INSTITUTO ANDALUZ DE CIENCIAS DE LA TIERRA

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Pesticide behaviour in soils after irrigation with treated wastewater

Modificación del comportamiento de plaguicidas en suelos por riego con aguas residuales

Memoria de Tesis presentada por el Licenciado en Química D. José Antonio Rodríguez Liébana para optar al grado de doctor por la Universidad de Granada

Esta Tesis Doctoral ha sido dirigida por la doctora María Aránzazu Peña Heras, Investigador Científico del CSIC en el Instituto Andaluz de Ciencias de la Tierra

Granada, Septiembre de 2016

VºBº de la directora

El doctorando

María Aránzazu Peña Heras

José Antonio Rodríguez Liébana

Editor: Universidad de Granada. Tesis Doctorales
Autor: José Antonio Rodríguez Liébana
ISBN: 978-84-9163-033-3
URI: http://hdl.handle.net/10481/44293

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presentada por

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Composición del Tribunal de Tesis:

Dr. María Jesús Sánchez Martín, Profesor de Investigación, Presidenta
Departamento de Procesos de Degradación del Medio Ambiente y su Recuperación,
Instituto de Recursos Naturales y Agrobiología de Salamanca (IRNASA, CSIC)

Dr. Antonio Sánchez Navas, Profesor Titular de Universidad, Secretario
Departamento de Mineralogía y Petrología, Universidad de Granada

Dr. Francisco José Martín Peinado, Profesor Titular de Universidad, Vocal
Departamento de Edafología y Química Agrícola, Universidad de Granada

Dr. Tomás Undabeytia López, Científico Titular, Vocal
Departamento de Agroquímica, Microbiología Ambiental y Conservación de Suelos,
Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS, CSIC)

Dr. Laura Delgado Moreno, Investigador Contratado, Vocal
Departamento de Protección Ambiental, Estación Experimental del Zaidín (EEZ, CSIC)

Esta Tesis Doctoral ha sido financiada por los proyectos CGL2007-60355 (plan nacional I+D+i) y A/023943/09 (AECID), y el grupo de investigación RNM-303 de la Junta de Andalucía, con contribución de fondos FEDER y una beca predoctoral del programa Junta de Ampliación de Estudios (CSIC). El trabajo de investigación se ha desarrollado entre la Estación Experimental del Zaidín (CSIC) y el Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR).

LIST OF PUBLICATIONS

Publications related with the thesis:

1. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. (2011). Sorption of hydrophobic pesticides on a Mediterranean soil affected by wastewater, dissolved organic matter and salts. *Journal of Environmental Management* 92 (3), 650-654
2. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. (2014). Role of irrigation with raw and artificial wastewaters on pesticide desorption from two Mediterranean calcareous soils. *Water, Air, and Soil Pollution* 225 (8), article number 2049
3. **Rodríguez-Liébana J.A.**, ElGouzi S., Mingorance M.D., Castillo A. and Peña A. (2014). Irrigation of a Mediterranean soil under field conditions with urban wastewater: Effect on pesticide behaviour. *Agriculture, Ecosystems and Environment* 185, 176-185

4. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. Characterization of the kinetic aspects related with pesticide adsorption to soils. *In preparation*

5. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. Influence of the quality of the irrigation water in the adsorption/desorption of dimethenamid and fenarimol in agricultural alkaline soils. *In preparation*

6. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. Impact of the irrigation water and fertiormont amendment on thiacloprid sorption and leaching through disturbed soil columns. *In preparation*

7. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. Laboratory degradation of three pesticides with different properties under incubation with treated wastewater and dissolved organic matter solutions. Contribution of soil biota. *In preparation*

Other publications:

8. Peña A., **Rodríguez-Liébana J.A.** and Mingorance M.D. (2011). Persistence of two neonicotinoid insecticides in wastewater, and in aqueous solutions of surfactants and dissolved organic matter. *Chemosphere* 84 (4), 464-470
9. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. (2013). Pesticide sorption on two contrasting mining soils by addition of organic wastes: Effect of organic matter composition and soil solution porperties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 435, 71-77

10. **Rodríguez-Liébana J.A.**, Mingorance M.D. and Peña A. (2014). Pesticide mobility and leachate toxicity in two abandoned mine soils. Effect of organic amendments. *Science of the Total Environment* 497-498, 561-569
11. **Rodríguez-Liébana J.A.**, López-Galindo A., Jiménez de Cisneros C., Gálvez A., Rozalén M., Sánchez-Espejo R., Caballero E. and Peña A. (2016). Adsorption/desorption of fungicides in natural clays from Southern Spain. *Applied Clay Science* (in press, DOI: 10.1016/j.clay.2016.07.006)

A mis padres

TABLE OF CONTENTS

Acknowledgements/Agradecimientos 23

Acronyms and abbreviations 27

Abstract/Resumen 33

SCOPE AND OBJECTIVES OF THE THESIS 41

CHAPTER 1: INTRODUCTION 47

- 1.1. PESTICIDES 49
  - 1.1.1. Concepts 49
  - 1.1.2. Historical usage of pesticides 49
  - 1.1.3. Pesticide market 51
  - 1.1.4. Pesticide classification 52
    - 1.1.4.1. Chemical classification 53
    - 1.1.4.2. Classification according to the target organism 53
    - 1.1.4.3. Classification according to the mode of action 54
    - 1.1.4.4. Toxicological classification 55
  - 1.1.5. Biopesticides 55
  - 1.1.6. Pesticide fate in soils 57
    - 1.1.6.1. Adsorption-desorption 57
    - 1.1.6.2. Degradation 60
    - 1.1.6.3. Leaching 63
    - 1.1.6.4. Runoff 63
    - 1.1.6.5. Volatilisation 64
    - 1.1.6.6. Plant uptake 64
  - 1.1.7. Factors controlling pesticide fate in soils 65
    - 1.1.7.1. Soil properties 65
    - 1.1.7.2. Soil solution properties: pH and ionic strength 73
    - 1.1.7.3. Pesticide properties 75

1.1.7.4. Climatic factors: temperature and water content 78

1.2. WASTEWATERS 80

1.2.1. Concepts and composition 80

1.2.2. Influence of the discharge of untreated wastewater on the receiving environment 81

1.2.3. Treatment of urban wastewater 81

1.2.3.1. Context and legislative framework 81

1.2.3.2. Compliance of the EU member states with the directive 83

1.2.3.3. Stages of urban wastewater treatment 85

1.2.4. Treated wastewater reuse 89

1.2.4.1. Context and legislative framework 89

1.2.4.2. Barriers and potential reuse of treated wastewaters in Europe 91

1.2.4.3. Applications of treated wastewaters reuse 91

1.2.4.4. National and local situation 92

1.2.4.5. Reuse of treated wastewaters in agriculture 93

1.2.4.6. Benefits and potential risks from wastewater reuse 95

CHAPTER 2: MATERIALS AND METHODS 99

2.1. EXPERIMENTAL METHODS FOR SOILS AND SOLUTIONS 101

2.1.1. Soil sampling and preparation 101

2.1.2. Soil texture 101

2.1.3. Field capacity 102

2.1.4. Soil pH and electrical conductivity 102

2.1.5. Cation exchange capacity 103

2.1.6. Total C and total N 103

2.1.7. Soil organic carbon 103

2.1.8. Soil moisture content 104

2.1.9. Soil carbonates 104

2.1.10. Soil dehydrogenase activity 105

2.1.11. Soil induced respiration 105

2.1.12. Soil chemical composition: X-ray fluorescence 106

2.1.13. Soil mineralogy: X-ray diffraction 106

2.1.14. Infrared spectroscopy 107

2.1.15. Determination and characterisation of dissolved organic carbon 107

2.1.15.1. Specific UV absorbance at 254 nm ($SUVA_{254}$) 107

2.1.15.2. Humification index (HIX) 108

2.1.16. Total dissolved solids 108

2.1.17. Inorganic anions determination 108

2.2. PESTICIDE INFORMATION AND ANALYSIS 109

2.2.1. General pesticide information 109

2.2.1.1. α-cypermethrin and deltamethrin 109

2.2.1.2. Pendimethalin 110

2.2.1.3. Fenarimol 110

2.2.1.4. Thiacloprid 112

2.2.1.5. Dimethenamid 112

2.2.2. Pesticide stock solutions 112

2.2.3. Pesticide extraction from aqueous samples 113

2.2.4. Pesticide extraction from soil samples 113

2.2.4.1. Microwave assisted extraction 113

2.2.4.2. Ultrasound assisted extraction 114

2.2.5. Pesticide analytical determinations 115

2.2.5.1. Gas chromatography 115

2.2.5.2. High performance liquid chromatography 115

2.3. SITE DESCRIPTION AND SOIL PHYSICOCHEMICAL PROPERTIES 117

2.4. CHEMICAL ANALYSIS OF SOILS 121

2.5. MINERALOGICAL STUDY BY X-RAY DIFFRACTION 123

2.6. FTIR STUDY OF SOILS 125

2.7. TREATED WASTEWATER, SEWAGE SLUDGE AND FERTIORMONT PROPERTIES 127

2.7.1. Treated wastewater 127

2.7.2. Sewage sludge 128

2.7.3. Fertiormont 130

2.8. STATISTICAL ANALYSIS OF THE DATA 131

CHAPTER 3: ADSORPTION–DESORPTION 133

3.1. INTRODUCTION 135

3.1.1. Adsorption kinetics 135

3.1.2. Adsorption–desorption isotherms 135

3.1.2.1. Classification of adsorption isotherms 136

3.1.2.2. Adsorption equilibrium models 137

3.1.2.3. Desorption isotherms and hysteresis 139

3.1.3. Advantages and drawbacks of the batch technique 140

3.1.4. Role of dissolved organic carbon in pesticide retention by soils 141

3.2. EXPERIMENTAL SETUP 142

3.2.1. Adsorption kinetics 142

3.2.1.1. Evaluation of equilibrium time and shape of the curves 142

3.2.1.2. Kinetic models 143

3.2.2. Adsorption of pendimethalin, α–cypermethrin and deltamethrin to glassware ... 145

3.2.3. Adsorption–desorption isotherms 146

3.2.3.1. Adsorption 146

3.2.3.2. Desorption 146

3.3. RESULTS AND DISCUSSION 147

3.3.1. Adsorption kinetics 147

3.3.1.1. Evaluation of equilibrium time and shape of the curves 147

3.3.1.2. Kinetic models 149

3.3.2. Adsorption of pendimethalin, α–cypermethrin and deltamethrin to glassware ... 161

3.3.2.1. Without soil ... 162

3.3.2.2. With soil ... 164

3.3.3. Adsorption isotherms ... 164

3.3.3.1. Pendimethalin, α–cypermethrin and deltamethrin in SV soil ... 165

3.3.3.2. Thiacloprid in SV soil ... 169

3.3.3.3. Dimethenamid and fenarimol in SV, RM1 and RM3 soils ... 173

3.3.4. Desorption isotherms ... 179

3.4. CONCLUSIONS ... 181

CHAPTER 4: RELEASE FROM SOILS ... 183

4.1. INTRODUCTION ... 185

4.2. EXPERIMENTAL SETUP ... 186

4.2.1. Soil fortification and desorption experiments ... 186

4.2.2. Analytical determinations ... 186

4.2.3. Data analysis ... 187

4.3. RESULTS AND DISCUSSION ... 187

4.3.1. Desorption with MQ and treated wastewater ... 187

4.3.2. Desorption with surfactant solutions ... 189

4.3.2.1. Thiacloprid ... 189

4.3.2.2. Fenarimol ... 192

4.3.3. Desorption with inorganic salt solutions and dissolved organic matter ... 193

4.3.3.1. Inorganic salts ... 193

4.3.3.2. Dissolved organic matter ... 195

4.4. CONCLUSIONS ... 198

CHAPTER 5: DEGRADATION ... 201

5.1. INTRODUCTION ... 203

5.2. EXPERIMENTAL SETUP ... 204

5.2.1. Degradation experiments ... 204

5.2.2. Analytical determinations.......... 206
5.2.3. Degradation models.......... 206
5.2.4. Data analysis.......... 208
5.3. RESULTS AND DISCUSSION.......... 209
5.3.1. Evolution of soil moisture content during incubation.......... 209
5.3.2. Experimental data fitting. Model comparison.......... 210
5.3.3. Pesticide degradation under incubation with the different solutions.......... 213
5.3.3.1. MQ water.......... 213
5.3.3.2. Treated wastewater.......... 216
5.3.3.3. Dissolved organic carbon solutions.......... 216
5.3.4. Soil sterilisation effects and biological contribution.......... 218
5.3.4.1. MQ water.......... 218
5.3.4.2. Treated wastewater.......... 218
5.3.4.3. Dissolved organic carbon solutions.......... 219
5.3.5. Dehydrogenase activity.......... 219
5.4. CONCLUSIONS.......... 221
CHAPTER 6: LEACHING.......... 223
6.1. INTRODUCTION.......... 225
6.2. EXPERIMENTAL SETUP.......... 226
6.2.1. Column experiments.......... 226
6.2.2. Analytical determinations.......... 229
6.2.3. Transport models.......... 229
6.2.4. Data analysis.......... 231
6.3. RESULTS AND DISCUSSION.......... 234
6.3.1. Leachate properties and water flow through columns.......... 234
6.3.2. Description of bromide breakthrough curves and modelling with STANMOD program.......... 236

6.3.3. Description of thiacloprid breakthrough curves and modelling with STANMOD program 240

6.3.4. Thiaclorprid amount remaining in soil 246

6.4. CONCLUSIONS 247

CHAPTER 7: FIELD EXPERIMENT 249

7.1. INTRODUCTION 251

7.2. EXPERIMENTAL SETUP 252

7.2.1. Properties of pesticides and irrigation fluids 252

7.2.2. Experimental site and climatic conditions 252

7.2.3. Field experiment 254

7.2.4. Pesticide adsorption isotherms 255

7.2.5. Analytical determinations 255

7.2.6. Evaluation and statistical treatment of the data 256

7.3. RESULTS AND DISCUSSION 257

7.3.1. Soil physicochemical properties 257

7.3.2. Pesticide adsorption isotherms 257

7.3.3. Bromide behaviour in the field plots 258

7.3.4. Pesticide dissipation in the field plots 261

7.3.5. Soil anion fate 265

7.3.6. Soil induced respiration and dehydrogenase activity 267

7.4. CONCLUSIONS 269

GENERAL CONCLUSIONS 271

REFERENCES 277

ACKNOWLEDGEMENTS

AGRADECIMIENTOS

ACKNOWLEDGEMENTS/AGRADECIMIENTOS

Una vez finalizada la redacción de esta memoria es momento de dedicar unas palabras a todos aquellos que, de una forma u otra, han formado parte del proceso.

En primer lugar, me gustaría destacar la labor de la Dra. Arancha Peña por brindarme la oportunidad de trabajar en investigación, participar de forma muy activa tanto en el trabajo de laboratorio como de escritorio, y mantener la confianza desde el primer hasta el último momento. En segundo lugar, a una de esas personas especiales y diferentes, la Dra. Mª Dolores Mingorance. Gracias por sus consejos, por el tratamiento de los datos, por incluirme en su grupo de investigación y porque siempre tuve la sensación de que era mi codirectora. Su esencia y su energía estarán siempre presentes.

También quería dar las gracias a la Estación Experimental del Zaidín y al Instituto Andaluz de Ciencias de la Tierra por permitirme hacer uso de sus instalaciones y equipos.

Thanks to Prof. Rai Kookana and his team for their warm welcome at CSIRO Land and Water centre in Adelaide and for helping me to grow as a scientist during my short stay. Special thanks to Lester Smith and Sheridan Martin for their guidance in the laboratory. In addition, special thanks to Divina, Martin and Sabela for the lunches, dinners, walks and funny moments around Adelaide and surrounds. I also would like to thank to Mien, Kevin and Miroslav of the Elm Tree Lodge for making me feel at home in that 'weird' place.

A todos los miembros del antiguo departamento de Geoquímica Ambiental de la EEZ. Especialmente, al Dr. Javier Huertas por permitirme usar el cromatógrafo iónico y, a la Dr. Concepción Jiménez por revisar la caracterización espectroscópica de los suelos y, sobre todo, al Dr. Rafa Bellver por sus sabios consejos y su sonrisa permanente.

A mis compañeros de grupo: a Jesús por enseñarme a muestrear suelos y llevarme a las minas de Alquife; a Antonia por su originalidad e introducirme en los experimentos de lixiviación; a Mariana, la chica de Mar del Plata que me enseñó a

disfrutar del mate; a Dani (‘el paraeño’) por alegrarnos el día a día y enseñarme técnicas de relajación; a Isa y Ana por vuestra ayuda en el laboratorio y mantener la amistad fuera de él, junto a Gerardo y David. A Siham, la flecha de ‘la paloma blanca’, porque me enorgullece haber sido tu ‘Ángel de laboratorio’ y haberte visto evolucionar durante estos años. Gracias por ser mi amiguita y haberte inventado tantas palabras y expresiones graciosas.

A mis amigos y compañeros de la EEZ e IACT: Marisa y familia, Chiara y Mauri, Mª Jesús, Álvaro y Alba, Amel, Iratxe, Pepeiño, Edu, Dani y Paula, y José Antonio por todas las conversaciones trascendentales durante los desayunos y el cerveceo dentro y fuera de horario laboral.

A todos los que han pasado por la peña de fútbol sala de la EEZ porque me he divertido mucho jugando con ellos. A mis amigos y familia de Peal por considerarme uno más desde el día en que llegué. A mis amigos de toda la vida de Jaén por tantos momentos inolvidables; en especial al Robles bajo cuyo paraguas he avanzado desde que éramos unos pardillos. A tu lado he conocido la verdadera dimensión del concepto amistad.

Gracias a mi extensa familia: hermanos, cuñados, sobrinos y, en especial, a mis padres, Juani y Antonio, por su amor y apoyo incondicional, y porque sin su confianza nunca habría llegado hasta aquí.

Por último a mi mejor amiga, Elena, porque tu sola presencia me calma y me hace más fuerte, por estar en los momentos malos y en los mejores. Junto a ti crezco cada día.

ACRONYMS AND ABBREVIATIONS

ACRONYMS AND ABBREVIATIONS

General

CEC, cation exchange capacity

CYP, α-cypermethrin

DHA, dehydrogenase activity

DIM, dimethenamid

DOC, dissolved organic carbon

DTM, deltamethrin

EC, electrical conductivity

FC, field capacity

FEN, fenarimol

GC-μECD, gas chromatography with μ-electron capture detection

HIX, humification index

HPLC-DAD, high performance liquid chromatography with diode-array detection

INT, 2-p-iodophenyl-3-p-nitrophenyl-5-phenyltetrazolium chloride

INTF, iodonitrotetrazolium formazan

IR, infrared

K_{ow}, octanol-water partition coefficient

LD_{50}, time to achieve 50% of initial solute concentration

LD_{90}, time to achieve 10% of initial solute concentration

LOD, limit of detection

MQ, MilliQ water

MSE, mean standard error

OC, organic carbon

OM, organic matter

PDM, pendimethalin

R^2, determination coefficient

RM1, soil

RM3, soil

SOM, soil organic matter

SUVA, specific UV absorbance

SV, soil

THC, thiacloprid

TWW, urban treated wastewater

XRD, X-ray diffraction

α, significance level

p, probability of an event to occur

Chapters

4: Adsorption-desorption and release

1/n, Freundlich sorption constant, related to soil heterogeneity

A22, Aerosol 22, commercial surfactant

B, kinetic constant, hyperbolic model

BP, Biopower, commercial surfactant

C, extent of the boundary layer thickness (Intraparticle diffusion model)

C_0, initial pesticide concentration

C_e, equilibrium concentration of the pesticide in solution

CMC, critical micelle concentration

D, total desorbed pesticide

E, efficiency coefficient

H, hysteresis coefficient

h, initial adsorption rate

k, kinetic rate

K_d, partitioning coefficient

K_f, Freundlich sorption constant, indicating adsorption capacity

K_{OC}, OC partitioning coefficient

L, Langmuir constant related to the affinity of the solute for the sorbent

PFO, pseudo-first order kinetic model

PSO, pseudo-second order kinetic model

R_E, equilibrium parameter in the Elovich model

R_i, initial adsorption factor in the intraparticle diffusion model

SS-MQ, sewage sludge extracted with MQ

SS-Ph, sewage sludge extracted with with NaH_2PO_4

TW-80, Tween 80, commercial surfactant

TX-100, Triton X100, commercial surfactant

X, pesticide concentration in soil

α, initial rate in the Elovich model

β, constant related to chemisorption in the Elovich model

5: Degradation

C, solute concentration in the liquid phase

k, degradation rate

FOMC, first order multicompartment model

SFO, single first order model

α, shape parameter in the FMOC model

β, shape parameter in the FMOC model

χ^2, chi-square test

6: Leaching

BTC, breakthrough curve

CDE, convection-dispersion equation

CXTFIT, one-dimensional transport model

D, apparent diffusion coefficient

f, fraction of equilibrium sorption sites

FERT, Fertiormont, commercial organic fertiliser

P, Peclet number

PV, pore volume

q, Darcy velocity

Q, elution flux at the column outlet

R, solute retardation factor

STANMOD, STudio of ANalytical MODels

α, first order rate

β, fraction factor

γ, zero-order production term

θ, volumetric water content

λ, column dispersivity

ν, pore-water velocity

ρ, soil bulk density

μ, first-order degradation coefficient

ω, mass transfer coefficient

7: Field experiment

A, plateau

DFOP, biexponential model

GUS, index used as environmental risk indicator

WL, well water

ABSTRACT

RESUMEN

ABSTRACT

The development of the chemical industry after the Second World War resulted in the synthesis of a huge amount of organic pesticides used in agriculture to boost crop productivity for the growing world population. However, their massive and, in some cases, improper use has given rise to the contamination of freshwater sources and soils. Therefore, with the spreading of an environmentally friendly awareness, the understanding of the physicochemical processes affecting pesticide fate in soils has raised considerable interest.

At the same time pressure on water resources in urban areas has been increasing in the last decades because of growing demand and limited water sources. Numerous initiatives focusing on the reuse of wastewaters have appeared worldwide, with special attention being paid to those areas with low rainfall and long drought periods such as the Mediterranean basin. In this sense, agricultural irrigation has become the main application of water reuse, after adequate treatment, thus preserving freshwater sources for other purposes such as drinking water supply. Water reuse allows a continuous water supply during the irrigation period, hence reducing the risk of crop losses. Despite the general advantages derived from treatment and reutilisation of wastewaters, limited awareness of potential benefits among stakeholders and the general public, and lack of a supportive and coherent regulatory framework for water reuse are two major barriers currently preventing a wider spreading of this practice in the EU. On the other hand, irrigation of agricultural lands with treated wastewaters may introduce great amounts of some constituents in the soil environment, especially dissolved organic matter, inorganic salts and surfactants, which have been reported to influence the main mechanisms involved in adsorption, degradation and mobility of pesticides.

Thus the **main objective** of this thesis was **to assess the influence of short-term irrigation with treated wastewater on the behaviour of different pesticides in three agricultural calcareous soils of the province of Granada (Southern Spain), with a special focus on the role of dissolved organic matter and inorganic salts present in wastewaters.**

This was assessed with treated wastewater corresponding to the effluents of the secondary sedimentation tank of the wastewater treatment plant of Churriana (Granada). Dewatered secondary sewage sludge from the same wastewater treatment plant was used as a source of dissolved organic matter. Additionally, a solid organic amendment (fertiormont) was employed in some experiments to evaluate the effect of this usual agricultural practice on pesticide behaviour.

Six pesticides covering a wide range of physicochemical properties were selected: two pyrethroid insecticides (α-cypermethrin and deltamethrin), a dinitroaniline herbicide (pendimethalin), a pyrimidine fungicide (fenarimol), a chloroacetamide herbicide (dimethenamid) and a neonicotinoid insecticide (thiacloprid).

The results show that treated wastewater increased significantly the adsorption of highly hydrophobic pesticides (log $K_{OW} > 4$), which was related with the amount and type of inorganic salts rather than with the presence of dissolved organic matter. However, the influence of the irrigation water quality in the retention of more polar compounds was practically negligible.

Pesticide solubilisation from soils previously contaminated depended on the type of soil, but was not altered by the use of treated wastewater. The presence of surfactants, inorganic salts and dissolved organic matter in the solution affected differently the release of thiacloprid and fenarimol, depending on both soil and solution characteristics.

No relevant effects were observed in the degradation of pesticides in soil incubated with treated wastewater and dissolved organic matter solutions. However, the use of wastewater depleted the activity of soil microorganisms in the early stages of incubation.

The use of treated wastewater did not significantly affect the leaching of thiacloprid through soil columns. However, irrigation with solutions at low dissolved organic carbon concentration and fertiormont amendment reduced the mobility of the insecticide. Although irrigation with dissolved organic carbon–rich solutions also delayed thiacloprid leaching, the total amount percolated was similar to the control treatment probably due to specific interactions between the insecticide and dissolved organic carbon during the experiment.

The field experiment confirmed laboratory findings. The disappearance of thiacloprid and pendimethalin from plots irrigated with wastewater was slower than from plots irrigated with water of higher quality. However, addition of fertiormont masked these differences. As in degradation experiment in the laboratory, wastewater irrigation seemed to have a negative effect on soil microbial population.

We can conclude that the use of treated wastewater for irrigation only produces small changes in the soil behaviour of pesticides (adsorption, desorption, degradation, mobility), and that the greatest variations correspond to the more hydrophobic compounds, that will require greater attention in the future. A remarkable aspect to consider is the effect of wastewater on the soil microbial population, which intervenes and regulates a wide variety of processes in the soil.

RESUMEN

El desarrollo de la industria química al finalizar la 2ª Guerra Mundial dio lugar a la síntesis de numerosos plaguicidas orgánicos usados en agricultura para potenciar la productividad de los cultivos, dado el aumento de la población. Sin embargo, su uso masivo y, en algunos casos, inadecuado ha conllevado un aumento de la contaminación de aguas y suelos. Todo lo anterior, unido a una mayor concienciación medioambiental de la población, ha promovido y alentado la comprensión de los procesos que afectan al destino y comportamiento de los plaguicidas en el suelo.

En las últimas décadas se ha producido también un aumento de la presión sobre los recursos hídricos, debido a una demanda creciente y a la previsión de su limitación como consecuencia del cambio global. Se han propuesto numerosas iniciativas, centradas fundamentalmente en la reutilización de aguas residuales depuradas, en especial en áreas caracterizadas por bajas precipitaciones y largos periodos de sequía, como la cuenca mediterránea. En este sentido, la aplicación más frecuente se ha concentrado en el riego agrícola con lo que se preservan las fuentes de agua fresca para otros fines, como el suministro de agua potable. Con esta práctica se asegura un suministro continuo de agua durante los periodos de riego, con lo que se reduce el riesgo de pérdida de los cultivos.

A pesar de las numerosas ventajas que se derivan del tratamiento y la reutilización de aguas residuales, existen dos barreras principales que limitan la expansión de esta práctica en la UE: por un lado, un conocimiento limitado de los beneficios potenciales por parte de las partes interesadas y de la población en general y, por otro, ausencia de un marco jurídico favorable y coherente sobre su reutilización. Asimismo, el riego de suelos agrícolas con aguas residuales tratadas puede introducir en el suelo grandes cantidades de algunas sustancias, en especial, materia orgánica disuelta, sales inorgánicas y/o tensioactivos, que podrían alterar los principales mecanismos implicados en la adsorción, degradación y movilidad de plaguicidas.

Por ello, el **objetivo principal** de esta tesis ha consistido **en evaluar la influencia a corto plazo del riego con aguas residuales tratadas en el comportamiento de diferentes plaguicidas en tres suelos de la provincia de Granada (sudeste de España), haciendo hincapié en el papel de la materia**

orgánica disuelta y de las sales inorgánicas presentes en dichas aguas residuales.

Para alcanzar este objetivo general se utilizaron aguas residuales depuradas correspondientes a los efluentes del tanque secundario de sedimentación de la estación depuradora de aguas residuales de Churriana (Granada). Igualmente se emplearon fangos o lodos desecados procedentes del tratamiento secundario, de la misma estación de tratamiento, como fuente de materia orgánica disuelta. En algunos experimentos se incluyó la adición de un fertilizante orgánico sólido (fertiormont) para evaluar el efecto de esta práctica agrícola en el comportamiento de los plaguicidas.

Se seleccionaron seis plaguicidas con un amplio rango de propiedades fisicoquímicas: dos insecticidas piretroides (α-cipermetrina y deltametrina), un herbicida de la familia de las dinitroanilinas (pendimetalina), un fungicida pirimidínico (fenarimol), un herbicida de la familia de las cloroacetamidas (dimetenamida) y un insecticida neonicotinoide (tiacloprid).

Los resultados demuestran que las aguas residuales depuradas generan un aumento considerable en la adsorción de plaguicidas altamente hidrófobos (log $K_{OW} > 4$), que está más relacionado con la cantidad y tipo de sales inorgánicas que con la presencia de materia orgánica disuelta. Sin embargo, la calidad del agua de riego tuvo una influencia prácticamente nula en la retención de compuestos más polares.

La solubilización de plaguicidas desde suelos previamente contaminados depende del tipo de suelo y no se vio alterada por el uso de aguas residuales. Por otra parte, la presencia de tensioactivos, sales y materia orgánica disuelta en el agua afectó de forma diferente a la liberación de tiacloprid y fenarimol, dependiendo de las características del suelo y de la propia solución. Este efecto parece ser más importante para compuestos menos solubles en agua.

No se observaron efectos relevantes en la degradación de plaguicidas en suelos incubados con aguas residuales tratadas y diferentes soluciones de materia orgánica. Sin embargo, el uso de aguas residuales indujo en los primeros días de incubación una menor actividad de los microorganismos del suelo.

El uso de aguas residuales depuradas no parece influir de forma significativa en la lixiviación de tiacloprid a través de columnas de suelo. Sin embargo, el riego con soluciones de baja concentración en carbono orgánico disuelto y el uso de fertiormont como enmienda orgánica produjeron una disminución en la movilidad del insecticida. Aunque el riego con soluciones ricas en carbono orgánico disuelto también retrasó la movilidad del compuesto, la cantidad total lixiviada fue similar a la del tratamiento control debido probablemente a interacciones específicas entre el insecticida y el carbono orgánico disuelto durante el experimento.

El ensayo de campo confirmó los resultados de laboratorio. La desaparición de tiacloprid y pendimetalina de parcelas regadas con aguas residuales fue más lenta que de las irrigadas con aguas de mayor calidad. Sin embargo, la adición de fertiormont redujo estas diferencias. Al igual que en los experimentos de degradación en el laboratorio, el riego con aguas residuales parece tener un efecto negativo en la población microbiana del suelo.

Así pues podemos concluir que el uso para riego de aguas residuales tratadas sólo produce en general pequeños cambios en el comportamiento y destino de plaguicidas en suelo (adsorción, desorción, degradación, movilidad), y que las mayores variaciones corresponden a los compuestos más hidrófobos, a los que será necesario prestar una mayor atención en el futuro. Un aspecto destacable a considerar es el efecto de las aguas residuales en la población microbiana del suelo, que interviene y regula una amplia variedad de procesos en el suelo.

SCOPE AND OBJECTIVES OF THE THESIS

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The development of the chemical industry after the Second World War resulted in the synthesis of a huge amount of organic pesticides used in agriculture to boost crop productivity for the growing world population. However, their massive and, in some cases, improper use has given rise to the contamination of freshwater sources and soils. Therefore, with the spreading of an environmentally friendly awareness, the understanding of the physicochemical processes affecting pesticide fate in soils has raised considerable interest.

At the same time pressure on water resources in urban areas has been increasing in the last decades because of growing demand and limited water sources. Numerous initiatives focusing on the reuse of wastewaters have appeared worldwide, with special attention being paid to those areas with low rainfall and long drought periods such as the Mediterranean basin. In this sense, agricultural irrigation has become the main application of water reuse, after adequate treatment, thus preserving freshwater sources for other purposes such as drinking water supply. Water reuse allows a continuous water supply during the irrigation period, hence reducing the risk of crop losses. Despite the general advantages derived from treatment and reutilisation of wastewaters, limited awareness of potential benefits among stakeholders and the general public, and lack of a supportive and coherent regulatory framework for water reuse are two major barriers currently preventing a wider spreading of this practice in the EU. On the other hand, irrigation of agricultural lands with treated wastewaters may introduce great amounts of some constituents in the soil environment, especially dissolved organic matter, inorganic salts and surfactants, which have been reported to influence the main mechanisms involved in adsorption, degradation and mobility of pesticides.

Thus the **main objective** of this thesis was **to assess the influence of short-term irrigation with treated wastewater on the behaviour of different pesticides in three agricultural calcareous soils of the province of Granada (Southern Spain), with a special focus on the role of dissolved organic matter and inorganic salts present in wastewaters.**

This was assessed with treated wastewater corresponding to the effluents of the secondary sedimentation tank of the wastewater treatment plant of Churriana

(Granada). Dewatered secondary sewage sludge from the same wastewater treatment plant was used as a source of dissolved organic matter. Additionally, a solid organic amendment (fertiormont) was employed in some experiments to evaluate the effect of this usual agricultural practice on pesticide behaviour.

Six pesticides covering a wide range of physicochemical properties were selected: two pyrethroid insecticides (α-cypermethrin and deltamethrin), a dinitroaniline herbicide (pendimethalin), a pyrimidine fungicide (fenarimol), a chloroacetamide herbicide (dimethenamid) and a neonicotinoid insecticide (thiacloprid).

In order to achieve the main goal of this research, the following partial objectives were addressed:

1. *Development and optimisation of analytical methodologies allowing the determination of pesticides in different aqueous and soil samples (chapter 2).*
2. *Study of the adsorption (kinetics and isotherms) of the pesticides in the three soils with solutions of different nature. Furthermore, the effects of wastewater composition on dimethenamid and fenarimol desorption from the three soils were also evaluated (chapter 3).*
3. *Evaluation of the influence of wastewater and different solutions on the release of thiacloprid and fenarimol previously adsorbed on two of the soils (chapter 4).*
4. *Analysis of the degradation of thiacloprid, pendimethalin and fenarimol in a soil incubated with different solutions including wastewater and dissolved organic matter at different concentrations. The biological contribution to pesticide degradation was established by comparison with sterilised soil. To further interpret the results several kinetic models were used for data fitting and dehydrogenase activity changes with time were measured (chapter 5).*
5. *Assessment of the transport parameters and the processes involved in the leaching of thiacloprid through soil columns. The impacts of using infiltrating solutions of different composition and amendment with fertiormont were also studied. Fitting of data was performed by CXTFIT modelling using STANMOD software package (chapter 6).*
6. *Field study to assess the dissipation of thiacloprid and pendimethalin under more realistic conditions. The effects of treated wastewater irrigation and fertiormont amendment were determined by comparison with a control treatment.*

Dehydrogenase activity and soil induced respiration were measured to help obtaining an overall picture of the entire process (chapter 7).

1. INTRODUCTION

1.1. PESTICIDES

1.1.1. Concepts

In general, a pesticide is a chemical or biological agent that deters, incapacitates, kills, or otherwise discourages pests. According to the Food and Agriculture Organisation of the United Nations (FAO, 2005), **pesticide** is *any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.*

The definition above implies that pesticides are toxic chemical agents that are deliberately released into the environment to combat crop pests and disease vectors. The most common use of pesticides is as plant or crop protection products, which in general protect plants from damaging influences such as weeds, fungi, or insects.

Active ingredient is defined as the biologically active part of the pesticide; and **formulation,** as purchased by users, is the combination of various ingredients designed to render the product useful and effective for the purpose claimed.

1.1.2. Historical usage of pesticides

Although the science of pest control is considered to be of recent origin (from the latter part of the 19^{TH} century), it is probably true that humans have practiced some form of pest control since the beginnings of agriculture around 10000 BCE in the Fertile Crescent of the Mesopotamian Civilisation (Smith and Secoy, 1975) to alleviate crop losses. Even today, direct yield losses caused by pathogens, animals, and weeds range between 20 and 40% of global agricultural productivity (Oerke, 2006; Savary et al., 2012). The first recorded use of pesticides is about 4500 years ago by Sumerians who used sulfur compounds to control insects and mites. About 3200 years ago the Chinese pioneered the use of mercury and arsenical compounds for controlling insects

(Unsworth, 2010). Apart from religious and folk magic practices, some forms of chemical methods for fungal, weed and insect control in classical Greece and Rome have been documented, such as the use of fumigation with a variety of smokes or the application of olive oil and sulfur with different additives ("Geoponika"; Smith and Secoy, 1975).

Until the 1940s, pest control chemicals were derived from plants and inorganic compounds. For instance, pyrethrum, which is derived from the flowers of *Chrysanthemum cinerariaefolium,* has been used as an insecticide for over 2000 years. Persians used the powder to protect stored grain, and it was used later in Europe to control head lice. On the other side, Bordeaux Mixture, based on copper sulfate and lime, is still used against various fungal diseases. The drawback for many of these products was their high rates of application, lack of selectivity and phytotoxicity. The growth in synthetic pesticides accelerated in the 1940s with the discovery of the effects of DDT, aldrin, dieldrin, endrin, chlordane, parathion, captan and 2,4-D (Jarman and Ballschmiter, 2012). Given their significant success at a relatively low cost, these synthetic products launched the modern chemical industry and began a new era in pest control. Nevertheless, some important drawbacks, like pest resistance to these compounds, rapidly appeared.

Throughout most of the 1950s, consumers and most policy makers were not overly concerned about the potential health risks in using pesticides. However, some problems derived from their indiscriminate use, such as bioaccumulation, were highlighted in the book Silent Spring (Carson, 1962).

Since the publication of Silent Spring, growing awareness and concern have led to more stringent regulations and the seeking of safer compounds. The 1970s and 1980s were characterised by the introduction on new chemical classes such as sulfonylureas and dinitroanilines for weeds, pyrethroids and benzoylureas for insects (Elliott, 1989), and azoles and pyrimidines for fungal control. In the 1990s research activities focused on finding new members of existing families with greater selectivity and better environmental and toxicological profiles (Briggs, 1994). This period also constituted the refinement of mature products in terms of use patterns with the introduction of newer and more user-friendly and environmentally safe formulations. In addition the use of Integrated Pest Management systems, which discourage the development of pest populations and reduce the use of agrochemicals, has also become more widespread.

These changes have altered the nature of pest control and have the potential to reduce and change the nature of agrochemicals used.

From recent decades, less toxic compounds of natural origin, known as biopesticides, have been introduced to partially substitute highly toxic synthetic chemicals (Pérez López, 2012).

1.1.3. Pesticide market

Pesticides help to increase farm yields and still have a large scope to improve the overall agricultural production of the world. Decreasing farmlands and increasing population pose a serious threat to food security. Furthermore, grains are also used to produce biofuel posing a risk to food security, especially in developing and under developed regions where price drastically influences consumption.

The global pesticide market (crop and non-crop plants) has been estimated at 58.4 billion $ in 2015 and is projected to reach 77.4 billion $ by 2020, at a compound annual growth rate of 5.79% during the forecast period (2015 to 2020), with herbicides accounting for 44% of total sales in 2015 (Figure 1.1).

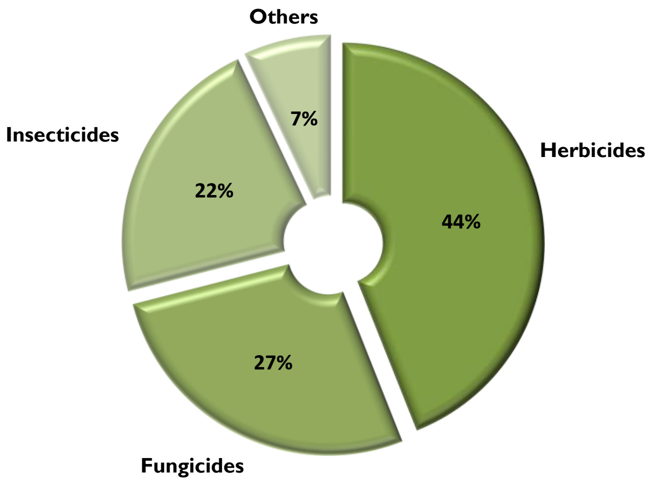


Figure 1.1. Global pesticide market in 2015 by segments

The current trend to survive in the market is the research and innovation route. Genetically modified plants have helped farmers increase their yields coupled with the reduction of use in some pesticides. Biopesticides adoption is also increasing all over the world, especially in developed and some developing countries due to the public awareness regarding food safety and environmental concern, as well as more stringent regulations. They are expected to grow at a compound annual growth rate of 15.5% to reach 3.2 billion $ by 2018.

The consumption of pesticides for crop protection in Spain has gradually increased since the mid-1990s (Figure 1.2). However, the economic situation and unfavourable climatic episodes in 2011 resulted in a 4% reduction, thus returning to values similar to those previous to the economic crisis. Sales of pesticides in the Spanish market reached a value of 925 million € in 2013, 8.2% higher than in 2012. Herbicides met 35% of the total sales, followed by insecticides (30%) and fungicides (25%), corresponding the rest (10%) to other types.

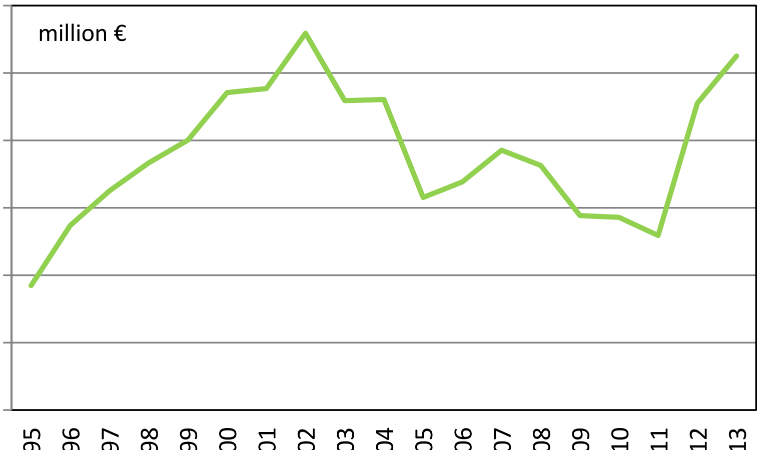


Figure 1.2. Evolution of pesticide sales in the Spanish market during the last two decades (million €)

Exports of pesticides decreased by 1.7% to 832 million €. Despite this fall, it is practically twice as much as that of 2009. It is worth noting the increase in sales to Germany and France (40% of the total). Imports totalled 597 million €, an increase of 5.1%. European countries are the main suppliers, especially Germany and France (47% of the total).

1.1.4. Pesticide classification

Due to the large number of pesticides currently in use with a wide range of physicochemical properties and chemical classes, pesticides can be classified according to different aspects such as the chemical nature, the target pest, the mode of action and the toxicity.

1.1.4.1. Chemical classification

A traditional classification of pesticides places them in one of two groups depending on the chemical nature: organic and inorganic. Organic pesticides can be subdivided in natural and synthetic compounds: the natural organic pesticides are derived from naturally occurring sources such as plants (i.e. rotenone, pyrethrum, nicotine…). Synthetic organic pesticides are produced artificially by chemical synthesis. The vast majority of modern pesticides are synthetic organic compounds, some of which are based on natural molecules (i.e. pyrethroids, neonicotinoids…).

Furthermore, organic pesticides can be classified according to the chemical structure, the presence of functional groups, or considering the ionic or nonionic character of the molecule (Figure 1.3).

1.1.4.2. Classification according to the target organism

Another important classification of pesticides is based on the type of organism against which they are directed (Table 1.1). Some pesticides control more than one class of pests and may be classified in more than a single category.

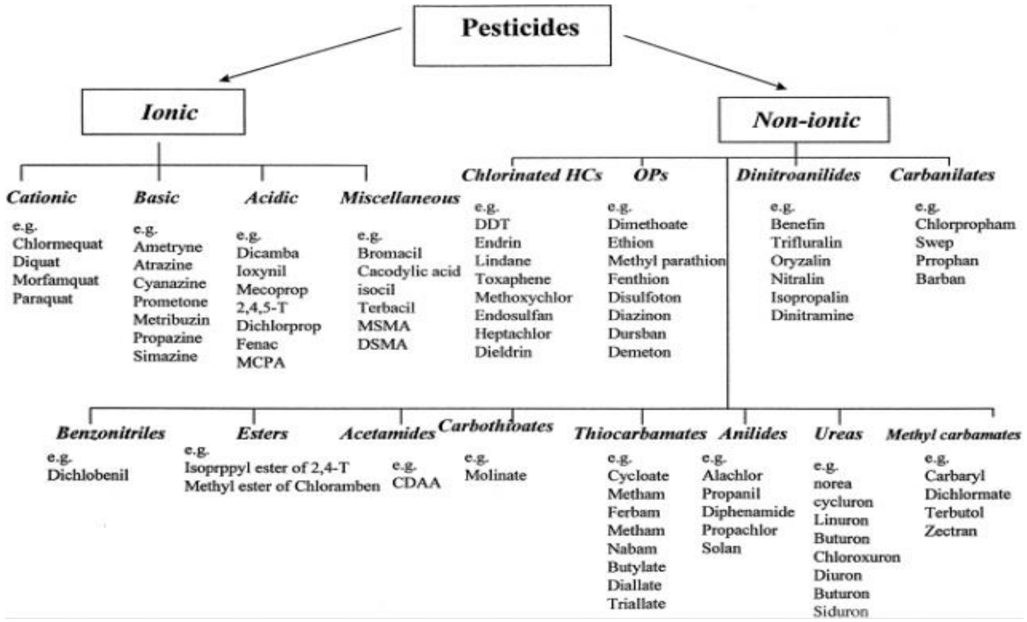


Figure 1.3. Chemical classification of organic pesticides (Gevao et al., 2000)

Table 1.1. Types of pesticides and the corresponding target organisms

Type of pesticide	Target organisms	Type of pesticide	Target organisms
Algaecides	Algae	*Insecticides*	Insects
Antimicrobials	Microorganisms	*Miticides (acaricides)*	Mites
Avicides	Birds	*Molluscicides*	Snails and slugs
Defoliants	Plant leaves	*Nematicides*	Nematodes
Disinfectants	Microorganisms	*Ovicides*	Insect eggs
Fumigants	Air or soil borne insects and diseases	*Piscicides*	Fishes
Fungicides	Fungi	*Repellents*	Insects, birds…
Herbicides	Weeds	*Rodenticides*	Rodents

Herbicides, insecticides and fungicides are the most widely used, and hence considered of major importance. Among herbicides, the most important classes correspond to phenoxies, triazines, thiocarbamates, ureas and uracils, sulfonylureas, dinitroanilines, benzoic acid derivatives and acetanilides.

Among insecticides, the most common classes are organochlorines, organophosphates, carbamates, pyrethroids and neonicotinoids. It is important to note that organochlorine insecticides have been included in the list of persistent organic pollutants (Stockholm Convention, 2011) and banned because of their high toxicity and environmental persistence (Radcliffe et al., 2009).

Most fungicides used belong to azoles, carbamates, pyrimidines, pyridines, strobilurins, dicarboximides, phenylamides, phenylpyrroles, anilinopyrimidines and carboxylic acid amides groups.

1.1.4.3. Classification according to the mode of action

Pesticides control pest organisms by physically, chemically or biologically interfering with their metabolism or normal behaviour. The route that brings a pesticide in contact with the target pest depends on the nature of the pesticide and the mode of application (spraying, fumigating and baiting).

Many pesticides are 'contact' pesticides. This means that, to be effective, they must be absorbed through the external body surface or the exposed plant tissue; for example, tetramethrin used in household fly sprays, or bipyridillium herbicides such as paraquat.

Other pesticides are systemic in action. Systemic pesticides can move (be translocated) from the site of application to another site within the plant or animal where they become effective; for example, insecticides that are absorbed by foliage or through the root and translocated throughout the plant where they kill chewing or sucking insects; or nematicides that are applied to the leaves of plants and are transferred to the roots of the plant to kill worms or caterpillars attacking the plant's roots. Similarly, blood anticoagulant rodenticides in baits take effect once they have been transferred from the digestive system to the bloodstream of rats or mice.

1.1.4.4. Toxicological classification

The use of agrochemicals may have toxic effects on human health, mainly derived from their handling and field application. There are two major types of toxicity: chronic and acute. The former refers to that caused by chemicals that are applied continuously at sublethal doses and can cause long-term effects generally associated with the accumulation in tissues and internal organs.

Acute toxicity refers to that produced suddenly. There are three types of acute toxicity: oral toxicity due to ingestion; dermal toxicity caused by contact with the skin; and toxicity by inhalation of the gases or vapours. The World Health Organisation has adopted the classification of the Globally Harmonised System of Classification and Labelling of Chemicals of the United Nations (Table 1.2) (WHO, 2009). This classification is based primarily on the oral and dermal toxicity to rats, since these determinations are standard procedures in toxicology. Acute toxicity is quantified by the mean lethal dose (LD_{50}), which represents the amount of product required to kill 50% of the test animals (expressed as mg of toxicant kg^{-1} of animal bodyweight, bw).

1.1.5. Biopesticides

The EPA defines biopesticides as *certain types of pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals.* Ware and Whitacre (2004) refer to biopesticides as 21st century pesticides because of their general low toxicity, high selectivity, high effectiveness at low doses, and relatively rapid degradation.

Table 1.2. Acute toxicity classification of pesticides (WHO, 2009)

Category	**Oral**		**Dermal**	
	LD_{50}[a] (mg/kg bw)	Hazard Statement	LD_{50}[b] (mg/kg bw)	Hazard Statement
Category 1	< 5	Fatal if swallowed	< 50	Fatal in contact with skin
Category 2	5-50	Fatal if swallowed	50-200	Fatal in contact with skin
Category 3	50-300	Toxic if swallowed	200-1000	Toxic in contact with skin
Category 4	300-2000	Harmful if swallowed	1000-2000	Harmful in contact with skin
Category 5	2000-5000	May be harmful if swallowed	2000-5000	May be harmful in contact with skin

[a]The rat is the preferred species; [b]Rats or rabbits are the preferred species

As of September 2015, there are 436 registered biopesticide active ingredients and 1401 active biopesticide product registrations. Three groups of compounds can be distinguished:

1. *Biochemicals.* They include hormones, pheromones, enzymes, and natural insect and plant regulators. Biochemical pesticides interrupt natural growth processes or communications in insects and weeds.
2. *Microbial pesticides.* The active ingredient of a microbial pesticide is a microorganism such as virus, bacteria, fungus or protozoan. Microbial pesticides can control many different kinds of pests, although each separate active ingredient is relatively specific for its target pest/s. The most widely used microbial pesticides are subspecies and strains of *Bacillus thuringiensis*.
3. *Plant-incorporated protectants.* They are pesticidal substances that plants produce from genetic material that has been added to the plant (i.e. genetically modified crops). Their use is controversial, especially in many European countries (EFSA, 2006).

1.1.6. Pesticide fate in soils

The fate of organic compounds in the environment is mainly regulated by their behaviour in soils. Pesticides may reach the soil environment by different ways. Direct soil application is normally employed for the control of pests such as weeds, insects or microorganisms. Pesticides may also reach the soil indirectly, when some pesticide fractions applied to the aerial part of crops drop to the soil during application, or lixiviate from the crops. Other ways the pesticides reach the soil are by transportation from a different compartment, e.g. with the irrigation water, or by atmospheric or runoff deposition (Sánchez-Brunete et al., 2008).

Once in soil, pesticides may undergo a series of physicochemical and biological processes that can be interrelated (Figure 1.4). They may be grouped into two classes: (1) distribution processes (adsorption-desorption, leaching, volatilisation, runoff, plant uptake) implying movement of pesticide molecules between different soil phases, or in the same phase; (2) transformation processes (degradation), which involves changes in pesticide structure.

1.1.6.1. Adsorption-desorption

The adsorption process is defined as the passage of a solute (sorbate) from a liquid or gas to the surface of a solid (sorbent) without causing changes in its composition (Osgerby, 1970). In soil, solid-liquid processes normally occur since soil particles are surrounded by a thin layer of water (soil solution). Solid-gas adsorption will occur only in cases of extreme aridity (Pignatello, 1989; Pignatello and Xing, 1996). Adsorption may be purely physical, as with van der Waals forces, or chemical in nature, as with electrostatic interactions.

Desorption is the inverse process of adsorption, that is, the release of sorbate from the sorbent surface to either the liquid or gas phase. The extent of desorption is negatively related with the adsorption energy, which determines the reversibility of adsorption (totally or partially reversible, or irreversible). Partial reversibility or hysteresis is an important aspect determining bioavailability of pesticides.

Adsorption-desorption phenomena are probably the most important modes of interaction between soil particles and pesticides and control the concentration of the latter in the soil solution, hence affecting the rest of the processes involved in pesticide fate (Koskinen and Harper, 1990; Boesten and van der Linden, 1991).

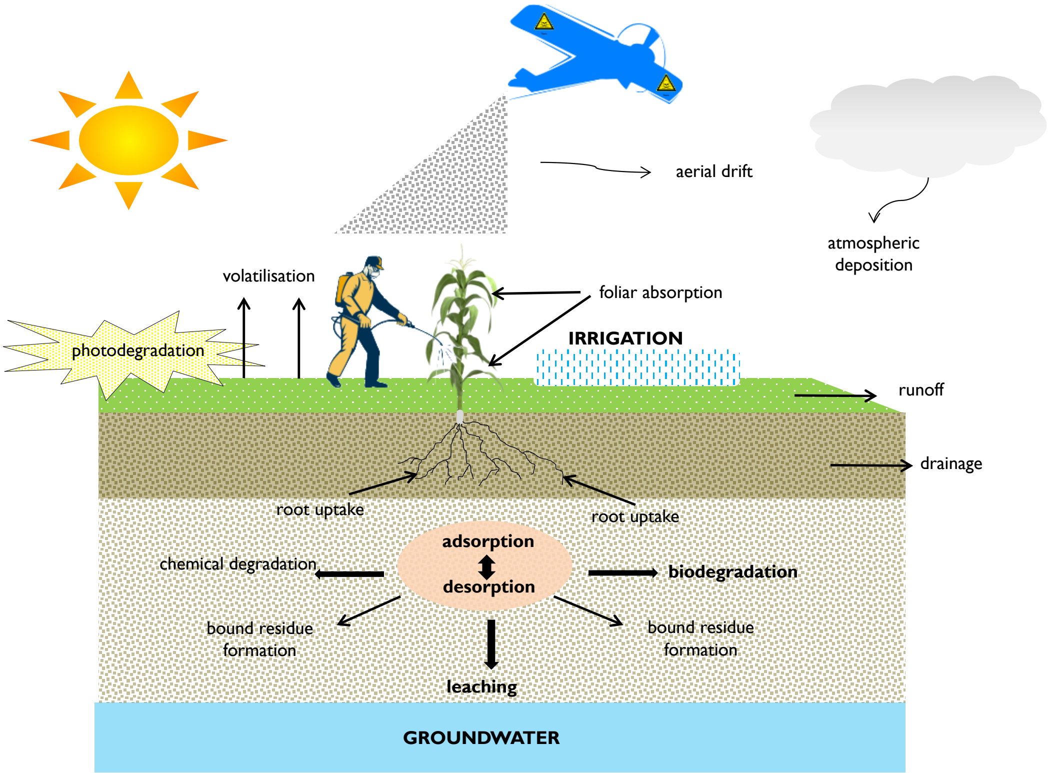


Figure 1.4. Main processes that control environmental pesticide fate

Adsorption mechanisms

The knowledge of the mechanisms involved in soil-pesticide interactions is important to better understand adsorption processes. According to the literature, these mechanisms include ionic bonding, covalent bonding, H bonding, charge transfer, ligand exchange, van der Waals forces, and hydrophobic bonding or partitioning (Calvet, 1989; Gevao et al., 2000). The description of adsorption mechanisms is a difficult task because of the wide range of solute chemical structures and of adsorbent properties of soil constituents. In fact, two or more mechanisms can occur simultaneously depending on the characteristics of the sorbent-sorbate system (Gevao et al., 2000).

Ionic bonding. Organic pesticides adsorbed by ionic bonding exist either in the cationic form in solution or can be protonated and become cationic. Bipryridilium pesticides (e.g. diquat, paraquat) bind to the negatively charged surfaces of mineral clays and humic substances via their cationic group. Weak base pesticides, such as triazines and triazoles, can be protonated and subsequently adsorbed (Weber et al., 1969; Gevao et al., 2000; Kah and Brown, 2006). Furthermore, anionic pesticides can be attracted by the positive charges of metallic oxides and oxohydroxides (Kah and Brown, 2006). The role of the pH is fundamental since it governs the existence of electrical charges in pesticide molecules and soil colloids (Li et al., 2001).

H bonding. It is a special case of dipole-dipole interaction where H acts as a bridge between two electronegative elements. Humic substances, with numerous oxygen and hydroxyl-containing functional groups, form H bonds with complementary groups on pesticide molecules, which compete with water for these binding sites (Senesi, 1992). H bonding is suggested to play a vital role in the adsorption of several nonionic polar pesticides, including substituted ureas and phenylcarbamates (Senesi and Testini, 1980; 1983). The role of pH is also important since acidic and anionic pesticides such as 2,4-D, dicamba or clopyralid may establish H bonding with soil organic matter (OM) at pH values below their pK_a in their nonionised form (Kah and Brown, 2006; Bukun et al., 2010).

van der Waals forces. These interactions consist of weak short-range dipole or induced dipole attractions that may be magnified by the hydrophobic effect (Gevao et al., 2000; Kah and Brown, 2006). Interactions between nonionic and nonpolar pesticides on suitable humic acid molecules are of particular relevance. Because these forces are additive (Senesi, 1992), their contribution increases with an increasing area of contact.

Ligand exchange. Adsorption by ligand exchange involves the replacement of relatively weak ligands (e.g. H_2O), partially holding polyvalent cations associated with soil OM or clay minerals, by suitable molecules such as anionic pesticides (Senesi, 1992). The ligand-exchange mechanism is implicated in the retention of many organic acids to oxide surfaces. Ligand exchange has also been proposed as a mechanism of retention for zwitterionic compounds such as imazaquin on highly weathered tropical soils (Regitano et al., 2000) and glyphosate on goethite (Sheals et al., 2002).

Charge transfer. Charge transfer involves the overlapping of the respective molecular orbitals and a partial exchange of electron density (Von Oepen et al., 1991). Humic substances contain within their structure both electron deficient structures, such as quinones, and electron rich moieties, such as diphenols, suggesting the possible formation of charge-transfer complexes via electron donor-acceptor mechanisms (π–π reaction). Depending on their chemical properties, pesticides can act as electron donor or electron acceptor agents (Senesi, 1992).

Hydrophobic bonding. The hydrophobic effect is the observed tendency of nonpolar substances to aggregate in aqueous solution and exclude water molecules (Chandler, 2005). Hydrophobic retention need not be an active adsorption mechanism, but can also be regarded as a partitioning between a solvent and a non-specific surface. The partitioning theory, which treats soil OM as a water-immiscible liquid phase, has been used to explain the hydrophobic interaction between pesticides and soils (Karickhoff, 1981). This means that humic substances both in the solid and dissolved phase are treated as a non-aqueous solvent into which the organic pesticide can partition from water (Chiou et al., 1986). However, soil OM is a solid phase with pH-dependent functional groups and a matrix of internal and external hydrophobic surfaces. Hydrophobic adsorption is proposed as the main mechanism for the retention of nonpolar pesticides by hydrophobic active sites of humic substances or clay (Gevao et al., 2000; Kah and Brown, 2006).

Covalent bonding. The formation of covalent bonds between pesticides and soil humic substances is often mediated by chemical, photochemical or enzymatic catalysts leading to stable, mostly irreversible incorporation to the soil. The pesticides which are more likely to undergo this interaction have functional groups similar to those of humus, and include acylanilides, phenylcarbamates, phenylureas, dinitroaniline herbicides, nitroaniline fungicides and organophosphate insecticides (Gevao et al, 2000).

1.1.6.2. Degradation

Pesticide degradation is the process by which a pesticide is transformed into a substance (metabolite) that is usually less hazardous for the environment that the parent compound. Alongside sorption, degradation is the second most important process used to predict the fate of pesticides in soils (Boesten and van der Linden, 1991; Beulke et al., 2005). It can lead to structural changes in pesticide molecules due to different chemical reactions (oxidation, reduction or hydrolysis), or complete mineralisation of the molecule to give inorganic compounds such as CO_2, H_2O, NH_3, PO_4^{3-}, etc. In soil systems, the transformation may occur by abiotic (chemical and photochemical degradation) or biotic (microbial degradation) pathways, the latter being predominant in the soil, due to the activity of microorganisms.

Microbial degradation

Microbial degradation or biodegradation is the decomposition of pesticides by soil microorganisms, especially bacteria, fungi and actinomycetes (Alexander, 1981; Häggblom, 1992; De Schrijver and De Mot, 1999). The biodegradation of pesticides is often complex, and involves a series of biochemical reactions. It constitutes the most important and effective process in the breakdown of pesticides in soils (Dabrowska et al., 2004). The ability of soil microorganisms to reduce the concentration of pollutants in soils is used in the bioremediation of contaminated sites, since this is an efficient, minimally hazardous, economical, versatile and environmental friendly strategy (Finley et al., 2010). This ability is directly linked to the long-term adaptation of microorganisms to environments where the pesticides are repeatedly applied. Moreover, genetic engineering is used to enhance the biodegradation potential of microorganisms (Schroll et al., 2004).

In soil, the microorganisms metabolise organic pesticides either aerobically or anaerobically. In most cases, the microorganisms degrade the molecules and utilise them as a source of energy and nutrients (Abdelhafid et al., 2000; Topp, 2001; Parales et al., 2002; Getenga, 2003; Boivin et al., 2005), or use them through cometabolism, which occurs when an organic compound is not directly used by the microorganisms for growth, but is metabolised in conjunction with another substrate used for growth (Häggblom, 1992; Kumar et al., 1996; Sánchez et al., 2004). According to Van Eerd et al. (2003), the microbial metabolism of pesticides may involve a three-phase process:

- In phase I, the parent compound is transformed through oxidation, reduction, or hydrolysis to generally produce a more water-soluble and usually a less toxic product.
- In phase II, the conjugation of the pesticide or its metabolite to a sugar or amino acid occurs. Conjugation of pesticides often involves the use of existing enzymatic machinery and is therefore called a cometabolic process.
- Phase III involves conversion of phase II metabolites into secondary conjugates, which are also nontoxic.

The extent and rate of biodegradation depend on the chemical structure, solubility and concentration of the compound being degraded, the type and number of microorganisms present, and the physicochemical properties of the environment that determine the amount of pesticide available for degradation such as type of soil, pH, temperature, moisture and OM.

Chemical degradation

The most important reactions implied in the chemical degradation of pesticides are oxidation, reduction, dehydrohalogenation and especially hydrolysis, with water functioning as the reaction medium, as reactant, or both (Goring et al., 1975; Wolfe et al., 1990). These mechanisms are similar to those of biodegradation, and can only be distinguished in sterile conditions. Chemical degradation rates may be influenced by clay surfaces, metal oxides, metal ions and soil OM (Goring et al., 1975; Menniti et al., 2003).

Photochemical degradation

Photolytic reactions of environmental relevance are those produced by sunlight, and hence it is necessary that the chemical absorbs the wavelength of solar radiation above 290 nm. It is especially important in the surface of soils and plants, as well as in aquatic environments, where pesticides can be transported in dissolution or adsorbed to particulate matter. The photolysis rate is dependent on the photons absorbed by the molecule at the considered wavelength (Stumm and Morgan, 1976; Zafiriou et al., 1984; Mill, 1999).

Pesticides may directly absorb the light, followed by the corresponding chemical reaction. Direct photolysis depends on the intensity and transmission rate of solar radiation in soil solution, as well as on intrinsic factors of the chemical such as the absorption rate of the light and the quantic efficiency of the reaction (Stumm and Morgan, 1976). Furthermore, the light may be absorbed by other constituents of the soil solution and either transmitted to the pesticide molecules, or lead to the formation of different species that react with pesticides. Indirect photolysis is of great importance on the total degradation of pesticides (Leifer, 1988; Remucal, 2014). Humic substances and inorganic ions may affect the photodegradation of pesticides (Katagi, 2004; Xie et al., 2011; Remucal et al., 2014; Carra et al., 2016).

Photochemical decomposition of pesticides in soils is limited by depth, texture, moisture content, temperature and OM content of soil (Romero et al., 1998; Sánchez et al., 2005).

1.1.6.3. Leaching

Leaching is the downward movement of pesticides with the waterfront through the soil profile, bypassing the unsaturated zone. It is considered as the main responsible of groundwater contamination (Southwick et al., 1995; van der Werf, 1996). Apart from pesticide and soil properties, rate of pesticide leaching decreases with increasing OM content and depth of the surface zone with high biological activity. In many soils the presence of macropores (cracks, worm holes, root channels) enhances the hazard of pesticides leaching to groundwater (van der Werf, 1996). The hypotheses proposed to explain this vertical transport of pesticides include preferential flow (Elliott et al., 2000; Roulier and Jarvis, 2003; Jarvis, 2007), cotransport with colloidal or particulate matter (Worrall et al., 1999; Villholth et al., 2000; Hesketh et al., 2001), and a combination of both (Williams et al., 2000).

Most of the simple indexes used to evaluate the risk of pesticide leaching include degradation and sorption as the main factors (Laskowski et al. 1982; Gustafson, 1989).

1.1.6.4. Runoff

Runoff is the movement of water and any contaminant across the soil surface. It occurs when the infiltration capacity of the soil is exceeded due to heavy rainfall or excessive irrigation. Water running off the land towards channels, streams, rivers and lakes can also move chemicals such as pesticides. Pesticides may be moving with the runoff water if dissolved or adsorbed to eroding soil particles. How far a pesticide moves from the area where it was applied will depend on a complex interaction of pesticide and soil properties with weather conditions and site characteristics. The most important factors are the slope and soil structure, the presence of vegetal cover, the intensity of rainfall or irrigation, pesticide physicochemical properties and formulation, and time elapsed from application (Cohen et al., 1995; Wauchope et al., 1995).

The total seasonal losses in runoff for soil-applied pesticides average about 2% of the application and rarely exceed 5-10% of the total applied amount (Schiavon et al., 1995; Carter, 2000). However, losses higher than 10% have been reported under simulated rainfall conditions (Kookana et al., 1998).

1.1.6.5. Volatilisation

Volatilisation is the physicochemical process by which a compound is transferred from the soil surface to the gas phase. Subsequent deposition may be the major source of pesticide contamination in some environments (Eisenreich et al., 1981; Cindoruk and Ozturk, 2016), even posing an important route of exposure to humans and animals (Paterson et al., 1990). Volatilisation decreases the amount of a pesticide available for control of pests and the potential for groundwater contamination but increases the potential for contaminating the atmosphere and surface water. For most pesticides, losses by volatilisation are negligible in comparison with those of leaching and runoff. However, for highly volatile pesticides, losses can reach 90% of the initial mass when applied to the surface of soils and plants (Taylor and Spencer, 1990).

Apart from pesticide properties, volatilisation rates depend on soil characteristics, climatic conditions and agricultural practices.

1.1.6.6. Plant uptake

Foliage and roots present the largest plant area for uptake from air and soil respectively. Foliar uptake of pesticide volatilised from the soil may contribute more to the total plant residues than root uptake (Topp et al., 1986). In soil, plant uptake can occur from interstitial water or air. Briggs and co-workers (1982) showed that uptake of nonionised compounds consists of two components: (1) an equilibration of the concentration in the aqueous phase inside the root with the concentration in the surrounding solution; and (2) sorption on hydrophobic root solids.

Uptake of pesticides from the soil by plants is probably a major source of food chain bioaccumulation and an important route of exposure to humans and animals (Paterson et al., 1990). Generally, low translocation through the plant to edible parts above ground is observed (Beck et al., 1996; Peña et al., 2014), but edible roots and tubers such as carrots may be contaminated. It has been reported that translocation to plant shoots is strongly dependent on pesticide lipophilicity (Briggs et al., 1982; de Carvalho et al., 2007).

Sorption, degradation, leaching and volatilisation processes limit the availability of chemicals for plant uptake.

1.1.7. Factors controlling pesticide fate in soils

The relative importance of the processes described above is controlled by the physicochemical properties of pesticides and soils, environmental variables and agricultural practices. As already mentioned, adsorption is the key process controlling pesticide fate in soils because detoxification mechanisms, such as degradation, plant uptake and mobilisation, involve only the non-sorbed fractions (Pignatello and Xing, 1996). Hence, discussion is made focusing adsorption.

1.1.7.1. Soil properties

Soils are heterogeneous and dynamic systems that undergo continual exchange of matter and energy with the atmosphere, hydrosphere and biosphere. It is a thin surface layer, covering the bedrock of most of the land area of the earth, and is the final product of the weathering action of physical, chemical, geological, hydrogeological, and biological processes on parent rocks (Brady and Weil, 2008). Some important functions of soils are included in Table 1.3.

Table 1.3. Some important functions of soils (adapted from Murphy, 2014)

• Base and medium for plant growth • Filtering and storage of water • Control of water flow • Pool of nutrients	• Resistance to erosion • Foundation and base for infrastructure • Reduction of movement of toxic compounds • Nutrient recycling and decomposition of soil biota

In addition to being the site of most food production, soil is the receptor of large quantities of pollutants and a key component of environmental chemical cycles (Chiou, 2002). In a recent study concerning 11 pesticides and 13 soils covering a wide range of physicochemical properties, Kodešová et al. (2011) have demonstrated that pesticide adsorption is dependent on a combination of soil physical and chemical properties, of which OM is usually the most relevant.

Soil texture

Soils are composed by particles of different size and reactivity. The terms sand, silt, and clay refer to relative sizes of the soil particles, being sand the larger size of particles, and clay the smaller one (Table 1.4). The combined portions of sand, silt, and clay in a soil determine its textural classification. Gravel or rocks greater than 2 mm in diameter are not considered when determining texture. Both distribution and interaction of these particles, especially the smallest ones (Cruz-Guzmán, 2007) determine largely most of the soil physical and chemical properties that may influence the fate of organic contaminants, such as structure, porosity, aeration, permeability, water retention capacity or cation exchange capacity (CEC).

Table 1.4. Size of the different soil particles

Particle name	Particle diameter (mm)
Very coarse sand	2.0-1.0
Coarse sand	1.0-0.5
Medium sand	0.5-0.25
Fine sand	0.25-0.10
Very fine sand	0.10-0.05
Silt	0.05-0.002
Clay	<0.002

The capacity of soils to adsorb organic pollutants is in general negatively correlated with particle size (Zhou et al., 2004; Cheng et al., 2014). Coarse-textured soils are chemically inert and have a great proportion of macropores through which water and solutes can infiltrate rapidly. Therefore, they present high risk of aquifer contamination by leaching. On the contrary, clayey soils are well-structured, retain water and solutes, and have low permeability. Therefore, they pose certain risk of surface waters contamination by runoff processes.

Soil structure

Soil structure describes the arrangement of soil particles and of the pore space located between them. It is determined by how individual soil granules bind together and aggregate. Like texture, it has a great influence on other soil properties.

Soil structure is determinant in soil hydrological characteristics and affects indirectly pesticide dynamics. In soils with preferential flow zones non-sorbed pesticides infiltrate rapidly to deeper soil layers with the consequent risk of groundwater contamination (Sánchez et al., 2006; Kördel and Klein, 2006; Delgado-Moreno et al., 2007a). Poor-structured soils difficult water infiltration thus favouring runoff through surface waters of non-sorbed compounds (Reichenberger et al., 2007). Under dry soil conditions pesticide percolation is lower in sandy than in clayey soils, while the opposite occurs when pesticides are applied to wet soils (Shipitalo et al., 1990; Edwards et al., 1993; Flury et al., 1995; Brown et al., 1995).

The activity of soil wildlife, as earthworms, can also originate preferential channels that may enhance the occurrence of pesticides in deeper soil layers (Edwards et al., 1993).

Colloidal fraction

Soil colloids are made up of the smallest particles (less than 1 μm) of organic and inorganic materials in the soil. They are considered the most active portion of the soil and determine the physical and chemical properties of soils. They have high surface area, external and internal electrical charges (mostly negative), adsorption capacity for cations and water molecules, and cohesion, adhesion, dispersion and flocculation properties. Due to this high reactivity the colloidal fraction of soil is the main responsible of the interactions with hydrophobic organic compounds. Two types of soil colloids are distinguished: inorganic and organic components.

Organic matter. Soil OM is the fraction of the soil that consists of plant and animal tissue in various stages of decomposition. Most of the agricultural soils have between 3 and 6% OM. It can be grouped into three major types: *1) plant residues and living microbial biomass, 2) active OM, also referred to as detritus; and 3) stable OM, often referred* *to as humus.* The first two types contribute to soil fertility because the breakdown of these fractions results in the release of plant nutrients such as N, P, K or S. The humus fraction has less influence on soil fertility because it is the final product of decomposition. However, it is still relevant for soil management because it contributes to soil structure, soil tilth, and CEC.

It is generally accepted that soil OM has beneficial effects on soil physical, chemical and biological properties, which in turn influence the productive capacity of soils (Table 1.5).

Table 1.5. Contributions of soil organic matter related to soil productivity (adapted from Stevenson, 1994 and Baldock and Skjemstad, 1999)

Physical	Chemical	Biological
• Enhances aggregate stability, improving water infiltration and soil aeration, reducing runoff • Improves water holding capacity • Reduces the stickiness of clay soils making them easier to till • Reduces surface crusting, facilitating seedbed preparation	• Increases the soil´s CEC or its ability to hold onto and supply over time essential nutrients • Improves the ability of a soil to resist pH change (buffering capacity) • Accelerates decomposition of soil minerals over time, making the nutrients in the minerals available for plants	• Provides food for the living organisms in the soil • Enhances soil microbial biodiversity and activity influencing bioavailability and pesticide effectiveness • Enhances pore space through the actions of soil microorganisms. This helps to increase infiltration and reduce runoff

Soil OM is composed of a wide variety of organic materials with different properties ranging from biopolymers such as polysaccharides, lipids, proteins and lignin, humic substances, and diagenetically matured kerogen and combustion-related black carbon (Aiken et al., 1985; Stevenson, 1994; Song et al., 2002). Lipids are strong sorbents for hydrophobic organic compounds, but their contents in many soils are often very low and may play an insignificant role. Other biopolymers have low affinity for organic contaminants and thus are not considered as dominant sorptive phases in soils (Xing et al., 1994; Weber et al., 2001).

Humic substances are major components of soil OM (65-80%) (Schnitzer, 1978, 1986; Stevenson, 1994; Senesi and Loffredo, 1999), contributing to the brown or black colour in surface soils. They affect the chemistry and bioavailability of chemical elements, as well as transport and degradation of xenobiotic and natural organic compounds. Humic substances are complex and heterogeneous mixtures of polydispersed materials (with molecular weights ranging from a few hundred to several hundred thousand Daltons) formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains (humification process).

Humic substances can be divided into three main fractions: humic acids, fulvic acids and humin. Humic and fulvic acids are extracted from soils using a strong base (NaOH or KOH). Humic acids are insoluble at low pH, and they precipitate by adding strong acid. Humin cannot be extracted with either a strong base or a strong acid (Stevenson, 1994). Because of its nonextractability, the physical and chemical nature of humin is the least understood of the three humic fractions. Humin may include complex soil OM ranging from unaltered or less-altered biopolymers such as lignin and polysaccharides (Hatcher et al., 1985), mineral-bound lipids and humic acid-like materials (Rice and MacCarthy, 1990), kerogen and black carbon (Song et al., 2002).

Humic substances are highly chemically reactive yet recalcitrant with respect to biodegradation. Despite of their chemical, structural and molecular heterogeneity, they may exhibit certain bulk physicochemical properties similar to those of organic polymeric materials (LeBoeuf and Weber, 1997, 2000a,b; Young and LeBoeuf, 2000).

Clay minerals. It has long been recognised that the minerals in the clay fractions of soils play a crucial role in determining their major physical and chemical properties. Chemically, clays are hydrous aluminium silicates, usually containing minor amounts of impurities such as potassium, sodium, calcium, magnesium, or iron. Clay minerals have a sheet-like structure and are composed of mainly tetrahedrally arranged silicate and octahedrally arranged aluminate groups. Clay minerals typically form over long periods of time as a result of the gradual chemical weathering and erosion of rocks, usually those composed of feldspars and micas, or through hydrothermal activity. There are two types of clay deposits: primary and secondary. Primary clays form as residual deposits in soil and remain at the site of formation. Secondary clays have been transported from their original location by any erosion agent and deposited in a new sedimentary deposit.

Soil clay minerals can be grouped into 1:1 and 2:1 clay minerals. The 1:1 clay minerals, primarily kaolinite, are found in most soils, but predominate in highly weathered soils of humid temperate and tropical regions (Schulze, 2002). The 2:1 clay minerals are grouped into non-swelling and swelling clays. The former have a high negative surface charge, however, swelling is inhibited by interlayer K^+ that is held tightly in the hexagonal siloxane cavities. The 2:1 swelling or expandable clays include the smectite and vermiculite groups. The 2:1 non-expandable clays include the illite group.

Soil clays may be of an extremely diverse and complex nature, reflecting both the variety of the parent rock as well as the transformation and neoformation processes that may have occurred in previous weathering environments (Wilson, 1999).

Metallic oxides. Similarly to clay minerals, metallic oxides, which are abundant in many soils worldwide, originate from the weathering of the minerals of which the rocks are composed (Segalen, 1971). They include hydroxides, oxohydroxides and oxides themselves, being those of aluminium and especially iron the most abundant (Schwertmann and Taylor, 1989). In these minerals, the active adsorption sites are the OH^- groups in the surface, which depending on the pH can behave as acceptors or donor of electrons (Hingston et al., 1972). Their high specific surface makes them good sorbents for organic compounds, mainly anionic (Celis et al., 1999; Dubus et al., 2001).

The sorption interactions of pesticides in soil may involve either the mineral or organic components, or both (Huang, 1997). Their relative importance is usually evaluated by using selected soils or soil clays (Cox et al., 1997, 1998a; Sheng et al., 2001), by determining sorption after removing soil components (Laird et al., 1994; Celis et al., 2006; Ahangar et al., 2008a), or by using model sorbents (Cox et al., 1998b; Sheng et al., 2001; Hyun and Lee, 2004; Celis et al., 2006).

It is traditionally considered that soil OM plays a vital role in the adsorption of nonionic organic contaminants, being hydrophobic bonding the main mechanism involved (Hamaker and Thompson, 1972). After the development of the partition theory (Chiou et al., 1979; Karickhoff et al., 1979), soil OM has long been recognised as the dominant soil phase in the sorption of nonionic pesticides and other organic compounds (Sánchez-Martín et al., 2000; Andrades et al., 2001; Wauchope et al., 2002; Ben-Hur et al., 2003; Cao et al., 2008; Báez et al., 2013), with its nature having no or little influence, especially in OM-rich soils (Bailey and White, 1964; Hayes, 1970; Jenks et al., 1998; Delgado-Moreno et al., 2010). However, in recent times, there has been an increasing awareness that not only the amount, but also the chemical composition of soil OM and its interaction with soil minerals can influence adsorption. It is recognised that humic and fulvic acids are the main soil OM components involved in pesticide adsorption (Delgado-Moreno et al., 2010). Ahmad et al. (2001) highlighted the importance of the aromatic fraction of soil OM as a good predictor of a soil´s ability to bind nonionic pesticides. Further studies have revealed that diuron adsorption is positively and negatively correlated with aryl C and O-alkyl C respectively (Ahangar et al., 2008 a,b; Smernik and Kookana, 2015). On the other hand, the lipid fraction competes for or blocks sorption sites on the soil OM, thus reducing adsorption (Ahangar et al., 2009; Delgado-Moreno et al., 2010).

The interactions of pesticides with clay minerals have been studied for a long time, but the research in this field has increased dramatically from the early 1990s onwards (Barriuso et al., 1994; Lagaly, 2001; Nir et al., 2006; Cornejo et al., 2008). In soils with low OM contents, the adsorption of pesticides often depends on active components of the inorganic fraction, which is predominantly the clay fraction (Sánchez-Camazano et al., 2000; Báez et al., 2015). Since the clay content of most soils significantly exceeds the soil OM content, overall sorption of certain pesticides could plausibly be controlled by their interactions with clays, especially the expandable smectites due to their high surface areas (Sheng et al., 2001; Cornejo et al., 2008). Sánchez-Camazano et al. (2000) found a significant correlation between linuron adsorption and clay content when soils with OM levels <2% were considered. Karickhoff (1984) reported that when clay:OM ratio was lower than 30, mineral contributions were masked, regardless of the mineral content. However, this ratio depends on sorbate hydrophobicity. Other studies (Mingelgrin and Gerstl, 1983; Liu et al., 2008) proposed a clay:organic carbon (OC) ratio of 25-60 as a threshold from which inorganic contribution became important.

In general, adsorption of nonionic compounds by clays is higher when both the charge density of clays and the hydration energy of the exchangeable cation are low (Boyd et al., 2011). Highly polar, nonionic pesticides can interact with interlayer cations either directly or through water bridges (Boyd et al., 2011). In both cases, the nature of the inorganic cation has a great influence (Lagaly, 2001; Sheng et al., 2001; Liu et al., 2009). The adsorption capacity of clays for nonionic and highly hydrophobic compounds is often considered to be very limited due to the very hydrophilic character of the clay surfaces (Mortland, 1970; Jaynes and Vance, 1996). The adsorption of this type of pesticides by clays has been related to the presence of hydrophobic microsites on the clay mineral surface. In these cases the organic compound can effectively compete with water molecules for such relatively hydrophobic regions (Laird, 1996; Hundal et al., 2001).

Adsorption of ionisable or polar pesticides may be largely controlled by inorganic colloids (von Oepen et al., 1991; Kah and Brown, 2006). Cationic pesticides can be readily adsorbed on clay minerals, in particular 2:1 phyllosilicates, by ion-exchange processes (Rytwo et al., 2004). Anionic pesticides can interact with clay minerals through positively charged clay edges or through cation bridges with certain multivalent metal ions at exchange sites. Nevertheless, these adsorption sites are often limited and anionic pesticides are generally not retained by clays due to repulsions with the negatively charged silicate surfaces (Cornejo et al., 2008).

The effect of metallic oxides on pesticide adsorption could be also significant. Wahid and Sethunathan (1979) reported that free iron oxide seemed implicated in lindane sorption on soils. Other works have reported that amorphous iron and aluminium oxides are relevant sorbent phases for phenoxy herbicides and other ionisable compounds (Regitano et al., 1997; Clausen and Fabricius, 2001; Rodríguez-Rubio et al., 2006; Werner et al., 2013). Cheng et al. (2014) showed that, while iron oxides contributed to DDT adsorption on soils, manganese oxides had an inhibitory effect. In a more recent study, Báez et al. (2015) found that the high adsorption of glyphosate on volcanic soils was mainly related to contents of amorphous aluminium oxides.

For ionisable or polar compounds and for soils with low OC content and/or high clay content, Hermosín and Cornejo (1994) stated that adsorption could be defined by the sum of organic and inorganic colloids, better than only by soil OM.

The associations among the different soil components may alter the sorption ability of the separated entities. There is growing evidence that interactions between organic and inorganic colloids strongly affect pesticide adsorption (Murphy et al., 1992, 1994; Celis et al., 2006; Ahangar et al., 2008 a,b; Ahangar, 2012; Smernik and Kookana, 2015). These studies show that interassociation processes may block functional groups for sorption on mineral and organic surfaces. However, because the soil mineralogy varies little across the field, the influence of these interactions is greatly diminished, allowing the effect of OM chemistry to be seen clearly (Ahangar et al., 2008b).

Cation exchange capacity

Soil CEC is a measure of the soil's ability to hold exchangeable cations, mainly Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} (Rayment and Higginson, 1992). It is an inherent soil characteristic influencing soil structure stability, nutrient availability, soil pH and the soil's reaction to fertilisers and other soil improvers (Hazelton and Murphy, 2007). Furthermore, CEC may be a significant factor in the fate of pesticides, especially ionisable and highly polar compounds.

Numerous studies have pointed out to the importance of CEC on pesticide adsorption (Jenks et al., 1998; Wethje et al., 2000; Zhu and Selim, 2002; Archangelo et al., 2004; Piwowarczyk and Holden, 2012). In fact, pesticide adsorption on soils has been frequently better correlated with CEC as compared with OM content because the CEC considers the sorptive capacity from both OM and clays and the likely reduction in sorption due to their interactions (Pusino et al., 1994). However, this positive correlation between pesticide adsorption and CEC has been attributed to the high contribution of OM to total CEC (Felsot and Willson, 1980; Archangelo et al., 2004) in the range 25-90% (van Dijk, 1971),

1.1.7.2. Soil solution properties: pH and ionic strength

The solution pH and ionic strength are among the factors that are likely to influence sorption characteristics. In agricultural fields, these parameters vary in time in response to climatic conditions, applications of fertilisers, manure, lime, and gypsum, and vary in space because rapid infiltration results in lower ionic strength in water-conducting macropores than in the soil matrix (de Jonge and de Jonge, 1999).

The soil solution can either directly or indirectly influence sorption mechanisms. The influence of pH on pesticide behaviour depends on other soil properties and the characteristics of the molecule. Unlike highly hydrophobic compounds, adsorption of ionisable and polar pesticides, such as phenoxy acids, triazines, sulfonylureas and imidazolinones, is highly sensitive to variation in pH (Regitano et al., 1997; Boivin et al., 2005; Delgado-Moreno et al., 2007b; Cao et al., 2008; Delgado-Moreno and Peña, 2008). This relationship mainly derives from the different proportion of ionic and neutral forms of the pesticide present at each pH level, but also from the presence of surfaces with pH-dependent charges in soils. Indirect effects are due to a change in the degree of aggregation of the soil, which is strongly linked to the soil solution composition. Clay dispersion is brought about by the presence of monovalent cations, high pH and low ionic conductivity, while stable aggregates are maintained in the presence of multivalent cations, low pH and high ionic strength (Goldberg and Glaubig, 1987; Chorom and Rengasamy, 1995). Dispersion causes surfaces to be more directly accessible for pesticide adsorption. On the other hand, soil colloids may go in suspension, which has been related to facilitated transport of strongly sorbing pesticides (McCarthy and Zachara, 1989).

Degradation of ionisable pesticides is also influenced by soil pH because it leads to changes in sorption, in composition and activity of the microbial community, and because it modifies the balance between different degradative mechanisms (Kah and Brown, 2006). A higher pH increases the rate of chemical processes, whereas a lower pH boosts the resistance of pesticide to degradation. Moreover, at lower pH the activity of microorganisms, particularly bacteria involved in pesticide degradation, is limited (van der Werf, 1996). El Sebai et al. (2007) related the spatial variability in the rate of isoproturon degradation in 50 soils with that of soil pH.

Results show that ionic strength of soil solution can influence the sorption of pesticides, either positively or negatively, according to the electrolyte composition and concentration, and characteristics of the pesticide and sorbent. Uncharged molecules seem to be much less sensitive to variation in ionic strength (Alva and Singh 1991; de Jonge and de Jonge; 1999; Clausen et al. 2001; Spark and Swift, 2002).

Increased pesticide adsorption with increasing ionic strength has been reported for a wide variety of pesticides (Regitano et al., 1997; de Jonge and de Jonge, 1999; Clausen et al., 2001; Spark and Swift, 2002; Ureña-Amate et al., 2005; chapter 3). To explain this fact, different causes have been suggested: i) the replacement of protons from the soil surface as ionic strength increases, causing a slight decrease in pH and shifting acidic compounds toward neutral forms that are more strongly sorbed than the anionic forms (Regitano et al. 1997; de Jonge and de Jonge 1999); ii) the presence of multivalent cations in the solution due to the formation of cation–pesticide–soil surface complexes (McConnell and Hossner, 1989; Clausen et al., 2001; Hyun and Lee, 2004); iii) the formation of neutral ion pairs between the anionic form of the pesticide and cations in the solution (Spadotto and Hornsby, 2003); iv) stabilisation of colloids at higher ionic strength (de Jonge and de Jonge, 1999); and v) the salting out effect, which leads to the decrease of pesticide solubility with the consequent higher affinity for soil particles (Lee et al., 1990; Ureña-Amate et al., 2005).

A negative relationship between adsorption and ionic strength has been also reported (Alva and Singh, 1990; Regitano et al. 1997; de Jonge and de Jonge 1999; Clausen et al., 2001; Hyun and Lee, 2004). Clausen et al. (2001) noted decreased adsorption of ionic pesticides on soil minerals with increasing $CaCl_2$ concentrations. Different reasons were postulated to explain this effect: i) enhanced competition with the chloride anion for anion exchange sites; ii) possible complexation between the anionic pesticides and Ca^{2+}, which results in nonsorbing solution complexes; and iii) a decrease in the activity of the charged ions caused by the increasing electrolyte concentration.

1.1.7.3. Pesticide properties

The physicochemical properties of a pesticide govern its behaviour and ultimately its biological activity. Pesticide properties such as water solubility, hydrophobicity, volatility and molecular characteristics are all key properties, which determine the fate of pesticides in soils (Senesi, 1992; Pignatello and Xing, 1996).

Molecular characteristics

Molecular characteristics, such as polarity, molecular size, ionisability or the occurrence of functional groups, are determinant factors affecting pesticide behaviour in soils, since they directly control the affinity of the chemicals for soil and water phases, and thus bioavailability.

In general, polar compounds with small molecules tend to dissolve in water, hence posing a risk of water bodies' contamination. On the contrary, nonpolar compounds with high molecular weight are strongly sorbed on soil OM. The presence of carboxile (–COOH), carbonile (–CO), oxhidrile (–OH) and amine ($-NH_2$) groups determines the intensity and type of binding mechanisms. It is also important the influence of steric hindrance and the presence of insaturations.

Ionisable compounds possess either weak acidic and/or basic functional group(s). As a consequence, they may be partially ionised within the range of normal soil pH, which strongly affects their soil reactivity. The adsorption of neutral organic compounds in soils occurs mainly by hydrophobic partitioning, whereas a number of additional mechanisms are postulated for the adsorption of ionisable pesticides, including ionic exchange, charge transfer, ligand exchange, and cation or water bridging. Anionic pesticides can be adsorbed by anion exchange, which is more likely to occur in tropical soils that contain significant quantities of positively charged surfaces in the form of aluminium and iron oxides (Kah and Brown, 2006). Anion exchange was involved in the adsorption of the dissociated form of chlorsulfuron (Shea et al., 1986), prosulfuron (Hyun and Lee, 2004), 2,4-D (Celis et al., 1999; Dubus et al., 2001), or mecoprop and bentazone (Clausen and Fabricius, 2001). Cation exchange is among the most prevalent mechanisms in the adsorption of cationic pesticides, because of the large proportion of negatively charged sites associated with clay and soil OM (Harper, 1994). Triazine herbicides and positively charged bipyridylium compounds have been reported to be adsorbed by cation exchange (Senesi et al., 1995; Herwig et al., 2001; Spark and Swift, 2002).

Due to the higher solubility of polar pesticides in water they are degraded much faster than nonpolar substances. Faster degradation was observed for anionic pesticides as compared to cationic ones. Moreover, the aromatic structures are more resistant to degradation processes than aliphatic compounds. It is stated, that pesticides containing the active chlorine atoms undergo nucleophilic substitution easily, for example hydrolysis. Resistance to oxidation processes was found among pesticides of high oxidation state. On the other hand, compounds of high reduction state undergo transformations in aerobic conditions easily (Topp et al., 1997).

Water solubility and hydrophobicity

The tendency of a chemical to dissolve in water is expressed through its water solubility. One of the routes of transport of contaminants in the environment is water; therefore water solubility affects the ability of a compound to be transported as well as its rates of transfer between water and other environmental compartments (Kühne et al., 1995). Chiou et al. (1983) demonstrated that the extent of solute insolubility in water is the primary factor affecting the soil OM-water partition coefficient of nonionic organic compounds.

The hydrophobicity of a pesticide is generally expressed by its octanol-water partition coefficient (K_{ow} or Log K_{ow}), which is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system. It is a key parameter in studies of the environmental fate of organic chemicals, related to water solubility, affinity for soils and sediments, and bioaccumulation in living organisms (Schwarzenbach et al., 2003).

It is generally accepted that pesticides with water solubility lower than 30 mg L^{-1} are considered as poorly mobile, and vice versa. Therefore, according to the solubility of the pesticides examined in this dissertation, which will be shown in chapter 2 (Figure 2.2), only thiacloprid and dimethenamid would be susceptible to soil percolation. On the other hand, pesticides with low Log K_{ow} values (e.g., less than 1) may be considered relatively hydrophilic; conversely, chemicals with high Log K_{ow} values (e.g., greater than 4) are very hydrophobic and tend to be strongly retained in soils and accumulate in animal tissues.

Numerous works have reported that pesticide adsorption on soils is inversely proportional to water solubility (De Wilde et al., 2008; El Bakouri et al., 2009; Rojas et al., 2014), and positively correlated to pesticide hydrophobicity (Fouqué-Brouard and Fournier, 1996; Rodríguez-Cruz et al., 2006, 2007; Rojas et al., 2014). However, Fouqué-Brouard and Fournier (1996) reported that binding of pesticides was related not only to pesticide characteristics but also to the composition of both the soil and the associated molecules. In fact, Chiou et al. (1986) and Kile and Chiou (1989) showed significant solubility enhancements of relatively water-insoluble compounds by the presence of soil-derived dissolved OM (DOM) and surfactants respectively in the soil solution, due to pesticide-DOM or pesticide-surfactant interactions. This enhancement was found to be inversely and directly proportional to water solubility and K_{ow}, respectively.

Volatility

The volatility of a pesticide represents its tendency to move to the air phase from other environmental compartments, such as soils. The greatest losses by volatilization occur in the period immediately following the application of pesticides to plants or moist soils (Taylor and Spencer, 1990). However, in dry environments continuous losses might be expected. Volatilisation is greatly reduced by incorporation of the pesticide into the soil, where the rate becomes dependent upon movement of the residues to the soil surface by diffusion or convective transport by soil water (van der Werf, 1996). Similarly, it may be also reduced the longer the compound stays in the soil.

A simple way to evaluate pesticide volatility is through the vapour pressure. It can be said that pesticides with vapour pressure higher than 1 Pa have a great volatilisation potential, whereas, below 10^{-6} Pa, the air affinity is very low. However, volatility is intimately related with water solubility, thus the Henry law´s constant (obtained as the vapour pressure/water solubility ratio) is a more appropriate criterion of the volatilisation rate of a pesticide than its vapour pressure alone (Jury et al., 1984; Spencer and Cliath, 1990). Henry´s constant usually ranges between 10^{5} and 10^{-9} Pa m^{3} mol^{-1}, but pesticides show values above 10 only in a few cases. While values higher than 10 are always indicative of very high volatility, for constants below 10^{-4} volatilisation is low or negligible. Intermediate values are affected by other parameters (Jury et al., 1984; Clendening et al., 1990; Vighi and di Guardo, 1995).

1.1.7.4. Climatic factors: temperature and water content

The main climatic factors that influence behaviour of organic compounds in soils are the temperature and moisture content of the soil (Alletto et al., 2006; El Sebai et al., 2010, 2011; Regitano et al., 2016).

Sorption may occur as the result of two types of forces: enthalpy-related and entropy-related forces (Hamaker and Thompson, 1972). Hydrophobic bonding is an example of an entropy-driven process. For polar chemicals, the enthalpy-related forces are greater, due to the additional contribution of electrostatic interactions. It is often assumed that adsorption is an exothermic process, whereby an increase in temperature leads to decreased adsorption and increased desorption rates (Calvet, 1989; Harper, 1994; Delle Site, 2001; Ureña-Amate et al., 2005). Due to the dependence of both sorption coefficients and solubility on temperature, the measured effect of temperature on sorption isotherms is the result of combined sorption and solubility contributions (Kipling, 1965). For ionisable pesticides, thermodynamic studies have shown a variable influence of temperature on the different binding mechanisms (Hayes, 1970). Although no apparent trend is observed for the neutral form, a clear decrease in adsorption with increasing temperature occurs for the ionised form (Eberbach, 1998; DiVincenzo and Sparks, 2001). Furthermore, pesticide degradation usually increases with temperature due to the lower adsorption, hence higher bioavailability, and the increase of the activity of degrader microorganisms (van der Werf, 1996; Kah et al., 2007).

Evidence suggests that soil moisture content is another important factor influencing pesticide fate. It is widely accepted that mobility, bioavailability and efficacy of pesticides generally decrease with soil dryness, probably because of an increase in sorption by soil colloids (Mangels, 1991; Latrille, 2013). This effect can be attributed to reduced competition of water for sorption sites and an increase of pesticide concentration in solution (Harper 1994). Indeed, some works have observed that temporarily drying and returning to field capacity generally increased sorption of pesticides due to a reduction in thickness of the water film coating the soil minerals, which serves to concentrate the pesticide near the sorption surface or facilitate precipitation (Haouari et al., 2007; Jablonowski et al., 2012). Ayeni et al. (1998) found that a delay in rainfall of up to 14 d after application of imazethapyr significantly reduced bioactivity in a coarse textured soil, but not in other finer textured soils. The effect of timing of soil wetting was probably related to sorption and, therefore, it would probably affect imazaquin mobility as well.

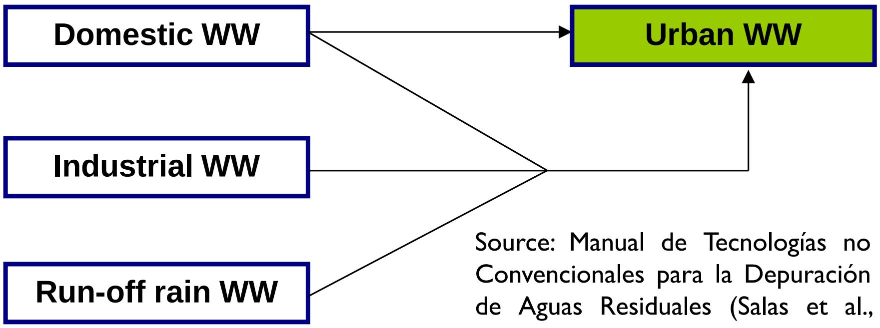
However, increased diffusion at high soil moisture content may cause additional sorption by ion exchange at colloid surfaces. Strong basic compounds may essentially adsorb due to ionic interactions, and their sorption would be enhanced at high soil moisture content due to diffusion. Increased sorption with increased water content has been observed with atrazine (Koskinen and Rochette, 1996; Rochette and Koskinen, 1996) and metsulfuron methyl (Berglöf et al., 2003). The transformation processes of pesticides are also closely related to soil moisture. Lower soil water content would reduce microbial activity and in this way the rate of transformation processes of pesticides would also decrease. However, excessive water content in soil may also have adverse effects on pesticide degradation (Topp et al., 1997).

1.2. WASTEWATERS

1.2.1. Concepts and composition

Wastewater (WW) is any water that has been adversely affected in quality by anthropogenic influence and can originate from a combination of domestic, industrial, commercial or agricultural activities, surface runoff or stormwater, and from sewer inflow or infiltration. WW is approximately 95% water. The rest is composed of a variety of constituents including pathogens, organic and inorganic matter, dissolved solids (such as salts, pharmaceuticals, drugs, etc.), and toxins. It is the last 5% that is detrimental to receiving waters, ecosystems, and human health. According to the Food and Agriculture Organisation of the United Nations (FAO) WW is defined as *water which is of no further immediate value to the purpose for which it was used or in the pursuit of which it was produced because of its quality, quantity or time of occurrence. However, wastewater from one user can be a potential supply to another user elsewhere* (AQUASTAT).

Urban or municipal WW is normally considered as domestic WW (from residential settlements) or a mixture of domestic WW and industrial WW (from premises used for trade or industry) and/or run-off rain water (Figure 1.5).



Source: Manual de Tecnologías no Convencionales para la Depuración de Aguas Residuales (Salas et al., 2007)

Figure 1.5. Composition of urban wastewaters

The generation of urban WW is an inevitable consequence of human activities. These activities alter the characteristics of water, contaminating it and limiting its subsequent discharge or application to other uses.

1.2.2. Influence of the discharge of untreated wastewater on the receiving environment

The discharge of untreated WW to freshwater sources causes environmental damage and puts human health at risk inducing the following aspects:

1. Incorporation of great amounts of sludges and suspended solids that may reduce light penetration (Moeller and Calkins, 1980) and block respiratory organs of many animals.
2. Incorporation of degradable organic substances that causes the consumption of the dissolved O_2 by degrader microorganisms. If O_2 demand exceeds aeration, an anaerobic cycle can be reached with the consequent appearance of ammonia, nitrogen and hydrogen sulfide, and sulfate reduction to sulfide. The water becomes dark, with unpleasant odor and may spread pathogens (virus, bacteria and protozoa).
3. Incorporation of organic and inorganic toxic compounds that may adversely affect the food chain.
4. Eutrophication due to the excess of nutrients (mainly N and P) (Qin et al., 2015).
5. Alteration of pH and the saline balance.

Because of the depletion of the dissolved O_2, the self-purifying capacity of freshwater sources after untreated WW discharge is reduced. Wastewater treatment plants (WWTPs) are designed to clean up the harmful constituents and return the water to a safe, reusable state.

1.2.3. Treatment of urban wastewater

1.2.3.1. Context and legislative framework

The European Union (EU) has over 500 million inhabitants. The WW generated by this large population and industry is a major source of pollution. It can affect the quality of drinking and bathing waters and increase the loss of biodiversity. The council directive 91/271/EEC (Directive 91/271/EEC), later modified in 1998 (Directive 98/15/EEC), was adopted in order to guarantee that urban WWs are adequately treated before their discharge to the environment. The directive is often perceived as costly but it addresses this challenge with benefits to both health and environment.

Briefly, the directive establishes two distinctive obligations: firstly, the urban agglomerations shall have systems for collecting and conducting urban WW to WWTPs; secondly, the existence of different treatments for WW purification before discharge to the environment.

The characteristics of the sites where WW are produced are taken into account when planning the treatments to be carried out. Accordingly, treatments will be more or less rigorous when performed in areas qualified as "sensitive", "less sensitive" or "normal".

In particular, the directive 91/271/EEC sets the following points:

- Deadlines for the installation of collecting systems depending on the size of the agglomerations, the characteristics of the dumping area (sensitive area) and requirements for these systems (Article 3).
- Deadlines for collected WW to receive secondary treatment depending on the size of agglomerations from which they proceed, as well as the requirements for effluents from the facility where this treatment occurs (Article 4 and Annex I point B).
- Criteria for the identification of sensitive and less sensitive areas (Annex II), the deadlines for the treatment of WW discharged into these areas, along with the characteristics of the treatment facilities and the requirements for their effluents (Articles 5 and 6; letter B and tables 1 and 2 of Annex I).
- Deadlines and appropriate treatments for discharges collected from agglomerations not covered by Articles above (Article 7).
- Environmental aspects that should be considered when preparing the authorisations for discharges of industrial facilities when these discharges, after purification, are carried out in collecting systems and treatment facilities for urban WW (Article 11, point C of Annex I).
- Conditions of use and disposal of sludges generated at the facilities of WW treatment, prohibiting their discharge to surface waters from December 31, 1998 (Article 14).
- Analytical controls of the WW and sludges from WWTPs, as well as those of receiving waters (Article 15, point D of Annex I).

- Content and structure of the information that Member States must provide to the Commission on the implementation of the Directive (Articles 16 and 17; Annexes I and III).

The directive 91/271/EEC also establishes the quality requirements for the effluents of WWTPs (Table1.6).

The transposition of the European directive into the Spanish law is contained in the Real Decreto RD11/1995. Furthermore, RD 509/1996 includes the Annexes of the directive that had not been initially incorporated. On the other hand, the changes introduced by directive 98/15/EEC are considered in RD 2116/1998.

According to the national legislation, it corresponds to the Autonomic Governments the delimitation of the urban agglomerations and the declaration of sensitive or less sensitive areas, except when two or more territories are involved.

Table 1.6. Requirements for effluents from wastewater treatment plants (WWTPs) after secondary treatment

Parameter	Concentration	Minimal % of reduction[a]
BOD_5	25 mg L^{-1} O_2	70-90
COD	125 mg L^{-1} O_2	75
Total Suspended Solids	35 mg L^{-1}	90

[a]With respect to the inflow

The programs of implementation of Directive 91/271/EEC, in Spain, have been considered in the Plan Nacional de Saneamiento y Depuración de Aguas Residuales (1995-2005), which develops the objectives and main lines of action of the management of public water in relation to discharges of urban WW.

1.2.3.2. Compliance of the EU member states with the directive

A European Commission report (2016) notes that a significant progress towards full implementation was achieved by 2012. Most member states, especially the 15 older EU countries, have collected a considerable part of their WW, with an average rate of compliance of the article 3 of 98%. Twenty member states have reached compliance rates of 100%. All member states have either maintained or improved previous results, except the Republic of Bulgaria. Only two member states showed compliance rates below 60%. There are still countries of the 13 new member states (those which joined the EU after 2004) where there is only partial collection of sewage, applying individual or other appropriate systems in a relatively high rate (above 20%).

Ninety two % of the WW in the EU received secondary treatment in compliance with the article 4 of the directive, 10 percentage points up from the previous report. Sixteen member states reached 90-100% compliance, another 5 had levels of compliance in the range of 50-90%, and 3 reached lower levels. Even though the compliance rates in EU 13 new member states are still trailing behind, with an overall rate of 68%, there has been a substantial improvement in comparison to the previous report, in which only 39% of the WW received appropriate secondary treatment.

Nearly 75% of the territory in the EU is now designated as sensitive area. Fifteen member states have designated their entire territory as such, whereas 13 member states have identified only certain water bodies as "sensitive". With an overall compliance rate of article 5 of 88%, there has been a substantial improvement since the previous report, of 11 percentage points. However, due to delays in implementation of more stringent treatment in EU 13 new member states, those countries show an average compliance rate of 32%. Overall, 9 member states reached levels below 50%, another 4 had levels in the range of 50-90% and, on the positive side, 12 countries show compliance rates of 90-100%.

There are 463 big cities (> 150000 inhabitants) covered by this report. This is over 100 less than in the previous report, mainly due to the non-inclusion of Italian and Polish data because of their low quality. The pollution load that is produced by big cities represents 46% of the total generated load. Approximately 89% of this load undergoes treatment that is more stringent than what would be required by the directive. The percentage of load non-collected or collected and untreated has decreased from 5% to 2.2% since the previous report. However, the degree of compliance varies significantly among big cities. For instance, only 14 of the 28 capitals can be considered to be in full compliance in 2011/2012, which are nevertheless 3 capitals more than at the time of the previous report.

This report concludes that, despite challenges such as substantial investment needs and long-term planning, high compliance rates are reached in EU 15 older members. For these countries the priority is to maintain and renew the infrastructure. In EU 13 new members, still significant compliance gaps exist, especially on treatment. Reinforced action and investments are needed to reach full compliance within reasonable time delays.

1.2.3.3. Stages of urban wastewater treatment

Half of the water treated worldwide is urban WW. The volume of WW continues to increase as a result of changing demographics, economic development and urban spread. Along with more stringent environmental safeguarding as a result of regulations and lifestyles, WW treatment is a major environmental challenge for local authorities.

Urban WW treatment is also a technological and economic challenge; the goal is to preserve biodiversity and protect water resources while ensuring the wellbeing of local populations.

Conventional technologies

In small rural areas septic systems are normally used. In these, a large septic tank settles out and stores solids, which are partially decomposed by naturally occurring anaerobic bacteria. The solids have to be pumped out and hauled by tank truck to be disposed of separately. Liquid wastes are dispersed through perforated pipes into soil fields around the septic tank.

In sewered urban areas WW purification typically requires several physical, chemical and biological treatment stages (Figure 1.6):

Preliminary treatment. During preliminary treatment, the incoming WW is strained to remove all large objects. The influent flows across bar screens, of a wide variety of shapes and sizes, and objects on the screens are raised out of the water (either mechanically or manually).

Another component of preliminary treatment is the grit channel where the velocity of the incoming WW is carefully controlled to allow sand, grit, and stones to settle down while keeping the majority of the suspended organic material in the water column. The grit is removed from the channel, added to the larger objects removed by the bar screens, and taken to the landfill for disposal.

Primary treatment. Its main purpose is to produce both a generally homogeneous liquid capable of being treated biologically and a sludge that can be separately treated or processed. Many plants have large tanks, commonly called primary clarifiers or primary sedimentation tanks, where the sludge settles and the floating material, such as grease and oils, rises to the surface to be skimmed off.

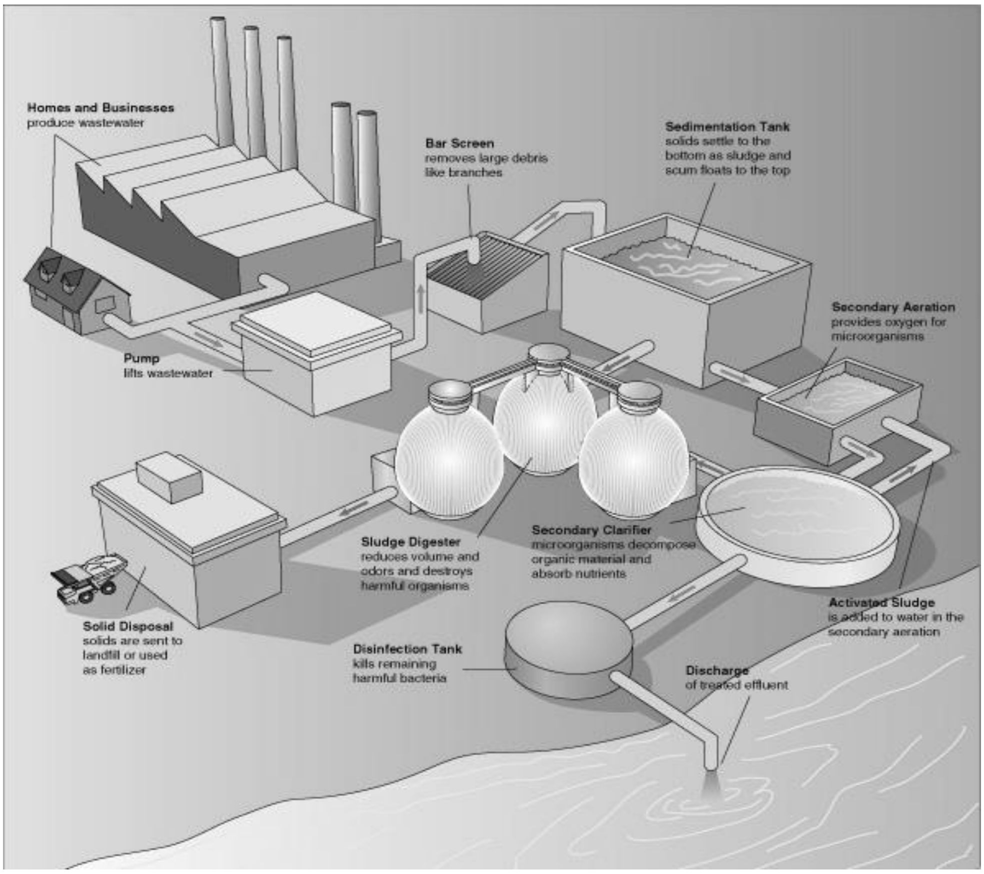


Figure 1.6. Conventional process of wastewater purification in WWTPs

Secondary treatment. This step can remove up to 90% of the OM in WW by using biological treatment processes. The two most common conventional methods are attached growth and suspended growth processes.

In attached growth (or fixed film) processes, bacteria, algae, fungi and other microorganisms grow and multiply on the surface of stone or plastic media, forming a microbial growth or slime layer (biomass) on the media. WW passes over the media along with air to provide oxygen, and the bacteria consume most of the OM. Attached growth process units include trickling filters, biotowers, and rotating biological contactors.

In suspended growth processes, the microbial growth is suspended in an aerated water mixture where the air is pumped in, or the water is agitated sufficiently to allow oxygen transfer. The suspended growth process speeds up the work of aerobic bacteria and other microorganisms that break down the OM by providing a rich aerobic environment. In the aeration tank, WW is vigorously mixed with air and microorganisms acclimated to the media for several hours. Suspended growth process units include variations of activated sludge, oxidation ditches and sequencing batch reactors.

After biological treatment, the water is pumped to secondary clarifiers where any leftover solids and the microorganisms sink to the bottom. These solids are handled separately from the supernatant. Secondary treatment is usually sufficient to meet legal requirements, and secondary treated WWs (TWW) can be discharged to water bodies or reused.

Tertiary treatment. This treatment involves advanced processes that generate an effluent of higher quality than secondary treatment can produce. This can be accomplished by a variety of methods such as chemical coagulation and sedimentation, filtration, reverse osmosis, and extending secondary biological treatment to further stabilise oxygen-demanding substances or remove nutrients. In various combinations, these processes can achieve any degree of pollution control desired.

Disinfection. The purpose of this step in the treatment of WW is to substantially reduce the number of microorganisms in the water to be discharged back into the environment and is almost always the final step in the treatment process regardless of the level or type of treatment used. The effectiveness of disinfection depends on the quality of the water treated, the type of disinfection used, the disinfectant dosage, and other environmental variables. Common methods of disinfection include ozonation, chlorine, and UV light. Innovative technologies include solar disinfection and TiO_2 photocatalysis.

Alternative technologies

In Southern Mediterranean countries, the removal or inactivation of excreted pathogens is the principal objective of WW treatment. Conventional options are often better at removing environmental pollutants than removing pathogens. Therefore, the application of new WW treatment technologies to overcome the limitations of conventional methods is becoming necessary.

Membrane bioreactors. This technology (Figure 1.7 A) combines biological-activated sludge process and membrane filtration. The costs are higher but the increase of water price and the need of water reuse, as well as more stringent regulations, are making this process competitive. Membrane bioreactors are highly efficient in removing nutrients, OM, suspended solids, pathogens, trace organic compounds and their degradation products (Radjenović et al., 2008).

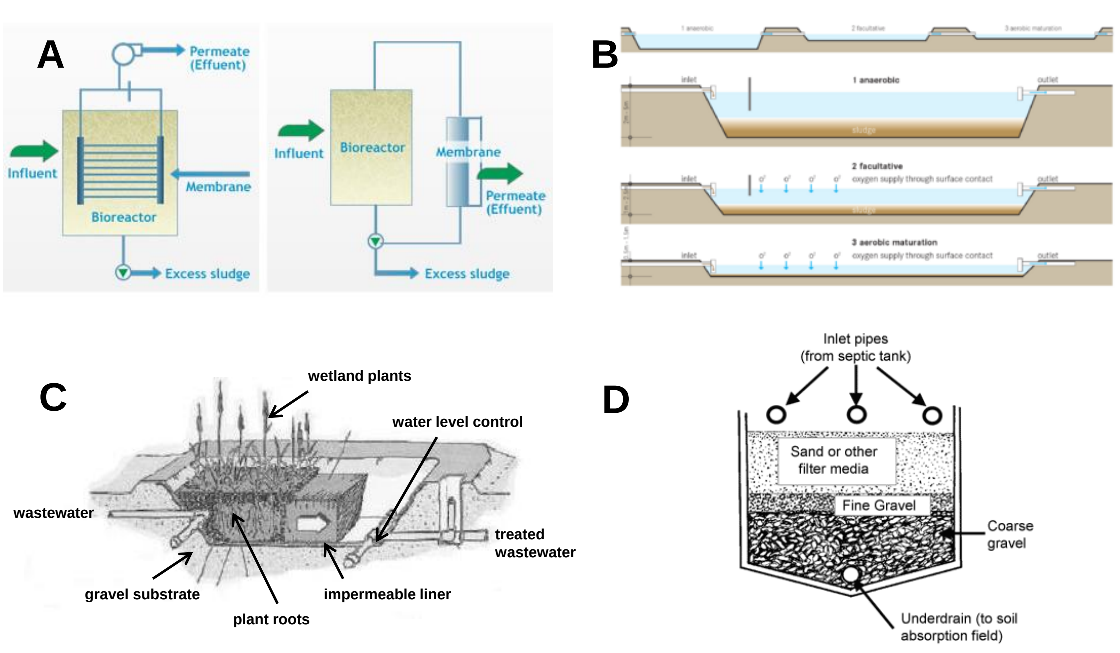


Figure 1.7. Schematic representation of membrane bioreactors (A), waste stabilisation ponds (B), constructed wetland (C), and sand filter (D)

Waste stabilisation ponds. These ponds or lagoons (Figure 1.7 B) are holding basins used for low-cost secondary WW treatment where decomposition of OM occurs naturally, with sunlight disinfection and a complex symbiosis of bacteria and algae, which stabilises the waste and reduces pathogens. The main disadvantages of waste stabilisation ponds are the large land areas required (Hosetti and Frost, 1995).

Constructed wetlands. This system (Figure 1.7 C) uses wetland vegetation, soils, and their associated microbial population to improve water quality. They efficiently remove suspended solids through water filtration. Organic pollutants are transformed and taken up by plants or transformed by wetland microorganisms. Nutrients in excess are often absorbed by wetland soils and subsequently consumed by plants and microorganisms.

Sand filters. Sand filtration (Figure 1.7 D) is one of the oldest WW treatment technologies known. They are beds of granular material, or sand, where pretreated WW can be collected, and distributed to the land application system. Their main advantages are: minimal equipment and investment; environmentally "green" technology; negligible electrical consumption; natural disinfection; and scalable technology suitable for commercial, industrial and institutional settings.

The choice of the purification system depends mainly on the population size, and the load and type of contamination.

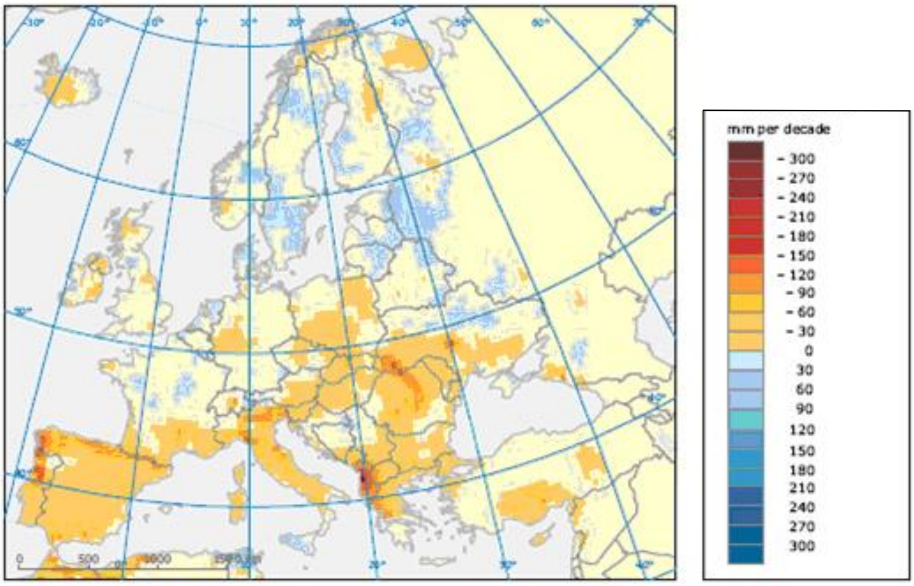
1.2.4. Treated wastewater reuse

1.2.4.1. Context and legislative framework

Water over-abstraction is a major cause of water stress. Main pressures from water consumption are concentrated on irrigation and domestic demand, including tourism. The "Communication on Water scarcity and Droughts" (European Commission, 2007) made clear that water scarcity and drought events are likely to be more severe and more frequent in the future due to climate change and increasing population. Over the past decades, droughts have dramatically increased in number and intensity in the EU (Figure 1.8) and at least 11% of the European population and 17% of its territory have been affected by water scarcity to date.

In Spain there are areas of low rainfall and long periods of drought, which forces to optimise water management. In this sense, TWW constitute a viable and optimal resource.

Numerous international organisations have proposed TWW reuse as an additional resource to be included in water management plans. Water reuse is a top priority area in the "Strategic Implementation Plan" of the European Innovation Partnership on Water (European Commission, 2012a), and maximisation of water reuse is a specific objective in the Communication "Blueprint to safeguard Europe's water resources" (European Commission, 2012b).



Source: The data come from two projects: ENSEMBLES (http://www.ensembles-eu.org) and ECA&D (http://eca.knmi.nl).

Figure 1.8. Observed changes in annual precipitation in Europe between 1961 and 2006

The European Directive 2000/60/EC (Directive 2000/60/EC), or the EU Water Framework Directive, was finally adopted on 23 October 2000, after several years of debate and proposals. It permits to set homogeneous environmental objectives among all the Member States for the water resources. Its general purpose is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwaters. Reutilisation of TWW is included among the complementary measures that can be introduced in order to comply with the environmental objectives.

The transposition of this directive into the Spanish law is contained in the *Ley de Aguas* (RD 1/2001), lately modified by the law 62/2003 in order to achieve an adequate protection of inland, coastal and transitional waters. Article 109 states that the government must develop the basic conditions for reutilisation and specify the required quality for reclaimed waters according to the intended use. It also establishes that the concession holders should fund the costs necessary for WW treatment and get the level of quality demanded.

Moreover, RD 1620/2007 establishes the quality conditions to be met by reclaimed water indicating the permitted and prohibited uses and the regime of responsibilities in relation to the maintenance of quality.

1.2.4.2. Barriers and potential reuse of treated wastewaters in Europe

Water reuse encounters numerous barriers in the EU, although this practice is commonly and successfully used in, for example, Israel, California, Australia, and Singapore. Limited awareness of potential benefits among stakeholders and the general public, and lack of a supportive and coherent framework for water reuse are two major barriers currently preventing a wider spreading of this practice in the EU.

At present, about 1 billion cubic metres of TWW is reused annually, which accounts for approximately 2.4% of the TWW effluents and less than 0.5% of annual EU freshwater withdrawals. But the EU potential is much higher, estimated in the order of 6 billion cubic metres. Both southern and northern Member States already have in place numerous initiatives regarding water reuse for irrigation, industrial uses and aquifer recharge. Cyprus and Malta already reuse more than 90% and 60% of their TWW respectively, while Greece, Italy and Spain reuse between 5 and 12% of their effluents, clearly indicating a huge potential for further uptake (Wintgens and Hochstrat, 2006). However in some areas, like the Canary Islands, Valencia or Murcia, the percentage of water reuse is quite higher (Iglesias et al., 2010).

On 2 December 2015, it was presented a new circular economy package (European Commission press release, 2015). In particular, it committed to develop a number of actions to promote further uptake of water reuse at EU level, of which the most important is to establish minimum quality requirements for TWW reuse in irrigation and aquifer recharge at the beginning of 2017.

1.2.4.3. Applications of treated wastewaters reuse

Several types of TWW uses are normally accepted worldwide depending on the quality achieved (Table 1.7). It is important to mention that in Spain the RD 1620/2007 prohibits the use of TWWs for drinking water supply, except in case of catastrophe. Their use is also banned in the food industry, except for processing and cleaning purposes; in hospitals; in aquaculture for growing molluscs; in recreational uses as bathing waters; in cooling towers and evaporative condensers; in fountains of public outdoor and indoor spaces; and any other use that the authorities may consider harmful to the environment and human health.

Table 1.7. Applications of treated wastewaters

Irrigation	Irrigation of food and non-food crops Landscape irrigation: parks, golf courses... Forest irrigation Land treatment
Environmental	Aquifer recharge Augmentation of surface water Fight against salt intrusion Recreational and environmental uses
Industrial	Recycling: cooling water, process water… Construction
Urban	Toilet flushing Cooling water for air conditioning Firefighting Ornamental use Street and road maintenance Car washing
Drinking water	Indirect reuse through augmentation of surface water Direct use (combined with conventional drinking water)
Other uses	Firefighting, artificial snow…

Adapted from Condom et al. (2012)

1.2.4.4. National and local situation

In 2007 the number of WWTPs in Spain was over 2500, which treated 3375 hm^3 per year. Their geographic distribution is shown in Figure 1.9.

According to Ortega de Miguel (2008), the volume of reused water in Spain reached approximately 368 hm^3 per year. Agricultural irrigation accounted for 71% of the total water reused, followed by environmental (17.7%), recreational (7%), urban (4%) and industrial (0.3%) uses. The regions where most water was reused were leadered by Comunidad Valenciana (148.66 hm^3/y) and Murcia (84.52 hm^3/y), followed by Cataluña (44.16 hm^3/y) and Baleares (28.24 hm^3/y), all in the Mediterranean arc. Andalusia, ranking fifth (24.21 hm^3/y), only reused 1-5% in the different basins.

In the Andalusian region water treatment and quality is regulated by the Decrees 54/1999 and 310/2003.

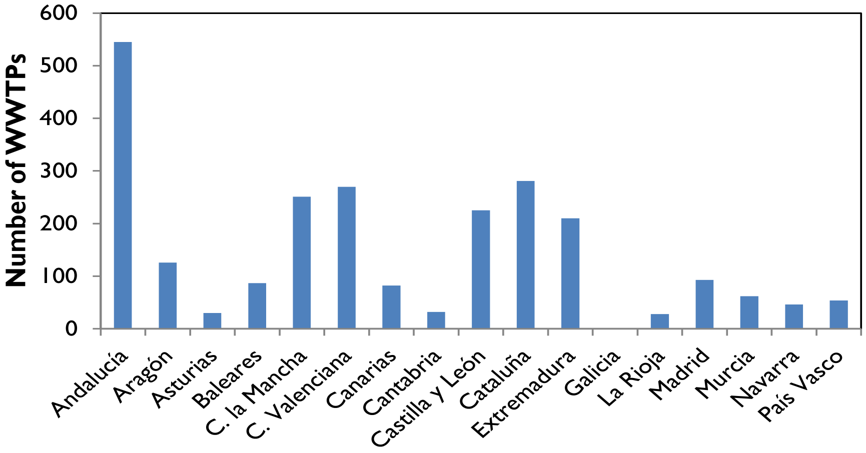


Figure 1.9. Distribution in Spain of WWTPs per Autonomic regions (Ministerio de Medio Ambiente, Medio Rural y Marino)

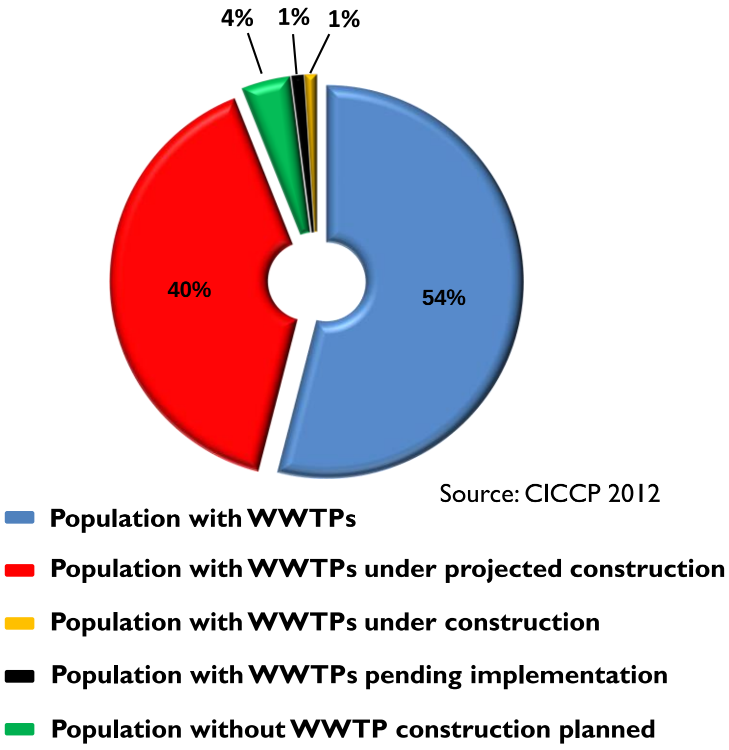
The province of Granada has a population of around 920000 inhabitants, but only 54% of the WW generated is adequately purified in WWTPs (Colegio de Ingenieros de Caminos, Canales y Puertos, 2012) (Figure 1.10).

The situation is similar in the metropolitan area of the city of Granada. This area has a population of approximately 530000 inhabitants, of which only 49% of the WW generated is collected and treated, being the rest directly discharged into the environment. Different projects are planned in order to achieve the purification of the entire WW generated, thus complying with the Water Framework Directive (Colegio de Ingenieros de Caminos, Canales y Puertos, 2012).

1.2.4.5. Reuse of treated wastewaters in agriculture

Agricultural irrigation is the main application of TWW reuse (Salgot and Huertas, 2006; Iglesias et al., 2010; Pedrero et al., 2010; Sato et al., 2013). TWW is being used for irrigation on an estimated 4.5 million ha worldwide (Jiménez and Asano, 2008). Therefore, this reuse becomes indispensable to minimise TWW discharge to the environment, thus preserving fresh water resources for other uses such as drinking water supply for human consumption (Sousa et al., 2011; Kayikcioglu, 2012).

Additionally, it can be considered a reliable water supply, quite independent from seasonal drought and weather variability and able to cover peaks of water demand. This can be very beneficial to farming activities that can rely on sustainable continuity of water supply during the irrigation period, consequently reducing the risk of crop failure and income losses. Appropriate consideration for nutrients in TWW could also reduce the use of additional fertilisers resulting in savings for the environment, farmers and WW treatment (Salgot and Huertas, 2006).



Source: CICCP 2012

Figure 1.10. General situation of wastewater treatment in the province of Granada

Many farmers in arid or semi-arid areas, given the increasing competition for water between agriculture and other sectors, rely on irrigation with TWW because: (1) it is the only water source available for irrigation throughout the year, (2) reduces the need for purchasing fertiliser, (3) involves less energy cost if the alternative clean water source is deep groundwater, or (4) enables farmers in peri-urban areas to produce high-value vegetables.

Nevertheless, one of the main problems in promoting the irrigation with TWW is the reluctance of farmers for fear of rejection of their products. Therefore, it is necessary to take measures to raise awareness of its safety. Hamilton et al (2007) indicated that significant gaps remained in the science of sustainable TWW irrigation:

- Long-term accumulation of bioavailable forms of heavy metals in soils
- An understanding of the balance of various factors affecting the environmental fate of organics in WW-irrigated soils
- The influence of reuse schemes on catchment hydrology, including the transport of salt loads
- Risk models for helminth infections (in particular in developing countries)
- Transfer efficiencies of chemical contaminants to plants
- Effects of chronic exposure to chemical contaminants through consumption of WW-irrigated food

1.2.4.6. Benefits and potential risks from wastewater reuse

Reuse of TWW can provide significant environmental, social and economic benefits. Water reuse can improve the status of the environment both quantitatively, alleviating pressure by substituting abstraction, and qualitatively, relieving pressure of discharge from WWTPs to sensitive areas. WW can often contain significant concentrations of OM and inorganic nutrients (N, P and K). Hence, when the water is recycled as an irrigation source for agriculture, it can improve soil structure, physicochemical properties and fertility, thus increasing crop productivity (Marschner et al., 2003; Gori et al., 2004; Sousa et al., 2011). Furthermore, OM increases soil moisture, retains metals (through cationic exchange and the formation of organometallic compounds) and enhances microbial activity (Meli et al., 2002; Ramirez-Fuentes et al., 2002; WHO, 2006). This capacity to improve soil characteristics gives TWW an additional advantage over synthetic fertilisers. Moreover, when compared to alternative sources of water supply such as desalination or water transfer, water reuse often turns out to require lower investment costs and energy, also contributing to reduce greenhouse gas emissions.

Nevertheless, the reuse of TWW for agricultural purposes poses several environmental risks, whose effects depend on the specific composition of TWW and how it is used. According to the World Health Organisation (WHO, 2006), the following components may have a negative impact on the environment:

- *Pathogens (viruses, bacteria, protozoa and helminths).* These organisms can contaminate crops, soils, surface waters and aquifers. From a health perspective, they are considered the primary hazard, especially when the WW is not adequately treated (Amoah et al. 2006; Angelakis and Snyders, 2015).
- *Salts.* The continuous irrigation with TWW may increase soil salinity. If this is not controlled, soil productivity can decrease in the long term due to changes in the osmotic pressure at the root zone, which may retard the water uptake of the plant, and specific ion toxicity (sodium, boron and chloride) (Hamilton et al., 2007). Thus, salts may destroy the soil structure by causing soil dispersion and clogging of pores, and affect hydraulic conductivity (Toze, 2006; Ruoss et al., 2008; Lado and Ben-Hur, 2009; Sousa et al., 2011; Lado et al., 2012).
- *Heavy metals.* They are easily and efficiently removed during common treatments and the majority of heavy metal amounts end up in the biosolid fraction (Sheikh et al., 1987; Stevens and McLaughlin, 2006). However, the use of TWW containing industrial discharges with high heavy metals concentration leads to metal accumulation in soils and crops and has been associated with health problems in crop consumers (Calheiros et al., 2008). Regardless the metal content of TWW, heavy metals will not be absorbed by plants unless they reach a threshold concentration in the soil and they are bioavailable in the mobile phase (Xiong et al., 2004).
- *Toxic organic compounds.* A great variety of toxic compounds may be present in TWW (Ying, 2006a). Domestic WW has normally low content of toxic organic compounds, but it can increase to hazardous levels because of industrial discharges, agricultural runoff, leaks from storage tanks or pipes, leachates from polluted soils, confinement sites and landfills, and air pollutants deposited in rain. Among them, the most common are industrial compounds (phthalates, biphenyl, PCBs, *p*-nonylphenol…), pesticides, petroleum components, disinfections by-products, hormones and pharmaceuticals (Pal et al., 2014; Luque-Espinar et al., 2015; Pereira et

al. 2016). These pollutants may have carcinogenic, teratogenic or mutagenic effects. Additionally, some of them may act as endocrine disrupting agents in animals or humans. In WW treatment, the concentration of many of these compounds is reduced by adsorption, volatilisation and biodegradation processes.

- *Nutrients.* It has been above mentioned that the addition of nutrients to agricultural soils through TWW irrigation increases crop productivity (Gori et al., 2004; Oliver et al., 2014). However, it is well known that if WW, treated or non-treated, is discharged into natural water bodies such as lakes, rivers and the coastal marine environments, it can cause severe degradation problems such as eutrophication and algal blooms (Oliver et al., 2014; Kumar and Pal, 2015).
- *Organic matter.* Despite the beneficial aspects of OM in soil properties and crop productivity, the presence of DOM in TWW may alter the fate of pesticides and other pollutants in soils (Müller et al., 2007; Gerstl and Graber, 2010).

2. MATERIALS AND METHODS

2.1. EXPERIMENTAL METHODS FOR SOILS AND SOLUTIONS

2.1.1. Soil sampling and preparation

Soil samples were collected from the plough layer (20 cm). Once in the laboratory, they were air dried, the aggregates were disaggregated with a wooden roller and passed through a 2 mm sieve. The coarser fraction (> 2 mm) was discarded, while the finer one (< 2 mm) was stored in plastic bags and used for soil characterisation.

2.1.2. Soil texture

The granulometric analysis of soils was performed according to the Robinson pipette method (Robinson, 1922), which is based on the different sedimentation velocity of soil particles (Stokes' equation). Ten g of soil were mixed with 100 mL of Milli Q (MQ) water (Millipore, Bedford, MA) and digested with small portions of H_2O_2 (33%, w:v; Panreac, Spain) to destruct the OM. To eliminate the dissolved salts, the samples were dialysed during 2 d utilising cellophane as a semipermeable membrane. Subsequently, 10 mL of a sodium hexametaphosphate ($(NaPO_3)_6$) (Panreac, Spain) solution was added to disperse clay particles. MQ water was added up to a volume of 150 mL and the suspensions were shaken for 8 h. For the differentiation of soil particles according to their size, the samples were passed through a 50 µm sieve thus obtaining the sand fraction. The suspensions were transferred to big volumetric cylinders and water was added up to a volume of 1 L. The suspensions were manually agitated and an aliquot of 20 mL was taken immediately (silt + clay fractions). Finally, the samples were let to settle down and an additional 20 mL aliquot was taken after 8 h at a depth of 8 cm (clay fraction). Both aliquots were oven-dried at 105 °C during 48 h, and the dry residues were weighed for the calculation of the percentage of each soil fraction.

Once the sand, silt, and clay percentages of a soil are known, the textural class can be read from the textural triangle (Figure 2.1). The nomenclature of the United States Department of Agriculture was used.

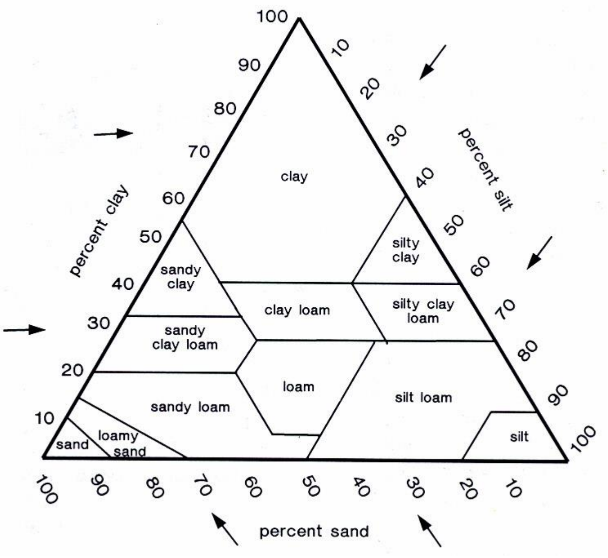


Figure 2.1. Soil texture diagram of the United States Department of Agriculture

2.1.3. Field capacity

The field capacity (FC) of a soil is an important agronomic characteristic that is primarily controlled by soil texture and soil OM content. It refers to the relatively constant soil water content reached after 48 h drainage of water from a saturated soil. The water and air contents of the soil at FC are considered to be ideal for crop growth.

The FC is measured using the Richards method (Richards 1941). Sieved soil samples were placed in the ceramic plates (Soilmoisture Equipment Corp., Santa Barbara, CA, USA), saturated with distilled water and pressurised at 1/3 bar. After 24 h, the moisture content in the soil sample is said to be at FC. The soil samples are then weighed (W1), placed in an oven at 105 °C for 24 h and then weighed again (W2). The FC is calculated with the following equation:

$$FC\ (\%) = \frac{W1 - W2}{W2} \times 100 \qquad [2.1]$$

2.1.4. Soil pH and electrical conductivity

Soil pH was determined by mixing 4 g of soil with 10 mL of MQ water in glass tubes (1:2.5 w:v). The mixture was shaken end-over-end for 1 h and the suspensions were settled during 10 min. Afterwards, pH was measured in the suspensions using a pH-meter (Eutech Instruments Cyberscan pH 2100, Singapore) calibrated with pH 4.00, 7.00 and 10.00 buffer solutions (XS Instruments Green Line, Italy).

Electrical conductivity (EC) was determined in the same soil:water suspensions using a conductivity-meter (XS Instruments COND 510, Italy). The EC was expressed in dS m^{-1} at 25 °C according to equation 2.2:

$$EC_{25} = EC \times \left[1 + \left(0.0191 \times (25 - T)\right)\right] \qquad [2.2]$$

2.1.5. Cation exchange capacity

The CEC of the soils was calculated according to the colorimetric method by Meier and Kahr (1999) based on the formation of a complex between triethylenetetramine (Trien) and Cu^{2+}. For the determination of CEC ($cmol_+ kg^{-1}$) 0.5 g of ground soil (<50 μm) was mixed with 20 mL of a Cu^{2+}-Trien solution at 0.05 M (pH 10), the mixture was shaken for 4 h and allowed to stand for 24 h. Then the absorbance at 620 nm of the supernatant was measured in a spectrophotometer (Helios Gamma, Thermo Scientific, Cambridge, UK).

The CEC of soils is calculated as the difference of absorbance before and after the complex formation.

2.1.6. Total C and total N

Total C and total N were determined in ground samples (<50 μm) with an elemental analyser (LECO TruSpec CN, MI, USA). The samples were subjected to combustion with pure oxygen (oxidation reactor) at a temperature of 900 °C. The different combustion products were transported with He through a reduction column (reduction reactor comprising Cu at 680 °C), obtaining the CO_2 and N_2 gases. N concentration was determined by thermal conductivity and that of C by IR.

The measurements were performed by the ionomics laboratory of the CEBAS-CSIC in Murcia (Spain).

2.1.7. Soil organic carbon

The soil OC was determined by a modification (Mingorance et al., 2007) of the Walkley and Black method (Walkley and Black, 1934). This method consists in oxidising the OC with $K_2Cr_2O_7$ in the presence of H_2SO_4. To do this, 0.05-0.2 g of ground soil (<50 μm) was mixed with 3 mL of 1N $K_2Cr_2O_7$ (Panreac, Spain) and 6 mL of 36 N H_2SO_4 (Scharlab, Spain) in Pyrex glass vials and gently shaken. To maintain the reaction temperature as long as possible, vials were introduced into a polystyrene block. After the reaction time (2.5 h) 10 mL of ultrapure water was added, and the samples were stirred and allowed to stand for 48 h. Subsequently, the supernatant absorbance at 590 nm was measured. The amount of OC in the samples was calculated with a calibration curve (0-5 mg L^{-1}) prepared from a standard solution of sucrose at 5 mg OC mL^{-1}. The quality of the analytical results was evaluated using two certified reference materials (LECO 308 and 62, LECO Corporation, NIST, USA).

The general convention now is to report results as soil OC rather than as soil OM (Baldock and Skjemstad 1999). Nevertheless, the percentage of soil OM can be estimated by equation 2.3:

$$\%OM = \%OC \times 1.724 \qquad [2.3]$$

where 1.724 is the correction factor of Van Bemmelen. This is an approximation assuming that soil OM contains 58% OC.

2.1.8. Soil moisture content

The moisture content of soil samples was determined on a dry weight basis by the gravimetric method. A known mass of soil was weighed in an analytical balance (Mettler AE240) and oven-dried (Selecta) at 105 °C during 24 h to ensure complete drying. Dry samples were placed in a laboratory desiccator, to reach room temperature, and weighed again. Equation 2.4 was used to calculate moisture content:

$$H(\%) = \frac{m_w - m_d}{m_d} \times 100 \qquad [2.4]$$

where m_w and m_d are the mass of wet and dry samples, respectively.

2.1.9. Soil carbonates

The carbonates of soil samples were determined with a methodology based on the classical method of Bernard calcimeter: the release of CO_2 after reaction of HCl with $CaCO_3$:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_{2(g)}$$

Approximately 0.5 g of oven-dried soil was mixed with 4 mL of a 6 M HCl (Scharlab, Spain) solution in a closed Pyrex 100 mL bottle connected to a gas pressure sensor (Vernier Science and Technology) monitoring the changes in pressure assumed to originate from the CO_2 levels produced during carbonate decomposition. The same procedure is followed with approximately 0.2 g of $CaCO_3$ (Merck Life Science, Germany) of known purity. Soil carbonates are calculated with the following equation:

$$Carbonates\ (\%) = \frac{M \times C}{P \times S} \times 100 \qquad [2.5]$$

where M and P are the maximum pressure (mm Hg) recorded for soil and carbonate respectively, C is the mass of carbonate and S that of soil sample (g).

2.1.10. Soil dehydrogenase activity

Classical methodologies for dehydrogenase activity (DHA) determination are based on the reduction of soluble tetrazolium salts to red coloured formazans. Several compounds have been proposed, though in soils the use of 2-p-iodophenyl-3-p-nitrophenyl-5-phenyltetrazolium chloride (INT) has been found to be more suitable than other salts due to its high electron affinity (Von Mersi and Schiner, 1991). DHA calculation of soil samples was based on a method by García et al. (1997): approximately 1 g of dry soil was incubated at 25°C for 20 h in a plastic tube with 0.2 mL of a 0.4% (w/v) 2-p-iodophenyl-3-p-nitrophenyl-5-phenyltetrazolium chloride (INT) (Sigma-Aldrich, USA) aqueous solution. The iodonitrotetrazolium formazan (INTF) formed after reduction of INT was extracted with a tetrachloroethylene/acetone mixture (2/3) by vigorous shaking in a vortex. The suspensions were centrifuged (Universal 320R centrifuge, Hettich) at 4000 rpm for 15 min, and the supernatants transferred to glass tubes and measured spectrophotometrically at 490 nm. A calibration curve between 0.5-10 mg L^{-1} of INTF (Sigma-Aldrich, USA) was constructed to determine INTF concentration in the samples. DHA was expressed as µg INTF g soil $^{-1}$ h^{-1}.

2.1.11. Soil induced respiration

The induced respiration of soils was measured using an automated respirometer (µTrac 4200, Sy Lab microbiology; Gomensoro, Madrid, Spain) based on the indirect impedance technique. The system operates by measuring changes in the impedance of a KOH solution that traps the CO_2 produced during the biological activity of the soil. The system consists of an incubation block with 21 cavities that can be maintained at a constant temperature during the procedure. Measuring airtight cells, closed by a screw cap, are inserted into each cavity of the system. The 2% KOH solution is poured into the measuring cells equipped with two electrodes that are connected to the base of the cavities. A second plastic vial containing the soil sample is placed in the KOH solution in the measuring cell.

Soil is preincubated with distilled water at 70% field capacity during 2 h. Then, 5 g of preincubated soil is mixed with 50 mg of a talc-glucose mixture (10:1, w:w) and transferred to a plastic vial. This vial is introduced inside the measuring cell to which is added 2 mL of fresh KOH solution (Panreac, Spain) at a concentration of 35.7 mM. The measuring cell is sealed, and then connected to the cavity of the respirometer. Each cell is allowed to stabilise during 1 h at 30 °C. Then, the impedance variation is measured every 5 minutes at this temperature for 20 h. Results are expressed as mg CO_2 100 g^{-1} h^{-1} (Mingorance and Peña, 2016). In all cases, the values during the first hour were considered as corresponding to a lag phase and discarded (Bailey et al., 2007; Butler et al., 2011, 2012).

2.1.12. Soil chemical composition: X-ray fluorescence

The chemical composition of soil samples was characterised in the scientific services of the Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR, Granada) by X-ray fluorescence (XRF). XRF spectrometry is based on the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays as primary radiation from an X-ray tube. Samples were analysed in a wavelength dispersive XRF spectrometer (S4 Pioneer, BRUKER) with a maximum power of 4 kW. The spectrometer has an Rh anode X-ray tube (60 kV, 150 mA), three analyser crystals (OVO-55, LiF 200 and PET), two collimators (0.23° and 0.46°), Pb, Cu, and Al beam filters, and a flow proportional counter for light element detection and a scintillation counter for heavy elements.

2.1.13. Soil mineralogy: X-ray diffraction

X-ray diffraction (XRD) is one of the most used techniques for the identification of clay minerals in soils. It is based on the diffraction of X rays by particulate matter (Jenkins and Snyder, 1996; Moore and Reynolds, 1997). The analyses were performed in the XRD laboratory of the Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR, Granada) equipped with a Philips PW 1710 apparatus, operated by a totally computerised system (XPOWDER), and a Panalytical X'Pert Pro MPD model with automatic charger and X'Celerator detector, allowing rapid, precise qualitative and quantitative study of the mineral composition of any geological sample. XRD patterns were recorded on powder specimens as well as on oriented and glycolated specimens.

2.1.14. Infrared spectroscopy

Infrared (IR) spectroscopy is used routinely for the rapid characterisation of a wide range of materials, such as soils. It is based on the interaction of molecules with electromagnetic energy in the IR spectral region. When a molecule absorbs IR radiation at frequencies matching that of its own molecular vibrations, it results in an increase of the amplitude of the vibrations at these frequencies.

The IR spectra were collected with a FTIR (Fourier-Transformed infrared) Perkin Elmer Spectrum-One spectrometer equipped with a lithium tantalate ($LiTaO_3$) detector. Every spectrum was recorded in the region 4000-450 cm^{-1} with accumulations of 100 scans, a wavenumber resolution of 4 cm^{-1} and an acquisition of 0.5 scan s^{-1}, by using KBr pellets obtained by pressing uniformly prepared mixtures of 1 mg of sample with 100 mg of KBr (FTIR spectroscopy grade; Merck Life Science, Germany) previously desiccated at 110 °C under reduced pressure. Grams/32 (Thermo Fisher Scientific Inc., 2011) program was used to plot and analyse the spectra.

2.1.15. Determination and characterisation of dissolved organic carbon

For the determination of the dissolved organic carbon (DOC) content in the soil supernatants and in aqueous solutions, samples were filtered through 0.45 µm PVDF filters and dried at low temperature (≤45 °C) to avoid OM decomposition. Then, the methodology of section 2.1.7 was followed.

For the characterisation of DOC two parameters were calculated: the Specific UV Absorbance at 254 nm ($SUVA_{254}$) and the humification index (HIX).

2.1.15.1. Specific UV absorbance at 254 nm ($SUVA_{254}$)

$SUVA_{254}$ is defined as the specific UV absorbance of an aqueous sample at 254 nm normalised for DOC concentration. It is normally expressed in L mg^{-1} m^{-1} and calculated according to the following formula:

$$SUVA_{254}(Lmg^{-1}m^{-1}) = \frac{A_{254}}{DOC} \times 100 \qquad [2.6]$$

This parameter has been shown to be a good indicator of the aromaticity of the DOC present in an aqueous sample, though it does not provide information about the reactivity of DOC. Sample pH, nitrate and iron may affect $SUVA_{254}$ measurements (Weishaar et al., 2003).

2.1.15.2. Humification index (HIX)

HIX (dimensionless) is an indicator of the degree of humification of DOC. Its calculation is based on the reports by Zsolnay et al. (1999) and Zsolnay (2003). Fluorescence emission spectra were recorded from 300 to 480 nm at an excitation wavelength of 254 nm in 1 cm cuvettes, using a Photon Technology International (model QM-2000) fluorescence spectrophotometer. Fluorescence values relative to the maximum were calculated. Previous to the fluorescence measurements, filtered samples were acidified with HCl 2 M at pH~2, since pH affects the fluorescence of DOC (Laane, 1982), and diluted when A_{254} was greater than 0.3 cm^{-1} to ensure low DOC concentration.

HIX was calculated as the relation between the area under the spectrum of the upper quarter (435-480 nm) and that of the lower quarter (300-345 nm). Humification can be considered to be associated with the C/H ratio (Stevenson, 1994; Lüttig, 1986). While the lower quarter corresponds to non-humified compounds with a low condensation degree, the upper one corresponds to aromatic condensed molecules typical from humic acids (Cox et al., 2007).

2.1.16. Total dissolved solids

The term “total dissolved solids” describes the inorganic salts and small amounts of OM present in solution in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, bicarbonate, chloride, sulfate and nitrate anions.

It was determined by a gravimetric method consisting in oven-drying (105 °C, 24 h) a known volume of sample. After reaching room temperature in a desiccator, the solid residue is weighed in an analytical balance. The total dissolved solids are calculated by dividing the mass of the solid by the sample volume. Results are expressed in mg L^{-1}. One drawback of this method is the loss of volatile organic compounds (Sawyer and McCarty, 1967).

2.1.17. Inorganic anions determination

Inorganic anions such as chloride (Cl^-), bromide (Br^-) and nitrate (NO_3^-) were determined in the leachates proceeding from the column and field assays.

Furthermore, the inorganic anions present in the irrigation waters used in the field study were also determined. A Metrohm 761Compact Ion Chromatograph equipped with a conductivity detector (Metrohm, Switzerland) was used. A 20 µL aliquot was injected in a Metrosep A Supp 4-250 column (250 x 4 mm), whose separation phase consists of polyvinyl alcohol particles with quaternary ammonium groups (9 µm particle size), protected with a Metrosep A Supp 4 guard column (5 x 4 mm, 5 µm particle size). The eluent consisted in an aqueous mixture of Na_2CO_3 (1.8 mM)/$NaHCO_3$ (1.7 mM) and 2% acetone at a flow rate of 1 mL min^{-1}. Sulfuric acid 50 mM was used as chemical suppressor. The retention times of F^-, Cl^-, Br^-, NO_3^- y SO_4^- were 3.7, 5.2, 7.3, 8.1 and 13.9 min respectively.

2.2. PESTICIDE INFORMATION AND ANALYSIS

2.2.1. General pesticide information

The structure and the main properties of the pesticides under study are depicted in Figure 2.2. Information below is extracted from Tomlin Pesticide Manual (2003) and Pesticide Properties DataBase (FOOTPRINT).

2.2.1.1. α-cypermethrin and deltamethrin

Both α-cypermethrin (CYP) [(R,S)-α-cyano-3-phenoxybenzyl(1R,S)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], and deltamethrin (DTM) [[(S)-cyano-(3-phenoxyphenyl)-methyl](1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate] are non-systemic insecticides with contact and stomach action which belong to the pyrethroid class. They act on the central and peripheral nervous system at very low doses, and are used to control a wide range of chewing and sucking insects in a wide range of crops.

CYP is approved for use in the EU. It has low aqueous solubility, is non-volatile and, based on its chemical properties, is not expected to leach to groundwater. However, it is considered to be a serious water pollutant. It is moderately persistent in soil and has been known to persist in water except at alkaline pH. It is highly toxic by ingestion to human beings and other mammals and a recognised irritant. It is relatively non-toxic to birds but is highly toxic to most aquatic organisms and honeybees. It is moderately toxic to earthworms.

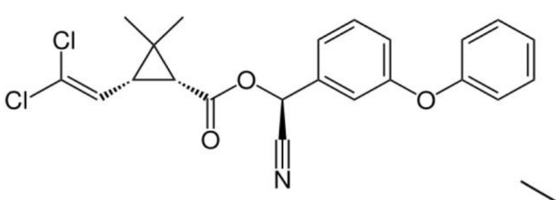
DTM is approved in the EU, Australia and the USA for use in agriculture and veterinary treatments. It has low aqueous solubility and leaching potential, and is non-volatile. It is not persistent in soil but it is stable in water. DTM is highly toxic to humans and other mammals and is a neurotoxin. It is relatively non-toxic to birds and earthworms although it presents a high risk to most aquatic organisms and honeybees.

2.2.1.2. Pendimethalin

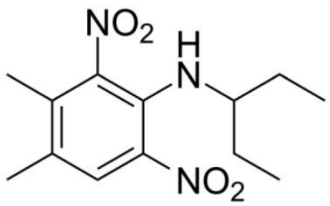
Pendimethalin (PDM) [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] is an herbicide of the dinitroaniline class used in pre-emergence and post-emergence applications. It controls most annual grasses and many annual broad-leaved weeds by inhibition of cell division and cell elongation. PDM has low aqueous solubility and soil leachability, and moderate volatility. It is moderately persistent in soil, relatively sensitive to sunlight irradiation and very resistant to aqueous hydrolisis. PDM is slightly toxic to humans with moderate eye irritation and harm if swallowed or absorbed through skin. It is considered to be slightly toxic to small mammals and some birds by ingestion. However, it is highly toxic to fishes and aquatic insects.

2.2.1.3. Fenarimol

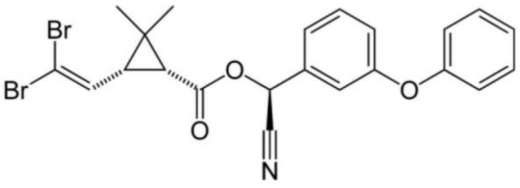
Fenarimol (FEN) [(±)-2,4'-dichloro-α(pyrimidin-5-yl)benzhydryl alcohol] is a systemic fungicide with protectant, curative and eradicating properties of the group of substituted pyrimidines. It is applied especially in fields and greenhouses of ornamental plants and horticultural crops such as strawberries, vineyards, tomatoes, peppers and eggplants, against powdery mildew and black spot. FEN has low water solubility and is persistent and not mobile in soil. In aqueous solutions, it is stable to hydrolysis but susceptible to rapid photolysis. The use of FEN presents low acute toxicity to wild birds and mammals, as well as for honeybees and earthworms. However, it is classified as harmful to fish or other aquatic life (http://www.inchem.org/documents/jmpr/jmpmono/v95pr20.htm).



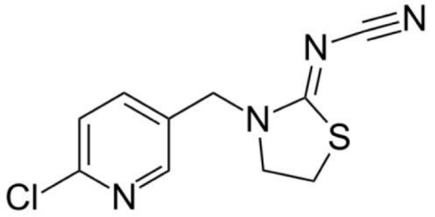
α-cypermethrin (CYP)
Class: pyrethroid insecticide
Mol. weight (g mol^{-1}): 416.3
Water sol. (mg L^{-1}): 0.01 (25 °C)
Log k$_{ow}$: 6.94



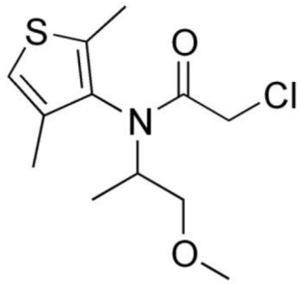
Pendimethalin (PDM)
Class: dinitroaniline herbicide
Mol. weight (g mol^{-1}): 281.3
Water sol. (mg L^{-1}): 0.3 (20 °C)
Log k$_{ow}$: 5.18



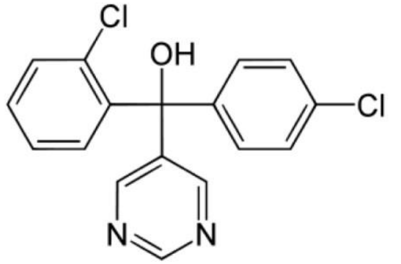
Deltamethrin (DTM)
Class: pyrethroid insecticide
Mol. weight (g mol^{-1}): 505.2
Water sol. (mg L^{-1}): < 2x10^{-4} (25 °C)
Log k$_{ow}$: 4.6



Thiacloprid (THC)
Class: neonicotinoid insecticide
Mol. weight (g mol^{-1}): 252.7
Water sol. (mg L^{-1}): 184 (20 °C)
Log k$_{ow}$: 1.26



Dimethenamid (DIM)
Class: chloroacetamide herbicide
Mol. weight (g mol^{-1}): 275.8
Water sol. (mg L^{-1}): 1200 (25 °C)
Log k$_{ow}$: 2.15



Fenarimol (FEN)
Class: pyrimidine fungicide
Mol. weight (g mol^{-1}): 331.2
Water sol. (mg L^{-1}): 13.7 (25 °C)
Log k$_{ow}$: 3.69

Figure 2.2. Chemical structure, class and main physicochemical properties of the pesticides under study (Tomlin, 2003; FOOTPRINT)

2.2.1.4. Thiacloprid

Thiacloprid (THC) [(Z)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide] is an insecticide of the neonicotinoid family which is the most important new class of synthetic insecticides produced during the past two decades. THC was developed in 2000 and its mechanism of action is similar to other neonicotinoids involving disruption of the nervous insect system by stimulating nicotinic acetylcholine receptors. It has activity not only against sucking insects but also against weevils, leaf miners and various beetle species. THC is moderately soluble in water and, according to its reported GUS index (0.14) (Gustafson, 1989), has low leachability. Although THC is very persistent in water, it is readily degraded in soil by microorganisms. This insecticide has moderate acute toxicity for mammals, fishes, aquatic invertebrates, honeybees and earthworms, but it is highly toxic to birds. However this insecticide has been temporarily banned from the European market due to studies that warn about the effect of neonicotinoids on the behaviour and survival of honey bees (Gill et al, 2012; Henry et al., 2012; Williams et al., 2015).

2.2.1.5. Dimethenamid

Dimethenamid (DIM) [(RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide] is a selective pre-emergence herbicide belonging to the chloroacetanilide class. It acts through inhibition of cell division by interfering with the synthesis of proteins, lipids and other components of the membranes. It is commonly used in the control of annual grasses and many broad-leaved weeds in maize, soya beans, sunflower and other crops. DIM is non-volatile and highly soluble in water. According to its calculated GUS index (2.41), it has a moderate leaching potential. Although DIM does not persist in soil, it is resistant to degradation in aqueous solutions.

2.2.2. Pesticide stock solutions

Analytical reference standards of the pesticides, all with purity ≥96%, were used without further purification (Dr. Ehrenstorfer, Augsburg-Germany). Individual stock solutions were prepared at 1 g L^{-1} in either acetone or acetonitrile (both Pesticide Residue Analysis grade) and stored at -20 °C until use. The stock solutions were then appropriately diluted in order to prepare the standards for calibration and working solutions for the different studies.

2.2.3. Pesticide extraction from aqueous samples

A microwave assisted extraction was used. The following procedure was performed for the extraction of the most hydrophobic pesticides (CYP, DTM and PDM) in SV soil supernatants (chapter 3). In a small closed PTFE tube (ca. 20 mL), 5 mL of the sample was vortexed with 10 mL ethyl acetate (Panreac, HPLC grade) and added with 20 µL of an internal standard (IS), bromopropylate (Dr. Ehrenstorfer, Augsburg-Germany; purity ≥ 98.5%), at 100 mg L^{-1} in hexane. The mixture was extracted in a microwave oven (Mars Xpress, CEM, Matthews, NC) at 800 W, ramping for 10 min to 110 °C, and then maintained for 5 min. The mixture was frozen (-80 °C) for 30 min and the organic phase concentrated to dryness in a rotary evaporator at 40 °C (Laborota 4000, Heidolph). The dry residue was dissolved in 1 mL hexane, poured into a vial and directly injected in a gas chromatograph (see below).

The recoveries of the pesticides at a concentration level of 2 mg L^{-1} from the different aqueous samples are shown in Table 2.1.

Table 2.1. Percentage of pesticide (±standard deviation) recovered from aqueous samples with the microwave assisted extraction method (n = 4)

Solution	CYP	DTM	PDM
MQ	79 ± 1.3	91 ± 1.5	70 ± 4
TWW	71 ± 2	84 ± 7	69 ± 8
DOC 3	85 ± 2	94 ± 4	81 ± 9
DOC 9	78 ± 1.3	92 ± 4	75 ± 3
DOC 30	76 ± 10	70 ± 14	82 ± 6
DOC 90	55 ± 9	54 ± 8	90 ± 4
$CaCl_2$ 5 mM	83 ± 3	91 ± 2	82 ± 4
$(NH_4)_2SO_4$ 5 mM	77 ± 3	88 ± 5	75 ± 9

2.2.4. Pesticide extraction from soil samples

2.2.4.1. Microwave assisted extraction

Another microwave procedure was developed (based in Hernández-Soriano et al., 2007a) for the extraction of CYP, DTM and PDM from SV soil in order to determine their sorbed amount (chapter 3). Wet soil from glass tubes (ca. 0.3 g) was transferred to PTFE closed vessels (ca. 30 mL) and added with 25 mL ethyl acetate (Panreac, HPLC grade). After addition of the IS as above, the sample was extracted in the microwave oven at 800 W, ramping for 10 min to 132 °C, and then maintained for 5 min. Hence, the same procedure as with aqueous samples was followed.

Recoveries (n = 8) for CYP, DTM and PDM in soil fortified at 1 mg kg^{-1} of each pesticide were 85 ± 5%, 93 ± 4%, and 86 ± 3% respectively.

2.2.4.2. Ultrasound assisted extraction

An ultrasound assisted extraction (Ultrasons, Selecta) was employed in the degradation, leaching and field studies (chapters 5, 6 and 7). Different conditions were used depending on the expected pesticide amount in soil samples (Table 2.2).

A known amount of soil (1.5-2.5 g, dry weight basis) was extracted in Pyrex glass centrifuge tubes with 15 mL of methanol (HPLC grade, Panreac). The suspensions were centrifuged during 15 min at 2500 rpm and controlled temperature (20 °C), and the supernatants filtered to eliminate suspended soil particles. This process was repeated twice. The combined supernatants were concentrated to dryness at 40 °C in a rotary evaporator, and the dry residue dissolved in different volumes of MQ water (A) and acetonitrile (B) mixtures (Table 2.2) depending on the subsequent analysis by HPLC-DAD.

Table 2.2. Conditions used in the ultrasound assisted extraction method depending on the experiment

Experiment	Soil mass (g)[a]	A:B mixtures[b] (%)	V of mixture (mL)
Leaching	1.5	50:50	1
Degradation	2.5	45:55	1.5
Field	2.5	45:55	1-5[c]

[a]dry weight basis; [b]A: acetonitrile, B: MQ water; [c]depending on sampling time and soil depth

Recoveries (n = 4) of the pesticides at a 1 mg kg^{-1} level were 89 ± 4% for THC, 101 ± 0.5% for FEN and 91 ± 6% for PDM.

2.2.5. Pesticide analytical determination

2.2.5.1. Gas chromatography

A gas chromatographic method was developed for the analysis of CYP, DTM and PDM in aqueous and soil samples. An Agilent 6890 Series II gas chromatograph equipped with a μ-electron capture detector (μECD) (Agilent technologies), and an automatic injector (Agilent technologies 7683B Series injector) with 100-positions (7683 Series autosampler) was used. Helium was used as the carrier gas and injector and detector temperatures were 250 and 300 °C, respectively. A 1-μL sample dissolved in hexane was injected splitless into a HP-5MS (5% phenyl methylsilicone) capillary column (Agilent; 30 m x 0.25 mm i.d. x 0.25 μm film thickness). Oven temperature was programmed starting at 45 °C (1 min), heating at 35 °C min^{-1} to 250 °C, then at 15 °C min^{-1} to 285 °C and maintained 10 min. Retention times were 10.0, 12.6, 16.7 and 21.0 min, for PDM, IS, CYP and DTM, respectively (Figure 2.3).

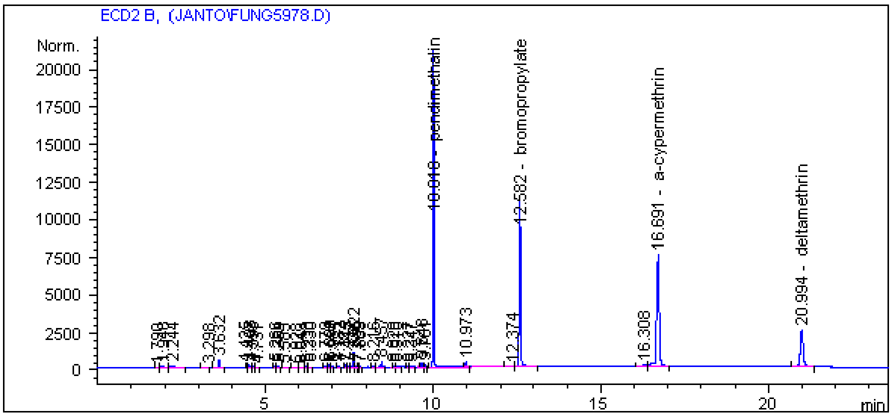


Figure 2.3. GC–μECD chromatogram of pendimethalin, bromopropylate (IS), α–cypermethrin and deltamethrin. Standard mixture at 0.5 mg L^{-1} each in hexane

The calibration curve was performed by triplicate injection of pesticide standards at concentrations between 0.05 and 2 mg L^{-1}, prepared in hexane by dilution of the stock solutions. R^2 value was 0.991 for PDM, 0.997 for CYP and 0.999 for DTM.

2.2.5.2. High performance liquid chromatography

A high performance liquid chromatograph (Agilent 1100 Series/Hitachi LaChrom Ultra) equipped with a diode-array detector (HPLC-DAD) was used in reversed-phase to determine the concentration of THC, DIM, FEN and PDM in different experiments. The mobile phase consisted in mixtures of acetonitrile (A) and MQ water (B), with a flow rate of 0.25 mL min^{-1}. A 10 µL aliquot of filtered (0.45 µm, PVDF filters) samples and standards was injected in a Zorbax C8 column (5 µm, 2.1 x 150 mm) connected to an Eclipse XOB-C8 (5 µm, 2.1 x 12.5 mm) guard column (Agilent Technologies). Column temperature was set at 40 °C.

An isocratic method (50% A: 50% B) (Figure 2.4, top) was designed for the simultaneous measurement of THC, FEN and DIM concentration. Detection wavelengths were set at 245 nm for THC, 210 nm for FEN and 238 nm for DIM. In these conditions, the retention times were 2.2, 5.8 and 6.4 min for THC, FEN and DIM respectively.

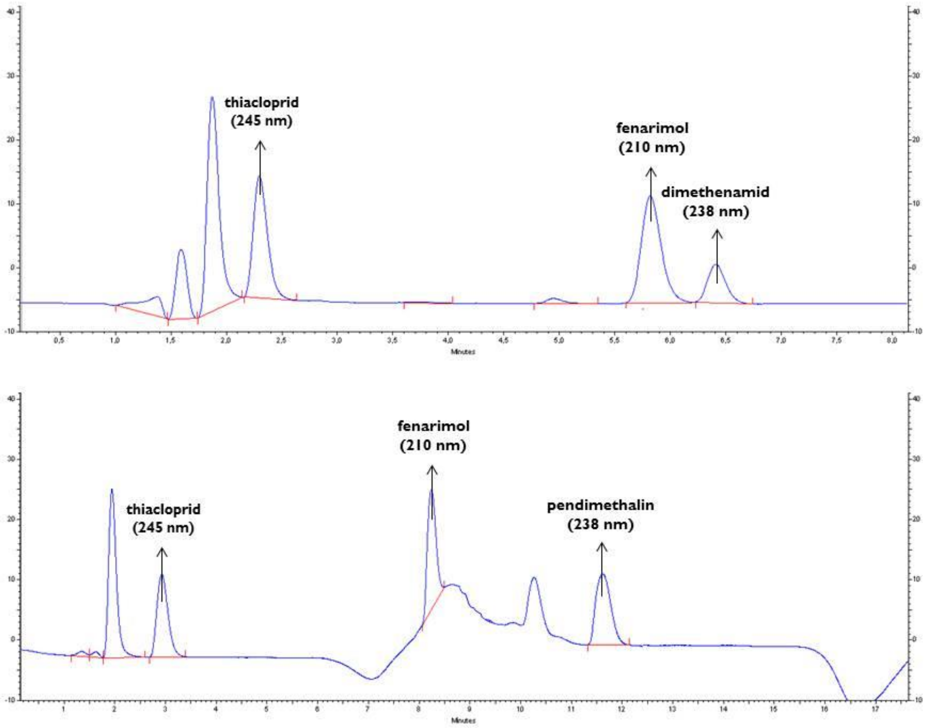


Figure 2.4. HPLC-DAD chromatograms of thiacloprid, fenarimol and dimethenamid according to the isocratic method (top), and thiacloprid, fenarimol and pendimethalin according to the gradient method (bottom). Standard mixtures at 1 mg L^{-1} each in acetonitrile:water (Table 2.2).

A gradient method was used for the join determination of THC, FEN and PDM with the following program: 0-2.5 min (40% A); 2.5-5 min (80% A); 5-12 min (80% A); 12-14 min (40% A) to reach the initial conditions, and maintained for 3 min. The measurement of PDM was performed at 238 nm. Retention times were 2.8, 8.3 and 11.5 for THC, FEN and PDM respectively (Figure 2.4, bottom).

Standards of the pesticides were prepared by dilution with A:B mixtures at the same proportion of the initial chromatographic conditions. Standard concentration ranged from 0.1 to 2 mg L^{-1} for PDM, and from 0.1 to 10 mg L^{-1} for THC, FEN and DIM. Calibration curves were performed by triplicate injection of these standards. R^2 value was 0.999 for THC and FEN in both methods, 1.0 for DIM and 0.998 for PDM. The limits of detection (Hernández-Soriano et al., 2007a) were 0.04 mg L^{-1} for DIM, and 0.08 mg L^{-1} for THC, FEN and PDM.

2.3. SITE DESCRIPTION AND SOIL PHYSICOCHEMICAL PROPERTIES

Three soils, SV, RM1 and RM3, representative of the Mediterranean semiarid climate were used. The plots, where the soils were collected, are located in the province of Granada (Southeast Spain) and are devoted to different land uses.

SV soil was collected from a plot located at approximately 540 m altitude with flat topography and well-drained, in the village of Vegas del Genil. It is a calcaric fluvisol devoted to different irrigated crops such as corn, tobacco and fruit trees.

RM1 soil was sampled from a bare steep land located 21 km from Granada beside an olive grove at 695 m altitude near the village of Pinos Puente. It is a chromic vertisol with deep cracks and is used for production of rainfed crops.

RM3 soil was collected from a steep land located in the borough of Puerto Lope (30 km from Granada) at 901 m altitude. It is a calcaric regosol with a characteristic white colour, devoted to olive groves.

The physicochemical properties of the soils studied are presented in Tables 2.3 and 2.4, and discussed below.

Soil texture is an important factor in soil productivity, since it influences the ease with which soil can be worked, the amount of water and air it holds, and the rate at which water can enter and move through soil. According to the percentage of sand, silt and clay, SV, RM1 and RM3 are classified as silt loam, clay and clay loam soils respectively (section 2.1.2). The textural composition of soils is again the main responsible of the variation in FC values. RM1 has the highest water retention capacity due to its higher content in clay minerals. Conversely, SV soil with low clay content has the lowest FC.

Table 2.3. Main physicochemical properties of the soils studied

Soil	Sand (%)	Silt (%)	Clay (%)	pH	EC (dS m^{-1})	FC (%)	CEC (cmol$_+$kg^{-1})	$CaCO_3$ (%)	OC (%)	OM (%)	Total C (%)	C/N
SV	31	58	11	8.1	1.2	27	8.1	26	1.2	2.1	5.5	6.9
RM1	10	39	51	7.9	0.24	38	18.3	42	0.62	1.1	5.7	7.9
RM3	26	41	33	8.1	0.22	30	12.6	62	0.91	1.6	8.5	11.3

Table 2.4. Concentration and spectroscopic characteristics of the dissolved organic carbon released by soils. Experiments performed in 1 g/10 mL soil:water suspensions

Soil	DOC (mg L^{-1})	A_{254} (cm^{-1})	$SUVA_{254}$ (L mg^{-1}C m^{-1})	HIX^{a}
SV	9.6	0.498	5.2	2.9
RM1	8.3	0.385	4.6	2.0
RM3	12.3	0.450	3.7	2.7

[a] samples were 1:2 diluted and acidified with HCl

Soil pH is determinant in many chemical processes that take place in the soil, specifically the availability of nutrients for plants. It can also influence plant growth due to its effect on the activity of beneficial microorganisms. Though the optimal pH values for most plants range between 5.5 and 7.5 (Table 2.5), many crops have adapted to thrive at pH values outside this range. Moreover, soil pH controls the adsorption–desorption phenomena of certain contaminants (chapter 1, section 7.2). The three studied soils have basic pH, characteristic of regions with limited rainfall, such as Southeastern Spain. Soil pH above 7.5 is generally related with calcareous soils, as corresponds to the three soils, with $CaCO_3$ contents higher than 15%, the threshold established by FAO for a soil to be considered calcareous. No signs of sodification exist since pH values are below 8.5 (Porta et al., 1994).

Soils contain more carbon (C) than the sum of atmosphere and vegetation, in both organic and inorganic forms (Swift, 2001). In most soils (with the exception of calcareous soils) the majority of C is held as soil OC. The term soil OM is used to describe the organic constituents in the soil (chapter 1, section 1.1.7.1), while the term 'soil OC' refers to the C occurring in soil OM. The soils used in this study have low OC content (close to or lower than 1%), as corresponds to the Mediterranean climate (Jones et al., 2005), and high content in inorganic C ($CaCO_3$). Soil OC concentration depends on the local environmental conditions, but it is also affected strongly by the soil management practices (Hontoria et al., 2004).

Soil OC is related to the sustainability of the agricultural systems affecting soil physical (aggregation, pore size distribution), chemical (pH, CEC) and biological (microorganisms' distribution and activity) properties linked to crop yield. Soil OC has a major influence on the soil's ability to store water, and the soil's ability to form complexes with metal ions and supply nutrients. Loss of soil OC can, therefore, lead to a reduction in soil fertility, land degradation and even desertification.

Soil EC is a measure of the amount of salts in soil (salinity of soil) and is used as an indicator of soil health (section 2.1.4). It affects crop yields, crop suitability, plant nutrient availability, and activity of soil microorganisms which in turn influence key soil processes including the emission of greenhouse gases. Long-term irrigation of SV soil with low-quality water may be the reason of its higher salinity (Qian and Mecham, 2005). However, since EC values are below 2 dS m^{-1}, this parameter does not limit plant growth or seed germination (Ye et al., 2002) and we can consider SV, RM1 and RM3 soils as non-saline soils.

Table 2.5. Plant growth related with soil pH

pH	Plant growth
>8.3	Too alkaline for most plants
>7.5	Iron availability becomes a problem
7.5	**Acceptable for most plants**
7.0	
6.8	
6.0	
5.5	Reduced soil microbial activity
<4.6	Too acid for most plants

Knowledge of a soil's CEC is basic to understand how to manage lime and fertiliser additions. Cations adsorbed on the surface of soil colloids, and those contained in the soil solution, are available for plant use (chapter 1, section 1.1.7.1.). Soils with high sand and silt content have a lower percentage of clay and OM, and thus have lower CEC. This explains why coarse-textured soils require more frequent applications of lime and fertiliser. In our case, CEC is ordered according to the content of clay minerals (RM1 > RM3 > SV), due to the low influence of the OM content of these soils.

Soil C/N ratio is a sensitive indicator of soil quality. It is often considered as a sign of soil nitrogen mineralization capacity (Springob and Kirchmann, 2003) and serves as a tool for calculating soil fertilisation. Generally, it is considered that a C/N ratio between 10 and 12 produces a correct release of N, while values above or below cause very little or excessive releases. It can be seen in Table 2.3 that only RM3 has an adequate C/N ratio, whereas SV and RM1 soils present lower values indicating a higher lability of the soil OM.

Concerning DOC, RM1 soil released the lowest amount of OC among the three soils studied (Table 2.4), in accordance with the lowest OC content (Table 2.3). The spectroscopic characteristics of the water-soluble fraction of soil OM is commonly used as an indicator of soil quality (Jones et al., 2014). It can be inferred from both

$SUVA_{254}$ and HIX that SV-derived DOM has a higher degree of aromaticity and molecular weight than the other two soils (Zsolnay et al., 1999; Weishaar et al., 2003; Zsolnay, 2003; He et al., 2011), indicating a greater stabilisation of OM (Table 2.4). This is confirmed by the fluorescence spectra of the soils (Figure 2.5), showing SV soil lower fluorescence at shorter wavelengths. In this figure, it can be observed the lower and higher fluorescence of RM1 at longer and shorter wavelengths respectively, which leads to its lower HIX.

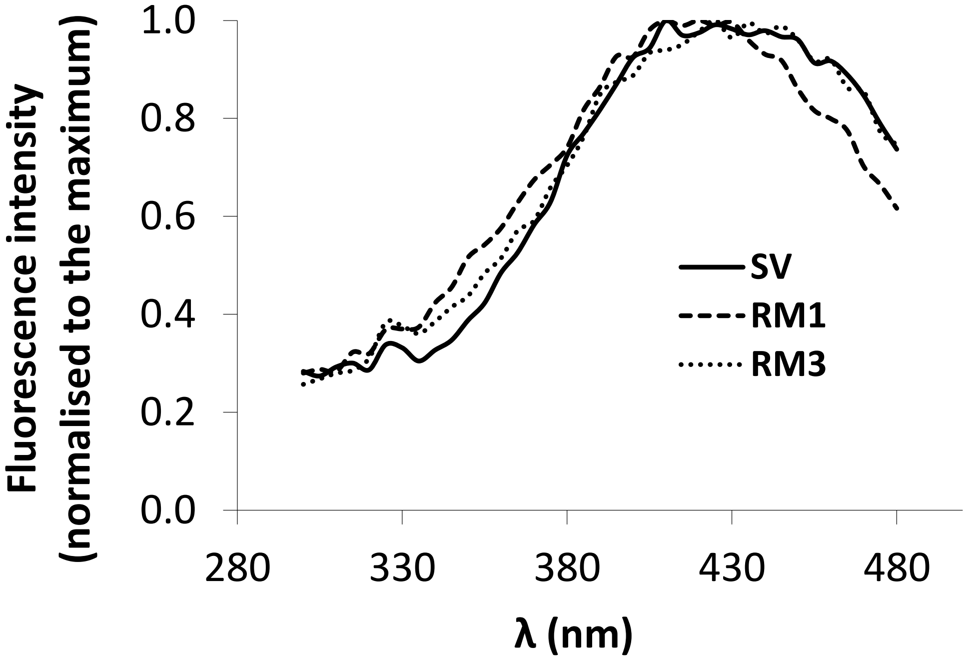


Figure 2.5. Normalised fluorescence spectra of the dissolved organic carbon released by soils (1:10 w:v soil/water) after shaking during 24 h

2.4. CHEMICAL ANALYSIS OF SOILS

The chemical composition of the soils was determined by XRF according to section 2.1.12. Results, expressed as oxides, are shown in Table 2.6. These data show that the main oxides present in the soils studied are oxides of silicon, aluminum, iron and calcium, with lower contribution of magnesium. The silica content is primarily related to clay minerals and free silica.

Table 2.6. Oxide content in soils (%)

Soil	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI†
SV	34.9	14.6	4.4	0.1	4.7	15.5	0.8	2.5	0.6	0.3	21.0
RM1	29.7	9.1	3.5	0.2	1.8	25.5	0.2	1.7	0.4	0.1	27.4
RM3	23.8	5.2	1.9	0.1	0.9	33.5	0.1	0.9	0.3	0.2	32.8

†LOI, loss on ignition

The CaO content can be associated to the presence of carbonates in the soil. As expected, a high correlation (r = 0.992) was found between $CaCO_3$ content determined with the calcimeter method (Table 2.3, section 2.1.9) and the CaO value obtained with XRF. It is noteworthy that the significant presence of Ca^{2+}, Mg^{2+} and Al^{3+} cations in the studied soils favour the stability and strength of aggregates. The loss on ignition (900 °C for 1 h) is high mainly due to the richness in $CaCO_3$ (RM3 > RM1 > SV), showing the OC content less influence (Dean, 1974).

SV soil contains more potassium than the other soils, which has been related to the presence of illite (Robert et al. 1988; Mimouni, 1990), as will be seen below through the characterisation by XRD. Feldspars may also be a source of potassium in the soil.

It is also remarkable the presence of TiO_2, probably related to minerals such as ilmenite and rutile. However, we did not identify them in the XRD study due to their low proportion. Other oxides such as P_2O_5, MnO and Na_2O are negligible (< 1%). Higher Na_2O values in SV soil can be also related with the quality of the water used for irrigation (Qian and Mecham, 2005; Jalali et al., 2008).

Regarding metallic elements (Table 2.7), it is observed that RM1 and RM3 soils contain a concentration of Zn below the minimum recommended by the European Union for agricultural soils (150-300 ppm Zn). That of Cr, Ni and Cu is within the recommended range for all soils (reference value for Cr, 50-100 ppm; for Ni 30-75 ppm; for Cu 50-140 ppm) (Kabata -Pendias et al., 1992).

Table 2.7. Concentration of some elements in soils (ppm)

Soil	S	Cl	Cr	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	I	Ba	Pb
SV	809	352	106	54	68	185	17	0	5	94	293	19	173	0	364	80
RM1	273	33	78	47	81	81	14	25	4	76	384	17	97	55	726	0
RM3	260	60	60	41	73	86	6	0	5	31	620	0	69	0	135	0

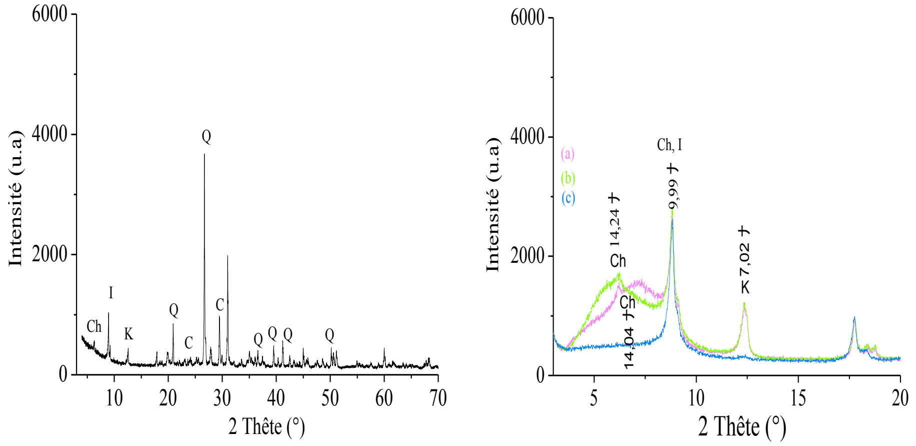
The relatively high level of S in SV soil may be linked to the agronomic practices or to the use of fungicides based on sulfur. Additionally this soil has been irrigated with low quality water which may contain high amounts of Cl^- and SO_4^{2-}, as will be shown below. RM1 and RM3 soils have received less management practices and therefore, less external inputs.

2.5. MINERALOGICAL STUDY BY X-RAY DIFFRACTION

The mineralogy of soils was studied by XRD according to section 2.1.13. The diffractograms obtained after different treatments (powder, orientated aggregates (OA), oriented aggregates treated with ethylene glycol (OAEG) and oriented aggregates treated with ethylene glycol at 550 °C (OAEG 550)) are shown in Figure 2.6. They reveal the presence of a significant peak of quartz in the three soils in agreement with the crystal properties of this type of mineral, in addition to the difficulty of its removal by sedimentation because of its small particle size.

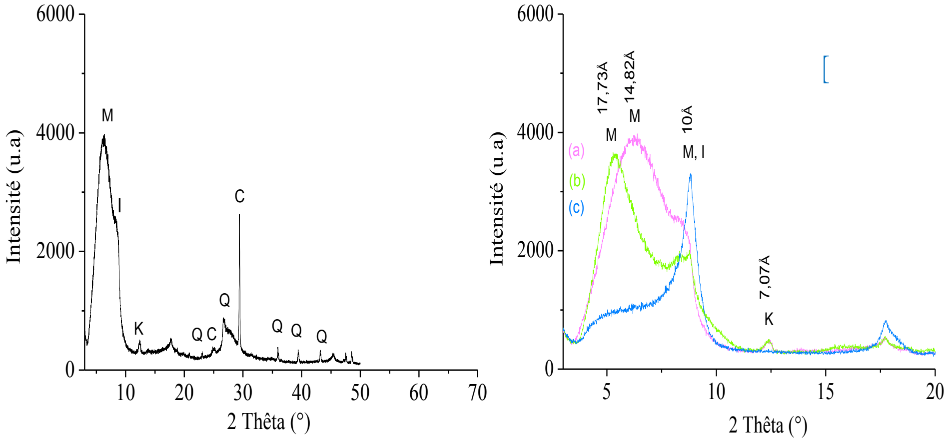
The XRD pattern of soil SV points to the presence of two non-swelling clays, chlorite (reflection d_{001} at 14.04 Å) and illite (reflection of 9.99 Å) (Figure 2.6 top). The chlorite content is very low since its peak does not occur after heat treatment. We also identified the presence of a significant peak to the d_{001} reflection equal to 7.02 Å. It corresponds to kaolinite as it disappears after the treatment at 550 °C. This corroborates the results obtained by XRF analysis.

The analysis of the XRD pattern of soil RM1 (Figure 2.6 middle) clearly shows that the clay fraction is essentially composed by swelling minerals with low crystallinity (reflection d_{001} = 14.82 Å), in accordance with its classification as a vertisol. This peak could be also assigned to chlorite, but we note that the peak at about 7 Å is low and the OAEG test causes a significant shift in this response to d_{001} equal to 17.73 Å. Both peaks marked a shoulder at d_{001} = 10 Å, related with the presence of illite.



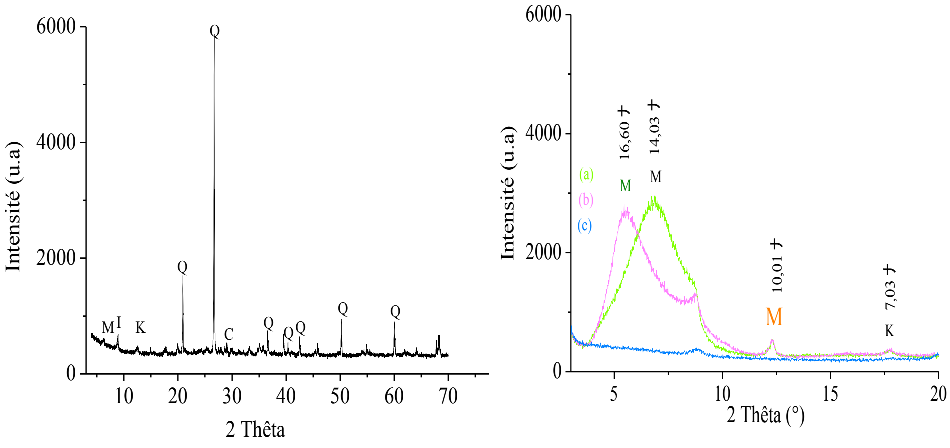
Ch: Chlorite. I: Illite. K: Kaolinite Q: Quartz.

(a) OA (b) OAEG (c) OAEG 550



M: Montmorillonite. I: Illite. K: Kaolinite Q: Quartz.
C: Calcite

(a) OA (b) OAEG (c) OAEG 550



M: Montmorillonite, I: Illite. K: Kaolinite Q: Quartz,
C: Calcite

(a) OA (b) OAEG (c) OAEG 550

Figure 2.6. Powder (left) and oriented aggregates (right) XRD patterns of SV (top), RM1 (middle) and RM3 (bottom) soils

This peak remains unchanged after the OAEG and OAEG 550 tests, which is in accordance with its non-swelling properties. The peak at d_{001} = 7.07 Å indicates the existence of kaolinite, which disappears after the treatment at 550 °C. The very low intensity of this peak reflects the low content of this mineral. We can conclude that the clay fraction of soil RM1 is essentially an interstratified smectite-illite. Other associated minerals are calcite and traces of quartz.

For soil RM3, the XRD pattern (Figure 2.6 bottom) shows the presence of a peak at 14.03 Å, which corresponds to the d_{001} reflection of montmorillonite, which is sensitive to the swelling test and the thermic treatment. The presence of illite is also possible due to the existence of a characteristic peak at about 10 Å. Kaolinite occurrence is revealed by a very narrow peak at 7.17 Å, which disappears after the treatment at 550°. The clay mineralogy of RM3 soil is essentially an illite-montmorillonite interstratified with traces of kaolinite.

2.6. FTIR STUDY OF SOILS

FTIR spectra of soils are given in Figure 2.7. Most bands correspond to clay minerals, as expected, given the low OM content of the soils. Assignment of peaks was performed according to Farmer (1974) and Madejová and Komadel (2001).

The first two bands are typical of smectites and vermiculites, consisting of a narrow band around 3620 cm^{-1} corresponding to the stretching vibration of the OH linked to cations in the octahedral layer, mainly Al^{3+}, and a wider one near 3400 cm^{-1} corresponding to the OH groups involved in the hydrogen bonds H_2O-H_2O. For SV and RM3 soils (Figure 2.7 A, C) a band appears at 3696 and 3698 cm^{-1} respectively, characteristic of kaolinite. Bands appearing in the range 3000-2850 cm^{-1} are attributable to C-H bonds of aliphatic hydrocarbons.

The bands at 1794 cm^{-1} for SV and 1798 cm^{-1} for RM1 and RM3 correspond to carboxylic acid derivatives. O-H bonds bending vibration of H_2O appears around 1620-1630 cm^{-1}. The bands at 1434 cm^{-1} for SV and 1432 cm^{-1} for RM1 and RM3, together with that observed around 875 cm^{-1}, are characteristic of calcite, which usually occurs in soil with smectites. The intense band at approximately 1030 cm^{-1} corresponds to the stretching of the Si-O bonds in montmorillonites.

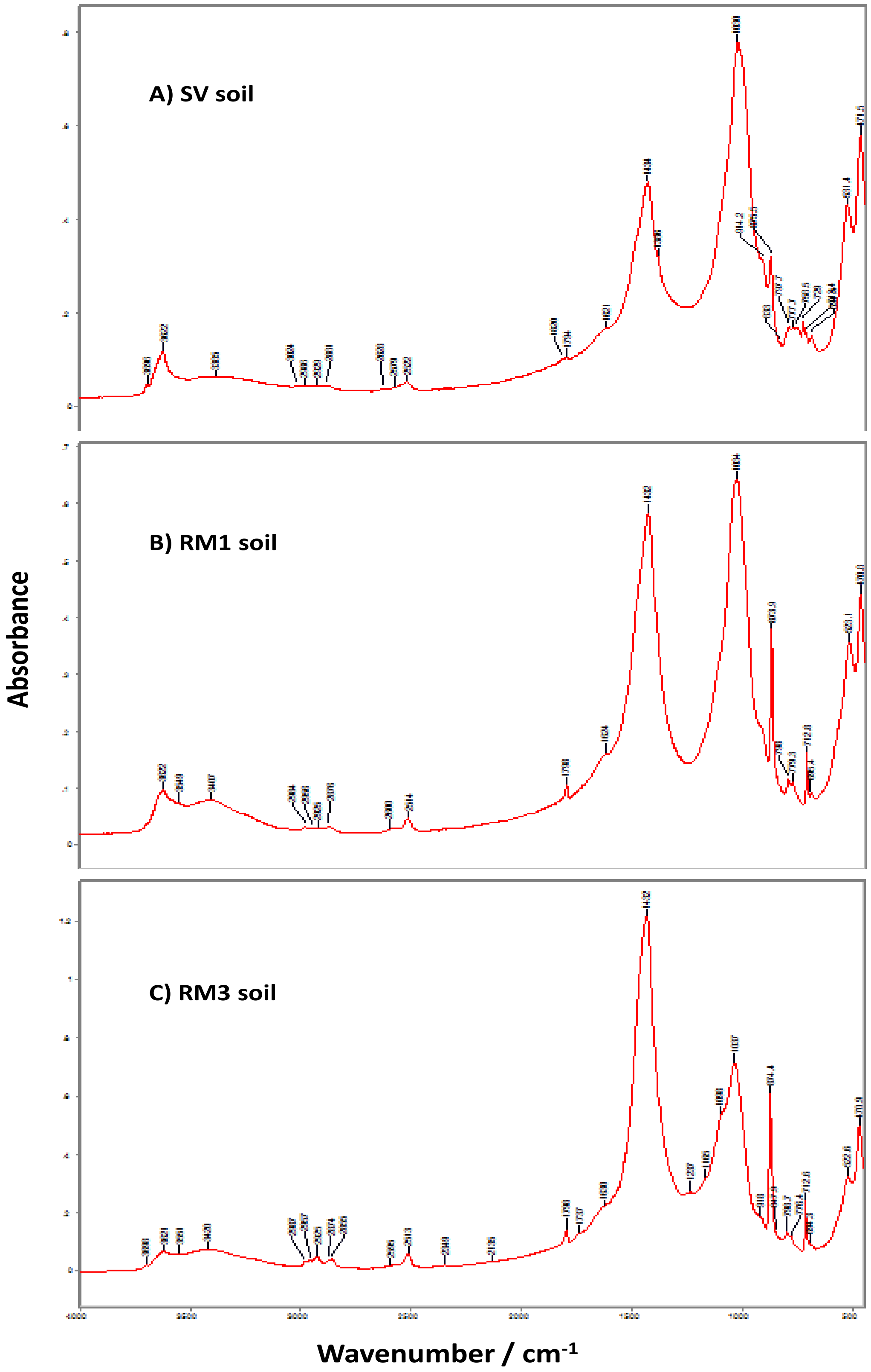


Figure 2.7. FTIR spectra of SV (A), RM1 (B) and RM3 (C) soils

A group of bands with low intensity, which generally appears in the range 920-690 cm^{-1}, corresponds to Al_2OH, AlOHFe, FeOHFe and Mg-OH. The peak at around 798 cm^{-1} is indicative of a significant occurrence of Fe^{3+} in the octahedral layer. It is generally accompanied by another peak at 870 cm^{-1}, which is normally masked, as in our spectra. Finally, in the region 530-465 cm^{-1}, two bands of similar intensity are observed, corresponding to the deformation of Si-O-Al bonds in the octahedral layer (531 cm^{-1} for SV, and ~523 cm^{-1} for RM1 and RM3), and deformation of Si-O-Si bonds in the tetrahedral layer (~471 cm^{-1}).

2.7. WASTEWATER, SEWAGE SLUDGE AND FERTIORMONT PROPERTIES

2.7.1. Treated wastewater

Treated wastewater was collected on different dates during the experimental period from the effluent of the secondary sedimentation tank (after biological treatment) of the WWTP of Granada Sur, located in Churriana de la Vega (Figure 2.8), which collects the WW of around 425000 population equivalents (EMASAGRA S.A.).

Figure 2.8. Aerial photograph of the wastewater treatment plant of Granada Sur

The physicochemical properties of TWW are presented in Table 2.8. Average parameters are within the range established by national and European regulations.

Table 2.8. Average properties of the treated wastewater used

Parameter	Units	Value
†pH		7.8 ± 0.2
SAR		3.5
†EC	dS m^{-1}	0.98 ± 0.13
BOD	mg O_2 L^{-1}	24
COD	mg O_2 L^{-1}	88
Suspended solids	mg L^{-1}	23
Dissolved solids	mg L^{-1}	575
†DOC	mg L^{-1}	25 ± 5
†$SUVA_{254}$	L mg^{-1}C m^{-1}	1.2 ± 0.2
†HIX		1.3 ± 0.1
Surfactants	mg L^{-1}	0.75
Grease	mg L^{-1}	25
Phenols	mg L^{-1}	0.5
Total N	mg L^{-1}	40
Total P	mg L^{-1}	6.9
NH_4^+	mg L^{-1}	45
NO_2^-	mg L^{-1}	0.1
†NO_3^-	mg L^{-1}	6.1 ± 3.4
†PO_4^{3-}	mg L^{-1}	7.1 ± 3.8
†Cl^-	mg L^{-1}	72 ± 14
†SO_4^{2-}	mg L^{-1}	77 ± 4
S^-	mg L^{-1}	0.03
Ca^{2+}	mg L^{-1}	32

†Determined in the laboratory (± standard deviation, n = 5). The rest of parameters were provided by the wastewater treatment plant (EMASAGRA S.A.)

2.7.2. Sewage sludge

The production of sewage sludge is one of the main environmental problems associated with the increase of the worldwide population. Therefore, its reuse, especially in agriculture, has become crucial to reduce its environmental impact. Sewage sludges have a huge content of water (approximately 95%) and pathogens, and considerable amounts of contaminants and OM, hence they are treated and stabilized before their use.

Table 2.9. Average properties of the sewage sludge used

Parameter	Units	Value
†*pH		7.3 ± 0.2
†*Electrical conductivity	dS m^{-1}	8.2 ± 1.0
†Organic carbon	%	33 ± 1.0
Humic acids	%	1.6
Fulvic acids	%	0.47
†*Dissolved organic carbon	g L^{-1}	5.8 ± 0.2
†^$SUVA_{254}$	L mg^{-1}C m^{-1}	1.3 ± 0.2
†^HIX		0.53 ± 0.03
†*Cl^-	mg L^{-1}	134 ± 6
†*NO_3-	mg L^{-1}	3.8 ± 0.4
†*SO_4^{2-}	mg L^{-1}	158 ± 6
Cd	mg kg^{-1}	2.5
Cr	mg kg^{-1}	60
Pb	mg kg^{-1}	349
Zn	mg kg^{-1}	772
Ni	mg kg^{-1}	103
Cu	mg kg^{-1}	284

†Determined in the laboratory (± standard deviation, n = 5). The rest of parameters from Sánchez (2002). *Determined in filtered (0.45 µm) SS-Ph extracts. ^Determined in filtered SS-Ph extracts diluted 100 times

Secondary sewage sludge was collected in the same WWTP after anaerobic digestion. It was air-dried, ground and sieved (< 2 mm) in the laboratory. One g of sewage sludge was shaken during 24 h at 20 °C with 10 mL of Na_2HPO_4 50 mM. This extract (SS-Ph) was afterwards used as a source of DOC. Similarly, extracts of sewage sludge with MQ water in the same conditions (SS-MQ) were also used in chapter 4 to evaluate the efficiency of a different DOC fraction in pesticide release from soil. Aqueous solutions at different DOC concentrations used in the experiments were obtained by adequate dilution of SS-Ph and SS-MQ. Both solutions extract preferentially low molecular size DOC fractions, but Na_2HPO_4 tends to enrich the extracts in hydrophobic compounds with a larger aromatic contribution (Reemtsma et al., 1999).

The main properties of sewage sludge are shown in Table 2.9. The concentration of heavy metals is below the limits established in the RD 1310/1990 concerning the use of sewage sludge in agriculture (Annex I B).

2.7.3. Fertiormont

An organic fertiliser, fertiormont (FERT), was kindly provided by Fertilizantes Orgánicos Montaño S.L. (Gilena, Sevilla).

Table 2.10. Average properties of fertiormont

Parameter	**Units**	**Value**
†*pH		8.8 ± 0.3
†*Electrical conductivity	dS m^{-1}	3.7 ± 0.3
†Organic carbon	%	26 ± 2
†*Dissolved organic carbon	g L^{-1}	1.7 ± 0.1
†*Cl^-	mg L^{-1}	214 ± 8
†*NO_3-	mg L^{-1}	85 ± 3
†*SO_4^{2-}	mg L^{-1}	48 ± 3
†*PO_4^{3-}	mg L^{-1}	64 ± 2
Organic nitrogen	%	1
P	%	0.62
K	%	4
Ca	%	9
Mg	%	2.2
Cu	%	0.0064
Fe	%	1.43
Mn	%	0.024
Zn	%	0.0059

†Determined in the laboratory (± standard deviation, n = 5). *Determined in filtered (0.45 μm) fertiormont extracts (1 g fertiormont/10 mL MQ water). The rest of parameters provided by Fertilizantes Orgánicos Montaño S.L.

It is composed by vegetal residues (mainly from olive, legumes, citrus and horticultural crops) composted during 2 years under controlled conditions. FERT was air-dried and sieved (< 2 mm) in the laboratory before its use. The main properties of FERT are presented in the Table 2.10.

FERT considerably improves some physicochemical properties of soils, such as the enhancement of the water retention capacity and nutrient availability for crops, the conservation and improvement of soil structure, and the incorporation of a beneficial microbial population.

2.8. STATISTICAL ANALYSIS OF THE DATA

Exploratory analysis was performed to check normality and outliers of the data sets. Differences among samples were established with ANOVA for normal data sets or with the Kruskal-Wallis test for non-normal data sets, using the Fisher's LSD or the Mann-Whitney tests for post-hoc comparisons. The relationship between variables was assessed by either correlation or regression analysis. The fitting of data to adsorption, desorption and dissipation equations was performed by non-linear regression. All statistical analyses were performed with SPSS v.21.0 (Illinois, USA) software program and the probability level was set to $P<0.05$.

3. ADSORPTION–DESORPTION

3.1. INTRODUCTION

3.1.1. Adsorption kinetics

Adsorption of pesticides on soils is a time-dependent process driven by the difference between the amount currently adsorbed and the amount that would be adsorbed if the system was in equilibrium (Huang et al., 2006). Therefore, sorption kinetic studies are needed to evaluate the equilibrium time and the mechanisms involved, as well as the order and rate of the reaction. Frequently, adsorption occurs rapidly over the short-term, which is attributed to diffusion of pesticide molecules to the soil surface (boundary diffusion) followed by a slower phase, known as particle diffusion, due to molecular diffusion phenomena within internal mesopores, micropores or capillaries of the soil structure until the equilibrium is reached (Hamaker and Thompson, 1972; Beulke et al., 2004; De Wilde et al., 2008; Fernández-Bayo et al., 2008; Báez et al., 2013). This may be linked to the existence in the sorbent of two regions with different accessibility (Streck et al., 1995): while region 1 is in direct contact with the solution phase, region 2 only exchanges with region 1. According to Kookana et al (1992), a combination of both phases is possible due to the presence of different types of reaction sites and/or their accessibility to the pesticides.

Sorption kinetic plots represent the amount of adsorbed pesticide versus the soil-solution contact time. Different mathematical models have been proposed in the literature to determine the rate and type of adsorption (Ho, 2006; De Wilde et al., 2008; Báez et al., 2013; Rojas et al., 2014). In our case experimental data were adjusted to the models described in the *Experimental Setup* section of this chapter.

3.1.2. Adsorption–desorption isotherms

The adsorption–desorption process of pesticides in soils is generally studied through isotherms using the batch equilibrium technique (OECD, 2000). In this method a known amount of soil (m, g) is shaken with a fixed volume (V, mL) of aqueous solutions of the pesticide at different initial concentrations (C_0, μg mL^{-1}) at a fixed temperature. After reaching the equilibrium, the two phases are separated by centrifugation, and the liquid phase is analysed. Desorption experiments are normally conducted by replacing a known volume of the supernatant with an equal volume of background solution without the pesticide after the adsorption experiments using sequential decanting and refilling steps.

Adsorption and desorption isotherms are constructed by plotting the concentration of the pesticide in the soil (X, µg g^{-1}) against the equilibrium concentration of the pesticide in the solution (C_e, µg mL^{-1}). The adsorption equilibrium, evaluated by kinetic experiments, is established when the liquid phase containing the pesticide has been contacted with the soil for sufficient time, and the pesticide concentration in the bulk solution reaches an equilibrium (Kumar and Sivanesan, 2007; Foo and Hameed, 2010).

Adsorption–desorption isotherms provide information about the adsorption mechanisms, surface properties and the degree of affinity of the sorbent for the sorbate (Bulut et al., 2008; Foo and Hameed, 2010). Nevertheless, isotherms are not able to describe completely the mechanisms involved without thermodynamic and kinetic data (Calvet, 1989).

3.1.2.1. Classification of adsorption isotherms

In spite of the great variety of behaviours observed depending on the soil–pesticide system, a general classification in four main types of isotherms, represented in Figure 3.1, is normally accepted (Giles et al., 1960):

C-isotherms. The curve is a line of zero-origin and corresponds to a constant partition of the solute between the bulk solution and the sorbent. Porous and flexible sorbents with regions of different solubility for the solute, and solutes with higher affinity for the sorbent than for the solvent favour this kind of isotherm (Calvet, 1989).

L-isotherms. This kind of isotherms occur when the sorbent has higher affinity for the solute than for the solvent at low solute concentration and vice versa. It suggests a progressive saturation of the solid. L-isotherms can be divided into two groups: (i) the curve reaches an asymptotic plateau (the sorbent has a limited adsorption capacity); (ii) the curve dos not reach any plateau (limited adsorption capacity is not clearly shown).

H-isotherms. This is a particular case of an L-isotherm where the sorbent has an extremely high affinity for the solute molecules. Therefore, the slope of the curve when C_e approaches zero is close to infinity (Hinz, 2001; Limousin et al., 2007), which is inconsistent with thermodynamic laws (Tóth, 1994).

S-isotherm. This type of isotherm exhibits a sigmoidal curve implying that adsorption becomes easier as solute concentration in solution increases. This behaviour is observed due to two causes. First, solute–solute attractive forces at the surface, causing cooperative adsorption. Second, existence of competing reactions within the solution, such as complexation with a ligand, which inhibits the adsorption of the solute (Hinz, 2001). S-curves are typical for adsorption of relatively polar non-ionic organic chemicals in clays, especially montmorillonites (Calvet, 1989).

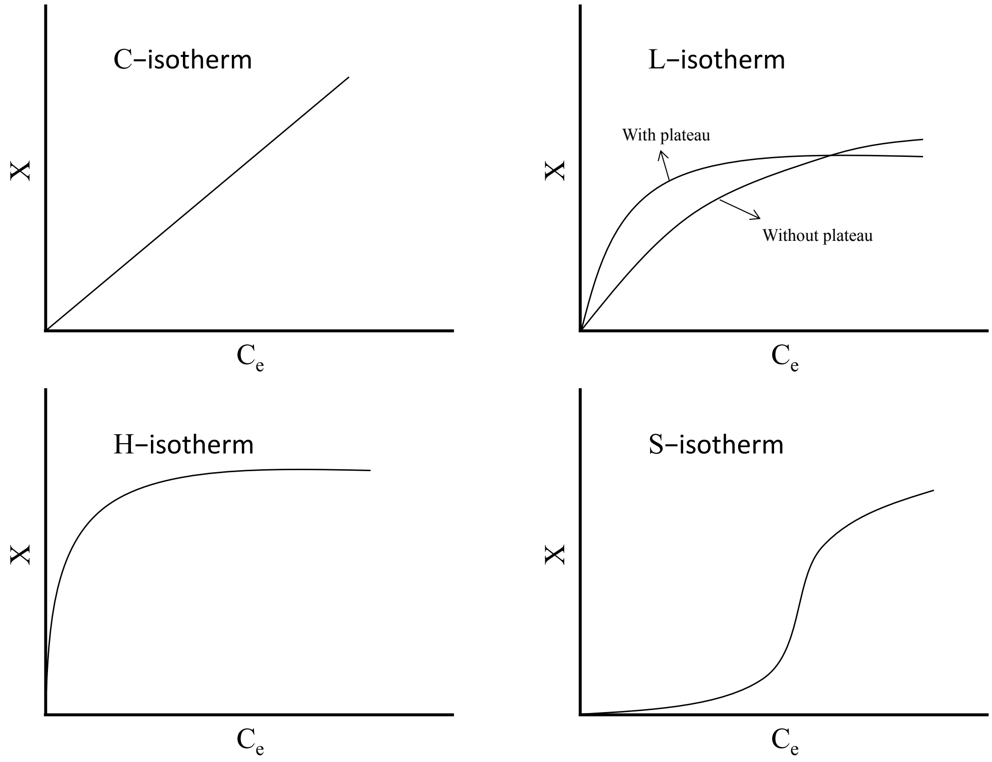


Figure 3.1. Classification of adsorption isotherms according to their shape (Giles et al., 1960)

3.1.2.2. Adsorption equilibrium models

Adsorption has been described as a complex distribution process that accumulates solutes at surfaces and interphases (Huang et al., 2003). Several models have been invoked to quantify and explain the equilibrium distribution of organic compounds between aqueous phases and soils, among which the most used ones are described below.

Linear model. A simple linear model was proposed in the late 1970s for describing the adsorption equilibria (Chiou et al., 1979; Karickhoff et al., 1979). The partitioning coefficient (K_d) is defined as:

$$K_d = \frac{X}{C_e} \qquad [3.1]$$

where X and C_e are the solid-phase and liquid-phase equilibrium concentrations of the solute, respectively. Adsorption of hydrophobic organic compounds on soils is mainly conducted by van der Waals attractions onto the hydrophobic part of the soil OM (Karickhoff et al., 1979). Although this statement has been discussed (Sheng et al., 2001), the OM predominates in most cases. Consequently, K_d is frequently normalised to the OC fraction (f_{OC}, kg kg^{-1}) of the solid, and the OC partitioning coefficient (K_{OC}, L kg^{-1}) is defined as (Chiou et al., 1979):

$$K_{OC} = \frac{K_d}{f_{oc}} = \frac{K_d * 100}{\%OC} \qquad [3.2]$$

K_{OC} has been used in the estimation of the leaching potential of pesticides in soils (Cleveland, 1996; Wauchope et al., 2002). The linear model assumes that adsorption occurs in an amorphous gel- or liquid-like OM with no limitation of active sites (Chiou et al., 1983). Various studies have shown that this model is inconsistent with a wide range of observed non-partitioning data such as isotherm nonlinearity, very slow rates of adsorption and desorption, adsorption–desorption hysteresis, and competition among solute molecules (Weber et al., 1992; Huang et al., 1997; Xing and Pignatello, 1997). Physical and chemical heterogeneity of soil OM may also explain the nonlinear adsorption of non-ionic organic compounds (Huang and Weber, 1997; Karapanagioti et al., 2001). Therefore, although partitioning is in part responsible for pesticide adsorption on soils, it cannot be considered the only mechanism involved (Mingelgrin and Gerstl, 1983).

Langmuir model. The Langmuir model (Langmuir, 1918) is the simplest one that describes a limited adsorption capacity (X_{max}). This model involves monolayer adsorption on a set of different localized adsorption sites with uniform energies. Thus, solute–solute interactions are not taking place. The Langmuir isotherm is expressed as:

$$X = X_{max} \frac{LC_e}{1+LC_e} \qquad [3.3]$$

In the linear form:

$$\frac{X}{C_e} = X_{max}L - LX \qquad [3.4]$$

The constant L corresponds to the affinity of the solute for the sorbent. A graphic representation of X/C_e *versus* X permits the calculation of L from the slope and X_{max} from the intercept. The value of $X_{max}L$ is often used as a distribution coefficient (K_d) when the concentrations are low enough (Limousin et al., 2007). The Langmuir model was originally developed to describe the adsorption of gas solutes onto activated carbon (Calvet, 1989; Foo and Hameed, 2010). The complexity of the soil matrix makes usually difficult the application of this model.

Freundlich model. The Freundlich isotherm (Freundlich, 1906) is the most widely used for quantifying adsorption of organic compounds on soils, since it considers the heterogeneity of the soil surface and multilayer adsorption resulting from extremely strong solute–solute interactions (Calvet, 1989; Adamson and Gast, 1997; Rojas et al., 2013). Its mathematical expression is:

$$X = K_f C_e^{1/n} \qquad [3.5]$$

The Freundlich constants K_f (L kg^{-1}) and 1/n (dimensionless) are correlated with the maximum multilayer adsorption capacity and adsorption intensity, respectively (El Bakouri et al., 2009). The constant 1/n is also related to surface heterogeneity, reflecting more heterogeneous surface as its value gets closer to zero (Foo and Hameed, 2010). While a value below unity implies chemisorption, 1/n above one is an indicative of cooperative adsorption (Haghseresht and Lu, 1998). When 1/n = 1, the Freundlich model is linear and K_f is equivalent to the distribution coefficient K_d. After logarithm linearization the experimental values of K_f and 1/n can be calculated by plotting log X *versus* log C_e.

$$logX = logK_f + \frac{1}{n} logC_e \qquad [3.6]$$

3.1.2.3. Desorption isotherms and hysteresis

Desorption, though less studied than adsorption, is an important process since it determines the release rate and the potential mobility of pesticides in soil. They can be also evaluated through isotherms and represented by the Freundlich equation as:

$$X = K_{fd} C_e^{1/nd} \qquad [3.7]$$

where K_{fd} and $1/n_d$ are the Freundlich desorption coefficients. The construction of desorption isotherms enables the characterization of retention reversibility. A relation between adsorption and desorption parameters, proposed by Hornsby and Davidson

(1973), allows characterizing the degree of adsorption hysteresis. As the first point of a desorption isotherm belongs to the adsorption isotherm, it can be written as:

$$K_f(C_e)^{1/n} = X = K_{fd}(C_e)^{1/n_d} \quad [3.8]$$

where X and C_e are the adsorbed and solution concentrations for the common point of both isotherms. Rearranging the terms:

$$K_{fd} = K_f C_e^{\frac{1}{n}(1-H)} \quad [3.9]$$

where $H = \frac{1/n_d}{1/n}$ is the coefficient of hysteresis. If we solve equation [3.9] for X:

$$K_{fd} = K_f^H X^{(1-H)} \quad [3.10]$$

indicating that desorption isotherms depend on the adsorbed amount of solute before desorption (X).

Hysteresis phenomena occur when desorption isotherms do not coincide with adsorption isotherms, and is commonly observed in pesticide adsorption–desorption by soils. When H decreases, hysteresis increases and adsorption is more irreversible (Barriuso et al., 1994; Mamy and Barriuso, 2007). The degree of irreversibility plays an important role in evaluating the movement of pesticides through the soil profile. Theoretically, there is no hysteresis when H = 1 ($1/n = 1/n_d$), but in practice no hysteresis is considered when $0.7 < H < 1$ (Mamy and Barriuso, 2007). However, it is advisable to consider secondary phenomena such as degradation or the formation of bound residues with increasing sorbent–sorbate contact time (Calvet, 1989; Lesan and Bhandari, 2003).

3.1.3. Advantages and drawbacks of the batch technique

The batch technique is the most frequently used method to evaluate pesticide adsorption–desorption (Calvet, 1989) because of its simplicity and reproducibility. However, several sources of error may be introduced such as losses by volatilisation and degradation, insufficient length of the experiments to reach equilibrium (need of evaluation of adsorption kinetics), or no complete separation between water and sorbent phase (Schrap et al., 1994; Delle Site, 2001). A special relevance corresponds to the solid/solution ratio which in numerous cases is either too high compared with the natural conditions in aqueous environments or too low compared with the natural conditions of porous media (Limousin et al., 2007). Furthermore, continuous shaking can lead to the destruction of the soil particles (Sposito, 1984, Dal Bosco et al., 2013). Consequently, the batch method is very helpful as a preliminary tool but extrapolation to porous media requires other conditions.

3.1.4. Role of dissolved organic carbon in pesticide retention by soils

The addition of OM through effluent irrigation or organic amendment supply results in an increase of DOC in the soil solution that can influence the environmental fate of pesticides (Müller et al., 2007). The role of DOC in pesticide retention by soils, although widely studied, is not fully understood because it depends on the specific DOC–pesticide–soil system (Celis et al., 1998; Cox et al., 2000; Rodríguez-Liébana et al., 2014a). In general, interactions between DOM and organic pollutants in solution and competition of DOM for sorption sites on soil particles result in reduced sorption of the solute (Graber et al., 2001; Li et al., 2005; Barriuso et al., 2011). In contrast, cumulative sorption and cosorption processes will enhance sorption to the solid phase (Cox et al., 2004; Ling et al., 2006; Rodríguez-Cruz et al., 2012). The net effect of DOM on the sorption of organic pollutants to soils is the sum of the abovementioned processes, which are all controlled by the binding affinity of the organic pollutant to the DOM, the binding affinity of the DOM and the organic pollutant to the soil matrix, and the sorption affinity of the DOM–organic pollutant complex to the soil solid phase.

Ling et al. (2006) have studied the effect of DOC in the adsorption of the herbicide atrazine on different soils. Adsorption of atrazine was enhanced at low DOC concentrations (0-62 mg L^{-1}) and decreased thereafter with increasing DOC concentrations. According to the authors, at low concentration the DOC would be retained on the soil, by mechanisms such as ligand exchange between DOC and hydroxyl groups on the soil mineral surface (Shen, 1999), leading to an increase in the soil OC content that promotes pesticide adsorption. But at the same time, as DOC concentration increases, the availability of adsorption sites decreases, then the higher DOC concentration would favour the presence of these hydrophobic compounds in solution.

Flores-Céspedes et al. (2006) have shown that the presence of DOC in the range 15-100 mg L^{-1} reduced the adsorption of the insecticide imidacloprid of low hydrophobicity (log K_{ow} 0.54) because of competence for the adsorption sites. In contrast, DOC increased the retention of two more hydrophobic compounds (3,4-

dichloroaniline, log K_{ow} 2.69; 4-bromoaniline, log K_{ow} 2.26) by co-sorption with DOC molecules to different extents depending on the nature of the DOC added. They proposed a modified distribution coefficient, K_{DOC}, as a safer parameter for soil adsorption predictions of organic pollutants.

3.2. EXPERIMENTAL SETUP

3.2.1. Adsorption kinetics

3.2.1.1. Evaluation of equilibrium time and shape of the curves

Kinetic experiments were performed per triplicate using the batch equilibration method. Different experimental conditions were used depending on the pesticide: CYP, DTM, PDM and THC sorption behaviour was only assessed in SV soil. In the case of DIM and FEN the three soils were considered in order to establish the influence of soil properties. Due to the low water solubility of CYP, DTM and PDM, and their expected high retention, 0.4 g of SV soil was weighed in 30 mL Pyrex tubes and mixed with a 20 mL aliquot of an aqueous solution of the pesticides at 0.5 μg mL^{-1} (solid/liquid ratio 1/50). In the case of THC, DIM and FEN, samples of 5 g of the respective soil were mixed with 20 mL of pesticide solution at 2 μg mL^{-1} (solid/liquid ratio 1/4). The tubes were shaken end-over-end in a thermostatic chamber at 20 ± 1 °C (Selecta Hotcold-M) during 15, 30, 60, 120, 240, 480, 960 and 1440 min and then centrifuged at 3000 rpm for 15 min (Hettich GmbH). The supernatants were treated differently depending on the subsequent analytical determination. Concentrations of PDM, CYP and DTM were determined by GC-μECD, while HPLC-DAD analysis was used for the other three pesticides (see 2.2.5.1 and 2.2.5.2 sections). A control without soil was run at each sampling time to account for possible pesticide losses due to other processes such as volatilisation, degradation or sorption to the glassware.

The amount of sorbed PDM, CYP and DTM (X, μg g^{-1}) was directly determined in soil after Microwave Assisted Extraction (MAE) (see 2.2.4.1 section). By contrast, the amount of sorbed THC, DIM and FEN was calculated by the difference between the initial and equilibrium concentrations (C_0 and C_e, μg mL^{-1}) in the aqueous phase, according to the equation:

$$X = \frac{V}{m}(C_0 - C_e) \qquad [3.11]$$

where V is the solution volume (mL), and m is the mass of soil (g).

Calculations were based on the assumption that no degradation of pesticides occurred during adsorption experiments.

3.2.1.2. Kinetic models

Hyperbolic model. This model was proposed by Biggar et al. (1978), and in its linear form can be expressed as:

$$\frac{1}{X_t} = \left(\frac{B}{X_{max}} \times \frac{1}{t}\right) + \frac{1}{X_{max}} \qquad [3.12]$$

where X_{max} and X_t are the amount of pesticide adsorbed at equilibrium and at time t respectively (μg g^{-1}), t is the contact time (min) and B is an empirical constant. This equation allows us to calculate X_{max} from the intercept of the $1/X_t$ *versus* 1/t plot.

Pseudo first order (PFO) model. The kinetic equation is:

$$\frac{dX_t}{dt} = k_1(X_{max} - X_t) \qquad [3.13]$$

The Lagergren equation (Lagergren, 1898) is obtained by integrating equation [3.13] for the boundary conditions of X = 0 at t = 0, and X = X at t = t:

$$\log(X_{max} - X_t) = logX_{max} - 0.4342k_1t \qquad [3.14]$$

where k_1 is the PFO rate constant (min^{-1}), which is determined from the slope of the plot of $\log(X_{max}-X_t)$ *versus* t.

Pseudo second order (PSO) model. This model considers that the driving force is proportional to the active sites available for sorption on the sorbent (Ho and Mckay, 1999). The kinetic rate equation is:

$$\frac{dX_t}{dt} = k_2(X_{max} - X_t)^2 \qquad [3.15]$$

Integrating for the boundary conditions and rearranging the terms, the following linear form is obtained:

$$\frac{t}{X_t} = \frac{1}{k_2 X_{max}^2} + \frac{t}{X_{max}} \qquad [3.16]$$

where k_2, calculated by plotting t/X_t *versus* t, is the PSO kinetic rate constant (g $μg^{-1}$ min^{-1}).

Elovich equation. This equation, first proposed by Roginsky and Zeldovich (1934), assumes that adsorption takes place in two phases: a fast initial reaction associated with the movement of the sorbate to readily external sites followed by slower diffusion to sorbent´s micropores:

$$\frac{dX_t}{dt} = \alpha \exp(-\beta X_t) \qquad [3.17]$$

Given that $X_t = 0$ when $t = 0$, the integrated form is:

$$X_t = \frac{1}{\beta}\ln(t + t_0) - \frac{1}{\beta}\ln t_0 \qquad [3.18]$$

This expression is simplified to obtain a linear equation by assuming that t is much larger than t_0, with $t_0 = 1/\alpha\beta$.

$$X_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad [3.19]$$

The intercept of the plot X_t *versus* ln t corresponds to the amount sorbed during the initial sorption phase and α (μg g^{-1} min^{-1}) is regarded as the initial rate. β (g $μg^{-1}$) is related to the extent of surface coverage and activation energy for chemisorption. For a particular system, t_{ref} is the longest time in the adsorption process and X_{ref} the solid phase concentration at time $t = t_{ref}$. Thus, equation [3.19] is rewritten as:

$$X_{ref} = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t_{ref} \qquad [3.20]$$

Subtracting equation [3.20] from equation [3.19] and dividing by X_{ref}:

$$\frac{X_t}{X_{ref}} = R_E \ln\left(\frac{t}{t_{ref}}\right) + 1 \qquad [3.21]$$

where $R_E = 1/(X_{ref}\beta)$ is the approaching equilibrium factor of the Elovich equation. When $R_E > 0.3$ the kinetic curve rises slowly. On the contrary, when $R_E < 0.02$ the curve instantly approaches equilibrium (Wu et al., 2009a).

Intraparticle diffusion model (Weber-Morris). This model, presented in the early 60s (Weber and Morris 1962; 1963), considers that sorption is influenced by diffusion in the sorbent and convective diffusion in the sorbate solution. The linear equation is:

$$X_t = C + k_{int}t^{1/2} \qquad [3.22]$$

where k_{int} (μg g^{-1} $min^{1/2}$) is the intraparticle diffusion rate constant, and C (μg g^{-1}) is a parameter proportional to the extent of the boundary layer thickness, that is, the larger C, the greater the boundary layer effect (Mckay et al., 1980). The initial adsorption behaviour in this model is determined by rewriting equation [3.22] as in Wu et al. (2009b):

$$X_{ref} = C + k_{int}t_{ref}^{1/2} \qquad [3.23]$$

where t_{ref} is the longest time in the adsorption process and X_{ref} is the adsorbed amount at $t = t_{ref}$. Subtracting equation [3.23] from equation [3.22] and rearranging the terms:

$$X_{ref} - X_t = k_{int}(t_{ref}^{\frac{1}{2}} - t^{\frac{1}{2}}) \qquad [3.24]$$

$$\frac{X_t}{X_{ref}} = 1 - R_i\left[1 - (\frac{t}{t_{ref}})^{1/2}\right] \qquad [3.25]$$

where $R_i = (K_{int}t_{ref}^{1/2}/X_{ref})$ is the initial adsorption factor. From equation [3.23] R_i can be also expressed as:

$$R_i = \frac{X_{ref} - C}{X_{ref}} = 1 - (\frac{C}{X_{ref}}) \qquad [3.26]$$

When R_i approaches 1 ($C = 0$), the contribution of fast initial adsorption is negligible and adsorption is entirely controlled by intraparticle diffusion. On the other hand, when $R_i = 0$ ($C = X_{ref}$), the adsorption occurs right at the beginning of the process (Wu et al., 2009b).

3.2.2. Adsorption of pendimethalin, α–cypermethrin and deltamethrin to glassware

As we will verify in the 3.3.2 section, adsorption to glassware of highly hydrophobic pesticides, especially pyrethroids, may be problematic when assessing their adsorption behaviour on soils by the batch technique. Mixtures of the three pesticides at 0.5 μg mL^{-1} were prepared in MQ water, TWW, and DOC solutions at various concentrations (3-90 mg L^{-1}), as well as in solutions of $CaCl_2$ and $(NH_4)_2SO_4$. Twenty mL of each solution per triplicate were placed in 30-mL Pyrex centrifuge tubes, which were then mechanically shaken end-over-end in a thermostatic chamber at 20 ± 1 °C for 24 h. To facilitate pesticide solubility in water and maintain pesticide detection in the analytical determination range, the solutions were prepared by dilution from standards in acetone at 1 g L^{-1}, keeping the organic solvent amount always below 0.5-0.8% in volume, to neglect any effect on adsorption. Pesticides were analysed in the solution and on the glassware. The latter was determined after placing the tubes upside down to let the drops drain. The dry tubes were sonicated for 10 min (200 W, Ultrasons, Selecta) with 3 x 10 mL acetone, the combined fractions were concentrated to dryness and the dry residue dissolved in 1 mL hexane. Finally, pesticide concentration was determined by GC-µECD (see 2.2.5.1 section).

Pesticide adsorption to the walls of the tubes was also considered in the presence of soil. After 24 h shaking, soil was eliminated from the tubes with a spatula and the residual soil was calculated by weight difference with the empty tube. The procedure was then conducted as above.

3.2.3. Adsorption-desorption isotherms

3.2.3.1. Adsorption

Adsorption isotherms of DIM and FEN on the three soils and of THC on SV soil were made in triplicate with different solutions in the initial concentration range 0.5-5 µg mL^{-1} using the same solid/liquid ratio as in the kinetic studies. For PDM, CYP and DTM, hydrophobic compounds whose adsorption on soil was expected to be high, single point sorption experiments were carried out at 0.5 µg mL^{-1} with 0.4 g SV soil and 20 mL solution, because ideally, 20-80% of the initially applied pesticide should be sorbed (Koskinen et al., 2006). The suspensions were shaken in a thermostatic chamber at 20 ± 1 °C during 24 h to ensure adsorption equilibrium, and the samples were subsequently treated as in the kinetic studies. Control solutions at each concentration without soil were run to check the influence of other processes such as pesticide degradation, volatilisation or adsorption onto glassware.

The amount of pesticide sorbed was calculated as previously detailed in the kinetic experiments. For THC, DIM and FEN experimental data were fitted to the Freundlich equation described above. For PDM and pyrethroids distribution coefficients (K_d) were calculated from the ratio X/C_e.

3.2.3.2. Desorption

Desorption of DIM and FEN from the three soils was performed at the highest initial pesticide concentration of the adsorption isotherms (5 µg mL^{-1}) with MQ, TWW, and DOC in the concentration range 30-300 mg L^{-1}. After the initial adsorption step, 10 mL of supernatant, where pesticide concentration was determined, was replaced by the same volume of the corresponding background solution. The tubes were thoroughly mixed in a vortex and shaken for 24 h at 20 ± 1 °C. This process was repeated four times, so four desorption steps were completed. As in sorption experiments, blanks without soil were conducted for each desorption step.

In this case, the amount of pesticide sorbed was calculated as:

$$X = \frac{V}{m}(C_0 - C_e) + X_0 \qquad [3.27]$$

where X_0 is the concentration of pesticide initially retained in soil (Limousin et al., 2007). The constructed desorption isotherms were fitted to the Freundlich model, and desorption coefficients K_{fd} and $1/_{nd}$ were obtained by linear regression. Hysteresis coefficients (H) were calculated as mentioned in section 3.1.2.3. The total desorbed pesticide (D, %) was obtained according to the expression:

$$D = \frac{(X_0 - X_f) * 100}{X_0} \qquad [3.28]$$

where X_0 represents the sorbed pesticide concentration before the first desorption step, and X_f the sorbed concentration after desorption is completed.

3.3. RESULTS AND DISCUSSION

3.3.1. Adsorption kinetics

3.3.1.1. Evaluation of equilibrium time and shape of the curves

As observed in Figure 3.2 adsorption equilibria were achieved within 24 h of soil–solution contact time for all the pesticides. The sorption capacity of SV soil was 14.5, 55.0, 68.2, 70.4, 91.8 and 94.8% of the initial amount applied for DIM, THC, FEN, PDM, DTM and CYP respectively, and correlated (r = 0.895) with pesticide hydrophobicity (log K_{ow}). In addition, a significant relationship ($P < 0.05$) was found between sorption capacity and pesticide solubility in water ($\%Adsorp. = -4.31 \times LnS_w + 66.22$, $R^2 = 0.723$). Soil RM1 retained more DIM as compared with the other two soils. In contrast, FEN sorption capacity was ranged as SV > RM3 > RM1.

In SV soil, PDM was rapidly adsorbed and reached X_{max} after approximately 2 h. Sorption kinetics of both pyrethroid insecticides (CYP and DTM) was similar and a longer time (approximately 8 h) was needed for the equilibrium to be reached. A rapid sorption of THC was observed in the first 15 min (35% of the initial amount applied), followed by a much slower process until an apparent equilibrium after 16 h.

Concerning the three soils no differences in the behaviour of DIM and FEN were observed. The adsorption of both pesticides was almost instantaneous with a sorbed

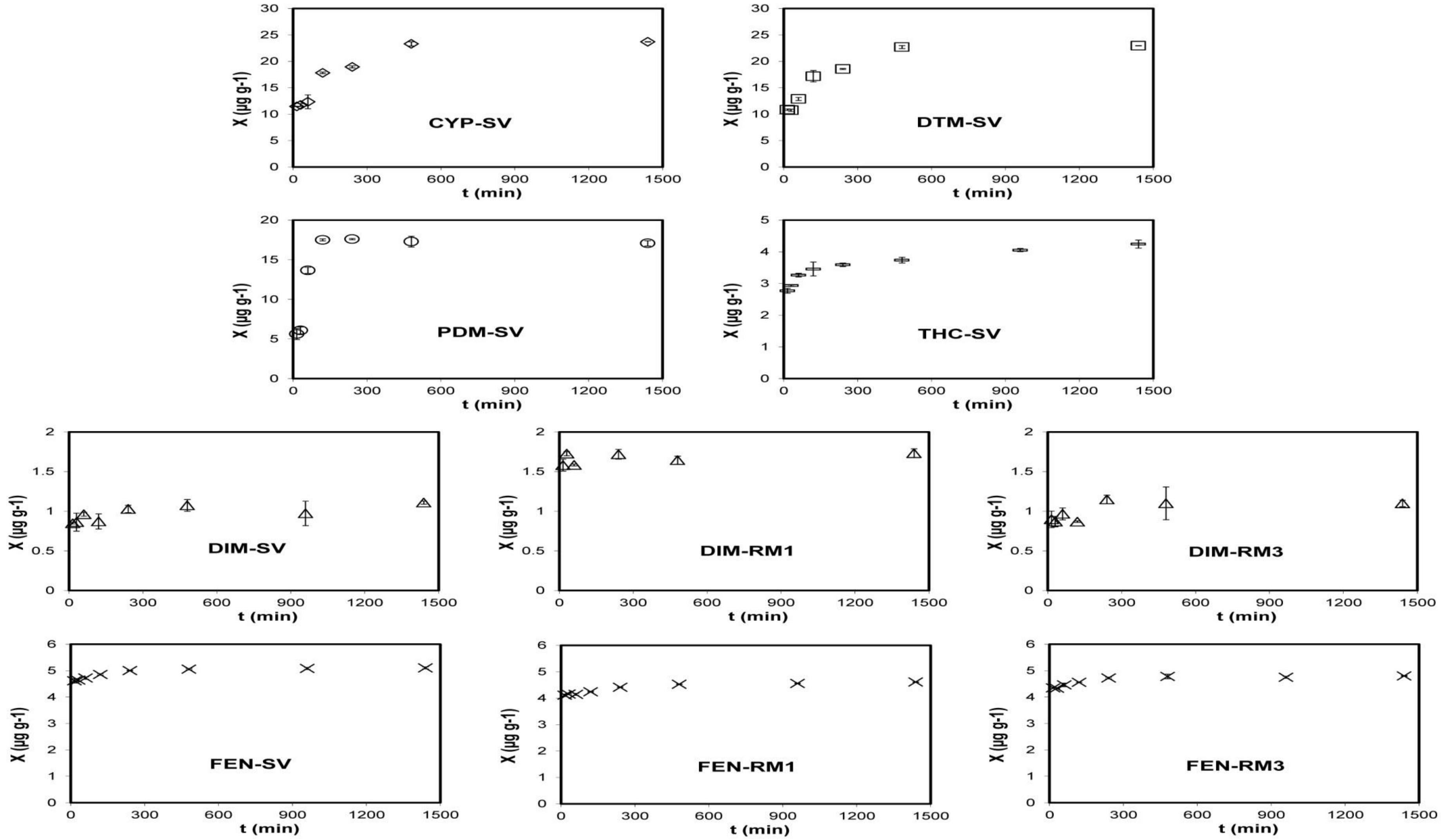


Figure 3.2. Kinetic curves for pesticide sorption on the different soils (SV, RM1 and RM3)

amount of 11-21% for DIM and 52-58% for FEN in the first 15 min of the experiment, followed by a much slower progress toward an apparent equilibrium after approximately 4 h. Shaking in batch experiments allows instantaneous contact of pesticide molecules with the most accessible soil particles (Regitano et al., 2002).

On the other hand, the shape of the curves indicates that the dominance of either surface or internal phenomena is dependent on pesticide properties. Diffusion of pesticide molecules within the internal soil structure is more important for the more hydrophobic pesticides CYP and DTM. On the other hand, sorption of DIM and FEN seems to be controlled by transport into the macropores as a consequence of their high adsorption at short contact times. Although a rapid initial adsorption of THC was observed, intraparticle diffusion cannot be excluded due to the constant increase of sorbed amount during the experimental time. In order to identify the mechanisms involved in pesticide adsorption, experimental data were fitted to different kinetic models.

3.3.1.2. Kinetic models

Hyperbolic model

Fitting of the experimental data to the hyperbolic model is depicted in Figure 3.3. According to the low values of R^2 obtained (Table 3.1), especially those for the herbicide DIM, this model was not appropriate to describe pesticide kinetics. This lack of fit has been associated with a long soil-solution contact time (Grébil et al., 2001; Fernández-Bayo et al., 2008). In this sense Cáceres et al. (2010) found a good fitting to this model for metsulfuron-methyl adsorption on soils at short contact times (180 min). However, this model was effective in the estimation of X_{max} (differences between 2 and 17%), providing values that were in general slightly lower than those experimentally calculated (Table 3.1).

Pseudo first and pseudo second order models

The fitting of the experimental data to the PFO and PSO kinetic models are depicted in Figures 3.4 and 3.5 respectively for all the pesticides, except for DIM in RM1 and RM3 soils where data could not be fitted to the PFO model. The estimated rate constants (k_{PFO} and k_{PSO}) and X_{max} are shown in Table 3.1, as well as the corresponding determination coefficients R^2. The experimental maximum X observed in each experiment was assumed to be X_{max} for k_{PFO} estimation.

Fitting to the PFO was not satisfactory when the whole data set was considered. However, at short contact times (2 h for PDM, 16 h for THC, and 8 h for the rest of the pesticides) data could be- fitted (Figure 3.4). Although the PFO model provided R^2 values ≥ 0.90 ($P < 0.05$), it failed to explain X_{max} experimental values (differences between 28 and 127%) and therefore the applicability of this model was found to be limited.

By contrast, data adequately conformed to the PSO kinetics with $R^2 > 0.99$ ($P < 0.01$). This model described the whole data set and the predicted X_{max} values that agreed with the experimental ones, with the lowest differences (0-3.5%). The ability of the PSO model to explain sorption of organic pollutants from aqueous solutions has been repeatedly reported (Fernández-Bayo et al., 2008; Cáceres et al., 2010; Pavlovic et al., 2013).

It has been described in the literature that PFO kinetics is mainly suitable in the first stages of the sorption process, when low coverage of sorptive sites occurs and the amount of unoccupied ones can be considered constant. As the reaction proceeds, unoccupied sites and pesticide concentration in solution constantly decrease and adsorption becomes a PSO reaction (Báez et al., 2013).

According to Azizian (2004) improved fitting to the PFO occurs when the initial concentration of pesticide increases. In our case, a better fit and prediction of X_{max} with the PSO model is expected because of the relative high coverage of active sites in the first 15 min with respect to the amount in equilibrium for each pesticide–soil system (35-91%).

Taking into account the k_{PSO} values, sorption rates were ranged in the order DIM > FEN > THC > PDM > DTM ≈ CYP. Sorption of DIM was slower for SV as compared with the other two soils. For FEN a faster sorption to RM3 soil was found, followed by SV and RM1 respectively.

Table 3.1. Kinetic parameters predicted from the fitting of pesticide sorption to the Hyperbolic, PFO, PSO and Elovich models

			Hyperbolic			**PFO**			**PSO**				**Elovich**				
Soil	Pest.	$X_{max\ exp}$	X_{max}	B	R^2	X_{max}	k (x 10^3)	R^2	X_{max}	k (x 10^3)	h	R^2	α	β	t_0	R_E	R^2
SV	CYP	23.7	19.7	13.6	0.686*	16.2	7.3	0.955**	24.3	1.0	0.60	0.999**	Not fitted				
	DTM	23.0	19.4	15.0	0.745*	16.5	8.1	0.953**	23.6	1.1	0.60	0.999**	Not fitted				
	PDM	17.6	19.1	40.2	0.865**	40.0	48.0	0.957*	17.4	3.0	0.92	0.998**	Not fitted				
	THC	4.2	3.8	6.6	0.831**	1.2	2.0	0.950**	4.3	8.4	0.15	0.998**	157	3.2	0.002	0.07	0.987**
	DIM	1.1	1.0	3.5	0.558*	0.27	4.3	0.903**	1.1	57.7	0.07	0.994**	58369	19.7	8.7 10^{-7}	0.05	0.693*
	FEN	5.1	5.0	1.6	0.734**	0.49	5.2	0.966**	5.1	43.9	1.1	1**	2.3 10^{14}	8.2	5.4 10^{-16}	0.02	0.956**
RM1	DIM	1.7	1.7	0.87	0.262#	Not fitted			1.7	100	0.30	1**	3.3 10^{30}	47.5	6.4 10^{-33}	0.01	0.268#
	FEN	4.6	4.5	1.6	0.587*	0.55	4.0	0.990**	4.6	30.0	0.64	1**	2.6 10^{12}	8.2	4.6 10^{-14}	0.03	0.941**
RM3	DIM	1.2	1.0	3.3	0.391#	Not fitted			1.1	106	0.13	0.999**	8310	16.8	7.2 10^{-6}	0.05	0.617*
	FEN	4.8	4.7	1.6	0.671**	0.52	6.9	0.991**	4.8	50.5	1.2	1**	2.5 10^{14}	8.8	4.6 10^{-16}	0.02	0.925**

Parameter units defined in the *Experimental Setup* section
*$P<0.05$; **$P<0.01$; #not significant ($P>0.05$)

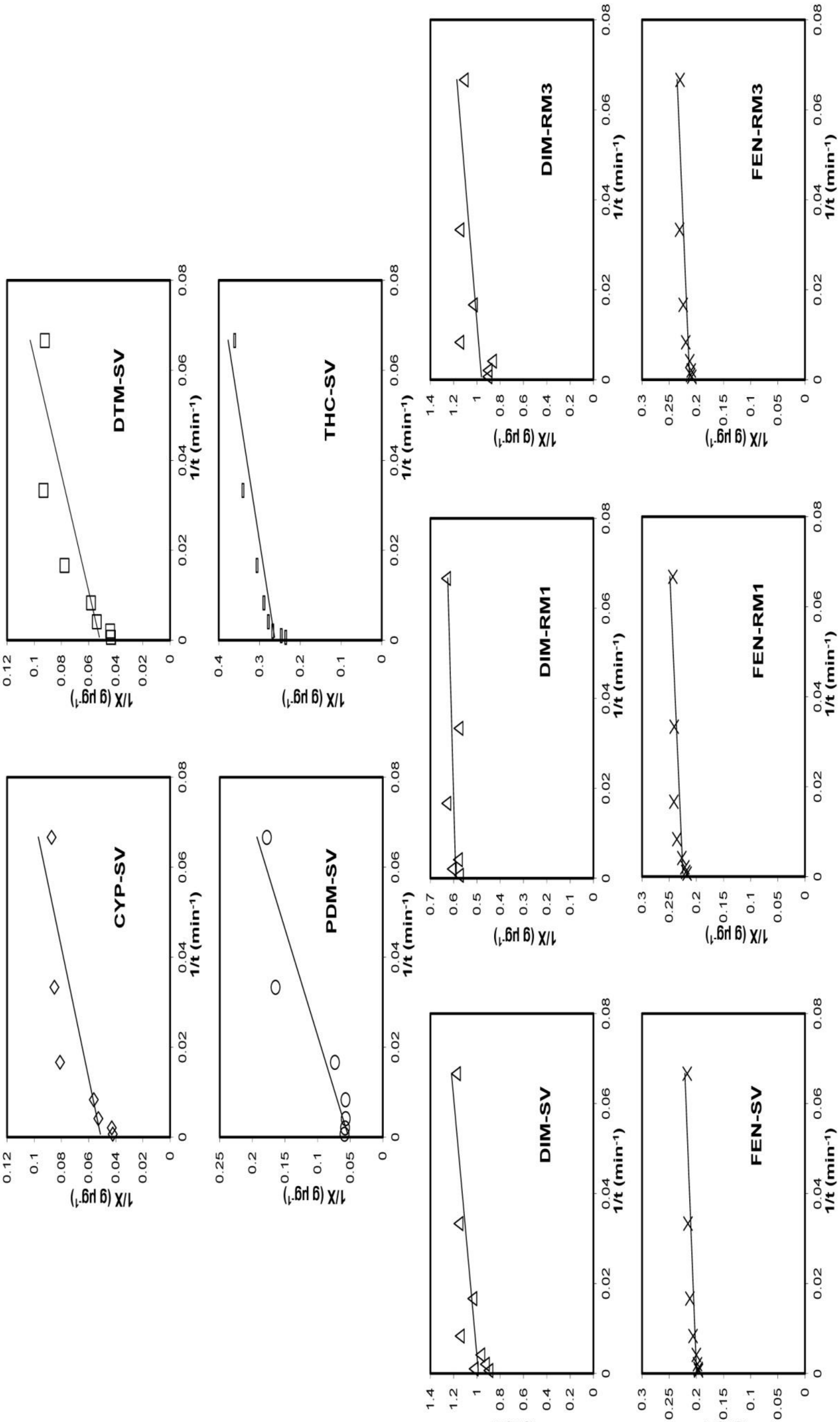


Figure 3.3. Fitting to the hyperbolic model for pesticide sorption on soils

An initial adsorption PSO rate was calculated as $h_{PSO} = k_{PSO} \times X_{max}^2$ (μg g^{-1} min^{-1}) (Ho, 2006) in order to determine the contribution of the initial mass transport in the whole process (Table 3.1). In all the cases, the initial rate was higher than the intrinsic one (k_{PSO}), but the difference was more pronounced for the most hydrophobic and less water-soluble pesticides. It is worth mentioning that, while the contribution of the initial rate to DIM sorption relative to k_{PSO} on SV and RM3 soils was low, h_{PSO} value was three times higher than that of k_{PSO} for RM1, suggesting a high initial accessibility of DIM molecules to RM1 surface, possibly related to the great clay content of this soil (51%).

Elovich equation

This model is useful to describe second order kinetics assuming that actual solid surfaces are energetically heterogeneous (Rudzinski and Panczyk, 2000). According to Table 3.1 and Figure 3.6, it may be considered that Elovich equation was suitable to describe THC and FEN sorption kinetics ($R^2 > 0.92$; $P < 0.01$), as well as that of DIM in SV and RM3 soil ($R^2 > 0.62$; $P < 0.05$). This poorer fitting for DIM, with relatively high water solubility, could be due to the fact that Elovich equation neglects the effects of simultaneously occurring desorption (Plazinski et al., 2009). Regarding PDM, CYP and DTM, although an apparent good fitting was achieved, especially for pyrethroids (Figure 3.6), the model was rejected due to the high standard error of the intercepts and consequently the negative values of the 95% confidence intervals.

Some authors have related the lack of fit to this model to a high coverage of the soil surface, being the effect dependent on pesticide properties (Fernández-Bayo et al., 2008). Despite the low initial concentration (0.5 μg mL^{-1}), this could be the case of PDM, CYP and DTM, due to the low amount of soil used (0.4 g) and the supposedly high affinity of these pesticides for soil. In addition, it has been reported that application of Elovich equation is restricted to the initial times of the sorption process, when the system is relatively far from equilibrium (Plazinski et al., 2009), which is not the case for DIM sorption on RM1, where equilibrium occurs almost instantaneously (Figure 3.2).

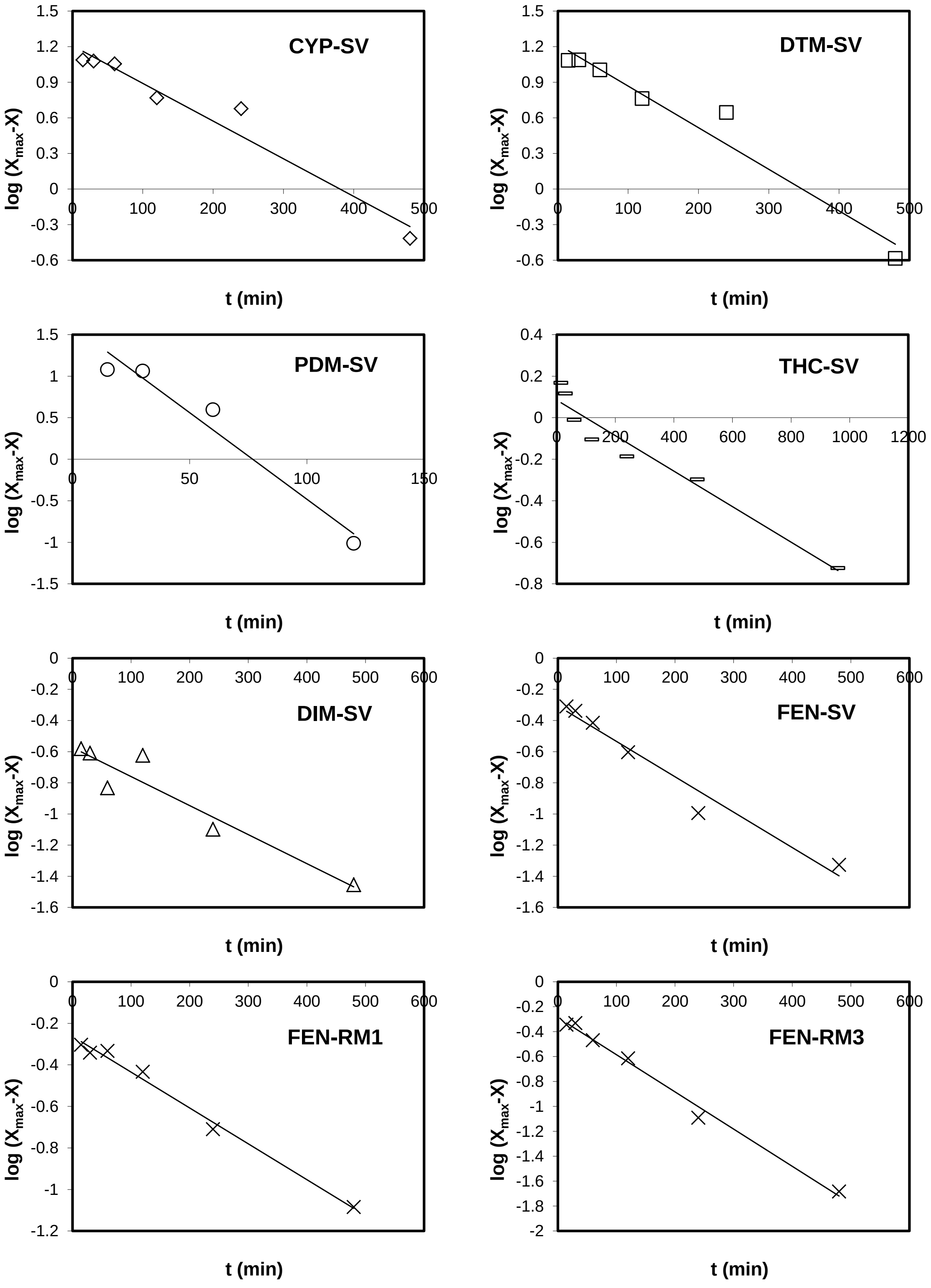


Figure 3.4. Fitting to the PFO model for pesticide sorption on soils at short contact times

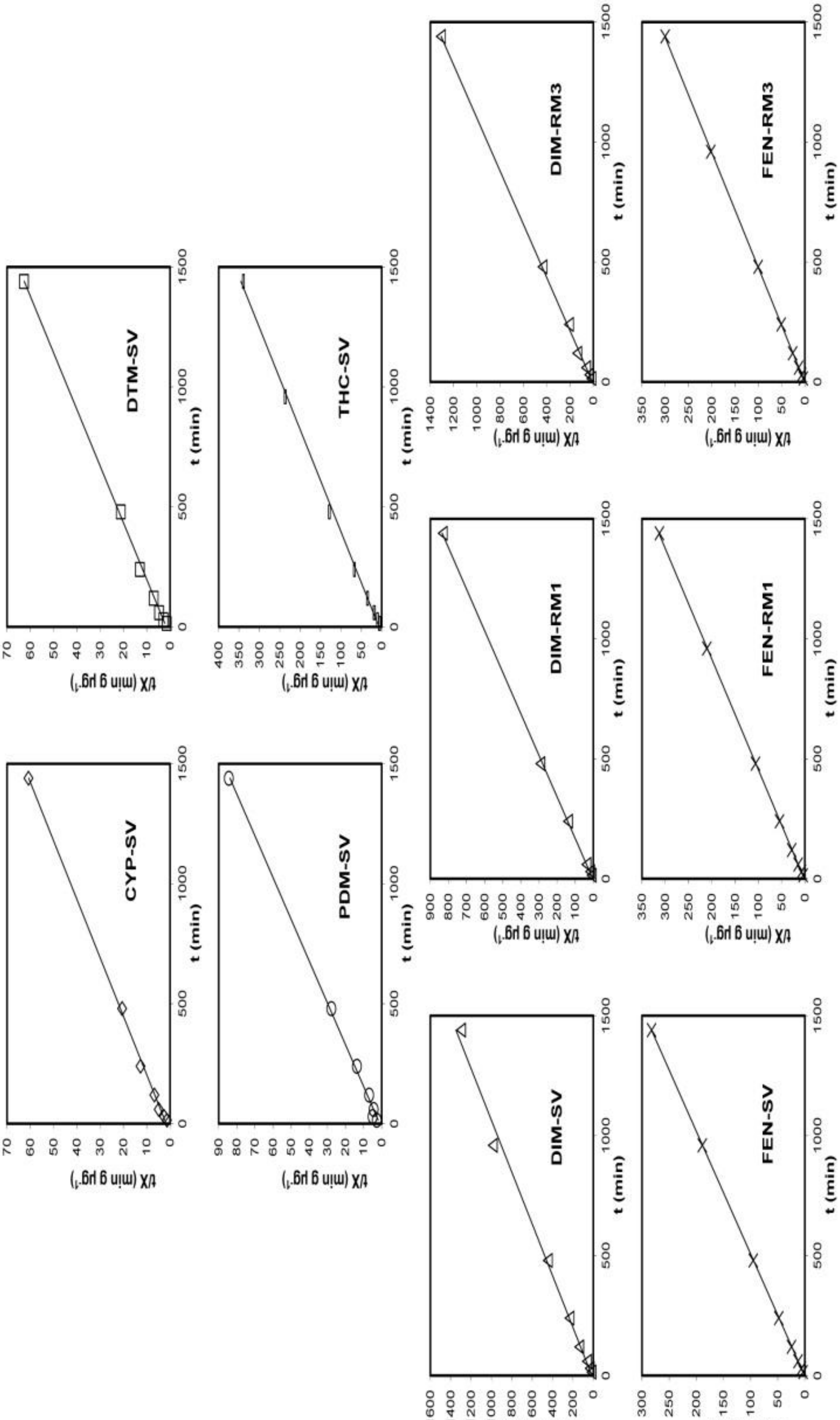


Figure 3.5. Fitting to the PSO model for pesticide sorption on soils

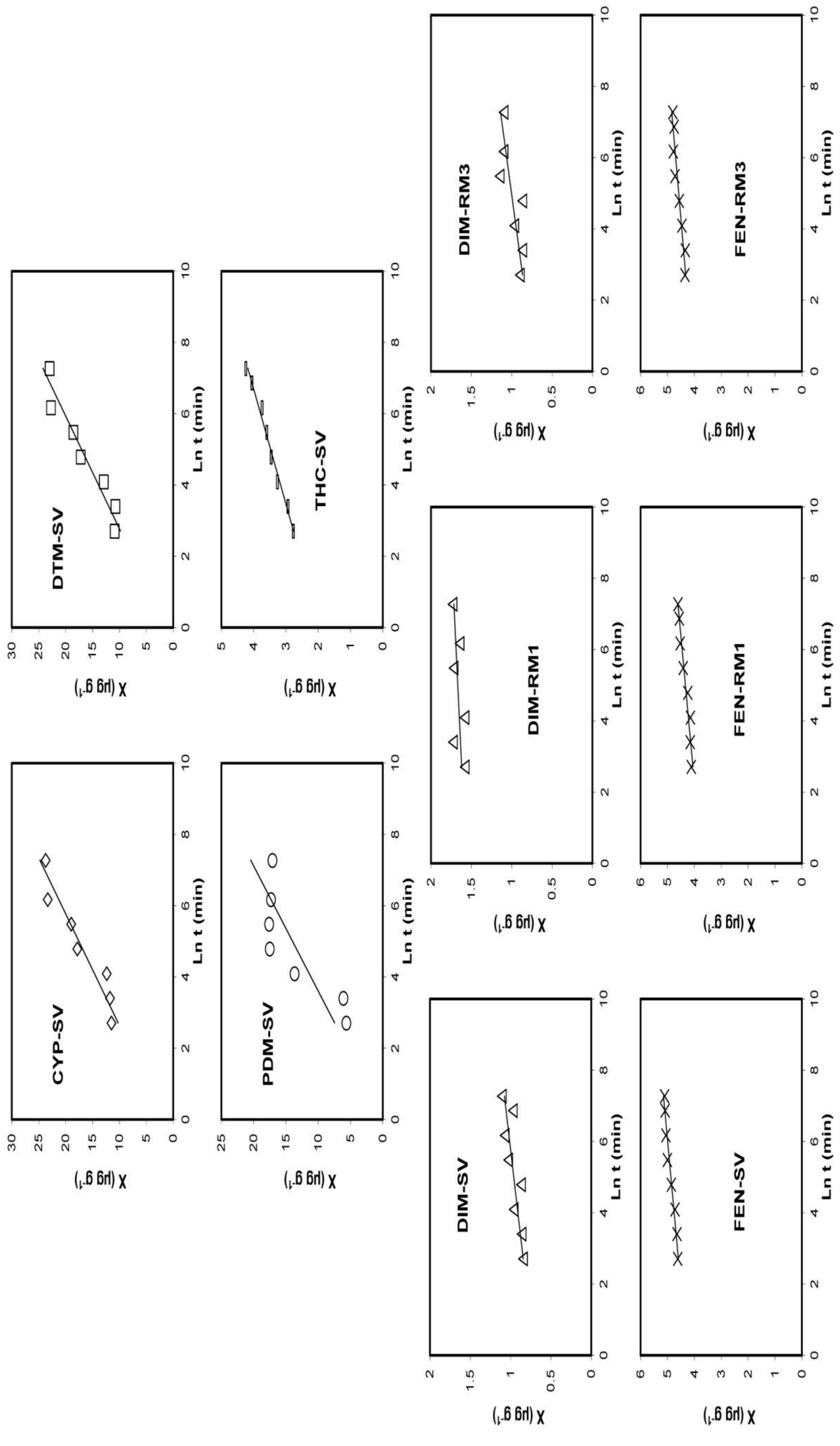


Figure 3.6. Fitting to the Elovich equation for pesticide sorption on soils

We can clearly consider that the fast reaction phase occurred within the first 15 min of contact time. The β values indicated a higher number of active sites available for DIM sorption, followed by FEN and THC in SV soil. On the other hand, the initial adsorption rate, expressed by α, was much higher for FEN, showing the high affinity of this relatively hydrophobic fungicide for the soil colloids. Regarding FEN sorption on the different soils no great differences in β values were found indicating a similar availability of active sites. However, the adsorption in the initial phase was two orders of magnitude faster for SV and RM3 than for RM1, the soil with less OC content.

From the linear form of the equation, the intercept is considered as the amount sorbed during the initial fast phase (Inoue et al., 2004). The corresponding values were 1.93 ± 0.08 μg g^{-1} for THC; 0.71 ± 0.07 μg g^{-1} for DIM–SV, 0.70 ± 0.11 μg g^{-1} for DIM–RM3; and 4.27 ± 0.06, 3.73 ± 0.07 and 4.01 ± 0.07 μg g^{-1} for FEN in SV, RM1 and RM3 respectively, equivalent to 45%, 76–78%, and 81–84% of the total amount sorbed for THC, DIM and FEN. These percentages represent the contribution to the whole process of a nearly instantaneous equilibrium, especially relevant for FEN sorption likely due to its higher hydrophobicity. The sorption rates (μg $g^{-1}min^{-1}$) of the slow phase, represented by the slope of the straight line, were 0.31 ± 0.01 for THC, 0.05 ± 0.01 for DIM–SV, 0.06 ± 0.02 for DIM–RM3, 0.12 ± 0.01 for FEN in SV and RM1 soils, and 0.11 ± 0.01 for FEN in RM3.

According to R_E values in Table 3.1, adsorption curves of THC, DIM and FEN are in the “rapid rising” region (Table 3.2),

Table 3.2. Classification of the kinetic curves based on the approaching equilibrium parameter (R_E) derived from the Elovich equation

R_E	Curve	Zone
$R_E > 0.3$	Slow rising	1
$0.3 > R_E > 0.1$	Mild rising	2
$0.1 > R_E > 0.02$	Rapid rising	3
$R_E < 0.02$	Instant approaching equilibrium	4

From Wu et al. (2009a)

These data indicate that slow diffusion is more important for THC, followed by DIM and FEN (lower R_E), in accordance with the sorbed amount in the initial phase. Although we have previously mentioned that the DIM-RM1 system did not fit the Elovich equation, it is important to note that the adsorption curve was in the “instant adsorption equilibrium" zone (Table 3.2), confirming the great affinity of DIM for RM1 soil.

Intraparticle diffusion (Weber-Morris model)

The intraparticle diffusion model has been recently applied to evaluate adsorption of pesticides on soils from aqueous solutions (Fernández-Bayo et al., 2008; Cáceres et al., 2010; Báez et al., 2013; Rojas et al., 2014). Normally, a straight line is obtained from the representation of X_t *versus* $t^{1/2}$ that does not necessarily pass through the origin. In other cases the plots present multilinearity pointing to the existence of two or three stages in the whole process: the first stage represents external surface adsorption (instantaneous adsorption); the second stage is the gradual adsorption step, where intraparticle diffusion is controlled; and the third stage is the final equilibrium step, where the solute moves from larger pores to micropores, causing a slow adsorption rate. The time required for the second stage is difficult to predict since it depends on the variations of the system, including temperature, solute concentration, and adsorbent particle size (Wu et al., 2009b).

Fitting plots and parameters are presented in Figure 3.7 and Table 3.3 respectively. The model was successfully applied in all the pesticide–soil systems except for DIM, for which the model only fitted poorly SV data, and PDM that presented multilinearity with good regression ($R^2 > 0.86$), but the high standard error of the parameters voided the model application (Figure 3.7). For the other pesticides data were fitted to a single straight line that did not pass through the origin.

As observed in Table 3.3 for SV soil, DIM exhibited the lowest rate constant, followed by FEN, THC and the pyrethroid insecticides. Furthermore, no great differences were observed for FEN sorption in the three soils, indicating again that textural soil composition was not a determinant factor.

In all the cases C values were positive (Table 3.3) which indicates rapid adsorption within a short period of time and therefore the process is not exclusively controlled by intraparticle diffusion (Wu et al., 2009b; Cáceres et al., 2010; Báez et al., 2013). According to Tables 3.3 and 3.4, the calculated values of C/X_{ref} and R_i indicated intermediate contribution of initial adsorption for pyrethroids (zone 2), while more strongly initial adsorption was observed for THC, DIM and FEN (zone 3), in agreement with the kinetic curves (Figure 3.2).

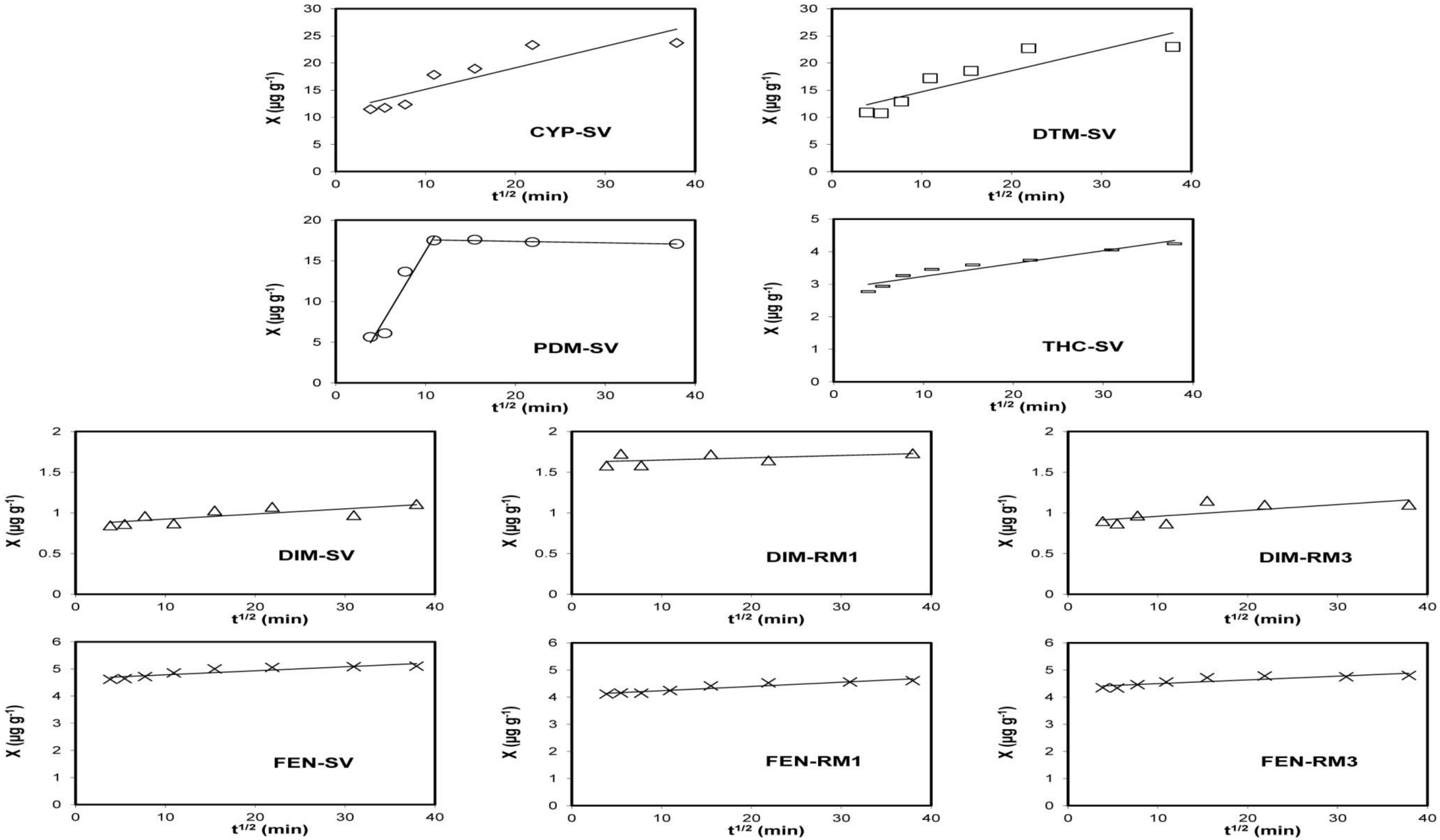


Figure 3.7. Fitting to the intraparticle diffusion model for pesticide sorption on soils

Table 3.3. Kinetic parameters (standard error) predicted from the Intraparticle Diffusion model

SOIL	SV	RM1	RM3
CYP			
k_{int} ($\mu g\ g^{-1} min^{1/2}$)	0.40 (0.09)		
C ($\mu g\ g^{-1}$)	11.19 (1.64)		
C/X_{ref}	0.43		
R_i	0.57		
R^2	0.799**		
DTM			
k_{int} ($\mu g\ g^{-1} min^{1/2}$)	0.39 (0.09)		
C ($\mu g\ g^{-1}$)	10.81 (1.63)		
C/X_{ref}	0.42		
R_i	0.58		
R^2	0.795**		
THC			
k_{int} ($\mu g\ g^{-1} min^{1/2}$)	0.039 (0.005)		
C ($\mu g\ g^{-1}$)	2.85 (0.10)		
C/X_{ref}	0.66		
R_i	0.34		
R^2	0.965*		
DIM			
k_{int} ($\mu g\ g^{-1} min^{1/2}$)	0.006 (0.002)		
C ($\mu g\ g^{-1}$)	0.86 (0.04)		
C/X_{ref}	0.78		
R_i	0.22		
R^2	0.623*	$0.264^{\#}$	$0.510^{\#}$
FEN			
k_{int} ($\mu g\ g^{-1} min^{1/2}$)	0.015 (0.003)	0.016 (0.002)	0.014 (0.003)
C ($\mu g\ g^{-1}$)	4.64 (0.06)	4.08 (0.04)	4.36 (0.06)
C/X_{ref}	0.89	0.87	0.89
R_i	0.11	0.13	0.11
R^2	0.818**	0.906**	0.773**

*P<0.05; **P<0.01; $^{\#}$not significant (P>0.05)
PDM was not fitted

Table 3.4. Initial adsorption behaviour according to intraparticle diffusion kinetic parameters

R_i	C/X_{ref}	Initial adsorption behaviour	Zone
$R_i = 1$	$C/X_{ref} = 0$	No initial adsorption	0
$1 > R_i > 0.9$	$0 < C/X_{ref} < 0.1$	Weakly initial adsorption	1
$0.9 > R_i > 0.5$	$0.1 < C/X_{ref} < 0.5$	Intermediately initial adsorption	2
$0.5 > R_i > 0.1$	$0.5 < C/X_{ref} < 0.9$	Strongly initial adsorption	3
$R_i < 0.1$	$C/X_{ref} > 0.9$	Approaching completely initial adsorption	4

From Wu et al. (2009b)

Therefore, intraparticle diffusion is more relevant for the pyrethroid insecticides (higher R_i and lower C/X_{ref}), followed by THC, DIM and FEN, for which ≈ 90% of total adsorption is reached in the rapid initial stage. Intraorganic matter diffusion has been established as the main rate-limiting mechanism for sorption of hydrophobic compounds (Brusseau et al., 1991). Two different processes can occur when OM is considered: i) instantaneous sorption on the more accessible OM domain, and ii) rate-limited steps due to the presence of complex associations between OM and mineral constituents (Báez et al., 2013). It has been found that as pesticide hydrophobicity and molecular size decrease, the importance of retarded intraparticle diffusion increases (Fernández-Bayo et al., 2008; Rojas et al., 2014). It does not occur in our work, since intraparticle diffusion is more important for pyrethroids, with higher log K_{OW} and molecular weight. However, the different experimental conditions used (soil/solution ratio and pesticide concentration) should be taken into account, since they highly influence intraparticle diffusion processes (Wu et al., 2009b).

3.3.2. Adsorption of pendimethalin, α–cypermethrin and deltamethrin to glassware

Previous experiments with pyrethroids had reported that a great proportion (> 60%) of these insecticides may remain adsorbed on the glass walls of the tubes used for batch assays and centrifugation (Zhou et al., 1995, 1997; Ali and Baugh, 2003). Although some reports indicated that the extent of adsorbed pesticide on the laboratory glassware was independent on pH, ionic strength and DOC (Zhou et al., 1997; Ali and Baugh, 2003), the influence of the composition of the background solution was investigated.

Additionally preliminary studies using Teflon tubes, as an alternative to using glass tubes (data not shown), also showed pesticide adsorption on the walls, in agreement with previous results (House and Zhou, 1992; Koskinen et al., 2006) and were not further considered.

3.3.2.1. Without soil

In the absence of soil, adsorption on the glass walls of the tubes was low for MQ water (< 1%) and for the different DOC solutions (0.9-3.8%) (Figure 3.8). A linear adsorption increase with DOC content in the solution employed was found in the whole DOC concentration range ($P \leq 0.05$), with R^2 values of 0.954 for PDM, 0.771 for CYP and 0.787 for DTM. The slopes of the straight lines (% adsorbed pesticide/mg L^{-1} DOC) were 0.034 ± 0.004, 0.018± 0.006 and 0.023 ± 0.007 respectively. By contrast, when using TWW as the background solution, adsorption of all the pesticides on the glass walls increased to 10-15%, significantly different ($P < 0.05$) from the assays concerning MQ water and DOC solutions. The complex composition of TWW may affect pesticide distribution between liquid and solid phases, not only by adding a relatively high DOC concentration, but also by inducing a possible alteration of pH and electrolytic composition of the solution (Müller et al., 2007). Nonetheless, DOC solutions were prepared by dissolving sewage sludge (SS-Ph) from the same TWW treatment plant, and DOC concentration seemed not to be responsible for the great increase of pesticide adsorption on the glass walls. However differences in composition of the DOC fractions between TWW and solutions extracted from sewage sludge (Celis et al., 1998; Ilani et al., 2005; Katsoyiannis and Samara, 2007), or contributions to the OM from non-dissolved fractions cannot be excluded. Another factor considered, i.e. solution pH, was not greatly modified with any of the solutions used in the assays (Table 3.5). On the contrary, the electrical conductivity of TWW was three orders of magnitude higher than that of MQ water (Table 3.5), a fact which could account for the observed pesticide adsorption increase.

Therefore, adsorption on glassware walls was also evaluated using background solutions containing the ions most commonly present in the TWW employed (Ca^{2+} and NH_4^+ as the cations and Cl^- and SO_4^{2-} as the anions). Solutions were prepared at a concentration providing a conductivity value similar to that measured in TWW (Table 3.5). Results show that adsorption on the glass walls of the tubes was high (25-35% for

$(NH_4)_2SO_4$) or very high (35-55% for $CaCl_2$) (Figure 3.8), and significantly different from the rest of background solutions evaluated ($P < 0.05$), a fact that highlights the importance of inorganic compounds in pesticide behaviour. The adsorption increase was higher for both pyrethroids than for PDM and seems to be inversely related with the compounds' solubility in water. A possible explanation is a salting out effect, which implies a reduction in aqueous solubility of neutral molecules in the presence of dissolved ions (Turner, 2003). This decrease in water solubility would favour the adsorption on hydrophobic sorbents, such as glassware walls, plastics, clays or sediments (Turner and Rowling, 2001; El-Nahhal and Lagaly, 2005).

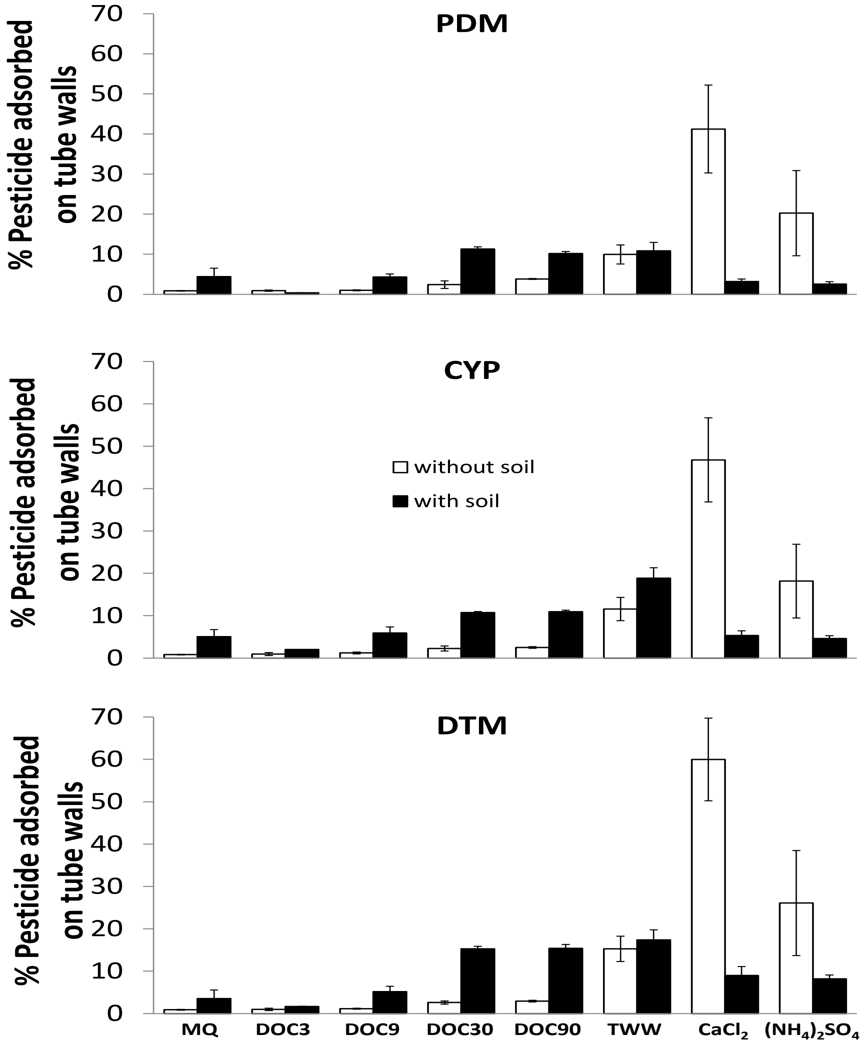


Figure 3.8. Percentage of pendimethalin (PDM), α-cypermethrin (CYP) and deltamethrin (DTM) adsorbed on the glass walls of the tubes with the different background solutions without or with SV soil. Vertical bars correspond to standard deviations (n = 4).

3.3.2.2. With soil

The presence of soil in the system alters the proportion of pesticide found on the glassware walls, due to the greater surface area of the soil particles as compared to the vessel walls (Koskinen et al., 2006). The amount retained ranged from 2 to 17% depending on the background solution and on the pesticide.

As can be seen in Figure 3.8, the main differences in pesticide behaviour are found when salts are used. For both salts, $CaCl_2$ and $(NH_4)_2SO_4$, the reduction of pesticide adsorption on the glassware may be linked to an increase of solubilised soil DOC (DOC_{sol}) as a consequence of the disruption of the organo-mineral linkages and the mobilisation of OC from soil into the aqueous phase. This DOC_{sol} increase has been usually connected to the presence of Na^+, with a known dispersive effect on soil clay particles, but this cation was deliberately not considered in this study. Recently it has been reported that counterions, such as SO_4^{2-} and Cl^-, may be responsible for the enhanced dissolution of soil carbonates present in calcareous soils, and the consequent increase of DOC_{sol} from soil OC trapped in the carbonate fraction (Artiola and Walworth, 2009). The increase in DOC_{sol} when compared to MQ water, reflected in Table 3.5, would favour pesticide solubilisation and reduce the proportion of pesticides retained on the glass walls. Therefore, the values of pesticide adsorption on glassware using the solution without soil are not good indicators of the behaviour of the pesticide when soil is present.

3.3.3. Adsorption isotherms

Due to the issue presented above, single point distribution coefficients (K_d) were calculated for PDM, CYP and DTM as explained in the section 2.2.1 of this chapter. For the other three pesticides multipoint adsorption isotherms (0.2-5 μg mL^{-1}) were carried out.

Adsorption of pesticides was ranged as CYP ≈ DTM > PDM > FEN > THC > DIM, which in general terms can be directly related with pesticide hydrophobicity after taking into account some considerations: adsorption of non-ionic pesticides on soils is mainly attributed to hydrophobic interactions or van der Waals forces with the soil OM (Báez et al., 2013). In the case of the highly soluble DIM (water solubility 1200 mg L^{-1}), interactions with the soil mineral fraction may be relevant in the adsorption process. On the other hand, some controversial reports about the log K_{ow} values of

PDM have been found in the literature: 5.18 (García-Valcárcel and Tadeo, 2003; Tomlin, 2003; Alister et al., 2009) or 4.18 (Sharma and Singh, 2007). If the latter was correct and we exclude DIM, adsorption would be ranked in accordance with pesticide hydrophobicity, a fact widely reported (Rodríguez-Cruz et al., 2006, 2007; Rojas et al., 2014). It is also important to mention that the order of adsorption is almost inversely proportional to pesticides water solubility (Figure 2.2), also in accordance with previous works (De Wilde et al., 2008; El Bakouri et al., 2009, Rojas et al., 2014).

The use of TWW and saline solutions affected the adsorption of PDM and the pyrethroid insecticides, but it did not influence that of THC, DIM and FEN; therefore, the discussion below will not refer to them.

3.3.3.1. Pendimethalin, α–cypermethrin and deltamethrin in SV soil

It has been reported that adsorption of pyrethroid insecticides (Ali and Baugh, 2003) and PDM (Rytwo et al., 2005; Sakaliene et al., 2007; Kjaer et al., 2011) is directly related to soil OC content rather than to the mineral fraction. Although SV has a low OC content, these three pesticides showed strong retention on soil (Table 3.6) as expected from their physicochemical properties, and therefore they present no or low risk of leaching through the soil profile. PDM adsorption constants (K_d and K_{OC}) with control water (Table 3.6) were in the range previously found in literature (Zheng and Cooper, 1996; Tomlin, 2003; Lu et al., 2006; Sakaliene et al., 2007; FOOTPRINT).

In contrast, while our results show that adsorption coefficients for pyrethroids coincide for DTM with those calculated by Zhu and Selim (2002), they were in general much lower than those reported (Tomlin, 2003; FOOTPRINT). This disagreement may be explained due to competence of pesticide molecules for the adsorption sites (Xing et al., 1996; Delgado-Moreno et al., 2007b; Delgado-Moreno and Peña, 2008; Rojas et al., 2014), to the experimental setup itself consisting in determining the pesticides directly from soil or else because some fractions of OM, mainly aromatic fractions, instead of total OC, can control pesticide adsorption (Ahmad et al., 2001; Smernik and Kookana, 2015).

DOC solutions from sewage sludge with different concentrations (3-90 mg L^{-1}) modified the retention of the three pesticides by soil (Table 3.6).

Table 3.5. Some properties of the background solutions used for batch assays, as well as supernatant and soil properties after batch equilibration (± confidence interval at $\alpha = 0.05$) (n = 4)

	Before batch experiments[a]			**After batch experiments**			
	Background solutions			**Supernatant**			**SV soil**
	DOC (mg L^{-1})	pH	Conductivity x 10^{-3} (dS m^{-1})	pH	Conductivity x 10^{-3} (dS m^{-1})	DOC (mg L^{-1})	OC (%)
MQ	0	7.6 ± 0.1	1 ± 0	8.8 ± 0.0	109 ± 0	16.4 ± 0.1	1.12 ± 0.11
DOC 3	3	7.4 ± 0.1	20 ± 1	8.4 ± 0.0	121 ± 2	21.7 ± 0.1	1.10 ± 0.09
DOC 9	9	7.6 ± 0.0	46 ± 0	8.2 ± 0.0	163 ± 1	23.3 ± 0.2	1.15 ± 0.12
DOC 30	30	7.8 ± 0.0	138 ± 0	7.8 ± 0.0	291 ± 0	34.9 ± 0.1	1.14 ± 0.12
DOC 90	90	7.8 ± 0.0	387 ± 1	7.3 ± 0.0	571 ± 2	92.9 ± 0.2	1.20 ± 0.10
$CaCl_2$ 5mM	0	6.6 ± 0.0	1229 ± 2	7.6 ± 0.0	1299 ± 3	41.2 ± 0.1	1.13 ± 0.11
$(NH_4)_2SO_4$ 5mM	0	6.2 ± 0.0	1367 ± 4	8.3 ± 0.0	1451 ± 4	36.2 ± 0.2	1.18 ± 0.12
TWW	24.8 ± 4.6	7.8 ± 0.2	980 ± 130	7.5 ± 0.0	1003 ± 1	35.9 ± 0.2	1.23 ± 0.09

[a] Batch experiments performed with 0.4 g SV soil and 20 mL of the background solution

At the lowest DOC concentration adsorption was significantly enhanced ($P < 0.05$) between 1.2 and 1.35 times for DTM and CYP, while PDM distribution constant remained unaffected ($P > 0.05$). The DOC solution at 9 mg L^{-1} did not significantly modify the K_d values of all the pesticides with respect to MQ water ($P > 0.05$). The two higher DOC concentrations (30 and 90 mg L^{-1}) led to a significant adsorption reduction (K_d and K_{OC}) of the three pesticides ($P < 0.05$). This behaviour is in accordance with the study by Ling et al. (2006) who found that atrazine adsorption increased at low DOC concentration and decreased thereafter with increasing DOC concentration.

After batch equilibration DOC concentration was measured in the supernatants for the different background solutions employed (Table 3.5), showing an increase of DOC content as the amount of initial DOC increased. On the contrary, soil OC after batch equilibration was not significantly modified with respect to MQ water ($P > 0.05$) when using DOC solutions between 3 and 90 mg L^{-1}. The extent to which a soil is able to retain DOC has been reported to be negatively related with soil OM content, and positively with clay content (Kaiser and Zech, 1998; Shen, 1999; Ling et al., 2006). The soil employed, with 1.2% OC and 11% clay content, has a relatively low ability to retain DOC and thus increase pesticide retention. Our results indicate that the increase of DOC, facilitating the presence of the hydrophobic pesticides in solution, plays in this case a more important role in pesticide retention than the modification of soil OC.

Saline solutions were also assayed, since they are major constituents of TWW. Solutions of $CaCl_2$ induced the highest enhancement of pesticide adsorption with respect to MQ water ($P < 0.05$) (more than 5 times for CYP), followed by $(NH_4)_2SO_4$ which also promoted significantly ($P < 0.05$) CYP adsorption (3.5 times) (Table 3.6). The increase in K_d values for DTM was lower but significant ($P < 0.05$) (approximately 2 times), while PDM adsorption was not significantly altered ($P > 0.05$).

Aqueous dissolution of a neutral compound involves overcoming water-water interactions and the formation and occupation of a cavity. According to Turner (2003) the addition of large inorganic salt concentration alters the water structure in the solution. In the presence of dissolved salt, water is more ordered and compressible, since the inorganic ions are surrounded by water molecules that are tightly bound in the hydration shell (El-Nahhal and Lagaly, 2005). This results at microscopic level in a reduction of the amount of water solvating the pesticide molecules, and therefore, their adsorption on soil increases by a partitioning mechanism.

Table 3.6. Distribution coefficients, K_d (± confidence interval at $\alpha = 0.05$), and organic carbon-normalised linear sorption constant, K_{OC}, for pendimethalin (PDM), α-cypermethrin (CYP) and deltamethrin (DTM) on SV soil. Effect of solution composition

	MQ	DOC 3	DOC 9	DOC 30	DOC 90	$CaCl_2$ 5mM	$(NH_4)_2SO_4$ 5 mM	TWW
CYP								
K_d	195 ± 8	264 ± 7	201 ± 4	118 ± 4	68 ± 2	1044 ± 25	683 ± 8	1040 ± 13
K_{OC}	17424	23908	17449	10346	5634	92648	57611	84472
DTM								
K_d	191 ± 6	228 ± 3	186 ± 4	106 ± 5	64 ± 2	397 ± 12	353 ± 3	441 ± 7
K_{OC}	17065	20674	16105	9313	5367	35221	29776	35866
PDM								
K_d	93 ± 4	92 ± 3	96 ± 3	70 ± 3	55 ± 2	104 ± 5	90 ± 5	108 ± 3
K_{OC}	8349	8326	8278	6118	4576	9243	7571	8784

The extent of this effect seems to depend on the compounds' hydrophobicity and also on other factors, such as molecular diameter or hydrophobic surface area (Turner, 2003). As a final consideration, the effects of ionic strength appear more strongly evident when using low soil/solution ratio, as is our case (a 1:50 ratio) (Spark and Swift, 2002).

When TWW was used as the background solution, the adsorption of all the pesticides drastically increased ($P < 0.05$) (Table 3.6), which could not be simply explained by a modification of soil OC content, since this parameter at the end of the batch assay was not significantly different ($P > 0.05$) from the rest of the solutions employed (Table 3.5). Besides, the measurement of DOC from TWW showed that it was as high as that corresponding to DOC solution at 30 mg L^{-1}, which had induced a significant reduction of pesticides' adsorption. On the other hand TWW supernatant conductivity was much higher than that corresponding to the DOC solutions employed (3-90 mg L^{-1}) and roughly similar to the solutions of the inorganic salts. Therefore, apart from the high DOC, the type and concentration of the inorganic salts in TWW are playing a role in the adsorption behaviour of the three hydrophobic pesticides.

3.3.3.2. Thiacloprid in SV soil

Experimental multipoint adsorption data for THC were well described by the Freundlich equation with $R^2 \geq 0.969$ (Figure 3.9 left). The 1/n values lower than unity (Table 3.7) indicate that adsorption isotherms are L-type (Giles et al., 1960), that is, a progressive saturation of the active sites occurs thus diminishing the affinity for soil with increasing pesticide concentration in solution. Non-linear isotherms are obtained when specific interactions between polar groups of the pesticide ($-C\equiv N$ group of THC) and the OM of the sorbent are involved (Spurlock and Biggar, 1994; Chiou et al., 2000). Taking into account that isotherms were nonlinear and to compare data with those available in literature, K_{OC} values were calculated from the distribution coefficients (K_d) determined by fitting experimental data to the linear model forced through the origin with $R^2 \geq 0.87$ (Marín-Benito et al., 2013) (Figure 3.9 right).

According to the K_d and K_{OC} values (Table 3.7), it can be said that THC is moderately adsorbed on SV soil, with adsorption constants slightly lower than those previously found (K_d 4.6-14.9 L kg^{-1}; K_{OC} 408-1584 L kg^{-1}) in Australian soils of tropical origin (Oliver et al., 2005a).

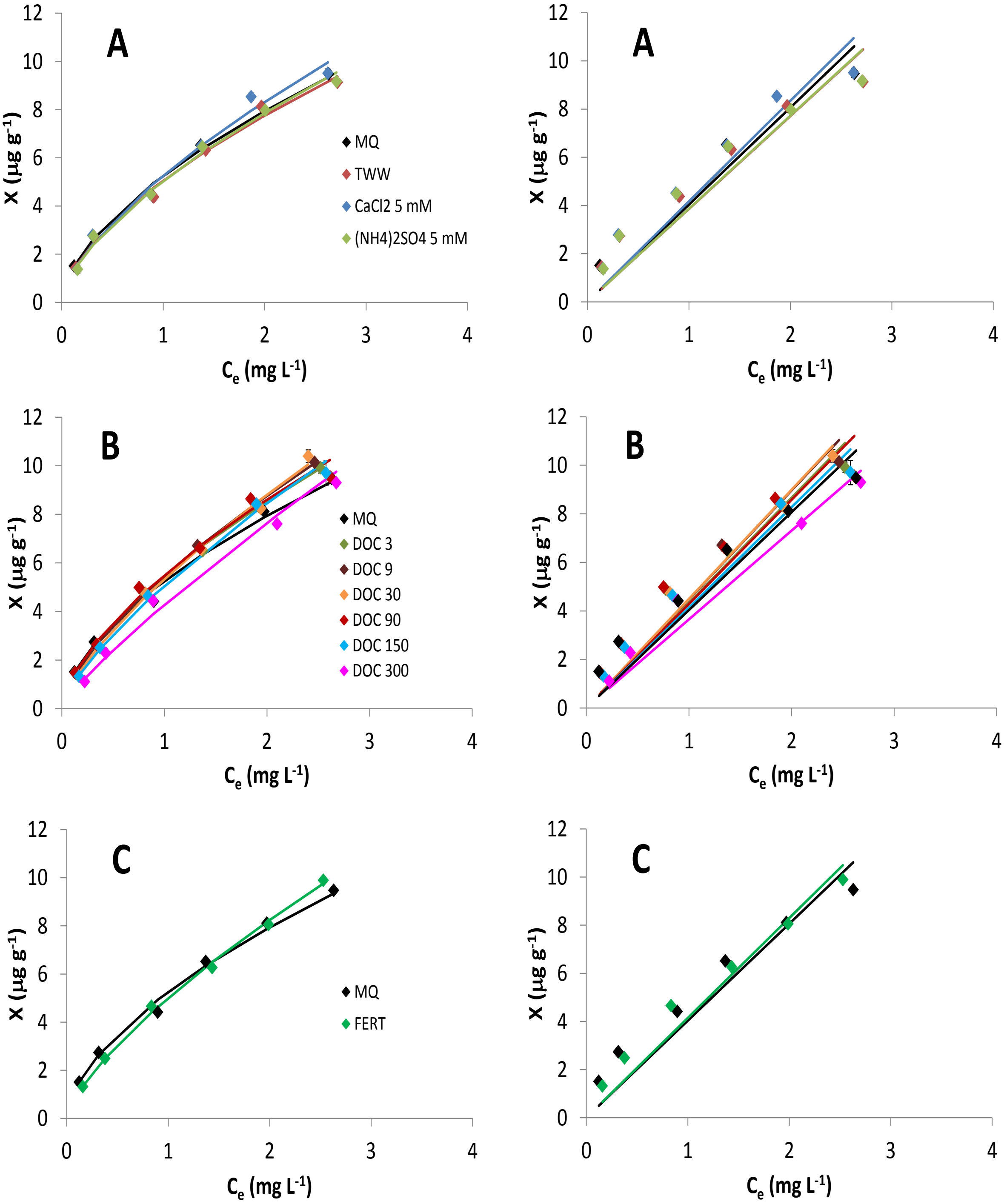


Figure 3.9. Freundlich (left) and linear (right) adsorption isotherms of thiacloprid (THC) in SV soil with TWW and saline solutions (A), DOC solutions at different concentrations (B), and SV soil amended with 1% Fertiormont (C). Comparison with control water MQ

In general, it was observed that the composition of the background solution did not greatly modify the adsorption of THC taking into account the low variation of K_d values (CV = 6.5%). Nevertheless, a special trend can be deduced when DOC is present in the background solution at different concentrations, though this behaviour was not as pronounced as for the most hydrophobic compounds. Firstly, THC adsorption increased up to a DOC concentration of 30 mg L^{-1} (K_d 4.5, K_{OC} 372), and it decreased thereafter with the lowest adsorption obtained for the DOC300 solution (K_d 3.7, K_{OC} 306). At DOC concentrations higher than 30 mg L^{-1} the affinity of THC for soil particles may decrease caused by the pesticide–DOM interactions which favour the presence of the contaminant in solution (Ling et al., 2006). It is worth mentioning that 1/n tends to increase with increasing DOC concentration, reaching a value of 0.84 when the solution at 300 mg L^{-1} DOC is used. This means that, although THC is adsorbed in less extent, the pesticide–soil interactions are more intense and a partitioning mechanism becomes more important. Flores-Céspedes et al. (2006) reported reduced adsorption of imidacloprid (a similar compound from the same neonicotinoid family) in a calcareous soil due to the co-presence of DOC in the solution but at lower levels (15-100 mg L^{-1}), as a consequence of blocking of the adsorption sites by DOM molecules. The DOC adsorbed could modify the hydrophilic–hydrophobic characteristics of the soil surface, so diminishing the available sites for adsorption of pesticides with no marked hydrophobic character (Barriuso et al., 1992; Celis et al., 1998). From our results it can be inferred that higher amounts of DOC could significantly reduce the adsorption of a relatively polar pesticide such as THC.

Amendment of soil with 1% (w:w) Fertiormont (FERT) did not modify THC adsorption coefficients. The slope of the Freundlich isotherm increased comparing to MQ water (1/n = 0.72), pointing to a more linear process. THC adsorption has been correlated with soil OC content (Rodríguez-Liébana et al., 2013), although this relationship was found to be significant only when soils were separated into different land uses (Oliver et al., 2005a). The low variation of K_{OC} (CV = 6%) taking into account all the soil–solution systems used coincide with these findings.

Table 3.7. Adsorption constants (± standard error) of thiacloprid (THC) in SV soil derived from the fitting to the Freundlich (K_f and 1/n) and linear (K_d and K_{OC}) models

	MQ	DOC 3	DOC 9	DOC 30	DOC 90	DOC 150	DOC 300	$CaCl_2$ 5mM	$(NH_4)_2SO_4$ 5mM	TWW	FERT
K_f[a]	5.3 ± 0.1	5.5 ± 0.1	5.5 ± 0.0	5.4 ± 0.1	5.5 ± 0.1	5.1 ± 0.1	4.3 ± 0.1	5.3 ± 0.2	5.0 ± 0.2	5.1 ± 0.1	5.0 ± 0.1
1/n[a]	0.60 ± 0.02	0.64 ± 0.01	0.68 ± 0.01	0.72 ± 0.01	0.64 ± 0.02	0.74 ± 0.03	0.84 ± 0.03	0.66 ± 0.04	0.64 ± 0.03	0.62 ± 0.02	0.72 ± 0.02
R^2	0.989	0.996	0.999	0.996	0.989	0.990	0.986	0.969	0.968	0.988	0.988
K_d[a]	4.0 ± 0.2	4.3 ± 0.2	4.5 ± 0.2	4.5 ± 0.2	4.3 ± 0.2	4.1 ± 0.2	3.7 ± 0.1	4.2 ± 0.2	3.9 ± 0.2	3.9 ± 0.2	4.1 ± 0.1
R^2	0.882	0.884	0.891	0.896	0.870	0.866	0.876	0.879	0.876	0.878	0.895
K_{OC}[b]	331	355	372	372	355	339	306	347	322	322	339

[a] mean value ± standar error

[b] $K_{OC} = (K_d \times 100) / \%OC$

3.3.3.3. Dimethenamid and fenarimol in SV, RM1 and RM3 soils

Retention of DIM and FEN in the three soils (SV, RM1 and RM3) was studied through multipoint adsorption isotherms. Adsorption data were well adjusted to the Freundlich model with R^2 values ≥ 0.91 for DIM, and ≥ 0.99 for FEN (Figure 3.10; Table 3.8). According to the K_f values, it can be inferred that DIM and FEN were weakly and moderately sorbed by soils, respectively. Adsorption isotherms of FEN were close to linearity (C-type) with 1/n values ≥ 0.90, as well as those of DIM in RM1 soil (1/n ≥ 0.83) pointing to a relatively high contribution of a partitioning mechanism. In contrast, adsorption isotherms of DIM in SV and RM3 soils were L-type, especially at high concentrations of DOC in the background solution (Table 3.8). It is noticeable that for these two soils the coefficients 1/n were the highest for the DOC30 solution, likely due to the contribution of partitioning on the DOC fraction adsorbed on soil colloids.

As DOC amount increases, the interactions with pesticide molecules in solution become more important and partitioning is less relevant. Other authors have obtained similar values of 1/n for DIM (Archangelo et al., 2004), and in the range 0.42-0.89 for FEN (Oliver et al., 2003). Due to this, the K_f constants would be adequate indicators of adsorption extent. Nevertheless, for comparison with the other pesticides K_d and K_{OC} constants were calculated from fitting sorption isotherms to linear regression forced through the origin (Figure 3.11; Table 3.8). Fitting to the linear model was satisfactory, with R^2 ≥ 0.85 and R^2 ≥ 0.88 for DIM and FEN respectively. When considering the three soils adsorption of FEN was ordered as SV > RM3 > RM1, whereas that of DIM was RM1 > SV ≈ RM3, indicating that different mechanisms are involved depending on pesticide and soil properties. Although RM1 has the lowest OC content, data of K_{OC} reflect that, either this OC is the most effective in retaining pesticides or other soil fractions contribute significantly to pesticide adsorption.

The distribution coefficients obtained for FEN (L kg^{-1}) were in accordance with those previously found for a mine soil with a similar OC content, but the authors found a much lower K_d in a degraded soil with a very low OC content (0.23%) (Rodríguez-Liébana et al., 2013).

A wide range of K_d values (7.41-50.94 L kg^{-1}) was reported for FEN adsorption on Australian surface soils for a wide range of OC contents (Oliver et al., 2003). The latter works suggest that OC content is the main factor controlling adsorption of FEN on soils, depending on their land use. In fact, in our study the adsorption of FEN was ranged according to the OC content of the soils. This hypothesis is supported by the relatively low coefficient of variation of K_{OC} (CV = 17%) when all the soil–solution systems are considered.

However it is difficult to establish a significant role of OM in pesticide adsorption on soils with low OC content (< 2%) (Hernández-Soriano et al., 2007b). Therefore the influence of soil OM cannot be explained on the basis of OC content alone but also of variation in the chemistry of the OC. Some authors have concluded that aromaticity is the key fraction of soil OC controlling adsorption of non-ionic pesticides (Ahmad et al., 2001; Smernik and Kookana, 2015). Another study has found a strong correlation between FEN adsorption and both the aromatic and alkyl fractions of soil OC (Oliver et al., 2005b). The increases of these two fractions, which represent predominantly the hydrophobic constituents of soil OC, were related with an enhanced adsorption of increasingly hydrophobic compounds. Additionally, contribution of the mineral fraction to the overall adsorption of FEN may occur by coulombic-based attractions between the negative charges of the minerals and the positively charged regions of FEN molecule (Wehtje et al., 2000).

The values of K_d obtained for DIM were in accordance with those reported in the range 0.39-6.87 L kg^{-1} (Vasilakoglou et al., 2001; Archangelo et al., 2004). This oscillation may be attributed to the high variability of the soils used in these studies in terms of clay content (22-75%) and OC content (0.68-8.53%). DIM adsorption on RM1 soil was approximately twice the one calculated on the other two soils. Since RM1 has the lowest OC content, our findings contradict other results which have shown that OM is the most important factor in the adsorption of chloroacetamides (Weber and Peter, 1982; Peter and Weber, 1985; Clay et al., 1997, Oliveira et al., 2001) through different interactions such as charge transfer, van der Waals forces or hydrogen bonds (Torrents et al., 1997). In fact, Archangelo et al. (2004) reported a strong relationship between DIM adsorption and OC content of soils. The great variation of DIM K_{OC} (CV = 63%) indicated that not only OC but also other soil fractions are relevant in the adsorption process, especially in RM1 with K_{OC} values approximately 3-fold than those for SV and RM3.

The relative importance of mineral soil components in the adsorption of chloroacetamide herbicides is subject to debate. Archangelo et al. (2004) have also found that the adsorption of DIM is positively correlated with CEC, indicating that other soil properties should be taken into account when evaluating the adsorption of this pesticide.

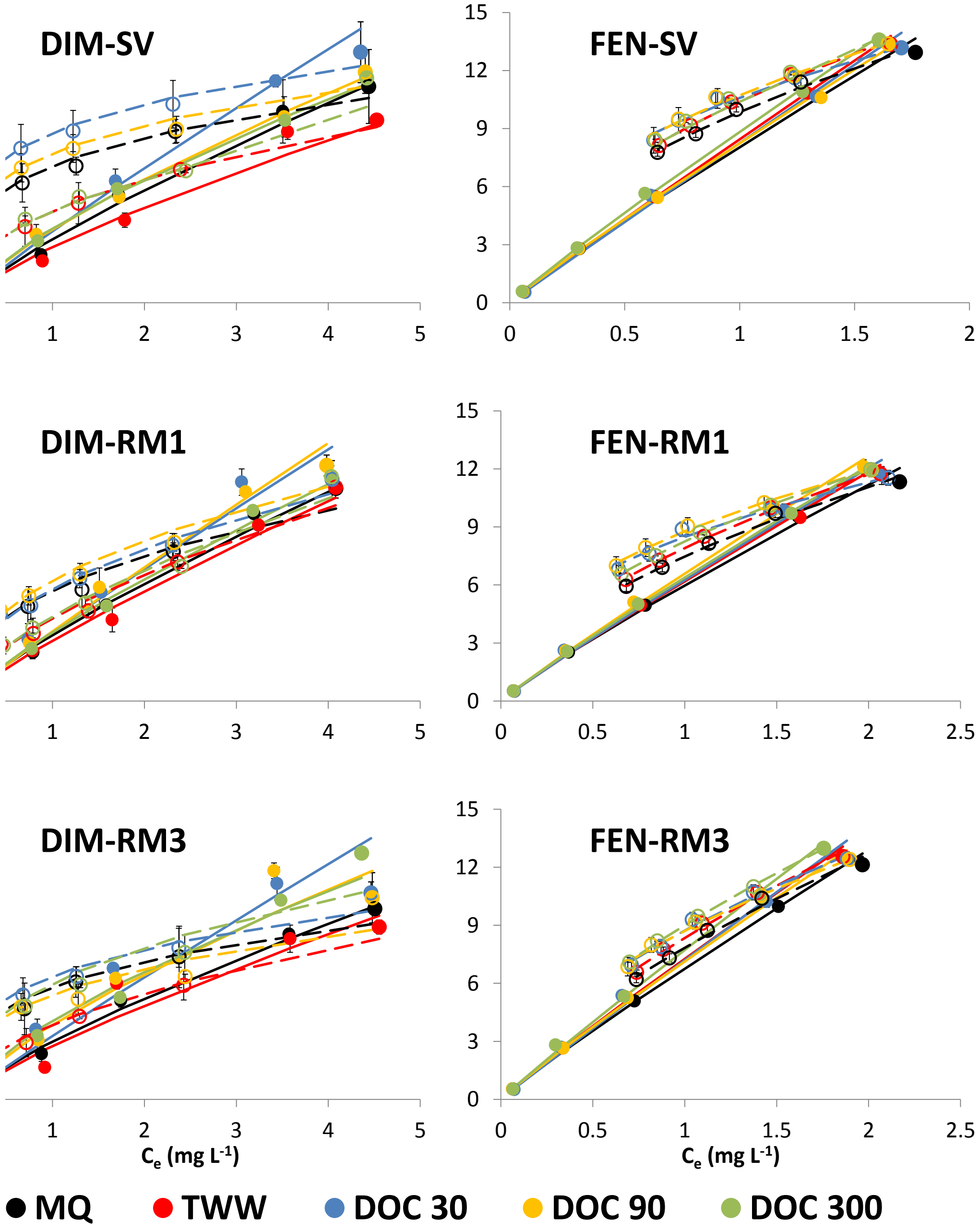


Figure 3.10. Adsorption isotherms (filled symbols and continuous lines) and desorption isotherms (unfilled symbols and dashed lines) of dimethenamid (DIM) and fenarimol (FEN) in the three soils (SV, RM1 and RM3). Points are the experimental data, whereas lines correspond to the fitting to the Freundlich model. Vertical bars represent the standard deviation of the mean value (n = 3)

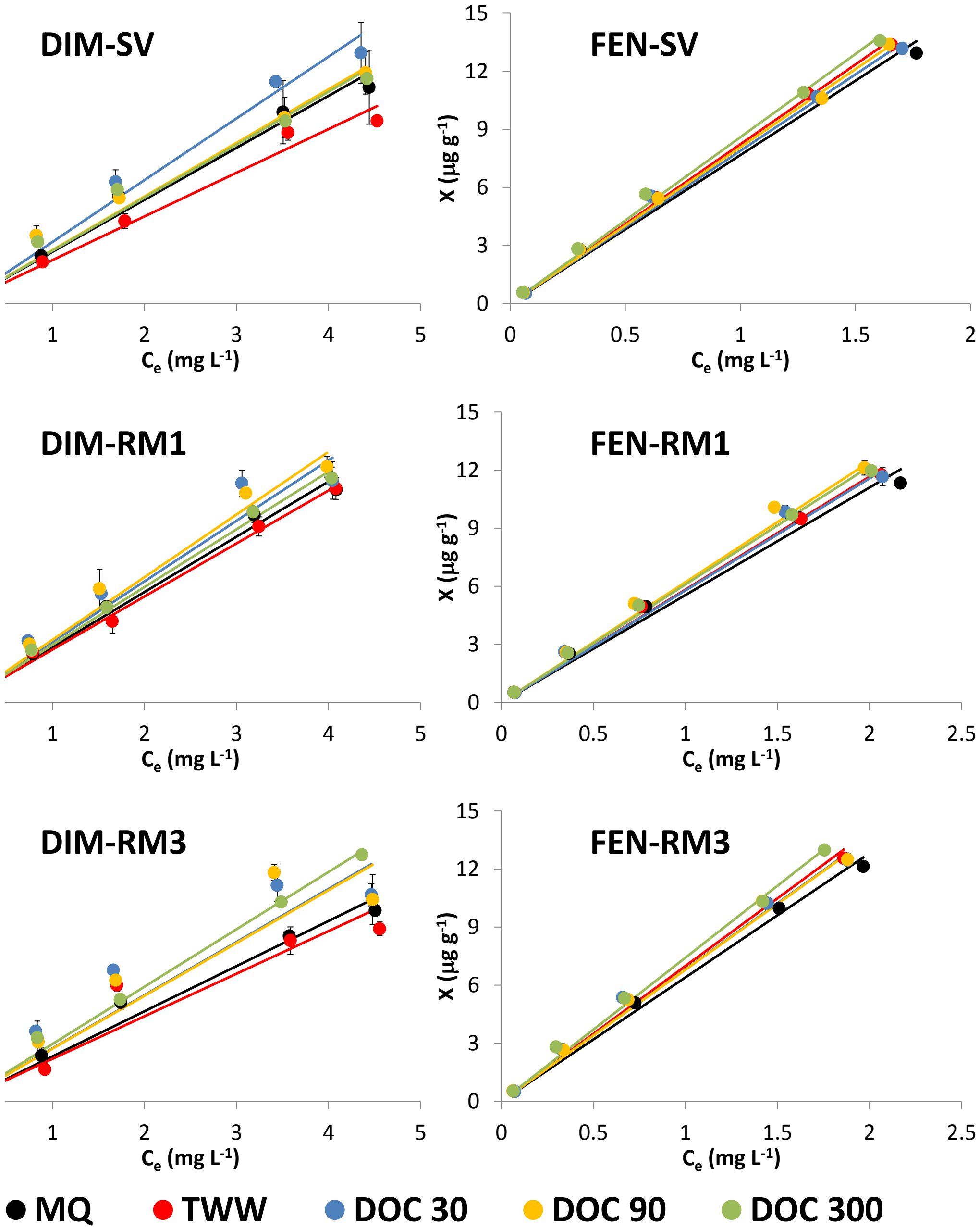


Figure 3.11. Adsorption isotherms of dimethenamid (DIM) and fenarimol (FEN) in the three soils (SV, RM1 and RM3). Points are the experimental data, whereas lines correspond to the fitting to the linear model. Vertical bars represent the standard deviation of the mean value (n = 3)

Similarly, Peter and Weber (1985) have found enhanced adsorption of other chloroacetamides with increasing clay content. Mineral contribution to adsorption may be significant or even dominate when the pesticide polarity is high and/or when soil clay:OC ratio is high (Karickhoff, 1984; Roy and Krapac, 1994), as is the case of RM1 soil (clay:OC ratio ≈ 80). A clay:OC ratio of 25-60 has been proposed as the threshold from which mineral contribution becomes important (Mingelgrin and Gerstl, 1983). In a recent work Smernik and Kookana (2015) have reported an important influence of OM–mineral interactions on K_{OC} of diuron, but the magnitude of these interactions is not reflected with such a simple measure as soil clay content.

Contrary to what happened with the rest of the pesticides, the adsorption of FEN seems to increase in a linear relationship ($R^2 \geq 0.90$, $P \leq 0.05$) with increasing concentration of DOC in the background solution, except for RM1 soil (Figure 3.12). This adsorption increase was more pronounced for RM3 soil as indicated for the slopes of the straight lines.

Adsorption increases in the presence of DOC could be justified considering initial adsorption of DOC on the soil surface, which would interact with pesticide molecules by hydrophobic or physical mechanisms. Similar results have been exposed for organic pollutants with hydrophobicity similar to that of FEN (Flores-Céspedes et al., 2006).

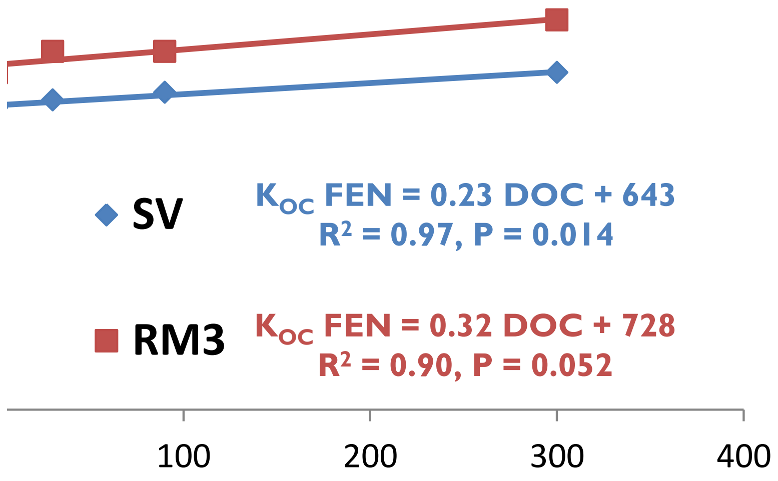


Figure 3.12. Relationship, in SV and RM3 soils, between organic-carbon normalised adsorption constants (K_{OC}) of fenarimol (FEN) and concentration of DOC in the background solution.

Table 3.8. .Adsorption constants (± standard error) of dimethenamid (DIM) and fenarimol (FEN) in SV, RM1 and RM3 soils derived from the fitting to the Freundlich (K_f and 1/n) and linear (K_d and K_{OC}) models

		MQ	DOC 30	DOC 90	DOC 300	TWW	MQ	DOC 30	DOC 90	DOC 300	TWW
Soil				*DIM*					*FEN*		
SV	K_f^a	0.66 ± 0.03	0.74 ± 0.05	0.76 ± 0.02	0.77 ± 0.02	0.58 ± 0.03	8.1 ± 0.3	8.3 ± 0.3	8.3 ± 0.1	8.9 ± 0.1	8.5 ± 0.2
	$1/n^a$	0.83 ±0.04	0.91 ± 0.06	0.75 ± 0.02	0.72 ± 0.02	0.77 ±0.04	0.93 ± 0.02	0.98 ± 0.03	0.93 ± 0.01	0.93 ± 0.01	0.96 ± 0.01
	R^2	0.980	0.962	0.991	0.990	0.975	0.994	0.993	0.999	1	0.998
	K_d^a	0.54 ± 0.03	0.64 ± 0.03	0.55 ± 0.02	0.55 ± 0.02	0.45 ± 0.01	7.7 ± 0.2	7.9 ± 0.2	8.1 ± 0.1	8.6 ± 0.1	8.2 ± 0.1
	R^2	0.867	0.875	0.887	0.877	0.880	0.884	0.896	0.899	0.887	0.888
	K_{OC}^b	45	53	45	45	37	636	653	669	711	678
RM1	K_f	1.1 ± 0.0	1.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.0	1.0 ± 0.0	6.0 ± 0.1	6.3 ± 0.2	6.6 ± 0.2	6.4 ± 0.1	6.2 ± 0.2
	1/n	0.83 ± 0.03	0.93 ± 0.04	0.94 ± 0.05	0.83 ± 0.02	0.86 ± 0.03	0.90 ± 0.01	0.94 ± 0.03	0.94 ± 0.02	0.93 ± 0.01	0.93 ± 0.02
	R^2	0.991	0.979	0.977	0.996	0.986	0.999	0.990	0.995	0.999	0.995
	K_d^a	0.95 ± 0.02	1.04 ± 0.05	1.08 ± 0.04	0.99 ± 0.02	0.91 ± 0.02	5.6 ± 0.1	5.8 ± 0.2	6.2 ± 0.2	6.1 ± 0.1	5.8 ± 0.1
	R^2	0.884	0.877	0.890	0.885	0.883	0.883	0.888	0.892	0.887	0.886
	K_{OC}^b	158	173	180	165	152	933	967	1033	1017	967
RM3	K_f	0.60 ± 0.02	0.66 ± 0.06	0.77 ± 0.04	0.82 ± 0.04	0.55 ± 0.06	6.8 ± 0.1	7.2 ± 0.2	7.2 ± 0.1	7.8 ± 0.4	7.3 ± 0.1
	1/n	0.80 ± 0.03	0.94 ± 0.07	0.74 ± 0.04	0.70 ± 0.04	0.82 ± 0.09	0.93 ± 0.02	0.98 ± 0.03	0.93 ± 0.01	0.95 ± 0.03	0.94 ± 0.01
	R^2	0.987	0.951	0.974	0.971	0.909	0.998	0.993	0.998	0.989	0.999
	K_d^a	0.47 ± 0.02	0.55 ± 0.04	0.55 ± 0.04	0.59 ± 0.02	0.44 ± 0.03	6.4 ± 0.1	6.8 ± 0.2	6.8 ± 0.2	7.4 ± 0.1	7.0 ± 0.1
	R^2	0.879	0.860	0.852	0.883	0.850	0.886	0.895	0.894	0.887	0.886
	K_{OC}^b	52	61	61	66	49	711	756	756	822	778

[a] mean value ± standar error

[b] $K_{OC} = (K_d \times 100) / \%OC$

3.3.4. Desorption isotherms

Experimental data for the three soils were satisfactorily fitted to the Freundlich isotherm with R^2 in the range 0.721-0.954 for DIM and 0.860-0.998 for FEN. Desorption isotherms are presented in Figure 3.10 together with the adsorption isotherms. The Freundlich desorption coefficients K_{fd} and $1/_{nd}$, as well as the hysteresis coefficients (H) and desorption percentages (D) are listed in Table 3.9.

Desorption isotherms of both compounds showed varying degree of hysteresis depending on the soil and the solution used, confirming that a redistribution process occurred continuously over the experimental time. This indicates that adsorption process was only partially reversible. In general, DIM desorption showed higher hysteresis effect (lower H) than that of FEN. In contrast, FEN desorbed less than DIM from the three soils reflecting the hydrophobic nature and the water solubility of each pesticide. It can be said that D values did not correspond with adsorption extent for both pesticides. On one hand, D values for FEN can be ranged as SV < RM1 ≈ RM3 (Table 3.9). This disagreement can be attributed to the less hysteretic behaviour (higher H coefficients) found in RM3 soil, resulting that FEN is desorbed in a similar extent from RM3 and RM1 soils. On the other hand, DIM desorption was practically ranged in an inverse order to that of adsorption, that is SV ≈ RM3 < RM1. Thus, hysteresis effect for DIM increased with increasing soil OC content, but it was not the case of FEN desorption. These findings reflect the complexity of the pesticide–soil interactions. For a particular soil no or low differences in FEN desorbed amount was observed for the different solutions, while that of DIM was higher with the solutions that exhibited the higher adsorption reversibility (higher H), that is TWW and DOC 300.

In all the cases K_{fd} is higher than the corresponding K_f for adsorption, indicating that greater proportion of pesticides were retained by soil during desorption as compared to adsorption at equilibrium (Krishna and Philip, 2008). This has been explained in the literature by breakdown of soil particles, thus increasing the number of sorption sites during the desorption phase, as a consequence of repeated centrifugation and resuspension of the soil followed by prolonged agitation in the batch method (Delle Site, 2001). Chemical and microbiological degradation, as well as the formation of bound residues have been also proposed (Clay and Koskinen 1990; Delle Site, 2001).

Table 3.9. Freundlich desorption coefficients (K_{fd} and $1/n_d$) (± standard error) of dimethenamid (DIM) and fenarimol (FEN) in soils. H: hysteresis coefficient, D: desorption percentage; E: efficiency coefficient

		MQ	**DOC 30**	**DOC 90**	**DOC 300**	**TWW**	**MQ**	**DOC 30**	**DOC 90**	**DOC 300**	**TWW**
Soil				*DIM*					*FEN*		
SV	K_{fd}	1.4 ± 0.1	1.8 ± 0.1	1.6 ± 0.0	1.0 ± 0.0	0.95 ± 0.05	9.9 ± 0.1	10.6 ± 0.2	10.8 ± 0.1	10.7 ± 0.0	10.4 ± 0.1
	$1/n_d$	0.27 ±0.04	0.22 ±0.05	0.25 ±0.03	0.45 ± 0.04	0.43 ± 0.05	0.51 ± 0.03	0.41 ± 0.05	0.45 ± 0.04	0.52 ± 0.01	0.53 ± 0.02
	R^2	0.838	0.721	0.845	0.928	0.877	0.976	0.860	0.918	0.995	0.985
	H[a]	0.33	0.24	0.33	0.63	0.56	0.55	0.42	0.48	0.56	0.55
	D[b]	48 ± 5	44 ± 4	48 ± 3	68 ± 2	64 ± 7	40 ± 1	37 ± 3	37 ± 2	38 ± 0	39 ± 1
	E[c]	1.00	1.24	1.09	0.73	0.67	1.00	1.08	1.09	1.09	1.05
RM1	K_{fd}	1.9 ± 0.1	1.9 ± 0.1	2.1 ± 0.1	1.5 ± 0.1	1.4 ± 0.1	7.5 ± 0.1	8.5 ± 0.1	8.8 ± 0.1	8.3 ± 0.0	7.9 ± 0.0
	$1/n_d$	0.39 ± 0.06	0.44 ± 0.04	0.41 ± 0.03	0.63 ± 0.05	0.61 ± 0.04	0.57 ± 0.03	0.42 ± 0.04	0.44 ± 0.04	0.53 ± 0.01	0.57 ± 0.01
	R^2	0.817	0.902	0.920	0.954	0.954	0.974	0.910	0.913	0.998	0.995
	H	0.47	0.47	0.44	0.76	0.71	0.63	0.45	0.47	0.57	0.61
	D	60 ± 8	62 ± 2	61 ± 2	75 ± 3	74 ± 0	48 ± 2	42 ± 1	42 ± 2	45 ± 0	47 ± 0
	E	1.00	1.02	1.09	0.76	0.75	1.00	1.14	1.17	1.10	1.06
RM3	K_{fd}	1.2 ± 0.1	1.3 ± 0.1	1.1 ± 0.1	1.2 ± 0.1	0.77 ± 0.04	7.8 ± 0.1	8.7 ± 0.2	8.7 ± 0.1	9.0 ± 0.0	8.4 ± 0.1
	$1/n_d$	0.30 ± 0.07	0.28 ± 0.04	0.32 ± 0.05	0.39 ± 0.06	0.50 ± 0.05	0.70 ± 0.04	0.58 ± 0.05	0.55 ± 0.04	0.65 ± 0.01	0.69 ± 0.03
	R^2	0.640	0.765	0.748	0.834	0.910	0.973	0.923	0.923	0.998	0.985
	H	0.38	0.30	0.43	0.56	0.61	0.75	0.59	0.59	0.68	0.73
	D	51 ± 16	50 ± 1	59 ± 3	64 ± 2	70 ± 2	49 ± 1	44 ± 1	45 ± 2	45 ± 0	48 ± 1
	E	1.00	1.09	0.94	1.03	0.66	1.00	1.11	1.11	1.15	1.07

[a] $H = 1/n_d / 1/n_a$

[b] $D (\%) = (X_0 - X_f) * 100 / X_0$

[c] $E = K_{fd} / K_{fd(MQ)}$

In order to establish the influence of the background solution in the sorption capacity of the soils, an efficiency coefficient (E) was calculated as $E = K_{fd\,(bckg)}/K_{fd\,(MQ)}$ (Rodríguez-Cruz et al., 2008). E values (Table 3.9) indicated that the use of TWW effectively reduced the adsorption capacity of soils for DIM, as well as DOC at the highest concentration, except for RM3 soil. In contrast, the affinity of soils for FEN was slightly increased in the presence of DOC without a defined pattern, but was practically not altered by TWW.

3.4. CONCLUSIONS

Kinetic studies show a high contribution of an initial rapid adsorption stage for all the pesticides. Diffusion into the soil micropores was relevant for the more hydrophobic compounds, CYP, DTM and PDM.

Pesticide adsorption was better explained by the Freundlich equation, confirming the heterogeneity of the substrate. Care has to be taken to avoid the retention on the laboratory glassware of the more hydrophobic compounds (CYP, DTM and PDM).

Adsorption is directly related to pesticide hydrophobicity and inversely dependent on water solubility. Treated wastewater increases the adsorption on soil of the more hydrophobic compounds (log K_{ow} > 4.2) without affecting the behaviour of more polar pesticides. Salt concentration seems to be the main factor involved in this process.

Adsorption of CYP, DTM and PDM is enhanced at low DOC concentrations (3-9 mg L^{-1}) but reduced at higher DOC concentrations (30-90 mg L^{-1}). Only a slight effect of DOC on the adsorption of more polar pesticides (DIM, FEN and THC) was found.

Hysteretic effects occurred in the desorption of DIM and FEN from soils, indicating that adsorption was partially reversible. The use of TWW and high DOC concentrations (300 mg L^{-1}) resulted in a higher reversibility of DIM adsorption.

4. RELEASE FROM SOILS

4.1. INTRODUCTION

In the field, pesticides are typically sprayed on the soil surface, which usually dries before rain or irrigation. After water is applied, a fraction of the pesticide is dissolved or desorbed into the soil solution, resulting in a potential risk of groundwater contamination in the medium- to long-term. The extent to what a pesticide is released from soil particles to the soil solution is expected to be highly dependent on pesticide and soil physicochemical properties, as well as on the composition of the irrigation solution. In general, pesticides with low water solubility and high log K_{OW} will tend to remain adsorbed, being less susceptible to desorption.

The increased pesticide–soil contact time (ageing) leads to the formation on non-extractable residues, due to the existence of stronger bonds or physical entrapment of the compound in the soil OM or mineral lattice (Gevao et al., 2000; Sharer et al., 2003; Walker et al., 2005).

It is well-known that DOM, added with the irrigation solution, may act as a mobile sorbent phase for pesticides (Chiou et al., 1986), thus increasing desorption by the formation of stable pesticide–DOM complexes (Graber et al., 2001; Li et al., 2005; Barriuso et al., 2011). This fact is enhanced by pretreating soil with the pesticide and allowing the carrier solvent to evaporate prior to the soil–solution contact (Williams et al., 2006). The concentration of DOC largely controls the concentration of hydrophobic contaminants in the soil solution, being the high-molecular-weight fraction (> 14000 dalton) the most effective one (Kögel-Knabner and Totsche, 1998; Kögel-Knabner et al., 2000). As we have seen in the adsorption chapter, it is well-recognized that the ability of a soil to adsorb non-ionic pesticides is related with the soil OM content. Conversely, soil OM can be a source of natural DOM that can increase the amount of solubilised hydrophobic organic compounds (Maxin and Kögel-Knabner, 1995; Williams et al., 2006). Therefore, not only the amount but also the nature of soil OM is an important factor to take into account.

Apart from the nature and concentration of DOM, irrigation water may contain some inorganic salts, known to affect pesticide sorption-desorption, as reflected in the adsorption chapter. Particularly relevant are surfactants, discharged into the sewer system from domestic or industrial activities, which are therefore present in wastewaters.

In this chapter we have assessed the effects of the irrigation solution composition on the availability (water-extractability) of THC and FEN previously adsorbed on soil. This approach is intended to be closer to real conditions in the field. The role in pesticide solubilisation of non-ionic and anionic surfactants, the most frequently used classes of surfactants (CESIO, 2013; Ying, 2006), as well as DOM from sewage sludge and some inorganic salts has been investigated.

4.2. EXPERIMENTAL SETUP

4.2.1. Soil fortification and desorption experiments

Aliquots of 10 g of SV and RM3 soils were finely ground and spiked with 5 mL of either THC or FEN at 1 g L^{-1} in acetone. After solvent evaporation, the aliquots were mixed with the rest of the soil samples (up to 250 g) to give a nominal initial pesticide concentration of 20 mg kg^{-1} (dry weight). Such high pesticide concentration was used to assure analytical sensitivity with the different solutions employed for desorption. Contaminated soil samples were sieved (2 mm), transferred to glass bottles and homogenised by shaking for two weeks at room temperature in the darkness (González et al., 2010). Afterwards, soil samples were stored (4 °C) for subsequent experiments.

Pesticide desorption was assessed by batch triplicate tests. Two grams of pesticide-fortified soils were placed in 30 mL Pyrex centrifuge glass tubes to which 20 mL of the corresponding solution was added, including MQ, TWW, anionic and non-ionic surfactants, two kinds of DOC from sewage sludge, and inorganic salts (Table 4.1). After 24 h shaking at 20 °C, the suspensions were centrifuged at 3000 rpm for 15 min and supernatants were filtered (PVDF filters, 0.45 μm) for subsequent analysis.

4.2.2. Analytical determinations

Solubilised pesticides were determined in the supernatants by HPLC-DAD, as indicated in section 2.2.5.1. Solution pH and EC were also measured before and after the batch experiments (Table 4.2). Fluorescence spectra of supernatants were recorded according to Zsolnay (2003) from 300 to 480 nm under excitation at 254 nm (see section 2.1.15.2). Fluorescence values relative to the maximal intensity were calculated for comparison among different spectra (Cox et al., 2000). Additionally, after desorption, soils were air-dried at room temperature to determine OC content.

Table 4.1. Solutions employed for desorption experiments

Solution	Supplier	Abbreviation	Concentration range	Critical micelle concentration (CMC) (g L^{-1})
Milli Q water		MQ		
Wastewater		TWW		
Sewage extracted with MQ		SS-MQ	3-30 mg DOC L^{-1}	
Sewage extracted with NaH_2PO_4 (50 mM)		SS-Ph	3-30 mg DOC L^{-1}	
Calcium chloride	Panreac	$CaCl_2$	5 and 10 mM	
Ammonium sulfate	Probus	$(NH_4)_2SO_4$	5 and 10 mM	
Aerosol 22	Sigma	A22	0.2-10 CMC	0.65
Biopower	Bayer	BP	0.2-10 CMC	2.70
Triton X100	Merck	TX-100	0.2-10 CMC	0.16
Tween 80	Sigma	TW-80	0.2-10 CMC	0.02

4.2.3. Data analysis

The results obtained for the different solutions were expressed as the percentage of desorption variation (D) relative to that corresponding to MQ water, performed with each batch series in order to control possible losses by volatilisation, degradation or adsorption on the glassware. D values were calculated according to the equation:

$$D(\%) = \frac{D_{SOL} - D_{MQ}}{D_{MQ}} \times 100 \qquad [4.1]$$

where D_{SOL} and D_{MQ} are the percentage of pesticide desorbed with each solution and MQ water, respectively.

Statistical analysis was performed following the rules established in the section 2.8.

4.3. RESULTS AND DISCUSSION

4.3.1. Desorption with MQ and treated wastewater

The absolute desorption rates were 49.1 ± 2.5% (MQ-SV), 48.9 ± 2.9% (TWW-SV), 58.2 ± 2.8% (MQ-RM3) and 59.7 ± 1.4% (TWW-RM3) for THC; and 34.6 ± 1.4% (MQ-SV), 35.1 ± 2.4% (TWW-SV), 38.9 ± 0.7% (MQ-RM3) and 41.0 ± 1.4% (TWW-RM3) for FEN. From these data, it can be said that THC was desorbed to a greater extent than FEN, approximately 1.5 times more from each soil, which is directly linked to its lower hydrophobicity and higher water solubility.

Table 4.2. Soil organic carbon content (%) and some properties of the supernatants after the desorption assay (± standard deviation) (n = 4)

Solutions	Concn.[a]	SV			RM3		
		Soil OC (%)	pH	EC x 10^3 (dS m^{-1})	Soil OC (%)	pH	EC x 10^3 (dS m^{-1})
MQ (Control)		1.19 ± 0.02	8.21 ± 0.05	493 ± 8	0.86 ± 0.01	8.36 ± 0.07	143 ± 6
SS-MQ	3	1.41 ± 0.11	8.23 ± 0.03	477 ± 5	0.90 ± 0.02	8.19 ± 0.05	129 ± 2
	9	1.28 ± 0.11	8.11 ± 0.03	501 ± 5	0.95 ± 0.03	8.09 ± 0.01	149 ± 3
	15	1.30 ± 0.08	8.02 ± 0.02	516 ± 6	1.05 ± 0.08	8.13 ± 0.02	170 ± 1
	30	1.30 ± 0.01	7.95 ± 0.03	549 ± 4	1.06 ± 0.06	8.08 ± 0.04	215 ± 3
SS-Ph	3	1.15 ± 0.05	8.35 ± 0.06	446 ± 3	0.84 ± 0.02	8.79 ± 0.01	121 ± 1
	9	1.13 ± 0.02	8.31 ± 0.05	474 ± 4	0.80 ± 0.02	8.47 ± 0.02	156 ± 1
	15	1.18 ± 0.04	7.81 ± 0.05	539 ± 11	0.91 ± 0.02	7.92 ± 0.04	218 ± 2
	30	1.15 ± 0.01	7.79 ± 0.03	590 ± 5	0.83 ± 0.00	7.90 ± 0.05	294 ± 2
$CaCl_2$	5	1.20 ± 0.00	7.94 ± 0.02	1578 ± 38	1.01 ± 0.02	7.82 ± 0.04	1306 ± 7
	10	1.17 ± 0.03	7.83 ± 0.03	2727 ± 112	0.90 ± 0.02	7.73 ± 0.02	2485 ± 64
$(NH_4)_2SO_4$	5	1.44 ± 0.06	7.80 ± 0.03	1661 ± 22	0.96 ± 0.04	7.83 ± 0.01	1320 ± 12
	10	1.15 ± 0.04	7.69 ± 0.03	2858 ± 52	0.95 ± 0.03	7.70 ± 0.02	2465 ± 51
A22	0.2	1.18 ± 0.00	8.25 ± 0.02	463 ± 7	0.88 ± 0.02	8.48 ± 0.01	149 ± 1
	2	1.21 ± 0.03	8.46 ± 0.02	566 ± 12	0.98 ± 0.01	8.78 ± 0.02	294 ± 2
	10	2.47 ± 0.16	8.94 ± 0.07	1278 ± 34	1.59 ± 0.05	9.18 ± 0.03	974 ± 18
BP	0.2	1.13 ± 0.01	8.23 ± 0.05	469 ± 1	0.78 ± 0.00	8.35 ± 0.01	198 ± 2
	2	1.55 ± 0.04	8.01 ± 0.04	931 ± 16	1.25 ± 0.02	8.09 ± 0.03	680 ± 2
	10	2.66 ± 0.10	7.87 ± 0.03	2270 ± 28	1.95 ± 0.05	7.92 ± 0.05	1920 ± 10
TW-80	0.2	1.10 ± 0.03	8.21 ± 0.02	454 ± 9	0.71 ± 0.01	8.41 ± 0.06	135 ± 3
	2	1.35 ± 0.01	8.17 ± 0.04	467 ± 5	0.77 ± 0.03	8.42 ± 0.02	136 ± 2
	10	1.37 ± 0.05	8.22 ± 0.03	514 ± 4	1.05 ± 0.03	8.42 ± 0.01	145 ± 1
TX-100	0.2	1.26 ± 0.04	8.13 ± 0.01	459 ± 7	0.97 ± 0.01	8.33 ± 0.02	145 ± 3
	2	1.46 ± 0.06	8.21 ± 0.01	448 ± 8	1.16 ± 0.02	8.34 ± 0.01	143 ± 1
	10	2.64 ± 0.01	8.29 ± 0.02	475 ± 10	1.91 ± 0.02	8.47 ± 0.04	140 ± 9

[a] Concentration units as described in Table 4.1

Additionally, these results evidence a greater difficulty in solubilising the pesticides from SV soil, due in part to a slightly higher OC content in SV. Despite the small difference in OC content (1.2 and 0.91%, respectively, Table 2.3) the high calcite content in RM3 (62%) may have further reduced the available OC, through the formation of aggregates between calcite and OM, as pointed out recently (El Arfaoui et al., 2010, 2012).

.In accordance with previous reports (González et al., 2010; Hernández-Soriano et al., 2012), and even though the experimental setup was not exactly identical (different soil-pesticide-solution proportions), pesticide desorption was not affected by TWW ($P > 0.05$), except for FEN in RM3 soil ($P = 0.037$). However, TWW is a complex mixture which may contain, among other constituents, large amounts of organic compounds, such as surfactants and other DOM molecules, as well as inorganic salts that could participate in the soil-pesticide-solution interactions (Barriuso et al., 2011; Müller et al., 2012; chapter 3). Additionally, seasonal and even hourly variations in TWW characteristics can occur, especially regarding the organic composition, due mainly to local factors such as temperature fluctuations and different domestic and industrial activities (Krzeminski et al., 2012; Camacho-Muñoz et al., 2014). Therefore, we have considered the role of each of these potential TWW components to be important for a better comprehension of the processes involved in the soil/solution interface.

4.3.2. Desorption with surfactant solutions

Two anionic and two non-ionic surfactants (Table 4.1) were assayed in a concentration range between 0.2 and 10 CMC. Pesticides desorbed differently depending on the type and structure of the surfactant, soil properties and pesticide polarity.

4.3.2.1. Thiacloprid

Desorption of THC increased with increasing BP concentrations for both soils ($P < 0.05$), especially for SV, for which a linear relationship was found between D and BP concentration ($D_{SV} = 21.86 + 1.37 \times CMC_{BP}$, $R^2 = 0.948$). For this surfactant D values were in the range 2.0-14.1% and 21.1-35.4% for RM3 and SV soils respectively. The other anionic surfactant assayed, A22, only increased significantly ($P < 0.05$) the desorption of this insecticide at the highest concentration (10 CMC) for both soils (D_{SV} = 18.4% and D_{RM3} = 12.0%) (Figure 4.1). Hernández-Soriano et al., (2012) also reported an enhanced desorption of the organophosphorous insecticide diazinon with BP solutions by bringing directly the pesticide into the aqueous medium. As it occurs in the present case, they also showed a slightly greater desorption of diazinon when using A22 at high concentrations. The lower effect of A22 when compared with BP in calcareous soils can be explained by the precipitation with Ca^{2+} of the surfactant salt (A22 is a tetrasodium sulfosuccinamate) due to a cation exchange of Ca^{2+} from soil with Na^{+} from the surfactant molecule (Hernández-Soriano et al., 2012). This precipitated salt could trap the desorbed molecules of THC, resulting in an apparent lower concentration in solution. A reduction of surfactant water solubility by divalent cations from soil has been also indicated for BP, but to a lower extent (Hernández-Soriano et al., 2011). Our results agree with them, resulting in an increase of THC desorption with an increase of BP micelle formation.

Regarding the non-ionic surfactants, TW-80 did not significantly affect THC desorption from both soils ($P > 0.05$) with D values ranging from -3.6% to 7.4%. On the other hand, as observed in Figure 4.1, TX-100 provided controversial results depending on the soil: it did not influence THC release from SV soil ($P = 0.271$), whereas its desorption from RM3 decreased with TX-100 concentration up to D = -44.3%.

It has been reported that soils with high clay content reduce the washing efficiency of non-ionic surfactants, which are adsorbed onto the soil particles, resulting in co-sorption of pesticides onto the hydrophobic moiety of the sorbed surfactant (Sánchez-Camazano et al., 2003; Wang and Keller 2008). In RM3 soil, clay particles (33%) may interact with TX-100 molecules, resulting in a stronger retention of THC on the soil matrix, by partitioning into immobile sorbed surfactant (Zhou and Zhu 2007). This is supported by the fact that the soil OC content after desorption with TX-100 increased linearly with surfactant concentration in both soils ($OC_{SV} = 1.21 + 0.14 \times CMC_{TX-100}$, R^2 = 0.994; $OC_{RM3} = 0.96 + 0.10 \times CMC_{TX-100}$, R^2 = 0.998), while when desorption is carried out with TW-80 this relationship is either not observed in SV or shows in RM3 a much lower slope than that of TX-100 ($OC_{RM3} = 0.70 + 0.03 \times CMC_{TW-80}$, R^2 = 0.978).

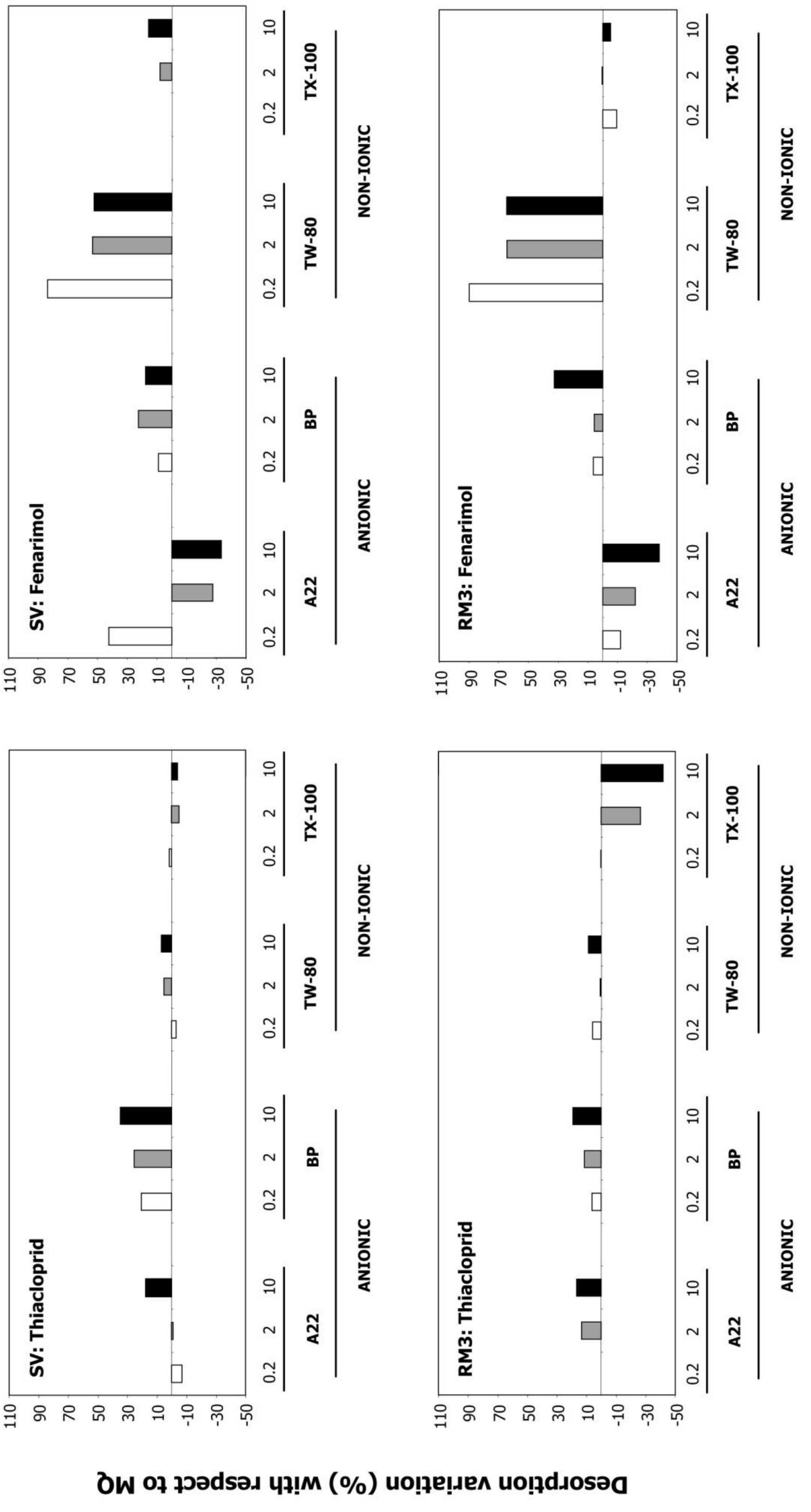


Figure 4.1. Effect of surfactant type and concentration (CMC) on the desorption extent (D, %) relative to that obtained with MQ water for thiacloprid and fenarimol, previously adsorbed on two calcareous soils, SV and RM3. A22, Aerosol 22; BP, Biopower; TW-80, Tween 80; TX-100, Triton X-100. For the same surfactant, concentration is presented in a range of colour from white (lower concentration) to black (higher concentration)

This finding is consistent with previous works which reported a greater difficulty of TX-100 in desorbing PAHs and pesticides from clay fractions and clayey soils (Zhou and Zhu 2007; Wang and Keller 2008).

The amount of non-ionic surfactants sorbed onto soil surface determines the overall pesticide desorbability, being clay content and CEC the soil properties controlling pesticide solubilisation (Wang and Keller 2008; Zheng et al., 2012).

4.3.2.2. Fenarimol

The desorption of FEN from both soils decreased significantly ($P < 0.05$) with A22 solutions at 2 and 10 CMC, likely again by complexation of the surfactant with Ca^{2+} from soils. However, it is worth mentioning that its desorption from SV soil increased considerably ($P < 0.05$) with A22 below the CMC up to D = 42.3% (Figure 4.1). In this soil, with lower amount of $CaCO_3$, the water solubility of A22 could be less affected by the presence of Ca^{2+} at this low concentration of surfactant (ca. 130 mg L^{-1}), leading to an enhanced release of the more hydrophobic FEN, by partitioning into the nonpolar core of A22 monomers (Zhou and Zhu 2007).

As it occurred with THC, FEN desorption showed a trend to increase with BP concentrations above the CMC, but without a defined pattern.

On the other hand, FEN desorption with non-ionic surfactants provided conflicting results. Firstly, TX-100 did not significantly affect the desorption process in RM3 soil ($P = 0.090$), although it increased in SV soil at 10 CMC (D = 15.6%; $P = 0.0017$). This suggests that higher concentrations of TX-100 would be required to effectively mobilise FEN from soils. The more difficult desorption of FEN from RM3 soil by TX-100 solutions could be probably due to its higher CEC and clay content, as occurred with THC.

Secondly, as can be seen in Figure 4.1, the amount of FEN desorbed was markedly enhanced in both soils ($P < 0.05$) by TW-80 solutions, especially below the CMC ($D_{SV} = 83.6\%$, $D_{RM3} = 89.8\%$). This result contradicts numerous studies that found that the release of hydrophobic organic contaminants from soils increases with the concentration of surfactants in solution (Sánchez-Camazano et al., 2003; Zhou and Zhu 2007; Wang and Keller 2008; Zheng et al., 2012). At low TW-80 concentration (0.2 CMC), surfactant monomers could improve FEN solubility by providing regions for specific interactions in solution. As TW-80 concentration increases (> CMC) some surfactant molecules could be weakly retained, as shown by the soil OC content (Table 4.2), providing additional sorbing points for FEN thus reducing its presence in solution. On the other hand, no significant differences were found between 2 and 10 CMC, probably because the soils do not have the capacity to adsorb more surfactant molecules (Wang and Keller 2008), as suggested by their OC content after the batch experiments (Table 4.2). Additional investigation would be useful to elucidate the saturation sorption capacity of the soils by surfactants.

4.3.3. Desorption with inorganic salt solutions and dissolved organic matter

The influence of DOC and inorganic salt solutions individually is shown in Figure 4.2. Two different kinds of DOC from sewage sludge (SS-Ph and SS-MQ) were used in a concentration range between 3 and 30 mg L^{-1}, which is that normally found in TWW. The two fractions, extracted from the same residue, have different polarity, as discussed below, and represent different DOC composition depending on the extracting solution used (Reemtsma et al., 1999). SS-Ph at 30 mg L^{-1} DOC had a pH 7.0 and EC 0.114 dS m^{-1}, while for SS-MQ at the same concentration pH was 6.9 and EC 0.074 dS m^{-1}. It must be emphasised that the highest DOC concentration used in this experiment does not correspond to the highest one employed in the adsorption chapter.

Likewise, $CaCl_2$ and $(NH_4)_2SO_4$ aqueous solutions were assayed at 5 and 10 mM. Both salts at 5 mM give an EC similar to that of TWW (Table 3.5).

4.3.3.1. Inorganic Salts

At the concentrations evaluated in this assay (5-10 mM), the effect of the salts on the relatively polar and water-soluble THC was negligible (Figure 4.2), in agreement with the results corresponding to adsorption using batch experiments (Figure 3.9, Table 3.7). On the other hand, desorption of the more hydrophobic FEN increased ($P < 0.05$) with $CaCl_2$ in RM3 (D = 21.7% for 5 mM and 17.5% for 10 mM) and showed a contradictory effect in SV when using $(NH_4)_2SO_4$ (D = 17.5% and -20.8%, for 5 and 10 mM respectively). These confuse results are in line with those in the literature, which underline the difficulty of identifying general trends in the environmental fate of pesticides in the presence of ubiquitous ions (El Arfaoui et al., 2010).

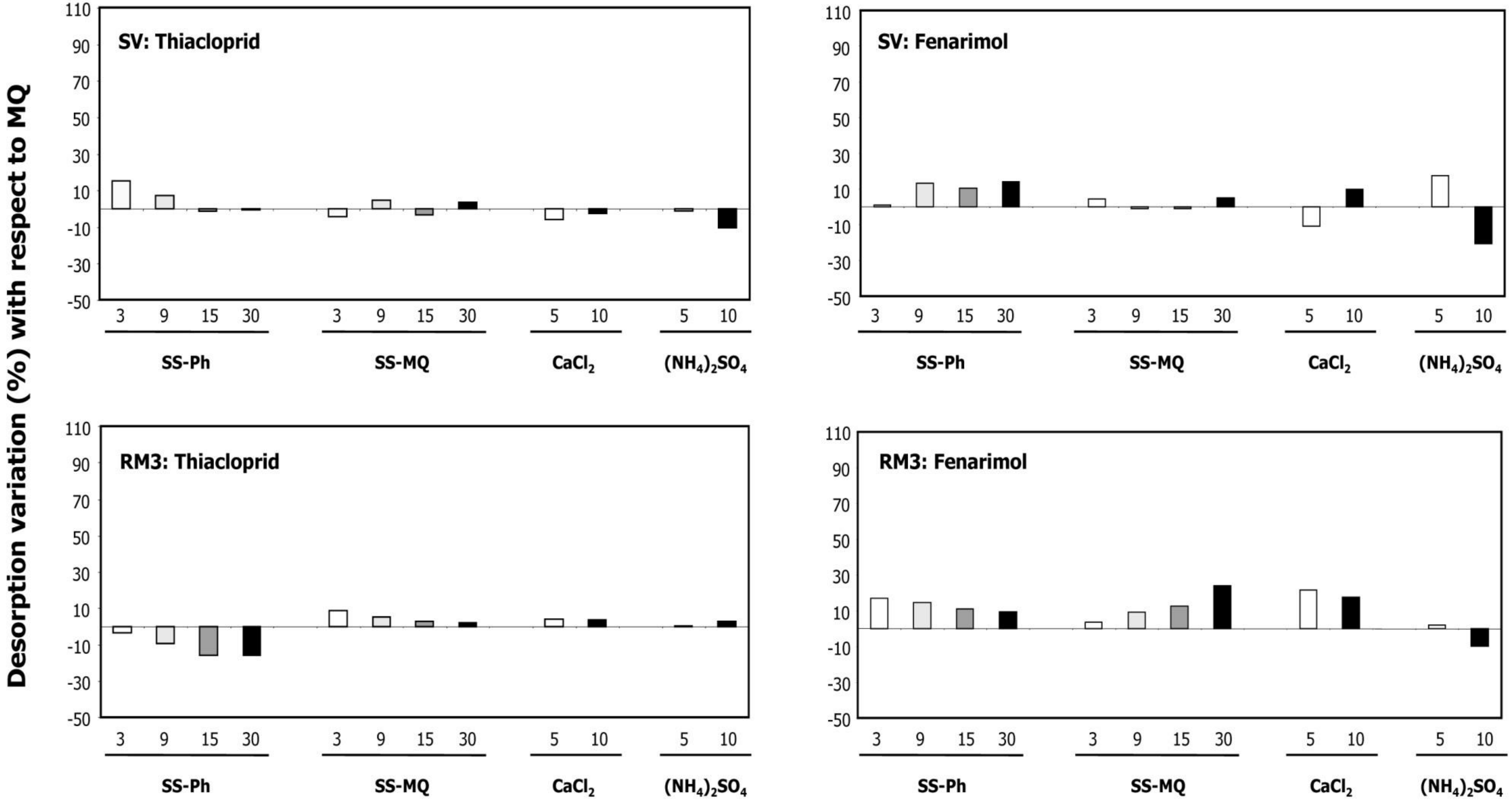


Figure 4.2. Effect of the type and concentration of sewage extracts (mg DOC L^{-1}) and of salt concentration (mM) on the desorption extent (D, %) relative to that obtained with MQ water for thiacloprid and fenarimol, previously adsorbed on two calcareous soils, SV and RM3. SS-Ph, sewage extracted with NaH_2PO_4 (50 mM); SS-MQ, sewage extracted with MilliQ water. For the same solution, concentration is presented in a range of colour from white (lower concentration) to black (higher concentration)

Literature reports have been found concerning the influence of salts on pesticide adsorption on soil (Alva and Singh, 1991; Spark and Swift, 2002; El Arfaoui et al., 2010), but not on pesticide desorption. Salts have been reported to affect the solubility of non-electrolytes due to a salting out effect, whose extent is related to temperature variation, effective pressure produced by salt dissolution and solvent compression in the presence of salts (Turner 2003; Saab et al., 2010). The solubility of different organic compounds decreases more with bivalent than with monovalent cations, with an increase in salt concentration and also with the increase in the ionic radius of the cation. For instance, the aqueous solubility of the fungicide metalaxyl, higher in pure water (8.4 g L^{-1}) than that of THC and FEN (Tomlin, 2003), was reduced by 2.5% (NaCl), 5.5% (KCl) or up to 30% ($CaCl_2$), using salt concentrations of 10 mM (Saab et al., 2011). On the contrary the solubility of the insecticide carbaryl (water solubility 120 mg L^{-1}) (Tomlin, 2003), increased with natural seawater but decreased with lab-made seawater (Saab et al., 2010). All these findings suggest that the nature of the organic compound largely affects the changes in solubility and that high salinity is needed to significantly affect the water solubility of the pesticides under study, thus modifying their water extractability from soil. Additionally, the presumable high amounts of Ca^{2+} in our experiments, due to the calcareous nature of both soils, could mitigate the effects of other ions present.

A further effect from salts in solution could be the mobilisation of soil OC, which could influence pesticide desorption even in these OC-poor soils. However, the soil OC content was not modified after desorption (Table 4.2) while the amount of DOC released by both salt solutions, estimated by the absorbance at 254 nm of the filtered supernatants after desorption (Artiola and Walworth 2009), was either not modified or even decreased with respect to MQ. This decrease was more pronounced for Cl^- than for SO_4^{2-}, in agreement with previous reports in the literature (Reemtsma et al., 1999; Rennert et al., 2007; Rashad et al., 2010). These findings highlight that the salt concentration range examined, similar or slightly higher than that normally found in TWW, had a low effect on the release of FEN and THC from both soils.

4.3.3.2. Dissolved organic matter

The effect of DOC solutions extracted from sewage sludge (SS-MQ and SS-Ph, Table 4.1) was evaluated by examining their fluorescence spectra. Both original solutions presented similar spectra with maximum absorbance close to 330 nm (Figure 4.3, top), a region which corresponds to non-humified compounds with a low condensation degree. Although both DOC solutions are obtained from the same residue, the normalized fluorescence spectrum of DOC in SS-Ph is higher at wavelengths > 400 nm, a region which corresponds to aromatic condensed molecules, typical from humic acids (Cox et al., 2007). This is confirmed by a higher HIX (0.54) and $SUVA_{254}$ (1.3, L $mg^{-1}C$ m^{-1}) for SS-Ph than the values corresponding to SS-MQ (0.43 and 1.1 L $mg^{-1}C$ m^{-1}, respectively).

After the batch assays with both soils, the fluorescence spectra of supernatants showed that both DOC solutions behaved similarly in the region > 400 nm, resembling those of the suspensions after desorption using MQ. However, at lower wavelengths the DOC solutions showed a different behaviour depending on the soil. For RM3 (Figure 4.3, bottom) the fluorescence spectra of the supernatants indicate that SS-MQ and SS-Ph almost overlapped indicating that they did not greatly differ in composition. In addition their polar fraction (in the range of 300-330 nm) was more abundant in the solution than when using MQ, suggesting a preferential binding of the higher molecular-weight DOC molecules to the soil in agreement with previous reports (Guo and Chorover 2003; Navon et al., 2011).This fact points to a lower retention of the polar DOC fraction with this soil.

Although the clay content of RM3 is higher than SV (33% vs 11%), the content in Fe and Al oxides, which has also been correlated with the soil binding capacity of DOC (Benke et al., 1999), is much higher in SV (Table 2.6). Therefore, the polar fractions of both DOC solutions are likely more bound to SV soil (Figure 4.3, middle).

Concerning pesticide desorption, no significant effect of any DOC solution was observed for the more polar THC for any soil ($P > 0.05$), in agreement with the adsorption behaviour described in the previous chapter (Table 3.7, Figure 3.9). The stronger absorbance of both DOC sources at $\lambda > 400$ nm, where the less polar and more complex organic compounds fluoresce, could explain the lack of interaction of both DOC sources with this relatively polar pesticide. In a previous report, the use of different DOC solutions only modified the desorption of the more hydrophobic pesticides, like DDT or α-cypermethrin (González et al., 2010).

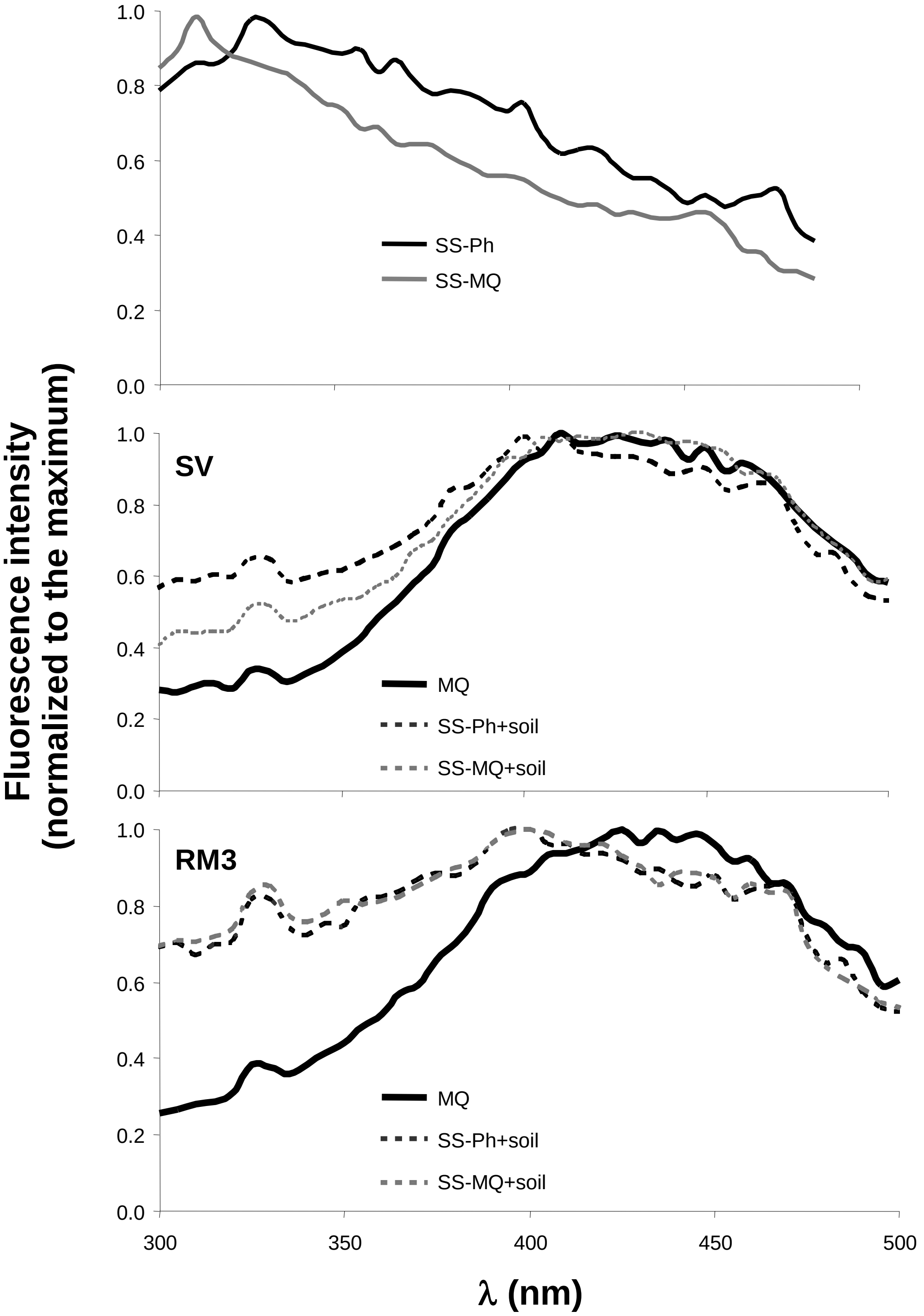


Figure 4.3. Normalized fluorescence spectra of DOC solutions (SS-Ph and SS-MQ) (top) and of the supernatant solutions from soils SV (middle) and RM3 (bottom), after desorption in batch, when using SS-MQ and SS-Ph at 30 mg OC L^{-1} each

In the case of FEN, more hydrophobic, desorption from SV was not significantly affected by SS-Ph or SS-MQ solutions (P = 0.06). In this soil the polar fractions were more bound to the surface, as above stated (Figure 4.3, middle). On the contrary, FEN desorption from RM3, always greater than that using MQ, depended on the type of solution used. It decreased as DOC concentration increased in the SS-Ph solution ($D_{SS-Ph} = 17.17 - 0.28 \times DOC_{conc}$; R^2 = 0.846), while it increased linearly with SS-MQ concentration ($D_{SS-MQ} = 1.60 + 0.75 \times DOC_{conc}$; R^2 = 0.994) reaching values up to D = 24.1% at the highest DOC concentration. Comparison with adsorption behaviour was only possible for DOC 30, for which FEN sorption was not greatly affected in any of the soils (Table 3.8, Figure 3.10).

The effect of DOC on pesticide solubilisation has been described to be two-fold. At low DOC concentrations, it can promote pesticide mobilisation from the soil matrix through the formation of pesticide-DOC complexes, a process which has been reported to be greater when soils are pretreated with pesticides (Williams et al., 2006). As DOC concentration increases, co-sorption with the pesticide molecules previously released to the solution due to the increased sorption capacity of the soil surface can occur (Flores-Céspedes et al., 2006). The relative extent of both solubilisation and co-sorption processes will depend on soil-DOC-pesticide system, and on the specific interactions between soil, solute and liquid phases (Cox et al., 2007). The current available data do not allow us to establish the mechanisms involved, which will determine the final environmental fate of the studied chemicals.

4.4. CONCLUSIONS

FEN solubilisation is linked to soil OC, but not that of THC, emphasizing the importance of pesticide properties. Likewise, the composition of the background solution plays a remarkable role in the release of both pesticides previously adsorbed.

Pesticide desorption largely depended on the soil-pesticide-surfactant system, suggesting that surfactants of the same type may behave differently. Anionic surfactants, especially BP was more effective in desorbing THC, while FEN was highly desorbed by the non-ionic TW-80. It is worth mentioning that the THC enhanced desorption was observed at BP concentrations of 27 g L^{-1}, far from the surfactant values normally found in wastewater. On the contrary, the high increase in FEN desorption occurred at a more environmentally sound concentration of TW-80

(4 mg L^{-1}). The environmental fate of A22 should be addressed for non-calcareous soils.

The effect of inorganic salts in the concentration range studied was variable for FEN but negligible for THC. Higher salt concentrations would be needed to effectively solubilise the pesticides.

The presence of DOC increased FEN desorption in all the cases with respect to the control, but in a different extent depending on the soil, and on DOC characteristics and concentration.

Water sources of similar characteristics (organic and inorganic composition) would be expected not to greatly affect the solubilisation from soil of relatively polar pesticides, such as THC.

5. DEGRADATION

5.1. INTRODUCTION

Beside sorption, degradation is the second most important process used to predict the environmental fate of pesticides and their potential risk of surface and groundwater contamination, since it directly controls the attenuation of pesticide residues in soil. The relative importance of this process depends on soil physicochemical (pH, OC content, textural composition) and biological properties (activity and distribution of microorganisms), climatic conditions (soil temperature and moisture content), and pesticide characteristics (water solubility, log K_{ow}) (Kah et al., 2007; Arias-Estévez et al., 2008; Grenni et al., 2012). Sorption and degradation have been in general negatively correlated due to a reduction of pesticide bioavailability with increased sorption (Guo et al., 1999; Kah and Brown, 2006; Grenni et al., 2012), because degradation occurs mainly in soil solution (Guo et al., 1999; Beulke et al., 2005).

Although abiotic factors may also be important (Delgado-Moreno and Peña, 2007; 2009), decomposition of most chemicals in the soil environment is mainly carried out by soil microorganisms (biodegradation), essentially bacteria and fungi (Kulshrestha et al., 2000; Ellegaard-Jensen et al., 2013), converting them generally into less toxic compounds. The extent of biodegradation can range from minor changes, which may not significantly affect the compounds' chemical and toxicological properties, to mineralisation processes (Von Wirén-Lehr et al., 2002; Ruoss et al. 2011; Kookana et al., 2014). The relative dominance of one process over another depends on the specific soil-pesticide system and cannot therefore be generalized (Kah et al., 2007). In most cases, soil microorganisms use pesticides as a source of energy and nutrients (Abdelhafid et al., 2000; Topp, 2001), or utilize them through cometabolism, which occurs when an organic compound is metabolised in conjunction with another substrate used for growth (Kumar et al., 1996; Sánchez et al., 2004).

Important amounts of DOC, salts and microorganisms may be incorporated to the soil environment through irrigation with TWW and other low-quality waters, which could interact with pesticides, and alter soil microbial populations (Assadian et al., 2005; Frenk et al., 2014). DOC can also potentially affect degradation and mineralisation kinetics of pesticides in two ways. Generally, DOC can increase the solubility of hydrophobic compounds, thus decreasing their adsorption and enhancing their availability to soil microorganisms, as a consequence of both the formation of stable pesticide−DOC complexes in solution or competitive adsorption (Celis et al., 1998; Spark and Swift, 2002; Li et al., 2005; Williams et al., 2006; Barriuso et al., 2011). On the other side, higher sorption due to pesticide−DOC−soil interactions has been also reported (Ling et al., 2006; Flores-Céspedes et al., 2006), driving to reduced bioavailability, which is directly related to xenobiotics degradability (Katayama et al., 2010). Therefore, the role of DOC in pesticide biodegradation is a subject of debate, since it depends on its source and concentration, soil type, and pesticide characteristics.

In the present study laboratory degradation parameters were determined for three non-ionic pesticides (THC, FEN and PDM) in SV soil. The effects of irrigation with TWW, as well as the role of DOC from fresh sewage sludge from the same WWTP were investigated. Soil was sterilised to evaluate the biotic contribution to pesticide degradation, and dehydrogenase activity (DHA) was determined to assess the effects of the treatments on soil microbial community. Although laboratory behaviour of pesticides may differ from that under real conditions due to simplistic assumptions, some authors have reported that field degradation can be extrapolated using standard laboratory methods (Beulke et al., 2005). Therefore, the results obtained in this work could be used to better understand the factors that influence pesticide persistence in soil irrigated with low-quality waters to ensure their safe use.

5.2. EXPERIMENTAL SETUP

5.2.1. Degradation experiments

Degradation experiments of THC, FEN and PDM in SV soil were carried out in the laboratory. In order to estimate the biological contribution to pesticide degradation, soil was sterilised by tyndallisation at 100 °C and atmospheric pressure for 1 h d^{-1} for three consecutive days. This system has proven its effectiveness in previous works of the research group (Delgado-Moreno and Peña, 2007, 2009; Hernández-Soriano et al., 2009; ElGouzi et al., 2015). Furthermore, to confirm this, 100 µL of soil suspensions (1 g soil/10 mL sterilised MQ water) was spread over the surface of Petri dishes containing LB (Lysogeny Broth) as culture medium. No growth was observed, contrary to natural soil suspensions, after incubation at 28 °C during 1 week (Figure 5.1).

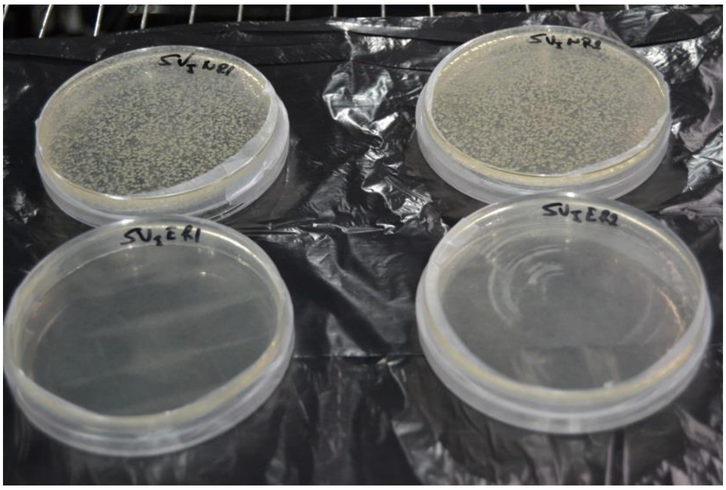


Figure 5.1. Petri dishes containing natural (top) and sterilised (bottom) soil suspensions. Incubation at 28 ºC during a week

Different aqueous solutions were used for soil pre-treatment and to provide soil humidity: MilliQ water (MQ) as control, TWW and sewage sludge extracts (SS-Ph) at 30 (DOC 30) and 300 (DOC 300) mg L^{-1} DOC.

Sterilised (SSV) and non-sterilised (SV) soil samples (1 kg for each treatment) were placed in plastic trays covered with aluminium foil and added with 110 mL of the corresponding solution to reach a moisture level equivalent to 40% soil FC (11% water content). Samples were homogenised and preincubated in a thermostatic chamber for 4 days at 15°C to activate microbiological populations.

Aliquots of 1.5 mL of a standard solution containing a mixture of the three pesticides at 1 g L^{-1} in acetone were homogeneously applied to give a nominal initial concentration in the whole soil sample of 1.5 mg kg^{-1} (dry weight) for each pesticide. This dose would be close to or lower than recommended for THC, PDM and FEN (Kulshrestha et al., 2000; Yagüe González and Yagüe Martínez de Tejada, 2006; Dong et al., 2014). After the solvent evaporated in a fume hood, samples were sieved twice through 2 mm and gently homogenised. Finally, soil moisture content was adjusted to 70% FC (19% water content) by further addition (80 mL) of the aqueous solutions corresponding to each treatment: MQ, TWW, DOC 30 or DOC 300. Each pesticide-treated soil sample corresponding to a single treatment was split into two subsamples of approximately 500 g each, which were transferred to autoclaved loosely capped glass jars to avoid anaerobic conditions and incubated at 15°C in the dark.

Both sterilised and non-sterilised treatments were sampled immediately after preparation (t = 0) and then at intervals during the subsequent 100 days. Two replicates of each subsample (four per treatment) were periodically collected and frozen until analysed. The moisture content of soil samples was controlled at each sampling time, and twice a week if the interval between two consecutive sampling times was extended. If needed, moisture content was maintained by addition of the corresponding solution followed by vigorous shaking.

5.2.2. Analytical determinations

Soil moisture content was evaluated as in equation [2.4] (chapter 2, section 2.1.8). Pesticide residues were extracted from soil samples by sonicating 2.5 g soil (dry weight) with 15 mL methanol (chapter 2, section 2.2.4.2). After filtration (0.45 µm PVDF), the three pesticides were determined by HPLC-DAD according to chapter 2, section 2.2.5.2.

Determination of dehydrogenase activity (DHA) along the experimental period was performed as described in chapter 2, section 2.1.10. The calibration curve (0.5-10 mg L^{-1} INTF) was measured daily with each sample batch. Four replicates of sterilised and non-sterilised soil were analysed. Simultaneously, a blank without soil was run for control purposes.

5.2.3. Degradation models

The single first order (SFO) kinetic model is normally used to describe pesticide degradation due to its simplicity. However, pesticide degradation frequently differs from SFO kinetics due to reasons related with: i) the complexity of soil environment, where the population of degrading microorganisms may vary considerably with time and climatic conditions; and ii) the distribution of pesticides between soil and solution by complex adsorption/desorption mechanisms that influence their availability to microbial degradation. Therefore, within the great number of postulated bi-phasic models, the first order multi compartment (FOMC) proposed by Gustafson and Holden (1990), one of the most frequently used (FOCUS, 2006), was also considered.

Single first order model (SFO). It assumes that the number of pesticide molecules is small relative to the number of degrading microorganisms and their enzymes. As a result, the rate of the decrease in pesticide concentration is at any time directly proportional to the remaining pesticide concentration in the system (equation [5.1]).

$$\frac{dC}{dt} = -kC \qquad [5.1]$$

By integrating equation [5.1], a simple exponential equation is obtained:

$$C = C_0 \times e^{-kt} \qquad [5.2]$$

where C (%) is the concentration of pesticide at time t (day), C_0 is the initial concentration (100%), and k (day^{-1}) the degradation rate constant. The half-life times, $t_{1/2}$, usually employed in the literature, will be named from now on DT_{50} which are easy to interpret. The SFO model is the one usually chosen to derive regulatory degradation endpoints, according to the equation [5.3].

$$DT_{50} = \frac{\ln 2}{k} \qquad [5.3]$$

First order multi compartment model (FOMC). In the FOMC, also known as Gustafson and Holden model, soil is considered as a heterogeneous medium formed of unconnected subcompartments, each with a different first-order degradation rate constant (Gustafson and Holden, 1990). A clear advantage of the FOMC model compared to other bi-phasic models is the relatively small numbers of parameters to be estimated (equation [5.4])

$$\frac{dC}{dt} = -\frac{\alpha}{\beta} C \left(\frac{t}{\beta} + 1 \right)^{-1} \qquad [5.4]$$

Equation [5.5] is obtained by integration of equation [5.4]

$$C = \frac{C_0}{\left(\frac{t}{\beta} + 1 \right)^{\alpha}} \qquad [5.5]$$

In this model, α is a shape parameter, determined by the coefficient of variation of rate constant values, and β a location parameter, respectively. Degradation in the FOMC model occurs more rapidly for higher α and lower β values. Regulatory endpoints can be calculated by the following equation:

$$DT_{50} = \beta \left(2^{\frac{1}{\alpha}} - 1 \right) \qquad [5.6]$$

.

5.2.4. Data analysis

Degradation curves were obtained by representing pesticide residual concentrations in soil (C, % of initially added amount C_0) *versus* the experimental time (t, days). The fitting of experimental data to the above described models was performed by non-linear regression using a Levenberg-Marquardt algorithm.

Recommendations of the FOCUS work group (FOCUS, 2006) were followed to evaluate the goodness of fit. Apart from visual assessment, the coefficient of determination (R^2), the residual standard error (RSE) and the chi-square (χ^2) test were used as indicators of the goodness of fit. The χ^2 test considers the deviations between observed and calculated values relative to the uncertainty of the measurements:

$$\chi^2 = \sum \frac{(C - O^2)}{\left(\frac{err}{100} - \overline{O}\right)^2} \quad [5.7]$$

where C and O are the calculated and observed values, Ō is the mean of all observed values and err is the measurement error percentage. To validate the model, the calculated χ^2 must be less than or equal to the tabulated values ($\chi^2_{m\alpha}$), being m the degree of freedom (number of measurements minus number of model parameters), and α the test significance level. In this study $\alpha = 0.05$ which indicates that the model has a 95% probability of being appropriate. Once the model is validated, the scaled error (err_{scaled}) can be determined on the basis of the error percentage (err):

$$err = 100 \times \sqrt{\frac{1}{\chi^2_{m,\alpha}} \times \sum \frac{(C - O)^2}{\overline{O}^2}} \quad [5.8]$$

$$err_{scaled} = \frac{err}{100} \times \overline{O} \quad [5.9]$$

The χ^2 test is recommended as a tool for model comparison (FOCUS, 2006). The err value at which the χ^2 test is fulfilled at a given degree of freedom should be below 15% (at a 5% significance level). The model with the lowest err_{scaled} is defined as the most suitable, because it describes the measured data in the most robust way.

The participation of soil microorganisms on pesticide degradation (biodegradation) was calculated from the Single First Order (SFO) kinetic fitting as:

$$\frac{k_{biotic}}{k_{total}} = 1 - \left(\frac{k_{abiotic}}{k_{total}}\right) \quad [5.10]$$

which assumes that the different mechanisms involved in pesticide degradation in soil are additive (Buser and Müller, 1995). Degradation rates k_{total} and $k_{abiotic}$ correspond to the degradation rate constants from the SV and SSV samples, respectively.

5.3. RESULTS AND DISCUSSION

5.3.1. Evolution of soil moisture content during incubation

Figure 5.2 represents the evolution of the moisture content of SV and SSV samples incubated with the different solutions along the whole duration of the experiment. This graph shows a higher difficulty of SSV samples to retain water, with a greater dispersion of the data. It is known that sterilisation of soils may lead to changes in their structure and physicochemical characteristics that may modify their capillarity and absorptive capacities (Liegel, 1986).

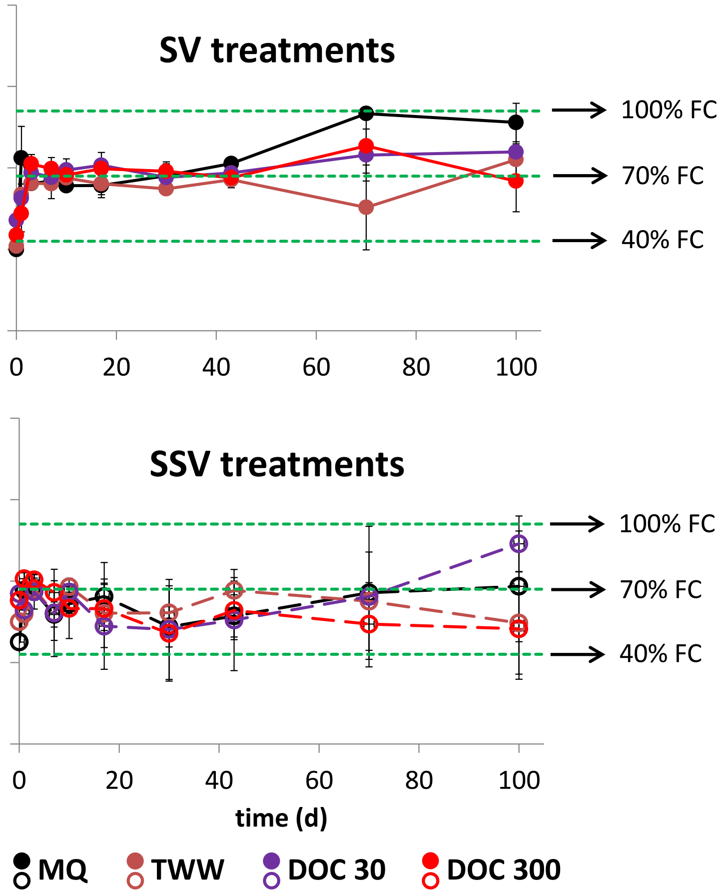


Figure 5.2. Moisture content of nonsterilised (top) and sterilised (bottom) soils under incubation with the different solutions during the experiment. Vertical bars represent the standard deviation of the mean (n = 4)

Greater deviations from the 70% FC level were found, however, at longer incubation times when degradation slows down or is totally completed (THC-SV samples).

5.3.2. Experimental data fitting. Model comparison

The experimental pesticide data in SV and SSV soils incubated with the different solutions were adjusted to the SFO and FOMC kinetic models (Figure 5.3).

In general, pesticide degradation was well-fitted to both models (Table 5.1), with $R^2 > 0.86$ for SV and $R^2 > 0.72$ for SSV samples, values which can be considered as adequate (FOCUS, 2006).This is supported by the fact that err parameter was < 15% in all the cases. However, the FOMC model was able to better describe the slower portion of the decay curves (Figure 5.3, right).

As shown in Table 5.1 THC data provided the best fitting among the three pesticides to both models for SV samples, with R^2 values ranging from 0.983 to 0.995. It can be said that THC degradation was closely fitted to both models, with practically no differences in the statistical parameters. In contrast, SSV treatments showed some differences, especially when TWW and DOC 30 solutions were used, probably due to the longer THC persistence with these solutions (Table 5.2). Although data were well fitted to the SFO model, THC degradation in sterile soils, where microorganisms were absent, appears to follow a bi-phasic pattern, since FOMC model yielded higher R^2 (>0.931), with lower RSE and err_{scaled} values. Liu et al. (2011) reported SFO degradation for THC in both sterilised and nonsterilised soils, although they did not test any other model.

The behaviour of PDM in SV soil samples was similar to that found for THC. In accordance with previous reports (Lee et al., 2000; Alister et al., 2009; Swarcewicz and Gregorczyk, 2012) degradation of PDM was well fitted to the SFO model, with R^2 values from 0.934 to 0.960. Nevertheless, fitting to the FOMC model was slightly better as shown by higher R^2 and lower RSE and err_{scaled} parameters (Table 5.1). Gaston et al. (2003) and García-Valcárcel and Tadeo (2003) have reported deviations from the SFO model of PDM dissipation from soil, although it was used as a first approximation. On the other hand, Swarcewicz and Gregorczyk (2012) reported that a bi-phasic model was not suitable, although they found a better fitting by introducing a final plateau concentration in the SFO equation.

Table 5.1. Statistical parameters derived from the fitting of experimental data of thiacloprid, pendimethalin and fenarimol under incubation with the different solutions to the single first order and the first order multi compartment kinetic models. SV refers to non-sterile samples and SSV to sterile samples

Samples	**R^2**	**RSE**	**χ^2**	**err (%)**	**err_{scaled}**	**R^2**	**RSE**	**X^2**	**err (%)**	**err_{scaled}**
	Single First Order (SFO)					First Order Multi Compartment (FOMC)				
SV	*THIACLOPRID*									
MQ	0.983	4.8	0.170	7.2	2.378	0.984	4.7	0.138	6.8	2.251
TWW	0.991	3.7	0.085	5.1	1.810	0.991	3.8	0.079	5.2	1.839
DOC 30	0.988	4.0	0.147	6.3	1.868	0.995	2.7	0.058	4.1	1.228
DOC 300	0.988	4.0	0.122	6.1	1.990	0.990	3.6	0.086	5.4	1.755
SSV										
MQ	0.905	7.0	0.079	6.8	4.787	0.937	5.7	0.046	5.5	3.826
TWW	0.789	8.7	0.127	8.7	6.040	0.964	3.6	0.019	3.6	2.462
DOC 30	0.779	7.8	0.088	7.4	5.478	0.986	2.0	0.005	1.8	1.352
DOC 300	0.920	6.7	0.075	6.6	4.572	0.931	6.2	0.057	6.0	4.168
SV	*PENDIMETHALIN*									
MQ	0.959	3.4	0.014	2.9	2.415	0.982	2.3	0.005	1.9	1.566
TWW	0.935	3.9	0.018	3.3	2.728	0.984	1.9	0.004	1.6	1.304
DOC 30	0.934	3.9	0.019	3.4	2.738	0.975	2.4	0.006	2.1	1.648
DOC 300	0.960	3.5	0.016	3.1	2.436	0.973	2.9	0.009	2.5	1.965
SSV										
MQ	0.821	2.6	0.006	2.0	1.851	Non fitted				
TWW	0.746	4.1	0.018	3.4	2.898	0.944	1.9	0.003	1.6	1.330
DOC 30	0.849	2.7	0.007	2.1	1.940	0.828	2.9	0.007	2.2	2.036
DOC 300	0.851	2.4	0.005	1.8	1.716	0.907	1.9	0.003	1.4	1.330
SV	*FENARIMOL*									
MQ	0.868	5.3	0.033	4.6	3.772	0.975	2.3	0.006	2.0	1.617
TWW	0.904	4.5	0.023	3.8	3.215	0.988	1.6	0.003	1.3	1.127
DOC 30	0.871	5.0	0.030	4.3	3.558	0.965	1.8	0.007	2.2	1.808
DOC 300	0.909	4.2	0.021	3.7	2.995	0.988	1.5	0.002	1.3	1.066
SSV										
MQ	0.745	2.2	0.004	1.7	1.585	Non fitted				
TWW	0.789	2.6	0.006	2.0	1.848	0.918	1.6	0.002	1.2	1.134
DOC 30	0.725	2.6	0.006	1.9	1.849	0.847	1.9	0.003	1.4	1.354
DOC 300	0.881	2.2	0.004	1.6	1.573	0.882	2.2	0.004	1.6	1.538

However, no final plateau concentration was observed in our experimental data (Figure 5.3, middle). PDM degradation in SSV samples with MQ did not conform to the FOMC model. For TWW and DOC 300 the FOMC fitting was better, while for DOC 30 a similar description using both models was found (Table 5.1).

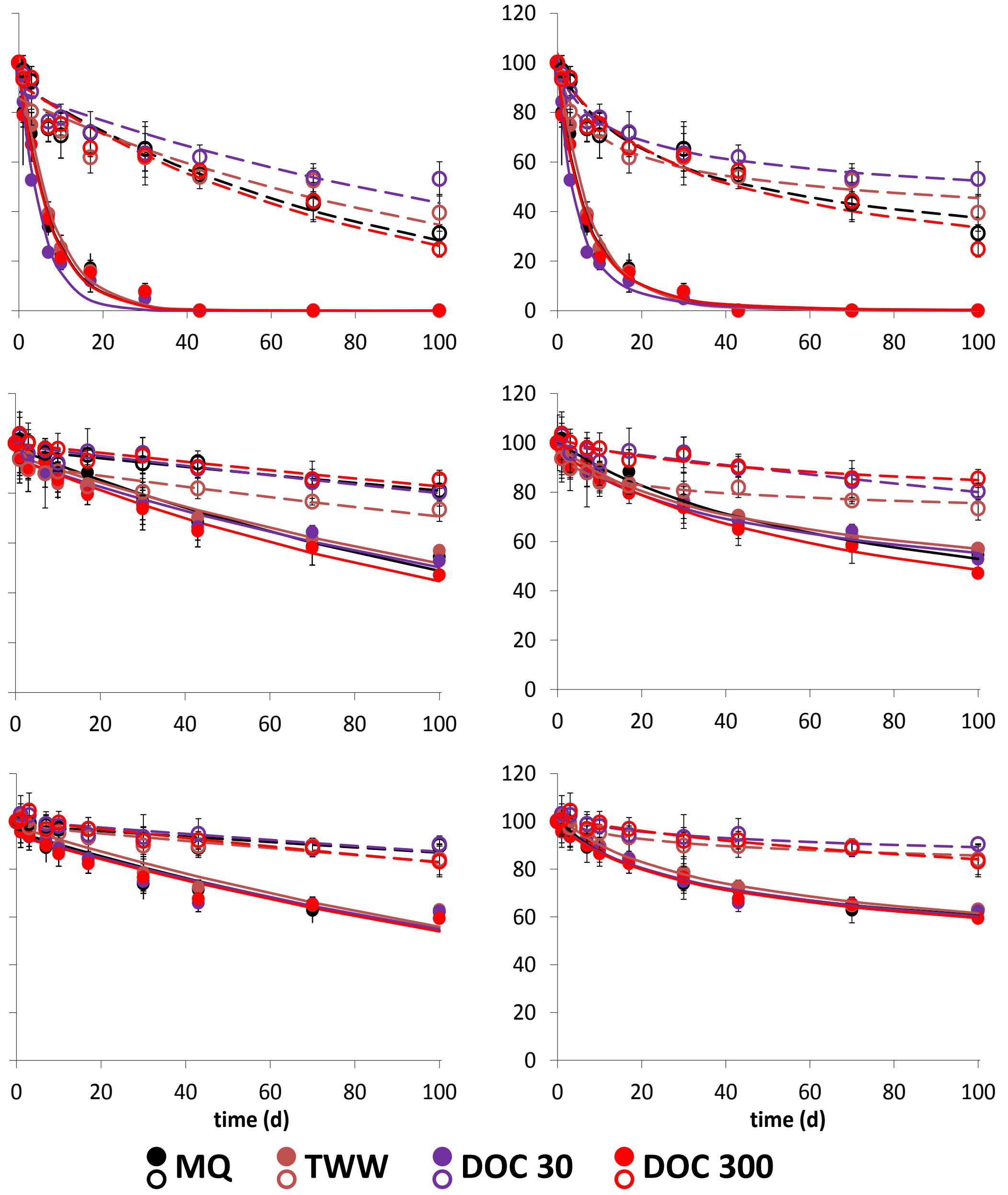


Figure 5.3. Evolution with time of thiacloprid, pendimethalin and fenarimol concentration (%) in nonsterilised (closed circles and continuous lines) and sterilised (open circles and dashed lines) soils under incubation with the different solutions. Experimental data fitted to the single first order (left) and first order multi compartment (right) kinetic models. Vertical bars represent the standard deviation of the mean (n = 4)

Degradation of FEN seems to clearly follow a bi-phasic pattern, as confirmed by the better fitting of the data to the FOMC model, which showed higher R^2 values and lower RSE and err_{scaled} (Table 5.1). In the case of sterilised soil, degradation was very slow and 80-90% of FEN remained in the soil at the end of the incubation experiment

(Figure 5.3, bottom). As it occurred with PDM, fitting of MQ-SSV data to the FOMC model was not possible. In the other SSV treatments the bi-phasic model was more adequate than the SFO, while for the DOC 300 solution the differences were negligible (Table 5.1).

According to the FOCUS guidelines (FOCUS, 2006), the simplest model that can provide an adequate description of the decline curves should always be preferred. In our case, although in general a slightly better fitting to the FOMC model was observed, the degradation behaviour of the pesticides will be discussed according to the SFO model to compare with previously reported data.

5.3.3. Pesticide degradation under incubation with the different solutions

5.3.3.1. MQ water

As shown in Table 5.2 the degradation rate constant (k) in non-sterile SV soil decreased in the order THC >> PDM > FEN and half-life time values (DT_{50}) with control MQ were 5.3, 99.4 and 122.4 days for THC, PDM and FEN respectively. These results indicate that THC is rapidly degraded, while PDM and FEN are moderately persistent in the studied soil under our experimental setup. Unlike expected, degradation rates were not related with the hydrophobicity and adsorption extent of pesticides, as degradation of PDM, the most hydrophobic (Figure 2.2) and more strongly adsorbed among the pesticides studied (chapter 3), was faster than that of FEN.

An initial fast decay in THC soil concentration during the first 10 days was followed by a slower decrease until disappearance below the limit of detection after approximately 43 days, a fact that occurs with all the solutions. It could happen that at t > 10 days an increase in the sorption of THC occurs due to ageing (Gevao et al., 2000), with the corresponding lower availability for degradation or else that the concentration of remaining THC was too low to allow effective microbial degradation (Egli, 2010). The rapid disappearance of THC is in accordance with a recent work, which has indicated 98.8% degradation after 15 days of laboratory incubation (Liu et al., 2011).

Our reported DT_{50} value for THC (5.3 days) was higher than that found by Liu et al. (2011) (1.3 days) and lower than the reported by other authors (Dong et al., 2014)

(11.8 days), probably because of the differences in soil characteristics and experimental setting, especially different incubation temperatures. The high degradation rate of THC could be related with the presence of the nitrile group in its structure (Figure 2.2) which has been reported to be easily attacked by soil microorganisms to form the corresponding amide (Delgado Moreno and Peña, 2009; Liu et al., 2011). Additionally the high THC bioavailability, due to its low soil adsorption capacity (chapter 3, Table 3.7), could have favoured a rapid dissipation.

Degradation of PDM was slow with a final residual concentration of 54% at the end of the incubation period (Figure 5.3, middle). Persistence of PDM has been reported to be influenced by several factors such as temperature, moisture content and soil type (Lee et al., 2000; Stranberg and Scott-Fordsman, 2004; Swarcewicz and Gregorczyk, 2012).

Half-life time for PDM (99.4 days) was in the range of those found in other laboratory experiments, between 22 and 182 days (Lee et al., 2000; Singh et al., 2002; Gaston et al., 2003; García-Valcárcel and Tadeo, 2003; Swarcewicz and Gregorczyk, 2012; FOOTPRINT). Swarcewicz and Gregorczyk, (2012) have related this variation with differences in soil texture and moisture content, as well as with the copresence of other pesticides in the soil. The major transformation mechanisms under aerobic conditions are N-dealkylation and reduction of the less hindered nitro group in the molecule (Kulshrestha and Singh, 1992; Kulshrestha et al., 2000) (Figure 2.2).

On the other hand, the relative high persistence of PDM in the soil studied may be also attributed to limited bioavailability due to its high adsorption (chapter 3, Table 3.6), or else to ageing processes (Barriuso et al., 1997).

The degradation pattern of FEN was similar to that obtained for PDM. A decrease in FEN concentration was observed in the first 40 days of the experiment to a concentration of 71% of the initial amount applied, followed by a slower decline until a practically constant level of approximately 62% at 100 days (Figure 5.3, bottom).

As already mentioned, the highest persistence of the pesticides studied corresponds to the fungicide FEN (DT_{50} = 122.4 days) with three aromatic rings in its structure and higher molecular weight (Figure 2.2). Hernández-Soriano et al. (2009) evaluated the laboratory dissipation behaviour of four organophosphorous insecticides and suggested that slower degradation could be related to the complexity of the chemical structure, likely due to a preferential decomposition of the more labile compounds. A similar behaviour was noted in the evaluation of the simultaneous disappearance of four triazine herbicides (Delgado-Moreno and Peña, 2009).

Table 5.2. Kinetic parameters derived from the fitting of experimental data of thiacloprid, pendimethalin and fenarimol under incubation with the different solutions to the single first order and the first order multi compartment kinetic models. (n = 4 for each date)

Samples	**C$_0$ ± SE (%)**	**K ± SE (x10^{-3})(d^{-1})**	**DT$_{50}$ (d)**	$\frac{k_{biotic}}{k_{total}}$	**C$_0$ ± SE (%)**	**α**	**β**	**DT$_{50}$ (d)**
	Single First Order (SFO)				First Order Multi Compartment (FOMC)			
SV	*THIACLOPRID*							
MQ	97 ± 4	132 ± 12	5.3	0.91	99 ± 4	3.6	23	4.8
TWW	103 ± 3	126 ± 8	5.5	0.93	104 ± 3	8.6	63	5.3
DOC 30	99 ± 3	186 ± 15	3.7	0.96	102 ± 3	2.4	9.7	3.2
DOC 300	96 ± 3	133 ± 11	5.2	0.91	98 ± 3	3.3	20	4.7
SSV								
MQ	92 ± 3	12 ± 2	59		99 ± 4	0.45	13	48.3
TWW	86 ± 4	9 ± 2	77		100 ± 3	0.21	2.2	62.4
DOC 30	88 ± 4	7 ± 1	98		100 ± 2	0.18	2.7	129
DOC 300	92 ± 3	13 ± 2	55		97 ± 4	0.66	25	46.5
SV	*PENDIMETHALIN*							
MQ	98 ± 2	7 ± 1	99	0.73	101 ± 1	0.58	49	114
TWW	95 ± 2	6 ± 1	114	0.57	99 ± 1	0.32	22	167
DOC 30	94 ± 2	6 ± 1	112	0.65	97 ± 2	0.34	23	158
DOC 300	94 ± 2	7 ± 1	93	0.75	97 ± 2	0.69	58	101
SSV								
MQ	98 ± 1	2 ± 0	374		Non fitted			
TWW	92 ± 2	3 ± 1	265		99 ± 2	0.06	0.91	1.4x10^{5}
DOC 30	99 ± 1	2 ± 0	323		99 ± 2	12.3	5703	330
DOC 300	100 ± 1	2 ± 0	367		102 ± 1	0.09	16	3x10^{4}
SV	*FENARIMOL*							
MQ	96 ± 2	6 ± 1	122	0.78	102 ± 2	0.21	9.7	242
TWW	98 ± 2	6 ± 1	124	0.70	103 ± 1	0.25	15	223
DOC 30	94 ± 2	5 ± 1	128	0.75	99 ± 2	0.24	15	243
DOC 300	94 ± 2	6 ± 1	125	0.65	99 ± 1	0.24	14	232
SSV								
MQ	99 ± 1	1 ± 0	555		Non fitted			
TWW	98 ± 1	2 ± 0	415		101 ± 1	0.05	4.6	1.9x10^{6}
DOC 30	100 ± 1	1 ± 0	507		102 ± 1	0.05	7.6	4.8x10^{6}
DOC 300	101 ± 1	2 ± 0	356		102 ± 1	0.19	58	2308

SE: standard error

Unfortunately, few papers about FEN degradation in soil in laboratory experiments have been published in the last decades. Some authors have reported very slow degradation with DT_{50} values ranging from 250 to 1833 days, depending on soil properties, and experimental conditions including FEN dose (Althaus and Beaty, 1982; Rainey, 1990; Jackson and Lewis, 1994; FOOTPRINT). Rainey (1990) identified a minor metabolite as α-(2-chlorophenyl)-α-(4-chlorophenyl)-1,2-dihydro-2-oxo-5-pyrimidinemethanol.

It is worth mentioning that FEN concentration at the end of the experiment was higher than 60% of the amount initially applied (Figure 5.3, bottom). This suggests that longer incubation periods would have been required for a proper evaluation of FEN persistence using SFO. With this model degradation rates could have been overestimated. In fact, the wide variability of reported FEN half-lives is probably due to inaccuracies in calculations, owing to the degree of extrapolation required. Therefore, as suggested in section 5.3.1 of this chapter, the bi-phasic FOMC model could be more suitable to describe FEN degradation (DT_{50} = 242 days).

Moreover FEN, as indicated for PDM, may have become less available for biodegradation along incubation due to ageing processes.

5.3.3.2. Treated wastewater

To our knowledge few works about the effects of TWW on pesticide degradation in soil have been reported to date. In our study the use of TWW for soil incubation did either not alter pesticide persistence (THC and FEN) or slightly increased it (PDM) (Table 5.2). Furthermore, the final residual concentration of PDM was the highest when using TWW (57%). This could be linked to the reported higher adsorption coefficient for PDM with TWW in the soil under study (Table 3.6), thus reducing bioavailability for degradation. Other authors have also observed no or negligible effects of TWW in dissipation rate of organophosphorous insecticides (Hernández-Soriano et al., 2009) or phenylurea herbicides (ElGouzi et al., 2015).

5.3.3.3. Dissolved organic carbon solutions

Sewage sludge is a source of microorganisms which, when added to the soil, may increase their capacity of transforming organic pollutants (Sánchez et al., 2004).

The use of DOC solutions from sewage sludge did not affect FEN degradation, but produced different effects on THC and PDM depending on DOC concentration.

While the DOC 300 solution did not alter THC persistence with respect to the control, the use of DOC 30 slightly reduced it, as shown in Figure 5.3 (top), resulting in DT_{50} of 3.7 days. This fact contradicts adsorption results, which show a slightly higher bioavailability of THC with DOC 300 solution (chapter 3, Table 3.7). The faster degradation of THC in DOC 30-incubated soil could be explained in terms of an addition of further microbial population capable of degrading this insecticide. However, this effect was counterbalanced when using a 10-fold DOC concentration likely due to a greater amount of labile compounds in the soil matrix competing with THC to become the main C source for microorganisms. Additionally, inhibitory effects on the microbial population responsible for degrading THC are also possible due to higher salinity and other toxic compounds present in relevant amounts.

In the case of PDM, the opposite effect was observed. Persistence was enhanced for the DOC 30 solution (112 days), but diminished for DOC 300 (93 days). The lowest residual concentration of PDM at the end of incubation (t = 100 days) corresponded to the DOC 300 solution (47%), confirming that incubating with high DOC concentrations increases PDM degradation. The lowest persistence of PDM when using DOC 300 is probably due to its higher availability according to the decrease of the distribution coefficient (K_d) with increasing DOC amount in solution, although this concentration was not assayed (chapter 3, Table 3.6), as well as to a high load of exogenous microorganisms. On the other hand, we observed an unexpected higher persistence of PDM with DOC 30 compared with MQ water.

Pesticide-DOM interactions have been postulated to increase pesticide apparent solubility and favour pesticide desorption, especially in the case of scarcely soluble and hydrophobic compounds like PDM (Huang and Lee, 2001; Li et al., 2005; Barriuso et al., 2011). It is possible that two converging processes occur at the same time, the capacity of DOC solutions to enhance the bioavailability of pesticides and the relative increase in the microbial population (Felsot and Dzantor, 1995; Sánchez et al., 2004). Moorman et al. (2001) have reported controversial effects of organic amendments on pesticide degradation and microbial activity of soil, and related their results with the OC source, application rate, and chemical nature of pesticides.

5.3.4. Soil sterilisation effects and biological contribution

Sterilised soils (SSV) were used to assess the breakdown of pesticides due to soil microbial activity for comparison with data from non-sterilised soil (SV). It is important to mention that, except MQ water which was passed through a 0.22 µm PVDF filter (GE Waters & Process Technologies), solutions were not sterilised to avoid OM decomposition and therefore, for each treatment, endogenous soil microorganisms are responsible for any difference observed with respect to SV treatments. Furthermore, the microbial load in TWW and DOC solutions may also contribute to pesticide biodegradation.

The overall results show that the microbial community has a significant role in pesticide degradation, with biological contribution ranged in the order THC > FEN ≈ PDM. This is in line with previous works showing that the transformation of THC in soil is mainly due to microbial processes (Kobayashi and Shimizu, 1994).

5.3.4.1. MQ water

Residual concentration of pesticides decreased slowly as compared with SV soil suggesting that pesticides could be partially degraded by abiotic processes. The residual concentration at 100 days was 31% for THC, 81% for PDM, and 90% for FEN of the initial amount applied. The half-life of pesticides was 59 days for THC, similar to the results found by Liu et al. (2011), and increased to 374 days for PDM and to 555 days for FEN. As above mentioned, the biological contribution for THC was the highest (0.91), followed by FEN (0.78) and finally PDM (0.73), and was inversely related with pesticide hydrophobicity (Figure 2.2), soil sorption capacity (chapter 3, Tables 3.6, 3.7 and 3.8), and consequently bioavailability.

5.3.4.2. Treated wastewater

Except for the rapidly degraded THC, the biological contribution to pesticide degradation in the presence of TWW was lower than that corresponding to the control water (Table 5.2) in agreement with Hernández-Soriano et al. (2009). This finding suggests that TWW could induce changes not only in soil microbiota (Frenk et al., 2014), but also in soil physicochemical properties (Müller et al., 2007) driving to enhanced chemical contribution to pesticide decay, especially for the more persistent pesticides. As observed in Figure 5.3 (middle), these effects were more noticeable in the decay curve of PDM with the lowest persistence (265 days) and biotic contribution (0.57) for this treatment (Table 5.2).

5.3.4.3. Dissolved organic carbon solutions

Different effects were observed on the half-life time of pesticides in SSV soil for both DOC solutions. THC persistence increased to 98 days for the DOC 30 solution compared with the control, whereas it remained practically unaltered (55 days) for DOC 300. For PDM, DT_{50} was 323 days for DOC 30, and similar to that of the control for DOC 300 (367 days). Finally, FEN persistence was lower for both DOC solutions than for MQ water, and showed a decreasing trend with increasing concentrations of DOC (Table 5.2).

In our study the greatest biotic contribution to THC degradation was found for DOC 30 solution (0.96), due to the highest degradation rate in natural soil and the lowest in sterilised soil. However, the DOC 300 solution had no effect on the biological contribution compared with the control. An unexpected lower biotic contribution to PDM degradation was found for DOC 30 (0.65) compared with MQ, though it increased to 0.75 for DOC 300. The opposite behaviour was observed for FEN, that is, biotic contribution decreased with increasing concentrations of DOC, suggesting that the role of exogenous microorganisms from sewage sludge should be taken into account, since they accelerate FEN degradation in sterilised soil.

It has been previously reported that the addition of organic amendments may influence strongly the structure and intensity of microbial activity of soils as a result of increased metabolism, pointing to enhanced pesticide biodegradation (Briceño et al., 2007; 2010). In our case, though the number of degrader-microorganisms would be higher in the DOC 300 irrigated soil, the presumably great amount of labile OM could constitute their main C source, and compete with pesticide decomposition even for the rapidly degraded THC. This hypothesis has been previously considered for different organic amendments (Moorman et al., 2001; Delgado-Moreno and Peña, 2009). On the other hand, as above mentioned, other constituents present in sewage sludge such as salts or heavy metals could have a negative effect on the microbial population responsible for biodegradation of THC comparing with the DOC 30 solution.

5.3.5. Dehydrogenase activity

Estimation of dehydrogenase activity (DHA) in soils has been considered a good measure of microbial oxidative activity (Casida, 1977; Camiña et al., 1998). Results obtained are depicted in Figure 5.4. In general, DHA during the incubation time followed a similar pattern for all the solutions assayed, with an increase in the first 7-10 days and a subsequent decrease to reach a constant level at t = 17 days. This trend is consistent with the higher degradability of THC in the first 10 days of the experiment (Figure 5.3, top). On the other hand, the final behaviour of these curves suggest a decrease of easily degradable and bioavailable substrates (Saviozzi et al., 2002).

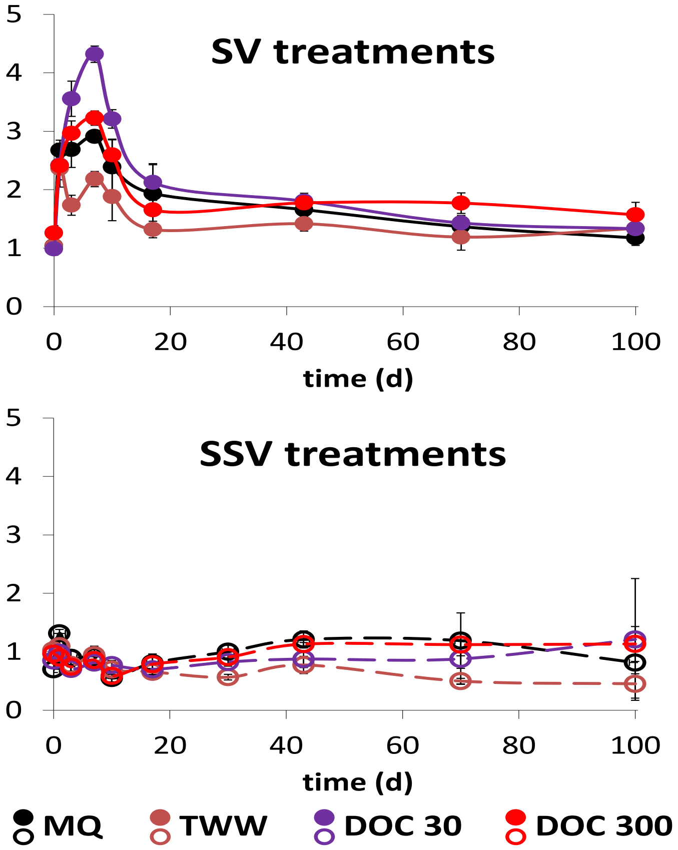


Figure 5.4. Dehydrogenase activity of nonsterilised (solid circles, top) and sterilised (open circles, bottom) soils under incubation with the different solutions during the experiment. Vertical bars represent the standard deviation of the mean (n = 4)

The presence of TWW yielded the lowest soil DHA, a fact linked to inhibitory effects on soil microbial population due to the presence of toxic compounds such as heavy metals, salts, surfactants or other organic contaminants (Hernández-Soriano et al., 2009). It is worth mentioning that at the end of the experiment DHA evolved to match the values of the other treatments. Frenk et al. (2014) concluded that soil bacterial community is not resistant to TWW during the irrigation season, yet is resilient in long term. This is in line with the general trend of TWW to reduce the biological contribution to the disappearance of relatively persistent pesticides. However, it is not reflected in pesticide degradation behaviour, practically not affected by irrigation with TWW, except in the case of PDM with the longest persistence for this solution.

DHA for the soils incubated with the DOC solutions behaved differently along time depending on DOC concentration. DHA values were slightly higher for DOC 30 incubated soil than those found for the DOC 300 solution in the first half of the experiment, which is consistent with the faster degradation rate found for THC and the high biotic contribution with DOC 30. As the experiment progressed, DHA for DOC 300 tended to increase, being slightly greater than that of DOC 30 in the second half of the incubation period. This finding could be related with the faster decay of the moderately persistent PDM and the increase in biological contribution at high DOC concentrations. Apparently an initial inhibition of microbial activity could occur in soil irrigated with high concentrations of DOC (DOC 300), which could be later reversed when microorganisms adapt to the new conditions.

5.4. CONCLUSIONS

THC was the less persistent pesticide followed by PDM and FEN. The degradation rate of FEN was not modified by the different solutions used.

TWW induced higher persistence of PDM, probably by inhibition of soil biota.

The effect of DOC on pesticide degradation and soil microbial activity was dependent on DOC concentration, incubation time, and chemical nature of the pesticide:

- At low concentration (30 mg L^{-1}) DOC solution was more effective in degrading slightly persistent pesticides such as THC.
- On the other hand, high concentrations of DOC (300 mg L^{-1}) had more influence in the degradation of the moderately persistent PDM.

The simultaneous presence of THC, as an accessible C source for microorganisms, could have limited the biodegradation of the other two pesticides at the first stages of the degradation process.

6. LEACHING

6.1. INTRODUCTION

Most agriculturally applied pesticides are slightly water-soluble organic compounds that can be transported from treated fields to surface water by runoff, or else they may be carried by water flowing through the soil profile thus contaminating groundwater. Pesticide contamination of groundwater is an issue of international importance because groundwater can be used as drinking water, especially in areas with periodic water shortage and intensive agricultural activity (Sato et al., 2013). Due to their massive and improper use in the last decades, several studies have revealed the presence of pesticides in surface and groundwater (Goodrich et al., 1991; Boxall et al., 2004; Kjaer et al., 2005; McManus et al., 2014; Silva et al., 2015).

The movement of pesticides through the soil profile is mainly controlled by sorption and degradation because both processes affect the availability of a pesticide in the soil solution (Allen and Walker, 1987; Walker, 2000). The most significant transport mechanism of pesticides in soil is mass flux, which is the movement that water provides to solutes (Bear, 1988). Besides, solutes are subject to molecular diffusion mechanisms and dispersion (Leeds-Harrison, 1995) (Figure 6.1). Transport of organic chemicals depends on soil structural and hydraulic properties. Apart from the formation of preferential flow channels (Ghodrati and Jury, 1992; Grochulska and Kladivko, 1994; Schoen et al., 1999; Elliott et al., 2000; McGrath et al. 2010), the association of pesticide molecules with soil colloids (Vinten et al., 1983; Seta and Karathanasis, 1997; de Jonge et al., 1998; McGechan and Lewis, 2002; Styczen et al., 2011; Katagi, 2013) and DOC (Graber et al., 1995; Williams et al., 2006; Jiang et al., 2008; Katagi, 2013) has been reported to contribute to pesticide enhanced transport. Cabrera et al. (2011) reported that not only the amount, but also the nature and composition of DOC play an important role in pesticide leaching.

A variety of chemical and physical nonequilibrium processes affect solute transport in the subsurface (Nielsen et al., 1986). Nonequilibrium conditions have been grouped in two categories: transport related and sorption-related (Brusseau et al., 1991). Transport related nonequilibrium, often referred to as physical nonequilibrium, results from heterogeneous material properties in the flow domain, affecting reactive and nonreactive solutes (Kamra et al., 2001). Sorption-related nonequilibrium may result from chemical nonequilibrium conditions that could be regulated by kinetic reactions, or controlled by molecular diffusion into aggregates (intraparticle and intraorganic matter diffusion) (Montoya et al., 2006).

The main objectives of this study were: i) to estimate the soil hydraulic transport parameters through the leaching of Br^- as the inert tracer; ii) to evaluate the effect of effluent irrigation composition and FERT amendment on THC leaching through SV soil columns under laboratory conditions; and iii) to estimate the parameters that control THC transport by fitting experimental data to the one-dimensional CXTFIT transport model.

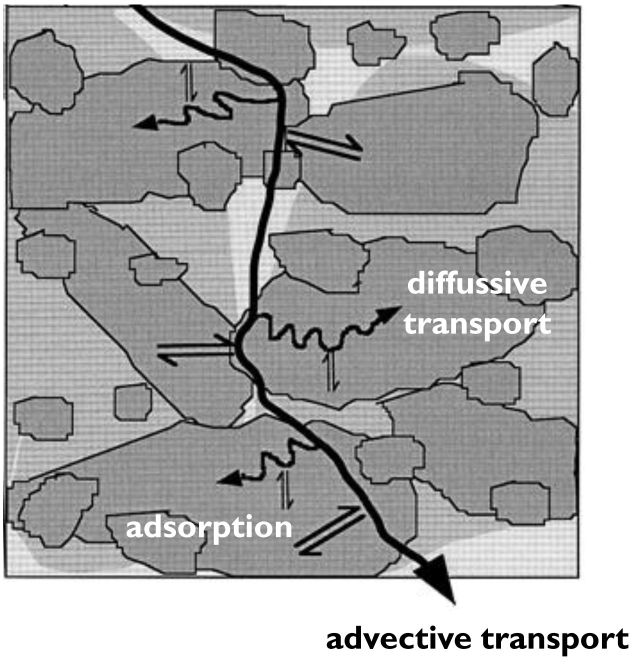


Figure 6.1. Scheme of solute leaching through a soil. Aggregates (dark) create immobile regions where mass transfer occurs exclusively by diffusion. Thick and thin lines indicate advective and diffusive solute flux. Adsorption (double arrows) may take place in both regions (Fesch et al., 1998)

6.2. EXPERIMENTAL SETUP

6.2.1. Column experiments

The solute transport assays were carried out at ambient temperature, per triplicate, in small polypropylene columns (2 cm i.d.; 10 cm length), which were homogeneously packed by addition of successive layers of non-amended SV soil and SV soil amended with FERT (1% w/w) to establish uniform bulk density up to a height of 5 cm (Peña et al., 2011a; Rodríguez-Liébana et al., 2014b). The soil and the amendment were sieved several times through 2 mm and shaken end-over-end overnight to assure homogeneous mixing before column packing. A fine layer of muslin was placed at the bottom of the soil column to avoid soil loss, and also at the column top to avoid soil disturbance during infiltration and to facilitate distribution of water on the surface.

To establish a steady-state flux, soil columns were saturated with 0.01 M $CaCl_2$ (Panreac), allowing them afterwards to drain excess water overnight, so the final soil moisture was close to FC. The pore volume (PV) was calculated as the difference in weight before and after saturation. After draining excess of water, saturated columns were covered with aluminium foil to avoid pesticide photodegradation during the experiments.

A 100 µL-aliquot of THC at 1 mg mL^{-1} (100 µg pesticide) in acetone (HPLC grade, Panreac) was carefully dropped on the top of the column and left in a fume hood until solvent evaporated to have a concentration of approximately 5 µg g^{-1}. Bromide ion was used as a non-reactive tracer at a rate of 6.4 mg per column (0.2 mL from a 0.2 M $MgBr_2$ solution in deionised water) to determine the dispersive characteristics of the columns. Milli Q water (MQ) as control, TWW, $(NH_4)_2SO_4$ 5 mM, and sewage sludge extracts (SS-Ph) at DOC concentration of 3 (DOC 3) and 300 mg L^{-1} (DOC 300) were used immediately as influent solutions for non-amended soil columns. To evaluate the influence of FERT amendment, amended-soil columns were leached with MQ water. The influents were applied through a plastic tube connected to a Boyle-Mariotte bottle at 5 cm constant-head boundary conditions from the top of the columns, allowing them to flow under positive pressure throughout the experiments (Fernández-Gálvez et al., 2012) (Figure 6.2).

Leachates were collected in glass tubes using a fraction collector (Model frac-920, General Electrics) programmed so that collection was more frequent at the beginning of the experiment, slowing down as it progressed. After filtering (PVDF 0.45 µm filters), an aliquot of the leachates was immediately used for the estimation of DOC and pesticide concentration. The rest was stored at 4 °C for the subsequent measurement of Br^- concentration, pH and EC, within 2-3 days. Some column parameters calculated from soil packing are shown in Table 6.1. At the end of each leaching experiment soil was allowed to drain and columns were segmented into two equal 2.5 cm layers (upper and lower) to determine THC concentration remaining in soil.

An aliquot of each soil section was oven dried at 105 °C for 24 h to calculate the moisture content (chapter 2, section 2.1.8), so the results were referred to dry weight. Pesticide loss by retention on the experimental materials has been previously discarded (Rodríguez-Liébana et al., 2014b).

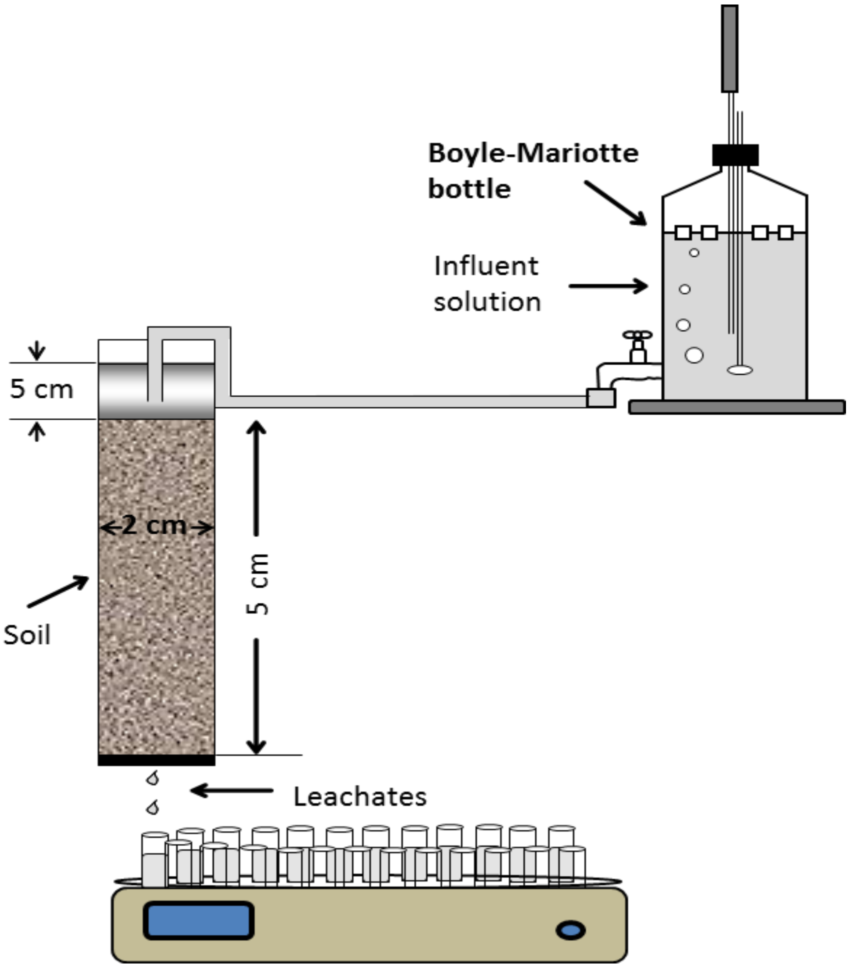


Figure 6.2. Description of the leaching experiments

Table 6.1. Column parameters (± standard deviation) calculated from soil packing (n=15 for SV and n=3 for FERT)

Soil	m^a (g)	ρ^b (g cm^{-3})	θ^c (cm^3 cm^{-3})	PV^d (cm^3)
SV	19.4 ± 0.1	1.23 ± 0.01	0.468 ± 0.010	7.35 ± 0.16
FERT	19.2 ± 0.1	1.22 ± 0.00	0.454 ± 0.010	7.13 ± 0.17

[a]m, soil mass; [b]ρ, soil density; [c]θ, volumetric water content; [d]PV, pore volume
FERT refers to the SV soil amended with Fertiormont (1% w/w)

6.2.2. Analytical determinations

Apart from THC concentration (HPLC-DAD as in as in chapter 2, section 2.2.5.2), several leachate properties were determined. As described in chapter 2, section 2.1.4, pH was directly measured in filtered leachates while EC was measured in 1:15 diluted samples due to the great contribution of salts proceeding from soil, most influent solutions, Br^- tracer and saturation solution. Absorbance at 254 nm (Helios Gamma, Thermo Scientific, Cambridge, UK) of the 1:10 diluted samples was used as a rapid estimation of DOC amount in leachates (Artiola and Walworth, 2009).

Bromide concentration was determined in 1:50 diluted leachates by ion chromatography (chapter 2, section 2.1.17).

Pesticide residues from the soil layers were analysed by HPLC-DAD (chapter 2, section 2.2.5.2) after ultrasound-assisted extraction (chapter 2, section 2.2.4.2). Duplicate analyses of each soil layer were performed.

6.2.3. Transport models

According to the miscible displacement theory, movement of a solute in porous media occurs as a result of the combined effects of diffusion and convection. The convection-dispersion equation (CDE) is the basic equation used in this mechanistic model. The one-dimensional CDE model, assuming steady state flow, linear adsorption, first-order degradation and zero-order production, is given by the following equation (Toride et al., 1999)

$$R\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} - \upsilon\frac{\delta c}{\delta x} - \mu c + \gamma(x) \qquad [6.1]$$

where c is the solute concentration in the liquid phase (mg L^{-1}), t is the time (h), D is the apparent diffusion coefficient (cm^2 h^{-1}), which refers to the combined influence of diffusion and hydrodynamic dispersion for dissolved chemicals in porous media, x is the spatial coordinate in the direction of flow (cm), ν is the pore-water velocity (cm h^{-1}), μ is the first-order decay coefficient for degradation of the solute (h^{-1}), γ is a zero-order production term (mg cm^{-3} h^{-1}), and R (dimensionless) is the solute retardation factor, which represents the effect of the sorption process on solute transport and is defined as

$$R = 1 + \frac{\rho K_d}{\theta} \qquad [6.2]$$

where ρ is the soil bulk density (g cm^{-3}), K_d is the distribution coefficient for adsorption (L kg^{-1}), described by a linear isotherm, and θ is the volumetric water content (cm^3 cm^{-3}). Assuming R = 1 for nonreactive solutes, equilibrium CDE is used to estimate transport hydraulic parameters (Montoya et al., 2006).

Dimensionless parameters allow reducing equation [6.1] to the form:

$$R\frac{\delta C}{\delta T} = \frac{1}{P}\frac{\delta^2 C}{\delta Z^2} - \frac{\delta C}{\delta Z} - \mu^E C + \gamma^E(Z) \qquad [6.3]$$

where C is the solute concentration in the liquid phase, P is the Péclet number, μ^E is a first-order decay coefficient (= Lμ/v), γ^E is a zero-order production coefficient for equilibrium transport (= $L\gamma/vc_0$), and Z and T are the dimensionless space and time variables (Toride et al., 1999).

Chemical nonequilibrium may occur as a result of kinetic adsorption while physical nonequilibrium is caused by a heterogeneous flow regime. Although both nonequilibrium CDE models are based on different concepts, they can be reduced to the same dimensionless form (equations [6.4] and [6.5]) if dimensionless parameters are used (Toride et al., 1999).

$$\beta R\frac{\delta C_1}{\delta T} = \frac{1}{P}\frac{\delta^2 C_1}{\delta Z^2} - \frac{\delta C_1}{\delta Z} - \omega(C_1 - C_2) - \mu_1 C_1 + \gamma_1(Z) \qquad [6.4]$$

$$(1-\beta)R\frac{\delta C_2}{\delta T} = \omega(C_1 - C_2) - \mu_2 C_2 + \gamma_2(Z) \qquad [6.5]$$

where β is a fraction factor, and ω is a mass transfer coefficient; the rest as described above. The subscripts 1 and 2 refer to equilibrium and nonequilibrium sites respectively.

The two-region approach assumes that the liquid phase is composed of a mobile (flowing water, macropore domain) and an immobile (stagnant water, matrix, or micropore domain) region. The exchange between the two liquid regions is modelled by a first-order kinetic equation. Flow occurs only in the mobile region. Sorption is assumed instantaneous on all sorption sites, and the sorption rate is limited here by the diffusion of the solutes to the exchange sites in the stagnant phase. In this model the dimensionless parameter β is associated with the mobile domain (equation [6.6]), and ω is related with the solute transfer between the two domains (equation [6.7]).

$$\beta = \frac{\theta_m + f\rho_b K_d}{\theta + \rho_b K_d} \qquad [6.6]$$

$$\omega = \frac{\alpha L}{\theta v} \qquad [6.7]$$

where θ_m is the volumetric water content of the mobile fraction, f is the fraction of sorption sites in the mobile region and α (h^{-1}) is a first-order mass coefficient governing the rate of solute exchange between mobile and immobile liquid regions (Montoya et al., 2006).

The two-site chemical nonequilibrium approach assumes that sorption is instantaneous at type 1 sites and is described by an equilibrium sorption isotherm. At type 2 sites, sorption follows first-order kinetics, being the rate-limiting step either chemical or diffusive (van Genuchten and Wagenet, 1989; Brusseau et al., 1991). In this model the transport parameter β (equation [6.8]) is associated with the fraction of instantaneous solute retardation, and ω (equation [6.9]) describes the ratio of hydrodynamic residence time to the characteristic time scale for sorption (Montoya et al., 2006).

$$\beta = \frac{\theta + f\rho K_d}{\theta + \rho K_d} \qquad [6.8]$$

$$\omega = \frac{\alpha(1-\beta)RL}{v} \qquad [6.9]$$

where f is the fraction of equilibrium sorption sites and α (h^{-1}) is the first-order rate for kinetics at nonequilibrium sites. A simplification of the model assumes negligible decay in the adsorbed phase, and the corresponding degradation rate in the liquid phase (μ_{liq}, h^{-1}) is related to μ by equation [6.10] (Montoya et al., 2006):

$$\mu = \frac{L\mu_{liq}}{v} \qquad [6.10]$$

6.2.4. Data analysis

Breakthrough curves (BTCs) for the tracer and the pesticide were obtained for each treatment by representing the concentration in the leachates *versus* the relative PV. Equilibrium and nonequilibrium models were used to describe Br^- and THC BTCs.

Some parameters in the transport model can be independently calculated from experimental measurements. The volumetric water content (θ, $cm^3\ cm^{-3}$) was calculated as the resident water content of the soil after the experiment by soil volume unit. The elution fluxes at the column outlet (Q, $cm^3\ h^1$) were measured by weighing the amount of solution eluted at regular time intervals. The Darcy's velocities (q, cm

h^{-1}) were evaluated by dividing Q by the cross sectional area of the soil column. The actual pore-water velocity (v, cm h^{-1}) was calculated as $v = q/\theta$.

Other parameters are obtained by fitting the leaching data to the CDE model with STANMOD (STudio of ANalytical MODels) free software package that includes a modified and updated version of the CXTFIT code (CXTFIT 2.1) (Toride et al., 1999). This program has been widely used to estimate pesticide transport parameters during steady one-dimensional flow (Montoya et al., 2006; van Genuchten et al., 2012; Marín-Benito et al., 2013; Rodríguez-Liébana et al., 2014b). The inverse problem is solved by minimising an objective function (SSQ) that consists on the sum of the squared differences between observed and fitted concentrations (Šimůnek et al., 1999). This function is minimised using a nonlinear least-squares inversion method according to Marquardt (1963).

For the Br^- tracer, R and D values were estimated by fitting the analytical solution of the CDE model under equilibrium conditions. These parameters are presented in Table 6.2.

For THC transport the two-site chemical nonequilibrium CDE model was used. As the pesticide was applied as a short pulse to the soil surface, Dirac delta input is mathematically approximated in the boundary value problem (Flury et al., 1998). Zero initial concentration in the initial value problem and zero order production in the production value problem were assumed. Pore-water velocity and dispersion coefficient (from Br^- data, assuming that THC underwent the same physical transport processes as the tracer) were set constant, linear pesticide sorption and pesticide degradation only in the liquid phase were considered. The retardation factor (R_{mod}) and nonequilibrium dimensionless parameters β, ω and μ, were estimated from the fitting. The parameters f (dimensionless), α (h^{-1}) and μ_{liq} (h^{-1}) were calculated from equations [6.8], [6.9] and [6.10], respectively. An experimental pesticide retardation factor (R_{exp}) was derived from equation [6.2] for comparison with R_{mod}. K_d values were taken from the adsorption chapter. The goodness of fit was evaluated by visual assessment, R^2 values, Mean Squared Errors (MSE), and the 95% confidence limits of the estimated parameters.

Comparison among group means was conducted according to chapter 2, section 2.8.

Table 6.2. Calculated soil column parameters (V, q, v, Q, t) (± standard deviation) and estimated transport parameter (R, D) (± standard error) for bromide tracer, both in SV using different influent solutions and in FERT (SV + Fertiormont at 1%, w/w) with MQ as influent solution. The values of D and R were derived from BTCs generated by the CXTFIT modelling using the equilibrium convection-dispersion approach. The values of λ were calculated as λ=D/v

Treatment	V^a (cm^3)	q^b (cm h^{-1})	v^c (cm h^{-1})	Q^d (cm^3 h^{-1})	t^e (h)	R^f	D^g (cm^2 h^{-1})	λ^h (cm)	R^2	MSE^i
MQ	137 ± 20	2.58 ± 0.42	4.80 ± 0.78	8.0 ± 1.3	23 ± 2	1.38 ± 0.04	2.30 ± 0.21	0.48	0.955	0.6 10^{-4}
TWW	99 ± 11	1.44 ± 0.24	2.72 ± 0.42	4.5 ± 0.7	32 ± 1	1.39 ± 0.02	0.81 ± 0.06	0.30	0.981	0.3 10^{-4}
$(NH4)_2SO_4$ 5mM	127 ± 11	1.98 ± 0.48	3.66 ± 0.84	6.2 ± 1.5	25 ± 4	1.38 ± 0.04	1.75 ± 0.16	0.48	0.955	0.6 10^{-4}
DOC 3	79 ± 6	0.96 ± 0.12	1.86 ± 0.36	3.0 ± 0.4	33 ± 1	1.23 ± 0.03	0.65 ± 0.07	0.35	0.963	0.7 10^{-4}
DOC 300	86 ± 9	0.96 ± 0.24	1.86 ± 0.48	3.2 ± 0.8	41 ± 8	1.58 ± 0.03	1.06 ± 0.07	0.57	0.983	0.2 10^{-4}
FERT#	76 ± 8	0.74 ± 0.24	1.38 ± 0.48	2.3 ± 0.8	47 ± 12	1.18 ± 0.02	0.28 ± 0.03	0.20	0.940	0.7 10^{-4}

[a]V, total volume leached; [b]q, Darcy velocity; [c]v, average pore-water velocity; [d]Q, average elution fluxes; [e]t, experimental time; [f]R, retardation factor; [g]D, dispersion coefficient; [h]λ, soil dispersivity; [i]MSE, mean squared error

#FERT eluted with MQ

6.3. RESULTS AND DISCUSSION

6.3.1. Leachate properties and water flow through columns

The physicochemical properties of the leachates showed good agreement among repetitions, so data for replicated columns were pooled. In general, leachate properties were in accordance with those of the influent solutions. No great variations of pH values were recorded, remaining practically stable around pH 8 along the experiments (Figure 6.3 A). Only elution with TWW slightly increased leachate pH above 8, whereas amendment with FERT led to pH values always below 8.

Leachate conductivity (Figure 6.3 B) corresponds to the contribution of soil, saturation solution, Br^- tracer, influent solution and FERT amendment. Salts from the soil were mainly eluted in the first leachates and then gradually fell as a consequence of the washing effect until a constant level was reached after approximately 2 PV. The contribution of the influent solution was noted in the final part of the EC curve, with a background level above that of the control (MQ) for TWW, $(NH_4)_2SO_4$ and DOC 300 solutions. On the other hand, the ionic composition of FERT resulted in the highest maximum EC value, considerably higher than that of SV eluted with MQ and the rest of solutions.

DOC from the columns peaked at approximately 1 PV, and then decreased to a constant level. In general, estimation of DOC in leachates from A_{254} measurements showed that no significant changes occurred for the different influent solutions, except for DOC 300 (Figure 6.3 C). This solution exhibited a much slower decrease, likely caused by DOC adsorption-desorption processes during the movement through the column. It is also remarkable the increase of the amount of DOC leached when SV soil was amended with 1% FERT, probably indicating that the amendment contained a great proportion of low-molecular weight and water-soluble DOC (Guo and Chorover, 2003; Rodríguez-Liébana et al., 2014b). In addition Guo and Chorover (2003) have reported that the adsorbed DOC fractions, with higher molecular weight and hydrophobicity, may not be completely desorbed leading to a strongly bound fraction.

The mean elution fluxes (Q) are presented in Table 6.2. Likewise, the evolution of Q of the different influents through the soil column is shown in Figure 6.4. Though a similar pattern was found in all cases, elution was slower than MQ water for all the treatments, with the lower values for FERT and DOC solutions (Table 6.2). This fact has been related with diminished soil porosity due to a reduction in larger pores and an important increase in finer pores when solutions rich in OM and salts are infiltrated (Cox et al., 1997b; Müller et al., 2102). DOC has been also reported to develop hydrophobic coatings which influence aggregate wetting processes (Fernández-Gálvez et al., 2012).

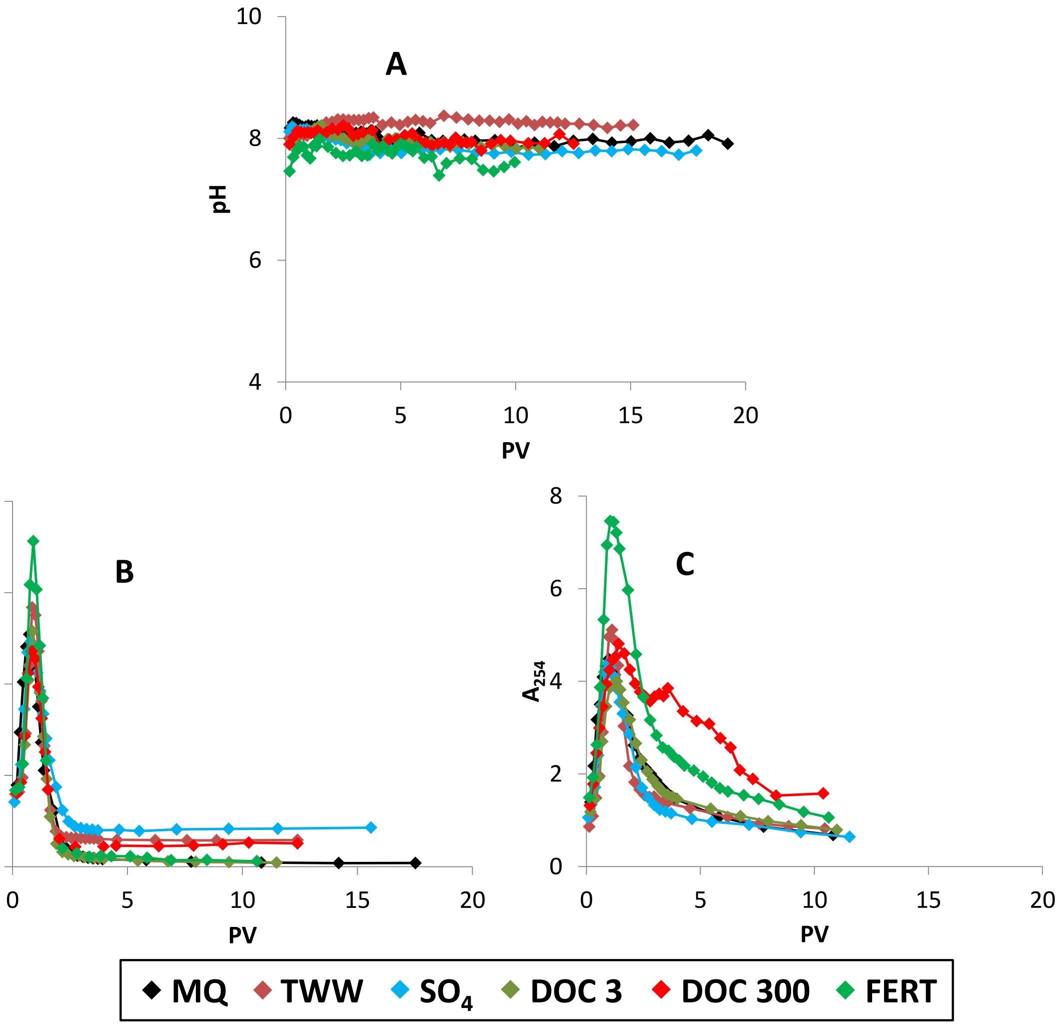


Figure 6.3. Evolution of leachate properties throughout the leaching experiments for the different treatments. A: pH; B: Electrical conductivity; C: Estimation of DOC content by measuring absorbance at 254 nm

Apart from salts, and suspended and dissolved OC which may block large size pores, González-Vila et al. (1992) have found a solubilisation–precipitation of soil carbonates in calcareous soils promoted by fulvic and humic acids. The association of DOC with soil carbonates could also contribute to the reduced soil porosity. A similar effect has been observed for anionic surfactant solutions (Peña et al., 2011a).

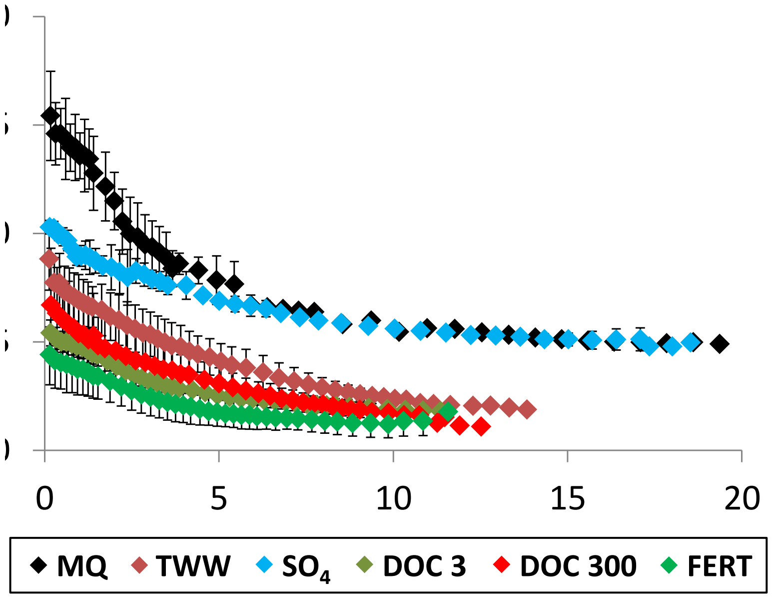


Figure 6.4. Evolution of flow rates throughout leaching experiments for the different treatments. Vertical bars represent standard deviation of the means (n = 3)

6.3.2. Description of bromide breakthrough curves and modelling with STANMOD program

Chloride was discarded as non-reactive tracer due to the contribution of soil and some of the influent solutions to the Cl^- balance in preliminary tests (the total leached amount was higher than 345% of the initially added even for the control). Therefore, Br^- was finally selected as in previous studies (Montoya et al., 2006; De Wilde et al., 2009; Rodríguez-Liébana et al., 2014b; Fernández-Bayo et al., 2015).

Figure 6.5 shows the experimental relative and cumulative Br^- BTCs, and Figure 6.6 the modelled BTCs for all the percolating solutions and for the FERT amended soil. No differences are observed for the different curves, except a slightly reduced peak maximum (PM) for DOC 300 solution, a fact previously reported for soils amended with different organic wastes (Marín-Benito et al., 2013; Rodríguez-Liébana et al., 2014b). Although a slight tailing is observed, the curves are quite symmetrical. Elution of Br^- started at approximately 0.5 PV and peaked never before 1 PV, suggesting physical equilibrium and uniform flow of water front (Sánchez et al., 2003; De Wilde et al., 2009; Fernández-Bayo et al., 2015). Moreover, the average mass recovery rate of Br^- in the leachates was 81±6% of the amount added to the top of soil columns, a value similar to those found by Lennartz and Kamra (1998) and Lennartz (1999).

The shape of the curves allowed simulation of Br^- transport under equilibrium conditions using the inverse modelling option of CXTFIT 2.1. As shown in Figure 6.6, the BTCs were well-fitted to the one dimensional deterministic equilibrium CDE model, with high determination coefficients ($R^2 > 0.94$) and low mean squared errors ($MSE < 0.7\ 10^{-4}$). Both, the retardation factor (R) and the dispersion coefficient (D) of the tracer were estimated from the fitting (Table 6.2).

The R values were slightly higher than 1 as confirmed by the visual assessment of the BTCs (Figure 6.5). The column amended with FERT displayed a considerably lower D value (Table 6.2), indicating less diffusion-dispersion for this treatment (Pang and Close, 1999; Dal Bosco et al., 2013). This could be due to the above suggested reduced soil porosity, which thereby implies more difficulty in water transport. In contrast, other authors have reported higher D values for soils amended with different organic wastes due to the greater heterogeneity of soil columns thus favouring a less homogeneous packing and the formation of preferential flow channels (Marín-Benito et al., 2013; Rodríguez-Liébana et al., 2014b).

Dispersivity (λ) is a soil hydrodynamic property calculated as D/v, assuming negligible molecular diffusion (Okada et al., 2014), which implies a linear relationship between D and v (Magesan et al., 1995). It is used as an indicator of local solute mobility in a soil (Montoya et al., 2006). Except for DOC 300, values of λ were slightly lower (Table 6.2) than those typically found for laboratory soil columns in the range 0.5-2 cm (Jury et al., 1991). The low λ is in accordance with a homogeneous soil packing and the short flow-path length (Shaw et al., 2000). If DOC 300 solution is excluded, soil λ was significantly related with averaged pore water velocities and elution fluxes ($R^2 = 0.695$; $P = 0.05$), in accordance with previous studies (Vanderborght et al., 2000; Nützmann et al., 2002; Latrille, 2013). Other reports have also related λ with the quality of the influent solution (Müller et al., 2012), and with pore size distribution (Radcliffe and Šimůnek, 2010).

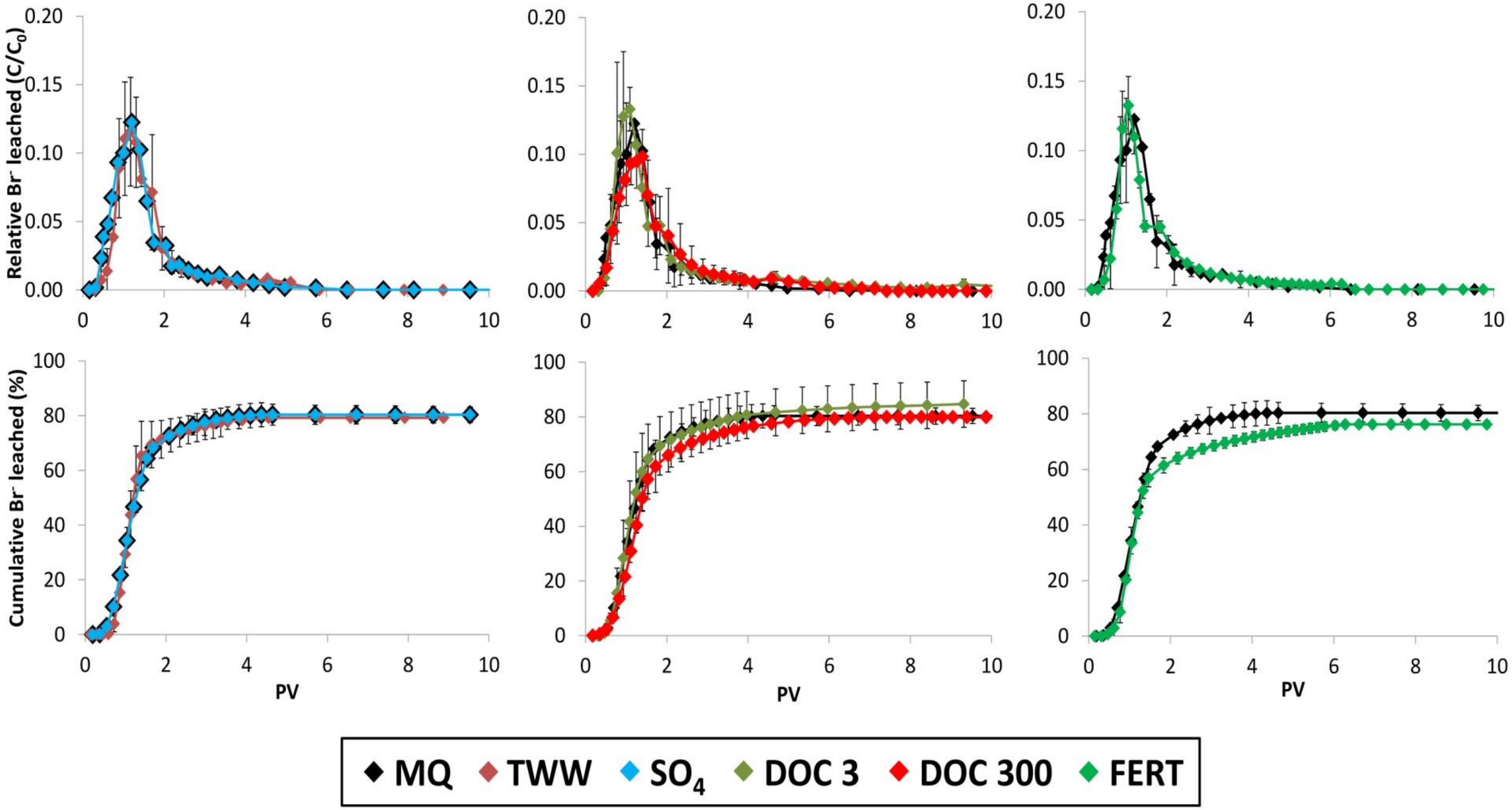


Figure 6.5. Experimental relative (top) and cumulative (bottom) breakthrough curves corresponding to the leaching of the non-reactive bromide ion in soil columns for the different treatments. Vertical bars represent standard deviation of the means (n = 3)

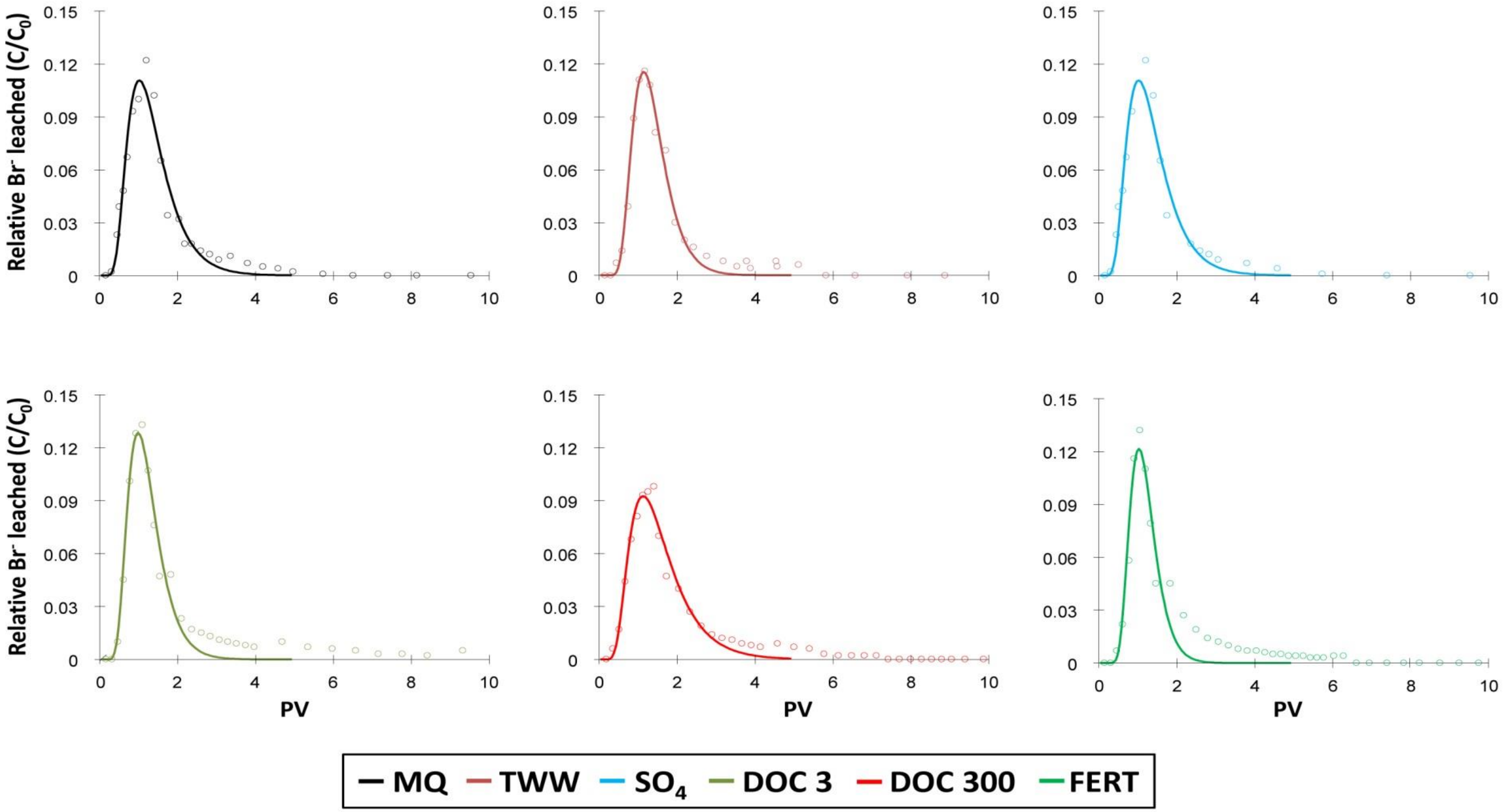


Figure 6.6. Modelled breakthrough curves corresponding to the leaching of the non-reactive bromide ion in soil columns for the different treatments

6.3.3. Description of thiacloprid breakthrough curves and modelling with STANMOD program

The experimental relative and cumulative BTCs corresponding to THC leaching in soil columns are represented in Figures 6.7 and 6.8, respectively. The PMs of THC occurred above 1 PV, which indicates that sorption processes are involved in leaching (Gamerdinger et al., 1991; Beck et al., 1993).

The curves were slightly asymmetrical, with a relatively extended tail. This asymmetry in solute BTCs, widely reported in the literature (Pot et al., 2011; Rodríguez-Cruz et al., 2011; Marín-Benito et al., 2013; Langeron et al., 2014; Rodríguez-Liébana et al., 2014b), has been attributed to non-equilibrium sorption due to time-dependent pesticide/soil interactions (Brusseau et al., 1989). With DOC solutions as influents, as well as when FERT was added, the rise was moderate, resulting in a more sigmoidal curve. This suggests that transport occurred closer to equilibrium conditions. Bouchard et al. (1988) observed increased equilibrium transport with decreasing pore water velocity, as is the case of DOC solutions and FERT amendment (Table 6.2).

Elution with MQ water led to an initial breakthrough of approximately 1 PV and a PM at 4.0 PV, corresponding to 20% of the pesticide initially added. At the end of the experimental time 66 ± 5% of THC was recovered in the leachates (Figure 6.7).

The solutions with less influence on THC leaching were $(NH_4)_2SO_4$ and TWW (Figure 6.7), leading to experimental values similar to MQ. On the contrary, main differences in leaching with respect to the control were observed with DOC solutions and FERT amendment. All these latter treatments resulted in curves shifted to the right with PM retarded to 4.7, 5.1 and 5.5 PV for DOC 3, DOC 300 and FERT, respectively. The intensity of the PM was either not modified for the DOC 300 solution (23% of the initially added), or reduced to values of 12% for DOC 3 and 13% for FERT. Total leached amount corresponded to 34 ± 4% for FERT, 37 ± 5% for DOC 3 and 54 ± 9% for DOC 300 (Figure 6.7). All these data suggest a greater retention of the pesticide by the soil, especially for DOC 3 and FERT treatments. Our findings contradict a previous study reporting enhanced mobility of prometryne by using sewage sludge derived DOM at 80 and 160 mg L^{-1} DOC as percolating solutions (Jiang et al., 2008). In the case of DOC 300, although pesticide elution was retarded, the high intensity of the PM (similar to that of MQ) and the less tailed desorption section are indicative of a more reversible THC retention in soil. It is possible that the pesticide co-eluted with DOC which leached from the column at longer PV and in higher amounts (Figure 6.3 C) (Cabrera et al., 2011). This fact is supported by the highest value of λ for DOC 300 (Table 6.2), which indicates a higher solute dispersivity in the soil solution (Montoya et al., 2006). However, an overall effect of reduction in the total amount of THC leached is clearly shown in the cumulative BTCs (Figure 6.7). Comparison between DOC 300 and FERT is not possible because neither the DOC amount nor the OM composition in the experimental setups are comparable.

As a consequence of the above-mentioned factors, it was necessary to simulate THC leaching through soil columns under non-equilibrium conditions, using the two-site chemical nonequilibrium CDE model. The observed nonequilibrium was interpreted as a sorption-related process, assuming that transport nonequilibrium did not occur. Only when DOC 300 was used as influent solution the software suggested equilibrium conditions, due to the proximity of β values to the unity and ω to 100 (Peña et al., 2011a).

The simulated BTCs are given in Figure 6.8, and the parameters generated by CXTFIT modelling are shown in Table 6.3.

According to the high determination coefficients ($R^2 \geq 0.965$) and the low mean squared errors ($MSE \leq 0.006$) it can be said that the experimental data were well described by the CXTFIT model. The values of β were 0.61 for MQ, 0.57 for TWW, 0.52 for $(NH_4)_2SO_4$, 0.75 for DOC 3 and 0.78 for FERT, indicating that retardation of THC was mainly regulated by instantaneous adsorption, especially for DOC 3 and FERT, as supported by the negative correlation between R_{mod} and α (r = 0.72). As a consequence, between 22 and 48% of pesticide retardation was controlled by slow kinetic adsorption. While infiltration with MQ water exhibited the highest α value, DOC 3 and FERT treatments yielded the lowest. Pignatello (2000) reported that the resistance of the soil matrix to solute diffusion is the only reasonably explanation of slow kinetics. Therefore THC diffusion was more difficult when DOC 3 solution was infiltrated, or when SV soil was amended with FERT. The *f* values indicated a proportion of instantaneous adsorption sites in the range 0.14-0.44, with the highest values for DOC 3 and FERT, because the experimental conditions likely provided new accessible sorption sites. It is also noticeable that μ values correlated negatively with the leached THC amounts at the end of the experiments (r = 0.99) (Table 6.4), with the highest degradation rates for DOC 3 and FERT (Table 6.3). However, this is not reflected in the calculated values of μ_{liq} which, compared with the corresponding μ value, were similar for MQ and SO_4, and 1.8, 2.7 and 3.6 times lower for TWW, DOC solutions and FERT soil respectively. Therefore, in addition to pesticide degradation in the soil solution, other processes are responsible for the differences in the recovered amounts. Montoya et al. (2006) indicated that degradation of atrazine in soil columns could be indirectly regulated by sorption to minerals and organic particles. In our case, DOC–soil interactions during infiltration could control sorption–desorption of THC in the soil (Jiang et al., 2008)

As shown by the estimated retardation factors (R_{mod}) low differences in the retention of THC through the soil columns were found, in line with the batch adsorption assays (chapter 3). Although in general an agreement between batch and column results exists (Pot et al., 2011; Marín-Benito et al., 2013), no relationship was found in our study ($P > 0.05$).

According to R_{mod}, retention of THC increased in all the cases to different extent with respect to control solution. Amendment of soil with 1% FERT led to the highest increase in pesticide retention, which can be partially explained by the slight increase of soil OC content (chapter 7, Table 7.1). In a previous work a linear relationship between R_{mod} of THC and soil OC was reported (Rodríguez-Liébana et al., 2014b). On the other hand the water movement through the soil columns was considerably slower when compared with MQ water (Table 6.2). This would result in increases in THC residence time in the columns, with the consequent delay in its leaching due to the slower exchange of THC by diffusion between mobile and less mobile water phases developed in small pores (Pignatello and Xing, 1996; Cox et al., 1997b).

The mentioned discrepancies between batch and column experiments are reflected in the differences between R_{mod} and R_{exp} (obtained from the batch adsorption experiments according to the equation [6.2]), the latter being always approximately 2-fold higher. These frequently observed divergences have been attributed to several reasons such as failure to attain local equilibrium in column experiments due to continuous removal of pesticide, possible increase of soil specific surface area in batch methods due to abrasion caused by continuous shaking, column flow variations and channelling, and much higher soil/solution ratio in columns (Brusseau et al., 1989;

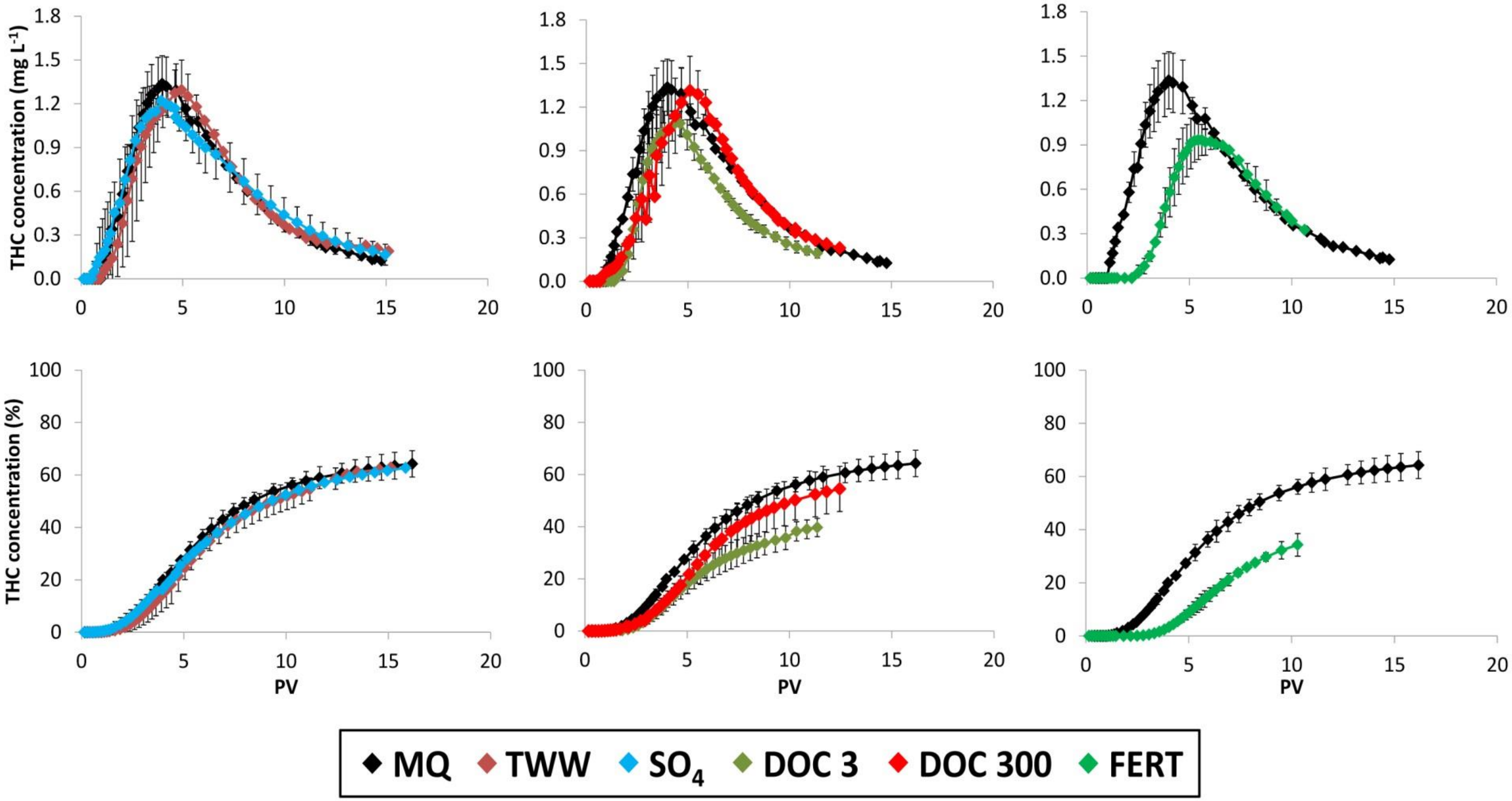


Figure 6.7. Experimental relative (top) and cumulative (bottom) breakthrough curves corresponding to the leaching of thiacloprid in soil columns for the different treatments. Vertical bars correspond to standard deviation of the means (n = 3)

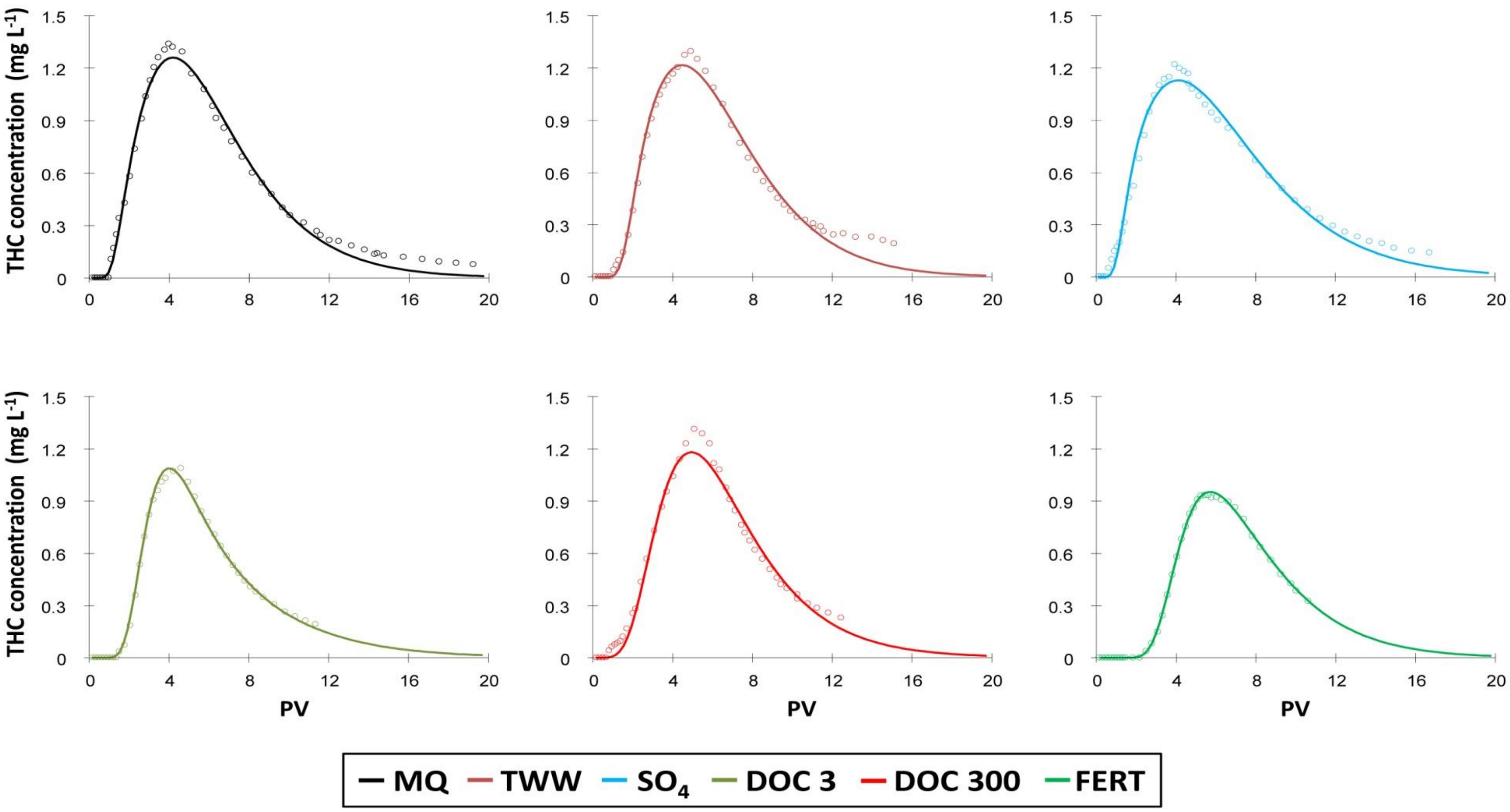


Figure 6.8. Modelled relative breakthrough curves corresponding to the leaching of thiacloprid in soil columns for the different treatments

Table 6.3. Thiacloprid sorption parameters (K_d, R_{exp}) ± standard deviation, and estimated transport parameters (R_{mod}, β, ω, μ) ± standard error in SV and FERT soils (SV + Fertiormont at 1% w/w), using different influent solutions, from BTCs generated by the CXTFIT modelling using the two-site chemical non equilibrium convection-dispersion approach. The values of ƒ, α and μ_{liq} were calculated from the estimated parameters

Treatment	**K_d[a]**	**R_{exp}[b]**	**R_{mod}**	**β**	**ω**	***f***	**α (h^{-1})**	**μ**	**μ_{liq}(h^{-1})**	**R^2**	**MSE[c]**
MQ	4.0 ± 0.2	11.51	6.41 ± 0.07	0.61 ± 0.03	3.54 ± 0.58	0.25	1.36	0.17 ± 0.02	0.16	0.987	0.003
TWW	3.9 ± 0.2	11.25	6.63 ± 0.08	0.57 ± 0.02	3.13 ± 0.36	0.20	0.60	0.20 ± 0.02	0.11	0.985	0.003
$(NH_4)_2SO_4$ 5mM	3.9 ± 0.2	11.25	6.89 ± 0.10	0.52 ± 0.02	3.39 ± 0.36	0.14	0.75	0.13 ± 0.02	0.10	0.983	0.003
DOC 3	4.3 ± 0.2	12.30	6.98 ± 0.12	0.75 ± 0.01	0.83 ± 0.04	0.41	0.18	0.51 ± 0.01	0.19	0.998	0.000
DOC 300†	3.7 ± 0.1	10.72	7.20 ± 0.07	≈1	≈100			0.30 ± 0.02	0.11	0.965	0.006
FERT#	4.1 ± 0.1	11.78	8.02 ± 0.07	0.78 ± 0.01	1.28 ± 0.06	0.44	0.20	0.54 ± 0.01	0.15	0.999	0.000

[a] Data from batch adsorption study (Table 3.7); [b] R_{exp} calculated as $R_{exp} = 1 + \frac{K_d \times \rho}{\theta}$; [c] Mean squared error

† Adjusted to the equilibrium CDE as suggested by the software; # FERT eluted with MQ

Boesten and Van der Linden, 1991; Kookana et al., 1992; Fesch et al., 1998; Chang and Wang, 2002).Nonlinearity in sorption isotherms may also affect since R_{exp} is derived from an adsorption constant calculated through forced linearization. Furthermore, some authors (Bouchard et al., 1988; Maraqa et al., 1998) have reported larger adsorption parameters determined by the batch technique than those found through column transport experiments due to the improved contact between pesticide and soil, thus resulting in lower retardation factors derived from the latter.

On the contrary, some works concluded that results from batch experiments can be used to predict pesticide transport in soil columns if non-equilibrium sorption is considered (Boesten et al., 1989; Streck et al., 1995; Altfelder et al., 2001; Ma and Selim, 2005).

6.3.4. Thiacloprid amount remaining in soil

Residues of THC retained in the soil column were distributed uniformly between both column segments, except for DOC 300 and FERT treatments for which a significant ($P < 0.01$) higher amount of pesticide was found in the lower layer (Figure 6.9; Table 6.4).

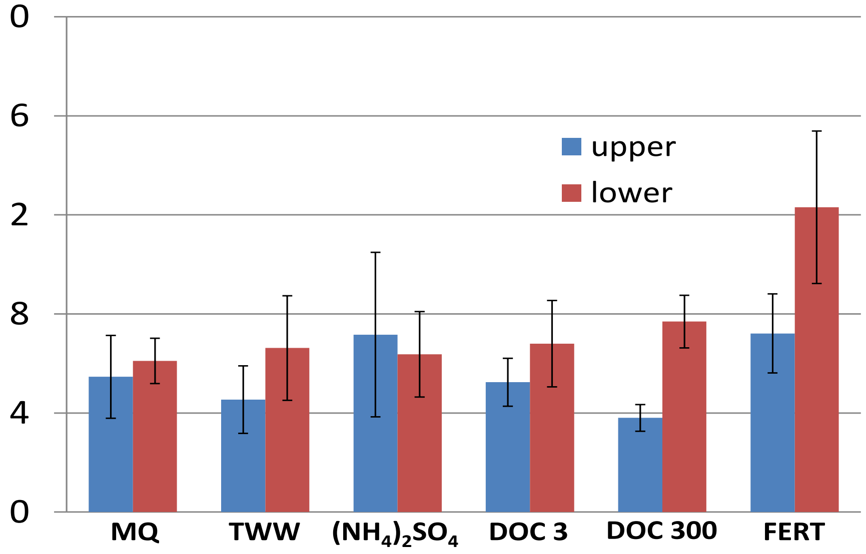


Figure 6.9. THC residues recovered from soil columns after leaching experiments for the different treatments. Vertical bars indicate standard deviation of the means (n = 6)

No statistical differences were found in the amount of pesticide retained in the top layer of soil column for any treatment ($P > 0.05$). In contrast, the amount of THC extracted from the lower layer was significantly higher for FERT soil with respect to the other columns ($P < 0.01$) confirming the higher affinity of THC for FERT-amended soil. The amount of pesticide recovered from both layers was always below 20% of the amount initially applied, being the total amount recovered (extracted + leached) in the range 50-80%. In spite of the short duration of the experiments, the relatively low pesticide recovered could be explained in part by degradation of THC entrapped in soil micropores (Cox et al., 1997b; Zeng et al., 2011). The dissipation of THC is supported by the rapid biological degradation already discussed in the degradation chapter and has been considered through μ and μ_{liq} parameters (Table 6.3). On the other hand, the small differences observed among treatments could be also attributed to differences in leached PVs, due to the difficulties in precisely establishing the experimental conditions, since flow rates were different (Table 6.2). Although the duration of the experiments was initially adjusted according to the observed flow (see time in Table 6.2 for DOC 300 and FERT), total PVs for both experiments were finally lower than those of MQ.

Table 6.4. Amount (%) of THC leached and retained in the soil columns (upper and lower layers), according to the different solutions percolated

Treatment	Leached (%)	Upper layer[a] (%)	Lower layer[b] (%)
MQ	66.2 ± 4.98	5.46 ± 1.67	6.10 ± 0.92
TWW	59.0 ± 5.64	4.54 ± 1.36	6.63 ± 2.11
$(NH4)_2SO_4$ 5mM	63.6 ± 1.31	7.17 ± 3.33	6.37 ± 1.73
DOC 3	37.5 ± 5.29	5.25 ± 0.97	6.80 ± 1.74
DOC 300	54.5 ± 8.65	3.80 ± 0.54	7.69 ± 1.06
FERT[#]	34.3 ± 4.26	7.21 ± 1.60	12.3 ± 3.08

[a]0-2.5 cm; [b]2.5-5 cm

[#]FERT eluted with MQ

6.4. CONCLUSIONS

In general it can be concluded that for THC, a relatively hydrophilic pesticide, a considerable proportion of the applied compound is leached from this poor-OC soil, that the composition of the irrigation solutions evaluated affects only slightly the movement of the pesticide through the soil profile, except when using DOC solutions at low concentration and that addition of an organic amendment reduces the fate of THC by increasing its retention to the soil.

7. FIELD EXPERIMENT

7.1. INTRODUCTION

Pesticides, applied in agriculture across entire fields, may adversely affect soil conservation and pose a potential risk of surface- and groundwater contamination. Moreover, the use of pesticides may decrease the biodiversity of soil, thus resulting in lower soil quality (Johnston, 1986; Edvantoro et al., 2003; Megharaj and Naidu, 2008).

A variety of agricultural factors such as pesticide application rate and mode, and repeated application are capable of affecting the fate of organic contaminants in the field. Persistence of pesticides has been found to increase with increasing application doses (Davidson et al., 1980; Gan et al., 1995), but to decrease with repeated pesticide application due to the adaptation of soil microorganisms and the acceleration of volatilisation processes (Piutti et al., 2002; Sørensen and Aamand, 2003; Marín-Benito et al., 2014).

Furthermore the increased contact time between soil matrix and pesticides (ageing) may decrease their bioavailability by increasing sorption onto soil particles, diffusion into soil macro- and micropores, and entrapment within soil OM (Brusseau et al., 1991; Pignatello and Xing, 1996, Gevao et al., 2000).

Although laboratory experiments provide information about the general behaviour of pesticides in soils, predictions based on laboratory data tend to overestimate pesticide persistence in the field due to fluctuating temperature and moisture conditions, as well as spatial and temporal changes in soil properties and microbial populations (Beulke et al., 2000; 2005; Bending et al., 2003). The effect of photodegradation and volatilisation may be also enhanced in the field for sensitive compounds.

Once evaluated the main processes that control pesticide dynamics in soil at laboratory scale, a field study becomes necessary to check the real fate. In this chapter we have evaluated the field dissipation of two pesticides, thiacloprid (THC) and pendimethalin (PDM) with contrasting properties, and their potential to contaminate groundwater. The effects of irrigation with well water (WL) and TWW, as well as the amendment of soil with an organic fertiliser (FERT) were also assessed. Finally, the effect of each treatment on some biological indicators, such as soil respiration or enzyme activities, was studied.

7.2. EXPERIMENTAL SETUP

7.2.1. Properties of pesticides and irrigation fluids

The behaviour of the herbicide pendimethalin (PDM) and the insecticide thiacloprid (THC) was studied in a field assay. The properties of both compounds can be found in Figure 2.2. Different pesticide standards were employed: high purity standards (purity ≥ 97%) (Dr. Ehrenstorfer GmbH, Augsburg, Germany) for laboratory analysis and commercial formulations for field studies: CALYPSO (Bayer Cropsciences, Alcácer, Valencia, Spain) a 48% w/v soluble concentrate for THC and BLUSS (Makhteshim Agan SA, Valencia, Spain) a 33% emulsifiable concentrate for PDM.

TWW and WL were both used for irrigation. TWW was directly pumped from an irrigation ditch located a few meters from the field plot. Meanwhile, the well from which the groundwater was pumped, was located in the field site. The analysis of both irrigation fluids during the field experiment, carried out as described in chapter 2, indicated that TWW had an average pH of 7.7 ± 0.1, EC 0.74 ± 0.04 dS m^{-1}, total solids content 547 ± 54 mg L^{-1} and DOC 23.0 ± 1.8 mg L^{-1}. The properties of the WL were pH 7.7 ± 0.2, EC 0.75 ± 0.001 dS m^{-1}, total solids content 353 ± 25 mg L^{-1} and DOC 4.6 ± 0.2 mg L^{-1}. Concerning different ions, analysis by ion chromatography indicated that TWW contained 99.0 mg L^{-1} Cl^- and 5.0 mg L^{-1} NO_3^- while WL contained 0.2 mg L^{-1} F^-, 20.8 mg L^{-1} Cl^-, 43.5 mg L^{-1} NO_3^- and 102 mg L^{-1} SO_4^{2-}.

7.2.2. Experimental site and climatic conditions

The field site of this experiment, 0.04 ha (aproximately 20 x 20 m), was located on the Vega de Granada aquifer (Southeastern Spain, 37° 10' 22.47" N 3° 38' 09.24"W, 631 m altitude), an area mainly devoted to agricultural activities. The plot under study (Figure 7.1) has been irrigated with TWW of the same WWTP in the last decades. However, it has not received previous pesticide treatments. During the field experiment the subsurface groundwater table depth oscillated between 40 and 43 m. Before the beginning of the experiments, four soil samples were collected at random within the experimental area from the top 10 cm. Soil samples were air dried, sieved through 2 mm and pooled. Soil physicochemical properties, according to the analytical methods described in chapter 2, consisted of 41% sand, 34% silt, 25% clay, pH 8.7 ± 0.2, EC 0.25 ± 0.03 dS m^{-1} (both at 1:2.5 w/v ratio), 1.0 ± 0.1 OC, 5.2% total C, 0.15% total N, 22% $CaCO_3$, 20% FC and 1.5 g cm^{-3} bulk density.

Figure 7.1. Preparing and levelling the field plots before the beginning of the experiments

Unit plot size was 2.6 m^2 (1.6 x 1.6 m) and a 1-m wide free zone was set between plots to prevent cross contamination. A total of nine plots were selected at the site, surrounded by a 25-cm border (Figure 7.2). Three of the plots were irrigated with TWW and another three with WL. The three final plots were also irrigated with TWW and amended five days before pesticide application with FERT at a rate of 3.2 kg per plot (F+TWW), equivalent to 1% dose considering the first 10 cm of soil. The organic fertiliser was incorporated by manual mixing with the upper soil layer. Each plot, irrigated by basin flooding, received the same irrigation volume, a total of 180 mm, during the field experiment.

Figure 7.2. General overview of the experimental plots, collection of soil samples and replenishment of sample holes (right)

Daily climate data (maximum and minimum temperature, precipitation, sun irradiation, and wind velocity) were acquired from the IFAPA meteorological station placed only some tenths of meters away from the plot (http://www.juntadeandalucia.es/agriculturaypesca/ifapa/ria/servlet/FrontController). During the sampling period mean daily temperature averaged 15.0 °C and ambient humidity 72%. Although the plots are placed in a Mediterranean zone, with typical low mean annual precipitation (average 357 mm for the period 1972-2000, http://www.aemet.es/es/serviciosclimaticos/datosclimatologicos), mainly concentrated during autumn and winter, abundant rainfall occurred (a total of 202.9 mm during the field experiment) starting 13 d after pesticide application (Figure 7.3).

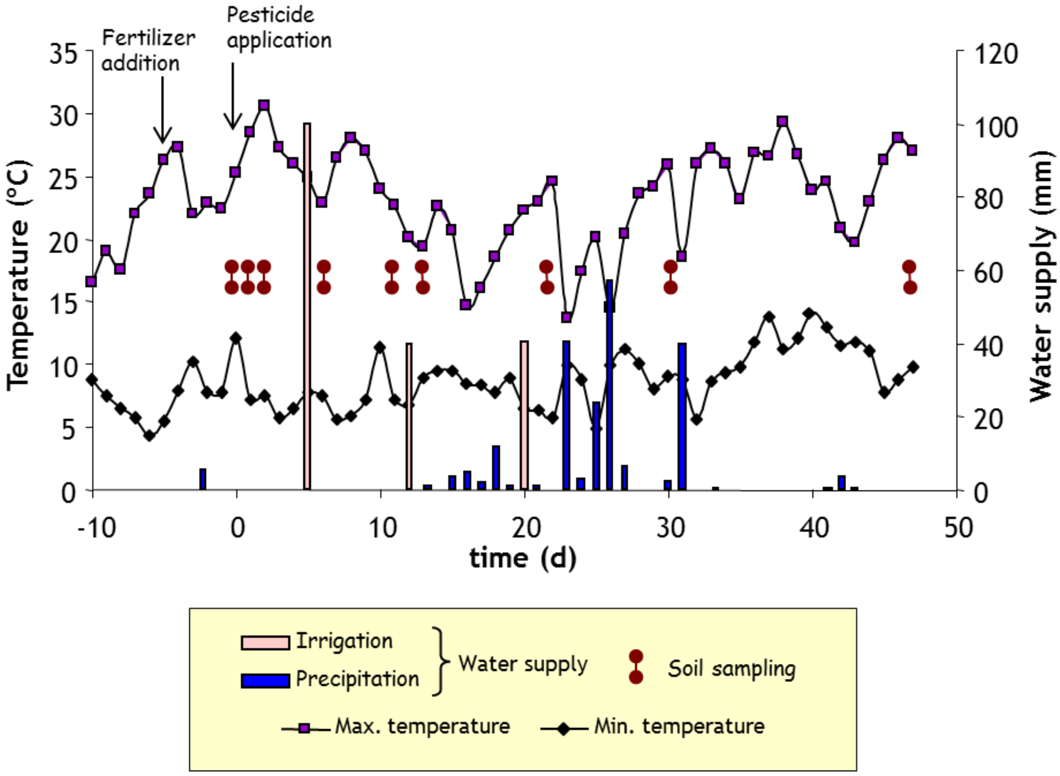


Figure 7.3. Maximal and minimal temperatures, water supply (irrigation or rain), pesticide and fertiliser application dates and soil sampling dates

7.2.3. Field experiment

A mixture of the commercial pesticide formulations was applied on bare soil, with a portable knapsack sprayer at a rate of 6 L ha^{-1}. Together with the pesticides, a non-retained tracer, magnesium bromide (Aldrich, Madrid, Spain), was also applied at a rate of 32.5 kg ha^{-1} (Kazemi et al., 2008). Pesticide initial concentration was only semi realistic, but was estimated necessary to achieve the monitoring of pesticide residues at various depths and along the experimental time.

Soils from the upper layer (0-5 cm) were periodically sampled per triplicate during almost 50 days, using a steel spade of 3.5 cm diameter. Nine and 22 days after pesticide application deeper soil samples (0-30 cm) were collected using a longer soil corer. To avoid the formation of preferential flow, the sample holes from all the sampling events were replenished with soil slurry prepared by mixing water with untreated sieved soil (4 mm) (Figure 7.2). Samples were packed individually in plastic bags, maintained in a portable freezer during collection and transport, and stored at -18 °C until analysis. Results are referred to on a dry weight soil basis, after drying overnight at 105 °C.

7.2.4. Pesticide adsorption isotherms

Isotherms were carried out using the batch equilibration method. Samples of soil (5 g for THC and 0.4 g for PDM) from the field plot were suspended in aliquots of 20 mL of aqueous pesticide solutions in the concentration ranges 0.2-10 and 0.2-1 mg L^{-1} for THC and PDM respectively, prepared in WL and TWW. The isotherms were conducted as described in chapter 3, section 2.3.1. The experiments were run in duplicate with a control of the pesticide solution without soil, to account for possible degradation or pesticide loss during the sorption process.

Sorption data were fitted to the linear and Freundlich models (equations [3.1] and [3.5]). The organic carbon distribution coefficient (K_{OC}) was calculated as equation [3.2]. The retardation coefficient (R) was calculated as in equation [6.2], where ρ_b is the soil bulk density and θ was approached by using soil FC.

7.2.5. Analytical determinations

The soil moisture content of each plot was determined per triplicate (n=9 per treatment) as in chapter 2, section 2.1.8.

Pesticides were extracted from soil samples (ca. 5 g d.w.) with methanol using ultrasound extraction, as described in section 2.2.4.2, chapter 2. Recoveries were 88.7% for THC and 91.0% for PDM. Pesticide analysis was accomplished by HPLC-DAD (chapter 2, section 2.2.5.2)

Bromide, together with Cl^- and NO_3^- in the soil, were determined by ion chromatography (section 2.1.17, chapter 2). In brief, ca. 1 g soil (d.w.) was shaken with 3 mL MQ water for 16 h at room temperature. Suspensions were centrifuged at 5000 rpm and 20 °C during 15 min and supernatants were passed through 0.45 µm PVDF filters. Sample ratios ranged from 1:10 to 1:2, depending on the sampling dates.

Soil induced respiration measurements were performed as explained in section 2.1.11 (chapter 2). Finally dehydrogenase activity (DHA) was determined in triplicated soil aliquots (1 g) during 20 h at 25 °C as previously described (section 2.1.10, chapter 2).

7.2.6. Evaluation and statistical treatment of the data

Exponential mathematical models were used to describe pesticide disappearance from soil under the three treatments. Different equations were used to fit the residual pesticide concentrations measured at different sampling dates (n= 9 dates x 3 replicates = 27): the single first-order kinetic (SFO) model ($C = C_0 \times e^{-kt}$), the one decay phase with plateau (SFO-P) ($C = (C_0 - A) \times e^{-kt} + A$), and the bi-exponential model ($C = C_1 \times e^{-k1t} + C_2 \times e^{-k2t}$), abbreviated as DFOP. The SFO model has been presented in chapter 5, equation [5.2]; the SFO-P model considers the formation of a plateau (A) without change in concentration with time; and the DFOP model assumes the simultaneous existence of two compartments or pools, in which the pesticide disappears at two different SFO kinetic rates (k_1 and k_2).

Model parameters were estimated from the best-fit model by fitting the data by non-linear regression, using a Levenberg–Marquardt algorithm that returns the best-fit parameters by minimising the sum of squares of the residuals between measured and fitted values. As in chapter 5, several criteria were adopted to determine the goodness-of-fit: visual graphical comparison, R^2 value, the confidence interval amplitude of the kinetic constant and mean standard error of the model. Values of $R^2 \geq 0.7$ were accepted as adequate (FOCUS, 2006).

Regulatory endpoints were derived by analysing data from field dissipation studies. DT_{50} and DT_{90} are the time taken for a 50/90% decline in mass or concentration of a pesticide after it has been applied to, formed in, or transferred to, an environmental compartment. DT_{50} and DT_{90} values are used as triggers for estimating environmental exposure and they should always be derived by best-fit kinetics. The SFO model has until recently been the preferred model for estimating DT_{50} or $t_{1/2}$ [ln 2/k] and DT_{90} values [ln 10/k] (García-Valcárcel and Tadeo, 2003; Herrero-Hernández et al., 2011).

The GUS index (Gustafson, 1989), used as an environmental risk indicator, was calculated as $GUS = \log(t_{1/2}) \times [4 - logK_{OC}]$. Comparison among treatments was done as described in chapter 2, section 2.8.

7.3. RESULTS AND DISCUSSION

7.3.1. Soil physicochemical properties

Soil pH, EC and OC content did not differ ($P > 0.05$) in soil samples from the same treatments taken at the beginning and at the end of the experiment (Table 7.1), as expected from short periods of irrigation with TWW and in agreement with other reports (Qian and Mecham, 2005; Kayikcioglu, 2012).

Table 7.1. Initial and final soil properties from the experimental plots

	TWW	**WL**	**TWW+F**
Initial pH	8.8 ± 0.0	9.0 ± 0.1	8.9 ± 0.1
Final pH	8.9 ± 0.0	8.9 ± 0.0	9.0 ± 0.1
Initial EC (dS m^{-1})	0.23 ± 0.07	0.28 ± 0.03	0.27 ± 0.04
Final EC	0.25 ± 0.03	0.23 ± 0.06	0.25 ± 0.02
Initial OC (%)	1.0 ± 0.1	0.9 ± 0.1	1.1 ± 0.2
Final OC	1.0 ± 0.2	1.1 ± 0.2	1.1 ± 0.2

The soil moisture content at each sampling time from pesticide application is represented in Figure 7.4. No differences were observed for the different treatments with a maximum coinciding with the first and main irrigation event at day 6. Although the last irrigation event was at day 20, soil moisture content was always higher than 50% FC due to abundant rainfall starting after 13 days of pesticide application (Figure 7.3).

7.3.2. Pesticide adsorption isotherms

Adsorption isotherms (Figure 7.5), run using the soil from the plot, show that while THC data were better fitted to the Freundlich equation, those of PDM were better described by the linear model (Table 7.2). It is also observed that for both pesticides there were no significant differences between the adsorption constants (K_f and K_d) when using WL or TWW ($P > 0.05$) (Table 7.2).

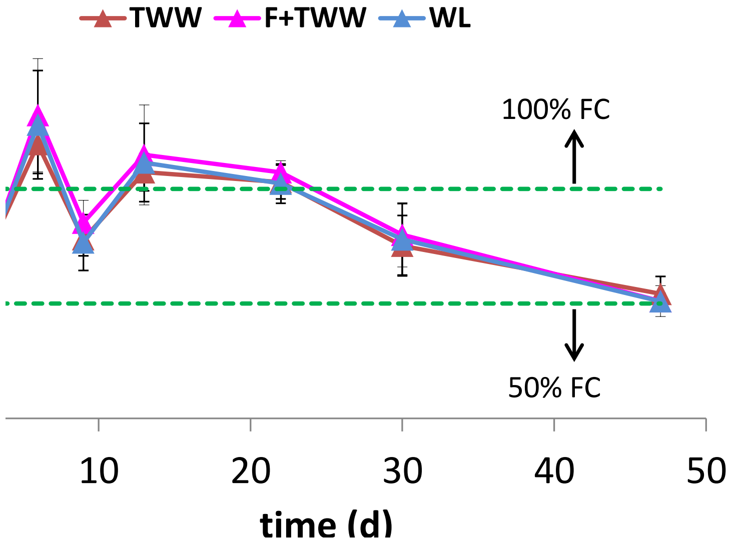


Figure 7.4. Moisture content of soil samples for the different treatments during the experiment. Vertical bars represent the standard deviation of the mean (n = 9)

The adsorption constants were much higher for PDM than for THC, as expected from their corresponding physicochemical properties (Figure 2.2) and in accordance with results presented in chapter 3. Adsorption isotherms of THC showed a high degree of non-linearity, exhibiting $1/n$ values < 0.6, in agreement with laboratory sorption results using SV soil (chapter 3, table 3.7). The low $1/n$ values classify these isotherms as type L (Giles et al., 1960), which indicates a decrease in specific sorption sites with increasing concentration as the adsorptive sites become occupied. On the other hand, the more hydrophobic PDM displayed a linear isotherm suggesting a partitioning mechanism without an apparent limit to sorption (Table 7.2; Figure 7.5). The retardation factors, R, show that THC is expected to be considerably less delayed than PDM when moving through the soil profile.

7.3.3. Bromide behaviour in the field plots

Bromide, used as a non-retained tracer, showed that the three plots behaved similarly (Figure 7.6). Bromide, applied together with the pesticides, disappeared rapidly from the surface soil layer, reaching stable values before 10 days had elapsed from its application.

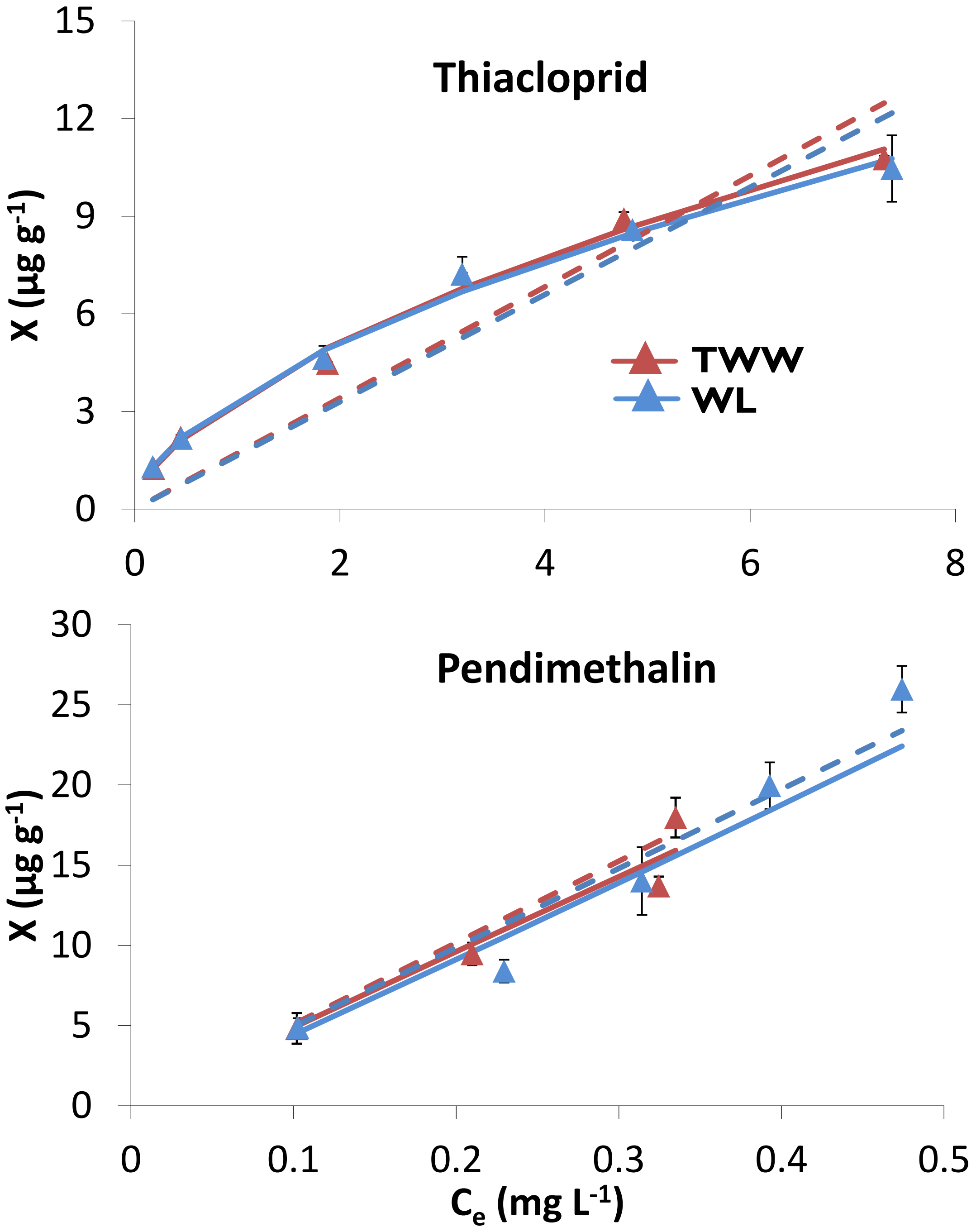


Figure 7.5. Adsorption isotherms of thiacloprid and pendimethalin in the soil collected from the field site with TWW (red) and WL water (blue). Experimental data were fitted to Freundlich (continuous lines) and linear (dashed lines) models. Vertical bars represent standard deviation of the mean (n = 3)

Table 7.2. Adsorption constants (± standard error) of thiacloprid (THC) and pendimethalin (PDM) in the soil collected from the field site derived from the fitting to the Freundlich (K_f and 1/n) and linear (K_d and K_{OC}) models

	WL	**TWW**	**WL**	**TWW**
	THIACLOPRID		PENDIMETHALIN	
K_f	3.5 ± 0.1	3.4 ± 0.1	49 ± 7	46 ± 13
1/n	0.57 ± 0.02	0.59 ± 0.01	1.0 ± 0.1	0.98 ± 0.16
R^2	0.991	0.994	0.882	0.766
K_d	1.6 ± 0.1	1.7 ± 0.1	49 ± 2	51 ± 4
R^2	0.855	0.868	0.902	0.859
K_{OC}[a]	165	171	4933	5082
R[b]	13.7	14.2	380.5	391.9

[a] $K_{OC} = (K_d \times 100) / \%OC$

[b] Retardation factor

This non-retained tracer disappeared more rapidly than pesticides from the upper soil layer, because pesticides can be retained (chapters 3 and 6) and may be subject to degradation (chapter 5) and volatilisation processes, hence reducing their presence in soil (Kazemi et al., 2008).

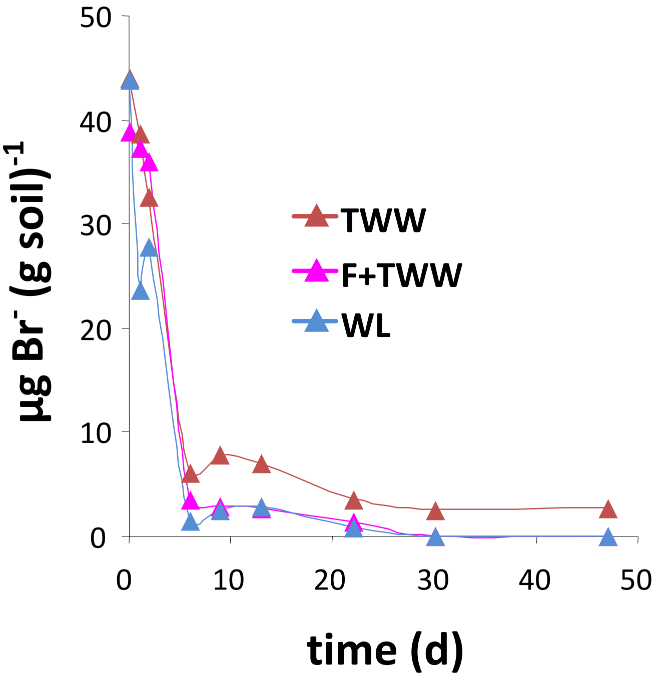


Figure 7.6. Evolution with time of Br- concentration in the upper soil layers

7.3.4. Pesticide dissipation in the field plots

In all cases the residual pesticide data were fitted well to the SFO model, with R^2 > 0.81. When using SFO-P or DFOP models the R^2 values continued to be good, the MSE values were improved, but the confidence intervals of the regression coefficients were too wide. Therefore it can be concluded that for all the treatments, THC and PDM behaviour can be adequately described by the SFO model (Table 7.3), in agreement with the incubation experiments described in chapter 5.

It is important to stress that main pesticide decay (up to 80% THC and 50% PDM) occurred during the first days after application (< 5 d) (Figure 7.7), even without irrigation or precipitation. The rate of disappearance of both pesticides appears to be directly related to the compounds' water solubility and field persistence and inversely related with their hydrophobicity (log K_{ow}) (Figure 2.2).

Table 7.3. Parameters (± standard error) from the best fitting model (SFO) describing thiacloprid (THC) and pendimethalin (PDM) dissipation in the field plots. Treatments: irrigation with wastewater (TWW), with well water (WL) and a combination of organic fertiliser with TWW (F+TWW)

Pesticide	Treatment	R^2	C_0 (%)	k (d^{-1})	DT_{50} (d)	DT_{90} (d)	GUS
PDM	F+TWW	0.888	83 ± 4	0.07 ± 0.01	11	35	
	TWW	0.808	79 ± 5	0.05 ± 0.01	13	43	0.32
	WL	0.829	84 ± 5	0.08 ± 0.01	9	31	0.30
THC	F+TWW	0.938	95 ± 4	0.24 ± 0.03	2.9	10	
	TWW	0.959	99 ± 3	0.20 ± 0.02	3.4	11	0.94
	WL	0.922	96 ± 5	0.28 ± 0.04	2.5	8	0.71

R^2: coefficient of determination. DT_{50}, DT_{90}: time required to reach 50 or 10% of the initial pesticide concentration, respectively. GUS: GUS index (Groundwater Ubiquity Score)

Half-lives of THC ranged between 2.5 and 3.4 d and R^2 values were always > 0.92 (Table 7.3). This insecticide should disappear more rapidly than PDM from the upper soil, because THC is expected to be transported with irrigation water since it is slightly adsorbed onto soil, in agreement with its adsorption coefficients (Table 7.2), though it is a non-volatile compound, relative stable under sunlight (Peña et al., 2011b). The half-lives calculated for this pesticide under the different treatments (Table 7.3) were lower than those found in the literature for field experiments, in the range 9-27 d (FOOTPRINT), but slightly higher than those recently reported by Sharma and Parihar (2013) of 1.8 days.

The literature concerning PDM suggests that loss at the first days after application by volatilisation (Cooper et al., 1990; Smith et al., 1995; García-Valcárcel and Tadeo, 2003; Triantafyllidis et al., 2009) or photodegradation (Parochetti and Dec, 1978; Lee et al., 2000; Triantafyllidis et al., 2009) are factors that strongly affect the dissipation of PDM under field conditions. The first two days after application, without water supply and with maximal temperatures between 28 and 30 °C (Figure 7.3), PDM residues ranged from 63 to 86% (day 1) and between 54 and 64% (day 2). In this sense Cooper et al. (1990) estimated the PDM volatilisation loss about 13% during the 5-day period following application.

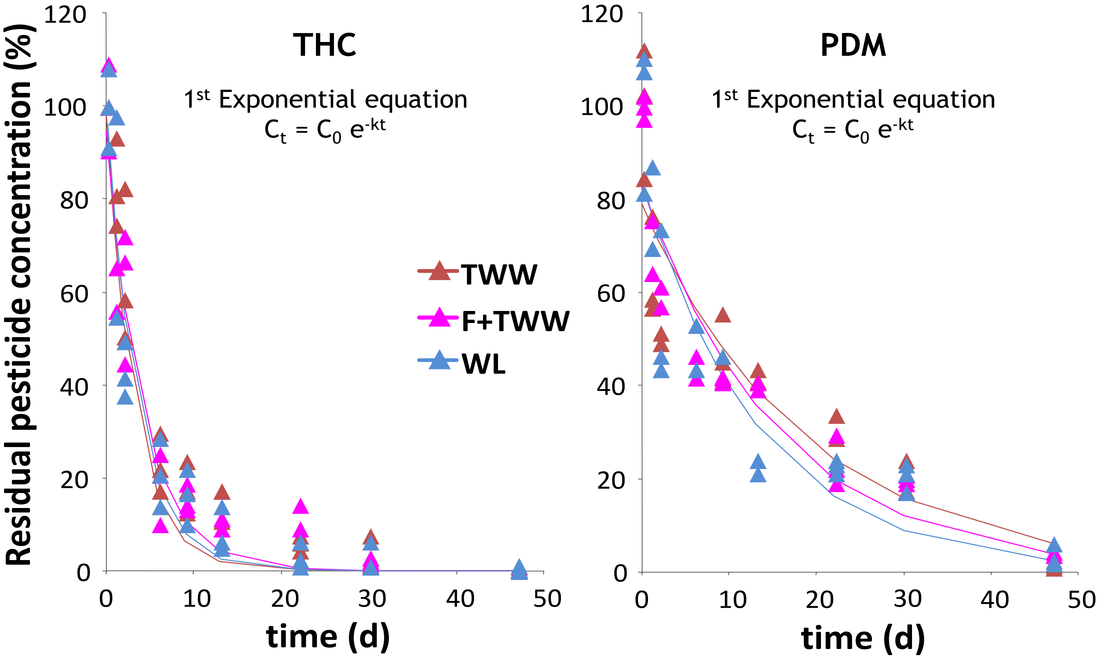


Figure 7.7. Experimental and fitted residues (% relative to initial concentration) of thiacloprid (THC) and pendimethalin (PDM) in the upper soil layer. Treatments: irrigation with wastewater (TWW), with well water (WL) and a combination of organic fertiliser with TWW (F+TWW)

On the other hand, due to its high retention by the plot soil (Table 7.2) this pesticide seems to be tightly adsorbed on the soil upper layer and the potential leaching loss of the herbicide applied to the soil and its environmental impacts are expected to be very limited (Lee et al., 2000). The first-order kinetic equation provided an adequate data fitting (R^2 0.81-0.89) in compliance with Cooper et al. (1994), Lee et al. (2000) or Sondhia (2012), while García-Valcárcel and Tadeo (2003) indicated that disappearance rate of PDM in soil did not totally conform to a firs-order kinetics. However attempts to fit the experimental data to the other kinetic models were unsuccessful. The calculated half-lives, between 9 and 13 d (Table 7.3), are in the range of those found by Cooper et al. (1994), and Sondhia (2012), but lower than other data previously reported in the range 9-31.5 d (Lee et al., 2000; Alister et al., 2009; Triantafyllidis et al., 2009).

In contrast with what was expected from PDM properties, residues of this pesticide continued to decrease in the upper soil layer during the field experiment. This result points to the formation of bound or non-extractable residues, because PDM is relatively persistent and highly retained by this soil (Table 7.2). Therefore disappearance due to biotic or abiotic degradation or to leaching was supposed to be negligible. The formation of non-extractable residues is a process which depends on pesticide and soil characteristics (Barriuso et al., 2008). This process has been already reported for PDM in another soil (Barriuso et al., 1997) and could also take place in this case.

By comparison of DT_{50} values with those of the laboratory degradation study (Table 5.2), persistence of both pesticides was considerably lower under field conditions, especially for PDM. As pointed out by different researchers (Walker, 1987; Herrero-Hernández et al., 2011), less persistence is observed in the field than in laboratory experiments because of uncontrolled climatic factors such as sun irradiation, important rainfall events that improve pesticide movement to lower soil layers, which increases pesticide decline, as well as constant change of temperature and moisture content, which results in fluxes in microbial and chemical reactivity of the soil. As above mentioned, losses by volatilisation and photodegradation accelerate PDM dissipation in field. Moreover, for this herbicide, Kjaer et al. (2011) have calculated a contribution of particle-facilitated transport via macropores in the range 16-31% in the leaching through a structured soil.

For the short-term persistence (DT_{50}) the use of TWW showed a trend to slow down pesticide disappearance (Table 7.3), as confirmed by the long-term persistence (DT_{90}) and in agreement with laboratory results (chapter 5). The effect of irrigating with TWW was initially mitigated by the addition of an organic fertiliser resulting in disappearance rates more close to irrigation with WL, probably because the fertiliser supplies a microbial population able to promote pesticide degradation or else because it provides a great amount of DOC to facilitate pesticide transport to lower soil layers

(Table 2.10). Herrero-Hernández et al. (2011) showed that sorption of tebuconazole in a field assay was directly correlated with soil OC and indirectly to DOC, especially in the first days after amendment application when DOC is produced in greater amounts.

Finally, according to the GUS indexes lower than 1 (Table 7.3), none of the pesticides and none of the treatments would represent an environmental hazard (Table 7.4).

Table 7.4. Leaching potential of pesticides according to the GUS index

GUS value	Leaching potential
< 0.1	Extremely low
0.1-1.0	Very low
1.0-2.0	Low
2.0-3.0	Moderate
3.0-4.0	High
> 4.0	Very high

Pesticide residues in the soil profile (0-30 cm) are presented in Figure 7.8. Nine days after application, pesticide residues were much higher in the upper soil layer (0-10 cm) than in deeper ones (10-30 cm) for all the treatments. The amounts in the sub-surface layer (10-20 cm) 9 days after application (total irrigation 100 mm) ranged between 0.05 and 0.11 μg g^{-1} for both pesticides, with higher concentrations in general in F+TWW and TWW treatments than in WL. After 22 days (total irrigation supply, 180 mm) pesticide residues in the 10-20 cm layer had decreased for THC but not for PDM, reflecting the higher PDM concentration in the upper soil layer which continued to leach to deeper soil profiles.

The values corresponding to the 20-30 cm were lower in all cases, even below detection limits after 22 days in many cases, suggesting that pesticide leaching was mainly limited to the upper soil layers, in accordance with the GUS indexes.

Considering the percentage of remaining pesticides in the subsurface layer (10-20 cm) with respect to the initial pesticide amount in the upper soil layer, residues of THC and PDM were very low (<1.0% after 9 days).

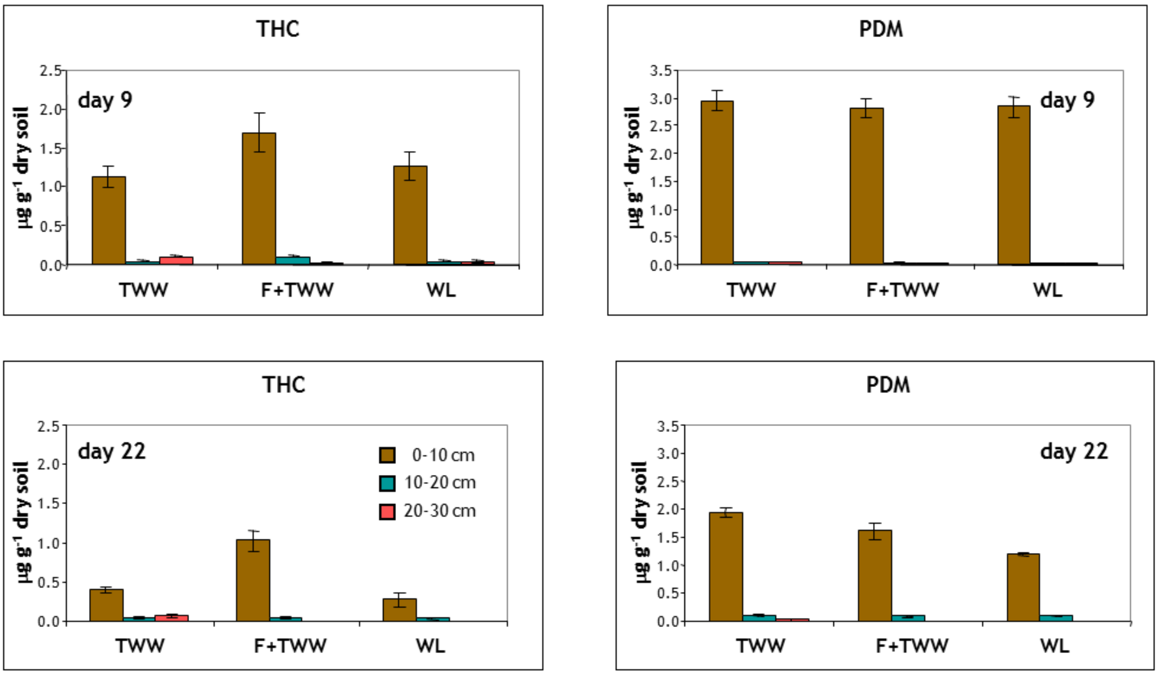


Figure 7.8. Distribution profile of thiacloprid (THC) and pendimethalin (PDM) 9 and 22 days after pesticide application. Error bars represent the standard error of the mean value (n = 6). Treatments: irrigation with wastewater (TWW), with well water (WL) and a combination of organic fertiliser with TWW (F+TWW)

In the case of THC the low concentration values comply with its moderate solubility in water (Figure 2.2), its relatively low retention by soil (Table 7.2) and its relatively low persistence (Table 7.3), which has been reported to be favoured by soil microbial activity (Liu et al., 2011). PDM, a highly stable pesticide, strongly retained on this soil (Table 7.2), remains mostly in the upper layer (Figure 7.8). In fact, after 22 days PDM residues at 20-30 cm depth did not represent a significant fraction of the total amount applied (<0.1-0.2%), being almost undetectable. Starret et al. (1996) also found 0.2% of the applied PDM, even under heavy irrigation in agreement with the results of Stahnke et al. (1991) in a silty clay loam soil. This indicates that downward movement of PDM in the soil is very limited, even under TWW irrigation or addition of an organic fertiliser, because of the strong adsorption on soil.

7.3.5. Soil anion fate

Apart from bromide, other anions, which can pose a hazard to soil quality or to cultivated plants, were also evaluated (Figure 7.9).

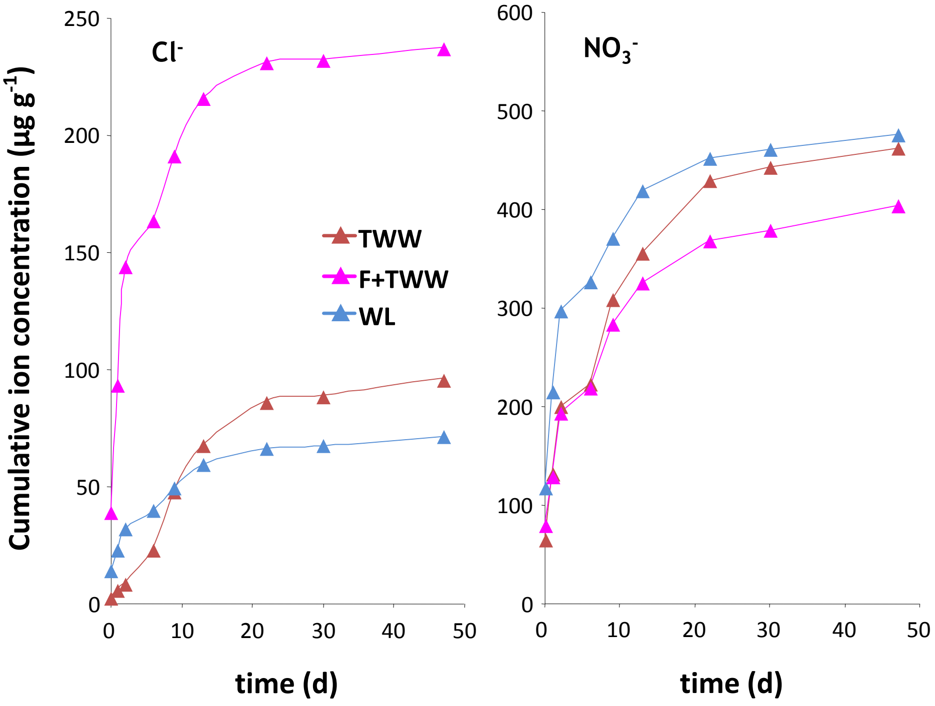


Figure 7.9. Cumulative concentration of chlorides and nitrates (µg g^{-1}) in soil samples from the upper soil layer. Treatments: irrigation with wastewater (TWW), with well water (WL) and a combination of organic fertiliser with TWW (F+TWW).

Chloride concentrations were higher for the plots amended with FERT (F+TWW), since this amendment contained approximately 2.1 mg g^{-1} Cl^- (Table 2.10), followed at a great distance by TWW and finally by WL. The actual values corresponding to the F+TWW treatment contained more Cl^- during the whole assay period, until the two last sampling dates (days 30 and 47) for which no significant differences among treatments were found ($P > 0.05$). After an initial Cl^- load in F+TWW, the concentration increased in all the treatments after irrigation (days 5, 12 and 22), because of the presence of this anion also in irrigation water (Figure 7.9).

On the other hand, NO_3^- concentration was high for TWW but also for WL, owing to the contamination of this agricultural area by nitrates, which percolate to the saturated zone from which WL is collected. FERT, which contained 0.85 mg g^{-1} NO_3^- (Table 2.10), evolved similarly to the other two treatments but without significant differences ($P > 0.05$) for any date due to the variability of the data. From the day 22 onwards, owing to repeated rain events (Figure 7.3), the concentration of NO_3^- in all the plots diminished as a consequence of washing (Figure 7.9). It is important to note that ponding is an irrigation system that may result in much faster flow through the soil profile compared to sprinkler or other irrigation systems. Therefore, the traditional irrigation procedure employed in the Vega de Granada, may facilitate the pollution by NO_3^- and salts favouring their rapid entrance into groundwater.

7.3.6. Soil induced respiration and dehydrogenase activity

Soil biological indicators, such as soil respiration and enzyme activities, can give us information on the presence of viable microorganisms, as well as on the intensity and on the kind and duration of the effects of pollutants or management practises on the metabolic activity of soil. Hence, they are well suited to measure their impact on soil health, and a good complement of chemical methods when evaluating the effects of pollutants in a soil (Margesin et al., 2000; Mingorance and Peña, 2016; Romero-Freire et al., 2016).

Soil microbial biomass, an important indicator of the status of soil vitality, can be estimated by the short-term substrate (glucose)-induced respiration. This method has been usually recommended to determine the effects of contaminants on the soil microflora (Schinner et al., 1996; Smolders et al., 2004; Fabrizio et al., 2009), though a recent report (Romero-Freire et al., 2016) has alerted about the advisability of using basal soil respiration as an indicator of metal pollution in certain soils. A drawback of the method employed in this study is that it registers only glucose-utilising microorganisms.

In our case the measurement of the rate of CO_2 evolution, was initially higher for F+TWW plots in agreement with the higher organic load provided by the amendment. In the rest of the treatments soil respiration was characterised by a peak occurring 1-2 days after pesticide application (Figure 7.10, left), followed in all cases by a gradual decline. The increase suggests that pesticides in soils constitute a readily available substrate, which can be used as carbon and energy source by soil microorganisms (especially THC, as suggested in chapter 5). According to the respiration data, irrigation with TWW, or addition of FERT combined with TWW irrigation (F+TWW) favoured microbial activity. Both treatments, rich in OM, are expected to increase microbial activity and, therefore, soil respiration. On the contrary, in the plots irrigated with WL, measured respiration rates were lower than but not significantly different from ($P > 0.05$) those corresponding to plots irrigated with TWW, fertilised or not, pointing to a lower microbial activity.

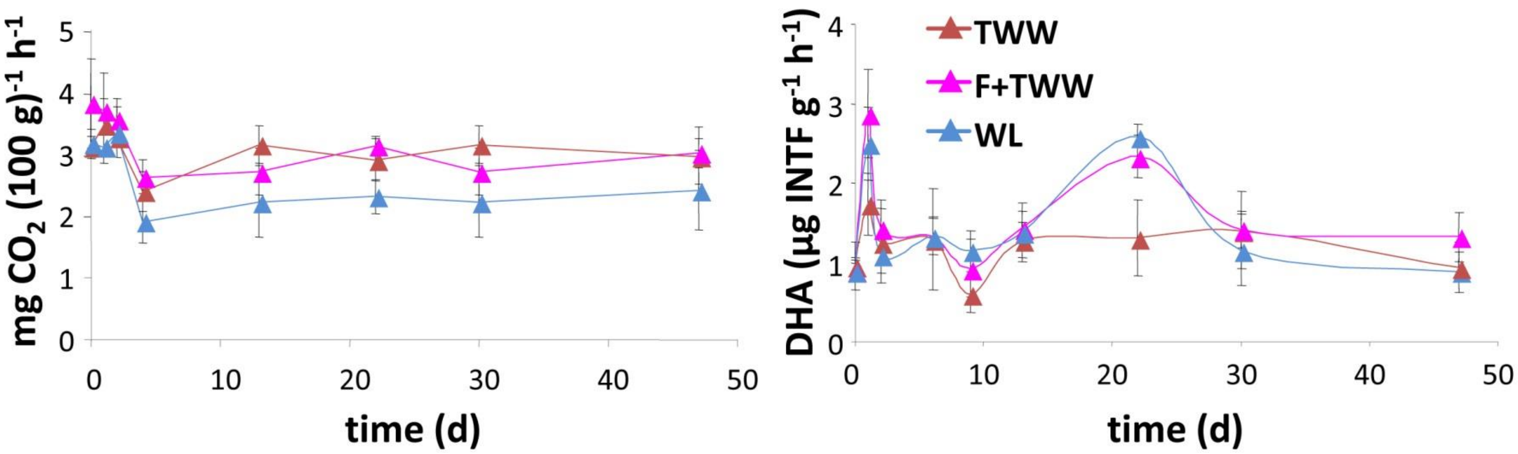


Figure 7.10. Evolution of soil induced respiration (left) and soil dehydrogenase activity (right) from the upper soil layer along the experimental period. Treatments: irrigation with wastewater (TWW), with well water (WL) and a combination of FERT with TWW (F+TWW).

Dehydrogenase activity, an intracellular process that occurs in every viable microbial cell due to the activity of several enzymes catalysing the transfer of hydrogen and electrons from one compound to another, represents the overall microbiological activity of the soils (Nannipieri et al., 2002). During the first 15 days, DHA was in general higher for WL and F+TWW plots than for TWW plots with an increase in all cases 1 day after pesticide application. A second peak was observed 22 days after application, the latter only for WL and F+TWW plots (Figure 7.10, right). Contrary to what was seen with soil respiration, WL plots showed in general higher DHA values than TWW, although without statistical significance. This behavior coincides with the lower DHA evolution observed when using TWW in laboratory degradation studies (chapter 5). From 30 days onwards, coinciding with the end of irrigation and the increase of rain (Figure 7.3), DHA values levelled for all treatments, reaching similar values.

Increase in DHA activity after amendment addition has been frequently reported (Marín-Benito et al., 2012) as a consequence of higher labile OC content. Previous DHA analysis have shown that irrigating soil with TWW may lead to a decrease in DHA (Hernández-Soriano et al., 2009; Kayikcioglou, 2012), probably due to higher water salinity or to negative effects of some ions present in TWW. This would mean that under TWW irrigation the microbial consortia involved in pesticide degradation could be negatively affected, in line with the observed lower pesticide degradation rate.

7.4. CONCLUSIONS

From this study it can be concluded that disappearance rates from the upper soil layers were dependent on pesticide properties and always ranged as THC > PDM. The effect of treatments depended on pesticide hydrophobicity, being negligible for the more polar (THC), while for PDM they resulted in slightly increased pesticide persistence in surface soil after irrigation with TWW. The increased persistence for PDM with TWW was alleviated by the addition of an organic fertiliser, likely due to enhanced pesticide degradation by the supplied microbial population or else to the facilitated pesticide transport as a consequence of higher DOC contribution. The abnormal climatic conditions, with 203 mm rainwater during the experiment (mean annual precipitation, 357 mm) while irrigation amounted to 180 mm, may have masked in part the effects of irrigation solution on pesticide behaviour. The dissipation of THC and PDM was adequately modelled by first-order kinetics.

The greater disappearance rates for both pesticides, which occurred the first days after application, coincided with higher CO_2 rates and dehydrogenase activities; both parameters have shown to be appropriate as biological indicators of enhanced pesticide degradation. However, while soil respiration increased with TWW irrigation, DHA alerted about a toxic or detrimental effect of irrigating with TWW, which could hamper microbial maintenance and growth. Finally, care has to be taken with the potential increase in soil, and consequently in groundwater, of the concentration of some anions (Cl^-, NO_3^-) when adding organic fertilisers and irrigating with low-quality waters.

GENERAL CONCLUSIONS
CONCLUSIONES GENERALES

GENERAL CONCLUSIONS

1. Adsorption of pesticides in soil was ordered according to pesticide hydrophobicity and inversely to water solubility, highlighting the importance of pesticide properties. Adsorption of the most hydrophobic pesticides (α-cypermethrin, deltamethrin and pendimethalin) to laboratory glassware needs to be taken into account.
2. The kinetic study shows that adsorption equilibrium was reached within the first 24 h of soil–solution contact time. High contribution of a rapid initial stage was observed for all the pesticides. Diffusion within the internal soil structure was more important for the pyrethroid insecticides. Conversely, adsorption of more polar compounds was controlled by transport into soil macropores, especially for dimethenamid and fenarimol, for which adsorption was almost instantaneous.
3. The use of treated wastewater, a practice commonly used for crop irrigation in regions with long water scarcity periods, increased the adsorption of hydrophobic pesticides (log $K_{OW} \geq 4$) on soil. This increase was related with the amount of inorganic salts rather than with the organic fraction present in wastewater. In fact, adsorption was enhanced at very low dissolved organic carbon concentration, but decreased thereafter with increasing dissolved organic carbon concentrations. The quality of the irrigation solution was less important for the retention of more polar compounds.
4. Release of pesticides from soils was dependent on soil type and was not affected by treated wastewater. On the other, hand the presence of surfactants, salts and dissolved organic carbon in the background solution affected fenarimol and thiacloprid desorption to a different extent depending on the soil and on the solution characteristics. Water sources of similar organic and inorganic composition would be expected not to greatly affect the solubilisation from soil of relatively polar pesticides, while they would have environmental importance for more hydrophobic compounds.
5. There were no relevant effects of the incubation solution on soil degradation of thiacloprid, pendimethalin and fenarimol, pesticides with contrasting

physicochemical properties. However, it was observed that irrigation with treated wastewater may deplete the activity of soil microorganisms in the short term, as shown by the dehydrogenase activity measurements.

6. The movement of the relatively polar thiacloprid was retarded with respect to the water front due to adsorption processes. No significant effects were observed by the use of treated wastewater and $(NH_4)_2SO_4$ at 5 mM as influent solutions. On the other side, both irrigation with water at very low dissolved organic carbon concentration and amendment of soil with fertiormont reduced thiacloprid mobility. The retained amount of pesticide was uniformly distributed in the soil columns, except for amendment with fertiormont, which tended to accumulate thiacloprid in the lower soil layer.
7. The field experiment confirmed laboratory findings. The dissipation of thiacloprid and pendimethalin from plots irrigated with treated wastewater was slower than from plots irrigated with higher-quality water, though the addition of fertiormont masked this difference. As in laboratory degradation assays, dehydrogenase activity measurements indicated that irrigation with treated wastewater may have a negative effect on soil microbial population.

CONCLUSIONES GENERALES

1. La adsorción de los plaguicidas en los suelos fue directamente proporcional a la hidrofobicidad de los compuestos e inversamente a su solubilidad en agua, poniendo de relieve la importancia de las propiedades físico-químicas de los plaguicidas. Hay que tener en cuenta la adsorción de los plaguicidas más hidrófobos (α-cipermetrina, deltametrina y pendimetalina) a las paredes de vidrio del material de laboratorio.
2. El estudio cinético muestra que, para todos los plaguicidas ensayados, el equilibrio de adsorción se alcanzó en las primeras 24 h de contacto entre el suelo y la fase líquida. Se observó una elevada contribución de una fase inicial rápida en la adsorción de todos los compuestos. La difusión molecular en la estructura interna del suelo resultó más importante para los insecticidas piretroides. Por el contrario, para los plaguicidas más polares, especialmente dimetenamida y fenarimol, la adsorción fue casi instantánea, lo que indica que el transporte en los macroporos del suelo controló la adsorción.
3. El uso para riego de aguas residuales depuradas, una práctica relativamente frecuente en cultivos de zonas con largos períodos de sequía, incrementó la adsorción en suelo de plaguicidas hidrófobos (log $K_{OW} \geq 4$). Este incremento estuvo más relacionado con la cantidad de sales inorgánicas que con la fracción orgánica presente en las aguas residuales. De hecho, la adsorción aumentó a muy baja concentración de carbono orgánico disuelto, pero disminuyó después a concentraciones más elevadas. La calidad del agua de riego fue menos importante en la retención de compuestos más polares.
4. La solubilización de plaguicidas desde suelos contaminados dependió del tipo de suelo y no se vio afectada por el uso de aguas residuales tratadas. Por otra parte, la presencia en la solución de agentes tensioactivos, sales o carbono orgánico disuelto afectó de forma variable a la desorción de tiacloprid y fenarimol, en función de las características del suelo y de la solución. Se espera pues que soluciones de composición orgánica e inorgánica similar no afecten en gran medida a la desorción de plaguicidas relativamente polares y que tengan una mayor importancia en la solubilización de compuestos más hidrófobos.

5. No hubo efectos relevantes en la degradación en suelo de tiacloprid, pendimetalina y fenarimol debido a la irrigación con aguas residuales depuradas y soluciones de carbono orgánico disuelto. Sin embargo, se observó que las aguas residuales depuradas pueden disminuir la actividad de los microorganismos del suelo a corto plazo, como demuestran las medidas de la actividad deshidrogenasa.
6. El movimiento de tiacloprid, plaguicida relativamente polar, a través de columnas de suelo se retrasó con respecto al flujo de agua debido a procesos de adsorción. No se observaron efectos significativos por el uso de aguas residuales tratadas o $(NH_4)_2SO_4$ 5 mM como soluciones de infiltración. Por otro lado, tanto el riego con una solución a muy baja concentración de carbono orgánico disuelto como la adición al suelo de fertiormont, redujeron la lixiviación del compuesto. La cantidad retenida de tiacloprid al final de los experimentos se distribuyó de manera uniforme en las columnas de suelo, excepto con fertiormont como enmienda, que tiende a acumular el insecticida en las capas inferiores del suelo.
7. El experimento de campo confirmó los hallazgos de laboratorio. La disipación de tiacloprid y pendimetalina en parcelas regadas con aguas residuales tratadas fue más lenta que en las parcelas regadas con un agua de mayor calidad, aunque la adición de fertiormont al suelo enmascaró estas diferencias. Al igual que en los ensayos de degradación realizados en laboratorio, las medidas de la actividad deshidrogenasa indicaron que el riego con aguas residuales tratadas puede tener un efecto negativo sobre la población microbiana del suelo.

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IACT
INSTITUTO ANDALUZ DE CIENCIAS DE LA TIERRA

CSIC
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ugr Universidad de Granada