PESTICIDE EMISSIONS FROM SOIL – FATE AND PREDICTABILITY

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Introduction

The need to safeguard global food supply has led to an increasing use of chemical pesticides during the last 60 Years. However, this need should be balanced with our responsibility also to safeguard human and environmental health. By definition, chemical pesticides are toxic compounds and can become pollutants of soil, water and air after their application. Such pollution can lead to human risk pathways, e.g. by the presence of pesticide residues in the food we eat, the water we drink, and the air we breathe. Once applied to the surface or subsurface of a soil, the fate of a pesticide compound is governed by its decomposition/degradation, its adsorption onto the solid phase of the soil, its dissolution in the liquid phase with subsequent movement by leaching, and its volatilization to the gas phase with subsequent diffusion through soil pores and/or emission to the atmosphere. Together with environmental variables (e.g. temperature, soil type and structure, soil moisture content), the physical and chemical properties of individual pesticides dictate the extent to which each of these processes acts upon a given compound. The potential for air contamination depends on the extent to which the pesticide converts to the gaseous state, i.e. its volatility. For some pesticides (e.g. the class known as fumigants), almost 100% of the chemical mass is potentially volatile under field conditions. In such a scenario, the potential for emissions from soil, and therefore air contamination, is very high. Research to understand the processes controlling pesticide emissions better can lead to the development of strategies that reduce these emissions; thereby assisting farmers in the protection of air quality and compliance with increasingly stringent air quality regulations. This article describes the extent of pesticide emissions from soil, the environmental and human health concerns of these emissions, and the efforts being made to predict these emissions using model simulations.

Pesticide Emissions from Soil

Recent estimates of pesticide use worldwide and in the USA have been reported by US Environmental Protection Agency (USEPA, 2011). Worldwide, total use was around 5.2 billion lbs of which the majority, 40%, was as herbicide, 17% as insecticide and 10% as fungicide (33% as 'other', including fumigants). In the USA, total use was around 1.1 billion lbs (22% of world use), again with the majority, 47%, as herbicide, but only 8% as insecticides and 6% as fungicide (39% as 'other', including fumigants). In the USA, 80% of all 2007 pesticide use was in agriculture, and of the 10 most highly used pesticides, 6 were herbicides and 4 were fumigants.

The emission potential of fumigant pesticides tends to be consistently high due to their extremely high volatility and vapor pressure across a wide range of environmental conditions. As such, a significant concern exists over their emission potential and their negative impact on localized air quality. The fumigants methyl bromide and methyl iodide have been found to emit over 80% of their total mass when injected into subsoil (Yagi *et al.*, 1993; Majewski *et al.*, 1995; Ashworth *et al.*, 2011). Other fumigants typically produce lower, but still highly significant, emissions from soil, such as 10–30% for chloropicrin and 30–50% for 1,3-dichloropropene (Gao *et al.*, 2008; McDonald *et al.*, 2008; Ashworth *et al.*, 2009). Reasons for lower emissions for these two fumigants when compared to methyl bromide and methyl iodide are their lower volatility and vapor pressures, and their greater level of degradation within the soil. The consistently high potential for soil fumigant emissions has led to the development of strategies that aim to reduce these emissions effectively. For example, relatively inexpensive approaches such as irrigation with water (to plug surface soil pores and thus prevent diffusion of the fumigant gas from the soil to air), compaction of the soil surface (to reduce the size of surface soil pores), and addition of reactive chemicals or organic materials (to increase the degradation of the fumigant within the soil and reduce the mass available for emission) have all been shown to be effective. The most popular approach however, and one often mandated by regulation, is the placement of plastic film over the soil surface after application of the fumigant. A variety of plastic films are available and the most impermeable of these have been shown to reduce the emissions of methyl bromide and methyl iodide to air very effectively.

Of the most highly used herbicides, both atrazine (ranked second in use statistics with approximately 78 million lbs used in USA in 2007) and metolachlor (ranked fourth in use statistics with approximately 35 million lbs used in USA in 2007) have been shown to volatilize readily and emit from soils after surface application. Gish *et al.* (2011) observed that following applications of these pesticides in consecutive years, atrazine emissions to air ranged from 2 to 12% in the 5 days following each application. During the same period, metolachlor emissions ranged from 5 to 63%. These workers noted that emissions were positively correlated with ambient temperatures, and also that highest emissions were found in years when surface soils were moist; due to enhanced adsorption of the pesticide onto the soil in dry conditions. Indeed, they

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found that under moist conditions, the total loss by emissions was greater than the loss by surface runoff. The most highly used insecticide in the USA, chlorpyrifos (ranked fourteenth in use statistics with approximately 9 million lbs used in USA in 2007), has also been found to emit readily from soil to air. In wind tunnel experiments, Wolters *et al.* (2003) measured a total emission loss of 44% during the 13 days after application. Again, these workers found that moisture at the soil surface enhanced emissions when compared to dry conditions. Although emissions of these traditional pesticide products are generally lower than fumigants due to their lower volatility and vapor pressure, and their greater susceptibility to environmental conditions, a significant potential for emissions does exist under certain conditions.

Figure 1. Measuring soil to air emissions of agricultural pesticides.

Problems associated with pesticide emissions from soil

Depletion of the stratospheric ozone layer is primarily associated with an increase in the presence of chlorine and bromine atoms which can destroy ozone molecules. Although ozone depletion is thought to be primarily due to chlorine, bromine is also highly significant because of the higher reactivity of bromine atoms (thought to be around 40 times more effective than chlorine at destroying ozone molecules). This has led to concerns over the role of fumigant methyl bromide in ozone depletion since each molecule of methyl bromide contains a bromine atom. The 1987 Montreal Protocol is an international treaty designed to limit the depletion of stratospheric ozone by phasing out the use and production of ozone depleting substances. In 1992, the Montreal Protocol called for a phase out of the use of methyl bromide in developed countries by the year 2010. In the USA, the phase out was initially scheduled for 2001 although this was later adjusted to 2005. Nevertheless, methyl bromide remains a highly used pesticide in the USA due to a number of exemptions to its banned use (termed Critical Use Exemptions). For example, in 2007, it was the third highest used fumigant in California. Therefore, the effect of emissions of methyl bromide on the stratospheric ozone layer remains a concern since depletion of this layer is associated with an increase in harmful ultraviolet light (UV-B) from the sun reaching the earth's surface.

Pesticide volatility and emissions from soils are a concern in terms of the direct inhalation of these chemicals by humans living and working close to the application sites. Such concerns are particularly acute in areas where pesticides are applied in the vicinity of especially sensitive populations, e.g. near schools and retirement homes. The health of agricultural workers in these areas is also likely to be at increased risk. Inhalation of pesticide products is associated with a number of human health impacts such as irritation of the respiratory tract, coughing, shortness of breath, dizziness and muscular twitching. More serious effects from exposure to pesticides are also reported. For example, atrazine, metolachlor, chlorpyrifos, methyl bromide and methyl iodide are considered toxic to human organs such as lungs, kidneys and the central nervous system. Moreover, atrazine is also thought to cause reproductive effects and methyl iodide to cause mutagenic effects. Both of these chemicals are also considered potentially carcinogenic.

The organic compounds released to the atmosphere following their emission from volatile pesticide products are termed volatile organic compounds (VOCs). These compounds may be the parent pesticide product itself, or a secondary product formed by degradation of the chemical within the soil. In addition to their direct potential toxicity, these compounds may also influence air quality via their role in the formation of near-surface (tropospheric) ozone. This type of ozone is formed by reaction between VOCs and nitrous oxides (e.g. from vehicle exhaust emissions) in the presence of sunlight. Near-surface ozone is a major component of photochemical smog and is therefore associated with human health effects via inhalation, such as irritation of the respiratory system, asthma and bronchitis. In summary, there are a number of ways in which pesticide emissions from soil can affect human and environmental health detrimentally.

Emission predictability

Due to their potentially adverse impacts on human and environmental health, it is important to quantify the extent of pesticide emissions from soil. Moreover, it is also necessary to assess the effectiveness of strategies that aim to minimize soil to air emissions of agricultural pesticides. To achieve this, laboratory and field experiments (Figure 1) can be conducted. However, these types of experiments are usually very time-consuming, expensive and difficult to replicate. In addition, it is practically impossible to conduct experiments to determine pesticide emissions for every soil, pesticide formulation, management practice, application method, and environmental condition. Also, in an outdoor environment, it is nearly impossible to isolate a single factor affecting the fate and transport process to determine its effect on emissions; instead all processes occurring during the experimental period affect the outcome.

Due to these constraints, computer simulation models have become increasingly used as powerful tools for risk assessment. Compared with laboratory and field experiments, they are a relatively simple and cost-effective approach to estimate pesticide emissions. Software code such as HYDRUS, CHAIN2D and PELMO are capable of predicting pesticide volatilization and movement, and ultimately, soil to air emissions. These models usually require the input of factors controlling pesticide behavior, including the physical and chemical properties of the pesticide (e.g. its volatility and vapor pressure), the ability of a given soil to conduct water and air and degrade or decompose the pesticide, the soil-air boundary conditions, and initial values of soil moisture, soil porosity, temperature, and pesticide concentrations in the system. In relation to simulating emission reduction strategies (e.g. the use of plastic films over the soil surface following the application of fumigants), the decreased potential for the volatile pesticide to move from soil to the air can be considered in the simulation.

Similar to any type of prediction model, there are three important issues to consider in relation to simulating pesticide emissions: 1) the availability and quality of input parameters, 2) testing and validation of the models, and 3) forecast. Firstly, the availability and quality of input parameters is essential for accurate prediction of pesticide emissions. Relatively accurate estimations of the physical and chemical properties of many pesticides are available (e.g., from the Material Safety Data Sheet for a given pesticide). General information about soil type and properties are also available to the public. However, due to potentially high spatial variation in soils, the movement and reaction of volatile pesticides in the soil is very site-specific. It is controlled by soil pore space, soil organic matter and clay contents, moisture, temperature, pesticide degradation rate in the soil, and adsorption onto soil particles. Management practices such as cultivation may result in temporal variation in these soil properties. Ideally, such variables are determined using simple field or laboratory methods to assist in the input of accurate numerical values to the simulation model. By taking account of the complex interactions between these variables, the model calculates the behavior of the pesticide i.e. its transport and fate in the liquid and gas phases of the soil.

Secondly, validation of the models against experimental measurements is of great importance. It ensures that the model represents the actual pesticide behavior in soils and at the soil-air interface. In other words, the validation process tells us how accurate the model is when compared to real data, and whether the results are acceptable or not. As an example, we validated a model (HYDRUS) for methyl iodide emissions by comparing experimental and simulated total emissions under treatments of a control (a bare soil with no emission reduction strategy imposed), and a soil covered by a type of plastic film known as virtually impermeable film (VIF) which was intended to reduce emissions to air (Luo *et al.*, 2012). The results showed that the model reasonably reproduced the shape and value of the experimental emission curves (Figure 2). Also evident from the figure is the excellent ability of the VIF to reduce methyl iodide emission from the soil compared to the bare soil. The slight increase in emissions at around 340 hours was due to the practice of cutting the plastic film at 2 weeks to allow for crop planting.

Thirdly, as an example of forecasting, we subsequently used the same model to predict methyl iodide emissions under a range of other, less expensive, emission reduction strategies (Figure 3). Here, a less effective (more permeable) plastic film known as high density polyethylene ('HDPE' in Figure 3) was shown to be relatively poor at reducing methyl iodide emissions, even when coupled with a deeper injection of the fumigant into the soil ('Deep' in Figure 3). The use of a chemical reagent, ammonium thiosulfate, ('Reagent' in Figure 3) which acted to enhance degradation of the methyl iodide within the soil was seen to be effective in reducing emissions, especially when used in conjunction with the application of irrigation water ('Irrigation' in Figure 3) and HDPE. Thus, using this approach, we are able to estimate the likely emissions from a range of scenarios without having to conduct field and laboratory experiments. Having initially validated the model against existing experimental data, we can have some degree of certainty that the model predictions are accurate. This highlights the potentially powerful nature of computer modeling in the prediction of pesticide emissions from soils.

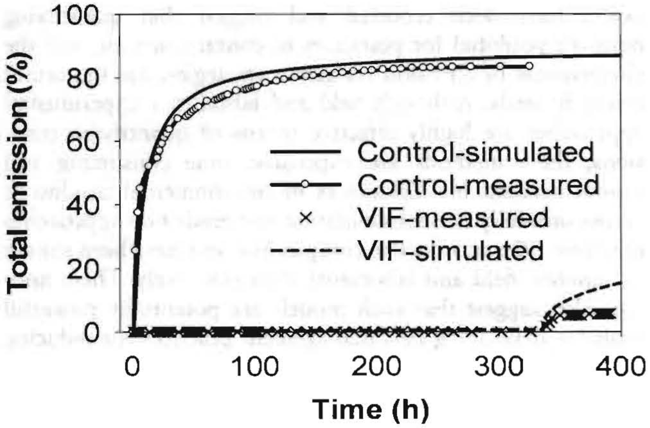

Figure 2. Demonstrating that the model reasonably reproduced the shape and value of the experimental emission curves.

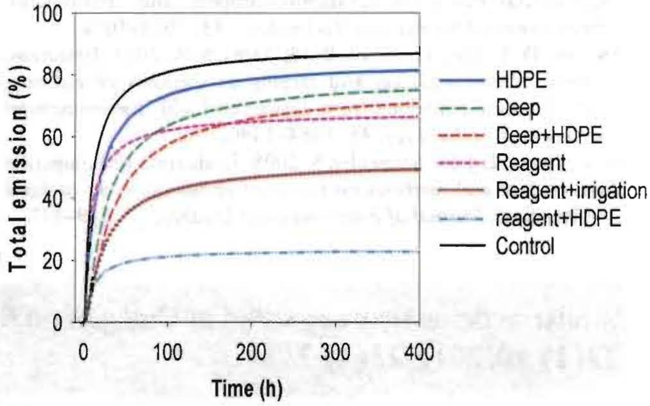

Figure 3. Predicting methyl iodide emissions under a range of emission reduction strategies.

Conclusions

The use of pesticides is an essential component of modern agriculture enabling farmers to meet the need for a safe, adequate food supply. However, care must be taken in the use of such pesticides due to their potential to cause environmental contamination. One aspect of this contamination is the volatilization of pesticides and their transport from soil to air. Subsequent potential effects on air quality and human health have been reported and suggest that quantifying both the potential for pesticides to contaminate air, and the effectiveness of emission reduction strategies, are important research needs. Although field and laboratory experimental approaches are highly effective means of quantifying emissions, these methods are expensive, time consuming and cannot account for differences in environmental conditions across sites fully. Model simulation and prediction approaches therefore offer an effective compromise and have been shown to simulate field and laboratory data effectively. These findings also suggest that such models are potentially powerful tools for developing best management practices for reducing pesticide emissions.

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