Fundación para el Fomento de la Investigación Sanitaria y Biomédica de la Comunitat Valenciana

GENERALITAT VALENCIANA

European Workshop on Pesticides in Ambient Air
26-27th May 2014

MONITORING OF PESTICIDES IN EUROPE

Dr. Clara Coscollà

Fundación para el Fomento de la Investigación Sanitaria y Biomédica de la Comunitat Valenciana

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OUTLINE

I. Introduction

II. Sampling of pesticides in ambient air

III. Analytical procedures:

- ❖ Extraction
- ❖ Clean-up
- ❖ Determination

IV. Occurrence of pesticides in air

V. Conclusions and future trends

PESTICIDE CONSUMPTION IN EUROPE (2008)

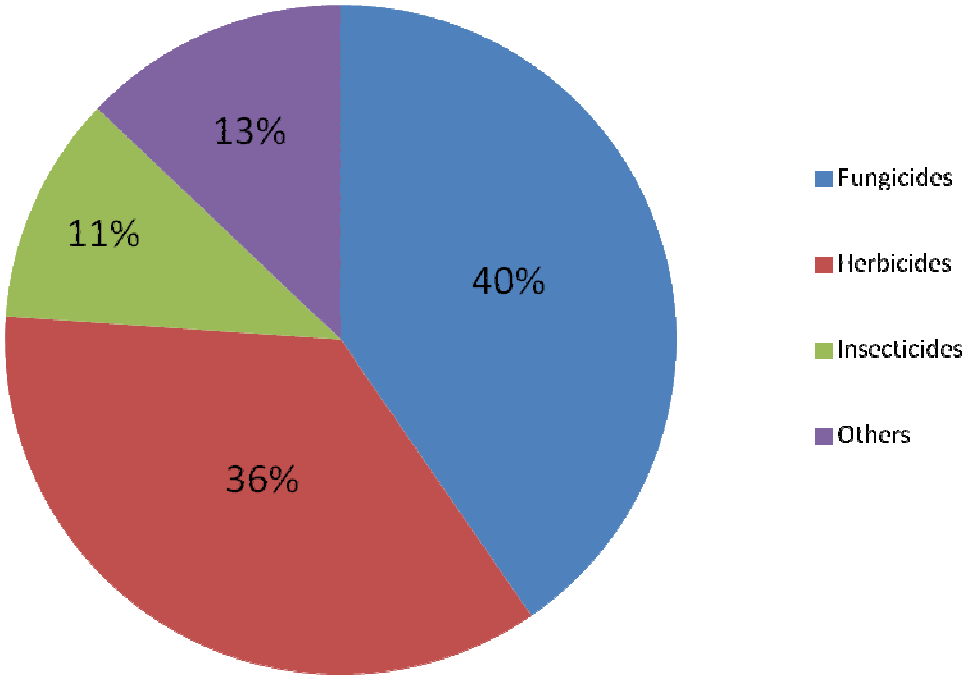
- Consumption of pesticides in European countries:

310 000 Tonnes

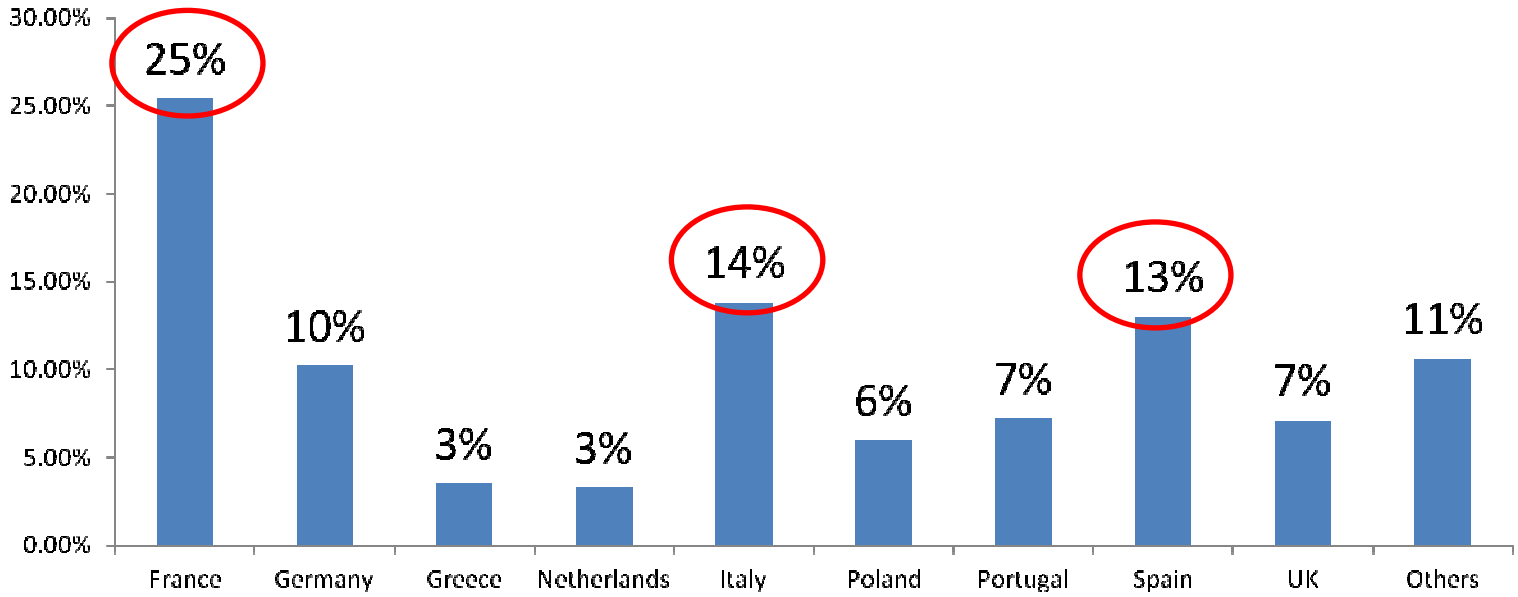
- Number of pesticides authorized and applied in EU (2010):

>350

- Newly introduced pesticides are:
  - ✓more polar
  - ✓less toxic
  - ✓more degradable in ambient air

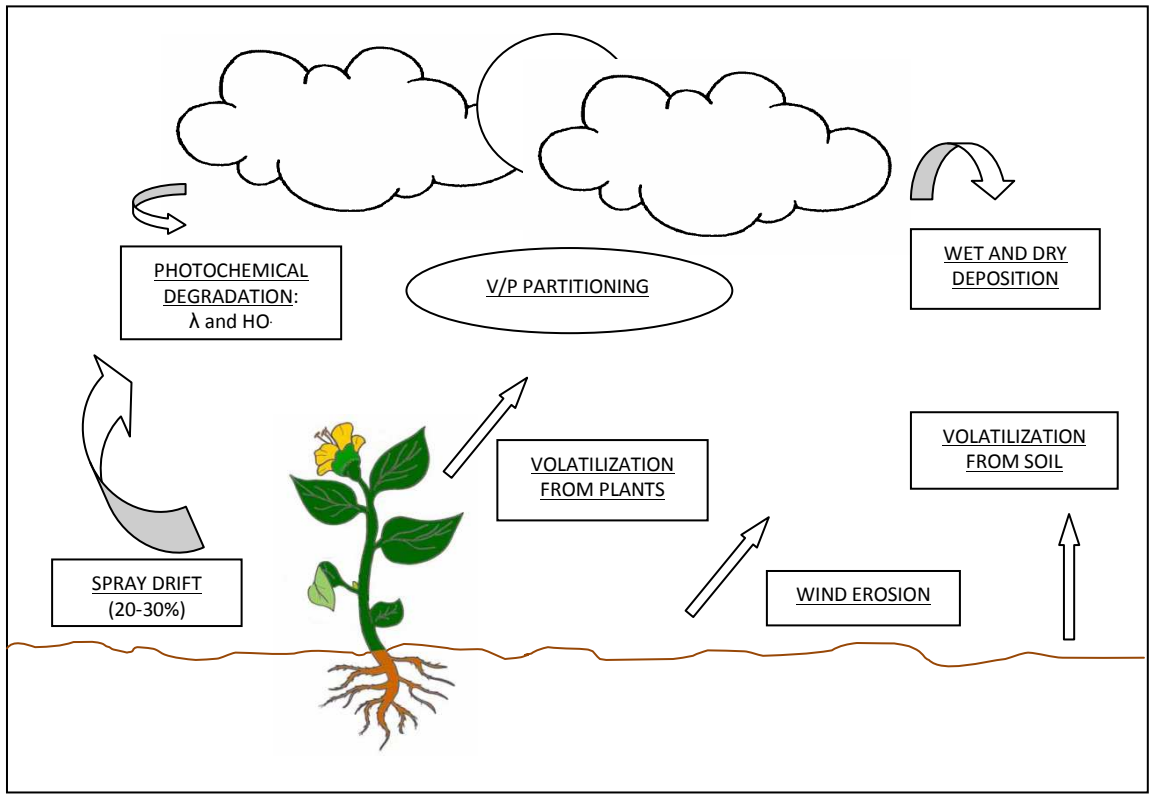


PESTICIDE CONSUMPTION IN EUROPE (2008)



Source: Agrow 2009

Emision and transformation of the pesticides in the atmosphere



Factors influencing emision, transport and transformation of pesticides

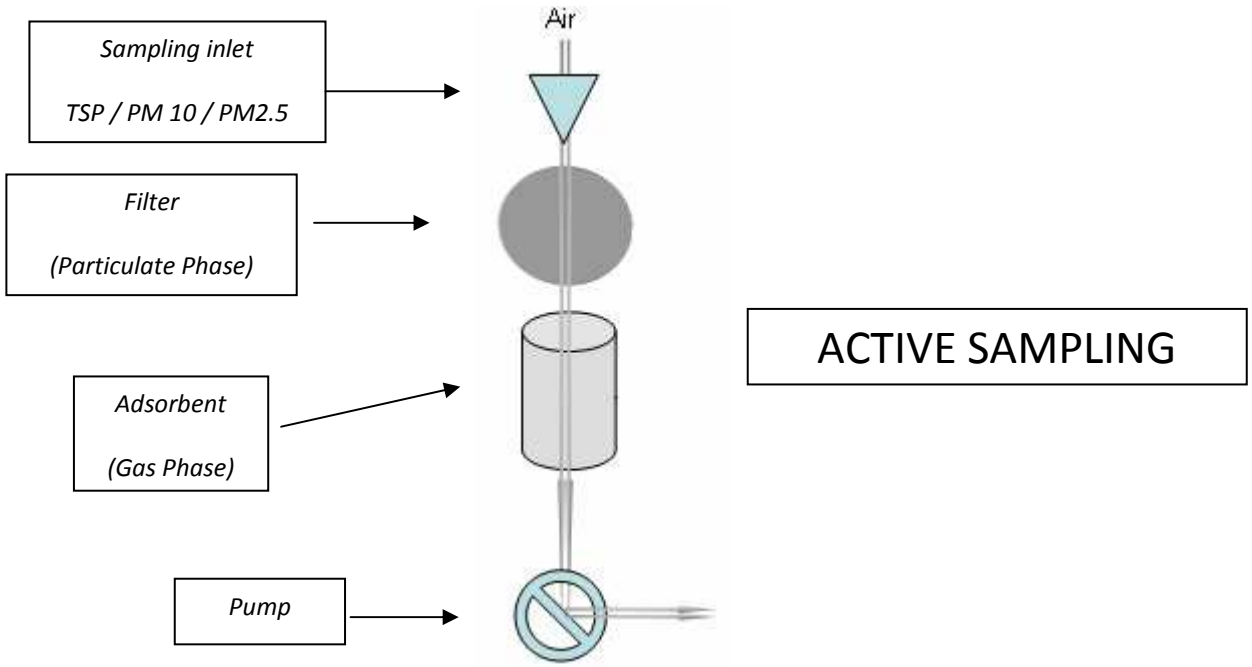
Phys-Chem properties

- **Vapour pressure**
- **-Henry´ s constant (H):** $H_{[Pa\,m^3 mol^{-1}]} = \frac{(V_p \cdot M)}{S}$
- **-Coefficient partition octanol-water (Kow):** $k_{ow} = \frac{Organic\ phase}{Aqueous\ phase}$

Metereological conditions

- **Temperature:** *(ΔT=10ºC →P' =xP x Є[3,4])*
- **-Wind speed**
- **-Wind direction**
- **-Rainfall episodies**

Half Life *(SRT = 1-1000 m, MRT=1-1000 km, LRT>1000 km)*



ACTIVE SAMPLING

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HVS: flow rate = 13-30 $m^3 h^{-1}$ (hours /days)

-Total sampled volume : 220 to 2700 m3

-Sampling times: 12h to 7 days. Normally 24h is generally enough to detect levels of pesticides with a flow rate sampler of 30 m^3h^{-1} (700 m^3/day)

-Air Monitoring Network of Valencia region

HVS: flow rate = 13-30 $m^3 h^{-1}$ (hours /days)

-Particle phase: QFFs, GFFs

-Gaseous phase: PUF, XAD-2, XAD-4, sandwich PUF/XAD

HVS: flow rate = 13-30 $m^3 h^{-1}$ (hours /days)

FILTERS	SORBENTS	REFERENCE
GFF	PUF	Alegria et al 2008
GFF	PUF/XAD-2	Aulagnier et al 2008
GFF	XAD-2	Scheyer et al 2008
QFF	PUF	Yang et al 2008
QFF	PUF/XAD-2	Choi et al 2009
GFF	PUF	Ozcan et al 2009

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HVS: flow rate = 13-30 $m^3 h^{-1}$ (hours /days)

FILTERS	SORBENTS	REFERENCE
GFF	XAD-2	Schummer et al 2010
GFF	XAD-2, XAD-4	Borras et al 2011
GFF	PUF	Cindoruk et al 2011
GFF	PUF	Park et al 2011
QFF	-	Hart et al 2012
QFF	-	Coscollà et al 2013
QFF	PUF	Jin et al 2013
QFF	PUF	Li et al 2014

LVS: flow rate = 0.03-3.6 $m^3 h^{-1}$ (days/few weeks)

QFFs +PUF

-Exposed time:
weekly

-Flow rate: 1m^3/h

-Total volume:
aprox 168 m^3

-Air Monitoring Network of Centre Region (France)

LVS: flow rate = 0.03-3.6 $m^3 h^{-1}$ (days/few weeks)

FILTERS	SORBENTS	REFERENCE
GFF	PUF	Bossi et al 2008
GFF	PUF	Coscollà et al 2010
GFF	PUF-XAD-PUF	Hayward et al 2010

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Cascade Impactors_LVS: Particle size distribution of pesticides

Samplig inlet: TSP

-Impactor measures gravimetric particle size distribution

-Flow rate: 2m^3/h, so 48 m^3 per day

-Total volume collected: 300 m^3 (per week)

-This sampler is situated in Alzira station (Valencia)

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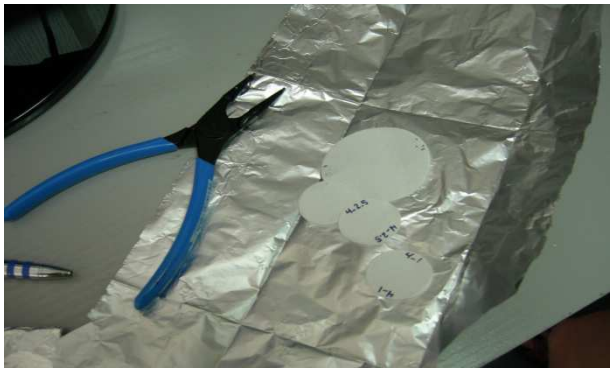
Cascade Impactors_LVS: flow rate = 0.03-3.6 $m^3 h^{-1}$ (days/few weeks)

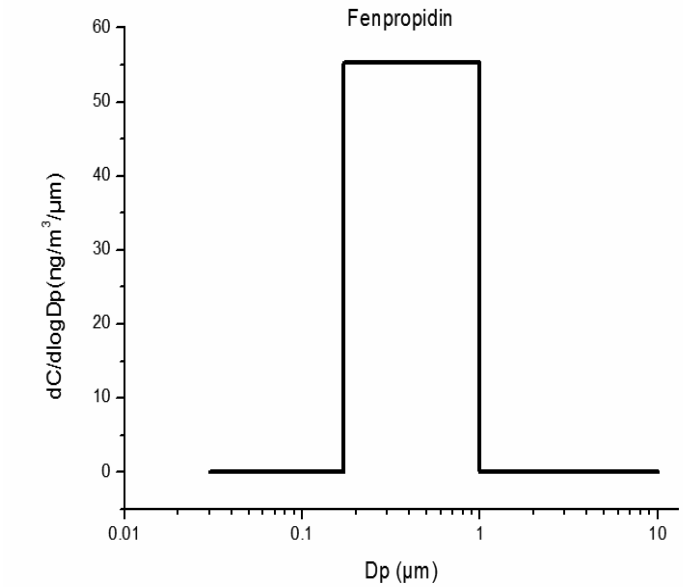


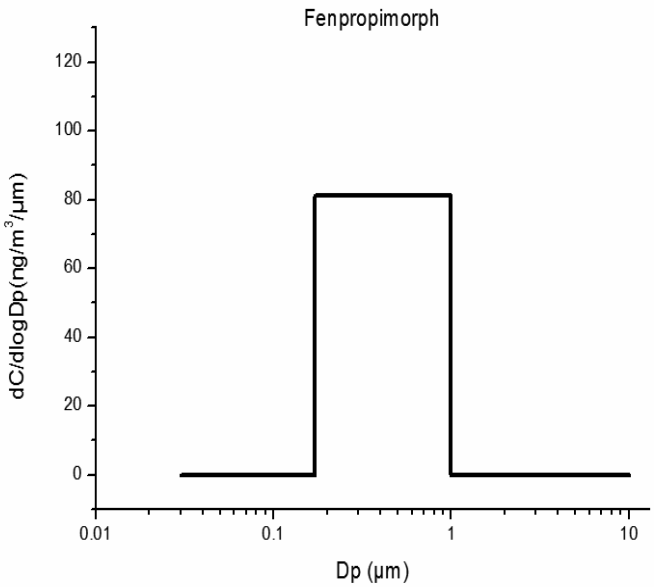
-Four size fractions:

<1, 2.5-1, 10-2.5 and >10 µm

-Two types of GFFs (25 and 47 mm diameter)

Cascade Impactors





Most pesticides were accumulated in the fine (0.1-1 µm) particle size fraction in a Centre Region (France)

Source: Coscollà et al 2013

Pesticides	Extraction	Clean-up	Determination	LOD (pg m-3)	Reference
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)

Research literature within period 2000-2008

Analysis of pesticides in ambient air

EXTRACTION

ULTRASONIC EXTRACTION

-Liquid-solid extraction (LSE) of pesticides trapped in filters and cartridges

-Solvents: n-hexane, methanol, dichloromethane

-Pesticides: OCPs, CUPs

-Matrices: GFF, XAD-2, XAD-4, PUF

-References: Fu et al (2009), Borras et al (2011), Cindoruk et al (2011)

Analysis of pesticides in ambient air

EXTRACTION

SOXHLET

-Advantage: simple, low-cost method and adopted in standarized analytical methodologies for deterrmining pesticides in ambient air.

-Disadvantage: time (6-24 h) and solvent (250-700 mL) consuming. Long-heating periods are prone to broke the integrity of polar thermally labile pesticides applied in modern agriculture.

-Solvents: acetone, DCM, hexane, cyclohexane or mixtures

-Pesticides: OCPs, CUPs

-Literature: Soxhlet is the most common extraction technique used in the literature for pesticides in ambient air

Analysis of pesticides in ambient air

EXTRACTION

PRESSURIZED LIQUID EXTRACTION

-PLE utilizes organic solvents under elevated temperature (50-200ºC) and pressures (1000-2000 psi) to extract organic pollutants from environemtal matrices.

-Advantages: 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.

-Pesticides: OCPs, OPPs, CUPs

Analysis of pesticides in ambient air

EXTRACTION

PRESSURIZED LIQUID EXTRACTION

-Matrices: QFFs, GFFs, PUFs, XAD-2, Tenax

-Solvents: hexane, DCM, diethyl ether, ethyl acetate

-Literature: Yang et al (2008), Rania et al (2008), Bailey et al (2007), Coscollà et al (2010)

Analysis of pesticides in ambient air

EXTRACTION

MICROWAVE ASSISTED EXTRACTION

-Advantages: reduction of both, extraction time and organic solvent consumption

-The main parameters for method optimization are solvent, temperature and time.

-Matrices: QFFs

-Pesticides: CUPs

-Solvents: ethyl acetate

-Literature: Hart et al. (2012) and Coscollà et al (2013)

Analysis of pesticides in ambient air

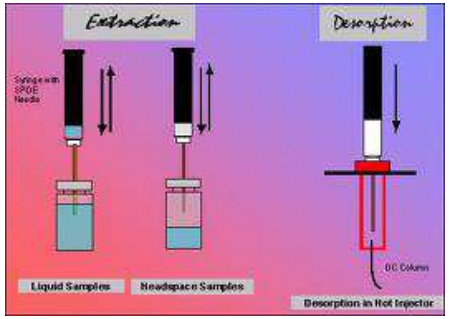
EXTRACTION

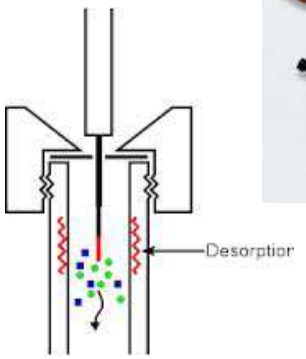
SOLID PHASE-MICROEXTRACTION (SPME)

-SPME is a simple, fast and solvent-free technique which combines extraction, concentration and sample introduction into GC injector in one single device.

-Pesticides: CUPs

-Literature: Raeppel et al 2014





Analysis of pesticides in ambient air

CLEAN-UP

SOLID PHASE EXTRACTION

-Polar sorbents: Florisil, alumina, silicagel or combination of them, used for most apolar pesticides

-Apolar sorbents: C18 for more polar pesticides

-Matrices: filters and PUFs

-Pesticides: OCPs, OPPs

-Literature: SPE is the most commonly used clean-up technique in pesticides in air

Analysis of pesticides in ambient air

CLEAN-UP

GEL PERMEATION CHROMATOGRAPHY

-GPC or size exclusion chromatography separates compounds on the basis of their size

-GPC is best suited for removing materials like waxes and fats

-Pesticides: CUPs

-Literature: Hart et al 2012

Analysis of pesticides in ambient air

DETERMINATION | GAS CHROMATOGRAPHY

PESTICIDES	DETERMINATION ANALYSIS	REFERENCE
OCs	GC-ECD	Alegria et al 2008
CUPs	GC-ECD	Scheyer et al 2008
OCs	GC-ECD	Ozcan et al 2009
CUPs	GC-MS	Aulagnier et al 2008
OCs	GC-MS	Choi et al 2009
OCs	GC-MS	Fu et al 2009
CUPs	GC-MS	Coscollà et al 2010
CUPs, OCs	GC-MS	Haywrad et al 2010
CUPs	GC-MS	Borras et al 2011
CUPs	GC-MS	Li et al 2014

Analysis of pesticides in ambient air

DETERMINATION

GAS CHROMATOGRAPHY

PESTICIDES	DETERMINATION ANALYSIS	REFERENCE
CUPs	GC-MS/MS	Schummer et al 2010
CUPs	GC-MS/MS	Hart et al 2012
OCs	GC-HRMS	Bossi et al 2008
OCs	HRGC/HRMS	Park et al 2011
OCs	HRGC/HRMS	Jine et al 2013

Analysis of pesticides in ambient air

DETERMINATION | GC-MS/MS Triple Q

-Volatility and thermal stability are required for amenable-GC pesticides

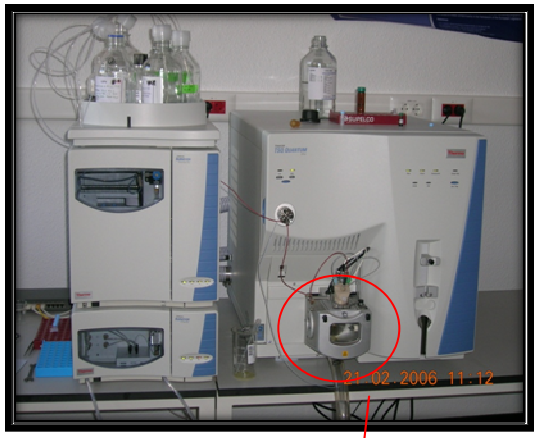
-GC-MS/MS is replacing traditional detectors and is nowadays the analytical technique most widely used.

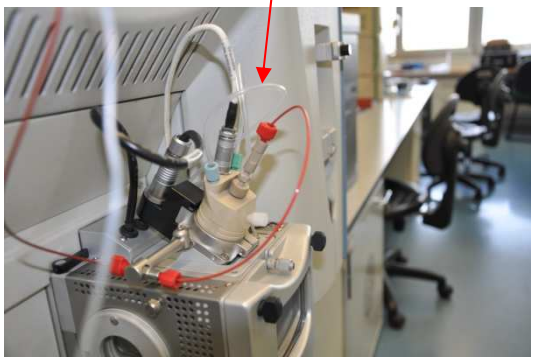
-Capacity to provide quantitative and confirmatory results, and high sensitivity.

Analysis of pesticides in ambient air

DETERMINATION

LC-MS/MS Triple Q





-Determination of these compounds:

- non amenable-GC pesticides
- polar compounds
- compounds with low-thermal stability and those requiring derivatization to improve volatility in GC

-LC-MS/MS presents wider scope, increased sensitivity and better selectivity.

-Electrospray ionization in the positive mode (ESI+) gave higher sensitivity for pesticides in air.

Analysis of pesticides in ambient air

DETERMINATION

LC-MS/MS Triple Q

-**Non-polar stationary phase**:

octadecyl carbon chain (C18) bonded to silica

-**Mobile phase:**

Aqueous, moderately polar (the most common organic solvents used are acetonitrile and methanol)

-**Literature:**

Coscollà et al 2010 and Coscollà et al 2013

Analysis of pesticides in ambient air

DETERMINATION

LC-HRMS

-Liquid chromatography combined with full scan high-resolution mass spectrometry has shown to be an effective approach for measuring the exact mass of pesticides.

-LC-HRMS enables a fully untargeted measurement with the ability to retrospectively detect additional compounds in the raw data, which were not anticipated to be of interest at the time of sample analysis (screening methodology).

-Important parameters are: retention time tolerances, accurate mass tolerances, adducts, isotopic pattern, fragment ions and response thresholds.

Occurrence of pesticides in ambient air

-In recent years, several monitoring studies have reported pesticide concentrations in remote, rural and urban zones of different countries.

-In general, the reported values are the sum of pesticides present in gas and particulate phases, although some studies reported the distribution between gas and particles.

-Concentrations of pesticides in ambient air ranged from few pg per m^3 to many ng per m^3.

-The presence of a pesticide in the air is dependent on its use, but other factors, such as V/P distribution, wet and dry deposition, transport and atmospheric degradation, are also important.

Occurrence of pesticides in ambient air

-The highest concentrations in air usually occur in the spring and summer months coinciding with application times and warmer temperatures.

-Pesticides have been detected at low levels during periods after use. This could be due to volatilization, wind erosion or the result of LRT from other areas.

-Until now 150 CUPs and their metabolites have been detected in ambient air.

-The results of the following tables correspond to PM10, PM 2.5 or TSP depending on the study.

Occurrence of pesticides in ambient air

COUNTRY	PESTICIDES	SAMPLING YEAR	SITE	LEVELS	REFERENCE
Mexico	OCs	2002-2004	Urban/ rural	239-2360 pgm^{-3}	Alegria 2008
Canadá	CUPs	2004	rural	4 pgm^{-3} - 8 ngm^{-3}	Aulagnier 2008
Greenland	OCs	2004-2005	urban	4.8-20.2 pgm^{-3}	Bossi 2008
Canadá	CUPs, OCs	2006-2007	rural	400-600 pgm^{-3}	Hayward 2010

Occurrence of pesticides in ambient air

COUNTRY	PESTICIDES	SAMPLING YEAR	SITE	LEVELS	REFERENCE
China	OCs	2005-2006	Urban, suburban	93-351 pgm^{-3}	Yang 2008
China	CUPs	2011-2012	Urban	150-3816 pgm^{-3}	Li 2014
Turkey	OCs	2006-2007	urban	4.78 ngm^{-3}	Ozcan 2009
Turkey	OCs	2008-2009	urban	1030.7 pgm^{-3}	Cindoruk 2011
Korea	OCs	2008	Urban, rural, remote	ND-344.3 pgm^{-3}	Park 2011

Occurrence of pesticides in ambient air

COUNTRY	PESTICIDES	SAMPLING YEAR	SITE	LEVELS	REFERENCE
France	CUPs	2006-2008	Urban, rural	1.32-12.15 ngm^{-3}	Coscollà 2010
France	CUPs	2007	urban	0.08-1428 ngm^{-3}	Schummer 2010
France	CUPs	2010	urban	0.2-85.8 ngm^{-3}	Raeppel 2014
Spain	CUPs	2010	Urban, rural, remote	From few to several hundred pgm^{-3}	Hart 2012
Spain	CUPs	2010	Urban, rural, remote	From few to several hundred pgm^{-3}	Coscollà 2013

CONCLUSIONS AND FUTURE TRENDS

-Further studies are necessaries to improve sampling procedures.There is a lack of consistency in sampling methodologies.

-Presently used analytical methods generally involve Soxhlet extraction that requires big solvent volumes and is time consuming. Consequently, efforts should be made to develop sample preparation techniques based on modern extraction techniques such as PLE or MAE.

-Analytical methodologies employed must be capable of residue measurements at very low levels, and must provide unambiguous evidence to confirm the identity of any residue detected.

CONCLUSIONS AND FUTURE TRENDS

-Consequently, MS or MS/MS are necessary tools in the modern analysis of pesticides in air, coupled to GC or LC.

-Also further developments involving techniques such as LC-HRMS or GC-HRMS could be necessaries in order to apply non-target analysis in monitoring pesticides and their degradation compounds in ambient air.

-Wider monitoring studies are required to achieve a better knowledge of the occurrence and fate of CUPs in ambient air.

-Wider sampling networks are necessaries to reach a better knowledge of the occurrence, fate, and impacts of CUPs.

-More effforts are required to implement an extensive Air Monitoring Network in Europe for pesticide control and to develop regulations or recommendations regarding safer pesticide levels in ambient air.

THANK YOU VERY MUCH

MERCI BEAUCOUP