NEW GAS-CHROMATOGRAPHY-BASED APPROACHES FOR THE MONITORING OF PESTICIDES

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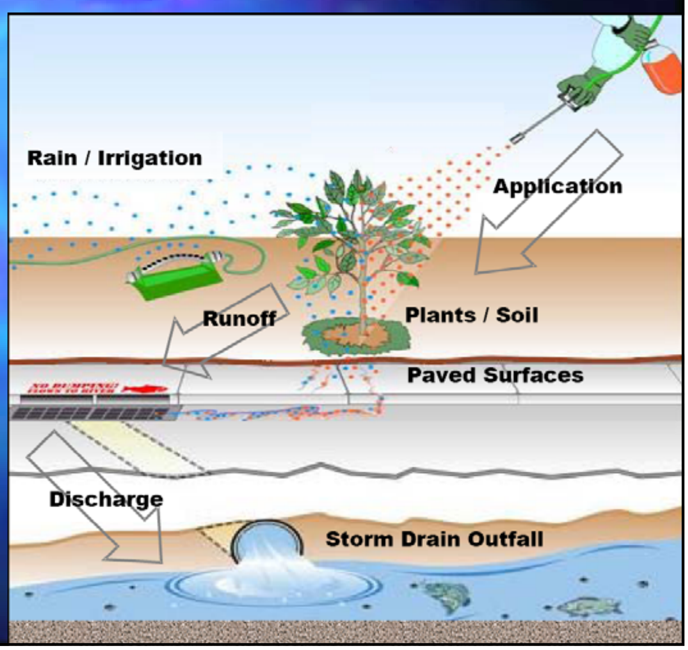
INTRODUCTION

Pesticides monitoring:



Bay Regional Water Board

- ✓ **Common outdoor urban/agricultural pesticides are also common in environmental samples**

1950s

Organochlorines
- DDT, Chlordane, Dieldrin…

1970s

Orgaphosphates
- Diazinon, Chlorpyriphos…

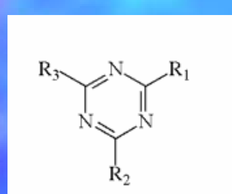
1990s

Pyrethroids

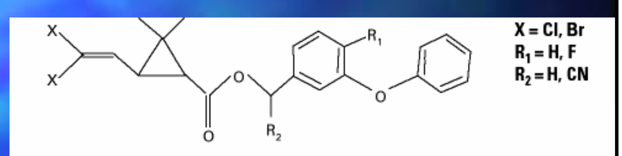
2010s

????

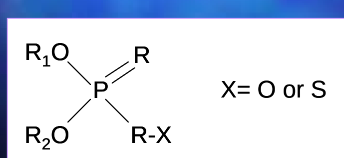
Triazines



Pyrethroids (emerging pollutants)



OPPs



- Almost all are regulated by laws intended to prevent environmental problems
- MRLs set in fruits to protect consumer´s health

Pesticides	MRL (mg/kg)			
	Orange	Apple	Pear	Grape
Diazinon	0.5 [a]	0.5 [a]	0.5 [a]	0.5 [a]
Parathion-methyl		0.2 [a]		0.2 [a]
Fenitrothion	2 [a]	0.2 [a]	0.2 [a]	0.2 [a]
Malathion	2 [a]			
Fenthion	0.05 [b]			
Chlorpyriphos-ethyl	0.3 [a]	0.5 [a]	0.5 [a]	0.5 [a]
Bromophos-methyl		0.02 [b]		
Methidathion	2 [a]		0.3 [a]	0.2 [a]
Azinphos-methyl	2 [a]	0.5 [b]		
Permethin			1 [b]	

a = EU MRL
b = Dutch MRL

Pesticides analysis in environmental samples

Extraction+Clean-up+Concentration + GC-detector

Sample prep. *Instrum. Anal.*

✓ **Technical advances in GC:**

- Fast(er) analysis
- Better detectability
- Improved separation

✓ **Limitations of conventional sample preparation methods:**

- Manual procedures (partly)
- Large quantities of sample, solvents, wastes
- Prone to loss and contamination

Faster sample preparation ?

Requirements:

- ✓ **Miniaturisation**
- ✓ Enhanced detectability:
  - Large aliquot injection
  - Improved detection (+ identification)
- ✓ Enhanced separation:
  - GCxGC
- ✓ On-line procedures

GC×GC applications:

- ✓ **Unravel the composition of complex mixtures:**
  - Aromas, essential oils
  - Petroleum mixtures
- ✓ **Identify individual components within complex families of pollutants:**
  - PCBs, PCDD/Fs
  - PBDEs, PCNs

  =>> Limited number of applications for pesticides
- ✓ **Group separation of related families of pollutants**

  =>> No tested for pesticides yet

INTRODUCTION

Current challenges in environmental chemistry:

✓ **New sample preparation methods for environmental and food analysis: trace pollutants and monitoring**

- Faster
- Miniaturised

} MSPD

✓ **Powerful separation (+ identification) techniques:**

- Selective and sensitive detectors: qMS, ITD(MS/MS)
- Powerful separation techniques: GC×GC

OBJECTIVES

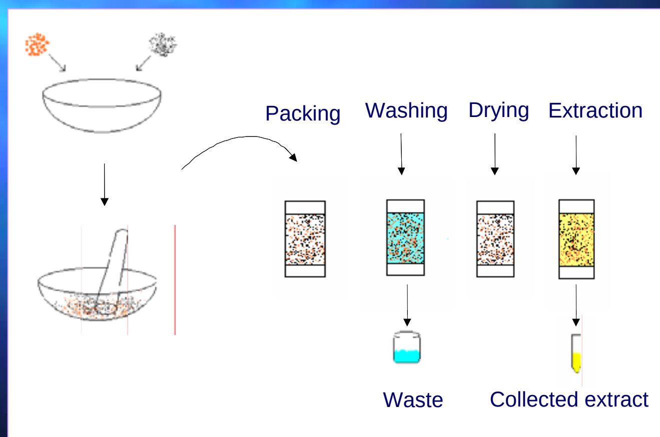
✓ **Fast monitoring of pesticides in environmental samples**

1. **Generic miniaturised sample prep method**
   - **Fruit: MSPD-based procedure**

2. **Determination of individual components**
   - GCxGC *vs* GC–qMS
   - Group separation (fast visual recognition: screening)
   - Individual components (accurate determination)

MSPD: MATERIALS and METHODS

✓ **Matrix solid phase dispersion**
applied to fruit samples



MSPD: MATERIALS and METHODS

✓ **Important aspects in MSPD[1]:**

1. **Selection of sorbent**
   - **best results with C8 material**
2. **Selection of extraction solvent**
   - **best results with ethyl acetate**
3. **Removal of interfering material**
   - **depending on samples**

[1] E.M. Kristenson *et al.*, J. Chromatogr. A 917 (2001) 277.

MSPD: MATERIALS and METHODS

Sample preparation method:

✓ Fast miniaturised sample prep: MSPD

1. **0.1 g of fresh peel + 0.1 g C8**
2. **Packing on an SPE cartridge**
3. **Washing with water (except for apple)**
4. **Elution with 700 µL EtOAc**

Samples:

Orange, pear, grape and apple

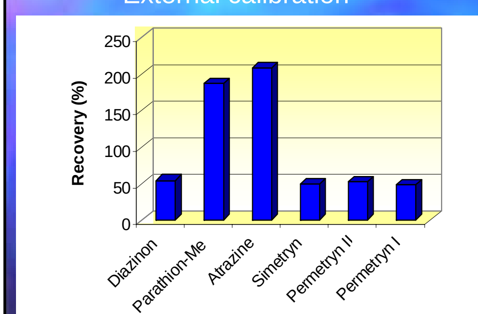
Pesticides:

✓ 15 Organophosphorous pesticides
✓ 10 Triazines
✓ 8 Pyrethroids

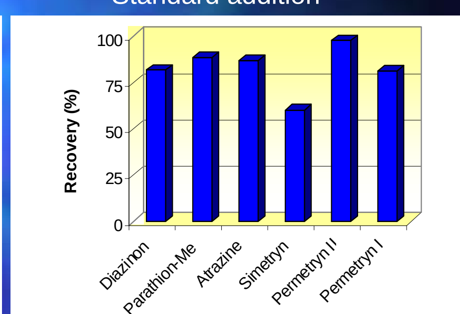
MSPD: RESULTS and DISCUSSION

Optimisation: MSPD plus GC-qMS (SCAN)

External calibration



Standard addition



✓ No extra clean up but severe matrix effect was observed: standard addition and careful selection of selective ions.

✓ Two separated GC-qMS runs for triazines and OPPs (SCAN) and for pyrethroids (SIM).

MSPD: RESULTS and DISCUSSION

Analytical performance of MSPD plus GC-qMS

	Percent average recovery (RSD)[1]			
	Orange	Apple	Grape	Pear
Malathion	95(5)	97(11)	78(6)	88(22)
Bromophos-Me	104(22)	84(22)	81(7)	87(18)
Chlorpyrifos-Et	103(9)	99(7)	49(4)	70(24)
Atrazine	111(18)	93(22)	88(3)	88(21)
Prometryne	107(4)	94(10)	69(5)	85(24)
Cypermetrin III+IV	102(1)	94(13)	93(5)	92(25)
Deltamethrin	99(9)	89(13)	99(26)	88(17)

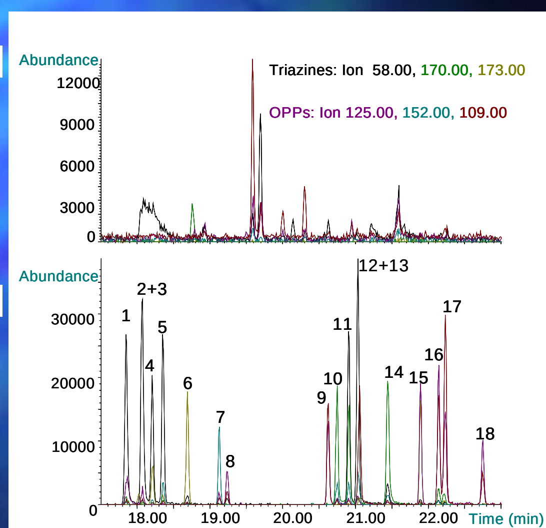
[1] n =4. Spiking level, 0.5 mg/kg

MSPD: RESULTS and DISCUSSION

MSPD plus GC-qMS: application to non-spiked samples

Non-spiked grape, 100 mg

Standard mixture, 0.5 mg/kg



Peak numbering: (1) atratron, (2) simazine, (3) prometron, (4) atrazine, (5) promazine, (6) terbuthylazine, (7) diazinon, (8) disulfoton, (9) parathion-Me, (10) simetryn, (11) ametryn, (12) prometryn, (13) paraoxon-Et, (14) terbutryne, (15) malathion, (16) fenthion, (17) chlorpyrifos, and (18) bromophos-Me.

GCxGC: MATERIALS and METHODS

Enhanced selectivity and sensitivity:

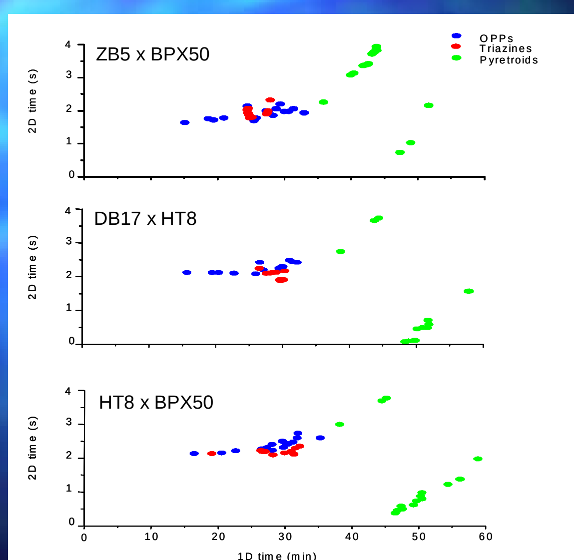
MSPD plus GCxGC-microECD: group analysis

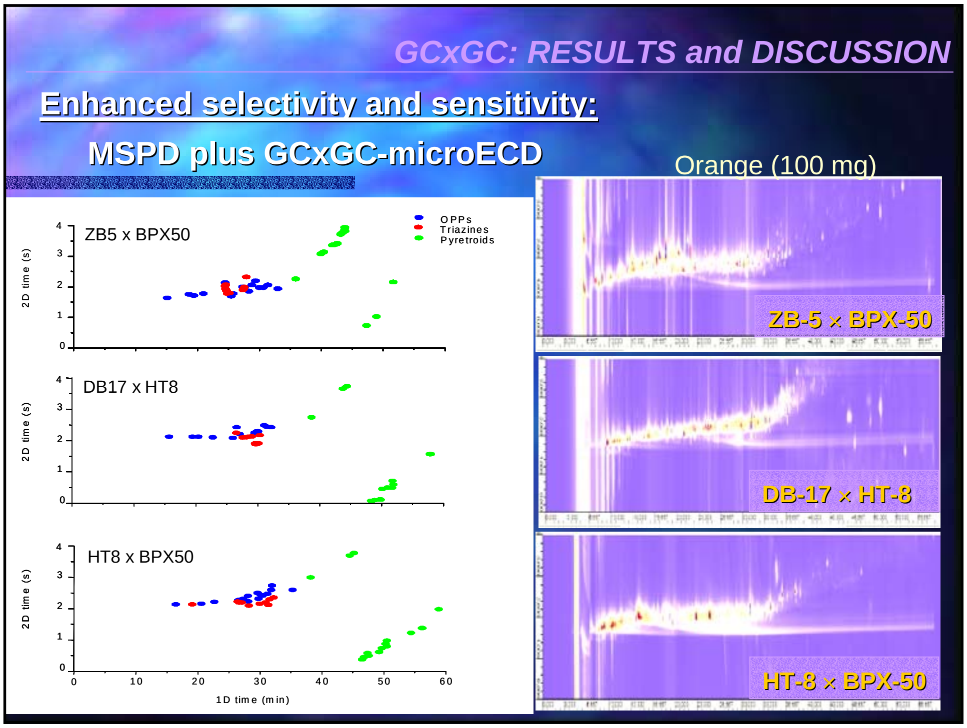
✓ GC×GC column combinations:

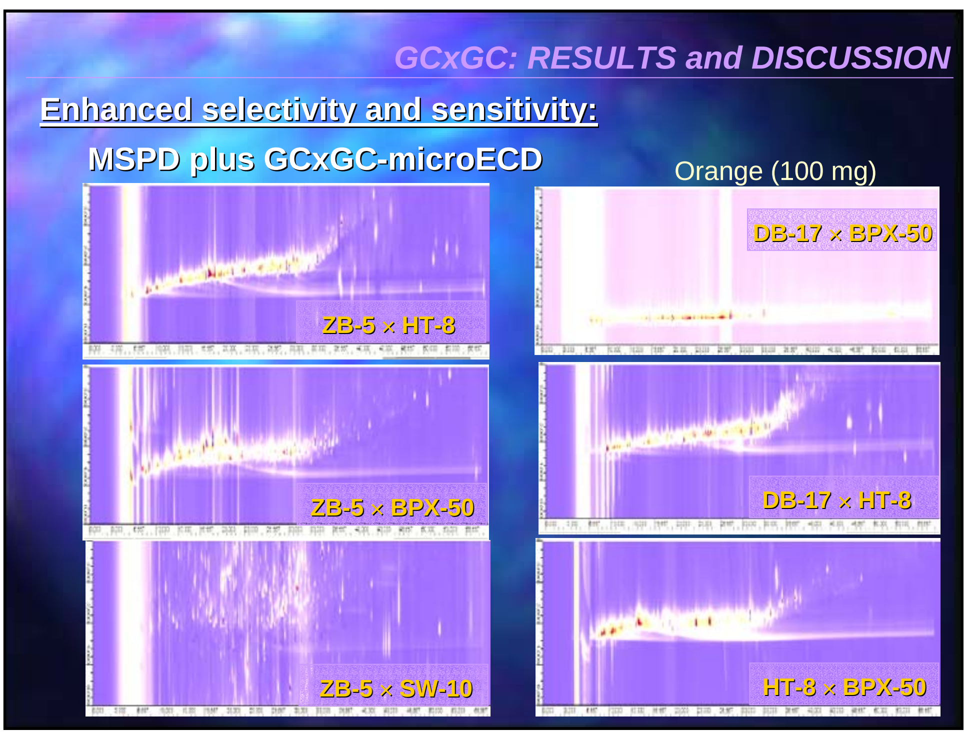
1D GC column (30 m × 0.25 m × 0.25 μm)	2D GC column (1 m × 0.1 m × 0.1 μm)
ZB-5 5% phenyl methylpolysiloxane	HT-8 8% phenyl methylsiloxane-carborane
HT-8 8% phenyl methylsiloxane-carborane	BPX-50 50% phenyl polysilphenilene siloxane
DB-17 50% phenyl methylpolysiloxane	Supelcowax-10 polyethylene glycol type

GCxGC: RESULTS and DISCUSSION

Enhanced selectivity and sensitivity: GCxGC-microECD

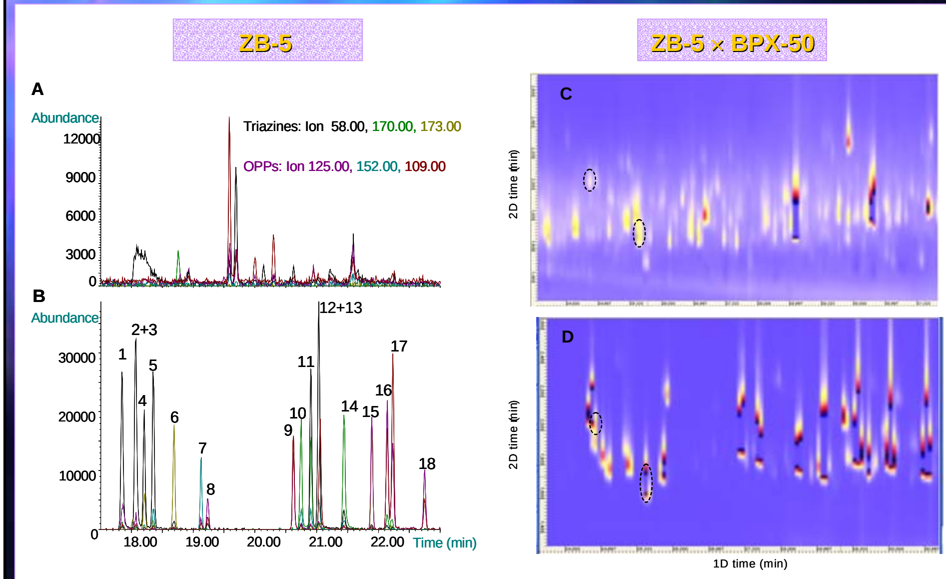



GCxGC: RESULTS and DISCUSSION
Enhanced selectivity and sensitivity:
MSPD plus GCxGC-microECD
Orange (100 mg)
OPPs
Triazines
Pyretroids
ZB5 x BPX50
DB17 x HT8
HT8 x BPX50
2D time (s)
1D time (min)
ZB-5 × BPX-50
DB-17 × HT-8
HT-8 × BPX-50


GCxGC: RESULTS and DISCUSSION
Enhanced selectivity and sensitivity:
MSPD plus GCxGC-microECD
Orange (100 mg)
ZB-5 × HT-8
ZB-5 × BPX-50
ZB-5 × SW-10
DB-17 × BPX-50
DB-17 × HT-8
HT-8 × BPX-50

GC–qMS vs GCxGC: RESULTS and DISCUSSION

Non-spiked grape (100 mg)



CONCLUSIONS

✓ **Miniaturisation good alternative**

- small amount of sample
- low solvent and sample consumption
- minimal wastes
- faster sample preparation: monitoring
- on-line or at-line coupling with GC (automation)

✓ **Combined with enhanced separation + detection techniques (GCxGC)**

- faster generic accurate analytical methods
- routine analysis and monitoring
- new studies

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