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**TESI DI DOTTORATO DI RICERCA**

**ASSESSING THE EFFICIENCY OF MODIFIED CLAYS FOR DECONTAMINATE  
AGRICULTURAL WASTE WATER BY PESTICIDE RESIDUES**

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# 1 General Introduction

Many anthropic activities, including the agricultural and food industries, give rise to environmental problems for which it is necessary to find solutions. The presence of undesirable substances in water, the soil and foodstuffs can pose a risk to the health and hygiene to humans and animals. It is therefore essential to study methods for removing pollutants from these matrices, as to make them compatible with the maintenance of healthy environmental conditions. This paper aims at verifying the possibility of using modified clays (or organic-clays) to remove contaminants from waste water coming from different areas. This work derives from the necessity to overcome the numerous, negative aspects of current techniques and offers new, effective, easy to use and economic methods.

A number of examples could be presented. This paper will provide two examples such as vineyards and greenhouses. These are two of many cases in which it is necessary to intervene with purification techniques. The systems in use today have several disadvantages which makes it necessary to find alternative methods which are as efficient, safe, easy to use and as economic as possible.

## 1.1 *Plant protection products*

Plant protection products (PPPs) most commonly known as *pesticides* are the chemical compounds mainly used in these areas. By their nature, PPPs are harmful to some forms of life. It is therefore not surprising that, at certain levels of exposure, they may be harmful to humans (Maddy et al, 1990; Mehler et al 1992). If PPPs are applied under appropriate cropping and climatic conditions in prescribed amounts using modern techniques according to good farming practices, they can be effective in pest control with little adverse effects on the surrounding environment. However, often measurements indicate the presence of PPPs on non-agricultural land, in the atmosphere, and in water.

PPPs emissions are generally due to both diffuse and point sources. Diffuse contamination via percolation, runoff, drainage and drift explains only a part of the applied PPPs that reach ground and surface water whereas to the direct losses can be attributed between 40 to 90% of surface water contamination by PPPs (Mason et al., 1999; Carter, 2000; Kreuger and Nilsson, 2001). Most direct losses are related to spillage resulting from the filling operation, spray excess and technical rest volumes in the tank as well as leakages of the spray equipment, pump and booms, rinsing water from cleaning the internal tank to avoid carry over effects onto the following crop, water from external cleaning of spray equipment, etc. (Isensee and Sadeghi, 1996; Torstensson and Castillo, 1997). In conclusion, these point sources are mainly linked to the filling and cleaning area on the farm. Therefore additional technological and infrastructural solutions are required to reduce these direct pesticide releases. Some possible solutions could include (a) the existence of a filling and loading area on the farmyard to minimize the release of pesticides (Rose et al., 2001; Rose, 2003) (b) the

cleaning process of the spray equipment in the field (Handbury, 1998; Balsari, 2003), (c) waste water treatment systems to separate and/or degrade the contaminants from the water fraction (De La Rocque, 2004; Osaer et al., 2001).

Concerning the greenhouses, even if in the actual European legislation (EC 1107/2009) states that these systems are considered growing systems that “prevents release of PPP into the environment” there are several studies which revealed the presence of PPPs and biocides in surface water nearby and in protected crop areas (Teunissen, 2005; Gonzalez- Pradas et al., 2002; Garratt et al., 2007). A first stage will be to understand if and in which way the PPPs used in greenhouses reach the water bodies and in which concentrations. A modelling approach seems to be the most appropriate tool for these studies. Positive results could represent a logic reason for developing decontamination schemes and will give important information for the latest development stage of the system. A cost-effective decontamination system could help to increase the use of these systems and to improve the environmental conditions by reducing water body contamination by pesticides. The use of a depuration system to collect and decontaminate the drained water from greenhouses could be a solution to avoid the PPPs surface water contamination. Furthermore, a depuration system which allows the use of water after the decontamination treatments could represent an important resource of water for greenhouses with closed loop irrigation systems. A comparison with the open-field cultivation will further help to collect important information for a future possible enlargement of use of decontamination system for other agricultural compartments than vineyards.

## ***1.2 Decontamination systems***

There are several types of decontamination systems which are proposed for treating agricultural waste water containing pesticides. A very recent study (Zapata et al., 2010) shows that combining a large-scale homogeneous solar photocatalysis with biological treatment in a composed system, to treat real industrial waste water polluted with commercial pesticide determinate the elimination of pesticides and reduces the dissolved organic carbon (DOC) and the chemical oxygen demand (COD) of the waste water.

Some other researchers focus attention only on biological treatment. The most world-diffuse biological system is the **biobed**, originally developed in **Sweden** and representing a simple and cheap construction intended to collect and degrade spills of pesticides on farms (Tortensson, 2000; Tortensson and Castillo, 1997). It consists of three components in a 60 cm deep pit in the ground: a clay layer at the bottom, a biomixture or biomix of straw, peat and soil filling the remaining depth and a grass layer covering the surface. The biobed is also equipped with a ramp to allow the sprayer to be driven and parked over the biobed. **Greenhouse biobeds** have also been developed, and their design varies from that of farm biobeds (Tortensson, 2002). However, the biobed has generated interest in several other countries (e.g., UK, Belgium, Italy, France, Peru and Guatemala) and its implementation has sometime led to modifications of the original biobed design into what are renamed biofilters, biomassbed, Phytobac, biobac and biotables. The **biofilters** are typical for **Belgium** and consist of two or three units of 1m<sup>3</sup> plastic containers stacked in a vertical pile

and connected with plastic valves and pipes. The biofilter substrate is a homogenized mixture of local soil, chopped straw and peat, or composted material or other materials (Pussemier et al., 2004; Pigeon et al., 2005). The biomass developed in **Italy** is the **biomassbed**, which utilizes biomixtures as filters through which pesticide-contaminated water is circulated and decontaminated (Fait et al., 2007; Coppola, 2007). Materials such as urban and garden composts, peach stones, vine branches, and citrus peel have been tested because of their availability and cheapness (Trevisan et al., 2004). Studies at laboratory scale using such mixtures have shown a high degradation of chlorpyrifos, metalaxyl, and imazamox (Vischetti et al., 2004). Two biobed systems have also been developed in **France** named **Phytobac** and **biobac**. **The Phytobac**, developed by Bayer Crop- Science, was inspired by the Swedish concept of the biobed. It consists of a 60 cm deep basin made of watertight materials to ensure complete retention of contaminants and effluents. The substrate consists of topsoil from the farm (70%) and chopped straw (30%). No grass layer is placed on the top, and a cover protects the bed from rainfall. **The biobac** is another system derived from the Swedish biobed and the Phytobac. It consists of a tank insulated from the subsoil and filled with a mixture of organic and mineral materials, mainly soil from the farm and chopped straw. The concept behind this system is that farm soil contains microorganisms, which over successive treatments have adapted to the degradation of pesticides used at the farm, and this natural detoxifying ability of the soil microflora can be maintained and encouraged in the biobac by the input of a supplementary source of carbon and energy, such as straw. In **Guatemala** the biobed takes the name **biotable** and consists of a cylinder half-buried in the ground and containing all of the elements of a biobed with a clay layer at the bottom, a biomixture (maize residues, soil, and peat), and grass layer at the surface. Because it is located above the ground level, it can be used as a table.

Generally the biological systems show a good efficiency on decontaminating water containing pesticides, 90% of pesticide contamination was removed from water treated in a prototype of the biomassbed installed in a vineyard and using a biomixture of vine branches, green compost, and topsoil (Fait et al., 2007). The mixture of topsoil and straw readily degrades pesticides in less than 1 year even at high concentrations in a Phytobac. In Denmark pilot and field-scale studies showed that most of the applied amounts of the pesticides were retained and degraded in the biobed but that significant leaching of the most mobile substances occurred.

However, due to the temperature and organic matrix dependence of the pesticide sorption in the system, its use in the field can sometimes be restricted (Castillo et al., 2008).

**The adsorption/filtration** is another well-known method used in the removal of hazardous compounds from polluted water. Adsorptive or reactive filters containing a medium that adsorbs or reacts with a water contaminant. Activated carbon filtration is an adsorptive process in which the contaminant is attracted to and held (adsorbed) onto the surface of the carbon particles (Yoshida et al., 1991). The efficiency of the adsorption process is influenced by carbon characteristics (particle and pore size, surface area, solubility of the contaminant, and contaminant attraction to the carbon surface). The medium for an activated carbon is typically petroleum coke, bituminous coal, lignite, wood products, coconut shell, etc. The carbon medium is

activated by subjecting it to steam and high temperature without oxygen. A variety of activated carbon materials have been used, such as, granular activated carbon (GAC), powdered activated carbon (PAC), carbon cloth, fibers, felts or carbon cloth electrodes, black carbon from wheat residues (WC), carbon black and commercial activated carbon (AC). The forms GAC and PAC are the most used since they are considered very capable and effective materials for the adsorption of a variety of pesticides. The treatment of pesticide waste water with activated carbon was reviewed by Kyriakopoulos and Doulia (2006). However, the high cost of active carbon together with the expensive process for its regeneration has led to the search for new inexpensive materials (Cruz-Guzman et al., 2005), such as the potential use of complexed organoclay adsorbents.

### ***1.3 Modified clays (organic-clays) and their adsorption function.***

The most frequently-used clay in the preparation of organic-clay is montmorillonite. Characterised by a structure of the 2:1 type, this clay has numerous isomorphic substitutions which give it a permanent negative charge. This is compensated by the cations (normally Na<sup>+</sup> and Ca<sup>2+</sup>) which can be exchanged by other cations present in a solution. The partial, positive charge in each cation makes it highly hydrophilic and, in the presence of water, greatly hydrated. This hydration, besides the presence of Si-O groups in the clay, also makes the surface of the mineral hydrophilic. Consequently, the adsorption of non-ionic, organic compounds by the clay is reduced in the presence of water because the organic compounds, relatively apolar, cannot compete with the water for adsorption sites on the clay surface. Modified clays are produced by means of substituting the cations originally present in the interlayers with organic cations. The most frequently-used organic cations are alkylammonium ions. The molecular structure of this substance has a central atom of nitrogen linked to four organic groups including a radical acid. Interaction between the clay and the organic molecule takes place by means of the charged part of the radical acid, which attaches itself to the walls of the interlayer by means of Coulomb mechanisms. The aliphatic part of the molecule renders the clay organophilic.

The insertion of the organic cation into the interlayer determines an increase in the basal distance of the clay and the removal of the water. When the cation is adsorbed to a lesser degree than the CEC of the clay, the mechanism involved is exclusively an exchange of cations. Van der Waal forces are responsible for the adsorption of greater quantities than the CEC. When the organic cation adsorbed exceeds the CEC, the organic-clay complex takes on a positive charge and is more hydrophobic than the unmodified clay (Zanetti et al., 2000). Moreover, the introduction of organic cations reduces the hydration of the clay and at the same time reduces the surface area of the mineral endowing it with hydrophobic characteristics. Krishna et al., (2000) observed a reduction in the surface area (BET) of a montmorillonite from 29.5 m<sup>2</sup>/g to 5.0 m<sup>2</sup>/g after interaction with the hexadecyltrimethylammonium (HDTMA). The structure of the modified clay is represented by regular organic/inorganic multilayers containing disorganised chains. According to the kind of organic cation used in the preparation of the organic-clays, these can prove to be suitable for interaction with both organic and inorganic compounds. This property makes them suitable for purifying soil and water

from pollutants of different kinds. The adsorption of the non-ionic compounds on the modified clay with quaternary ammonium cations having only one small or rigid functional group (methyl, ethyl or benzyl), appear very strong, of the competitive type and are expressed by non-linear isotherms. On the contrary, the adsorption of non-ionic compounds on a clay which has been modified by quaternary ammonium cations having long alkylic chains (12-18 C atoms) is inferior and in many cases produces a linear isotherm, of the not competitive type. It is inversely proportional to the solubility of the solute in water and it is quantitatively comparable to that of a natural soil. This is caused by the fact that the process takes place by partitioning. Therefore, according to the structure of the organic cation, the interlayer space, functions as an adsorbent or as a mean of partitioning of the non-ionic compounds present in the water. Tests on the adsorption of a mixture of benzene, toluene ethyl-benzene and o-xylene (BTEX) on bentonite modified with a quaternary ammonium salt have demonstrated that the organic compounds are absorbed by this matrix in greater quantity than unmodified bentonite forming a single plane in the clay interlayer which is perpendicular to the surface of the layer (Gitipour et al., 1997). The literature also reports studies on the adsorption of pesticides on organic-clay. Sanchez- Martin et al. (2006) showed that clays modified with octadecyltrimethylammonium bromide (ODTMA) were 100% more efficient than natural clays in eliminating the penconazol and the methalaxyl from the water.

Some researchers have also carried out studies on the simultaneous adsorption of organic pollutants and heavy metals on clay. Generally, the organic-clays have demonstrated a strong affinity with the organic molecules and little affinity with the heavy metals (Zhu and Chen, 2000). Several studies carried out by Herrera et al., (2000) show that montmorillonite treated with hexadecylpyridinium are effective in removing *Salmonella enteritidis* from watery solutions.

#### ***1.4 Models to estimate PPP emission from greenhouses***

A sector with relatively unknown impact on the environment is the horticultural sector. Greenhouse production is considered by the council regulation EC 1107/2009 to prevent release of PPPs into the environment, contrary to field conditions. This is one of the reasons for which the models able to estimate PPP emissions to ground and/or surface water from such kind of structures are limited or in some cases not even existing. Recently van der Linden (2009) showed in a position paper concerning the PPP emission from greenhouses by other routs than air that models which can be used to simulate leaching from soil bound protected crops exists whereas simulation models for emissions from hydroponic systems need to be developed. Coupling fate models to existing models of water flow for such systems seem promising. Existing models of water flow in hydroponic systems seem sufficiently detailed to be coupled to models on fate of PPPs. However the latter still need to be developed.

The models used at European level to calculate leaching to ground water after application of a PPP in the open field are the FOCUS models: MACRO, PEARL, PELMO and PRZM (FOCUS, 1995). In principle these models are also capable of calculating leaching of the PPP after applications to covered crops.



However, the models were not developed for simulating situations in which water and /or PPP are unevenly applied, i.e. applied spot wise or band wise. One may give preference to a particular model depending on prevailing circumstances (Dubus et al., 2002). For example, if interaction with ground water has to be considered and drainage to surface water may occur, then the use of the PEARL model (Tiktak et al., 2000) is suggested.

However, even if leaching models exist for soil bound cultivations, appropriate scenarios to calculate emissions have to be developed. According to sensitivity analyses of the existing leaching models most important parameters and data in the selection procedure are related to climate data and soil properties (Van der Linden, 2009). In this paper three scenarios were developed and the FOCUS PEARL MODEL was parameterised for soil tomato cultivation in open field and greenhouse situated in Italy a country with Mediterranean climate. Climate data for open field and greenhouse were taken from an open field and a greenhouse near Pisa in the Tuscany region of Italy.

## ***1.5 Conclusions***

The use of pesticides is more often limited due to the contamination of ground and surface water. Pesticide contamination of water can mainly be linked to point source contamination rather than to diffuse sources. Such point sources are areas on farms (vineyards) where pesticides are handled, filled into sprayers and where sprayers are cleaned. In order to reduce pesticide contamination from these point sources, different kind of chemical and biological systems are being researched. Biopurification is the use of living organisms, primarily microorganisms, to degrade the environmental contaminants into less toxic forms. The adsorption is one of the most used physic/chemical process for decontaminating waste water containing pesticides and consist of the attraction and held of this molecules on adsorbent surface. Low cost materials are more often researched as substitute adsorbents of activate carbon. Organoclay materials show a high efficiency on adsorbing pesticides and other organic pollutants from water. A new sector with important impact on environment seems to be the horticultural sector. However, very little information is available about the fate of plant protection products when released from greenhouses to aquatic systems. A modelling approach seems to be the most appropriate solution to quantify the releases from greenhouses and the magnitude of the impact. Such information will further be useful on the system development stage in order to obtain a cost – effective system which helpfully will contribute to increase the use of these depuration systems. However, both sectors, agricultural and horticultural, certainly need the implementation of on-site systems to reduce groundwater or surface water contamination.

## **Objectives**

Materials science is a field that is in constant evolution in today's world. Environmentally compatible materials, which are cheap and which have a great affinity with pollutants, are frequently used for

decontamination purposes in diverse, environmental compartments Clays are useful in various fields of science and technology. They are used for the purification of gases, to separate liquids, in catalytic processes and in environmental protection. These applications are possible due to their chemical and mechanical stability, their high specific area and their surface properties. The capacity of clay to adsorb substances is essentially determined by the structure of its pores and the chemical nature of its surface. Clay has a permanent negative charge caused by isomorphic substitution. This charge makes it suitable for absorbing cations. Moreover, the hydrophilic nature of clay makes it compatible with polar organic compounds. In order to make it possible for clay to adsorb both anions and hydrophobic organic compounds wide use has been made of the technique whereby the constituent cations are substituted with organic cations thus making the clay more hydrophobic and according to the quantity of organic cations adsorbed able to attract anions. In the light of the data reported in the general introduction regarding the interaction of clays modified with polar or apolar organic compounds and heavy metals, the present project aims at evaluating the possibility of using such materials for the decontamination of waste waters, coming from different areas such as greenhouses and vineyards. Both cases represent situations having a great environmental impact which require quick, effective solutions.

The specific objectives of the PhD thesis are:

- (a) To characterize and compare sorption kinetics and isotherms of pesticides on natural and modified clays.
- (b) To develop a depuration scheme in order to test the practical application of the most efficient modified clay for decontaminate pesticide-containing water from vineyards.
- (c) To find alternatives to the depuration scheme for pesticide containing on formulations anti-foaming agents.
- (d) To simulate pesticide emissions in horticultural and agricultural conditions (f.i. indoor and outdoor) in order to better understand the entity of the environmental concentration.

## 2 Pesticide Adsorption from Aqueous Solution by Modified Clays

### ABSTRACT

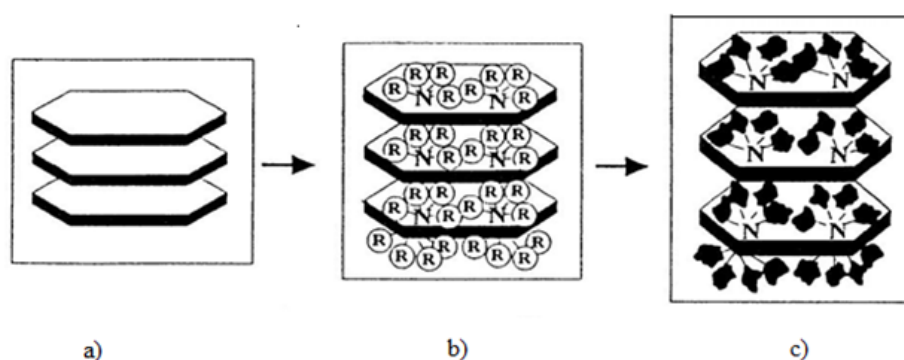
Sorption of three pesticides (chlorpyrifos, metalaxyl and penconazole) has been measured on a commercial clay montmorillonite and on the same mineral modified with either of two cationic-surfactant micelles. Both micelle–clay complexes, commercial names Cloisite 20A and Cloisite 30B, showed a good capacity to sorb all three pesticides from water, whereas their sorption on the natural montmorillonite was not described by an isotherm. Modelling sorption on both micelle–clay complexes showed that the Freundlich sorption constant ( $K_F$ ) was higher for chlorpyrifos on Cloisite 20A ( $K_F = 7.76$ ) than on Cloisite 30B ( $K_F = 5.91$ ), whereas the sorption of metalaxyl was stronger on Cloisite 30B ( $K_F = 1.07$ ) than on Cloisite 20A ( $K_F = 0.57$ ). Moreover the micelle–clay complex Cloisite 20A showed also a good affinity for penconazole, the maximum quantity adsorbed ( $q_m$ ) of  $6.33 \text{ mg g}^{-1}$  being 45% more than that on Cloisite 30B. Single-batch adsorption of each pesticide onto both micelle–clay complexes was studied using the Freundlich isotherm for chlorpyrifos and metalaxyl and the Langmuir isotherm for penconazole. The Cloisite 20A micelle–clay complex was predicted to require 23% less adsorbent to treat certain volumes of wastewater containing  $30 \text{ mg L}^{-1}$  chlorpyrifos, 43% more to treat metalaxyl similarly and 57% less to treat penconazole compared with Cloisite 30B.

### 2.1 Introduction

Contamination of soils, ground water and surface water by pesticides is currently a concern throughout the world because many of these compounds are detrimental to both human health and the environment. The increasing use of pesticides in agriculture and domestic activities is increasingly contaminating water resources. Among recently developed pesticides, organophosphate, triazole and phenylamide pesticides are commonly used. Chlorpyrifos is the most used organophosphate insecticide, although it is considered hazardous and has been included on the list of priority substances in the water policy established by the European Community (EC 2455/2001). Penconazole and metalaxyl are fungicides with a high level of use around the world especially in vineyards and greenhouses (Fait et al., 2007). Their residues in water leaving farmyards may be reduced by using a cost-effective depuration plan based on adsorption, which is one of the most efficient methods for removal of pollutants from water. Activated carbon is a very efficient adsorbent for removing many pesticides from water due to its high surface area and porosity (Leyva-Ramos et al., 1995) However its high cost restricts its use in the field (Sharma et al., 2007; Sharma et al., 2008) More recently, low-cost adsorbents, for example organoclay complex adsorbents, have been investigated as an alternative to activated carbon. These materials, often used in industrial and technological processes, have been proposed as sorbents for the immobilisation of industrial organic contaminants and pesticides (Boyd et

al., 1991; Xu et al., 1997; Sanchez-Martin et al. 2006), for the removal of pesticides from water (Cruz-Guzman et al., 2005, Polubesova et al., 2005), for the development of slow-release pesticide formulations (Carrizosa et al., 2000; Undabeytia et al., 2000), or for the examination of bioavailability potential (Singh et al., 2003) and photostabilization of sorbed pesticides (Margulis et al., 1992).

As explained on the previous Chapter, such organoclay complexes are clay minerals modified with a quaternary ammonium salt containing one or more aliphatic chains. The quaternary ammonium cations interact with clays and replace the exchangeable inorganic cations on their surfaces, forming a stationary phase in the clay particles. In addition, as a result of the larger size of the quaternary ammonium cations compared with that of the replaced cations, the interlamellar distance (basal spacing) of the mineral increases which facilitates the attraction of other organic compounds (Fig.1) (Brigitte et al., 1996).



**Figure 1.** Structure of modified clay; a) individual stack of expandable clay platelets; b) clay surface modified by a quaternary ammonium cation; c) organophilic clay saturated with organic contaminant; N, nitrogen; R, radicals.

To achieve practical use of the modified clay for depuration, the main objective of the present Chapter is to report the equilibrium of the adsorption of the three pesticides onto two micelle-clay complexes and unmodified montmorillonite clay adsorbents; such determination of the maximum quantity of these pesticides adsorbed by mineral clays should allow us to obtain dose-effect relationships for practical application.

## 2.2 *Materials and methods*

### 2.2.1 **Natural Clay and Micelle–clay Complexes**

Natural montmorillonite clay (< 0.01 mm), characterized by a cation exchange capacity (CEC) of 92 mequiv per 100 g clay (Stretz et al., 2005), and montmorillonite modified with either of two (15) quaternary ammonium salts yielding clay micelles were used in the study. All three low-cost minerals, Cloisite Na+

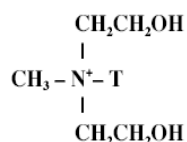
(montmorillonite), Cloisite 30A and Cloisite 30 B (Table 1), were bought from Southern Clays Products, Inc. (Texas).

**Table 1.** Characteristics of natural clay and micelle-clay complexes

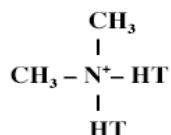
<i>Clays: commercial designation</i>	<i>Organic modifier</i>	<i>*Surfactant mol. wt.  (g mol<sup>-1</sup>)</i>	<i>Modifier concentration</i>		<i>d<sub>001</sub> (Å)</i>
			<i>meq/100g clay</i>	<i>g/100g clay</i>	
Cloisite Na <sup>+</sup>	None	none	none	none	11.7
Cloisite 30B	MT2EtOH <sup>**</sup>	372	90	33.5	18.5
Cloisite 20A	2M2HT <sup>***</sup>	550	95	52.3	24.2

\* WAXS d-spacing analysis (Stretz et al., 2005)

\*\* MT2EtOH: methyl, tallow ( T; ~ 65% C18; ~ 30% C16; ~ 5% C14), bis-2-hydroxyethyl, quaternary ammonium;



\*\*\* 2M2HT: dimethyl, dihydrogenated tallow (HT; ~ 65% C18; ~ 30% C16; ~ 5% C14), quaternary ammonium;



The d (001) basal spacing of the micelle–clay complexes increased from 11.7 Å (natural clay) to 18.5 and 24.2 Å (modified clays).

## 2.2.2 Pesticide

Chlorpyrifos (O,O-diethyl O-(3,5,6- trichloro-2-pyridinyl) phosphorothioate), metalaxyl (methyl N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-DL-alaninate) and penconazole (1-[2-(2,4-dichlorophenyl) pentyl]-1H-1,2,4-triazole) were used in the study. Chlorpyrifos is a solid with water solubility of 1.05 mg L<sup>-1</sup> and log Kow (where Kow is the 1-octanol/water partition coefficient) of 4.7. Metalaxyl is a solid with water solubility of 7100 mg L<sup>-1</sup> and log Kow of 1.75. Penconazole is a solid hydrophobic compound with water solubility of 73 mg L<sup>-1</sup> and log Kow of 3.72. Chlorpyrifos and metalaxyl (both 99.9% purity) were bought from Dow AgroScience, and penconazole (99.7%) from LabServ Analytica. Stock solutions (100 mg L<sup>-1</sup>) were prepared in methanol (Sigma-Aldrich, Steinheim, Germany) and stored at 4±2 °C in the dark. Working standard solutions were prepared daily. All reagents used were of analytical grade.

### 2.2.3 Clay Adsorption

Adsorption isotherms of pesticides by natural montmorillonite and the micelle-clay complexes were obtained using the batch equilibrium technique. Sorbent (50 mg) was treated with a solution (10 mL) of each pesticide in deionised water at concentrations of 5, 10, 15, 20, 25, 30 and 35 mg L<sup>-1</sup>, and the suspensions shaken at 20 ± 2 °C for 24 h. The suspension with the natural clay was shaken also at 35 °C in a thermostatted chamber. Subsequently, the suspensions were centrifuged at 5000×g for 15 min. After centrifugation, the suspensions were filtered using glass microfibre filters of 1,6 µm pore size, and an aliquot of solution (1 mL) was transferred to vials for analysis by high-performance liquid chromatography (HPLC). The teflon containers of 20 ml were used for the study.

### 2.2.4 HPLC Analysis

The pesticides were analyzed using an HPLC Agilent HP1100 Series, equipped with a Phenomenex Gemini® column C18 110A (100 mm x 4.60 mm i.d., 3 µm) and a diode-array detector. The column temperature was 25 °C. The mobile-phase reservoirs contained a 60/40 v/v % mixture of water (A) and acetonitrile (B) with a flow rate of 0.7 mL min<sup>-1</sup>. Elution was performed with a linear gradient: 0–5 min, A from 60 to 55%, B from 40 to 45%; 5–10 min, A from 55 to 44%, B from 45 to 56%; 10–15 min, A from 44 to 16%, B from 56 to 84%; 15–25min, A from 16 to 10%, B from 84 to 90%; 25–26min, A from 10 to 60%, B from 90 to 40%. The volume of the injection loop was 20 µL. The wavelength used for detection of chlorpyrifos was 290 nm and for metalaxyl and penconazole was 210 nm (Vischetti et al., 2008). The retention time was 7.9 min for metalaxyl, 14.4 min for penconazole and 19.1 min for chlorpyrifos; the instrumental limit of detection for all three analytes was 50 µg L<sup>-1</sup>.

### 2.2.5 Isotherm Calculations

#### 2.2.5.1 Langmuir isotherm

The Langmuir isotherm assumes monolayer sorption on a surface containing a finite number of binding sites, with uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as:

$$q_e = \frac{C_e K_L q_m}{1 + K_L C_e} \quad (\text{non-linear form}) \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (\text{linear form}) \quad (2)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  the equilibrium concentration of solute in the bulk solution ( $\text{mg L}^{-1}$ ),  $q_m$  the monolayer adsorption capacity ( $\text{mg g}^{-1}$ ) and  $K_L$  is the constant related to the energy of adsorption ( $\text{L g}^{-1}$ ).  $K_L$  is the reciprocal value of the concentration at which the adsorbent is half saturated.

### 2.2.5.2 Freundlich isotherm

The Freundlich isotherm assumes that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution varies with concentration. The Freundlich equation may be written as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (\text{non-linear form}) \quad (3)$$

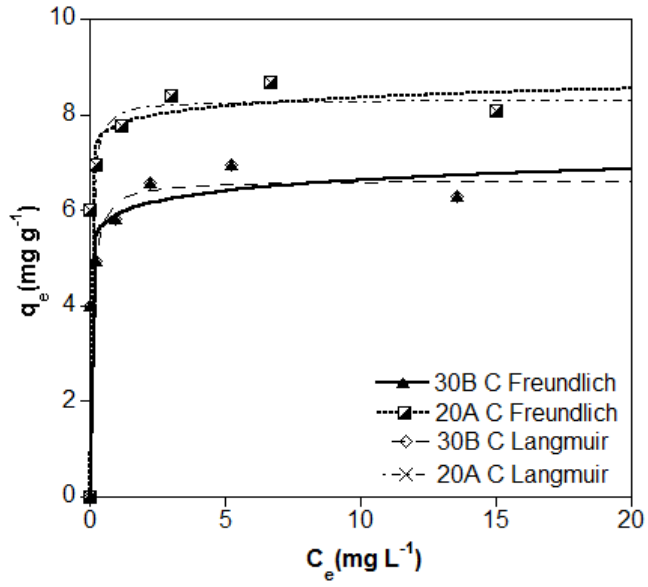
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{linear form}) \quad (4)$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  the equilibrium concentration of solute in the bulk solution ( $\text{mg L}^{-1}$ ),  $K_F$  the constant indicative of the relative adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ ) and  $1/n$  is the constant indicative of the strength of the adsorption.

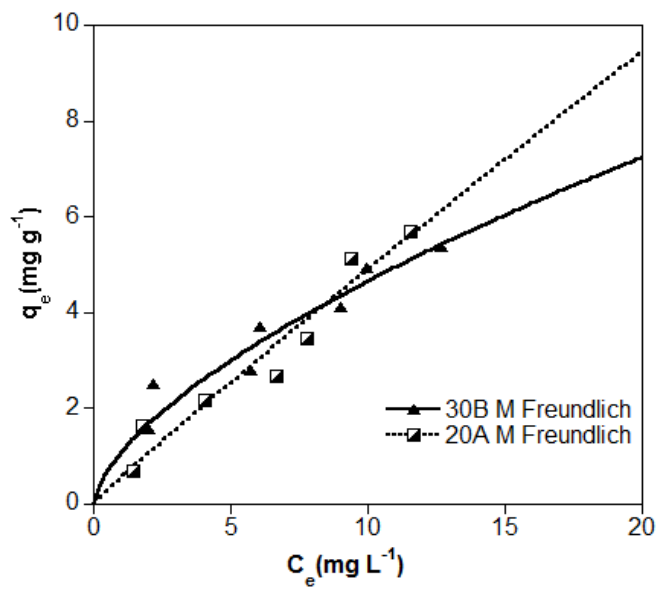
## 2.3 Results and discussion

### 2.3.1 Adsorption

The measurements of adsorption equilibrium provide the basic physicochemical data to allow evaluation of the applicability of the adsorption process, and two isotherm models commonly employed in this regard, the Langmuir and the Freundlich, were tested. The adsorption of the three pesticides on the natural clay (montmorillonite) was not described by an isotherm either at  $20 \pm 2$  or  $35$  °C, whereas isotherms were obtained for the two modified clay minerals. This first finding demonstrates that, even at the higher temperature, the basal spacing of the montmorillonite was not expanded sufficiently to allow entry of the pesticide molecules and the calculation of the isotherm. In contrast, the clay minerals modified with a quaternary ammonium salt (Cloisite 20A, Cloisite 30B) could be fitted with the Freundlich and Langmuir models respectively (Fig.2).

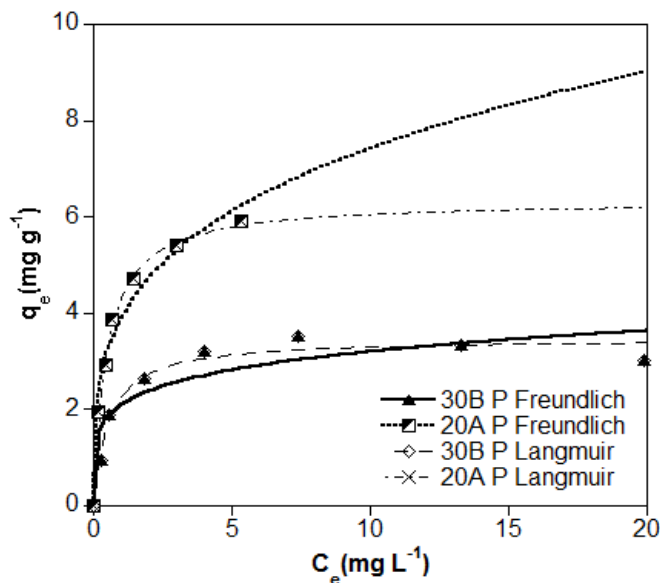


a)



b)





c)

**Figure 2.** Sorption isotherms of: a) chlorpyrifos (C), b) metalaxyl (M), c) penconazole (P) by the two micelle–clay complexes Cloisite 20A (20A) and Cloisite 30B (30B); data fitted to both the Freundlich and Langmuir models (only the former for metalaxyl).

The sorption isotherms of chlorpyrifos for both the modified clays were H-type (high affinity), subgroup 2 according to Giles et al. (1960) demonstrating a large or ionic affinity for the sorption sites. Solute molecules were completely absorbed at lower concentrations and there were decreasing sites available for adsorption on the adsorbent surface as the solution concentration was increased. For metalaxyl, both micelle–clay complexes gave double-layer isotherm types whereas the L-type isotherms (subgroup 2) observed for penconazole may indicate that sorption could also occur through physical forces (Witthuhn et al., 2005).

The constants for the isotherms of chlorpyrifos and penconazole were calculated from the non-linear form of both the Freundlich and Langmuir isotherm models, and those for metalaxyl from the non-linear form of the Freundlich model (Table 2). Measurements for chlorpyrifos were better fitted by the Freundlich isotherm with correlation coefficients of 0.98 on adsorption on Cloisite 20A, and 0.97 on adsorption on Cloisite 30B, than by the Langmuir isotherm (0.52 and 0.34). In contrast, penconazole sorption was better fitted by the Langmuir isotherm, with correlation coefficients of 0.99 for sorption on Cloisite 20A, and 0.97 for Cloisite 30B, than by the Freundlich isotherm (0.87 and 0.96). Metalaxyl sorption was fitted by the Freundlich isotherm, with correlation coefficients of 0.93 for Cloisite 20A and 0.92 for Cloisite 30B.

The Freundlich parameter  $K_F$  denotes the relative sorption capacity (or adsorption power) of the micelle–clay complex for the three pesticides: a high value of  $K_F$  reflects rapid sorption of the pesticides (Aksu and Donmez, 2006). The higher  $K_F$  values obtained for chlorpyrifos, 7.76 mg g<sup>-1</sup> for sorption on Cloisite 20A

and 5.91 mg g<sup>-1</sup> for Cloisite 30B, than for metalaxyl, 0.54 and 1.07 mg g<sup>-1</sup> on Cloisites 20A and 30B respectively, indicate that chlorpyrifos is more readily sorbed on both Cloisite 20A and Cloisite 30B than is metalaxyl. Furthermore, the higher K<sub>F</sub> observed for sorption of chlorpyrifos on Cloisite 20A than on Cloisite 30B showed that Cloisite 20A is the more efficient for the removal of chlorpyrifos from aqueous solutions. For the removal of metalaxyl, Cloisite 30B was the more efficient having the higher K<sub>F</sub> value.

There is general agreement that the strength of pesticide sorption onto micelle–clay complexes can be well represented by the constant 1/n. Sorption of chlorpyrifos and metalaxyl occurred favorably onto both micelle–clay complexes as shown by the value of 1/n being within the range 0–1.

The Langmuir parameters (q<sub>m</sub> and K<sub>L</sub>) were used to describe the sorption of penconazole onto both micelle–clay complexes (Table 2); the parameter q<sub>m</sub> reflects the maximum monolayer sorption capacity of these complexes and K<sub>L</sub> reveals the affinity of the sorbents. The maximum sorption capacity (q<sub>m</sub>) of Cloisite 20A for penconazole was 6.33 mg g<sup>-1</sup> and for Cloisite 30B was 3.47 mg g<sup>-1</sup> (Table 2).

**Table 2.** Freundlich and Langmuir constants for the removal of pesticides by modified clays

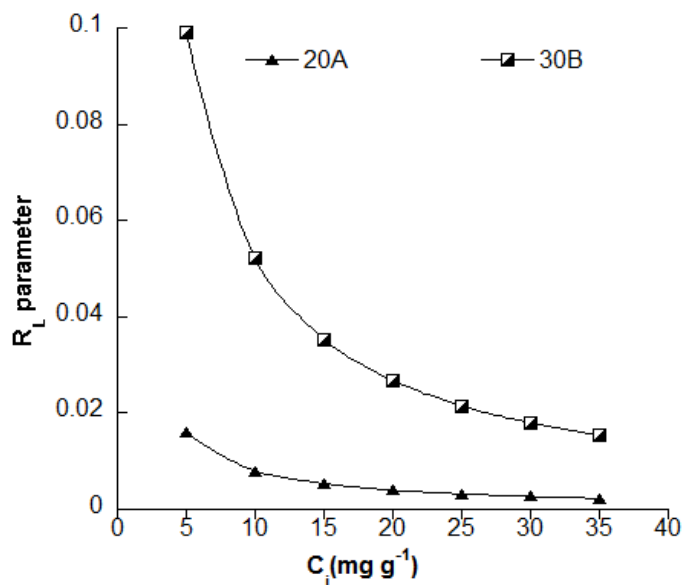
<i>Micelle-clay adsorbent</i>	<i>Pesticide</i>	<i>Freundlich</i>			<i>Langmuir</i>		
		<i>K<sub>F</sub></i> ( <i>mg g<sup>-1</sup></i> )	<i>1/n</i>	<i>R<sup>2</sup></i>	<i>K<sub>L</sub></i> ( <i>L g<sup>-1</sup></i> )	<i>q<sub>m</sub></i> ( <i>mg g<sup>-1</sup></i> )	<i>R<sup>2</sup></i>
Cloisite 20A	Chlorpyrifos	7.76	0.03	0.97	12.4	6.63	0.52
	Metalaxyl	0.54	0.95	0.93			
	Penconazole	2.13	0.18	0.87	2.12	6.33	0.99
Cloisite 30B	Chlorpyrifos	5.91	0.05	0.98	23.8	8.32	0.34
	Metalaxyl	1.07	0.63	0.92			
	Penconazole	3.88	0.28	0.96	1.82	3.47	0.97

The dimensionless constant separation factor or equilibrium parameter (R<sub>L</sub>) was used to determine the favorability of the adsorption of penconazole onto both adsorbents. The equation is given by:

$$R_L = 1 / (1 + K_L C_0) \quad (5)$$

The value of the parameter R<sub>L</sub> indicates the type of sorption. An R<sub>L</sub> value higher than unity indicates unfavorable sorption whereas an R<sub>L</sub> value of unity indicates linear sorption. Favorable sorption is shown by an R<sub>L</sub> value in the range 0 to unity. However an R<sub>L</sub> value equal to 0 indicates irreversible sorption (Vadivelan and Vasanth, 2005).

The calculated  $R_L$  values at different initial penconazole concentrations (Fig.3) showed that sorption by both micelle–clay complex adsorbents was more favorable at higher concentrations. Also the value of  $R_L$  in the range of 0 to 1 at all initial fungicide concentrations confirms the favorable uptake of the penconazole process, the adsorption of the fungicide being stronger on Cloisite 20A.



**Figure 3.** Separation factor ( $R_L$ ) for the adsorption of penconazole on the Cloisite 20A (20A) and Cloisite 30B (30B) micelle–clay adsorbents.

### 2.3.2 Mass Balance in Batch Experiments

The process of adsorption proceeds through various mechanisms, such as external mass transfer of solute onto the surface of the adsorbent followed possibly by an intraparticle diffusion mechanism. Therefore, to predict the adsorber size and efficiency in the removal of the pesticides by both micelle–clay complexes, an empirical procedure based on the adsorption equilibrium condition has been designed. Adsorption equilibrium is a dynamic concept based on the equal rates of both adsorption and desorption processes on the surface of the adsorbent. The physical chemistry involved may be complex and no single theory of sorption explains all the systems. However, adsorber design engineering requires only equilibrium data. Unuabonah et al. (2008) predicted the efficiency of a single-batch adsorber for the adsorption of an acid dye onto tetraborate-modified kaolinite clay adsorbent using such measurements.

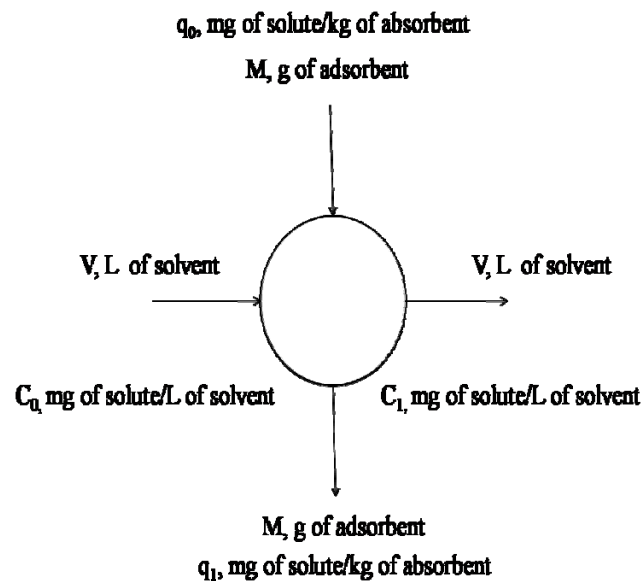
Sorption isotherm relations have been used to predict the design of single-stage batch-sorption systems to reduce the amount of pesticide in solution of volume  $V$  (L) from an initial concentration of  $C_0$  to  $C_1$  (mg L<sup>-1</sup>) (Fig.4). The theory underlying this objective is the following: at time  $t = 0$ ,  $q_0 = 0$  and as time proceeds, the mass balance requires that the amount of pesticide removed from the liquid equals that acquired by the solid. The mass-balance equation for the sorption system (Fig.5) can be written as:

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \quad (6)$$

wherein the amount of the adsorbent is  $M$  and the solute loading changes from  $q_0$  to  $q_1$  ( $\text{mg g}^{-1}$ ).

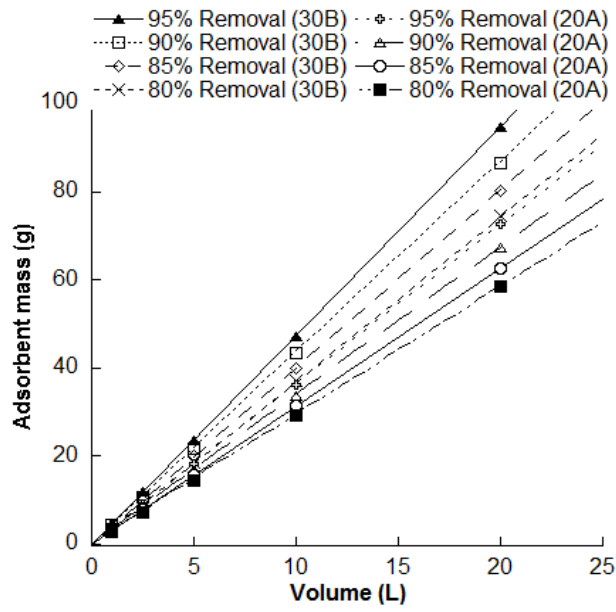
Under equilibrium conditions,

$$C \downarrow C_e \text{ and } q_1 \downarrow q_e. \quad (7)$$

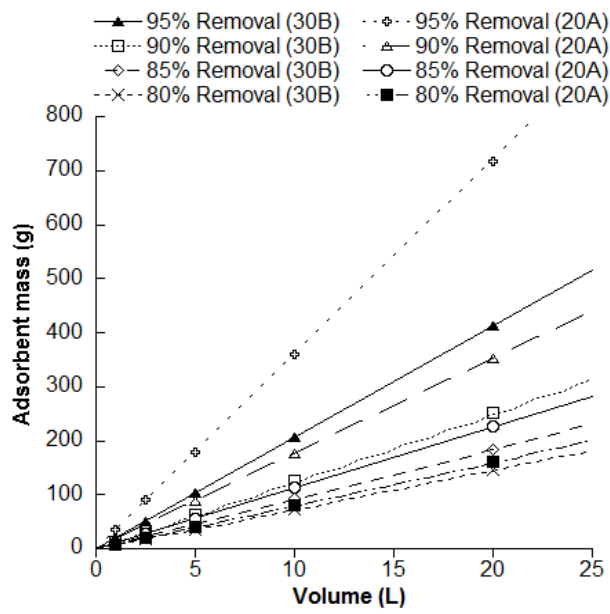


**Figure 4.** Schematic diagram for a single-batch adsorber for the adsorption of pesticides.

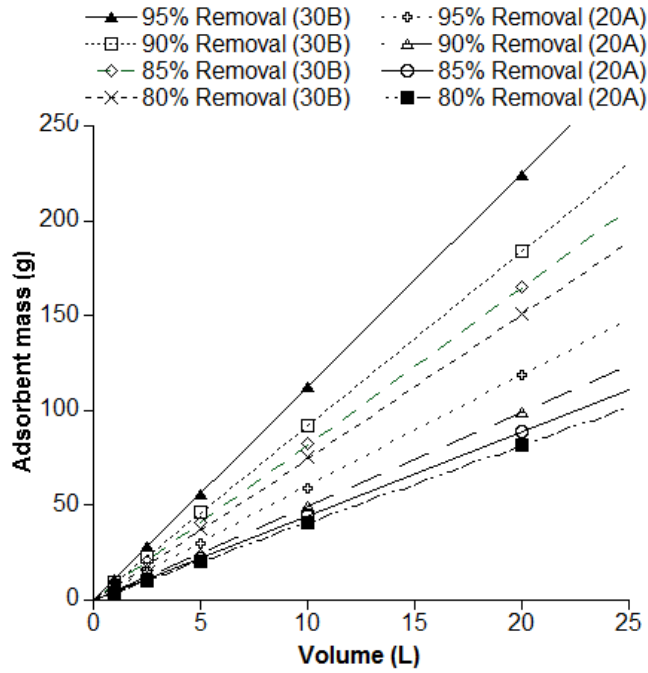
Based on the measured adsorption isotherms for Cloisites 20A and 30B, the Langmuir model for penconazole and the Freundlich model for chlorpyrifos and metalaxyl were selected to predict the amount of these adsorbents required to remove a certain percentage of each pesticide from various volumes of contaminated water.



a)



b)



c)

**Figure 5.** The predicted mass of Cloisite 30B (30B) and Cloisite 20A (20A) adsorbents required to remove specified percentages of pesticide from various volumes of polluted water containing: a) chlorpyrifos, b) metalaxyl, c) penconazole.

The equations include:

- For the Langmuir isotherm:

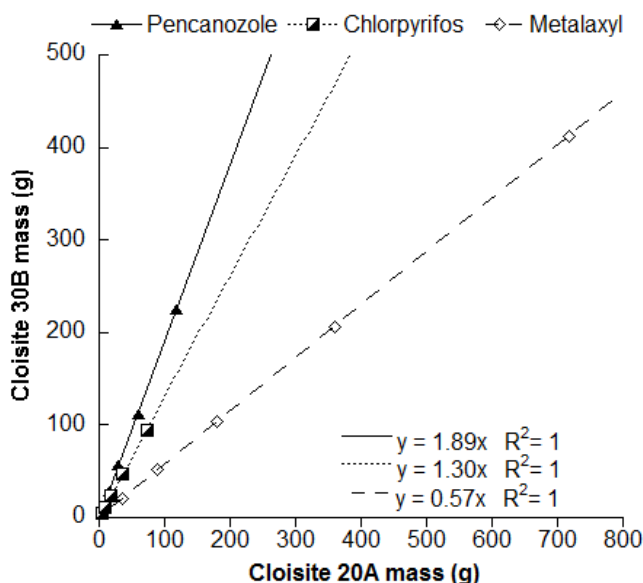
$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{\frac{q_m K_L C_e}{1 + K_L C_e}} \quad (8)$$

- For the Freundlich isotherm:

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{C_0 - C_e}{K_F C_e^{\frac{1}{n}}} \quad (9)$$

The predicted amounts of Cloisites 20A and 30B adsorbents required to remove a certain percentage of 30 mg L<sup>-1</sup> of each of the three pesticides from specific volumes of polluted water solution in a single-batch adsorber could thus be estimated (Fig.5). For example, to remove 95% of 30 mg L<sup>-1</sup> chlorpyrifos from 1, 2.5, 5, 10 and 20 L aqueous solution required 3.62, 9.06, 18.1, 36.3 and 72.5 g Cloisite 20A. Under identical conditions, a higher quantity of Cloisite 30B is required (4.72, 11.8, 23.6, 47.3 and 94.5 g). For metalaxyl under the same adsorption conditions, both micelle-clay complexes showed lower affinity; the quantity necessary for Cloisite 20A was 35.9, 89.8, 180, 359 and 718 g whereas for Cloisite 30B was 20.6, 51.6,

103.15, 206 and 413 g. For the efficient removal of penconazole under identical conditions, Cloisite 20A required 5.91, 14.8, 30.0, 59.2 and 118 g whereas Cloisite 30B required 11.2, 28.1, 56.1, 112 and 224 g.



**Figure 6.** Required mass of Cloisite 30B against that of Cloisite 20A micelle–clay adsorbent for removal from contaminated water of each of the three pesticides.

The quantities of Cloisite 20A needed to remove chlorpyrifos, metalaxyl and penconazole from water solution are respectively 1.89, 0.57 and 2.36 times lower than those of Cloisite 30B (Fig.6). This indicates that Cloisite 20A would be more efficient for use in treatment plants for the adsorption of chlorpyrifos and penconazole from aqueous solutions whereas Cloisite 30B would be more efficient for removal of metalaxyl.

## 2.4 Conclusions

The main objective of the present Chapter was to report the efficiency of different clay and modified clays in removing pesticide residues at concentrations that mimic the contamination level of waste water at the farmyard level. The adsorption of the three pesticides on the natural clay (montmorillonite) was not described by an isotherm either at 20±2 or 35 °C. This first finding demonstrates that, even at the higher temperature, the basal spacing of the montmorillonite was not expanded sufficiently to allow entry of the pesticide molecules and the calculation of the isotherm. Concerning the modified clays, the results obtained showed that the organic modifier increased the sorption of the pesticides by clay, depending on the type of organic modifier, and on the pesticide properties. The modified clay Cloisite 20A was showed to be more efficient for the adsorption of chlorpyrifos and penconazole from aqueous solutions whereas metalaxyl was showed to be more efficiently removed by Cloisite 30B. However, the adsorption of the three pesticides

onto the two micelle-clay complexes was measured to allow the determination of the maximum pesticide quantity adsorbed in order to obtain a dose-effect relationship for practical applications.

Work publication/presentation:

Suciu N. A. and Capri E. (2009) Adsorption of Chlorpyrifos, Penconazole and Metalaxyl from Aqueous Solution by Modified Clays. *J. Environ. Sci. Health, Part B.*, 44, 525-532

Suciu N. A., Capri E. Assessing Modified clays as adsorbent for decontaminate agricultural waste water by chlorpyrifos, penconazole and metalaxyl residues. 1st Young Environmental Scientists Meeting. 16-18 March 2009, Landau, Germany.



### **3 Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards**

#### **ABSTRACT**

The main objective in this Chapter was to develop and test a pilot scheme for decontaminating pesticide-containing water derived from pesticide mixtures used to protect vineyards, which scheme comprises adsorption by an organoclay and including a system where enhanced or rapid microbial degradation of the adsorbed residues can occur. In laboratory experiments, the Freundlich adsorption coefficients of formulations of two fungicides, penconazole and cyazofamid, onto the organoclay Cloisite 20 A were measured in order to predict the efficiency of this organoclay in removing these fungicides from the waste spray-tank water. Subsequently, the adsorption tests were repeated in the pilot system in order to test the practical operation of the depuration scheme. The adsorption tests with the pilot system show 96% removal of both fungicides over a few hours, similar to the efficiency of removal predicted from the laboratory adsorption tests. The formulation type may influence the efficiency of the adsorption. Regarding the waste disposal, for instance the organoclay composted after the treatment, cyazofamid showed significant dissipation after 90 days, whereas the dissipation of penconazole was negligible.

#### ***3.1 Introduction***

With the coming into force of the new European directive 2009/128/EC, the sustainable use of pesticides becomes a duty for all the European Member States. The directive establishes a framework to achieve sustainable use of pesticides by reducing the risks and impacts of pesticide use on human health and the environment and by promoting the use of integrated pest management.

Particular attention is accorded to pesticide contamination of surface and groundwater; appropriate measures to reduce exposure of water bodies to non-point sources (spray drift, drain flow and run-off) and point sources (pesticide handling procedures) should be adopted .

The current Chapter aims at validating the practical applications of the laboratory findings previously studied on Chapter 2 using waste water and at testing a possible approach to dispose of the adsorbed residues. The pesticides considered in this Chapter were penconazole and cyazofamid. Even if in the previous Chapter the fungicide metalaxyl was showed to be better adsorbed by Cloisite 30B than Cloisite 20A, his higher solubility in water in part determinate his low affinity for the organoclays and made it not appropriate for this study, a to much quantity of clay should has been required to remove it from water. The pesticide chlorpyrifos was as

well not considered further in the work principally due to his high octanol-water partition coefficient which made it easy absorbable by the plastic surfaces. In the previous Chapter Teflon containers were used for the adsorption study, but this was not possible in the present study.

Recent studies have shown that irradiation simulating sunlight could represent a suitable technique to photodegrade pesticide adsorbed on natural and modified clays (Tajeddine et al. , 2010). As an alternative, Kupper et al. (2008) demonstrated that the composting of 28 pesticides, adsorbed on an active biomix, was successful in full-scale composting plants, with a dissipation rate of more than 50% for more than two-thirds of the pesticides after 112 days of treatment. The objectives of this study were (1) to assess the adsorption of representative formulated pesticides on an organoclay and (2) to assess the mass balance in batch studies. The findings were then used (3) to test a pilot depuration system that could be utilized on farms. The depuration scheme comprises, beside the pilot plant for adsorption, a system where enhanced or rapid microbial degradation of the adsorbed residues can occur.

## 3.2 *Materials and methods*

### 3.2.1 Pesticide selection

The pesticides selected were cyazofamid (4-chloro-2-cyano-*N,N*-dimethyl-5-*p*-tolylimidazole-1-sulfonamide) and penconazole (1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole), two fungicides commonly used for integrated pest management in vineyards. Cyazofamid is used not more than three times per year for the treatment of grapevine against *Plasmopora*, according to the guideline of the “Integrated production disciplines” (<http://www.ermesagricoltura.it/Sportello-dell-agricoltore/Come-fare-per/Produrre-nel-rispetto-dell-ambiente/Fare-agricoltura-integrata-produzioni-vegetali/Disciplinari-di-produzione-integrata/Norme-general-2009>; [http://www.ermesagricoltura.it/content/download/8991/119268/file/d09\\_vite.pdf](http://www.ermesagricoltura.it/content/download/8991/119268/file/d09_vite.pdf) ). Penconazole was chosen as a fungicide used against powdery mildew (*Oidium*) also in viticulture. In integrated pest management in Italy, the chemical class of penconazole, called Sterol Biosynthesis Inhibitors (SBI), is authorized for use no more than three times per year. The commercial formulations of both pesticides are liquids, a suspension concentrate (SC) for cyazofamid and an emulsifiable concentrate (EC) for penconazole.

### 3.2.2 Chemicals

Analytical standards (99% purity) of cyazofamid and penconazole were purchased from Dr. Ehrenstorfer GmbH, Germany and LabServ Analytica, respectively. The two fungicides were used as the commercial formulations Mildicut (25 g L<sup>-1</sup> cyazofamid, ISK Bioscience Europe S.A., Brussels, Belgium) and Topas (100 g L<sup>-1</sup> penconazole, Syngenta Crop Protection S.p.A., Milan, Italy). Cyazofamid is a solid with water solubility of 0.114 mg L<sup>-1</sup> and log  $K_{ow}$  (where  $K_{ow}$  is the 1-octanol/water partition coefficient) of 3.2. Penconazole is a solid hydrophobic compound with water solubility of 73 mg L<sup>-1</sup> and log  $K_{ow}$  of 3.72. The

pesticide formulations were dissolved in deionised water at a concentration of 24 mg L<sup>-1</sup> for cyazofamid and 25 mg L<sup>-1</sup> for penconazole. The volume of pesticide formulation used was less than 1% of the final pesticide solution volume. All the reagents used were of analytical grade.

### 3.2.3 Adsorbent characteristics

The adsorbent used was the commercial organoclay, Cloisite 20 A, obtained by the modification of natural montmorillonite with a micelle of quaternary ammonium salts (Fig.1). The modification process and the main properties of the adsorbent have been discussed in detail in the previous chapters.

### 3.2.4 Laboratory studies

#### 3.2.4.1 Pesticide adsorption

Pesticide adsorption on the substrate was conducted using a batch equilibrium technique. Adsorbent (20 mg) was treated with pesticide solution (10 mL) at increasing concentrations. The concentrations of fungicides ranged from 16 to 24 mg L<sup>-1</sup> for cyazofamid and from 5 to 25 mg L<sup>-1</sup> for penconazole. Subsequently, the suspensions were shaken at 20 ± 2 °C for 3 h and centrifuged at 5000×g for 15 min. Preliminary experiments revealed contact for 3 h to be long enough for equilibrium to be reached. After centrifugation, the suspensions were filtered using glass microfibre filters of 1.6 µm pore size, and an aliquot of solution (1 mL) was transferred to vials for analysis by high-performance liquid chromatography (HPLC). The chromatographic parameters of the method have been described in detail in the Chapter 2. The wavelength used for detection of cyazofamid was 290 nm and of penconazole was 220 nm. The retention time was 17.5 min for cyazofamid and 15.9 min for penconazole. The instrumental limit of detection for both analytes was 20 µg L<sup>-1</sup>. The amounts of pesticide sorbed by Cloisite 20 A were determined from the difference in pesticide concentrations between the initial solution and the equilibrium solution.

Data were fitted to the Freundlich sorption isotherm:  $q_e = K_F C_e^{1/n}$  ; where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent (mg g<sup>-1</sup>),  $C_e$  the equilibrium concentration of solute in the bulk solution (mg L<sup>-1</sup>),  $K_F$  the constant indicative of the relative adsorption capacity of the adsorbent (mg g<sup>-1</sup>) and  $1/n$  is the constant indicative of the strength of the adsorption.

#### 3.2.4.2 Mass balance in batch experiments

The Freundlich equation for mass balance was employed as described in detail in Chapter 2 and was:

$$\frac{M}{V} = \frac{(C_0 - C_e)}{q_1} = \frac{(C_0 - C_e)}{q_e} = \frac{(C_0 - C_e)}{K_F C_e^{1/n}}$$

in which  $M$  ( $g$ ) is the amount of adsorbent and  $V$  ( $L$ ) is the pesticide solution volume.  $C_0$  and  $C_e$  represent the initial and equilibrium pesticide concentrations, while  $K_F$  and  $1/n$  are the experimentally determined Freundlich coefficients.

This equation was selected to predict the final pesticide concentration ( $C_f$ ) of a volume  $V$  ( $L$ ) with an initial pesticide concentration ( $C_0$ ) for a known amount of adsorbent  $M$  ( $g$ ). Under equilibrium conditions, the final pesticide concentration ( $C_f$ ) became the concentration at equilibrium.

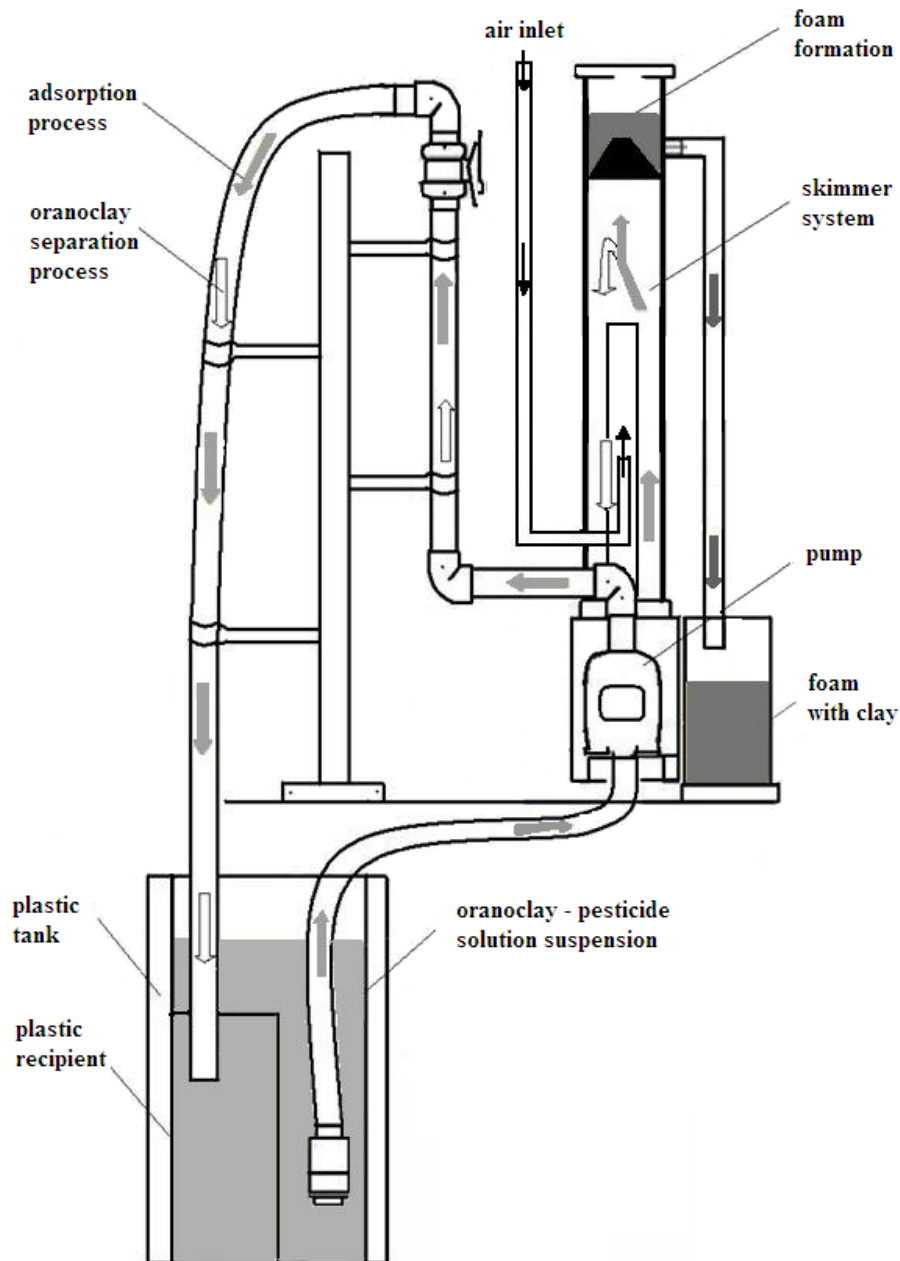
### **3.2.5 Pilot Adsorption Plant**

#### **3.2.5.1 Design and management**

A pilot adsorption plant was developed which included two parts, one where the adsorption takes place and the second where the adsorbent is separated from the suspension. The first part comprised a 120-L plastic tank, where the pesticide solution is added to the adsorbent. Subsequently, with an electric pump the suspension is pumped in a closed-tube circuit that starts and finishes in the plastic tank. This operation allows the agitation and so full contact of the pesticide solution with the adsorbent. At the end of the adsorption process, the suspension is pumped into the second part of the depuration system, a skimmer, where the clay particles are separated from the suspension in the form of foam. Foam fractionation has the capacity to remove dissolved organic compounds, proteins and small-sized particles from waste water (Qu et al., 2009). The skimmer is a cyclonic countercurrent system in which scum is trapped at the top and water is discharged from the bottom of a closed cylinder. The production of micro-bubbles is performed by the Venturi pump of the system, the “skimmer”, similar to analogous systems used in aquaculture that allows also the control of output of trapped scum. The water discharged at the bottom of the cylinder is recovered in the plastic tank and subsequently re-circulated to the skimmer system until no foam formation is visible. During the entire process, the foam is recovered under gravity in a 10-L plastic receptacle, installed near the bottom of the skimmer cylinder (Fig. 7).

For the adsorption process, the flow of suspension in the system was equal to the maximum outflow rate of the electric pump, whereas for the adsorbent separation process the suspension flow to the skimmer was one third of maximum outflow rate of the electric pump.

Preliminary tests revealed the use of the adsorbent as a concentrate suspension in water instead of as a powder at the beginning of the experiment considerably increased adsorbent recovery in the skimmer after adsorption.



**Figure 7.** Pilot system scheme

### 3.2.5.2 Adsorption tests

The pesticide concentrations used for the adsorption test in the pilot system were one third of the average fungicide concentrations measured in the field in a previous study (Fait et al., 2007), 34 mg L<sup>-1</sup> for cyazofamid and 10 mg L<sup>-1</sup> for penconazole. These concentrations could simulate the worst scenario occurring in vineyards: a residual fungicide volume in the spray tank after spraying one third of the total volume utilized that, subsequently, is diluted with the water used to wash the equipment. Generally the volume of water used to wash the spray tank is around two thirds of the capacity of the tank. To obtain these concentrations, formulations of cyazofamid (136 mL) and penconazole (10 mL) were added to water (98.5 L) in the tank. To obtain complete homogenization, the pesticide-contaminated water was re-circulated

around the first part of the system for 5 min and then sampled (10 mL) for determination of the pesticide concentration. Subsequently, the adsorbent, as a suspension concentrate, was added to the contaminated water and this final suspension re-circulated in the system for 3 hours. The concentrate adsorbent suspension was obtained by shaking for 15 min the powder adsorbent (100 g) with water (1.5 L) in a 2-L glass receptacle. At suitable time intervals, the suspension was sampled (10 mL), filtered and the filtrate analyzed for the remaining pesticide concentration by high-performance liquid chromatography. The initial pesticide concentrations were finally calculated considering the total volume of the contaminated water (100 L). The environmental temperature was  $26.8 \pm 1.8$  °C for the adsorption test with cyazofamid and  $22.7 \pm 1.4$  °C for that with penconazole ([http://www.arpa.emr.it/sim/?osservazioni\\_e\\_dati/dexter](http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter)).

### 3.2.5.3 Organoclay separation and quantification

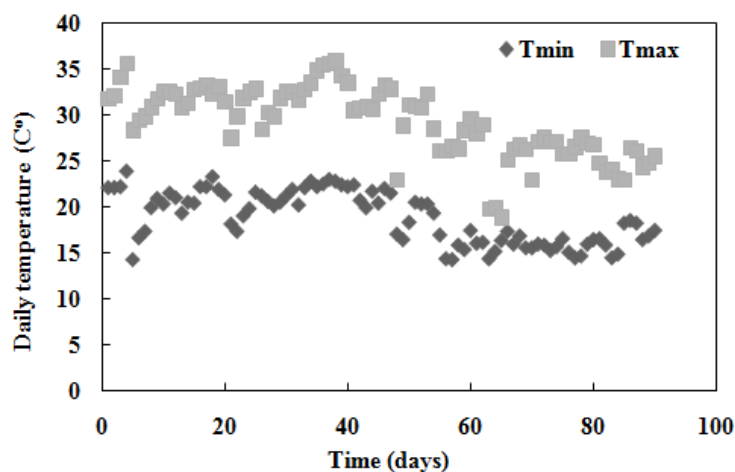
At the end of the adsorption process, the suspension was re-circulated in the skimmer system until foam formation stopped. The foam collected in the plastic receptacle was left to liquefy for 2 h, and then, to quantify its organoclay content, the liquid concentrate suspension was mixed to obtain a homogeneous suspension and 25 % of the total volume was taken and filtered using a Büchner funnel with weighed glass microfibre filters (1.6 µm pore size). Subsequently, the organoclay was heated for 12 h in an oven at 105 °C, and the total quantity of organoclay in the system was then calculated.

## 3.2.6 Degradation system

### 3.2.6.1 Design and management

The remaining suspension volume was then used to test for possible microbial degradation of adsorbed residues. The liquid concentrate suspension was mixed to obtain a homogeneous suspension, divided into two parts and passed under gravity through commercial compost. This compost (2 kg) was held in a 3-L plastic receptacle containing at the bottom a gravel layer of 2 cm. Holes at the bottom of the plastic receptacle, and the presence of a funnel between the first and a second plastic receptacle (5 L) placed below, permitted the collection and recovery of effluent. The gravel layer prevents the migration of small pieces of the compost. Subsequently, the recovered effluent was recirculated through the compost. At the surface of the compost, the suspension was distributed with a watering can to give a homogeneous distribution. On the first two days, the operation was done three times per day to allow the full deposition of clay with pesticide on the compost. Subsequently, the effluent was recirculated twice daily for seven days, daily until the 22<sup>nd</sup> day, once every two days until the 60<sup>th</sup> day and once each four days until the 90<sup>th</sup> day. On the 7<sup>th</sup>, 15<sup>th</sup>, 22<sup>nd</sup> and 60<sup>th</sup> days, a volume of tap water equal to the measured volume of effluent was added to the effluent. After the 7<sup>th</sup> day, a layer of plastic foam was placed on the surface of the compost to prevent the evaporation of water. For both fungicides, the experiments were carried out in duplicate. After two days a sample of the matrix was taken from each receptacle to determine the initial pesticide concentration. After this, samples were taken after 7, 15, 22, 42 and 90 days and analyzed. At the same time, a sample of effluent was taken

and analyzed in order to assess potential pesticide desorption. Any increase in pesticide concentration, for both penconazole and cyazofamid, could be detected in the effluent (data not shown). The minimum and maximum daily temperatures for the period of the study are presented in Fig. 8 ([http://www.arpa.emr.it/sim/?osservazioni\\_e\\_dati/dexter](http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter)).



**Figure 8.** Minimum and maximum daily temperature of the degradation period

### 3.2.6.2 Biochemical parameters

Prior to the degradation study, the compost was placed in the receptacles (six in total) and maintained wet, and after 4 days a sample was taken from each and used to determine the total aerobic population, the organic carbon content and the total nitrogen content of the compost. The same analyses were made at the end of the degradation study. Two compost receptacles were used as control samples.

The concentration of organic C in each sample of compost was determined by the Walkley–Black procedure (Nelson and Sommers, 1996); the total nitrogen ( $N_{\text{tot}}$ ) was measured by the Kjeldahl method (Bremner and Mulvaney, 1982). For the total aerobic population count, plating was done onto Plate Count Agar (PCA) and, after the incubation period of  $72 \pm 3$  hours at  $30 \pm 1^\circ\text{C}$ , the colonies were counted (Regione Lombardia 2002).

### 3.2.6.3 Pesticide extraction

Penconazole and cyazofamid was extracted from samples of the organic matrix ( $30 \pm 0.001$  g) of which the dry matter content was determined gravimetrically after drying at  $105^\circ\text{C}$  for 12 hours. Methanol (120 mL) was added to the organic matrix and shaken for 1 h at 180 rpm. The liquid phase was separated from the solid phase with a Büchner filter and glass microfibre filters of  $1.6 \mu\text{m}$  pore size. These steps were repeated three times after which the liquid phases were collected and concentrated with a rotary evaporator. After filtration, the glass microfibre filters were added to the organic matrix to avoid any pesticide loss.

Subsequently methanol (up to 10 mL) was added to the concentrated phase and dried under nitrogen. The pesticides were re-dissolved in methanol 90:10 (v/v) methanol – 0.1% H<sub>3</sub>PO<sub>4</sub> water solution (5 mL) and injected in the HPLC ( De Wilde et al., 2009).

### 3.2.7 Statistical analysis

For the degradation study, the linear regression model was used to evaluate the relationship between the variables of time (day) and active substance (a.s.) amount (% of a.s.) respectively. The amount found on the compost sampled after two days from application were considered to be the initial amount.

The first step was to calculate the regression curve:

$$y_1 = b_0 + b_1 x_1 \quad (10)$$

considering time as the  $x$  variable and the a.s. amount as the  $y$  variable. Using the Excel 2007 program, the  $b_0$  and  $b_1$  parameters were calculated:

$$b_1 = \frac{\sum xy - \frac{1}{n} \sum x * \sum y}{\sum x^2 - \frac{1}{n} (\sum x)^2} \quad (11)$$

where  $n$  is the number of observations (in this case  $n=6$ )

$$b_0 = \bar{y} - b_1 \bar{x} \quad (12)$$

where  $\bar{y}$  and  $\bar{x}$  are the averages of the variables time and a.s. amount respectively.

Subsequently, the deviance decomposition theorem was applied:

$$SS_y = SS_R + SS_e \quad (13)$$

The total deviance was calculated as:

$$SS_y = \sum (y)^2 - \frac{(\sum y)^2}{n} \quad (14)$$

The deviance of the regression model was calculated as:

$$SS_R = b_1^2 * \left[ \sum (x)^2 - \frac{(\sum x)^2}{n} \right] \quad (15)$$

and the error deviance was obtained with:

$$SS_e = SS_y - SS_R \quad (16)$$



At this point, a significance test was applied. The first hypothesis to verify was  $b_1 < 1$ , with a level of significance of 99% ( $\alpha=0.01$ ). A one-tailed test was used as it was in our interest to verify that  $b_1 < 0$  and not  $b_1 \neq 0$ .

Student's  $t$ -test was applied and a value of calculated  $t$  ( $t_c$ ) higher than the value of  $t$  tabulated ( $t_{tab}$ ) will indicate a value of  $b_1$  significantly  $< 0$ . The formula used to calculate  $t_c$  was:

$$t_c = \frac{b_1 - o}{\sqrt{\frac{SS_e}{n - 2} \sum (x_i - \bar{x})^2}} \quad (17)$$

### 3.3 Results and Discussion

#### 3.3.1 Pesticide adsorption in the laboratory tests

Over contact times in the range of 10–180 min, the removal efficiency of fungicide from solution (Fig. 9) increased with increasing agitation time and reached equilibrium at 60 min for penconazole and 180 min for cyazofamid. Therefore, shaking of the organoclay–water suspension for 3h was chosen as the equilibration time.

The Freundlich sorption model was fitted to the experimental sorption data (Table 3). The correlation coefficients ( $R^2$ ) were 0.93 for cyazofamid and 0.99 for penconazole. Comparing the adsorption behavior of the two pesticides, the highest  $K_F$  value was obtained for cyazofamid ( $26.9 \text{ mg g}^{-1}$ ), though the Freundlich isotherm exponent  $1/n$  was higher for penconazole. The strength of fungicide sorption on Cloisite 20 A can be explained by their aqueous solubility, as adsorption of organic compounds is generally inversely proportional to their aqueous solubilities (Giles et al., 1960). The aqueous solubility of penconazole is higher than that of cyazofamid, so making penconazole less adsorbed than cyazofamid. However, the higher  $1/n$  value for penconazole indicates a higher strength of adsorption of this fungicide on Cloisite 20 A. This higher strength is in agreement with its shorter equilibrium time.

**Table 3.** Freundlich parameters for cyazofamid and penconazole adsorption on Cloisite 20 A.

<i>Pesticide</i>	<i>Freundlich Coefficients</i>		
	$K_F (\text{mg g}^{-1})$	$1/n$	$R^2$
Cyazofamid	26.9	0.25	0.93
Penconazole	25.5	0.84	0.99

The slope ( $1/n$ ) values of  $< 1$  obtained for both fungicides (Table 3) indicate L-type isotherms, which are characterized by decreasing adsorption at higher concentrations; thus, sorption of both cyazofamid and

penconazole on Cloisite 20 A was concentration dependent (Briggs, 1981). This type of adsorption isotherm is observed when the molecules are adsorbed in a flat position, so not suffering strong competition from water molecules, which explains the high affinity to sorbent for solute at low concentrations. However, as the concentration increases, sorption sites become limiting, and therefore sorption decreases.

### 3.3.2 Pilot depuration system

#### 3.3.2.1 Pesticide adsorption tests

In the fungicide adsorption tests in the pilot depuration system (Table 4), the true initial fungicide concentrations experimentally determined were 31.2 mg L<sup>-1</sup> cyazofamid and 9.08 mg L<sup>-1</sup> penconazole. Starting from these concentrations, after 3 h of adsorption, the removal of both cyazofamid and penconazole from solution was 96.6 %. Comparing these results with those from the mass balance in batches, the percentage of removal of both fungicides from solution is similar to that predicted from the adsorption tests in the laboratory (Table 4).

**Table 4.** Removal of fungicides by adsorption on Cloisite 20A.

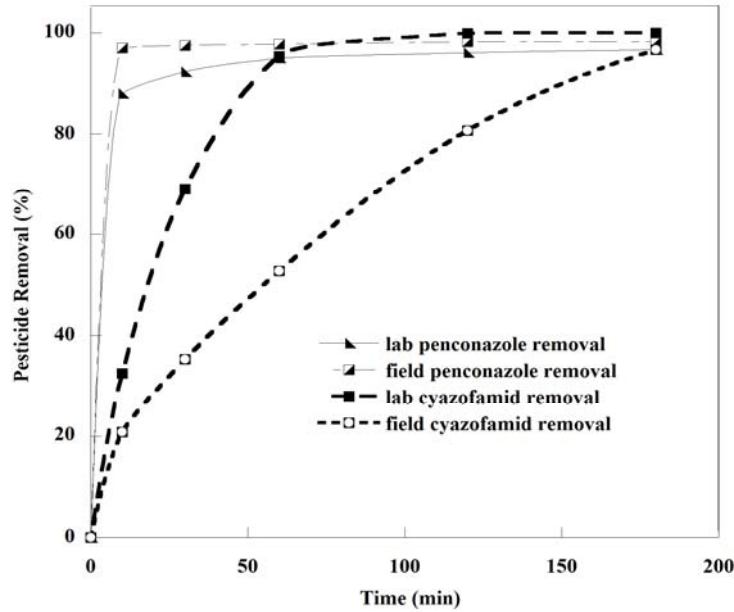
<i>Fungicide</i>	$C_{0R}^a$ ( <i>mg L<sup>-1</sup></i> )	$R_T^b$ (%)	$R_P^c$ (%)
Cyazofamid	31.2	95.3	96.6
Penconazole	9.08	96.9	96.6

<sup>a</sup> initial fungicide concentrations - determined experimentally

<sup>b</sup> fungicide theoretical removal – determined from mass balance in the batch system

<sup>c</sup> fungicide practical removal – determined in the pilot depuration system

The findings of the effect of contact time on fungicide removal from contaminated water in the pilot depuration system show that the time necessary to achieve 100% of the pesticide removal were comparable in both laboratory and field trials (Fig. 9). However, comparing the trend of pesticide removal, the adsorption in the pilot system for both compounds, is slower than in the laboratory. This could be explained by the differences between the solid/liquid ratios used in the laboratory and the pilot system. The solid/liquid ratio used in laboratory was 1:500 and in the pilot depuration system was 1: 1000.



**Figure 9.** Effect of contact time on fungicide sorption on Cloisite 20 A in laboratory and field tests; initial concentrations for laboratory tests were 14 mg L<sup>-1</sup> for cyazofamid and 20 mg L<sup>-1</sup> for penconazole.

### 3.3.2.2 Organoclay separation after the adsorption phase

After the adsorption phase the organoclay was separated from the suspension (Table 5). Around 65% and 45% of the organoclay utilized in the adsorption tests of penconazole and cyazofamid, respectively, was recovered in the foam. Approximately 5% of the total adsorbent amount utilized for adsorption of penconazole and 25% of that for cyazofamid remained in the skimmed water. This higher organoclay recovery in the foam for the adsorption test with penconazole can be explained by the presence of surfactants in its commercial formulation. However, the 5% that remained in the skimmed water is due to organoclay particles smaller than 5 µm, and which can be separated subsequently by sedimentation.

**Table 5.** Organoclay adsorbent separation after adsorption

<i>Fungicide</i>	<i>Foam</i>	<i>Skimmer system</i>	<i>Water after skimmer</i>
	(%)	(%)	(%)
Cyazofamid	45	30	25
Penconazole	65	30	5

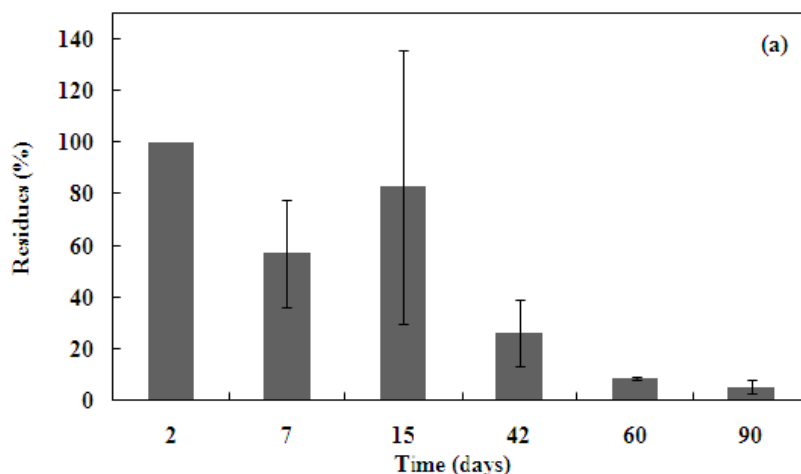
After the adsorption tests, the skimmer system was cleaned, with the washing water being recovered and the organoclay content quantified. Around 30% of the total organoclay utilized for adsorption, in both cases, was found to remain in the skimmer system stuck to the cylinder walls. After the adsorption test, this amount could be immediately recovered by washing the skimmer system or could be recovered later in the next adsorption cycle.

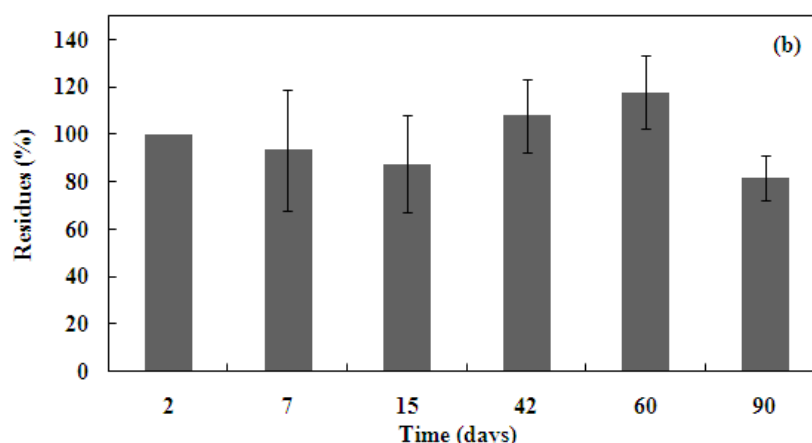
The organoclay separation from suspension in the skimmer system after adsorption was shown to be dependent on the presence of surfactants in the pesticide formulation. The adsorption test with cyazofamid, formulated as a suspension concentrate, gave an organoclay separation after adsorption 20% lower than that found for penconazole, which was formulated as an emulsifiable concentrate.

### 3.3.2.3 Removal of the pesticide residues

For both matrices considered, compost-clay with cyazofamid and compost-clay with penconazole, a study was made of their microbial development and of the amount of fungicide left in the clay over the experimental period. Bearing in mind the chemical structure of each pesticide, the chosen experiment time was 90 days, which represents the half-life ( $DT_{50}$ ) of penconazole (the more persistent of the two fungicides) under field conditions (<http://sitem.herts.ac.uk/aeru/footprint/it/Reports/509.htm>). It is assumed that the experiments include both chemical and biological degradation. Pesticide dissipation in similar matrices generally depends on their availability, persistence and affinity for organic matter. In this particular case, the fungicide dissipation depends also on their affinity for the modified clay, Cloisite 20A.

Looking at the persistence of the fungicides over the 90 days (Fig. 10), the concentration of cyazofamid decreased in the matrix compost-modified clay (Fig. 10a), whereas penconazole (Fig. 10b) showed no breakdown. Such difference in their behaviour could be expected as cyazofamid persistence is much lower ( $DT_{50}$  field = 4.5 days) than that of penconazole; furthermore, the Freundlich adsorption coefficient  $1/n$  is higher for penconazole on the modified clay, making it more strongly adsorbed and less available for degradation/dissipation.





**Figure 10.** Evaluation of fungicide residues in compost-clay matrices: (a) cyazofamid and (b) penconazole.

Student's  $t$  test was used to verify the existence of a relationship between the level of fungicide residue on the matrices compost-modified clay and time. The Student's  $t$  coefficient calculated ( $t_c=4.08$ ) confirms the significance for the degradation of cyazofamid with a value higher than the  $t$  tabulated ( $t_{0.05;4}=3.75; \alpha=0,01; n=4$ ), whereas for penconazole the  $t_c$  was 0.01 confirming that no significant degradation/dissipation occurred.

Concerning the changes in compost properties during the degradation study (Table 6), a decrease in organic carbon was observed which is the result of the mineralisation of the organic material with time. A slight increase in the total N content in the matrix containing cyazofamid and a significant decrease in the matrix containing penconazole was also observed. However the C/N ratio of all matrices, with and without modified clay with fungicides, was low, which could be attributed to the fairly high total N content.

**Table 6.** Chemical characteristics of the compost matrix without clay with fungicides and with clay with fungicides

	<i>OC</i> ( <i>g Kg<sup>-1</sup></i> )	<i>N<sub>(tot)</sub></i> (%)	<i>C/N ratio</i>
Initial <sup>a</sup>	238.9	24.1	9.9
Cyazofamid <sup>b</sup>	233	25.4	9.2
Penconazole <sup>b</sup>	216.9	21.8	9.9

<sup>a</sup> values obtained at the beginning of the experiment

<sup>b</sup> values obtained at the end of the experiment

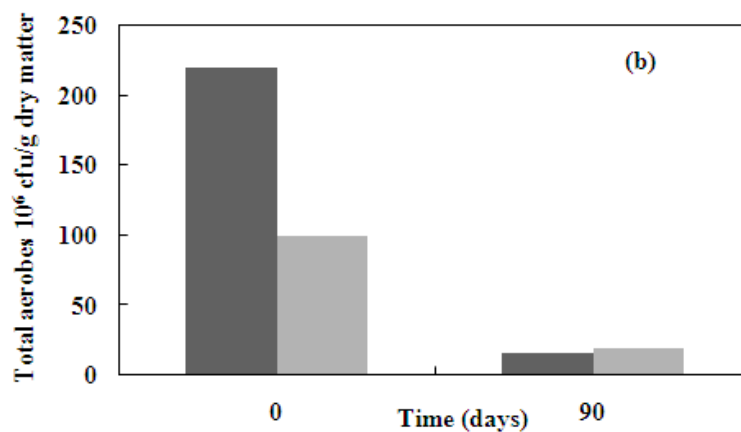
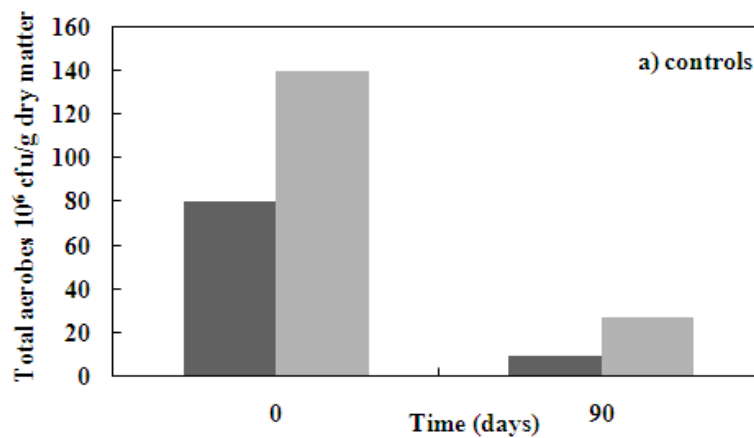
### 3.3.2.4 Development of the microbial population

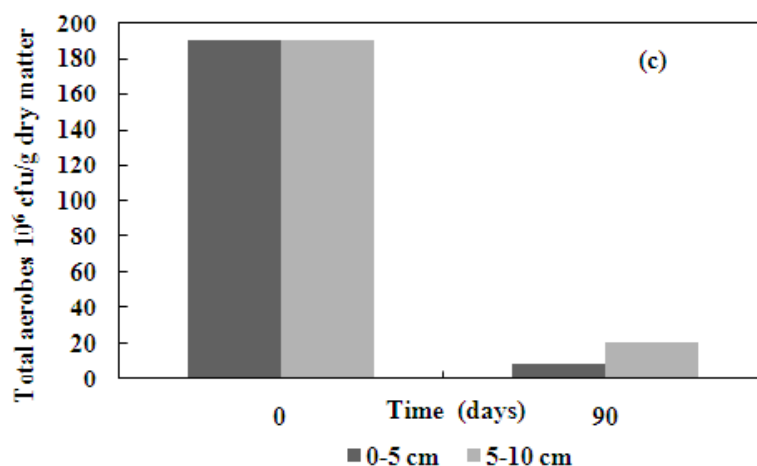
One of the possible reasons of the low dissipation rate measured could be due to the toxic effect of the quaternary salts. With this in mind, we studied the development of the total aerobic population in the different matrices, at two depths. The first layer was between 0 and 5 cm, and the second between 5 and 10 cm.

The general tendency in the microorganism populations in the controls (Fig. 11a) was a decrease in aerobes; after 90 days, the aerobes decreased approximately nine-fold with respect to time 0 in the first layer, and

approximately five-fold in the second layer. The same tendency could be observed on the compost-clay with cyazofamid and compost-clay with penconazole matrices (Fig. 11b, c). After 90 days on the matrices containing cyazofamid, the aerobes decreased approximately 14 times with respect to time 0 in the first layer, and 5 times in the second layer, while on the matrices containing penconazole the decrease was even higher, 22 times in the first layer and 9 times in the second layer.

The matrix used for control present a decrease on aerobes population similar with the decrease observed on the matrix with modified clay with cyazofamid. Thus the quaternary ammonium salt present on the modified clay does not have a toxic impact on the microbe population.





**Figure 11.** Evaluation of the total aerobe population in compost matrices: (a) control (no clay with pesticide), (b) clay with cyazofamid, (c) clay with penconazole.

Finally, it can be stated that mixing the modified clay after the adsorption with commercial compost and maintaining the obtained matrix under the described conditions did reduce the concentration of cyazofamid over the studied time frame; however no removal occurred for the persistent fungicide penconazole. Thus additional treatments still appear to be necessary in order to achieve lower concentrations that allow its disposal in the field as biomass. An improved composting process or a higher dilution in mass will allow agricultural use as required by the current legislations. If not this organoclay will represent hazardous waste and then is preferable the incineration rather than the composting.

### 3.4 Conclusion

The depuration scheme developed showed to be efficient for decontaminating pesticide-containing water derived from vineyards. The adsorption tests in the pilot system show a removal of both fungicides penconazole and cyazofamid similar to that predicted from the adsorption tests in the laboratory. The findings obtained in laboratory were completely repeatable at practical level and the mass-balance model developed show to be an essential tool for the development of the decontamination scheme. The recovery of the modified clay after the adsorption was shown to be dependent on the presence of surfactants in the pesticide formulation. For the adsorption test of penconazole, which contains a higher quantity of surfactants on the formulation, if compared with the formulation of cyazofamid, the recovery of Cloisite 20 A was 20% higher. This higher quantity of surfactants determines a longer foam formation process in the skimmer system. Concerning the waste disposal, for instance the organoclay composted after the adsorption, additional treatments appear to be necessary for persistent pesticides as penconazole, whereas fungicide cyazofamid shows a significant decrease after 90 days, in favourable conditions of compost humidity and environment temperature. However future decontamination research should be attempted for water contaminated with pesticides containing antifoaming agents in their formulations, in which case the present pilot system could not be applied.

Work publication/presentation:

Suciu N.A., Ferrari T., Ferrari F., Trevisan M., Capri E. (2010) Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards. Submitted to Environmental Science and Pollution Research

Suciu N. A., Ferrari T., Ferrari F., Trevisan M. and Capri E. Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards. Convegno SICA, Piacenza, Italy, 20-21 September 2010. Poster

Suciu N. A., Ferrari F., Trevisan M. and Capri E. Improving the Biomassbed™ efficiency by using modified clays. Pesticides Behaviour in Soils, Water and Air Conference, York, UK, 14-16 September 2009. Poster



## **4 Pesticide removal from waste spray-tank water by organoclay adsorption after field application to vineyards; alternative for pesticides containing antifoaming agents on formulation**

### **4.1 Introduction**

Considering the cost of treating water to remove pesticides, contamination should be treated at the source, more in particular on the farm before the discharge. On-farm adsorption system, profoundly described in Chapter 3, developed to treat pesticide-containing water, consists on adsorption of pesticides on commercial clays and the recovery of the clays from solution in a skimmer system. The adsorbed residues are subsequently deposited in a system where enhanced or rapid microbial degradation can occur. However, the system shows to have some leakages, for example, for pesticides that are formulated with agents which prevent the foam formation during the application. For these formulations the systems cannot be functional as the recovery of clay in the shimmer system cannot occur. Therefore, the current Chapter aims at evaluating alternatives for pesticides containing anti-foaming agents on formulations. One possible approach is the use of commercial compost as filter through which pesticide-clay suspension, at the end of the adsorption process, is passing and the clay is recovered. The objectives of this study were (1) to assess the adsorption of representative formulated pesticides on an organoclay and (2) to assess the mass balance in batch studies. The findings were then used (3) to test the alternative pilot depuration system that could be utilized on farms. The commercial compost with the recovered clay was used (4) to evaluate the degradation of the pesticide in time.

### **4.2 Materials and methods**

The pesticide selected was cyprodinil, a fungicide of the Anilinopyrimidine class commonly used for integrated pest management in vineyards. Cyprodinil is used in combination with fludioxonil not more than two times per year for the treatment of grapevine against *Botrytis cinerea*, according to the guideline of the “Integrated production disciplines”. The commercial formulation is a solid, water dispersible granule (WG).

#### **4.2.1 Chemicals**

Analytical cyprodinil standard (99% purity) was purchased from Dr. Ehrenstorfer GmbH, Germany. The commercial formulation used was CHORUS (50% cyprodinil, Syngenta Crop Protection, Milano, Italy). Cyprodinil is a solid with a water solubility of 13 mg L<sup>-1</sup> and log  $K_{ow}$  (where  $K_{ow}$  is the 1-octanol/water partition coefficient) of 4.

The fungicide formulation was dissolved in deionised water at a concentration of 10 mg L<sup>-1</sup> cyprodinil. The volume of pesticide formulation used was less than 1% of the final pesticide solution volume. All the reagents used were of analytical grade.

#### **4.2.2 Adsorbent characteristics**

The adsorbent used was the same as for adsorption of cyazofamid and penconazole, Cloisite 20 A, commercial organoclay obtained by the intercalation of a micelle of quaternary ammonium salts between the layers of natural montmorillonite (Fig.1). The main properties of the adsorbent are presented in the Table 1.

#### **4.2.3 Laboratory studies**

##### **4.2.3.1 Cyprodinil adsorption**

Cyprodinil adsorption on the substrate was conducted using a batch equilibrium technique. Adsorbent (20 mg) was treated with cyprodinil solution (10 mL) at increasing concentrations. The concentrations ranged from 2 to 10 mg L<sup>-1</sup>. Subsequently, the suspensions were shaken at 20 ± 2 °C for 3 h and centrifuged at 5000×g for 15 min. Preliminary experiments revealed contact for 3 h to be long enough for equilibrium to be reached. After centrifugation, the suspensions were filtered using glass microfibre filters of 1.6 µm pore size, and analysed as described on the previous Chapter for penconazole and cyazofamid. The chromatographic parameters of the method have been detailed in Chapter 2. The wavelength used for detection was 266 nm. The retention time was 13.5 min. The instrumental limit of detection was 20 µg L<sup>-1</sup>. The amounts of cyprodinil sorbed by Cloisite 20 A were determined from the difference in pesticide concentrations between the initial solution and the equilibrium solution.

Data were fitted to the Freundlich sorption isotherm which was deeply described in the Chapter 2.

##### **4.2.3.2 Mass balance in batch experiments**

The Freundlich equation for mass balance was employed to determinate the cyprodinil removal from 100 L solution with 100 g Cloisite 20A. The mathematical bases of the model were described in detail in Chapter 2.

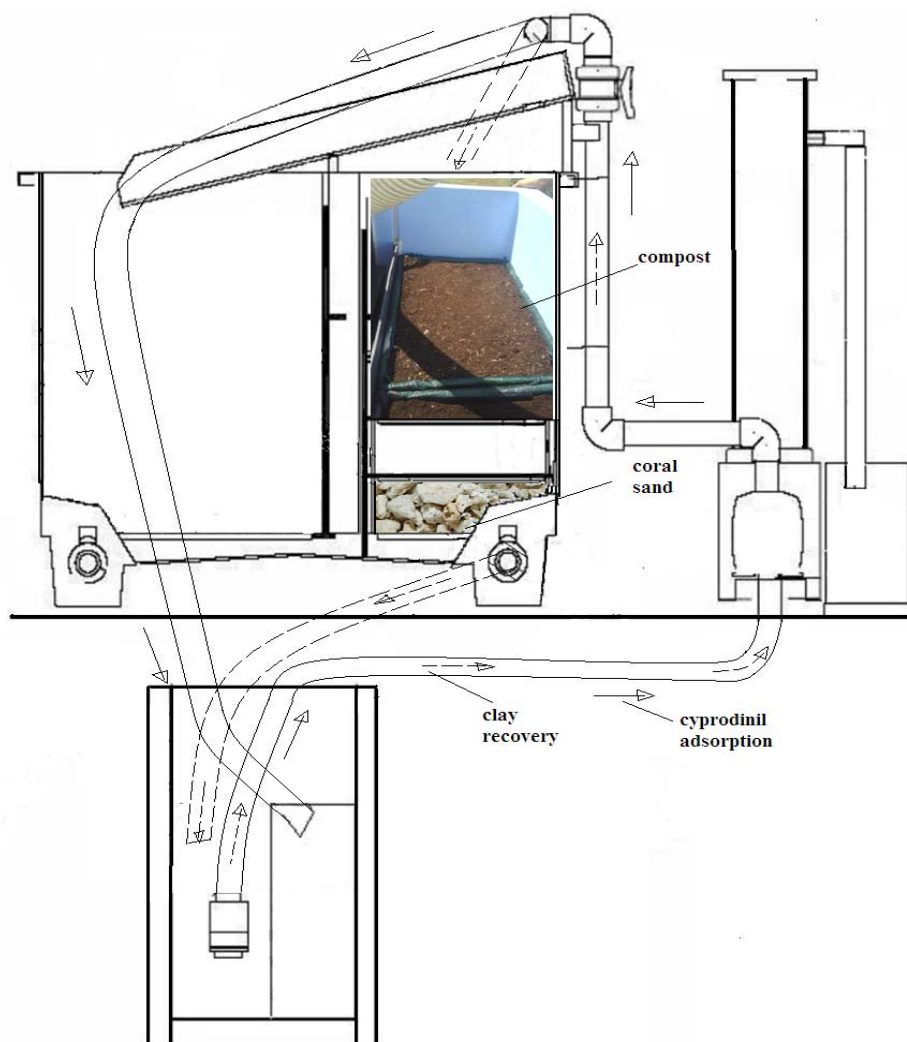
#### **4.2.4 Pilot Adsorption Plant**

##### **4.2.4.1 Design and management**

The pilot adsorption plant, previously developed and described in Chapter 3, was modified to allow the separation of clay particle from suspension also for pesticides containing on formulation antifoaming agents. The first part, where the adsorption takes place, was exposed in detail in the previous Chapter. The second

part, where the clay particles are separated from the suspension, is composed by a substrate of commercial compost through which the suspension under gravity is drained. The compost was previously placed in 4 plastic boxes, two layers, of 10 kg each, which were introduced in a plastic tank situated near the skimmer system (Fig.12). The suspension is pumped to the surface of the compost and after compost is collected in the tank. The operation is repeated until the totally amount of organic clay is separated from suspension by deposition at the compost surface. In the plastic tank, below the plastic boxes containing the compost, one layer of plastic boxes containing coral sand was added into the tank to avoid compost losses into the system. At the end of the separation process the water was pumped through the skimmer system, previously described in Chapter 3, in order to decrease the dissolved organic carbon (DOC) content and to remove proteins and small-sized particles from the collected water. The DOC was determinate as described in water analysis guidelines ISO/CEN 1484 (1997). However any difference in DOC value of water before and after skimmer system could be detected (data not shown).

For the entire process, the flow of suspension in the system was equal to the maximum outflow rate of the electric pump.



**Figure 12.** Pilot system for cyprodinil adsorption and organoclay recovery after adsorption

#### 4.2.4.2 Adsorption tests

The cyprodinil concentration used for the adsorption test in the pilot system was one third of the average cyprodinil concentration measured in the field in a previous study (Fait et al.,2007) 102 mg L<sup>-1</sup>. This concentration could simulate, as described in the previous Chapter for penconazole and cyazofamid, the worst scenario occurring in vineyards. To obtain this concentration, formulations of cyprodinil (20.4 g) was added to water (98.5 L) in the tank. The complete homogenization of the pesticide-contaminated water was obtained by its re-circulation around the first part of the system for 5 min. A sample (10 mL) was then taken for pesticide concentration determination. The adsorbent was subsequently added to the contaminated water and the suspension re-circulated in the system for 3 hours. The adsorbent was employed as concentrate suspension obtained by shaking for 15 min the powder adsorbent (100 g) with water (1.5 L) in a 2-L glass receptacle. As previously described for the other fungicides, in the previous Chapter, a time kinetic was obtained by sampling (10 mL) at suitable time intervals the suspension, filtering and analyzing the filtrate for the remaining pesticide concentration by high-performance liquid chromatography. The initial cyprodinil concentration was finally calculated considering the total volume of the contaminated water (100 L). The environmental temperature was 27.5±2°C ([http://www.arpa.emr.it/sim/?osservazioni\\_e\\_dati/dexter](http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter); web site on line the 23/11/2009).

#### 4.2.4.3 Degradation study

The compost-clay with cyprodinil matrix obtained after the adsorption was used to test for possible microbial degradation of the adsorbed residues. The matrix was maintained wet by irrigation with tap water. The operation was repeated once daily for seven days, daily until the 22<sup>nd</sup> day, once every two days until the 60<sup>th</sup> day and once each four days until the 90<sup>th</sup> day. On the first day two samples of the matrix were taken from each plastic box of each of the two layers to determine the initial pesticide concentration. After this, samples were taken after 7, 15, 22, 42 and 90 days and analyzed. At the same time, a sample of effluent was taken and analyzed in order to assess potential cyprodinil desorption. In any sample the cyprodinil could be detected (data not shown). The minimum and maximum daily temperatures for the period of the study are presented in Fig. 8 ([http://www.arpa.emr.it/sim/?osservazioni\\_e\\_dati/dexter](http://www.arpa.emr.it/sim/?osservazioni_e_dati/dexter); web site on line the 23/11/2009).

#### 4.2.5 Biochemical parameters

Prior to the adsorption study the compost was maintained wet and after 4 days, the starting day of the adsorption study, a sample was taken from each box and used to determine the total aerobic population, the organic carbon content and the total nitrogen content of the compost. The same analyses were made at the end of the degradation study. Two compost receptacles, prepared as described in the previous Chapter for the penconazole and cyazofamid degradation study, were used as control samples. The compost in the receptacles was irrigated at the same time intervals as the compost in the tank.

The concentration of organic C, the total nitrogen ( $N_{\text{tot}}$ ) and the total aerobic population were determined as described in Chapter 3, by the Walkley–Black procedure, by the Kjeldahl method and onto Plate Count Agar (PCA) respectively.

#### **4.2.6 Cyprodinil extraction**

Cyprodinil was extracted from the compost-clay matrix using as solvent the methanol. The extraction method was described in detail in the previous Chapter.

#### **4.3 Statistical analysis**

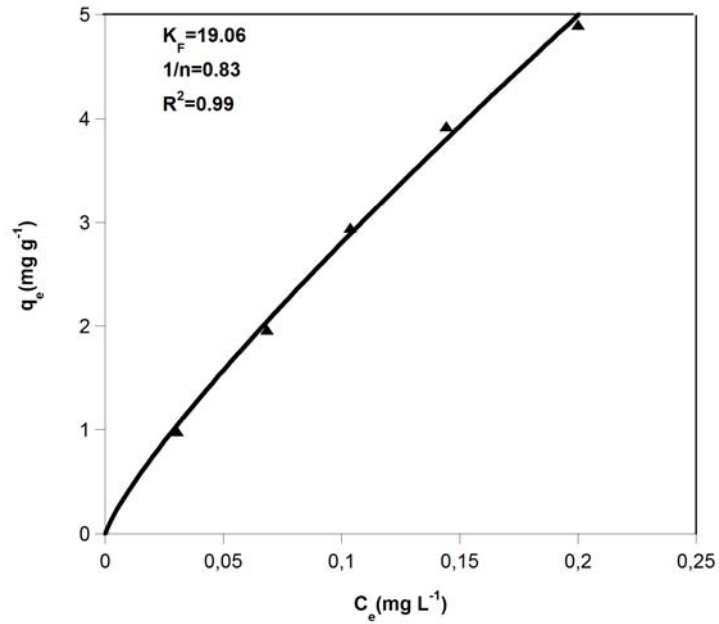
The linear regression model was used to evaluate the degradation/dissipation of cyprodinil in time. The mathematical bases of the model and the software used were described in the Chapter 3. The amount of the fungicide found on the compost sampled after the adsorption study was considered to be the initial amount.

#### **4.4 Results and Discussion**

##### **4.4.1 Cyprodinil adsorption in the laboratory**

The time kinetic in the range 10–180 min show an increase of cyprodinil adsorption on Cloisite 20A with increasing agitation time and reached equilibrium at 10 min. However, the equilibration time was chosen to be 3h.

The Freundlich adsorption isotherm and the relative coefficients of cyprodinil sorption on Cloisite 20 A are showed in the Fig. 13. The correlation coefficient ( $R^2$ ) was 0.99 whereas  $K_F$  and  $1/n$  were 19.06 ( $\text{mg g}^{-1}$ ) and 0.83 respectively. A correlation coefficient very close to 1 denotes a good fit of the model to the data. Comparing the adsorption behavior of cyprodinil with what was observed for penconazole and cyazofamid adsorption on the previous Chapter (Table 3) It can be stated that cyprodinil was less adsorbed than the other two fungicides but the strength of the adsorption ( $1/n$ ) is comparable with that of penconazole. This high strength is in agreement with its short equilibrium time.



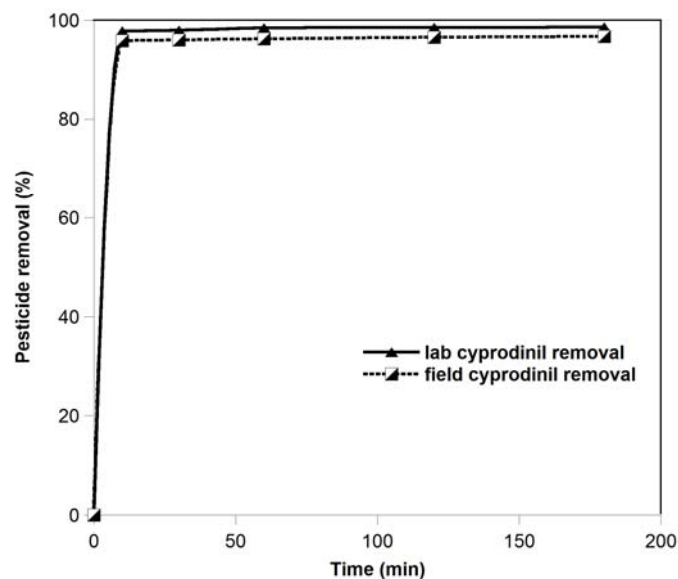
**Figure 13.** Adsorption isotherm of cyprodinil on Cloisite 20A

## 4.4.2 Pilot depuration system

### 4.4.2.1 Pesticide adsorption tests

The real initial cyprodinil concentration experimentally determined in the cyprodinil adsorption tests in the pilot depuration system was 102 mg L<sup>-1</sup>. After 3 h of adsorption, and starting from this concentration, the removal of cyprodinil from solution was 95.7 %. Comparing these results with those from the mass balance in batches, the percentage of cyprodinil removal from solution is similar to that predicted from the adsorption tests in the laboratory, 93.2%.

The findings of the effect of contact time on fungicide removal from contaminated water in the pilot depuration system show that the time necessary to achieve maximum cyprodinil removal were comparable in both laboratory and field trials (Fig. 14).

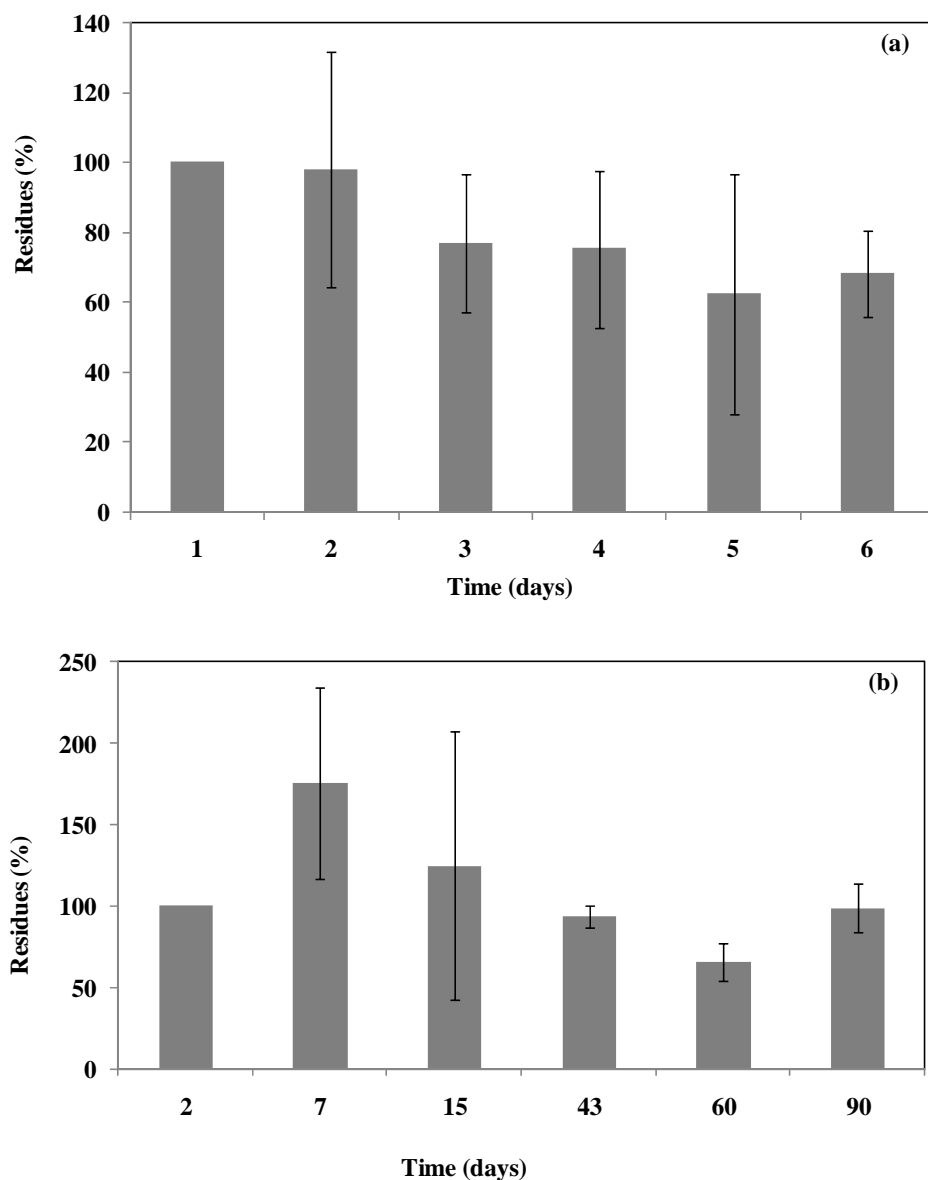


**Figure 14.** Effect of contact time on fungicide sorption on Cloisite 20 A in laboratory and field tests; initial cyprodinil concentration for laboratory test was 6 mg L<sup>-1</sup>

#### 4.4.2.2 Removal of the pesticide residues

The compost-clay matrix obtained after adsorption process was used to test its microbial development and the cyprodinil amount left in the clay over the experimental degradation period. The experiment time was 90 days, the same period as considered in the previous Chapter for penconazole and cyazofamid degradation study. It is assumed that the experiments include both chemical and biological degradation. Pesticide dissipation in similar matrices generally depends on their availability, persistence and affinity for organic matter. In this particular case, the cyprodinil dissipation may depend also on its affinity for the modified clay, Cloisite 20A. The experiment in the laboratory denotes a high strength of cyprodinil adsorption on Cloisite 20A.

Looking at the persistence of cyprodinil over the 90 days (Fig. 15a and 15b), the concentration in the first and second layer showed no breakdown. Such behaviour was not expected considering that cyprodinil has a moderate persistence in soil with DT<sub>50</sub> in field equal to 57 days. However this result is in agreement with what was observed for the persistent fungicide penconazole in Chapter 3. Furthermore, some researchers propose such a type of organo-clays for development of slow-release pesticides formulations. Therefore, these results suggest that after the adsorption on the organo-clay the fungicides tend to have a different behaviour than after the adsorption on soil. The cyprodinil concentration on the second layer after 7 days shows even an increase if compared with the concentration after 2 days This could be explained by the migration of the clay particles from the first layer to the second layer.



**Figure 15.** Evaluation of cyprodinil residues in compost-clay matrices: (a) first layer and (b) second layer.

The student's  $t$  test used to verify the existence of a relationship between the level of cyprodinil residue on the matrices compost-modified clay and time, revealed an insignificant degradation of cyprodinil in both the first and the second layer with a lower value of the Student's  $t$  coefficient calculated ( $t_c=2.73$  for the first layer and  $1.39$ ) than the  $t$  tabulated ( $t_{0.05;4}=3.75; \alpha=0,01; n=4$ ).

Concerning the changes in compost properties during the degradation study (Table 7), a decrease in organic carbon was observed which is the result of the mineralisation of the organic material with time. A slight increase in the total N content in the matrix sampled from the first layer and a significant decrease in the matrix sampled from the second layer were also observed. However the C/N ratio of all matrices, with and without modified clay with fungicides, was low, which could be attributed to the fairly high total N content.



**Table 7.** Chemical and microbial characteristics of the compost matrix without clay with cyprodinil and with clay with cyprodinil

	<i>OC</i> (g Kg <sup>-1</sup> )	<i>N</i> <sub>(tot)</sub> (%)	<i>C/N</i> ratio	<i>Total aerobs</i> <i>Ufc/g</i>	
				<i>0-5cm</i>	<i>5-10cm</i>
Initial <sup>a</sup>	242	24.3	9.9	9*10 <sup>7</sup>	13*10 <sup>7</sup>
Cyprodinil 1 <sup>st</sup> layer <sup>b</sup>	212.1	24.6	8.6	19*10 <sup>6</sup>	20*10 <sup>6</sup>
2 <sup>nd</sup> layer <sup>b</sup>	224.7	22.4	10.5	20*10 <sup>6</sup>	19*10 <sup>6</sup>
Control	-	-	-	9*10 <sup>6</sup>	27*10 <sup>7</sup>

<sup>a</sup> values obtained at the beginning of the experiment

<sup>b</sup> values obtained at the end of the experiment

One of the possible reasons of the low dissipation rate measured could be due to the toxic effect of the quaternary salts. With this in mind, we studied the development of the total aerobe population in the different matrices, at two depths. The first depth was between 0 and 5 cm, and the second between 5 and 10 cm.

The general tendency in the microorganism populations in the controls was a decrease in aerobes after 90 days. The aerobes showed a slightly higher decrease with respect to time 0 in the first layer (0-5 cm) than in the second layer (5-10 cm). The same tendency could be observed on the compost-clay with cyprodinil in both first and second layer.

## 4.5 Conclusions

The depuration scheme developed for pesticides containing antifoaming agents on them formulation showed to be efficient for the recovery of the modified clay after adsorption in less than one week. Concerning the adsorption process in the pilot system, the fungicide cyprodinil shows a removal from solution similar to that predicted from the adsorption tests in the laboratory. Moreover, cyprodinil, fungicide with moderate persistence in soil, after the adsorption on Cloisite 20A shows to have a similar behaviour as the persistent fungicide penconazole, with no significant degradation during and after the organoclay composting process. Therefore additional treatments still appear to be necessary in order to achieve lower concentrations that allow its disposal in the field as biomass.

Work publication/presentation:

Suciu N. A., Ferrari F., Trevisan M. and Capri E. Improving the Biomassbed™ efficiency by using modified clays. Pesticides Behaviour in Soils, Water and Air Conference, York, UK, 14-16 September 2009. Poster

## **5 Modelling approach to estimate emission of Plant Protection Products from protected crop systems to surface water in Mediterranean countries.**

### **ABSTRACT**

The FOCUS PEARL model was parameterized to perform simulations for Plant Protection Product (PPP) emissions from greenhouses to surface water, after application to a tomato crop. A comparison with the open field was made in order to investigate how the climatic conditions, which are more controlled under greenhouse conditions, influence the PPP emissions to surface water. Although only a limited number of runs were performed, the results show the existence of two hypothetical substances (subsequently indicated as CC and CC-M) in the water drained from greenhouses, contrary to what is stated in the European council Regulation 1107/2009. The irrigation amounts given during the crop cycle and the temperature conditions within the covered structure have an important influence on PPP's emission as increasing the irrigation volume and/or decreasing the temperature result in increased concentrations of CC and CC-M in drainage water whereas the opposite occurs when the temperature is increased. Flushing the soil at the end of the crop cycle and irrigating with minimum water excess during the crop cycles, as an alternative to over-irrigation for the entire cultivation period, resulted in lower CC and CC-M leaching/drainage. However to generalise these findings, additional runs for other substances and other crops than tomatoes are required.

### **5.1 Introduction**

Since the nineteen sixties PPPs have a major role in agriculture and the increase of crop production, but pesticides may affect human health and the environment via contamination of groundwater, surface water, soil, air and food. Therefore there is a need for further development of harmonised and scientifically based methodologies to support the risk assessment of PPPs in Europe.

A sector with relatively unknown impact on the environment is the horticultural sector. Greenhouse production is considered by the council regulation EC 1107/2009 to prevent release of PPPs into the environment, contrary to field conditions. However water boards frequently measure the occurrence of PPPs and biocides in surface water near and in protected crop areas. Teunissen (2005), for example, summarised the results for a number of glasshouse areas in The Netherlands over the period 2000-2004 and showed that the concentrations of PPP frequently exceeded up to 100 times the applicable Dutch Environmental Quality Standards for fresh surface water. Most standard exceedings were caused by insecticides and acaricides, followed by fungicides. This situation can occur both in areas with obsolete greenhouses and with up-to-date

greenhouses suggesting that replacement of structures over time will not automatically solve the problems associated with PPP emissions. Similar studies and results were also reported for horticultural areas in Mediterranean countries (Gonzalez- Pradas et al., 2002; Garratt et al., 2007).

At EU level several active substances have been listed in Annex I to Directive 91/414/EEC with reference to use in covered structures. The current risk assessment methodology does not differentiate between the emissions of a protected crop application and the emissions of a field application. Therefore, EFSA, via the Scientific Panel on Plant Protection Products and their Residues (PPR Panel), were mandated to compile an inventory of protected crop systems and to identify/investigate/address PPP emissions from these systems to relevant environmental receptors, for the support of the EU guidance document on the importance of emission routes including the circumstances under which they are relevant (EFSA, 2010c).

Protected crops are irrigated, at least for part of the year. Irrigation in excess of the crop's requirements is common (EFSA, 2010a). This is because the monetary value of over-irrigation is smaller than that of yield loss arising from insufficient irrigation. The excess water and associated PPP may reach groundwater and/or surface water. Water and PPP are often not evenly distributed over the surface and local areas with high flow rates and large PPP concentrations may occur. Soilless systems with closed-loop irrigation need to discharge water more or less frequently in order to reduce the risk of salinity stress, nutritional unbalances and root-born diseases; at this point any dissolved PPP will leave the system along with the discharge water. Condensation water and associated PPP may also be discharged to surface water. Emissions of PPPs from covered structures to air and water are thus not necessarily different from or less than emissions from open field cultivations (EFSA, 2010a). Therefore, the PPR Panel concluded that development of specific environmental risk assessment strategies for protected crops is needed for some cases.

Due to the large number of combinations of covered structures, crop growing systems, irrigation techniques, application methods etc it is not feasible to develop detailed risk assessment procedures for all situations. Therefore EFSA (2010a) developed an outline for a general decision scheme to select the conditions that might lead to emissions from protected crops different from field applications. The scheme poses the question whether the protection structure, growing system and/or application technique significantly influence the emission of PPPs to the relevant receptor or the exposure of organisms in the receptor. If this is the case a separate assessment should be made for the protected crop structure. Further decisions have to be made for each receptor separately.

In the present Chapter we evaluated whether and how the existing models used for calculating leaching and drainage of PPP from open field cultivations to surface water can be applied for estimating emissions from greenhouses to these receptors, under Mediterranean conditions, and whether emissions are different. In particular, this study aims at testing:

- (1) the influence of a more controlled climate in greenhouses on the emissions to surface water, compared to the open field

(2) the influence of temperature and irrigation amounts on the emissions.

Annual average concentrations in drainage water were usually used to compare the results of the calculations.

This paper has been written in the context of EFSA's work on the development of new Guidance on Emissions from Protected Crops.

## 5.2 *Materials and methods*

### 5.2.1 Selection of driving forces

The first part of the work focused on the selection of the main driving forces, growing media, structure type, emission receptor, crop and PPP application techniques.

**Growing medium.** In most Mediterranean countries (Cyprus, France, Greece and Italy) the growing medium mostly used for the cultivation of crops under protection is the **soil** (Sigrimis, 2010). The same applies to Spain, where in Almeria more than 65% of cultivation is soil-bound.

**Structure type.** The structure selected was **glasshouse (unheated)**, a structure which EFSA (2010a) considered to have possible different emissions as compared to the open field and therefore may result in possible different concentrations in the environment. In that case, a different risk assessment would be appropriate. According to EFSA (2010b) this type of structure belongs to the category of greenhouses and therefore the term greenhouse will be used to describe the growing system further on in the text.

**Emission receptor. Surface water** was selected as the receptor of PPP emission. In EFSA (2010a) the PPR Panel expressed their interest in calculations of emissions from greenhouses to this receptor.

**Crop. Tomato** appears to be the most important greenhouse crop species worldwide and, in particular, in Southern Europe (Sigrimis, 2010).

**PPP application technique. Spraying to the crop canopy** was selected as it is one of the most common PPP application techniques used on the greenhouse tomato.

### 5.2.2 Emission routes

Vermeulen et al. (2010) identified all theoretically possible emission routes from glasshouse cultivation systems in the Netherlands. In their scheme, the main emission routes from soil-bound cultivation to surface water were:

- condensation, if not collected and reused, which is directly discharged into surface water
- discharge of recirculation water into surface water, typical for The Netherlands
- leaching to a depth of approximately 1 m and then (artificial) lateral drainage to surface water

The above selected drivers were parameterised and used to simulate emissions via lateral drainage to surface water.

### 5.2.3 Model description

The PEARL – Pesticide Emission Assessment at Regional and Local scales - model (Tiktak et al., 2000) was used in this study. The PEARL model deals with the pesticide transformation and fate and is linked with the SWAP model (van Dam et al., 1997) for the water cycle and transport.

Water flow in soil is described by Richard's equation including a range of possible lower boundary conditions (for instance groundwater levels that fluctuate in response to the rainfall input). Soil evaporation and plant transpiration is calculated via multiplying a reference evapotranspiration rate with soil and crop factors. Crop growth is simulated with a simple growth model that assumes fixed length of the growing season. In this growth model, both the leaf area index and the rooting depth are a function of the development stage of the crop. Heat flow in soil is described by Fourier's law.

One of the PEARL's options for PPP applications is spraying the crop. The applied pesticide is distributed over the crop canopy using the soil cover fraction while the remainder of the dosage reaches/deposits into the soil. Then, PEARL simulates PPP volatilisation from the plant surface, penetration into the plant tissues, degradation (using first order kinetics) and wash-off due to rainfall. The soil pesticide mass balance is expressed as:

$$\frac{\partial c_{eq}}{\partial t} = -R_s - \frac{\partial J_l}{\partial z} - \frac{\partial J_g}{\partial z} - R_t + R_f - R_u - R_d \quad (18)$$

where  $c_{eq}$  is the pesticide concentration in the equilibrium domain of the soil system, ( $M L^{-3}$ );  $R_s$  is the rate of pesticide sorption in the non-equilibrium domain of the soil system;  $J_l$  and  $J_g$  are the mass fluxes of the pesticide in the liquid and gas phases ( $M L^{-2}$ ), respectively;  $R_t$  is the transformation rate;  $R_f$  is the formation rate;  $R_u$  is the root uptake rate;  $R_d$  is the lateral pesticide discharge rate (all rates are in  $M L^{-3} T^{-1}$ ).

The transport in the liquid phase includes the convection, dispersion and diffusion processes and is described as follows:

$$J_l = qc_1 - (D_{dis} + D_{diff,1}) \frac{\partial c_1}{\partial z} \quad (19)$$

where  $q$  is the soil water flux ( $L^3 L^{-2} T^{-1}$ );  $c_1$  is the PPP concentration in the liquid phase ( $M L^{-3}$ );  $D_{dis}$  and  $D_{diff,1}$  are the hydrodynamic dispersion and chemical diffusion coefficients ( $L^2 T^{-1}$ ), respectively.

The sorption in both the equilibrium and non-equilibrium phases is described by Freundlich isotherms. The partitioning of the pesticide between the liquid and the gaseous phases is described by Henry's law. The degradation of the pesticide is described by a first order equation, dynamically adjusted for the effects of

temperature and moisture in the soil and adjusted for soil depth. The temperature factor is described by the Arrhenius equation as:

$$f_t = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad (20)$$

where  $E_a$  is the molar activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the molar gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $T$  is the temperature (K) and  $T_r$  is the temperature at which the half-life of the substance was determined. The depth factor is specified in a tabular form, and the moisture effect factor ( $f_m$ ) is given as:

$$f_m = \min\left[1, \left(\frac{\theta}{\theta_{fc}}\right)^B\right] \quad (4)$$

where  $\theta_{fc}$  is the soil moisture at field capacity ( $\text{L L}^{-1}$ ), and  $B$  is an empirical factor. PPP uptake by roots is directly proportional to the volumetric water uptake. Similarly, the lateral PPP discharge is taken proportionally to the lateral water discharge.

Basic input data for the model include: daily meteorological data; soil textural properties; farming practices (crop planting and harvest dates, irrigation regime); information on the timing, type and quantity of PPP applications; environmental fate parameters (half-life, solubility in water, sorption on organic matter) for the substance under investigation. PEARL provides daily outputs of the concentration of PPP in the vadose zone (soil and water) and in the upper saturated zone.

#### 5.2.4 PEARL application for open field

The site for which the model was applied is located in Pisa in the Tuscany region of Italy ( $43^{\circ}71' \text{N}$ ,  $10^{\circ}39' \text{E}$ ). The daily meteorological data (solar radiation, maximum and minimum air temperature and pan evaporation) for an 18 year period have been taken from a local weather station database. The reference evapotranspiration was calculated from the pan evaporation. The period was extended to 26 years, so the last eight years were copied and six of these years were used as the “warming up period”. This approach of simulating for a period of 26 years was developed by FOCUS (2000) and is commonly used in risk assessment procedures on leaching.

Data for soil textural properties were not available; therefore, the FOCUS Piacenza soil scenario was used to perform the calculations. The crop cycle was between 10<sup>th</sup> May and 25<sup>th</sup> August, dates used in FOCUS Piacenza scenario for tomatoes. The development of the crop was characterised by maximum leaf area index (LAI), the maximum effective rooting depth and the crop coefficient. The values of these parameters were adapted from FAO (1998). The irrigation scheme as included in the FOCUS Piacenza scenario was also employed.

To perform the calculations a “dummy” substance (CC) and its metabolite (CC-M) were used. The substance CC and its metabolite are copies of the example substance C and its metabolite, available from the FOCUS leaching scenarios, with the modification of molar activation energy value. The main properties of the two compounds, requested by the model, are presented in Table 8. The PPP was sprayed to the crop canopy and the interception fraction was taken to be 0.7.

**Table 8.** CC and CC-M main properties requested by the model.

Properties	Substances	
	CC	CC-M
Molar mass (g mol <sup>-1</sup> )	200	150
Saturated vapour pressure measured at 20 °C (Pa)	1E-10	
Molar enthalpy of vaporisation (kJ mol <sup>-1</sup> )	95	
Solubility in water measured at 20 °C (mg L <sup>-1</sup> )	50	90
Molar enthalpy of dissolution (kJ mol <sup>-1</sup> )	27	
K <sub>om</sub> measured at 20 °C (L kg <sup>-1</sup> ) <sup>(a)</sup>	100	30
Freundlich sorption exponent	0.9	
DT <sub>50</sub> measured at 20 °C (d) <sup>(b)</sup>	20	100
Molar activation energy (kJ mol <sup>-1</sup> )	65.4	

(a): organic matter- water partition coefficient

(b): half-life time at reference conditions (top soil, 20 °C, field capacity)

Formation fraction of CC-M out of CC is 0.71.

### 5.2.5 PEARL application for greenhouse

The model was applied to a greenhouse in Pisa, near the location of open field application. The weather station of the greenhouse provided data for daily solar irradiation, air temperature and potential evaporation. The reference evapotranspiration (ET) was calculated from pan evaporation and the irrigation amount was assumed to be in excess (1.2 ET). Drainage subsequently was calculated by the model. The data set was only available for one year of cultivation with one crop cycle. In order to establish a data set for a long-term simulation (e.g. 20 years) a linear function correlation between the daily outdoor temperature from Pisa and daily indoor temperature was derived. The correlation was then applied to the 26 years open field temperature data and so an indoor temperature data set was obtained. The daily ET was obtained using the same approach; an empirical power function correlation between the indoor temperature and ET for one year (data available) was obtained and subsequently applied to the indoor temperature data set previously established. Moreover, the irrigation amount for the entire simulation period was calculated as described

above. Soil textural properties, PPP application scheme and characteristics were the same as those for the open field.

In order to compare the PPP emissions from greenhouse with the emissions from the open field two scenarios were created for the greenhouse cultivation:

- i) one tomato cultivation per year with a single PPP application one month after transplanting
- ii) two growing cycles per year with one single PPP treatment in the first cycle

In the first scenario, we assumed that the soil was not irrigated before and after the cultivation and that the reference ET corresponded to soil evaporation for the periods without crop. The second approach was used in order to create a scenario as realistic as possible, i.e. a dynamic situation with respect to irrigation for a full year.

For both types of growing systems, under cover (greenhouse) and open field, calculations were performed to determine the concentrations of the PPP and its metabolite in water drained to surface water. The drainage to surface water was realized assuming drainpipes at a depth of 80 cm. The drainage resistance was set to 43 days, and was calculated using a design discharge of 7 mm/day in combination with a desired maximum groundwater level midway between two drains of 0.5 m below soil surface. See Tiktak et al. (2010) for details. The use of a drainage system implies the knowledge of the ground water level over a period of time. A dataset of the ground water level from a greenhouse in The Netherlands was adapted as such a dataset was not available for the study area. The target concentration for comparing the scenarios was the 80<sup>th</sup> percentile of annual averaged drainage concentrations.

## **5.2.6 Influence of temperature and water amount on emissions from greenhouse**

In order to evaluate the influence of temperature and irrigation water amount on PPP emissions from the greenhouse several scenarios were constructed. For all scenarios the weather conditions for periods of 26 years were created by copying the available weather data to the desired period. For the scenarios in which the influence of the amount of water was studied, the irrigation amount given to the crop (equal to 1.2 ET) was multiplied 1.1-1.5 times. The soil textural properties and PPP characteristics were as described in the previous scenarios. The tomatoes were cultivated two times in separate cycles per year and the PPP was applied one month after the start of each cultivation cycle.

For the scenarios in which the influence of temperature was studied, the daily average temperature was modified as follows:

- one degree lower for the days with temperature higher than 20 °C (1C-20)
- one degree higher for the days with temperature lower than 20 °C (1C+20)



- one degree lower for all the days (1C-T)
- one degree higher for all the days (1C+T)

### 5.3 Results

The balances of annual water amounts used for tomato cultivation in the greenhouse and in the open field are presented in Table 9. For the greenhouse cultivation, two situations are presented, one with one crop cycle per year and one with two crop cycles per year. The values in the table for all variables are reported as averages over the 20 years period, i.e. averages over the simulation runs without the 6-year warm-up period. The irrigation and precipitation amounts were inputs, whereas the actual ET, leaching and drainage amounts were calculated by the model.

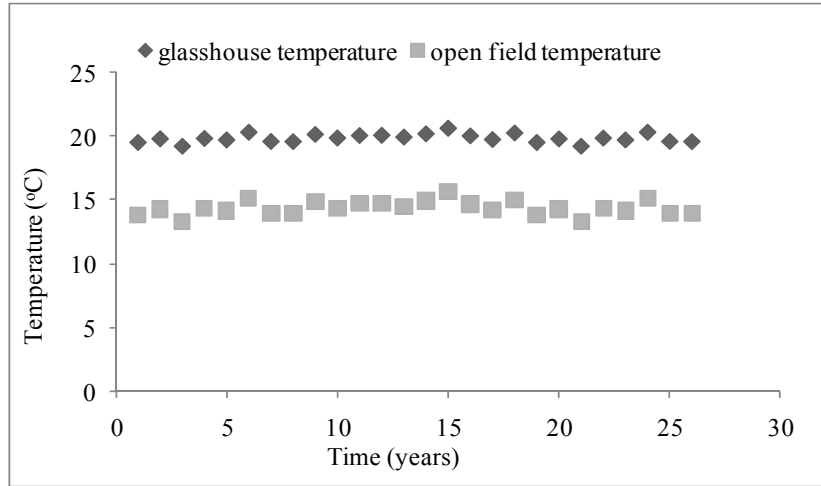
The total water amount used for tomato cultivation in the open field (irrigation amount plus precipitation amount) appeared to be 2.25 times higher than the amount of water used for 1 greenhouse cultivation cycle and 1.6 times higher than the amount used for 2 greenhouse cultivation cycles. The highest actual ET was shown for tomato cultivation in greenhouse with two crop cycles per year whereas the lowest was for open field cultivation. Temperature was found to have an important role in the calculated ET in greenhouse as well as open field cultivation (Fig. 16). The difference between the given water amount and actual ET amount is the sum of leachate and drainage water as storage over such a long period is negligible. The highest leaching was observed for the cultivation of tomatoes in the open field and the lowest for cultivation of tomatoes in the greenhouse with one crop cycle per year. The amount of drainage water was the same for all the situations considered.

**Table 9.** Annual water balance for cultivation of tomatoes in the greenhouse and in the open field.

<i>Type of grow</i>	<i>Irrigation</i> <i>(mm/year)</i> <i>(a)</i>	<i>Precipitation</i> <i>(mm/year)</i> <i>(a)</i>	<i>ET</i> <i>(mm/year)</i> <i>(a)(b)</i>	<i>Leachate</i> <i>(mm/year)</i> <i>(a)</i>	<i>Drainage</i> <i>(mm/year)</i> <i>(a)</i>
<b>Greenhouse</b> <b>1 cycle</b>	668.4	0	600	6	3.8
<b>Greenhouse</b> <b>2 cycles</b>	957.4	0	816.2	13	3.8
<b>Open field</b>	381.5	1121.1	520	97	3.8

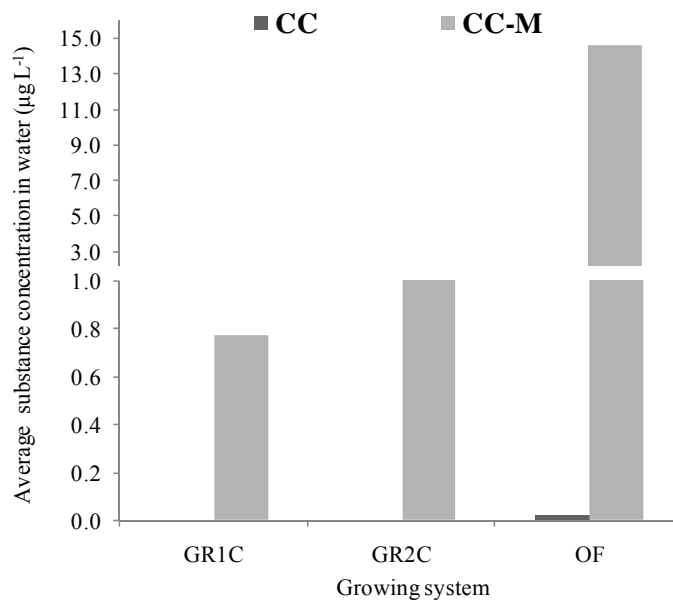
(a): average over 20 years

(b): ET represents the actual evapotranspiration



**Figure 16.** Annual average temperature in greenhouse and open field.

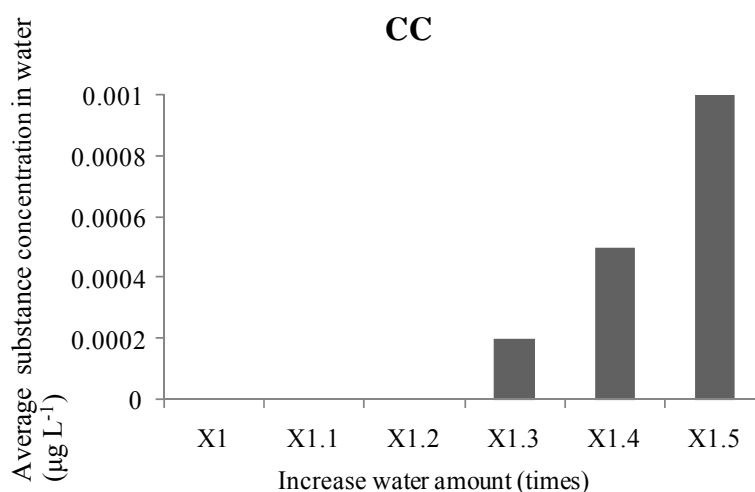
The concentrations of the “dummy” substance, CC, and its metabolite, CC-M, found in the drained water were highest for the cultivation of tomatoes in the open field (Fig. 17). For both types of cultivation in the greenhouse the average concentration of substance CC in drained water was below  $0.0005 \mu\text{g L}^{-1}$  whereas for the cultivation of tomatoes in the open field the average concentration was  $0.020 \mu\text{g L}^{-1}$ . Metabolite CC-M was found in higher concentrations in the drained water than the parent, with values up to  $14.5 \mu\text{g L}^{-1}$  for cultivation of tomatoes in the open field,  $2.09 \mu\text{g L}^{-1}$  for the greenhouse with two crop cycles per year and  $0.77 \mu\text{g L}^{-1}$  for the greenhouse with one crop cycle per year.



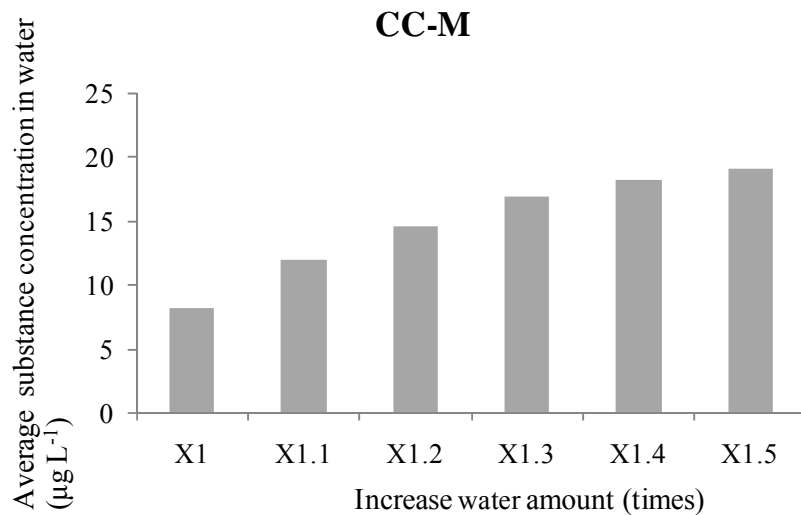
**Figure 17.** Annual average concentration closest to 80<sup>th</sup> percentile for substances CC and CC-M in drained water during cultivation of tomatoes in the greenhouse (GR1C: one crop cycle per year; GR2C: two crop cycles per year) and in the open field (OF).

The average concentrations of CC and CC-M in drained water were found to be influenced by the irrigation volume (Fig.18a and b) and indoor temperature (Fig.19). The simulation did not reveal the presence of CC in the drained water when minimal water amounts were considered for calculations. When the water supply was increased up to 1.2 times no effects on average substance CC concentration in drained water could be observed whereas for higher gifts, 1.3-1.5 times the minimal value, the concentration increased considerably. Effects on drainage of CC-M were found earlier, i.e. at lower water supply, and were more pronounced. The average concentrations of the metabolite in drained water increased 1.47, 1.8, 2.08, 2.26 and 2.36 times respectively when water supply was 1.1, 1.2, 1.3, 1.4 and 1.5 times the original values.

Regarding the influence of the inside greenhouse temperature, the results showed an increase in the concentration of metabolite CC-M in drained water up to 1.27 times when the annual average temperature was lowered by 1 °C and a 1.29 times decrease when the annual average temperature was raised by 1 °C. The inside greenhouse temperature did not show a noticeable influence on the annual average concentration of substance CC in drained water during the tomato cultivation. For all situations, the concentration in drained water was below the minimum reported level of 0.0005 µg L<sup>-1</sup>.

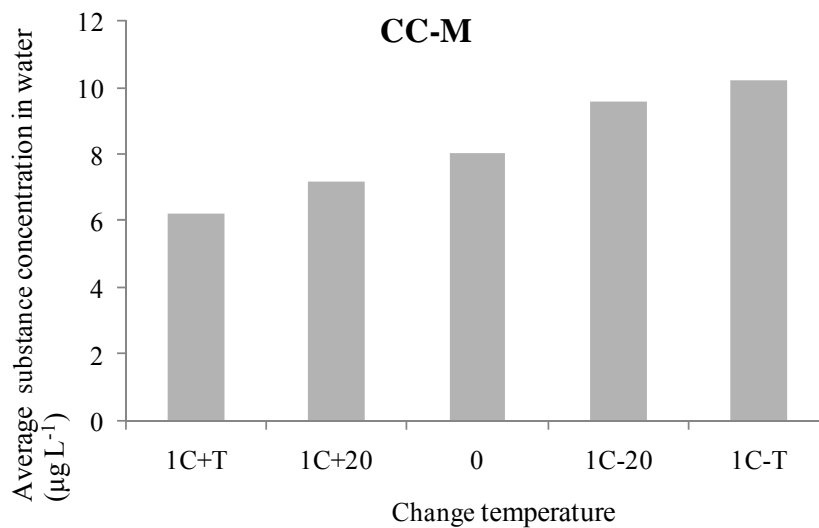


a)



b)

**Figure 18.** Average concentrations closest to the 80<sup>th</sup> percentile of substances CC (a) and CC-M (b) in drained water as influenced by the irrigation volume. The original value (x1) corresponded to the volume calculated as the product of crop ET times 1.2.



**Figure 19.** Annual average concentration (80<sup>th</sup> percentile) of substance CC-M in drained water as influenced by temperature: (1C-20), one degree less for the days with temperature higher than 20 °C; (1C-T), one degree less for all the days; (1C+20), one degree more for the days with temperature lower than 20 °C; (1C+T), one degree more for all the days; (0) original temperature.

## 5.4 Discussion

The drainage is the result of leaching of water to the depth, to the artificial drains and the transport via these drains to surface water. The concentrations in the drain water were used as the endpoint of the calculations as

we did not define and model concentrations in the surface water. The differences between pesticide emissions from greenhouse to surface water compared to the open field are shown in Fig. 17. Drainage concentrations in open field cultivation are much higher than in greenhouse cultivations. This was expected as the values of main driving factors, amount of water and temperature, favour the leaching to the depths of PPP in the open field. The effect of the total water supply can be understood when extrapolating the results of Fig. 18 and 19. The higher amount of water received by the crop and the lower temperature for open field cultivation than for greenhouse cultivation result in a higher amount of leaching water to the depths and in higher drainage concentrations. Additional calculations (data not shown), using free drainage as the lower boundary condition, showed similar behaviour regarding the leached concentrations to ground water, higher in the open field than in the greenhouse, but compared to the concentrations in drained water the values were higher. The lower temperature in the open field probably limited CC transformation in CC-M, following the Arrhenius equation, thus resulting in a higher concentration in drained water compared to the greenhouse cultivation. At the same time the evaporation of water from soil and its uptake by plants will have been influenced by the lower temperatures.

Regarding the metabolite CC-M, average concentrations in drained water were much higher than the concentrations of the parent substance. These results could be explained by the high conversion of CC into its metabolite CC-M and the higher mobility of CC-M. It is well known that compounds with low  $K_{om}$  value generally present a high leaching potential (Boesten and Van der Linden, 1991).

Greenhouse tomato cultivation is more realistically described by the second scenario but some aspects are still missing. If tomato is cultivated twice per year and the same PPP is applied in both cycles, the PPP and/or metabolite average concentrations in drained water are expected to be higher than the concentrations determined in the present study. For the sake of easy comparison only one application was assumed. In practice, alternative PPP may be used in each of the cycles. Even with one single application in two successive cycles, PPP emissions from the greenhouse were higher than one would argue from the statement reported in the European Regulation 1107/2009/EC on “Placing plant protection products (PPP) on the market”, which considers greenhouses as a closed growing system that “prevent release of PPP into the environment”.

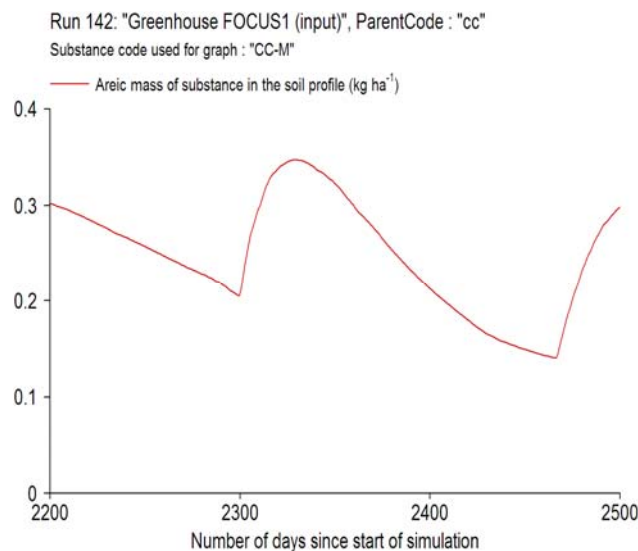
The results reported in Fig. 18 and 19 show that a small variation of irrigation volume or indoor temperature can have a big influence on pesticide concentration in the water drained from greenhouse cultivation. The CC-M concentration in drained water shows a sigmoidal increase with increasing the irrigation volume and an almost linear variation when the temperature is increasing and decreasing respectively (for the limited temperature range considered). In order to find out which of the two factors has a higher impact on CC-M emissions the necessary relative changes in temperature and, respectively, irrigation volume to obtain a 50% increase in leaching concentrations were determined. It was observed that a 50% increase in CC-M concentration in drained water was obtained when the irrigation volume was increased by 14% whereas for the same increase only a decrease from  $21C^0$  to  $19.2C^0$  of temperature is necessary. Therefore, for the

investigated scenarios, it could be concluded that temperature has a higher relative influence on CC-M emissions from the greenhouse than the irrigation volume in this study.

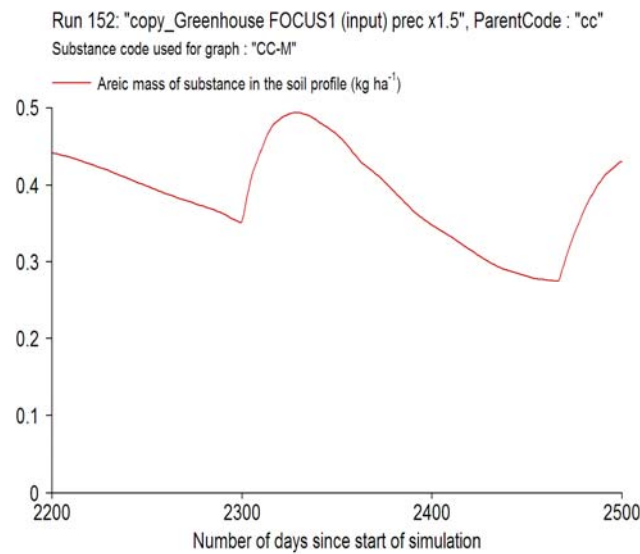
The irrigation type assumed in the study, rain, is a common irrigation type for the open field but not very common for greenhouses. The drip irrigation and gutter irrigation are the most common for greenhouses. A different type of irrigation could have an influence on the leaching and therefore on the drainage to surface water. This will also depend on the way the substance is applied. If the substance is applied with the irrigation water, the effect will most probably be a higher leaching with a factor of two or more (Leistra, 1985). The substance will then be in the spots with higher water flow and additionally brought in at some depth. If the substance is sprayed, then the opposite might be true. The substance will then be (at least partly) in the spots with lower flow. Gutter irrigation might have effects pointing in the same direction, possibly more extreme.

Greenhouse crops are generally over-irrigated (EFSA 2010a), principally to avoid soil salinisation and this results in the leaching of both PPP/metabolite and fertilisers. Therefore, an optimisation of irrigation management is crucial to minimize the environmental impact associated with irrigation, fertilisation and PPP application. A solution could be irrigating at minimum water excess during the crop cycle followed by a soil flush before the next crop cycle, which indeed is a common practice in many greenhouse areas, for instance in Almeria, Spain (Thompson et al., 2006). Fig. 20 shows that the areic mass of CC-M in the soil profile 8 days after the end of the crop cycle ( day 2431) is 1.82 times lower when the irrigation is at minimum water excess (original value) than at maximum water excess (1.5 times the original value). The higher value for the scenario with 1.5x can be explained by the movement of the substance to deeper, less bioactive layers. The areic mass of substance CC in the soil, in the same day, 2431, was the same for the both types of irrigation regime.

Therefore, based on the data in Fig. 20 it can be concluded that avoiding over-irrigation during the cycles and applying the irrigation necessary to prevent soil salinisation before the following crop can significantly reduce the leaching of PPP and/or its metabolites.



a)



b)

**Figure 20.** Areic mass of metabolite CC-M in the soil profile when irrigation is at minimum water excess (a) and at maximum water excess (b). The graphs are referring to the 7<sup>th</sup> year of simulation. The cultivation starts at day 2269, CC was applied at day 2301 and the flush of the soil was considered to be performed at day 2431; 8 days after the end of crop cycle.

## 5.5 Conclusions

The FOCUS PEARL model, generally used for calculating leaching and drainage of PPP from open field cultivations to ground/surface water, can also be parameterized to simulate PPP emissions from greenhouses to surface water.

In this case study, weather conditions were found to have a major role on the PPP emissions from glasshouses and the open field. The more controlled climate in the greenhouse prevented a substantial precipitation excess as was observed for the open field, which had a large effect on the leaching concentrations.

Regarding the greenhouse cultivation it was noticed that the temperature has a slightly higher influence on CC-M emissions from the greenhouse than the irrigation excess volume. A 50% increase of CC-M concentration in drained water was observed when the irrigation volume increased by 14% and the temperature decreased from 21°C to 19.2°C.

Although a limited number of runs have been performed, it can be concluded that there are potential PPP emissions to surface water associated with crop cultivation in greenhouses, contrary to what is stated in the European Council Regulation 1107/2009, article 3.

The lower areic mass of CC and CC-M in the soil profile at the end of the crop cycle and the lower CC and CC-M average concentration in drained water when the crop is irrigated with a minimum water excess indicates that there are possibilities for optimising water regimes in greenhouse cultivations. For the substance under investigation, flushing the soil after the crop cycle in order to lower salt contents will lead to lower leaching compared to the situation with the same amount of water but applied more evenly to the crop. For other substances, the situation might be totally different. More work is necessary to derive a more generally applicable advice.

## **5.6 Recommendations**

The present study could be used as input to understand the PPP fate in greenhouses. However additional research is needed especially to understand how others routes, such as condensation, if not collected and reused, and discharge of recirculated water, could influence the PPP concentration in surface water. Furthermore, additional runs for substances with different properties than CC in the same scenarios are required in order to confirm the hypotheses.

Movement of PPPs to ground and surface water is influenced by the type of crop and the crop parameters, due to effects on the volume of water that percolates to deeper depths. The temperature optimum of the crop determines the temperature conditions within the covered structure. The application technique, the amount of spray intercepted by the crop and the application timing also differ between different crops and this will influence emissions of PPPs. The tomato, in this study, is considered a crop with a high temperature optimum and is assumed to be irrigated as rain. Therefore scenarios for other crops, with cooler conditions for growth and different irrigation technique are also required.

Work publication/presentation:

This work is the property of European Food Safety Authority.

European Food Safety Authority (2010) .Modelling approach to estimate emission of Plant Protection Products from protected crop systems to surface water in Mediterranean countries. EFSA Journal 2010; 8(8):1615 [18 pp.]. doi:10.2903/j.efsa.2010.1615

Suciu. N.A. Modelling approach to estimate emission of Plant Protection Products from protected crop systems to surface water in Mediterranean countries.47th Plenary Meeting of the Scientific Panel on Plant Protection Products and their Residues, Parma, 22-23 September 2010. Oral Presentation.

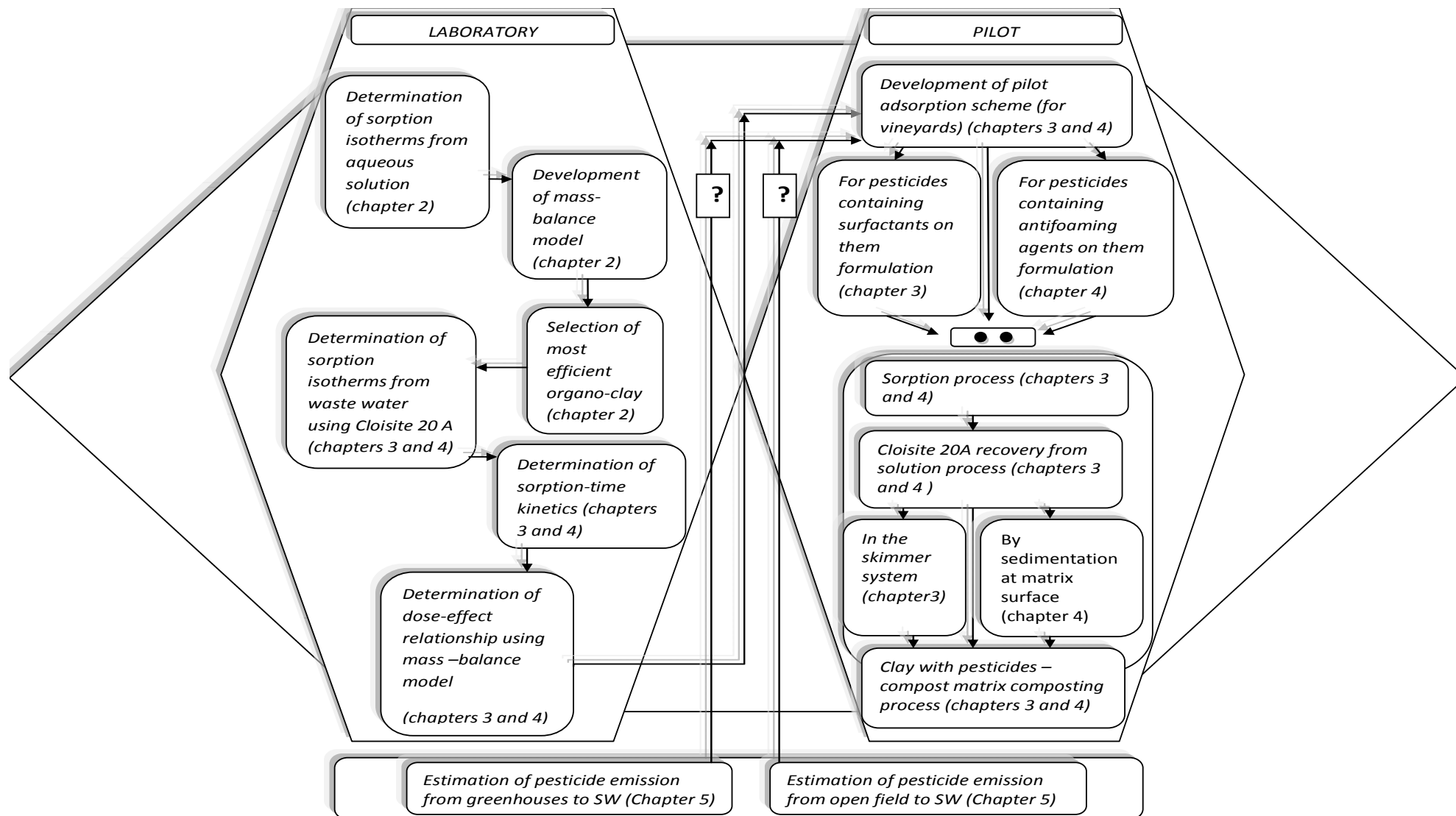


## 6 General Conclusions

Inadequate management of pesticides can give rise to residues in surface- and groundwater, which is a major-environmental issue in Europe (Carter, 2000; Mason et al., 1999). One source of contamination is the use of pesticides in agriculture. A large fraction of this contamination is generated on-farm and is called point-source pollution. The point source pollution can significantly be reduced by applying agricultural best management practices and routines. However, some releases may still occur which makes it difficult to respect the quality standard of pesticides in drinking water which are specified by the EU Directive (98/83/EEC).

To comply to these standards, additional technologies are required to reduce direct pesticide releases. A possible approach is the use of purification systems to capture and treat contaminated water. Out of the agricultural sector, the horticultural sector seems to have a major impact on the environment. However the actual European legislation (EC 1107/2009) considers these greenhouse systems to “prevents release of PPP into the environment”. Therefore a modeling approach to estimate emissions of PPPs from protected crops area was choose to be the most appropriate way to better understand the entity of the environmental concentration and later on using this information for the development of a cost –effective decontamination systems. A comparison with open field cultivation was also performed in order to investigate how the climatic conditions, which are more controlled under greenhouse conditions, influence the PPP emissions to surface water. However the information could further be considered for a possible enlargement of the developed decontamination system use in the agricultural sectors, in addition to vineyards.

Fig. 20 presents the schematic representation of the these whereas Fig. 21 show the questions behind the development process.



**Fig.20** Schematic representation of the theses

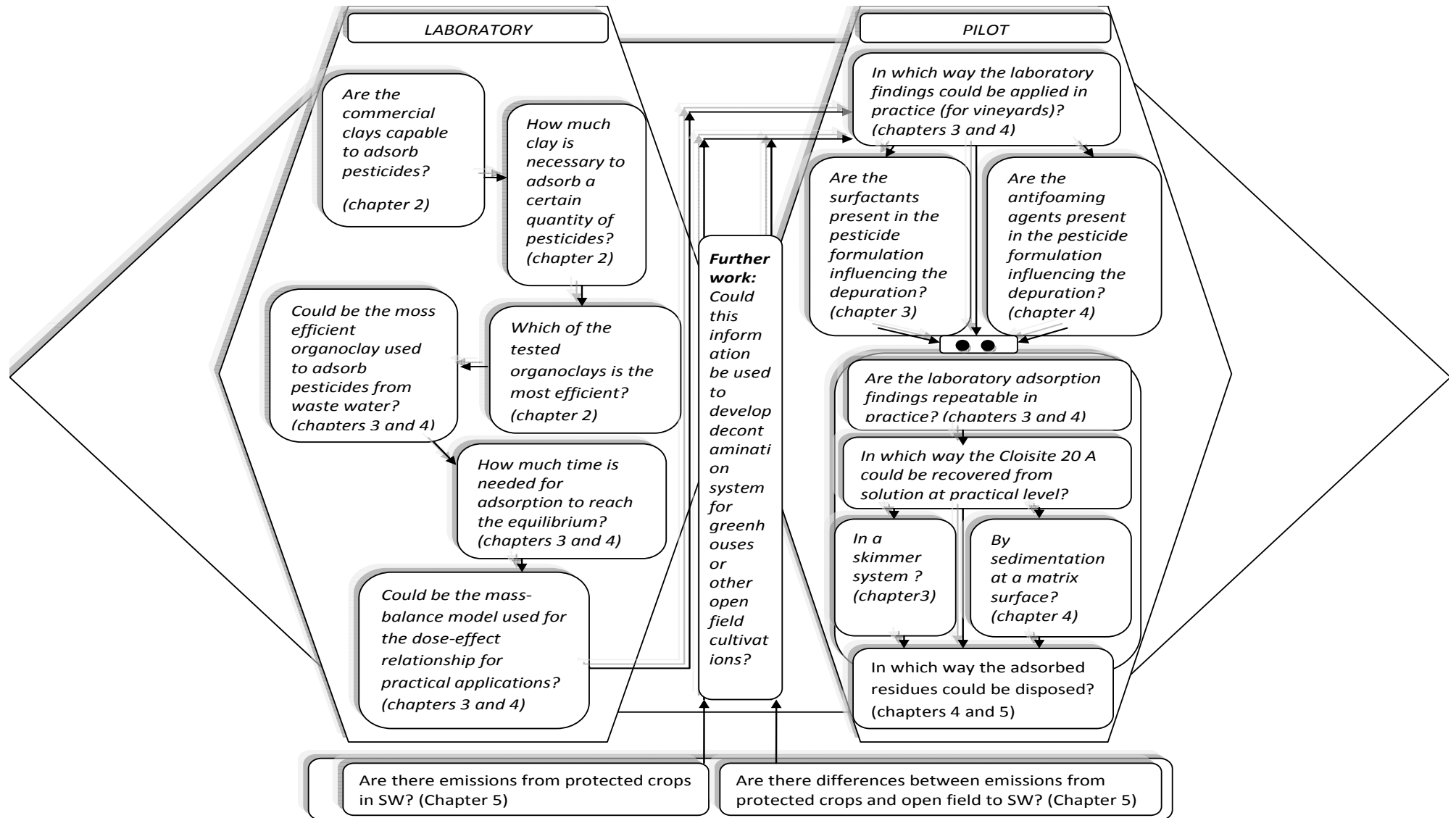


Fig.21 Questions posed to define the objectives

The adsorption of the different pesticides onto micelle-clay complexes and unmodified montmorillonite clay were measured to allow the determination of the maximum pesticide quantity adsorbed in order to obtain a dose-effect relationship for practical applications. The modified clay Cloisite 20A was showed to be more efficient for use in treatment plants for the adsorption of chlorpyrifos and penconazole from aqueous solutions whereas metalaxyl is more efficiently removed by Cloisite 30B. Adsorption tests in laboratory using Cloisite 20 A were also developed for cyazofamid and cyprodinil and the results showed a high affinity of the both fungicides for the organoclay. Therefore Cloisite 20 A was show to be the most efficient organoclay from those tested in this study. This, in part, is explained by the structure of the modifier quaternary salt which contains two aliphatic chains on the structure and determinate a higher space between the layers of the montmorillonite.

Subsequently a depuration scheme was developed to test the practical applicability of the Cloisite 20A organoclay and the results showed it to be efficient for decontaminating pesticide-containing water derived from vineyards. The adsorption tests in the pilot system show a removal of three of the pesticide considered, cyazofamid, penconazole and cyprodinil, to be similar to that predicted from the adsorption tests developed in the laboratory. Concerning the other two pesticides, for instance metalaxyl, even if it showed to be better adsorbed by Cloisite 30B than Cloisite 20A, the higher solubility in water determinate, in part, it's low affinity for the organoclays and made it not appropriate for this study in the pilot system. A high quantity of clay should have been required to remove it from the water. The pesticide chlorpyrifos was as well not considered further in the work principally due to his high octanol-water partition coefficient which made it easy absorbable by the plastic surfaces, there by crating technical problems. The recovery of the modified clay after the adsorption was shown to be dependent on the presence of surfactants in the pesticide formulation. For the adsorption test of penconazole, which contains a higher quantity of surfactants in the formulation, if compared with the formulation of cyazofamid, the recovery of Cloisite 20 A was 20% higher. This higher quantity of surfactants determinates a longer foam formation process in the skimmer system. For the fungicide cyprodinil, formulated with antifoaming agents, an alternative treatment of the clay-water suspension was necessary. After adsorption the suspension was passed through a compost layer which determinates the sedimentation of the clay at the compost surface.

Concerning the waste disposal, for instance the organoclay composted after the adsorption, additional treatments appear to be necessary for pesticides with moderate and high persistence in soil as penconazole and cyprodinil. The fungicide cyazofamid shows a significant decrease after 90 days, in favourable conditions of compost humidity and environment temperature.

The results of the modelling exercise shows that the FOCUS PEARL model, generally used for calculating leaching and drainage of PPP from open field cultivations to ground/surface water could be parameterised to simulate PPP emissions from greenhouses to surface water.

For the case study, weather conditions were found to have a major role on the PPP emissions from glasshouses and the open field. The more controlled climate in the greenhouse prevented a substantial precipitation excess as was observed for the open field, which had a large effect on the leaching concentrations. Furthermore, in greenhouse cultivation it was noticed that the temperature has a slightly higher influence on CC-M emissions from the greenhouse than the irrigation excess volume.

However, the main conclusion of this exercise was that there are potential PPP emissions to surface water associated with crop cultivation in greenhouses, contrary to what is stated in the European Council Regulation 1107/2009, article 3. Therefore a possible use of the outputs of this exercise is in future work to develop decontamination systems for greenhouses or for open field cultivation.

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