DEPARTAMENT DE MEDICINA PREVENTIVA I SALUT PÚBLICA, CIÈNCIES DE L’ ALIMENTACIÓ, TOXICOLOGIA I MEDICINA LEGAL

MULTI-RESIDUE METHODS FOR THE ANALYSIS OF PESTICIDES IN AIRBORNE PARTICULATE MATTER BY LC-MS/MS AND GC-MS/MS. MONITORING LEVELS IN THE ATMOSPHERE.

CLARA COSCOLLÀ RAGA

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MULTI-RESIDUE METHODS FOR THE ANALYSIS OF PESTICIDES IN AIRBORNE PARTICULATE MATTER BY LC-MS/MS AND GC-MS/MS. MONITORING LEVELS IN THE ATMOSPHERE.

EUROPEAN DOCTORAL THESIS

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MONITORING LEVELS IN THE ATMOSPHERE.

Memoria que presenta para optar al Título de Doctora:

Clara Coscollà Raga

València, Julio 2011

Vicent Yusà Pelechá Doctor en Ciencias Químicas, y Agustín Pastor García Doctor en Ciencias Químicas y Catedrático de Universidad

CERTIFICAN que:

Clara Coscollà Raga, Licenciada en Farmacia por la Universidad de Valencia, ha estado trabajando bajo nuestra dirección para la elaboración de la tesis “**Multi-residue methods for the analysis of pesticides in airborne particulate matter by LC-MS/MS and GC-MS/MS. Monitoring levels in the atmosphere”,** y que presenta para optar al Título de Doctora por la Universidad de Valencia.

Y para que así conste a los efectos oportunos, firmamos el presente documento en Valencia, a 20 de Junio de 2011.

Vicent Yusà Pelechá

Agustín Pastor García

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Als meus pares

A la meua germana

ÍNDICE/INDEX

I. ABSTRACT, RESUMEN, RESUM, RÉSUMÉ

Abstract

Currently used pesticides (CUPs) appear in the atmosphere as a consequence of its massive use in agricultural areas during application periods. More than 300 active substances are nowadays authorised by the European Union for their application on different crops according to the Directive 91/414 of CEE. The total use of plant protection products in the European Union (EU-27) during 2008 was about 310 011 tons of active ingredients, with France (25.3%), Spain (12.9%) and Italy (13.3%) as the three main consumer countries.

The emissions of pesticides during application, volatilization from soil and plants after application and wind erosion of soil particles containing sorbed pesticides are the key processes driving to their presence in ambient air. Once in the air pesticides can suffer different mechanisms such as transportation, degradation and deposition.

The research aim of this thesis was to develop different analytical methods for the determination of currently used pesticides in airborne particulate matter and to provide information about the levels of these pesticides in two European regions (France and Spain).

This thesis is composed of one review study and four experimental chapters. The scope of the review study is focused on current collection and analytical methods for determination of CUPs in ambient air. Additional considerations about the occurrence of pesticides in ambient air are included.

In the first chapter an analytical method was developed in order to determine nine CUPs in PM 2.5. Pesticides were extracted by PLE and analyzed by LC-MS/MS. PLE conditions as well as parameters in the ESI source ionization were optimized using a statistical design of experiments.

In the second chapter an analytical method for analysing 30 CUPs in PM 2.5 was developed. Pesticides were extracted by MAE and analyzed by LC-MS/MS. MAE conditions were also optimized using a statistical design of experiments.

In the third chapter an analytical methodology in order to analyze 40 CUPs in PM 10 by CG-MS/MS triple Q was developed. A GPC clean-up was introduced in this study.

The analytical methods developed in chapters 1, 2 and 3 were applied to analyze real samples in Valencia region (Spain) during 2007-2010 in order to evaluate the presence of pesticides in ambient air. Valencia region has an intensive agricultural production mainly of citrus fruits. Samples were collected in different sampling sites focused on rural, urban and remote stations.

Chapter 4 describes a study about the presence of CUPs in Centre region (France). Centre region is one of the country´s largest regions with many agricultural activities focused mainly in arable crops. Some spatial and temporal studies were carried out. The influence of the meteorological conditions, such as humidity and wind direction were also evaluated. Rural and urban stations were sampled from 2006 to 2008 in Centre region.

The analytical methods developed and the concentration levels of CUPs provided by this thesis could be very useful in order to establish a monitoring and surveillance network of pesticides in ambient air around different countries of the European Union.

Resumen

Los plaguicidas actualmente utilizados en agricultura (CUPs) pueden encontrarse en la atmósfera como consecuencia de su uso intensivo en zonas agrícolas sobre todo durante el periodo de aplicación. Más de 300 sustancias activas están actualmente aprobadas por la UE y pueden ser aplicadas en distintos cultivos según la Directiva 91/414/CEE. La cantidad total de plaguicidas utilizados en la (EU-27) durante el 2008 fue de unas 310.011 toneladas de sustancia activa, con Francia (25.3%), España (12.9%) e Italia (13.3%) como los tres países con mayor consumo.

La emisión de los plaguicidas durante la aplicación, la volatilización desde el suelo y las plantas después de su aplicación y la erosión del suelo con partículas cargadas con plaguicidas son los procesos fundamentales por los que los plaguicidas pueden llegar a la atmósfera. Una vez en el aire ambiente los plaguicidas pueden someterse a mecanismos de transporte, degradación y deposición.

El objetivo fundamental de esta tesis es desarrollar métodos analíticos para analizar estos CUPs en la fase particulada del aire y proporcionar información sobre concentraciones de estos plaguicidas en dos regiones europeas (Région Centre y Comunidad Valenciana), en Francia y España.

Esta tesis se compone de un estudio de revisión y cuatro capítulos experimentales. El estudio de revisión se fundamenta en una revisión bibliográfica sobre métodos de muestreo y análisis, y sobre concentraciones detectadas en la literatura de plaguicidas en el aire ambiente.

En el primer capítulo se desarrolló un método analítico para determinar nueve CUPs en PM 2.5. Los CUPs fueron extraídos utilizando PLE y se analizaron por LC-MS/MS. Las condiciones del PLE y de la fuente de ionización ESI se optimizaron utilizando el diseño estadístico de experimentos.

En el segundo capítulo, se desarrolló un método analítico para analizar treinta CUPs en PM 2.5. Los CUPs fueron extraídos por MAE y se analizaron mediante LC-MS/MS. Las condiciones del MAE también se optimizaron utilizando un diseño estadístico de experimentos.

En el tercer capítulo, una metodología analítica para determinar cuarenta CUPs en PM 10 se desarrolló por CG-MS/MS. Se introdujo en este capítulo una purificación por GPC.

Las metodologías analíticas desarrolladas en los capítulos 1, 2 y 3 se aplicaron para el análisis de muestras en la fase particulada del aire en la atmósfera de la Comunidad Valenciana durante los años 2007-2010 para evaluar la presencia de los plaguicidas en el aire ambiente. La Comunidad Valenciana es una región con muchos cultivos de cítricos y con una importante actividad agrícola. El muestreo se realizó en distintas estaciones rurales, urbanas y remotas.

El capítulo 4 trata de un estudio sobre presencia de los CUPs en la Región Centre de Francia durante los años 2006-2008. La Región Centre es una de las regiones más grandes de Francia con una intensa producción agrícola, especialmente de cultivos intensivos como el trigo o el maíz. En este capítulo estudios sobre la distribución espacial y temporal de los plaguicidas, así como la influencia de las condiciones meteorológicas como la humedad y la dirección del viento fueron evaluadas y estudiadas para comprender el comportamiento de los plaguicidas en el aire.

Como consecuencia de los pocos trabajos publicados en la literatura sobre plaguicidas en el aire ambiente, además de desarrollar nuevas metodologías analíticas y estudiar la presencia de los plaguicidas en la atmósfera para aportar un mejor conocimiento de estos contaminantes en el ámbito científico, los trabajos realizados y los resultados obtenidos pueden ser una aportación útil, junto con posteriores estudios, para futuras reglamentaciones de la UE sobre plaguicidas en aire, pues actualmente existe un vacío legal en este aspecto.

Resum

Els plaguicides que actualment s´estan aplicant en agricultura poden trobar-se en l´atmosfera com a conseqüència del seu ús intensiu en àrees agrícoles durant els periodes d´aplicació. Més de 300 substàncies actives estan actualment aprovades per la Unió Europea i poden ser aplicades en diferents cultius segons la Directiva 91/414/CEE. La quantitat total de plaguicides utilitzats en la Unió Europea (EU-27) durant l´any 2008 va ser unes 310.011 tones de sustància activa, amb França (25.3%), Espanya (12.9%) i Itàlia (13.3%) com els tres països amb major consum.

L´emissió dels plaguicides durant l´aplicació, la volatilització des del sòl i les plantes després de l´aplicació i l´erosió del sòl amb partícules carregades amb plaguicida són els processos fonamentals pels quals els plaguicides poden arribar a l´atmosfera. Una vegada en l´aire ambient els plaguicides poden estar sotmesos a mecanismes de transport, degradació i deposició.

L´objectiu fonamental d´aquesta tesi és desenvolupar metodologies analítiques per analitzar aquestos plaguicides d´ús actual en agricultura en la fase particulada de l´aire i proveir dades sobre concentracions d´aquestos plaguicides en dues regions europees (Région Centre i Comunitat Valenciana), en França i Espanya.

Aquesta tesi s´estructura amb un estudi de revisió i quatre capítols experimentals. L´estudi de revisió es fonamenta en una revisió bibliogràfica sobre els métodes de mostreig i anàlisi i les concentracions detectades en la literatura sobre plaguicides en l´aire ambient.

En el primer capítol, s´ha desenvolupat un mètode analític per determinar nou CUPs en PM 2.5. Els plaguicides s´extragueren utilitzant PLE i s´analitzaren mitjançant LC-MS/MS. Les condicions del PLE i de la font d´ionització ESI s´optimitzaren utilitzant un disseny estadístic d´experiments.

En el segon capítol, s´ha desenvolupat un mètode analític per analitzar trenta CUPs en PM 2.5. Els plaguicides s´extragueren amb MAE i s´analitzaren per LC-MS/MS. Les condicions del MAE també s´optimitzaren utilitzant un disseny estadístic d´experiments.

En el tercer capítol, una metodologia analítica per determinar quaranta CUPs en PM 10 s´ha desenvolupat per CG-MS/MS. En aquest estudi una purificació amb GPC va ser introduida.

Les metodologies analítiques desenvolupades en els capitols 1,2 i 3 s´han aplicat per a l´anàlisi de mostres en la fase particulada de l´aire en l´atmosfera de la Comunitat Valenciana durant els anys 2007-2010 per tal d´avaluar la presència dels plaguicides en l´aire ambient. La Comunitat Valenciana és una regió amb molts cultius de cítrics i amb una important activitat agrícola. El mostreig es realitzà en diferents estacions rurals, urbanes i remotes.

El capítol quatre tracta d ´un estudi sobre la presència dels CUPs en la Regió Centre de França durant els anys 2006-2008. La Regió Centre és una de les regions més grans de França amb una intensa producció agrícola, especialment de cultius intensius com el blat i la dacsa. En aquest capítol estudis sobre la distribució espacial i temporal dels plaguicides, així com la influència de les condicions metereològiques com la humitat i la direcció del vent varen ser avaluades i estudiades per comprendre el comportament dels plaguicides en l´aire.

Com a conseqüència dels pocs treballs que hi ha publicats sobre plaguicides en aire en la bibliografia, a més de desenvolupar noves metodologies analítiques i estudiar la presència dels plaguicides en l´aire ambient per aportar un millor coneixement d´aquestos contaminants en l´àmbit científic, els treballs realitzats i els resultats obtinguts poden ser una aportació útil, junt a posteriors estudis, per a futures reglamentacions de la Unió Europea sobre plaguicides en aire, doncs actualment existeix un buit legal en aquest aspecte.

Résumé

Les pesticides actuellement utilisés en agriculture peuvent se retrouver dans l'atmosphère du fait de leur usage intensif dans les zones agricoles pendant les périodes d'application. Actuellement plus de 300 substances actives approuvées par l'Union Européenne et elles peuvent être appliquées dans différentes cultures selon la Directive 91/414/CEE. La quantité totale de pesticides utilisée dans l'Union Européenne (EU-27) pendant l'année 2008 a été de 310.011 tonnes de substance active, et la France (25.3%), l'Italie (13.3%) et l'Espagne (12.9%) sont les trois pays avec la plus forte consommation.

C'est l'émission des pesticides pendant l'application, la volatilisation à partir du sol et des plantes après l'application et l'érosion du sol avec des particules chargées de pesticides qui sont les processus fondamentaux à l'origine de la dissipation des pesticides dans l'atmosphère. Une fois qu'ils sont dans l'aire ambiant, ils peuvent être soumis à des mécanismes de transport, de dégradation et de dépôt.

L'objectif fondamental de ce travail de thèse est de développer des méthodologies analytiques pour analyser des pesticides utilisés en agriculture dans la phase particulaire de l'air et de fournir des données sur les concentrations de ces pesticides dans deux régions européennes (la Région Centre et la Communauté Valencienne), en France et en Espagne.

Cette thèse est structurée par une revue bibliographique et quatre chapitres expérimentaux. L'étude bibliographique porte essentiellement sur les méthodes d'échantillonnage et l'analyse pour déterminer des pesticides dans l'air ambiant. Dans cette étude on y trouve aussi une synthèse des niveaux de pesticides dans l'atmosphère de par le monde.

Dans le premier chapitre a été développé une méthode analytique pour déterminer neuf pesticides dans des PM 2.5. Les pesticides ont été extraits en utilisant la PLE et ont été analysés par LC-MS/MS. Les conditions de la PLE et la source d'ionisation ESI ont été optimisées en utilisant un modèle statique d'expériences.

Dans le deuxième chapitre a été développée une méthode analytique pour analyser trente pesticides dans des PM 2.5. Les pesticides ont été extraits par MAE et ont été analysés par LC-MS/MS. Les conditions de la MAE ont été optimisées aussi en utilisant un design statistique d'expériences.

Dans le troisième chapitre, une méthodologie analytique pour déterminer quarante pesticides en dans des PM 10 a été développée par CG-MS/MS. Dans cette étude une purification avec par GPC a été introduite.

Les méthodologies analytiques développées dans les chapitres 1, 2 et 3 ont été appliquées pour l'analyse d'échantillons de phase particulaire de l'air de la Communauté Valencienne. Celle-ci, c'est une région qui possède beaucoup de cultures d'agrumes et avec une important activité agricole. L'échantillonnage est effectué au niveau de différentes stations rurales, urbaines et éloignées.

Le quatrième chapitre traite d'une étude de la présence du CUPs dans la Région Centre de la France pendant les années 2006-2008. La Région Centre est une des régions les plus grandes de la France avec une production agricole intensive, essentiellement de cultures intensives comme le blé et le maïs. Dans ce chapitre on y trouve une étude sur la distribution spatiale et temporelle des pesticides, ainsi que sur l'influence des conditions météorologiques telles que l'humidité et la direction du vent. Ceci a été fait pour tenter de comprendre le comportement des pesticides dans l'air.

À cause du peu de travaux publiés sur les pesticides dans l'air dans la bibliographie, en plus de développer nouvelles méthodologies analytiques pour étudier la présence des pesticides dans l'air ambiant afin de fournir une meilleure compréhension de ces polluants pour la communauté scientifique, les travaux effectués et les résultats obtenus peuvent être une contribution utile, avec des études ultérieures, pour de futures actions réglementaires au niveau de l'Union Européenne sur pesticides dans l'air, car actuellement il y a un vide juridique dans ce domaine.

II. INTRODUCCIÓN

II.a El uso de plaguicidas químicos en agricultura

Las plagas y enfermedades de los cultivos agrícolas pueden causar cuantiosas pérdidas en los mismos, comprometiendo seriamente la cantidad, calidad y regularidad de las producciones agrícolas. Se estima, a nivel mundial, que a pesar de los avances científicos en el control de plagas los ataques de insectos, ácaros, nemátodos, hongos, bacterias, virus, microplasmas y otros patógenos, así como las malas hierbas producen disminuciones en un promedio del 35-40% de la producción agrícola potencial (Peshin, 2002), pérdidas que podrían ser mucho mayores en ausencia de métodos de control.

Por ello, en una agricultura moderna, es imprescindible una adecuada defensa contra las plagas y enfermedades que afectan a los cultivos. Entre los diferentes métodos de control, tanto profilácticos (prácticas de cultivo preventivas) como directos (lucha biológica, control biotécnico utilizando feromonas u otros mecanismos fisiológicos de las plagas, lucha genética empleando variedades resistentes, utilización de plaguicidas naturales, bien de origen mineral o procedentes de seres vivos, etc.) juega actualmente un papel predominante el uso de plaguicidas químicos de síntesis. En realidad, desde el final de la 2ª Guerra Mundial han sido el instrumento más utilizado por los agricultores para la defensa de sus cultivos contra las plagas, hasta el punto de convertirse los tratamientos químicos en una práctica habitual en los cultivos agrícolas.

II.a.1 Los plaguicidas químicos

Los plaguicidas son sustancias o productos destinados a luchar contra las plagas en agricultura o con otros fines (jardinería, tratamientos de madera, mantenimiento de vías de transporte, silvicultura, etc.), aunque la agricultura es, con diferencia el sector que más recurre a los plaguicidas.

Los plaguicidas legalmente se consideran como “productos fitosanitarios” (Reglamento (CE) 1107/2009 de la Unión Europea). Los productos fitosanitarios comprenden tanto las sustancias activas como los preparados destinados a proteger los vegetales o los productos vegetales contra los organismos nocivos. Según su función se clasifican en insecticidas, acaricidas, nematicidas, molusquicidas, rodenticidas, fungicidas, bactericidas, herbicidas, desinfectantes de suelo, etc.

También pueden clasificarse según su composición química por ejemplo dentro de los insecticidas/acaricidas: organoclorados, organofosforados, carbamatos, piretroides, sulfoorgánicos, derivados del estaño, benzoilureas, o dentro de los fungicidas: ditiocarbámicos, ftalimidas, tiofanatos, acilalaninas, nitrofenoles, benzimidazoles, triazoles, pirimidinas, imidazoles, etc., o según su mecanismo de actuación (neurotóxicos, sobre la respiración celular, sobre el metabolismo de los glúcidos o sobre la biosíntesis de lípidos y proteínas, sobre la división celular, etc.).

Actualmente el uso de plaguicidas es necesario en muchos casos para defender los cultivos contra las plagas y enfermedades que les afectan. Su empleo además de garantizar la producción de alimentos en suficiente cantidad, contribuye a la calidad de los mismos y a la regularidad en su disponibilidad, presentando además ventajas económicas obvias. Desde el punto de vista económico, a nivel mundial se considera que por cada dólar invertido en plaguicidas se obtiene un beneficio de aproximadamente 4 dólares evitando pérdidas en los cultivos (Peshin , 2002).

Además, la industria fitosanitaria es un poderoso agente económico, importante en el mercado mundial y europeo. En Europa da empleo a unas 35.000 personas (Comisión de las Comunidades Europeas, 2002). Por todo ello presentan un claro interés económico y social.

Pero, por otra parte, la mayoría de los plaguicidas químicos presentan propiedades que los hacen peligrosos para la salud y el medio ambiente, ya que actúan alterando procesos vitales. Respecto a la peligrosidad para la salud, sus efectos negativos o toxicológicos pueden ser agudos o crónicos. Los primeros son más frecuentes entre la población directamente expuesta (operadores que los manipulan) aunque pueden afectar a todo tipo de personas, mientras que los crónicos afectan a la población general que está indirectamente expuesta a los mismos a través del aire, agua y residuos en alimentos, e incluye los efectos debidos a la bioacumulación y persistencia, y pueden suponer efectos como carcinogenecidad, mutagenicidad, genotoxicidad y alteraciones inmunitarias o del sistema endocrino, que la reciente normativa europea trata de evitar (López Crespí et al., 1998) (Coscollà , 2004).

Desde el punto de vista toxicológico para las personas se clasifican en tres categorías: nocivos, tóxicos y muy tóxicos. Adicionalmente, pueden tener otros efectos: corrosivos, irritantes, etc. Aunque estas clasificaciones son útiles para conocer la peligrosidad general de un producto fitosanitario debido a la gran variedad de los mecanismos de actuación, la realidad es mucho más compleja.

Por otra parte la aplicación agrícola de los plaguicidas también tiene repercusiones ecológicas considerables. En la Unión Europea se aplicaron unas 310.011 toneladas de materias activas durante el año 2008 (Agrow, 2009). Solo un 1-5% alcanza el organismo nocivo objetivo; el restante 95-99% contamina el medio, tanto la planta (incluyendo la parte comestible) como el suelo, el agua, el aire y los seres vivos presentes en el ecosistema.

Ello puede ocasionar una serie de efectos secundarios indeseables como alteración del equilibrio biológico, apareciendo nuevas plagas por la destrucción de sus enemigos naturales, mortandad de abejas y polinizadores, aparición de fenómenos de resistencia, residuos en alimentos, acumulación y biomagnificación a lo largo de la cadena trófica, pérdida de biodiversidad y contaminación general del medio.

II.a.2 Importancia de la Agricultura Europea: situación particular en dos regiones europeas.

II.a.2.1 La Agricultura Europea

La agricultura y la selvicultura cubren la inmensa mayoría del territorio de la U.E. y desempeñan un papel fundamental para la producción de alimentos y otros productos, para la gestión del paisaje y conservación de la naturaleza y para la economía y mantenimiento de la población rural.

Según datos de Eurostat (Eurostat, 2007) el número de explotaciones agrícolas en 2005/2006/2007 en la U.E. era de 14.478.600, ocupando una superficie de 182,30 millones de Has. y dando trabajo a tiempo total a 12,7 millones de personas. La superficie agrícola útil representa más del 43% de la superficie total de la U.E. El valor total de la producción vegetal anual supera los 185.220 millones de euros. El principal país productor es Francia (20,3% del total) seguido por Italia (14,2%), España (12,7%) y Alemania (12,6%).

Las principales producciones en 2006/07 han sido cereales (258,4 millones de toneladas), remolacha azucarera (110,4 millones de Tm.), patatas (56,8 millones de Tm.), frutas (73,9 millones de Tm) y hortalizas (63,6 millones de Tm). Dentro de los cereales, predomina el trigo con el 46% de la producción. En el caso de las frutas destacan las manzanas (12,9%) y las naranjas (9,2%), y en el de las hortalizas los tomates (30,8%).

La mayor parte de los cultivos agrícolas europeos reciben tratamientos químicos con plaguicidas, pues en el año 2005 solo un 4,3% de la superficie agrícola está considerada como “agricultura ecológica” donde no se permiten los tratamientos con productos químicos sintéticos. La superficie agrícola destinada a la agricultura ecológica varía mucho entre países, desde un 11% en Austria a menos del 1% en Irlanda, Polonia y Malta, pasando por algo menos del 4% en España (Eurostat Year Book, 2009). En España, en el año 2008, la superficie se incrementó y supuso el 5% de la superficie agrícola útil (Comité de Agricultura Ecológica de la Comunidad Valenciana, 2009).

II.a.2.2 La Agricultura Valenciana (España)

Hasta la mitad del siglo XX la agricultura representó el sector más importante de la economía valenciana, la cual fue proporcionando recursos para el desarrollo de otros sectores. Sin embargo a lo largo de la 2ª mitad del siglo XX y de la primera década del siglo XXI ha ido perdiendo peso relativo en la economía por el desarrollo de otros sectores hasta representar en 2008 solo un 2% del PIB valenciano, aunque genera mucha actividad económica derivada.

Sin embargo esa modesta cifra macroeconómica no debe ocultar el hecho de que con 693.600 Has ocupa un 30% del territorio de la Comunidad Valenciana (el 50% es forestal y el 20% restante para otros usos: eriales, rios y lagos y usos no agrícolas), da empleo a unas 70.000 personas y genera una producción anual que supera los 5,6 millones de toneladas, valoradas (2008) en 2.091 millones de euros, destinando las 2/3 partes de su producción a la exportación. Además es un elemento fundamental para la seguridad alimentaria, configuración del paisaje y mantenimiento del medio rural (CAPA, 2009b).

La agricultura valenciana es muy variada, registrándose una marcada dualidad entre el regadío litoral y el secano interior, caracterizándose por su gran parcelación, el escaso peso de la ganadería, la variedad de cultivos que permite su clima mediterráneo, su preocupación por la calidad y la tradición exportadora. La Tabla 1 muestra la distribución de la superficie y la producción de los cultivos más relevantes.

En cuanto a producción destaca el predominio absoluto del cultivo de los cítricos que suponen como media el 70% del valor de la producción vegetal total, ocupando 182.951 Has (datos de 2008) lo que representa más del 30% de la superficie agrícola. (CAPA, 2009b).

En cuanto a frutales no cítricos, aunque ocupan el 23,1% de la superficie agrícola, solo representan el 2,5% de la producción agrícola por el predominio de la superficie del cultivo del almendro en secano. Otros cultivos en regadío son los frutales de hueso (melocotones, nectarinas, ciruelos, albaricoques) y otros como níspero y caqui.

Las hortalizas de regadío intensivo, aunque solo ocupan un 4% de la superficie agrícola, representan un 10,5% de la producción total, destacando las producciones de tomates y sandias, seguidas por alcachofas, melones, cebollas, pimientos, bróculi y otras.

El viñedo ocupa un 14,1% de la superficie agrícola (85.849 Has entre uva de mesa y uva de vinificación) y supone el 7,02% de la producción. El olivo que ocupa un 15,6% de la superficie agrícola supone un 2,5% de la producción.

Los cereales tienen una importancia relativa escasa pues solo ocupan el 7,5% de la superficie agrícola, destacando el cultivo del arroz en la zona del parque natural de la Albufera y representando el 3,3% de la producción final agrícola. La agricultura de regadío de la zona costera, que supone más de la mitad de la superficie cultivada es bastante intensiva, con los tratamientos químicos que esto supone.

La superficie de agricultura ecológica, donde con seguridad no se aplican tratamientos químicos representa en 2009, 36.000 Has, lo que solo supone un 5% de la superficie agrícola total.

Tabla 1: Principales superficies y producciones por grupos de cultivos en la Comunidad Valenciana (2008) (CAPA, 2009b).

Cultivo	Superficie (Has)	Superficie (%)	Producción (Tm)	Producción (%)
Cítricos	182.951	30,2	3.947.889	70,0
Frutales no cítricos	140.635	23,1	152.028	2,5
Hortalizas	24.398	4,0	587.129	10,5
Vid	85.849	14,1	432.729	7,02
Olivo	95.008	15,6	132.538	2,5
Cereales	45.618	7,5	180.655	3,3
Otros	33.534	5,5	190.327	3,5
TOTAL	**607.933**	**100**	**5.632.295**	**100**

La producción del sector agroalimentarioa valenciano representó en el 2007 alrededor del 8-9% del total español (MERCASA, 2007).

II.a.2.3 La Agricultura en la Région Centre (Francia)

Francia es el país europeo con un mayor consumo de productos fitosanitarios (Eurostat, 2007). La Région Centre está situada en el centro de Francia y tiene una intensa actividad agrícola. En 2008 el territorio dedicado a la agricultura en esta región es de 60%, superando la media francesa de 52%.

La superficie total de la Región Centre es de 3.953.600 Has (2008), distribuidos en 2 403.300 Has para la agricultura, 789.900 Has para los bosques y la madera y 760.500 Has para otros usos. Las 2.403.300 Has de tierra agrícola utilizable se repartieron en 2.063.600 Has para cultivos extensivos, 296.300 Has para pastizales, 23.600 para viña y 4.500 Ha para frutales.

Las principales producciones agrícolas en 2008 fueron: los cereales (trigo, cebada y maíz), los cultivos oleaginosos (colza y girasol), los cultivos proteoginosos (guisantes), los cultivos industriales (remolacha industrial, lino y cáñamo), las patatas, los frutales (peras y manzanas) y la viticultura. La Tabla 2 muestra la superficie (Ha) y producción de estas producciones agrícolas.

Tabla 2: Principales superficies y producciones por grupos de cultivo en la Région Centre (Francia) según el Ministère de l´Agriculture, de l´alimentation, de la pêche, de la ruralité et de l´amenágement du territoire (MAAP, 2008)

Cultivo	Superficie (Has)	Producción (Tm)
Cereales	1.304.070	9.222.420
Oleaginosos	372.865	1.174.519
Proteoginosos	17.720	-
Remolacha	22.845	2.073.014
Patatas	10.126	513.039
Forraje	35.310	287.525
Vino	23.585	1.006.052 hl

hl = hectolitros

II.a.2.4 Problemas fitosanitarios y tratamientos químicos recomendados en la agricultura valenciana

Los cultivos de la agricultura valenciana, debido a las favorables condiciones climáticas (temperaturas suaves o cálidas y frecuencia de altas humedades relativas, que favorecen el desarrollo de insectos y el ataque de hongos) son objeto de numerosos ataques de plagas y enfermedades y necesitan defenderse contra los mismos, recurriendo, en muchas ocasiones a los tratamientos químicos.

Los principales problemas fitosanitarios en los cultivos más importantes y los tratamientos recomendados que normalmente se aplican para la protección de estos cultivos[1] se detallan en la Tabla 3.

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana

	CULTIVO: CITRICOS	
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
“poll roig” (*Aonidiella aurantii)*	primavera (mayo-junio)	clorpirifos
“poll gris” (*Parlatoria pergandei*)	fin de verano (agosto-sept.)	piriproxyfen
“serpetas” (*Cornuaspis beckii y C. gloveri)*		metil-clorpirifos
		aceites parafínicos
		metidation
“caparreta negra” (*Saissetia oleae*)	febrero-marzo	piriproxifen
	agosto	fosmet
		metil-azinfos
		metidation
		fenitrotion
“cotonet” (*Planoccocus citris*)	fin de verano	clorpirifos
		metil-clorpirifos
		diazinon
	fin verano-otoño	
"mosca de la fruta" (*Ceratitits capitata*)	primavera-principios verano	malation
		triclorfon
		lambda-cihalotrin
		spinosad
		metil-clorpirifos
		etofenprox
"pulgones" (*Aphis citricola*)	abril-mayo	dimetoato (ometoato)
"pulgones" (*Aphis gossipy*)		clorpirifos
"pulgones" (*Toxoptera aurantii*)		pirimicarb
"pulgones" (*Mizus persicae*)		acetamiprid
		pimetrocina
		etofenprox
		etiofencarb
		carbosulfan
		carbofuran
		benfuracarb
		metomilo
"araña roja" (*Tetranychus urticae*)	fin verano	clofentezin
“ácaro rojo” *(Panonychus citri)*	o principios de otoño	etoxazol
		fenazaquin
		fenbutestan
		fenpiroximato
		hexitiazox
		propargita
		tebufenpirad
		spirodiclofen
		dicofol

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: CITRICOS		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"cochinilla acanalada" (*Icerya purchasi*) "mosca blanca algodonosa" (*Aleurothrixus floccosus*)	Fines de verano	buprofecin acetamiprid fenazaquin lufenuron piridaben
"minador de las hojas" (*Phyllocnistis citrella*)	Primavera-verano-otoño	abamectina acetamiprid diflubenzuron flufenoxuron imidacloprid lufenuron
"polilla del limonero" (*Prays citri*)	Primavera	clorpirifos metil-clorpirifos
"ácaro de las maravillas" (*Eriophyes sheldoni*)	Primavera	abamectina
"piojo blanco" (*Aspidiotus nerii*)	Mayo-junio Agosto-septiembre	aceites clorpirifos piriproxifen metidation
"trips" *(Pezothrips kellyanus)*	Ocasionalmente en primavera	dimetoato metil-clorpirifos
"caracoles" *(Theba pisana, Helix aspersa*)	Ocasionalmente todo el año, periodos lluviosos	metiocarb
"Aguado del fruto y gomosis" (*Phytophtora citrophtora*)	Otoños lluviosos con temperaturas suaves	cúpricos etil-fosfito de aluminio mancozeb metalaxil
"Hongos en fruta recolectada" (*Penicillium digitatum, Penicillium italicum, Alternaria spp., Phytophtora citrophtora*, etc.)	Tratamientos en almacén para conservación frutos	imazalil tiabendazol ortofenil-fenol miclobutanil procloraz fosetil-Al guazatina pirimetanil

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: VID		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"polilla del racimo" (*Lobesia botrana*)	Junio-julio Agosto	clorpirifos metil-clorpirifos flufenoxuron tebufenocida metoxifenocida tiodicarb (metomilo)
"oidio" (*Uncinula necator*)	3-4 aplicaciones desde la floración al envero (abril-agosto)	azufre boscalida miclobutanil quinoxifen ciproconazol diniconazol fenbuconazol fluquinconazol flusilazol penconazol tebuconazol triadimenol kresoxim-metil azoxistrobin
"mildiu" (*Plasmopara viticola*)	Dependencia de la pluviometría (abril-octubre)	cúpricos captan folpet maneb mancozeb metiram azoxistrobin cimoxanilo dimetomorf famoxadona piraclostrobin fosetil-Al benalaxil metalaxil
"Podredumbre gris" (*Botrytis cinérea*)	Lluvias o rocíos intensos cuando la uva está madurando (agosto-octubre)	ciprodinil fludioxonil fenhexamida iprodiona mepanipirim metil-tiofanato carbendazima

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: VID		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
“mosquito verde” (*Empoasca spp*.)	Ocasional (junio-septiembre)	clorpirifos acrinatrin flufenoxuron imidacloprid
“el cotonet” (*Planococcus vitis*)	Ocasional (junio-septiembre)	clorpirifos metil-clorpirifos imidacloprid
“Trips” (*Frankliniella occidentalis*)	Ocasional en primavera	metiocarb acrinatrin spinosad
“araña roja” (*Tetranychus urticae*)	Ocasional (primavera-verano)	dicofol fenbutestan fenpiroximato hexitiazox piridaben propargita

CULTIVO: FRUTALES		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"mosca de la fruta" (*Ceratitits capitata*)	Verano-otoño	malation lambda-cihalotrin deltametrin
"piojo de San José" (*Quadraspidiotus perniciosus*)	Primavera-verano-otoño	clorpirifos metil-clorpirifos fenoxicarb fenitrotion
“pulgones” (*Myzus persicae* y otros)	Primavera	acetamiprid clorpirifos metil-clorpirifos tiacloprid tiametoxam
"polillas" (*Cydia molesta)*	Primavera-verano	diflubenzuron fosmet metil-clorpirifos

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: FRUTALES		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"agusanado" (*Carpocapsa pomonella*)	Primavera-verano	hexitiazox etoxazol fenpiroximato fenazaquin
"Oidio" (*Sphaerotheca pannosa*, *Podosphaera tridactyla*)	Primavera-verano	bitertanol bupirimato ciproconazol miclobutanil penconazol tetraconazol tebuconazol triflumizol azoxistrobin trifloxistrobin
"Monilia" *(Monilia laxa,* *Monilia fructigena*)	Primavera-verano	captan iprodiona tebuconazol metil-tiofanato (CBZ) difenoconazol
"Moteado" *(Venturia spp.,* *Fusicladium spp.*)	Primavera-verano	captan folpet clortalonil bitertanol kresoxim-metil tetraconazol difenoconazol

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: OLIVO		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"mosca del olivo" (*Bactrocera oleae*)	Verano-otoño	dimetoato
"repilo" (*Cycloconium oleaginum*)	Primavera-otoños lluviosos	difenoconazol, compuestos de cobre

CULTIVO: ARROZ		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"cucat" (*Chilo supressalis)*	Verano	fenitrotion tebufenocida confusión sexual
"hongo" (*Piricularia oryzae)*	Verano	carbendazima flusilazol tebuconazol triciclazol triflumizol

CULTIVO: HORTALIZAS		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
"orugas de lepidópteros en tomate y pimiento" (*Tuta absoluta*, *Heliotis spp.*, *Spodoptera spp.*)	Fin primavera-verano-principio otoño	bifentrin cipermetrin clorpirifos deltametrin esfenvalerato flufenoxuron L-cihalotrin
"moscas blancas en tomate y pimiento" (*Trialeurodes vaporariorum, Bemisia tabaci*)	Primavera-verano-otoño	bifentrin L-cihalotrin oxamilo imidacloprid piridaben piriproxifen
"mildiu en tomate y pimiento" (*Phytophtora infestans, Phtytophtora capsici*)	Primavera-verano-otoño	benalaxil cimoxanilo metalaxil famoxadona captan ciazofamida

Tabla 3: Principales problemas fitosanitarios, cultivos y tratamientos en la agricultura valenciana (continuación)

CULTIVO: HORTALIZAS		
PLAGA	**PERIODO DE APLICACIÓN**	**TRATAMIENTO**
“orugas de lepidópteros en tomate y pimiento” (*Tuta absoluta*, *Heliotis spp.*, *Spodoptera spp.*)	Fin primavera-verano-principio otoño	bifentrin cipermetrin clorpirifos deltametrin esfenvalerato
“moscas blancas en tomate y pimiento” (*Trialeurodes vaporariorum, Bemisia tabaci*)	Primavera-verano-otoño	bifentrin L-cihalotrin oxamilo imidacloprid
“mildiu en tomate y pimiento” (*Phytophtora infestans, Phtytophtora capsici*)	Primavera-verano-otoño	benalaxil cimoxanilo metalaxil
“escarabajo de la patata” (*Leptinotarsa decemLineata*)	Primavera-verano	cipermetrin L-cihalotrin lufenuron deltametrin imidacloprid
"mildiu" (*Phytophtora infestans*) en patata	Primavera-verano	benalaxil metalaxil ditiocarbamatos
“Rizoctonia” (*Rizoctonia solani*)	Otoño	metiltolclofos metiltiofanato
"mildiu" (*Peronospora destructor*) en cebolla	Primavera	benalaxil metalaxil azoxistrobin ditiocarbamatos
“orugas de la col” (*Pieris brassicae* y otras)	Verano-otoño	cipermetrin deltametrin ciflutrin
“moscas blancas de la col” (*Aleyrodes proletella*)	Otoño-invierno	imidacloprid A-cipermetrin L-cihalotrin
“oidio de las cucurbitáceas” (*Erysiphe cichoracearum*)	Verano	bupirimato ciproconazol penconazol

[1] *Esta información se ha obtenido de consultas a los Boletines de Avisos Agrícolas que emite la Conselleria de Agricultura, Pesca y Alimentación (CAPA 2008, 2009a, 2010) y de encuestas a los técnicos del Servicio de Sanidad Vegetal de la citada Conselleria (2010).*

Cítricos

Son atacados por diversas plagas, algunas endémicas e importantes, que requieren normalmente tratamientos químicos.

En primer lugar, con carácter general a todos los cítricos, están las cochinillas diaspinas, entre las que destaca el "poll roig" (*Aonidiella aurantii)* y secundariamente el "poll gris" (*Parlatoria pergandei*), las "serpetas" (*Cornuaspis beckii y C. gloveri)* y otros. Suelen tratarse en primavera (mayo-junio) o fin de verano (agosto-septiembre), que son los momentos de máxima sensibilidad de la plaga, con clorpirifos, piriproxyfen, metil-clorpirifos o aceites parafínicos (estos últimos preferentemente en verano). Hasta el año 2007, inclusive, el metidation, actualmente prohibido fue el insecticida más empleado.

Hay otras cochinillas que solo ocasionalmente pueden requerir alguna aplicación química. Entre ellas están la lecanina "caparreta negra" (*Saissetia oleae*), que suele estar bien controlada por sus enemigos naturales. En caso de requerir tratamiento químico, puede hacerse contra la primera generación de formas sensibles (febrero-marzo) o contra la segunda (agosto). Los productos recomendados son aceite, piriproxifen y fosmet. Anteriormente se han empleado metil-azinfos (hasta 2005) y metidation (hasta 2007) y fenitrotion (hasta 2008), actualmente prohibidos.

Una cochinilla psedoccocina que ocasionalmente requiere alguna aplicación es el "cotonet" (*Planoccocus citris*), aunque se controla bien biológicamente con el depredador *Crytolaemus montrouizieri*, insecto que se produce y se entrega a los agricultores en los Servicios Oficiales para su suelta en primavera. Sólo cuando el tratamiento biológico no es suficiente se recurre a tratamientos químicos a fines de verano con clorpirifos o metil-clorpirifos. Anteriormente también se empleó el diazinon (hasta fines de 2008), actualmente prohibido.

Una plaga clave que ataca en la maduración del fruto y que normalmente requiere tratamientos químicos en las variedades precoces (por sus ataques a fin de verano-otoño) o las tardías (por sus ataques en primavera principios de verano) es la mosca de la fruta (*Ceratitits capitata*). Hasta 2008 se realizaban tratamientos masivos aéreos, con malation (hasta 2008) y también por vía terrestre con esos productos y con triclorfon. Actualmente, debido a la prohibición de uso de estos fosforados (se ha solicitado la readmisión de malation), se recomiendan lambda-cihalotrin, spinosad, metil-clorpirifos y etofenprox en tratamientos terrestres.

Diversos pulgones (*Aphis citricola, Aphis gossipy, Toxoptera aurantii, Mizus persicae*) atacan principalmente a clementinas y plantones. Suelen tratarse en primavera, cuando aparecen las primeras colonias (abril-mayo) con dimetoato, (metabolizable a ometoato) clorpirifos, pirimicarb, acetamiprid, pimetrocina o etofenprox. También se han empleado etiofencarb (hasta 2007), carbosulfan (hasta 2008), carbofuran y benfuracarb (hasta 2009), actualmente eliminados, aunque han solicitado la readmisión. También hasta 2008 se empleó metomilo.

También las clementinas son normalmente atacadas por la araña roja (*Tetranychus urticae*), por lo que suelen requerir aplicaciones de acaricidas, en cualquier momento del año, pero especialmente a fines de verano o principios de otoño. Pueden emplearse numerosos acaricidas (clofentezin, etoxazol, fenazaquin, fenbutestan, fenpiroximato, hexitiazox, propargita, tebufenpirad o spirodiclofen. También ha sido muy empleado anteriormente dicofol (hasta 2010).

Otro ácaro que puede atacar a cualquier tipo de cítricos, pero sólo ocasionalmente requiere tratamientos es *Panonychus citri*, para el que se emplean los mismos acaricidas anteriormente citados, normalmente a fin de verano o principios de otoño, aprovechando el tratamiento contra las cochinillas.

Otras plagas pueden controlarse bastante bien por métodos biológicos, como la cochinilla acanalada (*Icerya purchasi*) y hasta cierto punto la mosca blanca algodonosa (*Aleurothrixus floccosus*) que solo ocasionalmente puede requerir algún tratamiento a fines de verano con buprofecin, acetamiprid, fenazaquin, lufenuron o piridaben, o el minador de las hojas (*Phyllocnistis citrella*) que en plantonadas puede requerir tratamientos con abamectina, acetamiprid, diflubenzuron, flufenoxuron, imidacloprid o lufenuron.

El limonero suele requerir tratamientos específicos contra la polilla (*Prays citri*) normalmente en primavera. Aunque puede emplearse lucha microbiológica con preparados de *Bacillus thuringiensis* también pueden utilizarse productos químicos como clorpirifos y metil-clorpirifos. También en el limonero para combatir el ácaro de las maravillas *(Eriophyes sheldoni*) puede emplearse abamectina y para el piojo blanco (*Aspidiotus nerii*) aceites, clorpirifos y piriproxifen (anteriormente, hasta 2007, se empleaba metidation y metil-pirimifos, actualmente prohibidos).

Ocasionalmente los cítricos pueden requerir tratamientos contra trips (dimetoato, metil-clorpirifos) o contra caracoles (metiocarb).

En el caso de enfermedades criptogámicas en campo, la única importante y que requiere aplicaciones químicas en el caso de que la fruta está madura y se producen lluvias con temperaturas suaves (especialmente en otoños lluviosos) es la debida al hongo *Phytophtora citrophtora*, que causa el “aguado” de las frutas y la podredumbre del cuello y gomosis en el árbol. Los fungicidas empleados para su control son productos cúpricos, etil-fosfito de aluminio, mancozeb y metalaxil.

Además de los tratamientos químicos en campo, otros tratamientos químicos que normalmente reciben los frutos cítricos previamente a su comercialización son los tratamientos fungicidas en almacén para asegurar su conservación. Se emplean diversos productos, siendo el más empleado imazalil, seguido por tiabendazol y ortofenil-fenol. También se emplean miclobutanil, procloraz, fosetil-Al, guazatina y pirimetanil.

Vid

La plaga básica sobre la que se aplican normalmente tratamientos es la polilla del racimo (*Lobesia botrana*). Aunque puede combatirse con lucha microbiológica (*Bacillus thuringiensis*) o biotécnica (feromonas de confusión sexual), normalmente se utiliza la lucha química con clorpirifos, metil-clorpirifos, flufenoxuron, tebufenocida o metoxifenocida, aplicados en junio-julio (contra la 2ª generación) y agosto (contra la 3ª generación). Hasta 2007 se pudo utilizar tiodicarb, metabolizable a metomilo.

Entre las enfermedades, son endémicas los ataques de hongo del oidio (*Uncinula necator*), que requiere normalmente 3-4 aplicaciones desde la floración al envero. Los fungicidas utilizados son azufre, boscalida, miclobutanil, quinoxifen, inhibidores de la síntesis del ergosterol (ciproconazol, diniconazol, fenbuconazol, fluquinconazol, flusilazol, penconazol, tebuconazol, triadimenol) y las estrobirulinas (kresoxim-metil, azoxistrobin, trifloxistrobin).

Otro hongo que normalmente requiere aplicaciones químicas para su control, aunque muy irregulares en función de la pluviometría es el del mildiu (*Plasmopara viticola*). Pueden emplearse fungicidas de contacto (productos cúpricos, captan, folpet, ditiocarbamatos: maneb, mancozeb, metiram), penetrantes (azoxistrobin, cimoxanilo, dimetomorf, famoxadona, piraclostrobin), o sistémicos (fosetil-Al, benalaxil, metalaxil).

Si cuando la uva está madura, suceden lluvias o rocíos intensos pueden aplicarse tratamientos para evitar la podredumbre del racimo causada por el hongo *Botrytis cinerea.* Los fungicidas recomendados son ciprodinil, fludioxonil, fenhexamida, iprodiona, mepanipirim, metil-tiofanato metabolizable a carbendazima y pirimetanil. Anteriormente también se han utilizado procimidona (hasta 2007) y vinclozolina (hasta 2007), actualmente eliminados.

Otras plagas que pueden requerir algún tratamiento ocasional son el mosquito verde (clorpirifos, acrinatrin, flufenoxuron, imidacloprid), el cotonet (clorpirifos, metil-clorpirifos, imidacloprid), los trips (metiocarb, acrinatrin, spinosad) o los ácaros (dicofol, fenbutestan, fenpiroximato, hexitiazox piridaben, propargita).

Frutales

La principal plaga es la mosca de la fruta (*Ceratitits capitata)*, contra la que se efectúan tratamientos desde que se inicia la maduración de los primeros frutos de hueso (junio) y durante todo el verano hasta entrado el otoño. Hasta final de 2008 el producto más utilizado fue malation. Actualmente se recomiendan lambda-cihalotrin, deltametrin y otros.

Otra plaga importante es el piojo de San José (*Quadraspidiotus perniciosus)* contra el que se aplica clorpirifos, metil-clorpirifos, fenoxicarb y hasta 2008 fenitrotion. También contra pulgones, especialmente en primavera se aplica acetamiprid, clorpirifos, metil-clorpirifos, tiacloprid, tiametoxam y diversos insecticidas contra otras plagas: bifentrin, deltametrin, etc., contra polillas (*Cydia molesta)* diflubenzuron, fosmet, metil-clorpirifos etc. contra el agusanado (*Carpocapsa pomonella*), hexitiazox, etoxazol, fenpiroximato, fenazaquin, tebufenpirad contra ácaros, etc.

Contra enfermedades la más tratada es el oidio, con fungicidas como bitertanol, bupirimato, ciproconazol, miclobutanil, penconazol, tetraconazol, tebuconazol, triflumizol, azoxistrobin y trifloxistrobin, contra los ataques de Monilia se emplea captan, iprodiona, tebuconazol metil-tiofanato (metabolizable a carbendazima), difenoconazol. Contra el moteado se emplean captan, folpet, clortalonil, bitertanol, kresoxim-metil, tetraconazol y difenoconazol.

Olivo

En el olivar la única plaga que requiere habitualmente tratamientos químicos es la mosca del olivo (*Bactrocera oleae*) que se trata generalmente con dimetoato. En primaveras u otoños lluviosos el hongo causante del repilo del olivo (*Cycloconium oleaginum*) se trata con productos cúpricos o fungicidas orgánicos como difenoconazol.

Arroz

Su plaga principal es el "cucat" (*Chilo supressalis)* que aunque se ha venido tratando con insecticidas (fenitrotion, tebufenocida) en años pasados actualmente se han suprimido, pues se combate con la técnica de la confusión sexual.

La única enfermedad que se trata es la causada por el hongo *Piricularia oryzae*. Se han empleado fungicidas como carbendazima, flusilazol, tebuconazol, triciclazol y triflumizol.

Hortalizas

En el caso de las hortalizas existe una gran variedad de cultivos, por lo que son muy diversas las plagas y enfermedades que les atacan, siendo muy intensas y variadas las aplicaciones químicas en las mismas.

Como plagas más frecuentes en tomate y pimiento pueden citarse diversas orugas de lepidópteros (tratadas con bifentrin, cipermetrin, clorpirifos, deltametrin, esfenvalerato, flufenoxuron, L-cihalotrin, teflubenzuron, etc.), moscas blancas (bifentrin, L-cihalotrin, oxamilo, imidacloprid, piridaben, piriproxifen, tiametoxam, Z-cipermetrin, etc.), mildiu (benalaxil, cimoxanilo, metalaxil, famoxadona, captan, ditiocarbamatos, o ciazofamida, etc.) y de reciente introducción la polilla (*Tuta absoluta*) contra la que se están ensayando diversos insecticidas.

En el caso de la patata, la principal plaga es el escarabajo (*Leptinotarsa decemLineata*), combatido con cipermetrin, L-cihalotrin, lufenuron, deltametrin, imidacloprid, teflubenzuron, y tiametoxam. La enfermedad más peligrosa es el mildiu (*Phytophtora infestans*) combatida con fungicida como benalaxil, metalaxil o ditiocarbamatos. Otras enfermedades como la causada por *Rizoctonia* son combatidas con metiltolclofos o metiltiofanato.

También el mildiu (*Peronospora destructor*) es la principal enfermedad de la cebolla, combatido con benalaxil, metalaxil, azoxistrobin y ditiocarbamatos, al igual que el mildiu de la lechuga y el de la col. Las orugas de la col son combatidas con insecticidas piretroides (cipermetrin, deltametrin, ciflutrin) o con *Bacillus thuringiensis* y sus moscas blancas con imidacloprid, A-cipermetrin o L-cihalotrin.

El oidio de las cucurbitáceas (melón, sandia, etc.) es combatido con fungicidas como bupirimato, ciproconazol, penconazol, tetraconazol, triadimefon, etc.). Similares fungicidas sirven para el control de otros oidios (alcachofa, etc.).

En realidad en hortalizas son utilizados todo tipo de plaguicidas, considerando la gran variedad de cultivos existentes y la variedad de plagas dentro de cada cultivo.

Herbicidas

Además de los insecticidas y fungicidas empleados en la protección de los cultivos en la parte aérea, se emplean cantidades importantes de herbicidas aplicados al suelo para el control de las malas hierbas.

En el arroz tienen importancia los tratamientos herbicidas que se han realizado con sustancias tales como cicloxidim, cletodim, propanil, oxadiazon, azinsulfuron, profixidin, bentazona, cihalafop-butil, molinato, etc.

Además de los indicados para el arroz, donde su empleo es sistemático, otros herbicidas muy empleados son diuron (en cítricos, olivar y frutales), fluazifop (en frutales, cítricos, viñedo y hortícolas), fluroxipir (en frutales, cítricos y vid), MCPA (en frutales y cítricos), pendimetalina (en frutales, cítricos, vid y olivo), terbutilazina (en frutales, cítricos y olivo), y hasta 2009 trifluralina (en cítricos y hortícolas) y glifosato (cítricos).

En ocasiones también se efectúan aplicaciones al suelo previos a la plantación de cultivos (hortícolas, vid, etc.) de nematicidas como 1,3-dicloropropeno, etoprofos y otros.

II.a.3 Consumo de plaguicidas

Aunque no se dispone de datos detallados sobre el consumo de plaguicidas en la Unión Europea a nivel de materias activas y cultivos, situación que trata de remediar el reciente Reglamento 1185/2009 relativo a las estadísticas de plaguicidas, cuya aplicación se iniciará a partir de 2011, sí se han realizado algunas estimaciones globales aproximadas que proporcionan una interesante información.

En un estudio realizado por Eurostat (Eurostat, 2007) referente a la evolución de consumo de plaguicidas en la U.E. en el período 1992-2003, se observa que aunque fue creciendo ligeramente hasta 1999, a partir de ese año decreció ligeramente, tanto por reducción del número de tratamientos al emplear mejores métodos de previsión como a la reducción de dosis de aplicación. Sin embargo, aún en 2003 superaron 219.717 Tm, siendo Francia el país más consumidor con el 28,1% del total, seguido por España (14,5%), Italia (14%) y Alemania (10,6%).

En todo caso el consumo de plaguicidas en Europa es elevado. En 2007 el mercado mundial de plaguicidas representó 33.390 millones de dólares, de los cuales 7.080 millones, es decir el 21,2%, fueron consumidos en Europa. La Figura 1 muestra el consumo por tipo de plaguicida en Europa. Predomina en primer lugar el consumo de herbicidas (42,9%) seguido por el de fungicidas (38,7%), insecticidas (13,9%) y otros (4,5%) (AEPLA, 2009).

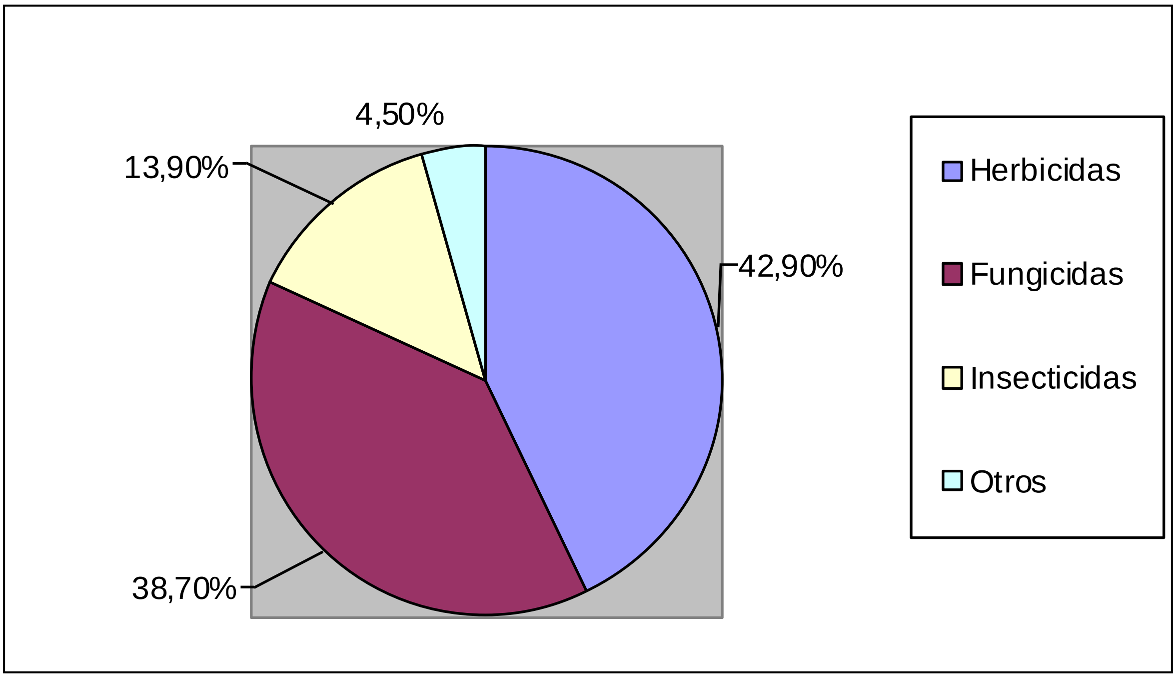


Figura 1: Consumo de plaguicidas (% del consumo total en millones de dólares) en Europa durante 2007 (AEPLA, 2009)

En el año 2008 se aplicaron en Europa 337.660 Tm. de plaguicidas, 310.011 Tm en países de la U.E., de las cuales el 12,9% correspondieron a España y el 25,3% correspondieron a Francia. Francia fue el país donde más cantidad de plaguicidas se vertieron al medio (78.557 Tm), seguido por Italia (43.085 Tm) y España (40.013 Tm) (Agrow, 2009).

De la cantidad total de plaguicidas vertidos en 2008 en Europa, 136.688 Tm (el 40,4%) lo fueron de fungicidas, 120.633 (35,7%) de herbicidas, 3.709 (11%) de insecticidas y el resto de otros fitosanitarios. En cambio en valor económico los herbicidas representaron el 42,8%, los fungicidas el 35,7% y los insecticidas el 12,3% (Agrow, 2009).

En España, debido a un clima más cálido y seco que favorece el desarrollo de las plagas de insectos y ácaros, cobra mayor peso proporcional el consumo de insecticidas/acaricidas. La Figura 2 muestra el consumo de plaguicidas por grupos en España durante 2009. En cantidad de plaguicida vertido en campo, el 33% fueron insecticidas, seguidos por herbicidas (26%) y fungicidas (24%) (AEPLA, 2009).

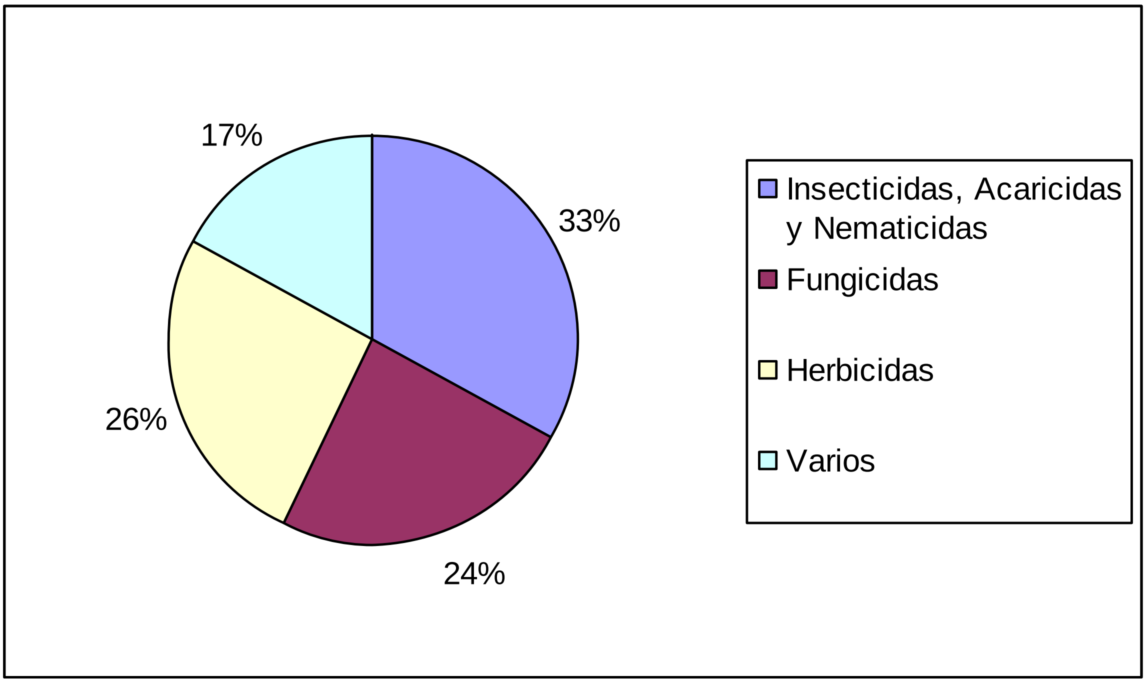


Figura 2: Consumo de plaguicias en España en 2009. Tipos de producto (% del total de toneladas en 2009)

La agricultura valenciana es importante consumidora de plaguicidas. Del total de plaguicidas consumidos en España es la segunda Comunidad (tras Andalucía) en el volumen utilizado de los mismos, en cantidades oscilando entre el 16,3% (2002) al 11,7% (2007) del total español; en 2008 y 2009 representó un 12,1% del total español (datos tomados de las memorias anuales de AEPLA). En cuanto al consumo por unidad de superficie agrícola (€/Ha) ocupa el segundo lugar en las agriculturas peninsulares, tras la región de Murcia (AEPLA, 2003) (AEPLA , 2008) (AEPLA, 2009) (AEPLA, 2010).

II.a.4 Medidas legislativas de la Unión Europea sobre plaguicidas

Aunque los plaguicidas tienen una gran importancia desde el punto de vista agrícola, económico y social, como sustancias tóxicas que son, pueden tener una incidencia considerable sobre la salud de las personas y sobre el medio ambiente en toda su complejidad, que son cuestiones a las que, lógicamente, es muy sensible la opinión pública europea. No olvidemos que anualmente se vierten al ambiente más de 300.000 Tm (310.011 Tm en 2008 en los países de la UE) de sustancias tóxicas en Europa, que pueden contaminar alimentos, aire, suelo, aguas y los seres vivos.

Por todo ello la U.E. desde hace años, viene ocupándose de regular diversos aspectos del empleo de plaguicidas. La primera norma, de 1976 (Directiva 76/895/CEE, 1976) se dirigió a proteger a los consumidores fijando unos límites máximos de residuos (LMRs) en alimentos y fue completada por más de cincuenta directivas posteriores. Actualmente están derogadas y han sido sustituidas por el Reglamento 396/2005.

En la actualidad la U.E. regula el empleo de los plaguicidas, tanto al inicio de la cadena es decir la autorización de materias activas que pueden emplearse (Directiva 91/414/CEE, Reglamento 1107/2009), al final de la cadena, fijando límites máximos de residuos en alimentos (Reglamento 396/2005) y aguas (Directiva 2000/60/CE, 2006/118/CE y 2008/105/CE) y también en la fase intermedia o de uso (Directiva 2009/128/CE para el uso sostenible de plaguicidas).

Autorización de materias activas

Hasta 1991 cada Estado tenía su propio Registro y concedía las autorizaciones de plaguicidas. En 1991 la promulgación de la Directiva 91/414/CE, que entró en vigor en 1993 supuso un cambio radical, ya que dispuso que las materias activas debían ser autorizadas por la U.E., dando un plazo de 10 años (que se alargó hasta 2009) para que se revisasen por la U.E. las 955 materias activas que en ese momento estaban en uso en la U.E.

Como consecuencia de un exigente y escrupuloso proceso de revisión se han eliminado el 75% de las materias en uso en 1993. Durante ese período (hasta 2009) solo se han aprobado 80 materias activas nuevas, por lo que al inicio de 2010 solo se dispone de 313 materias activas aprobadas, aunque hay algunas más (50) en fase de estudio. En definitiva, se dispone en 2010 solo de una tercera parte del número de materias activas de las que se disponía 17 años antes, lo que supone una reducción muy considerable de la farmacopea fitosanitaria y un replanteo de las estrategias de control de plagas.

Por otra parte a fines de 2009 se ha promulgado el Reglamento 1107/2009 relativo a la comercialización de productos fitosanitarios que sustituirá, a partir de junio de 2011 a la Directiva 91/414/CE, y que es aún más exigente al introducir criterios de corte para la autorización de materias activas (eliminará sustancias cancerígenas, mutágenas o tóxicas para la reproducción categorías 1 y 2, disruptores endocrinos, contaminantes orgánicos persistentes, etc.), lo que se supone que eliminará además al menos un 10% de las sustancias ya autorizadas. Es decir, se está en un proceso de disminución del número de materias activas utilizables.

Uso sostenible de plaguicidas

Hasta ahora la normativa sobre utilización de plaguicidas (formación de aplicadores, condiciones de uso, limitaciones a su empleo, etc.), ha sido competencia de cada Estado. Con la publicación de la Directiva 2009/128/CE sobre uso sostenible de plaguicidas la U.E. dicta normas referentes a su utilización que empezarán a aplicarse a partir de diciembre de 2012.

Entre ellas prevé la programación de planes nacionales para reducir los riesgos y la dependencia de los plaguicidas (con objetivos, medidas, calendarios e indicadores cuantitativos), la realización de cursos de formación para los aplicadores profesionales, la revisión periódica de los equipos de aplicación, la prohibición de la pulverización por medios aéreos salvo casos especiales, la adopción de medidas especiales para proteger el medio acuático y agua potable, reducción de su uso en zonas públicas, normas para la venta, almacenamiento de plaguicidas y eliminación de envases y restos y especialmente la gestión integrada de plagas que, combinando la lucha química con otros métodos alternativos, cuando sea posible, será obligatoria a partir de 2014, aunque ya se está desarrollando con carácter voluntario en muchos casos.

Residuos en alimentos, agua y aire

El Reglamento 396/2005 relativo a los límites máximos de residuos en alimentos y piensos (LMRs) y los posteriores que lo desarrollan fijan las concentraciones máximas admisibles de residuos en productos alimenticios expresadas en mg/kg de alimento o pienso. Se han fijado más de 100.000 LMRs para las distintas combinaciones plaguicida/producto vegetal, teniendo encuenta la “ingestión diaria admisible” (ADI) del plaguicida, su dosis aguda de referencia (ARfD), la composición de la dieta media y la “buena práctica agrícola”.

Para vigilar el cumplimiento de esta normativa en todos los países europeos se realizan estrictos planes de vigilancia y control, auditados por la U.E. y, caso de ser necesario, se lanzan alertas comunitarias al respecto.

Respecto a las aguas, varias Directivas, particularmente la 2000/60/CE, la 2006/118/CE y la 2008/105/CE fijan las concentraciones máximas admisibles en aguas y prevén planes de vigilancia.

La U.E. está implementando actualmente una rigurosa normativa sobre autorización y uso de plaguicidas, así como una estricta vigilancia sobre su control, con el objeto de reducir al mínimo los riesgos y peligros que supone la utilización de plaguicidas para la salud y medio ambiente. También se está implementando una rigurosa legislación sobre concentraciones máximas de plaguicidas admisibles en alimentos, piensos y aguas, pero, todavía no en el aire, posiblemente por falta de suficientes estudios al respecto.

No obstante, el Reglamento 1107/2009 (cuya aplicación se prevé a partir de junio de 2011) indica claramente (art. 4.3) que para autorizar un producto fitosanitario, aplicado en buena práctica fitosanitaria no ha de tener efectos nocivos para la salud humana o sobre el medio ambiente, a través del agua potable, alimentos, piensos o aire. La Directiva 95/36/CE sobre valoración de riesgo ambiental de los plaguicidas previamente a su autorización, exige la realización de estudios sobre el destino y comportamiento en suelo, agua y aire, proponiendo expresamente la realización de estudios sobre vías de degradación en la atmósfera.

En el proceso de autorización de un plaguicida se evalúan aspectos de presencia en el aire y transporte. La EFSA (European Food Safety Authority) emite informes científicos de cada uno de los plaguicidas susceptibles a ser admitidos en el Anexo I de la Directiva 91/414/CEE. Por ejemplo, en el caso de la trifluralina, este plaguicida fue excluido de dicho anexo el 20 de septiembre de 2007. Se solicitó la re-admisión de este producto químico y en respuesta la EFSA emitió en 2009 un informe de esta sustancia donde se evaluaba su riesgo. Uno de los apartados de este informe trata del transporte en la atmósfera a larga distancia del trifluralin. Debido a su elevada volatilidad (Presión de vapor = 9,50E-03 Pa a 25^{o}C y constante de Henry = 10.2 Pa m^{3} mol^{-1} a 20^{o}C) la EFSA afirma que es posible detectarla en la atmósfera a pesar de que su vida media fotoquímica es corta en aire (5,3h) (EFSA Scientific Report, 2009).

II.b Aerosol atmosférico o fase particulada del aire (PM)

El término materia particulada se utiliza habitualmente en el contexto de los estudios de la calidad del aire y hace referencia a partículas sólidas o líquidas suspendidas en medio gaseoso. Este término es sinónimo de aerosol atmosférico, si bien éste último es más común en el campo de la ciencia atmosférica. Se trata de una mezcla compleja de partículas suspendidas con diferentes características físicas, químicas y biológicas que determinan su comportamiento y sus efectos sobre la salud y el medio ambiente (EPA, 2004).

Las partículas pueden llegar a la atmósfera procedentes de fuentes naturales como la erosión del suelo originada por el viento, el aerosol marino o procedente de las emisiones volcánicas o incendios naturales. Los incendios son una de las mayores fuentes de productos de combustión a la atmósfera. La mayoría de los incendios ocurren en los trópicos. La combustión de vegetación es una fuente importante de emisión de CO_2, CO, NO_x, CH_4, hidrocarburos y partículas orgánicas. El polvo con el aerosol mineral es arrastrado por el viento desde el suelo. Las regiones áridas y semiáridas del mundo, que ocupan un tercio de la superficie terrestre, son las mayores localizaciones de polvo. La fuente más importante es el Sahara-Sahel del norte de África; Asia central es la segunda fuente importante de polvo. Otro tipo de fuente es la derivada de la actividad antropogénica, como la combustión del petróleo. (Seinfeld et al., 2006).

Las fuentes se pueden clasificar en primarias y secundarias. Las primarias son las enumeradas anteriormente, naturales y antropogénicas, donde las partículas son emitidas directamente desde el foco emisor a la atmósfera. También existen las fuentes secundarias de emisión donde las partículas se forman en la atmósfera por conversión gas-partícula a través de reacciones químicas con el O_2, vapor de agua, especies reactivas como el ozono, radicales como hidroxilos y nitratos, contaminantes como dióxido de azufre y óxido de nitrógeno, y gases orgánicos procedentes de fuentes naturales y antropogénicas. La figura 3 muestra un esquema de la formación de los aerosoles secundarios inorgánicos (SIA). Los procesos de formación de partículas se producen por nucleación de partículas a partir de gases de baja presión de vapor emitidos desde diversas fuentes o formados en la atmósfera, condensación de gases de baja presión de vapor en partículas que ya existen, y coagulación de partículas. (Wilson et al., 2002).

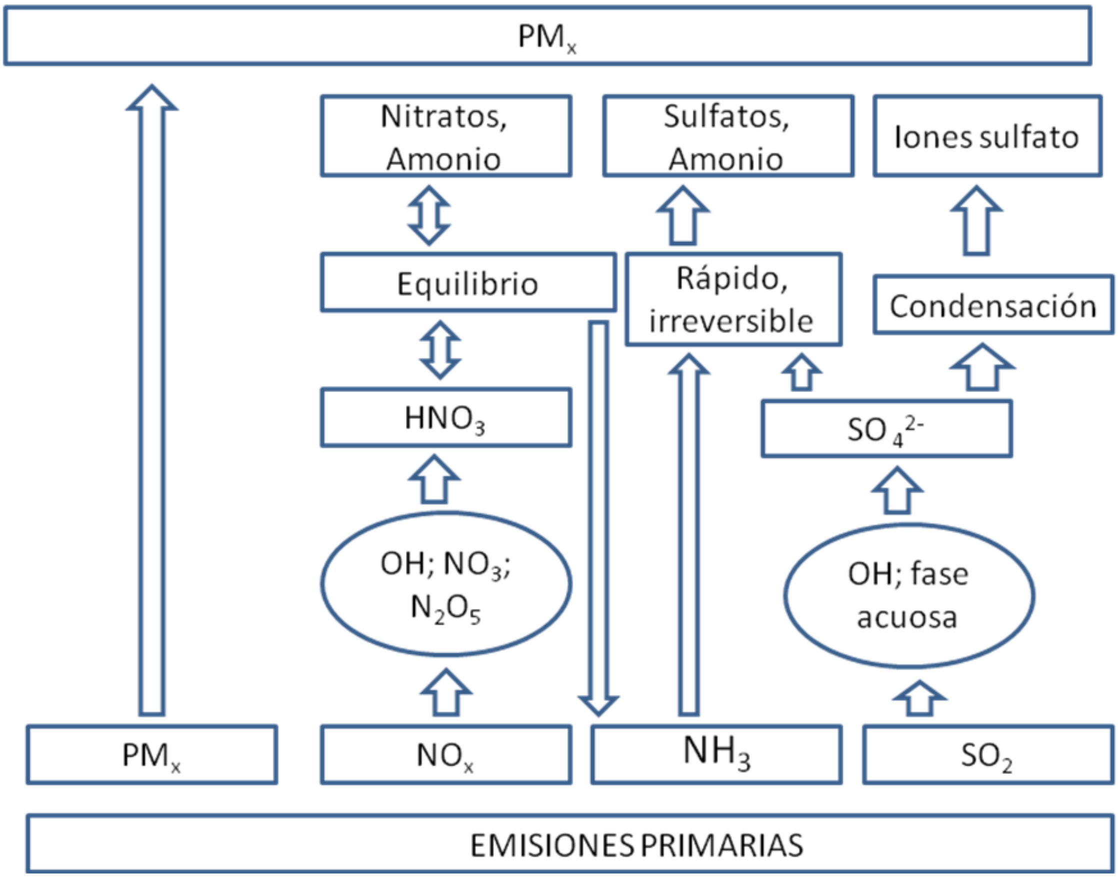


Figura 3: Mecanismos de formación de aerosoles secundarios inorgánicos (SIA)

La Tabla 4 muestra los principales compuestos de la materia particulada (PM). La composición y concentración de las partículas es muy variable y depende de muchos factores como variaciones climáticas, fuentes de emisión y posición geográfica (Polichetti et al., 2009). La Tabla 5 detalla la composición promedio de las PM 10 en estaciones de muestreo de distinta tipología.

Tabla 4: Esquema de la composición de las partículas (PM)

Aerosoles secundarios inorgánicos (SIA)	
Sulfatos:	22-45% (fracción másica) en aerosoles continentales. La mayoría procede de la conversión G-P del SO_2. En partículas finas.
Amonio:	Es el principal catión asociado al sulfato en aerosoles continentales. Se produce por la reacción del NH_3 con el ác. súlfurico. En partículas finas.
Nitratos:	Deriva mayoritariamente de la condensación del ác. nítrico sobre las partículas minerales alcalinas. En partículas finas y gruesas.
Naturales	
Cloruros:	En aerosoles marinos (Cl^-, Na^+, Mg^{2+} ..)
Elementos minerales:	Son los "crustal elements" (SiO_2, Al_2O_3, Fe, Ca, P, Ti, Mg, Mn). En partículas gruesas.
Compuestos Orgánicos (OC)	
Alcanos y alquenos de alto peso molecular, hidrocarburos aromáticos policíclicos, plaguicidas, dioxinas.. Compuestos emitidos directamente o por condensación de los compuestos fotooxidados.	
Carbón elemental (EC)	
"black carbon", "graphitic carbon" se emite directamente a la atmósfera en los procesos de combustión.	
Agua	
Partículas biogénicas (polen, esporas, fragmentos plantas..)	

Tabla 5: Concentración media anual (μg m^{-3}) de PM 10, y sus componentes en estaciones españolas (Querol et al., 2004)

Componente	**PM 10**	**OC+EC**	**Mineral**	**Marino**	**SIA**
Estación rural	21	3	6	2	7
Estación urbana	31-42	7	10	2	7
Estación cerca tráfico	45-55	13	16	2	9

OC: compuesto orgánicos; EC: carbón elemental; SIA: aerosoles secundarios inorgánicos

Las partículas en la atmósfera tienen distintas densidades y no son esféricas. El diámetro aerodinámico es importante para el transporte, eliminación, muestreo y deposición de las partículas en el tracto respiratorio. Este diámetro se define como el diámetro de una partícula esférica con una densidad de 1 g cm^{-3}. Partículas con el mismo tamaño físico y forma pero distintas densidades tendrán diferentes diámetros aerodinámicos. Los estudios sobre distribución de tamaños de partículas utilizando impactores dan medidas directas del diámetro aerodinámico de la partícula (Wilson et al., 2002).

Existen distintas clasificaciones de la materia particulada ligada a diferentes campos de estudio o enfoques metodológicos. Wilson et al. (2002) señalaron 4 tipos de clasificación de las partículas: (1) modal, basado en la distribución de tamaño observado y mecanismos de formación (ver tabla 6); (2) punto de corte, normalmente basado en el 50% del punto de corte en un equipo concreto de muestreo; (3) tamaño ocupacional, basado en la entrada dentro de los distintos compartimentos del tracto respiratorio; y (4) clasificación legal según distintas normas de calidad ambiental.

La clasificación modal divide las partículas en 4 modos: *modo grueso o "coarse"*, la distribución de las partículas con diámetros más grandes que el mínimo en la distribución de masas de las partículas, generalmente entre 1 y 3 µm. Estas partículas se originan normalmente por procesos mecánicos, como por ejemplo por la erosión del viento; *modo fino*, la distribución de partículas con diámetros más pequeños que el mínimo en la distribución de masas de las partículas, generalmente entre 1 y 3 µm. Estas partículas normalmente proceden de la combustión o se forman a partir de gases. El modo fino incluye el de acumulación y el nucleación; *modo nucleación*, comprende partículas finas con diámetros por debajo de 0,1 µm. Este modo se observa en áreas remotas y limpias o cerca de fuentes de nueva formación de partículas. Los toxicólogos llaman a estas partículas ultrafinas o nanopartículas; *modo acumulación*, son partículas finas con diámetros por encima de 0,1 µm. Las partículas en este modo normalmente no crecen en el modo grueso. Sin embargo, las partículas en el modo nucleación pueden crecer por coagulación (dos partículas que se unen y forman una tercera más grande) o por condensación (moléculas con bajo equilibrio en la presión de vapor que condensan en una partícula) y pasar al modo acumulación.

Tabla 6: Clasificación modal de las partículas (PM) según su diámetro y mecanismo de formación

CLASIFICACIÓN	DIÁMETRO (µm)	MECANISMO FORMACIÓN
Modo grueso	>1-3	Procesos mecánicos (erosión del viento)
Modo fino	<1-3	Combustión o a partir de gases
Modo nucleación	<0,1	Áreas remotas y limpias o cerca de fuentes de nueva formación de partículas
Modo acumulación	>0,1	Por coagulación o condensación del modo nucleación

Otra clasificación se basa en el punto de corte de las partículas durante el muestreo. El muestreo selectivo según tamaño se refiere al muestreo de las partículas por debajo o en un especificado rango de tamaño aerodinámico, normalmente definido por encima del punto de corte del 50%, basándose en criterios de salud, visibilidad, etc. Los captadores que someten las partículas a ciclones separan las partículas en fracciones más grandes y más pequeñas que se recogen en distintos filtros. Los impactadores en cascada utilizan múltiples tamaños de corte para obtener una distribución de las partículas según masa o composición química.

En salud laboral las partículas se clasifican en inhalables, torácicas y respirables que agrupan las partículas según su capacidad de entrada en diversos compartimentos del sistema respiratorio. Las partículas inhalables entran en el tracto respiratorio y llegan a las vías aéreas. Las partículas torácicas pasan la laringe y alcanzan los pulmones. Y las partículas respirables son un tipo de las torácicas que llegan más fácilmente a los pulmones (CEN, 1993).

En los estudios y control de la calidad del aire las fracciones de interés son las PM 10 y PM 2.5 definidas en la Directiva 1999/30/CE. Las PM 10 se definen como las partículas que pasan a través de un cabezal de tamaño selectivo para un diámetro aerodinámico de 10 µm con una eficiencia de corte del 50%. Las PM 2.5 se definen como las partículas que pasan a través de un cabezal de tamaño selectivo para un diámetro aerodinámico de 2.5 µm con una eficiencia de corte del 50%.

A pesar de que el impacto sobre la salud derivado de las partículas ha sido descrito en distintos episodios sucedidos durante el siglo pasado, la comunidad científica no empezó a estudiar los efectos perjudiciales para la salud de la exposición a PM hasta la última década. Distintos estudios epidemiológicos han demostrado que un aumento a la exposición ambiental de contaminantes atmosféricos produce un incremento de los ingresos hospitalarios por enfermedades cardiovasculares (Lanki et al., 2006; Ballester et al., 2006). Otros trabajos han confirmado que un incremento de 10 µg m^{-3} en las PM 10 produce un aumento en el riesgo de hospitalización por infarto de miocardio (Lanki et al., 2006; Miller et al., 2007). En otros estudios también se ha demostrado la relación entre el aumento de la contaminación atmosférica y el desarrollo de arteriosclerosis en experimentación en animales y en humanos.

A escala mundial, La OMS ha estimado que 800.000 muertes son producidas cada año por exposición a PM (WHO, 2002). Un estudio llevado a cabo en 19 ciudades europeas ha calculado que una reducción en las concentraciones de PM 10 de sólo 5 µg m^{-3} podría prevenir de entre 3300 y 7700 muertes por año (Medina et al., 2004).

En el ámbito europeo, La Agencia Europea del Medio Ambiente emitió un informe en 2009 sobre los niveles de PM en toda la Unión Europea durante el 2005. La legislación europea sobre calidad del aire establece dos límites legales para las concentraciones de PM 10, a las que los ciudadanos europeos no deberían estar expuestos: niveles de media anual que exceda los 40 µg m^{-3} y concentraciones de PM 10 superiores a 50 µg m^{-3} durante más de 35 días al año. Los resultados en todos los países de la UE durante el 2005 muestra que un 9% de los países europeos estuvieron expuestos a valores superiores de la media anual legislada (40 µg m^{-3}). Este valor fue excedido en más de un 75% en las áreas urbanas de la región de los

Balcanes. La probabilidad de superar estos valores también fue elevada en la República Checa, Polonia, Hungría y el sur de España.

Los resultados indicaron que en 2005, aproximadamente el 28% de la población europea estuvo expuesta por más de 35 días a unas concentraciones de PM 10 por encima del valor límite de 50 µg m^{-3}. Esto sucedió especialmente en países del este de Europa, en Italia, España, Portugal, Grecia, algunos países de los Balcanes, Bélgica, Holanda y Luxemburgo. El número de muertes prematuras por millón de habitantes atribuible a la exposición por PM 10 se estimó entre 510 y 1150 casos por millón, con una mediana estimada de 830 muertes por millón (EEA, 2009).

La calidad del aire y la protección de la atmósfera está legislado a través de normativas europeas y estatales. Con el fin de proteger la salud humana y el medio ambiente es importante combatir las emisiones de contaminantes en la fuente y determinar y aplicar medidas de reducción de emisiones.

En el ámbito europeo, la Directiva 2008/50/CE del Parlamento Europeo y del Consejo, relativa a la calidad del aire ambiente y a una atmósfera más limpia en Europa, recopila y actualiza diversas normas anteriores. Las partículas son unos de los contaminantes evaluados para determinar la calidad del aire ambiente. Esta directiva fue transpuesta a nuestro ordenamiento jurídico a través del Real Decreto 102/2011, relativo a la mejora de la calidad del aire. La Directiva 96/62/CE del Consejo sobre evaluación y gestión de la calidad del aire ambiente, estableció con carácter general el régimen jurídico sobre la contaminación atmosférica en la Unión Europea, incluyendo las partículas. Esta directiva fue incorporada a nuestro ordenamiento jurídico a través del Real Decreto 1073/2002.

A partir de la Directiva 96/62/CE se publicaron diversas “directivas hijas” como la Directiva 1999/30/CE del Consejo y la 2004/107/CE del Parlamento Europeo y del Consejo. La primera establece valores límite y evalúa a partir de métodos y criterios comunes las partículas (PM 10) y otros contaminantes (dióxido de azufre, dióxido de nitrógeno, óxidos de nitrógeno y plomo) en el aire ambiente. La segunda directiva establece un valor objetivo de concentración además de métodos y criterios comunes de evaluación de concentraciones para metales (arsénico, cadmio y níquel) e hidrocarburos aromáticos policíclicos (benzo(a)pireno) en PM 10.

En el ámbito estatal la Ley 34/2007 de calidad del aire y protección de la atmósfera establece las bases para prevenir, vigilar y reducir la contaminación atmosférica. Asimismo, en el ámbito de la Comunidad Valenciana a través de Decreto 161/2003 se creó la Red Valenciana de Vigilancia y Control de la Contaminación Atmosférica como dispositivo de medición para la evaluación de la calidad del aire ambiente. A partir de este decreto en la Comunidad Valenciana existe una red para el control y vigilancia de metales e hidrocarburos aromáticos policíclicos en PM 10 y PM 2.5. No existe hasta la fecha ninguna legislación que regule la presencia de plaguicidas en la fase particulada de la atmósfera.

II.c Emisión, transporte y transformación de los plaguicidas en la atmósfera

II.c.1 Mecanismos de emisión de los plaguicidas en la atmósfera

Los plaguicidas se están aplicando sobre áreas agrícolas en cantidades importantes en las últimas décadas, por lo que su presencia en alimentos, aguas y suelo está siendo ampliante estudiada en todo el mundo. Contrariamente a lo que ocurre con otras matrices ambientales como agua y suelo (Arias-Estévez et al., 2008) (Vryzas et al., 2009), pocos datos existen actualmente sobre la presencia de estos contaminantes en el aire ambiente. Sin embargo, cabría señalar que el uso intensivo de los plaguicidas podría producir contaminación no solo del suelo y las aguas, sino también de otros compartimentos ambientales como la atmósfera.

Los plaguicidas se introducen en la atmósfera por distintos mecanismos. El primero es la emisión durante la aplicación, donde entre el 20 y 30% del total de la dosis aplicada nunca llega al cultivo y puede perderse en el aire, o depositarse en áreas adyacentes a la zona de tratamiento. La magnitud de este efecto deriva o “spray drift” depende de diversos factores, como del tipo de formulación de los plaguicidas (viscosidad y volatilidad), la técnica de aplicación, la habilidad del aplicador y las condiciones climáticas durante la aplicación (velocidad y dirección del viento, temperatura, humedad relativa, estabilidad atmosférica en el lugar de aplicación) (Van der Berg et al., 1999) (Gil et al., 2005).

El segundo mecanismo es la emisión post-aplicación, que se puede producir por transferencia de los residuos de plaguicidas a la fase gaseosa (volatilización) tras varios días o semanas después de una aplicación (Bedos et al., 2002) (Voutsas et al., 2005). Los factores que pueden influir en la volatilización de los plaguicidas desde el suelo o los cultivos hacia la atmósfera dependen de las características fisico-químicas de los compuestos (la presión de vapor, la constante de Henry, la solubilidad, el coeficiente de adsorción, reactividad..), de las propiedades del suelo (contenido en agua, temperatura del suelo, contenido en materia orgánica, densidad del suelo, pH..), de las prácticas agrícolas (flujo de aplicación, tipo de formulación) y las condiciones ambientales durante y después de la aplicación (temperatura del aire, viento, humedad aire) (Van der Berg et al., 1999).

Los flujos de volatilización desde el suelo oscilan entre unos pocos a varios cientos de ng m^{-2} s^{-1} (Bedos et al., 2006). Wang et Jones (1994) sugirieron que la volatilización de compuestos orgánicos desde el suelo depende del ratio entre el coeficiente de partición octanol-agua (k_{ow}) y la constante de Henry (H).

La constante de Henry es un parámetro importante para compuestos aplicados al suelo con cierto contenido en agua, porque considera la solubilidad y la presión de vapor. La constante de Henry (H) se expresa como el resultado de (V_p x M)/S, donde “V_p” es la presión de vapor, “M” el peso molecular y “S” la solubilidad en agua, por lo que plaguicidas con “H” elevada tendrán alta presión de vapor y serán poco solubles en agua, siendo más probable su volatilización y susceptibles de encontrarse en el aire ambiente. En la tabla 7 se detalla la constante de Henry para los plaguicidas objeto de estudio.

El coeficiente de partición octanol-agua (k_{ow}) es un parámetro que indica la polaridad del plaguicida pues mide la distribución de la sustancia entre la fase orgánica (FO) y la fase acuosa (FA): k_{ow}= (FO/FA). Un plaguicida con un k_{ow} elevado y por tanto bastante apolar que se encuentre en un suelo rico en materia orgánica, será más susceptible de quedarse retenido en el suelo y de no pasar a la atmósfera. Sin embargo, este mismo plaguicida en un suelo con elevado contenido en agua, debido a su baja polaridad no sería soluble en el agua y sería más susceptible de volatilizarse al aire ambiente (Cousins et al., 1999).

Finalmente, la partición suelo-aire k_{SA} puede expresarse como: $K_{SA} = 0.411\ f_{OC}\ \rho\ (K_{OW}/H)$, donde "$f_{oc}$" es la fracción de carbono orgánico y "ρ" es la densidad del suelo. Cuanto más pequeña es la relación "K_{OW}/H" más susceptible es el compuesto de pasar del suelo al aire (Wang et Jones , 1994).

Además de la volatilización desde el suelo, se ha estudiado la volatilización de los plaguicidas desde las plantas o los cultivos, demostrándose que la volatilización desde las plantas es tres veces superior respecto a la del suelo bajo las mismas condiciones climáticas, debido a que las plantas tienen menos puntos de adsorción que el suelo (FOCUS Working Group, 2008). En la volatilización desde los cultivos influyen los mismos factores que desde el suelo (Leistra et al., 2006). Una ecuación similar a la utilizada en el suelo se puede aplicar a los plaguicidas distribuidos entre la vegetación y el aire, introduciéndose el concepto de coeficiente de partición planta/aire ($K_{pa} = K_{OW}/H$) (Bidleman, 1999).

Los compuestos con una presión de vapor elevada presentan una volatilidad alta, y poca influencia de otros factores. Sin embargo, compuestos con una presión de vapor media presentan una dependencia de factores ambientales y condiciones de aplicación. Bedos et al.. (2002) señalaron que compuestos con altas presiones de vapor como el heptaclor, la trifluralina o el lindano, presentaron inicialmente unos altos flujos de volatilización (>30 g ha^{-1} d^{-1}) seguidos de un descenso rápido. Sin embargo, la volatilización de compuestos con bajas presiones de vapor como dieldrin, endrin o DDT fue inicialmente baja (1 g ha^{-1} d^{-1}) pero descendió más lentamente.

De acuerdo con Bidleman (Bidleman, 1998) la presión de vapor es el principal parámetro que influye en la partición de una sustancia semi-volátil entre la fase particulada y gaseosa del aire. Sustancias con una presión de vapor superior a 10^{-2} Pa se encuentran principalmente en la fase gaseosa del aire ambiente, mientras que aquéllas que tienen una presión de vapor inferior a 10^{-5} Pa están casi exclusivamente en la fase particulada. La mayor parte de los plaguicidas tienen una presión de vapor entre los valores mencionados y se distribuyen entre las dos fases.

Sanusi et al. (1999) informaron que algunos plaguicidas organoclorados y carbamatos con presiones de vapor entre 5,6 y 0,031 MPa se encontraban únicamente en la fase gaseosa, mientras que algunos herbicidas (urea) e insecticidas (carbamatos) cuyas presiones de vapor estaban entre 0,041 y 0,0003 MPa se encontraron en más de un 70% en la fase particulada.

Van Dijk et al. (1999) concluyeron que algunos plaguicidas como el deltametrin, fenpropimorph, carbofuran, chlorothalonil, 3,6-dichloro-2-methoxybenzoic acid (dicamba), 4-chloro-2-methylphenoxy acetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D), con presiones de vapor entre 1.6 x 10^{-3} y 1.3 x 10^{-8} Pa estaban solo en la fase particulada. Otros plaguicidas como el lindano, trifluralin, clorpirifos y metolachlor (presiones de vapor entre 0.0027 y 0.0062 Pa) aparecieron casi exclusivamente en la fase gaseosa.

La atrazina y la simazina se distribuyeron en un 40% en la fase particulada en los meses de invierno, mientras que se encontraban completamente en la fase gaseosa en el periodo Mayo-Junio. Recientemente Li et al. (2007) describieron que debido a las altas temperaturas atmosféricas en el área subtropical de Guangzhou y Hong Kong, China, los plaguicidas organoclorados (OCPs) estudiados se encontraban predominantemente en la fase gaseosa en todas las estaciones del año. La fracción particulada osciló entre un 1-32%. Sin embargo, para el α-endosulfan y los compuestos DDT ocasionalmente alcanzó el 75% en invierno.

En estudios recientes, Scheyer et al. (2008) relacionaron las condiciones climáticas como la temperatura y la humedad relativa con la distribución entre la fase vapor y gaseosa (V/P) de estos cuatro plaguicidas (alaclor, lindano, metaloclor y trifluralin). No se encontró relación entre la concentración total de partículas y la partición V/P en los cuatro plaguicidas estudiados.

Es importante conocer la presión de vapor del compuesto para identificar su potencial para volatilizarse y también en la autorización de un producto fitosanitario (Reglamento 1107/2009). En este proceso se tiene en cuenta la volatilidad del plaguicida utilizando su presión de vapor (Vp) como factor clave en la volatilización.

Plaguicidas aplicados al suelo con Vp más altas que 10^{-4} Pa (20ºC) y aplicados a las plantas con Vp más altas que 10^{-5} Pa (20ºC), serán difíciles de autorizar. La tabla 7 describe la presión de vapor para la mayoría de los plaguicidas estudiados. Diversos autores han clasificado las plaguicidas en función de su volatilidad (baja, media y alta) según su presión de vapor. La tabla 8 presenta la clasificación realizada por distintos autores y la “European Plant Protection Organization (EPPO)” proponiendo distinta clasificación en función de si se trata del suelo o las plantas.

Tabla 7: Presiones de vapor y constante de Henry para los plaguicidas estudiados (BCPC, 2000)

Plaguicida	Presión de vapor (mPa)	Constante de Henry (Pa m^3 mol^{-1})
Acetamiprid	1,00E-03	5,30E-08
Acetochlor	2,20E-05	2,10E-03
Aclonifen	1,60E-05	3,03E-03
Alachlor	2,00 E-03	3,20E-03
Azoxystrobin	1,10E-07	7,30E-09
Bifenthrin	2,40E-02	-
Bitertanol	2,20E-07	2,00E-08
Bupirimate	1,00E-01	1,44E-03
Buprofezin	1,25E+00	4,24E-01
Captan	4,20E-04	1,18E-01
Carbaryl	4,10E-05	9,20E-05
Carbendazima	9,00E-02	3,60E-03
Chlorothalonil	7,60E-05	2,50E-02
Chlorpropham	2,40E+01	4,70E-02
Chlorpyrifos	2,70E+00	6,76E-01
Chlorpyrifos-m	3,00E+00	3,72E-01
Cyfluthrin	9,60E-04	1,30E-02
Cypermethrin	2,00E-04	2,00E-02
Cyprodinil	5,10E-01	6,60E-03
Deltamethrin	1,24E-05	3,12E-02

Tabla 7: Presiones de vapor y constante de Henry para los plaguicidas estudiados (continuación)

Plaguicida	Presión de vapor (mPa)	Constante de Henry (Pa m^3 mol^{-1})
Diazinon	1,20E+00	6,09E-02
Dichlobenil	1,40E-07	1,32E+00
Dichlorvos	2,10E-03	2,58E-02
Dicofol	5,30E-03	2,45E-02
Diflufenican	4,25E-06	1,18E-02
Dimethenamid	2,50E-03	4,80E-04
Dimethoate	2,50E-01	1,20E-06
Dimethomorph I	9,70E-07	2,04E-05
Dimethomorph II	9,70E-07	2,04E-05
Epoxiconazole	1,00E-05	4,71E-04
Esfenvalerate	6,70E-05	1,70E-08
Ethofumesate	6,50E-04	6,80E-04
Ethoprophos	7,80E-02	1,35E-02
Fenazaquin	3,40E-03	4,74E-03
Fenhexamid	4,00E-04	5,00E-06
Fenitrothion	1,80E-01	-
Fenoxycarb	8,67E-07	3,30E-05
Fenpropidin	1,70E-02	1,07E+01
Fenpropimorph	3,50E-03	3,00E-01
Fipronil	3,70E-04	3,70E-05
Fluazinam	7,50E-03	25,9E+00
Fludioxonil	3,90E-07	5,40E-05
Flufenoxuron	6,52E-09	7,46E-06
Flusilazole	3,90E-02	2,70E-04
Folpet	2,10E-05	7,80E-03
Hexythiazox	3,40E-03	2,40E-03
Imazalil	1,58E-01	2,61E-04
Imidacloprid	9,00E-07	2,00E-10
Iprodione	5,00E-07	7,00E-06
Iprovalicarb	4,40E-05	1,30E-06
Kresomin-methyl	2,30E-03	3,60E-04
Lambda-cyhalothrin	2,00E-04	2,00E-02
Malathion	5,30E+00	1,21E-02
Mepanipyrim	2,32E-02	1,67E-03
Metalaxyl	7,50E-01	1,60E-05
Metazachlor	9,30E-05	5,90E-05
Methidathion	2,50E-01	3,30E-04
Methiocarb	1,50E-02	1,20E-04
Methomyl	7,20E-04	2,13E-06
Methyl parathion	1,00-03	5,82E-06
Metolachlor	4,20E-03	2,40E-03
Myclobutanil	2,13E-01	4,33E-04

Tabla 7: Presiones de vapor y constante de Henry para los plaguicidas estudiados (continuación)

Plaguicida	Presión de vapor (mPa)	Constante de Henry (Pa m^3 mol^{-1})
Omethoate	3,30E+00	-
Oryzalin	<1,30E-05	<1,73E-04
Oxadiazon	1,00E-04	3,50E-02
Oxydemeton-S-methyl	4,79E-04	4,70E-06
Oxyfluorfen	2,60E-05	2,40E-02
Penconazole	3,70E-01	6,60E-04
Pendimethalin	1,94E-03	2,73E-03
Permethrin (cis, trans)	2,9E-03/9,2E-04	5,8E-03/2,8E-03
Phosmet	6,50E-05	8,25E-04
Pirimicarb	4,00E-01	3,60E-05
Pirimiphos-m	2,00E+00	6,00E-02
Prochloraz	1,50E-01	1,64E-03
Procymidone	1,80E-01	-
Propachlor	3,06E-02	3,65E-03
Propargite	6,00E-06	3,33E-06
Propyzamide	5,80E-05	7,60E-04
Pyrazophos	22,00E-02	2,57E-04
Pyridaben	2,50E-02	-
Pyrimethanil	2,20E-02	3,6E-03
Pyriproxyfen	1,30E-02	1,02E-04
Quinoxyfen	1,20E-02	3,19E-02
Spiroxamine	5,70E-03	3,80E-03
Tebuconazole	1,70E-03	1,00E-05
Tebufenozide	1,56E-04	6,59E-05
Tebufenpyrad	1,00E-02	1,25E-03
Tebutam	8,90E-02	1,50E-02
Thiabendazole	4,60E-04	2,70E-08
Tolclofos-methyl	5,70E-01	-
Tolylfluanid	2,00E-04	7,70E-02
Triadimefon	2,00E-02	9,00E-05
Triflumizole	1,80E-01	5,60E-06
Trifluralin	6,10E-03	1,50E-01
Vinclozolin	1,60E-05	3,80E-03
α-endosulfan	8,30E-04	1,48E+00
γ-HCH	4,40E-03	1,50E-02

Tabla 8: Clasificación de los plaguicidas según su presión de vapor (FOCUS Working Group, 2008)

	Presión de Vapor (Pa)		
Volatilidad del compuesto	**Seiber, Woodrow, 1983** **Unsworth et al., 1999**	**Koerdel et al., 1999**	**EPPO**
Volátil	$> 10^{-1}$	$> 10^{-3}$	Suelo : $> 10^{-1}$ Plantas : 10^{-3}
Volatilidad media	entre 10^{-1} y 10^{-5}	entre 5×10^{-3} y 10^{-6}	Suelo : entre 10^{-1} y 10^{-3} Plantas : entre 10^{-3} y 10^{-5}
Poco o no-volátil	$< 10^{-5}$	$< 10^{-6}$	Suelo : $< 10^{-3}$ Plantas : $< 10^{-5}$

EPPO: European Plant Protection Organization

La temperatura es un factor importante en la volatilización, principalmente por su efecto sobre la presión de vapor. La presión de vapor de un plaguicida con un peso molecular medio, aumenta tres o cuatro veces por cada 10ºC que aumenta la temperatura. Se ha demostrado que los flujos de volatilización aumentan desde el amanecer, alcanzando un máximo a mediodía, seguido por una disminución hasta el anochecer (Rice et al., 2002).

El tercer mecanismo por el que el plaguicida puede introducirse en el aire ambiente es el proceso de erosión del viento, el cual puede arrastrar partículas del suelo cargadas con plaguicidas. La emisión de plaguicidas adsorbidos al suelo fue descrita por Scharf et Baechmann (1993) para plaguicidas con baja volatilidad en el aire. Esto se pudo demostrar con el comportamiento de deposición temporal del fenpropimorph. Este plaguicida alcanzó tres picos de concentración en precipitación durante tres periodos distintos: Abril/Mayo, Julio y Octubre. La presencia del fenpropimorph en el primer periodo se explica porque coincide con su aplicación, el segundo periodo coincide con la cosecha y el tercero con el sembrado para la cosecha del año próximo (cereales). Estas actividades agrícolas causan que partículas del suelo y las plantas con antiguos residuos de plaguicidas entren en la atmósfera, ya que el segundo y tercer pico no se pueden explicar por volatilización de los residuos.

Como resultado de estos tres mecanismos (figura 4), fracciones importantes de los plaguicidas aplicados pueden llegar a la atmósfera.

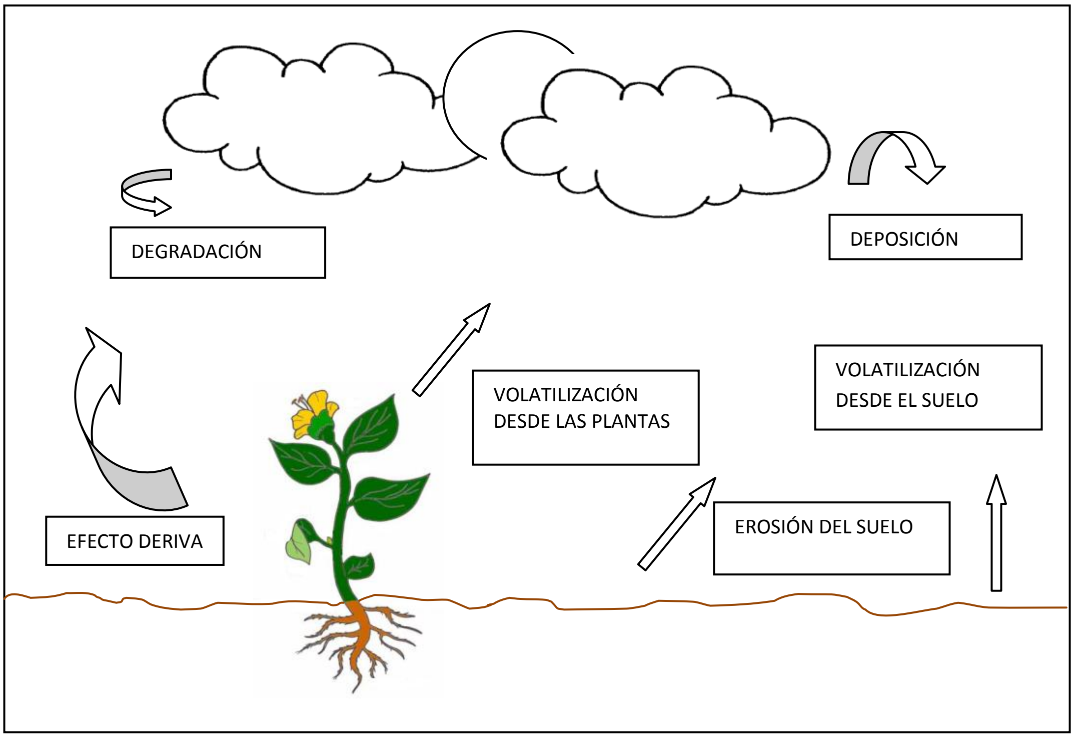


Figura 4: Procesos de transferencia de los plaguicidas a la atmósfera

II.c.2 Transporte de los plaguicidas en la atmósfera

Una vez el plaguicida entra en la atmósfera, suele permanecer en la capa más cercana a la superficie terrestre, es decir, la troposfera con una altura de hasta 15 km. Esta capa tiene un papel importante en el movimiento vertical y la distribución horizontal de los contaminantes en el aire. La troposfera tiene fluctuaciones en la altura debido a que depende de las propiedades de la superficie como la temperatura, accidentes geográficos y vegetación (tipo y cantidad) (Majewski et al., 1995)

La dispersión local de los plaguicidas dura desde unos pocos minutos hasta una hora y está principalmente influenciada por la velocidad del viento. En consecuencia, los plaguicidas con una vida muy corta (vida media de unos minutos), se dispersan en el ámbito local (transporte a corta distancia, desde 1 a 1000 m del punto de aplicación), ya que los procesos de transformación y deposición requieren más tiempo.

El transporte a media distancia (entre 1 a 1000 km) es el que suelen tener los CUPs con vidas medias cortas (minutos/horas) y que suelen recorrer desde decenas hasta centenares de kilómetros desde el lugar de aplicación.

Por otro lado, a escala regional (transporte a larga distancia, >1000 km) se produce un transporte vertical a capas superiores de la atmósfera, donde procesos de intercambio y eliminación como la transformación y la deposición húmeda o seca son factores que influirán en este tipo de transporte (Bidleman, 1998) (Asman et al., 2005). Los plaguicidas persistentes suelen desplazarse largas distancias debido a que tardan en degradarse más de dos días.

Una vez en la atmósfera el plaguicida se distribuye entre la fase gaseosa y particulada. La distribución entre ambas depende de las características fisico-químicas de los compuestos considerados, como la presión de vapor o la solubilidad en agua. También influyen los factores ambientales, especialmente la temperatura, la humedad y la naturaleza y concentración de las partículas en suspensión.

La partición entre la fase particulada y gaseosa es importante para determinar el destino de estos compuestos en el aire ambiente, principalmente la deposición húmeda (deposición de las partículas por precipitación como lluvia o nieve) o seca (deposición en las plantas o suelo por gravedad o impacto de las partículas), la degradación fotoquímica y el transporte atmosférico.

Por otra parte, para estudiar el transporte de los plaguicidas en el aire es interesante conocer las trayectorias del aire durante el periodo de muestreo y de aplicación, es decir, conocer las direcciones del viento en el periodo estudiado para poder establecer relación entre los plaguicidas aplicados en una zona determinada y concentraciones detectadas en otra zona próxima o alejada (Alegria et al., 2008).

II.c.3 <u>Degradación y deposición de los plaguicidas en la atmósfera</u>

Los plaguicidas en la atmósfera pueden sufrir procesos de transformación y/o degradación. Las principales vías de transformación de los plaguicidas en la atmósfera son: reacciones de degradación por la luz solar (fotólisis directa) y procesos fotoxidativos (fotólisis indirecta). Los procesos fotoxidativos son reacciones químicas con radicales HO·, NO_3· (Le Person et al., 2007) (Feigenbrugel et al., 2006) y ozono (O_3). Las reacciones con radicales HO· son la via más importante de degradación (Atkinson et al., 1999).

La vida media "half life" de los plaguicidas en el aire se define como el tiempo necesario para que la concentración inicial de los plaguicidas se reduzcan a la mitad por procesos fotoxidativos y/o fotolíticos. Para evaluar los procesos de degradación y calcular la vida media de los plaguicidas, se utilizan los estudios experimentales en cámaras (Le Person et al., 2007).

Sin embargo, debido a la falta de determinaciones experimentales en muchos casos, para calcular la degradación fotoxidativa de los plaguicidas en la atmósfera se utilizan programas como el "Atmospheric Oxidation Program" (AOP), conocido como "el método Atkinson", que calcula los procesos de transformación de estos compuestos en el aire.

Este método calcula la constante de reacción teórica de diferentes compuestos respecto a los radicales HO·, y en el caso de compuestos que contienen dobles y triples enlaces la constante de reacción con respecto al ozono. No obstante, este método no es muy fiable para el cálculo de compuestos que contienen varios heteroátomos, o de moléculas "voluminosas" que pueden tener impedimento estérico en el posible ataque del radical HO·, como es el caso de la mayor parte de los plaguicidas estudiados. Además en el cálculo de la vida media por el método AOP no están incluidos los procesos de degradación directa (fotólisis), que si bien para la mayoría de los plaguicidas no es importante, es el proceso de degradación principal para algunos de ellos.

La tabla 9 muestra la vida media "half life" de algunos de los plaguicidas estudiados. No obstante, hay que tener en cuenta las limitaciones anteriormente indicadas respecto al método utilizado para calcular la vida media.

Tabla 9: Vida media "Half Life" de los plaguicidas estudiados

Plaguicida	Vida media	Referencia
Acetamiprid[2]	0,140 d	(EC, 2004)
Aclonifen	1,2 d	(EFSA, 2008a)
Captan[2]	1,5h	(EFSA, 2009c)
Carbendazim[2]	0,606 h	(EC, 2007a)
Chlorothalonil[2]	4,7 años	(EC, 2006)
Chlorpyrifos[2]	1,4 h	(EC, 2005)
Cyprodinil[2]	2,1h	(EFSA, 2005a)
Diazinon[2]	1,33 h	(EFSA, 2006f)
Diflufenican	3,3 d	(EFSA, 2007c)
Dimethenamid	2,45 h	(EFSA, 2005b)
Dimethoate[2]	1,6 h	(EFSA, 2006a)
Dimethomorph[2]	3,6 h	(EFSA, 2006b)
Epoxiconazole[2]	4 d	(EFSA, 2008b)
Ethofumesate[2]	4,1 h	(EC, 2002a)
Ethoprophos[2]	0,155 d	(EFSA, 2006c)
Fenhexamid[2]	7,4 h	(EC, 2001a)
Fenpropidin[2]	1 h	(EFSA, 2007a)
Fenpropimorph[2]	2,9 h	(EFSA, 2008c)
Fludioxonil[2]	3,6 h	(EFSA, 2007b)
Flusilazole[2]	20,8 h	(EC, 2007b)
Fluzinam	163 d	(EFSA, 2008d)
Imazalil	1,8 h	(EC, 2007c)
Imidacloprid[2]	0,85 h	(EFSA, 2008e)
Iprodione[2]	85 min	(EC, 2002b)
Malathion[2]	0,414 d	(EFSA, 2005c)
Metalaxyl M[2]	4-6 h	(EC, 2002c)
Metazachlor[2]	6,5 h	(EFSA, 2008f)
Methiocarb[2]	13,8 h	(EFSA, 2006d)
Pendimethalin[2]	12 h	(EC, 2003)
Spiroxamine[2]	0,8 – 1,15 h	(EC, 1999)
Tebuconazole[2]	2,647 d	(EFSA, 2008g)
Thiabendazole[2]	2 – 3,5 h	(EC, 2001b)
Trifluralin (1),(2)	5,3 h	(EFSA, 2009a)
	1 h	(Le Person et al., 2007)

d=dia; h=horas

[1] La vida media teórica (método Atkison) de la trifluralina es de 5,3 h; sin embargo existen estudios experimentales (Le Person et al., 2007) que evidencian que el tiempo de vida en aire es mucho menor (1 h) debido a procesos de fotólisis.

[2] La vida media para estos plaguicidas ha sido calculada por el método Atkinson.

Otra vía de desaparición de los plaguicidas en el aire ambiente puede ser la deposición húmeda o seca (Asman et al., 2002). La deposición es la vía de entrada de los plaguicidas desde el aire a la superficie terrestre (compartimento acuático o terrestre). Ambas deposiciones deben considerarse por separado ya que están sujetas a distintos procesos físicos atmosféricos.

La deposición húmeda de los plaguicidas, ya sea en la fase gaseosa o particulada del aire, se produce durante periodos lluviosos. Este tipo de deposición depende fundamentalmente del flujo de precipitación y del coeficiente de partición aire/agua del plaguicida. La deposición es más intensa al inicio de un episodio lluvioso, especialmente tras largos periodos de sequía.

La deposición seca de los plaguicidas en ambas fases (gaseosa y particulada) suele producirse después de procesos de volatilización (post-aplicación). Los plaguicidas se depositan desde la atmósfera al suelo, agua o plantas. La deposición seca no debe confundirse con la sedimentación por el efecto deriva que se produce durante el momento de la aplicación de los plaguicidas. La velocidad y dirección del viento junto con la temperatura son factores importantes en este tipo de deposición.

Ambos procesos, la deposición húmeda y seca, dependen de la distribución de los plaguicidas en la fase gaseosa y particulada del aire. Los compuestos adsorbidos en la fase particulada suelen eliminarse por deposición húmeda (Unsworth et al., 1999), mientras que los compuestos que mayoritariamente se encuentran en la fase gaseosa es más probable que sufran ambas deposiciones.

II.d Sampling of pesticides in ambient air

Pesticides in ambient air are generally present at very low concentrations, requiring appropriate sampling and pre-concentration techniques to achieve sensitivity of the analytical instruments. The most common sampling techniques for pesticides in ambient air can be grouped into two categories: active (Tadeo, 2008) and passive (diffusive) sampling (Namiesnik et al., 2005) (Esteve-Turrillas et al., 2007).

II.d.1 Active sampling

Active samplers enable pesticides present in the gaseous and particulate phases to be trapped by pumping air through a filter and a solid adsorbent. The pesticides in the particulate phase are first retained in the filter, whereas those present in the gas phase are subsequently trapped by the adsorbent (See Figure 5). Ambient air pesticides can be sampled by using low-volume samplers (LVS) or high-volume samplers (HVS).

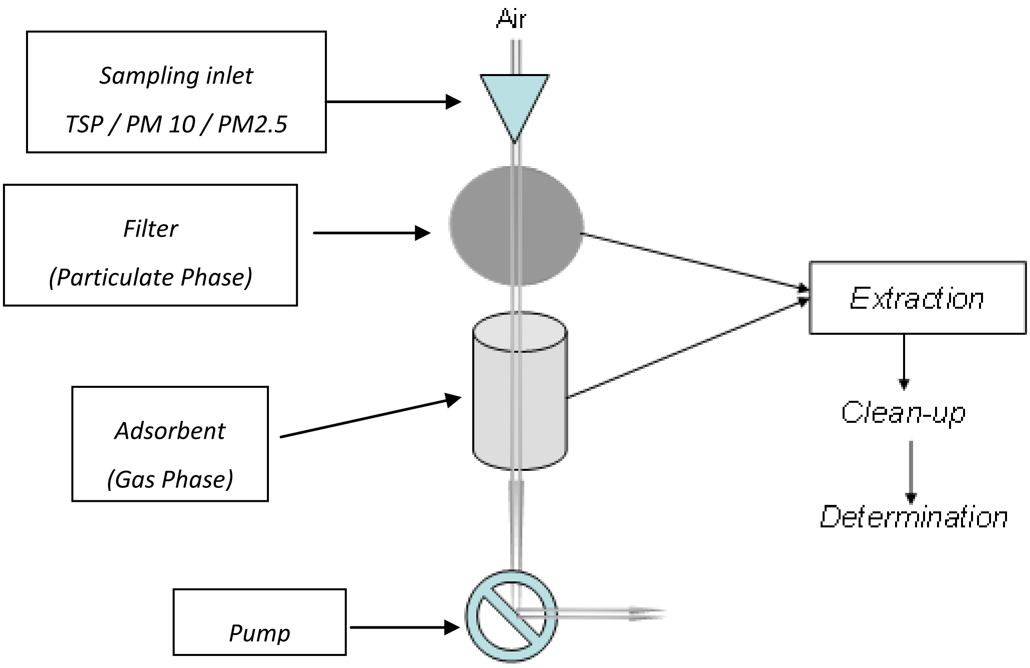


Figure 5: Schematic diagram of a typical active air sampling system and the analysis steps of filters and adsorbents.

Pesticides are present in the atmosphere at concentrations usually ranging from 0.1 pg m^{-3} to 10 ng m^3 for each pesticide (Bedos et al., 2002). Because of these low concentrations, samplers need to be in contact with a large quantity of air; consequently, pesticides in ambient air are most frequently sampled by HVS (capable of pumping at a flow rate of 13-30 m^3 h^{-1}).

Table 10 shows data about the volumetric flow rates and sampling durations used in different monitoring studies of pesticides in ambient air. It also indicates the pesticides sampled and the filters and absorbents used in each case. The total volume sampled ranged between 220-2700 m^3 with sampling times ranging from 12 hours to 7 days. Specific sampling time, however, depends on the purpose of the sampling, the sampler flow rate, and the detection limit of the analytical method. In general, with high volume sampling flow rates around 30 m^3 h^{-1} (EPA, 1999) (AFNOR, 2007a), 24 hours is generally enough to detect the levels of pesticides in mid-latitude regions and to avoid clogging up the filters.

Table 10: Examples of active sampling methods recently used for pesticides in ambient air

Flow rate ($m^3 h^{-1}$)	**Duration (h)**	**Filter type (particulate phase)**	**Adsorbent (gas phase)**	**Pesticides**	**Reference**
12.6-25.8	5.5-9	TCGF	XAD-2, 100g, s-PUF	9 multiclass pesticides	(Waite et al., 2006)
11-15	24	GFF, 30 cm Ø	XAD-2, 20g	11 multiclass pesticides	(Sanusi et al., 1999)
26	23	QFF, 78/516 cm2	PUF	9 OCPs	(Lammel et al., 2007)
15	168	GFF, 10.2cm Ø	XAD-2, 10g, s-PUF	40 multiclass pesticides	(Yao et al., 2006)
18.5	12	QFF, 10-5 Ø	XAD-2, s-PUF	23 multiclass pesticides+OCPs	(Sofouglu et al., 2001)
30	24	QFF	PUF	OCPs	(Gioia et al., 2005)
4.6	24	QFF, 9 cm Ø (PM2.5-10)	_	OCPs	(Xu et al., 2005)
42	24	GFF	PUF, 827 cm3	OCPs	(Harrand et al., 2004)
5.8-29.1	24	GFF, 30 cm Ø	XAD-2, 20 g	11 multiclass pesticides	(Sanusi et al., 2000)
1.1-15	24-168	QFF	PUF	52 multiclass	(Lig´Air, 2006)
12.5	168	GFF	XAD-2, 25 ml, s-PUF	10 herbicides	(Waite et al., 2005)
8.33	84	GFF, 10.2cm Ø	XAD-2 , 25 ml, s-PUF	2 herbicides	(Cessna et al., 2000)
20.8	24	GFF, 10cm Ø	PUF (Ø 8 cm x 7.5 cm)	24 OCPs	(Alegria et al., 2006)
34	24	QFF	XAD-2	OCPs	(Burhler et al., 2001)
2.3-12.5	24/48	QFF	XAD-2	15 multiclass pesticides	(Baraud et al., 2003)
8.33	84	GFF	XAD-2 , 25 ml, s-PUF	2 herbicides	(Waite et al., 2002)
10-15	24	GFF, 30 cm Ø	XAD-2, 20g	27 multiclass pesticides	(Scheyer et al., 2005)
12-48	24	GFF	XAD-2, 40 g	51 multiclass pesticides	(Peck et al., 2005)
10.4	24	QFF, 10.2 cm Ø	PUF, Ø 8.0 cm x 7.5 cm thick	20 OCPs	(Yang et al., 2008)
10-15	24	GFF, 30 cm Ø	XAD-2, 20 g	28 CUP	(Scheyer et al., 2007)
16	168	GFF, 10.2cm Ø	XAD-2, 7 g + Tenax-TA, 7g , s-PUF	13 OP+ 13 degradation products	(Rania et al., 2008)
16	168	GFF, 10.2cm Ø	XAD-2, 7 g + Tenax-TA, 7g , s-PUF	3 fungicides	(Bailey et al., 2007)
8.33	84	GFF, 10.2cm Ø	XAD-2, 25 ml s-PUF	5 fungicides	(Waite et al., 2004)
30	24	GFF, 15.0 cm Ø	_	9 multiclass pesticides	(Chapter 1)
34	24	QFF	XAD-2, 40 g	OCPs	(Burhler et al., 2004)
0.35	18-67	GFF, 9 cm Ø	PUF	OCPs	(Alegria et al., 2000)
12-18	24	QFF	PUF	OCPs	(Dvorska et al., 2008)

Few studies have used LVS to monitor pesticides in ambient air (see Table 10). However, LVS (0.03-3.6 m^3 h^{-1} flow rate) are mainly used in studies related with volatilization, both in chamber (Garcia-Valcarcel et al., 2003), and field studies (Bedos et al., 2006) (Ferrari et al., 2003) (Rice et al., 2002); in spray drift (Briand et al., 2002) (Clément et al., 2000), greenhouse air (Tsiropoulos et al., 2006) (Segura Carretero et al., 2003), or occupational safety (indoor) air studies (Bouvier et al., 2006) (US Department of Labor Occupational Safety & Health Administration, 1999) (NIOSH, 2003).

Pesticides in particulate matter are trapped using glass fiber filters (GFF) or quartz fiber filters (QFF). The filter diameter varies between 9 and 30 cm, depending on the sampler used (Table 10). Few absorbents, on the other hand, have been employed in the collection of pesticides present in the ambient air gas phase. One of the most commonly used absorbents is the hydrophobic polymeric resin, Amberlite XAD-2 (see Table 10). This is a crosslinked polyestyrene copolymer sorbent with a large surface area (300 m^2 g^{-1}) that mainly interacts with the analytes through Van der Waals forces and π-π interactions of aromatic rings (Fontanals et al., 2007).

XAD-2 is a universal adsorbent, very efficient for trapping herbicides, fungicides or insecticides. Generally 10-40 g of XAD-2 resin are employed to collect pesticides present in the gaseous phase in volumes up to 2000 m^3. It is employed alone or sandwiched between polyurethane foam (PUF) cylinders. The latter has been used to monitor different pesticide classes such as banned OCPs, organophosphate pesticides (OPPs), triazines and phthalimides (see Table 10).

Although XAD-4 has not been used in many monitoring studies, it has been employed in some studies in order to compare the trap efficiency of different solid sorbents (Clément et al., 2000). XAD-4 is a polymeric adsorbent supplied as white insoluble beads. It is a nonionic crosslinked polymer which derives its adsorptive properties from its macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), its high surface area (800 m^2 g^{-1}), and the aromatic nature of its surface.

PUF “polyurethane foam” is a type of foam generally used for furniture upholstery, pillows, and mattresses. It is white and turns yellow upon exposure to light. It is easy to use and inexpensive, and generally consists of a polyether with a density of 0.0225 g/cm^3. PUF has been used in many studies mainly focused on monitoring organochloride pesticides (OCPs) and other priority pollutants, such as PCBs, PBDEs, etc. This adsorbent has been tested by the EPA (Environmental Protection Ageny, USA) for sampling 57 common pesticides (scope of the EPA Method TO-4A) (EPA, 1999), including banned OCPs (aldrin, alachor or p,p’-DDT or lindane), OPs (Malathion, diazinon, dicofol) and polar pesticides such as simazine (log Kow: 2.1), monuron (log Kow: 1.46), carbaryl (log Kow: 1.85) or dicrotophos (log Kow: -0.35). Using this EPA method, LigAir (2007) conducted annual campaigns for monitoring up to 52 pesticides in ambient air, including both banned and currently used pesticides (CUPs), such as fungicides, herbicides and insecticides.

Another sorbent employed is the porous polymer Tenax TA, a resin based on 2,6-diphenylene oxide with low surface area (35 m^2/g) and low water affinity. It has been used in combination with XAD-2 to monitor OPPs or fungicides such as folpet, captan or captafol (Table 10). However, it is a traditional sorbent for trapping compounds with medium to high boiling points and is mainly used to collect volatile compounds with low volume samplers (Clément et al., 2000) (Barro et al., 2006) (Egea Gonzalez et al., 2004). Both the EPA and NIOSH specify the use of Tenax TA in their standard methods for determination of volatile organic compounds (VOCs) in ambient air and indoor air, respectively (EPA, 1999) (NIOSH, 2003).

Some studies have evaluated the trapping efficiency of different solid sorbents for collecting pesticides in the gaseous phase. Dowson et al. (2006) have compared the efficiency of different types of adsorbents for trapping 27 currently used pesticides, including PUF, XAD-2 resin, XAD-4 resin, and both resins sandwiched between PUF. Efficiency was tested by simultaneously sampling pesticides with high-volume samplers, each one incorporating one type of adsorbent. It appears that the PUF/XAD-2/PUF and PUF/XAD-4/PUF sandwiches are the most efficient, followed by the XAD-2 and XAD-4 resins. The PUF by itself was the least efficient. The authors recommend the use of XAD-2, because the efficiency of sandwiches is only slightly greater than XAD-2 alone, and decreased pumping efficiency occurs with sandwiches.

In order to establish a procedure for sampling four fungicides (pyrimethanil, metalaxyl-M, myclobutanil and fenhexamid) and the insecticide malathion, Tsiropoulus et al. (2006) evaluated the retention efficiency and carried out breakthrough tests for four solid sorbents (XAD-2, XAD-4, Supelpak-2, Florisil and C-18). In general, the retention efficiency remained constant for all the sorbents and compounds except in the case of fenhexamid on XAD-4 and Florisil, where a decrease in trapping efficiency was observed when the amount of pesticides was increased. Retention efficiency was examined by fortification of the sampling cartridge into the front bed with different amounts of pesticides, and ambient air was pulled through the tubes at different rates. However, this study used low volume rates (1-2 L min^{-1}) and the method was not applied for monitoring ambient air, but to monitor malathion and fenhexamid after application in greenhouse air. Supelpak-2 and Florisil were selected based on their performance characteristics.

Before sampling new pesticides or using different sorbents, sampling efficiency (ability of the sampling medium to trap analytes of interest), retention efficiency (ability of the sampling medium to retain a compound spiked to it in liquid solution) and breakthrough tests should be performed (EPA, 1999) (AFNOR, 2007a).

II.d.2 Passive sampling

A passive air sampler (PAS) is a device that collects chemicals from the atmosphere without the aid of a pump, and consists of an accumulating medium that has a high retention capacity for the target analytes. Such samplers allow for integrative (time - averaged concentrations, TWA) sampling in locations where active samplers would not be practical over long periods, such as remote locations with a lack of electricity (Namiesnik et al., 2005). Nevertheless, passive samplers are usually able to collect only the free gaseous phase pollutants and the duration of sampling ranges from a few weeks to several months (see Table 11), significantly longer than the usual time required using active samplers.

Table 11: Examples of passive sampling devices employed recently for the determination of OCPs and other pollutants in air

Type	Duration [Sampling rate (m^3 day^{-1})]	Uptake regime	Type of study/Country	Pollutants	Concentrations	Reference
PUF disk	4 month	K	Seasonality of air concentrations/Canada	α-HCH, γ-HCH, chlordanes, dieldrin, toxaphene, DDTs, α-endosulfan	1.3-1283 pg m^{-3}	(Motelay-Massei et al., 2005)
PUF disk	6 weeks [3-4]	K	Monitoring at continental scale/ Europe	α-HCH, γ-HCH, HCB, DDTs	<0.4-390 pg m^{-3}	(Jaward et al., 2004)
PUF disk	4 months [3.1]	K	Monitoring the Laurnetian Great Lakes/Canada-USA	α-HCH, γ-HCH, α-endosulfan, dieldrin	15-430 pg m^{-3}	(Gouin et al., 2005)
POG	7 days [3]	E/CL	Vertical profiling of the atmosphere/Canada	PCBs	0.75-730 pg m^{-3}	(Farrar et al., 2005)
PUF disk	2-month [4.8]	K	Investigation of concentrations at remote sites	PCBs, α-HCH, γ-HCH, α-endosulfan, dieldrin, toxaphene	0.6-7 pg m^{-3}	(Pozo et al., 2004)
XAD-2	1 year [1]	K	Atmospheric distribution and long-range transport	chlordanes, heptachlor, DDTs, α-endosulfan, hexachlorobenzene	0.07-260 pg m^{-3}	(Shen et al., 2005)
XAD-2	5-8 months [1]	K	Monitoring at three rural sites/ Canada	γ-HCH, DDTs, α-endosulfan, β-endosulfan	0.6-66 pg m^{-3}	(Wania et al., 2003)
PUF disk/SPMD	4 month	K	Assessment of urban-rural trends/ Canada	chlordanes, dieldrin, α-endosulfan, DDTs	0.17-817 pg m^{-3}	(Harner, 2004)
POG	7 days	E	short-term spatial variability	lindane, γ-HCH	0-1775 pg m^{-3}	(Farrar et al., 2006)
PUF disks	28 days[3-4]	K	Impact of local points sources	DDTs, HCHs	20-120 pg m^{-3}	(Klánová et al., 2006)
PDMS-coated stir bar /silicone tube	14 [108/719 ml h^{-1}]	K	Control polluted area	HCB, α-HCH, γ-HCH	19.5-7469 ng m^{-3}	(Wennrich et al., 2002)
SPMD	7 days	K	Evaluation air quality/Spain	diazinon, chlorpyrifos	5-1325 ng m^{-3}	(Esteve-Turrillas et al., 2008)
VERAM	48 hours	CL	Indoor air quality/Spain	chlorpyrifos, metalaxyl, oxyfluorphen, lindane, carbon disulfide, 2,2,4-trimethylpentane, ethylbenzene and xylene	1-2200 ng m^{-3}	(Sanjuán-Herráez et al., 2011)

K: kinetic; E: equilibrium; CL: curvi-linear

A range of PAS$_s$ are available for sampling different chemical species in air (Seethapathy et al., 2008). The majority of studies that use PAS for monitoring pesticides in ambient air are focused on sampling OCPs, along with other persistent organic pollutants (POPs). Different devices have been used such as semipermeable membrane devices (SPMDs), Versatile-Easy-Rapid Atmospheric Monitors (VERAM) and Polymer-coated Glass (POG) samplers with several adsorbents like polyurethane foam (PUF) disks or XAD resins. Table 11 shows an overview of recent studies concerning the monitoring of OCPs in ambient air using PAS.

Most of the passive air sampling done to date has been performed using PUF disks (see Table 11). PUF is used regularly as a sorbent in active high-volume sampling devices. Because of its properties it has also been applied as a passive sampler in the form of a disk. Such passive air samplers consist of PUF disks housed in stainless steel, domed chambers in order to reduce the influence of wind speed on uptake rate and also to protect the PUF disks from precipitation, direct particle deposition, and UV sunlight (Jaward et al., 2004) (see figure 6). Motelay et al.. (2005) investigated the seasonality of air concentrations for OCPs and other pollutants using PUF disks as passive samplers. PAS were deployed for 4-month integration periods along an urban-rural transect in Toronto. They concluded that such a simple sampling technique can yield insightful data.

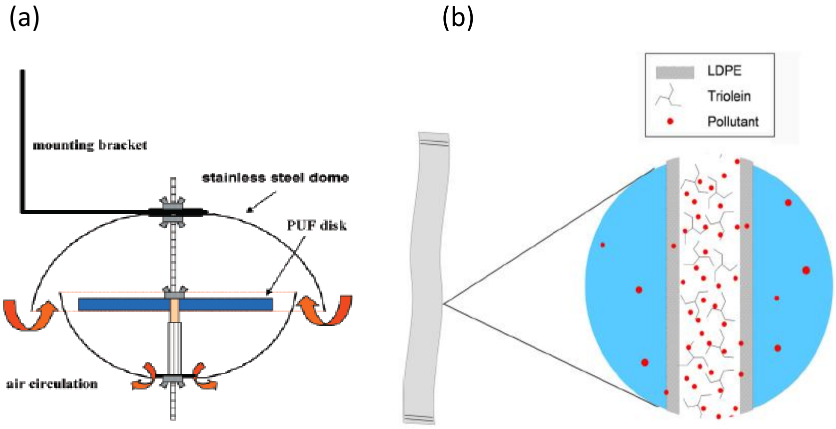


Figure 6: Schematic diagram of typical passive air samplers: a) Design of a PUF passive air sampler (Pozo et al., 2004); b) Design of a SPMD (Esteve-Turrillas et al., 2007).

Semi-permeable membrane devices (SPMDs) comprise a low-density polyethylene (LDPE) bag, 70–90 µm wall thickness, filled with triolein (1,2,3-tris-cis-9-octadecenoyl glycerol). Standard devices are 106 cm long, 2.54 cm wide, and contain 1 mL of triolein (Petty et al., 2000). The operation of a SPMD as a passive sampler is based on the diffusion of compounds through the polymeric membrane bag and their subsequent accumulation in the lipophilic solvent (see figure 6).

SPMDs have been used mainly for sampling a variety of non-polar and moderately polar organic contaminants in water (Esteve-Turrillas et al., 2007) (Huckins et al., 2002). However, some authors have used them for sampling pollutants in ambient air (Soderstrom and Bergqvist, 2004) (Lohmann et al., 2001). Harner et al. (2004) used SPMD housed in protective chambers for sampling POPs, including some OCPs. The samplers were deployed in six sites for 4 months of sampling. The results demonstrated the feasibility of using such devices to determine air concentrations of pesticides and to assess their spatial distribution.

Recently, a Versatile, Easy and Rapid Atmospheric Monitor (VERAM) has been developed for the sampling of some VOCs and pesticides (OCPs, OPPs, pyrethroids and others) in indoor air. VERAM samplers are based on a low-density polyethylene layflat tube filled with a solid-phase or a combination of solid-phases (florisil and activated carbon), which is able to adsorb a wide range of compounds with different physicochemical properties. Moreover, it provides other great advantages, such as: versatility in the sampling of compounds with different physical-chemical properties, low price and higher sensitivity than SPMD samplers. Ly-Verdú et al. (2010) monitored the air quality within seven packaging factories located in different parts of Spain by passive sampling of VOCs in air using two kinds of samplers, the developed VERAM and SPMD. The equivalence of the two employed methodologies was demonstrated and both samplers can be used to estimate the atmospheric concentrations of VOCs and evaluate the air quality in occupational environments (Ly-Verdú et al., 2010). Sanjuán-Herráez et al. detected high quantities of chlorpyrifos at thousand ng m^{-3} and also metalaxyl, oxyfluorphen and lindan at ng m^{-3} in indoor air (Sanjuán-Herráez et al., 2011).

Polymer-coated Glass (POG) samplers are created by applying a thin polymeric stationary phase (ethylene vinyl acetate-EVA) to a solid glass surface. The characterisation and principles of POG sampling have been described by Harner et al. (2003). Farrar et al. (2005) reported the first application of POG samplers for a process based study of OCPs in ambient air. The same authors used POG samplers to investigate short-term spatial variability of POPs including lindane and HCB (Farrar et al., 2006). The passive air samplers were deployed in 38 sites across 19 European countries with an exposure time of 7 days.

As shown above, XAD-2 is used routinely as a sampling medium in active samplers. Wania et al. (2003) developed and calibrated a PAS based on the sorption of gaseous pollutants to XAD-2. The sampler consists of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a steel can with an open bottom. They concluded that the XAD-2-based passive samplers are suitable for obtaining time weighted, semiquantitative information on the concentrations of vapour-phase POPs, including OCPs, in the atmosphere over a time scales of months to years. Shen et al. (2005) deployed the same XAD-2 resin passive sampler over 40 stations across North America in order to evaluate the distribution and long range transport of OCPs. The samplers were deployed for an entire year to yield the annual average concentration in each station.

A major challenge in understanding the data obtained from PAS is to estimate the air concentrations from the concentrations found in the samplers, which can allow comparison between passive samplers deployed at various locations and times. Gas phase compounds partitioning into the PAS during uptake can reach equilibrium if the exposure time is long enough. In general, there are three different phases for chemical uptake in a PAS. The uptake is initially linear with time, followed by a curvilinear region, and finally a constant phase when equilibrium is established between the air and the PAS (Shoeib and Harner, 2002).

The capacity and time to reach equilibrium can be varied by the choice of sampler type, storage medium and size. Moreover, the total capacity of the sampler at equilibrium also differs between compounds. Chemicals with high equilibrium partition coefficients will take longer to reach equilibrium than others with low partition coefficients. The equilibrium concentration depends on the PAS-air partition coefficient ($K_{PAS\text{-}A}$), which correlates with the octanol-air partition coefficient, K_{OA} (Harner, 2004).

Sampling can therefore be conducted using two principal air phase strategies: the kinetic (linear) or the equilibrium sampling mode. The relationship between the amount of pollutants absorbed by the PAS and their concentrations in air can be obtained by mathematical models. These calculations can be governed by linear or equilibrium models after establishing the corresponding experimental parameters (e.g. $K_{PAS\text{-}A}$ or sampling rate (m^3 d^{-1}) for each compound studied). During the kinetic period, the sampling rate remains linear at values ranging from 1 to 4.8 m^3 d^{-1} (Table 11) for the different sampler types and OCPs. The experimental parameters can be established by field calibration experiments (Harner et al., 2003) (Chaemfa et al., 2008) or using performance reference compounds (PRCs), also named depuration compounds (Pozo et al., 2004) (Bartkow et al., 2006).

Currently PAS can allow estimations of air concentrations within a factor of 2-3 of the “true” air concentrations (Harner et al., 2006). For many situations, this may be an acceptable level of accuracy. Nevertheless, further improvements may be possible, although PAS will probably always be less reliable than active methods.

II.e Analytical procedures

II.e.1 Extraction

Analytical methods for extracting pesticides from water, food and soil have been widely studied (Nollet, 2011). For aqueous samples, SPE (solid phase extraction) has become a common and effective multi-residue technique for extracting pesticides from water. SPE, such as LiChrolut®EN and Bond Elut™Plexa™, prepares multiple samples in parallel, uses relatively low quantities of solvents, and can be readily automated. Another extraction technique applied to water samples is solid phase microextraction (SPME). It uses a fused-silica fiber coated externally with an appropriate stationary phase and integrates sampling, extraction, concentration and analyte desorption into a single procedure (Picó et al., 2004).

In food samples, PLE has been especially recommended not only for grain and cereal samples but also for fruits and vegetables. Pesticides are extracted with an organic solvent or water at high pressure and temperature. Another technique used for food is matrix solid phase dispersion (MSPD). MSPD has shown very good characteristics for analyzing fatty samples, fruits and vegetables. The sample is dispersed with a solid phase (C_{18} or Florisil) until a homogeneous mixture is obtained. This dispersion is then placed onto a column and pesticide residues are eluted with a few milliliters of organic solvent (Soler and Picó, 2007). In recent years, QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology (used for extraction and clean-up steps) has been applied successfully with several non-fatty food matrices such as fruits and vegetables (Anastassiades, 2007) and low fatty food matrices such as milk, egg and avocado (Lehotay et al., 2005). A recently modified QuEChERS methodology has been applied to meat-based baby food, olive oil, flaxseeds and peanuts (Koesukwiwat, 2010).

For soil samples, Soxhlet is one of the most frequently used techniques because it has been adopted in many standardized analytical methodologies for determining pesticides in soils. However, this technique uses drastic conditions that often break the structural integrity of thermolabile pesticides. In addition, long extraction time and large consumption of solvent are required in Soxhlet. To facilitate pesticide extraction in soils, new extraction procedures based on instrumental techniques such as PLE or MAE have been tested. Both techniques have the advantages of fast extraction times and low solvent consumption (Andreu and Picó, 2004).

Air

In contrast to water, food and soils, the extraction of pesticides from air particulate matter is much less developed. In air samples, Soxhlet is the first choice (see table 12) when pesticides are to be extracted from filters and cartridges used in active air samplers, because it has the advantage of being a simple and low cost method, and it has been adopted in some standardized analytical methodologies for determining pesticides in ambient air (EPA, 1999) (ASTM, 2005).

Soxhlet extraction is performed with different solvents used either alone, such as acetone, DCM, or as solvent mixtures such as hexane-DCM, DCM-petroleum ether (PE), cyclohexane-acetone or hexane-acetone (see Table 12). Prior to the sampling, the traps need to be cleaned. The more usual cleaning method is Soxhlet, with the same solvents used for extraction. Sanusi et al.. (2000) pre-extracted the GFF and the XAD-2 resin with Soxhlet for 24 hours using n-hexane-DCM (85:15), and then dried it in a 60ºC oven and stored it in polyethylene bags and bottles, respectively. Peck and Hornbuckle (2005) pre-cleaned the XAD-2 resin with 24-h Soxhlet extraction with methanol, acetone, dichloromethane, hexane and 50:50 hexane-acetone. The XAD-2 resin was put into stainless steel sampling in the laboratory. The resin filled cartridges were stored in aluminium canisters sealed with a Teflon tap and placed in sealed plastic bags during transport to and from the sampling locations.

As with other matrices, soxhlet extraction has the disadvantage of being both, time (from 6 to 24 hours) and solvent (250-700 mL), consuming. These two drawbacks together with the long heating periods in the Soxhlet flask that are prone to break the structural integrity of polar thermally labile pesticides applied in modern agriculture (N-methylcarbamates, sulfonyl urea, and chlorophenoxy acid herbicides), are leading to the use of alternative procedures such as PLE (Abdou et al., 2001).

It is widely recognized that PLE gives recoveries comparable to those obtained with Soxhlet and other techniques in use. PLE utilizes organic solvents under elevated temperature (50–200ºC) and pressure (1000–2000 psi) to extract organic pollutants from environmental matrices (Fitzpatrick et al., 2000) (Dean, 1998). PLE increases the speed of the extraction process with low solvent consumption, and can be automated. The main parameters for method optimization are solvent, temperature and time. Pressure is not considered a critical experimental parameter (Dionex, 2000). Nevertheless, PLE has been scarcely used for the extraction of pesticides from air samples (see table 12).

Recently, some authors have used PLE to extract OCPs from air samples. Yang et al. (2008) extracted loaded QFF and PUF plugs individually, using a mixture of hexane-DCM-ethyl ether (7:1:2, v/v), at 100ºC for 15 min (four times). Recoveries ranged from 62 to 100 %. Rania and Sun (2008) extracted 10 organophosphorus pesticides (OP) and 14 OP degradation products from a GFF and a PUF/XAD-2/Tenax/PUF sorbent cartridge using PLE. They used ethyl acetate as solvent, at 100ºC for 30 min. No degradation of OP pesticides was observed and the recoveries ranged from 70-100%, with relative standard deviations from 1 to 21% , except for phorate oxon and malathion monocarboxylic acid, which were not sufficiently extracted by PLE with ethyl acetate, due to their affinity for sorbent material. Likewise, the same extracting method was used by Bailey and Welzer (2007) to extract the fungicides captan, captafol and folpet, also using PLE. Surrogate recoveries (diazinon d10) were 85-105%, and a second extraction with acetone showed no presence of pesticides in the extracts.

As a pre-cleaning procedure, some authors used PLE with different solvent mixtures. For pre-cleaning of PUF plugs, Yang et al. (2008) used a mixture solvent of hexane-DCM-ethyl ether (7:1:2), with PLE operated at a temperature of 100°C for 15 min. The extraction procedure was repeated six times using fresh solvent each time. The PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon-lined lids before use. QFFs were baked at 450°C for 8 h to remove organic contaminants. A similar PLE pre-cleaning procedure for QFF was followed by Sofuoglu et al. (2001), who baked overnight the filters previously wrapped loosely with aluminium foil, in a muffle furnace at 450°C. Bailey and Welzer (2007) also used PLE for PUF, XAD-2 and Tenax-TA cleaning, but they utilized ethyl acetate for the first extraction and acetone for the second.

Other techniques for the liquid-solid extraction (LSE) of pesticides trapped in filters and cartridges, have been applied using appropriate organic solvents. Lammel et al. (2007) extracted some OCPs regulated under the global POP convention (UNEP, 2001), from particulate matter trapped on filters with n-hexane using ultrasonic extraction for 30 minutes. Shen et al. (2005), using a method first described by Wania et al. (2003), extracted organochlorine pesticides from a XAD-2 passive air sampler transferring the XAD-2 material to an elution column and passing 250 mL of methanol through it, followed by 350 mL of dichloromethane. For extracting OCPs trapped in a Polymer-coated Glass (POG) passive air sampler with a coating of ethylene vinyl acetate (EVA), Farrar et al.. (2005) just dissolved the EVA coating by immersion in 35 mL of dichloromethane (DCM).

It is well-known that microwave-assisted extraction (MAE) allows reduction of both, extraction time and organic solvent consumption, and increases sample throughput in the extraction of different pollutants from environmental matrices (Bayen et al., 2004) (Wurl and Obbard, 2005). Applications of MAE for extracting pesticides from soils (Patsias et al., 2002) (Fuentes et al., 2007), sediments (Carvalho et al., 2008) and foods (Fuentes et al., 2008) (Sanusi et al., 2004) (Sinhg et al., 2004) have been proposed. However, no studies have been published related to the extraction of pesticides from air traps.

A complete method for pesticide analysis in ambient air, as in other matrices, includes additionally to the sampling step, a sample preparation procedure and a pesticide determination method. Table 12 gives a summary of the analytical methods proposed for identification and quantification of pesticides in ambient air. The steps involved are extraction, clean-up, and determination.

Table 12: Overview of methods proposed for the analysis of pesticides in ambient air.

Pesticides	Extraction	Clean-up	Determination	LOD (pg m^{-3})	Reference
9 multiclass pesticides	Soxhlet, 16h,		GC-MS	0.70-89	(Waite et al., 2006)
11 multiclass pesticides	Soxhlet, 12h, n-Hx:DCM	HPLC, silica	GC-ECD; HPLC-UV		(Sanusi et al., 1999)
9 OCPs	Soxhlet, 8h, acetone; Ultrasonic, 30 min, n-Hx		GC-ECD	1.4-73	(Lammel et al., 2007)
40 multiclass pesticides (OCPs, OPPs, neutral herbicides	Soxhlet, 12h, acetone	Silica gel; Florisil	GC-ECD; GC-MS	4.0-20	(Yao et al., 2006)
23 multiclass pesticides	Soxhlet, 12 h, DCM:PE	Alumina	GC-ECD		(Sofouglu et al., 2001)
22 OCPs	Soxhlet, 24 h, PE/DCM	Alumina	GC-NI-MS	0.002-0.13	(Gioia et al., 2005)
OCPs	Soxhlet 24h, c-Hc:acetone	Alumina	GC-ECD; GC-MS	0.005-0.1	(Xu et al., 2005)
OCPs	Soxhlet, 16h, DCM	L-L partitioning; Florisil	GC-MS	0.1	(Harrad and Mao , 2004)
11 multiclass pesticides	Soxhlet, 12h, Hx-DCM	Silica	GC-ECD; HPLC-UV	_	(Sanusi et al., 2000)
54 multiclass pesticides	Soxhlet, 16h, DEE+Hx	Alumina/Florisil	GC-MS; HPLC-UV	1	(Lig´Air, 2006)
10 multiclass herbicides	Soxhlet, 8h, acetone	_	GC-MS; GC-MS/MS	5-0-25	(Waite et al., 2005)
2 herbicides	Shoxlet, 16h, aceteone	Florisil	GC-ECD; GC-MS	40	(Cessna et al., 2000)
17 OCPs	Soxhlet 12h, n-Hx-DCM	no clean up	GC-ECD	5.0-8.0	(Scheyer et al.,2005)
24 OCPs	Soxhlet 16 h, PE	Alumina	GC-ECNI-MS	0.1-14	(Alegria et al., 2006)
44 OCPs	Soxhlet 24h, PE	Florisil+Alumina	GC-MS	0.24-9	(Jaward et al., 2004)
14 OCPs	Soxhlet 24h, Acetone:Hx	Silica gel	GC-ECD	_	(Burhler et al., 2001)
19 OCPs	Soxhlet, 18 h, PE	Alumina	GC-MS	0.7-1.3	(Gouin et al., 2005)
4OCPs	Inmersion in DCM	Silica gel	GC-NI-MS	1.2-26	(Farrar et al., 2005)
OCPs	Soxhlet, 24 h, PE	Alumina	GC-NI-MS	0.01-0.48	(Pozo et al., 2004)
15 multiclass pesticides	Soxhlet, 24 h, nHx-DEE	_	HPLC-UV	70-13800	(Baraud et al., 2003)
27 multiclass pesticides	Soxhlet, 12 h, DCM-Hx	_	GC-MS/MS	2.5-1250	(Scheyer et al.,2005)
51 multiclass pesticides	Soxhlet, 24 h, Hx-acetone	Florisil	GC-EI-MS	0.71-110	(Peck and Hornbuckle, 2005)
20 OCPs	PLE, Hx-DCM-EE	Silica	GC-EI-MS	0.4-1.6	(Yang et al., 2008)
28 multiclass pesticides	Soxhlet, 12h, Hx-DCM	no clean up	GC-MS/MS	2.5-1250	(Scheyer et al.,2007)
10 OP	PLE, Eac	C18	LC-MS/MS	0.2-10	(Rania and Sun , 2008)
3 fungicides	PLE, EAc	C18	GC-NI-MS	0.8-3.8	(Bailey and Welzer, 2007)
5 herbicides	Soxhlet, 12h, acetone	Florisil	GC-MS	40	(Waite et al., 2004)
OCPs	Soxhlet 24h, PE	Silica	GC-ECD;GC-NI-MS	0.1	(Alegria et al., 2000)

Taking into account table 12, PLE extraction has been used only in three studies of pesticides in ambient air (Yang et al., 2008; Rania and Sun, 2008; Bailey and Welzer, 2007). Moreover, MAE extraction has never been used in the analysis of air samples. Both techniques present some advantages such as fast extraction and low solvent consumption. For these reasons, these procedures have been selected as extraction techniques in this thesis.

II.e.2 Clean-up

During the extraction of pesticides from food and environmental samples, not only the analytes are isolated. There are different types of interfering compounds, mainly fats, carbohydrates, water, chlorophyll and others, which get co-extracted. Therefore, usually another analytical step is needed, i.e. extract purification. Liquid-liquid partitioning (LLP) and SPE are the most popular clean-up techniques for pesticide residues in food.

LLP clean-up can be efficiently applied using organic solvents, such as dichloromethane and ethyl acetate-cyclohexane (Picó et al., 2006). Regarding SPE, current literature points out that the retention affinity of graphitized black carbon and polymers were stronger than those of octadecyl (C_{18}) and octyl (C_8) bonded silicas. The introduction of various types of co-polymeric sorbents has helped to make SPE a more robust clean-up technique with a wider application range than the conventional silica-based sorbents. A polymeric sorbent frequently used for the clean-up of pesticides in food samples is Oasis-HLB®. This is a hydrophilic-lipophilic balanced copolymer (HLB) of N-vinylpirrolidone and divinylbenzene. Polar basic benzimidazoles and azoles can be separated from co-extractants by a MCX (a polymeric sorbent substituted with sulfonyl groups) that represents the combination of reversed-phase and cation exchange properties (Picó et al., 2006).

Another clean-up technique commonly applied to pesticides in food and environmental matrices is GPC (Gel permeation chromatography). This procedure is generally recommended for purifying extracts obtained from biological samples; it can be used for separating large molecules (e.g., lipids), because its operational principle is based on size exclusion (Beyer and Biziuk, 2008). Likewise, QuEChERS methodology is used as a clean-up method for food and environmental samples. This procedure has obtained good results for non-fatty food matrices such as fruits and vegetables (Anastassiades, 2007) and low fatty food matrices such as milk, egg and avocado (Lehotay et al., 2005).

Air

Regarding air samples, SPE has become the most common clean-up approach for the purification of pesticide residues (see Table 12). The most frequent sorbents include normal phase sorbents (Hennion, 1999) such as Florisil (synthetic magnesium silicate), alumina, silica gel, or a combination of them (alumina/silica or alumina/Florisil). In these polar sorbents, only extracts in a non-polar solvent, typically hexane or isooctane, are percolated through the sorbent after conditioning. Step elution with solvents of increasing polarity allows a fractionation on the basis of polarity differences.

Alumina was employed for the clean-up of filters and PUF air sample extracts for the determination of OCPs (Alegria et al., 2006). The extract was obtained from Soxhlet extraction with petroleum ether (PE) and concentrated by rotary evaporation, blown down with a gentle stream of nitrogen and exchanged into isooctane.

Clean-up was performed on a column of 1 g of neutral alumina (Al_2O_3). The column was pre-eluted with 10 mL dichloromethane followed by 10 mL PE. Extracts were applied in 1 mL isooctane and the column was eluted with 15 mL (5% DCM/PE). The eluate was concentrated by nitrogen blow-down and solvent-exchanged into isooctane before analysis. Polar sorbents provide a good clean-up for most apolar pesticides such as organochlorine and some organophosphorus compounds, but are less suitable for the clean-up of analytes covering a wide polarity range.

Reversed-phase C18 silica has been used for the clean-up of more polar pesticides, such as OP herbicides and OP degradation products (Rania and Sun, 2008), and some fungicides (Bailey and Welzer, 2007). Extracts in methanol were loaded onto the preconditioned C18 cartridge and eluted with 5 mL of ethyl acetate. However, no macroporous polymeric sorbents, such as LiChrolut EN, Oasis HLB, Bond Elut PPL and Isolute ENV+, have been used, probably because of the low number of polar pesticides monitored in the atmosphere.

Gel permeation chromatography (GPC) or size exclusion chromatography separates compounds on the basis of their size (EPA, 1994). Jaward et al. (2004) used GPC with Biobeads SX3, in a two-step clean-up procedure to detect OCPs and other persistent organic pollutants (POPs), after an alumina-silica chromatographic column for purification of extracts from PUF passive sampler.

In some cases, mainly when using very selective detectors such as GC-MS/MS (Scheyer et al., 2007) and LC-MS/MS, no clean-up was necessary. However, it is essential to study the matrix effect (signal enhancement or suppression) (Haslová and Zrostlíkova, 2003), ruggedness and instrumental maintenance prior to deciding whether or not to perform a clean-up step.

II.e.3 Determination

Over the past decades, approaches to detect trace levels of pesticides have changed significantly, moving away from the use of GC with classical detectors to GC-MS because of the sensitivity and selectivity offered by the MS detector. Likewise, the increasing use of polar and sometimes thermal-labile compounds, mainly herbicides, has promoted the use of LC-MS based methods.

II.e.3.1 GC Methods

Pesticide residues in air, as in other matrices, are mainly analyzed by gas chromatography (GC). Volatility and thermal stability are required for GC-amenable pesticides. The detectors most widely used are the electron-capture detector (ECD), the nitrogenphosphorus detector (NPD) and the mass spectrometry detector (MS).

Detection and analysis by ECD is commonly used for the analysis of OCPs. Many studies related to air monitoring of POPs including some OCPs such as Aldrin, *cis* and *trans*-Chlordane, DDT and transformation products, Dieldrin, Endrin, Heptachlor, HCB, Mirex. These studies are still using this very sensitive and selective detector (Table 12). Columns employed are nonpolar or semipolar, 5% phenyl/ 95% polydimethylsiloxane (DB-5, Optima-5), mostly with 30m x 0.32mm i.d. x 0,25µm or 60m x 0.25mm i.d x 0.10µm film thickness. They commonly utilize helium as the carrier gas and operate in the splitless injection mode.

Because of uncertainty of pesticide identification with GC-ECD, some authors conduct confirmation of pesticides by GC-MS (see Table 12). GC-MS is increasingly replacing traditional detectors in the determination of pesticide residues in air, and is nowadays the analytical technique most widely used. GC-MS is a favoured approach for the analysis of pesticides in air because of its capacity to provide quantitative and confirmatory results, and for its high sensitivity.

The MS analyzer most frequently used is quadrupole, mainly working in selected ion monitoring (SIM) mode, which provides a higher sensitivity than full scan mode. In multiresidue analysis by GC-MS, electron ionization (EI) in positive mode is most commonly used. Peck and Hornbuckle (2005) have analyzed 51 currently used pesticides (CUPs) in ambient air by GC-MS, using a quadrupole analyzer in SIM mode, with EI+. A 30-m 5 % phenyl methylsiloxane capillary column was utilized (HP-5MS; 0.25 mm i.d., 0.25 µm film thickness). All analytes were identified by retention time and by two characteristic ions, and the internal standard method was used for quantification. The analytes presented retention times ranging from 23.86 to 85.22 min.

Chemical ionization (CI) is a softer ionization approach that tends to give lower LOQ depending on the pesticide, but is not widely applicable in multiclass pesticide methods and does not provide as much structural information about the analyte as EI does. The GC-MS technique has been also used with negative chemical ionization (NCI), mainly for analysis of OCPs (see Table 12).

Some polar pesticides can not be analyzed directly by GC (pesticides not amenable to GC). However, different polar pesticides have been also determined by GC-MS, both in EI and NCI ionization mode, after a prior derivatization step. Waite et al. (2005) analysed ten polar herbicides, including Aryloxyalkanoic acids (2,4-D, MCPA), triazines (atrazine) and thiocarbamates (triallate), by GC-MS after methylation with ethereal diazomethane. The same derivatizing agent was used in a previous study (Waite et al., 2004) to analyse five polar herbicides such as trifluralin, dicamba, diclofop, MCPA and trifluralin. Scheyer et al. (2005) used pentafluorobenzylbromide (PFBBr) to derivatize urea herbicides (Diuron Isoproturon, Chlorotoluron) and Aryloxyalkanoic acids (2,4-D, MCPP, MCPA).

Some authors, looking to optimize sensitivity and specificity, have used GC coupled to mass spectrometry in tandem (MS/MS) using ion trap (IT) instruments (Sauret et al., 2000). Scheyer et al. (2005) developed a multiresidue method using GC-IT-MS/MS for the analysis of 27 multiclass pesticides, some of them requiring a derivatization step (ureas). Owing to its high specificity, this method does not require a clean-up step. Precise optimization of MS/MS parameters is needed in order to maximize the signal for each pesticide. Usually the first step is the selection of parent ions studying the fragmentation pattern (full scan spectra) of each analyte. Precursor ions are then isolated in the ion trap and fragmented by collision-induced dissociation (CID) (Naert et al., 2004) and the two most abundant product ions for each congener are selected. Different parameters can potentially affect CID fragmentation as well as the analytical response of the ITMS system, depending on the instrument used. The optimization can be made by software, by the approach of changing-one-factor-at-a-time (COST), or using statistical design of experiments (DOE). Methods for multiresidue determination of pesticides by GC-MS/MS have been widely established for other matrices such as vegetables, soils or sediments, using both IT (Gamón et al., 2001) and triple quadrupole detectors (QqQ) (Pihlström et al., 2007). Until now, this last detector has not been used for the analysis of pesticides in air.

II.e.3.2 HPLC Methods

GC coupled to MS (GC-MS) is now a routine technique for analysis of non-polar, semi-polar, volatile and semi-volatile organic compounds. In contrast, LC coupled to MS (LC-MS) is the technique of choice for polar and non-volatile substances, and in recent years it has experienced a growing use in the field of food and environmental analysis.

While GC-MS provides fingerprint spectra by electron ionization (EI), atmospheric pressure ionization (API) techniques usually generate unfragmented spectra. Tandem MS (MS/MS), or in-source collision-induced dissociation (CID), is required to obtain structural information, to improve selectivity and sensitivity, and to confirm the identity of analytes. Among the analyzers capable of MS/MS, triple-quadrupole and ion-trap instruments are the most commonly utilized for the analysis of toxic compounds (Núñez et al., 2005).

Electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) complement one another in regards to polarity, molecular mass of analytes, and chromatography conditions. However, ESI remains the ionization source most frequently used for analysis of toxic compounds in different fields due to the high polarity and ionization characteristics of these substances (Núñez et al., 2005).

There are several instrumental parameters that influence the ESI ionization efficiency such as: spray voltage, sheath gas, auxiliary gas or capillary temperature. Thus, a careful optimization of the mass spectrometer is required to achive maximum sensitivity. Also, the composition of the mobile phase and the nature and amount of ionic additives added to support ion formation influence the yield of analyte ions.

Three major chromatographic modes are utilized for the separation of pesticides in tandem MS: reversed-phase, ion-pair reversed-phase and ion-exchange. Because of its robustness, reversed-phase covers more than 80% of LC applications. In reversed-phase, medium polarity, polar and ionic pesticides are separated according to the difference in hydrophobicity by partitioning between an apolar stationary phase and a polar mobile phase. Most stationary phases are based on silica that has been chemically modified with octadecyl (C_{18}) or octyl (C_8). Aminopropyl, cyanopropyl or phenyl silica can also be used for reversed-phase separations. Other apolar stationary phases are based on synthetic polymers such as the styrene-divinyl-benzene co-polymer. The selection of mobile-phase constituents in reversed-phase mode is not an easy task, and the conditions described in literature are not always optimized. Methanol and/or acetonitrile are usually used as organic modifiers (Picó et al., 2004).

Air

Although the main determination technique for pesticides in ambient air is GC with different detectors (see Table 12), some studies have analyzed non amenable-GC pesticides (polar compounds or compounds with low thermal stability such as urea herbicides, carbamates, triazines or phenoxy acids) using HPLC.

Sanusi et al. (1999, 2000) fractionated the extracted pesticides from XAD-2 resin and filters, and analyzed two out of three fractions by HPLC-UV, including phosalone, mecoprop, atrazine, diuron, isoproturon, carbofuran and carbaryl. They used a reverse phase column C18 (4µm, 3.9 mm i.d. x 30 cm), with a binary solvent (methanol-acetonitrile, 80:20) as mobile phase.

Baraud et al. (2003) developed a multiresidue method for the determination of sixteen polar pesticides from nine different chemical families in the atmosphere, using HPLC-UV. After extraction with Soxhlet using n-hexane:diethylether (90:10, v/v) for 24 hours, and subsequent evaporation, the deposit was dissolved in 2 mL of mobile phase (acetonitrile:water:acetic acid, 30:59:2, v/v). The limits of detection ranged from 0.7 to 13.8 ng m^{-3}.

Some authors have described the benefits that LC coupled to tandem mass spectrometry (MS/MS) presents: wider scope, increased sensitivity and better selectivity (Alder et al., 2006) for pesticide analysis. For this reason, in other fields such as food safety, the development of multiresidue pesticide methods by LC-MS/MS has become essential in order to achieve higher sensitivity and specificity, as well as confirmatory procedures (Alder et al., 2006) (Matuszewski et al., 2003). However, few methods have been developed and validated for multiresidue analysis of pesticides in ambient air samples.

Rania and Sun (2008) have developed a LC-MS/MS method for the determination of 24 organophosphorus pesticides and their degradation products in air samples using electrospray ionization in positive mode (ESI+). They reported that APCI ionization mode gave poorer sensitivity for these molecules than ESI+. For most compounds, two characteristic transitions with the best sensitivity for each compound were selected, choosing the most intense for quantitative analysis (SRM1) and the second transition (SRM2), along with the ratio SRM1/SRM2 for confirmation of the compound. The method detection limits ranged typically from 0.2 to 10 pg m^3 for typical air volumes of 2700 m^3.

II.f Occurrence of pesticides in air

In recent years, several monitoring studies have reported pesticide concentrations in remote, rural and urban zones of different countries. Table 13 identifies more than a hundred pesticides that have been determined in ambient air from studies conducted in recent years (2000- 2010) using active sampling, mainly high volume samplers. Also, their regulatory status in the European Union (EU) (European Union, 2008) is reported.

In general, the reported values (Table 13) are the sum of pesticides present in gas and particulate phases, although some studies report separately the distribution between gas and particles. Concentrations of pesticides in ambient air ranged from a few pg per cubic meter to many ng per cubic meter.

Taking into account the compounds listed in Table 13, more than 40% of the substances detected in ambient air are herbicides, mostly chloroacetamides, thiocarbamates, triazines and aryloxyalkanoic acids. Approximately half of these herbicides detected are nowadays forbidden according to the EU regulations.

Insecticides make up 33% of the substances detected in ambient air, mainly organochlorines, organophosphorus, carbamates and pyrethroids, all of which are now forbidden according to EU regulations. The use of delthametrin and fenpropathrin (pyrethroids), however, is still permitted.

Table 13 also shows fungicides detected (26%) from the total compounds. 33 fungicides were detected out of the 126 pesticides studied. Fungicides belong to different chemical classes, such as morpholines (fenpropidin, fenpropimorph, spiroxamide), benzimidazole (carbendazim, thiabendazole) or ftalamides (captan, folpet). Some of these fungicides are currently forbidden throughout the EU, such as vinclozolin, HCH, fenarimol, triadimefon and trycyclazole.

Some authors have shown that atmospheric concentrations of CUPs are correlated to the proximity of sampling to source areas and that the occurrence is usually linked with local use (Majewski et al., 1998). However, Peck and Hornbuckle (2005) showed that the amount of pesticide used in an area of USA is only slightly correlated to the detection frequency and not correlated to average concentrations. This means that the presence of a pesticide in air is dependent not only on its use, but on other factors, such as V/P distribution, wet and dry deposition, transport and atmospheric degradation, are also important. Nevertheless, the overall concentration at the regional scale is expected to be higher during the period when a given pesticide is applied over large areas (Tuduri et al., 2006).

Locally high concentrations of pesticides in air are very seasonal and are correlated to local use patterns. The highest concentrations in air usually occur in the spring and summer months, coinciding with application times and warmer temperatures. However, for some CUPs that are detected, it is not always clear if their concentration and frequency in air is associated with local use and/or long range transport (LRT) from other sources (Tuduri et al., 2006).

Pesticides have also been detected at low levels during periods after use, but determination of their sources has proven difficult. These off-season occurrences could be due to volatilization and wind erosion or the result of long-range transport from other areas. White et al. (2006) found that the herbicide metribuzin was detected in an overnight sample more than 2 months after its application on the farm's fields. They attribute this fact to the relative persistence of metribuzin in soil (half-life is 106 days) and, therefore, the possibility of post-application volatilization of metribuzin from soil even 2 months after application.

Table 13: Concentrations of pesticides in ambient air

Compound	Chemical Class	Regulatory EU	VP^1	W solu.^{1}	Concentration (ng m^{-3})		Site/Country	Phase	Reference
			(Pa)	(mg L^{-1})	Average	Range			
2,4-D	Aryloxyalkanoic acid (H)	In	1.90E-05	23180	0.219	0.0286-0.897	rural/Canada	G+P	(Waite et al., 2005)
						ND-37	rural/France	G+P	(Baraud et al., 2003)
					0.35		rural/Canada	G	(Yao et al., 2006)
					0.440	ND-1.306	rural/Canada	G+P	(Aulagnier et al., 2008)
DDTs		Out							(Scheyer et al., 2005)
2,4'-DDE		Out			0.56	ND-5.01	Greenland	G+P	(Bossi et al., 2008)
2,4'-DDT		Out			0.191	0.007-0.673	Urban/Hong Kong	G	(Li et al., 2007)
					0.912	0.086-2.010	Urban/Guangzhou	G	(Li et al., 2007)
4,4'-DDD		Out			0.43		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
4,4'-DDE		Out			0.021	ND-0.032	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.026	0.006-0.057	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.07		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
					0.41	ND-0.94	Greenland	G+P	(Bossi et al., 2008)
					0.054	0.008-0.151	Urban/Hong Kong	G	(Li et al., 2007)
					0.222	0.034-0.579	Urban/Guangzhou	G	(Li et al., 2007)
4,4'-DDT		Out			0.358	0.006-2.63	Urban/Hong Kong	G	(Li et al., 2007)
					0.718	0.022-2.84	Urban/Guangzhou	G	(Li et al., 2007)
Acetochlor	Chloroacetamide (H)	Out	4.00E-01	223	4.6	ND-53.5	rural/Iowa	G	(Peck and Hornbuckle, 2005)
Aclonifen	Diphenyl ether (H)	In	1.60E-05	1.4		ND-4.2	Rural /France	G+P	(Lig´Air, 2006)
					1.78	0.64-4.50	Urban/France	G+P	(Schummer et al., 2010)
Alachlor	Chloroacetamide (H)	Out	2.00E-03	170.3	1.1	ND-8.5	Iowa	G	(Peck and Hornbuckle, 2005)
						ND-0.0049	Rural/Canada	G+P	(Waite et al., 2005)
					0.01		Canada	G	(Yao et al., 2006)
						ND-2.8	Urban/France	G+P	(Lig´Air, 2006)
					1.20	0.26-2.39	Urban/France	G+P	(Schummer et al., 2010)
					0.468	0.125-0.9	rural/Canada	G+P	(Hayward et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP[1] (Pa)	W solu.[1] (mg L^{-1})	Concentration (ng m^{-3}) Average	Range	Site/Country	Phase	Reference
Aldrin	Organochlorine (I)	Non, banned	8.60E-03	0.027	0.0048	ND-0.0087	rural/China	G	(Sofouglu et al., 2001)
					0.006	0.003-0.011	rural/Turkey	G+P	(Gioia et al., 2005)
						0.01-0.466	urban/France	G+P	(Scheyer et al., 2005)
					0.077		USA	G	(Yang et al., 2008)
					0.07		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Ametryn	Triazine (H)	Out	3.65E-04	200	0.69		rural/USA	G	(Peck and Hornbuckle, 2005)
Atraton	Methoxytriazine (H)				0.69	ND-2	rural/USA	G	(Peck and Hornbuckle, 2005)
Atrazine	Triazine (H)	Out			1.2	ND-8.5	rural/USA	G	(Peck and Hornbuckle, 2005)
					0.294	ND-1.4	remote /France	G+P	(Sanusi et al., 2000)
					2.125	0.640-5.97	rural/France	G+P	(Lig´Air, 2006)
					0.0043	ND-0.0199	Canada	G+P	(Yao et al., 2006)
					0.02		Canada	G	(Waite et al., 2005)
					0.3	ND-0.688	urban/France	G+P	(Scheyer et al., 2007)
					1.2	ND-8.5	rural/USA	G	(Peck and Hornbuckle, 2005)
					1.121	0.645-1.905	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.407	ND-0.407	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.587	0.352-0.823	rural/Canada	G+P	(Hayward et al., 2010)
Azinfos-methyl	Organophosphorous (I)	Out	5.00E-07	28	14.5	ND-16.5	rural/Canada	G+P	(White et al., 2006)
						ND-0.095	rural/Canada	G+P	(Bailey and Welzer, 2007)
Azinfos-methyl oxon	Metabolite					ND-0.0061	rural/Canada	G+P	(Bailey and Welzer, 2007)
Bifenthrin	Pyrethroid (I)	Out	2.40E-02	< 0.001	0.15	0.06-0.31	Urban/France	G+P	(Schummer et al., 2010)
Boscalid	Carboxamide (F)	In	7.20E-04	4.6	0.53	0.35-0.81	Urban/France	G+P	(Schummer et al., 2010)
Bromoxynil	Hydroxybenzonitrile(H)	In	6.30E-05	130	0.185	0.0086-0.791	Canada	G+P	(Yao et al., 2006)
					0.070	ND-0.211	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.098	ND-0.158	rural/Canada	G+P	(Aulagnier et al., 2008)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP[1] (Pa)	W solu.[1] (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Butachlor	Chloroacetamide(H)	Out	2.40E-04	20	0.09	ND-0.15	rural/USA	G	(Peck and Hornbuckle, 2005)
Butylate	Thiocarbamate (H)	Out	1.73E+00	36	5.3	ND-5.3	rural/USA	G	(Peck and Hornbuckle, 2005)
Captan	Phthalimide (F)	In	1.00E-05	3.3		ND-22.8	rural/France	G+P	(Lig´Air, 2006)
						0.032-4.86	rural/Canada	G+P	(Bailey and Welzer, 2007)
					2.057	0.713-4.9	rural/Canada	G+P	(Aulagnier et al., 2008)
					2.899	0.111-5.074	rural/Canada	G+P	(Aulagnier et al., 2008)
					10.07	4.12-25.19	Urban/France	G+P	(Schummer et al., 2010)
Carbaryl	Carbamate (I)	Out	4.10E-05	120		ND-0.18	remote /France	G+P	(Sanusi et al., 2000)
					0.348	0.140-0.696	rural/France	G+P	(Sanusi et al., 2000)
					0.557	ND-1.289	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.051	ND-0.051	rural/Canada	G+P	(Aulagnier et al., 2008)
Carbofuran	Carbamate, N-methyl (I)	Out	3.10E-05	351	0.626	ND-3.10	remote /France	G+P	(Sanusi et al., 2000)
					2.85	ND-8.1	rural/France	G+P	(Sanusi et al., 2000)
					0.038	ND-0.038	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.787	ND-0.787	rural/Canada	G+P	(Aulagnier et al., 2008)
Carboxin	Oxathiin (F)	Out	2.50E-05	199	0.24		rural /USA	G	(Peck and Hornbuckle, 2005)
Chlordane, trans-, gama	Organochlorine (I)	Out	1.30E-03	insoluble	0.158	0.013-0.894	rural /Turkey	G+P	(Sofouglu et al., 2001)
					0.007	ND-0.011	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.01	0.003-0.018	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.40	0.27-0.72	Greenland	G+P	(Bossi et al., 2008)
					0.389	0.006-1.6	Urban/Hong Kong	G	(Li et al., 2007)
					0.922	0.192-1.79	Urban/Guangzhou	G	(Li et al., 2007)
					0.006	0.0009-0.020	rural/Canada	G+P	(Hayward et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP[1] (Pa)	W solu.[1] (mg L^{-1})	Concentration (ng m^{-3}) Average	Range	Site/Country	Phase	Reference
Chloridazone	Pyridazinone (H)	In	1.00E-06	422	2.54	0.41-11.23	Urban/France	G+P	(Schummer et al., 2010)
Chloroneb	Aromatic (F)		4.00E-01	8	0.4	ND-2.4	rural/USA	G	(Peck and Hornbuckle, 2005)
Chlorothalonil	Chloronitrile (F)	In	7.60E-05	0.81		ND-107.7	rural/France	G+P	(Lig´Air, 2006)
						ND-458	rural/Canada	G+P	(White et al., 2006)
					0.015	ND-0.015	rural/Canada	G+P	(Aulagnier et al., 2008)
					1.227	0.930-1.724	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.15	0.06-0.55	Urban/France	G+P	(Schummer et al., 2010)
					0.48		Urban/Canada	G	(Gouin et al., 2008)
					1.740		rural/Canada	G	(Gouin et al., 2008)
					0.918	0.008-2.845	rural/Canada	G+P	(Hayward et al., 2010)
Chlorpyrifos	Organophosphorous (I)	In	2.70E-03	1.4	0.391	0.038-1.068	rural /Turkey	G+P	(Sofouglu et al., 2001)
					1	ND-2.9	rural/USA	G	(Peck and Hornbuckle, 2005)
						ND-97.8	rural/France	G+P	(Lig´Air, 2006)
					0.134	ND-0.233	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.641	ND-0.868	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.330		Urban/Canada	G	(Gouin et al., 2008)
					0.065		rural/Canada	G	(Gouin et al., 2008)
					0.041	0.006-0.121	rural/Canada	G+P	(Hayward et al., 2010)
Chlorpyrifos oxon	Metabolite					0.196-0.189	rural/Canada	G+P	(Rania and Sun, 2008)
Chlorthal	Benzenedicarboxylic acid (H)	Out			0.0089	ND-0.033	rural/USA	G	(Peck and Hornbuckle, 2005)
					0.007	ND-0.007	rural/Canada	G+P	(Aulagnier et al., 2008)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
cis-Chlordane	Organochlorine (I)	Non, banned	1.30E-03	0.1		0.015-0.062	urban/France	G+P	(Scheyer et al., 2005)
					0.042	0.005-0.214	rural/Mexico	G+P	(Alegria et al., 2006)
					0.079	ND-0.25	rural/China	G	(Xu et al., 2005)
					0.0035	ND-0.019	rural/China	P	(Yang et al., 2008)
						ND-0.0041	urban/China	P	(Yang et al., 2008)
					0.869	ND-2.444	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.46	0.11-0.87	Greenland	G+P	(Bossi et al., 2008)
					0.380	0.007-1.5	Urban/Hong Kong	G	(Li et al., 2007)
					1.43	0.191-4.18	Urban/Guangzhou	G	(Li et al., 2007)
					0.008	0.00098-0.056	rural/Canada	G+P	(Hayward et al., 2010)
cis-Nonachlor					0.002	ND-0.004	rural/Mexico	G+P	(Alegria et al., 2006)
trans-Nonachlor					0.0059	0.00083-0.031	rural/Canada	G+P	(Hayward et al., 2010)
Clomazone	(H)		1.92E-02	1100	0.33	0.14-0.68	Urban/France	G+P	(Schummer et al., 2010)
Clopyralid	Pyridinecarboxylic acid (H)	In	1.60E-03	emulsifiable	0.235	ND-0.235	rural/Canada	G+P	(Aulagnier et al., 2008)
Cycloate	Thiocarbamate (H)	Out	2.13E-03	75	0.22	ND-0.74	rural /USA	G	(Peck and Hornbuckle , 2005)
Cyfluthrin beta	Pyrethroid (I)	In	9.60E-04	0.0025	0.18	0.07-0.29	Urban/France	G+P	(Schummer et al., 2010)
Cypermethrin alfa	Pyrethroid (I)	In	2.00E-04	0.004	0.45	0.11-1.02	Urban/France	G+P	(Schummer et al., 2010)
Cyproconazole	Triazole (F)	In/Out	4.00E-05		11.08	1.47-20.50	Urban/France	G+P	(Schummer et al., 2010)
Cyprodinil	Anilinopyrimidine (F)	In	5.10E-04	13		ND-3.3	rural/France	G+P	(Lig´Air, 2006)
Dacthal	Benzoic acid (H)		2.10E-04	disperses	0.1		Urban/Canada	G	(Gouin et al., 2008)
				0.02			rural/Canada	G	(Gouin et al., 2008)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
DEA	Metabolite			3200	0.51	ND-1.3	rural /USA	G	(Peck and Hornbuckle, 2005)
Deltamethrin	Pyrethroid (I)	In	1.24E-08	0.0002		ND-1130	urban/France	G+P	(Baraud et al., 2003)
						ND-4770	rural/France	G+P	(Baraud et al., 2003)
					27.41	5.80-79.00	Urban/France	G+P	(Schummer et al., 2010)
DEP	Metabolite	Out				ND-0.102	rural/Canada	G+P	(Aulagnier et al., 2003)
Desethylatrazine	Metabolite	Out			0.132	ND-0.132	rural/Canada	G+P	(Aulagnier et al., 2008)
Desmedipham	Carbamate (H)	In	4.10E-02	7	0.15	0.03-0.39	Urban/France	G+P	(Schummer et al., 2010)
DIA	Metabolite				1.2		rural/USA	G	(Peck and, Hornbuckle, 2005)
Diazinon	Organophosphorous (I)	Out	1.20E-02	60	6.7	ND-59.1	rural/USA	G	(Peck and Hornbuckle, 2005)
						ND-1.5	urban/France	G+P	(Baraud et al., 2003)
						1.4-612.4	rural/Canada	G+P	(Aulagnier et al., 2008)
					1.128	ND-1.171	rural/Canada	G+P	(Aulagnier et al., 2008)
Diazinon oxon	Metabolite					ND-0.696	rural/Canada	G+P	(Aulagnier et al., 2008)
Dicamba	Auxine(H)	In	1.67E-03	6100	0.184	0.019-0.615	rural/Canada	G+P	(Yao et al., 2006)
					0.12		Canada	G	(Yao et al., 2006)
					0.171	ND-0.477	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.009	ND-0.009	rural/Canada	G+P	(Aulagnier et al., 2008)
Dichlobenil	Benzonitrile (H)	Out	8.80E-02	14.6		ND-0.74	urban/France	G+P	(Lig´Air, 2006)
					0.182	ND-0.328	rural/Canada	G+P	(Aulagnier et al., 2008)
Dichlorvos	Organophosphorous(I)	Out	2.10E+00	18000	0.84	ND-2.3	rural/USA	G	(Peck and Hornbuckle, 2005)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP[1] (Pa)	W solu.[1] (mg L^{-1})	Concentration (ng m^{-3}) Average	Range	Site/Country	Phase	Reference
Dieldrin	Organochlorine	Non, banned			0.035	0.003-0.114	rural /Turkey	G+P	(Sofouglu et al., 2001)
						0.008-0.136	urban/France	G+P	(Scheyer et al., 2005)
					0.015		rural/USA	G+P	(Gioia et al., 2005)
					0.015	0.002-0.037	rural/Mexico	G+P	(Alegria et al., 2006)
					0.159		urban/USA	G+P	(Burhler et al., 2001)
					0.014	ND-0.014	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.06		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
					1.94	ND-4.30	Greenland	G+P	(Bossi et al., 2008)
Difenoconazole	Triazole (F)	In	3.33E-02	15	0.35	0.15-0.80	Urban/France	G+P	(Schummer et al., 2010)
Diflufenican	Pyridinecarboxamide (H)	In				ND-0.1	urban/France	G+P	(Lig´Air, 2006)
			4.25E-06	0.05	0.164	ND-0.462	urban/France	G+P	(Scheyer et al., 2007)
					0.32	0.12-1.22	Urban/France	G+P	(Schummer et al., 2010)
Dimethachlor	Chloroacetamide (H)	In	0.64E-03	2300	110.42	7.09-271.39	Urban/France	G+P	(Schummer et al., 2010)
Dimethenamid	Amide (H)	Out	2.50E-03		1.024	ND-2.588	rural/Canada	G+P	(Aulagnier et al., 2008)
Dimethoate	Organophosphorous (I)	In	2.50E-04	23800		0.0013-0.019	rural/Canada	G+P	(Baraud et al., 2003)
Dimethomorphe	Cinnamic acid (F)	In	1.00E-06	18		ND-0.1	urban/France	G+P	(Lig´Air, 2006)
Dinocap	Dinitrophenyl (F)	Out			13.46	3.27-38.08	Urban/France	G+P	(Schummer et al., 2010)
Disulfoton	Organophosphorous (I)	Out	7.20E-03	25	1.4		rural/USA	G	(Peck and Hornbuckle, 2005)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Diuron	Urea (H)	In	1.10E-06	36.4	0.524	ND-1.6	remote /France	G+P	(Sanusi et al., 2000)
					3.214	ND-12.8	rural/France	G+P	(Scheyer et al., 2007)
					0.455	0.048-1.534	urban/France	G+P	(Scheyer et al., 2007)
Endosulfan I	Organochlorine (I)	Out		0.32	0.168		urban/USA	G+P	(Peck and Hornbuckle, 2005)
					0.367	0.073-1.373	rural/Mexico	G+P	(Alegria et al., 2006)
		Out		0.33	0.02	0.003-0.03	rural /Turkey	G+P	(Sofouglu et al., 2001)
					0.002		rural/USA	G+P	(Peck and Hornbuckle, 2005)
					0.38		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
					0.092	0.001-0.321	rural/Canada	G+P	(Hayward et al., 2010)
Endosulfan sulfate	Metabolite				0.369	0.046-1.271	rural /Turkey	G+P	(Sofouglu et al., 2001)
					0.001		rural/USA	G+P	(Gioia et al., 2005)
					0.005		Urban/Canada	G	(Gouin et al., 2008)
					0.008		rural/Canada	G	(Gouin et al., 2008)
					0.51		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Endosulfan, alpha-	Organochlorine (I)	Out		0.32		ND-81.3	rural/France	G+P	(White et al., 2006) (Lig´Air, 2006)
						0.007-0.1	urban/France		(Scheyer et al., 2005)
					6.3	ND-14.8	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.628	ND-1.177	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.630	ND-0.892	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.550		Urban/Canada	G	(Gouin et al., 2008)
					0.82		rural/Canada	G	(Gouin et al., 2008)
					4.83	ND-10.25	Greenland	G+P	(Bossi et al., 2008)
					0.124	ND-0.840	Urban/Hong Kong	G	(Li et al., 2007)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP (Pa)^1	W solu. (mg L^{-1})^1	Average(ng m^{-3})	Range(ng m^{-3})	Site/Country	Phase	Reference
Endosulfan, beta-	Organochlorine (I)	Out		0.33	2.2	ND-7.2	rural/Canada	G+P	(White et al., 2006)
						0.007-0.137	urban/France	G+P	(Scheyer et al., 2005)
					0.120		Urban/Canada	G	(Gouin et al., 2008)
					0.125		rural/Canada	G	(Gouin et al., 2008)
Endrin	Organochlorine (I)	Non, banned	2.00E-08	insoluble	0.016	0.005-0.025	rural /Turkey	G+P	(Sofouglu et al., 2001)
						0.008-0.891	urban/France	G+P	(Scheyer et al., 2005)
						0.03	Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Endrin, Keto-	Organochlorine (I)				0.041	0.006-0.082	rural /Turkey	G+P	(Sofouglu et al., 2001)
					0.50		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Epoxyconazole	Triazole (F)	In	< 1E-05	6.63		ND-0.4	urban/France	G+P	(Lig´Air, 2006)
EPTC	Thiocarbamate (H)	Out	1.00E+01	375	0.17	ND-0.85	rural/USA	G	(Peck and Hornbuckle, 2005)
					6.11	ND-9.545	rural/Canada	G+P	(Aulagnier et al., 2008)
					7.866	ND-7.866	rural/Canada	G+P	(Aulagnier et al., 2008)
Ethalfluralin	Dinitroaniline(H)	Out	1.17E-02	0.3	0.115	ND-0.453	rural/Canada	G+P	(Yao et al., 2006)
		Out		0.007			Canada	G	(Waite et al., 2005)
Ethofumesate	Benzofuran (H)	In	6.50E-04	50		ND-1.2	rural/France	G+P	(Lig´Air, 2006)
					0.32	0.07-1.13	Urban/France	G+P	(Schummer et al., 2010)
Ethoprop	Organophosphorous (I)	In			0.35	ND-1.2	rural/USA	G	(Peck and Hornbuckle, 2005)
Etridiazole	Aromatic hydrocarbon (F)	Out	1.43E+00	117	0.045	ND-0.23	rural/USA	G	(Peck and Hornbuckle, 2005)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP (Pa)^1	W solu.(mg L^{-1})^1	Average(ng m^{-3})	Range(ng m^{-3})	Site/Country	Phase	Reference
Fenarimol	Pyrimidine (F)	Out			0.09	0.03-0.16	Urban/France	G+P	(Schummer et al., 2010)
Fenhexamid	Hydroxyanilide (F)	In	4.00E-04	20	0.30	0.06-0.53	Urban/France	G+P	(Schummer et al., 2010)
Fenoprop	Phenoxypropionic (H)	Out	1.00E-04	140	0.026	ND-0.026	rural/Canada	G+P	(Aulagnier et al., 2008)
Fenoxycarb	Carbamate (I)	In/Out	8.67E-01	7.9	6.40	2.04-14.87	Urban/France	G+P	(Schummer et al., 2010)
Fenpropathrin	Pyrethroid (I,A)	Out	0.76E-03	0.33	1.13	0.46-2.67	Urban/France	G+P	(Schummer et al., 2010)
Fenpropidin	Morpholine (F)	In	1.70E-02	530		ND-3.5	rural/France	G+P	(Lig´Air, 2006)
						ND-2.8	urban/France	G+P	(Lig´Air, 2006)
					0.15	0.06-0.46	Urban/France	G+P	(Schummer et al., 2010)
Fenpropimorph	Morpholine (F)	In	3.50E-03	4.3		ND-0.7	urban/France	G+P	(Lig´Air, 2006)
						ND-13.2	rural/France	G+P	(Lig´Air, 2006)
Flusilazole	Triazole (F)		3.90E-02	54	20.04	2.14-70.32	Urban/France	G+P	(Schummer et al., 2010)
Fluazifop-P-butyl	Aryloxyphenoxypropionate (H)		5.50E-05	1.1	0.04	ND-0.07	rural/Canada	G+P	(White et al., 2006)
Folpet	Phthalimide (F)	In	2.10E-05	0.8		ND-82.2	rural/France	G+P	(Lig´Air, 2006)
						ND-5.8	urban/France	G+P	(Bailey and Welzer, 2007)
						0.022-4.88	rural/Canada	G+P	(Aulagnier et al., 2008)
					5.86	0.39-11.30	Urban/France	G+P	(Schummer et al., 2010)
Fonofos	Organophosphorous (I)	Out			0.0085	ND-0.099	rural/USA	G	(Peck and Hornbuckle, 2005)
HCB	Organochlorine (F)	Non, banned	1.45E-03	insoluble	0.594	0.081-1.62	remote /France	G+P	(Sanusi et al., 2000)
					0.053	ND-0.35	rural/USA	G	(Peck and Hornbuckle, 2005)
					0.074		rural/	G	
					0.031	0.008-0.055	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.035	ND-0.055	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.047	0.0007-0.133	rural/Canada	G+P	(Hayward et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP (Pa)^1	W solu.(mg L^{-1})^1	Average(ng m^{-3})	Range(ng m^{-3})	Site/Country	Phase	Reference
HCH, alpha-	Organochlorine (I)	Out			0.048	0.0056-0.299	rural /China	G	(Sofouglu et al., 2001)
					0.17	0.070-0.423	remote /France	G+P	(Sanusi et al., 2000)
					0.218	0.075-0.415	rural/France	G+P	(Scheyer et al., 2005)
					0.111	0.004-0.462	rural /Turkey	G+P	(Yang et al., 2008)
						0.014-3.853	urban/France	G+P	(Sanusi et al., 2000)
					0.027	0.007-0.062	rural/Mexico	G+P	(Alegria et al., 2006)
					0.49		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
					20.19	10.29-66.35	Greenland	G+P	(Bossi et al., 2008)
					0.046	0.005-0.109	Urban/Hong Kong	G	(Li et al., 2007)
					0.139	0.041-0.313	Urban/Guangzhou	G	(Li et al., 2007)
					0.009	0.0007-0.026	rural/Canada	G+P	(Hayward et al., 2010)
HCH, beta-	Organochlorine(I)	Out			0.026	ND-0.086	rural/China	G	(Xua et al., 2005)
					0.32	0.063-0.631	rural /Turkey	G+P	(Sofouglu et al., 2001)
						0.0063-0.0237	urban/China	P	(Yang et al., 2008)
					0.038	0.024-0.053	rural/Turkey	G+P	(Sofouglu et al., 2001)
						0.0005-0.0049	urban/China	P	(Yang et al., 2008)
					0.53		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
HCH, gamma-	Organochlorine (I)	Out			0.117	0.001-0.666	rural/Turkey	G+P	(Sofouglu et al., 2001)
			0.0044	8.52E+00	1.034	0.751-1.567	remote /France	G+P	(Sanusi et al., 2000)
						0.048-0.946	urban/France	G+P	(Scheyer et al., 2005)
					0.47	0.029-1.643	urban/France	G+P	(Scheyer et al., 2007)
					0.38		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
					5.1	1.87-11.42	Greenland	G+P	(Bossi et al., 2008)
					0.051	0.005-0.261	Urban/Hong Kong	G	(Li et al., 2007)
					0.523	0.005-2.64	Urban/Guangzhou	G	(Li et al., 2007)
					0.008	0.0014-0.025	rural/Canada	G+P	(Hayward et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP (Pa)^1	W solu.(mg L^{-1})^1	Average(ng m^{-3})	Range(ng m^{-3})	Site/Country	Phase	Reference
Heptachlor	Organochlorine (I)	Non, banned	5.30E-02	0.056	0.304		rural/USA	G+P	(Sofouglu et al., 2001)
					0.007	0.002-0.024	rural /Turkey	G+P	(Sofouglu et al., 2001)
						0.0008-0.0101	urban/China	P	(Xua et al., 2005)
					0.057	0.006-0.156	rural/Mexico	G+P	(Alegria et al., 2006)
					0.12		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Heptachlorepoxy	Metabolite				0.072			G	(Yang et al., 2008)
					0.018	ND-0.029	rural/Mexico	G+P	(Alegria et al., 2006)
					0.79	0.33-2.74	Greenland	G+P	(Bossi et al., 2008)
IMP	Metabolite					ND-0.226	rural/Canada	G+P	(Rania and Sun, 2008)
Iprodione	Dicarboximide (F)	In	5.00E-04	13	11.12	3.89-42.31	Urban/France	G+P	(Schummer et al., 2010)
Isofenfos	Organophosphorous (I)	Out	4.40E-04	18	0.19	ND-0.54	rural/USA	G	(Peck and Hornbuckle, 2005)
Isomalation	Metabolite					ND-0.0036	rural/Canada	G	(Rania and Sun, 2008)
Isoproturon	Urea (H)	In	3.15E-06	65	0.215	ND-0.720	remote /France	G+P	(Sanusi et al., 2000)
					0.861	ND-3.3	rural /France	G+P	(Sanusi et al., 2000)
						ND-1.3	urban/France	G+P	(Baraud et al., 2003)
						ND-19	rural/France	G+P	(Baraud et al., 2003)
Kresomim-m	Strobilurin (F)	In	2.30E-03	2	1.54	0.22-3.58	Urban/France	G+P	(Schummer et al., 2010)
Lindane	Organochlorine (I)	Out	4.40E-03		2.592	ND-2.623	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.100		Urban/Canada	G	(Gouin et al., 2008)
					0.070		rural/Canada	G	(Gouin et al., 2008)
Linuron	Urea (H)	In	5.10E-05	63.8		ND-5.1	urban/France	G+P	(Baraud et al., 2003)
Malathion	Organophosphorous(I)	In	5.30E-03	145		ND- 0.2	urban/France	G+P	(Lig´Air, 2006)
						ND-1050	urban/France	G+P	(Baraud et al., 2003)
						ND-4450	rural/France	G+P	(Baraud et al., 2003)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Malathion oxon	Metabolite					0.0029-0.611			(Rania and, Sun, 2008)
MCPA	Aryloxyalkanoic acid (H)	In	2.30E-05	273.9	0.513	0.0095-4.96	rural/Canada	G+P	(Yao et al., 2006)
					0.27		Canada	G	(Waite et al., 2005)
					734	ND-5130	rural/France	G+P	(Lig´Air, 2006)
					1.613	0.099-3.890	rural /France	G+P	(Lig´Air, 2006)
					0.024	ND-0.053	rural/Canada	G+P	(Aulagnier et al., 2008)
MCPB	Aryloxyalkanoic acid (H)	In	4.00E-07	4400	0.101	ND-0.114	rural/Canada	G+P	(Aulagnier et al., 2008)
Mecoprop	Aryloxyalkanoic acid (H)	In	1.60E-03	250000	0.038	ND-0.038	rural/Canada	G+P	(Aulagnier et al., 2008)
Mepanipyrim	Anilinopyrimidine (F)	In	2.32E-02	3.10	0.31	0.18-0.44	Urban/France	G+P	(Schummer et al., 2010)
Metalaxil	Acylalanine (F)	In	7.50E-04	8400	0.63	ND-1	rural/Canada	G+P	(White et al., 2006)
									(Yao et al., 2006)
			7.50E-04	8400	0.496		rural /Canada	G+P	(Sofouglu et al., 2001)
Metamitron	Triazinone (H)	In	7.44E-01	1770	6.79	1.88-16.18	Urban/France	G+P	(Schummer et al., 2010)
Metazachlor	Chloroacetamide(H)	In	9.30E-05	430		ND- 0.8	rural/France	G+P	(Lig´Air, 2006)
						ND- 0.3	urban/France	G+P	(Lig´Air, 2006)
Methamidofos	Organophosphorous (I)	Out	2.30E-03	200000	7.3	ND-10.5	rural/Canada	G+P	(White et al., 2006)
Methidathion	Organophosphorous(I)	Out	2.50E-04	200		ND-0.3	urban/France	G+P	(Lig´Air, 2006)
Methoxychlor	Organochlorine(I)	Out		0.1	0.22	0.043-0.99	rural /Turkey	G+P	(Sofouglu et al., 2001)
					0.48		Urban/Turkey	G+P	(Ozcan and Aydin, 2009)
Metobromuron	Urea (H)	Out	4.00E-04	330	1.2	ND-3.1	rural/Canada	G+P	(White et al., 2006)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^{1} (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Metolachlor	Chloroacetamide (H)	Out	4.20E-03		488	ND-0.5	urban/France	G+P	(Lig´Air, 2006)
						ND-0.9	rural/France	G+P	(Peck and Hornbuckle, 2005)
					2.3	ND-27,5	rural/USA	G	(Peck and Hornbuckle, 2005)
					7.713	3.031-19.06	rural/Canada	G+P	(Aulagnier et al., 2008)
					1.42	0.266-3.364	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.25	0.09-0.45	Urban/France	G+P	(Schummer et al., 2010)
					0.513	0.145-0.822	rural/Canada	G+P	(Hayward et al., 2010)
Metribuzin	Triazinone (H)	In	5.80E-05	1050	0.79	ND-0.96	rural/Canada	G+P	(White et al., 2006)
					0.050		Urban/Canada	G	(Gouin et al., 2008)
					0.015		rural/Canada	G	(Gouin et al., 2008)
Metsulfuron methyl	Triazinylsulfonylurea (H)					ND-11	urban/France	G+P	(Baraud et al., 2003)
Mirex	Organochlorine (I)	Non, banned	7.00E-05	0.0001	0.079	0.0066-0.255	urban/China	G+P	(Yao et al., 2006)
Molinate	Thiocarbamate (H)	In	7.46E-01	990		ND-0.015	rural/USA	G	(Peck and Hornbuckle, 2005)
Myclobutanil	Triazole (F)	In/Out	2.13E-01	142	0.358	ND-0.358	rural/Canada	G+P	(Aulagnier et al., 2008)
					1.03	0.04-3.09	Urban/France	G+P	(Schummer et al., 2010)
Napropamide	Alkanamide (H)	In	5.30E-04	74	0.025	ND-0.025	rural/USA	G	(Peck and Hornbuckle, 2005)
Omethoate	Metabolite	Out				0.0009-0.0027	rural/Canada	G+P	(Rania and Sun, 2008)
Oxychlordane	Organochlorine				0.00022		rural/USA	G+P	(Gioia et al., 2005)
Oxyfluorfen	Diphenyl ether (H)	Out	2.67E-05	0.116		ND- 3	rural/France	G+P	(Lig´Air, 2006)
Parathion-Methyl	Organophosphorous(I)	Out	2.00E-04	55	2.2	ND-6	rural/USA	G	(Peck and Hornbuckle, 2005)
Pebulate	Thiocarbamate (H)	Out	4.70E+00	60	3.3	ND-12	rural/USA	G	(Peck and Hornbuckle, 2005)
Penconazole	Triazole (F)	In	3.70E-01	73 g/m3	5.78	1.22-19.41	Urban/France	G+P	(Schummer et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3}) Average	Range	Site/Country	Phase	Reference
Pendimethalin	Dinitroaniline (H)	In	4.00E-03	0.3		ND-117.3	rural/France	G+P	(Lig´Air, 2006)
						ND- 1.3	rural/France	G+P	(Lig´Air, 2006)
					3.18	0.32-7.83	Urban/France	G+P	(Schummer et al., 2010)
					0.050		Urban/Canada	G	(Gouin et al., 2008)
					0.14		rural/Canada	G	(Gouin et al., 2008)
					0.029	0.003-0.091	rural/Canada	G+P	(Hayward et al., 2010)
Phorate	Organophosphorous (I)	Out	8.50E-02	50	25	ND-91.2	rural/USA	G	(Peck and Hornbuckle, 2005)
Phosalone	Organophosphorous (I)	Out	< 6.00E-05	3.05	0.705	ND-3.670	remote /France	G+P	(Sanusi et al., 2000)
					0.412	ND-2.533	rural /France	G+P	(Sanusi et al., 2000)
					0.188	ND-0.281	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.236	ND-0.419	rural/Canada	G+P	(Aulagnier et al., 2008)
Phosmet	Organophosphate (I)	In	6.50E-05		0.826	ND-1.913	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.366	ND-0.646	rural/Canada	G+P	(Aulagnier et al., 2008)
Primicarb	Carbamate (I)	In	4.00E-04	3000	1.6	ND-5.1	rural/Canada	G+P	(White et al., 2006)
Prochloraz	Amide (F)	In/Out	1.50E-01	34.4	39.32	11.78-64.01	Urban/France	G+P	(Schummer et al., 2010)
Prometon	Triazine (H)		3.06E-04	750	0.57	ND-4.3	rural/USA	G	(Peck and Hornbuckle, 2005)
Propachlor	Chloroacetamide (H)	Out	1.00E-02	580	0.097	ND-0.15	rural/USA	G	(Peck and Hornbuckle, 2005)
						ND-1.7	rural/France	G+P	(Lig´Air, 2006)
						ND-1	urban/France	G+P	(Lig´Air, 2006)
Propargite	(A)	Out	6.00E-06	632		ND-45.6	rural/France	G+P	(Lig´Air, 2006)
Propazine	Triazine (H)	Out	3.90E-06	5	0.071	ND-0.12	rural/USA	G	(Peck and Hornbuckle, 2005)
Propyzamide	Benzamide (H)	In	5.80E-05	15	0.23	ND-0.33	rural/USA	G	(Peck and Hornbuckle, 2005)
Simazine	Triazine (H)	Out	2.94E-06	6.2	0.23	ND-0.4	rural/USA	G	(Peck and Hornbuckle, 2005)
					0.050	ND-0.055	rural/Canada	G+P	(Aulagnier et al., 2008)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W solu.^{1} (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Simetryn	Methylthiotriazine (H)		9.50E-05	400	0.09	ND-0.09	rural/USA	G	(Peck and Hornbuckle, 2005)
Spiroxamine	Morpholine (F)	In		200000		ND-12.1	rural/France	G+P	(Lig´Air, 2006)
TCP	Metaolite					0.026-0.131	rural/Canada	G+P	(Rania and Sun, 2008)
Tebuconazole	Triazole (F)	In	1.70E-03	36	1.49	0.23-5.03	Urban/France	G+P	(Schummer et al., 2010)
Tetrachlorvinphos	Organophosphorous (I)	Out	1.00E-03	145	0.49	ND-0.61	rural/USA	G	(Peck and Hornbuckle, 2005)
Tetraconazole					0.14	0.07-0.29	Urban/France	G+P	(Schummer et al., 2010)
Tolylfluanid	Sulphamide (F)	In	2.00E-04	0.9		ND-9.7	urban/France	G+P	(Lig´Air, 2006)
						ND-86.4	rural/France	G+P	(Lig´Air, 2006)
Toxaphene	Organochlorine (I)	Non, banned		3	0.505	0.319-0.771	rural/Mexico	G+P	(Alegria et al., 2006)
Triadimefon	Triazole (F)	Out	2.00E-05	64	1	ND-2.9	rural/USA	G+P	(Peck and Hornbuckle, 2005)
Triallate	Thiocarbamate (H)	In	1.60E-02	4	2.88	0.402-15.3	rural/Canada	G+P	(Yao et al., 2006)
					10.16		rural/Canada		(Waite et, 2005)
					0.22	ND-0.8	rural/USA	G	(Peck and Hornbuckle, 2005)
Tricyclazole	Reductase (F)	Out	2.70E-05	1600	0.17	ND-0.17	rural/USA	G	(Peck and, Hornbuckle, 2005)
Trifloxystrobin	Strobilurin (F)	In	3.40E-01	0.61	2.62	0.49-4.58	Urban/France	G+P	(Schummer et al., 2010)

Table 13: Concentrations of pesticides in ambient air (continued)

Compound	Chemical Class	Regulatory EU	VP^1 (Pa)	W $solu.^1$ (mg L^{-1})	Concentration (ng m^{-3})		Site/Country	Phase	Reference
					Average	Range			
Trifluralin	Dinitroaniline (H)	Out	6.10E-03	0.221	0.52	ND-8.2	rural/USA	G	(Yao et al., 2006)
					3.66	0.4-7.98	remote /France	G+P	(Sanusi et al., 2000)
					0.17	ND-0.811	rural/Canada	G+P	(Waite et al., 2005)
					0.15		rural/Canada		(Peck and Hornbuckle, 2005)
					0.09	ND-0.182	urban/France	G+P	(Scheyer et al., 2007)
						ND- 40.7	rural/France	G+P	(Scheyer et al., 2007)
						ND- 11.8	urban/France	G+P	(Scheyer et al., 2007)
					0.887	0.317-1.617	rural/Canada	G+P	(Aulagnier et al., 2008)
					1.09	0.507-1.935	rural/Canada	G+P	(Aulagnier et al., 2008)
					0.12	0.06-0.22	Urban/France	G+P	(Schummer et al., 2010)
					0.030		Urban/Canada	G	(Gouin et al., 2008)
					0.050		rural/Canada	G	(Gouin et al., 2008)
					0.16	ND- 1.95	Greenland	G+P	(Bossi et al., 2008)
					0.041	0.004-0.120	rural/Canada	G+P	(Hayward et al., 2010)
Vernolate	Thiocarbamate (H)	Out		90	0.16	ND-0.19	rural/USA	G	(Peck and Hornbuckle, 2005)
Vinclozolin	Dicarboximide (F)	Out	1.30E-04	2.6		ND-0.2	rural/France	G+P	(Lig´Air, 2006)
						ND-0.2	urban/France	G+P	(Lig´Air, 2006)

In = included, Out = excluded from the annex I Directive 91/414ND
[1] (BCPC, 2009)
Non detected; G: gas phase; P: particulate phase; F: fungicide; H: herbicide; I: insecticide; A: acaricide

III. OBJECTIVES

The general research aim of this thesis was to develop different analytical methods for the determination of CUPs in airborne particulate matter using LC-MS/MS and GC-MS/MS, and to provide information about the atmospheric levels of these pesticides in two European regions (France and Spain).

Within this aim, the following specific objectives were defined:

1- To review literature dating from 2000 to present focused on currently used collection and analytical methods for the determination of pesticides in ambient air. Likewise, considerations about the occurrence and fate of pesticides in ambient air were included.

2- To develop a rapid and sensitive procedure for the determination of some CUPs used extensively in the treatment of citrus fruits and other fruits (like grapes) in fine airborne particulate matter (PM 2.5) at trace levels using PLE and LC-MS/MS. Secondly, this method was to be applied to PM 2.5 collected from the monitoring network of the Regional Valencia Government (Spain).

3- To investigate the feasibility of using microwave energy for the efficient extraction of CUPs from fine airborne particulate matter (PM 2.5) and consequently to develop a rapid, sensitive, selective and reproducible method for the multi-residue determination of LC-amenable CUPs in PM 2.5 using MAE and LC-MS/MS, the ultimate goal being to apply this method to ambient air monitoring programs.

4- To develop an analytical methodology for sensitive and confirmatory determination of GC-amenable CUPs in airborne particulate matter using MAE and GC(EI)-MS/MS with a triple quadrupole analyzer for subsequent application to samples collected from the air monitoring network of the Regional Valencia Government (Spain).

5- To improve knowledge of the atmospheric behaviour of some CUPs and legacy insecticides in the Centre region of France, to monitor these pesticides in rural and urban sites in this area from 2006-2008 and finally, to analyze the overall occurrence and the spatial and temporal variations of the pesticides detected.

IV. CHAPTER 1:

ANALYSIS OF CURRENTLY USED PESTICIDES IN FINE AIRBORNE PARTICULATE MATTER (PM 2.5) BY PRESSURIZED LIQUID EXTRACTION AND LIQUID CHROMATOGRAPHY–TANDEM MASS SPECTROMETRY

IV.a INTRODUCTION

Pesticide extraction from airborne particulate matter is usually performed using Soxhlet with different solvents such as light petroleum (Gioia et al., 2005) (Alegria et al., 2006) (Motelay-Massei et al., 2005), acetone (Waite et al., 2005) (Cessna et al., 2000) (Waite et al., 2002) or *n*-hexane:methylene chloride (Scheyer et al., 2005) (Sanusi et al., 2000). These routine methods are time (up to 6–24 h) and solvent consuming (up to 250–300mL). It is widely recognized that pressurized liquid extraction (PLE) gives recoveries comparable to those obtained with Soxhlet for organic pollutants. This technique increases the speed of the extraction process with low solvent consumption (Fitzpatrick et al., 2000) (Yusà et al., 2006). Despite this, it has scarcely been used for the extraction of pesticides from particulate filters until now. In this study, PLE was selected and validated as an extraction method.

The conventional determination of pesticides in air, both in gas and particulate phase, is usually carried out by gas chromatography (GC) in combination with electron-capture detection (ECD) (Lammel et al., 2007) (Scheyer et al., 2005) (Shen et al., 2005) or mass spectrometric detection (MS) (Yao et al., 2006) (Motelay-Massei et al., 2005) (Harrad and Mao, 2004). In other areas, such as food and water control, there is a clear trend showing increased use of LC-MS for pesticide-residue analysis (Hernández et al., 2005) (Soler and Picó, 2007) (Alder et al., 2006). This owes to the evolution of LC–MS instruments (dramatic improvement in performance quality, wider scope of application) and to the fact that the greater polarity of CUPs makes LC-MS a good option for their determination. Nine pesticides were selected in this study for evaluation of their concentrations in airborne particulate matter. Their physico-chemical properties and agricultural usage are described in Tables 14 and 15. Although the number of papers on the analysis of polar pesticides in ambient air by LC–MS are scarce, the analytical methodology used in this study was LC-MS/MS triple quadrupole.

The selection of PM 2.5, rather than total suspended particulate (TSP) matter, as indicator of air pollution is based on health considerations and is intended to focus regulatory concern on those particles small enough to enter the thoracic region (Wilson et al., 2002).

The selection of the CUPs (see Table 14) was based on their polarity (suitable for being determined by LC-MS/MS) and their intensive use in the application area, rather than their volatility. Pesticides selected presented medium volatility (vapour pressure between 10^{-1} and 10^{-6} mPa). Pesticides with vapour pressure lower than 10^{-5} mPa such as IMCP and BTN are more likely to be found in the particulate phase. Pesticides with vapour pressure higher than 10^{-2} mPa such as CBZ, IMZ and MTD are more likely to be found in the gaseous phase. The rest of the pesticides could be distributed between both phases.

The aim of this study was to develop a rapid and sensitive procedure for the determination of nine currently and extensively used pesticides in the treatment of citrus fruit, other fruit and grapes, in fine airborne particulate matter (PM 2.5) at trace levels. The procedure includes the extraction of PM 2.5-bound pesticides by PLE followed by direct injection into a liquid chromatograph with a tandem MS detection. The method was applied to samples of PM 2.5 filters collected from the monitoring network of the Regional Valencia Government (Spain).

Table 14: Physico-chemical properties of the studied pesticides

Analyte	Type	Vapour pressure (mPa)[1]	Henry's law constant (Pa m^3 mol^{-1})[1]	log k_{ow}[1]	Period of application	Way of application
Carbendazim (CBZ)	fungicide	1.50E-01	3.60E-03	1.38	Spring-Autumn	Spraying
Imidacloprid (IMCP)	insecticide	9.00E-07	2.00E-10	0.57	March-Oct.	Spraying
Thiabendazole (TBZ)	fungicide	4.60E-04	2.70E-08	2.39	all year	Indoor
Imazalil (IMZ)	fungicide	1.58E-01	2.61E-04	3.82	all year	Indoor
Methidathion (MTD)	insecticide	2.50E-01	3.30E-04	2.2	May-Sept.	Spraying
Methiocarb (MTC)	helicide	3.60E-02	1.20E-04	3.08	Spring	Granulate bait, spraying
Bitertanol (BTN)	fungicide	2.20E-07	2.00E-08	4.1	Nov.-January; March-May	Spraying
Pyriproxyfen (PYPF)	insecticide	<1.30E-02		5.37	February-Sept.	Spraying
Hexythiazox (HXTZ)	acaricide	3.40E-03	2.40E-03	2.53	Spring-Summer	Spraying

[1](BCPC, 2009)

Table 15: Agricultural usage of the studied pesticides, mainly applied in citrus fruit, grapes and other fruit treatments

Pesticide	Type	Chemical class	Crop	Pest
Carbendazim	fungicide	benzimidazole	fruits citrics grapes	Monilia Aphidae F.eriobotriae B.cinerea Postharvesting in citrics
Imidacloprid	insecticide	nitroguanidine	citrics fruits vegetables watermelon	P. citrella M. persicae Aphidae Carterpiller White fly B. tabaci T.vaporariorum
Thiabendazole	fungicide	benzimidazole	citrics stone fruits grapes	Postharvesting in citrics
Imazalil	fungicide	imidazole	citrics	Postharvesting in citrics
Methidathion	insecticide	organophosphate (dithiophosphate)	citrics	Coccidae
Methiocarb	helicide	carbamate	citrics grapes vegetables	Snails Trips
Bitertanol	fungicide	triazole	fruits	S. pannosa P. tridactila P. leucotricha V. pirina F. eriobotriae
Pyriproxyfen	insecticide	pyridine	vegetables citrics fruits	A. aurantii A. nerii P. pergandii S. oleae B. tabaci T.vaporariorum
Hexythiazox	acaricide	carboxamide	citrics fruits grapes	P. citri T. urticae P. ulmi Acars

IV.b MATERIALS AND METHODS

IV.b.1 *Reagents*

High purity standard pesticides, bitertanol (98%), carbendazim (99%), hexythiazox (99.3%), imazalil (97.5%), imidacloprid (98%), methidathion (98.5%), methiocarb (98.5%), pyriproxyfen (98%), thiabendazole (98.5%) and the internal standard isoproturon D6 (98.5%) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). For these pesticides, some physical constants and their agricultural usage is shown in Tables 14 and 15.

Individual stock standards were prepared by weighing 10 mg of pure standard using a 5 decimal analytical balance and dissolving each compound in 50 mL of acetone. They were stored in capped amber vials at −21ºC (SANCO/2007/3131). Mix working solutions at 10 and 1 mg L^{-1} were prepared with methanol. An internal standard solution was prepared by appropriate dilution of the stock solution with isoproturon D6 in methanol.

Calibration solutions (0.01, 0.05, 0.1, 0.5, 1, 5 µg mL^{-1}) were prepared by adding variable volumes of the mix working solutions to the PM 2.5 filters, as well as 0.5 µg mL^{-1} of [2H6] isoproturon (ISP-*d*6).

HPLC grade methanol and acetonitrile were supplied by Scharlau (Barcelona, Spain). HPLC grade acetone and water were purchased from Merck (Darmstadt, Germany). Acetic acid was provided by Panreac (Barcelona, Spain).

Statistical data manipulation and numerical analysis of data resulting from experimental design were carried out by means of the statistical package MINITAB forWindows, Release 14 (Minitab, Birmingham UK).

IV.b.2 *Equipment and sample analysis*

The extraction of pesticides from PM 2.5 filters was carried out using an ASE 200 PLE system (Dionex, Sunnyvale, CA, USA). Samples were introduced into 22 mL stainless-steel cells containing a cellulose filter in the cell outlet. The cell was refilled with Hyflo Super Cell diatomaceous earth from Sigma–Aldrich (Steinheim, Germany). The optimized extraction conditions were as follows: extraction solvent, acetone; oven temperature, 50ºC; pressure, 1750 psi; heat up time, 2 min; static cycles, 2; static time, 1 min. The flush volume amounted to 100% of the extraction cell volume. The extracted analytes were purged from the sample cell using pressurized nitrogen (125–150 psi) for 1 min.

The LC–MS/MS system consists of a Finnigan Surveyor Autosampler, a Finnigan Surveyor LC quaternary pump and a Finnigan TSQ Quantum Ultra detector (San José , CA, USA). All pesticides were detected using electrospray ionization (ESI) in positive mode. The main ion source parameters were optimized by design of experiments (DoE). The optimized operating conditions were: spray voltage, 4500V; sheath gas pressure, 20 psi; capillary temperature, 350 ºC and auxiliary gas pressure, 5 arbitrary units (a.u.).

The extraction of pesticides from PM 2.5 filters was carried out using the ASE 200 PLE system. Afterwards, the extracts were concentrated under a gentle stream of N_2 at 40ºC using a Sample Concentrator (Techne, Cambridge, UK), re-dissolved in 0.5 mL of methanol and filtered through a 0.22 µmGHP Acrodisc filter from Pall Life Science (Ann Arbor, MI, USA) prior to LC–MS/MS analysis.

IV.b.3 Sampling and site characterization

PM 2.5 samples were collected using a large-volume sampler from Digitel (Madrid, Spain) and quartz fiber filters 150 mm in diameter from Schleicher & Schuell Microscience (Dassel, Germany). A sampling flow of 30 m^3h^{-1} was used, providing a total volume of filtered air around 760 m^3.

Three rural sampling stations (Alzira, Sant Jordi, Burriana) and one urban sampling station (Burjassot), part of the airborne particulate matter monitoring network of the Regional Valencia Government (Generalitat), were selected. Samples were collected from August to October 2007, and during this period the temperatures ranged from 12 to 35ºC.

The first station used in this study is located in a rural area in the centre of the Valencia region, approximately 1km from the city of Alzira (ALZ) (0º27´28´´W, 39º09´00´´N). Alzira has 42,543 inhabitants and is situated 43km from the city of Valencia. It has in its vicinity many citrus groves, such as orange trees. Samples were collected about 60m above ground level.

The second station is in Burriana (BUN), in the north of the Valencia region (0º05´23´´W, 39º53´41´´N). Burriana is a town (31,281 inhabitants) situated 63km north of Valencia, surrounded by irrigated land. Samples were collected 20m above ground level and in the vicinity of citrus groves.

The third station is located in the town of Sant Jordi (STJ). It is a rural area in the north of the Valencia region (0º22´22´´E, 40º33´17´´N) that has 744 inhabitants and is situated 110 km northeast of Valencia. This town is surrounded by different groves such as almond trees, olive trees, carob trees and vineyards. Samples were collected 181m above ground level. This station is located inside a golf course and very close to orange trees.

The fourth station is located in an urban area in Burjassot (BUR) (0º25´04´´W, 39º30´34´´N) (37,394 inhabitants). This town is 7 km northeast of the centre of Valencia city, without any agricultural activity. It was installed at the back of the Valencia University campus and inside a park with gardens. Samples were collected 25m above ground level.

To perform the PM 2.5 determination, a micro-balance Mettler- Toledo MX5 from Mettler-Toledo (Bedford, MA, USA) was used. Filters were previously conditioned according to EN 12341:1998 standard, at temperature (20±1ºC) and at relative humidity (50±5%) for at least 48 h, and then weighed.

A field filter was placed in the oven for 24 hours at 130ºC to volatilize any compounds it may contain in order to obtain a blank filter. A blank filter was used in each sequence of analysis for checking the pollutants' backgrounds. Moreover, some blank filters were spiked in each sequence analysis in order to evaluate the recoveries of each pesticide. These filters were also used for preparing the standards using matrix matched standard calibration.

IV.b.4 Optimization of PLE conditions

The use of solvents at elevated temperatures increases the capacity of solvents to solubilize analytes and increases the diffusion rate. In addition, increased temperatures also decrease the viscosity of liquid solvents (better penetration of matrix particles) and can disrupt the strong solute–matrix interactions caused by Van der Waals forces, hydrogen bonding and dipole attractions of the solute molecules and active sites of the matrix (Ritcher et al., 1996) (Dean, 1998).

Ethyl acetate, acetone, methanol and acetonitrile were investigated as extraction solvents under PLE standard operating conditions. The experiments were carried out on spiked filters (0.025 µg/filter). Spiked filters were obtained adding variable volumes of the mix working solutions to the blank filters.

The main parameters influencing the performance of PLE are temperature (*T*), pressure (*P*) and extraction time (Fitzpatrick et al., 2000). The optimization of these three parameters can be made using an approach of changing-one-factor-at-a-time (COST). However this method is very tedious and does not give information on interactions between factors, so it can miss the optimal settings when interactions exist (Massart et al., 1997).

A CCD design was chosen to study the relative influence of these three parameters on the recovery of pesticides and was carried out with spiked filters (0.025 µg/filter) using the selected solvent (acetone). The selected CCD model consisted of a full factorial design, including 8 cube points, 6 axial points and 6 central points in cube involving 20 chromatographic injections. The 20 runs were randomized to provide protection against the effect of hidden variables. The design matrix is shown in Table 16.

Table 16: Experimental conditions using the Central Composite Design (CCD) for optimizing PLE conditions

		Factors	
Run	Temp. (°C)	Pressure (psi)	Static time (min)
1	69	1605	3
2	69	1605	8
3	100	1375	6
4	69	1145	8
5	131	1145	8
6	131	1605	8
7	69	1145	3
8	100	1375	6
9	131	1605	3
10	131	1145	3
11	100	1375	6
12	100	1375	6
13	100	1000	6
14	150	1375	6
15	100	1375	10
16	100	1375	6
17	50	1375	6
18	100	1750	6
19	100	1375	1
20	100	1375	6

IV.b.5 Optimization of ESI ion source settings

IV.b.5.1 Screening design

The most important part of MS/MS optimization is source related. Although the TSQ Quantum detector has an automated source tuning, improvement in the analyte responses could be achieved by using statistical design of experiments (DoE) (Massart et al., 1997), mainly when a multiresidue method is needed. Taking into account the literature (Niessen, 1999), the main factors affecting the ESI ion source efficiency are: spray voltage (SP), sheath gas pressure (SGP), capillary temperature (CT) and auxiliary gas pressure (AGP).

The relative influence of these factors on the analytical response (arbitrary units of peak area of the ions with majority relative abundance) was studied with a Plackett–Burman (P–B) design (Massart et al., 1997) (Table 17). This screening design allows us to find the parameters that have the largest influence with a reduced number of experiments. In order to have generous degrees of freedom for testing the statistical significance of the estimated effects, 12 runs plus a triplicate centre point were used.

Table 17: Experimental conditions for the Plackett-Burman design for studying the influence of the different parameters in the analytical response

	FACTORS			
RunOrder	Spray Voltage (V)	Sheath Gas (psi)	Aux Gas (psi)	Cap Temp (^{o}C)
1	2000	5	5	350
2	2000	5	20	350
3	2000	40	5	200
4	3500	23	13	275
5	3500	23	13	275
6	5000	40	5	350
7	2000	5	5	200
8	2000	40	20	200
9	3500	23	13	275
10	2000	40	20	350
11	5000	5	20	200
12	5000	5	5	200
13	5000	5	20	350
14	5000	40	5	350
15	5000	40	20	200

IV.b.5.2 Central composite design

To obtain a more accurate optimization of the significant parameters, central composite design (CCD) (Massart et al., 1997) was used. This type of experimental design permits the response surface to be built and the factor settings or operating conditions that maximize pesticide response to be found.

IV.b.6 Quality control

Each set of filters was analyzed under quality assurance protocols, including process blanks, field blanks and reagent blanks. In order to determine the pollutants' backgrounds, a procedural blank was employed as a control and was treated in the same way as the samples.

Two field blanks were used; each consisted of a sealed envelop containing a filter, and were used as quality control (QC) samples during deployment, retrieval and transportation of the field filters. These field blanks were processed and analysed in the same way as the analytical samples.

The analysis of filters was performed immediately after sampling or after storage period at −20°C (3 months maximum). In order to check potential losses during the storage period, spiked blank filters were stored and analysed as field samples.

IV.c RESULTS AND DISCUSSION

IV.c.1 PLE extraction

Ethyl acetate, acetone, methanol and acetonitrile were investigated as extraction solvents under PLE standard operating conditions. The experiments were carried out on spiked filters (0.025 µg/filter). Table 18 illustrates the effect of the three selected solvents (ethyl acetate, acetone and acetonitrile) on the recoveries and the signal to noise ratio of each pesticide in the spiked filters. Methanol extracts contained co-extracts resulting in strong interference. Consequently, methanol was discarded as an extractant.

Table 18: Effect of solvent on recoveries of pesticides in spiked PM 2.5 (recovery % ±s); (signal/noise); n=5

Pesticides	Acetone	Ethyl acetate	Acetonitrile
IMCP	95±7 (1795)	94±8 (1518)	97±6 (1640)
CBZ	95±6 (3604)	95±9 (3592)	99±7 (3442)
TBZ	95±9 (4512)	83±7 (4238)	97±5 (2521)
IMZ	101±7 (3398)	87±15 (991)	110±3 (2598)
MTD	99±6 (215)	101±5 (172)	109±5 (197)
MTC	101±9 (2894)	97±9 (2454)	72±5 (240)
BTN	108±1 (8605)	106±3 (5398)	105±6 (5397)
PYPF	110±4 (13262)	108±4 (12262)	109±8 (8107)
HXTZ	84±3 (7388)	78±4 (6640)	118±9 (2994)

PFE conditions: temperature, 60°C; pressure, 1500 psi; static time, 1 min; cycles, 2; preheated, 2 min. The flush volume was 100% of the extraction cell volume and the purge time was 1 min.

Statistical analysis of the obtained data was carried out using a two-sample *t*-test approach at 95% confidence level (Gardiner, 1997) and no significant differences were found between them. However, all pesticides provided higher signal to noise responses with acetone, so acetone was selected as the extraction solvent.

A CCD design was chosen to study the relative influence of the three parameters (temperature, pressure and static time) on the recovery of pesticides. The experiment was carried out with spiked filters (0.025 µg/filter) using acetone as extraction solvent. The design matrix and the analytical response are shown in Table 19.

Table 19: Experimental conditions and response (peak area) of the central composite design used for optimization PLE extraction of pesticides from spiked PM 2.5

	Factors			Pesticides						
Run	**Temp. (°C)**	**Pressure (psi)**	**Static time (min)**	**CBZ m/z160**	**IMCP m/z209**	**TBZ m/z131**	**IMZ m/z159**	**BTN m/z269**	**PYPF m/z185**	**HxTZ m/z228**
1	69	1605	3	56493150	57340114	815452346	36631863	264565345	5009845	89680712
2	69	1605	8	45157478	47817353	709134396	30655128	214066588	3752667	71288062
3	100	1375	5	46663356	60136930	709776835	38193883	237209593	4301702	74397327
4	69	1145	8	43541144	60514428	676528037	39492471	216790413	3453815	66213077
5	131	1145	8	33488627	69281927	557560593	24232847	210798867	3455814	63849132
6	131	1605	8	39299064	58779598	606106808	25716490	215521122	3657997	62597078
7	69	1145	3	38757173	56644840	532633119	29223905	174104666	2646767	49791089
8	100	1375	5	36097060	64490402	535397243	29007564	200868769	2958851	55916103
9	131	1605	3	29811192	60509693	476404967	31296194	175081913	2485683	44467539
10	131	1145	3	34228698	60572132	543696821	36798898	187158181	2527874	45974841
11	100	1375	5	31838645	56300839	510424907	31201981	169440523	2514676	43970135
12	100	1375	5	33393093	54838210	546274094	38120490	173628832	2761389	46252137
13	100	1000	5	34376697	53651346	529722413	25890199	171042146	2834821	43163913
14	150	1375	5	25479036	48467643	466077686	29008230	152938848	1988725	33656235
15	100	1375	10	32034648	53852792	550148969	34753809	167041993	2634015	40817202
16	100	1375	5	27919888	55220854	521936537	26414424	153930924	2510621	38260236
17	50	1375	5	33760101	51459979	527624522	38717745	163034147	2538325	37605563
18	100	1750	5	31036152	54836161	547832249	36969921	163903661	2472065	35846802
19	100	1375	1	27803447	48942564	455509783	32284864	154388921	2549986	31705632
20	100	1375	5	28399964	52642352	513048786	32850410	162627353	2514405	33457636

The following step was to select the factor settings (values for temperature, pressure and static time) that maximize pesticide response. The factor settings that simultaneously maximize the responses of the ten compounds were selected using the "response optimizer" in the MINITAB program.

As we have multiple responses (one for each pesticide), and as the response surfaces are different for each compound, it is necessary to find a factor setting that simultaneously maximizes the desirability for each response. The desirability is 0.0 for the lowest values obtained in the CCD. This number increases as response values increase, with 1.0 being the highest response value obtained in the experiments. For this reason, a composite desirability was maximized to combine the individual desirability of all the response variables into a single measure, taking into account that all the response variables have the same importance. The optimized conditions (optimized factor settings) were as follows: temperature, 50ºC; pressure, 1750 psi; static time, 1min.

Figure 7 shows, as an example, some response surfaces obtained by using the three dimensional response surfaces for TBZ, CBZ and MTD. Three dimensional response surfaces show the effect of two independent variables (temperature and pressure) on a given response, at a constant value of the other independent variable (extraction time).

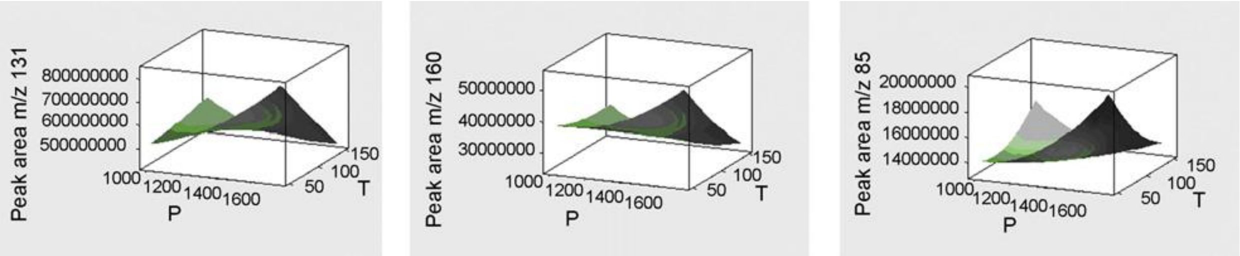


Figure 7: Response surface for TBZ, CBZ and MTD. Fixed conditions: extraction time, 5 min.

IV.c.2 MS/MS experimental parameters

IV.c.2.1 Screening design

Table 20 shows the estimated effects of spray voltage, sheath gas pressure, auxiliary gas pressure and capillary temperature on the optimization of ion source conditions, as well as their statistical significance at 95% confidence level ($\alpha < 0.05$). The parameters that had a significant effect ($p < 0.05$) on the response of one or more pesticides were spray voltage, sheath gas pressure and capillary temperature.

Consequently, these factors were selected for further optimization. The non-significant factor, auxiliary gas pressure, was fixed at the minimum value checked (5 a.u.) because it had a negative effect on all analytes.

Table 20: Estimated effects and p-values (α= 0.05) of the four main factors obtained from experimental design by Plackett–Burman used in the optimization of ion source conditions.

	FACTORS			
	Spray voltage	Sheath gas pressure	Auxiliary gas pressure	Capillary temperature
Pesticide	Effect (P-value)			
Carbendazim m/z 160	5895810 (0.000)	5704594 (0.000)	-36614 (0.892)	-535839 (0.071)
Imidacloprid m/z 209	11280346 (0.000)	3461238 (0.011)	-155543 (0.889)	-256495 (0.819)
Thiabendazole m/z 131	97120241 (0.000)	89610946 (0.000)	-5138008 (0.527)	-15461326 (0.079)
Imazalil m/z 201	-374634 (0.174)	-70113 (0.789)	57189 (0.827)	-343343 (0.020)
Methidathion m/z 85	-549970 (0.006)	-183417 (0.262)	-253866 (0.132)	135667 (0.399)
Methiocarb m/z 169	-10825795 (0.004)	-3997789 (0.195)	-5302099 (0.096)	1468658 (0.619)
Bitertanol m/z 269	-9385429 (0.009)	-1560580 (0.598)	-3131013 (0.301)	1636297 (0.580)
Pyriproxyfen m/z 185	-79659 (0.007)	-18508 (0.445)	-45711 (0.080)	13030 (0.587)
Hexythiazox m/z 228	-2076418 (0.006)	-759207 (0.228)	-1010797 (0.119)	403564 (0.509)
Isoproturon D6 m/z 171	-1791065 (0.069)	-775958 (0.394)	-739795 (0.415)	519705 (0.563)

The minimum, central and maximum values used in the P-B were: SP (2000-3500-5000 V), SGP (5-22.5-40 psi), CT (200-275-350ºC) and AGP (5-10-20 psi).

IV.c.2.2 Central Composite design (CCD)

To obtain a more accurate optimization of the three significant parameters (spray voltage, sheath gas pressure and capillary temperature), a central composite design (CCD) (Massart et al., 1997) was used. This type of experimental design permits the response surface to be built and the factor settings or operating conditions that maximize pesticide response to be found.

This design consists of a full factorial 23 design (8 hypercube points), 2 axial points and 10 central points. The 20 runs were randomized to provide protection against the effect of hidden variables. The values corresponding to every factor in each experiment and the responses for each pesticide are shown in Table 21.

Table 21: Experimental conditions and response (peak area) of the central composite design used for optimization of ion source conditions in LC–MS/MS analysis of pesticides

Run	Spray Voltage (V)	Sheath gas pressure (psi)	Cap. temp. (^{0}C)	CBZ m/z160	IMCP m/z209	TBZ m/z131	IMZ m/z159	MTD m/z85
1	5000	23	275	20892359	302667	10350724	3159129	100219
2	3500	23	275	16984230	247555	8680489	3261538	100346
3	2608	33	320	11719421	154081	5507621	3527164	112304
4	2000	23	275	7156450	72237	4050613	3425855	101388
5	3500	23	275	17294244	247506	8910568	3341056	99000
6	4392	33	230	11618971	276423	9076421	3104682	89528
7	3500	23	350	18062513	302468	8767232	3672311	127144
8	4392	33	320	14378397	395809	11084883	3837767	126875
9	4392	12	320	10338432	293333	8432963	3795608	152296
10	3500	5	275	5641494	164764	5244367	3420606	129161
11	2608	12	230	5098442	128336	3991525	3393226	110751
12	4392	12	230	9026860	234352	7209828	3212656	100066
13	2608	12	320	5843268	168269	4798718	3658540	139987
14	3500	23	275	11241635	277331	8551909	3654768	132343
15	3500	23	275	11158133	298050	8370299	3715615	138699
16	3500	23	200	8865600	202035	6799974	3324290	104531
17	3500	40	275	10331306	235281	7447729	3669605	124284
18	3500	23	275	11496625	300318	8632851	3773583	145716
19	3500	23	275	11245521	271220	8884592	3861380	145513
20	2608	33	230	7161624	161273	5237012	3945440	145756

Table 21: Experimental conditions and response (peak area) of the central composite design used for optimization of ion source conditions in LC–MS/MS analysis of pesticides (continued)

Run	Spray Voltage (V)	Sheath gas pressure (psi)	Cap. temp. (^{0}C)	MTC m/z169	ISPD6 m/z171	BTN m/z269	PYPF m/z185	HxTZ m/z228
1	5000	23	275	521906	396034	720569	1477004	174797
2	3500	23	275	515385	396581	742710	1513579	170385
3	2608	33	320	563943	395683	757656	1557835	171116
4	2000	23	275	538563	401245	743086	1552970	171709
5	3500	23	275	517207	387775	737308	1546138	169787
6	4392	33	230	485225	390745	735181	1493147	171264
7	3500	23	350	604494	405227	801473	1659435	195598
8	4392	33	320	652386	443892	839175	1735635	204178
9	4392	12	320	712799	479532	840500	1730630	206948
10	3500	5	275	654876	458847	774697	1623217	207759
11	2608	12	230	594818	456328	785136	1611874	195700
12	4392	12	230	585860	428979	749497	1546793	182375
13	2608	12	320	718123	465692	771591	1630498	200116
14	3500	23	275	706016	487961	825411	1650139	222126
15	3500	23	275	696574	492714	767300	1666247	214175
16	3500	23	200	619165	478918	781199	1621658	205171
17	3500	40	275	746788	504582	809292	1716008	222990
18	3500	23	275	767908	511142	825621	1738648	230809
19	3500	23	275	779842	530369	843120	1858949	240493
20	2608	33	230	767976	578712	879754	1892898	266982

For each pesticide, the analytical responses obtained were fitted into a linear equation that included second-order (curvature) and interaction terms. The model was validated using regression analysis of variance (ANOVA).

In order to maximize pesticide response, the factor settings for MS/MS had to be selected, as was the case for PLE extraction. Since each pesticide produces its own response, and the response surfaces are different for each compound, it is necessary to select the factor settings that maximized all pesticide responses. This was achieved in the same manner as for PLE extraction, by selecting the “response optimizer” in the MINITAB program.

The optimized factor settings were: spray voltage 4500V, sheath gas pressure 20 psi, capillary temperature 350^{o}C and auxiliary gas pressure 5 psi, which provided a composite desirability of 0.78.

Collision gas pressure and tube lens offset voltages were optimized for each pesticide using the automated optimization procedure in syringe infusion mode provided by the manufacturer. Selected reaction monitoring mode (SRM) was used for all analytes. Table 22 shows the monitored transitions obtained for each pesticide.

Table 22: Monitored transitions obtained for each pesticide

Time window (min)	Analyte	MW	Precursor ion (m/z)	Product ions (m/z) and their relative abundance	Collision energy	Tube lens
0-13	Carbendazim	191.2	192	160 (100%)	21	78
				132 (20%)	29	
	Imidacloprid	255.7	256	209 (70%)	11	84
				175 (100%)	20	
	Thiabendazole	201.2	202	131 (70%)	26	86
				175 (100%)	34	
13-15.30	Imazalil	296	297	159 (100%)	26	88
				201 (60%)	17	
	Isoproturon D6	206.3	213	171 (23%)	13	92
				78 (100%)	22	
	Methidathion	302.3	303	85 (100%)	18	97
				145 (80%)	19	
	Methiocarb	225.3	226	169 (100%)	15	91
				121 (98%)	19	
15.30-20	Bitertanol	337.4	338	269 (100%)	10	106
				99 (40%)	13	
	Pyriproxyfen	321.4	322	185 (100%)	24	83
				199 (14%)	23	
	Hexythiazox	352.9	353	228 (100%)	17	100
				168 (65%)	25	

IV.c.3 *Chromatographic determination*

The LC–MS/MS system consists of a Finnigan Surveyor Autosampler, a Finnigan Surveyor LC quaternary pump and a Finnigan TSQ Quantum Ultra detector (San José , CA, USA). Separation was performed on a Luna C18(2) column (150mm × 2.00mm ID, particle size 5 µm) from Phenomenex (Madrid, Spain).

Selected eluents were H2O with 0.01% acetic acid (A) and methanol (B), using a flow rate of 200 µl min^{-1}. Optimized gradient conditions were as follows: 0–8 min, linear from 30 to 35% B; 8–12min, linear from 35 to 90% B; 12–22 min, isocratic 90% B; 22–23 min, linear from 90% to 30%; 23–25 min, isocratic 30%. The autosampler and column temperatures were set at 20 and 22^{o}C, respectively, and a 10 µl volume injection was used.

IV.c.4 *Method Validation*

There is no available reference material for pesticides in fine airborne particulate matter, so the validation of the method was carried out using spiked filters. Spiked filters were prepared as explained in section IV.b.4. Recovery efficiencies ranged from 72 to 93% (see Table 23). Good linearity with R^2 > 0.99 was obtained in all pesticides with concentration ranges of 0.01–5 µg mL^{-1} in vial. The limit of quantification (LOQ) of the whole method was 32.8 pg m^{-3} for IMCP and 6.5 pg m^{-3} for the rest of the pesticides, when air volumes of 760 m^3 were collected.

Table 23: Range, limit of quantification, linearity, recoveries (R%) and standard deviation (SD) for the studied pesticides

Pesticide	Concentration range (µg mL^{-1})	R^2	LOQ (µg mL^{-1})	LOQ (pg m^{-3})	Recoveries (R%±SD)
Carbendazim	0.01-1	0.9997	0.01	6.5	86 ± 13
Imidacloprid	0.05-5	0.9993	0.05	32.8	85 ± 20
Thiabendazole	0.01-1	0.9993	0.01	6.5	93 ± 25
Imazalil	0.01-1	0.9996	0.01	6.5	90 ± 21
Methidathion	0.01-1	0.9993	0.01	6.5	89± 12
Methiocarb	0.01-1	0.9990	0.01	6.5	72± 18
Bitertanol	0.01-1	0.9995	0.01	6.5	87± 14
Pyriproxyfen	0.01-1	0.9993	0.01	6.5	75± 15
Hexythiazox	0.01-1	0.9995	0.01	6.5	82± 11

IV.c.5 Study of the matrix effect

Signal suppression or enhancement as a result of matrix effect (ME) can severely compromise quantitative analysis of pesticides at trace levels. The matrix effect must be evaluated and discussed within the context of method development before studying its performance characteristics, and an appropriate calibration technique which compensates these effects should be used.

ME was studied as described by Matuszewsky et al. (2003). Two different sets of solutions were prepared (set A: standard solutions in mobile phase; set B: spiked blank PM2.5 filter extracts) and determined using the ESI interface and the optimized factor setting. The absence or presence of matrix effects on quantification was evaluated by comparing the absolute peak areas of the two sets (ME%= B/A×100). Both sets A and B had concentrations of 1 µg mL^{-1}.

Table 24: Matrix effect (ME) (%) for the studied pesticides

Pesticide	Matrix effect (ME) (%)
CBZ	75
IMCP	91
TBZ	90
IMZ	48
MTD	91
MTC	38
BTN	89
PYPF	32
HXTZ	52

Table 24 shows that all compounds presented matrix effect. Some pesticides such as IMZ, MTC, PYPF and HXTZ showed high ion suppression (ME << 100%) with values of ME ranging from 32 to 52%. Others like CBZ, IMCP, BTN, TBZ and MTD had moderate ion suppression (ME < 100%), with ME ranging from 75 to 91%. This indicates that is necessary to minimize the matrix effect, using matrix matched standard calibration and internal standard methodology. Calibration standards were obtained by spiking blank filters. Spiked filters were obtained by adding variable volumes of the mix working solutions and a constant volume of internal standard (isoproturon D6) to the blank filters at the beginning of the sample preparation.

IV.c.6 Analysis of air samples

A breakdown of pesticide concentrations measured at the four sampling sites is presented in Table 25. For IMCP, MTC and MTD all samples had concentrations less than their limit of quantification; consequently, these pesticides are not included in the Table 25. Figure 8 shows the ion chromatogram of a sample collected in ALZ station in August 2007.

Table 25: Range and percentile concentrations of PM 2.5- bound pesticides in four stations in Valencia Region (Spain) (pg m^{-3})

Pest.	%>LQ[1]	Station															
		ALZ (N=11)				BUN (N=16)				STJ (N= 17)				BUR (N=16)			
		m	M	p50	p75	m	M	p50	p75	m	M	p50	p75	m	M	p50	p75
CBZ	100	82.8	466.0	225.4	325.0	133.0	572.0	259.0	379.9	48.9	268.2	124.3	162.9	41.0	203.0	102.6	120.6
TBZ	45	6.5	235.7	6.25	11.3	6.5	1371.0	22.4	101.6	6.5	81.0	13.5	27.3	6.5	18.8	6.25	11.6
IMZ	10	-	6.5	-	-	6.5	637.0	6.5	38.2	-	6.5	-	-	6.5	66.9	6.25	24.8
BTN	83	6.5	116.4	28.4	95.1	6.5	118.0	33.6	69.0	6.5	100	65.3	75.7	14.8	77.2	21.8	25.2
PYPF	40	6.5	333.3	133.6	258.0	6.5	155.6	51.7	85.2	6.5	33.9	6.5	6.25	6.5	51.2	6.25	6.25
HXTZ	78	15.1	88.0	25.0	43.0	51.3	434.9	148.0	254.0	6.5	119.8	21.8	30.0	6.5	20.3	13.4	13.6

[1] percentage of samples with pesticide concentrations >LQ; LQ = 6.5

Samples with pesticide concentrations <LQ=6.5

N: number of samples collected; P50: median; P75: percentile 75; m: minimum; M: maximum

CBZ was detected in all samples collected. The median, minimum and maximum values found were 145.6, 41.0 and 572.0 pgm^{-3}, respectively. Variations between stations were observed, with stations 1 (ALZ) and 2 (BUN) presenting larger values than those found in stations 3 (STJ) and 4 (BUR) (ANOVA, $p<0.01$). No monthly variations were found in any of the stations.

TBZ was detected in 45% of the samples collected. The values ranged from <LOQ to 1371 pg m^{-3}. Only 25% of the samples in station 4 contained TBZ, significantly less than the other three stations (45–52%). No seasonal variations within the stations were found, except a high increase in the sample concentrations in station 2 in September. TBZ is a fungicide used mainly indoor, in warehouses that store citrus fruit and other fruit.

IMZ was detected only in ten out of 60 samples analysed (16%). No samples with IMZ were detected in stations 1 and 3. This pesticide was detected mainly in samples taken during September and October. Three out of five samples collected in September showed very high concentrations of this pesticide (637.6, 309.8 and 134.5 pg m^{-3}). All samples collected in August showed concentrations of IMZ less than LOQ. Like TBZ, IMZ is a fungicide used on citrus fruit and other fruit in warehouses.

BTN was detected in 83% of samples analysed. The median and maximum values found were 29.2 and 118.0 pgm^{-3}, respectively. No significant differences between stations were found (ANOVA, $p>0.05$). The higher concentrations were found in August, except for station 3 where September concentrations were similar to those found in August.

PYPF was detected in 40% of samples analysed. The highest concentrations were found in station 1 with median and maximum values of 133.6 and 333.3 pg m^{-3}, respectively. This insecticide was not found in samples taken in stations 2–4 in October.

The acaricide HXTZ was found in 78% of samples analysed. The highest concentrations were found in station 2, with a median of 148 pg m^{-3} and a range between 61.30 and 434.9 pg m^{-3}. The maximum values achieved in these samples were collected in October.

No data exists in literature about the concentrations of these pesticides in PM 2.5 (see table 13). However, as an example, Xu et al. (2005) studied the concentrations of some pesticides in PM 2.5 and PM 10 in Beijing (China), but the substances analysed are banned organochlorine pesticides such as HCHs, DDTs and chlordanes. The concentrations found ranged from 7.7 to 32.8 pg m^{-3}, from 3.1 to 72.2 pg m^{-3} and from ND to 401 pg m^{-3}, respectively.

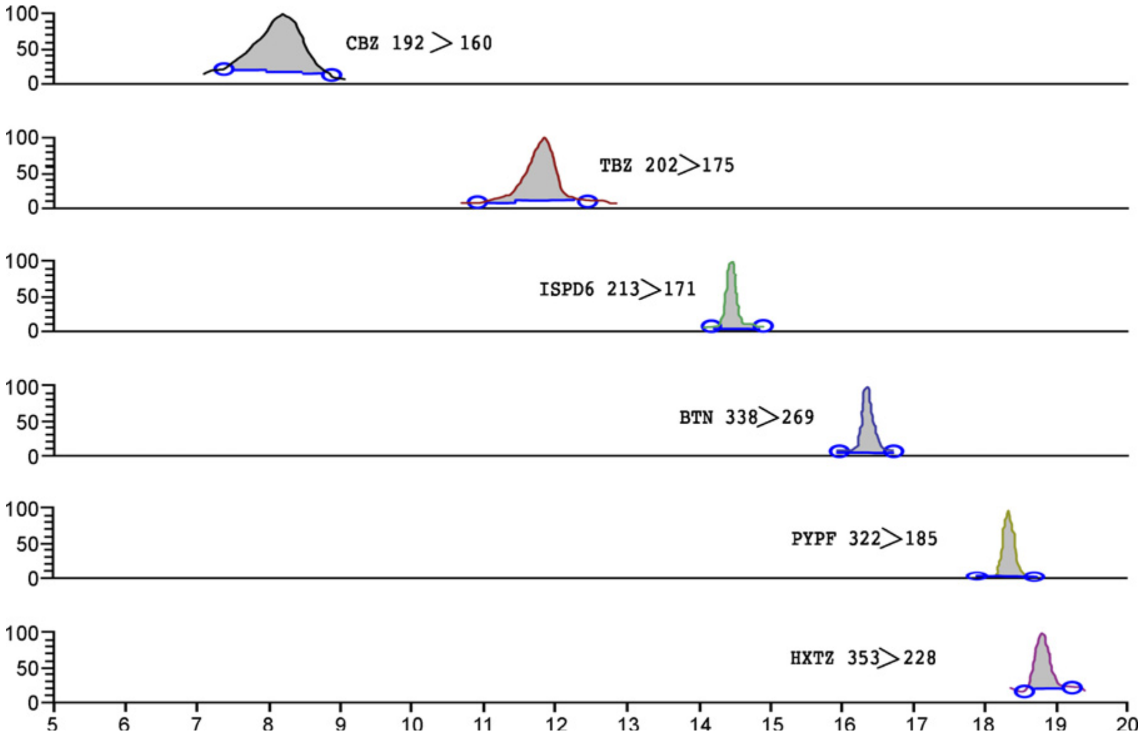


Figure 8: Ion chromatogram of a sample collected in Alzira station in August 2007 with concentrations of CBZ: 431 pg m^{-3}; TBZ: 159 pg m^{-3}; BTN: 95 pg m^{-3}; PYPF: 332 pg m^{-3}; HXTZ: 50 pg m^{-3}.

IV.d CONCLUSIONS

A very simple and confirmatory method to analyse nine CUPs in fine airborne particulate matter (PM 2.5) was developed. This is the first time these nine CUPs are analyzed in ambient air. The method is based on an extraction of pesticides by PLE followed by a direct injection into LC–ESI-MS/MS. Studies using PLE and LC-MS/MS for the analysis of pesticides in ambient air are scarcely found in literature.

Four solvents were studied for pesticide extraction. Acetone was selected because it presents good recoveries and provides higher signal to noise response. Acetone was previously used for extracting pesticides in ambient air but using Soxhlet extraction (Lammel et al., 2007) (Yao et al., 2006) (Waite et al., 2005) (Peck and Hornbuckle, 2005).

When comparing spiked blank filter extracts with the standard solution in the mobile phase, all pesticides showed ion suppression. For this reason, all pesticides presented matrix effect, which was minimized by using matrix matched standard calibration and internal standard methodology for quantitative analysis.

Optimization of ESI ion source settings and PLE conditions was achieved by statistical design of experiment approach. The optimized ESI ion source settings were: spray voltage, 4500V; sheath gas pressure, 20 psi; capillary temperature, 350°C and auxiliary gas pressure, 5 arbitrary units (a.u.). The optimized PLE conditions were as follows: temperature, 50°C; pressure, 1750 psi; static time, 1min.

The optimized method presented a LOQ of 6.5 pg m^{-3} (except for IMCP, which was 32.8 pg m^{-3}) when air volumes of $760m^3$ were collected. Recoveries ranged from 72 to 93%.

Using the optimized method, pesticide concentrations were investigated in 60 samples from four stations within Valencia Region´s monitoring network. The measured concentrations ranged from not detected to 1371 pg m^{-3}. The median in all stations was 178 pg m^{-3} for CBZ, 12 pg m^{-3} for TBZ, 6.37 pg m^{-3} for IMZ, 37.25 pg m^{-3} for BTN, 49.68 pg m^{-3} for PYPF and 52 pg m^{-3} for HXTZ. For IMCP, MTC and MTD, all samples gave concentrations less than their limit of quantification.

V. CHAPTER 2

MULTI-RESIDUE ANALYSIS OF 30 CURRENTLY USED PESTICIDES IN FINE AIRBORNE PARTICULATE MATTER (PM 2.5) BY MICROWAVE-ASSISTED EXTRACTION AND LIQUID CHROMATOGRAPHY–TANDEM MASS SPECTROMETRY

V.a INTRODUCTION

Pesticide extraction from airborne particulate matter is usually performed using Soxhlet with different solvents (see table 12), such as light petroleum (Gioia et al., 2005) (Alegria et al., 2006) (Motelay-Massei et al., 2005), acetone (Waite et al., 2005) (Cessna et al., 2000) (Waite et al., 2002) or n-hexane:methylene chloride (Scheyer et al., 2005) (Sanusi et al., 2000). This classical extraction technique has the disadvantage of being both time (from 6 to 24 h) and solvent (250–700 mL) consuming. These drawbacks, together with the long heating periods in the Soxhlet flask, which are likely to break the structural integrity of polar thermally labile pesticides applied in modern agriculture (N-methylcarbamates, sulphonyl urea, and chlorophenoxy acid herbicides), are leading to the use of alternative procedures, like pressurized liquid extraction (PLE) using a mixture of hexane–DCM–diethyl ether (7:1:2, v/v) (Yang et al., 2008), ethyl acetate (Rania and Sun, 2008) (Bailey and Welzer, 2007) or acetone (Chapter 1) as extraction solvents.

Similar to PLE (the extraction method used in Chapter 1), it is well known that microwave assisted extraction (MAE) allows reduction of both extraction time and organic solvent consumption, and increases sample throughput in the extraction of different pollutants from environmental matrices (Bayen et al., 2004) (Wurl and Obbard, 2005).

Applications of MAE for extracting pesticides from soils (Esteve-Turrillas et al., 2006) (Fuentes et al., 2007) sediments (Carvalho et al., 2008) (Smalling and Kuivila, 2008) and foods (Fuentes et al., 2008) (Sanusi et al., 2004) have been proposed. However, no studies have been published related to the extraction of CUPs from air traps.

On the other hand, the majority of methods developed for the determination of pesticides in ambient air are focused on legacy pesticides, such as those belonging to the persistent organochlorines class. Therefore, methods for newly introduced pesticides, and specifically for those that are currently used in agricultural practice, are required in order to study their occurrence in air and to implement monitoring programs.

The method has been designed to effectively extract and analyze 30 compounds belonging to different chemical classes, such as organophosphorous (i.e. methidathion), triazoles (i.e. bitertanol, myclobutanil and tebuconazole), imidazoles (prochloraz, triflumizole and imazalil), neonicotinoids (imidacloprid and acetamiprid), benzimidazoles and others. Apart from malathion and chlorpyrifos, the target pesticides are not compounds easily amenable to analysize by GC.

In general, the pesticides selected have medium or high water solubility (mg L^{-1} to g L^{-1}) and present a wide range of polarities, from compounds with very low octanol–water partitioning coefficients such as omethoate, imidacloprid or acetamiprid (log k_{ow} = −0.74, 0.57, 0.80, respectively), to apolar compounds such as fenazaquin (log k_{ow} = 5.51) and pyribaden (log k_{ow} = 6.37). Regarding their acid–base properties, the majority are neutral pesticides, but there are some acidic ones, such as acetamiprid (pKa = 0.7), flusilazole (pKa = 2.5) or triflumizole (pKa = 3.7).

The selected pesticides have different ranges of volatilities. Most of them have high volatility with high vapour pressure, such as omethoate (3.3E+00 mPa), carbendazim (9.0E-02), dimethoate (2.5E-01) and imazalil (1.5E-01). Some of them have low volatility with low vapour pressure such as imidacloprid (9.0E-07), azoxystrobin (1.1E-07) and bitertanol (2.2E-07). Other pesticides have medium volatility, such as acetamiprid (1.0E-03), thiabendazole (4.6E-04) and tebufenozide (1.5E-04).

In addition, the compounds selected are CUPs applied mainly to citrus fruit, other fruit, vegetables and grapes. In general, the active substances are approved by EU regulations. Others, such as the insecticides tebufenozide and buprofezin, or the acaricides hexythiazox, pyribaden or fenazaquin, may be withdrawn at the end of 2012, according with the EU regulations (Directive 91/414/CEE). However, the resubmission of applications for use of these pesticides such as pyridaben or malathion is now in progress and they could be included in annex I of directive 91/414/EEC. Some physical constants and the agricultural usage of the 30 studied CUPs are shown in Table 26.

The purpose of this study was to investigate the feasibility of using microwave energy for the efficient extraction of 30 CUPs from fine airborne particulate matter (PM 2.5) and to develop a rapid, sensitive, selective and reproducible method that can be used in air ambient monitoring programs. The procedure includes the extraction of PM 2.5-bound pesticides by MAE, followed by direct injection into a liquid chromatograph with tandem MS detection. The method was applied to samples of PM 2.5 filters collected from Valencia Region´s monitoring network, supplied by the Regional Government (Spain).

Table 26: Physicochemical properties and agricultural usage of pesticides studied

Analyte	Type	Vapour pressure (mPa)[1]	Henry's law constant (Pa m^3 mol^{-1})[1]	log kow[1]	Water solubility (mg L^{-1})[1]	Period of application	Way of application
Omethoate	Insecticide	3.3E+00		-0.74		May-Oct.	Spraying Dusting
Imidacloprid	Insecticide	9.0E-07	2.00E-10	0.57	610	March-Oct.	Spraying
Carbendazim	Fungicide	9.0E-02	3.60E-03	1.38	8	Spring, autumn	Spraying
Acetamiprid	Insecticide	1.0E-03	5.30E-08	0.80	4250	March-April	Spraying
Dimethoate	Insecticide	2.5E-01	1.20E-06	0.704	23800	May-Oct.	Spraying Dusting
Thiabendazole	Fungicide	4.6E-04	2.70E-08	2.39	30	All year	Indoor
Imazalil	Fungicide	1.5E-01	2.61E-04	3.82	180	All year	Indoor
Malathion	Insecticide	5.3E+00	1.21E-02	2.75	145	Spring, autumn	Spraying-bait Aerial
Flusilazole	Fungicide	3.9E-02	2.70E-04	3.74	54	April-June	Spraying
Metalaxyl	Fungicide	7.5E-01	1.60E-05	1.75	8400	March-Nov.	Spraying
Methidathion	Insecticide	2.5E-01	3.30E-04	2.20	200	May-June,August-Sep.	Spraying
Azoxystrobin	Fungicide	1.1E-07	7.30E-09	2.50	6	March-July	Spraying
Methiocarb	Helicide	1.5E-02	1.20E-04	3.08	27	Spring	Spraying Granulated bait
Fenhexamid	Fungicide	4.0E-04	5.00E-06	3.51	20	September-Oct.	Spraying
Iprovalicarb	Fungicide	4.4E-05	1.30E-06	3.20	11	May-July	Spraying
Bitertanol	Fungicide	2.2E-07	2.00E-08	4.10	2.7	March-May, Nov.-Jan.	Spraying
Myclobutanil	Fungicide	2.1E-01	4.33E-04	2.94	142	All the year	Spraying Indoor
Tebuconazole	Fungicide	1.7E-03	1.00E-05	3.70	36	March-July	Spraying
Tebufenozide	Insecticide	1.5E-04	6.59E-05	4.25	0.83	June-September	Spraying
Prochloraz	Fungicide	1.5E-01	1.64E-03	4.12	34.4	July and all the year	Spraying Indoor
Triflumizole	Fungicide	1.8E-01	5.60E-06	5.06	12500	April-July	Spraying
Cyprodinil	Fungicide	5.1E-01	6.60E-03	3.90	13	January and Septe.	Spraying
Tebufenpyrad	Acaricide	1.0E-02	1.25E-03	5.04	2.8	June-October	Spraying
Buprofezin	Insecticide	1.2E+00	4.24E-01	4.30	0.9	May-September	Spraying
Pyriproxyfen	Insecticide	1.3E-02	1.02E-04	5.37	5.3	April-Sept., Feb.-March	Spraying
Hexythiazox	Acaricide	3.4E-03	2.40E-03	2.53	0.5	Spring, autumn,summer	Spraying
Chlorpyrifos	Insecticide	2.7E+00	6.76E-01	4.70	1.4	All the year	Spraying
Flufenoxuron	Insecticide	6.5E-09	7.46E-06	4.00	0.004	June-October	Spraying
Pyridaben	Acaricide	2.5E-02		6.37	0.012	June-October	Spraying
Fenazaquin	Insecticide	3.4E-03	4.74E-03	5.51	0.22	June-October	Spraying

[1] (BCPC, 2009)

V.b MATERIALS AND METHODS

V.b.1 *Reagents*

High purity standard pesticides, omethoate (97%), imidacloprid (98%), carbendazim (99%), acetamiprid (99%), dimethoate (98%), thiabendazole (98.5%), fenhexamid (99.5%), imazalil (97.5%), azoxystrobin (99.5%), methidathion (98.5%), malathion (99.5%), metalaxyl (99.5%), myclobutanil (99%), methiocarb (98.5%), iprovalicarb (97.5%), tebufenozide (99%), flusilazole (99.5%), tebuconazole (98.5%), bitertanol (98%), prochloraz (99.5%), cyprodinil (97.5%), triflumizole (98.5%), tebufenpyrad (98%), buprofezin (99%), pyriproxyfen (98%), hexythiazox (99.3%), chlorpyrifos (98.5%), flufenoxuron (99.5%), pyridaben (99%) and fenazaquin (97%) were supplied by Dr. Ehrenstorfer (Augsburg, Germany).

Individual stock standards were prepared by weighing 10 mg of pure standard using a 5 decimal analytical balance and dissolving each compound in 50 mL of acetone. They were stored in capped amber vials at −21ºC (SANCO/2007/3131). Mix working solutions of 10 and 1mg l^{-1} were prepared with methanol. Calibration solutions (0.01, 0.02, 0.1, 0.2 and 0.5 µg mL^{-1}) were prepared by adding variable volumes of the mixed working solutions to the PM 2.5 filters.

HPLC grade methanol and acetonitrile were supplied by Scharlau (Barcelona, Spain). HPLC grade acetone, ethyl acetate and water were purchased from Merck (Darmstadt, Germany). Acetic acid glacial (Reag. Ph. Eur.) and formic acid 98% were provided by Panreac (Barcelona, Spain). Ammonium acetate for HPLC (97%) was purchased from Scharlau (Barcelona, Spain). Ammonium formate, solution Ultra (100 mL, 10M in water) was provided by Fluka (Steinheim, Switzerland).

PM 2.5 quartz fiber filters of 150 mm of diameter were supplied by Munktell filter AB (Falun, Sweden).

Statistical data manipulation and numerical analysis of data resulting from experimental design were carried out using the statistical package MINITAB for Windows, Release 14 (Minitab Inc., Birmingham, UK).

V.b.2 Equipment and sample analysis

Microwave extraction of pesticides from PM 2.5 filters was carried out using a Mars system from CEM corporation (Mathews, NC, USA), equipped with Teflon®TFM 100 mL extraction vessels. The MAE conditions were optimized for the extraction of pesticides from PM 2.5 filters. The final optimized method was as follows: the filters were extracted at 50ºC for 20 min, using a power of 1200 W, and 30 mL of ethyl acetate.

After cooling, the reactor was opened and the extracts were filtered. After 100 µl of diethylene glycol were added to the extract and concentrated with Turbo Vap 500 (Zymark, Idstein, Germany), the extracts were re-dissolved with 1mL of water:methanol (70:30) and filtered through a 0.22 µmGHP Acrodisc filter from Pall Life Science (Ann Arbor, USA) prior to LC–MS/MS determination.

The LC–MS/MS system consists of a Finnigan Surveyor Autosampler, a Finnigan Surveyor LC quaternary Pump and a Finnigan TSQ Quantum Ultra detector (San Jose, CA, USA). Chromatographic separation was performed on a Luna C18 (2) column (150mm×2.00mm I.D., 5 µm particle size) from Phenomenex (Madrid, Spain). The mobile phase was optimized and set to gradient mode. The flow rate was 200 µl min^{-1}. The autosampler and column temperatures were set at 20ºC and a 10 µl volume injection was used. All pesticides were detected using ESI in positive mode. The drying gas and nebulising gas was nitrogen Alfagaz B50 (99.99%), and the collision gas was argon C50 (99.99%). Both gases were from Air Liquide (Madrid, Spain). The main ion source parameters were set to the same conditions as described in Chapter 1 using a design of experiments (DOE) (previously optimized in Chapter 1).

V.b.3 Sampling and site characterization

Three sampling sites included in the PM2.5 monitoring network of the Regional Valencia Government (Generalitat Valenciana) were selected. The particulate phase of air samples were collected using quartz fiber filters of 150 mm in diameter and a large-volume sampler from Digitel (Madrid, Spain). The sampling flow used was 30 m^3 h^{-1}, with a total volume of filtered air ranging from 718 to 760 m^3.

Atmospheric sampling stations included three rural sites (Torre Endomenech, Beniganim and Burriana). All of them were situated in Eastern Spain (Valencia region).

The first station was placed in a rural area in Torre Endomenech in the north of Valencia region (0º04´44´´E, 40º16´10´´N). Torre Endomenech is a town located in la Plana Alta (Castellon province). This town is surrounded by many crops, such as almond trees, olive trees and cereals. The sampling period was May–June 2009. Samples were collected 259 m above ground level.

The second station was also placed in a rural area in Beniganim in the south of Valencia region (0º26´31´´W, 38º56´15´´N). Beniganim is a town located in la Vall d'Albaida (Valencia province). This town is surrounded by vineyards, olive trees and cereals. Samples were collected 195 m above ground level during April 2009.

The third station was installed in Burriana, in the north of Valencia region (0º05´23´´W, 39º53´41´´N). Burriana is a town (31,281 inhabitants) situated 13 km southeast of Castellon and 63 km north of Valencia, surrounded by irrigated land. Samples were collected 20m above ground level and very close to orange trees during June–July 2009.

To perform the PM 2.5 determination, a micro-balance Mettler-ToledoMX5 from Mettler-Toledo (Bedford, MA, USA) was used. Filters were conditioned before use according to EN 12341:1998 standard, at a temperature of 20±1ºC and a relative humidity of 50±5% for at least 48 h, and then weighed.

Before use, filters were heated in an oven for 24 hours at 130ºC in order to obtain a blank filter. A blank filter was used in each sequence of analysis. Moreover, some blank filters were spiked in each analysis sequence to evaluate the recoveries of each pesticide. These filters were also used for preparing standards using matrix matched standard calibration.

V.b.4 Quality control

Each set of filters was analyzed under quality assurance protocols, including process blanks, field blanks and reagent blanks. A procedural blank was employed as a control and was treated in the same way as the samples.

Two field blanks were used; each consisted of a sealed envelope containing a filter. They were used as quality control (QC) samples during deployment, retrieval and transportation of the field filters. These field blanks were processed and analyzed in the same way as the analytical samples. The analysis of filters was performed immediately after sampling or after storage at −20ºC (3 months maximum). In order to check potential losses during the storage period, spiked blank filters were stored and analyzed as field samples.

V.c RESULTS AND DISCUSSION

V.c.1 MAE extraction

V.c.1.1 Study of pesticide thermostability

The interaction between pesticides and particulate matter can result in the formation of bound residues. To obtain acceptable recoveries, an extraction procedure is needed to quantitatively remove the pesticides from the fine particulate matter. Consequently, the main parameters affecting the MAE recoveries, such as solvent, temperature, time and extraction volume, need to be optimized.

Prior to optimization of the extraction step, an initial study was necessary in order to test the stability of the pesticides. The majority of analytes studied are pesticides not amenable to GC owing to their polarity and thermolability. Therefore, a preliminary study was carried out to establish the range of temperature stability in the microwave oven.

Working standard solutions of pesticides at 0.2 µg mL^{-1} dissolved in ethyl acetate were used and their stability checked at 50, 80, 95 and 120ºC for 15 min. Degradation was observed for different pesticides at temperatures higher than 80ºC (Figure 9). Stability problems with MAE conditions for some thermally labile pesticides have also been reported by other authors (Smalling and Kuivila, 2008) (Cheng et al., 2007) (Lopez-Avila et al., 1998).

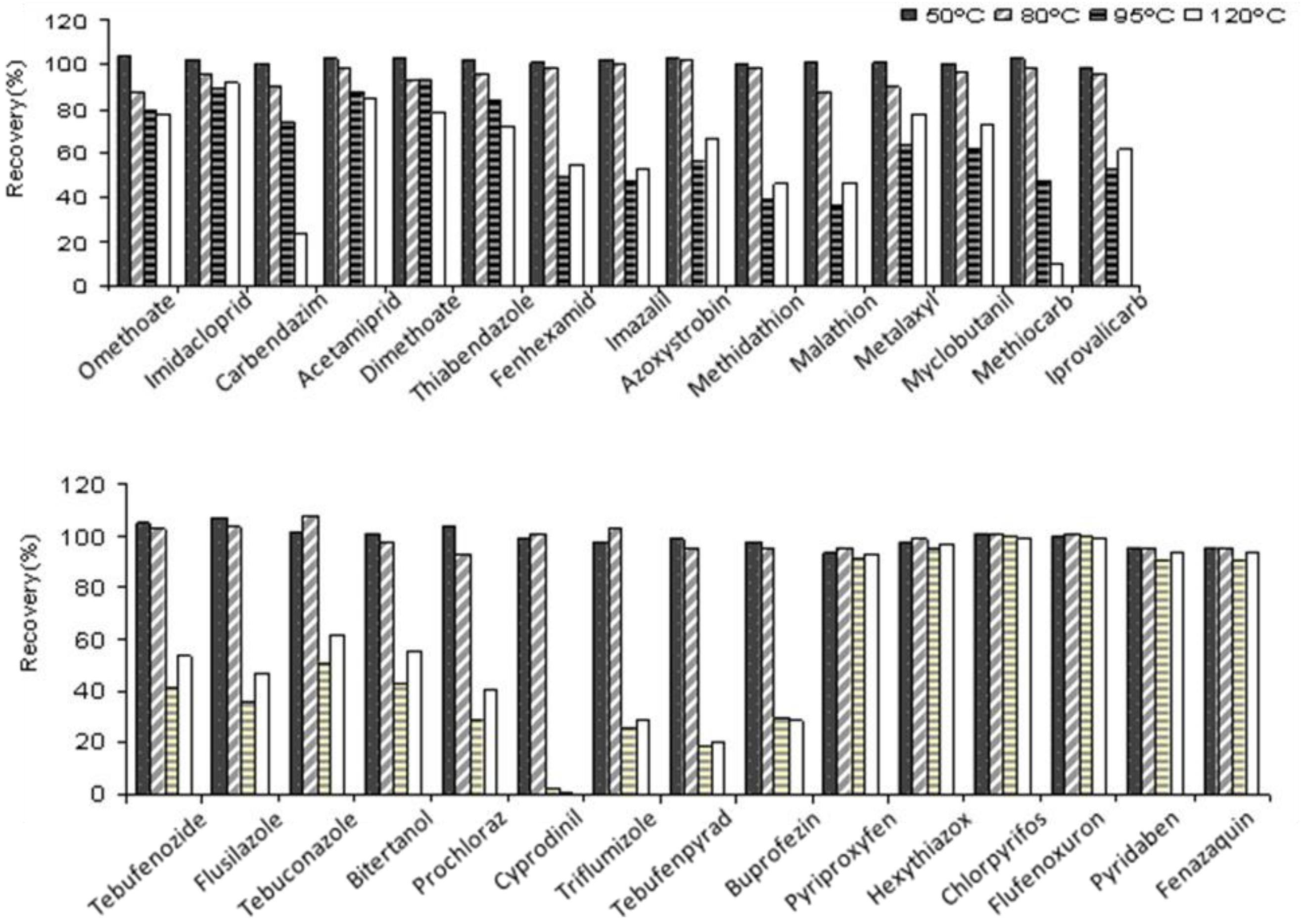


Figure 9: Stability of a standard solution of pesticides (0.2 ng mL^{-1}) under different MAE temperatures applied during 15 min (n = 4; solvent: 25 mL of ethyl acetate)

V.c.1.2 Study of extraction solvents

In order to select an appropriate solvent for the quantitative extraction of all 30 pesticides from atmospheric particulate matter, studies were performed using three different solvents commonly employed in the extraction of pesticides with a wide range of polarities from food and environmental matrices: acetone, ethyl acetate and acetonitrile.

These three solvents possess a suitable polarity and permitivity (ε) to absorb the microwave energy and transform it into thermal energy (Jassie et al., 1997). The use of solvents at elevated temperatures increases the capacity of solvents to solubilize analytes and also increases the diffusion rate. In addition, increased temperatures decrease the viscosity of liquid solvents (better penetration of matrix particles) and can disrupt the strong solute–matrix interactions caused by Van der Waals forces, hydrogen bonding and dipole attractions of the solute molecules and active sites of the matrix (Dean, 1998).

Microwave extraction was performed on spiked blank filters (0.2 µg/filter) with one 15-min cycle, using 30 mL of each solvent and an extraction temperature of 50^{o}C. Table 27 illustrates the effect of the three solvents on the recoveries of each pesticide from PM 2.5 filters. Statistical analysis of the obtained data was carried out using a two-sample t-test approach at 95% confidence level, and no significant differences were found between them. However extracts with ethyl acetate provide, in general, more precision and higher signal to noise responses due to lower ion suppression effects, so this solvent was selected.

In Chapter 1 using PLE, acetone was selected because it provided better signal to noise ratios for the majority of the nine pesticides determined. In this study, acetone only gave slightly higher signal to noise ratios for carbendazim, imidacloprid, thiabendazol, imazalil and bitertanol.

Ethyl acetate is a typical solvent used in the multi-residue analysis of pesticides in matrices, such as foods, using shaking or other conventional extraction methods. However, it has not been used in MAE methods to extract pesticides from environmental matrices. Vryzas and Papadopoulou-Mourkidou (2002) used acetonitrile to extract some herbicides from soils with MAE. Others authors have carried out the microwave extraction of pesticides from different matrices with the mixtures acetonotrile:water (soils), toluene:water (10:1) (soils) (Esteve-Turrillas et al., 2006) or acetone (vegetables) (Singh et al., 2004).

Table 27: Effect of solvent on recoveries (R%±SD) of pesticides from spiked PM 2.5 filters (0.2ng/filter)[1].

Pesticide	Ethyl Acetate	Acetone	Acetonitrile
Omethoate	97 ± 5	107 ± 10	82 ± 13
Imidacloprid	96 ± 4	92 ± 7	101 ± 6
Acetamiprid	102 ± 6	89 ± 15	95 ± 5
Dimethoate	96 ± 3	97 ± 15	96 ± 12
Carbendazim	101 ± 5	99 ± 18	97 ± 11
Thiabendazole	89 ± 8	64 ± 12	101 ± 15
Metalaxyl	91 ± 3	96 ± 11	84 ± 4
Methidathion	103 ± 6	80 ± 12	84 ± 5
Azoxystrobin	96 ± 2	88 ± 17	86 ± 3
Methiocarb	102 ± 7	82 ± 11	91 ± 4
Myclobutanil	89 ± 6	97 ± 15	103 ± 6
Fenhexamid	102 ± 5	88 ± 13	89 ± 9
Malathion	97 ± 7	89 ± 10	88 ± 11
Iprovalicarb	99 ± 7	94 ± 11	89 ± 8
Tebufenozide	101± 5	91 ± 16	77 ± 6
Flusilazole	92 ± 2	94 ± 14	86 ± 12
Imazalil	96 ± 6	97 ± 12	75 ± 12
Tebuconazole	94 ± 4	85 ± 10	89 ± 16
Bitertanol	97 ± 4	99 ± 11	93 ± 9
Cyprodinil	99 ± 6	102 ± 17	101 ± 10
Prochloraz	105 ±7	64 ± 11	103 ± 12
Triflumizole	97 ± 4	86 ± 7	78 ± 9
Buprofezin	108 ± 3	113 ± 12	104 ± 14
Tebufenpyrad	101 ± 4	90 ± 13	88 ± 14
Pyriproxyfen	98 ± 2	80 ± 14	99 ± 15
Hexythiazox	96 ± 2	90 ± 8	83 ± 17
Chlorpyrifos	96 ± 7	75 ± 13	85 ± 11
Flufenoxuron	108 ± 6	80 ± 12	85 ± 12
Pyridaben	101 ± 6	96 ± 10	106 ± 14
Fenazaquin	104 ± 7	89 ± 17	79 ± 9

SD: standard deviation; n = 4

[1] MAE conditions: temperature, 50ºC; solvent volume, 30 mL and time, 15 minutes

V.c.1.3 Optimization of MAE parameters

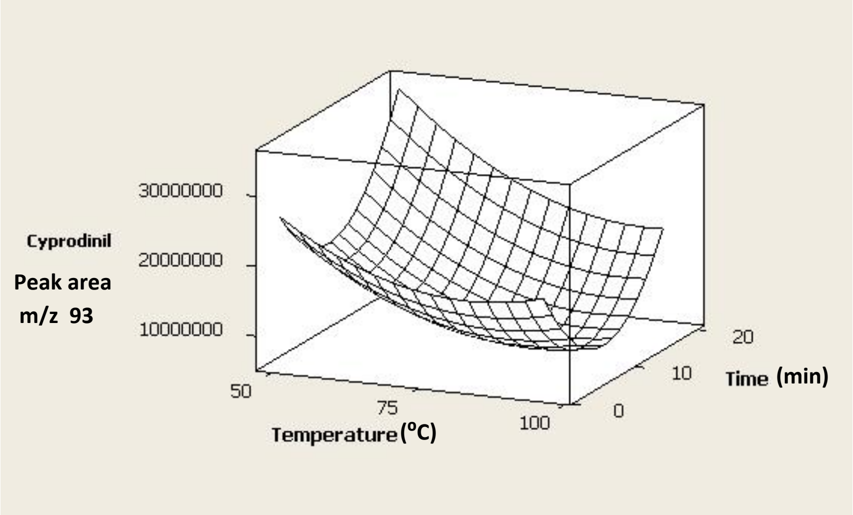
Once ethyl acetate was selected as the extraction solvent, the optimization of the three main factors (time, volume and temperature) affecting MAE recoveries (Jassie et al., 1997) was carried out by a design of experiment approach (DOE) using a central composite design (CCD) (Massart et al., 1997). This type of experimental design permits to build the response surface for each compound, and find the factor settings (operating conditions) that maximize the extraction efficiency. The CCD selected was composed of a full factorial 23 design (8 cube points) to which 6 axial points and 6 central points were added, involving a total of 20 randomized chromatographic runs divided in two blocks, and was carried out with spiked PM 2.5 filters (0.2 µg/filter).

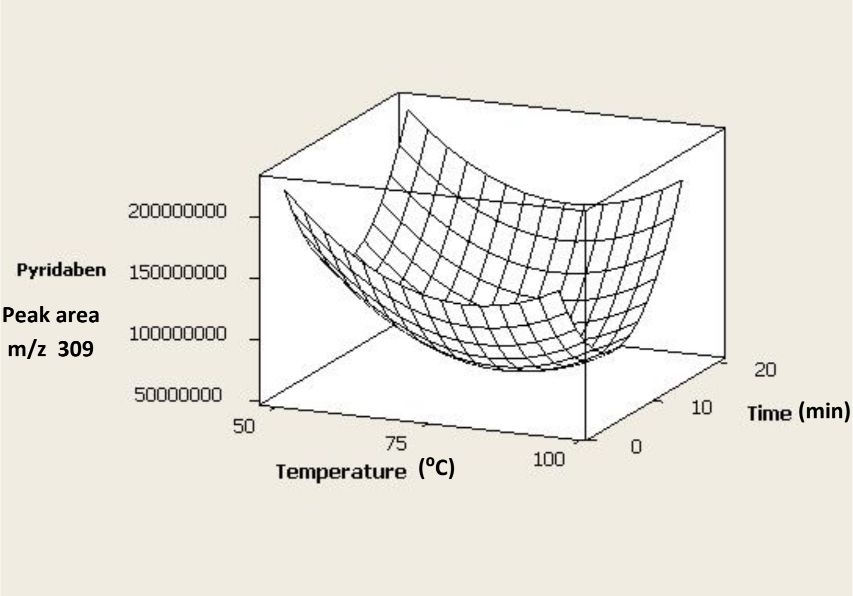
The extractions corresponding to each block were carried out in two consecutive days. The design matrix and, as an example, the analytical response of three pesticides (cyprodinil, pyridaben, fenhexamid), are shown in Table 28.

Three-dimensional response surface analysis shows the effect of two independent variables on a given response, at a constant value of the independent variables. Figure 10 presents, as an example, some response surfaces developed by the model for cyprodinil (m/z 93), pyridaben (m/z 309) and fenhexamid (m/z 97) at a constant value of the volume solvent (30 mL). To select the factor settings that maximize the compound responses, the “response optimizer” from the response surface design option in MINITAB program was used. This parameter simultaneously maximizes the desirability for each compound. The optimized factor setting was a time of 20 min, a temperature of 50^{o}C and a volume of 30 mL. These conditions provide a composite desirability of 0.995.

Table 28: Experimental conditions and response (peak area) of the central composite design used for the optimization of MAE extraction efficiency of pesticides from spiked PM 2.5 filters

Run	Temperature (^{0}C)	Time (min)	Volume (mL)	Cyprodinil (m/z 93)	Pyridaben (m/z 309)	Fenhexamid (m/z 97)
1	73	11	30	12150129	84180227	4075269
2	95	11	45	13254248	122509169	6919063
3	73	11	45	622681	11628126	282498
4	73	11	60	287044	10583796	115702
5	73	1	45	24320045	204451844	14096604
6	73	11	45	23003532	175522699	12279025
7	73	20	45	24334687	185772575	12789830
8	50	11	45	21063765	174896538	10570648
9	59	16	36	21371929	168027060	10139501
10	73	11	45	22008513	196168885	11466106
11	86	5	54	15459491	131543466	6131032
12	86	5	36	12195591	110425632	5321137
13	73	11	45	9536253	101122665	4368636
14	73	11	45	6909220	90132322	3209990
15	59	5	54	11168634	146766158	5265048
16	73	11	45	14449840	135801335	6169832
17	86	16	36	16774702	160381576	6615738
18	59	5	36	15422550	149097182	6679469
19	59	16	54	20148197	197542038	8477942
20	86	16	54	19471969	170388062	7588217





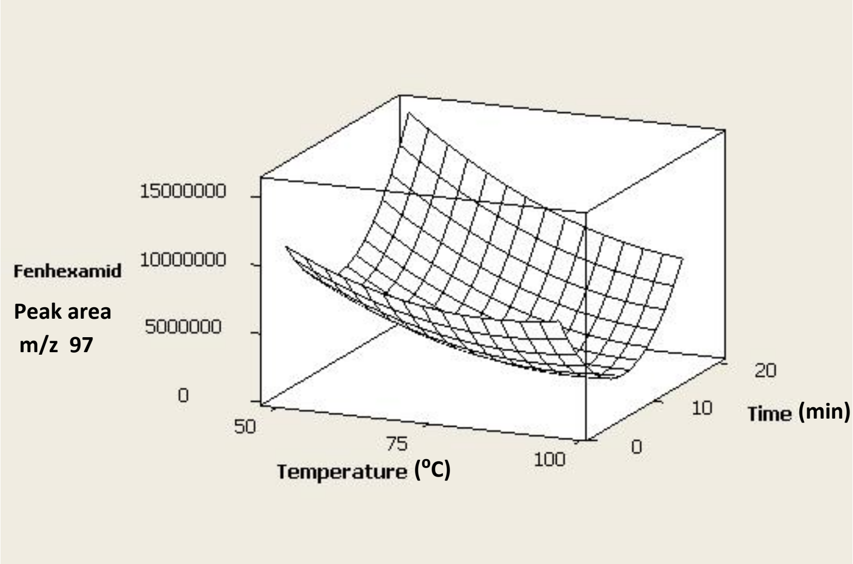


Figure 10: Response surface for cyprodinil, pyridaben and fenhexamid. Fixed conditions: volume, 30 mL ethyl acetate.

V.c.2 LC-MS/MS Optimization

Individual standard solutions (2 µg mL^{-1}) were prepared in methanol–H_2O, 50:50 containing 0.1% HCOOH for MS optimization. Both full-scan and MS–MS spectra were acquired to obtain information about the maximum number of transitions available for each compound. The most sensitive results were always obtained with ESI in the positive ionization mode, using $[M+H]^+$ as precursor ion. The most sensitive transition was selected as the quantification, while trying to avoid non-specific transitions generated by losses of M–H_2O or M–CO_2, in order to improve selectivity. The remaining transitions were used for confirmation.

The enhanced selectivity afforded by MS–MS permits the detection of pesticides that are partially separated or not separated at all; however, the simultaneous analysis of a high number of compounds requires, at least, a sufficient chromatographic separation in order to increase sensitivity. The gradient was optimized in order to render a rough separation between the 30 analytes, obtaining a consistent distribution between three time windows. The retention times (Rt) are shown in Table 29 and they corresponded to analytes with high polarities, such as omethoate (log P =−0.74) (Rt = 2.92 min), to non-polar analytes, such as fenazaquin (log P = 5.51) (Rt = 21.07 min).

The number of transitions covered in one LC–MS^2 run was 60 (two per pesticide), distributed throughout an acquisition time of 22 min. When acquiring in SRM mode, it is important to maximize the chromatographic signal to noise ratios (sensitivity) and it is also important that the peak to be quantified should be defined by at least 12 data points to assure a satisfactory peak shape and a reproducibility of area measurement. Accordingly, three time windows (segments) with dwell times ranging from 20 to 200 ms were selected. Likewise, the distribution of the analytes along the time windows try to center the chromatographic peak in windows, minimizing the risk of peak loss due to unexpected slight changes in retention time.

Apart from chromatographic separation, mobile phase composition is known to have a significant effect on LC–MS, both on correct chromatographic peaks as well as on signal sensitivity, so adequate modifiers could be added to the mobile phase in order to obtain efficient chromatography and to favour ionization (Mallet et al., 2004). Four different buffer constituents were tested: 0.1% acetic acid at pH 3.26, 0.1% formic acid at pH 2.69, 5 mM ammonium acetate at pH 6.54 and 0.1% formic acid with 5 mM ammonium formate at pH 3.16. In general, the highest signals were achieved with the ammonium formate buffer. However, for fenhexamid, malathion, metalaxyl, myclobutanil, pyriproxyfen and pyridaben the signal using formic acid was, on average, 20% higher than the signal achieved with ammonium formate buffer.

The lowest signal was provided by acetic acid and ammonium acetate, with responses for most compounds ranging from 45 to 85% of the signal with an ammonium formate buffer. Consequently, because of these results 0.1% formic acid with 5 mM ammonium formate was added to both the aqueous and organic mobile phases.

Selected reaction monitoring mode (SRM) was used for all analytes. Table 29 shows the two transitions monitored for each pesticide.

Table 29: Selected LC–MS/MS experimental parameters for each pesticide

Analyte	Retention time (min)	MW	Precursor ion (m/z)	Products ions (m/z) and their relative abundance	Collision energy	Tube lens
Omethoate	2.92	213.2	214	183 (100%)	12	82
			214	125 (70%)	25	69
Imidacloprid	8.58	255.7	256	209 (70%)	38	85
			256	175 (100%)	24	85
Carbendazim	4.94	191.2	192	160 (100%)	21	78
			192	132 (20%)	29	78
Acetamiprid	11.15	222.7	223	90 (40%)	36	90
			223	126 (100%)	20	90
Dimethoate	11.07	229.3	230	199 (100%)	11	90
			230	171(40%)	17	90
Thiabendazole	6.92	201.2	202	131 (70%)	26	86
			202	175 (100%)	34	86
Fenhexamid	15.66	302.2	302	97 (100%)	27	97
			302	55 (23%)	45	97
Imazalil	13.87	296	297	159 (100%)	26	88
			297	201 (60%)	17	88
Azoxystrobin	14.99	403.4	404	372 (100%)	14	90
			404	344 (29%)	27	90
Methidathion	15.04	302.3	303	85 (100%)	18	97
			303	145 (80%)	19	97
Malathion	15.41	330.4	331	285 (100%)	22	102
			331	127(93%)	14	102
Metalaxyl	14.71	279.3	280	220 (100%)	14	94
			280	248 (22%)	11	94
Myclobutanil	15.50	288.8	289	70 (98%)	18	90
			289	125 (100%)	34	90
Methiocarb	15.32	225.3	226	169 (100%)	15	91
			226	121 (98%)	19	91
Iprovalicarb	15.71	320.4	321	203 (49%)	11	101
			321	119 (100%)	19	101
Tebufenozide	15.92	352.5	353	133 (90%)	18	110
			353	297 (100%)	10	110
Flusilazole	15.86	315.4	316	247 (100%)	19	100
			316	165 (78%)	32	100
Tebuconazole	16.32	307.8	308	70 (100%)	30	97
			308	125 (37%)	40	97

Table 29: Selected LC–MS/MS experimental parameters for each pesticide (continued)

Analyte	Retention time (min)	MW	Precursor ion (m/z)	Products ions (m/z) and their relative abundance	Collision energy	Tube lens
Bitertanol	16.68	337.4	338	269 (100%)	10	106
			338	99 (40%)	13	106
Prochloraz	16.70	376.7	377	308 (100%)	14	78
			377	266 (17%)	13	78
Cyprodinil	16.58	225.3	226	108 (45%)	25	84
			226	93 (100%)	36	84
Triflumizole	17.41	345.7	346	278 (100%)	12	83
			346	73 (6%)	16	83
Tebufenpyrad	17.81	333.9	334	145 (73%)	26	109
			334	117 (100%)	35	109
Buprofezin	18.08	305.4	306	201 (100%)	13	89
			306	116 (36%)	18	89
Pyriproxyfen	18.41	321.4	322	185 (100%)	24	83
			322	199 (14%)	23	83
Hexythiazox	18.66	352.9	353	228 (100%)	17	100
			353	168 (65%)	25	100
Chlorpyrifos	18.75	350.6	351	198 (100%)	14	102
			351	97 (85%)	22	102
Flufenoxuron	18.78	488.8	489	158 (100%)	22	128
			489	141 (64%)	52	128
Pyridaben	20.52	364.9	365	309 (100%)	13	104
			365	147 (77%)	24	104
Fenazaquin	21.07	306.4	307	161 (100%)	16	95
			307	147 (26%)	20	95

V.c.3 Method Validation

There is no available reference material for pesticides in fine airborne particulate matter, so the validation of the method was carried out using spiked blank PM2.5 filters at three concentrations (0.01, 0.2 and 0.5 µg/filter), with five replicates at each level. Mean recoveries ranged from 72 to 109% (see Table 30), with coefficients of variation below 15%. Analytical characteristics evaluated were sensitivity, accuracy (measured as mean recovery), precision (expressed as repeatability), and specificity.

Table 30: Mean recoveries and coefficients of variation (n=5) from spiked PM 2.5 filters

	0.01 ng/filter		0.2 ng/filter		0.5 ng/filter		LOQ
PESTICIDE	Recovery (%)	CV (%)	Recovery (%)	CV (%)	Recovery (%)	CV (%)	(pg m^{-3})
Omethoate	107.2	7	107.2	5	70.1	3	6.5
Imidacloprid	75.3	13	106.9	2	109.4	2	6.5
Acetamiprid	98.2	5	107.9	2	85.1	2	6.5
Dimethoate	88.5	4	108.3	3	78.0	1	6.5
Carbendazim	75.3	13	104.4	1	71.2	11	6.5
Thiabendazole	84.1	5	99.8	11	87.6	27	6.5
Metalaxyl	75.8	7	109.2	2	88.8	3	6.5
Methidathion	101.6	14	103.2	1	74.2	8	6.5
Azoxystrobin	99.0	3	106.4	2	88.8	8	6.5
Methiocarb	98.7	4	101.7	7	95.1	10	6.5
Myclobutanil	97.7	6	106.9	6	83.0	4	6.5
Fenhexamid	100.0	7	106.5	1	71.8	4	13.5
Malathion	91.7	5	108.2	2	72.0	6	6.5
Iprovalicarb	98.3	3	110.7	3	81.3	5	6.5
Tebufenozide	115.4	2	115.4	2	82.0	6	6.5
Flusilazole	97.3	5	107.5	2	96.2	5	6.5
Imazalil	96.7	2	107.5	6	81.6	15	13.5
Tebuconazole	104.1	4	104.1	1	83.3	4	6.5
Bitertanol	99.5	4	108.5	1	88.3	4	6.5
Cyprodinil	98.7	4	108.5	1	78.9	7	6.5
Prochloraz	77.3	16	104.6	2	82.1	8	13.5
Triflumizole	92.9	4	104.0	4	90.2	16	6.5
Buprofezin	112.9	15	108.0	1	82.9	5	6.5
Tebufenpyrad	96.7	4	108.7	1	77.5	5	6.5
Pyriproxyfen	99.5	5	97.6	2	85.5	3	6.5
Hexythiazox	104.0	4	113.5	2	86.5	8	6.5
Chlorpyrifos	75.4	20	95.8	17	80.6	12	32.5
Flufenoxuron	103.6	9	107.9	2	77.0	2	6.5
Pyridaben	102.3	3	101.3	1	89.0	2	6.5
Fenazaquin	100.5	2	104.1	3	91.7	9	6.5

The limit of quantification (LOQ) was established as the lowest concentration tested for which recovery and precision were satisfactory (70–110% and <20% RSD, respectively), in accordance with the criteria established for the analysis of pesticide residues (SANCO/2007/3131). The LOQ of the whole method was 32.5 pg m^{-3} for Chlorpyrifos, 13.5 pg m^{-3} for fenhexamid, imazalil and prochloraz and 6.5 pg m^{-3} for the rest of pesticides, when air volumes of 760 m^3 were collected.

Linearity was studied using matrix-matched standards, analyzing each of them in triplicate at six concentrations in the range of 0.01–0.5 µg mL^{-1} in vial. Matrix-matched calibration plots showed good linearity with correlation coefficients (R^2) > 0.99 between 0.01 and 0.5 µg mL^{-1} in vial. The specificity of the method was tested by analyzing blank samples. The absence of any chromatographic peak at exactly the same retention time of the target pesticides, indicated there were no matrix compounds that might give a false positive signal in these samples.

For a positive identification (confirmation criteria) in accordance with the EU guidelines (SANCO/2007/3131), the following rules were applied: (i) two SRM transitions per compound were monitored, (ii) the LC retention time of the analyte in the sample had to be within 2.5% of the retention time in the standard, (iii) the relative abundance of the SRM transition signals had to be within 20% of the ratio obtained for the standards, and (iv) the S/N of the two diagnostic ions had to be >3.

V.c.4 Study of the matrix effect

In HPLC–MS, both in ESI and APCI ionization modes, the co-extractive matrix components can lead to suppression or enhancement of the analyte signal as a result of the interferences in the ionization mechanism of the analytes (Niessen, 2006). The matrix effect (ME) can severely compromise quantitative analysis at trace levels, so it must be evaluated and discussed in the context of method development before studying its performance characteristics. If necessary, an appropriate calibration technique compensating for the matrix effect should be used.

The matrix effect was evaluated by comparing the peak areas from standard solutions (n = 4) of the 30 pesticides in mobile phase (set A) with the peak areas of spiked blank PM 2.5 filters extracted with ethyl acetate (n=4) (set B). Spiked blank filters were obtained by spiking blank filters with the same concentration of the mixed working solutions, obtaining in all cases a concentration of 0.2 µg mL^{-1} in the vial (Matuszewski et al., 2003). The matrix effect was calculated via the formula:

ME% = B/A × 100. Both sets A and B had concentrations of 0.2 µg mL^{-1}.

Table 31: Matrix effect (ME) (%) of the studied pesticides

PESTICIDE	ME (%)
Omethoate	18
IMCP	89
CBZ	70
Acetamiprid	44
Dimethoate	33
TBZ	75
Imazalil	35
Malathion	30
Flusilazole	46
Metalaxyl	41
MTD	85
Azoxystrobin	31
MTC	36
Fenhexamid	44
Iprovalicarb	37
BTN	75
Myclobutanil	52
Tebuconazole	63
Tebufenozide	35
Prochloraz	38
Triflumizole	27
Cyprodinil	25
Tebufenpyrad	41
Buprofezin	38
PYPF	26
HXTZX	50
Chlorpyrifos	40
Flufenoxuron	77
Pyridaben	45
Fenazaquin	32

Table 31 shows the ion suppression of all compounds. Consequently, all pesticides displayed some matrix effect. When the average matrix effect is lower than 80%, it can generally be considered to have a significant effect on the quantitative analytical results (Zrostílková et al., 2001). In general, the ME can be eliminated by removing the co-eluting matrix components from the sample extract with an appropriate clean-up step. However, this can lead to a more complex and time consuming procedure. A compensation approach, such as the use of matrix matched standards, is considered a useful method to eliminate the consequences of matrix effects on the reliability (accuracy and precision) of the data. Consequently, a matrix matched calibration curve of six points was used for quantification.

V.c.5 Analysis of air samples

To put into practice the developed method, 54 samples were collected in three rural sites during three periods: April 2009 (Benigànim), May–June (Torre Endomenech) and June–July (Burriana). In these three sites, the levels of PM 2.5 ranged from 8 to 25 µg m^{-3}. A breakdown of pesticide concentrations measured at the three sites is presented in Table 32.

Table 32: Concentrations of PM 2.5 bound pesticides (pg m^{-3}) in three stations of Valencia Region (Spain)

Pesticide	Torre Endomenech[1] (N=21)				Burriana[2] (N=19)				Benigànim[3] (N=14)			
	n	m	M	Mean[4]	n	m	M	Mean	*n*	m	M	Mean
Omethoate	12	63.0	1208.0	399.7	19	65.3	205.1	126.2	*7*	15.0	36.0	22.0
Carbendazim	11	12.0	78.0	42.4	19	31.4	320.9	99.5	*6*	22.0	161.0	58.6
Acetamiprid	1		8.3	8.3								
Thiabendazole	1		25.0	25	7	21.9	35.4	18.0				
Malathion					3	6.8	17.4	11.5				
Flusilazole	1		9.7	9.7								
Metalaxyl	2	7.8	8.5	8.1	17	6.8	25.8	18.4	*6*	20.4	36.8	24.3
Azoxystrobin	2	8.2	8.4	8.3	8	7.3	9.5	8.4				
Iprovalicarb	1		9.8	9.8	5	6.5	10.0	7.7				
Myclobutanil									*7*	17.7	51.7	35.2
Tebuconazole	7	7.0	52.0	24.4	5	6.5	7.2	6.8				
Triflumizole	4	21.9	22.3	22.2								
Cyprodinil					2	11.0	20.4	15.7				
Tebufenpyrad					5	10.3	33.8	19.1				
Buprofezin					19	99.4	248.0	171.7				
Pyriproxyfen	2	6.9	67.0	36.9	19	26.7	274.0	99.6				
Hexythiazox	1		16.7	16.7	19	25.5	103.4	47.0				
Flufenoxuron					3	6.5	8.1	7.2				
Fenazaquin					4	6.7	12.0	8.2				

[1] Sampling period: May–June.

[2] Sampling period: June–July.

[3] Sampling period: April; N, total samples; n, number of samples > LQ; m, minimum concentration; M, maximum concentration.

[4] Mean values calculated only for samples with concentrations above detection limits.

Most of the pesticides detected have relatively high volatility (Vp >1×10^{-2} mPa), such as malathion (Vp: 5.3E+00 mPa), omethoate (Vp: 3.3E+00 mPa), buprofezin (Vp: 1.2E+00 mPa), metalaxyl (Vp: 7.5E-01 mPa) or myclobutanil (Vp: 2.1E-01 mPa). Others, however, present relatively low volatility, such as flufenoxuron (Vp: 6.2E-09 mPa), azoxystrobin (Vp: 1.0E-07 mPa), tebuconazole (Vp: 6.5E-05) or iprovalicarb (Vp: 4.4E-05 mPa). That means that their presence in the atmosphere is not only linked to their volatility but also to meteorological factors, atmospheric transport and removal, proximity of sampling to sources and period of application.

Nineteen out of thirty pesticides investigated were found in at least one sample. The insecticide omethoate (transformation product of dimethoate) and the fungicide carbendazim were the active substances most frequently detected (70% of total samples collected), with maximum concentrations ranging from 15 to 1208 pg m^{-3} and from 12 to 320.9 pg m^{-3}, respectively. Both pesticides have relatively high vapour pressures and are currently used against some pests found in olive trees and cereals, respectively. These crops are surrounding both Torre Endomenech and Benigànim sampling sites.

Their presence at the Burriana site could be linked to their medium-range transport from other areas in the vicinity. These pesticides are sprayed during spring and summer. The only reference in literature related to the presence of omethoate in ambient air has been provided by Raina and Sun (2008), who detected concentrations of 2.7 and 0.2 pg m^{-3} in two samples (gas + particulate phase) in British Columbia (Canada). In Chapter 1 carbendazim was detected in four stations (including Burriana) in Valencia region (Spain), at concentrations ranging from 41 to 572 pg m^{-3}.

Pesticide concentrations and profiles vary widely by site. The Burriana site shows the highest number of pesticides detected. The insecticides fenazaquin, flufenoxuron, pyriproxyfen, buprofezin, malathion; the acaricides hexythiazox, tebufenpyrad and the fungicides cyprodinil, thiabendazole, tebuconazole, azoxystrobin and metalaxyl were found in samples collected at this site, at concentrations ranging from 6.5 to 274 pg m^{-3}. All these plant protection products are used intensively in the area surrounding the town of Burriana, mainly in citrus fruit, but also in vegetables (tomato, pepper, lettuce, cauliflower) and fruit (peach, pear, watermelon, melon, apricot).

Figure 11 shows the ion chromatogram of a sample containing 8 pesticides collected in Burriana in June of 2009. Other authors have reported the presence of cyprodinil (Lig´Air, 2006) and malathion (Lig´Air, 2006) (Baraud et al., 2003) in ambient air at maximum concentrations of 3300 pg m^{-3} and 4450 ng m^{-3}, respectively. In Chapter 1, thiabendazole, pyriproxyfen and hexythiazox were detected at concentrations ranging from 6.5 to 1371 pg m^{-3}. The fungicide metalaxyl, apart from the 17 samples from Burriana (mean 18.4 pg m^{-3}), was also found in two samples from Torre Endomenech (mean 8.1 pg m^{-3}) and six samples collected in Benigànim (mean 24.3 pg m^{-3}). This fungicide is not only used in citrus fruit orchards, but also in the vineyards surrounding these other two sampling sites. Metalaxyl has also been reported by Yao et al. (2006) and White et al. (2006) in samples (gas + particulate phase) collected in three potato farm sites on Prince Edward Island (Canada), with concentrations ranging from 150 to 496 pg m^{-3}. The fungicide myclobutanil was detected in seven samples from Benigànim. Their presence could be related to its use in the vineyards around the sampling site during the period of sampling (April).

No data exists in literature about the concentrations in ambient air of fenazaquin, flufenoxuron, pyriproxyfen, buprofezin, triflumizole, tebuconazole, myclobutanil, iprovalicarb, azoxystrobin, flusilazole and acetamiprid. Some authors have shown that atmospheric concentrations of CUPs are correlated with the proximity of sampling to source areas and that the occurrence is usually linked with local use (Majewski et al., 1998). Locally high concentrations of pesticides in air are very seasonal and are correlated to local use patterns. The highest concentrations in air usually occur in the spring and summer months coinciding with application times and warmer temperatures. However, for some CUPs that are detected, it is not always clear if their concentration and frequency in air is associated with local use and/or medium range transport (MRT) from other sources (Tuduri et al., 2006).

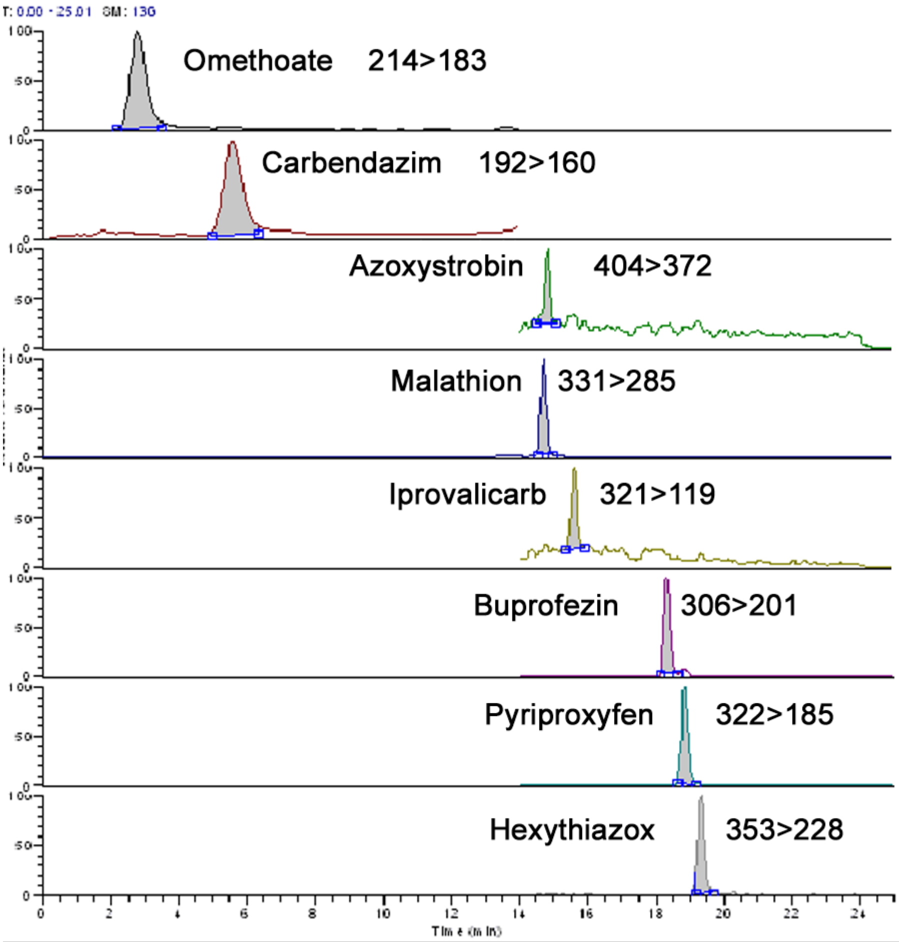


Figure 11: Ion chromatogram of a sample collected in Burriana station in June 2009 with concentrations of omethoate: 127.9 pg m^{-3}, carbendazim: 65.8 pg m^{-3}, azoxystrobin: 8.4 pg m^{-3}, malathion: 10.4 pg m^{-3}, iprovalicarb: 6.6 pg m^{-3}, buprofezin: 220.0 pg m^{-3}, pyriproxyfen: 182.8 pg m^{-3}, hexythiazox: 67.3 pg m^{-3}.

V.d CONCLUSIONS

A rapid and confirmatory method to analyze 30 CUPs in fine airborne particulate matter (PM2.5) was developed. The method is based on the extraction of pesticides by MAE followed by a direct injection into LC–ESI-MS/MS. This is the first time MAE has been used as an extraction technique for the analysis of pesticides in ambient air.

Three solvents were studied for pesticide extraction: acetone, ethyl acetate and acetonitrile. Ethyl acetate has been widely used for the determination of pesticides in food and environmental matrices. This solvent has been used in PLE to analyze ambient air samples (Rania and Sun, 2008). In this chapter, ethyl acetate was selected for MAE because it provided greater precision and higher signal to noise ratios for most pesticides.

All pesticides showed ion suppression when we compared spiked blank filter extracts with standard solutions in mobile phase. For this reason, matrix matched standard calibration was used for quantitative analysis, to counteract matrix effects.

The main parameters affecting MAE extraction (time, temperature, volume of solvent) were optimized by statistical design of the experimental approach. The optimized factor settings were: time 20 min, temperature 50ºC and solvent volume 30 mL.

The optimized method gave recoveries ranging from 72 to 109%. The limit of quantification (LOQ) was 32.5 pg m^{-3} for chlorpyrifos, 13.5 pg m^{-3} for fenhexamid, imazalil and prochloraz, and 6.5 pg m^{-3} for the remaining pesticides, when air volumes of 760 m^3 were collected.

Using the optimized method pesticide concentrations were investigated in 54 samples from three stations of the atmospheric monitoring network of the Regional Valencia Government (Spain). Nineteen out of 30 pesticides investigated were found in at least one sample: omethoate, carbendazim, acetamiprid, thiabendazole, malathion, flusilazole, metalaxyl, azoxystrobin, iprovalicarb, myclobutanil, tebuconazole, triflumizole, cyprodinil, tebufenpyrad, buprofezin, pyriproxyfen, hexythiazox, flufenoxuron and fenazaquin.

The measured concentrations ranged from 6.5 to 1208 pg m^{-3}. Eleven of the pesticides detected (fenazaquin, flufenoxuron, pyriproxyfen, buprofezin, triflumizole, tebuconazole, myclobutanil, iprovalicarb, azoxystrobin, flusilazole and acetamiprid) have been reported for the first time in ambient air. This method could be used in monitoring programs of currently used pesticides in air using the network of samplers which exist already to monitor fine particulate matter.

VI. CHAPTER 3

DETERMINATION OF 40 CURRENTLY USED PESTICIDES IN AIRBORNE PARTICULATE MATTER (PM 10) BY MICROWAVE-ASSISTED EXTRACTION AND GAS CHROMATOGRAPHY COUPLED TO TRIPLE QUADRUPOLE MASS SPECTROMETRY

VI.a INTRODUCTION

GC-MS is increasingly replacing traditional detectors in the determination of GC-amenable pesticides in air, and is nowadays the analytical technique most widely used. The MS analyser most frequently used is quadrupole, mainly working in selected ion monitoring (SIM) mode, which provides a higher sensitivity than full scan mode. In multiresidue analysis by GC–MS, electron ionization (EI) in positive mode is most commonly used.

However, in recent years, the application of tandem mass spectrometry (MS/MS) has been considered an advantageous tool which allows high selectivity and low analyte detectability (mass spectral noise reduction, both in matrix and vacuum background). The use of tandem mass spectrometry (MS/MS) with a triple quadrupole (QqQ) analyzer takes advantage of adequate precursor and product ion selection and can operate in selective or multiple reaction monitoring mode (SRM).

Several authors have reported the application of GC-MS/MS using a QqQ analyzer for the determination of pesticide residues in different matrices, such as animal feed (Walorczyk, 2008), fruits and vegetables (Cervera et al., 2010), soil (Rashid et al., 2010), and water (Pitarch et al., 2007). All these authors have highlighted that GC–MS/MS (QqQ) provides excellent selectivity and sensitivity, allowing reliable identification and accurate quantification of target analytes. However, GC–MS/MS with an EI-QqQ analyzer has not been investigated for the analysis of pesticides in ambient air, where the low levels of these residues require a powerful technique that permits low LOD_s and a confirmatory approach.

The selection of PM 10 (particulate matter which passes through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter), rather than total suspended particulate (TSP) matter, as indicator of air pollution is based on health considerations, since the respirable fraction of PM is the most dangerous for human health (Valavanidis et al., 2008) (Ballester et al., 2002), and the environment. Consequently, the regulatory concern is today focused on PM 10 and PM 2.5.

The 40 GC-amenable CUPs that have been selected belong to different chemical classes, such as pyrethroids, pyrimidinol, phtalamides, organophosphorus and organochlorines. These pesticides are, in general, thermally stable compounds with vapour pressures between 1.24E-05 and 46.5 mPa (see Table 33). The selected pesticides are, in general, approved by EU regulations, except diazinon, fenitrothion, isofenphos-m, permethrin, pyrazophos, trifluralin and vinclozolin, which have recently been forbidden. Therefore, an unlawful use of these pesticides could be checked.

An analytical methodology for sensitive and confirmatory determination of the 40 CUPs in airborne particulate matter using GC(EI)-MS/MS with triple quadrupole analyzer was developed. The procedure includes the extraction of PM10-bound pesticides by MAE, followed by Gel Permeation Chromatography (GPC) clean-up. The method was applied to samples collected from the air monitoring network which belongs to the Regional Valencia Government (Spain).

Table 33: Physicochemical properties and agricultural use of pesticides studied (^{1} BCPC, 2009)

Analyte	Type	Vapour pressure (mPa)^1	Henry's law constant (Pa m^3 mol^{-1})^1	log K$_{ow}$^{1}	Water Solubility^1	Period of application
Bifenthrin	Insecticide	2.4E-02		> 6	< 1 ug L^{-1}	Spring-Summer
Bupirimate	Fungicide	1.0E-01	1.4E-03	3.9	22 mg L^{-1}	Spring
Captan	Fungicide	1.3E+00	1.1E-01	2.8	3.3 mg L^{-1}	Spring- Autumn
Cypermethrin	Insecticide	2.0E-04	2.0E-02	6.6	0.004 mg L^{-1}	All year
Chlorpropham	Herbicide	2.4E+01	4.7E-02	3.8	89 mg L^{-1}	
Chlorothalonil	Fungicide	7.6E-02	2.5E-02	2.9	0.81 mg L^{-1}	All year
Cyfluthrin	Insecticide	9.6E-04	1.3E-02	6	2.5 ug L^{-1}	Spring-Summer
Deltamethrin	Insecticide	1.2E-05	3.1E-02	4.6	< 0.2 ug L^{-1}	All year
Diazinon	Insecticide	1.2E+00	6.1E-02	3.3	60 mg L^{-1}	March-Sept.
Dichlorvos	Insecticide	2.1E-03	2.5E-02	1.9	18 g L^{-1}	
Dicofol	Acaricide	5.3E-03	2.4E-02	4.3	0.8 mg L^{-1}	August-October
Diphenylamine	Fungicide			3.5		
Chlorpyrifos-e	Insecticide	2.7E+00	6.7E-01	4.7	1.4 mg L^{-1}	All year
Ethoprophos	Insecticide	4.6E+01		3.6	700 mg L^{-1}	All year
Fenitrothion	Insecticide	1.8E+01		3.4	14 mg L^{-1}	Spring-Summer-Autumn
Fipronil	Insecticide	3.7E-04	3.7E-05	4.0		
Fludioxonil	Fungicide	3.9E-04	5.4E-05	4.1	1.8 mg L^{-1}	September
Folpet	Fungicide	2.1E-02	7.8E-03	3.1	0.8 mg L^{-1}	Spring-Summer
Iprodione	Fungicide	5.0E-04	7.0E-06	3.0	13 mg L^{-1}	March-Oct.
Kresomin-methyl	Fungicide	2.3E-03	3.6E-04	3.4 (25ºC)	2 mg L^{-1}	Spring-Summer
Lambda-cyhalothrin	Insecticide	2.0E-04	2.0E-02	7 (20ºC)	0.005 mg L^{-1}	Spring-Summer-Autumn
Malathion	Insecticide	5.3E+00		2.7	145 mg L^{-1}	Spring-Summer-Autumn
Chlorpyrifos-m	Insecticide	3.0E+00	3.7E-01	4.2	2.6 mg L^{-1}	Spring-Summer-Autumn
Isofenphos-m	Insecticide					
Mepanipyrim	Fungicide	2.3E-02	1.6E-03	3.3	3.10 mg L^{-1}	August-October
Metalaxyl	Fungicide	7.5E-01	1.6E-05	1.7	8.4 g L^{-1}	Spring-Autumn
Pirimiphos-m	Insecticide	2.0E+00	6.0E-02	4.2 (20ºC)	11 mg L^{-1}	Spring-Summer-Autumn
Penconazole	Fungicide	3.7E-01	6.6E-04	3.7	73 g L^{-1}	Spring-Autumn
Permethrin	Insecticide	2.9E-03/9.2E-04	5.8E-03/2.8E-03	6.1 (20ºC)	6E-03 mg L^{-1}	
Pyrazophos	Fungicide	2.2E-01	2.5E-04	3.8	4.2 mg L^{-1}	
Pyrimethanil	Fungicide	2.2E+00	3.6E-03	2.8 (25ºC)	0.121 g L^{-1}	Agosto-Octubre
Pirimicarb	Insecticide	4.0E-01	3.6E-05	1.7	3 g L^{-1}	Spring
Procymidone	Fungicide	1.8E+01		3.1	4.5 mg L^{-1}	All year
Propargite	Acaricide	6.0E-03	3.3E-06	3.7	632 mg L^{-1}	Summer-Autumn
Quinoxyfen	Fungicide	1.2E-02	3.1E-02	4.6	116 ug L^{-1}	May-July
Tolclofos-methyl	Fungicide	5.7E+01		4.6	1.10 mg L^{-1}	November
Tolyfluanid	Fungicide	2.0E-01	7.7E-02	3.9	0.9 mg L^{-1}	Summer-Autumn
Triadimefon	Fungicide	2.0E-02	9.0E-05	3.1	64 mg L^{-1}	Spring-Summer
Trifluralin	Herbicide	6.1E+00	1.5E+01	4.8	0.221 mg L^{-1}	
Vinclozolin	Fungicide	1.3E-01	1.4E-02	3.0 (pH 7)	2.6 mg L^{-1}	

VI.b MATERIALS AND METHODS

VI.b.1 Reagents

High purity standard pesticides, bifenthrin (99.5%), bupirimate (97.7%), captan (98.5%), cypermethrin (91%), chlorpropham (99.5%), chlorothalonil (99.5%), cyfluthrin (98%), deltamethrin (99%), diazinon (96%), dichlorvos (97%), dicofol (99%), diphenylamine (99%), ethyl chlorpyrifos (99.5%), ethoprophos (93%), fenitrothion (97.5%), fipronil (98%), fludioxonil (99%), folpet (99%), iprodione (99.5%), kresomim-methyl (98%), lambda-cyhalotrin (99%), malathion (99%), methyl chlorpyrifos (98.5%), methyl isofenphos (96%) (%), mepanipyrim (99.4%), metalaxyl (99.5%), pirimiphos methyl (99%), penconazole (99%), cis-permethrin (94%), trans-permethrin (94%), pyrazophos (98%), pyrimethanil (97.5%), pirimicarb (98.7%), procymidone (98%), propargite (94.5%), quinoxyfen (99%), tolclofos-methyl (98.3%), tolylfluanid (98%), triadimefon (99.5%), trifluralin (99.5%) and vinclozolin (99%) were supplied by Dr. Ehrenstorfer (Augsburg, Germany).

Individual stock standards were prepared by weighing 10 mg of pure standard using a 5 decimal analytical balance and dissolving each compound in 50 mL of acetone. They were stored in capped amber vials at -21ºC (SANCO 10684/2009). Mixed working solutions of 0.1, 0.5 and 5 µg mL^{-1} were prepared with acetone. Calibration solutions (1, 10, 20, 30, 40 and 50 ng/mL) were prepared by adding variable volumes of the mix working solutions to the PM 10 filters (matrix matched standards).

Ethyl Acetate (UV-IR-HPLC-HPLC preparative) was purchased from Panreac (Barcelona, Spain), acetone for gas chromatography (SupraSolv®) from Merck (Darmstadt, Germany), dichloromethane (Pestinorm for pesticide residue analysis) was provided by Prolabo (Leuven, Belgium), HPLC grade n-Hexane 99% by Scharlau (Sentmenat, Spain) and nonane for GC was supplied by Fluka (Steinheim, Switzerland).

VI.b.2 Equipment and sample analysis

Chromatographic analyses were performed on a Trace GC Ultra and Triplus autosampler coupled to triple quadrupole mass spectrometer from Thermo-Finnegan (TSQ Quantum GC, San José, CA, USA). Separation was carried out on a TR-5MS capillary column (Thermo Fisher Scientific, Bellefonte, PA, USA) 30 m x 0.25 mm i.d., 0.25 µm film. High-purity helium (99.99%) and argon C50 (99.99%) were employed as carrier gas (constant flow of 1.2 mL min^{-1}) and collision gas, respectively, both from Air Liquide (Madrid, Spain).

The mass spectrometer was operated in electron impact mode (EI) using a voltage of 70 eV and a filament current of 25 µA. The ion source temperature and the GC-MS/MS interface were set to 250ºC. Selected reaction monitoring mode (SRM) was used for all analytes.

Microwave extraction of pesticides from PM 10 filters was carried out using a Mars system from CEM corporation (Mathews, NC, USA) equipped with Teflon® TFM 100 mL extraction vessels. The method was as follows: the filters were extracted at 50ºC for 20 min, using a power of 1200 W, and 30 mL of ethyl acetate. After cooling, the reactor was opened and the extracts filtered. After this, 20 µl of nonane as keeper were added to the extract and concentrated with a Turbo Vap 500 (Zymark, Idstein, Germany).

The extracts were re-dissolved in 700 µl of dichloromethane before injection in the GPC clean-up. The Waters Gel Permeation Chromatography Clean Up System was employed, integrated with a Waters 515 high-pressure liquid chromatography pump, a Waters 717 sample input module.

VI.b.3 Sampling and site characterization

PM 10 samples were collected using a large-volume sampler from Digitel (Madrid, Spain) and quartz fiber filters of 150 mm in diameter were supplied by Munktell filter AB (Falun, Sweden). A sampling flow of 30 $m^3 h^{-1}$ for 24 hours was used to provide a total filtered air volume of around 720-760 m^3 .

Samples were collected in Alzira (42,543 inhabitants), a city in the centre of Valencia region (43 km from Valencia city), which has in its vicinity many citrus crops such as orange trees. The sampling station was placed in a rural area, approximately 1 km from the city of Alzira (0^o27´28´´W, 39^o09´00´´N). A total of 38 samples were collected from April to June 2010. Samples were collected about 60 m above ground level.

To perform the PM 10 determination, a micro-balance Metter-ToledoMX5 from Mettler-Toledo (Bedford, MA, USA) was used. Filters were conditioned according to the EN 12341:1998 standard, temperature (20±1^{o}C) and relative humidity (50±5%) conditions for at least 48 h, and then weighed.

VI.b.4 GPC clean-up conditions

The Waters Gel Permeation Chromatography Clean Up System was employed, integrated with a Waters 515 high-pressure liquid chromatography pump, a Waters 717 sample input module, tandem columns Envirogel GPC clean up 19 mm x 150 mm and 19 mm x 300 mm, and a Waters 2487 UV detector (254 nm), together with a Gilson FC 204 Fraction Collector.

The experimental conditions were as follows: a mobile phase of methylene chloride, a flow rate of 5 mL min^{-1}, and a volume injection of 700 µl. The collected fractions extended from 11 min to 18 min. Before each multiple-sample procedure, the GPC was calibrated by establishing an elution profile with a calibration solution which consisted of corn oil, bis(2-ethylhexyl)phthalate, methoxychlor, perylene (EPA, 1994). The calibration chromatograms were examined to ensure that the relative retention times and peak shapes were as expected.

VI.b.5 Quality control

Each set of filters were analysed under quality assurance protocols, including process blanks, spiked blank samples, blank sample and reagent blanks. Two process blanks were used; each consisted of a sealed envelope containing a filter, and were used as quality control (QC) samples during deployment, retrieval and transportation of the field filters. These field blanks were processed and analysed in the same way as the analytical samples. The analysis of filters was performed immediately after sampling or after storage at -20^{o}C (3 months maximum).

In order to check potential losses during the storage period and assess recoveries during sample preparation, spiked blank samples were stored and analysed as field samples. Blank samples were baked for 24 hours at 130^{o}C in the oven to eliminate pesticides.

VI.c RESULTS AND DISCUSSION

VI.c.1 MAE extraction and GPC clean-up

In Chapter 2, ethyl acetate was selected as an appropriate solvent for quantitative MAE extraction of 30 amenable LC-pesticides. In that chapter, an optimization of the main MAE parameters (time, volume and temperature) was carried out using a design of experiments (DOE) approach. In order to develop a comprehensive extraction method for both GC and LC-amenable pesticides, the same extraction method was used in the present chapter, after checking the recoveries and other performance parameters in the validation of the method.

However, before evaluating the analytical performance, a study on the stability of these new pesticides at different MAE temperatures was performed using a standard solution of pesticides (10 ng mL^{-1}) with ethyl acetate under different MAE temperatures. No degradation was observed for any pesticide at the extraction temperature (50ºC) and extraction time (20 min) optimized in Chapter 2.

A GPC clean-up step after MAE was introduced to remove some matrix interferences. A standard solution was injected in the GPC system and different time window fractions were analyzed. The fraction collected between 11 to 18 minutes permits a quantitative recovery of pesticides. So, this time window was selected. The collected fractions were evaporated under a nitrogen flow at 40ºC, using 20 µl of nonane as keeper, and then re-dissolved with 1 mL of hexane before being injected in the GC-MS/MS.

VI.c.2 Chromatographic determination and injection mode

The GC temperature program was optimized: initial 90ºC, hold 5 min; rate 25ºC min^{-1} , to 180; rate 5ºC min^{-1} to 280ºC, hold 3 min; rate 10ºC min^{-1} to 300ºC, hold 3 min. Splitless injection conditions were as follows: split flow, 50 mL min^{-1}; splitless time, 2.00 min; surge pressure, 300 kPa; surge duration, 2.00 min; injection volume, 1 µl.

The injection mode was also optimized. The introduction of the sample into the gas chromatograph is a significant step, influencing sensitivity, accuracy, precision and matrix effect (Haslová and Zrostlíkova, 2003). At present, the use of pulsed splitless injection for the determination of trace pollutants has been often reported (Ling et al., 2006). This injection mode increases the gas pressure on the head of the injector (surge pressure), which leads to a faster transport of the sample vapour onto the column, and may consequently avoid thermal discrimination effects and heat degradation of more thermally labile pesticides such as dicofol, captan and folpet. Moreover, it forces less-volatile or “sticky” compounds onto the column.

Two parameters need to be optimized: pulse pressure and pulse time. Figure 12 shows the response obtained for each pesticide in a standard solution of 10 ng mL $^{-1}$ when surge pressure was tested in the range from 100 kPa to 300 KPa. A value of 300 KPa was selected with a surge time of 2 min (the same value as the optimized splitless time). Although the Programmable Temperature Vaporizer (PTV) (Stajnbahera and Zupancic, 2008) injection technique was also tested, no improvements were observed.

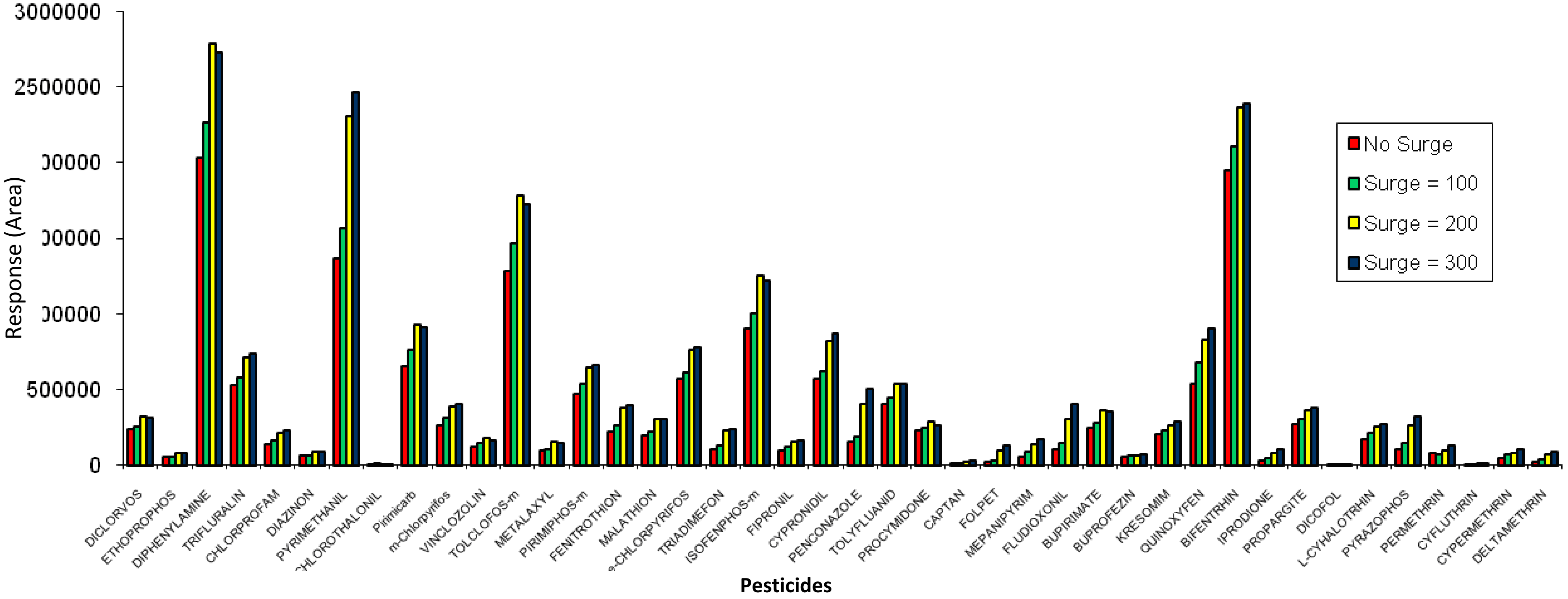


Figure 12: Response for each pesticide in a standard solution of 10 ng mL^{-1} with or without surge pressure in splitless injection mode. Surge pressure ranged from 100 kPa to 300 KPa.

VI.c.3 MS/MS experimental parameters

The use of selected reaction monitoring (SRM) mode based on the QqQ mass analyzer allows low analyte detectability and is one of the most selective approaches at present for the trace analysis of environment pollutants. However, for multiclass, multirresidue methods, a precise optimization of MS/MS parameters is needed in order to maximize the signal for each pesticide.

Optimization was performed using standard solutions of each pesticide with the mass spectrometer operating in EI ionization mode. The first step is the selection of the parent ions (precursor ions), which were chosen after examining the full scan spectra of each pesticide, taking into account a compromise between selectivity and sensitivity.

That means that the base peak was not always preferred (highest intensity), but for some pesticides a more selective peak (higher mass) was chosen (see figure 13). For some substances, two parent ions were selected, one for each transition. All the parent ions are shown in Table 34.

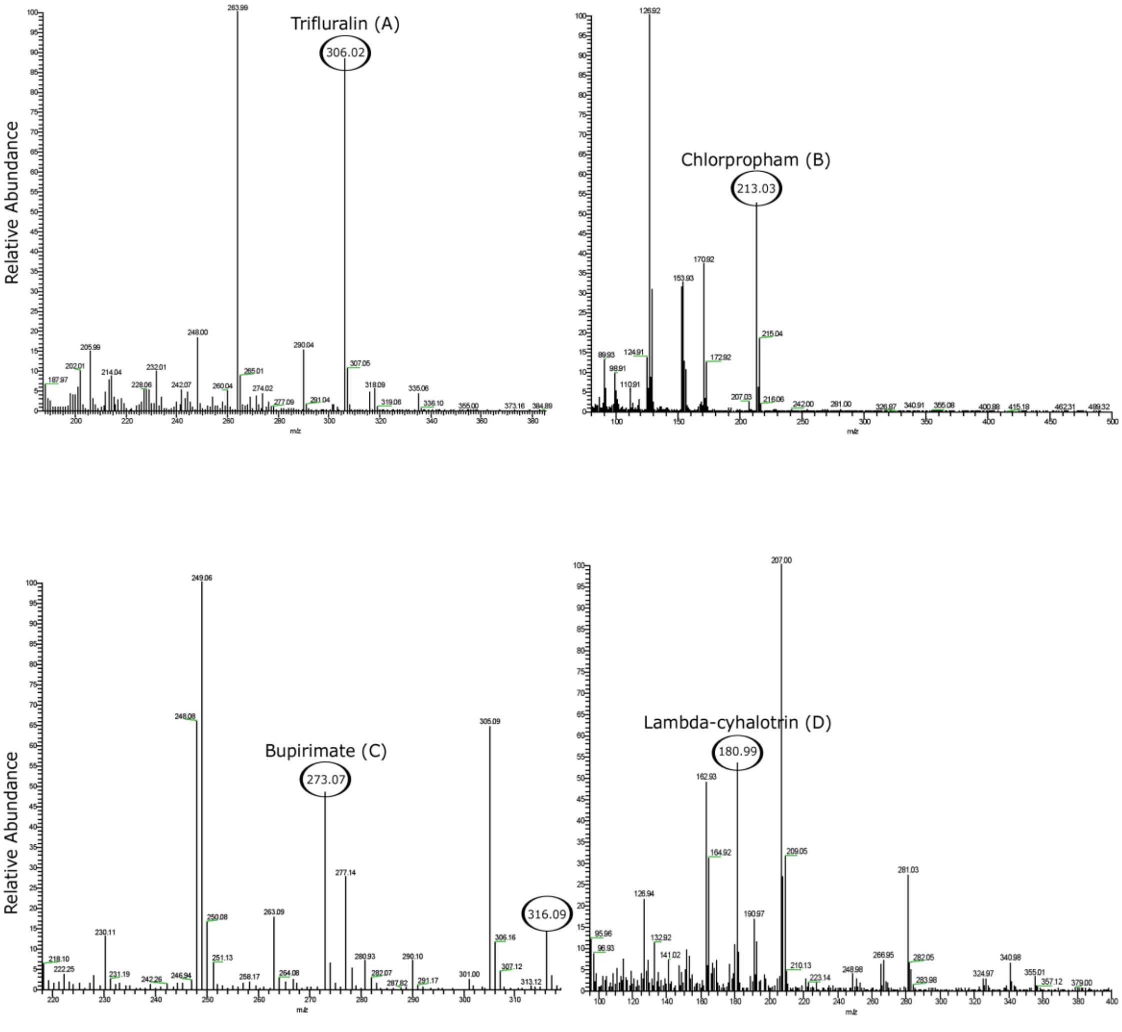


Figure 13: Full Scan spectrum and selected precursor ions for trifluralin, chlorpropham, bupirimate and lambda-cyhalotrin in a standard solution of pesticides (1 µg mL^{-1}).

Table 34: Selected GC–MS/MS experimental parameters for each pesticide

Analyte	Retention time (min)	Transitions (m/z)	Collision energy (eV)
Diclorvos	7.79	**108.96>78.95**[1]/185.02>92.96	5/10
Ethoprophos	10.99	157.91>129.81/**157.91>113.82**	5/5
Diphenylamine	11.04	**169.06>168.05**/169.06>167.04	10/20
Trifluralin	11.07	**306.16>264.10**/306.16>159.95	5/20
Chlorpropham	11.23	213.03>126.96/**213.03>170.98**	10/5
Diazinon	12.56	**179.13>137.04**/179.13>164.06	20/20
Pyrimethanil	12.87	**199.18>198.16**/198.11>117.95	10/30
Chlorothalonil	13.05	**266.97>132.88**/266.99>230.97	40/20
Pirimicarb	13.24	**166.21>95.90**/238.12>166.09	10/10
Chlorpyrifos-m	13.87	**286.06>271.03**/286.06>240.98	10/10
Vinclozolin	13.96	212.04>144.91/**212.04>171.96**	20/10
Tolclofos-methyl	14.11	**265.04>250.05**/265.04>220.03	10/20
Metalaxyl	14.22	**206.16>131.97**/206.16>116.94	20/40
Pirimiphos-m	14.53	**290.16>233.11**/290.08>124.89	10/10
Fenitrothion	14.77	**277.19>260.09**/277.19>108.98	5/20
Malathion	14.90	173.08>126.96/**173.08>98.89**	5/10
Chlorpyrifos-e	15.10	**314.07>257.99**/198.89>170.92	10/10
Triadimefon	15.48	**208.09>181.02**/208.09>110.88	5/20
Isofenphos-m	15.90	**199.04>120.92**/241.17>199.06	10/5
Fipronil	16.09	367.02>255.02/**367.08>213.03**	20/30
Penconazole	16.38	**248.13>156.97**/248.13>192.04	20/10
Tolyfluanid	16.45	**237.94>136.98**/136.99>91.02	5/20
Procymidone	16.79	283.16>255.16/**283.16>95.99**	5/5
Captan	16.92	**148.99>104.94**/148.99>79.01	5/20
Folpet	17.14	**260.03>129.92**/260.03>232.07	10/5
Mepanipyrim	17.78	**222.14>206.12**/223.23>207.17	20/20
Fludioxonil	18.16	248.14>153.98/**248.14>126.96**	10/20
Bupirimate	18.45	**273.23>193.19**/316.10>208.25	5/5
Kresomin-methyl	18.53	206.05>131.03/**206.05>116.00**	5/5
Quinoxyfen	20.84	272.13>237.16/**237.04>208.11**	5/20
Propargite	21.47	**135.05>107.02**/135.05>76.99	5/30
Bifenthrin	22.46	**181.05>165.01**/181.05>166.04	20/5
Iprodione	22.47	**314.08>245.02**/314.08>271.16	5/5
Dicofol	23.09	250.99>110.94/**250.99>138.94**	40/5
Lambda-cyhalothrin	24.38	196.99>141.02/**181.02>151.97**	5/20
Pyrazophos	24.83	373.00>232.19/**221.17>193.04**	5/5
Permethrin	26.03	**183.07>168.01**/183.07>153.02	5/5
Cyfluthrin	27.08	206.02>151.00/**206.02>177.09**	5/20
Cypermethrin	27.72	**181.07>152.20**/163.01>126.98	20/5
Deltamethrin	31.48	252.88>93.18/**180.98>151.92**	20/5

[1] Transition in bold used for quantification

Secondly, two transitions were monitored for each pesticide after checking the fragmentation of each parent ion. The software permits a rapid evaluation of all product ions formed from applying an energy ramp between 5-30 eV. Finally, the SRM collision energy was optimized for each selected transition. As an example, figure 14 shows the responses for the two SRM transitions for bifenthrin, bupirimate and penconazole when collision energies ranging from 5 to 60 eV were applied. In general, when energies higher than 30 eV were used, the signal decreases dramatically. The optimized collision energies are summarized in Table 34.

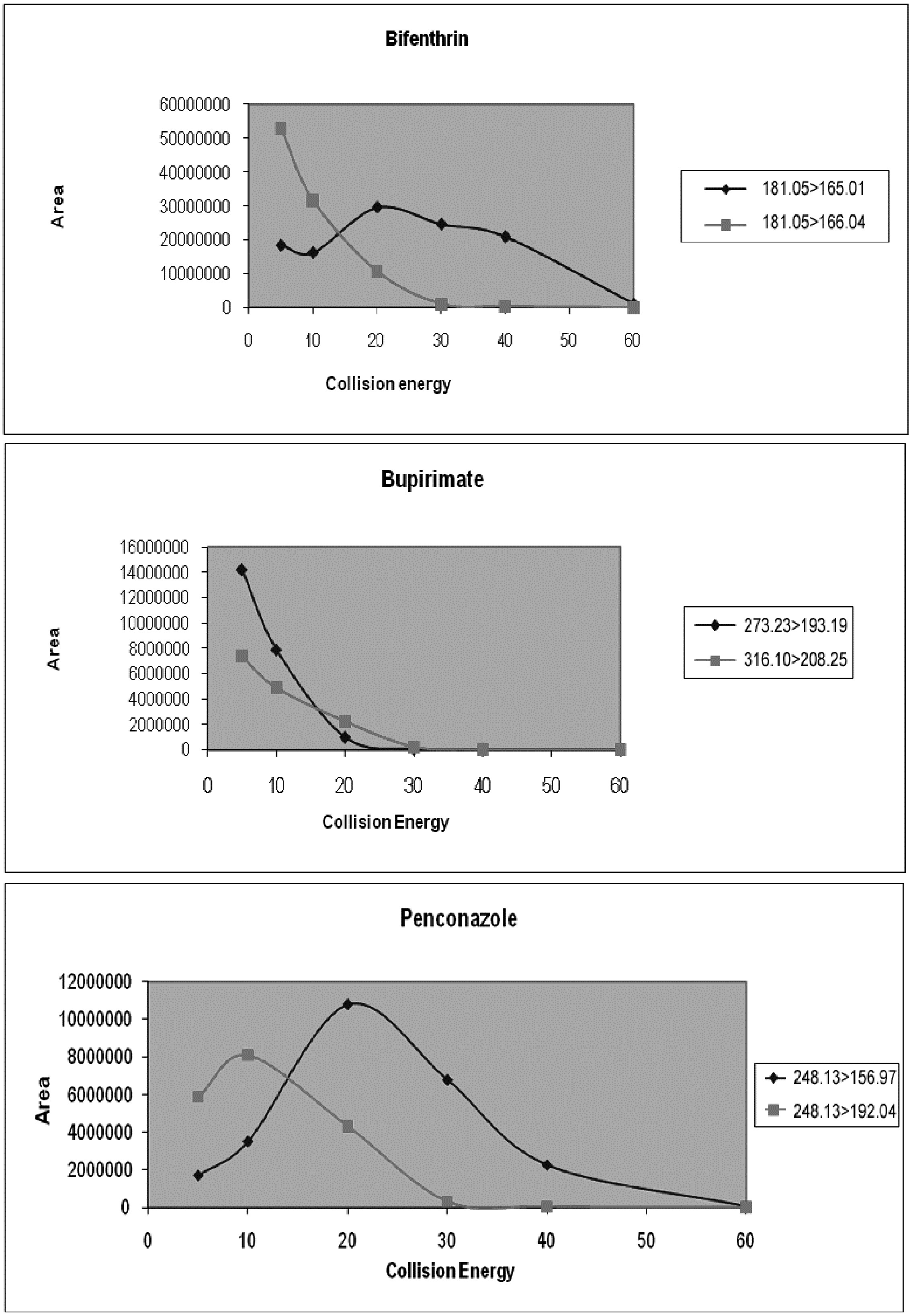


Figure 14: Responses for two SRM transitions for bifenthrin, bupirimate and penconazole applying collision energies from 5 to 60 eV during MS/MS optimization.

Based on the elution profile of the pesticides, a time-scheduled acquisition method was built up, comprising 10 time windows (segments) each comprising between 8 to 12 transitions. For each transition, an appropriate scan time (dwell time) was fixed, taking into account that increasing dwell time will increase the signal to noise ratio, but over long dwell times may result in insufficient time points being sampled in the peak (at least 12 peaks across any peak is a good practice). The scan time selected was 0.01 to 0.1 s.

In SRM mode the quadrupole filters Q1 and Q2 are working in conjunction and both are parked on a particular m/z value. The values of some relevant parameters, such as peak width and scan width, need to be chosen to improve selectivity. The peak width is related to mass resolution. In general, we have used 0.7 Full Width Half Maximum (FWHM), which is equivalent to 1 mass width at base of peak, however, in some cases a higher resolution of 0.4 FWHM could be used if there are interfering compounds with very similar masses. However, in this case, the mass calibration of the instrument must be working very well because the mass could be missed completely with this very narrow width.

Another parameter affecting the selectivity of the system is the scan width. The default width is 1 amu. This means that if we have a target m/z of 350 we actually measure every mass from 349.50 – 350.49. Reducing the scan width can also reduce the amount of noise being measured and therefore can improve the signal to noise ratio, however, it is important to be centered on the mass of interest. This means avoiding the use of nominal masses when setting up a SRM transition and instead using the correct decimal. Two decimals have been used for all the transitions.

VI.c.4 Method Validation

Linearity was studied using matrix matched standards, analyzing each of them in triplicate at five concentrations in the range 1-80 ng mL^{-1} in vial. The limit of quantification (LOQ) was established by checking the signal to noise (S/N) ratio of the quantification ion at decreasing concentrations in a spiked matrix solution, establishing it at S/N>10. The signal to noise ratio for the confirmation ion was in all cases above 3.

Matrix matched calibration plots showed good linearity with correlation coefficients (R^2) > 0.99 between 1-80 ng mL^{-1} in vial. The specificity of the method was tested by analyzing blank samples. The absence of any chromatographic peak at exactly the same retention time of the target pesticides indicated there were no matrix compounds that might give a false positive signal in these samples.

There is no available reference material for pesticides in airborne particulate matter, so the accuracy (recovery) of the method was carried out using spiked blank samples. Spiked filters were obtained by adding mixed working solution at three concentration levels (n=5) to the blank filters.

Accuracy and precision were estimated by means of recovery experiments (n=5) at three concentration levels (10, 20 and 40 pg m^{-3}). Table 35 shows the results obtained for each compound. As it can be seen, most pesticides presented suitable recoveries with values between 70 and 120% at three spiked levels and CV < 30%. The limit of quantification (LOQ) ranged from 1.32 to 39.47 pg m^{-3} when air volumes of 760 m^3 were collected (see Table 35).

Table 35: Mean recoveries, coefficients of variation and limits of quantification (n = 5) from spiked PM 10 filters

	LEVEL 1 (10 ng ml^{-1})		LEVEL 2 (20 ng ml^{-1})		LEVEL 3 (40ng ml^{-1})		LOQ
	Recovery (%)	CV (%)	Recovery (%)	CV (%)	Recovery (%)	CV (%)	(pg m^{-3})
Bifenthrin	95	17	90	9	99	9	1.32
Bupirimate	-	-	-	-	95	30	39.47
Captan	48	42	63	23	95	9	
Chlorothalonil	73	11	78	9	89	7	3.95
Chlorprofam	120	18	112	11	98	10	6.58
Chlorpyrifos-e	108	19	101	14	104	7	1.32
Chlorpyrifos-m	110	18	109	8	97	8	2.63
Cyfluthrin	-	-	-	-	102	30	39.47
Cypermethrin	84	30	71	11	92	8	13.16
Deltamethrin	82	18	77	4	111	14	13.16
Diazinon	108	10	110	22	91	10	1.32
Diclorvos	101	20	97	20	107	7	2.63
Dicofol	70	20	115	20	72	25	13.16
Diphenylamine	100	12	75	14	92	19	3.95
Ethoprophos	85	17	100	7	112	8	13.16
Fenitrothion	102	18	90	11	102	9	6.58
Fipronil	100	18	98	11	109	10	3.95
Fludioxonil	94	25	84	14	114	18	1.32
Folpet	63	7	83	17	99	10	13.16
Iprodione	81	19	80	17	120	18	13.16
Isophenfos-m	70	25	73	9	93	9	2.63
Kresomim-m	117	22	100	6	96	8	1.32
L-cyhalotrin	73	23	73	8	100	7	13.16
Malathion	104	14	100	13	92	4	2.63
Mepanipyrim	-	-	-	-	108	30	39.47
Metalaxyl	95	21	86	12	94	11	3.95
Penconazole	87	12	92	20	120	17	1.32
Permethrin	100	30	71	11	101	16	6.58
Pirimicarb	-	-	-	-	-	-	-
Pirimiphos-m	120	20	115	23	92	10	6.58
Procymidone	98	8	99	10	98	8	2.63
Propargite	91	11	88	11	76	26	13.16
Pyrazophos	76	14	82	7	101	14	2.63
Pyrimethanil	-	-	-	-	61	32	
Quinoxyfen	96	14	85	11	91	13	1.32
Tolclofos-m	111	22	105	9	98	5	1.32
Tolylfluanid	109	18	100	8	100	8	2.63
Triadimefon	108	23	94	6	95	7	3.95
Trifluralin	105	20	108	8	103	6	1.32
Vinclozolin	104	24	109	11	105	8	2.63

Two pesticides (pyrimethanil and pirimicarb) provided bad recoveries at all levels. Moreover, bupirimate, cyfluthrin and mepanipyrim presented good recoveries only at high levels. For these five pesticides, further studies are necessary in order to achieve better knowledge about this problem. Additionally, captan presented low recoveries, especially at the lowest level. This is a thermally labile pesticide that degrades in the injector, and it is difficult to measure in multiresidue analysis (Walorczyk, 2008). Dicofol and folpet also are subject to difficulties related to their degradation.

For a positive identification (confirmation criteria) in accordance with the EU guidelines (SANCO 10684/2009), the following rules were applied: i) two or more SRM transitions were monitored per compound, ii) the GC relative retention time of the analyte in the sample had to be within 0.5% of the retention time in the standard, iii) the relative abundance of the SRM transition signals had to be within 20-50% of the ratio obtained for the standards, and iv) the S/N ratio of the two diagnostic ions had to be >3.

VI.c.5 Study of the matrix effect

The matrix effect was evaluated by comparing the response of reference standards prepared in pure solvent with the response of matrix matched standards. The ratio between response in matrix and response in pure solvent was used as the absolute matrix effect. Figure 15 shows the matrix effect tested at a level of 20 ng mL^{-1}. Contrary to what usually happens with LC-MS/MS, most pesticides showed a high signal enhancement in the presence of matrix (without clean-up). However, for all pesticides this severe matrix effect decreased when a GPC clean-up step was added to the analytical procedure.

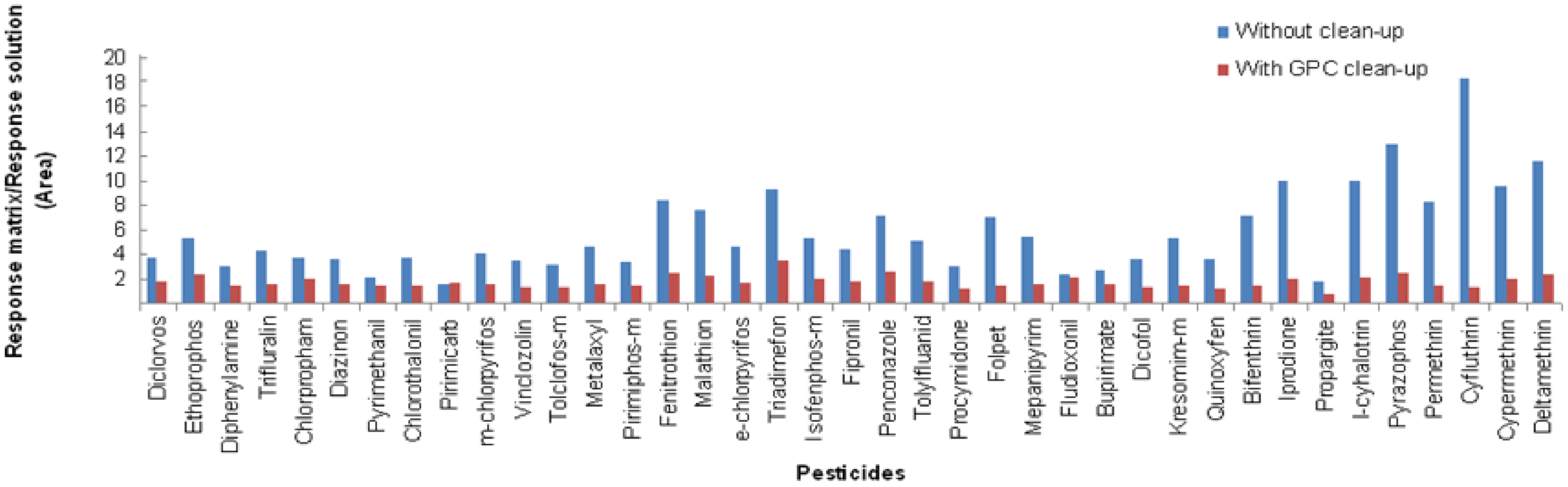


Figure 15: Matrix effect observed for each pesticide with and without GPC clean-up in spiked filters (n=3) at 20 ng mL^{-1}

Matrix-induced enhancement occurs mainly because matrix components mask active sites in the injector and column, minimizing the adsorption and decomposition of pesticides (Poole, 2007). Despite the matrix burden reduction, the matrix enhancement is still high. Therefore, an appropriate calibration method (matrix matched standards) needs to be used to aid accurate quantification (Garrido et al., 2009).

The introduction of a clean-up step also reduces the build-up of matrix components in the GC system that may negatively affect its robustness and GC-MS/MS performance. Likewise, a heavy matrix burden generally results in an increase of system maintenance requirements that diminishes productivity.

VI.c.6 Analysis of air samples

In order to study the applicability of the methodology developed, 38 samples were collected in a rural station situated in Alzira (center of Valencia region) during the spring (April and May) in 2010. The results obtained are shown in Table 36. Figure 16 shows a chromatogram of a sample collected in Alzira during June 2010.

Table 36: Concentrations of PM 10-bound pesticides (pg m^{-3}) from Alzira station in Valencia region (Spain)(N=38)[1]

Pesticide	n > LOQ	LD< n < LoQ	m	M	Mean[2]	Median[2]
Bifenthrin	33	4	1.6	83.4	24.6	18.1
Chlorothalonil	23	7	4.4	28.0	6.6	8.7
Chlorpyrifos-e	36	2	1.3	625.8	122.1	12.4
Chlorpyrifos-m	11	2	2.7	10.4	4.0	7.8
Clorpropham	4	1	7.8	9.4	7.4	9.2
Diazinon	14	0	8.1	252.9	58.3	27.8
Dicofol	12	0	14.4	53.2	19.7	16.5
Diphenylamine	10	13	4.9	6.7	5.8	-
Fipronil	1	5	-	14.0		-
Fludioxonil	10	0	9.0	38.7	19.3	16.2
Folpet	14	0	25.3	83.1	26.1	32.3
Malathion	32	3	2.9	94.6	12.1	9.0
Metalaxyl	38	0	4.4	174.9	45.4	20.6
Penconazole	22	2	1.4	44.0	5.9	4.7
Quinoxyfen	2	0	1.1	2.2	1.6	-
Triadimefon	5	5	6.0	26.9	9.9	6.1
Trifluralin	12	1	2.2	10.4	4.4	2.9
Vinclozoline	3	1	6.7	6.8	6.8	6.8

N, total samples; n, number of samples; m, minimum concentration; M, maximum concentration.

[1] PM10 of samples ranged from 7.08 to 43.43 µg m^{-3}.

[2] Mean and median values calculated only for samples with concentrations above quantification limits (LoQ).

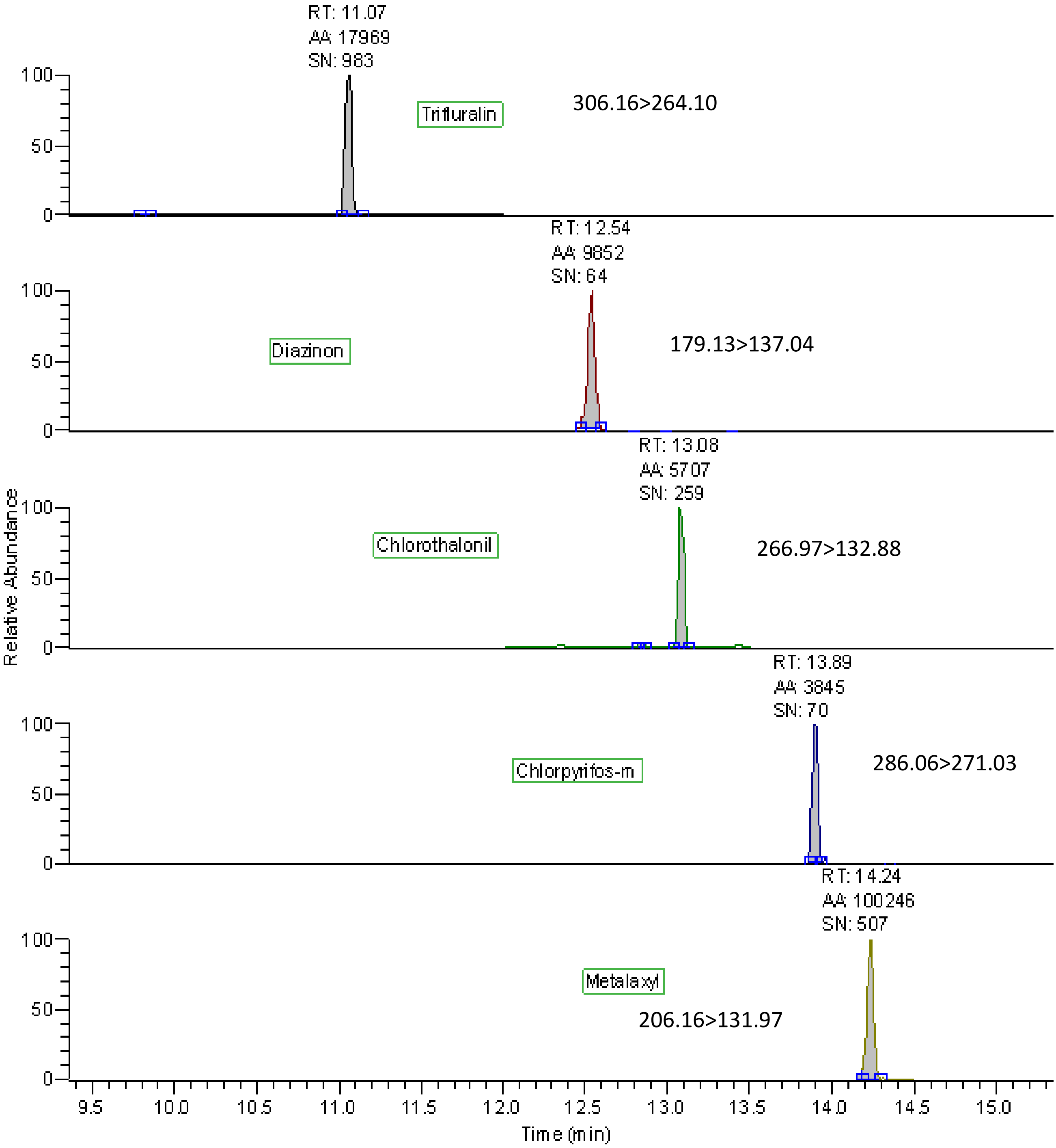


Figure 16: Ion chromatogram of a sample collected in Alzira station in June 2010 with concentrations of chlorothalonil: 2.78 pg m^{-3}, chlorpyrifos methyl: 1.6 pg m^{-3}, diazinon: 13.3 pg m^{-3}, metalaxyl: 51.9 pg m^{-3}, trifluralin: 2.9 pg m^{-3}

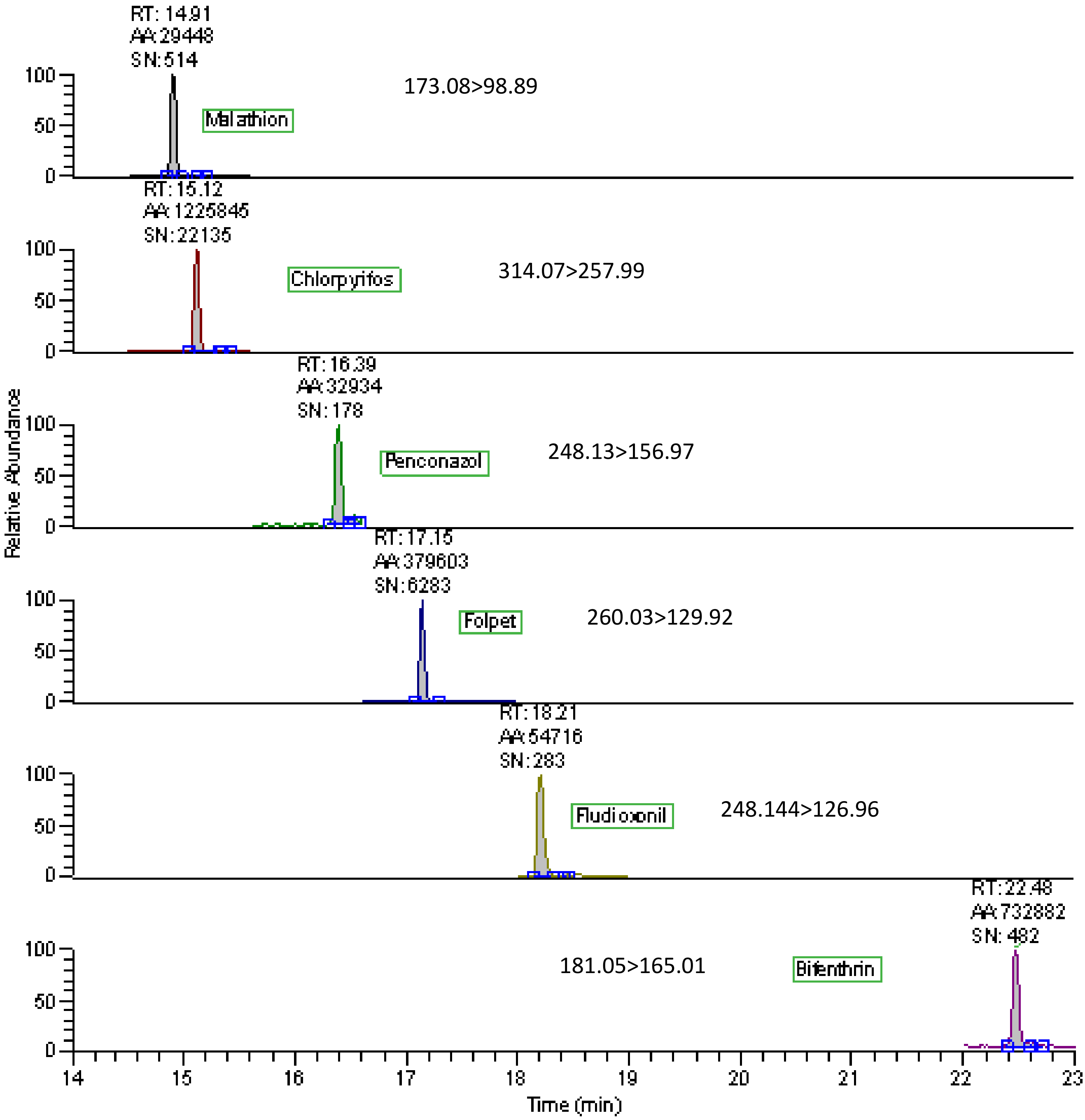


Figure 16 (continued): Ion chromatogram of a sample collected in Alzira station in June 2010 with concentrations of bifenthrin: 18.1 pg m^{-3}, chlorpyrifos ethyl: 145.3 pg m^{-3}, fludioxonil: 11.8 pg m^{-3}, folpet: 83.1 pg m^{-3}, malathion: 4.9 pg m^{-3}, penconazol: 4.8 pg m^{-3}

Of the 40 active substances monitored, 18 (nine fungicides, six insecticides, two herbicides and one acaricide) were detected in at least one sample, which highlights both the applicability of the analytical method and the intense use of pesticides in this area. The frequency of detection (percentage of samples above the limit of detection, LOD) ranged from 5 to 100%, with chlorpyrifos ethyl, metalaxyl, bifenthrin, malathion, chlorothalonil, penconazole, diphenylamine, folpet, diazinon and dicofol presenting the highest detections. The concentrations of the detected pesticides ranged from 1.3 to 625.8 pg m^{-3} .

Eight of the pesticides detected (bifenthrin, penconazole, diphenylamine, dicofol, fludioxonil, fipronil, clorpropham and quinoxyfen) have not been reported previously in ambient air in literature. Bifenthrin was detected in 37 out of the 38 samples analyzed, with an average concentration (mean) of 24.6 pg m^{-3}. Bifenthrin is a synthetic pyrethroid used as an insecticide and acaricide in vegetables, fruit and grapes.

Penconazole is a fungicide applied in fruits, such as peach, apricot and apples. It was detected with a frequency of 63%, and a concentration ranging from 1.4 to 44.0 pg m^{-3}. Diphenylamine is used in warehouse treatment applied to apples and pears. Although it was excluded from the annex I of the Directive 91/414/ECC in May 2010, it can be used until May 2011. This explains its application during the sampling period, and was detected with a mean concentration of 5.8 pg m^{-3}.

Another pesticide that was detected with a high frequency (92%) is malathion. This organophosphate insecticide has been forbidden since December 2008, which means that its presence could be linked with unlawful use in citrus crops, fruits, grapes and vegetables. Three more active substances that are nowadays prohibited, such as diazinon, trifluralin and vinclozolin, have also been detected, although with less frequency.

Two pesticides were detected in all samples analyzed: chlorpyrifos ethyl and metalaxyl, with mean concentration values of 122.1 and 45.4 pg m^{-3}, respectively. The first is an insecticide extensively used mainly for the treatment of citrus crops, while the fungicide metalaxyl is used to protect grapes and vegetables.

The 18 pesticides detected present a wide range of vapour pressures, from relatively high volatility ($Vp > 10^{-3}$ Pa), such as chlorpiriphos ethyl, diazinon and trifluralin, to low volatility ($Vp < 10^{-5}$), such as dicofol, fludioxinil or fipronil. However, their occurrence in ambient air and specifically in the particulate phase depends not only on its volatility, but also on its atmospheric half-life, the conditions of its application and the meteorological conditions. Locally high concentrations of pesticides in air are very seasonal and are correlated to local use patterns. The highest concentrations in air usually occur in the spring and summer months, coinciding with application times and warmer temperatures.

VI.d CONCLUSIONS

A sensitive and confirmatory method to analyze 40 CUPs in airborne particulate matter (PM 10) was developed. The method includes an extraction of pesticides by MAE, followed by GPC clean-up and injection into GC(EI)-MS/MS. GC-MS/MS with a triple quadrupole analyzer was shown to be a very suitable tool for multiresidue analysis of pesticides in ambient air. The selection and optimization of two SRM transitions, gives excellent sensitivity and selectivity, and the identification criteria established by the European Union was achieved.

Most pesticides showed a high signal enhancement in the presence of a matrix, but this matrix effect decreased significantly when a GPC clean-up step was added into the analytical procedure. However, in order to achieve an accurate determination, matrix matched standard calibration methodology was used to carry out quantitative analysis.

Recoveries ranged from 70 to 120%, except for pyrimethanil and pirimicarb. The limit of quantification (LOQ) ranged from 1.32 to 39.47 pg m^{-3}, when air volumes of 760 m^3 were collected.

Using the optimized method, pesticide occurrence was investigated in 38 samples from a rural station of the monitoring network of Regional Valencia Government (Spain). Eighteen out of 40 pesticides investigated were found in at least one sample: bifenthrin, chlorothalonil, chlorpyrifos ethyl, chlorpyrifos methyl, clorpropham, diazinon, dicofol, diphenylamine, fipronil, fludioxonil, folpet, malathion, metalaxyl, penconazole, quinoxyfen, triadimefon, trifluralin and vinclozolin (8 of the pesticides detected have been reported for the first time in literature).

This method could be used in monitoring programs of currently used pesticides in air, using the network of samplers which already exist to monitor particulate matter in air.

VII. CHAPTER 4

OCCURRENCE OF CURRENTLY USED PESTICIDES IN AMBIENT AIR OF CENTRE REGION (FRANCE)

VII.a INTRODUCTION

Centre Region, situated in the core of France, is one of the country's largest regions, with an area approximately 40,000 km^2. Although important cities like Tours and Orléans are located in this region (Figure 17), about 57.5% of the surface is used for agricultural activities focused mainly on arable crops (maize, soybean, wheat, sunflower, barley and beet), vineyards, vegetables and fruit trees (MAAP, 2008). These farming activities are intensive in the use of pesticides and consumed a total of 4,179 tons of active ingredients in 2001, representing about 5.5 % of the national consumption (FREDEC, 2004). France is the top consumer of pesticides in the European Union (Eurostat, 2007).

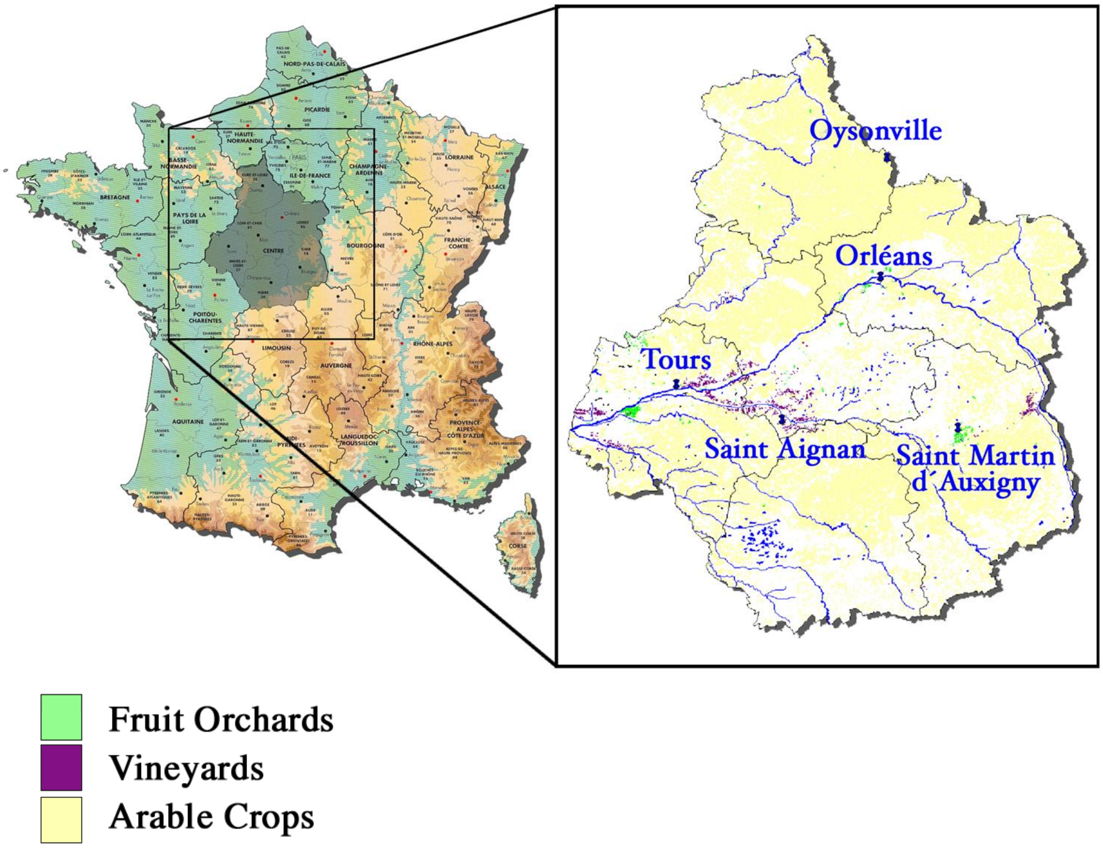


Figure 17: Sampling sites, types of agricultural crops and population density across Centre region (France)

During spray application of CUPs, a fraction of the dosage applied to the target area can be deposited onto the adjacent non-target areas (spray drift) and another fraction lost in the atmosphere. Emissions during application can range from a few percent to 20-30% (Van der Berg et al., 1999) of the dosage applied. Post-application emissions that involve volatilization from soil and plants and wind erosion of soil particles containing sorbed pesticides represent further significant pesticide input into the troposphere for several days or even weeks after application (Bedos et al., 2002) (Voutsas et al., 2005).

The FOCUS Air group (FOCUS, 2008) has considered that vapour pressure (Vp) is a key factor driving volatilization and is therefore a good trigger for screening compounds in a tiered risk assessment scheme. This group has also considered that substances applied to soil with Vp higher than 10^{-4} Pa and substances applied to plants with Vp higher than 10^{-5} Pa have a potential to reach the air, and require a risk assessment evaluation before authorisation. Moreover, it is known that semi-volatile organic compounds, such as pesticides in the atmosphere, are simultaneously present in both the gas and particulate phases (Sadiki and Poissant, 2008), and that the ability of a pesticide to travel short or long distances depends essentially on the amount of time it resides in the atmosphere, which in turn is related to the properties of the pesticide as well as meteorological factors (Addo et al., 1999).

The aim of this study is to improve the knowledge base of atmospheric behaviour of some CUPs and legacy insecticides in Centre Region, France. For this purpose, 56 pesticides (see Table 37) were monitored in three rural and two urban sites in this area during the 2006-2008 period. The concentrations measured were used to analyze the overall occurrence and the spatial and temporal variations of the pesticides detected.

Table 37: Physicochemical properties, agricultural use and legal situation of pesticides studied

Pesticide	Chemical class	Agricultural use	Legal situation (European Union)	Vapour pressure (Pa) (25ºC)[3]	Henry's law constant (Pa m^3 mol^{-1})[3]	Half life[4]
Insecticides						
2,4′ DDE	Organochlorine	-	banned	-	-	
2,4′ DDD	Organochlorine	-	banned	-	-	
2,4′ DDT+ 4,4′ DDD	Organochlorine	-	banned	-	-	
4,4′ DDE	Organochlorine	-	banned	-	-	
4,4′ DDT	Organochlorine	-	banned	-	-	
α-endosulfan	Organochlorine	arable crops, vegetables	out (since 2007)	8.30E-04	1.48	
Carbaryl[1]	Carbamate	vineyard, potato, peach, apple, asparagus	out (since 2008)	4.10E-05	7.39	
Chlorpyrifos ethyl	Organophosphate	vineyard, peach, pear, apple	in	2.70E-03	6.76E-01	1.40 hours
Diazinon	Organophosphate	vegetables, fruits	out	6.09E-05	6.09E-02	1.33 hours
Esfenvalerate	Pyrethroid	arable crops, vegetables, flowers	in	6.70E-05		
Ethoprophos	Organophosphate	potato, vegetables	in	4.65E-02		0.15 days
Fenoxycarb[1]	Carbamate	vineyard, peach, pear, apple, plum	in	8.67E-07	3.30E-05	
γ-HCH	Organochlorine	-	out (since 1998)	4.40E-03	1.5E-01	
Malathion	Organophosphate	vineyard, arable crops, vegetables	out (since 2008)	5.30E-03	1.21E-2	0.41 days
Methidathion	Organophosphate	fruits	out	2.5E-04	3.3E-04	
Methomyl[1]	Carbamate	vineyard, vegetables	in	7.20E-04	2.13E-06	
Methyl parathion	Organophosphate	-	out (since 2003)	0.20E-03		
Oxydemeton-S-methyl	Organophosphate	arable crops, pear, apple	out (since 2008)	3.80E-03	<1E-05	
Phosmet	Organophosphate	pear, apple, potato	in	6.50E-05	8.25E-04	
Propargite	sulfite ester	Acaricide	in	4.00E-02	6.40E-02	

Table 37: Physicochemical properties, agricultural use and legal situation of pesticides studied (continued)

Pesticide	Chemical class	Agricultural use	Legal situation (European Union)	Vapour pressure (Pa) (25ºC)[3]	Henry's law constant (Pa m^3 mol^{-1})[3]	Half life[4]
Herbicides						
Aclonifen	diphenyl éter	arable crops (sunflower, peas), potato	in	1.60E-05	3.03E-03	1.20 days
Alachlor	Chloroacetamide	arable crops (maize, soybean)	out	2.70 E-03	4.30E-03	
Dichlobenil	Benzonitrile	Vineyard	out (since 2009)	1.44E-01	1.14	
Ethofumesate	alkylsulfonate	arable crops (beet, beans)	in	0.65E-03	6.80E-03	4.10 hours
Diflufenican	Carboxamide	arable crops (wheat, barley)	in	4.25E-06	1.18E-02	3.30 days
Metazachlor	Chloroacetamide	cabbage, arable crops (rape)	in	9.30E-05		6.50 hours
Metolachlor	Organochlorine	-	out (since 2003)	4.20E-03	2.40E-03	1.80 hours
Oxadiazon	Oxadiazole	rice, vineyard, carrot	in	1.00E-04	3.50E-02	
Oxyfluorfen	diphenyl éter	Vineyard	in	2.60E-05	8.33E-02	12 hours
Pendimethalin	Dinitroaniline	arable crops, vegetables, vineyard	in	1.94E-03	2.73	12 hours
Propachlor	Chloroacetamide	cabbage, onion	out (since 2009)	0.01	3.65E-03	
Propyzamide	Benzamide	arable crops, vegetables	in	5.80E-05	9.9E-04	
Tebutam	Benzamide	-	out (since 2003)			
Trifluralin	Dinitroaniline	arable crops (soybean, sunflower), cabbage	out (since 2009)	6.10E-03	15	5.3 hours
Acetochlor[2]	Chloroacetamide	arable crops (maize)	in	2.20E-05		
Oryzalin[1]	Dinitroaniline Sulfonamide	vineyard, fruit trees, asparagus	in	<1.30E-06	<1.73E-04	
Dimethenamid	Amide	potato, arable crops (beet), onion	out (since 2008)	3.67E-02	8.32E-03	2.45 hours

Table 37: Physicochemical properties, agricultural use and legal situation of pesticides studied (continued)

Pesticide	Chemical class	Agricultural use	Legal situation (European Union)	Vapour pressure (Pa) (25ºC)[3]	Henry's law constant (Pa m^3 mol^{-1})[3]	Half life[4]
Fungicides						
Azoxystrobin	Strobilurin	arable crops, vegetables, vineyard	in	1.10E-04	7.30E-09	
Captan	Phtalimide	vineyard, fruit tres	in	<1.30E-03	3.00E-04	1.50 hours
Chlorothalonil	Phtalimide	arable crops, vegetables, fruit trees	in	7.60E-05	2.50E-02	4.70 years
Cyprodinil	Pyrimidine	arable crops (wheat, barley), pear, apple	in	5.10E-04	6.60E-03	1.20 hours
Dimethomorph I	Morpholine	vineyard, flowers	in	9.70E-07	5.40E-06	3.60 hours
Dimethomorph II	Morpholine	vineyard, flowers	in	1.00E-06	2.50E-05	3.60 hours
Epoxiconazole	Triazole	arable crops	in	1.00E-05	4.71E-04	4 days
Fenpropidin	Piperidine	arable crops (wheat, barley)	in	1.70E-02	10.70	1 hour
Fenpropimorph	Morpholine	arable crops (wheat, barley, sunflower)	in	3.50E-03	0.30	2.90 hours
Fluazinam	phenylpyridinamine	vineyard, potato	in			>48 hours
Fludioxonil	Phenylpyrrole	Vineyard	in	3.90E-07	5.40E-05	3.60 hours
Folpet	Phtalamide	potato, vineyard, apple, pear, arable crops	in	2.10E-05	7.80E-03	6.16 hours
Spiroxamine	Morpholine	arable crops, vineyard	in	5.7E-03	2.50E-03	1 hour
Tolylfluanid	Phenylsulfamide	almond, hazelnut, apple, pear, vineyard	in	2.00E-04	7.70E-02	
Vinclozolin	Dicarboxamide	vineyard, vegetables	out (since 2007)	1.30E-04	1.43E-02	
Iprodione[2]	Dicarboximide	vineyard, vegetables, fruit tres	in	5.00E-07	7.00E-06	85 min

[1] Pesticides not searched in 2006-2007

[2] Pesticides not searched in 2006

In = included, Out= excluded from the annex I Directive 91/414

[3] (BCPC ,2009)

[4] (EFSA, 2005-2009), (EC, 1999-2007)

VII.b MATERIALS AND METHODS

VII.b.1 Sampling, site characterization and meteorological parameters

Sampling was undertaken at two urban and three rural sampling sites located throughout the Centre Region, France (Figure 17, Table 38). Sampling was carried out according to (AFNOR, 2007a), using a Partisol 2000 low-volume sampler purchased from the Thermo Electron Corporation (East Greenbush, NY, USA).

Particulate and gaseous samples were collected together on 47-mm diameter quartz fibre filters (QFFs) followed by 26 x 76 mm (diameter x length) polyurethane foam (PUF) plugs. The filters and PUF plugs were exposed weekly at an air flow of 1 m^3 h^{-1}. The total air volume collected was approximately 168 m^3.

After sampling, and prior to extraction, the sampling module containing the particulate and gaseous phases was wrapped with aluminium foil and sealed in polyethylene bags. These were stored in the dark below 4°C for up to 24 h after sampling, or at -18°C when 24 h had passed since the sampling.

Meteorological data, such as air temperature (T), wind direction (WD) and wind speed (WS), were collected from two weather stations located in Orléans and Tours.

Table 38: Description of the sampling sites and periods[1]

Sampling site	Latitude	Longitude	Description
Tours (To)	47°25’62’’N	00°41’90’’E	Commercial and residential area. Samples collected at ground level.
Orléans (Or)	47°91’19’’N	01°89’54’’E	Parking in the city centre. Samples collected at 3.5 m above ground level.
Saint Martin d’Auxigny (SM)	47°20’34’’N	02°42’37’’E	Rural and agricultural area surrounded by apple tree fields. Samples collected at ground level.
Oysonville (Oy)	48°23’35’’N	01°56’57’’E	Rural and intensive agricultural area with mainly arable crops such as maize, wheat, soybean, barley and sunflowers. Samples collected at ground level.
Saint Aignan (SA)	47°26’63’’N	01°37’17’’E	Rural and agricultural area (vineyards). Samples collected at 6 metres above ground level.

[1] Sampling campaign in 2006: 14 March-12 September (26 sampling weeks). Sampling campaign in 2007: 11 April-11 July, except for Saint Martin d’Auxigny (until 11 September). Sampling campaign in 2008: 9 April-2 July, except for Saint Martin d’Auxigny (until 5 November).

VII.b.2 Sample analysis

The extraction of the studied pesticides (see Table 37) from the samples was carried out using an ASE 300 PLE system (Dionex, Sunnyvale, CA, USA). QFFs and PUFs were extracted together in stainless-steel cells. The extraction conditions were as follows: extraction solvent, dichloromethane; oven temperature, 90°C; pressure, 100 bars; heat-up time, 5 min; static cycles, 4; static time, 5 min. The flush volume amounted to 90% of the extraction cell volume. The extracted analytes were purged from the sample cell using pressurized nitrogen for 150 s (AFNOR procedure, 2007b).

Prior to extraction, each sample was fortified with a mixture containing 8.5 ng each of d_{14} trifluralin and d_{10} chlorpyrifos, which served as surrogates for assessing method recoveries. Samples were spiked with d_{14} trifluralin and d_{10} chlorpyrifos, producing within laboratory recoveries ranging from 75 to 115%. Afterwards, the extract was divided into two fractions. One fraction was concentrated by N_2 and solvent-exchanged with methanol.

Sample volume was adjusted to 1 mL and analyzed using an Alliance (Waters, Milford, MA, USA) liquid chromatograph equipped with a Quattro (Micromass, UK) mass spectrometer in Selected Reaction Monitoring Mode (SRM), in order to detect and quantify captan, carbaryl, epoxiconazole, fenoxycarb, phosmet, iprodione, methomyl, oryzalin, oxydemeton methyl and fluazinam. Experimental parameters for LC-MS/MS are shown in Table 39.

The other fraction was redissolved with 1 mL of hexane and analyzed by gas chromatography coupled with mass spectrometry (GC-MS) using an Agilent gas chromatograph equipped with an Agilent 5973 mass spectrometer (Agilent, Santa Clara, CA, USA) in SIM mode (Selected Ion Monitoring), following the AFNOR procedure (2007b). Selected ions and limits of detection for GC-MS are shown in Table 40. Concentrations were not recovery corrected.

Table 39: Selected LC–MS/MS experimental parameters for each pesticide[1]

Pesticide	Precursor ion (m/z)	Products ions (m/z)	Polarity ESI	LOQ (ng m^{-3})
Carbaryl	202	145.127	+	0.05
Epoxiconazole	330	121.101	+	0.05
Fenoxicarbe	302	88.116	+	0.05
Phosmet	318	160.133	+	0.05
Iprodione	228	141	-	0.05
Methomyl	163	88.106	+	0.12
Oxydementon methyl	247	169.109	+	1.19

[1] Chromatographic conditions: column; Gemini-NX3u C18 100A (Phenomenex). Eluents; water and methanol with 5mM of formate ammonium in a gradient mode. Flow rate; 200 µl min^{-1}.

Table 40: Selected ions for GC–MS analysis in SIM mode, and LOQ for each pesticide Table

Pesticide	Ions (m/z)	LOQ (ng m^{-3})
2,4’ DDD/ 4,4’ DDD	235, 237, 165/235, 237, 165	0.05
2,4’ DDE/ 4,4’ DDE	246, 248, 318/246, 318, 316	0.05
2,4’ DDT/4,4’ DDT	235, 237, 165/235, 237, 165	0.05
Acetochlor	146, 162, 223	0.05
Aclonifen	264, 212, 194	0.24
α-endosulfan	231, 207, 195	0.24
γ-HCH	219, 183, 181	0.05
Alachlor	237, 160, 146	0.05
Azoxystrobin	388, 372, 345	0.24
Chlorothalonil	268, 266, 264	0.27
Chlorpyrifos ethyl	316, 314, 286	0.05
Cyprodinil	225, 224, 210	0.05
Diazinon	304, 179, 152	0.05
Dichlobenil	173, 171, 136	0.05
Diflufenican	267, 246, 226	0.05
Dimethenamid	230, 203, 154	0.05
Dimethomorph	389, 387, 301	0.24
Esfenvalerate	181, 167, 152	0.24
Ethofumesate	286, 207, 161	0.24
Ethoprophos	200, 158, 139	0.05
Ethyl parathion	291, 235, 218	0.24
Fenpropidin	273, 145, 117	0.05
Fenpropimorph	303, 173, 145	0.05
Fludioxonil	248, 182, 154	0.05
Folpet	295, 285, 260	0.24
γ-HCH	219, 183, 181	0.12
Malathion	285, 256, 173	0.05
Metazachlor	277, 209, 134	0.05
Methidathion	146, 145, 125	0.05
Methyl parathion	263, 233, 125	0.05
Metolachlor	162, 238, 240	0.05
Oxadiazon	344, 302, 258	0.05
Oxyfluorfen	331, 302, 274	0.05
Pendimethalin	281, 252, 191	0.05
Propachlor	176, 120, 93	0.36
Propargite	230, 215, 173	0.24
Propyzamide	255, 175, 173	0.05
Spiroxamine	198, 126, 100	0.05
Tebutam	233, 190, 106	0.05
Tolylfluanid	346, 238, 181	0.05
Trifluralin	306, 264, 290	0.12
Vinclozolin	285, 213, 212	0.05

VII.b.3 Quality control protocol

Each set of samples were analysed under quality assurance protocols. In order to determine the pollutant backgrounds, a blank sampling module (QFF +PUF) and a spiked sampling module were employed as the control and quality-control samples during deployment, retrieval and transportation of the field filters. The analysis of samples was performed after sampling or after a storage period at -18^{o}C.

The retention capacity for PUF and the extraction recoveries for PUF plus filter were tested for all pesticides according to AFNOR standards (2007a), obtaining retention capacities from 60 to 120% and recoveries from 70 to 110%, respectively.

VII.c RESULTS AND DISCUSSION

VII.c.1 Overall air pesticide concentration

Three sampling campaigns were conducted on five sampling sites during the 2006-2008 study period. With few exceptions (see Table 38), the campaigns were conducted from April to mid-July as a consequence of the results of the previous studies for the period 2001-2005 (Lig'Air, 2005), which linked the presence of CUPs mainly to the growing season. The overall frequency of detection and the average pesticide concentrations are summarized in Table 41.

Table 41: Overall concentrations (gas +particulate phases) of detected pesticides in all sampling sites during the period 2006-2008

Pesticide	Frequency of detection (%)	Range (ng m^{-3})	Average+/-SD[3] (ng m^{-3})
4,4' DDD[1]	7	0.37 - 0.55	0.45 ± 0.06
4,4' DDE[2]	3	0.27 - 0.36	0.31 ± 0.03
Acetochlor[1]	52	0.30 - 8.87	1.32 ± 1.48
Aclonifen[2]	7	0.23 - 4.15	1.37 ± 0.81
α-endosulfan[2]	28	0.37 - 81.31	4.31 ± 10.99
Alachlor[2]	44	0.12 - 6.03	0.64 ± 0.75
Azoxystrobin[2]	1	0.66 - 1.79	1.21 ± 0.57
Captan[2]	3	1.19 - 67.62	22.49 ± 20.53
Chlorothalonil[2]	58	0.11 - 107.93	12.15 ± 17.05
Chlorpyrifos ethyl[2]	42	0.11 - 97.77	2.86 ± 10,96
Cyprodinil[2]	24	0.12 - 3.29	0.55 ± 0.67
Diazinon[2]	1	0.28-1.49	0.89 ± 0.85
Dichlobenil[2]	10	0.10 - 2.39	0.51± 0.64
Diflufenican[2]	5	0.11 - 0.56	0.22 ± 0.13
Dimethenamide[2]	2	0.16 - 0.74	0.38 ± 0.21
Dimethomorph I[2]	0.38	-	0.7
Dimethomorph II[2]	2	0.13 - 0.65	0.26 ± 0.22
Epoxiconazole[2]	17	0.12 - 3.99	0.44 ± 0.65
Ethofumesate[2]	2	0.54 - 1.16	0.92 ± 0.25
Ethoprophos[2]	1	0.21 - 0.48	0.35 ± 0.19
Fenpropidin[2]	30	0.11 - 3.54	0.51± 0.64
Fenpropimorph[2]	28	0.12 - 13.20	0.99 ± 2.10
Fluazinam[2]	3	0.12 - 2.20	0.47 ± 0.70
Fludioxonil[2]	1	0.53 - 2.08	1.21 ± 0.79
Folpet[2]	10	0.14 - 82.22	13.96 ± 18.37
γ-HCH[2]	76	0.12 - 1.21	0.34 ± 0.19
Iprodione[1]	0.68	-	0.18
Malathion[2]	0.38	-	0.21
Metazachlor[2]	8	0.17 - 3.13	0.93 ± 0.90

Table 41: Overall concentrations (gas +particulate phases) of detected pesticides in all sampling sites during the period 2006-2008 (continued)

Pesticide	Frequency of detection (%)	Range (ng m^{-3})	Average+/-SD[3] (ng m^{-3})
Methidathion[2]	0.38	-	0.27
Metolachlor[2]	37	0.12-2.49	0.37 ± 0.36
Oxyfluorfen[2]	3	0.65-3.01	1.10 ± 0.75
Parathion methyl[1]	1	0.67-0.75	0.71± 0.05
Pendimethalin [2]	66	0.07-117.33	1.84 ± 9.31
Phosmet[2]	3	0.15-1.33	0.56 ± 0.41
Propachlor[2]	20	0.14-3.48	0.53 ± 0.66
Propargite[2]	2	2.80-45.60	13.24 ±18.20
Spiroxamine[2]	34	0.15-9.01	1.12 ± 1.65
Tolylfluanid[2]	23	0.10-86.42	6.92 ± 15.48
Trifluralin[2]	84	0.12-58.79	1.93 ± 5.75
Vinchlozolin[2]	2	0.14-0.19	0.17 ± 0.02

[1] Total samples analyzed (N) = 149

[2] Total samples analyzed (N) = 262.

[3] The average and 95% confidence intervals were calculated from the arithmetic mean and standard deviation (SD) of samples with concentration superior to LOD.

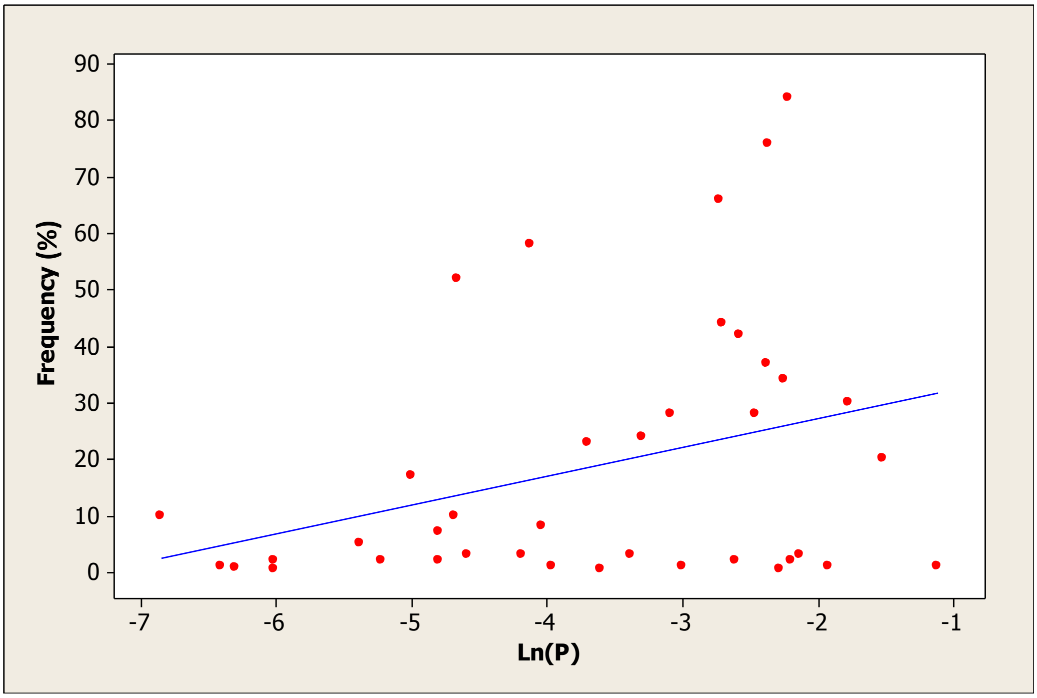
Of the 56 active substances monitored during this three-year study, including currently used and legacy pesticides, 41 were detected in the atmosphere in at least one sample, which highlights the intense use of pesticides in this region. Among the herbicides, 13 out of 18 substances monitored were detected at frequencies ranging from 2 to 84 %, with trifluralin, pendimethalin, acetochlor, alachlor and metolachlor presenting the highest detections, ranging from 37 to 84 %. In a study carried out by Peck and Hornbuckle (2005) in the atmosphere of Iowa during the period 2000-2002, these five herbicides showed a similar frequency of detection ranging between 18 and 78%. The mentioned herbicides, along with others less-frequent ones like aclonifen, dichlobenil, dimethenamid and oxyfluorfen, were found both in rural and urban (receptor) sites. All these herbicides are relatively volatile (Vp > 10^{-3} Pa) or have medium volatility (10^{-3}-10^{-5} Pa), with an atmospheric half life ($t_{1/2}$) of a few hours.

All sixteen monitored fungicides were detected, with frequencies ranging from 0.38 to 58%. The most frequent fungicides were chlorothalonil (58%) and fenpropidin (30%). Others, such as spiroxamine, fenpropimorph, cyprodinil, tolyfluanid and epoxiconazole, were also found in all sampling sites with frequencies higher than 17%. This is the first time these last five fungicides have been reported in literature. Some of them have a relatively high volatility e.g. fenpropidin or spiroxamine, while others have medium to low volatility, which is the case with chlorotalonil, folpet or iprodione (see Table 37).

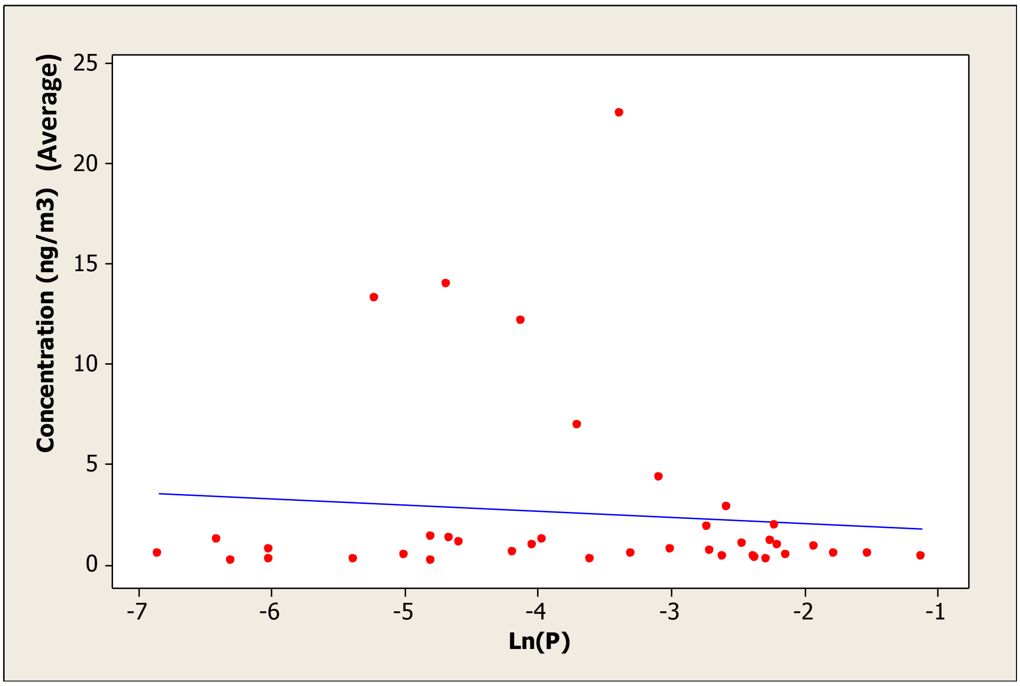
With respect to insecticides, 12 of the 22 substances monitored were detected, at frequencies ranging from 0.38 to 76%. Apart from the persistent insecticide lindane (γ-HCH), which has been banned since 1998, the most frequently detected insecticides were chlorpyrifos ethyl, which was observed at all sites with an overall frequency of 42%, and α-endosulfan, which was found at all sites with a detection frequency of 28%. The other insecticides detected presented very low frequencies (<7%).

For the pesticides studied, there was a statistically significant correlation between frequency of detection and the natural logarithms of vapour pressure ($p = 0.038$). However, no correlation was found between their average concentrations in the atmosphere and the natural logarithm of their vapour pressure (see Figure 18). This could be explained by the fact that the level of a pesticide in the atmosphere depends not only on its volatility, but also on its atmospheric half-life, the conditions of its application, the usage volume and the meteorological conditions.

The majority of the CUPs detected are presumably related to their application in vineyards, apple trees, potatoes and arable crops such as wheat, beet, maize, barley and sunflowers, which are the main crops in the vicinity of the three rural sites (source sites) sampled.



(A)



(B)

Figure 18: Frequency of detection (A) and Concentrations (B) vs. Vapour of Pressure (Ln P) for the pesticides detected during the study.

VII.c.2 Temporal variations in pesticide air concentrations

Figure 19 depicts the average concentrations of the pesticides detected during each of the three years of study. Some differences during this period are highlighted. A decline in levels has been observed for pesticides such as tolyfluanid, chlorpyrifos ethyl, alachlor and α-endosulfan. This last organochlorine insecticide has been banned since 2007, which could explain its decreasing levels.

On the other hand, for the fungicides spiroxamin and captan, and the herbicide dimethenamide, a slight increase has been observed, although the frequencies of detection of the latter two compounds were very low (<3%). Some pesticides such as vinchlozolin, phosmet, methidation, iprodione and fluazinam were detected only in 2007, whereas ethoprophos, dimethomorphe I and azoxystrobin were found only in the samples collected in 2008.

There are no easy explanations for these differences in the annual pattern of pesticides. Much more interesting than the overall variations between the three years are the observed seasonal variations. Figure 20 shows the concentration time series for some frequently detected pesticides.

As expected, for many CUPs a seasonal trend was observed, with higher detections and concentrations during spring and early summer. This, in general, could be related to the application period, although we do not have enough information to correlate farmers' practices (rate of application, exact dates of application, etc..) with pesticide occurrence in the atmosphere. Pesticide concentrations outside of their application periods remain very low and episodic and are probably the result of emissions from soils or plants or from erosion of contaminated soils.

For legacy pesticides such as lindane, a continuous background presence in the atmosphere of Centre region was detected. A regular concentration pattern was observed during all three years and at all five stations. Figure 21 shows its profile, with similar concentrations throughout the year, analogous spatial distribution and low concentrations.

A similar study was conducted by the Lig'Air (2005) group from 2001-2005 at the Saint Martin d'Auxigny (SM) sampling site, with 23 pesticides in common between both studies. Average concentrations for these compounds are compared in Figure 22. For α-endosulfan, alachlor, cyprodinil, fenpropimorph and lindane, the concentrations are very similar in both periods, with concentrations between 0.23 and 6.52 ng m^{-3}. Others, such as propargite and tolyfluanid, have increased dramatically from levels < LOQ to average concentrations of 10.2 and 11.5 ng m^{-3}, respectively. Likewise, chlorothalonil, captan, chlorpyrifos, folpet and trifluralin have increased significantly. This may indicate an increase in the use of these pesticides in Centre region, but we have no current usage data to confirm this.

In contrast, the herbicide metolachlor has decreased from an average concentration of 2.27 ng m^{-3} in the first study to 0.19 ng m^{-3} in the present one. This may be related to the banning of this pesticide in 2003. Contrary to our results, Schummer et al. (2010) reported a considerable decrease in the average concentrations of alachlor, and similar average concentrations for trifluralin from 2002 to 2007. However, an important increase found in the average concentrations of captan is similar in both studies. Schummer´s study was carried out from April to May (2007) and from March to June (2002).

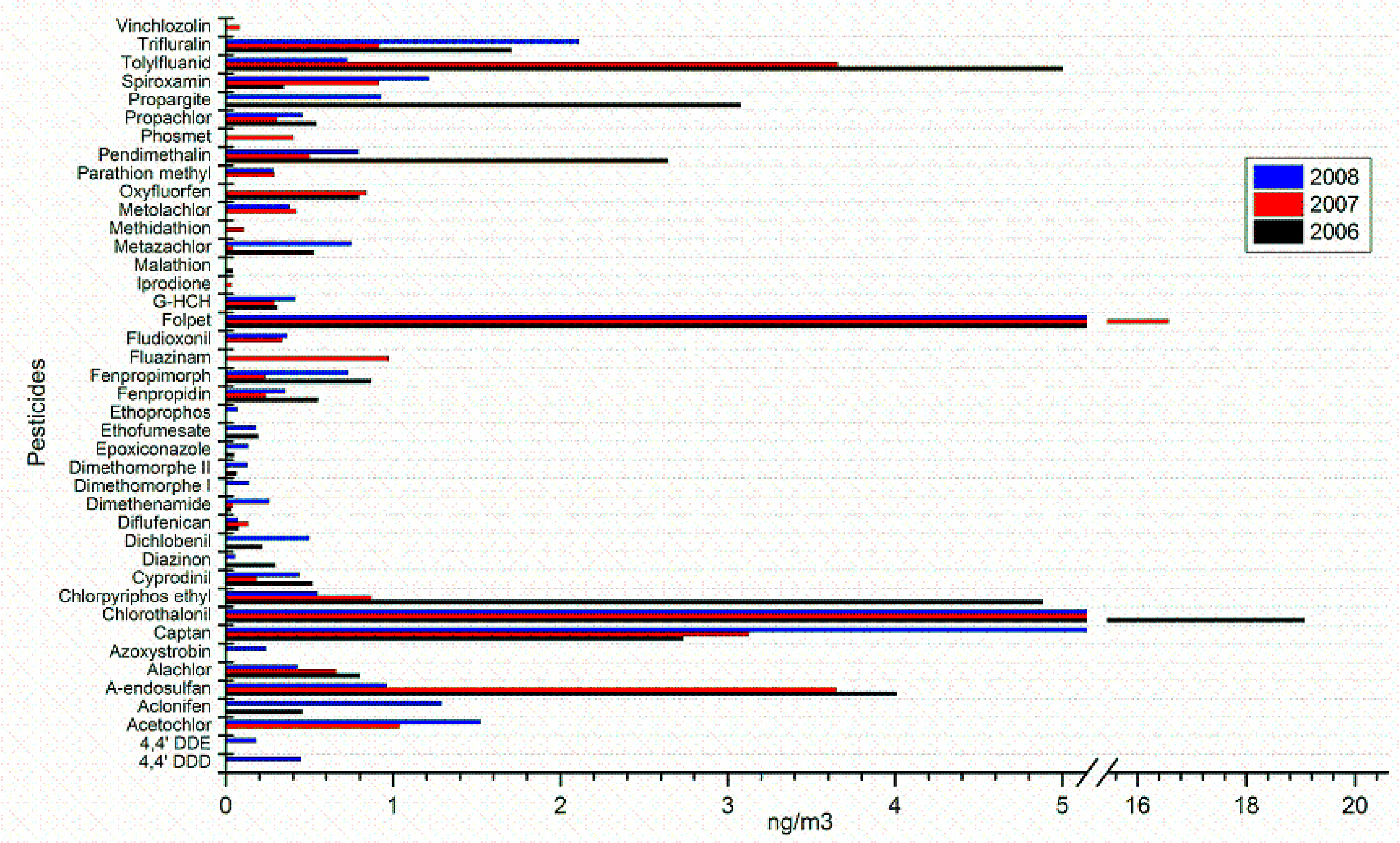


Figure 19: Average concentrations of the pesticides detected from 2006 to 2008.

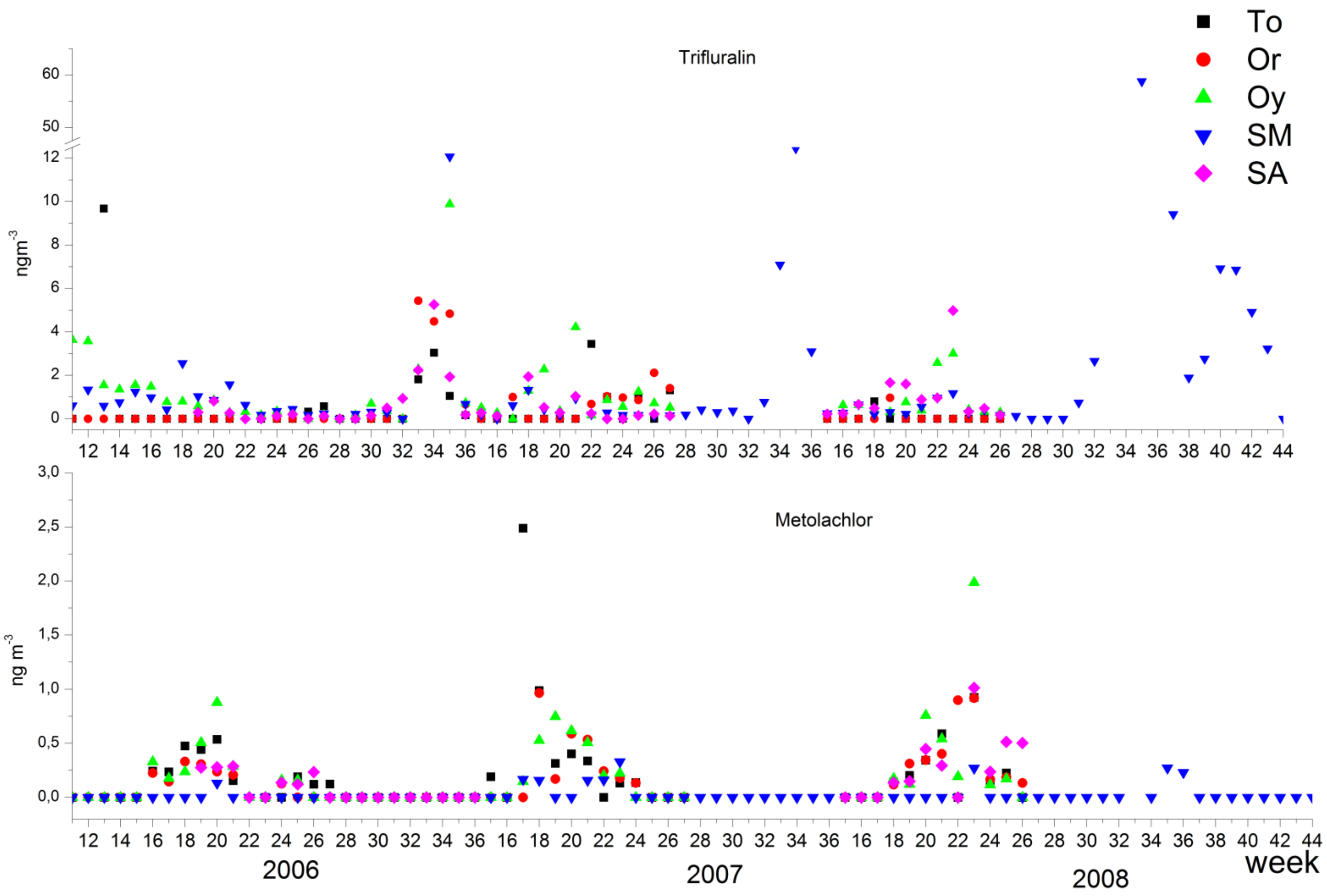


Figure 20: Concentration time series for some frequently detected pesticides (trifluralin and metolachlor) during each of three years of study in all sampling sites.

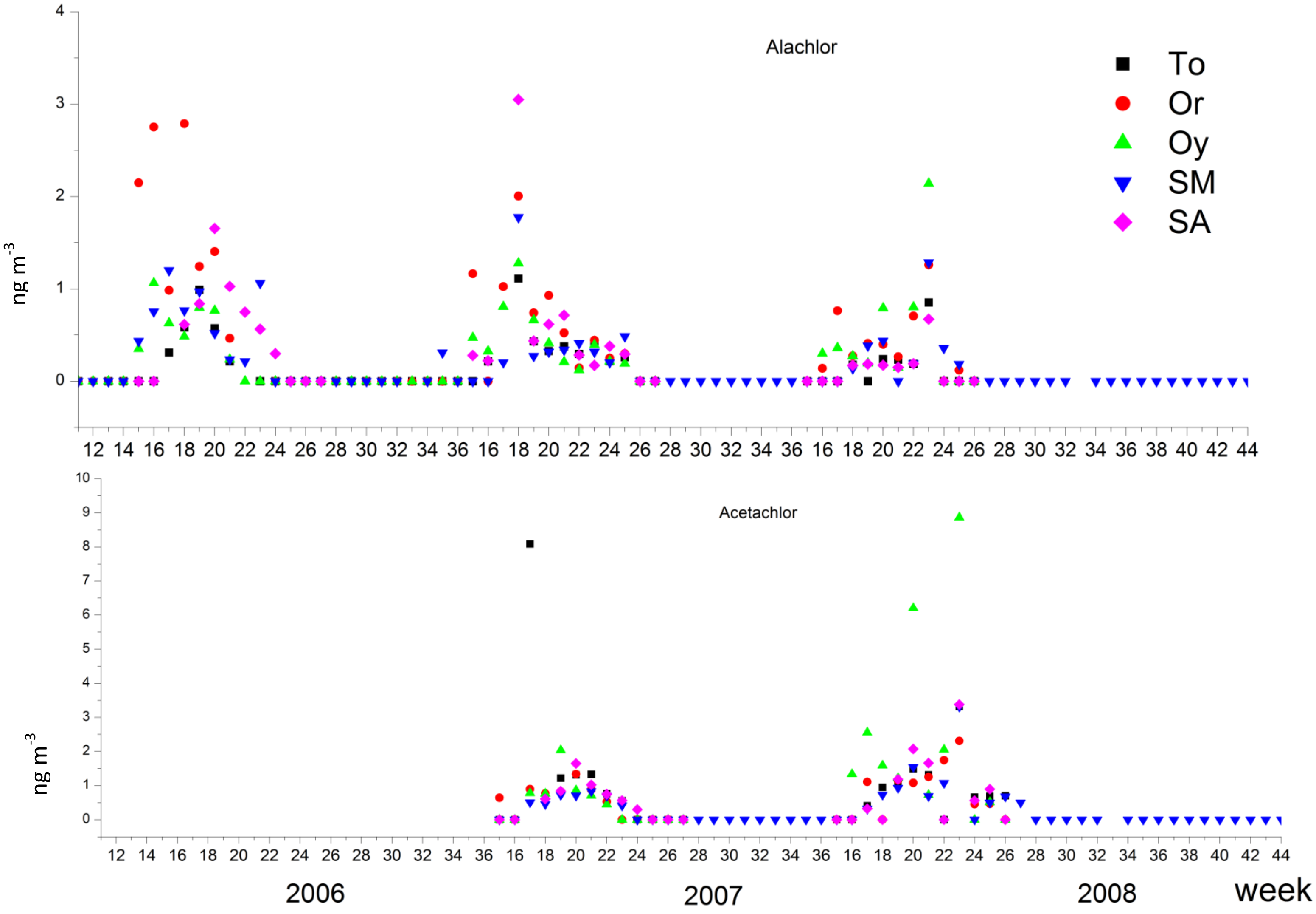


Figure 20: Concentration time series for some frequently detected pesticides (alachlor and acetachlor) during each of three years of study in all sampling sites.

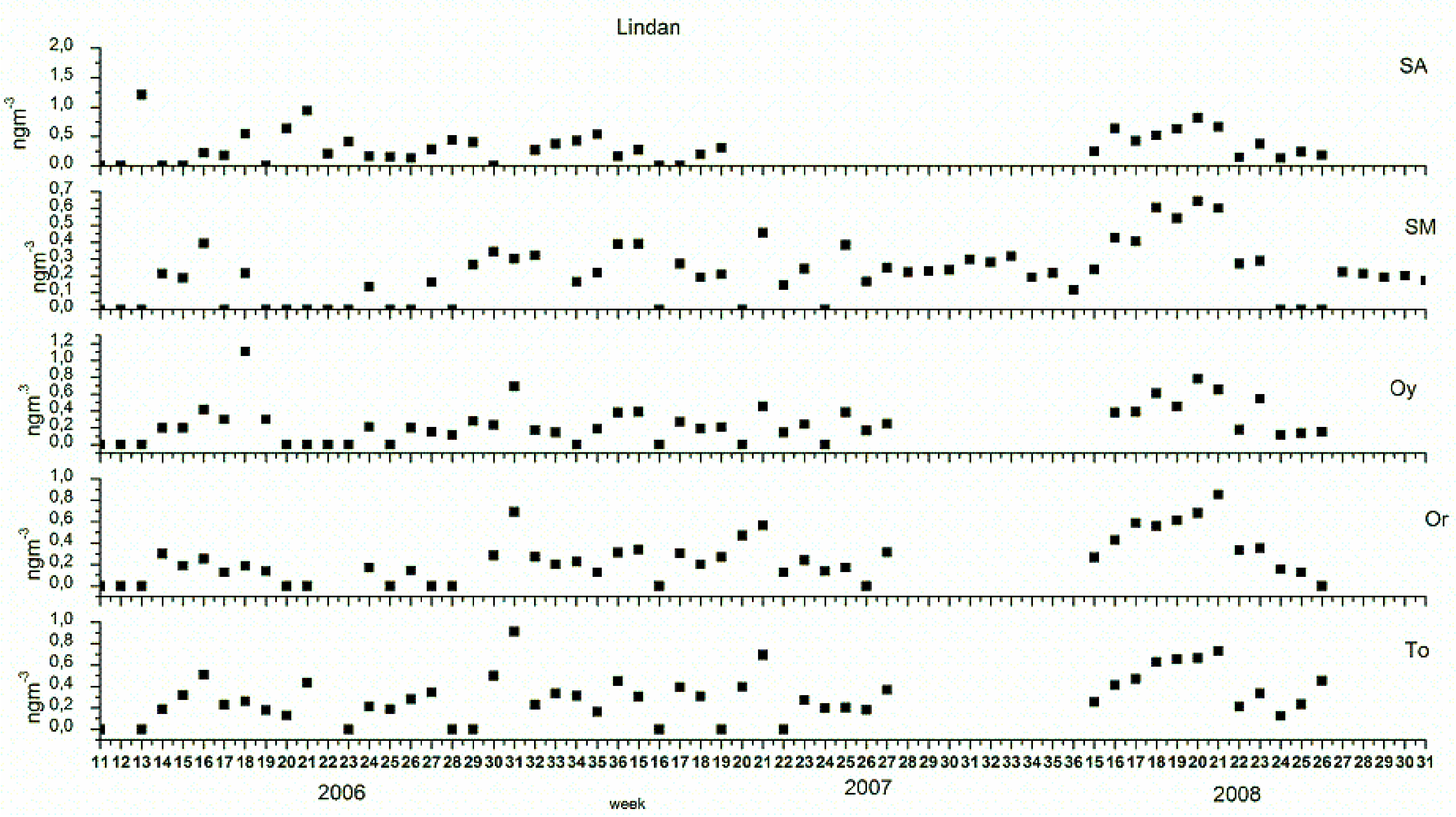


Figure 21: Temporal distribution of lindane from 2006 to 2008 in rural and urban sampling sites.

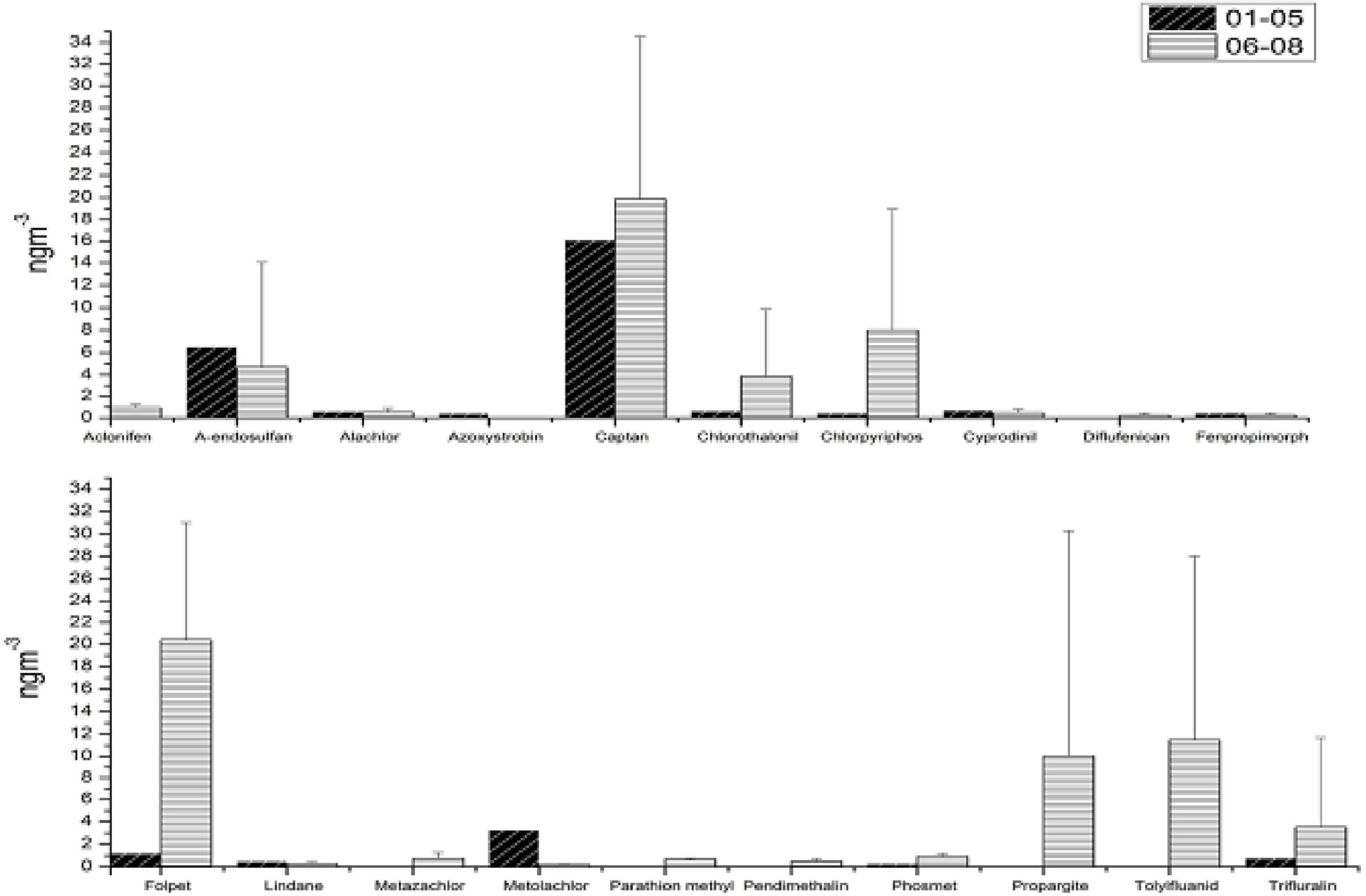


Figure 22: Temporal distribution of 23 pesticides during 2001-2008 in Saint Martin d´Auxigny site.

VII.c.3 *Spatial distribution of pesticide air concentrations*

From Figure 23 and Table 42, it can be seen that pesticide patterns and concentrations are similar at the three rural sites. Likewise, and although the rural sampling sites are nearest to the sources of emission, numerous pesticides showed no significant differences between rural and urban sites. The distance between the treatment area and the sampling site either may not be very significant or may be compensated by the huge amounts of pesticides in the region.

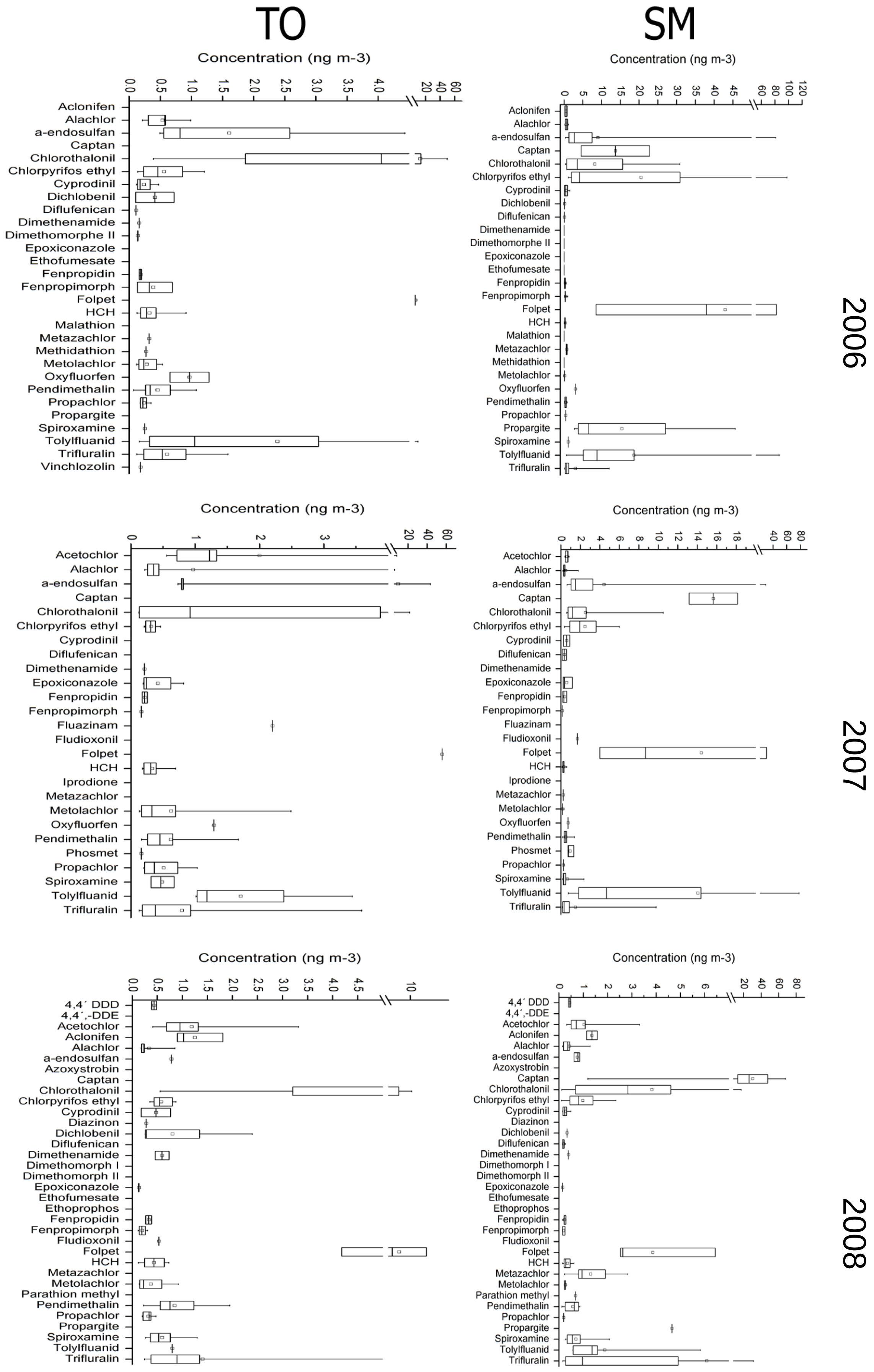


Figure 23: Pesticide air concentrations in Tours and Saint Martin d´Auxigny stations from 2006 to 2008

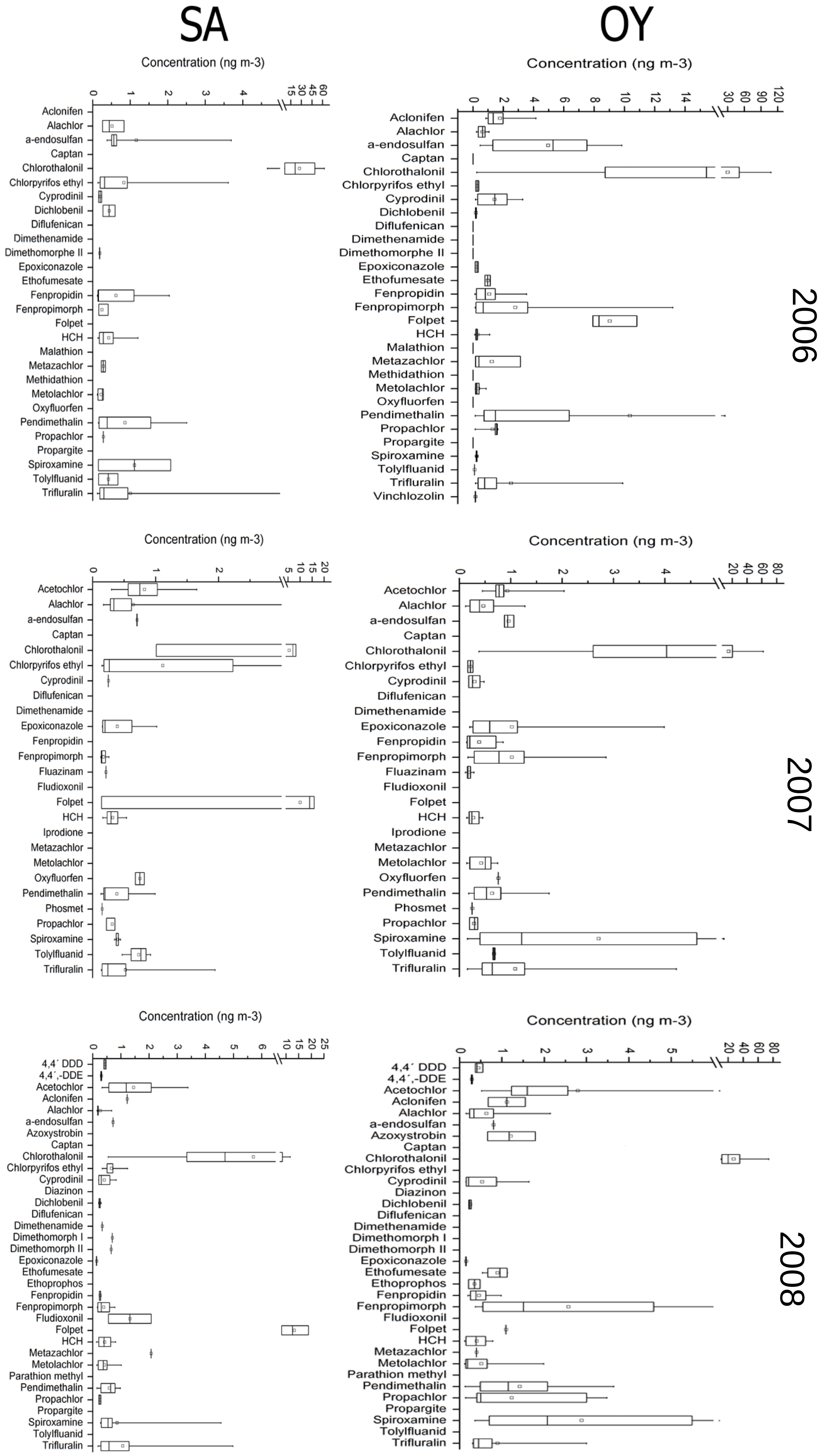


Figure 23: Pesticide air concentrations in Saint Aignan and Oysonville stations from 2006 to 2008

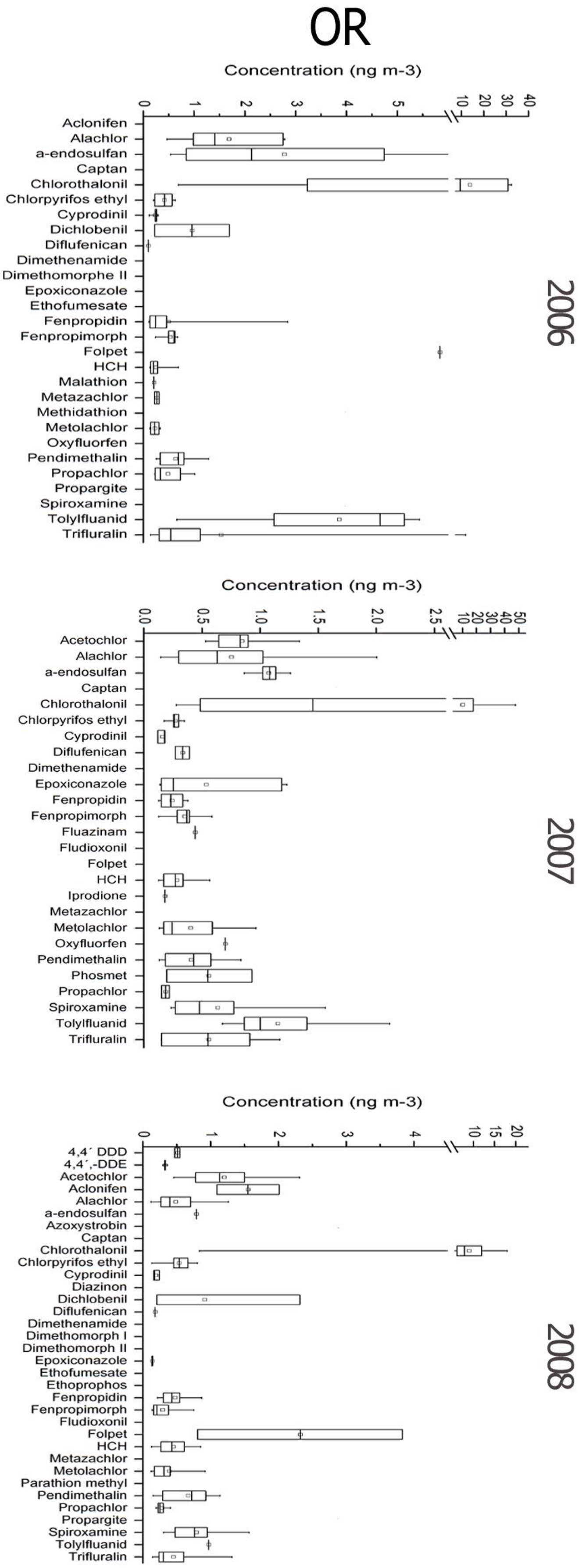


Figure 23: Pesticide air concentrations in Orléans station from 2006 to 2008

Table 42: Overall Spatial distribution of detected pesticides during 2006 at all stations

STATION	Oysonville (n=25)			Saint Martin d´Auxigny (n=24)			Tours (n=24)			Saint Aignan (n=17)			Orléans (n=23)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})
Aclonifen	24	0.86-4.15	1.78	8	0.23-0.83	0.53	n.d.	-	-	n.d.	-	-	n.d.	-	-
α-endosulfan	24	0.47-9.83	4.96	62	0.36-81.30	8.99	33	0.49 - 4.43	1.61	29	0.38-3.69	1.16	26	0.53 - 6.29	2.78
Alachlor	28	0.24-1.06	0.62	46	0.21-1.20	0.65	21	0.21 - 0.99	0.53	18	0.26-0.83	0.51	30	0.46 - 2.79	1.68
Captan	n.d.	-	-	8	4.54-22.82	13.68	n.d.	-	-	n.d.	-	-	n.d.	-	-
Chlorothalonil	60	0.26-107.93	29.77	46	0.30-30.89	8.15	46	0.39 - 49.78	12.65	41	4.65-62.76	27.22	30	0.69 - 32.42	13.79
Chlorpyrifos ethyl	60	0.18-0.38	0.28	42	1.18-97.77	20.49	46	0.14 - 1.21	0.56	47	0.14-3.61	0.83	30	0.20 - 0.63	0.41
Cyprodinil	44	0.18-3.29	1.41	37	0.14-1.56	0.54	17	0.12 - 0.47	0.23	12	0.16-0.24	0.2	22	0.12 - 0.30	0.23
Diazinon	n.d	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-	4	-	1.49
Dichlobenil	12	0.17-0.23	0.19	4	-	0.15	8	0.10 - 0.72	0.41	12	0.27-0.60	0.43	9	0.23 - 1.70	0.96
Diflufenican	n.d	-	-	4	-	0.13	4	-	0.11	n.d.	-	-	4	-	0.14
Dimethenamide	n.d	-	-	n.d.	-	-	4	-	0.16	n.d.	-	-	n.d.	-	-
Dimethomorph II	n.d	-	-	n.d.	-	-	8	0.13 - 0.14	0.14	12	-	0.18	n.d.	-	-
Epoxiconazole	12	0.15-0.35	0.25	n.d.	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-
Ethofumesate	8	0.79-1.15	0.97	n.d.	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-
Fenpropidin	60	0.13-3.54	1.07	25	0.13-0.46	0.25	8	0.16 - 0.20	0.18	23	0.12-2.04	0.62	52	0.11 - 2.84	0.50
Fenpropimorph	48	0.14-13.19	2.79	25	0.14-0.97	0.39	12	0.13 - 0.70	0.38	18	0.16-0.41	0.24	22	0.24 - 0.68	0.53
Folpet	12	7.91-10.82	9.02	12	8.53-82.22	42.89	4	-	5.71	n.d.	-	-	4	-	5.84
γ-HCH	68	0.12-1.11	0.31	50	0.13-0.39	0.25	79	0.13 - 0.51	0.32	70	0.14-1.21	0.42	65	0.13 - 0.69	0.24
Malathion	n.d	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-	4	-	0.21

n = number of samples with one or more pesticides detected.

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD.

Table 42 (continued)

Spatial distribution of detected pesticides during 2006 at all stations

STATION	Oysonville (n=25)			Saint Martin d´Auxigny (n=24)			Tours (n=24)			Saint Aignan (n=17)			Orléans (n=23)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})
Metazachlor	12	0.17-3.13	1.23	8	0.55-0.80	0.67	4	-	0.32	12	0.22-0.33	0.28	9	0.22 - 0.31	0.27
Methidathion	n.d	-	-	n.d.	-	-	4	-	0.27	n.d.	-	-	n.d.	-	-
Metolachlor	32	0.16-0.88	0.34	4	-	0.13	37	0.12 - 0.54	0.28	35	0.12-0.28	0.22	30	0.13 - 0.33	0.23
Oxyfluorfen	n.d	-	-	4	-	3.01	8	0.65 - 1.28	0.97	n.d.	-	-	n.d.	-	-
Pendimethalin	84	0.14-117.32	10.35	10	0.13-0.82	0.38	50	0.07 - 1.08	0.45	23	0.15-2.51	0.86	48	0.25 - 1.28	0.64
Propachlor	20	0.15-1.66	1.29	4	-	0.42	25	0.18 - 0.35	0.24	6	-	0.28	17	0.23 - 1.01	0.48
Propargite	n.d	-	-	17	2.80-45.60	15.39	n.d.	-	-	n.d.	-	-	n.d.	-	-
Spiroxamine	16	0.20-0.31	0.24	4	-	1.12	4	-	0.25	12	0.15-2.08	1.11	n.d.	-	-
Tolylfluanid	4	-	0.1	33	0.61-86.42	18.59	29	0.16 - 9.68	2.38	12	0.15-0.67	0.41	17	0.66 - 5.44	3.85
Trifluralin	88	0.16-25.80	2.51	92	0.17-40.74	2.97	75	0.12 - 1.59	0.61	70	0.12-5.26	1	74	0.15 - 11.82	1.53
Vinchlozolin	16	0.14-0.19	0.16	n.d.	-	-	4	-	0.18	n.d.	-	-	n.d.	-	-

n = number of samples with one or more pesticides detected.

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD.

Table 42 (continued)

Spatial distribution of detected pesticides during 2007 at all stations

STATION	Oysonville (n=12)			Saint Martin d´Auxigny (n=21)			Tours (n=13)			Saint Aignan (n=10)			Orléans (n=13)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})
Acetochlor	50	0.45-2.04	0.93	33	0.41-0.84	0.62	54	0.71 - 8.08	2	70	0.30-0.65	0.82	54	0.53 - 1.34	0.84
α-endosulfan	25	0.88-1.06	0.96	52	0.63-29.40	4.39	38	0.73 - 43.27	9.28	20	0.69-0.70	0.7	38	0.86 - 1.26	1.07
Alachlor	83	0.12-1.28	0.46	38	0.20-1.77	0.48	77	0.21 - 6.03	0.97	80	0.17-3.05	0.64	77	0.14 - 2.00	0.75
Captan	n.d	-	-	9	3.50-15.64	15.63	n.d.	-	-	n.d.	-	-	n.d.	-	-
Chlorothalonil	67	0.38-61.86	14.78	38	0.59-10.49	2.51	54	0.12 - 21.46	4.15	30	1.01-8.27	5.44	54	0.28 - 47.61	10.03
Chlorpyrifos ethyl	17	0.17-0.26	0.21	62	0.37-6.00	2.46	54	0.21 - 0.46	0.31	60	0.14-3.59	1.11	38	0,17 - 0.35	0.27
Cyprodinil	33	0.18-0.48	0.29	9	0.25-0.91	0.58	n.d.	-	-	10	-	0.25	23	0.12 - 0.18	0.16
Diflufenican	n.d	-	-	9	0.13-0.56	0.35	n.d.	-	-	n.d.	-	-	15	0.27 - 0.39	0.33
Dimethenamide	n.d	-	-	n.d.	-	-	8	-	0.21	n.d.	-	-	n.d.	-	-
Epoxiconazole	67	0.20-3.99	1.02	14	0.23-1.16	0.58	38	0.19 - 0.82	0.41	40	0.15-1.02	0.39	46	0.14 - 1.23	0.54
Fenpropidin	58	0.14-0.85	0.38	14	0.20-0.59	0.37	15	0.17 - 0.26	0.21	n.d.	-	-	31	0.13 - 0.38	0.24
Fenpropimorph	50	0.16-2.86	1.02	5	-	0.14	8	-	0.16	40	0.13-0.26	0.17	38	0.13 - 0.58	0.35
Fluazinam	45	0.12-0.28	0.19	n.d.	-	-	8	-	2.2	10	-	0.21	8	-	0.44

n = number of samples with one or more pesticides detected.

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD.

Table 42 (continued)

Spatial distribution of detected pesticides during 2007 at all stations

STATION	Oysonville (n=12)			Saint Martin d´Auxigny (n=21)			Tours (n=13)			Saint Aignan (n=10)			Orléans (n=13)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})
Folpet	n.d	-	-	14	3.99-30.49	14.39	8	-	55.62	30	0.14-15.91	10.01	n.d.	-	-
γ-HCH	83	0.14-0.46	0.27	86	0.12-0.59	0.27	77	0.18 - 0.69	0.33	80	0.16-0.54	0.32	85	0.13 - 0.57	0.28
Iprodione	n.d	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-	8	-	0.18
Metazachlor	n.d	-	-	5	-	0.23	n.d.	-	-	n.d.	-	-	n.d.	-	-
Metolachlor	58	0.15-0.75	0.42	24	0.16-0.33	0.19	61	0.13 - 2.49	0.62	n.a.	-	-	54	0.13 - 0.96	0.4
Oxyfluorfen	8	-	0.76	5	-	0.73	8	-	1.29	20	0.68-0.82	0.74	8	-	0.7
Pendimethalin	100	0.18-1.74	0.63	86	0.17-1.39	0.49	77	0.16 - 1.67	0.61	90	0.13-0.99	0.38	77	0.13 - 0.83	0.41
Phosmet	8	-	0.25	14	0.72-1.32	0.94	8	-	0.16	10	-	0.15	23	0.20 - 0.93	0.56
Propachlor	25	0.20-0.36	0.29	5	-	0.24	38	0.20 - 1.03	0.51	30	0.21-0.35	0.3	15	0.15 - 0.22	0.19
Spiroxamine	67	0.16-9.02	2.71	28	0.18-2.35	0.64	23	0.31 - 0.67	0.48	50	0.35-0.44	0.39	54	0.23 - 1.56	0.63
Tolylfluanid	17	0.65-0.68	0.67	62	0.75-78.32	14.05	31	1.01 - 3.44	1.7	40	0.47-0.92	0.73	54	0.68 - 2.11	1.15
Trifluralin	92	0.16-4.22	1.09	90	0.13-12.45	1.47	77	0.13 - 3.59	0.79	90	0.13-1.94	0.52	54	0.15 - 1.17	0.56

n = number of samples with one or more pesticides detected.

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD.

Table 42 (continued)
Spatial distribution of detected pesticides during 2008 at all stations

STATION	Oysonville (n=10)			Saint Martin d´Auxigny (n=29)			Tours (n=12)			Saint Aignan (n=12)			Orléans (n=12)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average^{1} (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average^{1} (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average^{1} (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average^{1} (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average^{1} (ng m^{-3})
4,4' DDD	30	0.37-0.55	0.44	7	0.39-0.48	0.44	17	0.39 - 0.49	0.44	17	0.39-0.47	0.43	17	0.47 - 0.55	0.51
4,4' DDE	20	0.27-0.30	0.28	n.d.	-	-	n.d.	-	-	25	0.28-0.31	0.3	42	0.29 - 0.36	0.33
Acetochlor	80	0.52-8.87	2.79	21	0.32-3.32	1.03	75	0.41 - 3.32	1.18	58	0.32-3.38	1.44	67	0.45 - 2.31	1.2
Aclonifen	20	0.67-1.55	1.11	10	1.13-1.58	1.36	25	0.90 - 1.81	1.25	8	-	1.22	17	1.09 - 2.01	1.55
α-endosulfan	18	-	0.8	10	0.62-0.85	0.75	8	-	0.78	8	-	0.72	8	-	0.79
Alachlor	90	0.15-2.14	0.63	24	0.14-1.29	0.42	42	0.18 - 0.85	0.34	60	0.15-0.67	0.26	75	0.12 - 1.26	0.48
Azoxystrobin	30	0.66-1.79	1.2	n.d.	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-
Captan	n.d.	-	-	14	1.19-67.62	30.32	n.d.	-	-	n.d.	-	-	n.d.	-	-
Chlorothalonil	100	10.67-74.43	27.36	62	0.11-17.22	3.82	100	0.56 - 9.31	5.36	100	0.55-11.66	5.7	100	0.83 - 18.04	8.97
Chlorpyrifos ethyl	n.d.	-	-	52	0.10-2.34	0.97	58	0.36 - 0.87	0.58	42	0.33-1.24	0.66	67	0.13 - 0.80	0.53
Cyprodinil	70	0.15-1.64	0.53	21	0.15-0.49	0.26	17	0.18 - 0.77	0.47	33	0.20-0.83	0.41	25	0.16 - 0.24	0.19
Diazinon	n.d.	-	-	n.d.	-	-	8	-	0.28	n.d.	-	-	n.d.	-	-
Dichlobenil	30	0.21-0.27	0.24	3	-	0.33	33	0.26 - 2.39	0.8	33	0.21-0.30	0.24	25	0.20 - 2.32	0.91
Diflufenican	n.d.	-	-	17	0.13-0.27	0.19	n.d.	-	-	n.d.	-	-	8	-	0.18
Dimethenamide	n.d.	-	-	3	-	0.39	17	0.46 - 0.74	0.6	8	-	0.33	n.d.	-	-
Dimethomorph I	n.d.	-	-	n.d.	-	-	n.d.	-	-	8	-	0.69	n.d.	-	-
Dimethomorph II	n.d.	-	-	n.d.	-	-	n.d.	-	-	8	-	0.65	n.d.	-	-

n = number of samples with one or more pesticides detected.

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD.

Table 42 (continued)
Spatial distribution of detected pesticides during 2008 at all stations

STATION	Oysonville (n=10)			Saint Martin d´Auxigny (n=29)			Tours (n=12)			Saint Aignan (n=12)			Orléans (n=12)		
PESTICIDE	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})	Frequency of detection (%)	Range (ng m^{-3})	Average[1] (ng m^{-3})
Epoxiconazole	20	-	0.15	14	0.13-0.15	0.14	25	0.12 - 0.14	0.13	25	0.12-0.14	0.13	33	0.13 - 0.15	0.14
Ethofumesate	40	0.54-1.17	0.89	n.d.	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-
Ethoprophos	20	0.21-0.48	0.35	n.d.	-	-	n.d.	-	-	n.d.	-	-	n.d.	-	-
Fenpropidin	80	0.19-0.98	0.45	17	0.13-0.29	0.22	17	0.27 - 0.38	0.33	25	0.23-0.27	0.26	42	0.21 - 0.87	0.47
Fenpropimorph	70	0.37-7.42	2.57	10	0.15-0.24	0.18	33	0.11 - 0.30	0.2	33	0.16-0.78	0.38	75	0.13 - 0.75	0.29
Fludioxonil	n.d.	-	-	n.d.	-	-	8	-	0.53	17	0.55-2.07	1.31	n.d.	-	-
Folpet	10	-	1.09	10	2.53-6.43	3.86	25	4.18 - 12.96	7.95	25	8.27-18.88	13.22	17	0.81 - 3.83	2.32
γ-HCH	100	0.12-0.78	0.4	65	0.13-0.64	0.35	100	0.13 - 0.73	0.43	100	0.13-0.81	0.42	92	0.13 - 0.85	0.45
Metazachlor	10	-	0.4	27	0.23-2.83	1.29	n.d.	-	-	8	-	2.07	n.d.	-	-
Metolachlor	80	0.18-1.99	0.51	10	0.23-0.27	0.26	58	0.14 - 0.92	0.37	67	0.14-1.01	0.41	75	0.12 - 0.92	0.39
Parathion methyl	n.d.	-	-	3	-	0.68	n.d.	-	-	n.d.	-	-	n.d.	-	-
Pendimethalin	100	0.13-3.64	1.41	34	0.12-0.86	0.57	92	0.23 - 1.95	0.84	83	0.14-0.98	0.58	83	0.15 - 1.14	0.67
Propachlor	70	0.14-3.48	1.22	7	-	0.19	42	0.20 - 0.47	0.32	17	0.21-0.29	0.25	42	0.20 - 0.41	0.28
Propargite	n.d.	-	-	3	-	4.65	n.d.	-	-	n.d.	-	-	n.d.	-	-
Spiroxamine	100	0.36-8.12	2.87	31	0.25-2.07	0.69	75	0.27 - 1.30	0.59	83	0.27-4.56	0.86	83	0.30 - 1.57	0.79
Tolylfluanid	n.d.	-	-	21	0.57-5.83	1.88	8	-	0.8	n.d.	-	-	8	-	0.97
Trifluralin	100	0.30-3.00	0.89	83	0.13-58.79	6.07	92	0.24 - 5.33	1.4	100	0.18-4.98	1.06	92	0.14 - 1.31	0.45

n = number of samples with one or more pesticides detected;

[1] The average was calculated from the arithmetic mean of samples with concentration above LOD

The majority of the pesticides studied have an atmospheric half-life of only a few hours and, consequently, are not prone to transport over long distances (>1000 km) (FOCUS, 2008). Nevertheless, their persistence in the atmosphere is long enough to allow them to be transported at the local and regional scale (medium-range transport), and this, along with their volatility, could explain their presence in urban areas. Likewise, the transport of pesticides in air is strongly dependent on wind speed and direction. Thus, to demonstrate how the transport from rural to urban areas occurs, wind patterns need to be considered.

Figure 24 shows the integrated wind rose for the two urban sites during the sampling period. Winds blowing from Oysonville arrived at Orléans from NNW-N-NNE directions, which happened with a relatively high frequency (about 20%). Winds from Saint Aignan and Saint Martin reached Orléans from SSW-SW (18%) and SSE-SE (8%) directions. Winds passing over SA and SM arrived at Tours (SSE-SES directions) with frequencies near 15%. And, winds that passed through Oysonville get to Tours with NNE-ENE directions and with a frequency near 25%.

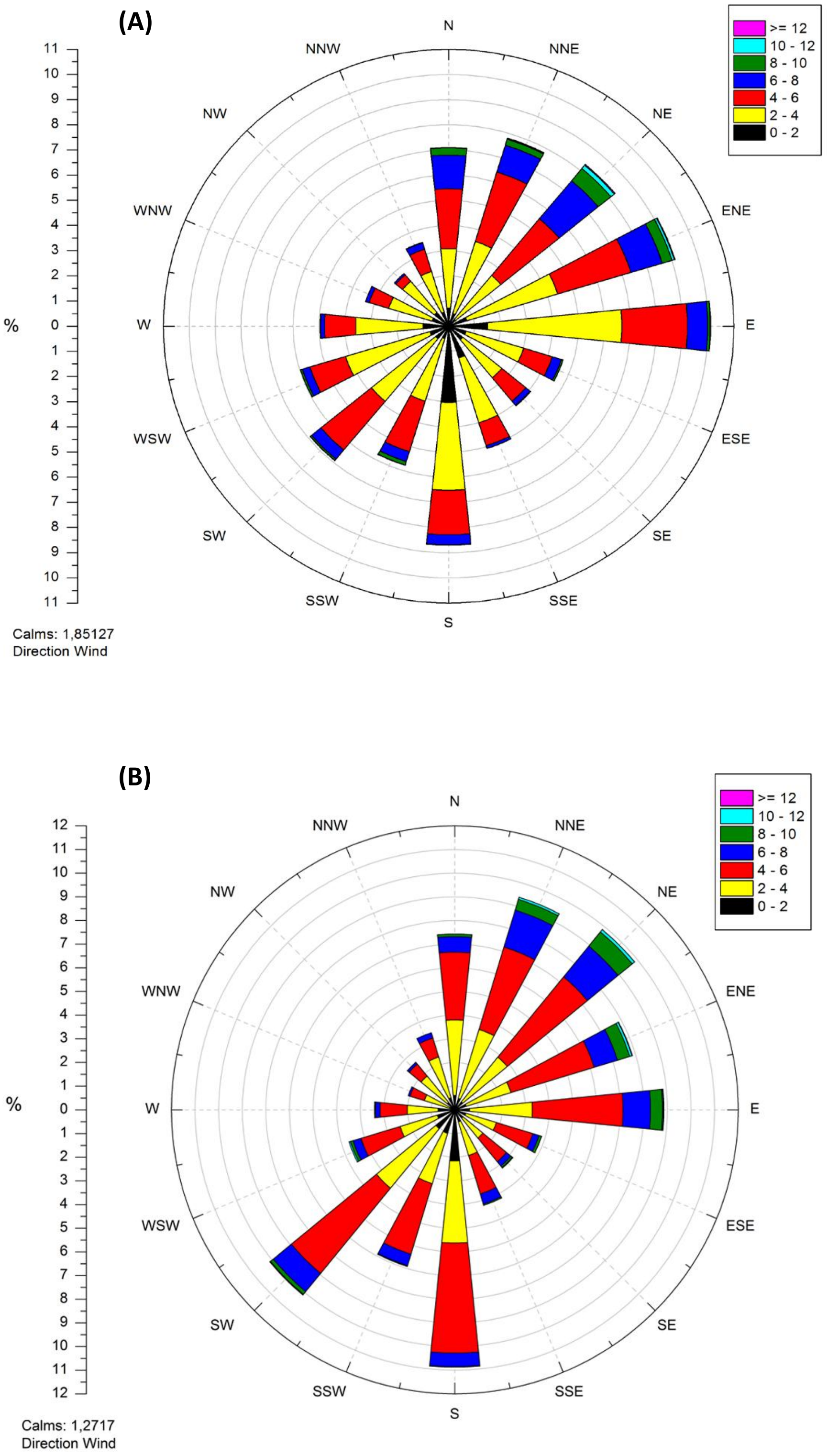


Figure 24: Integrated wind rose for the two urban sites: Orléans (A) and Tours (B) during the sampling period

Therefore, pesticides applied in the three rural areas could be transported to the urban sites when wind direction and velocity are appropriate, which during the period studied has happened with significant frequency. Transport between rural and urban areas can also be studied using trajectory analysis (Hayward et al., 2010). This tool was difficult to apply because of the use of weekly integrated samples.

Nevertheless, a qualitative approach could sometimes be applied. As an example, we studied the presence of acetochlor in Tours during 2007. Table 43 shows the concentrations of acetochlor for each week. It can be observed that this pesticide was detected in all samples from weeks 17 to 23, with concentrations ranging from 0.5 to 8.0 ng m^{-3}. As this pesticide is used mainly on maize crops in the area of Oysonville, its arrival at Tours should be linked to some wind trajectory.

Table 43: Concentrations of acetochlor in Tours during 2007

week	ng m^{-3}
15	<LOQ
16	<LOQ
17	8.08
18	0.71
19	1.22
20	1.32
21	1.33
22	0.76
23	0.55
24	<LOQ
25	<LOQ
26	<LOQ
27	<LOQ

Figure 25 depicts the 24 h back trajectories for one day of each week for the air mass passing over Oysonville and arriving at Tours (NNE-NE directions), which could explain the transport of acetochlor from the rural source to the urban site.

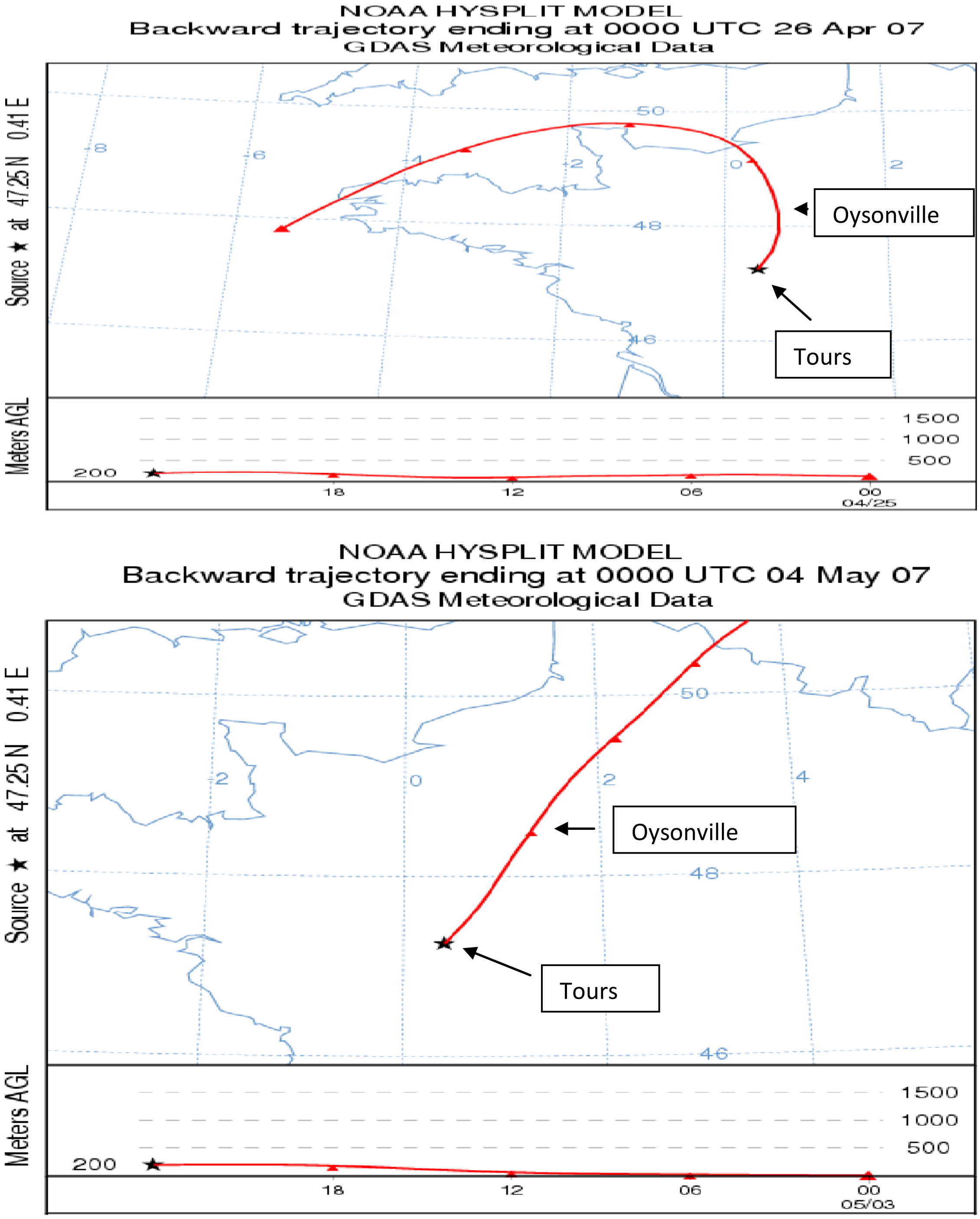


Figure 25: Backward trajectory for one day (weeks 17 and 18) for the air passing over Oysonville and arriving at Tours (April-June, 2007). The trajectory was calculated with NOAA's HYSPLIT model at 200 m above ground level.

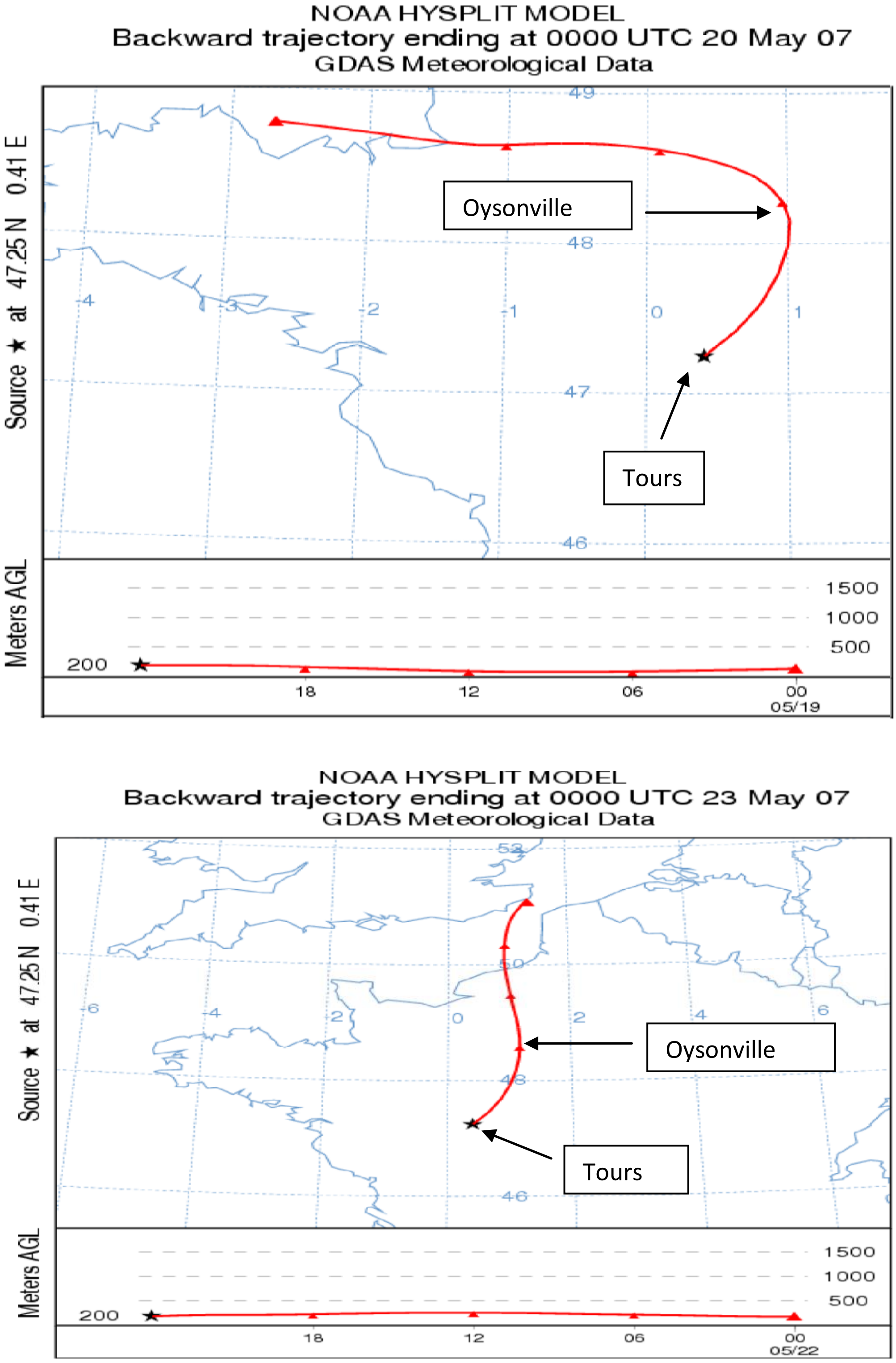


Figure 25: Backward trajectory for one day (weeks 20 and 21) for the air passing over Oysonville and arriving at Tours (April-June, 2007). The trajectory was calculated with NOAA's HYSPLIT model at 200 m above ground level.

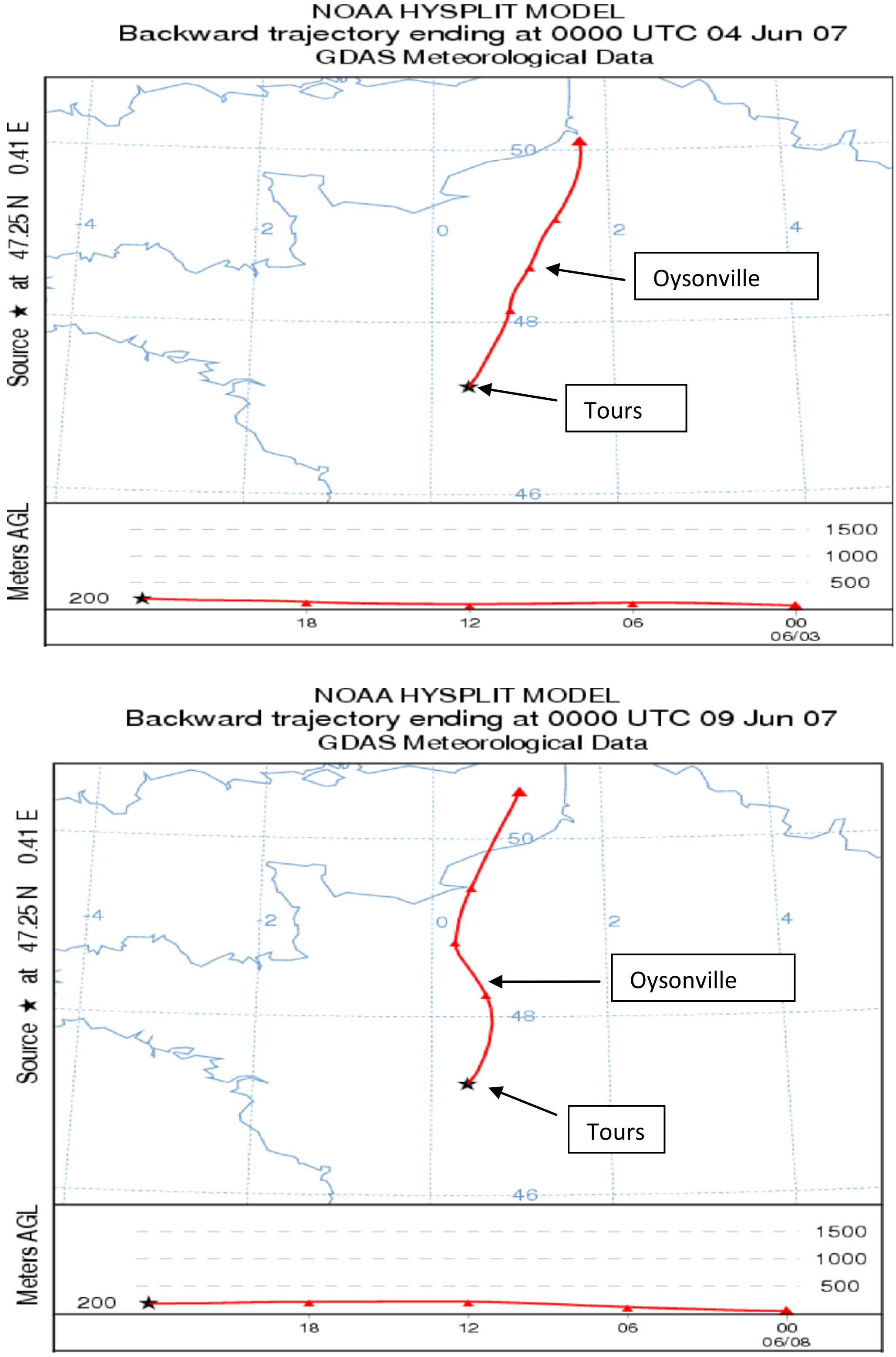


Figure 25: Backward trajectory for one day (week 23) for the air passing over Oysonville and arriving at Tours (April-June, 2007). The trajectory was calculated with NOAA's HYSPLIT model at 200 m above ground level.

In the following paragraphs of this section there is a discussion about the occurrence of the most frequently detected herbicides, fungicides and insecticides.

VII.c.3.1 Herbicides

The most detected herbicide was trifluralin, which appears at concentrations ranging from 0.12 to 58.79 ng m^{-3}. This selective soil herbicide is commonly used for the control of grass and broad- leaved weeds in arable crops (EFSA, 2009a). As all the sampling sites of Oy are surrounded by arable crops, this area could be considered the main source for trifluralin in Centre region.

Nevertheless, higher concentrations were detected in SM, where the arable crop cultivation area is smaller, meaning that the distance of the sampling site to the source is not always directly related to the concentrations detected. Alachlor concentrations ranged from 0.12 to 6.03 ng m^{-3}. The presence of this herbicide in Centre region could be related mainly to its use in the surroundings of Oy, where it is applied on maize and soybean crops. Air concentrations of pendimethalin ranged from 0.07 to 117.33 ng m^{-3}, with an average of 1.84 ng m^{-3}. As this herbicide is used for the treatment of arable crops, vegetables and vineyards, its presence in the atmosphere could mainly be explained by its use in the rural areas of Oy and SM. Its relatively high volatility and its half life (12 h) permit its medium-range transport (EC, 2003).

In a recent study, Schummer et al. (2010) detected trifluralin in the atmosphere of Strasbourg (France) in 9 out of 10 samples, with concentrations from 0.06 to 0.22 ng m^{-3}. Likewise, they reported the presence of alachlor and pendimethalin, with average concentrations of 1.20 ng m^{-3} and 3.18 ng m^{-3}, respectively. Metolachlor was found in both rural and urban sites, with an average concentration of 0.37 ng m^{-3} and a concentration pattern that peaked between April and June. This indicates that despite being banned since 2003, it is still applied to treat arable crops, and that despite its rapid degradation in the atmosphere (half-life of 1.8 h), it is transported from rural to urban areas.

Higher concentrations were detected by Scheyer et al. (2007). They reported maximum concentrations of 7.7 ng m^{-3} of metolachlor at a rural site in Alsace Region (France). In this study, samples were collected during spring 2003, when this pesticide was still authorized. Another frequently detected herbicide was acetochlor, which was found on all five sampling sites in 2007 and 2008 (not sampled in 2006) from weeks 16 to 25, at concentrations ranging from 0.30 to 8.87 ng m^{-3}. Propachlor was most frequently detected and presented highest concentrations in Oy, indicating a large local source of this compound around this site, although it has a widespread source, as it is applied in cabbage and onion fields in different areas of Centre region.

A lower frequency of detection (<10%) was obtained for oxyfluorfen, aclonifen, dichlobenil, and dimethenamid. The first one was found in all five stations, mainly during 2007, with an overall frequency of 3%, and concentrations ranging from 0.65 to 3.01 ng m^{-3}. Its presence in the Centre region could be attributed to its application on vineyards in the vicinity of the SA sampling site, where it was detected with an average of 0.74 ng m^{-3}. This compound has not been reported previously in literature.

VII.c.3.2 Fungicides

The most frequently detected fungicide was chlorothalonil, a broad-spectrum fungicide currently applied in arable crops, vegetables and vineyards. Chlorothalonil was detected in air samples collected at all five sites, with concentrations between 0.11 and 107.93 ng m^{-3} (average concentration of 12.15 ng m^{-3}). It is a relatively persistent substance that can be transported far from its emission source, which explains its occurrence in urban areas.

Apart from chlorothalonil, maximum average concentrations were measured for folpet and tolyfluanid. Folpet is a contact fungicide used to control various fungi in winter wheat, apples and wine grapes. It was detected at all five sites with concentrations ranging from 0.14 to 82.22 ng m^{-3}. Its presence in Centre region is due to its use around SA (vineyards), Oy (wheat), and SM (apple trees) although, owing to its capacity for medium-range atmospheric transport (half life: 6.16 h), it was also observed occasionally on the urban sites. Other fungicides detected in ambient air were fenpropimorph, cyprodinil, epoxiconazole and spiroxamine. All four of these fungicides are used mainly in arable crops and were detected in concentrations ranging from 0.12 to 13.20 ng m^{-3}.

According to the EFSA (EFSA, 2009b), concentrations of folpet in the air are expected to be negligible, due to its low volatility and relatively low persistence in the atmosphere. Likewise, the EFSA scientific report (EFSA, 2008b) indicates that epoxiconazole has no tendency to enter the air due to its low volatilization both from plants and soil after application. However, this active substance was detected at all sampling sites, mainly during 2007, in the period from mid-April to the first week of June, with a global detection frequency of 17%. The theoretical models presented by EFSA are based entirely on the vapour pressure of the substance, and do not account for the possibility of particle-bound transport. The levels of folpet and epoxiconazole found might be associated with particles.

In the study carried out by Schummer et al. (2010), chlorothalonil and folpet were found in lower concentrations than in this thesis. They also reported a lower range of concentrations of the systematic foliar fungicide fenpropidin than the one detected in this chapter (from 0.11 to 3.54 ng m^{-3}). On the other hand, in this thesis iprodione, a fungicide used on vines, fruits and vegetables, was detected in only one sample, and at a concentration of 0.18 ng m^{-3}, whereas Schummer et al. (2010) found iprodione in all their samples and at higher concentrations ranging from 3.84 to 42.31 ng m^{-3}. Vinchlozolin, which was not detected by Schummer et al. (2010) but was found in the present study only during 2006 and at the Oy sampling site; displayed a frequency of detection of 16% and concentrations between 0.14 and 0.19 ng m^{-3}, befitting its local use on vegetables. The authorization for the use of this fungicide was withdrawn on 1 January 2007, which could explain why it was not detected in 2007 and 2008.

VII.c.3.3 Insecticides

As regards the insecticides, 12 of the 22 substances monitored were detected, at frequencies ranging from 0.38 to 76%, with the highest frequencies for γ-HCH (76%), chlorpyrifos ethyl (42%) and α-endosulfan (28%). The other insecticides detected presented very low frequencies (<7%).

The detection of lindane could be explained by its persistence in local soils and by its long-range transport both from weathered sources and from fresh sources where it is still in use, although volatilization residues could not be distinguished from atmospheric transport because the ratio of α/γ-HCH was not studied. The second organochlorine insecticide most detected was α-endosulfan, banned since 2007. This volatile pesticide was used for the treatment of arable crops and vegetables. The detected levels were in the range of 0.37-81.21 ng m^{-3}, and it was present in both rural and urban stations with a similar temporal pattern.

However, during 2008 (after its banning), the frequency of detection and the concentration levels decreased significantly (see Figure 23). Its presence at rural sites would be linked to its use, resulting in increasing concentrations during its application period (spring); in contrast, its detection at urban sites could be attributed both to its persistence in air and to meteorological conditions.

According to Li et al. (2007), α-endosulfan is present mainly in the gas phase, and they detected lower concentrations than those found in the present study. Likewise, lower concentrations were also reported by Scheyer et al. (2005) in the urban atmosphere of Strasbourg.

Among the organophosphate insecticides, chlorpyrifos was the most frequently detected, with an average concentration of 2.86 ng m^{-3}. Other pesticides such as phosmet, diazinon, malathion, methidation and methyl parathion, were detected at much lower frequencies. Aulagnier et al. (2008) detected chlorpyrifos with a similar frequency but lower average concentrations than in the present study. These authors also found phosmet and diazinon more frequently, but with lower average concentrations. Likewise, Peck and Hornbuckle (2005) reported average concentrations of chlorpyrifos, diazinon and methyl parathion of 1.0, 6.7 and 2.2 ng m^{-3}, respectively, in the air of Iowa. Malathion has also been reported previously (Baraud et al., 2003) as well as in Chapters 2 and 3 of this thesis.

Despite the similar patterns between rural sites, some differences are apparent. The most relevant is the presence of captan only in SM. This fungicide was found in about 14% of the samples collected in SM with relatively high concentrations ranging from 1.1 to 67.6 (average of 30.3 ng m^{-3}). Its presence at this rural site can be attributed to its intense use in the apple orchards surrounding the SM sampling site. Concentrations of captan in the atmosphere in the same range of magnitude have been reported by Aulagnier et al. (2008) and Schummer et al. (2010) with average concentrations of 2.89 and 10.07 ng m^{-3}, respectively.

Likewise, the acaricide propargite was found only in SM; its three-year average concentration was 13.24 ng m^{-3}. The presence of the fungicide tolyfluanid is also characteristic of the SM site. Although it was also found at the three rural sites during 2006 and 2007, the concentrations at SM were more than one order of magnitude higher (three-year average of 16 ng m^{-3}). This could be linked to its application to the apple and pear trees surrounding this site.

Apart from some samples collected at the urban sites, mainly in Or, diflufenican appears only in the samples from SM, with a frequency of detection of 17% during 2008, and with concentrations ranging from 0.13 to 0.27 ng m^{-3}. Similar levels for this herbicide were reported by Schummer et al. (2010) in the atmosphere of Strasbourg, France, during 2007.

Three active substances were detected exclusively at the Oy rural site: azoxystrobin, ethofumesate and ethoprophos. The fungicide azoxystrobin was detected during spring with an average concentration of 1.20 ng m^{-3}. Azoxystrobin is a pesticide for use on cereals and vines, with a very low volatility. Its presence in Oy could be explained by its application to the fields of wheat, barley, maize and rape in the vicinity of the sampling site. This fungicide has been reported in Chapter 2 in the atmosphere of Valencia Region (Spain) during April-July 2009, detecting an average concentration of 0.008 ng m^{-3} in fine airborne particulate matter (PM2.5). Ethofumesate was found in spring at an average concentration of 0.89 ng m^{-3}. Its presence is linked to its use in the beet fields near this sampling site. Similar concentrations of ethofumesate were reported by Schummer et al. (2010) in the atmosphere of Strasbourg.

Ethoprophos is an insecticide and nematicide used to control a broad spectrum of insects and nematodes in potatoes. It was detected in only two samples during 2008, at concentrations of 0.48 and 0.21 ng m^{-3}. Although it has a high vapour pressure, its volatility in the soil seems to be minimal and is mainly due to the granular formulation incorporated into the soil after application (EFSA, 2006c). Its presence is linked to local use in the potatoe fields around Oy.

Likewise, the fungicide fluzinam, also used to treat potato crops was detected in Oy in 2007, at concentrations ranging from 0.12 to 0.28 ng m^{-3}. Contrary to expectations, however, it was not present in any of the samples taken from SM and it was found in only one sample from SA (0.21 ng m^{-3}), where it was expected to be used on apple trees and vines, respectively. Its medium to high potential for volatilization and its relative persistence in air (half life> 2d) (EFSA, 2008d) could explain its sporadic detection in urban areas. There are no previous reports in literature about the presence of these two last substances in air. Three additional fungicides, chlorothalonil, fenpropimorph and spiroxamine, are common on the Oy site where they appear at significantly higher concentrations than on the other sites studied (see Figure 23).

Two fungicides appear to be unique to the rural site of SA: dimethomorph and fludioxinil. The former was detected in two samples in 2006 and in one sample in 2008, showing concentrations during 2008 of 0.69 and 0.64 ng m^{-3} for I and II isomers, respectively. Aulagnier et al. (2008) checked for this pesticide but found no concentrations higher than the LOQ. Fludioxonil is a fungicide applied to wine and table grapes. It was detected in two samples during 2008, at concentrations of 0.55 and 2.07 ng m^{-3}, respectively. There are no previous references in the literature about the presence of this substance in ambient air.

It should also be stressed that pesticide patterns and concentrations at Or and To (urban sites) present only minor differences, which means that the CUPs are quite homogenously distributed in the atmosphere of the region during the growing season.

VII.c.4 Influence of temperature on air pesticide concentration

The temperature dependence of pesticide air concentrations was studied by plotting natural logarithms of the partial pressures (ln P) against the reciprocal time-averaged temperature for each sampling event (1/T) at the two urban sites. The slopes and correlation coefficients were analyzed and the p-values calculated to check whether both parameters were correlated. It was found that only 4 pesticides in Orléans (see Figure 26) and three in Tours (chlorothalonil, tolyfluanid and fenpropimorph) showed a statistically significant correlation ($p < 0.05$). Figure 26 shows that temperature predicts 76%, 40%, 38% and 16 % of the concentration variation for α-endosulfan, cyprodinil, propachlor and chlorothalonil, respectively.

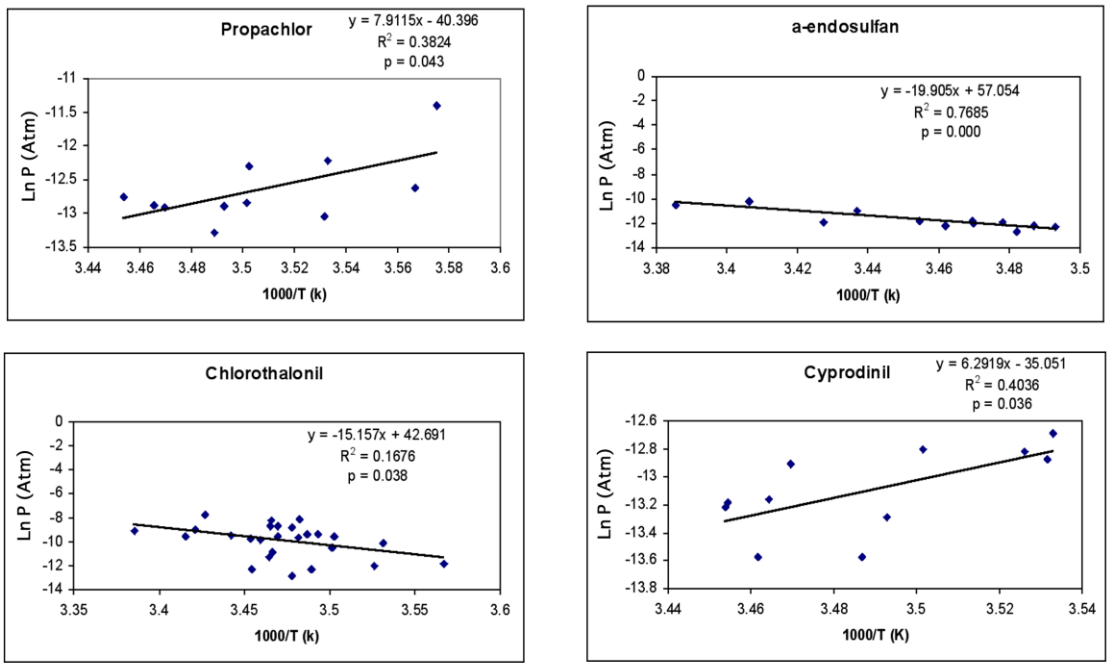


Figure 26: Influence of temperature on air pesticide concentrations. Plots of partial pressures (ln P) vs 1000/T at the two urban sites (Orléans and Tours).

For α-endosulfan and chlorotalonil, concentrations rise when temperature increases; this indicates that these pesticides volatilize from surfaces, and the volatilization is influenced by temperature. However, for propachlor and cyprodinil a positive slope was found, indicating a decreasing concentration in air with increasing temperatures. Apart from the temperature, other diverse factors could affect air concentrations, but no explanation can be offered for this behaviour with the current data.

Wania et al. (1998) suggested that for SOCs the slope of the ln P vs 1/T relationship could be used to qualitatively assess the relative magnitude of evaporative sources close to the sample locations (short-medium range transport) vs advection of background air into the area (long-range transport). However, we have found that for the majority of the CUPs detected, air concentrations were essentially independent of temperature (see Figure 27). This could mean that many other factors, such as application during the sampling period, wind speed or degradation process, could play a role in the air concentrations (Venier and Hites, 2010). The narrow temperature range during the sampling periods could also have contributed to this little or no temperature dependence.

(A) TOURS

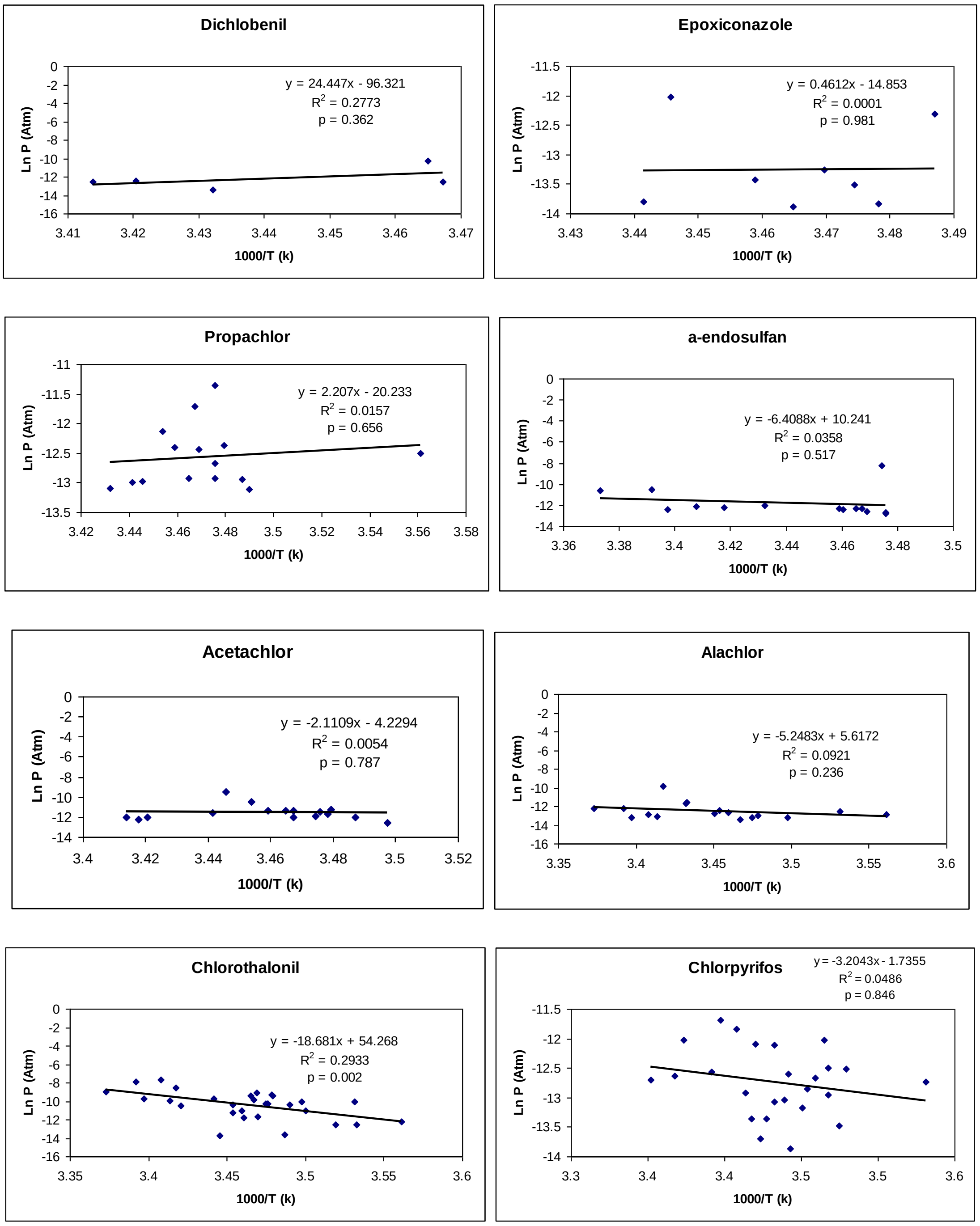


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (A) Tours in 2006-2008

(A) TOURS

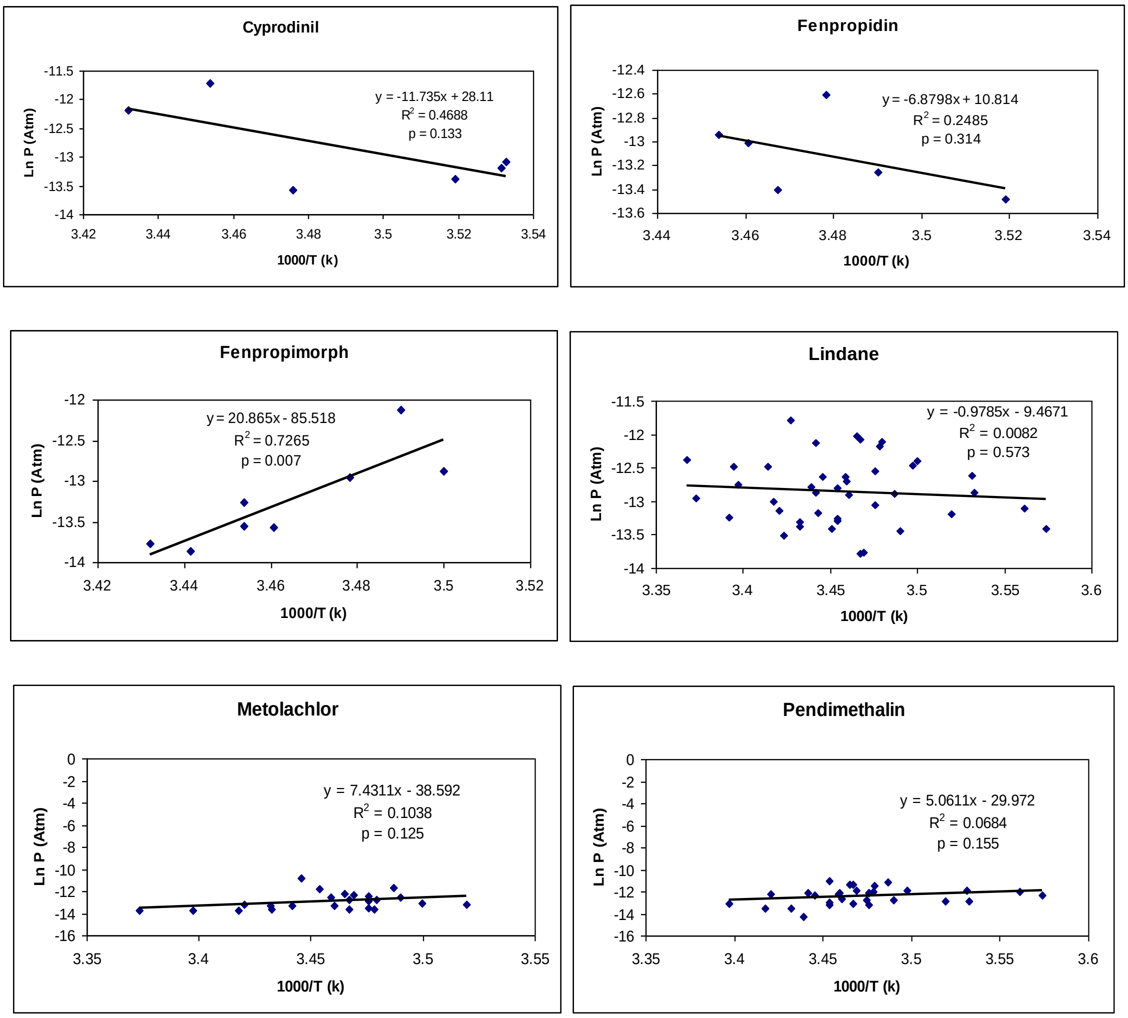


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (A) Tours in 2006-2008

(A) TOURS

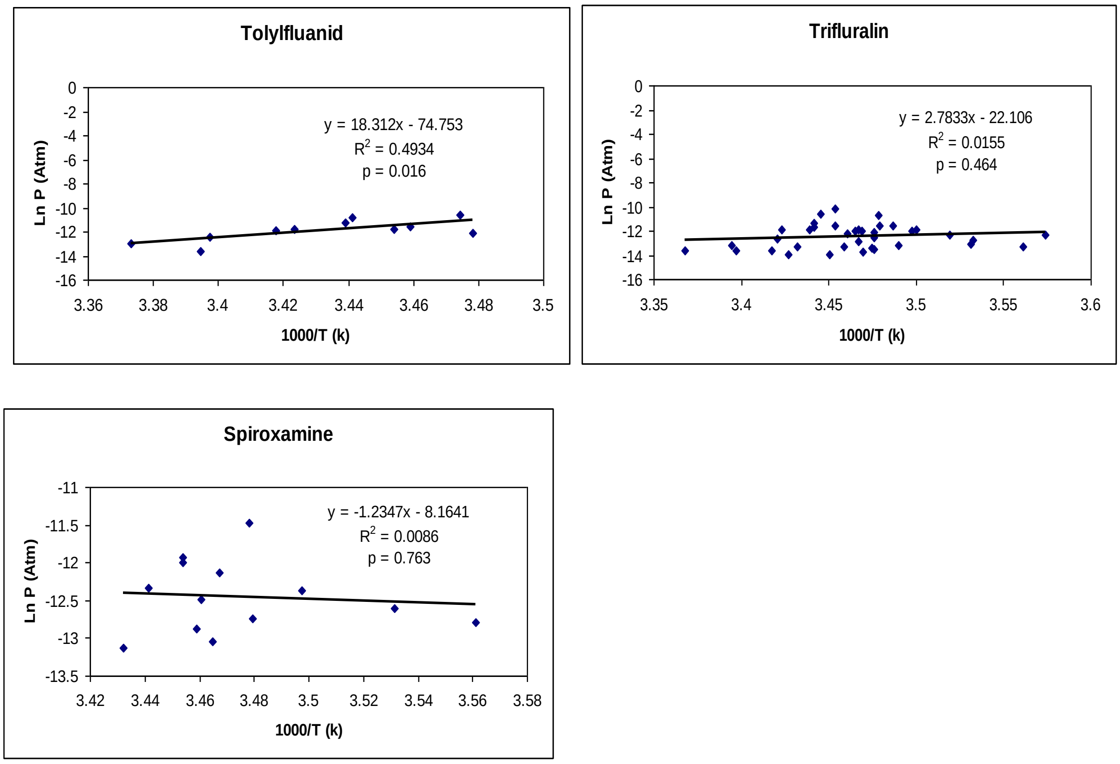


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (A) Tours in 2006-2008

(B) ORLÉANS

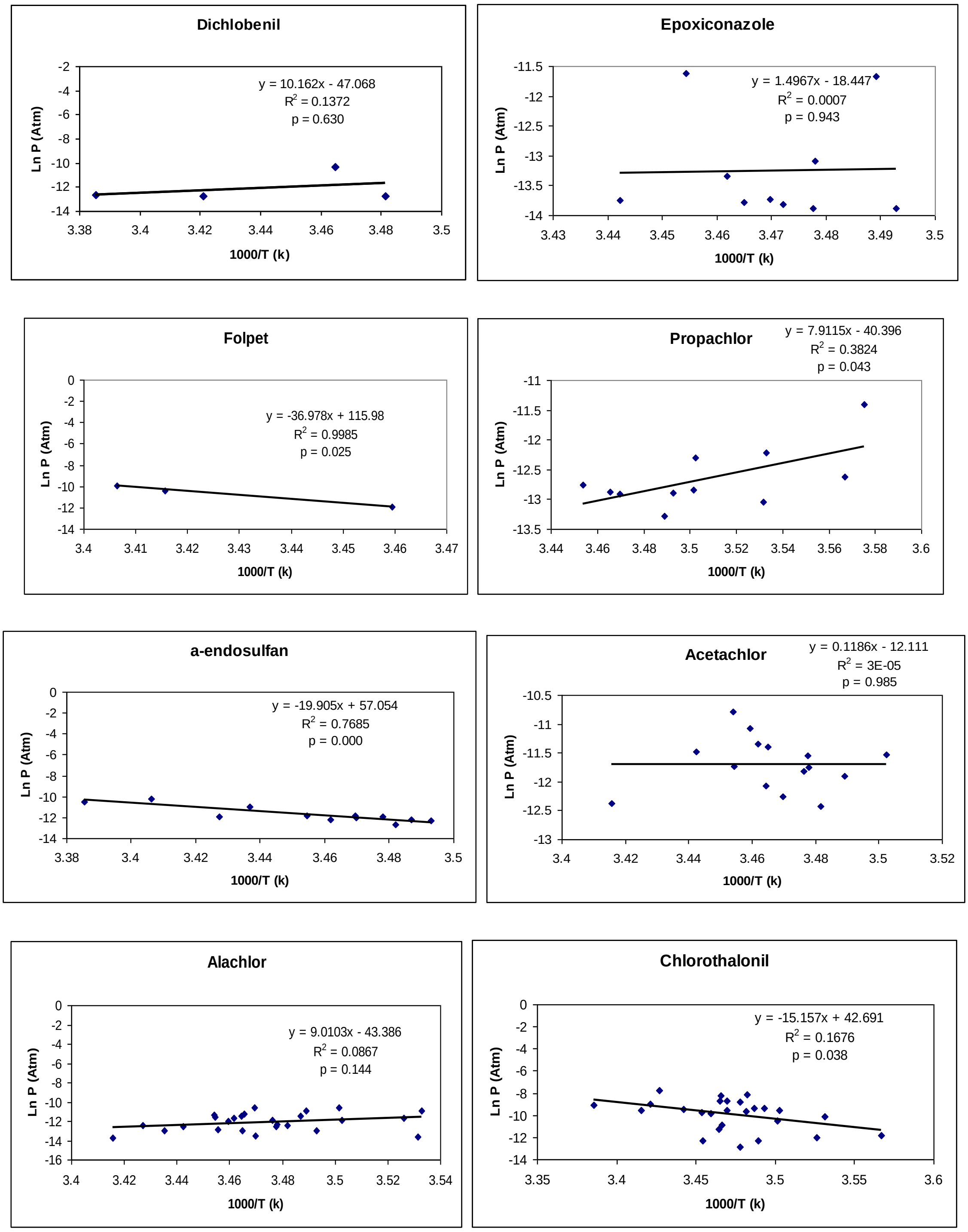


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (B) Orléans in 2006-2008

(B) ORLÉANS

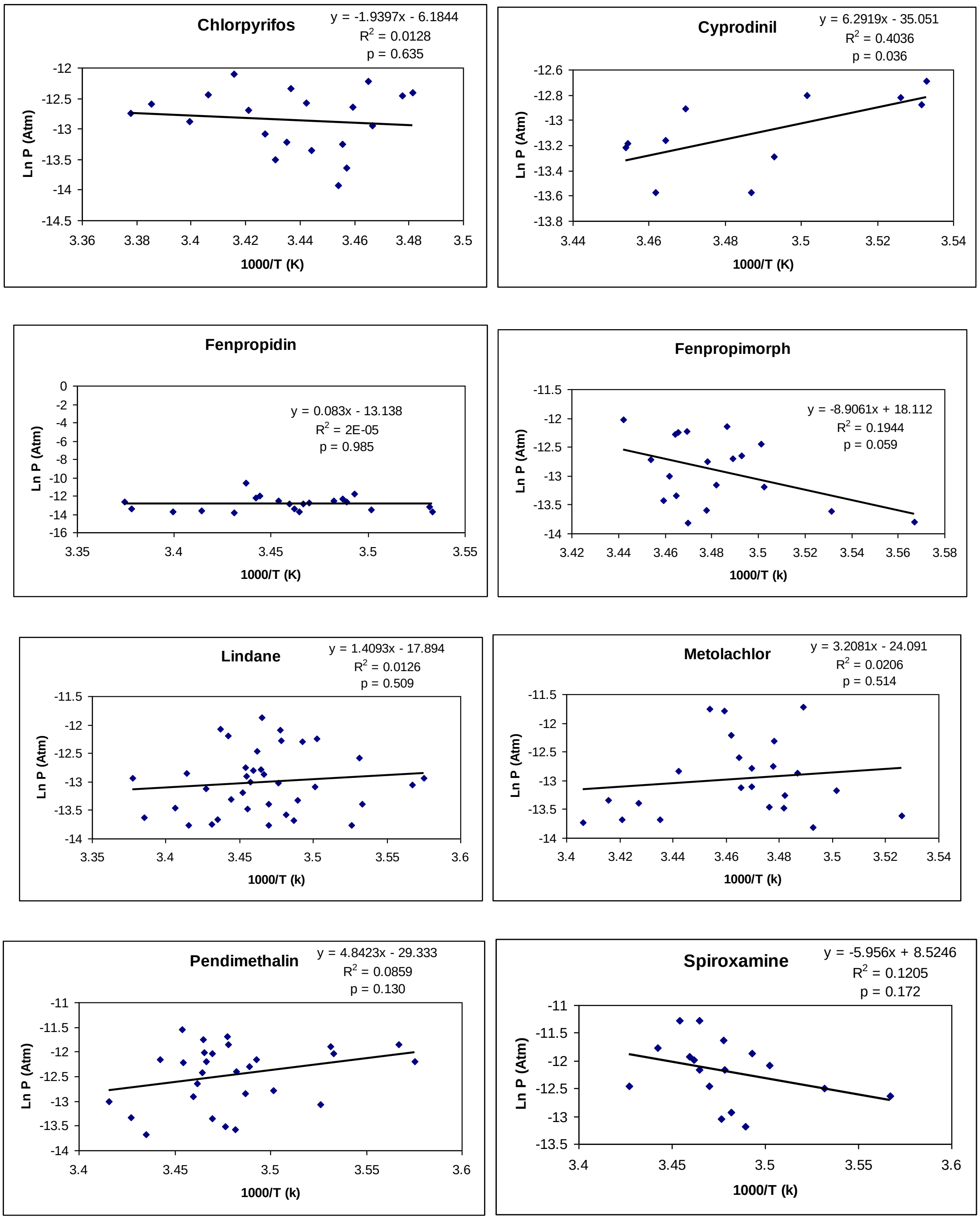


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (B) Orléans in 2006-2008

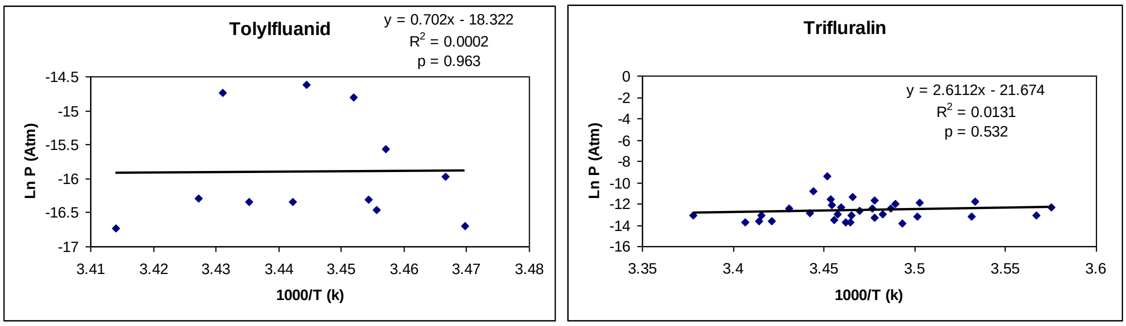


Figure 27: Plots of ln P vs 1000/T for selected pesticides detected in (B) Orléans in 2006-2008

VII.d CONCLUSIONS

Of the 56 pesticides investigated during the years 2006-2008 in three rural and two urban sites in Centre region, France, 41 were identified and quantified in at least one sample. Their overall concentrations ranged from 0.1 to 117.33 ng m^{-3}, and 18 active substances showed frequencies of detection higher than 10%.

Apart from the persistent and banned lindane, the four most detected compounds were the herbicides trifluralin, acetachlor and pendimethalin and the fungicide chlorotalonil. They were found in 52-78% of all the samples taken, and at average concentrations of 1.93, 1.32, 1.84 and 12.15 ng m^{-3}, respectively. Among the pesticides detected, concentrations of eight fungicides (sporoxamine, fenpropimorh, cyprodinil, tolyfluanid, epoxiconazole, vinchlozolin, fluazinam, fludioxinil), two insecticides (propargite, ethoprophos), and one herbicide (oxyfluorfen) were reported for the first time in literature, which could contribute to reducing the gap for experimental measurements of CUPs in the atmosphere.

Although the most characteristic crops surrounding the three rural sites are different and, consequently, the pattern of pesticides applied near these sites is dissimilar, only minor differences could be found in their profiles and concentrations. Nor did we find many differences in pesticide patterns and concentrations when we compared the Or and To sites with the rural areas. This means: (1) that although the atmospheric half life of most of the pesticides studied is in the range of a few hours, their persistence is long enough to allow them to be transported around the region (medium-range transport), and (2) that the distance between the area of treatment and the sampling site is either not significant enough, or could be compensated for the huge amounts used in the region.

Except for some banned persistent pesticides such as lindane, the concentrations of the most detected pesticides are linked to their use on arable crops such as maize, soybean, wheat and sunflower, and their application in vineyards and fruit orchards, the main crops in this region. This shows that the main sources of pesticides in ambient air are local rather than from background atmospheric contamination, and their detection in air occurs mainly during the application period.

VIII. GENERAL CONCLUSIONS

-Modern extraction techniques such as PLE and MAE provided good results for the extraction of CUPs from airborne particulate matter. These techniques are fast and are low in solvent consumption.

-Analytical methodologies developed using LC-MS/MS and GC-MS/MS were capable of muti-residue pesticide measurements at very low levels, and provided unambiguous evidence of the identity of any residue detected.

-A very simple and confirmatory method to analyze 9 CUPs in fine airborne particulate matter (PM 2.5) air was developed. The method was based on the extraction of pesticides with acetone by PLE followed by direct injection into LC–ESI-MS/MS. The LOQ was 6.5-32.8 pg m $^{-3}$ when air volumes of 760 m ^{3} were collected.

-A rapid and confirmatory method to analyze 30 LC-amenable CUPs in fine airborne particulate matter (PM2.5) air was developed. The method was based on the extraction of pesticides with ethyl acetate by MAE, followed by direct injection into LC–ESI-MS/MS. The LOQ was from 6.5 to 32.5 pg m^{-3} when air volumes of 760 m^{3} were collected.

-A sensitive and confirmatory method to analyze 40 CUPs in airborne particulate matter (PM 10) was developed. The method includes the extraction of pesticides with ethyl acetate by MAE, followed by GPC clean-up and injection into GC(EI)-MS/MS. The LOQ ranged from 1.32 to 39.47 pg m^{-3} when air volumes of 760 m^{3} were collected.

-In the three developed methods, where pesticides were analyzed by LC-MS/MS and GC-MS/MS, all of them presented a matrix effect. All pesticides analyzed by LC-MS/MS showed signal suppression; on the contrary, when analyzed by GC-MS/MS they showed high signal enhancement in the presence of the matrix. Consequently, matrix matched standard calibration was used for quantitative analysis.

-A statistical design of experiment approach was suitable for the optimization of PLE and MAE conditions and the ESI ion source in LC-MS/MS.

- Monitoring studies in two European regions were carried out providing more data about the levels of CUPs in different regions around the European Union. The overall concentrations of monitored pesticides ranged from 0.1 to 117.33 ng m^{-3} in Centre region (France). Apart from the persistent and banned lindane, the four most detected compounds were the herbicides trifluralin, acetachlor and pendimethalin and the fungicide chlorotalonil which were found in 52-78% of all the samples taken, and at average concentrations of 1.93, 1.32, 1.84 and 12.15 ng m $^{-3}$, respectively. Among the pesticides detected, concentrations of eight fungicides, two insecticides and one herbicide were reported for the first time in ambient air.

-The overall concentrations of pesticides associated with particulate matter ranged from not detected to 1371 pg m^{-3} in Valencia region. All pesticides from the first study, 11 from the second and 8 from the third were detected in ambient air and reported for the first time in literature. The most detected pesticides were carbendazim, bifenthrin, chlorpyrifos-e and metalaxyl, with a frequency of detection of 80, 98, 100 and 100%, respectively.

-The highest CUP concentrations were obtained during the application period, normally from April to September. In Valencia region, samples were collected during the application period and in Centre region a temporal study year round was carried out, indicating increased levels during the spring period.

-Many of the active substances studied in literature are now banned pesticides and only a small percentage can be considered CUPs. Additional monitoring studies and wider sampling networks are necessary to enhance our knowledge of the occurrence, fate, and impacts of currently used pesticides.

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X. ANNEXES

Annexe 1-Tables

Annexe 2-Figures

Annexe 3-Abreviations and Acronyms

AEPLA: Asociación Empresarial para la Protección de las Plantas
AGP: Auxiliary Gas Pressure
ALZ: Alzira station
AOP: Atmospheric Oxidation Program
APCI: Atmospheric Pressure Chemical Ionization
API: Atmospheric Pressure Ionization
ARfD: Dosis aguda de referencia/Acute reference dose
ASE: Accelerated Solvent Extraction
BTN: Bitertanol
BUN: Burriana station
BUR: Burjassot station
CAPA: Conselleria de Agricultura, Pesca y Alimentación de la Generalitat Valenciana
CBZ: Carbendazim
CCD: Central Composite Design
CID: Collision-induced dissociation
COST: Changing-one-factor-at-a-time
CT: Capillary Temperature
CUPs: Currently Used Pesticides
DCM: Dichloromethane
DOE: Statistical Design of Experiments
Eac: Ethyl acetate
EE: Ethyl ether
EFSA: European Food Safety Authority
EI: Electron Ionization
EPA: Environmental Protection Agency
ESI: Electrospray Ionization
EVA: ethylene vinyl acetate
FA: Fase acuosa/ Aqueous phase
FO: Fase orgánica/Organic phase
GC-ECD: Gas Chromatography-Electron Capture detector
GC-MS/MS: Gas Chromatography-Mass Spectrometry in tandem
GC-MS: Gas Chromatography-Mass Spectrometry detector
GC-NPD: Gas Chromatography-Nitrogephosphorus detector
GFF: Glass Fiber Filter
GPC: Gel Permeation Chromatography
H: Henry´s law constant
Has: Hectáreas/Hectares

HPLC-UV: High Performance Liquid Chromatography-Ultraviolet detector

HVS: High-Volume Sampler

HxTZ: Hexythiazox

IDA/ADI: Ingestión diaria admisible/Acceptable Daily Intake

IMCP: Imidacloprid

IMZ: Imazalil

ISPD: Isoproturon

IT: Ion Trap detector

Kow: Patition coefficient octanol/water

LC-MS/MS: Liquid Chromatography-Mass Spectrometry in tandem

LLP: Liquid-liquid partitioning

LOD/LD: Detection limit

LOQ/LQ: Quantification limit

LRT: Long-range transport

LVS: Low-Volume Sampler

MAAP: Ministère de l´alimentation, de l´agriculture et la pêche du Governement de la République Française

MAE: Microwave-assisted extraction

ME: Matrix Effect

MRT: Medium-range transport

MSPD: Matrix solid-phase dispersion

MTC: Methiocarb

MTD: Methidathion

MW: Molecular weight

NCI: Negative Chemical Ionization

n-Hx: n-Hexane

OCPs: Organochloride pesticides

OPPs: Organophosphate pesticides

Or: Orléans station

Oy: Oysonville station

PAS: Passive Air Sampler

P-B: Plackett-Burman design

PE: Petroleum ether

PIB/GNP: Producto Interior Bruto/Gross National Product

PLE: Pressurized Liquid Extraction

PM: Particulate Matter

POG: Polymer-coated Glass

POPs: Persistent Organic Pollutants

PTV: Programmable Temperature Vaporizer

PUF: Polyurethane Foam

PYPFN: Pyriproxifen

QC: Quality Control

QFF: Quartz Fiber Filter
QqQ: Triple Quadrupole detector
S/N: Signal to Noise
S: Solubility in water
SA: Saint Aignan station
SD: Standard desviation
SE: Solvent-extraction method
SGP: Sheath Gas Pressure
SIA: Secondary Inorganic Aerosol
SIM: Selected Ion Monitoring
SM: Saint Martin d´Auxigny station
SP: Spray Voltage
SPE: Solid Phase Extraction
SPME: Solid-Phase Microextraction
SPMD: Semimpermeable Membrane Devices
SRM: Selected Reaction Monitoring
SRT: Short-range transport
STJ: Sant Jordi station
$t_{1/2}$: Vida media/Half-Life
TBZ: Thiabendazole
Tm: Tonelada/Ton
To: Tours station
UE/EU: Unión Europea/European Union
VERAM: Versatile, Easy and Rapid Atmospheric Monitor
V/P: vapour/pressure distribution
VOCs: Volatile Organic Compounds
Vp: Vapour pressure
XAD: Hydrophobic polymeric resin Amberlite

Annexe 4- Results Spread: Papers published

Coscollà C, Yusà V, Martí P, Pastor A. *Analysis of currently used pesticides in fine airborne particulate matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry*. **Journal of Chromatography A (2008)1200(2); 100-107**

IMPACT FACTOR: 4.101

Coscollà C, Yusà V, Beser MI, Pastor A. *Multi-residue analysis of 30 currently used pesticides in fine airborne particulate matter (PM 2.5) by microwave-assisted extraction and liquid chromatography-tandem mass spectrometry*. **Journal of Chromatography A (2009) 1216; 8817-8827**

IMPACT FACTOR: 4.101

Clara Coscollà, Patrice Colin, Abderrazak Yahyaoui, Olivier Petrique, Vicent Yusà, Abdelwahid Mellouki and Agustin Pastor. *Ocurrence of Currently Used Pesticides in Ambient Air of Centre region (France)*. **Atmospheric Environment (2010) 44; 3915-3925**

IMPACT FACTOR: 3.584

Coscollà C, Castillo M, Pastor A, Yusá V. *Determination of 40 currently used pesticides in airborne particulate matter (PM 10) by microwave-assisted extraction and gas chromatography coupled to triple quadrupole mass spectrometry*. **Analytica Chimica Acta (2011) 693; 72-81**

IMPACT FACTOR: 3.757

Yusà V, Coscollà C, Mellouki W, Pastor A, De la Guardia M. *Review: Sampling and analysis of pesticides in ambient air*. **Journal of Chromatography A (2009) 1216; 2972-2983**

IMPACT FACTOR: 4.10

Congresses

AUTHORS: Coscollà C, Yusà V, Martí P, Pastor A.
TITLE: *"Analysis of Currently Used Pesticides in Fine Airborne Particulate Matter (PM 2.5) by Liquid Chromatography-Tandem Mass Spectrometry"*
CONGRESS: 4th International Workshop on Liquid Chromatography-Tandem Mass Spectrometry for Screening and Trace Level Quantitation in Environmental and Food Samples
PUBLICATION: Abstract Book
PLACE: Barcelone (Spain)
YEAR: 2008

AUTHORS: Coscollà C, Ibáñez C, Yusà V, Martí P, Pastor A.
TITLE:*"Determination of 30 pesticides in fine airborne particulate matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry"*
CONGRESS: "5th European Conference on Pesticides and Related Organic Micropollutants in the Environment" and *"11th Symposium on Chemistry and Fate of Modern Pesticides"*
PUBLICATION: Abstract Book
PLACE: Marseille (France)
YEAR: 2008

AUTHORS: Coscollà C, Yusà V, Carbonell E, Pastor A.
TITLE: *"Analysis of Currently Used Pesticides in Fine Airborne Particulate Matter (PM 10) by Liquid Chromatography-Tandem Mass Spectrometry using Pressurized Liquid Extraction and SPE clean-up"*
CONGRESS: "*Pesticide Behaviour in Soils, Water and Air Conference"*
PUBLICATION: Abstract Book
PLACE: York (United Kingdom)
YEAR: 2009

AUTHORS: Coscollà C, Yusà V, Carbonell E, Pastor A
TITLE: *"Analysis of 30 Currently Used Pesticides in Fine Airborne Particulate Matter (PM 2.5) by Liquid Chromatography-Tandem Mass Spectrometry"*
CONGRESS: "*I Jornadas de Investigación en Seguridad Alimentaria"*
PUBLICATION: Abstract Book
PLACE: Valencia (Spain)
YEAR: 2009

AUTHORS: Coscollà C, Yusà V, Carbonell E, Pastor A.
TITLE: *"Analysis of 30 Currently Used Pesticides in Fine Airborne Particulate Matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry"*
CONGRESS: "*IV Reunión de la Sociedad Española de Espectrometría de Masas"*
PUBLICATION: Abstract Book
PLACE: Universitat Jaume I de Castellón (Spain)
YEAR: 2009

AUTHORS: Coscollà C, Yusà V, Mancebo M, Pastor A
TITLE: *"Determination of Currently Used Pesticides (CUPs) in fine airborne particulate matter by Gas Chromatography-Triple Quadrupole Mass Spectrometry"*
CONGRESS: "6th European Conference on Pesticides and related organic micropollutants in the Environment and 12th Symposium on Chemistry and modern Pesticides"
PUBLICATION: Abstract Book
PLACE: Matera (Italy)
YEAR: 2010

AUTHORS: Coscollà C, Yusà V, Castillo M, Pastor A.
TITLE: *"Determination of Currently Used Pesticides (CUPs) in fine airborne particulate matter using Microwave-Assisted Extraction and Gas Chromatography coupled to Triple Quadrupole Mass Spectrometry"*
CONGRESS: ISC 2010
PUBLICATION: Abstract Book
PLACE: Valencia (Spain)
YEAR: 2010

Participation in Research Projects

Project title: *Atmospheric Fate and Impact of Pesticides*

Financial Entity: Interreg IIIC Sud part-financed by the European Union

YEAR: 2007-2008

Project title: *Estudio del comportamiento atmosférico de plaguicidas*

Financial Entity: Ministerio de Educación y Ciencia (CGL 2007-65223)

YEAR: 2007-2010

Project title: *Degradación en la atmósfera de los plaguicidas de uso más común en la Comunidad Valenciana*

Financial Entity: Conselleria de Empresa, Universidad y Ciencia (Generalitat Valenciana) (GV/2007/257)

YEAR: 2007-2008

Project title: "*Desarrollo de nuevos muestreadores pasivos de membranas semipermeables: determinación de contaminantes orgánicos en aguas y aire*"

Financial Entity: Ministerio de Educación y Ciencia (CTQ 2008-05719/BQU)

YEAR: 2009-2011

Project title: *"Control de plaguicidas en la atmósfera de la Comunidad Valenciana"*

Financial Entity: Conselleria de Sanitat (033/2009)

YEAR: 2009

Project title: *“Distribución espacial y temporal de los plaguicidas de uso habitual en la atmósfera de la Comunidad Valenciana”*

Financial Entity: Conselleria de Sanitat (046/2010)

YEAR: 2010

Project title: *“Control e impacto de los plaguicidas en la atmósfera de la Comunidad Valenciana”*

Financial Entity: Conselleria de Educación (GV/2011/007)

YEAR: 2011

Project title: “*Impacto de plaguicidas en la atmósfera: niveles en aire y agua de lluvia, cinéticas y degradación en aire”*

Financial Entity: Ministerio de Ciencia e Innovación (CGL2010-18474)

YEAR: 2011