4	Temperature studies
#5	Kinetics and mechanisms: effects of seawater
#6	Toxicology in soil and water: control by pesticide chemical kinetics and mechanisms
#7	Multidisciplinary model: integration of chemical kinetics and mechanisms with hydrology engineering
#8	Pesticides at the solution—solid interfaces: physical chemistry

#; Item numbers.

First, the analytical chemical methods could be improved or replaced and automated. Kinetics and mechanisms calculations need more and better measurements. Costs could be reduced. Secondly, the number of labile sorption sites has to be measured for kinetics calculations [1,2]. Experimental time-dependent kinetic rate coefficients are necessary for predictions [1–4]. Temperature experiments are needed at two levels. First, the number of sorption sites in the solution—solid interface is expected to be temperature-dependent. Calculations using this data might next reveal time-dependent kinetic rate coefficients.

In additions to field conditions, the molecular level effects on the solution—solid interfaces are not yet understood. A five-year Great Lakes program investigated farm field runoff into fresh water [13]. Pesticide contamination of the lakes and connected aquifers was documented. The effects of seawater should also be investigated. As currently conducted, research on the toxicology of pesticides in soil and water does not account for the time-dependent effects of kinetics and mechanisms [14,15]. That is unrealistic. The problem of pesticides in soil and water is multidisciplinary [15,16]. Chemical kinetics and mechanisms should be integrated with hydrology engineering. Time-dependent sorption, desorption, and chemical reactions influence leaching and surface transport. Finally, at the level of fundamental science, the physical chemistry of organic chemicals in the solid—solution interface needs to be better understood.

4. What Is Still Going Wrong

For 50 years, pesticide soil investigators measured the wrong variables, used the wrong units, calculated the wrong parameters, and totally ignored chemical stoichiometry. The eight projects listed in Table 1 are not being undertaken. Instead, chemically incorrect parameters continue to be used with neither stoichiometry nor the separate descriptions of sorption, desorption, intraparticle diffusion, and chemical reactions. The number of publications is so voluminous that there are even too many reviews to be cited [1]. This continues. Spot checks are the only practical way of testing what is still being done. Because it should have been the most authoritative choice, the published proceedings of the 2014 IUPAC-AgroChem Symposium were selected as a case study [17,18].

The chapter by Sabljic and Nakagawa is fundamentally flawed. The title of the symposium and its published proceedings focused on pesticide soil kinetics. However, the distribution coefficients k_D and k_{OH} that these authors presented are not related to kinetics. They are not even correct descriptions of pesticide soil equilibria. Pesticide sorption by soil has two reactants. They are: dissolved pesticide and empty sorption sites, a and b. The reaction product is filled sorption sites, c [1]. The early pages of first year chemistry textbooks all describe the equilibrium with an equation of the form:

$$K = c/ab \tag{1}$$

The symbols a, b, and c are the reactants and product mentioned above. This is derived from chemical thermodynamics and verified by experiments. The widely used distribution coefficient found in soil science reference textbooks is described with the equation:

$$k_D = c/a. \tag{2}$$

The above equation incorrectly neglects one of the two reactants, empty sorption sites, b [1,17]. In addition to its other problems [1,17], the octanol—water coefficient k_{OH} also does not account for empty sorption sites. This chapter not only ignores chemical kinetics and mechanisms, it also ignores first year chemistry descriptions of equilibria.

Chen, Laabs, Kookana, and Koskinen are the authors of the other chapter. Their proposed "non-first order kinetics" is flawed for the following reasons.

1   Chemical kinetics order is defined for individual processes or reactions, not groups of them lumped together as these authors have done [17].
2   For each pesticide soil process, all of the reactants and products have to be accounted for. That includes empty and filled sorption sites. Stoichiometry was ignored in this chapter.
3   Contrary to experimental evidence [17], the authors assumed that the kinetic rate coefficients were constants.
4   Constant half-lives are not obtainable from variable kinetic rate coefficients [17]. The authors ignored that.
5   Chemical units were not used. That prevented the use of chemical stoichiometry [1,17].
6   Rate determining kinetic processes could not be identified, because the processes were not separately described.

The flawed concept of "non-first order kinetics" from this confused chapter was carried over to the title of the whole book.

A random example suggests that these types of problems persist in recent publications [17].

5. Conclusions

There are three reasons why this decades-old mind set must change. First, soil and water supply the food for 7 billion people. The worldwide population must somehow be fed without poisoning people and their surroundings in the process. Secondly, with high energy particle physics, astronomy, and genetics making remarkable advances, environmental science will lose credibility if it does not keep up. Finally, the concepts and methods now available for progress must be improved and used instead of being ignored. When they are ignored, the money and manpower needed for the research program in Table 1 is wasted.

A reviewer has brought to our attention the importance of volatile pesticide interactions with soils. If money and manpower can be found to extend the research, head space analysis should be added to the kinetics experiments and the relevant research of other authors should be taken into account.

Conflicts of Interest: The author declare no conflict of interest.

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