Understanding of pesticides in waters and soils using a novel *in situ* dynamic sampling technique

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By

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Abstract

There has been increasing concern about the widespread occurrence and persistence of pesticides in the environment. Pesticides can transport among and between environmental compartments, causing pollution in water, soil and air, and posing potential risks to humans and the ecosystem. There is a need to study the fate and behaviour of pesticides in the environment.

Over the last few decades passive sampling approaches have aroused attention in detecting pesticides, but they are still under development. In this thesis, the passive sampling technique of diffusive gradients in thin-films (DGT) was developed and validated for pesticides in water and soils for the first time.

The DGT technique was developed for *in situ* measurement of 9 pesticides in water. The compounds were carefully selected to represent a wide range of properties and classes, so that the technique may have wider applicability in future. Two types of binding material (HLB and XAD 18) were used and compared. Laboratory testing was carried out with various controlled experiments. HLB showed higher binding capacity but with slower uptake than XAD 18. The principle of DGT was confirmed as the mass accumulated by DGT was inversely related to the thickness of diffusive layer and proportional to the deployment time. The performance of the DGT sampler was found to be independent of pH (4.7-8.2), dissolved organic matter concentration (<20 mg L^{-1}) and ionic strength (0.01-0.25M). Several laboratory and field trials were conducted to confirm the usage of DGT for *in situ* measurement of pesticides in water and soils. DGT has great potential to be applied to trace organic contaminant studies in soils and sediments, but so far work research on this line has been very limited. DGT was therefore investigated for *in situ* measurement of atrazine (ATR) and its 5 metabolites in soils, and compared with other two approaches to predict bioavailability to maize and to assess the ATR

degradation pathway. The results showed that DGT performed best in measuring the bioavailability of total ATR (ATR and its metabolites) to maize. Hydroxylation was the dominant degradation procedure during aging and maize growth in the test soils. This could be well characterized using DGT.

DGT was also deployed in a group of aged soils with different pH, soil types and ATR contaminated levels, to explore the behaviour of atrazine in soils and its sorption/desorption. Soil properties had influence on the labile pool size (K_d) and re-supply capability of ATR (R), while aging affected the labile pool in some soils, but had only a slight influence on re-supply. The DIFS (DGT-induced fluxes in soil/ sediment) model was employed to further characterize the kinetics of desorption from the solid phase to the solution phase, this showed that desorption kinetics and the labile pool size commonly affected the re-supply.

Owing to the frequently simultaneous occurrence of ATR and arsenic (As) in the environment, DGT equipped with precipitated ferrihydrite binding gel was deployed to investigate the effect of ATR on the availability of As in soils. The addition of ATR did not impact on the measurements of As availability in the test soils, in the concentration range (up to 50 mg kg^{-1}) used.

This research has demonstrated that DGT is an effective tool for measuring pesticides in soils and waters. It can be used for monitoring purposes, and in experiments designed to better understand pesticide fate, behaviour, availability and to help with assessment of their risk in the environment.

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Abbreviations

A	Exposure window area of DGT device, cm^2
ACN	Acetonitrile
AF	Ammonium formate
As	Arsenic
ATR	Atrazine
C_b	Analyte concentration in the bulk solution
C_{DGT}	Analyte concentration measured by DGT
CHL	Chloridazon
CLO	Clomazone
C_{SE}	Analyte concentration in soil solution
C_{SS}	Analyte concentration measured by solvent extraction
CYA	Cyanuric acid
δ	Thickness of diffusive boundary layer, mm
Δg	Thickness of the diffusive layer, mm
D_{25}	Diffusion coefficient of analyte at 25 ºC, $cm^2\ s^{-1}$
DACT	Desisopropyl-desethyl-atrazine
DBL	Diffusive boundary layer
D_e	Diffusion coefficient of analyte, $cm^2\ s^{-1}$
DEA	Deethylatrazine
DGT	Diffusive gradients in thin-films
DIA	Deisopropylatrazine
DIFS	DGT-induced fluxes in soils
DOM	Dissolved organic matter
D_t	Diffusion coefficient of anaylte at temperature T, $cm^2\ s^{-1}$
ETH	Ethofumesate
FLU	Fluometuron
GHP	GH Polypropylene
h	Hour
HA	Hydroxyatrazine
HCl	Hydrochloric acid
HLB	Hydrophilic-lipophilic-balanced

HPLC	High performance liquid chromatography
IDLs	Instrument detection limits
IS	Ionic strength
ISs	Internal standards
K_d	Soil- water distribution coefficient
k_1	Adsorption rate constant
k_{-1}	Desorption rate constant
K_{ow}	Octanol-water partition coefficient
LC-MS	Liquid chromatography – mass spectrometer
LIN	Linuron
M	Analyte mass accumulated in the passive sampler
MeOH	Methanol
MDLs	Method detection limits
MQ	Milli-Q
MWHC	Maximum holding capacity water
NaCl	Sodium chloride
NaOH	Sodium hydroxide
PA	Polyacrylamide
PIR	Pirimicarb
POCIS	Polar organic chemical integrative sampler
PYR	Pyrimethanil
PRCs	Performance reference compounds
R	Ratio of DGT estimated to actual pore-water concentration
rpm	Revolutions per minute
R_S	Sampling rate
SPE	Solid-phase extraction
t	Time
T	Temperature
T_c	Response time
TEMED	N,N,N',N'-Tetramethylethylenediamine
THI	Thiabendazole
TWA	Time-weight average

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Chapter 1: Introduction

1.1 Rationale for the study

Pesticides are one of the most potent tools to maintain food supply. It is estimated that from 2000 to 2008, 0.3 million tonnes of pesticides were applied to agricultural crops in 20 European countries each year (Chiaia-Hernandez et al., 2017), nearly 0.4 million tonnes were sold in 28 European countries (Eurostat). They have protected crops and improved yield. However, a large fraction of the residues are persistent in the environment, transport among environmental compartments, transform by degradation into more stable structures, cause contamination in waters, soils and air, and may reach humans through the food chain (Gavrilescu, 2005). It is important to measure pesticides and understand their fate and behavior in the environment, especially in water and soil.

The conventional methods for detecting pesticides in waters are difficult to deliver and pre-treatment procedures are required (Gavrilescu, 2005). New techniques in passive sampling and screening pesticides have experienced growth over the last decades but are still under development. Limitations have been discussed, such as interferences from hydrodynamic conditions, the need for *in situ* calibration and there are limited reports so far monitoring pesticides in aqueous environments (Mills et al., 2014a). The traditional methods for measuring pesticides in soils are evolving as well, but they are either cheap but time-consuming and not environmentally friendly, or efficient but expensive and also need clean-up procedures.

Diffusive gradients in thin films (DGT), a novel passive sampler which has been used both in water and soil studies, is more than a monitoring tool. It is cost-effective, easy to operate and relatively unaffected by hydrodynamic conditions when sampling analytes in waters (Chen et al., 2015b). DGT focuses on the bioavailable fraction of compounds in soils, instead of the total concentration, while dynamic information of compounds in soils can also be provided with

DGT measurement (Zhang et al., 2001). Although DGT was invented for inorganic compounds, such as heavy metals (Zhang and Davison, 1995; Zhang et al., 1995) and phosphorus (Zhang et al., 1998a), its application has been developed for organics in recent years. It has been applied in waters for detecting antibiotics (Chen et al., 2012), pharmaceuticals (Chen et al., 2017), bisphenols (Guan et al., 2017) and anionic pesticides (such as bentazon and chlorsulfuron) (Guibal et al., 2017), while kinetic information on bisphenols and antibiotics has also been obtained by DGT. These studies show the possibility for DGT to measure pesticides in waters and soils.

1.2 Research aims

The aim of this project was to develop a dynamic sampling technique for *in situ* measurements of pesticides, which could be applied to understand their behaviour in waters and soils. Specific objectives of the PhD project were:

(1) to develop the DGT technique for *in situ* measurement of a range of pesticides in the aquatic environment and soil;

(2) to investigate the bioavailability of pesticides in soils using different chemical measurements (porewater extraction and organic solvent extraction) and compare them with DGT measurement;

(3) to extend the application of the newly developed technique in soils, to assess aging effects, labile pool size and kinetic resupply of pesticides in soils using DGT and DGT induced fluxes in soils (DIFS);

(4) to explore potential for interactions between a pesticide (atrazine) on the availability of a heavy metal/metalloid (arsenic) in soils, using DGT.

1.3 Structure of the thesis

The following literature review in **Chapter 2** comprises an introduction to pesticides and a description of passive sampling techniques. The review starts with the importance of pesticides for a range of uses. The environmental behavior and fate of pesticides residues in soil and water is discussed, because of concerns over their efficacy and potential for adverse effectson the environment and human health. In order to track pesticides in the environment, a reliable and informative measurement and monitoring approach is required. A variety of methods in current use to measure pesticides in water and soil are therefore discussed.

Passive sampling techniques are then introduced, and the principles of passive samplers and criteria for their design are described. This focusses on 3 designs - POCIS and Chemcatcher passive samplers which have been used for pesticides in previous work, but have still not been widely adopted because of their limitations - then DGT. DGT is introduced with its application for inorganic chemicals in natural waters, soils, sediments, its applications for organic compounds are recommended and its potential advantages introduced. This lays the foundation for the studies presented in this thesis.

Chapter 3 described the laboratory test of DGT for 9 pesticides with two types of resin (HLB and XAD 18) as binding layer materials. The diffusion coefficients of these 9 pesticides were measured. The capacity and uptake kinetics of these two resins were measured and both validated by the principle of DGT through time dependence and diffusive layer thickness dependence tests. The effects of environmental factors, including pH, ionic strength and dissolved organic matter were investigated. The application of DGT in the environment was the confirmed by field work in rivers and soils.

Pot experiments were conducted in **Chapter 4** using maize growing in 5 different types of soils which cover a range of pH and organic matter contents. Atrazine was applied at two concentrations. The diffusion coefficients of atrazine and its 5 metabolites in DGT gels were

measured, so that experiments with the soils and plant uptake could be interpreted. Concentrations of available atrazine and its metabolites in soils were measured by DGT, pore water extraction and organic solvent extraction. All the measurements were compared with the concentrations in maize to investigate the bioavailability of atrazine and its metabolites. The degradation pathway of atrazine was also discussed.

In **Chapter 5**, the DGT devices were deployed in a group of aging soils with different pH and soil types, dosed with two levels of atrazine. The DIFS model which described the diffusional transport and dynamic exchange of solute between solid phase and solution was used to estimate the desorption rate constants and the labile pool size of atrazine in the soils through the ratio (R), distribution coefficients (K_d) and response time (T_c). The aging effect on these parameters was discussed.

Chapter 6 presents an investigation into the effect of atrazine application on the availability of arsenic in soils. Test soils were contaminated with three levels of atrazine. DGT, pore water extraction and sodium bicarbonate extraction were carried out to measure arsenic concentrations in soils. The effects of atrazine on R and K_d were also discussed.

Chapter 7 provides the conclusions of the thesis and discusses the possibilities of the future work arising from this study.

Chapter 2: Literature Review

2.1 Pesticides

According to the U.S. Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), a pesticide is defined as: 'any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. The pest refers to insects, rodents, nematodes, fungi, weeds, other forms of terrestrial or aquatic plant or animal life or viruses, bacteria, or other micro-organisms, except viruses, bacteria, or other micro-organisms on or in living man or other animals, or any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant' (Marrs and Ballantyne, 2004).

2.1.1 Introduction of pesticides

2.1.1.1Classification

There are more than 136 categories of pesticides classified, with respect to the target organism, chemical structure or mode of action (Marrs and Ballantyne, 2004) as listed in **Table 2.1**.

Table 2.1 Classification of pesticides

Classification dependence	Examples
Organism attacked	herbicides, fungicides, insecticides etc.
Chemical structure	organophosphorus, carbamates, organochlorines, pyrethrums etc.
Mode of action	anticholinesterases, glutamine synthetase inhibitors, chitin synthesis inhibitors etc.

2.1.1.2 Development

The history of the utilization of pesticides can be broadly divided into two stages. Before the 1940s, natural and mineral medicines based on natural resource and inorganic compounds were applied widely. From the early 1940s, the synthetic organic pesticides came into use, and the protection of crops has been changed tremendously.

The development of the synthetic organic pesticides started from the development of organochlorine pesticides, the period of 1940s was charaterized by the discovery and application of dichlorodiphenyltrichloroethane (DDT) and other chlorinated hydrocarbon insecticides (Krieger, 2001). DDT was found to be effective against almost all kinds of insects, which made it become the most widely used pesticide in the world (Rathore and Nollet, 2012). In Europe, the traditional botanical insecticides supply was restricted by wartime shortages and blockades, so there was pressure on chemical factories to synthesize or manufacture replacements, to secure the provision of crops and protect people from diseases. France and the UK found the insecticidal properties of hexachlorocyclohexane almost simultaneously. Then the discovery of insect-killing properties of lindane, followed by the wide spread of DDT, led to the extensive development and commercialization of new synthetic insecticides.

In Germany in 1937, the insecticidal activity of organophosphorus compounds was discovered; at the same time, these compounds were found to be powerful inhibitors of cholinesterase and toxic to mammals. Bladan was the first commercial production of organophosphorus insecticides, then many less toxic analogues were synthesized for use as insecticides, fungicides and plant growth regulators (Krieger, 2001).

In recent years, the high residue and environmental pollution of pesticides all over the world has attracted widespread concern. Many pesticide companies are now attempting to develop a series of high efficiency, low toxicity and good selectivity new pesticides.

For insecticides, the development and application of bionic pesticides such as pyrethroids and neristoxin insecticides are thought to be a breakthrough. In addition, the insect growth regulators containing chitin synthesis inhibitors were introduced into the market. Some insecticides like buprofezin, triflumuron, teflubenzuron, chlorfluazuron and methoprene are widely used.

For fungicides, the main products can be classified as morpolines, piperazidines, imidazoles, triazoles, pyrazoles and miazines; they are all chlorine heterocyclic compounds such as tridemorph, triforine, imazalil, prochloraz and triazolone. They can protect and cure diseases caused by bacteria in plants simultaneously, since they can be absorbed and translocated within plants. The efficiency of these fungicides has been improved by an order of magnitude.

Herbicides have been through major development, due to the mechanization and modernization of agriculture. They have high activity, selectivity, degradability and appropriate duration, which can solve long-standing weed problems effectively. The introduction of sulfonylurea and imidazolinone herbicides has been a revolution. They work for a variety of annual and perennial weeds, by blocking the synthesis of branched chain amino acids, and they are safe for human and animals. The major types of herbicides used currently are chlorsulfuron, metsulfuron-methyl, diclofop-methyl, buthidazole, imazaquin and glyphosate.

Table 2.2 Development of widely used pesticides in the history

Pesticide type	Examples
Insecticides	DDT, lindane, organophosphorus pesticides (like bladan), pyrethroid, neristoxin, buprofezin, triflumuron, teflubenzuron, chlorfluazuron, methoprene etc.
Fungicides	tridemorph, triforine, imazalil, prochloraz, triazolone etc.
Herbicides	chlorsulfuron, metsulfuron-methyl, diclofop-methyl, buthidazole, imazaquin, glyphosate etc.

2.1.2 Fate of pesticides residues in soil and water

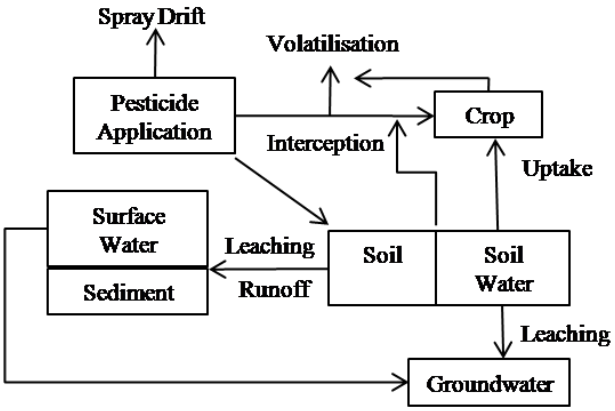


Figure 2.1 Pathways of a pesticide applied to a crop

Most agricultural pesticides are introduced as liquids sprayed on the soil and/or crops. They disperse among environmental compartments once released/used (Fig. 2.1) (Arias-Estévez et al., 2008).The pesticides which reach the target area will largely be adsorbed and bound by soil components and then begin to degrade, be taken up by target plants or non-target soil organisms, runoff or leach into surface water and groundwater, or volatilise into the atmosphere (van der Werf, 1996). Reduced pest control may be due to these transfers since pesticides must remain within a certain soil area to reach the target. Surface and ground water may become contaminated, and other species may be exposed during the distribution of pesticides. The interactions between pesticides and soil, water or plants are controlled by numerous and complex chemical, biological and physical reactions.

2.1.2.1 Pesticides in the soil

The transport of pesticides within the soil and their transfer from the soil to other environmental compartments (i.e. degradation, uptake by plants, volatilization, runoff and leaching) is directly determined by sorption-desorption processes. The physico-chemical properties of the pesticide compound and soil characteristics play an important role in these processes (Linn et al., 1993).

Adsorption and desorption

Adsorption is an important physicochemical process governing the fate of pesticides in the soil (Kan et al., 1994). It occurs as a result of an aqueous molecule attracted and retained on the surface of a solid (Rathore and Nollet, 2012). Adsorption can be either physical, as with van der Waals forces, or a chemical process as with coulombic forces and results from bond formation between the adsorbent and adsorbate. (Bailey and White, 1964). The sorption process of most pesticides is composed of an initial fast step followed by a much slower step tending towards final equilibrium (Pignatello, 1998). It affects pesticide leaching in the subsurface and transport to other environmental compartments. Bioavailability of pesticides can be reduced by adsorption to mineral surfaces or soil organic matter, leading to reduced pest control, since pesticides cannot be taken by the root of the target plant (Foght et al., 2001). With longer residence time in the soil, bound pesticides tend to lose their biological activity, until they become resistant to degradation and extraction. Desorption is also of significant importance, since it determines the release rate and the potential mobility and availability of pesticides in soil. Desorbed pesticides may become surface water contaminants and non-target plants around may be impaired if pesticides applied are re-released from the soil particles (Kan et al., 1994).

The tendency of a pesticide to be adsorbed by soil can be expressed by its distribution coefficient, K_d, which is defined as the ratio of the concentration in the solid phase to the dissolved concentration (Equation 2.1):

$$K_d = \frac{C_s}{C_d} \quad \textbf{(2.1)}$$

Where K_d is the distribution coefficient of a pesticide molecule between soil and water; C_s is the amount of pesticide adsorbed per unit of adsorbent mass; and C_d is the concentration of pesticide in the solution phase (Tuzimski and Sherma, 2015).

A high K_d value refers a strong sorption of a pesticide onto the soil particles, and thus it will not tend to leach (Carlile, 2006). K_d has been found to be related to the levels of clay and organic matter in the soil and is related to the pesticide soil organic partition coefficient (K_{oc}) (Equation 2.2):

$$K_d = \frac{K_{oc}\ OC}{100} \quad \textbf{(2.2)}$$

where K_{oc} is the soil organic partition coefficient and OC is the organic carbon content (%). Hydrophobic pesticides with a high K_{oc} value will have a high affinity to be retained in soil. This tends to give compounds greater persistence – measured as a long half-life in the soil (Hildebrandt et al., 2007).

The adsorption process depends on a variety of factors, including physicochemical properties of soils (such as soil texture, moisture, organic matter content, pH, soil particle distribution, soil temperature) and properties of the pesticides (pesticide molecular structure, electrical charge, solubility, polarity and octanol-water partition coefficient (K_{ow}) (Gavrilescu, 2005). The organic matter content has a large influence on the adsorption process. Walker and Crawford (1968) found that with an organic matter content up to about 6%, mineral and organic surfaces both contributed to adsorption. At higher organic content, adsorption occurred mostly on organic surfaces (Connell and Miller, 1984).

Dao and Lavy (1978) claimed that atrazine adsorption increased with the reduction of soil moisture, and was positively correlated with soil temperature and electrolytes concentration in soil solution. The study from Jenks et al. (1998) indicated that the decrease of soil pH and increase of organic matter content led to the increase of atrazine adsorption. Organic matter content was the best single predictor of atrazine adsorption ($r^2 = 0.98$), followed by soil pH ($r^2 = 0.82$), using multiple regression. Huang et al. (Huang et al., 1984) showed that the soil particle size fraction < 20μm provided more adsorption sites for atrazine.

Degradation

After application, degradation is the major loss process of many pesticides from soil. Degradation refers to the breakdown of parent molecules to degradation products or complete mineralization to carbon dioxide. Degradation may be via microbial, chemical and photo-chemical decomposition. It may change most pesticide residues in the soil into harmless nontoxic compounds, but some by-products may still be hazardous.

Microbial degradation

Biodegradation, which is the result of microbial metabolism of pesticides, occurs when fungi, bacteria and other microorganisms in the soil consume pesticides as a source of food and energy, or use the pesticides along with other sources of carbon. It is often the main pathway of pesticide degradation in soils. Soil organic matter content, moisture, temperature, aeration and pH are all factors that affect biodegradation. Microbial growth is favoured in warm, moist soils with a neutral pH. Adsorption also has influence on biodegradation, since sorbed pesticides are not instantaneously accessible to microorganisms and sorption reduces their degradation, as well as their transport (Koskinen et al., 2001). Most of the biotransformation requires enzymes as catalysts. Hence, biodegradation depends on sufficient biomass and sufficient contact between pesticides and enzymes. The ability of microorganisms to produce requisite enzymes and ideal environmental conditions for the reactions determines the degradation process.

Chemical degradation

Chemical degradation occurs by the breakdown of a pesticide without a living organism (Levine, 2007). It can be via hydrolysis, oxidation-reduction, substitution, elimination, dehalogenation and ionization.

Hydrolytic reaction is the most common reaction that takes place for pesticides in which the molecules split apart with the addition of water molecules (Manahan, 2011). This process depends on several factors. The hydrolytic reactions are catalyzed by hydrogen or hydroxide

ions, so soil pH or pH of the medium strongly contributes to the reaction rate. Temperature also positively affects the reaction rate, as with higher temperature the molecules move and react faster. Organic matter and clay content can enhance hydrolytic degradation by providing larger surface area. Soil moisture and pesticide concentration both have influence on the reaction rate and type of chemical reactions (Levine, 2007; Rathore and Nollet, 2012). Some functional groups of the original pesticides are replaced with a hydroxyl group in the hydrolysis reactions; the new compounds are usually less toxic.

Photodegradation

Photodegradation is the breakdown of pesticides by sunlight (Singh, 2016). It occurs when radiant energy in the form of photons breaks the chemical bonds of a molecule (McKeon and Segna, 1987). Compounds which absorb light within the solar spectrum (λ>290 nm) can be directly photodegraded by absorbing a photon to the target molecule. Indirect photolysis occurs more commonly. It is introduced by a photosensitizer which absorbs the photon to produce reactive species (Tsipi et al., 2015). The photodegradation is influenced by intensity of sunlight, time of exposure, properties of the site, method of application and the properties of the pesticide (Rathore and Nollet, 2012). It is a major reaction that often occurrs in surface water and soil. Hebert and Miller (1990) found that the direct photolysis of flumetralin and disulfoton was restricted to the photic depth of soils (0.2-0.3 mm) under laboratory irradiation, while the mean indirect photolysis depths were greater than 0.7 mm for outdoor exposures. The half-life of niclosamide was reported to increase from 95 to 195 h as soil depth increased from 0.5 mm to 3.0 mm in the moisture-maintained, while with air-dried soil the half-lives showed a much broader range of 199 h at 0.5-mm to 1064 h in 3.0-mm (Frank et al., 2002).

Potential forms of pesticides in the soil

After the contact and reaction with the soil, pesticides may become more strongly associated with soil components. The forms of pesticides in the soil can be classified as the extractable

fraction and bound (non-extractable) fraction at any time after the pesticides enters the soil. The extractable fraction of pesticides refers to the portion of pesticides that can be extracted by chemical methods from the soil, but it is affected by the nature of the extractant and the experimental conditions, since the time and intensity of extraction varies among different extraction procedures. On the contrary, bound pesticide residues are defined more clearly as the pesticides non-extractable after exhaustive sequential extraction. The importance of the study of these bound residues is not to explore their non-extractability, but to investigate their bioavailability, the availability to living organisms (Reid et al., 2000a; Semple et al., 2004; Gevao et al., 2000; Gunther and Gunther, 2012). The study of Gevao et al. (2001) indicated that some of the bound fraction of pesticides in the soil could still be taken up by earthworms. Bound DDT and HCH were still available to grain, maize, rice and earthworms (Verma and Pillai, 1991b; a). The bioavailable fraction of the pesticide in the soil is most significant for risk assessment. The readily available, extractable and bound fraction of compounds in soils changing with time is presented in Fig. 2.2 (Semple et al., 2003).

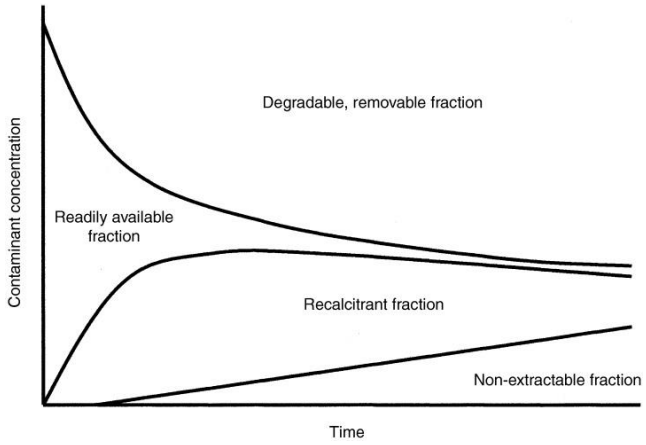


Figure 2.2 The influence of contact time on the extractability and bioavailability of a contaminant

2.1.2.2 Uptake by plants

Pesticides can be accumulated in plant tissues after they are moved from the soil into plants. The uptake of pesticides by plants can be a source of food chain bioaccumulation and an

important route of exposure to humans and animals (Paterson et al., 1990). There are four possible pathways for pesticides to enter plants from soil: root uptake into conduction channels and translocation by the transpiration stream; uptake from vapour in the air; external contamination by solids, followed by retention in the cuticle or penetration through it; transport in oil-containing plants through oil cells (Topp et al., 1986). Uptake of pesticides by the roots is generally considered the most important route, it occurs more readily with hydrophilic pesticides rather than lipophilic ones (Connell and Miller, 1984). The half-life of pesticides is of great importance, affecting the availability and supply for plant uptake. A pesticide with a half-life <10d is less likely to enter the plant. When the half-life becomes longer, the plant has a greater potential to take up the pesticide with the increasing growth period of the plant. Apart from the above properties, soil characteristics like temperature, organic matter content, clay fraction, pH and soil moisture also affect plant uptake. Properties of pesticides, such as water solubility, vapour pressure, molecular weight, K_{ow} and the method of application influence the uptake. The uptake process may also be related to the plant species (Cockerham and Shane, 1993).

Once they enter the plants, pesticides can translocate upwards or acropetally or basipetally through the xylem or phloem (Ahmad, 2014). Redistribution of pesticides and their metabolites is usually limited in plants (Matsumura, 2012).

Pesticides which have penetrated into plant tissue can remain in the plant or be metabolized to other compounds. Pesticide metabolites can be classified as free compound, conjugated metabolites and bound residues (Tsipi et al., 2015). Free metabolites derived from oxidation, reduction and hydrolytic reactions producing functional groups into pesticide molecules are primary metabolites. These reactions may be mediated by a range of enzymes; this is often the first step to detoxifying pesticides. Conjugation reactions refer to an endogenous substrate, where chemicals generated within the plants chemically bond to the pesticide and mainly occur

with glutathione (GSH), sugar and amino acids (Hoagland et al., 2001). Conjugates are more polar than most free compounds and often soluble only in water or other highly polar solvents. Sometimes the pesticides are covalently bonded to an insoluble portion of the cell matrix to form bound residues which are often not bioavailable in the plant. These residues cannot be extracted non-destructively from the plant tissue either. Finally, some pesticide metabolism processes in the plant can be conducted completely to carbon dioxide (Zweig and Sherma, 2016).

2.1.2.3 Pesticides in aquatic environments

Water may disperse pesticides into the environment via foliar wash-off, surface runoff and leaching. Pesticide runoff leads to contamination of surface water and leaching contributes to pollution of groundwater.

Surface runoff occurs when water application to the ground surface is faster than infiltration and exceeds the surface storage capacity. The water moving over a sloping surface and carrying pesticides from agricultural areas can cause serious pollution to surface water bodies such as rivers, lakes, oceans or seas (Agrawal et al., 2010). Once entering the water body, pesticides may be diluted through transport. The form in which the compounds exist in water and the hydrodynamics of the system determine the transport of pesticides in surface runoff (Larson et al., 1997). A pesticide molecule can exist in the dissolved phase, with transport depending on water flow. If the pesticide is associated with a particle or colloid, transport relies on the type of substrate with which it is associated and the movement of the particle or colloid. For substrates like dissolved organic matter or colloids, water flow governs the transport of pesticides as that of dissolved molecules. Pesticides associated with particles such as sands and clays, or coagulated with very fine particles are predisposed to settle out in lakes, reservoirs and backwaters. Hydrophobic organic pesticides tend to associate with natural organic matter. They are likely to accumulate in bed sediments with relatively high organic matter content

(>1%). The hydrodynamics of the system distributes the sediments after pesticides are desorbed from these areas.

Pesticides in the aquatic environment may be transformed or degraded through photochemical, chemical and biological reaction. The degradation process is important to the impact of leaching. Not only the movement of pesticides but also their disappearance from soil determines whether the pesticides will contaminate the groundwater by reaching the water table (Gavrilescu, 2005). Leaching is the movement of pesticides through the soil rather than over the surface. If the rate of leaching is sufficiently rapid, the parent pesticides will not degrade before they reach the groundwater and will induce environmental problems, but in some situations the degradation products will be more harmful (Khan, 2013).

2.1.3 Environmental and human health impact of pesticides

In 1962, biologist Rachel Carson alerted the public to the potential negative effects of pesticides in her book, *Silent Spring*. Questions were raised about the actual (rather than the perceived) benefits of pesticides, along with questions about environmental and public health risks (Rathore and Nollet, 2012).

Pesticides now attract a great deal of attention from the public (Stenersen, 2004), since most of the applied pesticides in the agricultural lands may affect non-target organisms and contaminate soil and water media.

Potential effects in Soil

Pesticides are designed to kill target organisms. Usually, however, only a small proportion of applied pesticides reach the target pests, in most cases <1% (Pimentel, 1995). So, often>99% remains in/moves through the environment and may cause unintended environmental effects. Pesticides can be hazardous to the indigenous organisms like beneficial competitors, predators and parasites of target pest insects (van der Werf, 1996). For example, atrazine can reduce

the earthworm population (Ramachandra, 2006). Some studies show that pesticides inhibit soil microbial diversity and activities (Ingram et al., 2005; Littlefield-Wyer et al., 2008), adversely influence soil biochemical processes, even disturb soil ecosystems (Hussain et al., 2009). It is important to consider the potential of pesticides to reduce soil enzymatic activities that act as a bio-indicator of soil fertility (Antonious, 2003). Soil fertility can also be affected by pesticides through disturbing the dynamic balance in the reservoir of organic and inorganic nutrients, possibly disrupting the supply of nutrients available to plants (Ramachandra, 2006).

In recent years, precautions have been employed to decrease potential negative environmental effects of agrochemical use. Stricter legislation, such as reducing pesticide application rates and usage of pesticides with lower toxicity and persistency, and new technology like buffer zones and low drift technology, have been adopted (Phipps and Park, 2002).

Potential effects of Water Contamination

Pesticides not absorbed by plants and soils or broken down by sunlight, soil organisms, or chemical reactions may ultimately reach groundwater sources of drinking water. Approximately one-half of the global population obtains water from wells. Once groundwater is contaminated by pesticides, the residues could remain for long periods of time since there are just a few microorganisms that have the potential to degrade pesticides, but the groundwater recharge rate averages <1% per year. Humans may be exposed to pesticides by eating contaminated fish or directly consuming the contaminated water.

Potential effects on Humans

The potential harm caused by pesticides to humans can be distinguished as short-term effects (acute poisoning) and long-term effects (chronic hazards) (Hallenbeck and Cunningham-Burns, 2012). Human contact with pesticides via oral or respiratory pathways has sometimes led to acute pathological responses, causing reports of neural paralysis and even death.

Farmers working the agricultural lands, mixing and spraying pesticides are certain to have higher dermal and respiratory exposures to pesticides than the general public.

Nowadays people are generally more concerned about the effect of long-time exposures to trace levels of pesticides (Levine, 2007). Some pesticides can accumulate in human tissues after long-term exposure or eating food containing pesticide residues. Concerns have centred around whether they have a potential threat to human health, if they can affect the nervous system, damage liver function, cause immune disorder, and even lead to cancer (Pimentel et al., 1992). Human pesticide poisonings and illnesses caused by pesticide usage are clearly the highest price paid for maintaining high crop production (Pimentel, 1995). Based on some animal tests, the International Agency for Research on Cancer claimed that 18 types of widely used pesticides were carcinogenic, while 16 types displayed a potential. Studies have linked the rising incidence of non-Hodgkin's lymphoma (NHL), a form of cancer, to the increased use of organophosphate pesticides and phenoxy herbicides and the cumulative effects of these pollutants on the human system (Nollet and Rathore, 2016). There are various categories of pesticide exposure for humans, the major route is through residues in the food supply. They may also be absorbed from drinking water or contaminated air.

2.1.4 Methods to measure pesticides in soil and water

2.1.4.1 In soil

The measurement of pesticides is conventionally performed directly by extraction. Before the final analytical measurements, sample preparation ideally needs to be rapid, simple and cheap. The procedure for obtaining purified extracts should avoid pesticide degradation during the treatment.

Several traditional liquid-solid extraction (LSE) methods have been conducted extensively since they are simple and cost effective, such as Soxhlet extraction (Wang et al., 2007) and

mechanical shaking (Babić et al., 1998), but they are also laborious, time-consuming, difficult to automate and need large volumes of toxic organic solvents (Sun and Lee, 2003).

Facing these disadvantages, more efficient environmentally friendly techniques for the rapid analytical-scale extraction are required. Some modern techniques have been introduced, including accelerated solvent extraction (ASE) (Gan et al., 1999), also known as pressurized liquid extraction (PLE), microwave- assisted extraction (MAE) (Vryzas and Papadopoulou-Mourkidou, 2002), supercritical fluid extraction (SFE) (Snyder et al., 1992), ultrasonic solvent extraction (USE) (Goncalves and Alpendurada, 2005) and solid-phase micro-extraction (SPME) (Aulakh et al., 2005; Beltran et al., 2000).

ASE has a similar principle to Soxhlet extraction, but it can be completed within a short time and with a smaller quantity of solvent, because it is applied at temperatures in the range of 40-200 ºC and pressures in the range of 1000-25000 psi. The solvents which have been heated and pressurized are able to solubilize the chemicals and penetrate the sample matrices more effectively, but the high temperature may cause degradation of pesticides during extraction.

MAE is operated with microwave energy to heat the solvent and the sample for extracting organic chemicals, by causing molecular movement and rotation of liquids with a permanent dipole. It has gained wide acceptance, since it can reduce solvent consumption and shorten extraction time. The usage of multi-vessel systems leads to an increase in sample numbers.

Compared with the traditional methods, SFE is superior in extraction efficiency, faster and selective. In SFE, both pressure and temperature are above the critical values of the extraction. In the supercritical fluids, the viscosity of analytes is lower than that of liquids, and the diffusion coefficients are higher. However, SFE does not save time and the initial equipment cost is more expensive than the conventional methods. It cannot handle large sample amounts and recoveries can be lower for markedly polar pesticides and metabolites.

USE, which is performed with ultrasonic baths, is easy to operate, little or even no sample preparation is needed, with low extraction temperature and low equipment cost. The solvent type and solvent mixture can be selected prior to the extraction to obtain maximum efficiency and selectivity. A large number of samples can be extracted simultaneously, in the absence of additional clean up procedures.

The techniques described above focus on efficient and complete extractions – designed to yield the 'total concentration' of pesticide in the soil. However, the 'relevant portion' environmentally is the 'bioavailable fraction' which is more important for risk assessment. It is also not possible to acquire any kinetic information from the extraction procedures described above. There is therefore interest in the use/development of methods which can quantify the readily available fractions in soils and could give information on the release kinetics/processes. Solid-phase micro-extraction (SPME) is a step in the direction of measuring the 'free' or 'labile' portion of pesticide in soils. It is a solvent-free extraction technique that employs a fused-silica optical fiber coated with a hydrophobic polymer. The analytes come into equilibrium with the SPME that is usually housed in a modified syringe, according to their affinity for the solid phase. This approach is simple, reproducible, and has low detection limits as it concentrates the analytes.

These methods have been more and more favoured in recent years, but many of the methods mentioned need expensive, sophisticated equipment. After extraction, a clean-up or pre-concentration procedure is usually required (Pose‐Juan et al., 2014; Alvarez-Benedi and Munoz-Carpena, 2004).

2.1.4.2 Methods to sample pesticides in waters

Several water samplers have been created and manufactured for different aquatic environments. The samplers need to provide rapid immersion in water, drift minimally from the vertical

position, have a suitable sealing mechanism to preserve the sample, have an adequate capacity, and be user friendly. The selection of water samplers is determined by the location of the sampling site, the depth at the sampling point, the distance from the bottom to where it is situated, sample size and type, site accessibility, and the type of matrix (Namiesnik and Szefer, 2009).

For surface water sampling, a held-hand open mouth bottle can be adopted to collect nearshore small samples, assuming that the depth and the water flow rate are smaller compared to the minimum for depth-integrating samplers. In the analysis of trace pesticides, large volume samples are usually required. The sample can be pumped through tubes into a larger container. If the sample should be taken from a selected depth, the container needs to be able to collect water at the required depth and transport the sample in undisturbed form. A weighted bottle stoppered with a cork connected to the bottle neck by a line used to open the bottle at the required depth is the simplest sampler used in this case.

For groundwater sampling, the type and location of the well, depth of water from the land surface, the physical properties of the well and the target chemicals are the most significant factors affecting the selection of samplers. In groundwater monitoring, pumps designed specifically for monitoring wells or pumps installed in supply wells, bailers, and thief-type samplers are most commonly applied.

The automatic sampling system is a portable sampler unit designed to take discrete sequential samples, time-composite samples or flow-composite samples over a given time period. Samples can be collected at about 0.5 m below the water surface. The auto-sampler will be triggered by the set flow volumes to fill up to 24 discrete bottles per week. These bottles can then be composited into one sample after one week. This offers more consistent results without manual intervention (Engineers, 2007; Namiesnik and Szefer, 2009).

2.2 Passive samplers

As mentioned in many documents, a number of pollutants which can be harmful to both human health and ecosystems are detected in the aquatic environment and terrestrial systems. It is essential to monitor these toxic compounds to determine the water quality (Vrana et al., 2005).Some institutions have set up directives for the measurement of priority pollutants which are on the lists of the US Environmental Protection Agency (EPA) and the Water Framework Directive of the European Union (EU). Sampling and analysis of such a broad range of inorganic and organic compounds is really a challenge.

In the conventional method of sampling, based on collecting discrete grab, spot or bottle samples of water, large volume samples should be collected when the pollutants are present at trace levels. However, this approach cannot cope with episodic pollution events, when pollutant concentrations vary over time - it only provides concentrations at the time of sampling. Increasing the frequency of sampling or automatic sampling systems could help with this problem, but it is costly and time-consuming as more samples should be taken from the spots over the entire duration of sampling and more treatment is required. The pre-treatment applied also affects the results, which may not be able to reflect the real contamination level.

Therefore, a rapid, effective and cost efficient sampling method is required to monitor the fate and concentrations of pollutants in the environment and evaluate the impact of these compounds in the environment. Passive sampling techniques – if properly understood and deployed - are able to satisfy these requirements (Namieśnik et al., 2005). There has been a tremendous increase in the use of passive samplers in recent years. The concentration of the analyte is measured as a weighted function of the time of sampling. Passive sampling is less sensitive to accidental, extreme variations of the analytes in natural waters. Passive samplers use a diffusion gradient to collect the analytes and an extraction process is often used after sampling (Tadeo, 2008).

2.2.1 Principle of passive samplers

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials of the analyte in the two media (Zabiegała et al., 2010).

Nearly all of the passive samplers are comprised of two components: a barrier and a sorbent. There are two types of barriers, one is a static layer of the surrounding medium (diffusion-type samplers), or a polymer membrane (permeation-type samplers). The net transport within the barrier happens mainly following Fick's law. The analyte begins to diffuse through the barrier to the sorbent when the sampler is exposed to the sample matrix. The uptake of the analyte, which is conducted by passive diffusion, will not stop until the chemical potentials of the analyte in the sorbent and in the sample matrix become equilibrium, or until the sampling period is stopped (Vrana et al., 2005).

Different material and geometry of the barrier and sorbent are selected, relying on the specific type of analyte and the matrix. Some other components have been introduced to these samplers and various designs of passive samplers are available (Seethapathy et al., 2008). They can be used for the detection of both inorganic and organic compounds in a variety of matrices, including air, water and soil.

A first-order, one compartment mathematical model can be used to fit experimental measurements of the exchange kinetics between a passive sampler and water phase:

$$C_s(t) = C_w \frac{k_1}{k_2}(1-e^{-k_2 t}) \qquad \textbf{(2.3)}$$

Where $C_S(t)$ is the concentration of the analyte in the sampler at exposure time t, C_W is the analyte concentration in the aqueous environment, and k_1 and k_2 are the uptake and offload rate constants, respectively.

The passive samplers designed for accumulating pollutants can be used either as equilibrium samplers or kinetic samplers (Nollet and De Gelder, 2000). The analyte is absorbed or adsorbed from the sample matrix into the sampling system following the model shown in Fig.2.3 (Vrana et al., 2005).

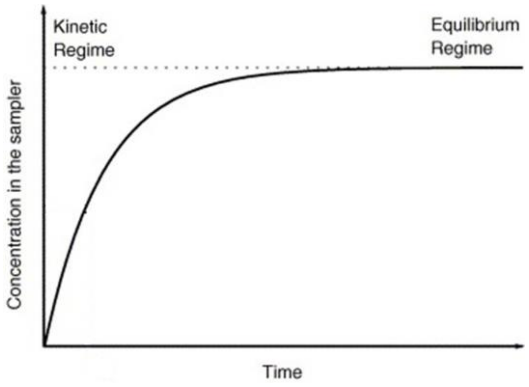


Figure 2.3 Principle of the passive sampler

Equilibrium samplers

Equilibrium samplers have been mostly used to measure concentrations of pollutants in ground water and in sediment pore water (Mayer et al., 2003). In the sampling process, samplers should be deployed for a sufficiently long time period to permit the thermodynamic equilibrium between the environmental matrix and the sorbent. In this situation, equation (2.3) can be reduced to:

$$C_s = C_w \frac{k_1}{k_2} = C_w K \qquad \textbf{(2.4)}$$

The phase-water partition coefficient (K) can be used to deduce the dissolved analyte concentration.

Equilibrium sampling reflects equilibrium concentrations over the deployment period, the amount of analyte collected by the sampler should not change once equilibrium has been reached, provided that the analyte concentration in the environmental matrix does not fluctuate and the ambient conditions remain the same. The basic requirements for this sampling method

are that the sampler capacity should be controlled well below that of the sample to avoid depletion and the device response time needs to be shorter compared to any fluctuations in the environmental matrix. The concentration of analyte can then be acquired according to the coefficient *K* or experimental calibration of the device (Zabiegała et al., 2010).

Kinetic samplers

A wider range of kinetic samplers is available than thermodynamic samplers, and they have been used for all chemical classes of pollutants (Greenwood et al., 2007). In kinetic sampling, the sampling process continues until the sampling session is terminated by the user, the mass of analyte in the sampled matrix - which is called the time-weighted average (TWA) concentration- integrates analytes in the sampler over the exposure time (Górecki and Namieśnik, 2002).For this type of sampling, it is assumed that the rate of mass transfer is linearly proportional to the difference in chemical potential of the analyte in the dissolved phase and that in the receiving sorbent, and it remains constant during the deployment time. In the kinetic regime, elimination rate k_2 is negligible, and equation (2.3) reduces to:

$$C_s(t) = C_w k_1 \quad \textbf{(2.5)}$$

Equation (2.6) can be expressed according to Eq. 2.5:

$$M_s(t) = C_w R_s t \quad \textbf{(2.6)}$$

Where M_S(t) is the mass of analyte accumulated in the receiving phase after an exposure time (t) and R_S is the sampling rate, which is the product of the first-order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of receiving phase. R_S may be described as the volume of water cleared of analyte per unit of exposure time by the device. When R_S is known, C_W can be calculated from the sampling rate (R_S), exposure time (t) and the amount of the analyte taken by the sorbent (M_S(t)).

In most cases, passive sampling immensely simplifies sampling and sample preparation, so that it is more suitable for *in situ* sampling and real-time monitoring. Secondly, there is always an

inherent force caused by chemical potential before the equilibrium has been reached to drive the target compounds transferring from sample medium into the receiving phase. So this method eliminates power requirements. Thirdly, passive sampling is a cost effective method (Chen et al., 2015b). Finally, passive sampling techniques can be applied to simulate bioaccumulation. Publications show that passive sampling methods can also be used to determine the TWA concentration of polar organics, non-polar organics, organo-metallics, and volatile organics and to evaluate their potential for bioaccumulation (Greenwood et al., 2009; Górecki and Namieśnik, 2002)

2.2.2 Design of passive samplers

Several criteria must be taken into account for the design of a passive sampler.

A suitable sorbent should have high affinity with the target compounds and be insensitive to interfering matrices in the environment; compounds ought to be stable on the sorbent during the storage. For kinetic sampling, a large capacity is also required to maximise the amount of analyte collected in a sufficient deployment time.

A barrier is present between the sampled medium and the sorbent, such that it determines the rate at which the target compounds are taken up. It may also decide the selectivity of the sampler and limit certain classes of analytes or species sampled. A basic requirement for the barrier is that it should not irreversibly hold or react with the target compounds (Vrana et al., 2005; Namieśnik et al., 2005).

If a holder body is used, the material should not react with the target compound or adsorb it. Tests to check whether the material is available for the body holder should be conducted prior to the deployment.

2.2.3 Passive sampling devices for pesticides

Two designs of sampler have generally been used for pesticides so far, the polar organic compound integrative sampler (POCIS) and the polar version of the Chemcatcher®.

2.2.3.1 POCIS

POCIS is a passive sampling technology developed by Alvarez et al. (2004), first reported to collect hydrophilic contaminants with log $K_{ow} < 4$ in aquatic environments. It is an abiotic device that enables assessment of the cumulative aqueous exposure to bioavailable hydrophilic organic chemicals and allows determination of the biologically relevant TWA concentrations in water.

As Fig. 2.4 shows, the POCIS consists of a solid material (sorbent) enclosed between two hydrophilic microporous polyethersulfone (PES) membranes to form a membrane-sorbent-membrane sandwich. Two compression holder washers are placed over each membrane. Water and target compounds flow through the membrane to reach the sorbent where the chemicals are trapped, while matrix and larger materials are excluded (Alvarez et al., 2005). The type of sorbent used is altered for particular chemicals or chemicals classes.

A standard POCIS comprises a sampling surface area (surface area of exposed membrane) to sorbent mass ratio of 180 cm^2 g^{-1} to reach an effective sampling surface area of 18 cm^2. Two configurations of the POCIS are usually available, each containing different sorbents. A pesticide-POCIS configuration contains a mixture of three sorbent materials (Isolute ENV+ and Ambersorb 1500 dispersed on SX-3 Bio Beads) and is used for most pesticides, natural and synthetic hormones, many wastewater-related chemicals, and other water-soluble organic chemicals. The pharmaceutical-POCIS configuration contains an Oasis HLB (Hydrophilic-Lipophilic-Balanced) sorbent designed for sampling most pharmacuetical classes. It is

common to deploy POCIS of several different configurations together to maximize the types of chemicals sampled (Bartelt‐Hunt et al., 2011).

(a) (b)

Figure 2.4 (a) Description of POCIS components; (b) POCIS deployment (EST-Lab)

2.2.3.2 Chemcatcher

Chemcatcher is a passive sampling device developed by researchers at the University of Portsmouth, Portsmouth, UK and Chalmers University of Technology, Göteborg, Sweden for the measurement of TWA concentrations of organic contaminants in waters (Kingston et al., 2000). The Chemcatcher consists of a polytetrafluoroethylene (PTFE) body, in which an Empore disk is placed as the receiving phase, a diffusion-limiting PES membrane is placed above the sorbent (shown in Fig. 2.5) (De la Cal et al., 2008). Different combinations of membranes and sorbents are available in different designs of Chemcatcher to monitor polar and nonpolar contaminants (Anjum et al., 2017).

(a) (b)

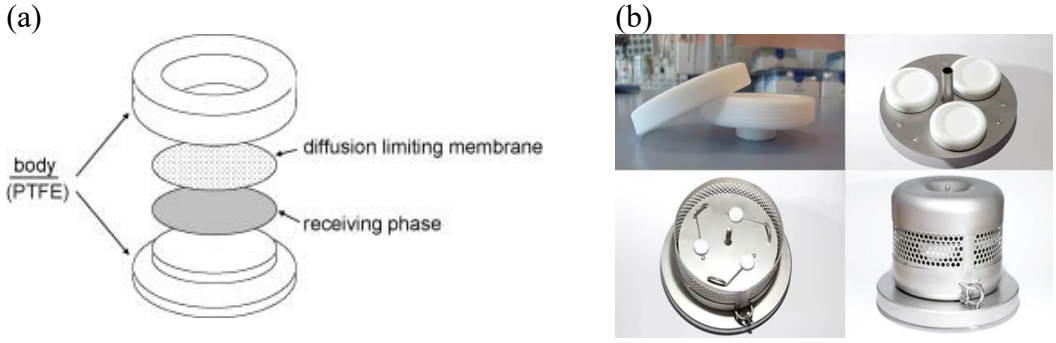


Figure 2.5 (a) Chemcatcher configuration; (b) Chemcatcher deployment (TelLab)

2.2.3.3 Applications

POCIS is commonly used for monitoring polar organic pollutants in different types of water. For pesticides monitoring, before regular applications, several studies focused on the laboratory calibration, sampling rates and the reliability of the Performance Reference Compound (PRC) of POCIS (Thomatou et al., 2015; Bartelt‐Hunt et al., 2011; Ibrahim et al., 2013). The PRCs are a group of compounds which are preloaded into samplers prior to deployment to overcome the influence from changing exposure conditions analytically. They are not detected in the environment and their release follow the same mass transfer principles as the uptake of target analytes, so they can be used to estimate the uptake of contaminates *in situ* (Harman et al., 2011).

This technique has been used extensively to characterize pesticides in surface waters such as rivers, streams and lakes. Lissalde et al. (2014) used POCIS in two rivers of France to monitor a selection of 23 polar pesticides and 8 metabolites, van Metre et al. (2017) detected 141 pesticides in 100 streams in the Midwest US, Thomatou et al. (2011) investigated the efficiency of POCIS for 13 pesticides in Lake Amvrakia. Some studies also investigated the performance of POCIS in groundwater for screening pesticides at low concentrations which could not be detected by spot sampling (Berho et al., 2013).

Similarly with Chemcatcher, the monitoring of pesticides has been conducted in rivers (Moschet et al., 2015), streams (Schäfer et al., 2008b), and even in sea waters (Shaw et al., 2010).

The pesticides shown in Table 2.1 are some examples of POCIS and Chemcatcher applications for detecting in the laboratory or in the field.

Although these two types of samplers are widely used, they still have some drawbacks. One is that extensive laboratory-based calibration experiments are essential, because of the lack of

theoretical models to determine the uptake of a compound into a POCIS or Chemcatcher according to its physicochemical properties. Before the samplers can be deployed in the environment, the uptake rates of the target compounds should be measured in the laboratory (Morin et al., 2012).

The other main drawback is that PRCs are often required. The use of PRCs is based on the assumption that their release rate and the uptake rate are isotropic, but this is not always the case in reality. Although some groups have shown that preloading the receiving phase with deuterated (d5) deisopropylatrazine can possibly be used for this purpose (Mazzella et al., 2010), these factors limit the utility of these samplers beyond screening or qualititative/semi-quantitative assessment of pollutants (Mills et al., 2014a).

As explained below, the development of the diffusion in thin films (DGT) device is promising. The addition of a thick diffusion gel layer helps control the uptake of analytes into the sorbent and limits the effects of water flow, so the thickness of the DBL is negligible. This may address the problem of the lack of a PRC approach for the polar Chemcatcher and POCIS samplers.

Table 2.3 Some examples of pesticides detected by POCIS and Chemcatcher

Category	Compound	Sampler	Waterbody/location	*R*s (L d^{-1})	LOQ (ng L^{-1})	Con. (ng L^{-1})
Fungicide	Thiabendazole[1]	POCIS	Lab	0.264		
Herbicide	Atrazine[1,2]	POCIS	Lab	0.290		
		Chemcatcher	Lab	0.12-0.52		
Herbicide	Linuron[3,4]	POCIS	Lab	0.196-1.059	4.3	nd-12
		Chemcatcher	16 streams			
Insecticide	Pirimicarb[5,4]	POCIS	Surface water		0.03	nd-3.27
		Chemcatcher	16 streams		4.5	nd-66

References: 1: (Bartelt-Hunt et al., 2011); 2: (Vermeirssen et al., 2009); 3: (Bayen et al., 2014); 4: (Schäfer et al., 2008b); 5: (Aisha et al., 2017).

*R*s: uptake rate

LOQ: limit of quantification for a sample obtained with the respective method

Con.: concentration of target compound detected in the water

nd: below detection limit

2.2.4 DGT

2.2.4.1 Principles of DGT

The diffusive gradient in thin film (DGT) technique was developed in 1994 to measure labile inorganic compounds quantitatively *in situ* in natural water (Davlson and Zhang, 1994b). It has been very extensively tested and applied to various analytes, including heavy metals, phosphate, sulphide and radionuclides. It has also been deployed in a wide range of environments - for example, soils, sediments, rivers and effluents (Zhang et al., 1995).

It consists of a series of layers which dissolved chemicals can go through over a given deployment time. A time averaged concentration of chemicals at the point of *in situ* deployment can be obtained after laboratory analysis. The *in situ* accumulation of the analyte allows DGT to achieve lower limits of detection than classical analysis of a spot sampler. Changes in water quality can be identified using a series of deployments. DGT typically utilizes a three-layer system: a resin-impregnated hydrogel layer, a hydrogel diffusion-layer and a filter membrane as shown in Figure 2.6 (Davison, 2016).

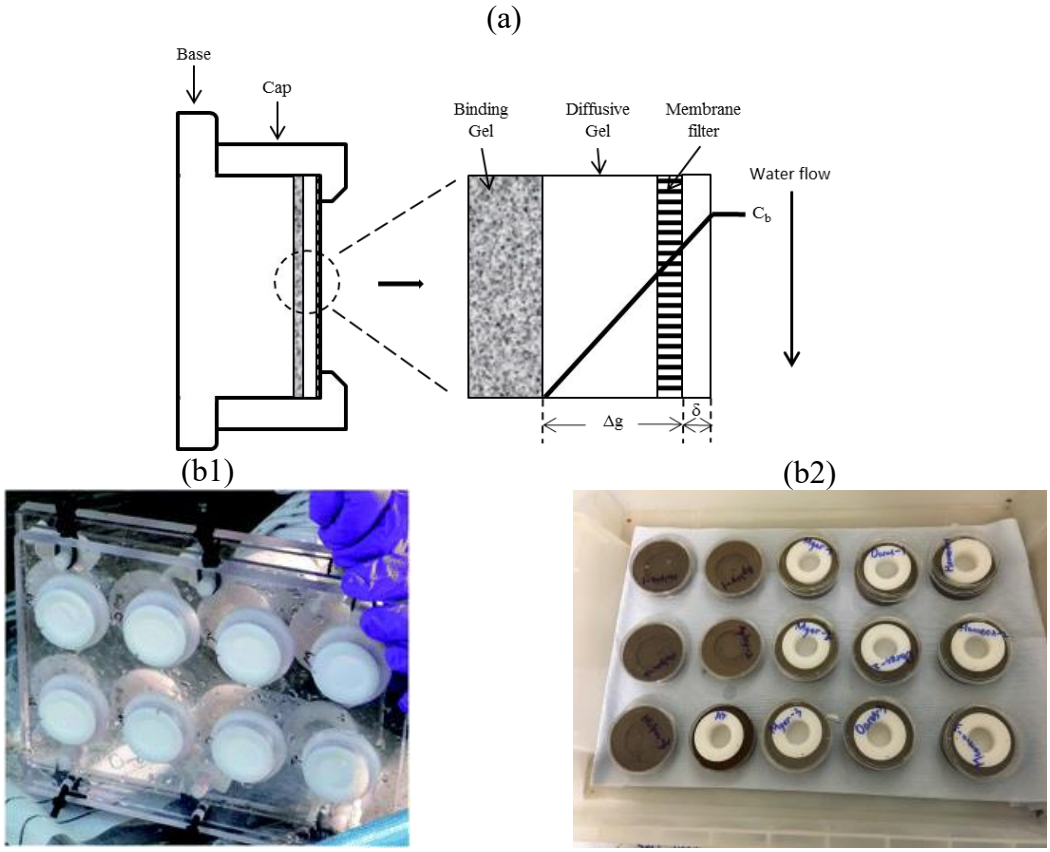


Figure 2.6 (a): A schematic diagram of a DGT device. C_b: concentration in the bulk water, δ: diffusive boundary layer (DBL); (b1): DGT deployment in the water (Turner et al., 2014); (b2): DGT deployment in the soil

The filter membrane isolates the polyacrylamide surface from the deployment medium. Target chemicals in solution diffuse through the filter and gel layers and are pre-concentrated on the resin. The concentration of target chemicals in solution can be calculated using the measured mass of analyte accumulated on the resin, the sampler exposure time and the temperature-corrected molecular diffusion coefficient for the metal of interest, based on the diffusion principles and the established characteristics of the diffusive path in the DGT sampler. The mass accumulated by DGT can be expressed by equation (2.7):

$$M = \frac{D_e C_b A t}{\Delta g + \delta} \quad \textbf{(2.7)}$$

D_e: the diffusion coefficient of analyte in the DGT
C_b: concentration of the analyte in the bulk solution
A: the sampling area of DGT
Δg: the diffusion path length of analyte before being trapped by the binding phase

C_b can be obtained by rearranging equation (2.7) to (2.8):

$$C_b = \frac{M(\Delta g + \delta)}{D_e A t} \quad \textbf{(2.8)}$$

The calculated labile-chemical concentration depends on the diffusion coefficient, D_e. D_e may be affected by the hydrogel, ionic strength, pH, and solution composition, which can influence the rate of diffusion.

2.2.4.2 Measurements in natural waters

DGT assembled with Chelex-100 as binding gel was demonstrated to be an *in situ* method of quantitatively measuring Cd, Fe, Mn and Cu in aqueous solution (Zhang and Davison, 1995). It can be used as a speciation tool for Cu and Cd in wastewater as well (Buzier et al., 2006). Mercury could be captured by DGT in river water (Dočekalová and Diviš, 2005). The results from DGT assembled with two kinds of binding gels showed that DGT measured inorganic ions and labile species rather than inert organic species and colloids. DGT measurement made over concurrent tidal phases detected significantly higher concentration of Cu, Zn and Ni during flood phase (Dunn et al., 2007). The use of DGT measuring organic compounds was developed in 2012. Chen et al. (Chen et al., 2012) measured for the first time the performance characteristics of DGT for quantifying polar organic compounds, antibiotics. Then they applied this new configuration of DGT in wastewaters - the first evidence of the use of DGT for organics in a real environment (Chen et al., 2013).

2.2.4.3 Principles and applications in soils and sediments

DGT locally lowers analyte concentrations in the soil solution at the DGT-soil interface, which stimulates re-supply from the solid phase by diffusion (Zhang et al., 2001).This mechanism

mimics the processes in the rhizosphere(Muhammad et al., 2012), avoids the separation of soil solution from the solid phase, making DGT an *in situ* method to measure soil concentration. DGT describes the diffusional transport and dynamic exchange of analytes between the solid phase and soil solution, making it possible to obtain kinetic and labile pool size parameters of the soil from the DGT measurements (Zhang et al., 1998b).

DGT has been proposed for measuring the dynamics of metals and nutrients with minimal disturbance to the soil. Ernstberger et al. (2005) has provided kinetic information simultaneously with pool size information for Cd, Zn and Ni on 5 different soils using DGT. Naylor et al. (2004) deployed new combined DGT probes in marine harbour sediments to understand the complex nature of trace metal and sulphur chemistry in sediments. A similar approach has been used for characterising the dynamics of soil-solution interactions for antibiotics (Chen et al., 2014a).

2.2.4.4 DGT and bioavailability

The performance of DGT on the assessment of metal and phosphorus bioavailability has been validated in a number of studies. DGT can predict the bioavailability of Cu, Pb and Zn in greenhouse soils, as the effective concentration obtained by DGT correlated significantly with uptake by sorghum (Agbenin and Welp, 2012). Another study (Zhang et al., 2001) showed DGT can be applied for Cu measurement in soil with demonstrations of plant yield response to Cu. Besides the plant bioavailability assessment, DGT is also able to be used as a bio-mimic surrogate of heavy metal uptake in earthworms (Bade et al., 2012). For nutrients, DGT technology has provided an effective way of assessing phosphorus (P) availability for plants. The work published by Six et al. (2013) indicated that the concentration of P measured by DGT gives a better correlation to maize uptake than other measurements. DGT can also predict wheat responsiveness to applied P more accurately than Resin-exchangeable P test and Colwell P

extraction (Mason et al., 2010). These cases provide the potential to measure pesticide bioavailability in soil by DGT.

2.2.4.5 State of DGT for organics

Although DGT was invented for inorganic substances, the usage has been expanded to organics in recent years. This started from antibiotics, and has extended to pharmaceuticals, PPCPs, bisphenols, illicit drugs and anionic pesticides as described in Table 2.4 below.

Table 2.4 Studies of organics with DGT to date

Category	Analytes	Binding gel	Research purposes	Ref.
Antibiotics	40 antibiotics (16 sulfonamides (SAs), 12 fluoroquinolones, 6 macrolides, 2 ionophores, 2 diaminopyimidines, 1 aminocoumarin and 1 lincosamide)	XAD18	Performance of DGT in detecting these antibiotics in wastewaters	(Chen et al., 2013)
Antibiotics	3 sulphonamides	XAD18	Desorption kinetics and *in situ* measurement of these antibiotics	(Chen et al., 2014a) (Chen et al., 2015a)
Polar organic contaminants	34 target chemicals (Antibiotics, PPCPs and pesticides)	HLB	Development, calibration, DBL impact measurement and field evaluation	(Challis et al., 2016)
Pharmaceuticals	Ciprofloxacin	XAD18	Desorption kinetics	(D'Angelo and Starnes, 2016)
Herbicide and its degradation product	Glyphosate and aminomethylphosphonic acid	TiO2	Development and validation	(Fauvelle et al., 2015)
Bisphenols	BPA, BPB, BPF	Activated charcoal (AC)	Development, validation and field trial	(Zheng et al., 2014)
Bisphenols	BPA, BPB, BPF	Activated charcoal (AC)	Desorption kinetics	(Guan et al., 2017)
Anionic pesticides	Bentazon, Chlorsulfuron, Ioxynil and Mecoprop	HLB and MAX	Development, validation and field trial	(Guibal et al., 2017)
Illicit drugs	Ketamine (KET), methamphetamine (METH), and amphetamine (AMP)	XAD18	Development, validation and field trial in wastewaters and rivers	(Guo et al., 2017)

2.2.5 Environmental factors affecting the performance of passive samplers

Theoretically, the quantitative correlation between the uptake mass of the target compound and its concentration in the environment is based on the scenario that the passive sampler is applied to a steady-state condition. However, the physicochemical properties of the analytes and the environmental parameters will both affect the reliability of this technique.

Water flow

There will be a layer close to any solid surface in a flowing solution where there is effectively no flow, called the diffusion boundary layer (DBL). The uptake of analytes by passive samplers is often dominated by this boundary layer at the membrane-water surface, rather than by the microporous membrane. Water flow affects the thickness of the boundary layer, the layer becomes thinner with the increase of the flow rate, but some DBL will remain even when the sampled solution is vigorously stirred. It has often been assumed that the DBL is sufficiently thin that it can be ignored in laboratory deployments when the flow rate is above a threshold (Gimpel et al., 2001). General estimates suggest the DBL thickness in fast flowing waters, such as rivers, streams, and the well-mixed surface water of lakes and sea, is in the range of 0.01-0.1 mm (Zhang and Davison, 1995). If the DBL is not negligible in the real environment, the value of DBL can be obtained by deploying different thicknesses of DGT devices and calculated through Eq. 2.7 (Warnken et al., 2006).

pH

pH is a major factor that can affect the properties of analytes and environmental surfaces. Pesticides have many functional groups which can be ionized or neutral at various pH. If the sampler accumulates neutral and ionized forms of the target compounds at different rates, this impact becomes more obvious. Li et al. (Li et al., 2011) investigated the effect of pH on the uptake of 21 PPCPs(pharmaceuticals and personal care products) and EDS (endocrine disrupting substance) by POCIS, and found that the sampling rate increased with pH for basic analytes and decreased with pH for acidic analytes. With neutral compounds, the sampling rate was relatively constant across the pH range.

Ionic strength

Increasing the ionic strength leads to the decrease of water solubility of many organic compounds, but most types of passive samplers only uptake the dissolved fraction, so the

sampling rate of analytes with higher salinity will be reduced. Shi et al. (2014) claimed that the sampling rate of POCIS was increased for most of the test antibiotics and EDCs when the salinity was increased from 0‰ to 14‰. A decrease occurred when the salinity was further increased to 35‰, which indicated the sampling rates reached their maximum at 14‰. Bayen et al. (2014) found that the sampling rates for POCIS of most test compounds with the presence of 30 gL^{-1}NaCl were lower than the rates in the absence of NaCl.

DOM (dissolved organic matter)

DOM present in natural waters may affect the uptake of analytes by passive samplers, mainly by bonding, interacting or competing with the target compounds. Li et al. (2011) and Harman et al. (2012) both found no statistical difference in sampling rate for some pharmaceuticals and PPCPs (such as ibuprofen) with added DOM spiked at 3-5 mg L^{-1} in lake water, which may be due to a narrow range. Charlestra et al. (2012) also noted no significant effect of natural DOM (0.1-5 mg L^{-1} as total organic carbon) on sampling of pesticides (like propiconazole) by POCIS. Gourlay et al. (2005) reported that the presence of DOM reduced the accumulation of PAHs in SPMDs, owing to the formation of complexes that were too large or too polar to pass the SPMD membrane.

Temperature

Passive samplers accumulate the dissolved fraction of the compounds and those bound to small particles. Water solubility and desorption from suspended particles of organic chemicals were enhanced with an increase of temperature. Water temperature fluctuates seasonally and daily and this can have a large effect on the uptake of target compounds. It was reported that the uptake of atrazine and diuron was positively correlated with temperature in Chemcatcher (Kingston et al., 2000). Togola and Budzinski (2007) investigated the effect of temperature on the accumulation of 14 pharmaceuticals, and showed that the increase of temperature from 15 to 21ºC led to an increase in sampling rate for most test compounds.

Biofouling

Algal and microbial growth on the surface of the membrane can inhibit the transfer of the analytes into the passive sampler and affects quantification of water concentrations (Wilderer, 2010). The PES membrane which is usually used in POCIS was less affected than growth on the SPMD membrane (Alvarez et al., 1999). Fouling of POCIS has different impacts on the uptake of organic compounds.

2.2.6 Selection of target pesticides for this work

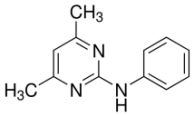
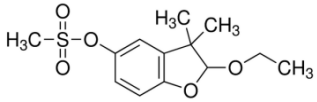
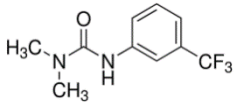
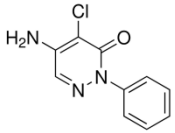
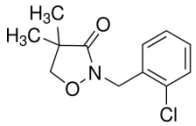
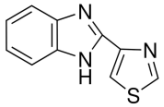
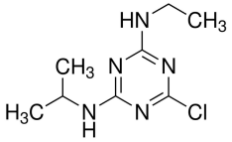
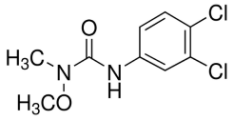
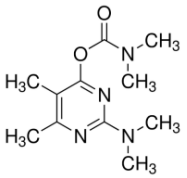
The mechanism of DGT depends on the diffusion of analytes through diffusive gel from the environment, thus the polarity of a compound largely affects the uptake to DGT. After searching for 'polar pesticides', about 370 pesticides appearing in published laboratory or field research studies were compiled on the list. Of these, 116 pesticides have been commonly used in research studies; some of them were detected using other passive samplers e.g. POCIS and Chemcatcher. A logK_{ow} value < 3 was required for these compounds (for compounds already studied by other two passive samplers logK_{ow} values didn't have a limit as they were designed for polar chemicals). Most of the pesticides applied in the environment are herbicides, fungicides and insecticides, so 54 pesticides which were detected in the aqueous environment belonging to the above classification were on a preliminary 'first-cut' list for consideration in this project. From this list, these 54 pesticides were classified into different groups, depending on their functional groups. From these, a shorter list was needed for the research focus here. Selection criteria were: to cover the different groups; their use/application in the UK in recent years; a range of molecular weight/properties, to test the potential wider application for DGT sampling; previous work with other passive samplers (as shown in Table 2.1). Additional practical considerations included availability and cost of analytical standards. Finally, based on

this range of criteria, 9 pesticides were selected for method development and testing, as will be described in the next Chapter. This list is shown as Table 2.5.

2.3 Summary

The importance of pesticides for a range of uses is briefly summarised here. The concern over their efficacy and potential hazards to the environment and humans requires a reliable and informative measurement and monitoring technique to track them in the environment and understand their behaviour and fate. Some conventional and current monitoring methods are discussed and compared. Passive sampling has been adopted recently for a limited number of pesticide studies, but has not yet been widely accepted. The DGT sampler may have advantages over other passive samplers, and applications in waters and soil environments have been demonstrated. The use of DGT has been expanded from inorganics to organics in recent years. This review lays the foundation for the studies presented in this thesis.

Table 2.5 Target pesticides in this study

Category	Classification	Compound	Structure	*MW* (g mol^{-1})	Log*K*$_{ow}$	*S*$_w$ 25℃ (mg L^{-1})	pKa
Fungicide	Anilinopyrimidine	Pyrimethanil		199.26	2.84	165.8	2.26 12.56
Herbicide	Methyl methoxyacrylate	Ethofumesate		286.35	2.7	72.86	
Herbicide	Phenylurea	Fluometuron		232.21	2.42	253.9	13.22
Herbicide	Pyridazinone	Chloridazon		221.65	1.14	3585	
Herbicide	Unclassified	Clomazone		239.7	2.5	197.5	
Fungicide	Benzimidazole	Thiabendazole		201.25	2.47	335.2	4.08 10.28
Herbicide	Chlorotriazine	Atrazine		215.69	2.61	214.1	3.2
Herbicide	Phenylurea	Linuron		249.1	3.2	44.27	4.85 7.09
Insecticide	Dimethylcarbamate	Pirimicarb		238.29	1.7	969.5	4.99

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Chapter 3: Development of a dynamic passive sampler for measuring pesticides in waters and soils

3.1 Introduction

Pesticides contribute significantly to the provision of world food. However, their potential adverse effects on biodiversity, environment, food quality and human health have raised great concern.

Pesticides enter the soil system through either direct application (Huang and Iskandar, 1999), or some indirect pathways such as washing-off from treated foliage (Rial Otero et al., 2003), crop residues, leaf fall in the autumn and root exudates (Pimentel and Levitan, 1986). Only a small proportion of applied pesticides could reach the target pests, in most cases less than 0.3% and with an average about 0.1% (Pimentel, 1995), more than 99.7% remaining in the soils. These may cause unintended environmental effects as pesticides are hazardous to the indigenous microorganisms like beneficial competitors, predators and parasites of target pest insects (van der Werf, 1996). Some studies showed that pesticides inhibit soil microbial diversity and activities (Ingram et al., 2005; Littlefield-Wyer et al., 2008), adversely influence soil biochemical processes and disturb soil ecosystem (Hussain et al., 2009). In recent decades there has been an increasing concern that pesticides constitute a risk to human by entering in the food chain (Margni et al., 2002), through direct contact with soil, inhalation of vaporized pesticides (Malik et al., 2013), and through groundwater contamination by pesticides leaching from soils.

It is clear that we need to measure pesticides in soils to understand their fate and dissipation. The measurements of pesticides in soils are usually performed using various extraction methods (Tadeo, 2008). They are complicated, expensive, laborious and time-consuming (Sun and Lee, 2003). Furthermore, these extraction methods focus on the 'total concentration' instead of the bioavailable fraction which is more important in risk assessment. No kinetic parameters of *in situ* processes of pesticides in soils can be obtained by extraction methods.

Therefore, a new dynamic technique considering kinetic aspects and bioavailability to determine pesticides in soil is desperately in need.

Pesticides can enter the surface waters through diffused pollution and leaching. Some pesticides are persistent pollutants for aquatic systems. It is essential to monitor these toxic chemicals to ensure the water quality. Grab sampling, which is widely used in water monitoring, is an effective way to measure the occurrence of organic contaminants in aquatic systems, but it only provides single point information at the time of sample collection; episodic contaminant events may be missed (MacLeod et al., 2007; Kingston et al., 2000). The development of passive sampling approaches, which can give time-weighted average concentrations has increased in recent years.

Passive samplers are able to retain trace level analytes by pre-concentration; the *in situ* sampling does not affect the environment (Alvarez et al., 2004). Passive samplers also limit the degradation of trapped chemicals during transport and storage (Morin et al., 2012). Techniques such as POCIS and Chemcatcher (Ibrahim et al., 2013; Schäfer et al., 2008a) are currently commercially available for the measurement of pesticides in waters. However, they can be dependent on hydrodynamic conditions during field deployment and/or rely on a laboratory calibration and losses of performance reference compounds to estimate sampling rates (Mills et al., 2014b). DGT (diffusive gradients in thin-films) is a passive sampling technique which has distinct advantages in these respects (Chen et al., 2012). It is also a dynamic technique that can be used in soils for measuring bioavailable species (Luo et al., 2014).

The development and use of DGT for inorganics has a long and well-published pedigree. The principles were first published in 1994 in Nature (Davlson and Zhang, 1994a) and now over 800 peer-reviewed papers have been published on testing and applying of the technique in different environmental media such as waters (Denney et al., 1999; Dunn et al., 2007), soils (Zhang et al., 1998b) and sediments (Harper et al., 1998b).. Until recently, the focus has been on metals, nutrients and radionuclides. DGT typically utilizes a three-layer system: a resin-

impregnated hydrogel layer, a hydrogel diffusion-layer and a filter membrane. The thick diffusion gel layer which controls the uptake of analytes into the receiving phase limits the influence of hydrodynamic conditions by making the effect of the diffusive boundary layer (DBL) negligible (Zhang and Davison, 1995).

The principle of DGT is based on Fick's first law (Davlson and Zhang, 1994a), such that the concentration of target chemicals in solution can be calculated using equation 3.1:

$$C_{\mathrm{DGT}} = \frac{M(\Delta g + \delta)}{D_e A t} \quad \textbf{(3.1)}$$

where, D_e is the diffusion coefficient of the analyte in the DGT, A represents the sampling area of DGT, Δg is the diffused length through which the analyte passes before being taken up by the binding phase, and δ is the thickness of diffusive boundary layer (DBL).

There is great potential for applications of DGT to organic chemicals, but the first application to organic compounds was not until 2012 by Chen et al. (2012). They investigated the performance characteristics of DGT for quantifying polar organic compounds (with logK_{ow} value <4). The newly developed 'organic DGT' has been applied in rivers, wastewater treatment plants and soils to sample antibiotics with XAD18 as the binding gel (Chen et al., 2013; Chen et al., 2014b). Zheng et al. (Zheng et al., 2014) subsequently applied activated charcoal as the binding layer for DGT to detect bisphenols (BPs) in the aquatic environment. Fauvelle et al. (Fauvelle et al., 2015) extended the application of DGT to glyphosate (PMG) and amino methyl phosphonic acid (AMPA) using titanium dioxide (TiO2) as the binding layer. Recently, more researches have been carried out on developing DGT technique for household and personal care products, illicit drugs and pesticides (Challis et al., 2016; Guo et al., 2017; Guibal et al., 2017; Chen et al., 2017). Although there are two publications on DGT measurements for pesticides (Challis et al., 2016; Guo et al., 2017; Guibal et al., 2017; Chen et al., 2017), the technique has not been developed for many important and widely used pesticides nor solved some essential technical issues. DGT devices in these two recent papers were deployed without filter membranes, possibly due to significant adsorption of the target

chemicals on to the filter membrane which can affect the accuracy of the measurements. However, there is little use for environmental measurements in DGT without filter membrane as hydrogel cannot be directly exposed in waters and soils.

The aim of this work was to develop the DGT technique to measure the available concentration of a wide range of pesticides in waters and soils. In evaluating the performance characteristics of the new DGT device, 9 pesticides were selected as test chemicals and two kinds of binding material were tested. The binding kinetics and capacity of the binding gels were determined, and the effects of deployment time, diffusive gel thickness, pH, ionic strength, and organic matter were studied. A field study of deploying DGT in waters and the application of DGT in soils were also undertaken to validate the performance and applicability of the technique.

The 9 target chemicals selected from various pesticides in use in UK and China were based on covering a range of different classifications (pesticides, insecticides and fungicides) and different functional groups (detailed properties are listed in Table S3.1). They represent most of the polar pesticides in use. The method was also tested for some of the metabolites.

3.2 Methods and materials

3.2.1 Chemicals and reagents

High purity (98.5-99.9%) standards of the 9 pesticides (Pyrimethanil (PYR), Ethofumesate (ETH), Fluometuron (FLU), Chloridazon (CHL), Clomazone (CLO), Thiabendazole (THI), Atrazine (ATR), Linuron (LIN) and Pirimicarb (PIR)), atrazine metabolites (Atrazine-2-hydroxy (HA), deethylatrazine (DEA), desisopropylatrazine (DIA), -desisopropyl-desethyl-atrazine (DACT), cyanuricacid (CYA)) and 2 internal standards (Atrazine-d5 and Linuron-d6) were purchased from Sigma-Aldrich or Dr. Ehrenstorfer. The details of these test compounds are listed in Table S3.1, including their classification, use and some of their physicochemical properties. Two different materials -Amberlite^{TM} XAD 18 (Rohm and Haas Company) and Oasis HLB (Waters, UK) were used as binding material. Sodium chloride (NaCl), sodium

hydroxide (NaOH), hydrochloric acid (HCl), ammonium formate (AF) and methanol (MeOH, HPLC grade) were obtained from Fisher Scientific (Loughborough, UK).

3.2.2 Analytical methods and detection limits

The separation of the target chemicals was performed with a Phenomenex Kinetex Biphenyl column (50×2.1mm, 2.6μm). For the 9 pesticides, liquid chromatography with mass spectrometric detection (LC–MS) was carried out using an Agilent LC coupled with a HP single quadrupole mass spectrometer detector with an ESI interface. The mobile phase consisted of 5mM ammonium formate in methanol (solvent A) and 5mM ammonium formate in MQ water (solvent B). The elution gradient began with 55% B from 0 min, then increased to 80% B at 1min and kept for 1.5 min, then raised to 100% B at 2.6 min and kept constant for 3.4 min, followed by returning to the initial conditions within 0.5 min. Finally, the column was re-equilibrated for 15min. The flow rate was 0.3 mL min^{-1}, the injection volume was 5 μL, and the temperature was set to 25 °C.

For atrazine metabolites, the mobile phase composition (A:B) was started from 85:15 (v:v) and kept for 0.5min. Then it was changed to 50:50 with in 3.5min and was kept for 1min. Then changed to 40:60 and kept for 2 min. Linearly increased the composition of B to 100% within 0.2 min and kept constant for 3.6 min, followed by returning to the initial conditions within 0.2min. The flow rate was 0.2 mL min^{-1}, the injection volume was 5μL, and the column oven temperature was set to 25 °C. The metabolites samples were analysed by a Shimadzu Nexera X2 UPLC coupled with a Shimadzu LCMS-8030 triple quadrupole mass spectrometer detector. The instrumental detection limits (IDLs) for LS-MS were calculated according to the signal/ noise ratio (S/N) >3 and method detection limits (MDLs) were calculated based on IDLs, the recoveries for water samples and DGT samples and the dilution factors. The results are shown in Table S3.2.

3.2.3 Gel preparation and DGT assemblies

Polyacrylamide resin gels were made by mixing 4 g/ 1.5 g (wet weight) binding resins HLB (particle size 60 µm) and XAD 18 (particle size < 75 µm), 10ml gel solution (made by appropriate amounts of acrylamide solution, cross-linker and MQ water), 60µl of ammonium persulphate and 15µl of TEMED. The solutions were then pipetted between two glass plates separated by spacers which have a certain thickness and allowed to set at 42-45 °C for about 45 min (Chen et al., 2012; Zhang and Davison, 1999; Davlson and Zhang, 1994a).

Agarose diffusive gel (containing 1.5% agarose) was prepared by dissolving an appropriate amount of agarose in an appropriate volume of pre-heated MQ water in a boiling water bath until all the agarose was dissolved and the solution became transparent. The hot gel solution was immediately pipetted into a preheated, gel-casting assembly and left to cool down to room temperature (Chen et al., 2012). All gels were hydrated in MQ water and stored in 0.01M NaCl solution. The DGT device was assembled using a plastic base housing consisting of a base and a cap, the diffusive gel was sandwiched between the binding gel and a filter membrane.

3.2.4 Adsorption by DGT holder, filter membrane and diffusive gel

All materials used for DGT devices were assessed for possible adsorption of the target compounds. Plastic DGT holders (piston and cap) (rinsed with methanol, followed by MQ water), polyacrylamide (PA), agarose gels (AG), 6 different filter membranes (polyethenesulfone membrane, PES; nuclepore track-etch membrane, PC; nylon membrane, NL; Cellulose Acetate membrane, OE; mixed celluse ester membrane, ME; hydrophilic polypropylene membrane, GHP) were exposed to 50 µg L^{-1} of the mixture of compounds in 10 mL solution (DGT holders were in 100 mL solution). They were shaken for 20 h on a shaker (Orbital, DOS-20L, Sky Line, ELMI). All materials were immersed in MQ water as blanks and the pesticides solution alone served as controls. The concentrations in the solution before and after experiment were measured to obtain the mass adsorbed.

3.2.5 Binding capacity and uptake kinetics of resin gels

To measure the binding capacity of the resin gels for accumulating the target pesticides, resin gel discs were immersed for 21 h in well-stirred solutions containing 0.01 M NaCl and a range of concentrations of mixed compounds (1, 2, 4, 6, 8, 10 mg L^{-1}).

The resin gel disc was immersed in 40 mL of 200 μg L^{-1} mixed compounds solution with a matrix of 0.01 M NaCl and shaken for 33 h. Samples were taken out at various times from 5 min to 33 h to measure the sorption kinetics of target compounds on two types of resin gels.

3.2.6 Diffusion coefficient measurements

The diffusion coefficients of the pesticides were measured using a diffusion cell that has been reported previously (Zhang and Davison, 1999). The diffusion cell comprises two compartments, each with an interconnecting 1.5 cm diameter connecting window. A 2.5 cm diameter disc of 1 mm thick diffusive gel was placed between the windows and the whole assembly clamped together. Both compartments were rinsed with methanol and subsequently MQ water. The source compartment contained 100mL of 1mg L^{-1} mixed pesticides in 0.01 M NaCl solution and 100 mL of 0.01 M NaCl only solution was introduced into the other compartment as the receptor solution. Both compartments were stirred continuously using an overhead stirrer. Sub-samples of 0.2 mL were taken from each compartment at various intervals. The temperature during the experiment was 21.5 ± 1.6 °C.

The slope of the linear plot of the mass of the measured chemical compound diffused into the receptor compartment versus time of the measurement was used to calculate the diffusion coefficient, D_e

$$D_e = \frac{\text{slope} \times \Delta g}{C_s \times A_s} \quad \textbf{(3.2)}$$

where Δg is the thickness of the diffusive gel; C_s is the concentration of compounds in the source compartment; and A_s is the area of the connecting window of the diffusion cell.

3.2.7 Time dependence

The DGT devices with both binding layers were deployed in 10 μg L^{-1} mixed pesticides solution (0.01 M NaCl, pH 6.9 ± 0.2, Temperature 24 ± 2°C) for different time periods up to 84 h. The devices were on a floating holder, and the solution was stirred by a magnetic bar.

3.2.8 Diffusive layer thickness dependence

The DGT with HLB binding gel containing diffusive gel of different thicknesses (0.5 to 1.5 mm) were immersed in 2 L of 10 μg L^{-1}mixed pesticides solution (0.01 M NaCl, pH 6.9 ± 0.2, Temperature 21 ± 2°C) for 15 h to determine the relationship between mass accumulated by DGT and diffusive gel thickness.

3.2.9 Effect of pH, ionic strength and DOM

To investigate the effect of pH and ionic strength on DGT performance, DGT devices were deployed in solutions with various pH and ionic strength. As the pH for natural water is normally between 5 and 8 (Chester, 2009; Hahn et al., 2007), DGT devices were deployed in 2 L of 10 μg L^{-1}mixed pesticides solution (0.01 M NaCl) of pH range from 4.7 to 8.2 for 17.8 h at 20 ± 1°C. For the effect of ionic strength, DGT devices were exposed to 2L of 10 μg L^{-1}mixed pesticides solution with NaCl ranging from 0.01 to 0.5 M (pH 6.9 ± 0.2, temperature 20 ± 2 °C). The effect of dissolved organic matter (DOM) was tested by deploying the DGT devices in 2L of 10 μg L^{-1} mixed pesticides solution with DOM ranging from 0 - 20 mg L^{-1} (0.01 M NaCl, pH 6.9 ± 0.2, temperature 21 ± 1 °C) for 16 h.

After deployment, all the devices were rinsed with MQ water thoroughly before they were disassembled. The diffusive gel was peeled off, and the binding gel was placed in a pre-cleaned amber vial. Two consecutive 5 mL portions of methanol were added to the vial to extract target pesticides from the binding gel by 30 min ultrasonic bath. The concentrations of the pesticides were then analysed following the procedure in **Section 3.2.2**.

3.2.10 DGT for atrazine metabolites

Verification of DGT measurement for metabolites was carried out in solution of pH 7 and ionic strength 0.01 M containing atrazine and its metabolites (HA, DEA, DIA, DACT, CYA). DGT devices with HLB resin gel were deployed in the solution for 24 hours at 21 ± 1°C.

3.2.11 Field applications in waters and soils

A field trial was undertaken by deploying DGT devices in two sampling sites of the She River in Fushun, China, for *in situ* measurement of pesticides. Each site had 3 sampling locations. DGT devices were deployed in triplicate, 30 cm below the surface water for 4 and 7 days. Traditional grab samples were also taken on day 4 and day 7 of the DGT deployment using 1 L amber bottles. They were filtered and pre-concentrated using a well-established solid-phase extraction (SPE) method (Loos et al., 2010). Detailed information is shown in the SI. At the end of the deployment, the retrieved DGT devices were rinsed with MQ water and then placed in clean plastic bags for transport. The sample treatments and analysis were the same as per the methods above. To test the DGT applicability in soils, five soils of different properties collected from the UK and China were spiked with ATR at the concentration of 100 mg kg^{-1}. The details of soil sites and properties are listed in Table S3.4. All soils were collected from the upper soil horizon and passed through a 2 mm sieve after air-dry to remove roots and stones prior to experiments.

The soils were then wetted to 25 - 30% maximum holding capacity water (MWHC) by adding appropriate amounts of MQ water, mixing well until ATR distributed in soils homogenously and allowing them to equilibrate at room temperature for 23 days before DGT deployment.

3.3 Results and discussion

3.3.1 Sorption by DGT holder, filter membrane and diffusive gel

There was no appreciable sorption of target compounds on the two types of diffusive gels or DGT mouldings as shown in Figure S3.1(a). However, compounds were sorbed substantially by PES, NL, OE and ME filter membranes (Figure S3.1(b)). Sorption to the PES filters was

marked (>50%) – this filter type has been used for POCIS (Alvarez et al., 2004) and Chemcatcher (Schäfer et al., 2008a); loss on the ME filter was also considerable. PC and GHP showed little sorption of the compounds, especially PC membrane performed the best, with < 5% adsorption for 5 compounds and < 15% for the other 4. So it was selected for the subsequent experiments.

Agarose gel was chosen as the diffusive gel as it is easy to prepare and cheaper, the thickness was set as 1mm.

3.3.2 Binding capacity of resin gels

The DGT samplers are normally deployed in the environment to accumulate target compounds over periods of weeks or more. Knowledge of the binding capacity of the resin gel is important, to help determine optimum sampling times for accurate measurements (Zhang and Davison, 1995). For the HLB binding gel, the uptake masses of all 9 pesticides increased linearly with increasing concentration in the bulk solutions (see Figure 3.1 and Figure S3.2). The binding capacity is dependent on the amount of resin used. According to the test concentration, the capacity of these pesticides on the HLB gel disc was at least within the range of 19 - 44 μg per disc (the lowest for CHL and the highest for PYR) assuming only half the resin would be available during DGT deployment. If the devices were deployed for 2 weeks, the concentration of CHL that can be accurately measured (within the binding capacity) would be at least 75 μg L^{-1} and that of PYR would be at least 200 μg L^{-1}, calculated according to Equation (3.1). These are much higher than environmental concentrations that have been detected (Berenzen et al., 2005; Seeland et al., 2013). The masses accumulated on the XAD18 gels were all lower than those for the HLB gels. One of the reasons is that the amount of XAD18 resin in each gel disc is less than the amount of HLB since XAD 18 powder was easier to get saturated in the gel solution. The masses of pesticides bound to the XAD18 gel increased linearly with increasing solution concentrations for most of the compounds, except for ATR and CHL. The mass of ATR accumulated on the resin gel decreased when the solution concentration reached 6 mg L^{-}

[1]and the mass was greater than 30mg per disc. This could be caused by the competition between the compounds (Morin-Crini et al., 2017). The mass of CHL did not increase with solution concentration, indicating that there were no significant binding of CHL on the XAD18 resin. Although the binding capacity of XAD18 gel is lower in the present configuration, it is still enough for at least 2 weeks deployment in a polluted environment.

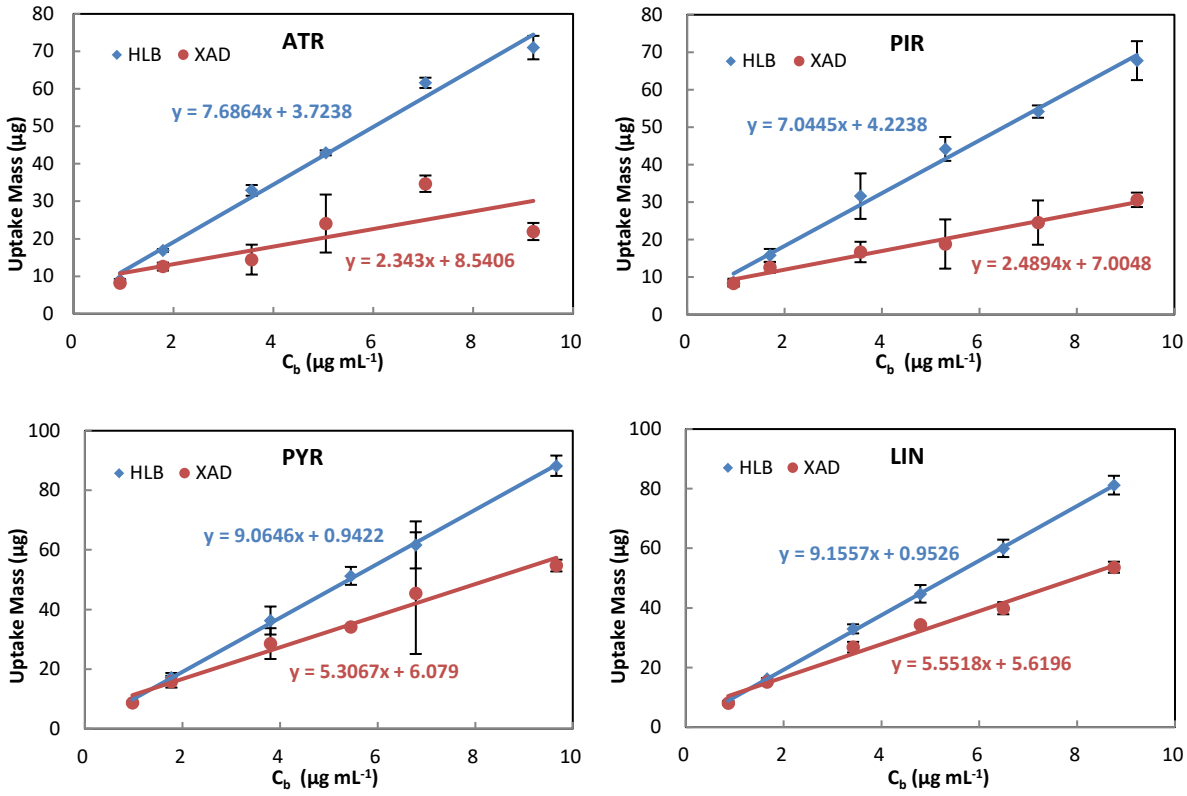


Figure 3.1 Masses of four pesticides (ATR, LIN, PIR and PYR) taken up by two types of binding gels with HLB and XAD18 resins at different concentrations (1 - 10 mg L^{-1}) (IS = 0.01 M, pH = 5.8 ± 0.2, T = 20 ± 2 ℃; n = 3). Error bars were calculated from the standard deviation (SD) of three replicates

3.3.3 Uptake kinetics of the resin gels

To ensure fully quantitative measurement by DGT, it is crucial to have rapid uptake of the target chemical by the resin gel, creating zero concentration at the resin gel/diffusive gel interface. The uptake of target compounds by XAD18 gel increased sharply and linearly within 2 h (Figure 3.2 and Figure S3.3), then slowly increased up to 8 hours. After 8 hours interaction, 6 compounds were adsorbed by >80% of their total amount added; most of the target chemicals (near 100%) were adsorbed within 12 h. The kinetic of the uptake by the HLB gel was slower

than that of the XAD18 gel, but still completed within 24 h. According to the DGT equation (3.1), the minimum uptake amount of target pesticide by the resin gel needs to be about 10 ng at the first 5 minutes. The results presented in Figure 3.2 show minimum of 50 ng for all test chemicals and for both resin gels. The results show that the target compounds bound onto these two types of gels sufficiently rapidly to ensure the concentration of these compounds at the diffusive/ binding gel interface to be zero, which enabled good performance of DGT.

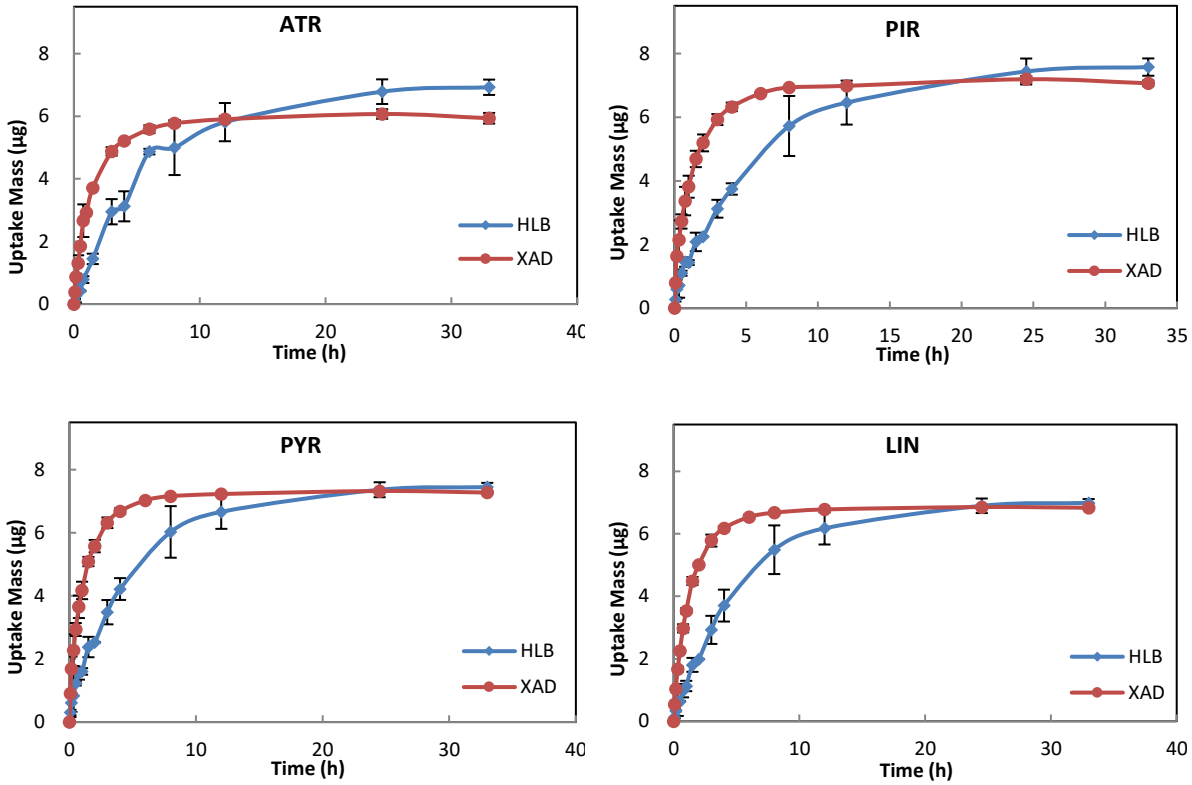


Figure 3.2 Binding kinetics of selected test chemicals by HLB and XAD resin gels in 40 mL solutions of 200 μg L^{-1} test chemicals (IS = 0.01 M, pH = 6.0±0.1, T = 21±1 ℃; n=3). Error bars were calculated from the standard deviation (SD) of three replicates

3.3.4 Diffusion coefficient measurement

Diffusion coefficient of a targeted chemical, D_e, is an essential parameter to calculate its concentration, C_b, using Equation (3.1). It is measured independently using the diffusion cell (Zhang and Davison, 1999). Based on the methods mentioned above, the diffusion coefficients of the 9 pesticides were measured at 21.5 °C and the standard diffusion coefficient at 25 °C was obtained by the equation (3.3):

$$\log D_t = \frac{1.37023(t\text{-}25)+(8.36\times10^{-4})(t\text{-}25)^2}{109+t} + \log\frac{D_{25}(273+t)}{298} \quad \textbf{(3.3)}$$

The diffusion coefficient of the target compound at the solution temperature t (°C) during the diffusion cell experiment is D_t, and D_{25} is the diffusion coefficient of the target compound at 25°C.

The typical plot of mass diffused versus experiment time for the target pesticides in the diffusion cell gave slopes shown in Figure S3.4. All the data are shown in Table S3.3.

In order to compare with POCIS and Chemcatcher passive samplers, the sampling rate per unit for DGT was calculated using Equation (3.4) (Greenwood et al., 2007; Chen et al., 2013).

$$R_{S/A} = \frac{R_s}{A} = \frac{D_e}{\Delta g} \quad \textbf{(3.4)}$$

Table 3.1 shows that the $R_{S/A}$ value for the DGT sampler ranged from 0.76 to 32.7 mL (d cm^2)$^{-1}$. For THI, ATR and LIN, the $R_{S/A}$ values for DGT were comparable with $R_{S/A}$ values reported in the literature for POCIS and Chemcatcher.

Table 3.1 Comparison of $R_{S/A}$ (mL(d cm^2)$^{-1}$) for DGT at 25°C and some other passive samplers

	CHL	THI	FLU	ATR	PIR	LIN	PYR	CLO	ETH
DGT $R_{S/A}$	5.68	5.33	5.51	4.90	4.88	4.92	4.95	4.89	4.59
POCIS $R_{S/A}$	-[a]	3.97[1] - 16.77[1]	-	0.76[1] – 5.83[2]	-	3.43[1] – 23.12[1]	-	-	-
Chemcatcher $R_{S/A}$	-	-	-	4.78[3] – 32.70[5]	6.29[4] – 23.9[6]	3.27[3] – 8.18[7]	-	-	-

a: no data available

References: 1: (Bayen et al., 2014); 2: (Mazzella et al., 2007); 3: (Camilleri et al., 2012); 4: (Moschet et al., 2015); 5: (Vermeirssen et al., 2009); 6: (Gunold et al., 2008a); 7: (Gunold et al., 2008b)

3.3.5 Effect of deployment time and diffusive gel thickness

Two experiments, to test the relationships of accumulated mass versus deployment time and diffusion layer thicknesses, were carried out to validate the principle of DGT for measuring pesticides. The masses of targeted chemicals accumulated by DGT increased linearly (for 7 chemicals sorbed by HLB and 5 chemicals with XAD18, r^2 values were higher than 0.99) with time up to 87 h and agreed well with the theoretical line calculated by Equation (3.1) for most

chemicals (see Figure S3.5). For DGT devices with HLB resin gel, the results of ETH showed significant deviation from the theoretical line after the deployment of 36 hours. For devices with XAD resin gel, only three target chemicals, ATR, THI and CLO, followed the theoretical line. The other six chemicals showed different degrees of deviation at different deployment times. These results indicate that the performance of DGT with HLB is better than that with XAD18 gel for measuring pesticides. A further test of DGT principle for pesticides was carried out using HLB DGT devices with different thicknesses of diffusive gel in a well stirred solution. The measured mass of the target compounds that diffused through the diffusive gel layer was inversely proportional to the diffusion layer thickness (Figure S3.6). The experimental data agreed well with the theoretical line obtained from the equation (3.1). Both results of time dependence and diffusion layer thickness confirm the principle and mechanism of the DGT technique for pesticides in solution.

The results obtained from the different diffusion layer thicknesses also indicate the diffusive boundary layer (DBL) at the surface of the device is insignificant during the experiment under stirred condition and it can be neglected in calculations. In the real environment, the DBL usually cannot be negligible, the value of DBL can be obtained by deploying different thicknesses of DGT devices and calculated through Eq. 3.1 (Warnken et al., 2006).

3.3.6 Effect of pH, ionic strength and DOM

Pesticides are ionic organic chemicals, which possess at least one polar functional group. They can be neutral, cationic, anionic or zwitterionic, depending on the pH of the solution. Their physicochemical properties may change with the environmental conditions, which can also affect the performance of DGT.

To assess the pH effect on the DGT measurement, DGT devices were immersed in solutions with the pH ranged from 4.7 to 8.2. The ratio of the target compound concentrations measured by DGT (C_{DGT}) to their concentrations in the bulk solutions (C_b) were plotted against pH values (Figure S3.7). The results indicate that pH of the solution had no marked effect on the

measurement by DGT with HLB binding gel as most of the ratios (C_{DGT}/C_b) were between 0.9 and1.1. However, for DGT with XAD18 binding gel, the C_{DGT}/C_b ratios were below 0.9 at the pH 7 for all tested compounds and at pH 6 and 7.5 for most compounds. These results demonstrate that the DGT with HLB binding gel can accurately measure concentrations of pesticides in the aquatic environment with a wide range of pH, whereas DGT with XAD 18 binding gel has its limitation.

The effect of ionic strength on DGT measurements was investigated in solutions with ionic strength similar to freshwater, estuary water and seawater, ranging from 0.01 M to 0.5 M. For DGT with HLB binding gel, there was no significant effect observed in the range of 0.01 M to 0.25 M, as shown in Figure S3.8. The ratios of C_{DGT} to C_b were within 0.9 and 1.1 for all tested chemicals. At the ionic strength of 0.5 M (close to seawater), the DGT measured concentrations were slightly lower than expected. The ratio of C_{DGT} to C_b was below 0.9 for ATR, THI and CLO, and close to 0.9 for other six chemicals. This is probably because the viscosity of the solution was higher on addition of a large amount of NaCl, which led to an impediment to the mass transfer process (Castells et al., 2003).

The effect of dissolved organic matter (DOM) on measurements of target chemicals by DGT devices with HLB resin as binding phase was demonstrated in Figure S3.9. The ratios of C_{DGT}/C_b were between 0.9 and 1.1 for majority of the chemicals at various DOM concentrations up to 20 mg L^{-1}. There was very little difference between the various DOM concentrations for all nine chemicals. The C_{DGT}/C_b ratios of some chemicals, such as CHL, FLU, PIR and CLO were below 0.9, they are similar to the ratios for the control solution where the DOM concentration was zero. These findings suggest that the performance of DGT is independent of DOM concentration. Similar phenomena have been observed in the study of Li et al. (Li et al., 2011) on the impact of POCIS for PPCPs (pharmaceuticals and personal care products) and EDS (endocrine disrupting substance), where R_s was not affected by DOM. Li et al.'s research (Li et al., 2016) on perfluorinated chemicals has also shown the similar results.

In general, the performance of DGT devices with HLB resin gel was better than the DGT devices with XAD18 resin as binding gel. DGT with HLB resin gel was therefore selected as the suitable devices for the future experiments and measurements.

3.3.7 DGT for metabolites

Apart from CYA, all other 4 metabolites were detected and measured quantitatively by DGT devices. The results are expressed in ratio of DGT measured concentration (C_{DGT}) and the concentration in solution by conventional method (C_b) (Figure S3.10). The ratios for all compounds are between 0.9 and 1.1 and most of them are close to 1.0. The results indicate that DGT can be used for measuring not only the pesticides, but also their metabolites.

3.3.8 Field applications in waters and soils

3.3.8.1 *In situ* DGT deployments in river water

The results of DGT deployments in She River and Dahuofang Reservoir, north of China are presented in Figure 3.3, ATR was the only detectable target compound. More information on sampling sites is in the SI.

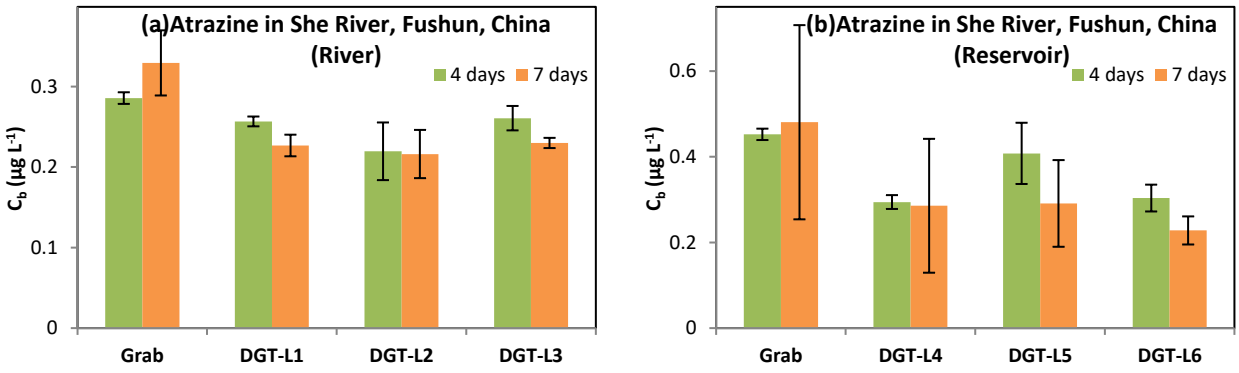


Figure 3.3 Average concentration of ATR measured by DGT devices *in situ* during two different deployment times (4 days, in green, and 7 days, in orange) in (a) She River (in three different locations, L1, L2, and L3) and (b) in She River reservoir (in three different locations (L4, L5, and L6). Grab samples were taken for both deployment period.

DGT provides time weighted average concentrations of ATR over the exposure period. The similar concentrations in the 3 locations of the river (Figure 3.3a) between two different deployment periods, 4 days and 7 days, indicate: i) the concentration of ATR during the 7 days

was consistent without significant variation; ii) the distribution of ATR in the 3 locations (about 50 meters apart) was uniform and iii) DGT performance was good during the deployment period and it was not affected by environmental factors up to 7 days, such as biofouling. As the river water flow was fast, the diffusive boundary layer (DBL) was neglected in calculating C_{DGT} as thickness was estimated much smaller than the thickness of the diffusive gel. The deployment in the reservoir showed slightly greater variation in DGT measured concentrations of ATR between three different locations and between two different deployment times (Figure 3.3b), especially for locations L5 and L6. It is reasonable as the mixing in the reservoir may be less efficient compared to the river. The concentrations of ATR in grab samples were higher than DGT measured *in situ* concentrations. DGT only measures the available fraction which is dissolved and able to diffuse through the diffusive gel. The measurement from the grab samples provides the total concentration, including colloids and complexed fractions that may not be measured by DGT. Several studies have shown the advantage of DGT over grab sampling when measuring chemical concentration in a changing environment (Dunn et al., 2007; Allan et al., 2007).

3.3.8.2 DGT measurements in soils

DGT devices were deployed in five different soils (Table S3.4) to test the applicability of the technique for measuring pesticides and their metabolites in soils. ATR and it metabolites have been chosen as testing compounds. The results are shown in Table 2. HA and DEA were the primary metabolites measured and DIA and DACT were not detected in these soils. The concentration of HA was much higher than that of DEA, implying that hydroxylation was the dominant metabolism process occurred. Although CYA was detected in soil F, the result was not presented here since HLB resin gel could not uptake CYA in the DGT performance test experiment. The extremely low concentration of ATR in soil F indicates the fast degradation of ATR in that soil. Soil F was collected from a highly active agriculture land with excessive

amount of fertilisers. The microbial activities could be much higher than other soils, and therefore, much faster ATR degradation.

Table 3.2 DGT measured concentrations of ATR and its metabolites in soils expressed in mg L^{-1}

	Soil M	Soil D	Soil F	Soil R	Soil K
ATR	3.430	3.305	0.001	4.059	4.034
HA	0.331	0.406	0.029	0.269	0.141
DEA	0.042	0.039	0	0.007	0.003

Although ATR was spiked to the same total concentration for all the soils, DGT measured concentrations, C_{DGT}, varied between soils. The available ATR concentrations in soils M and D were similar, but less than concentrations in soils R and K. This is mainly due to much lower pH in soils M and D, since the adsorption of ATR on the soil would increase with the reduction of pH (Auld and Medd, 1987). The concentrations of metabolites in soils M and D were greater than those in soils R and K, consistent with the findings by other researchers that hydrolysis rate of ATR decreased with the increasing soil pH (Armstrong et al., 1967). Although organic matter content enhanced the degradation of ATR (Gavrilescu, 2005), the pH seemed to have more dominant influence in those soils due to the large difference in pH.

3.4 Conclusions

In this study, a DGT method for measurement of pesticides from a range of chemical classes in waters and soils has been successfully developed. The test of time dependence and different diffusion thickness has validated the DGT theory for measuring pesticides. The uptake kinetic of the tested pesticides compounds by XAD18 binding gel was faster than that of HLB binding gels, but both of them satisfied the DGT requirements. The binding capacity of HLB binding gel is greater than that of XAD18 binding gel. The capacity is large enough to use DGT devices in polluted environment for long time. When DGT with HLB binding gel was used, pH between 4.7-8.2, ionic strength between 0.01-0.25M and DOM concentration up to 20mg/L had no significant effect on DGT performance. The performance of DGT with XAD18 binding gel

was adequate for measuring pesticides, but HLB was better overall. The results of field application in waters and soil have demonstrated that DGT with HLB binding gel can be used to measure available pesticides concentrations with good accuracy and precisions in waters and soils. It can also provide more information on speciation in waters and process mechanisms in soils.

Supporting information

The supplementary tables and figures are listed in Supporting Information.

3.5 Supporting Information

CONTENTS

Analytical method

Field water samples extraction – solid phase extraction (SPE)

The water samples were transported to the lab after collection and stored in the dark room at 4ºC. The pre-treatment of water samples was conducted based on published procedure (Loos et al., 2010; Carvalho et al., 2008) with minor modification. Briefly, water samples were filtered (Whatman GF/F filter, 0.7 μm) to remove suspended particles and then were divided into duplicate samples (500 mL). 100 ng of internal standards were added into filtered samples. SPE cartridges with HLB (200 mg, 6 mL, Sigma-Aldrich, UK) were preconditioned with 10 mL methanol (MeOH) and 10 mL MQ water, then water samples were introduced into the cartridge at a flow rate of 5-10 mL min^{-1}. After the loading of water samples, the cartridges were rinsed with 10mL of MQ water and vacuum dried for 2 h. The pesticides retained on the cartridges were eluted with 10 mL MeOH and the eluates were evaporated to near dryness under a gentle stream of nitrogen and re-dissolved in 1 mL of MeOH. Filtration through a 0.22 μm filter membrane was followed by transferring the extract to a 2 mL amber vial. All samples were stored at -20ºC in the freezer. Prior to the LC-MS analysis, 200 μL aliquot of each water sample extract was dried and reconstituted in 100 μL of mixed solvent (MeOH:MQ = 10:90 v/v).

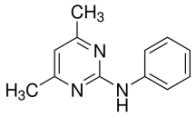
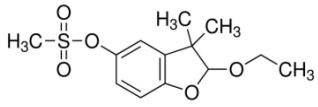
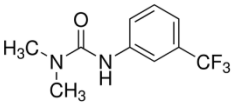
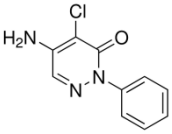
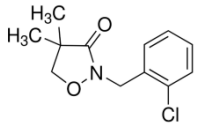
Information on sampling sites

The sampling points of water samples were on the She River, a tributary of Hun River, water flew through the territory of Fushun (Liaoning, China) into Dahuofang Reservoir. This river had a length of 59 km. The banks of the river were both farmland, planting corn, muskmelon ect. The farmland had a long history of ATR application.

The sampling sites of soil samples were in China and UK. The soil from the bank of She River was taken as Soil F. The other four sampling sites in UK were on farms from: Old castle mill, Malpas, Cheshire (Soil M); Daresbury, Cheshire (Soil D); Reddish, Stockport, Manchester

(Soil R); Kettering, Northamptonshire (Soil K). They were meadows with several years in the absence of organic pesticides.

Table S3.1 (a) Typical chemicals

Classification	Compound	*MW*	log*K*ow	*S*w25℃ (mg L^{-1})	pKa (0-14)	Formula	Structure
Fungicide	Pyrimethanil	199.26	2.84	165.8	2.26 12.56	$C_{12}H_{13}N_3$	
Herbicide	Ethofumesate	286.35	2.7	72.86		$C_{13}H_{18}O_5S$	
Herbicide	Fluometuron	232.21	2.42	253.9	13.22	$C_{10}H_{11}F_3N_2O$	
Herbicide	Chloridazon	221.65	1.14	3585		$C_{10}H_8ClN_3O$	
Herbicide	Clomazone	239.7	2.5	197.5		$C_{12}H_{14}ClNO_2$	

(b) Typical Chemicals studied by other passive samplers

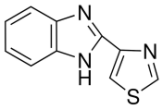
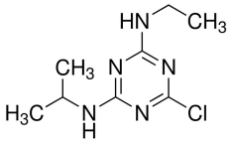
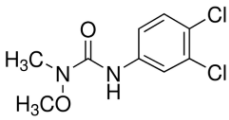
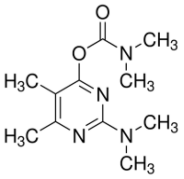
Classification	Compound	*MW*	log*K*ow	*S*w25℃ (mg L^{-1})	pKa (0-14)	Formula	Other Samplers	Structure
Fungicide	Thiabendazole	201.25	2.47	335.2	4.08 10.28	$C_{10}H_7N_3S$	POCIS	
Herbicide	Atrazine	215.69	2.61	214.1	3.2	$C_8H_{14}ClN_5$	POCIS Chemcatcher	
Herbicide	Linuron	249.1	3.2	44.27	4.85 7.09	$C_9H_{10}Cl_2N_2O_2$	POCIS Chemcatcher	
Insecticide	Pirimicarb	238.29	1.7	969.5	4.99	$C_{11}H_{18}N_4O_2$	Chemcatcher	

Table S3.2 Recoveries of test chemicals for SPE and DGT and detection limits (IDLs and MDLs) for both water and DGT samples during the lab experiments detected by LC-MS

Test Chemicals	IDL[b] (μg L^{-1})	Recoveries (%)		D_e at 25°C	Lab sample MDL[c] (μg L^{-1})		Field sample MDL (ng L^{-1})	
		SPE	DGT	(E-06 cm^2s^{-1})[a]	Water	DGT	Water	DGT
CHL	6.81E-2	89.06	99.33	6.58	7.57E-2	3.71E-2	1.53E-01	5.29E-1
THI	2.24E-1	72.53	98.92	6.17	2.49E-1	1.30E-1	6.17E-01	1.86E0
FLU	1.04E-1	106.42	98.32	6.38	1.15E-1	5.87E-2	1.95E-01	8.39E-1
ATR	4.13E-2	100.76	97.91	5.67	4.58E-2	2.64E-2	8.19E-02	3.77E-1
PIR	2.71E-1	93.41	96.52	5.70	3.01E-1	1.77E-1	5.81E-01	2.53E0
LIN	7.65E-2	98.61	96.79	5.65	8.51E-2	4.93E-2	1.55E-01	7.05E-1
PYR	1.25E-1	87.83	93.22	5.73	1.39E-1	8.32E-2	2.85E-01	1.19E0
CLO	9.11E-2	87.11	93.27	5.66	1.01E-1	6.14E-2	2.09E-01	8.77E-1
ETH	6.7E-4	86.76	98.14	5.31	7.46E-4	4.58E-4	1.55E-03	6.54E-3

a: D_e values were acquired from Table S3.3

b: IDLs were calculated based on IDL = 3SD, where SD is the standard deviation from a measured concentration of standard (8 times)

c: MDLs were calculated based on MDL= $\frac{IDL}{R \times CF}$, where R is the recovery for water or DGT samples and the CF is the concentration factor(dilution ratio)

DGT MDLs were calculated according to the DGT MDLs for 1-day deployment in the lab experiments and 7-daydeployment in the field application under 25°C condition

Table S3.3 Diffusion coefficient of 9 pesticides in DGT gel at test temperature (21.5°C, measured) and standard temperature (25°C, calculated)

Chemical	D_e at 21.5°C (E-06cm^2s^{-1}) (measured)	D_e at 25°C (E-06 cm^2s^{-1}) (calculated)
CHL	5.98	6.58
THI	5.60	6.17
FLU	5.79	6.38
ATR	5.15	5.67
PIR	5.18	5.70
LIN	5.13	5.65
PYR	5.20	5.73
CLO	5.14	5.66
ETH	4.83	5.31

Table S3.4 Properties of soils used for DGT applications

Soil	M	D	F	R	K
pH (H_2O)	4.8	5.7	6.0	6.7	7.7
Organic Mater Content (%)	3.9	5.4	6.1	4.8	8.1
Background ATR C_{DGT} (μg L^{-1})	0	0	0.35	0	0

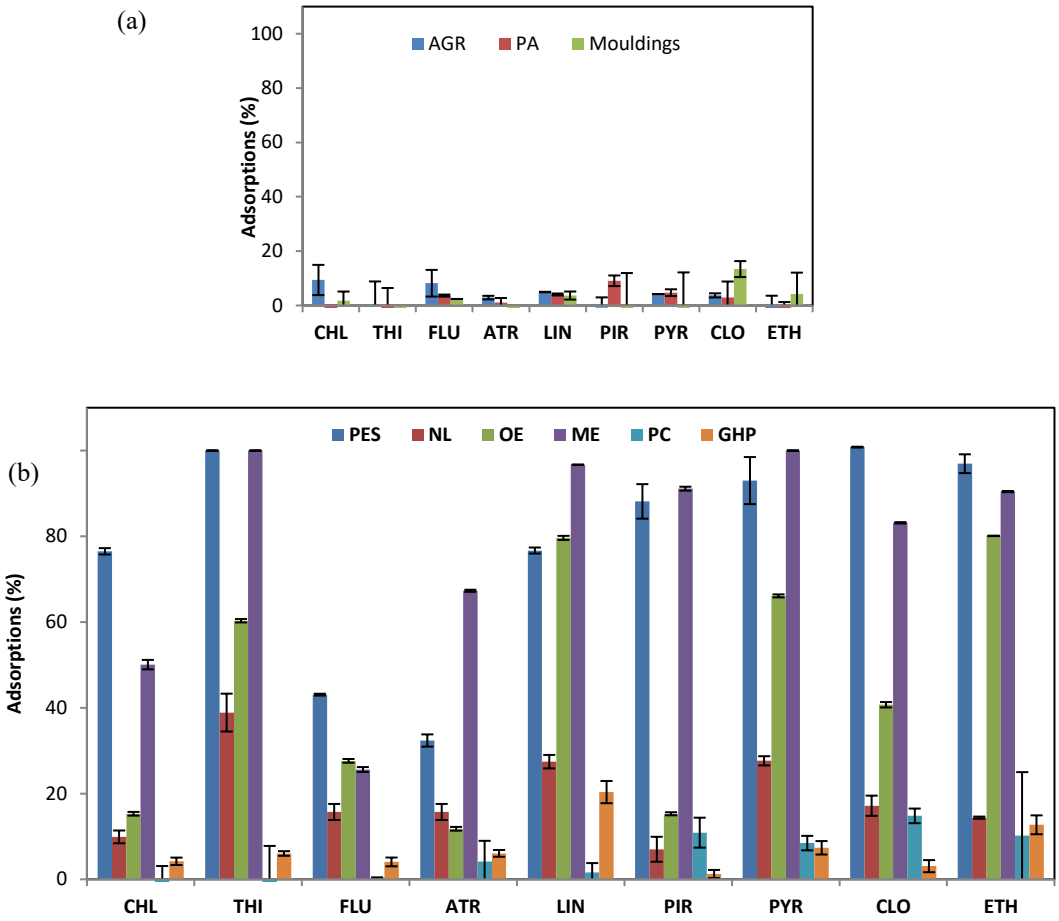


Figure S3.1 Adsorption of 9 target compounds onto (a) PA and agarose diffusive gels, DGT mouldings and (b) 6 kinds of filter membranes.

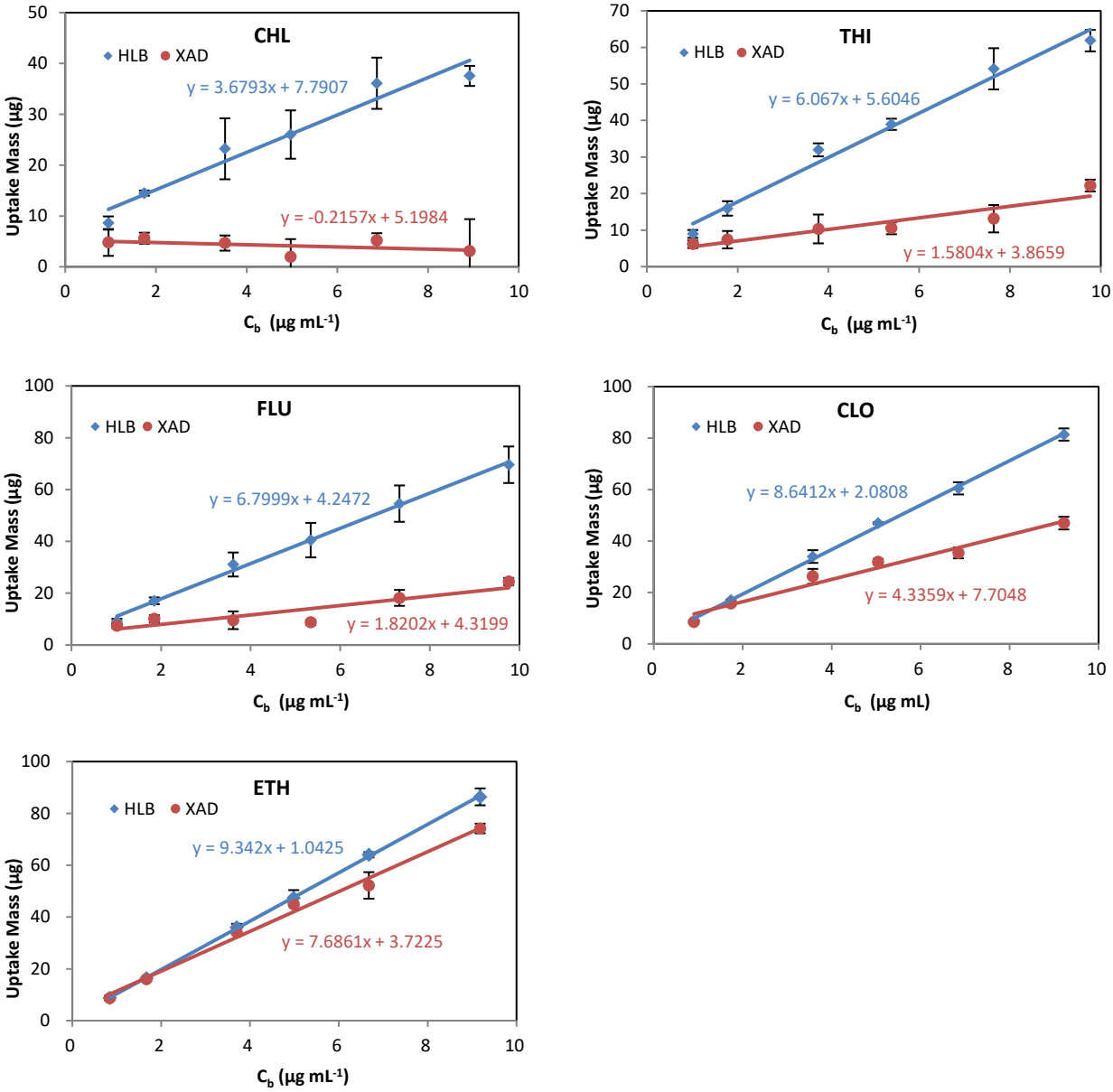


Figure S3.2 Masses of 5 other pesticides taken up by two types of binding gels at different concentrations (1-10 µg mL^{-1})

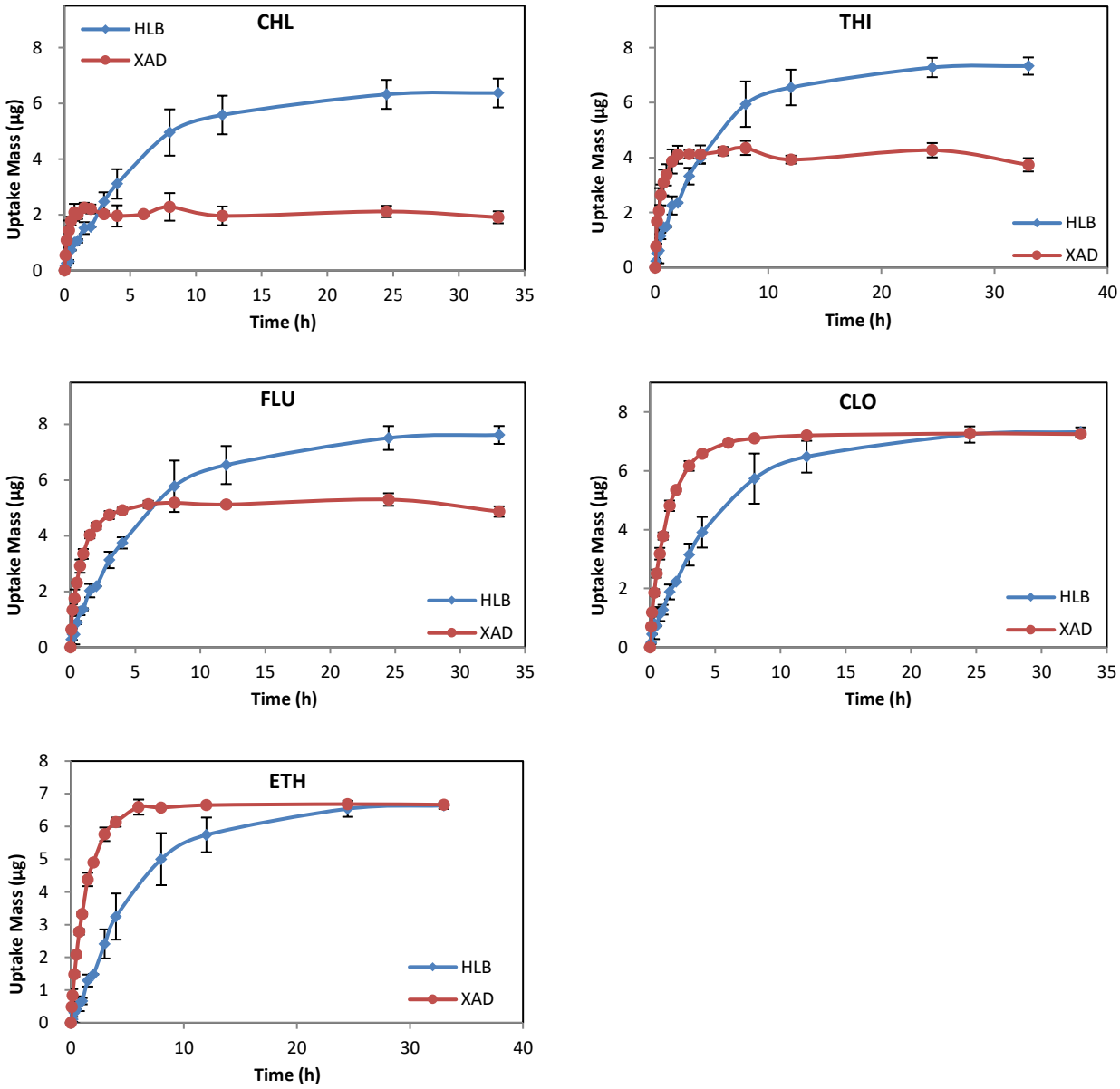


Figure S3.3 Time dependence of the masses of 5 other pesticides accumulated by two kinds of binding gels

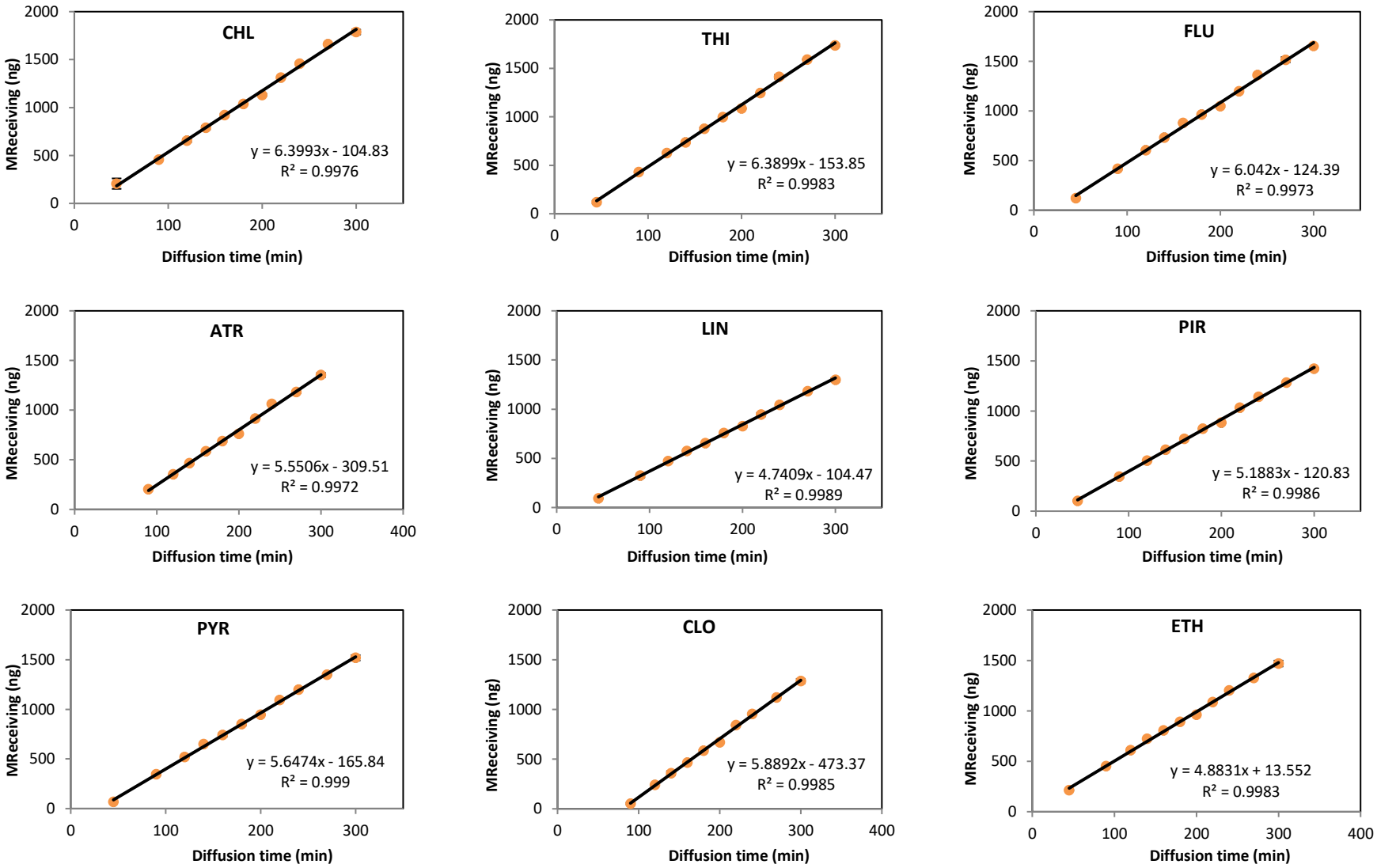


Figure S3.4 The masses of 9 pesticides diffused through agarose gel at different times under 21.5 °C, pH of 6.8 and ionic strength of 0.01 M

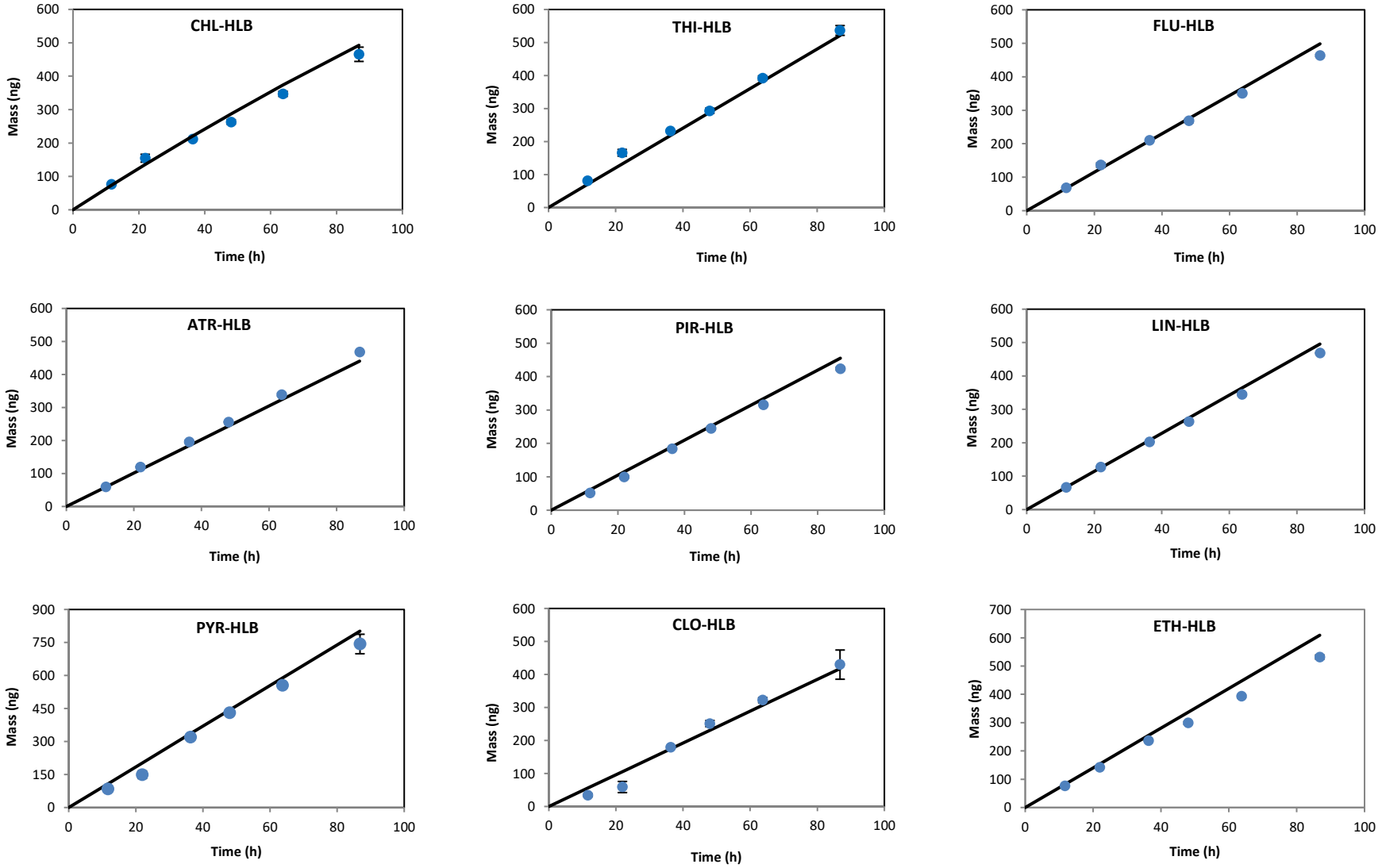


Figure S3.5 (a) Measured masses of 9 pesticides in the binding layer of DGT devices (HLB) for different times

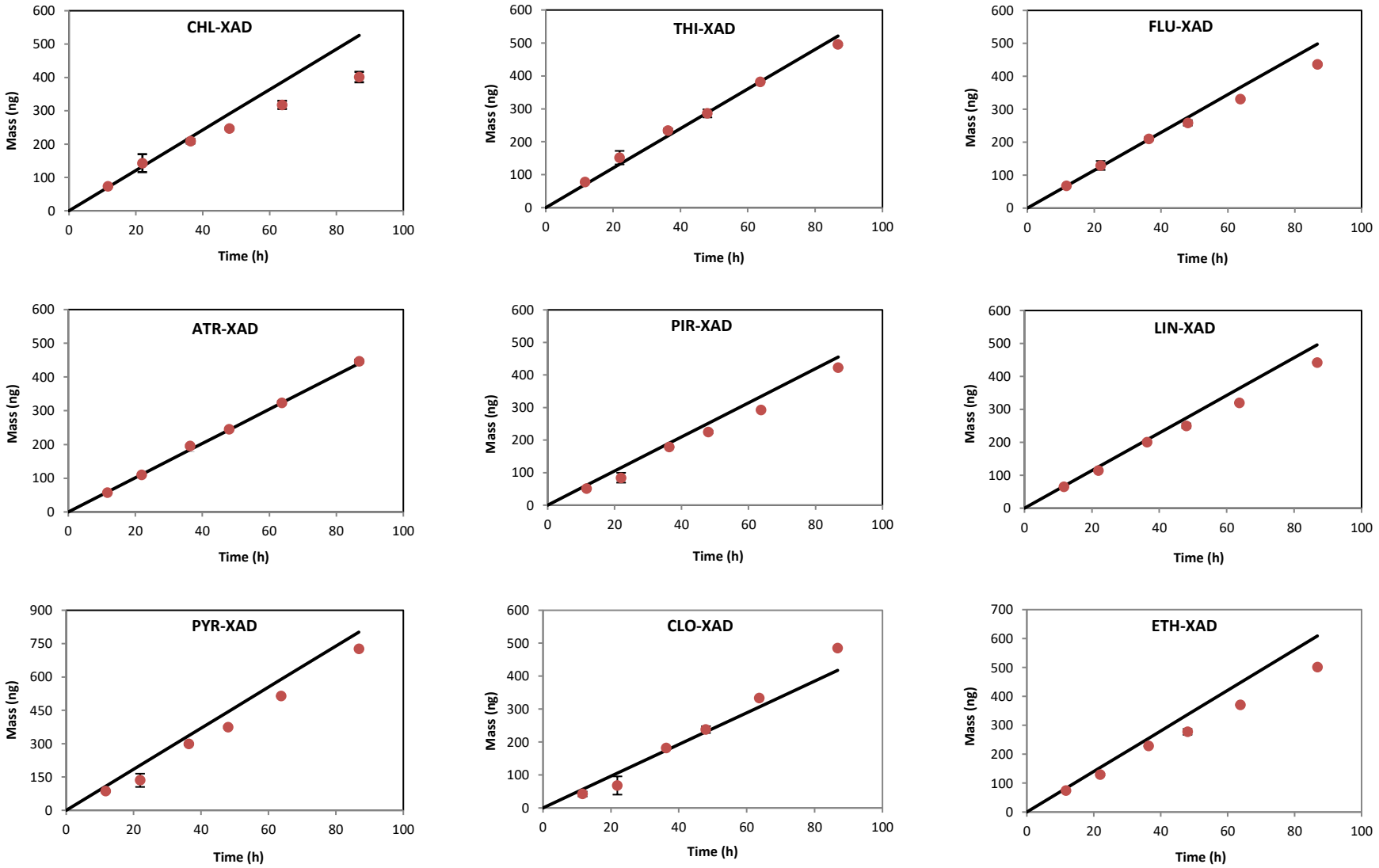


Figure S3.5 (b) Measured masses of 9 pesticides in the binding layer of DGT devices (XAD 18) for different times

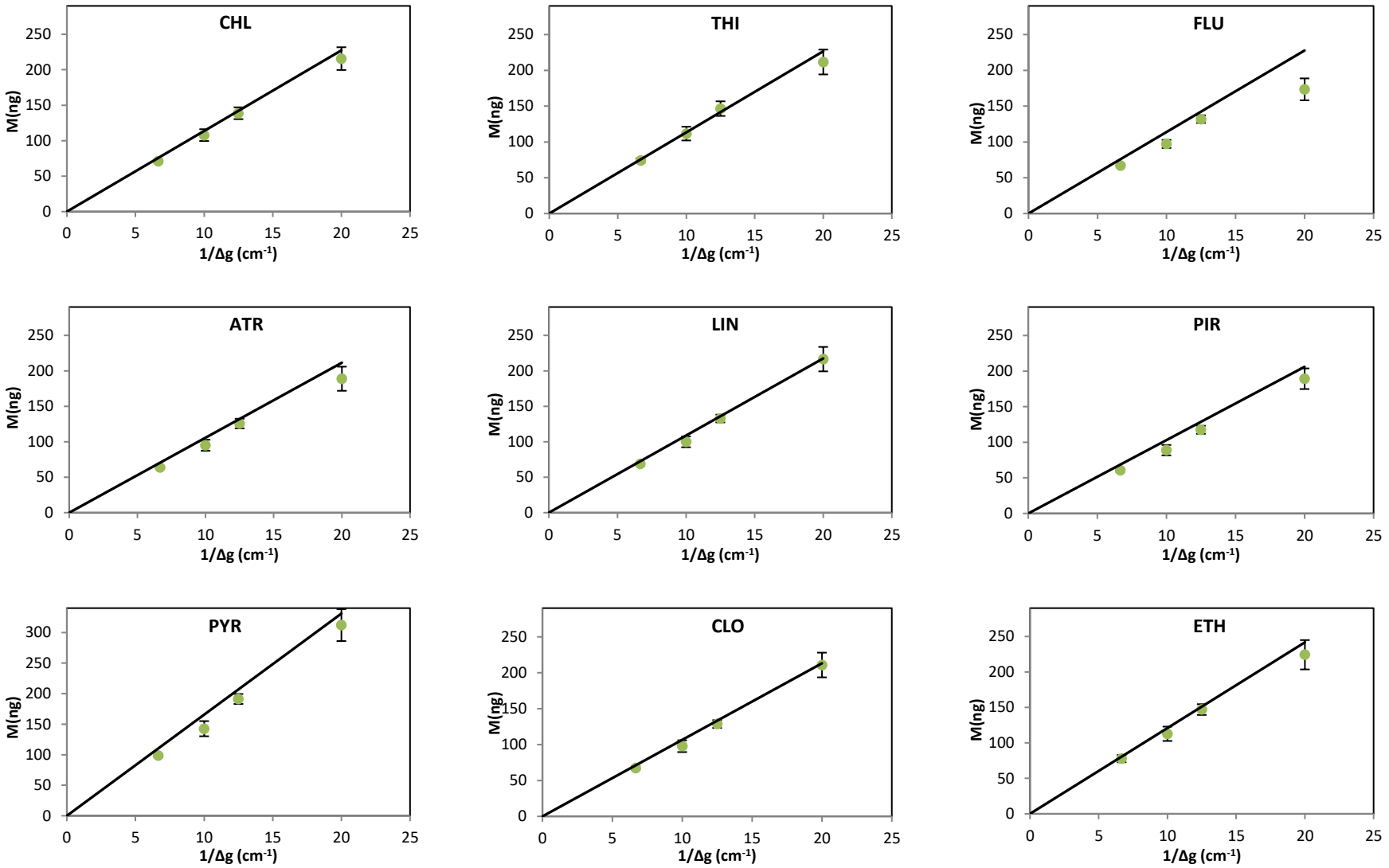


Figure S3.6 Measured masses of 9 pesticides for DGT with different diffusive gel thicknesses

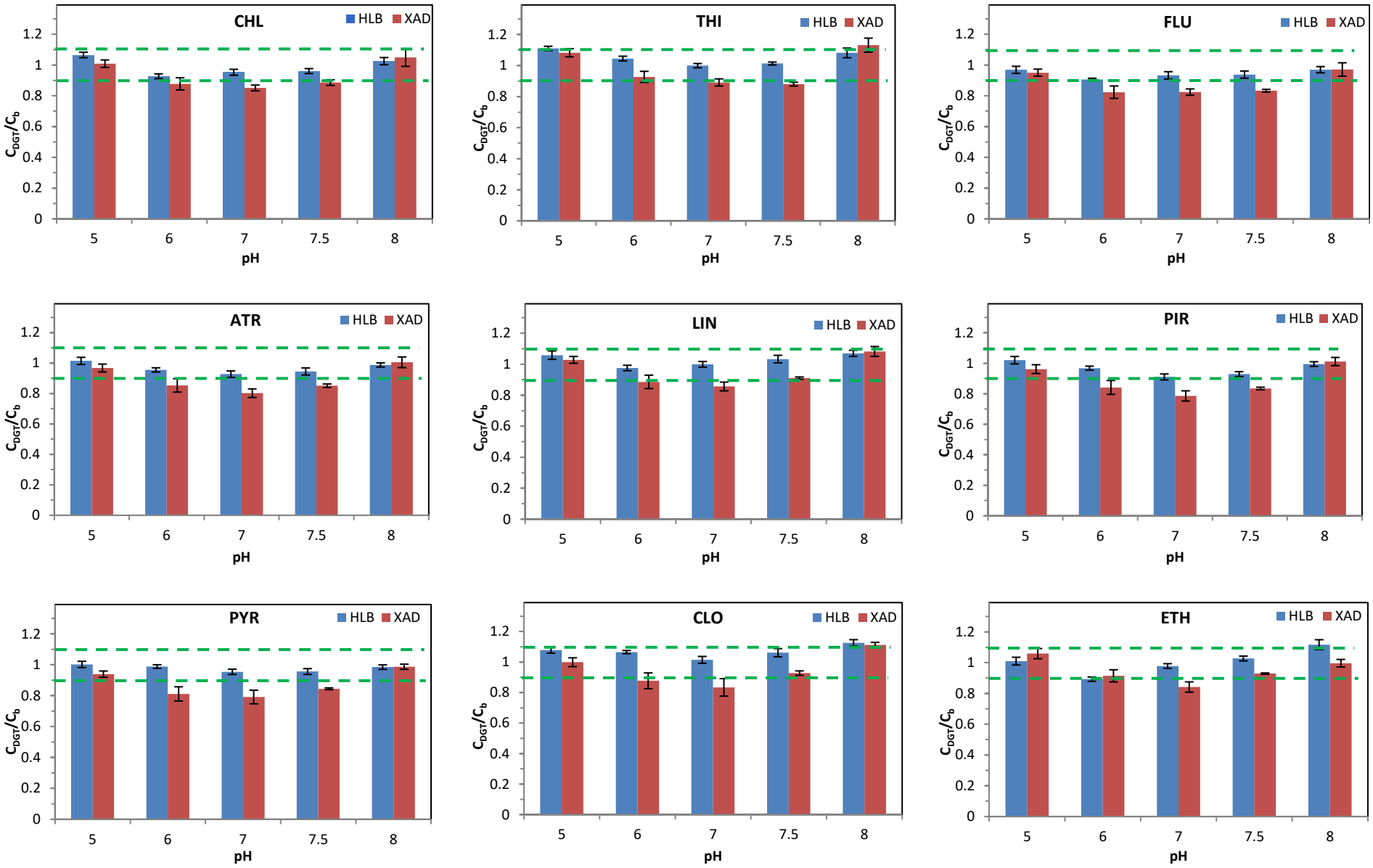


Figure S3.7 Effect of solution pH on the ratio of DGT measured concentrations of 9 pesticides, to their concentrations in the bulk solutions

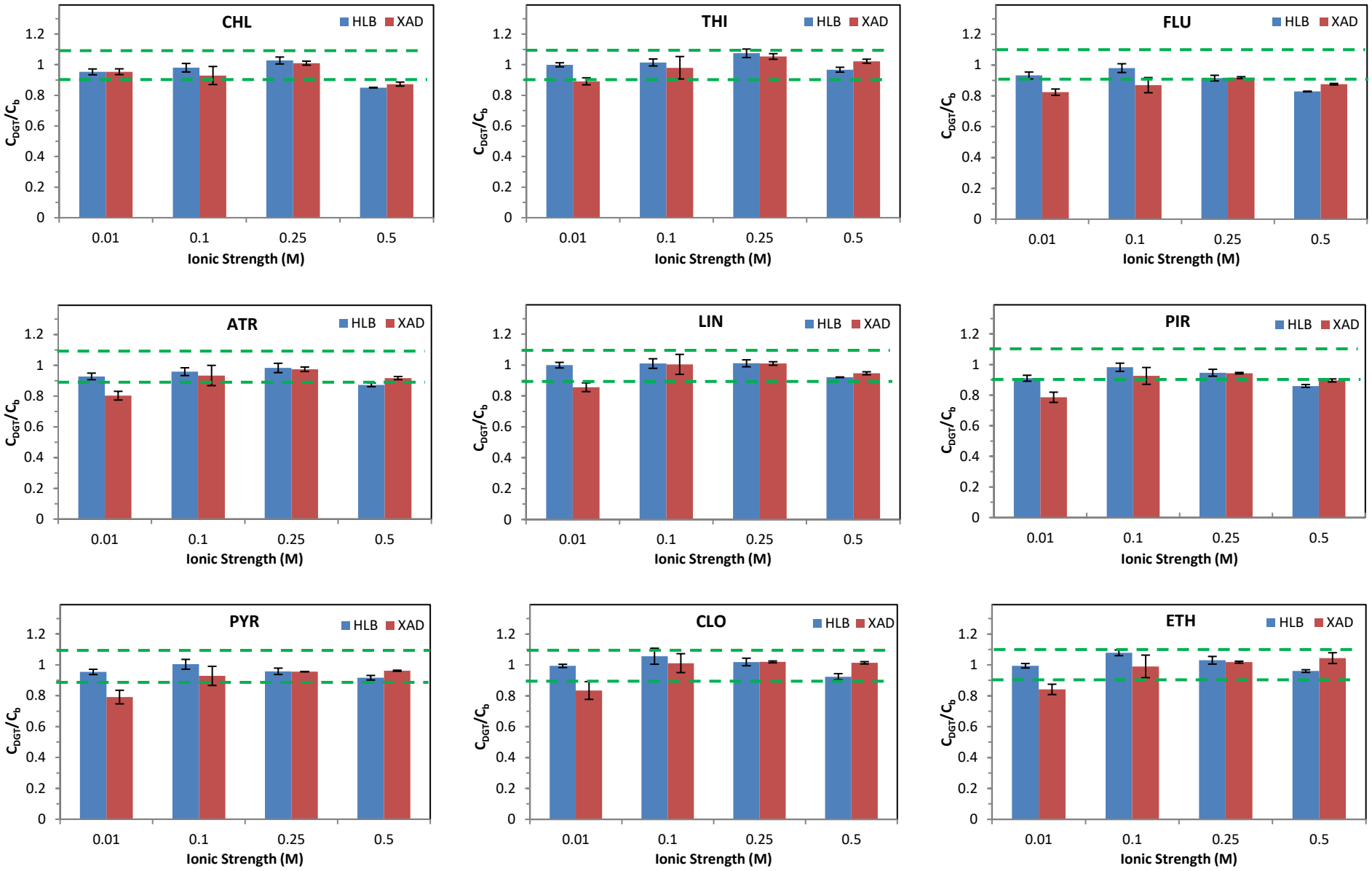


Figure S3.8 Effect of solution ionic strength on the ratio of DGT measured concentrations of 9 pesticides, to their concentrations in the bulk solutions

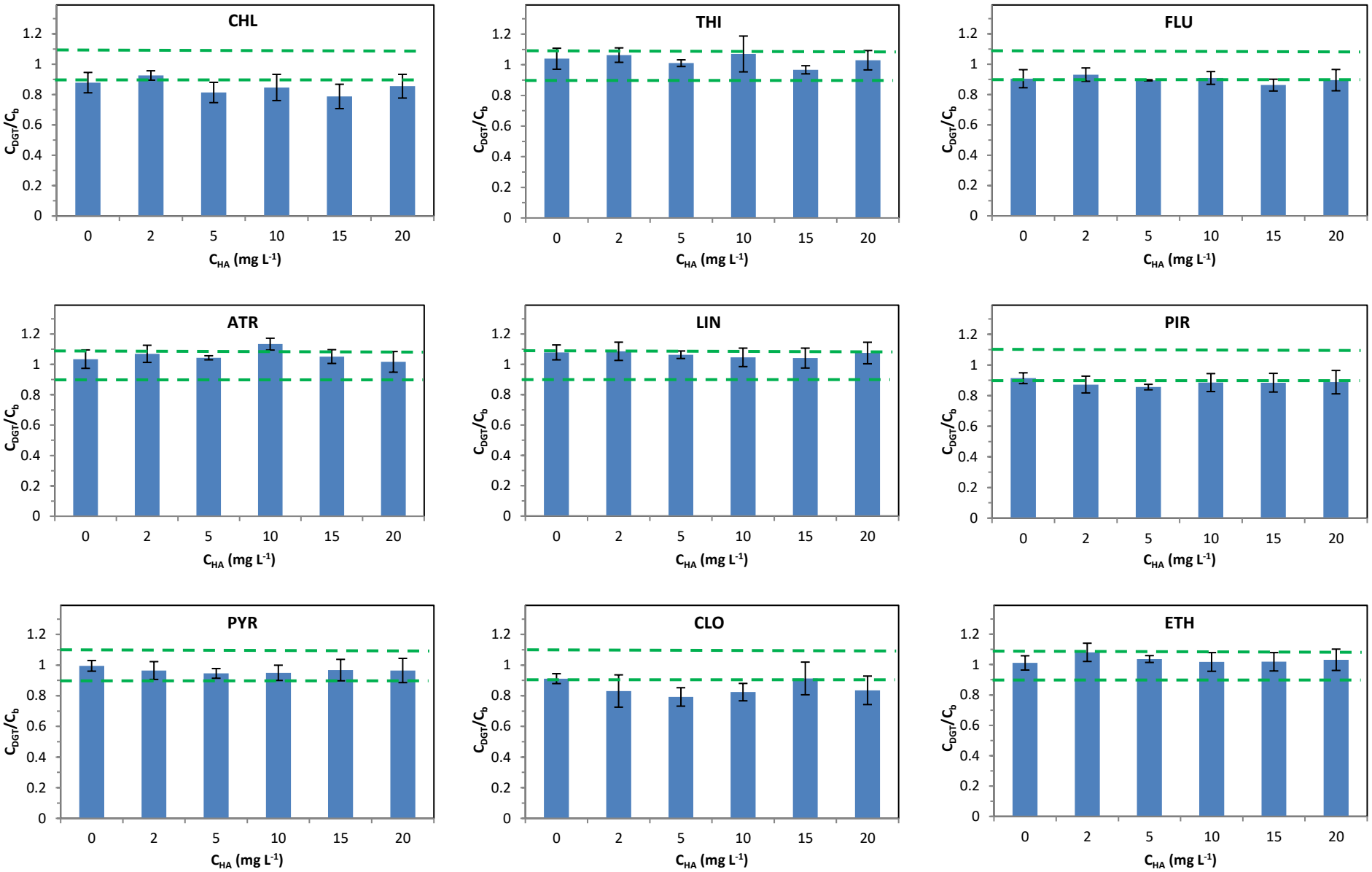


Figure S3.9 Impact of DOM on the performance of DGT with HLB binding gel

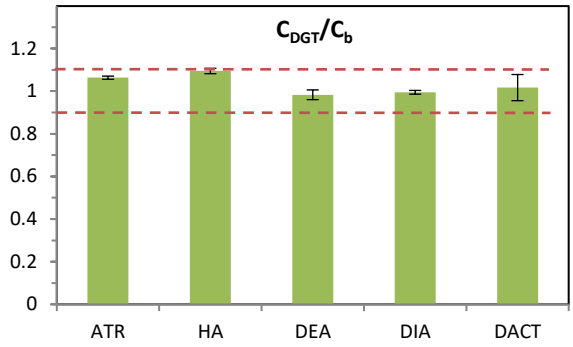


Figure S3.10 Performance of DGT in measuring ATR and its metabolites in a standard solution (pH = 5.7, Ionic strength = 0.01M) for 24 hours at 21 ± 1°C.

Chapter 4: Pesticide bioavailability and metabolism in a soil-crop system: testing a novel DGT sampling technique

4.1 Introduction

Pesticides are designed to protect crops by killing target pests. However, only an extremely small percentage (in most cases <0.1%) of the applied pesticides actually reach target organisms (Pimentel, 1995). So, >99.9% of the applied pesticides remain in the soils or move through environmental compartments. Some pesticides have long persistence in the soil, perhaps years or decades. Some residues become bound or non-extractable through interactions with the soil (Mordaunt et al., 2005), while the bioavailability of these residues are reduced. Studies have demonstrated that non-extractable (bound) pesticides may still be taken up by plants and earthworms (Fuehr and Mittelstaedt, 1980; Gevao et al., 2001). Due to the interests in the efficacy of pesticides after application and concerns over their potential non-target effects, there is a need for studies to contrast the performance of different monitoring approaches to assess the form, fate and bioavailability of pesticides in soil-plant systems.

The triazine herbicides are often considered the most important class of agricultural chemicals ever developed. Atrazine (ATR) is one of the most well-researched herbicides and often selected for studies on pesticide fate and behaviour in soils and plants (Farland et al., 2011). This broad-leaf herbicide which has been used widely to control weeds in corn, sorghum, sugarcane, rangeland and other crops in agriculture for several decades (Grigg et al., 1997). It is often applied to the soil surface both before and after the emergence of the crops, owing to its high selectivity (Haith et al., 1979). Its extensive usage has led to widespread contamination of soils and water. ATR is the pesticide most frequently found in groundwater in the US (Benotti et al., 2009). It has often been detected in groundwater in Europe; its use in Europe is now restricted. Although it is generally considered as a moderately persistent herbicide, with half-lives ranging from several weeks to months, ATR residues have been detected in agricultural

soil for up to 9 years after initial application (Capriel et al., 1985). It remained the most abundant pesticide in groundwater in Germany even years after it was banned (in 1991) (Tappe et al., 2002). There has been evidence that exposure to ATR may cause cancers in human and rats, and disrupt the oestrous cycle in rat strains (Rusiecki et al., 2004; Cooper et al., 2000). Its fate and degradation pathway has been well studied (Khromonygina et al., 2004; BoundyMills et al., 1997). Hence ATR was selected for this study.

It has been reported that the degradation of ATR occurs mainly through three pathways (shown in Figure 4.1). These are: i). hydroxylation at carbon atom 2, in which the chlorine is replaced with a hydroxyl group; ii). N-dealkylation at carbon atom 4 or 6; and iii). triazine ring cleavage (Eisler, 2007). Hydrolysis of ATR to hydroxyatrazine (HA) is the primary chemical degradation route (Boxall, 2009). It usually occurs in higher plants, with the help of an active catalyst (Shimabukuro, 1968) or in soil where it is catalysed by soil organic matter. Benzoxazinone can act as the catalyst and initiates the reaction in some higher plants such as corn, sorghum and poplar trees. The phytotoxicity of ATR is lost by hydroxylation (Shimabukuro and Swanson, 1969). In soil, low soil pH, high organic matter content, low moisture content, high temperature and high clay content all enhance the hydrolysis of ATR to form a less mobile metabolite, HA (Ware and Gunther, 1995). De-alkylation of ATR, encountered by both fungi and bacteria, is the main biodegradation pathway (Rosen et al., 2012). This process prefers the removal of the ethyl side chain to form de-ethylatrazine (DEA), rather than the isopropyl side chain to form deisopropylatrazine (DIA) in soil (Farland et al., 2011). De-alkylation occurs in most higher plants. All intermediate metabolic products can be further degraded to desisopropyl-desethyl-atrazine (DACT), ammeline (AMN) and cyanuric acid (CYA) following the combination of hydrolysis and dealkylation (Frear et al., 1972), and then eventually are mineralized into inorganic compounds such as CO_2, H_2O or NH_3.

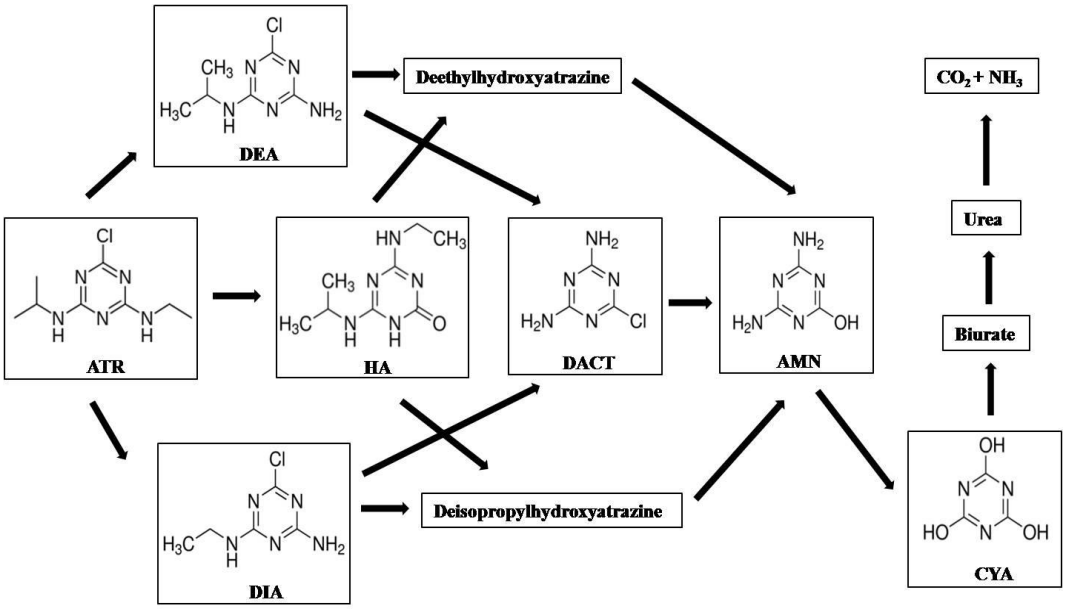


Figure 4.1 Degradation pathways of ATR

Several traditional simple and cost effective soil extraction methods have been conducted to measure pesticides, such as ATR and its metabolites in soils. These include traditional Soxhlet extraction (Wang et al., 2007) and mechanical shaking (Babić et al., 1998), but they consume labour, time and solvent (Sun and Lee, 2003). Some more efficient and environmentally friendly techniques have been introduced, including accelerated solvent extraction (ASE) (Gan et al., 1999), microwave- assisted extraction (MAE) (Vryzas and Papadopoulou-Mourkidou, 2002), supercritical fluid extraction (SFE) (Snyder et al., 1992), ultrasonic solvent extraction (USE) (Goncalves and Alpendurada, 2005) and solid-phase micro-extraction (SPME) (Aulakh et al., 2005). However, the determination of environmental fate and risk assessment requires the bioavailable fraction of ATR (Reid et al., 2000b). Exhaustive extractions determine the 'total' compound concentrations, which is the normal approach for regulatory soil tests. Although Tao et al. (2004) used the ASE procedure and obtained a positive relationship between the amount of total DDT (Dichlorodiphenyltrichloroethane and its metabolites) accumulated in the wheat root and the quantities extracted by n-hexane (r = 0.998), for most of the pesticides such as ATR, exhaustive extraction usually overestimated their bioavailability.

Hence, there is a need to assess the mobile, labile and bioavailable portions, to better inform pesticide risk assessments specifically. Direct characterization of ATR bioavailability in soil using plants or micro-organisms uptake can be costly and time-consuming. From the biological perspective, the biodegradable fraction of compounds can be considered as bioavailable. Radiorespirometry assays are often employed by assessing mineralisation of ^{14}C-labelled analogues to $^{14}CO_2$ (Gevao et al., 2001), which have been applied extensively. But this cannot confirm parent/metabolites and it needs the addition of radiolabelled chemicals which can't be applied *in situ*. In some cases, water-extractable residues were assumed to be available (Stalder and Pestemer, 1980), but measurements of ATR in soil solution are not able to account for the ability of the soil to resupply the solution concentration after depletion by uptake. Bioavailability is limited by mass transfer kinetics. More recently, less exhaustive techniques (Barriuso et al., 2004; Kelsey et al., 1997) have been widely used to predict the bioavailability of ATR. 80% aqueous methanol has been used for ATR extraction in some researches to measure ATR in soils (Huang et al., 2006) or acquire ATR bioavailability to antimicrobials (Barriuso et al., 2004). But these approaches do not provide any kinetic information.

In order to predict the bioavailability of pesticides to plants, it is necessary to understand both solution and solid phase supply processes in soils. The Diffusive Gradients in Thin Films (DGT) technique locally lowers analyte concentrations in the soil solution at the DGT-soil interface and stimulates re-supply from the solid phase by diffusion (Zhang et al., 2001). It has been successfully applied to the prediction of heavy metal and phosphorous bioavailability. DGT can predict the bioavailability of Cu, Pb and Zn in soils, for example, the effective concentrations obtained by DGT correlated significantly with uptake by sorghum (Agbenin and Welp, 2012). The work published by Six et al. (2013) indicated that the concentration of P measured by DGT has been shown to give a better correlation to maize uptake than other measurements. DGT has already been used successfully to measure antibiotics and to study

their release kinetics in soils and to characterize the dynamics of soil-solution interactions (Chen et al., 2014a). These studies raised interest in the potential for DGT to be used to measure ATR bioavailability in soil.

The object of this study was to obtain an integrated assessment of concentrations of ATR and its metabolites in soils and a reliable technique to determine the bioavailability of ATR in soils to a crop plant. DGT, water extraction and chemical extraction were employed in 5 different soils treated with ATR and compared with each other in time course experiments. ATR and breakdown products were determined. In addition, ATR and its products were also determined in maize grown in the soils, so the soil extraction/removal tests could be assessed for their ability to assess bioavailability of ATR. The metabolic pathways of ATR in this soil-maize system were thoroughly investigated as well, again focussing on the scope for DGT to add value and information.

4.2 Materials and methods

4.2.1 Chemicals

Atrazine (ATR) and its 6 metabolites: hydroxyatrazine (HA), deethylatrazine (DEA), deisopropylatrazine (DIA), deisopropyldeethylatrazine- (DACT), ammeline (AMN), cyanuric acid (CYA) were purchased from China. Their physiochemical properties are given in Table S4.1.

ATR was stored as 38% suspension liquid. All ATR metabolite stock solutions were dissolved in pure methanol. Acetonitrile (ACN) and methanol (MeOH) were purchased from Fisher (Poole, U.K.).

4.2.2 Soil samples

Five soils of different properties were collected from UK and China. The details of soil sites and properties are listed in Table S4.2. All soils were collected from the soil sub-surface (10-

20 cm) after surface vegetation and stones were removed, then air-dried and passed through a 2 mm sieve to remove roots and stones prior to experiments.

The soils were dosed with ATR at concentrations of 5 (as normal test lab soil) and 100 (as contaminated soil) mg kg^{-1} (dry matter basis). The soils were then wetted to 25-30% maximum holding capacity water (MWHC) by adding appropriate amounts of MQ water, mixing well until ATR distributed in soils homogenously and allowing them to equilibrate at room temperature in sealed bags in dark for 23 days.

4.2.3 Pot experiment

Maize seeds (*Zea mays*) were purchased from Johnsons Seeds (Suffolk, UK). They were soaked in MQ water for 48h, then pre-germinated on moist filter paper in the glasshouse for 48 h prior to sowing. Each plastic pot received 400 g ATR contaminated soil. Triplicates were prepared for each ATR treatment, 5 and 100 mg kg^{-1} for 5 soils. The soils were wetted to 100% pot MWHC 24 h before transplanting the pre-germinated seeds. Soil moisture was maintained at 100% MWHC during plant growth. The surface of each pot was covered with aluminium foil to minimize photo-degradation and to avoid loss of water. The experiment was conducted in a controlled-environment glasshouse which maintained a daily 14 h light period. The temperature was 25 °C during the daytime and 20 °C at night. The plants were grown for 3 weeks and harvested at the three-leaf stage. A mix of nutrients was added after two weeks.

The pots were left without watering one day prior to harvest. Shoots and roots were harvested separately. They were carefully rinsed with MQ water to remove any adhering soil particles, wiped with tissue paper and weights were recorded. Then these samples were freeze-dried for 48 h, weighed immediately, and stored at -20 °C. Before analysis, stored maize samples were cut and homogenized with a mortar and pestle. About 0.1 g samples were extracted using 10 mL of 80% aqueous MeOH by shaking on a rotary shaker for 48 h. The eluent was N_2 blown

to dryness and made up to 1 mL with MeOH, then filtered with 0.2 μm PTFE syringe filter prior to analysis.

4.2.4 DGT deployment and soil sampling

DGT devices assembled with 0.4mm HLB resin gels, 0.85mm agarose diffusive gels and GH Polypro (GHP) filter membranes were prepared prior to the experiment.

After 23 days aging, soils were wetted to 100% MWHC and mixed to obtain a soil slurry, then the slurry was left for 24 h before deployment. For DGT deployment, soil paste was smeared onto the filter of one DGT device, then the device was gently pressed into the soil to ensure maximum contact between the soil surface and the DGT device, the deployment was maintained at room temperature for 24 h. All treatments were triplicated.

After 24 h deployment, DGT devices were retrieved, and the filter surface was jet washed with MQ water. The resin gels were removed and placed into 20 mL amber glass vials. 10 mL ACN was added for each vial, the vials were put in an ultrasonic bath for 30 min to extract. The eluents were filtered through 0.2 μm syringe filter (PTFE, Whatman, UK) prior to analysis.

After retrieving, the triplicate soils were mixed and stirred, about 50 g soil paste was sampled into a 50 mL tube and centrifuged at 3500 rpm for 30 min. The soil solution obtained from the centrifuge was filtered with a 0.2 μm syringe filter (PTFE hydrophilic, Whatman, UK) into 1 mL vials prior to analysis.

5 g samples of the soils were taken and extracted with 20 mL ACN, then centrifuged at 3000 rpm for 30 min. The supernatants were filtered through 0.2 μm syringe filters (PTFE, Whatman, UK) into 20 mL vials waiting for analysis.

After harvest, all soils were sampled and extracted, as described above, to obtain ATR concentrations in soil after maize planting.

4.2.5 Diffusion coefficients of ATR and its metabolites and binding gel elution efficiency measurements

The diffusion coefficients (D_e) of ATR and its metabolites were measured by immersing DGT devices into 10 μg L^{-1} mixed pesticides solution (0.01 M NaCl, pH 6.0 ± 0.2, Temperature 24 ± 1°C). A 22 h deployment was conducted. All the devices were treated as mentioned above. The diffusion coefficients of target chemicals were calculated using the following equation:

$$D_e = \frac{M \times \Delta g}{C_b A t} \quad \textbf{(4.1)}$$

where, M is the measured mass of target chemicals in the binding gel, Δg is the diffused length of analyte before being trapped by the binding phase, A represents the sampling area of DGT, t is the exposure time, C_b is the concentration of chemicals in the bulk solution.

The elution efficiencies of test chemicals were defined as the ratios of measured chemicals in the extracts from HLB binding gels to the chemicals adsorbed by the binding gels. HLB gels were soaked into 10 mL solutions of 1mg L^{-1} mixed chemicals and shaken for 24 h. Then binding gels were taken out for ultrasonic extraction.

4.2.6 Chemical analysis (ATR and metabolites)

Prior to LC-MS/MS analysis, 0.2 mL of each stored sample was dried under a gentle N_2 flow and reconstituted in 0.2 mL with MQ: MeOH prepared in a ratio of 9:1.

A Shimadzu Nexera X2 LC coupled with a Shimadzu LCMS-8030 triple quadrupole mass spectrometer detector was used to analyse ATR and its metabolites. The separation of these chemicals was performed with a Phenomenex Kinetex Biphenyl column (50×2.1mm, 2.6 μm). The mobile phases consisted of 5mM ammonium formate in methanol (solvent A) – 5mM ammonium formate in MQ water (solvent B). The analytes were eluted with the following gradient program: 15%B from 0 min to 0.5 min, then increased to 50%B at 4 min and kept for 1 min, raised to 60%B after 0.5 min and kept for 2 mins, then raised to 100%B at 7.7 min and

kept constant for 3.6 mins, followed by returning to the initial conditions within 0.2 mins. Finally, the column was re-equilibrated for 4.5 mins. The flow rate was 0.2 mL min^{-1}, the injection volume was 5 μL, and the column oven temperature was set to 25 °C, dry gas flow was 15 L min^{-1}.The MS was set at positive ion mode and using multiple reaction monitoring (MRM) mode. The MS parameters were shown in Table S4.3.

4.3 Results and discussion

4.3.1 Distribution of total ATR (ATR and its metabolites) in soils

The 5 soils varied in pH (4.8 - 7.7) and organic matter content (OM) (3.9% - 8.1%). As presented in Table S4.2, soil Malpass (M) had the lowest pH and OM, soil Dares (D) and soil Fushun (F) were both acidic and had more OM than soil M, soil Reddish (R) and soil Kettering (K) were neutral, soil K had the highest OM while soil R had relatively low OM among these soils. Soil F was the only soil containing ATR at detectable levels when it was collected from the field. It had been used for maize in China with a concentration of 3.5×10^{-4} mg L^{-1} ATR detected with DGT.

After 23 days of aging, ATR had dispersed into the soil phases. As shown in Figure S4.1, < 2% of the total ATR applied was in the soil solution, 50% or more of the total ATR could be measured (water or ACN extractable), while it was not detectable in the other fractions (extractable but more hydrophobic solvent needed, bound, volatilized or mineralized).

The distribution of total ATR varied between the soils and with the amount of ATR applied to soils. For example, in the 5 mg kg^{-1} dosed soils, around 1% of the total ATR was in the soil solution in soils M and K, higher pH (soil K) and lower OM (soil M) enhanced the desorption of ATR in soil and lead to more dispersion in the soil solution, consistent with previous studies (Barriuso et al., 1992; McGlamery and Slife, 1966). Around 0.6% of total ATR was in soil solution in soils D and R, and only 0.12% in soil F. In the 100 mg kg^{-1} dosed soils, greater proportions of soluble total ATR were in soil R and soil K among the 5 soils.

Soil M at both dose levels had a larger extractable fraction than the other soils, probably because of its low OM. In soil F, the soil solution contained very little of the total ATR, but for 5 mg kg^{-1} dosed soil, the ACN extractable fraction was similar as in other soils, which indicated the desorption of total ATR in soil F was suppressed at this dosed level. In 100 mg kg^{-1} dosed soil F, only 27% of total ATR was ACN extractable, most was bound on the solid phase or mineralized.

4.3.2 Diffusion coefficients (D_e) and elution efficiencies of ATR and its metabolites in DGT measurement

The diffusion coefficient (D_e) is an essential parameter in calculating the chemical concentration through equation (4.1). D_e is temperature dependent (Zhang and Davison, 1995) and in this study it was measured directly using DGT devices. The D_e of target chemicals were measured at 24ºC and standard D_e values at 25ºC were obtained by equation (4.2)

$$\log D_t = \frac{1.37023(t-25)+(8.36010^{-4})(t-25)^2}{109+t} + \log \frac{D_{25}(273+t)}{298} \quad \textbf{(4.2)}$$

The diffusion coefficient of the target compound at the solution temperature t (°C) during the diffusion experiment is D_t, and D_{25} is the diffusion coefficient of the target compound at 25°C. All these data are shown in Table S4.5.

As the data in Table S4.6 shows, the elution efficiencies of ATR and 3 of its metabolites are all > 95% using 10 mL ACN for 30 min ultrasonic extraction, HA gave a lower recovery of 77.8 ± 1.6%. After the test, it was found that the HLB binding gel adsorbed a small amount of CYA, but the mass of CYA that could be eluted from the binding gel was only the mass in the gel solution, which means elution efficiency of CYA from HLB resin was 0%, consistent with a previous study (Meng et al., 2015). This means DGT can be used in the diffusive equilibration in thin films (DET) mode - when the bulk solution contains a large amount of CYA, C_{DET} should be equal to concentration in soil solution (C_{ss}). In this study, DGT measured

concentration (C_{DGT}) of CYA was assumed to be 10% of C_{DET}, since for other chemicals C_{DGT} was ~10% of $C_{solution}$ (5-19%).

4.3.3 DGT measurement of total ATR

After 23 days of aging, total ATR concentrations measured by DGT varied between different soils as indicated in Figure 4.2. In 5 mg kg^{-1} dosed soils, C_{DGT} in soil M was about twice that of the C_{DGT} in soil R, C_{DGT} in soil D and soil K were nearly equal, between C_{DGT} in soils M and R. C_{DGT} in these four soils were not very different from each other; they were all much larger than C_{DGT} in soil F. The results for C_{DGT} values in 100 mg kg^{-1} dosed soils were similar, except for soil R, which was the one that had the largest C_{DGT}. In both dosed levels, the C_{DGT} in soil F were the lowest; we hypothesise that this maybe because soil F was used for growing maize and had been treated with ATR and fertilizer in the field continuously, the microbial activity in the soil may be boosted (Haynes and Naidu, 1998; Zhong and Cai, 2007), leading to a stronger adsorption of ATR on the solid phase or further degradation of ATR.

Figure 4.2 also shows the distribution of total ATR between the parent compound and metabolites. Parent ATR was dominant in all the soils, except the higher dosed soil F. In this soil, the secondary metabolite CYA was almost the only detectable target compound (with a tiny proportion of HA). In other soil samples, HA was normally the dominant metabolite.

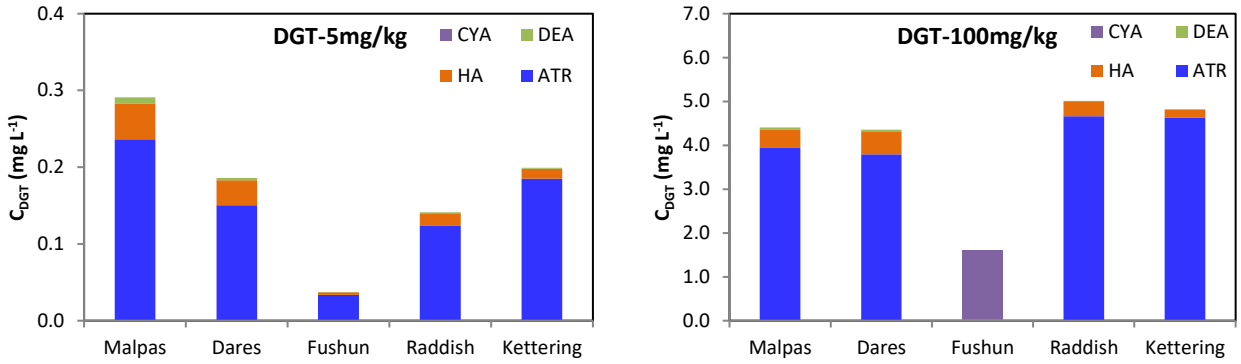


Figure 4.2 Concentrations of ATR and its metabolites measured using DGT in 5 soils (24 h deployment after 23 days of aging).

4.3.4 Uptake of residues by maize

As shown in Figure 4.3, some residues were taken up by maize roots from the soils and translocated in the xylem following root absorption to shoots (Sicbaldi et al., 1997).

Usually the concentrations measured in maize tissue were higher than concentrations measured in soils using different methods, indicating that maize did not only uptake ATR residues but also accumulated these chemicals. In 5 mg kg^{-1} dosed soils R and K, the concentrations of total ATR were higher in roots than in shoots in soils. The roots and shoots had similar concentrations of total ATR in maize in soil F, while in maize from soils M and D, the total ATR concentrations were higher in shoots. In 100 mg kg^{-1} dosed soils, the scenario was almost the opposite; the maize roots in soils M and D had higher concentrations of total ATR, indicating that the amount of ATR added also affected the maize uptake.

The present study demonstrates that the major metabolite of ATR in maize was HA, with very little DEA and DIA detected in roots. This means chemical degradation dominated the metabolism in maize at first, with de-alkylation taking place due to the presence of CYA (Singh, Switzerland, 2016),while the degradation of ATR in soils during aging may initially be affected by benzoxazinone from maize root exudates and by soil microorganisms,.

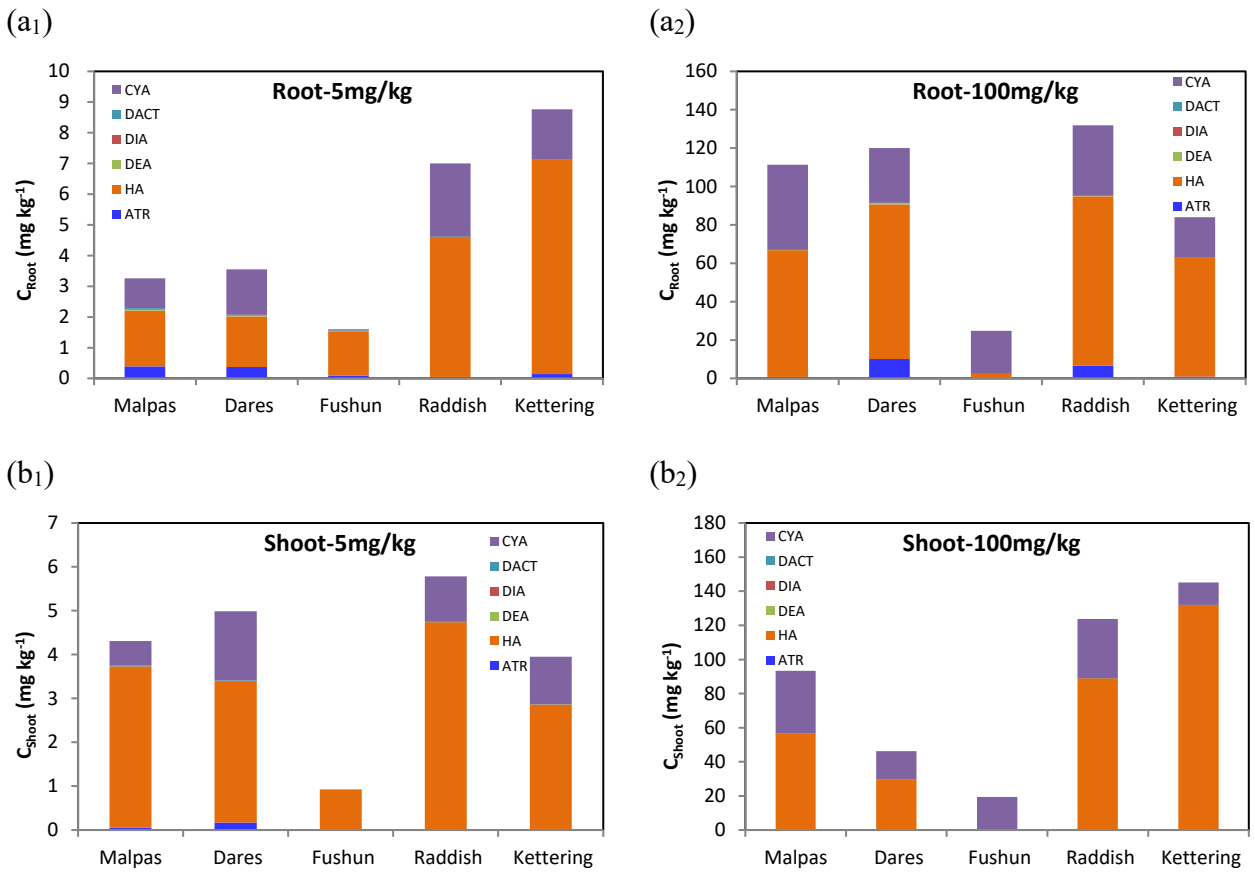


Figure 4.3 ATR and its metabolites in maize (a) roots and (b) shoots; ATR applied (1) 5 mg kg^{-1}, (2) 100 mg kg^{-1}

4.3.5 Comments on the ATR degradation pathways

The measurement of ATR and its metabolites along the translocation pathway of maize grown in soils are presented as the proportion of chemical in total ATR in Figure S4.2.

Before maize growth, ATR was the dominant chemical, the most abundant metabolite was HA and in some soils a small proportion of DEA was detected, revealing that hydroxylation of ATR was the preferential degradation mechanism in the soils here, rather than de-alkylation. ATR in soil F at 100 mg kg^{-1} was far more degraded than in the other soils and than in lower dosed soil F. CYA accounted for the highest proportion of all compounds, > 90% in soluble and DGT measured fraction whilst 70% in ACN-extractable fraction. As noted earlier, soil F was used previously to grow maize for several years. It seems likely that microorganisms capable of

degrading ATR had developed in soil F, and these microorganisms were activated by a high initial concentration of ATR addition.

A greater proportion of metabolites occurred in the soils after maize growth than before, emphasizing the breakdown of parent ATR during the 21days of maize growth. Proportions of HA and CYA increased significantly; no DEA, DIA or DACT were detected in soils, indicating that hydroxylation dominated the metabolism of ATR in soils during maize growth.

Transformation reactions occurred along the translocation pathway from soils to maize roots and leaves. The degree of degradation differed between different soil compartments and soil types, and the transformation along the pathway differed between the two ATR application levels.

After maize growth in soil D with the application of ATR at 5 mg kg^{-1}, CYA accounted for ~97% of total chemical in the soil solution, with no ATR detected. This indicated that soluble ATR was fully hydrolysed and de-alkylated, but in the solvent extraction sample HA - a less metabolized compound had the highest proportion (43%) and some parent ATR was detected. ATR in the solution phase was degraded further than in the solid phase, presumably because adsorption reduced the accessibility and degradability of ATR (Koskinen et al., 2001). Use of the DGT technique also enabled detection of small amounts of ATR. The proportion of ATR in the DGT sample was 0.86%, since ATR in the solid phase could be re-supplied to the solution during deployment. Hence the degradation level measured by these three methods was: soil solution> DGT measurement >solvent extraction. This scenario was similar in other soils of the two ATR application levels.

The degree of degradation varied between the soils. Soils M, D and F had greater proportions of metabolites than soils R and K; these three soils had lower pH and the degradation rate of ATR can be greater in slightly acid soils (Howard, 1991). The proportions of metabolites were

higher in 100 mg kg^{-1} soils. Higher doses can boost soil microbial growth and activity, leading to an increase in soil respiration (Gan et al., 1996).

In most soils, the proportion of parent ATR decreased along the translocation pathway. For instance, in soil D with the application of ATR at 5 mg kg^{-1}, the proportion of ATR was 33% in soil, 10% in roots, and only 3.4% of the total ATR in the shoots, implying that ATR metabolism occurred along the translocation pathway, with degradation of ATR continuing once entering the maize. A small portion of ATR appeared in roots and shoots; maize is known to rapidly convert ATR to HA (Shimabukuro, 1968).

4.3.6 Total ATR bioavailability

The log-log relationship (after linear fitting) between total ATR concentration in maize tissues and the different measurements of total ATR in the soils (at different doses and before/after maize growth) are shown in Figure 4.4. Log-log relationships were used, since log transformation enhanced the distribution of data.

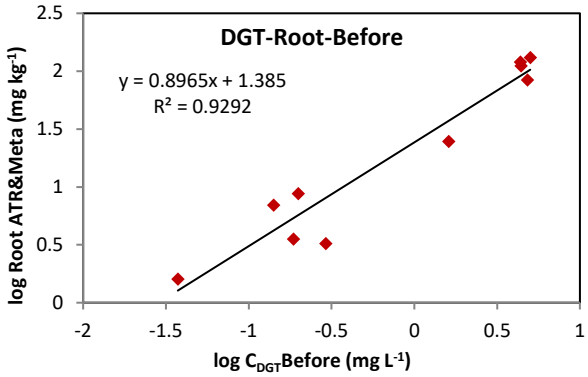
From a predictive perspective, the best measures of maize root-available total ATR were C_{DGT} measured before maize growth (r^2 = 0.929) and soil solution measured after maize growth (r^2 = 0.931). Other predictors of root total ATR concentration also had good relationships with total ATR concentration in roots (r^2 = 0.895-0.917), except for solvent extraction measurement after maize growth (r^2 = 0.734). The best measure of total ATR concentrations in the maize shoots across all soils were C_{DGT} (r^2 = 0.947) and C_{SS} (r^2 = 0.949), measured before maize growth. Other measurements were inferior, especially solvent extraction measurement after maize growth (r^2 = 0.626). DGT measurement in soils before maize growth was therefore the most effective in predicting the bioavailability of ATR to maize. This is an important finding since DGT has previously been shown to be a good predictor of bioavailability for inorganic substances, but this is the first study to show the result for an organic chemical.

The prediction approach mimicking bioavailability must be correlated with a specific organism, since bioavailability can vary between the types of biota. Previous researches have focused on the prediction of ATR bioavailability to microbes which were capable of degrading ATR or earthworms. Kelsey et al. (Kelsey et al., 1997) compared soil-aged ATR extracted by a variety of organic solvents with the proportions of these compounds which could be either accumulated by earthworms or mineralised by bacteria (*Pseudomonas R*). They found that ATR bioavailability to earthworm and bacteria could be predicted by extracting soils using MeOH:water (9:1) and MeOH:water (1:1). Less attention has been paid to predict ATR bioavailability to plants. A mild extraction approach, ACN extraction, was conducted in this study. C_{SE} before maize growth was positively correlated with maize uptake (see Figure 4.4 Red(e) and Blue(e)), but the data points were insufficiently dispersed, they could be placed as two distinct groups characterized by two total ATR concentration levels. For each group with 5 soils, the C_{SE} values had entirely different correlation with maize uptake, they were even not positively related in the lower C_{SE} group. Hence in this study, ACN extraction was not an appropriate approach in predicting total ATR bioavailability to maize.

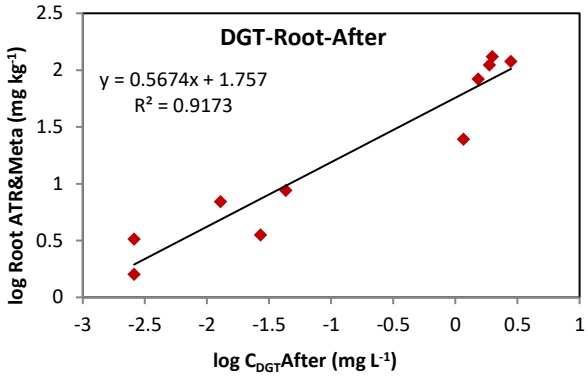
Chemicals in soil solution were once considered as bioavailable, since the mobile fraction was treated as bioavailable. However, a desorption process driven by plant uptake often occurred based on the equilibration of compounds between solid phase and the pore water (Posthuma et al., 1998). C_{SS} couldn't offer any information about this resupply and therefore was not able to represent bioavailability. In this study, the resupply was limited as the values of C_{DGT}/C_{SS} were < 0.2 (not shown) implying that the rate of desorption from the solid phase was so slow that there was insignificant resupply (Harper et al., 1999) and the maize could hardly absorb the chemicals from the solid phase, so C_{SS} was highly positively correlated with the maize uptake. DGT mimics the processes in the rhizosphere (Muhammad et al., 2012). It is an *in situ* approach to integrate chemicals supply kinetics from the solid phase with the bioavailable concentration

in soil. In this study, DGT was able to predict maize tissues uptake of total ATR, regardless of the soil properties. DGT has been demonstrated to be a good surrogate for plant uptake of inorganic compounds such as metals and phosphorus. This is the first research on the bioavailability of organic compounds in soils measured by DGT. These results show promise for those interested in predicting organic chemical degradation and plant uptake in soils, such as those involved with contaminated land remediation or pesticide efficiency, risk assessment and testing.

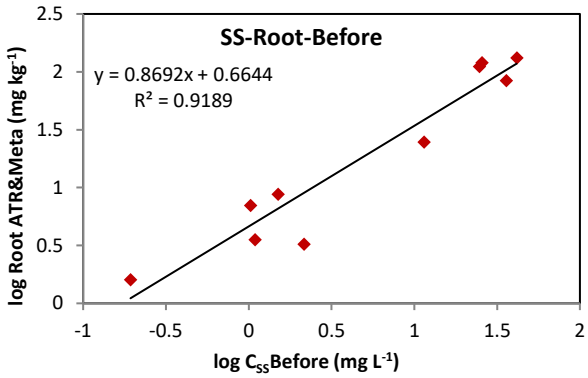
(a)


DGT-Root-Before
y = 0.8965x + 1.385
R² = 0.9292
log Root ATR&Meta (mg kg-1)
log CDGTBefore (mg L-1)

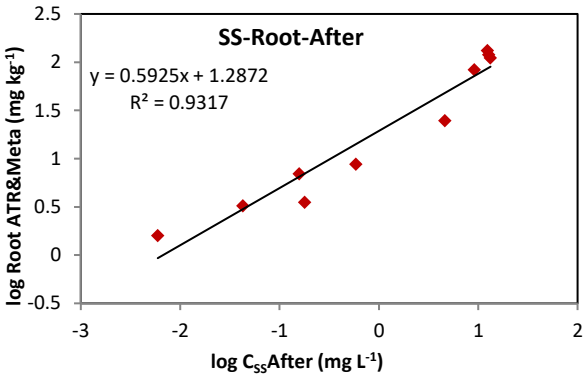
(b)


DGT-Root-After
y = 0.5674x + 1.757
R² = 0.9173
log Root ATR&Meta (mg kg-1)
log CDGTAfter (mg L-1)

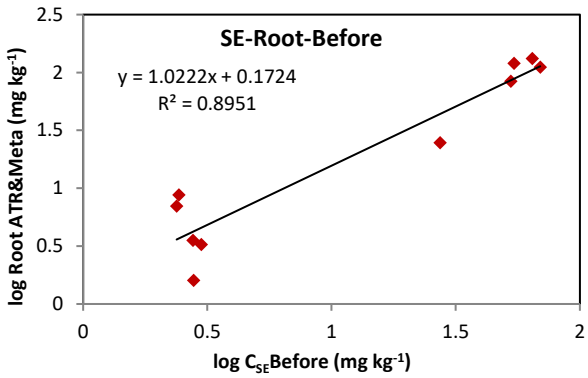
(c)


SS-Root-Before
y = 0.8692x + 0.6644
R² = 0.9189
log Root ATR&Meta (mg kg-1)
log CSSBefore (mg L-1)

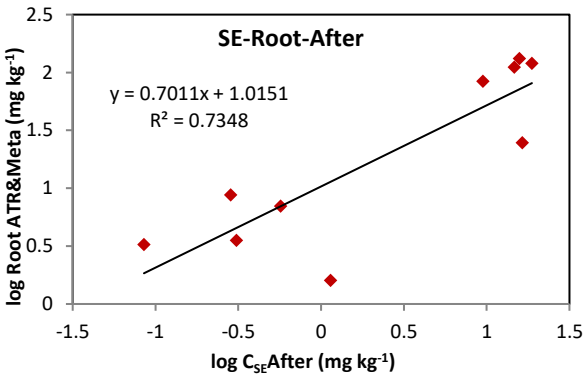
(d)


SS-Root-After
y = 0.5925x + 1.2872
R² = 0.9317
log Root ATR&Meta (mg kg-1)
log CSSAfter (mg L-1)

(e)


SE-Root-Before
y = 1.0222x + 0.1724
R² = 0.8951
log Root ATR&Meta (mg kg-1)
log CSEBefore (mg kg-1)

(f)


SE-Root-After
y = 0.7011x + 1.0151
R² = 0.7348
log Root ATR&Meta (mg kg-1)
log CSEAfter (mg kg-1)

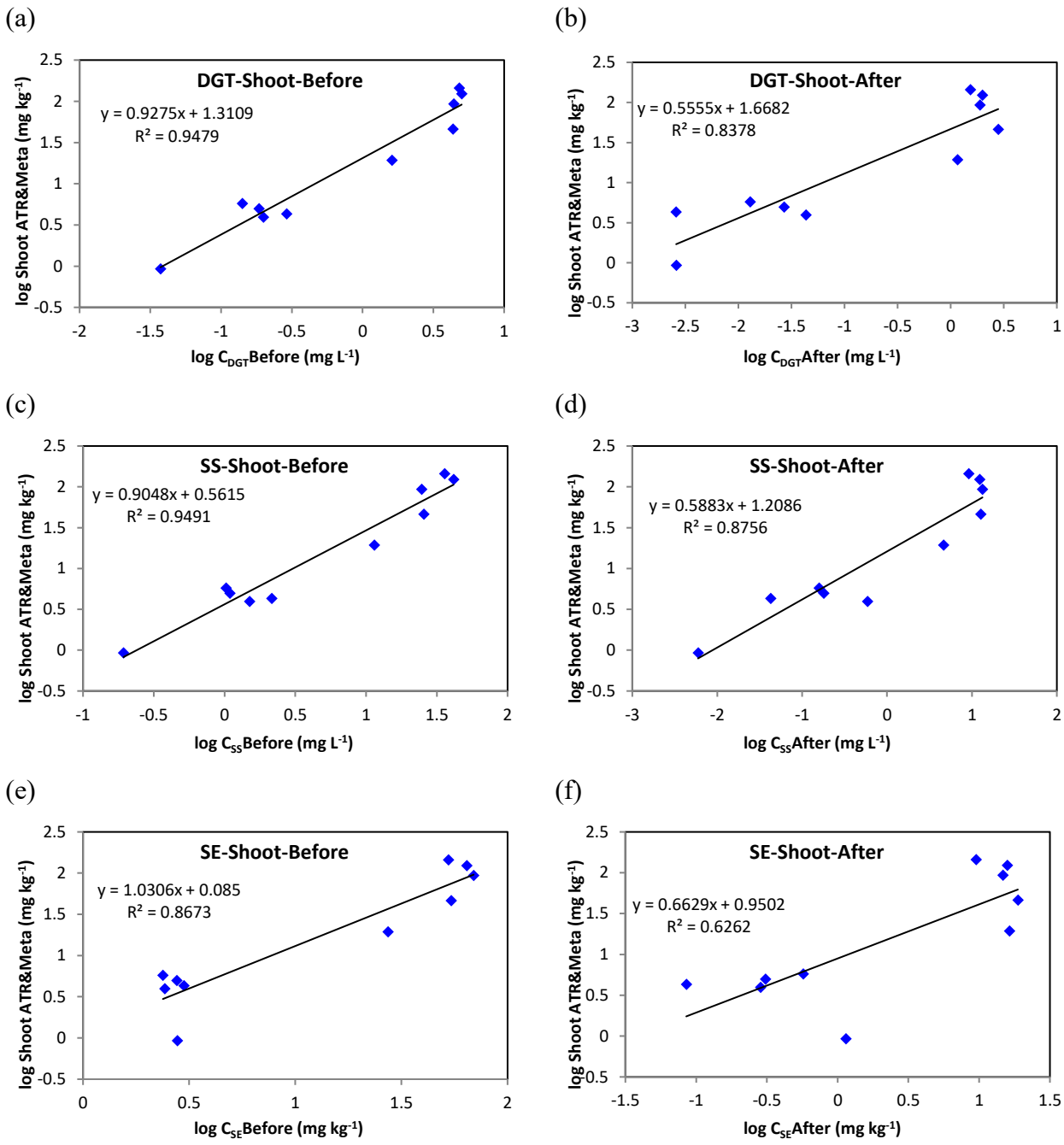


Figure 4.4 Dependence of total ATR concentration in maize (Red): root; (Blue): shoot on the (a) DGT concentration, before growth, (b) DGT concentration, after growth, (c) soil solution ATR, before growth, (d) soil solution ATR, after growth, (e) ACN-extracted ATR, before growth, (f) ACN-extracted ATR, after growth.

4.4 Conclusions

The results obtained in this study suggest that after 23 days of aging, a large proportion of total ATR was still ACN-extractable and the major constituent in soils was parent ATR. The growth of maize accelerated the binding and degradation of ATR in soils. In both soils and maize,

hydroxylation was the dominant degradation procedure of applied ATR, since little DIA or DEA were detected, the metabolism of ATR occurred along the compound translocation pathway. The relationships of ATR concentrations in maize and ATR measured in soil solution, solvent extraction and by DGT showed that the best correlation was with DGT measurement, suggesting the DGT method is superior to the other two conventional methods for predicting the bioavailability of ATR to maize.

This is the first time DGT has been applied to a soil-plant system for organic compounds, in the attempt to establish the relationship between plant uptake and DGT measured labile concentrations of pesticides. DGT has the potential to mimic plant uptake as it integrates the information and processes of analytes from soil solution and solid phase compartments and the kinetic exchange between the two compartments. Future work should be carried out to further characterize the dynamic exchange and transfer of pesticides in soils, to understand the mechanisms of their behaviour. DGT shows promise as a tool to provide useful information in this regard.

Supporting information

The supplementary tables and figures are listed in Supporting Information.

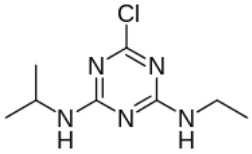
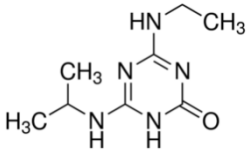
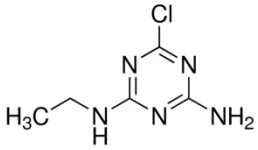
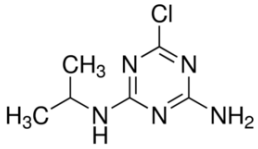
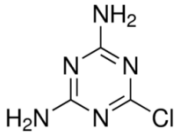
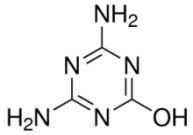
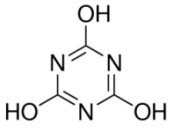
4.5 Supporting Information

CONTENTS

Supplementary Tables

Supplementary Figures

Table S4.1 Physico-chemical properties of atrazine (ATR) and its metabolites

Compound	Abb.	*MW*	Log*K*ow	*S*w25°C (mg L^{-1})	pKa (0-14)	Formula	Structure
Atrazine	ATR	215.69	2.6	214.1	1.7	$C_8H_{14}ClN_5$	
Hydroxyatrazine	HA	197.24	1.4	10e(+6)	5.1	$C_8H_{15}N_5O$	
Deisopropylatrazine	DIA	173.60	1.2	6160	3.4	$C_5H_8ClN_5$	
Deethylatrazine	DEA	187.63	1.5	2593	3.4	$C_6H_{10}ClN_5$	
Deisopropyl-Desethyl -atrazine	DACT	145.55	0.3	4.2e(+4)	0.6	$C_3H_4ClN_5$	
Ammeline	AMN	127.10	-4.1	10e(+6)	9	$C_3H_5N_5O$	
Cyanuricacid	CYA	129.07	-0.5	1994	13.6	$C_3H_3N_3O_3$	

https://chemicalize.com/#/

Table S4.2 Properties of soils

Soil Name	Abb.	Sample Location	pH(H_2O)	Organic Mater Content (OM, %)	Background ATR C_{DGT} (mg L^{-1})	Phosphorus (DGT) (ugmL^{-1})
Malpass	M	Old Castle Mill (UK)	4.8	3.9	0	0.5
Dares	D	Daresbury (UK)	5.7	5.4	0	0.2
Fushun	F	Fushun (China)	6.0	6.1	3.5×10^{-4}	0.6
Reddish	R	Reddish (UK)	6.7	4.8	0	0.1
Kettering	K	Kettering (UK)	7.7	8.1	0	0.5

Table S4.3 LC-MS parameters for target chemicals

Chemical	Ionisation mode	Retention time (min)	Molecular mass (g mol^{-1})	Precursor ions (m/z)	Product ions (m/z)	Q1 Pre Bias (V)	CE	Q3 Pre Bias (V)
ATR	+	7.360	215.69	216.20	174.15	-10	-17	-17
					132.15	-13	-24	-22
					104.15	-10	-29	-17
HA	+	5.475	197.24	197.80	156.00	-13	-18	-27
					113.95	-13	-22	-20
DEA	+	4.900	187.63	187.95	145.85	-19	-18	-26
					103.90	-19	-26	-17
DIA	+	3.850	173.60	173.75	145.85	-11	-19	-26
					132.00	-11	-20	-24
					96.05	-11	-19	-16
DACT	+	1.170	144.55	146.05	104.10	-15	-20	-16
					79.25	-16	-19	-29
AMN	+	0.650	127.10	128.10	86.20	-13	-18	-30
					69.10	-13	-28	-25
CYA	-	0.620	129.08	128.15	42.10	22	18	16
ATR-d5	+	7.360	220.69	220.80	179.15	-23	-20	-17
					101.25	-14	-26	-18

Table S4.4 ATR and its metabolites distribution in soils

(1) ATR and its metabolites distribution in soils (Initial dose = 5mg kg^{-1})

Soil	Malpas		Dares		Fushun		Raddish		Kettering	
Proportion	SS[a]	SE[b]	SS	SE	SS	SE	SS	SE	SS	SE
ATR	0.92%	50.77%	0.52%	47.62%	0.11%	40.24%	0.56%	46.20%	0.93%	47.67%
HA	0.14%	7.89%	0.10%	7.15%	0.008%	15.28%	0.05%	1.06%	0.05%	0.62%
DEA	0.044%	1.01%	0.012%	0.46%	0.0007%	0.10%	0.006%	0.31%	0.008%	0.17%
CYA	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Sum	1.11%	59.67%	0.62%	55.23%	0.12%	55.62%	0.61%	47.57%	0.99%	48.46%

a: propotion of the chemical in soil solution; b: propotion of the chemical in solid phase obtained from chemical extraction

(2) ATR and its metabolites distribution in soils (Initial dose = 100mgkg^{-1})

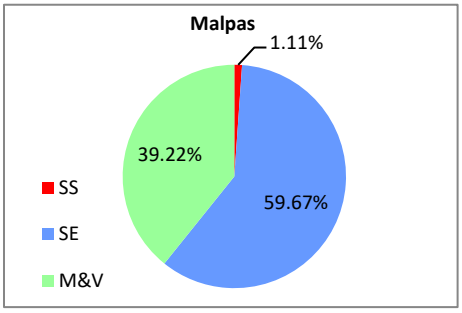
Soil	Malpas		Dares		Fushun		Raddish		Kettering	
Proportion	SS	SE	SS	SE	SS	SE	SS	SE	SS	SE
ATR	0.55%	67.19%	0.66%	52.74%	0.015%	3.93%	1.18%	63.62%	1.15%	52.40%
HA	0.07%	1.86%	0.06%	1.27%	0.0028%	4.29%	0.06%	0.49%	0.03%	0.29%
DEA	0.01%	0.17%	0.009%	0.18%	0.0028%	0.00%	0.0028%	0.05%	0.001%	0.01%
CYA	0.00%	0.00%	0.00%	0.00%	0.32%	19.09%	0.00%	0.00%	0.00%	0.00%
Sum	0.64%	69.22%	0.73%	54.19%	0.34%	27.31%	1.24%	64.17%	1.18%	52.69%

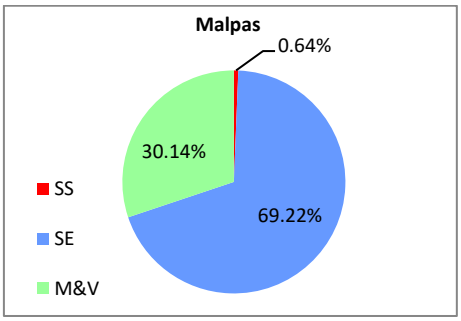
Table S4.5 Diffusion coefficient (D_e) of ATR and metabolites in diffusive gels measured using DGT devices at test temperature (24°C, measured) and standard temperature (25°C, calculated)

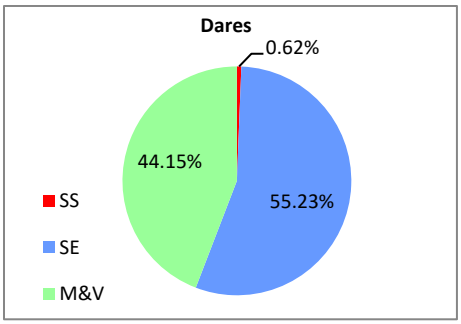
Chemical	D_e at 24°C (E-06cm^2s^{-1}) (measured)	D_e at 25°C (E-06 cm^2s^{-1}) (calculated)
ATR	5.05	5.19
HA	3.67	3.76
DEA	4.15	4.26
DIA	3.92	4.02
DACT	0.52	0.54

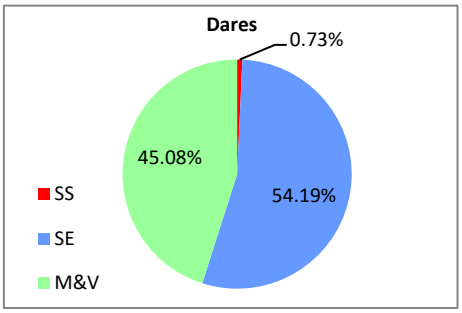
Table S4.6 Elution efficiencies of ATR and its metabolites determined for HLB binding gels

Chemical	Elution efficiency (%)
ATR	95.2±4.1
HA	77.8±1.6
DEA	120±4.7
DIA	130±5.2
DACT	120±8.0


Malpas
1.11%
39.22%
59.67%
SS
SE
M&V


Malpas
0.64%
30.14%
69.22%
SS
SE
M&V


Dares
0.62%
44.15%
55.23%
SS
SE
M&V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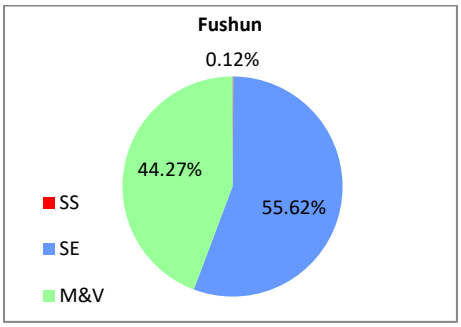
54.19%
SS
SE
M&V


Fushun
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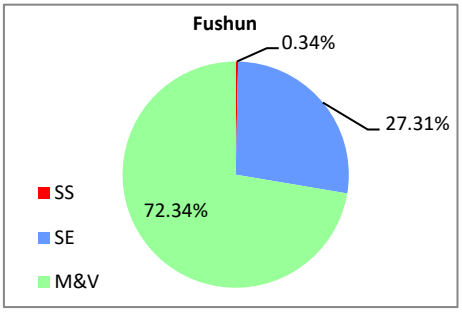
44.27%
55.62%
SS
SE
M&V


Fushun
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27.31%
72.34%
SS
SE
M&V

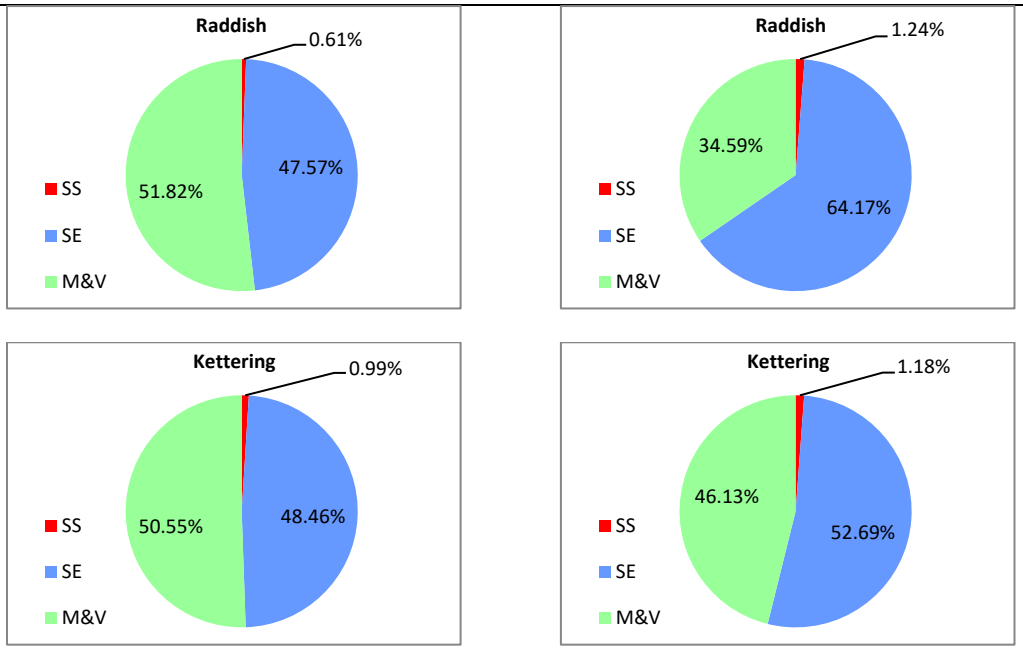


Figure S4.1 ATR and its metabolites distribution in soils (before growing maize, after 23 days of aing). SS: chemicals in soil solution; SE: chemicals in soil solid phase obtained from chemical extraction; M&V: chemicals could not be measured (extractable but more hydrophobic solvent needed, bound, volatilized or mineralized); left: 5mg kg^{-1}, right: 100 mg kg^{-1}.

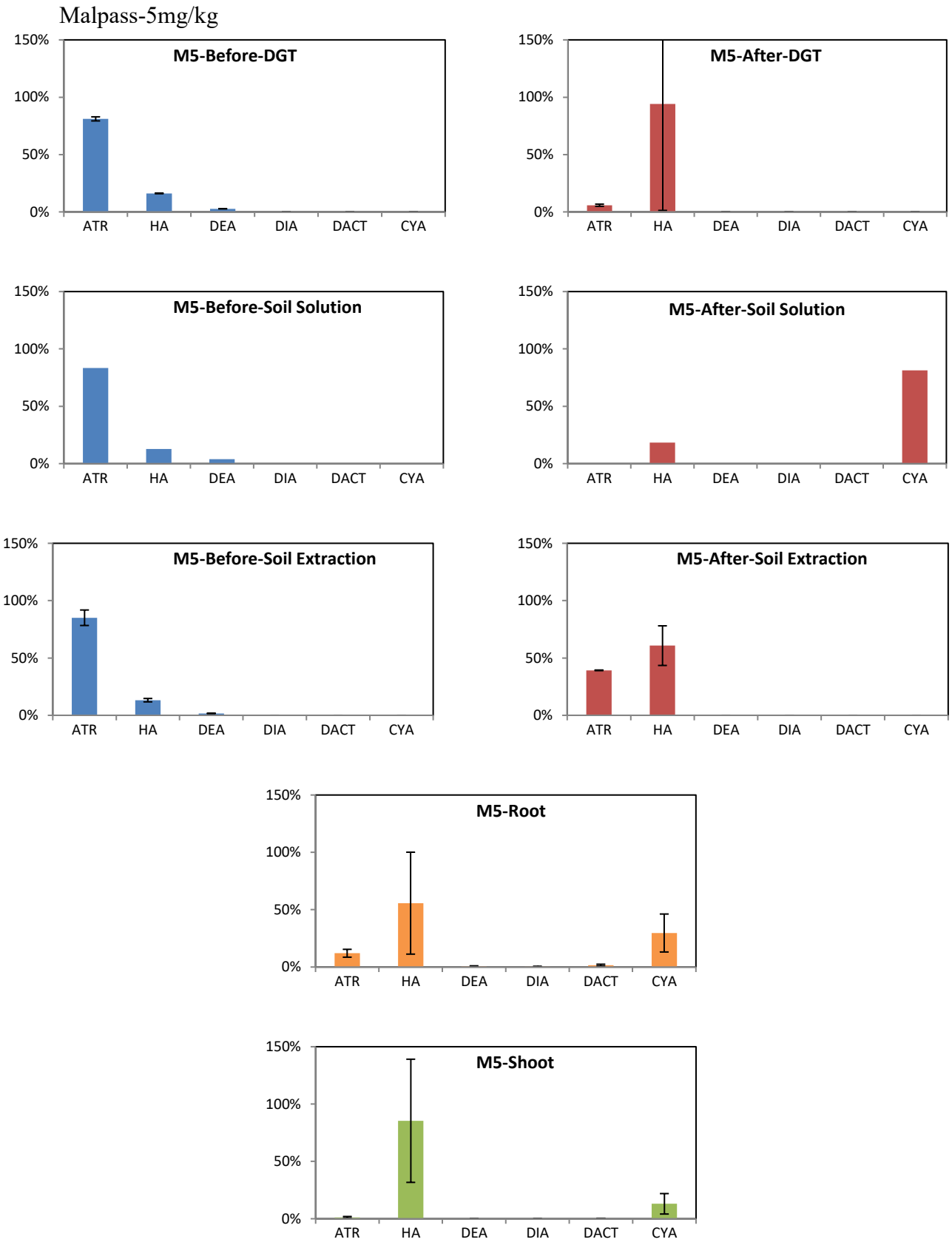


Figure S4.2a ATR degradation pathway in soil M at ATR dosed level of 5 mg kg^{-1}

Figure S4.2ATR degradation pathway (proportion of chemical in total ATR).

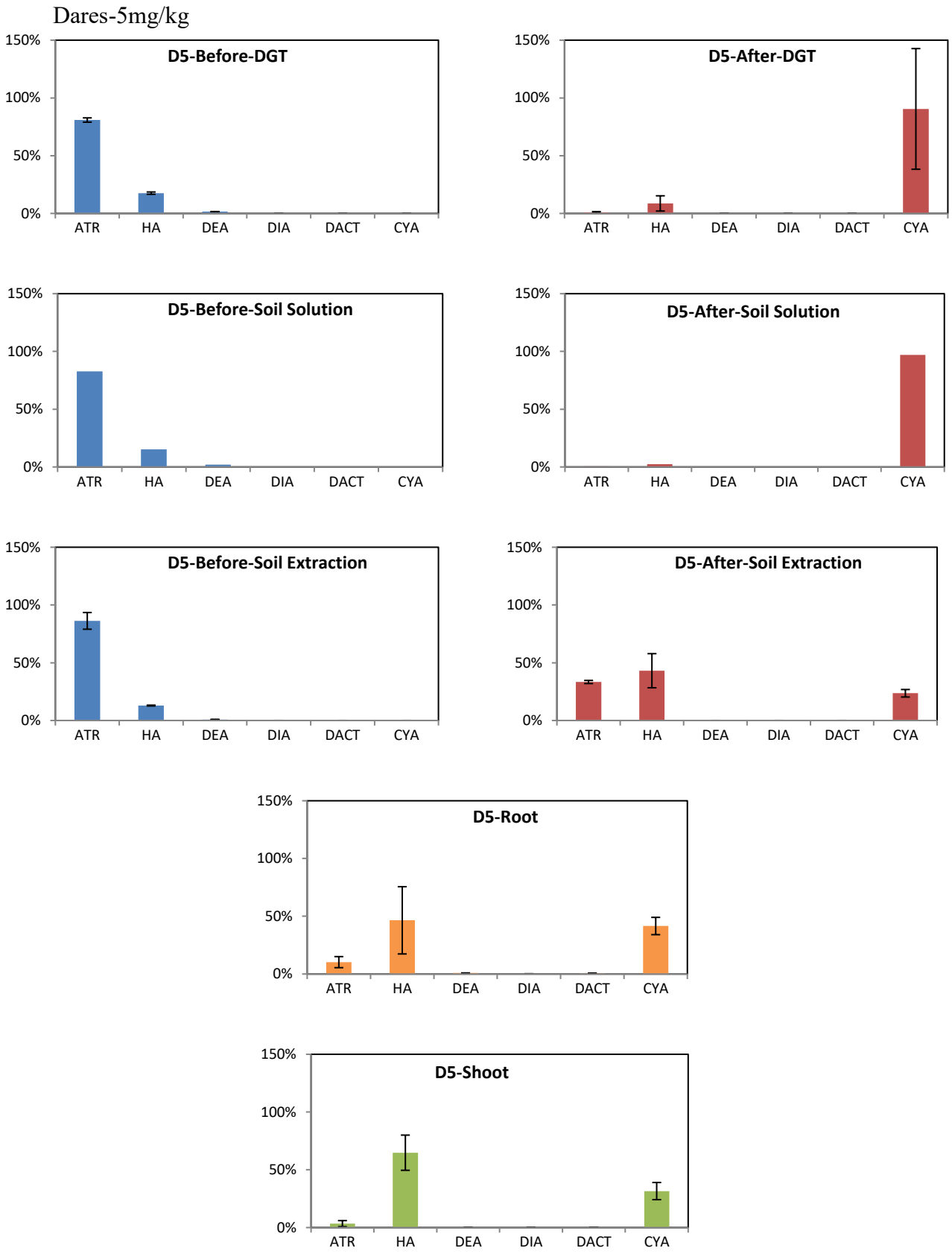


Figure S4.2b ATR degradation pathway in soil D at ATR dosed level of 5 mg kg^{-1}

Fushun-5mg/kg

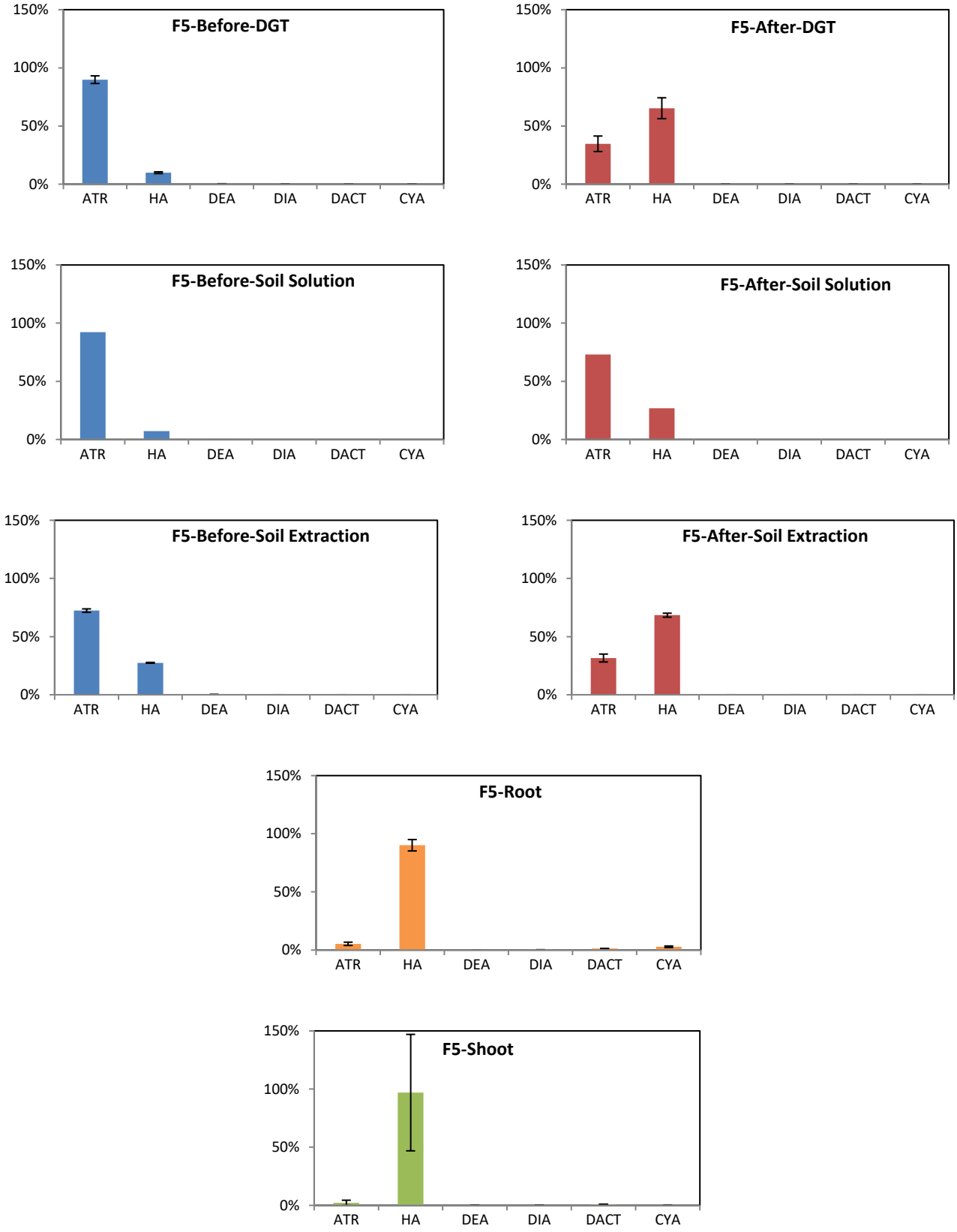


Figure S4.2c ATR degradation pathway in soil F at ATR dosed level of 5 mg kg^{-1}

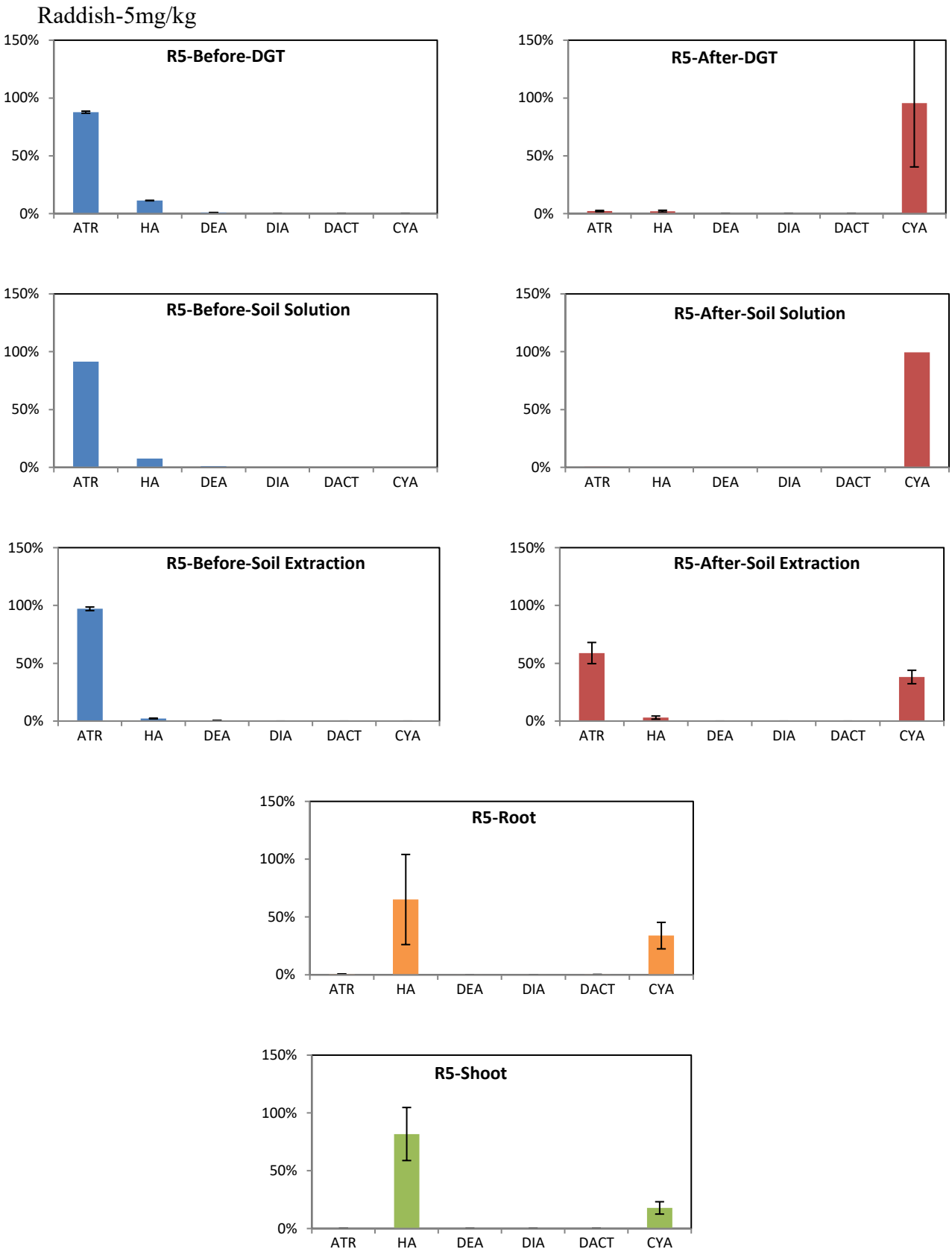


Figure S4.2d ATR degradation pathway in soil R at ATR dosed level of 5 mg kg^{-1}

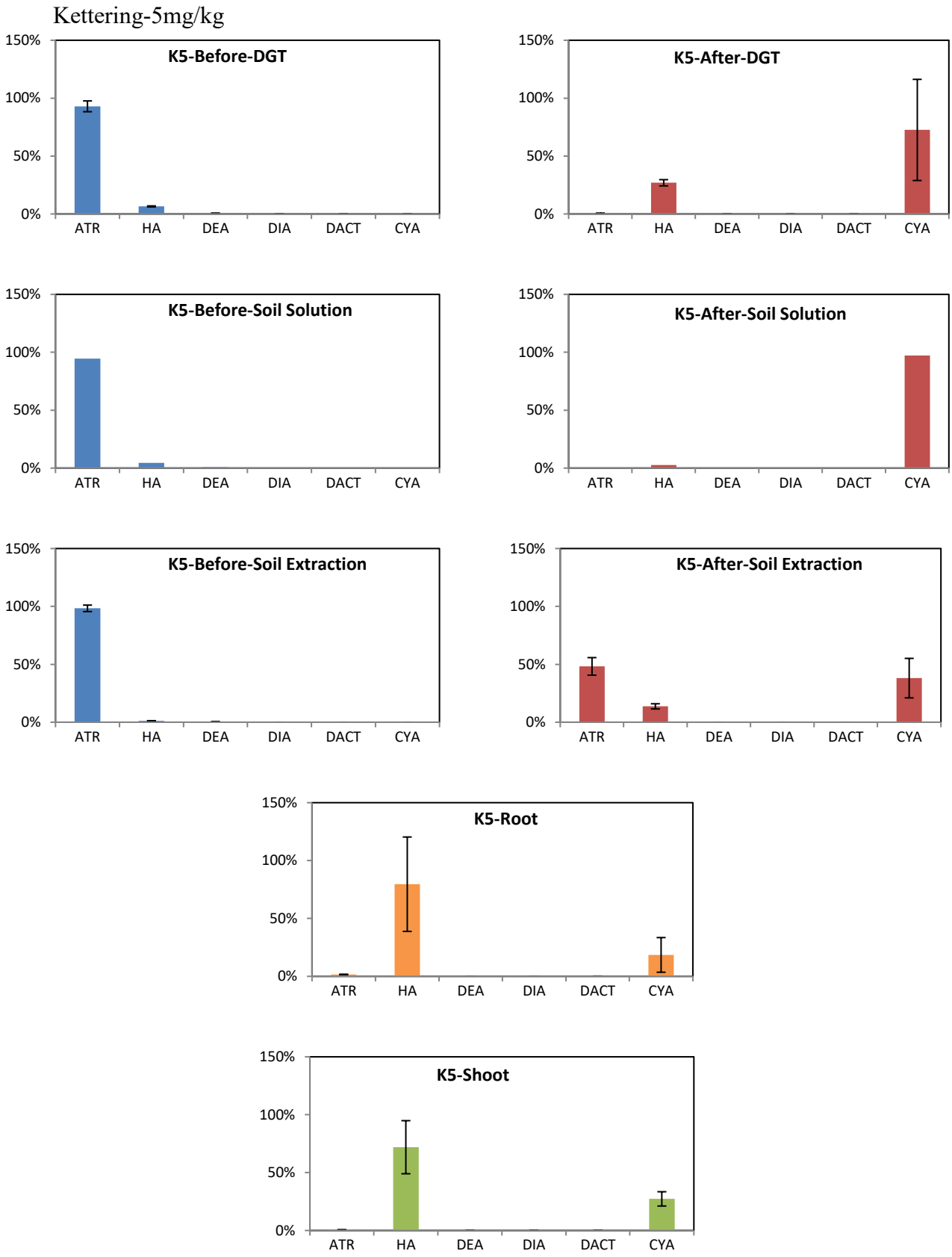


Figure S4.2e ATR degradation pathway in soil K at ATR dosed level of 5 mg kg^{-1}

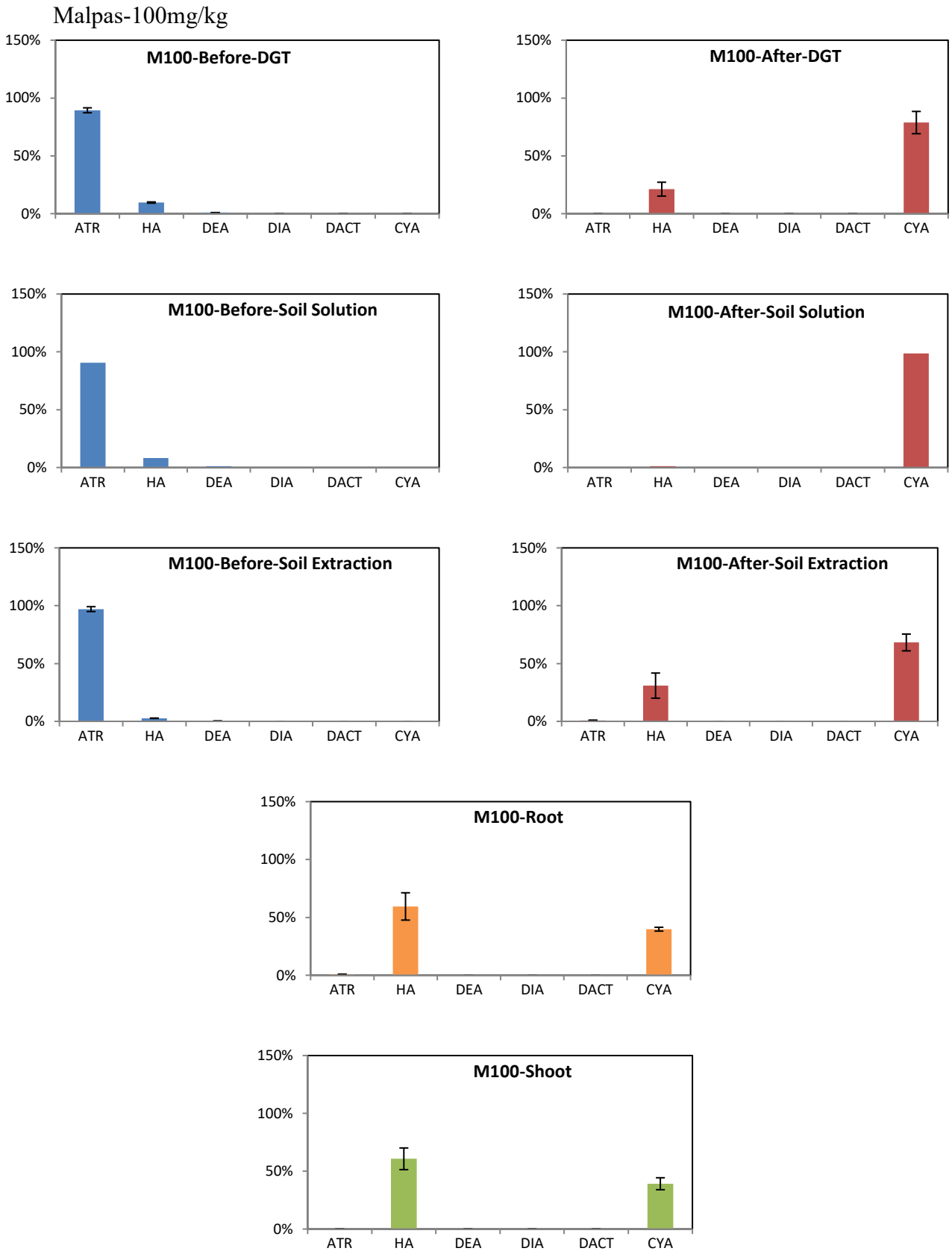


Figure S4.2f ATR degradation pathway in soil M at ATR dosed level of 100 mg kg^{-1}

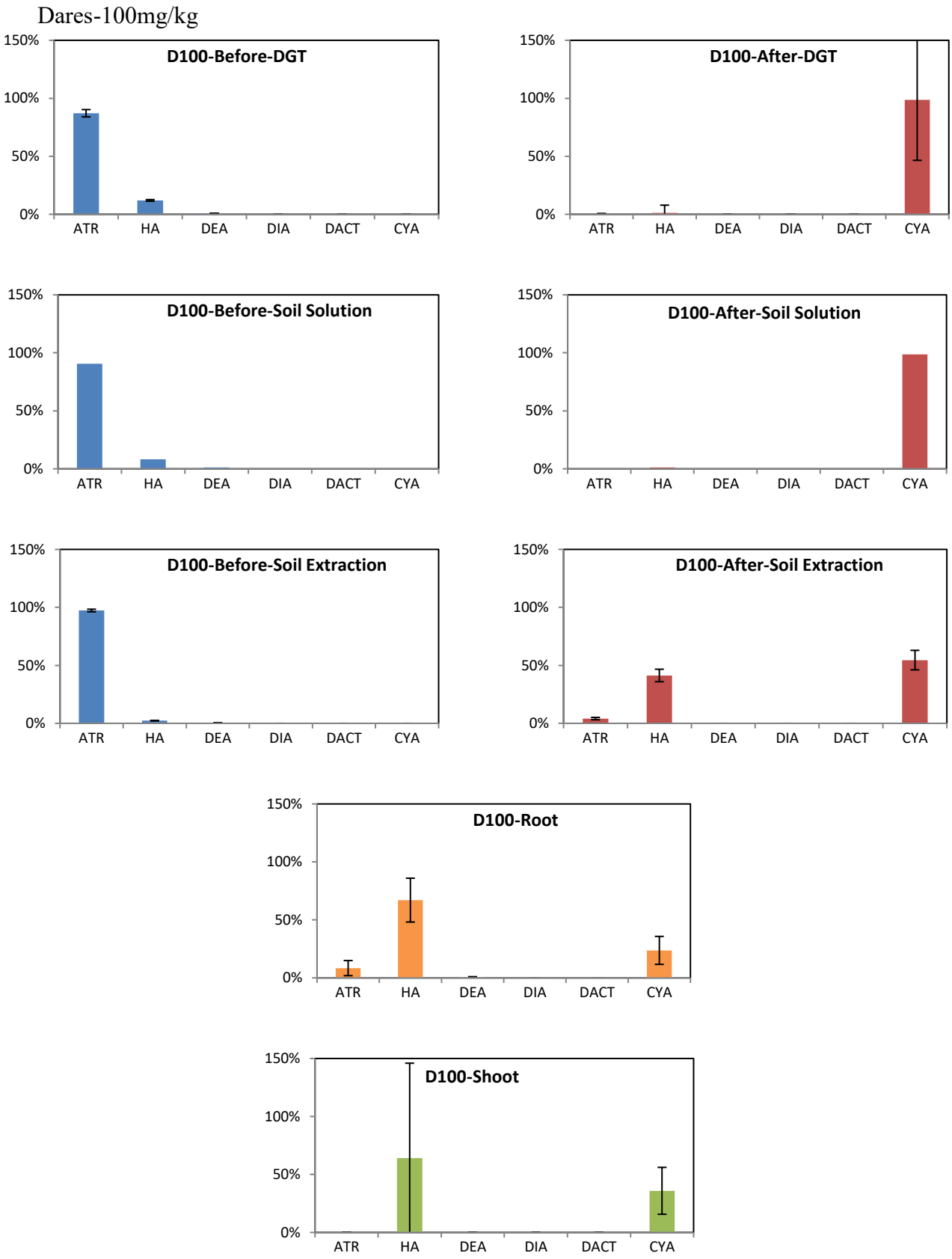


Figure S4.2g ATR degradation pathway in soil D at ATR dosed level of 100 mg kg^{-1}

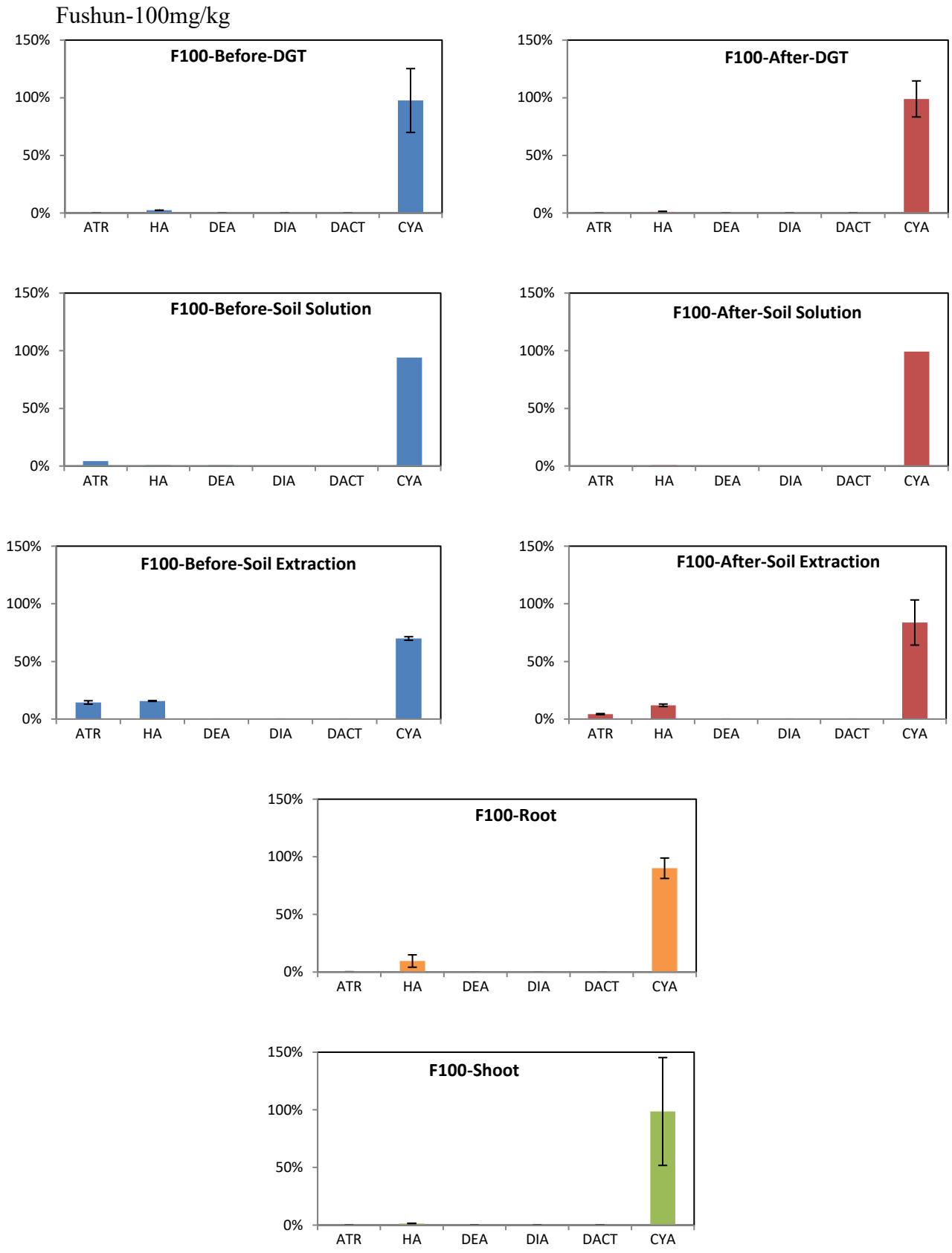


Figure S4.2h ATR degradation pathway in soil F at ATR dosed level of 100 mg kg^{-1}

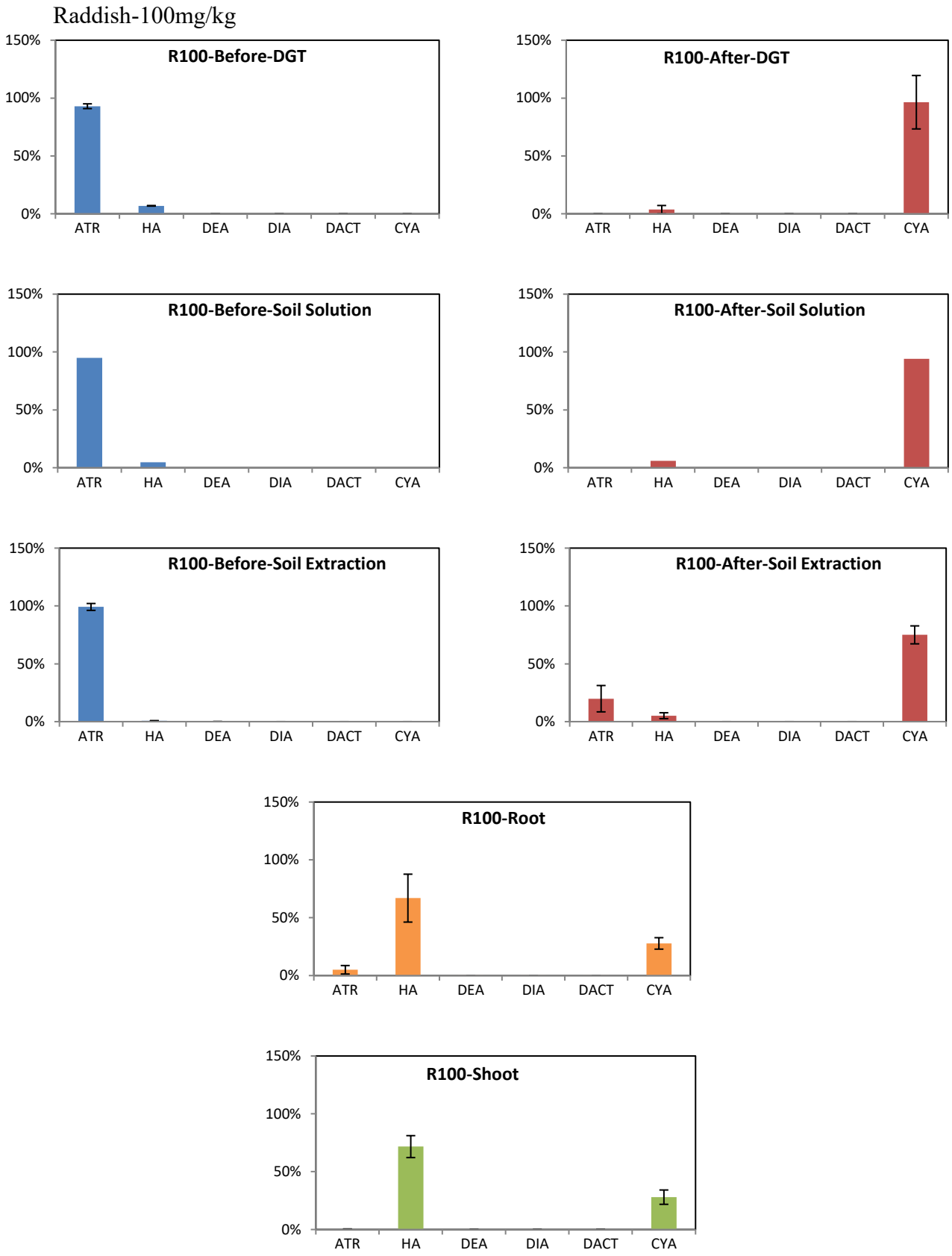


Figure S4.2i ATR degradation pathway in soil R at ATR dosed level of 100 mg kg^{-1}

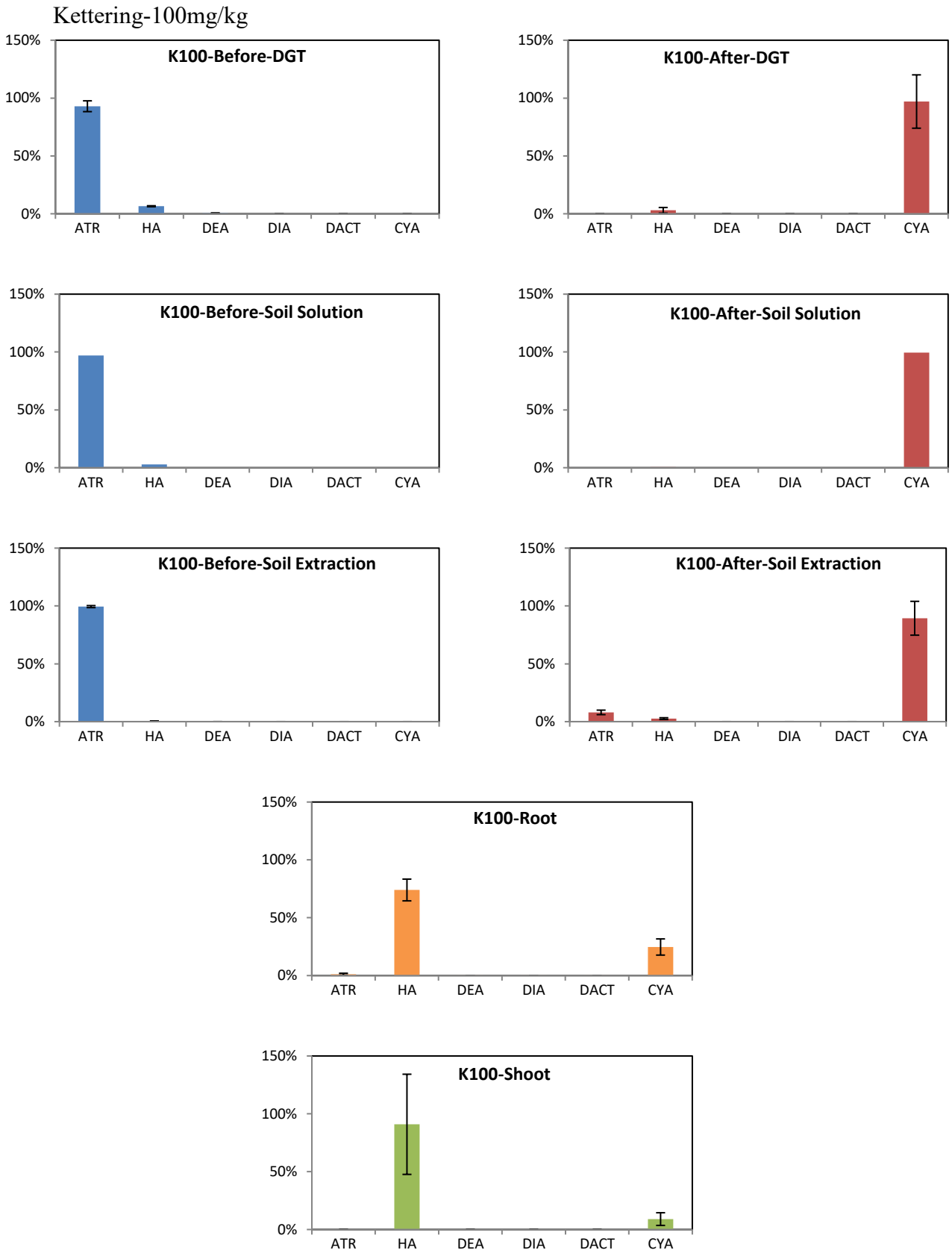


Figure S4.2j ATR degradation pathway in soil K at ATR dosed level of 100 mg kg^{-1}

Chapter 5: Assessment of aging effects, labile pool size and kinetic resupply of atrazine in soils

5.1 Introduction

Pesticides give benefits by the protection to crops and improvements of food supply, but they may contaminate the environment and may cause health problems by reaching humans through the food chain (Gavrilescu, 2005). Atrazine (2-chloro-4-ethylamino-6-isopropylamino- 1,3,5-triazine, ATR) is one of the most frequently detected and well researched pesticides. It has been used since 1958 and is registered in more than 70 countries worldwide (Farland et al., 2011; Kauffmann et al., 2000). It is applied to control broad-leaf weeds in the production of corn, sorghum, sugarcane, rangeland and other crops pre- and post-emergence (Grigg et al., 1997; Haith et al., 1979). The soil concentration of ATR after application may typically be ~3 - 6 mg kg^{-1} as a result of a normal application rate of 1.12 - 2.24 kg ha^{-1} (Alvey and Crowley, 1996). However, in some contaminated soils the concentration of ATR could be 10s - 100s mg kg^{-1}. It's half-life in soils is usually reported as weeks to months (Montgomery, 2007; Kamrin and Montgomery, 1999), but it also has been detected in soils for up to 9 years after initial application (Capriel et al., 1985). There has been evidence that exposure to ATR may delay reproductive development in laboratory rodents, reduce sperm quality in humans, and cause cancer in human and laboratory rats (Rusiecki et al., 2004; Laws et al., 2003; Swan et al., 2003). The use of ATR has been prohibited in most EU countries, but it is still in use in many other parts of the world. It is essential to understand its bioavailability, fate and behavior in soils and to assess the risks it poses.

Several factors have been reported to affect the availability of ATR in soils, such as soil moisture, pH, soil organic matter (SOM), soil type and initial applied concentrations (Jenks et al., 1998; Dao and Lavy, 1978). After application, ATR distributes in soils and interacts with soil particles; freshly added ATR has been observed to be more available than that which has persisted in the field for some time (Alexander, 2000). This time-dependent decline in availability, which is often referred to as 'aging', results from the formation of stronger bonds between ATR and soils and/or physical 'occlusion' of residues in soil micro-structures/organic matter (Gevao et al., 2000). Aging may not include the alteration of the molecular structure, but be a purely physical process – diffusion within some components of SOM (Brusseau et al., 1991), or diffusion into/entrapment within small pores in soil aggregates (Steinberg et al., 1987), and alteration of these sorbents to 'hide' ATR from micro-organisms.

The availability for transport and degradation processes of ATR in soils is determined by adsorption-desorption interactions of ATR with soil (Barriuso et al., 2004). It is traditionally characterized by a sorption coefficient (K_d), which is the ratio of the amount of chemical sorbed in the solid phase to that in soil solution (Tuzimski and Sherma, 2015). Many models have used this value to predict the amount of chemical that could be available in solution at a given time. However, not only the pesticide in the soil solution, but also that which is readily desorbable from the solid phase is potentially bioavailable (Koskinen et al., 2002). A reservoir of pesticide can build up, associated with soil particles and organic matter. When a pesticide is depleted from the available pool, following uptake by plants, leaching or degradation, the pesticide

adsorbed on the solid phase will be released to resupply the bioavailable pool. So dynamic sorption-desorption processes can be characterized by the capacity (labile pool size) for re-mobilization and the rate of re-supply of the pesticides from the solid phase. Traditional approaches of adsorption/desorption studies (sequential extraction, batch experiments) (Boivin et al., 2005; Barriuso et al., 2004) can't represent *in situ* conditions or provide dynamic information. However, DGT (diffusive gradients in thin-films) is an *in situ* technique which can measure the concentrations and fluxes of chemicals in soils (Zhang et al., 1998b). DGT measurements depend on labile concentrations in the soil solution and their re-supply from the solid phase. To interpret further the information obtained by DGT, the DGT-induced fluxes in soils (DIFS) model has been developed to provide a numerical simulation of the DGT-soil dynamic system. It has been successfully applied to exchange kinetic studies of metals (Ernstberger et al., 2005; Ernstberger et al., 2002) and to interpret DGT measurements of metals in soils in terms of kinetic and partitioning parameters. Only two previous application have been made for organic compounds so far – for antibiotics (Chen et al., 2014a; Chen et al., 2015a). These papers lay the foundation for this study on ATR availability, resupply kinetics and labile pool size in soils.

More specifically, the aims here were to investigate the effects of aging, soil pH and soil type on the availability of ATR in moderately treated soils. Two treatment levels were used; the labile pool size of ATR and the ability of soils to re-supply after depletion were assessed. The DIFS model was used to quantify and understand the

dynamic processes of ATR in soils, by estimating response time and kinetic rate constants of desorption.

5.2 Materials and methods

5.2.1 Chemicals

Atrazine (ATR) was purchased from Sigma. Atrazine metabolites were purchased from China. Their physiochemical properties are given in Table S4.1. ATR product was stored as 38% suspension liquid. ATR and its metabolites stock solutions were dissolved in pure methanol (MeOH). ACN (Acetonitrile) and MeOH were purchased from Fisher (Poole, U.K.).

5.2.2 Soil samples and treatments

Five soils of different properties were collected from the UK and China and used for the experiments. They were selected to represent a range of agricultural soils, with varying pH (4.8 - 7.7) and organic matter content (3.94% - 8.12%). The details of soil sites and properties are listed in Table S4.2. All soils were collected from the sub-surface (10 - 20 cm), then air-dried and passed through a 2 mm sieve to remove roots and stones.

6.6 mg and 131.6 mg of 38% ATR suspension liquid were mixed with 20 mL MQ water to obtain two levels of ATR solutions at 0.125 mg mL^{-1} and 2.5 mg mL^{-1}. These two concentrations of ATR were added into 500 g soils, the soils acquired ATR at concentrations of 5 (as normal test lab soil) and 100 (as contaminated soil) mg kg^{-1} (dry matter basis). The soils were then wetted to 25 - 30% MWHC (maximum water holding

capacity), by adding appropriate amounts of MQ water, and then mixed well to ensure ATR was distributed homogenously. These soil samples were then transferred to plastic bags which were kept partly open to maintain aeration. Soil samples were weighed every two days and moisture was kept constant by adding MQ water. The soils were then stored in the dark at room temperature for the experiments.

5.2.3 DGT deployment and soil sampling

DGT devices assembled with 0.4 mm HLB resin gels, 0.85 mm agarose diffusive gels and GH Polypro (GHP) filter membranes were prepared prior to the experiment.

After 1, 3, 6, 10, 15 and 23 days of aging, soils were wetted to 100% MWHC and mixed to obtain a soil slurry, then the slurry was left for 24 h before DGT deployment. For DGT deployment, soil paste was smeared onto the filter of the DGT device, then the device was gently pressed into the soil to ensure maximum contact between the soil surface and the DGT device. The deployment was maintained at room temperature for 24 h. All experiments were triplicated.

After 24 h deployment, DGT devices were retrieved, and the filter surface was jet washed with MQ water. The resin gels were removed and placed into 20 mL amber glass vials. Then 10 mL ACN was added to each vial; the vials were put in an ultrasonic bath for 30 min to elute. The eluents were filtered through 0.2 μm syringe filters (PTFE, Whatman, UK) prior to analysis.

After retrieving, the triplicate soils were mixed and stirred. Then ~50 g soil paste was sampled into a 50 mL tube and centrifuged at 3000 rpm for 40 min. The soil solution

obtained from the centrifuge was filtered with 0.2 μm syringe filter (PTFE hydrophilic, Whatman, UK) into 2 mL vials prior to analysis.

Finally ~5 g of the remaining soils after centrifuge were taken out and shaken on a rotary shaker with 20 mL ACN for 2 h, centrifuged at 3000 rpm for 30 min, and the supernatants filtered through 0.2 μm syringe filters (PTFE, Whatman, UK) into 20 mL vials. All experiments were replicated. They were then stored awaiting analysis.

5.2.4 Chemical analysis

All samples were analyzed for ATR by HPLC-MS. Details are given in Section 3.2.2.

5.2.5 Principle of DGT in soils and DIFS model

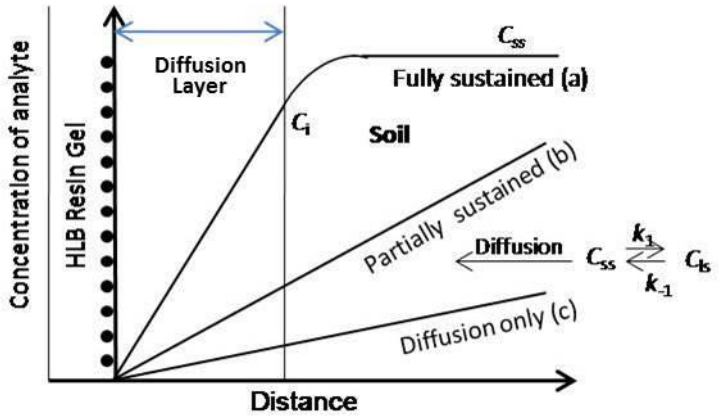


Figure 5.1 Processes induced by deployment of a DGT device in soil.

The mass (M) of analyte is accumulated by diffusion across the diffusion layer. Analytes in the soil solution (C_{SS}) become progressively depleted. Desorption (rate constant k_{-1}) from the soil particles (with concentration of labile analyte of C_{ls}) is induced. C_i is the instantaneous concentration of analyte at the interface between DGT and the soil solution, k_1 is the sorption rate constant.

When DGT is deployed in soil, the HLB resin gel binds the analytes that diffuse through the diffusion layer, leading to the formation of a linear concentration gradient in the

diffusion layer after an initial steady state (shown as Figure 5.1). The gradient depends on the thickness of the diffusion layer (Δg), and the interfacial concentration of labile analyte (C_i). According to Fick's first law of diffusion (Eq. 5.1), the flux ($F(t)$) is determined. D is the diffusion coefficient of the labile analyte. In this study, D of ATR at 25 °C was 5.67×10^{-6} cm^2s^{-1}, based on data from Chapter 3. With increasing deployment time, the accumulation of analyte by the resin gel tends to decline Ci, which induces a flux of analyte from solid phase to soil solution to resupply C_i. This flux contributes to the flux to DGT. The extent of the re-supply (the efficiency with which analyte concentrations are sustained in soil solution relative to their initial level) is determined by the soil's sorption capacity for the analyte and the kinetics of the adsorption and desorption processes.

$$F(t)= \frac{DC_i(t)}{\Delta g} \quad \textbf{(5.1)}$$

$$M= \int_0^T F(t)dt \quad \textbf{(5.2)}$$

$$C_{DGT}= \frac{M\,\Delta g}{DAT} \quad \textbf{(5.3)}$$

$$R(t)= \frac{C_{DGT}(t)}{C_{ss}} \quad \textbf{(5.4)}$$

The accumulated analyte (M), over the deployment time (T), is provided by integrating the flux over the deployment time as Eq. 5.2. The time averaged interfacial concentration (C_{DGT}) is calculated from M (Eq. 5.3), which can be determined analytically after extracting the analyte from binding gel, and A is the exposed area of the diffusion layer. An indicator of the extent of the depletion of soil solution concentrations at the DGT interface, R, is the ratio of C_{DGT} to the initial soil solution

concentration (C_{SS}) as presented in Eq. 5.4. The value of R is affected by the soil pool size of the analyte and the response time of the process (T_c) (Harper et al., 1998a).

The DIFS model (Harper et al., 2000; Sochaczewski et al., 2007) was developed to quantify the above processes. K_{dl} is the distribution coefficient based on labile solid-phase components that can exchange with the solution phase. The model uses K_{dl} (Eq. 5.5) and the T_c (Eq. 5.6) to describe the labile pool size and the kinetics of adsorption (rate constant k_1) and desorption (rate constant k_{-1}). P_c is the particle concentration of the tested soil.

$$K_{dl} = \frac{C_{ls}}{C_{ss}} = \frac{k_1}{P_c\, k_{-1}} \quad \textbf{(5.5)}$$

$$T_c = \frac{1}{k_1 + k_{-1}} = \frac{1}{k_{-1}(1 + K_{dl}\, P_c)} \quad \textbf{(5.6)}$$

In this study, the concentration of labile ATR (C_{ls}) was measured by ACN extraction as C_{SE}, so the value of K_{dl} was represented with K_d, the distribution coefficient estimated by measuring the concentrations of ATR in soil solution and extracted by ACN. T_c was calculated using 1D model of DIFS (1999, Lancaster, UK) and k_{-1} was obtained from 2D model of DIFS (2005, Lancaster, UK) when the R and K_d values were used as input parameters.

5.3 Results and Discussion

The 5 soils varied in pH (4.8 - 7.7) and organic matter content (OM) (3.9% - 8.1%). As presented in supporting information of chapter 4. Table S4.2, soil Malpass (M) had the lowest pH and OM, soil Dares (D) and soil Fushun (F) were both acidic and had more OM than soil M, soil Reddish (R) and soil Kettering (K) were neutral, soil K had the highest OM, while soil R had relatively low OM among these soils. Soil F was the only

soil containing ATR at detectable levels when it was collected from the field. It had been used for maize in China with a concentration of 3.5 $\times 10^{-4}$ mg L^{-1} ATR detected with DGT.

5.3.1 The effects of aging, pH and soil types on ATR availability

5.3.1.1 Soil Solution

As presented in Figure 5.2, the soil solution concentrations (C_{SS}) of ATR in 5 soils had no marked change after 10 days, illustrating the added ATR has nearly reached equilibrium with the soils in 10 days. . In 5 mg kg^{-1} dosed soils, C_{SS} basically decreased during aging with a little variation in some soils as expected (Barriuso et al., 2004). The picture was different in the 100 mg kg^{-1} dosed soils, there was very little change in C_{SS} after 6 days of aging for all soils. Soil M and D showed constant C_{SS} in the first 6 days, while C_{SS} values in soil R and K decreased at day 3 and increased at day 6. The C_{SS} trend in soil F was very different with sharp decrease between day 3 and day 6, as discussed below. Although ATR was spiked at the same level into all the soils (either 5 mg kg^{-1} or 100 mg kg^{-1}), the resulting C_{SS} varied between soils from the first day of the application. In lower dosed soils, soil M – the soil with the lowest OM content - had the highest C_{SS}. Previous research has shown that OM may reduce the release of ATR to soil solution, because sorption is greater on the soils enriched with organic carbon (Stehouwer et al., 1993). The C_{SS} sequence in the lower dosed soils then followed the sequence: soil M > soil K > soils D and R > soil F. C_{SS} in soil F was much lower than that in the other 4 soils. Soil K had high OM (8.1%) and a high soil pH of 7.7. Sorption of ATR by soils has been shown to decrease with increasing pH. Less ATR was sorbed

by soil with a pH of 7 or greater than in soils in the pH range 4-6 (Auld and Medd, 1987). This phenomenon was repeated in the higher dosed soil K. In higher dosed soil R, OM seemed to have much more influence than in the lower dosed soil, since it had the highest C_{SS} with a relatively low OM, while soils M and D were more affected by soil pH.

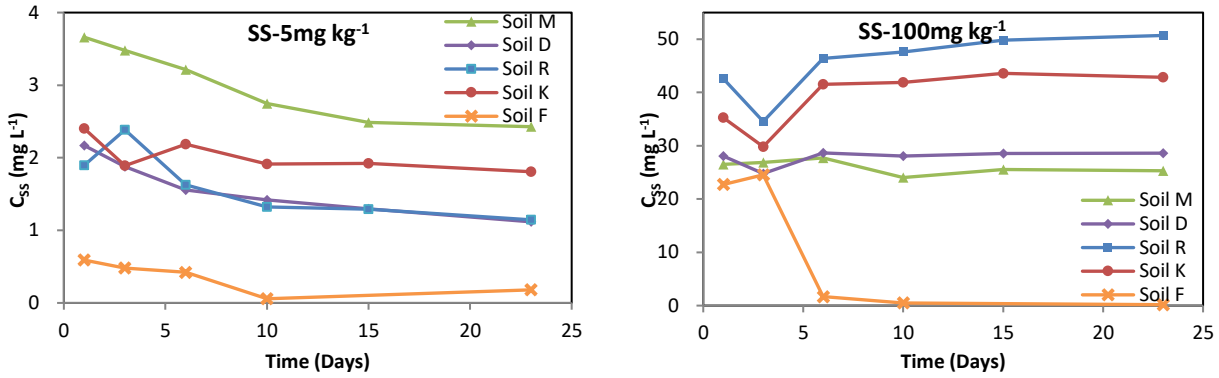


Figure 5.2 ATR concentration in soil solutions over aging time in 5 soils dosed at 2 levels

5.3.1.2 Extractable fraction

Compared to exhaustive extraction, shaking with ACN is a relatively mild solvent extraction. It has been proposed that it may access the labile pool of analyte in soils. After aging for 1 day, the concentrations of ATR measured by solvent extraction (C_{SE}) in lower dosed soils ranged from 3.9 - 4.9 mg kg^{-1}, close to the initial application rate. It was similar in the higher dosed soils, where measured C_{SE} values ranged from 95 - 99 mg kg^{-1}. The C_{SE} values all declined in the two dosed soils during aging. This was most marked in the higher dosed soil F. As reported in previous research, the ultimate result of aging processes was a reduction in extractability (Reid et al., 2000a). Most applied ATR was relatively easily desorbed in the early part of the aging process, but

larger portions of the amount added became less extractable due to more and stronger binding of ATR to the soil over time (Pignatello and Huang, 1991). Although ATR in all soils became more resistant to extraction with increasing aging time, the extractable concentrations were half or more of the initial concentrations after 23 days, demonstrating that over 50% applied ATR were still available by ACN extraction. This was more apparent in the higher dosed soils, except for soil F; C_{SE} in the other 4 soils only decreased < 30%, and the downward trend slowed down in soils M and R after 15 days. This is consistent with research which showed that the percentage sorbed to soil decreased as the competition for sorption sites increased with increasing ATR concentration (Mingelgrin and Gerstl, 1983).

The influence of aging effects varied among different soils. In lower dosed soils, after 1 day, soil F had the highest C_{SE}, followed by soil M, soil K, soils D and R, showing that faster sorption of ATR occurred in soils D and R. Soils F and M adsorbed ATR less tightly in the beginning though, the aging boosted adsorption in these two soils, since the decline of C_{SE} in these soils was greater than in the other soils. This phenomenon was different from some reports claiming that OM enhanced sorption as soil organic matter had a high affinity for ATR (Barriuso et al., 1992; Farland et al., 2011). However, pH is also playing an important role as soil M had the lowest pH which contributed to sorption. Johnson et al. (1993) found little correlation between ATR sorption and soil OM content in 26 surface and subsoil samples from 6 soils revealing that sorption was a complex synergism of many mechanisms; it could not be interpreted with a single factor.

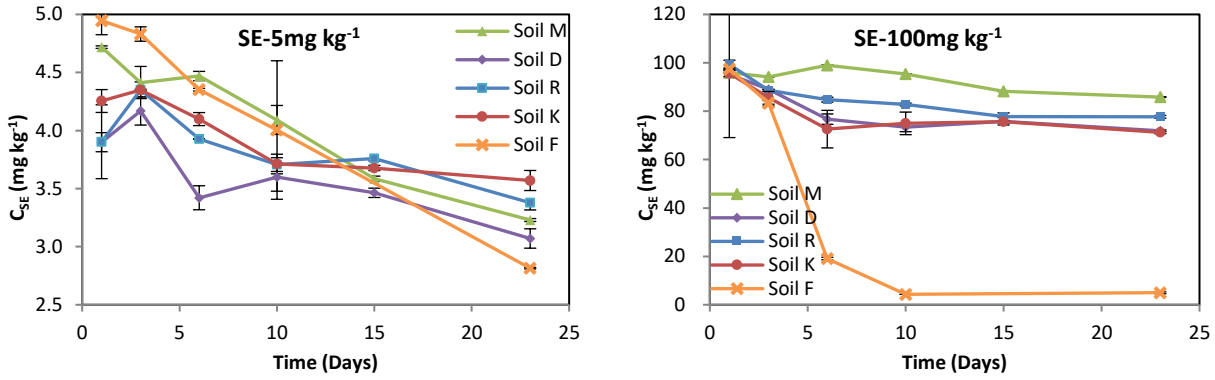


Figure 5.3 ATR concentrations as solvent (ACN) extractable over aging time in 5 soils dosed at 2 levels

5.3.1.3 DGT measured labile fraction

The DGT technique is capable of measuring metal bioavailability in soils and predicting plant metal uptake (Nolan et al., 2005), now its ability to measure pesticide bioavailability to maize uptake has been confirmed (shown in Chapter 4). The concentration measured by DGT (C_{DGT}) reflects the flux of an analyte supplied from the solid phase to the soil solution (Luo et al., 2010b). It embraces the concentrations in soil solution, the labile pool on the solid phase and the kinetic exchange between solution and solid phase.

In lower dosed soils, decreases in C_{DGT} were observed in all soils, indicating that the availability of ATR was decreased by increasing soil - ATR contact time (Figure 5.4). However, C_{DGT} in the higher dosed soils basically remained stable after 10 days. Within the first 10 days, except for the dramatic drop in soil F, C_{DGT} slightly increased in soils R and K, while it slightly decreased in soils M and D, with small variations. The trend of C_{DGT} and the order of their quantities in two dosed level soils resembled C_{SS}. C_{DGT} values were much less than the corresponding C_{SS}, implying that for all soils, the supply

from the solid phase to the soil solution could not be fully sustained to the removal of pesticide by DGT demand.

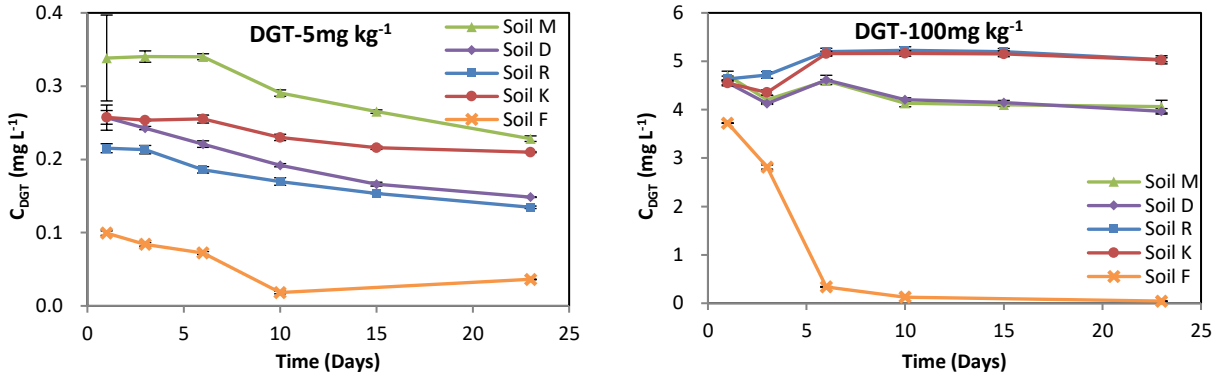


Figure 5.4 ATR concentration measured by DGT over aging time in 5 soils dosed at 2 levels

5.3.2 ATR degradation during the aging process

The reduction of ATR availability during aging is caused by it becoming increasingly sorbed/ sequestered by the soil solid phase. However, as noted earlier, there was a very marked reduction in the soil solution, solvent extraction and DGT derived concentrations for soil F. The changes with time and the extent of the decline in this soil point the influence of different process (es). Given that soil F was the only soil to be pre-exposed to ATR in the field, it was hypothesized that this could have led to the development and revitalising of microbial systems capable of degrading ATR more rapidly in the laboratory aging experiment.

After 23 days of aging, ATR and its degradation products (as described in Table S4.1) were determined using the three approaches described in Section 5.2.3. Parent ATR was dominant in all soils, except the higher dosed soil F (see Figure 5.5). There was evidence of some degradation, because of the presence of the metabolites HA and DEA

(see Figure 5.5). In the lower dosed soil F, C_{DGT} and C_{SS} of parent ATR were lower than in any of the soils. Little metabolite was detected. Although soil F had some HA as the dominant metabolite, the availability of ATR in other 4 soils and lower dosed soil F was mainly governed by adsorption-desorption.

The situation was a little different in the higher dosed soils. Soil F contained little (in C_{SE}) or no (in C_{ss} and C_{DGT}) parent ATR, but the metabolite CYA was abundant. Clearly in soil F, degradation losses of parent ATR are important. This may because soil F was used for growing maize and had ATR residues in the field. Hence the growth and activity of microorganisms likely already existed in the soil and were stimulated by the laboratory applications of ATR. Respiration and activity of the microorganisms could be strengthened (Gan et al., 1996), leading to a stronger adsorption of ATR on the solid phase and further degradation of ATR. The quantities of metabolites in soils M and D were greater than in soils R and K, consistent with the research revealing that hydrolysis rate of ATR decreased with the increasing soil pH (Armstrong et al., 1967). High organic matter content may also enhance the microbial activity and degradation of ATR, although in this study, pH seemed to have more influence.

Soil F will not be considered in the next section on adsorption-desorption, owing to the dominant effects of degradation on ATR in this soil.

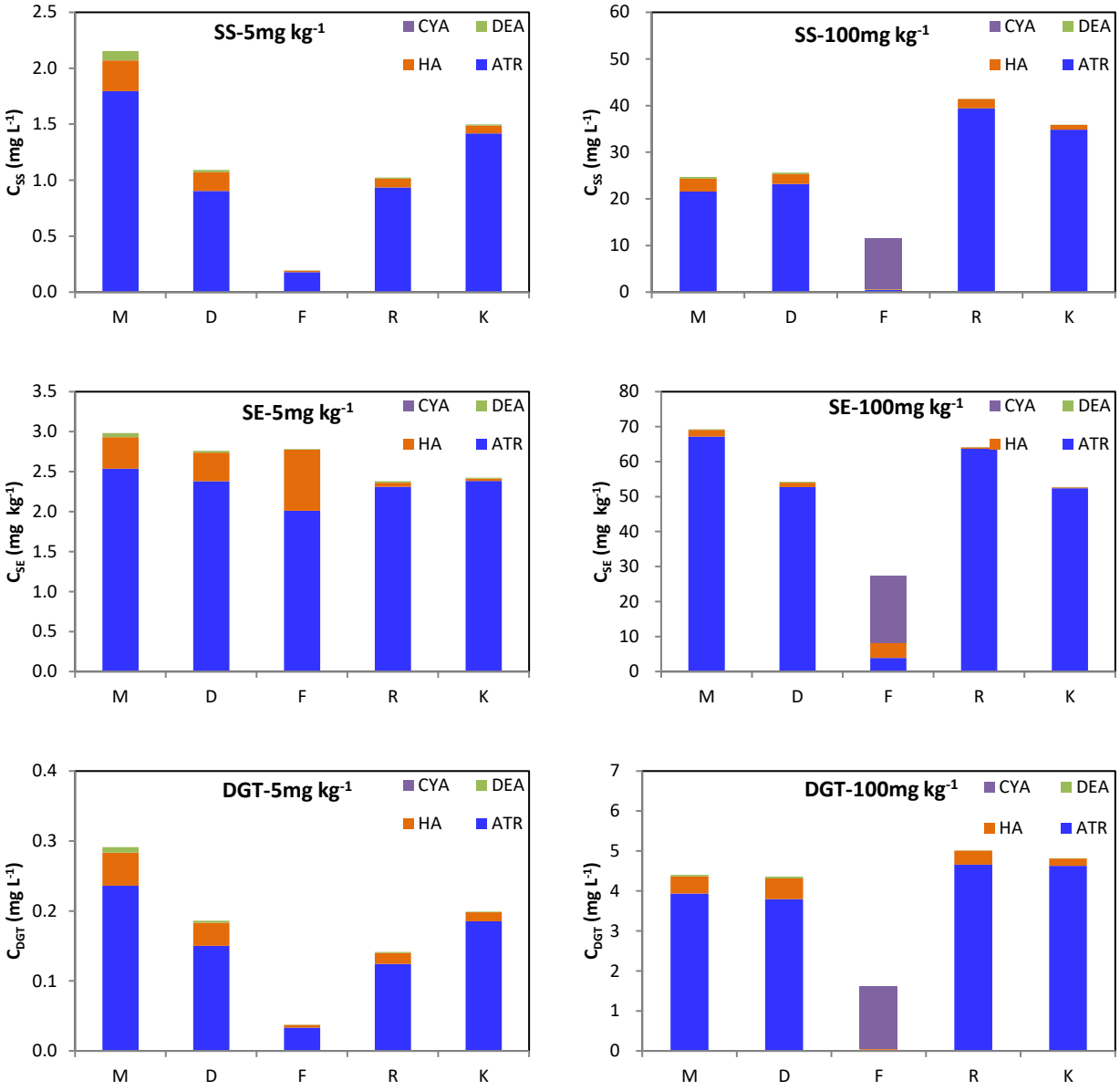


Figure 5.5 ATR and its metabolites measured in soil solution, by solvent extraction and by DGT after 23 days aging

5.3.3 Labile pool size and the ability to resupply ATR in different soils

It is generally accepted that – apart from the compound in the soil solution - there are two soil-associated pools relevant to compound availability after it has had contact with soils. These are a rapidly released fraction namely the 'labile sorbed fraction', and the 'non-labile fraction' which is more slowly desorbed (Pignatello and Xing, 1996).

To contribute to DGT-labile concentration, ATR in the labile solid phase pool will dissociate during DGT deployment, to counteract the depletion of ATR from soil solution. The distribution coefficient (K_d) - expressed as the ratio between the concentration of labile ATR in the solid phase extracted by ACN and its concentration in soil solution - was used as an indicator for the labile pool size of ATR in soils.

Several studies have been performed on the adsorption-desorption of ATR in soils, from which K_d values have been derived. These have ranged from 0.01 to 64 $cm^3\ g^{-1}$ (Ben-Hur et al., 2003; McGlamery and Slife, 1966; Ling et al., 2005; Payaperez et al., 1992). The values derived in this study are between 1.27 to 3.97 $cm^3\ g^{-1}$ (see Figure 5.6) so they lie within this range.

The K_d values in the lower dosed soils varied with aging. K_d values in soils R and D increased with aging time, C_{SE} decreased in these soils with aging (see Figure 5.3) and C_{SS} diminished as well (see Figure 5.2), indicating that the process of converting mobile ATR into sorbed ATR was faster than that of the sorbed ATR becoming non-available. This led to the expansion of labile pools in these two soils. A study on simazine also observed an increase of K_d as a result of the stronger but reversible sorption of the pesticide on soils with the increasing incubation time (Louchart and Voltz, 2007). K_d values in soil M basically remained stable during aging, except the value after 3 days of aging. In higher dosed soils, the situation was totally different. After a slight increase in the first 3 days, K_d values in 3 soils decreased after another 3 days and remained stable thereafter. This is incompatible with most of the research which reports that the K_d of pesticides increases with aging time. However, Sharer et al. (2003) reported that

the K_d values for ATR decreased within 30 days of incubation. This may be caused by the stronger binding between ATR and the soils particles, which formed more non-labile ATR.

K_d values in soils R and D were higher than in the other two soils in the lower dosed treatments. After 23 days of aging, K_d in soil M was less than half of that in soils R and D, displaying a smallest labile pool. Soil M is low in OM, which is a dominant sorbent for ATR (Ling et al., 2005). As a weakly basic herbicide, the adsorption of ATR would weaken due to increasing pH. Lee et al. (1989) also found enhanced release of native OM from the solid phase into soil solution with increasing pH. This could be an explanation for the low K_d value in soil K, despite its high OM content. Despite a 20 fold difference in application rate, K values in higher dosed soils didn't increase, but declined slightly in soils D and K, nearly half in soil R and increased almost three times in soil M. This demonstrates that the effect of applied concentration on the labile pool size of ATR was different between soils. The adsorption sites seemed to be saturated in soil R, but not in soils D and K. McGlamery et al. (McGlamery and Slife, 1966) reported that the degree of adsorption and desorption was independent of concentration in a clay loam and increasing the application of ATR over reasonable limits (0.375 – 40 ppm) appears to not saturate the adsorption sites. However, the concentration range here was far beyond 'reasonable limits' and soil properties varied.

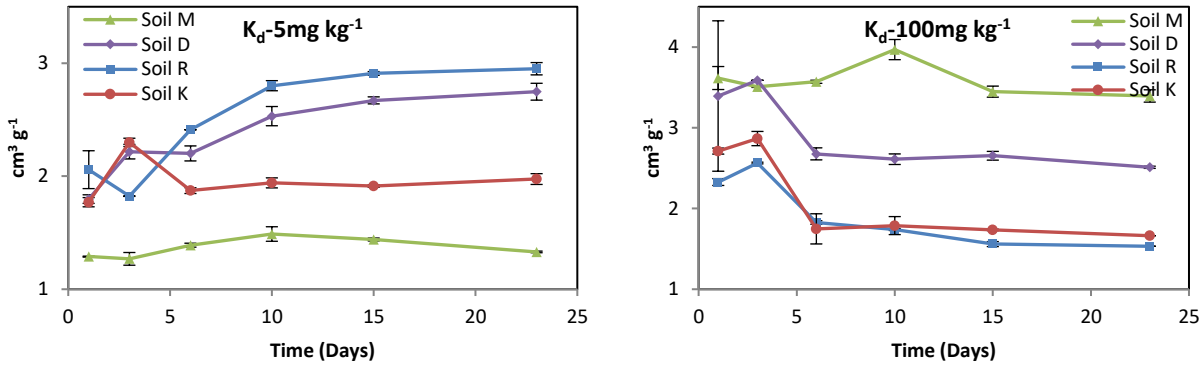


Figure 5.6 K_d of ATR at two dosed levels in 4 soils changed with aging time

The *R* value reflects ATR supply from both soil solution and solid phase in soils. It is indicative of the capability of soils to supply analytes to the DGT. The *R* value progressively decreases during deployment. The extent of this decrease over a given deployment time is determined by the ability of the soil to resupply analyte to the device surface, caused by analyte depletion in the soil solution (Harper et al., 1998a; Zhang et al., 1998b). Zhang et al. (1995) identified the 3 possible modes of analyte supply to the DGT devices which can be represented with the help of *R* (shown in Figure 5.1):

(a) Fully sustained case: the analyte taken up from the pore water is resupplied from the solid phase at a rate that can sustain the initial concentration in soil solution ($R \geq 0.95$)

(b) Partially sustained case: there is some resupply from the solid phase, but it is insufficient to maintain the initial C_{ss} ($0.1 < R < 0.95$)

(c) Diffusive case: there is no resupply from the solid phase to the soil solution. The supply of analyte is mainly accounted for by diffusion ($R < 0.1$)

In general, case (b) is the most common situation in the real environment. It is related to the DGT demand, as in case (a).

The *R* values from this experiment are shown in Figure 5.7. They varied from 0.09 to 0.18 in all the soils and doses. Therefore ATR was poorly resupplied in all soils or even not re-supplied as the modes described above. The *R* values in lower dosed soils fluctuated with aging time and increased slightly after 23 days of aging, while in higher dosed soils a slight and gradual decline of *R* (except *R* values after 3 days aging) was observed, illustrating that in both dosed levels the soil resupply capacities were little affected by soil aging.

In contrast to the K_d values, the difference of resupply capabilities between soils were reflective of their corresponding labile pool sizes. However, the *R* values in lower dosed soils didn't have the same trend with increasing aging time as K_d (shown in Figure 5.6), indicating that the ATR re-supply from soil does not merely depend on the labile pool size.

K_d and *R* values generally vary little with aging over 23 days in this study. Other studies on ATR soil aging have been performed over 1 week to 8 months or even years (Kelsey et al., 1997; Chung and Alexander, 2002; Park et al., 2004). Longer aging periods may make it easier to detect underlying trends and variations.

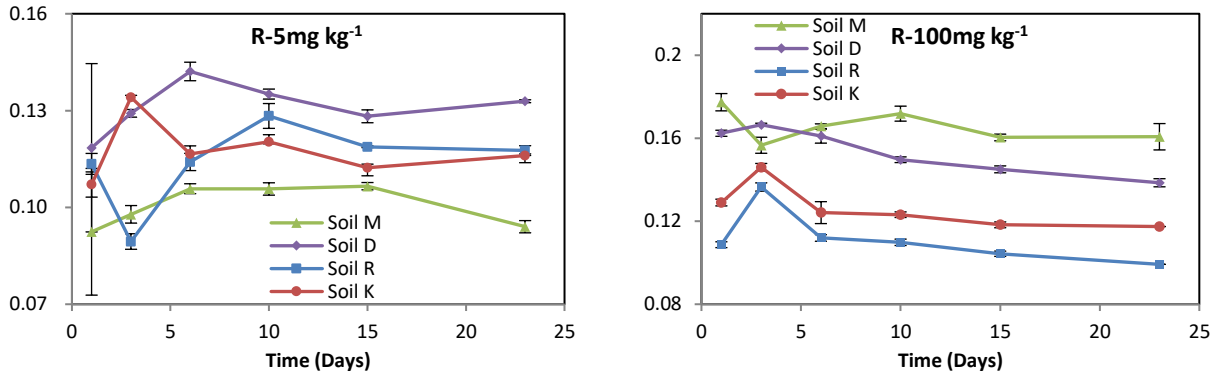


Figure 5.7 *R* values of ATR at two dosed levels in 4 soils plotted with aging time

5.3.4 Re-supply kinetic characteristics of ATR in different soils

K_d ultimately determines the quantity of ATR that can be re-supplied by the solid phase, while T_c and k_{-1} directly relate to the rate of this re-supply to the concentration in the soil solution, thereby controlling the ability to re-supply the analyte in soils (Harper et al., 1998a). When there is a large reservoir, T_c is significant to the availability of the analyte and the kinetics of desorption from the solid phase becomes the limiting factor (Chen et al., 2014a). However, T_c has little effect on the uptake of DGT if the labile pool size is small, since the pool will be depleted rapidly (Lehto et al., 2006).

In the lower dosed soils, T_c values fluctuated greatly with aging time. T_c values in soil D showed the least variation during aging as they were in the same order of magnitude and they increased after 10 days of aging. Soil R had the largest T_c values, leading to the slowest re-supply. This is consistent with soil R having the smallest C_{DGT}, even though it had the largest labile pool.

The desorption rate (k_{-1}) measures the ATR release rate from solid phase to solution. Except for several extreme values (maximal values in soils M and K after 3 days, in soil D after 6 days, and minimal value in soil R after 3 days), k_{-1} values remained in the

same order of magnitude - indicating that aging had a slight influence on the release rate of ATR in these soils. Only soil D was affected after 10 days, but it didn't reflect on the concentration of ATR. k_{-1} values for soil R were lower than in other soils, which was consistent with the lowest C_{DGT} in soil R, presenting the influence of k_{-1} on the resupply kinetics, but it didn't strongly correlate with C_{DGT} in other soils, revealing that k_{-1} was not a limiting factor in ATR resupply.

In higher dosed soils, C_{SS} values were about 10 times of the C_{SS} values in lower dosed soils. However, the labile pool sizes didn't differ much (K_d values in higher dosed soils were 1-3 times of that in lower dosed soils). There were not much difference between the R values in soils of two contaminated levels. As shown in Table 5.2, T_c values were abnormally and irregularly smaller than that in T_c values in Table 5.1, some of them were even < 0.1 s. Previous researches reported that a nearly fully sustained situation ($R \geq 0.95$) could be obtained from $K_d > 10^3$ and $T_c < 10$ s (Harper et al., 1998a). However, in this study, labile pools were not large enough to support such fast resupply. Furthermore, T_c values fluctuated enormously with aging time despite of the minor differences between other parameters. The uncertainty and inconsistency of these results may due to the error of DIFS models and they should be further investigated. Lehto et al. (Lehto et al., 2008) used an error function (E) for the quantitative assessment of how well the estimation of K_d and T_c using DGT measurements and the 2D DIFS. He discovered that the estimation using DIFS sometimes had large uncertainty.

Table 5.1 T_c and k_{-1} over time in the 4 tested soils dosed with 5 mg kg^{-1} ATR

	Aging times (days)	Soil Types			
		Soil M	Soil D	Soil R	Soil K
T_c (s)	1	1.6E+4	2.3E+3	9.2E+3	1.0E+4
	3	2.5E+3	2.0E+3	2.6E+4	6.4E+2
	6	6.8E+3	1.4E+3	1.0E+4	6.3E+3
	10	1.4E+4	4.6E+3	1.1E+4	6.5E+3
	15	6.9E+3	4.2E+3	1.0E+4	8.4E+3
	23	1.5E+4	3.2E+3	7.7E+3	4.6E+3
k_{-1} (s^{-1})	1	1.7E-5	9.1E-5	2.0E-5	2.1E-5
	3	1.1E-4	8.9E-5	8.1E-6	2.7E-4
	6	3.7E-5	1.2E-4	1.6E-5	3.2E-5
	10	1.8E-5	3.5E-5	1.4E-5	3.1E-5
	15	3.6E-5	3.6E-5	1.4E-5	2.4E-5
	23	2.5E-9	4.6E-5	1.8E-5	4.2E-5

Table 5.2 T_c and k_{-1} over time in the 4 tested soils dosed with 100 mg kg^{-1} ATR

	Aging times (days)	Soil Types			
		Soil M	Soil D	Soil R	Soil K
T_c (s)	1	2.9E-2	4.0E-2	1.3E+4	4.3E+3
	3	1.1E+3	3.2E-2	1.9E+3	7.6E+2
	6	2.0E-2	2.6E-2	8.0E+3	4.2E-2
	10	1.5E+3	6.7E+2	1.3E+4	3.9E+3
	15	3.0E-3	2.4E-2	9.7E+3	8.2E+2
	23	6.3E-4	2.5E-2	1.3E+4	1.0E-1
k_{-1} (s^{-1})	1	4.0E+0	3.1E+0	1.4E-5	1.2E-5
	3	1.1E-4	3.6E+0	8.5E-5	1.9E-4
	6	5.8E+0	5.9E+0	2.6E-5	5.1E+0
	10	7.0E-5	2.3E-4	1.6E-5	5.4E-5
	15	4.1E+1	6.3E+0	2.4E-5	2.6E-4
	23	1.9E+2	6.4E+0	1.9E-5	2.2E+0

5.4 Conclusions

This project has shown that increasing the aging time strengthened the adsorption of ATR on the soil particles, leading to the decrease in both soil solution and solvent extractable fraction. Since the aging time was relatively short (only 23 days), the reduction was not significant in lower dosed soils, in some highly polluted soils the availability of ATR even slightly increased. Soil properties also played an important role in the behaviour of ATR during aging, the availability of ATR was promoted with higher pH and lower OM theoretically, but these properties had an integrated impact on ATR in the real environment.

Apart from the adsorption process, degradation is another vital process which occurred during aging. ATR in all soil samples went through the hydroxylation, especially in soil F which was collected from a maize grown field in China where considerable amounts of fertilizers and ATR were applied.

The effect of initial concentration of ATR applied to soils was significant. The labile pool size of ATR in lower dosed soils increased to different extents, while it decreased in higher dosed soils. The same situation was observed in the study of the availability of ATR to resupply, in response to depletion. All soils were poorly sustained by solid phase; diffusion dominated the resupply process. The information on resupply kinetics (response time and rate constants) fluctuated substantially during aging between soils. It could be from the limits and uncertainties of the DIFS model as reported by Lehto et al. (Lehto et al., 2008).

The findings in this study demonstrated that the kinetics of release from solid phase to soil solution and labile pool size control the supply of ATR to a sink, such as DGT devices or plant roots. With the increasing aging time, the risk of leaching from soil to aqueous environment decreased, together with the bioavailability, which reflected in the reduced labile concentrations measured by DGT, but the potential availability of ATR didn't decrease much.

Chapter 6: Impact of atrazine on the availability of arsenic in soils

6.1 Introduction

Environmental contaminants and chemicals are usually studied individually, rather than interactively, yet they occur together in soils and waters, and biological systems are routinely exposed to mixtures. In this chapter, a study was conducted to see whether a major inorganic contaminant (arsenic) and a major organic contaminant (atrazine) underwent any interactions in soils, the environmental compartment where they frequently occur together. They were chosen to be illustrative, important contaminants and to test a methodology which can be used to explore interactions of trace substances in soil systems.

Arsenic (As) is present in the natural environment, but elevated levels occur from activities such as smelting of metal ores, wood preservatives, coal combustion, lead-acid automobile batteries, semiconductors in telecommunications and use of As-containing by-products (Smith et al., 1998). As contamination is common in natural waters and soils. Crop plants grown on contaminated soils and contaminated ground waters used as drinking water can be sources of human exposure. People chronically exposed to toxic levels of inorganic As may have health problems including skin lesions, neurotoxicity, skin cancer, lung, bladder, kidney, lymphoma and myelogenous leukaemia (Ferrario et al., 2016; Chen et al., 2003).

There have been numerous scientific papers suggesting that As is a worldwide and widespread contaminant. As was measured up to 3050 μg L^{-1} in rural groundwater in Vietnam with an average value of 159 μg L^{-1} (Berg et al., 2001). Razo et al. (Razo et

al., 2004) estimated a maximum concentration of 265 μg L^{-1} in pluvial water storage ponds and levels ranging from 29 to 28600 mg kg^{-1} of As from a mining site in Mexico. The soil background concentration of As varies from ~5 - 15 mg kg^{-1} but soil in contaminated areas could contain up to 172,000 mg kg^{-1} As (Wang and Mulligan, 2006b). Bangladesh is known for facing the most serious As contamination problem in the world. The concentrations are up to 83 mg kg^{-1} in soils, > 1000μg L^{-1} in groundwater and from 3 to1500 μg kg^{-1} have been reported in food and forage plants (Hossain, 2006).

Besides inorganic pollutants like As, humans are also often exposed to multiple toxicants, since elevated levels of organic chemicals such pesticides are also applied on farmlands. Atrazine (ATR) is one of the most widely used pesticides. Although it has been restricted in some parts of the world, it has been detected together with As in surface waters in the US (Lewis et al., 2002). ATR is a widely accepted chloro-S-triazine herbicide used to control broadleaf weeds in corn, sorghum and sugarcane (Grigg et al., 1997). Only a small fraction of ATR applied actually reaches the target pest, with a large amount of ATR remaining in the soil or transporting to aqueous environment (Pimentel, 1995).

It has been reported that ATR presents slight to moderate toxicity for humans and other animals. It can disrupt the oestrous cycle in rat strains (Cooper et al., 2000), cause premature reproductive senescence and increase the incidence of mammary tumours in female rats from lifetime exposure (Stevens et al., 1994). ATR also has the potential to enhance the toxicity of As in human cells (Castelo-Grande et al., 2005). As two

commonly used chemicals, As and ATR have been detected together in the environment. For example, 59 - 130 mg kg^{-1} As was detected in an ATR contaminated soil in South Australia (Ying et al., 2005).

Co-exposure studies of ATR and As have focused on the impact of toxicity and gene expression on organisms, such as the albino rat in the nigrostriatal system (Bardullas et al., 2013), mice in utero and juvenile (Cimino-Reale et al., 2008) and zebrafish embryos (Adeyemi et al., 2015). Not many published studies have addressed the effect of ATR on the As behaviour and availability in soils.

In this study, two levels of ATR (5 and 50 mg kg^{-1}) were applied to different types of soils with different concentrations of As, and the possible effects of ATR on the availability of As in these soils was evaluated with increasing aging time. Because of its ability to sample environmentally relevant fractions from the soil solution, DGT was used to explore potential interactive effects between As and ATR in the soils.

6.2 Method and Materials

6.2.1 Chemicals and reagents

As standard solution was purchased from (UK), while ATR product (38% suspension liquid) was obtained from China. Information on the reagents used in the experiments can be found in the Supporting Information (SI).

6.2.2 Soil samples and treatments

Six soils varying widely in pH and organic matter content were collected from China. Soil 1 and 2 were from As highly contaminated farmlands, growing vegetable and

maize, respectively; soil 3 and 4 were from moderate contaminated farmlands used for maize and green bean; soil 5 and 6 were from uncontaminated farmlands; they contained different levels of As, varying between 32.3 - 595.8 mg kg^{-1}. The details of soil properties are listed in Table S6.1. All the soils were air-dried and passed through a 2 mm sieve to remove roots and stones prior to experiments. 3.9 mg and 39 mg of 38% ATR suspension liquid were mixed with 20 mL MQ water and applied to 300 g of each soil to achieve concentrations of 5 and 50 mg kg^{-1}. The soils were then wetted to 25 - 30% MWHC (maximum water holding capacity) by adding appropriate amounts of MQ water, then mixed well to ensure ATR was distributed homogenously in the soils. The soil samples were then transferred to plastic bags, sealed and stored in the dark at room temperature for aging.

The sampling and analysis work involved determination of the following: As and ATR as determined by DGT; As determined as 'Olsen As'; direct determination of As and ATR soil solution concentrations. The sampling and analytical procedures are as described below.

6.2.3 DGT deployment and soil sampling

6.2.3.1 DGT preparation

The polyacrylamide diffusive gels were prepared with a 0.25mm spacer, as reported in a previous study (Zhang et al., 1995). After washing with MQ water, gels were immersed in 0.1 M Fe^{3+} solution (13.5 g $FeCl_3 \cdot 6H_2O$ in 500 mL MQ water) and shaken for at least 2 h for equilibration. 0.05 M MES (2-(N-morpholino)-ethanesulfonic acid, biochemical, BDH) buffer solution was adjusted with 1 M NaOH to pH 6.7. The gels

were soaked in the MES solution, after ensuring the Fe^{3+} ions were uniformly distributed. Gels were shaken for over 1 h, until the ferrihydrite was formed, then rinsed in MQ water several times. The precipitated ferrihydrite gels were soaked in 0.03 M NaCl solution before assembling.

DGT devices consisting of a 0.04 mm precipitated ferrihydrite gel, a 0.08 mm diffusive gel and a PES filter were prepared prior to deployment.

6.2.3.2 DGT deployments

After application of ATR, measurements of As were made by DGT at different times to investigate the ageing effect of ATR on the availability of As in soils. Before the DGT deployment, soils were wetted to 100% MWHC and mixed to obtain a soil slurry, then the slurry was left for 24 h. For the deployment, soil paste was smeared onto the filter of the DGT device. Then the device was gently pressed into the soil for good contact between the soil surface and the DGT device; the deployment was maintained at room temperature for 24 h. All experiments were triplicated. DGT devices were deployed after 1, 3, 11, 21 days of aging.

6.2.3.3 DGT retrieval, soil solution sampling and Olsen As measurement

After 24 h deployment, DGT devices were retrieved. The filter surface was jet washed with MQ water. The resin gels were removed and placed into 1 mL vials. The resin gels were eluted with 1 mL of 1 M HNO_3 for 24 h. The solution was diluted at least 10 times before analysis for As concentrations.

After retrieval, the triplicates soils were mixed and stirred and about 50 g soil paste was sampled into a 50 mL tube and centrifuged at 3500 rpm for 10 min. The soil solution

obtained from the centrifuge was filtered with a 0.45 μm syringe filter (non-pyrogenic, Corinig, Germany) into 1 mL vials prior to As analysis. Sub-samples were obtained by filtering through a 0.2 μm syringe filter (PTFE hydrophilic, Whatman, UK) for ATR analysis.

In addition, the soils were sampled for 'Olsen As'(Olsen et al., 1982), as follows: triplicate 1 g soil samples were taken and transferred to 3 separate 50 mL centrifuge tubes. A 0.5M $NaHCO_3$ solution was prepared and adjusted to pH 8.5 by adding appropriate amount of 1 M NaOH. Then 20 mL $NaHCO_3$was added to each soil sample tube and the tubes were shaken on a rotary shaker for 30 mins. The tubes were then centrifuged at 3500 rpm for 10 minutes. About 1 mL of the solution was then taken and filtered through a 0.45 μm syringe filter. Samples were diluted 20 times before analysis.

6.2.4 Chemical analysis

A Thermo Elemental X7 ICP-MS was used to determine As concentrations.

Concentrations of ATR in soil solution were determined by LC-MS. Detailed information of LC-MS measurement is provided in the SI.

6.3. Results and Discussion

6.3.1 Soil properties and As in soils before application of ATR

Selected physiochemical properties of the 6 soils are listed in Table S6.1. The soils had a range of properties. Soil pH varied between 4 (soil 5) and 7.6 (soil 3). Soil texture varied between sandy loam (soil 6) and clay loam (soils 3 and 4). Soil organic matter contents varied between 0.6% (soil 5) and 2.7% (soil 2).

The concentrations of As in soil solution (C_{SS}), the solid phase (C_{SE}) and measured by DGT (C_{DGT}) in the 6 soils before the addition of ATR are shown in Figure 6.1, as these soils have been contaminated by As and stored for a long time, As in the soils have already reached equilibrium with the soils. Soils 1, 2 and 4 contained the highest As concentration in the soil solution, all>40 mg L^{-1}. The C_{SS} of soils 5 and 6 were much lower, < 5 mg L^{-1}. Similar trends were observed in the C_{SE}, with soils 1, 2 and 4 the most contaminated (~4 - 5 mg L^{-1}) and soils 5 and 6 the lowest. The C_{SE} in soil 4 was lower than that in soil 1 and 2, indicating As in soil 4 had a small mobile fraction. The C_{SE} in the uncontaminated farmland soils 5 and 6 were the lowest, at <0.2 mg kg^{-1}. DGT measurements indicate the analyte both in soil solution and solid phase, C_{DGT} varied between these 6 soils, with highest value in soil 1 and lowest in soils 5 and 6, just like C_{SE}. As described in chapter 5, R is an indicator of the extent of the depletion of solution concentrations at the DGT interface, it is the ratio of C_{DGT} to the independently measured initial soil solution concentration (C_{SS}) (Zhang et al., 1998b). The R values of these 6 soils ranging from 0.10 to 0.52, indicating that As in the solid phase could partially sustained the soil solution (Chen et al., 2014a; Harper et al., 1998a).

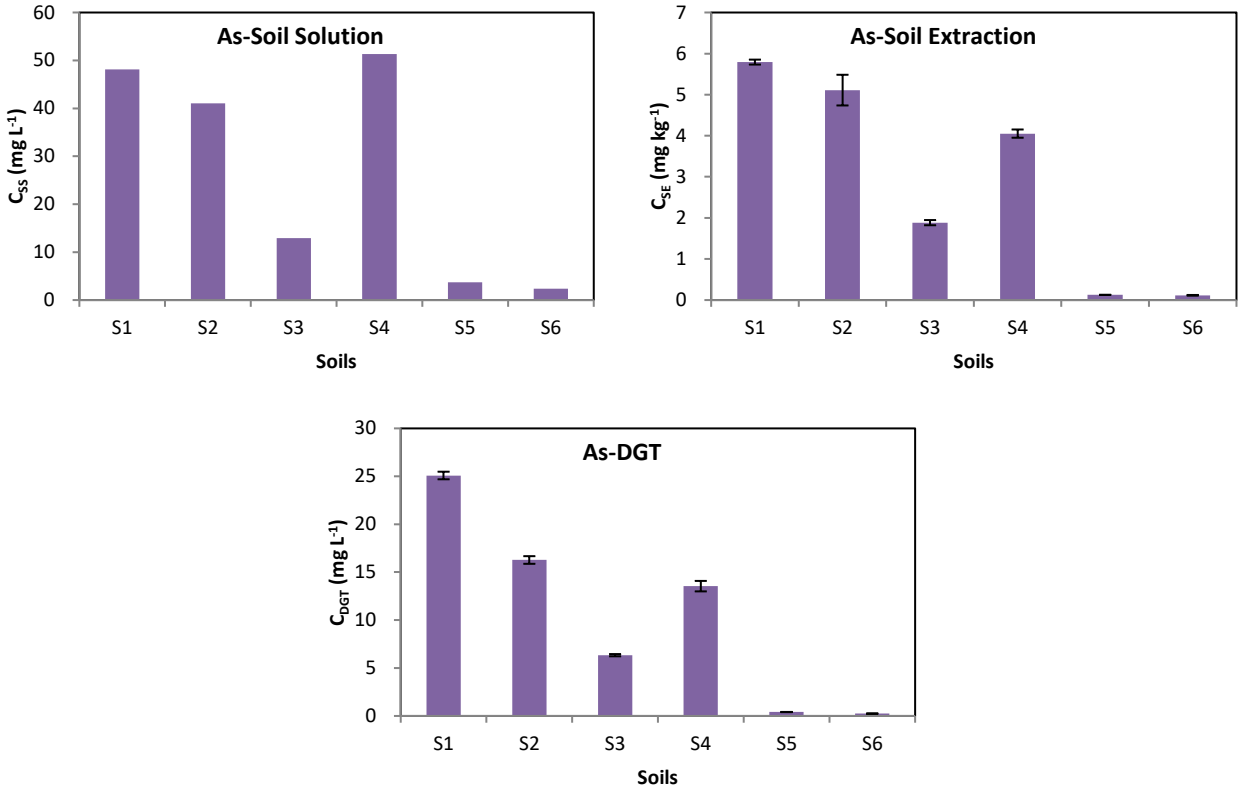


Figure 6.1 Concentration of As in the test soils measured by 3 methods (DGT, SS: soil solution extraction; SE: sodium bicarbonate extraction) prior addition of ATR.

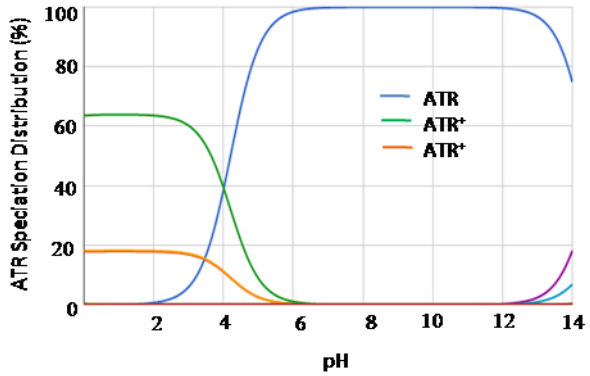
6.3.2 Effect of ATR on As availability and concentrations

6.3.2.1. Possible interaction processes between As and ATR in soils

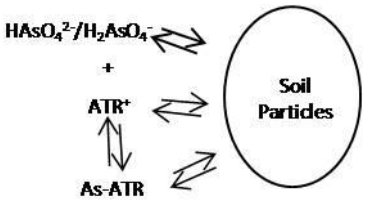
Figure 6.2 shows a schematic representation of ATR speciation under different pH conditions. This suggests that some ATR existed as ATR^+ in soil solutions when pH is below 6, i.e. all soil solutions except soil 3 are likely to have ATR^+. There are two cationic forms of ATR with positive charge in the solution (Figure 6.2(c)). $H_2AsO_4^-$ is the major species of As below pH 6, while $HAsO_4^{2-}$ is dominant above 6 (Smedley and Kinniburgh, 2002), they were both negatively charged. When the soil pH > 6, there was no interaction between the neutral ATR and arsenate. Whereas the soil pH became <6, electrostatic force controlled the adsorption between ATR^+ and $H_2AsO_4^-$. Since they

were oppositely charged, they would not compete for adsorption sites on soil particles. ATR^+ behaved as a sorbent in the soil solution, which may compete with the organic matter in solid phase for arsenate. When ATR was applied into As contaminated soil, it may adsorb As (in the form of $H_2AsO_4^-$) leading to the release of As from the solid phase. ATR in the solution phase may interact with itself by hydrogen bonding, so if the application rate of ATR increased, the interaction between ATR and As may be replaced by the H-bonding between ATR, resulting in the adsorption of As on soil particles.

(a)



(b)



(c)

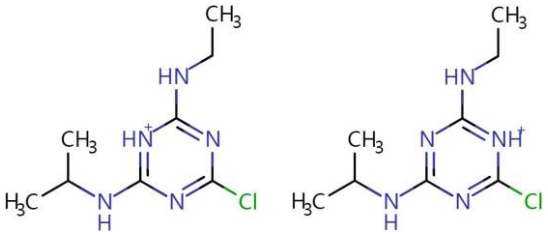


Figure 6.2 (a) ATR speciation in soil solutions; (b) Possible sorption/ desorption and interaction processes of As and ATR in soil; (c) two forms of ATR^+ existing in the soil solution

6.3.2.2 As in soil solution

Soil solution concentrations of As reflect the immediately available As in soils. The results of concentrations of As measured in soil solutions at different time after the

addition of ATR to the soils are presented in Figure 6.2.With the increasing aging time for ATR, concentration of As in the soil solution decreased a little from Day 2 to Day 4, then increased after that. This happened almost for all 6 soils at both ATR addition levels. It seems after 4 days of ATR addition, the adsorption of As on the solid phase increased, then water soluble As increased with longer time to the similar concentrations the initial concentration except for soil 4. In soil 4, C_{SS} dropped to nearly half from Day 2 to Day 4 and did not increase at Day 12 and Day 22.

There was no obvious net effect of ATR addition on the C_{SS} of As seen in Figure 6.3. In some cases, the As *C*SS was higher with the 5 mg ATR L^{-1} treatment than in the absence of ATR with the same aging time. One hypothesis to explain such an observation is that interaction of As and ATR enhanced the release of As from the soil solid phase (see Figure 6.2). This may be more likely in the first a few days, if freshly applied ATR had not equilibrated between the soil solution and solid phase. If As-ATR complexes were less adsorbable than $H_2AsO_4^-$ and $HAsO_4^{2-}$on the solid phase, more As may be detected in the soil solution. Kashem et al. (Kashem and Singh, 2001) found that the soluble concentration of Cd, Ni and Zn was lower in organic matter treated soils and dependent on soil Eh and pH.

After 12 days of ATR addition, there was no difference between the untreated As C_{SS} and that with the addition of 5 mg L^{-1} ATR. As shown in Figure S6.1(a), mobile ATR in soil solution decreased since it adsorbed on the solid phase with increasing aging time and some sorption sites were occupied. The study of Wang et al. (Wang and Mulligan, 2006a) implied that the competition for available adsorption sites and formation of

aqueous complexes between As and organic matter in soils would increase desorption of As, leading to the increase of C_{SS}, but in this study ATR was neutral or positively charged, it would not compete with the negatively charged As. The ATR may act as sorbent to adsorb As, it competed with the soil particles and resulted in more As dissociated back into solution.

However, the As C_{SS} in the 6 soils with 50 mg L^{-1} ATR were not higher than those with no added ATR or addition of 5 mg ATR L^{-1}. This indicates that the further 10 times addition of ATR didn't enhance the effect of ATR on As availability.

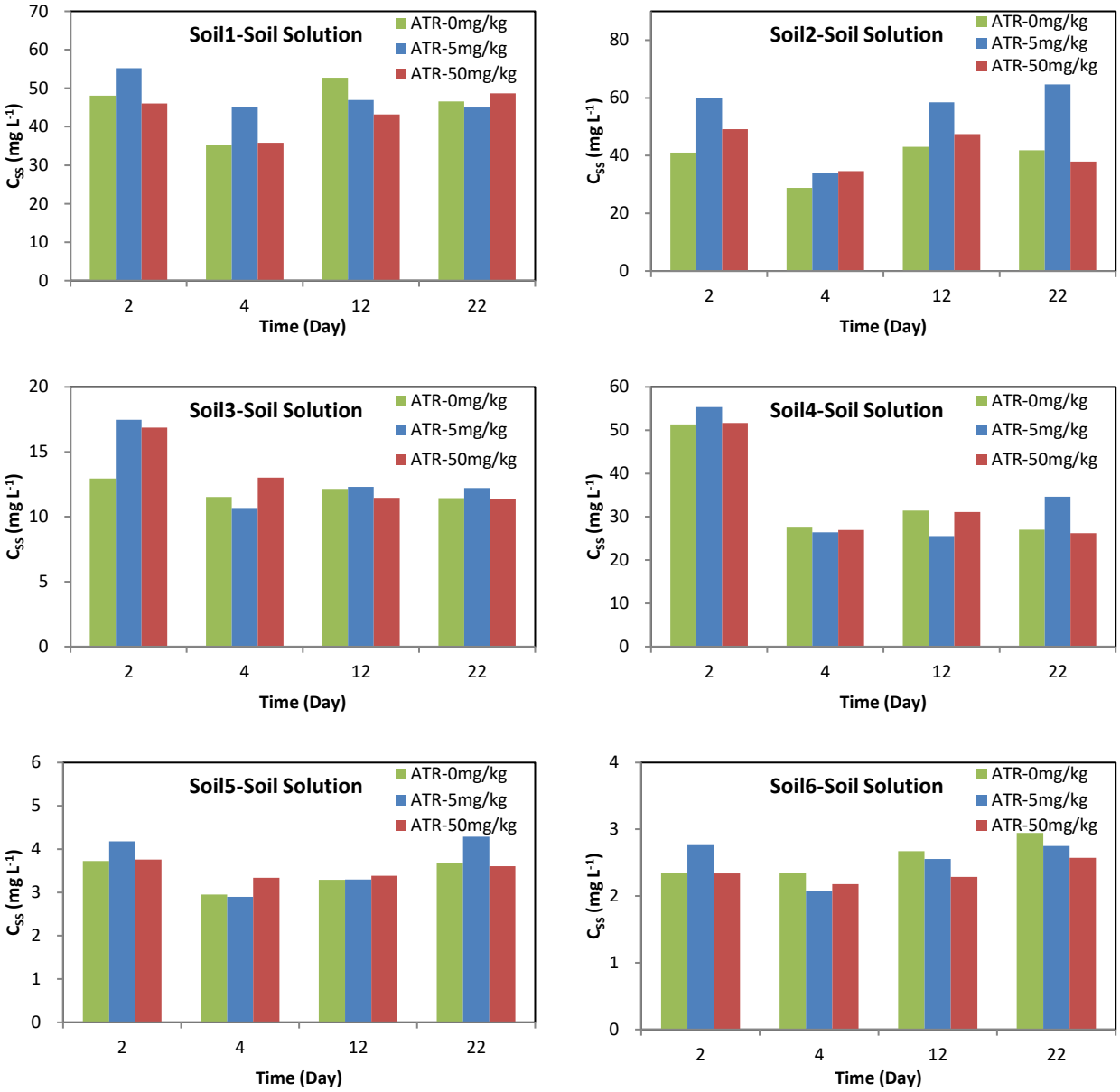


Figure 6.3 As concentrations in soil solution at three treatment levels of ATR with 4aging times in the 6 test soils

6.3.2.2 As measured by $NaHCO_3$ extraction

Extraction with $NaHCO_3$ is considered to release readily labile (bioavailable) As associated with soil mineral surfaces, compared to total As digested with concentrated HCl-HNO_3 (Adriano, 2001). In this study, As was extracted by $NaHCO_3$, so C_{SE} here represents the fraction of extractable As adsorbed on the solid phase.

As presented in Figure 6.4, unlike the trend of C_{SS}, C_{SE} on Day 4 was slightly higher than C_{SE} on the other days. This may indicate that during the equilibrium of ATR with soil the more soluble As adsorbed on the solid phase. In soil 1 and 2, C_{SE} with the presence of ATR increased from Day 2 to Day 4, but reduced after that to a similar C_{SE} as in Day 2. This was most obvious in soil 1 compared to the C_{SE} in the absence of ATR, implying that the addition of ATR only caused a small interference on the adsorption of As on solid phase during its equilibration with soils. This finding was different from Halim's research revealing that addition of organic matter generally reduced the extractability of the exchangeable forms of metals (Halim et al., 2003). In soil 3, C_{SE} with the presence of ATR increased on Day 22 with a dramatic reduction of soluble ATR which was puzzling. In general, the impact of ATR addition on the concentrations of $NaHCO_3^-$ extractable As in these test soils was not significant.

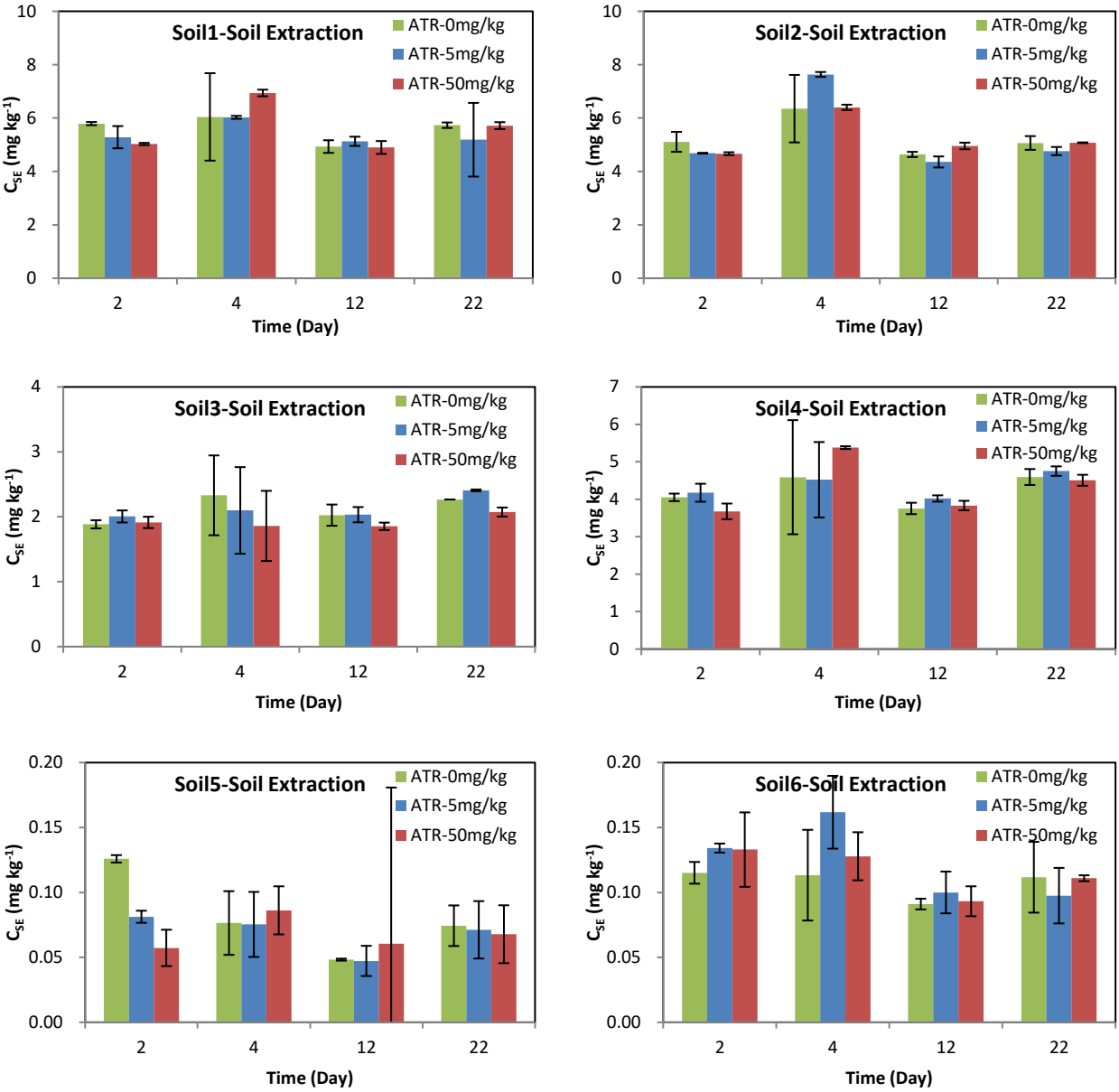


Figure 6.4 As concentrations in soil measured by $NaHCO_3$-extractionat three treatment levels of ATR with 4 aging times in the 6 test soils

6.3.2.3 DGT measurement

DGT measured concentration, C_{DGT}, offers an integrated measurement of labile (available) As in soils, reflecting supply from both solution and solid phase (Zhang et al., 2001). The diffusion coefficient of As in gel used for the calculation C_{DGT} was 5.25×10^{-06}, as obtained in a previous study (Luo et al., 2010a).

The change of C_{DGT} with aging time showed a similar trend to C_{SS} in most soils and most ATR dosed levels, declining from Day 2 to Day 4, then ascending a little or being comparable with Day 4 after that, as presenting in Figure 6.5 and Figure S6.1 (e) and (f), except for soil 6. In soil 6, C_{DGT} increased with the increasing aging time, may because with a coarser sandy soil texture (shown in Table S6.1), As was easier to desorb and to resupply to the solution phase, which is in agreement with the study from Alloway et al. (Alloway, 1995) claiming that Zn adsorption was suppressed in the sandy soil with large particle size.

C_{DGT} of As in the absence of ATR on Day 2 was higher or almost higher than C_{DGT} with the presence of ATR. But with the aging time increased C_{DGT} of As in the absence of ATR was no longer the highest concentration compared to C_{DGT} in the other two ATR contaminated soils, suggesting that the addition of ATR suppressed C_{DGT} of As to some extent.

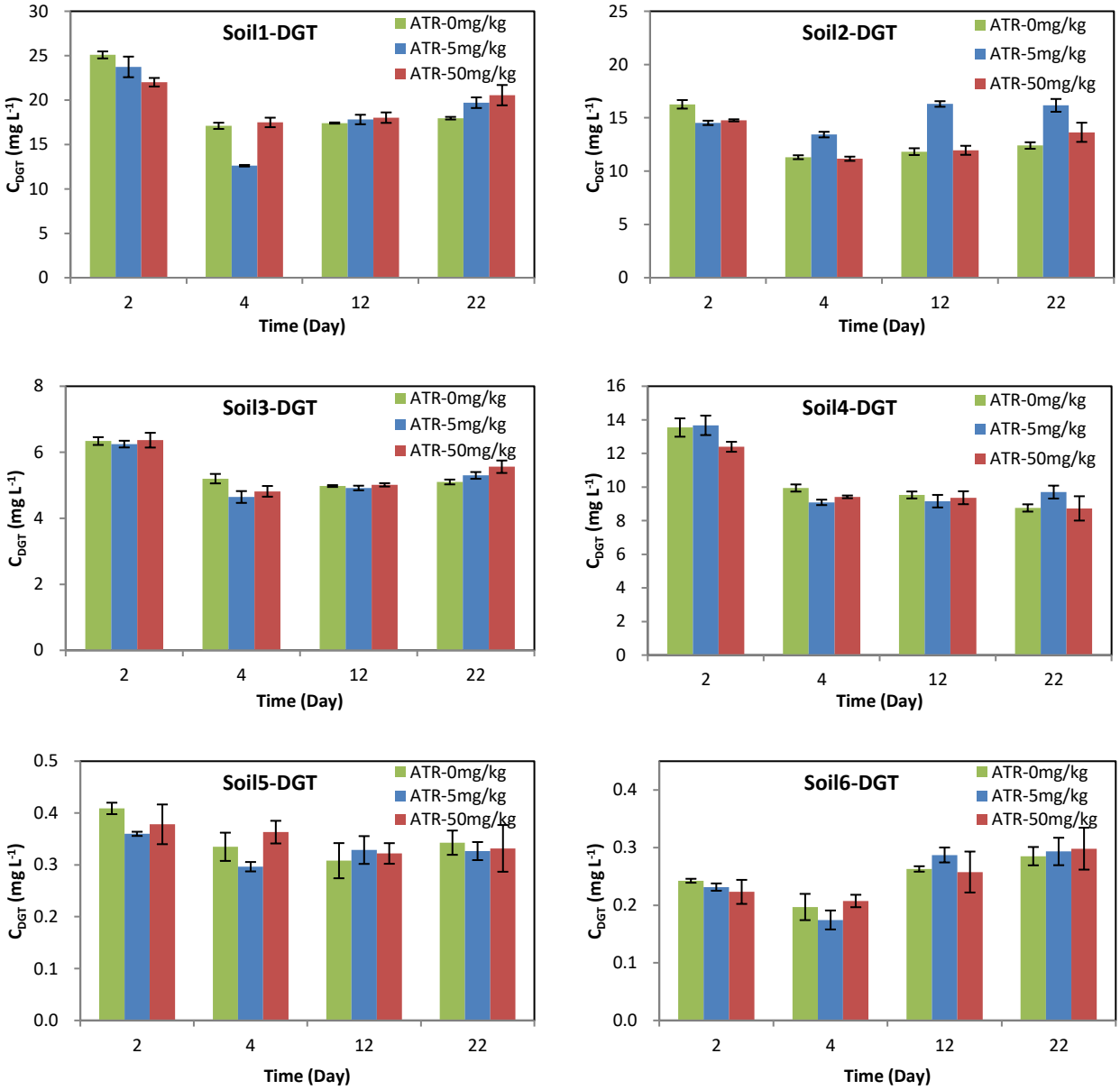


Figure 6.5 As concentrations in soil measured by DGT at three treatment levels of ATR with 4 aging times in the 6 test soils

6.3.3 Effect of ATR on *R* and K_d of As in soils

DGT continuously takes As out of the soil system during deployment. It depletes soil solution concentrations adjacent to the interface of DGT and soil. Resupply of As from the solid phase to the soil solution counteracts this depletion (Fitz et al., 2003). The extent to which soil solution concentrations adjacent to the DGT device are sustained

at their initial value during the deployment can be indicated using the ratio (R) of C_{DGT} to C_{SS}:

$$R = \frac{C_{DGT}}{C_{SS}} \quad \textbf{(6.1)}$$

The value of R is affected by the labile solid phase-solution phase partition coefficient, K_{dl} (Ernstberger et al., 2005), which is an indicator of the labile pool size of available As. It can be estimated as the distribution coefficient (K_d) of As in soils:

$$K_d = \frac{C_{SE}}{C_{SS}} \quad \textbf{(6.2)}$$

The R values in these soils are shown in Figure 6.6. They were between 0.1 and 0.55 in soils 1,2,3 and 4, which indicates that C_{SS} was partially sustained by resupply from the solid phase (Harper et al., 1999). The R values in soils 5 and 6 were ~0.1 implying that the resupply of As in these two soils depends on diffusion of As in soil solution. This is consistent with the K_d values shown in Figure 6.7 ; the K_d values for soils 5 and 6 were lower than in the other soils, illustrating that these two soils had a greater fraction of non-labile As and a smaller labile pool size of As, leading to less resupply to the pore water.

There appears to be no systematic change in R with time (see Figure 6.6). With the aging time increased, R was slightly decreased for soil 5, indicating a stronger adsorption of As on the solid phase. The addition of ATR also did not have an obvious effect on the R value (see Figure 6.6).The R value at 50 mg L^{-1} ATR dosed level in most soils (except for soil 2) would be higher than in the absence of ATR after aging for some time (at least 4 days). It may because neither a lower dose of ATR addition nor a short aging time for ATR to equilibrate with the soil could affect the resupply ability of soils.

ATR addition also had negligible impact on K_d with the increasing aging time (see Figure 6.7). An increase in labile pool size did not obviously affect the re-supply, since the increase of K_d in Day 4 did not cause a general increase of R on Day 4. However, in soil 2 at 5 mg L^{-1} ATR dosed level, R increased from 0.24 to 0.40 while K_d increased from 78 to 225 cm^3 g^{-1}. In soil 4 at 50mg L^{-1} ATR dosed level, R increased from 0.24 to 0.35 while K_d increased from 71 to 199 cm^3 g^{-1}, demonstrating that the increase in the labile pool size can reflect on the ability of resupply of As from solid phase to soil solution.

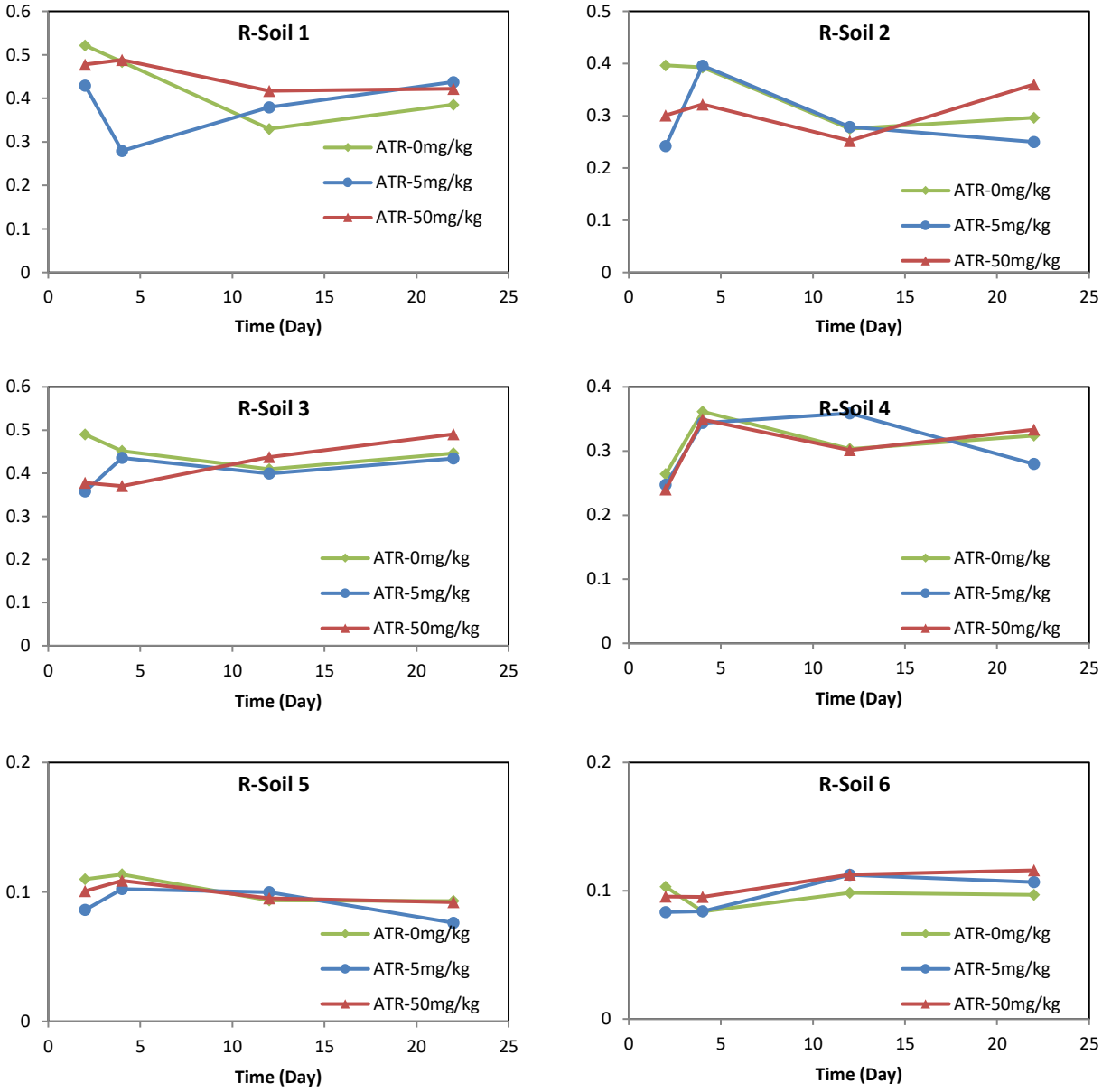


Figure 6.6 The *R* values of As at three ATR dosed levels with 4 aging time in 6 different soils.

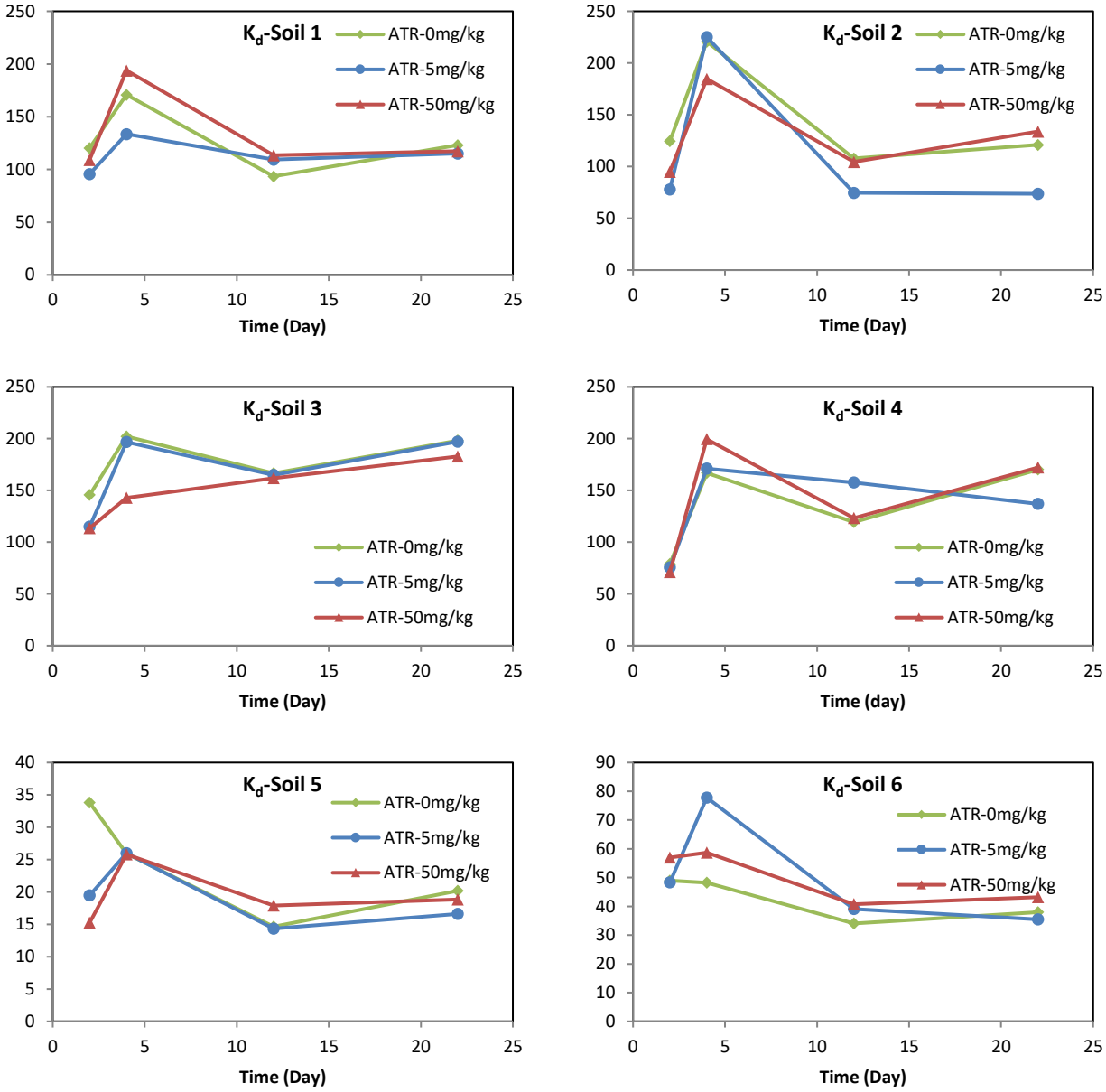


Figure 6.7 The K_d values of As at three ATR dosed levels with 4 aging time in 6 different soils.

6.4 Conclusions and environmental implications

The addition of ATR does not have obvious impact on the availability of As in the tested soils, so when ATR is applied in an As contaminated soil, the risk of organisms having greater exposure to As will not increase much. A lower dose level of ATR slightly increased the soluble fraction of As in some cases, but further addition counteracted

this effect. The labile pool size of As was slightly enhanced by the ATR addition, but did not affect the resupply ability much.

There is a need to investigate the availability of As affected by ATR in waters to understand the mechanism of the interaction between As and ATR.

Supporting information

Information including chemical standards, reagents, analytical methods, supplementary tables and figures was listed in the Supporting Information.

6.5 Supporting Information

CONTENTS

Chemicals and Reagents

Iron (III) chloride hexahydrate (FeCl3·6H2O), 2-(Nmorpholino) ethanesulfonic acid (MES), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$) and nitric acid (HNO_3) were all purchased from Sigma-Aldrich (UK).Water used in the experiments was supplied from a Milli-Q water purification system (>18.2 MΩ/cm,Millipore, UK). For making gels, gel solution was prepared and provided by DGT Research Ltd (UK), ammoniumpersulfate (APS) andN,N,N′,N′-Tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich(UK).

LC-MS analytical method

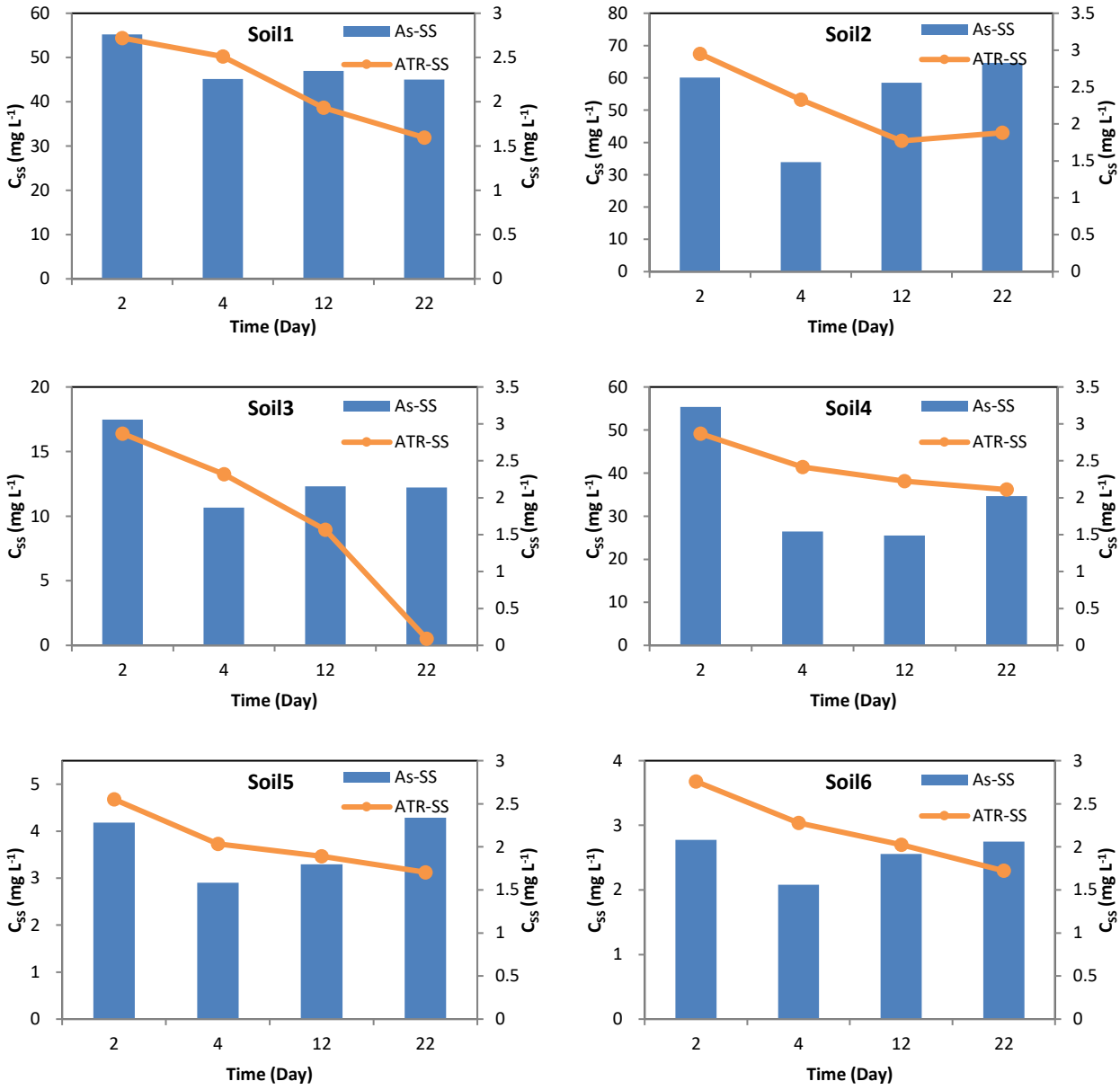
The measurement of atrazinewas performed with a PhenomenexKinetex Biphenyl column (50×2.1 mm, 2.6 μm). Liquid chromatography with mass spectrometric detection (LC–MS) was carried out using an AgilentLC coupled with a HP single quadrupole massspectrometer detector with an ESI interface. The mobile phase consisted of 5 mM ammonium formate in methanol (solvent A) – 5mM ammonium formate in MQ water (solvent B). The elution gradient began with 55% B from 0 min, then quickly increased to 80% B at 1 min, then kept for 1.5 min, then raised to 100% B at 2.6 min and kept constant for 3.4 min, followed by returning to the initial conditions within 0.5 min. Finally, the column was re-equilibrated for 15 min. The flow rate was 0.3 ml min^{-1}, the injection volume was 5 μL, and the temperature was set to 25 °C.

Table S6.1 Chemical and physical properties of tested soils

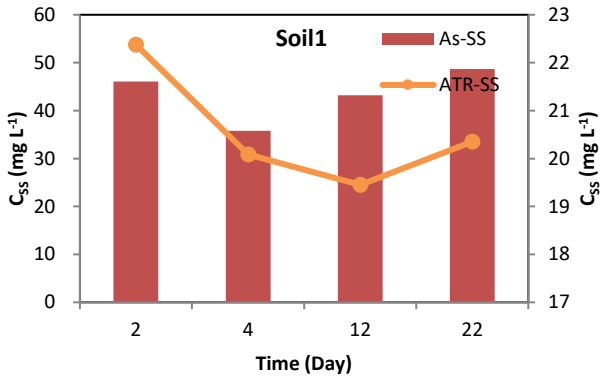
Soil ID	Soil type	Particle size (%)				pH	STOC[a]	CEC[b]	Total As	Available Fe	Available Al	Total Fe
		2-0.2 mm	0.2-0.02 mm	0.02-0.002 mm	<0.002 mm		g kg^{-1}	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}
Soil 1	loam	25.4	18.7	40.1	15.8	5.10	26.2	8.8	595.8	44.2	3.42	26.2
Soil 2	loam	33.1	15.3	38.2	13.4	4.96	27.1	8.7	499.0	44.4	3.65	27.1
Soil 3	clay loam	5.9	6.0	57.5	30.5	7.63	14.9	13	122.4	18.8	5.79	32.3
Soil 4	clay loam	3.6	1.0	59.4	36	5.22	13.3	13	143.7	85.2	3.07	32.3
Soil5	loam	35.0	23.8	30.2	11.0	4.00	5.6	14	26.0	19.8	3.84	36.2
Soil 6	sandy loam	57.4	14.3	19.2	9.1	4.39	6.7	12	32.3	36.1	3.22	49.4

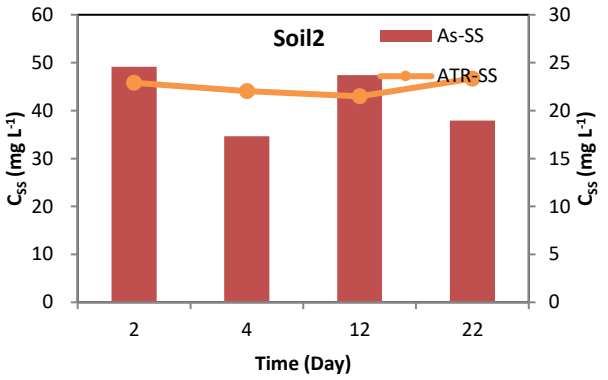
[a]STOC: soil total organic matter; [b]CEC: cation exchange capacity

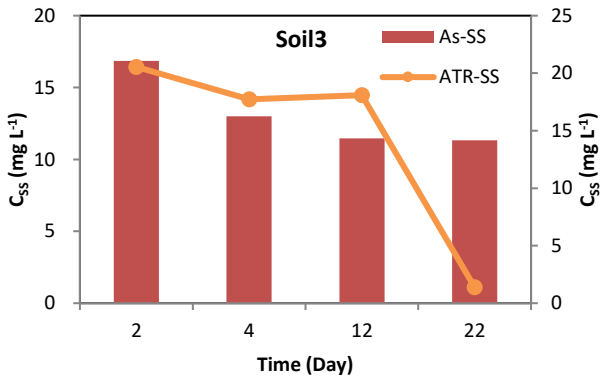
(a)

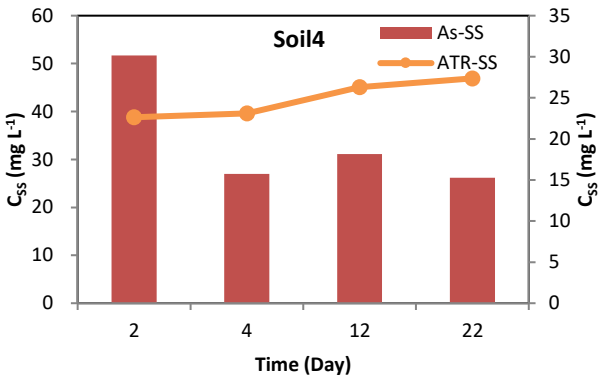

Soil1
As-SS
ATR-SS
C_{SS} (mg L^{-1})
Time (Day)
Soil2
Soil3
Soil4
Soil5
Soil6

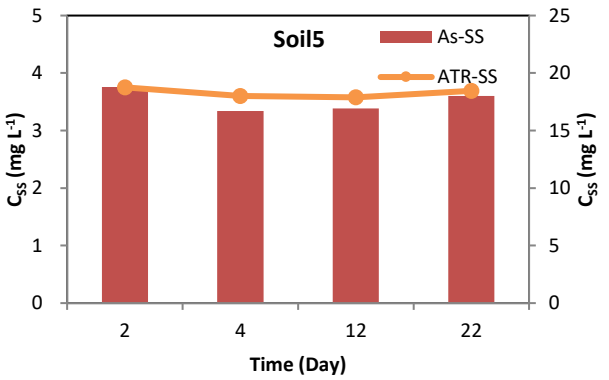
(b)

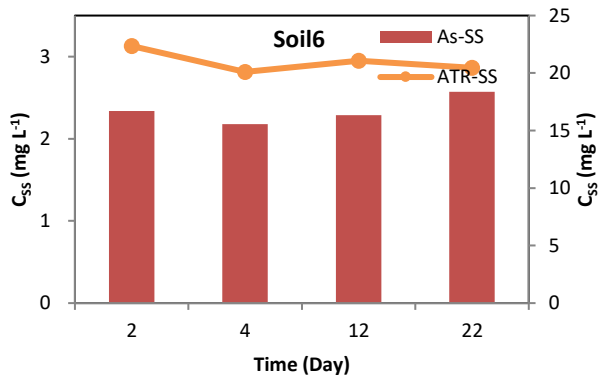

Soil1
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22


Soil2
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22

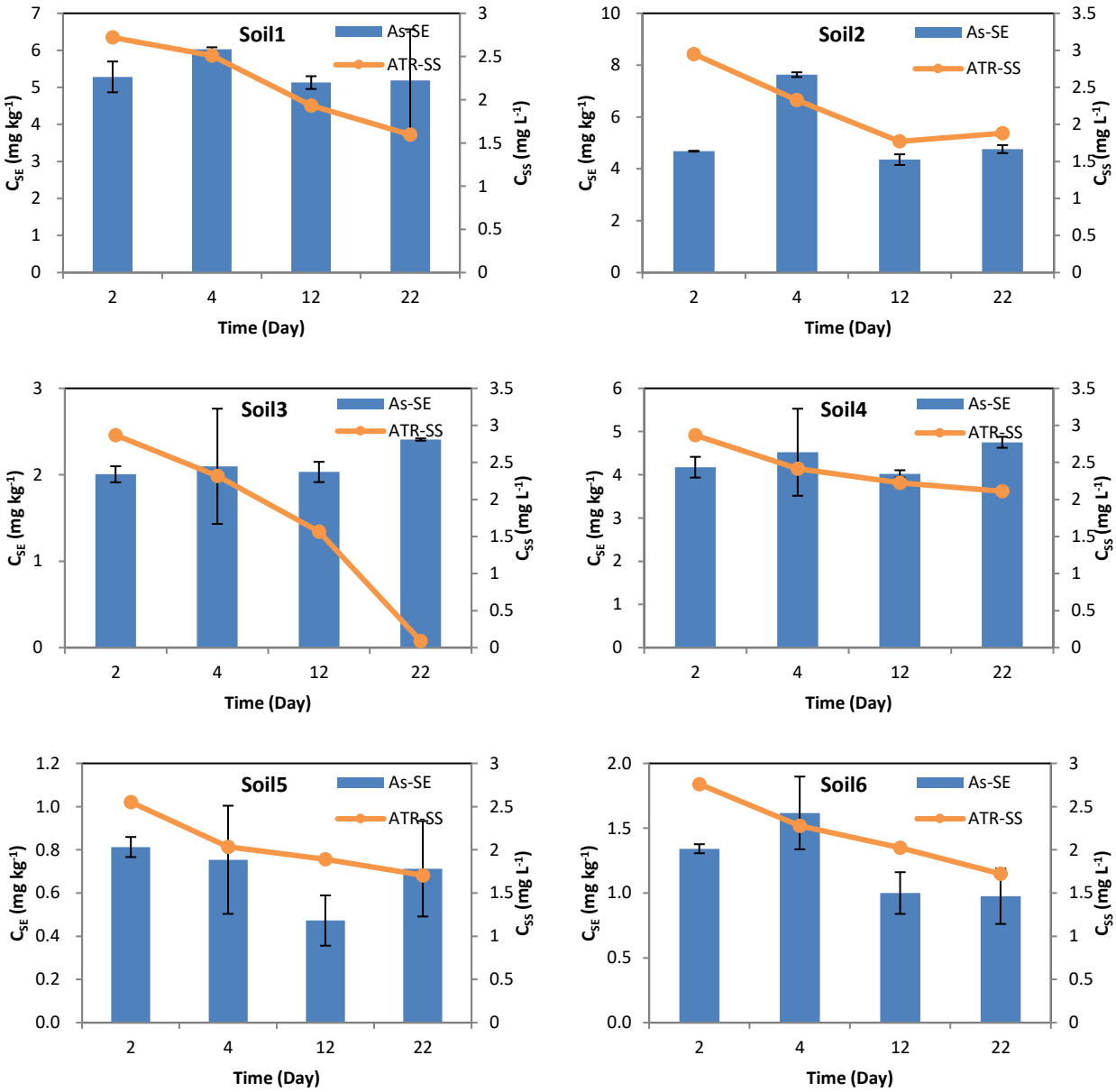

Soil3
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22


Soil4
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22

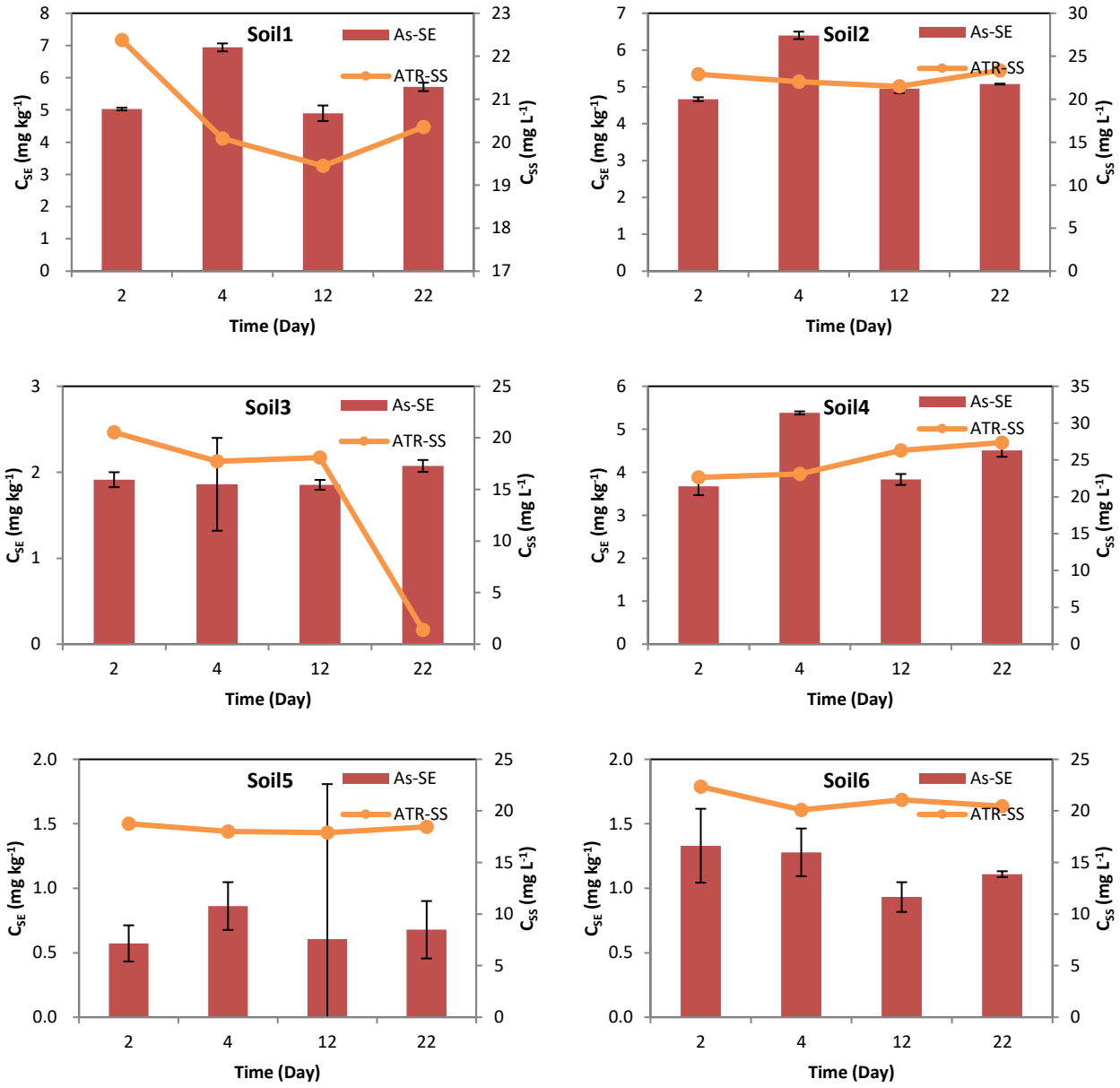

Soil5
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22


Soil6
As-SS
ATR-SS
C_{SS} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22

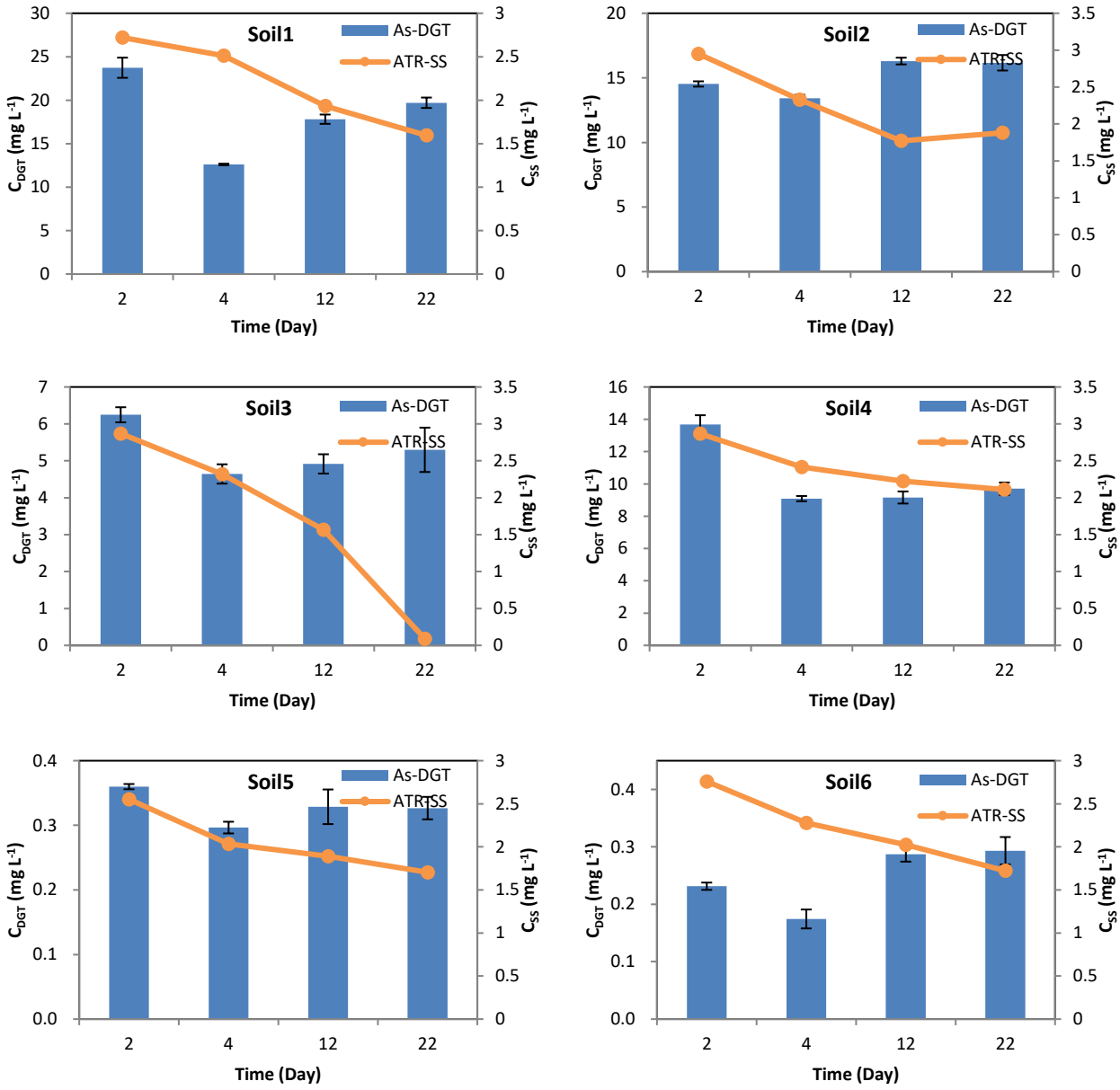
(c)


Soil1
Soil2
Soil3
Soil4
Soil5
Soil6
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
2
4
12
22

(d)


Soil1
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil2
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil3
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil4
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil5
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil6
As-SE
ATR-SS
C_{SE} (mg kg^{-1})
C_{SS} (mg L^{-1})
Time (Day)

(e)


Soil1
As-DGT
ATR-SS
C_{DGT} (mg L^{-1})
C_{SS} (mg L^{-1})
Time (Day)
Soil2
Soil3
Soil4
Soil5
Soil6

(f)

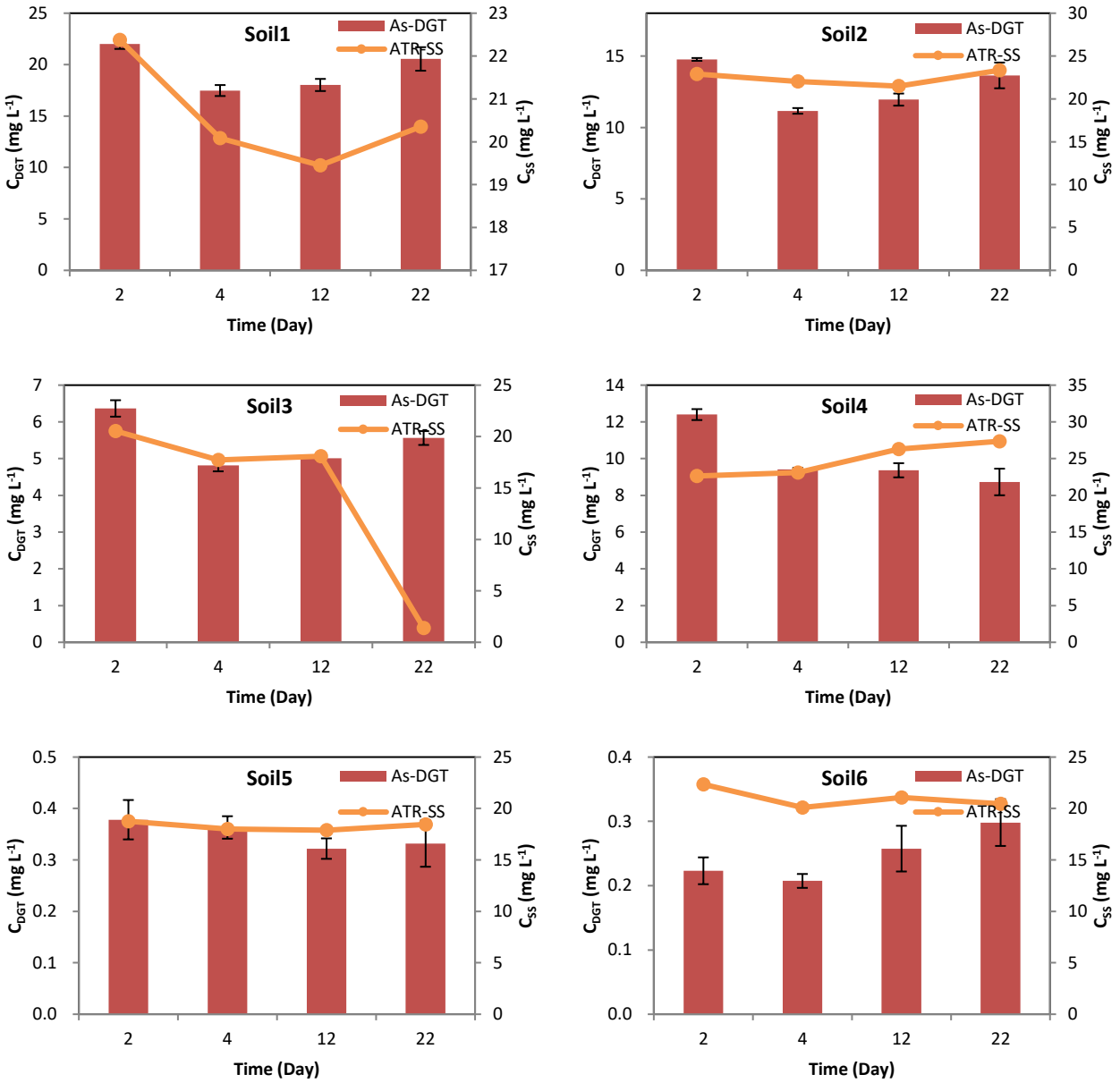


Figure S6.1 As concentrations measured by different methods in 6 soils with 4 aging times, with at two ATR dosed levels. As concentrations are shown on the left axis and ATR concentrations are shown on the right axis (a): As in soil solution at 5mg L^{-1} ATR; (b) As in soil solution at 50mg L^{-1} ATR; (c):$NaHCO_3$-extractable As at 5mg L^{-1} ATR; (d):$NaHCO_3$-extractable As at 50mg L^{-1} ATR; (e): As concentration measured by DGT 5mg L^{-1} ATR; (f): As concentration measured by DGT 50mg L^{-1} ATR.

Chapter 7: Conclusions and Future work

7.1 Conclusions

A novel DGT technique has been successfully developed for measuring pesticides quantitatively in waters and soils. It has been applied to predict the bioavailability of atrazine (ATR) to maize and assess the aging effect to the labile pool size and re-supply kinetics of atrazine in soils. The effect of ATR on the availability of arsenic (As) in As contaminated soils was also investigated with a previously developed DGT equipped with ferrihydrite binding gel. Method development was carried out with important pesticides selected from a range of chemical classes. Both tested binding gels (HLB and XAD 18) can be used for DGT devices as their capacities are large enough for polluted environment. However, HLB gel has a larger capacity. The uptake kinetics of both binding gels are fast enough to satisfy the requirements of an effective DGT sampler. However, XAD18 binding gel has a faster uptake rate. Tests of time dependence and different diffusion thickness validated the DGT theory. The performance of the DGT using the HLB binding gel was independent of conditions tested in the ranges of pH between 4.7 - 8.2, of ionic strength between 0.01 - 0.5 M and DOM concentration up to 20 mg L^{-1}. The DGT with HLB was selected for the subsequent research studies in soils and waters since it performed better overall. The technique was successfully validated in field conditions for in situ measurements and in different types of soils for obtaining available concentrations of pesticides with good accuracy and precision.

The ability of the DGT technique to predict the uptake of atrazine by plants was investigated using pot experiments with maize grown in 5 different soils. Results were interpreted by relating residues (parent compound and metabolites) in the soils and plants, in relation to soil properties, and the form and bioavailability of the residues. The results have shown that DGT could be used to investigate the bioavailability and degradation pathways of pesticides in soils. ATR and its 5 metabolites could be sampled and tracked in the soil-plant system. Hydroxylation

instead of N-dealkylation was the dominant degradation procedure observed along the analyte translocation pathway. Comparing with the other two measuring approaches (soil solution and solvent extraction), DGT performed best in predicting bioavailability of total ATR to maize. This was the first time DGT has been applied to the study in bioavailability of organic compounds and it was concluded that DGT could be a useful tool for tests of pesticide fate and bioavailability which are needed for regulation and risk assessment.

To further understand the fate and behavior of ATR in soils with time (aging), DGT devices were deployed in different types of soils at two ATR contaminated levels, and the DIFS model was employed to quantify/parameterize release of compounds from the soil solid phase to the soil solution. With increasing aging time, adsorption of ATR on the soil particles was generally strengthened, leading to the concentration decrease in both soil solution and the solvent extractable fraction. Soil properties influenced the behavior of ATR during aging; the availability of ATR is generally promoted by higher pH and lower OM, but these properties have an integrated impact on ATR when they came together in the real environment. The labile pool size of lower dosed soils increased to different extents, while it decreased in higher dosed soils. The same situation occurred in the study of the availability to resupply and the change of desorption kinetics of ATR from solid phase was also varied, which may result from the uncertainty of estimation using DIFS models.

Due to the lack of studies on the co-exposure and interferences of ATR and arsenic (As) in soil environments, DGT devices equipped with a precipitated ferrihydrite binding gel were deployed in six As contaminated soils with different properties and two ATR addition levels. The measurements of labile As showed that ATR didn’t greatly affect the availability of As, so the risk of organisms having greater exposure to As due to the existence of ATR would be insignificant. This could be the overall net effect of different processes and interactions between As and ATR in soils and soil solutions. However, the ATR addition slightly enhanced the labile pool size of As, but did not affect the resupply ability much.

7.2 Future perspective

This is the first time that DGT has been applied to measure pesticides in water and soils. Some work still needs to be undertaken to improve this technique and more applications of DGT should be conducted in the future.

This thesis only focused on the measurement of polar pesticides under various environmental conditions, but the use of DGT can be extended to a wider range of chemicals and conditions.

The field trials were conducted in rivers and ATR was the only target analyte detected. As DGT can be deployed in both water and soil, further applications can focus on the integrated measurements of analyte transport and fate through and within environmental compartments (water and soil).

Many research studies using DGT for metal bioavailability to biota have shown good correlations between the DGT-sampled metal fractions and plant concentrations; DGT can mimic the uptake of metals by roots. Bioavailability of pesticides is of great importance to risk assessment and it is specific to different organisms. Different thicknesses of diffusive layers of DGT could be employed to simulate the uptake of pesticides by different organisms to establish a database.

Modelling is a useful tool to study the fate and behaviour of pesticides in the environment. DGT can be incorporated with toxicological research to improve pesticide risk assessment.

The interaction between pesticides and metals is also needed to be investigated.

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