ADAPTATION OF ANALYSIS AND SAMPLING METHODS OF PESTICIDES AND THEIR DEGRADATION PRODUCTS IN AIR.

Gas-phase and particulate products study from the atmospheric degradation of pesticides.

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In colaboration with Universidad Politecnica de Valencia

Introduction

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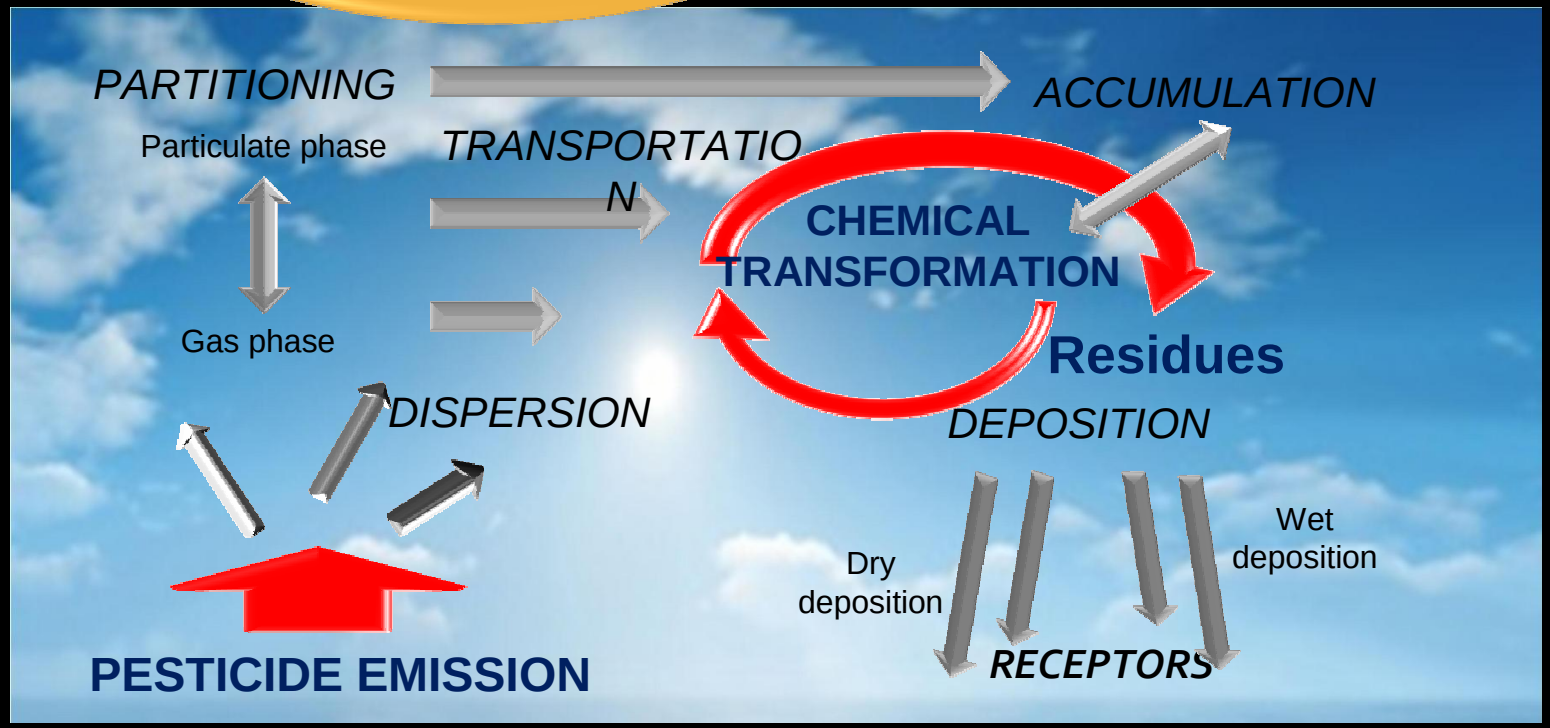
PESTICIDES

Current agriculture is based on the intensive use of synthetic pesticides. The original molecules or their residues are detected in the **atmosphere**

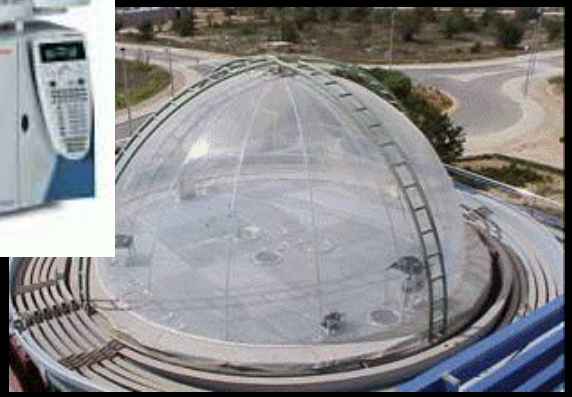
GASEOUS PHASE
PARTICULATE PHASE

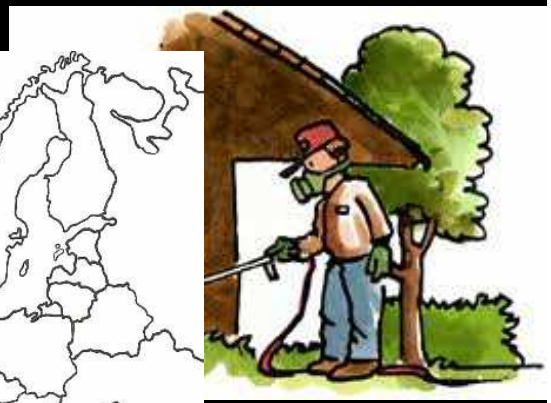


Objetive 1

Analytical method efficient and selective for pesticide monitoring

Gaseous and particulate





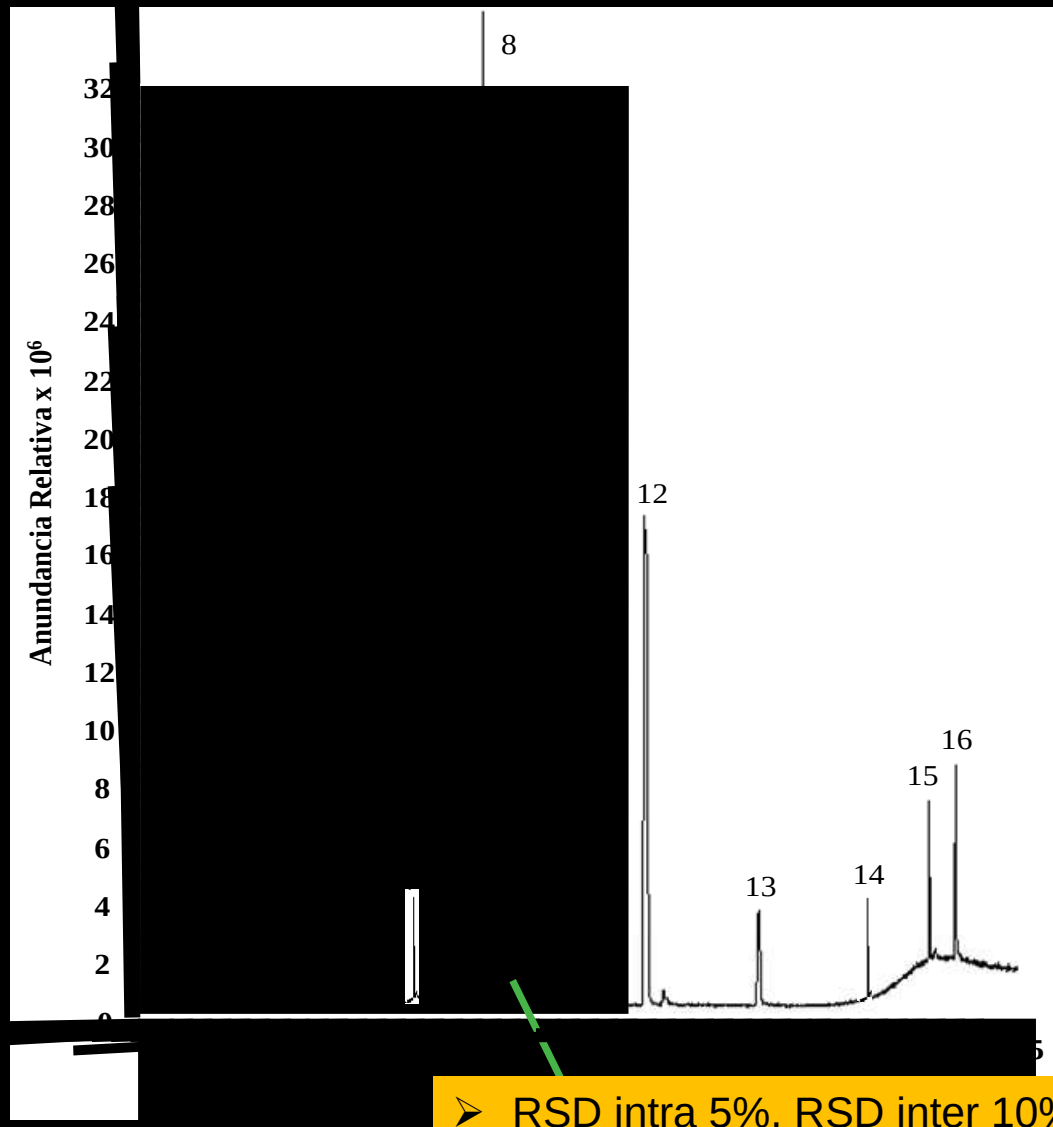
Laboratory studies

Sampling campaigns

Chromatography GC-MS

16 PESTICIDES

Most common application in Valencia region



1. Propacloro
2. Etalfluralina
3. Trifluralina
4. Benfluralina
5. Lindano
6. Metilclorpirifos
7. Propanil
8. Malatión
9. Clorpirifos
10. Fentión
11. Clorfenvinfos
12. Metidatión
13. Buprofezin
14. Tebuconazol
15. Piriproxifen
16. Bitertanol

(*). Estándar interno

- RSD intra 5%, RSD inter 10%
- Concentration range between 0,05 mg L^{-1} to 20 mg L^{-1}

E. Borras et al. Analytica Chimica Acta 699 (2011)

Sample treatment

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Sampling → **Liquid extraction** → **Concentration**

Filter type

Ultrasonic

Solvent
Cycles

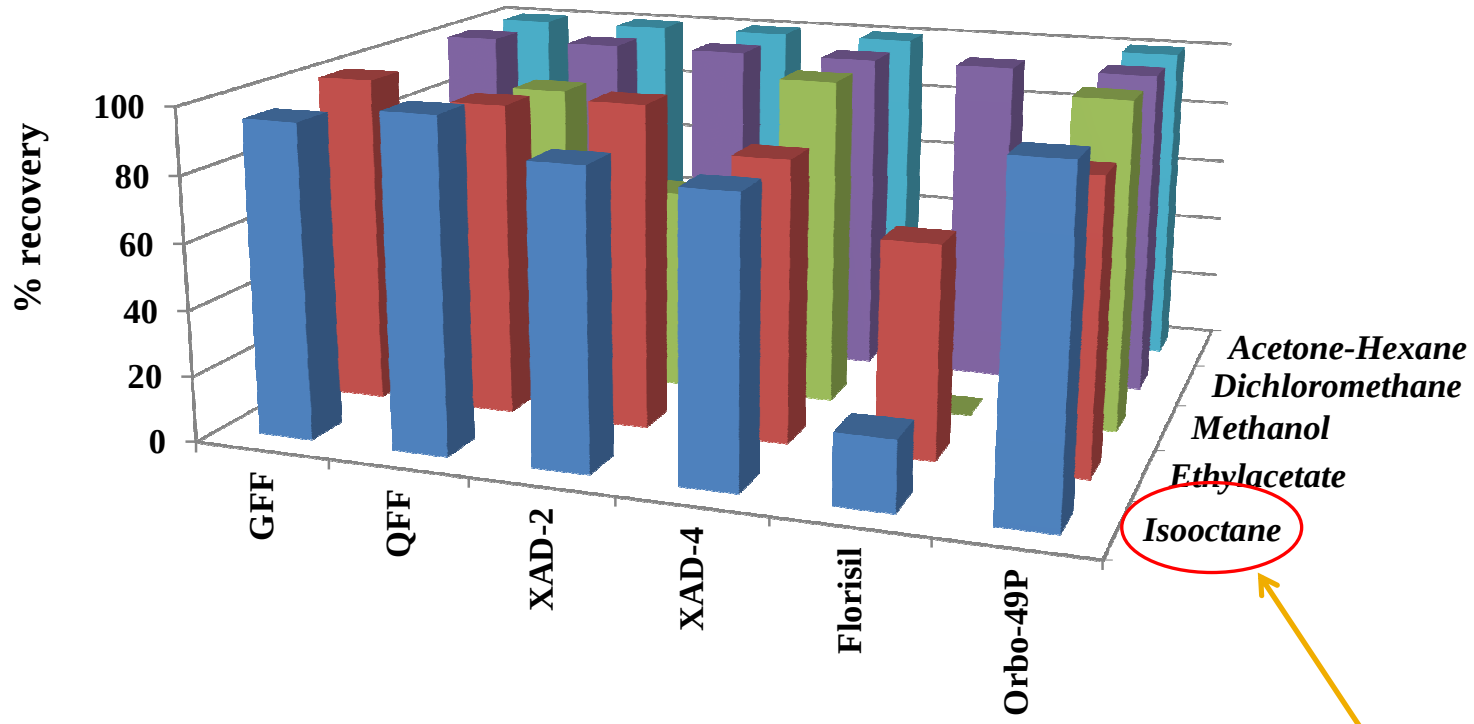
Rotavapor time

↓

Concentration → **Injection GC-MS**

Evaporation
N_2 air stream

OPTIMIZATION OF SAMPLING SUPPORT AND SOLVENT



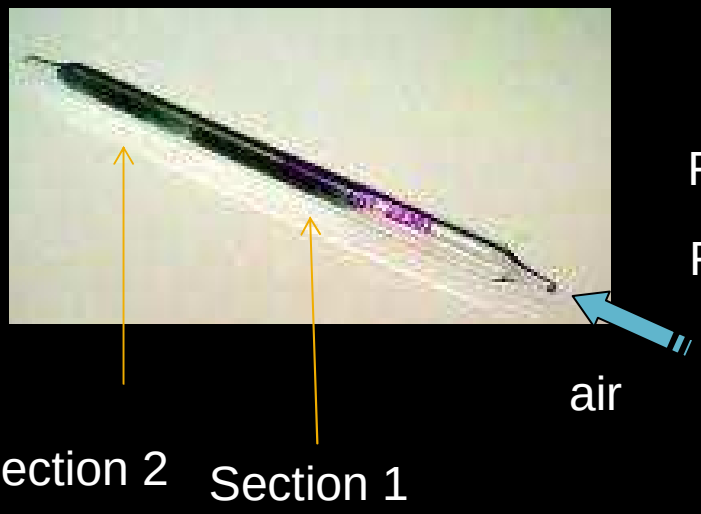
GFF = 95 ± 11% Particulate matter

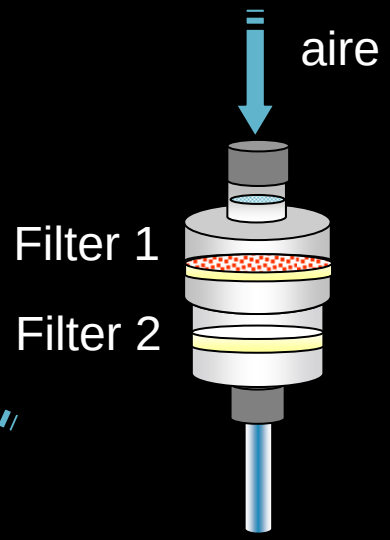
XAD-2 = 89 ± 6%
XAD-4 = 85 ± 15% Gaseous phase

Efficiency, cost, safety and properties associated with green chemistry

EVALUATION OF SAMPLING CONDITIONS

SATURATION





Sampling conditions
PM 24h, 30 m^3/h
Gas 24h 1 L/min

Absence of pesticides in the second section of the cartridges or in the second filter

Quantitative sampling

STABILITY

Chlorpyrifos-methyl, propanil, malathion and chlorpyrifos were unstable in GFF filters at time storage of 7 days, at 4ºC

Validation – EUPHORE

PESTICIDES → ATMOSPHERIC REACTOR

Pesticide	Cartridge	Sampling time (min)	Gas phase: cartridge (ppbV)	Gas phase: IR (ppbV)	% gas phase	Particulate phase: GFF ($\mu g\ m^{-3}$)	Particulate phase: TEOM ($\mu g\ m^{-3}$)
Propachlor	-	Inicial [1]	-	209 ± 4	100.0	-	ND
	XAD-2	60-90	121 ± 5	129 ± 3	61.8	158 ± 7	197 ± 5
	XAD-4	180-210	109 ± 4	120 ± 3	57.9	120 ± 7	141 ± 4
Benfluralin	-	Inicial [1]	-	204 ± 1	100.0	-	ND
	XAD-2	60-90	63 ± 3	71 ± 2	35.1	177 ± 5	197 ± 5
	XAD-4	180-210	63 ± 2	68 ± 2	33.4	131 ± 3	141 ± 4
Malathion	-	Inicial [1]	-	250 ± 3	100.0	-	ND
	XAD-2	60-90	138 ± 4	142 ± 4	55.9	193 ± 8	197 ± 5
	XAD-4	180-210	117 ± 4	126 ± 3	49.7	134 ± 5	141 ± 4

[1] Concentration after injection, ND: not detected

- ✓ Effectiveness of the proposed method
- ✓ SVOCs: necessary their determination in both phases

GAS / PARTICLE PARTITIONING

Environmental samples

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FIVE LOCATIONS

	LICENSE Sampling campaigns	Particulate %	Gas %
Propachlor	Yes until 31/10/2009	42	6
Ethalfluralin	No	-	-
Trifluralin	Yes until 31/12/2008	6	-
Benfluralin	Yes	6	-
Lindane	No	-	-
Chlorpyrifos-methyl	Yes	30	15
Propanil	Yes until 31/10/2009	-	-
Malathion	Yes until 06/08/2008	30	6
Chlorpyrifos	Yes	18	39
Fenthion	No	18	12
Chlorfenvinfos	No	6	3
Metidathion	No	-	6
Buprofezin	Yes until 31/09/2009	-	-
Tebuconazole	Yes	-	-
Piryproxifen	Yes	-	-
Bitertanol	No	-	-

FORBIDDEN

N.D: not detected
Error < 5%

33 SAMPLES
21 positives
9 of 16 detected pesticides

ng m^{-3}

	LICENSE Sampling campaigns	License Actual	PARTICULATE PHASE		GAS PHASE	
			min	max	min	max
Propachlor	Yes until 31/10/2009	No	0.18	5.83	5	82
Ethalfluralin	No	Yes	N.D	N.D	N.D	N.D
Trifluralin	Yes until 31/12/2008	No	0.08	0.3	N.D	N.D
Benfluralin	Yes	Yes	0.09	0.14	N.D	N.D
Lindane	No	No	N.D	N.D	N.D	N.D
Chlorpyrifos-methyl	Yes	Yes	0.13	1.23	21	51
Propanil	Yes until 31/10/2009	No	N.D	N.D	N.D	N.D
Malathion	Yes until 06/08/2008	Yes	0.45	4.5	185	577
Chlorpyrifos	Yes	Yes	0.22	2.66	29	1428
Fenthion	No	No	0.08	4.46	20	1268
Chlorfenvinfos	No	No	1.1	3.09	187	N.D
Metidathion	No	No	N.D	N.D	48	512
Buprofezin	Yes until 31/09/2009	No	N.D	N.D	N.D	N.D
Tebuconazole	Yes	Yes	N.D	N.D	N.D	N.D
Piryproxifen	Yes	Yes	N.D	N.D	N.D	N.D
Bitertanol	No	No	N.D	N.D	N.D	N.D

N.D: not detected

Error < 5%

CORRELATION ⇒ Chlorpyrifos-methyl: orange and peach crops (85%)

Other detected pesticides: crops of apricot, pear, plum, cherry and tomato 15%

HPLC-MS Method

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Sample treatment

- Filters extracted 3 times in ultrasonic bath with 10 ml of ethyl acetate for 15 min
- Extracts were accumulated and taken to dryness in a vacuum drier
- Samples were reconstituted with 500 µL of methanol and reduced to 100 µL

Chromatographic conditions

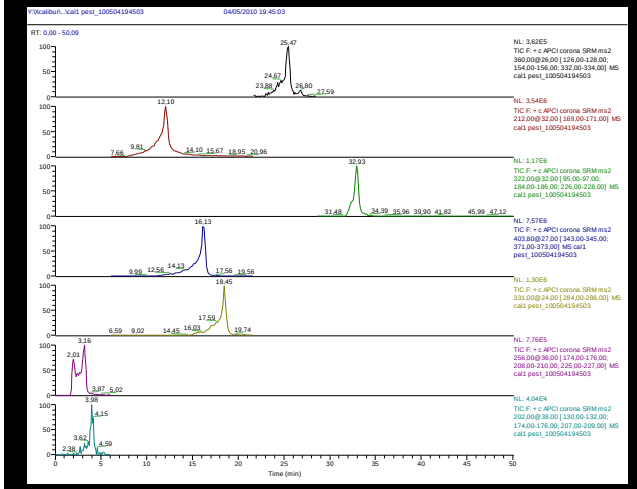
- ProntoSil 120-5 C18 column (150 x 2 mm; 5 um) Mobile phases A: methanol and B: water at 0.1% acetic acid
- Flow at 200 ml min^{-1}
- Gradient profile at 0 min 50% A, from 0 to 35 min linear gradient to 90% A, and at 90% A until the end of the chromatogram (50 min)

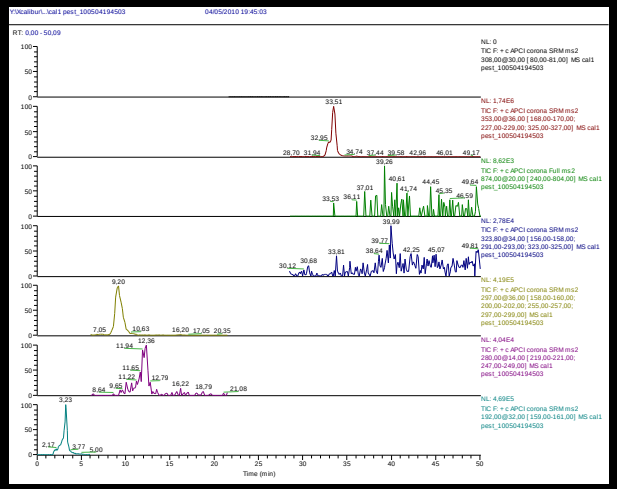
LC Surveyor and LCQ Advantage mass spectrometer

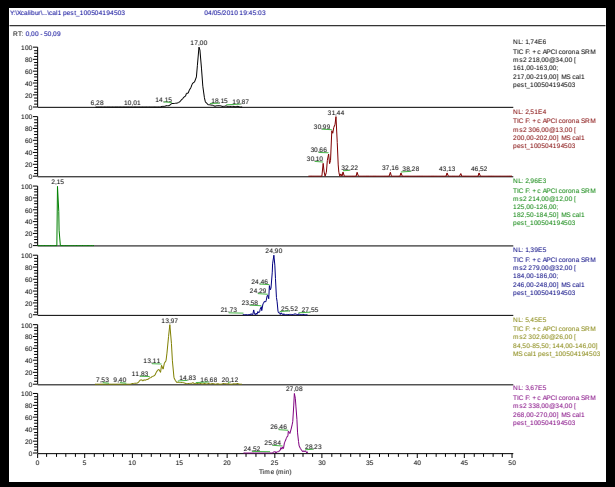
Detection conditions

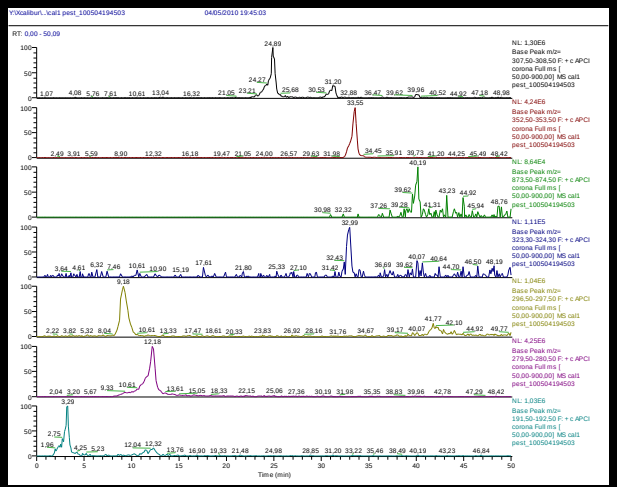
- **APCI+ mode**
- vaporizer temperature 400 ºC
- sheath gas flow rate 37 (arb)
- auxiliary gas flow rate 20 arb
- discharge current 5 uA
- capillary temperature 185 ºC
- capillary voltage 46 V
- tube lens offset 20 V
- **Full-scan mode range 50-900 m/z**
- **Selected Reaction Monitoring mode (SRM) to detect and quantify**

HPLC-MS Method









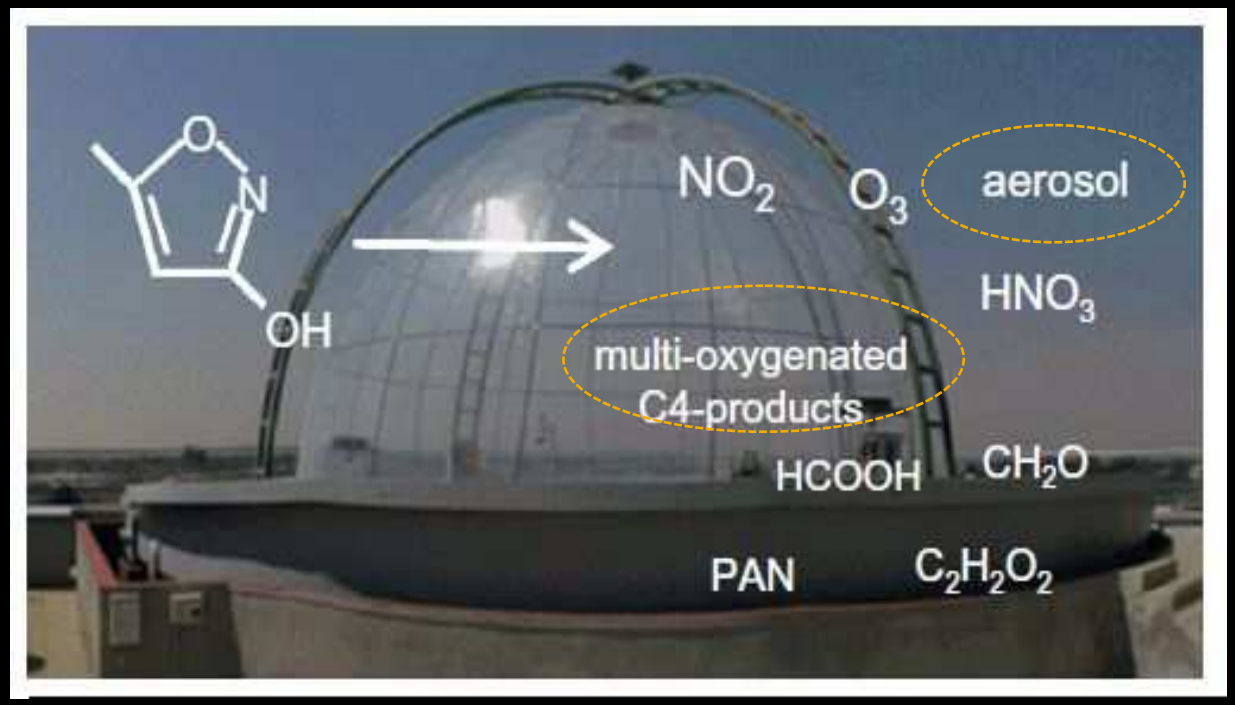
Conditions

- ✓ Samples were quantified using response factors from the daily calibrations made together with the injection of the samples
- ✓ Range of 20 to 0.2 ppm in solution.

chlorfenvinphos	chlorpyriphos-methyl
propachlor	imazalil
pyriproxifen	metalaxyl
azoxystrobin	carbendazim
malathion	propanil
imidacloprid	buprofezin
thiabendazole	omethoate
tebuconazol	fenthion
hexythiazox	methidathion
abamectin	bitertanol

Objetive 2

Atmospheric degradation of pesticides and the products generated



Reaction products

ANALYSIS

PESTICIDES

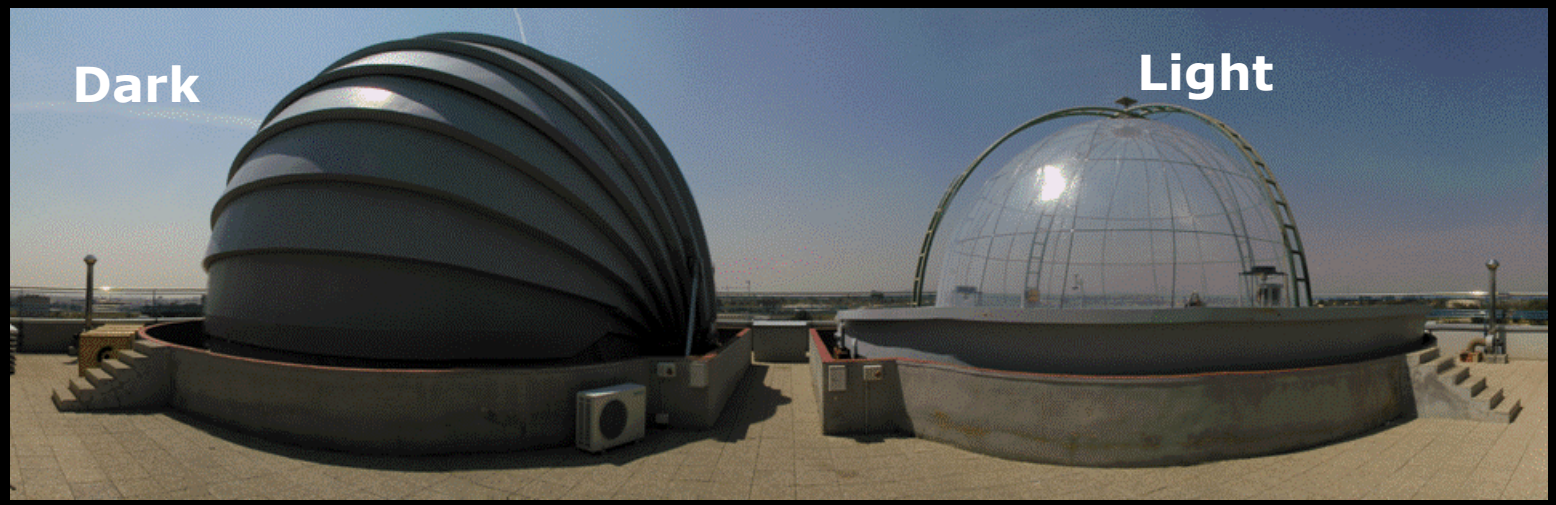
DIAZINON
HYMEXAZOL
CHLORPYRIFOS-METHYL → PRECURSOR
PROPACHLOR
TRIFURALIN

GC-MS Method : Pesticides

PRODUCTS

GAS PHASE
PARTICULATE PHASE → MULTI-OXYGENATED PRODUCTS

GC-MS
Derivatization PFBHA/MSTFA



Particulate matter formation

Type of Experiment	Y (%)
Photolysis of diazinon	-
Photo-oxidation of diazinon	44
Ozonolysis of hymexazol	0
Photolysis of hymexazol	0.09
Photo-oxidation of hymexazol in the absence of NO_x	4.73
Photo-oxidation of hymexazol in the presence of NO_x	4.81
Ozonolysis of chlorpyrifos-methyl	-
Photolysis of chlorpyrifos-methyl	-
Photo-oxidation of chlorpyrifos-methyl in the absence of NO_x	8
Photo-oxidation of chlorpyrifos-methyl in the presence of NO_x	21
Ozonolysis of propachlor	-
Photolysis of propachlor	-
Photo-oxidation of propachlor	15
Photolysis of trifluralin	42.5
Photo-oxidation of trifluralin	15

$$Y = \frac{\Delta HC}{\Delta M_0}$$

Aerosol yield

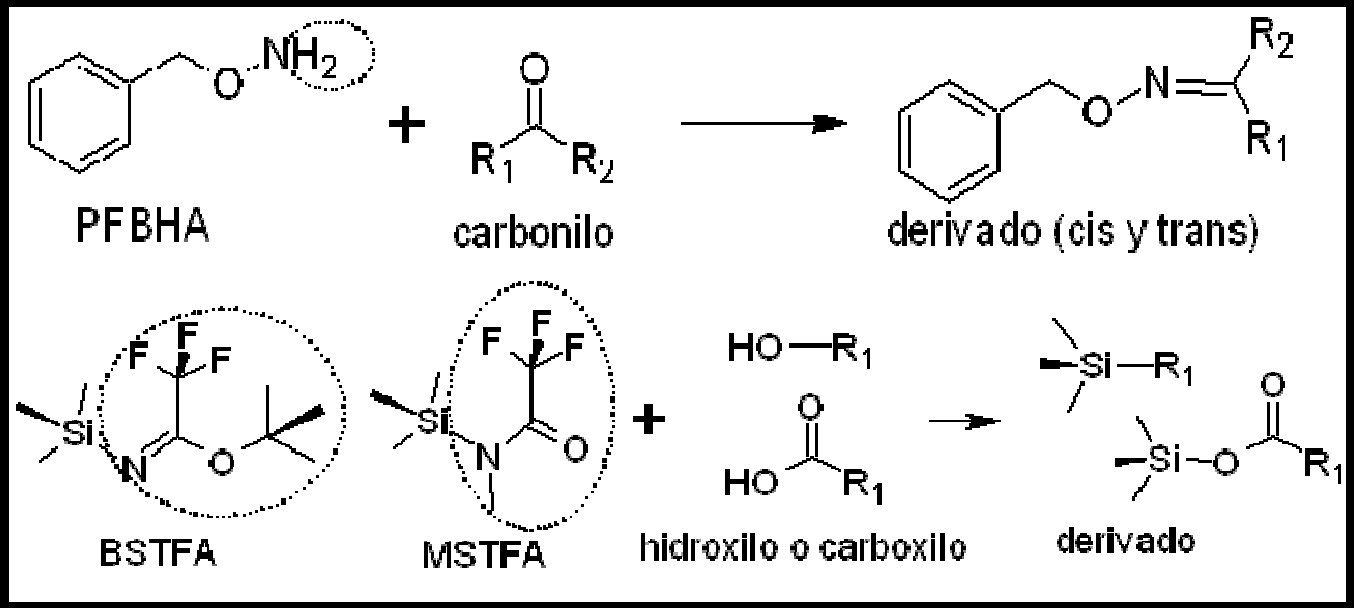
Exceptional behavior

Analytical method

ANALYTES

Alkanols, poli-hydroxylated compounds, aldehydes, ketones, hydroxy-ketones, carboxylic acids, dicarboxylic acids and other multi-oxygenated compounds

DERIVATIZATION PROCESS



1st step

2nd step

Sequential derivatization

- Yields > 99%
- Reproducibility > 90%
- Linearity r^2 > 0,99
- Reduced number of artifacts

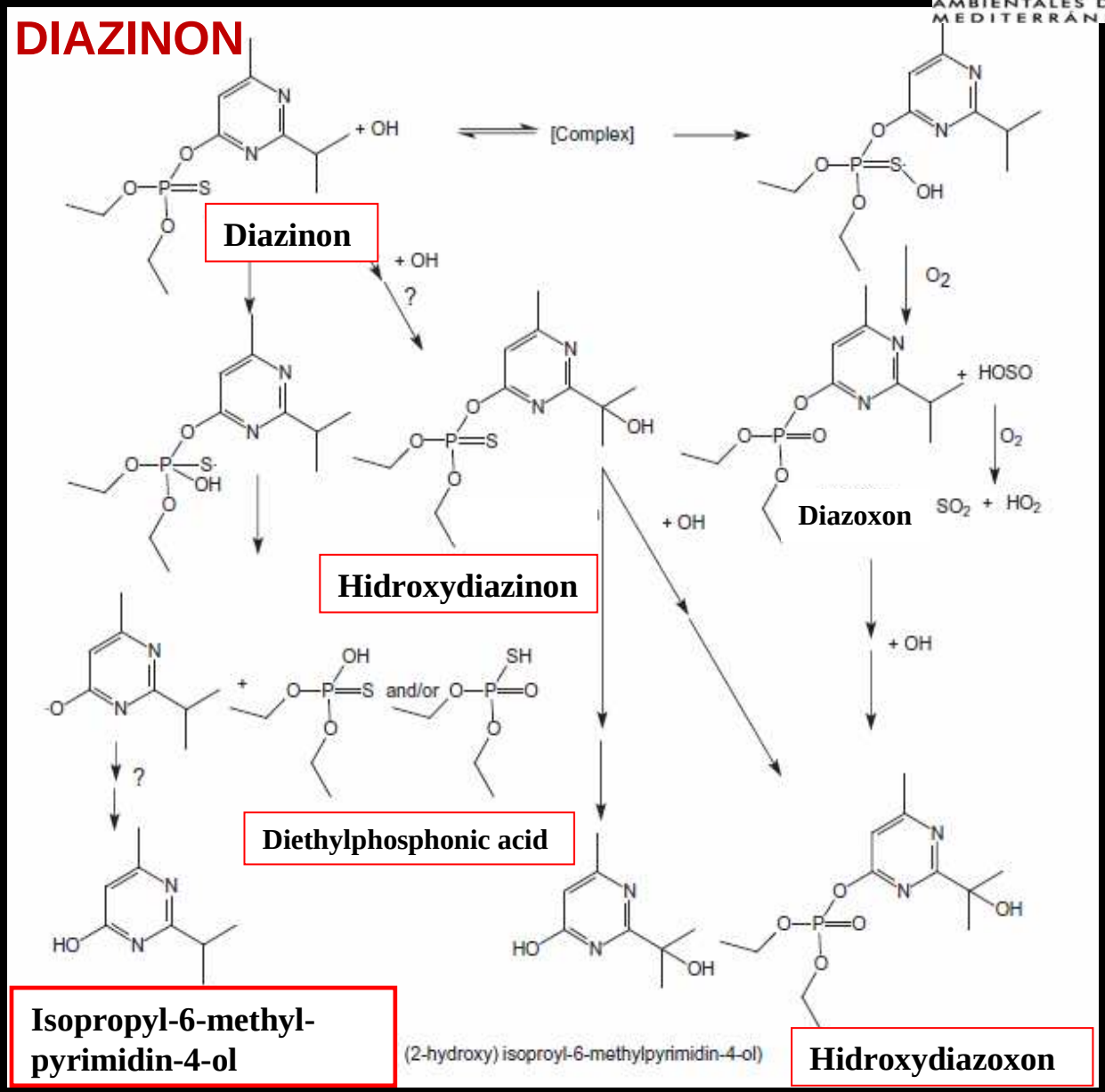
E. Borrás et al. Intern. J. Environ. Anal. Chem. 2012, 92, 110-124

Example. Diazinon

MECANISM

- Identification of gaseous and particulate compounds
- Support of mechanism design

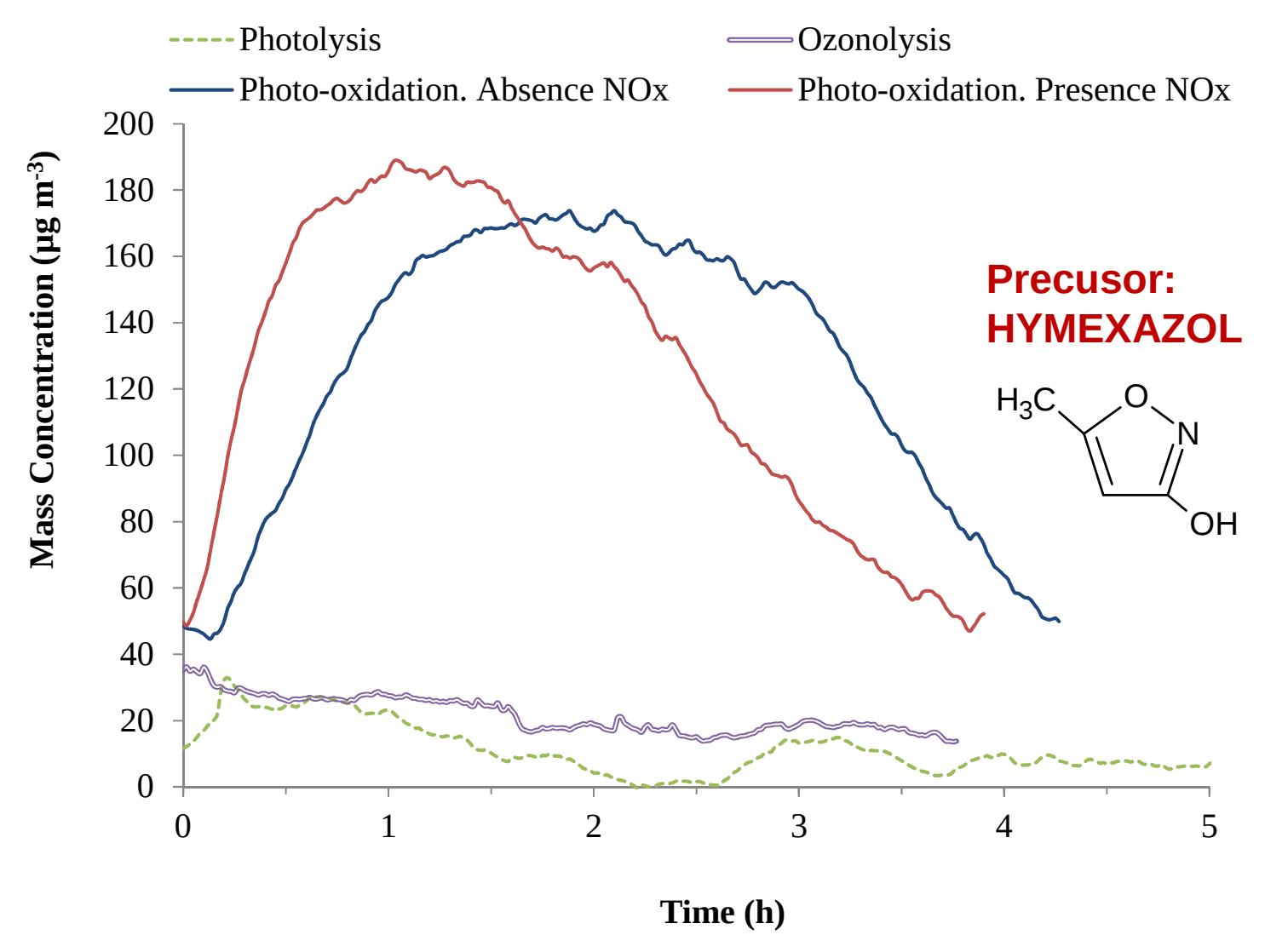
- Chromatographic techniques
- Spectroscopic tecniques (PTR-MS)
- Optical techniques



Muñoz et al., Chemosphere, 2011a , 724-730

Example. Hymexazol

PARTICULATE MATTER FORMATION



E. Borras et al. Chemosphere 92 (2013) 1035–1041

HYMEXAZOL

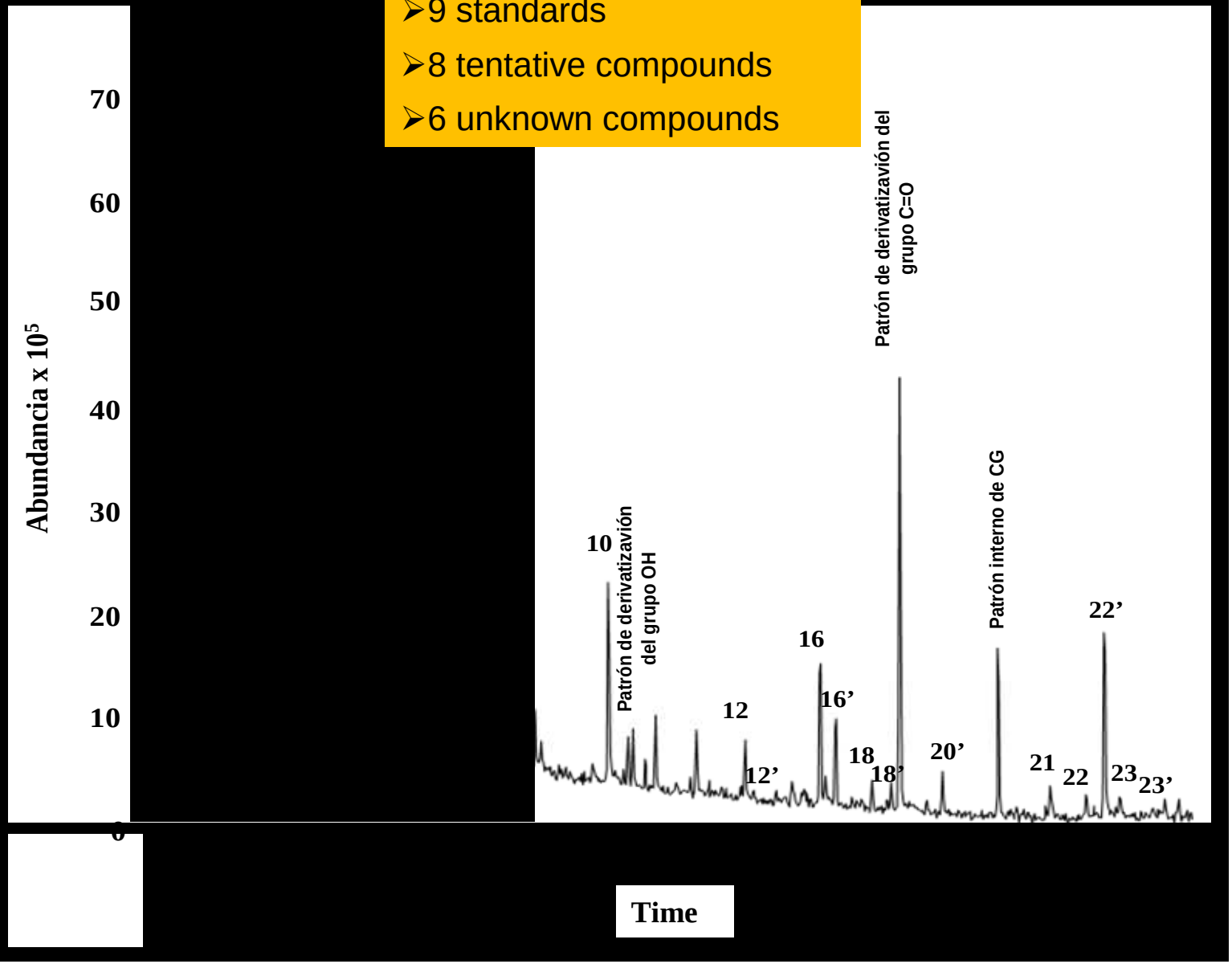
MULTI-OXYGENATED COMPOUNDS

PHASE
- GAS
- PARTICLES

GC-MS
Derivatization
PFBHA/MSTFA

Clasification

- 9 standards
- 8 tentative compounds
- 6 unknown compounds



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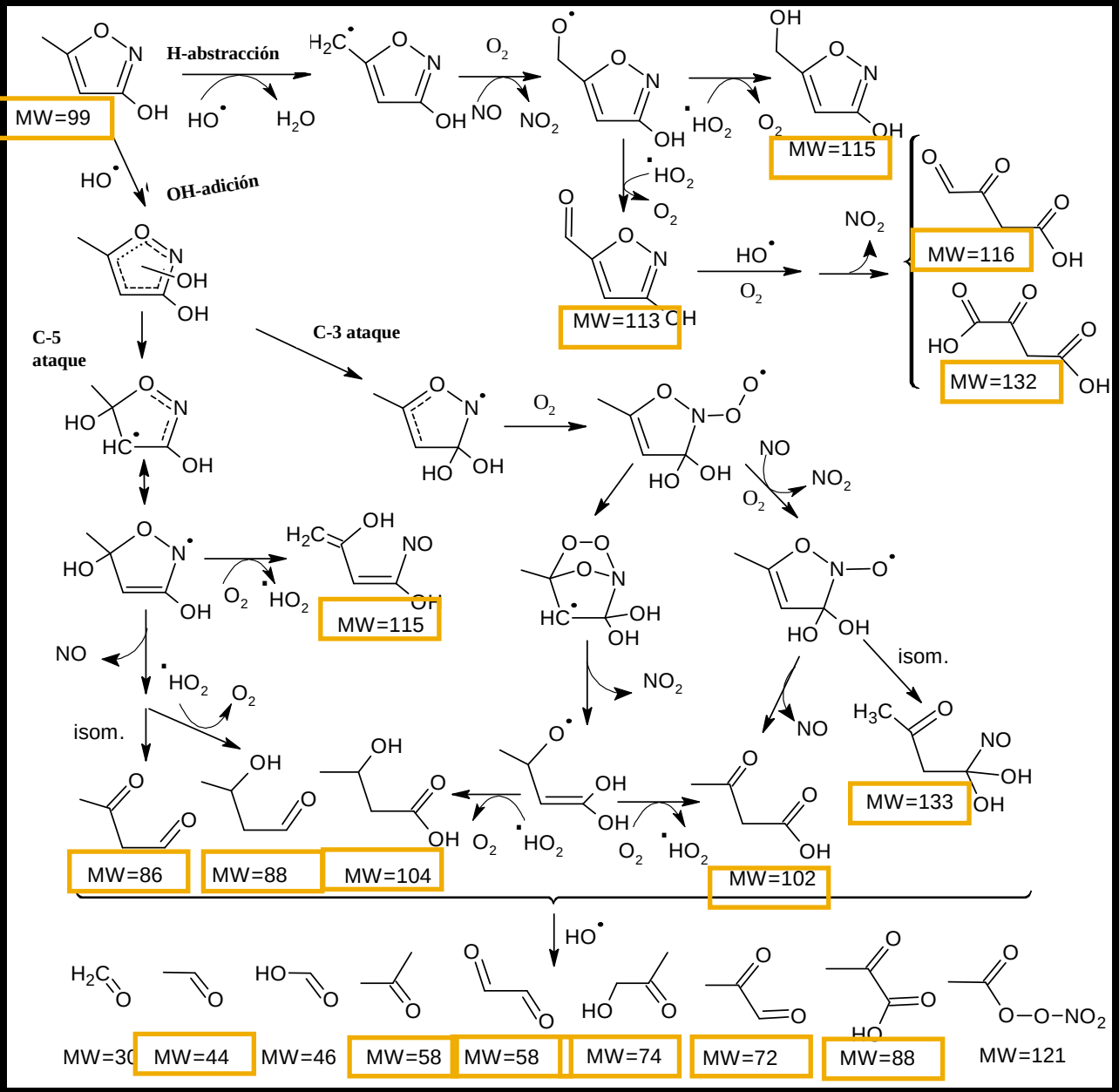

Borrás et al., Chemosphere, 2013

Atmospheric Implications

- Sensitive **methodology**, validated in simulation chambers EUPHORE applied to **control air quality** and proposed to routinely analysis.
- **Applicability** to determine pesticides in environmental campaigns, and monitoring of **allowed** and **forbidden** pesticides.
- Advance knowledge of the pesticides degradation - new pollutants and different applications -.
- **Significantly organic PM** formation in the environment. Need to determine degradation products - multi-oxygenate compounds.

CONCLUSIONS

- Progress in **physical and chemical characterization** of atmospheric organic **PM**
- The total number of identified species has increased; many of them firstly identified in atmospheric particles
- **Development** of new, sensitive, reproducible and validated analytical **methodologies**
- Advance **knowledge** of the degradation of **pesticides**

FUTURE TASKS

- ✓ Establishing **new degradation** mechanisms.
- ✓ Move degradation studies **from** simulation chambers **to** field
- ✓ Application in **routine monitoring** of Air Quality.
- ✓ Inclusion of data generated in atmospheric models.
- ✓ **Developing** new analytical methodologies focused on progress in the identification of organic PM fraction.
- ✓ Searching for **tracer or marker** species

THANKS FOR YOUR ATTENTION