Pesticides in air in Alsace

Maurice MILLET, Pr
Université de Strasbourg – CNRS
Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé
(ICPEES – UMR 7515)
Groupe de Physico-Chimie de l'Atmosphère
1 rue Blessig
67084 Strasbourg Cedex
Tél : 03.68.85.04.22
E-mail : mmillet@unistra.fr

UNIVERSITÉ DE STRASBOURG

- Research on pesticides in air stats in 1992 (LPCA),

- Ph.D thesis of M. Millet (1992) = second in France on the research area,

- 8 Ph.D on the area of research (actually one in work)

Resarches on :

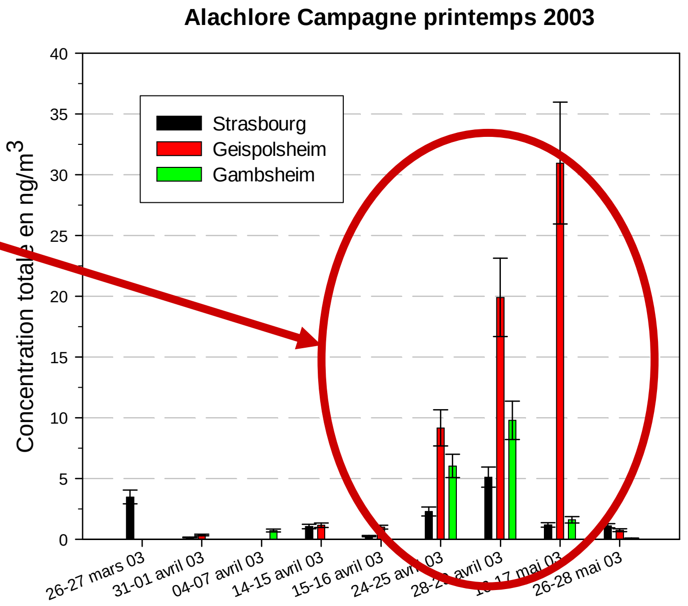
- analytical development,
- Drift and Volatilisation,
- Ecotoxicology,
- Sampling development (strategies and methods),
- Indoor air,
- Others(runoff, precipitation transfer to urban drainage,…)

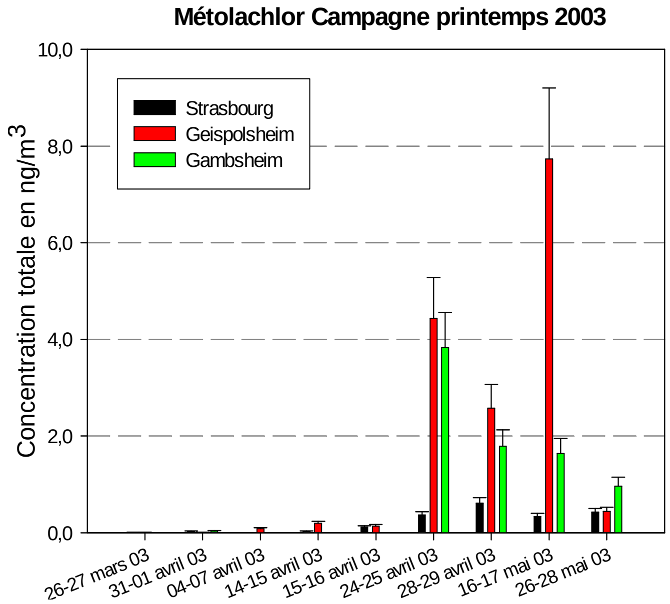
cnrs

Spatial and temporal variations of airborne pesticides concentrations.

Short range transport

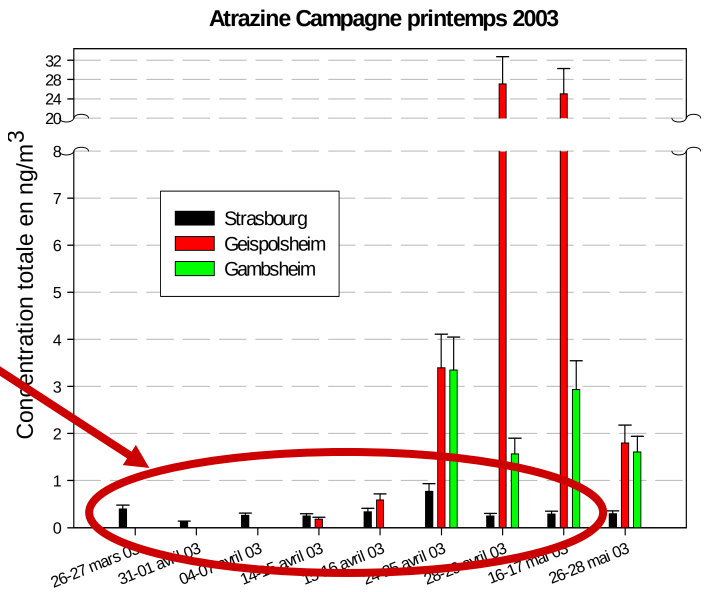
Seasonal profile correlated with applications

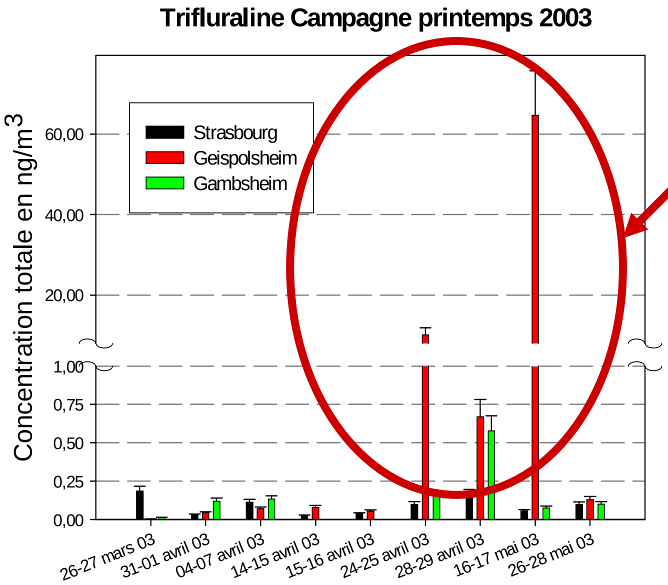




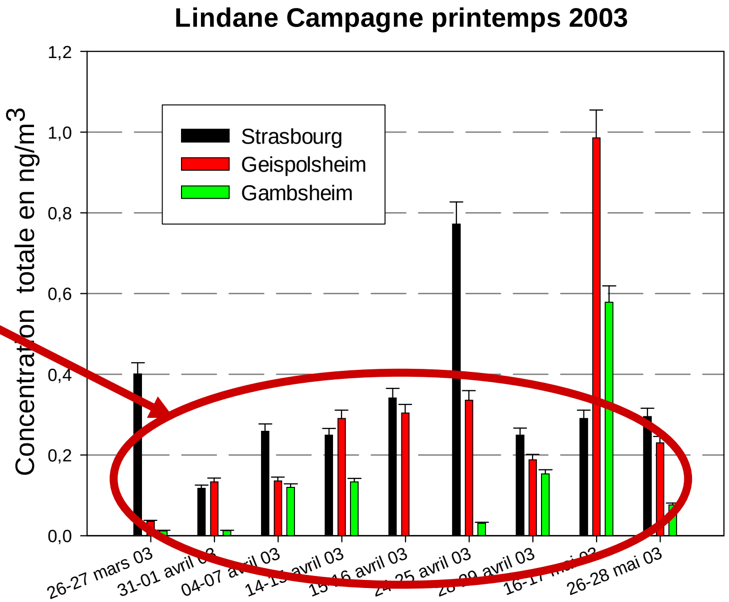
Higher concentrations in Geispolsheim

Lower concentrations in Strasbourg



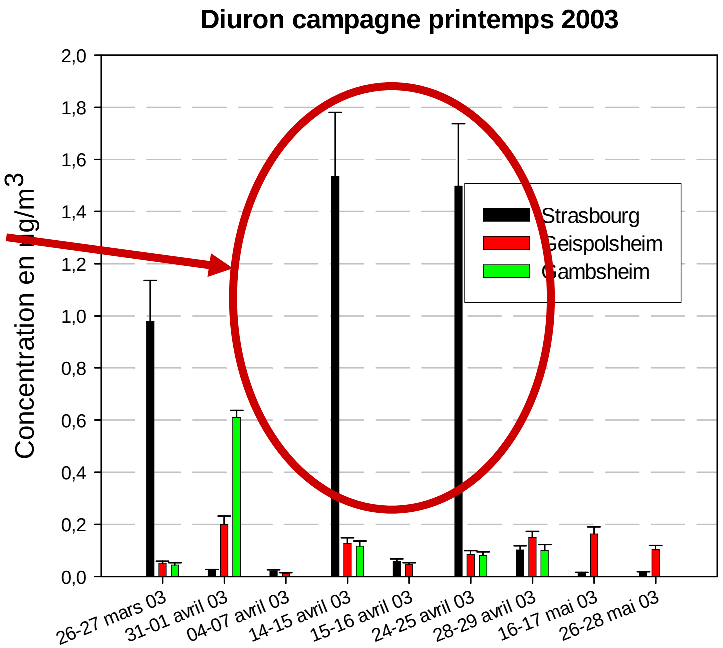


No seasonal profile



➢Lower concentrations than CUP mean below 500 $pg.m^{-3}$

Urban pesticides



➢Diuron more concentrated in urban area

➢ Comparison of two successives years of application

$$C_{pondérée} = \frac{C_{pluie} * H_{ech}}{H_{moyenne}}$$

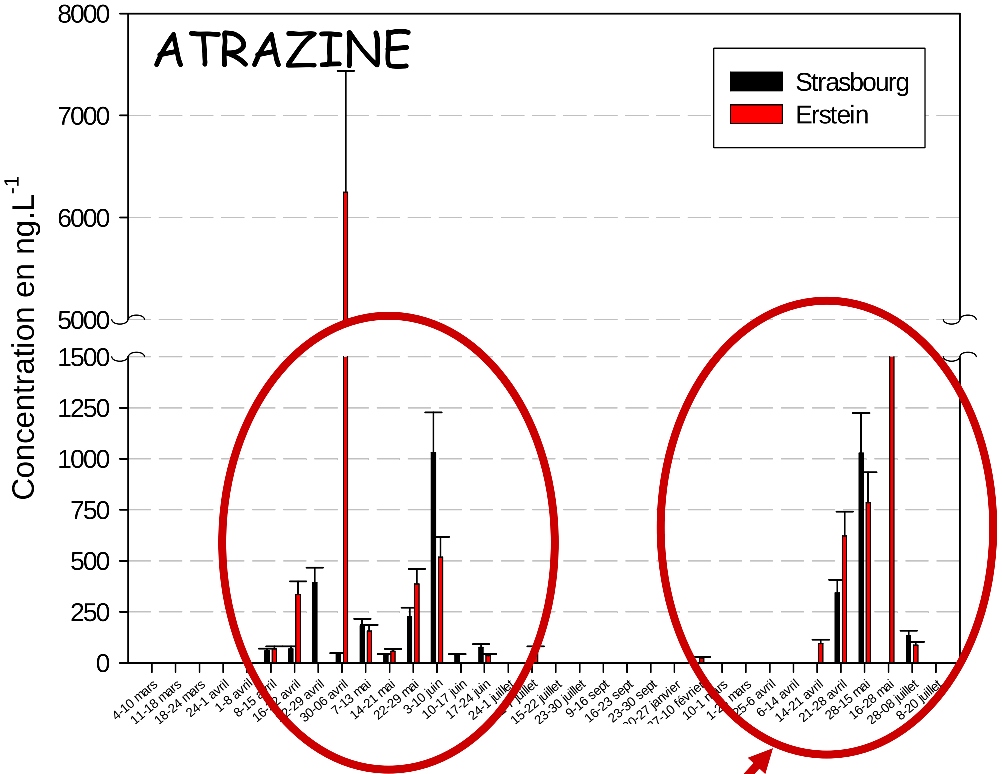
Height of rain in mm

Height of rain by week

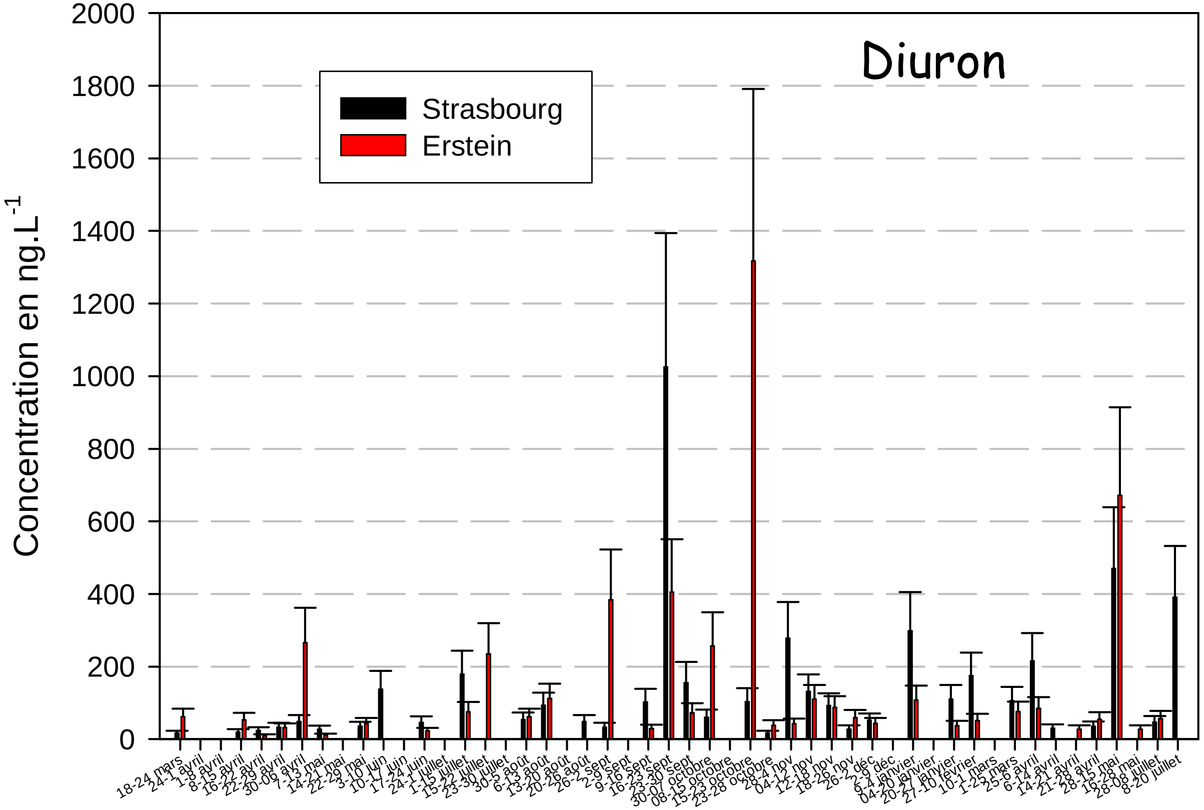
mean 26,1 et 25,2 mm

➢ Comparison between urban and rural site

➢ high concentration until 6250 $ng.L^{-1}$



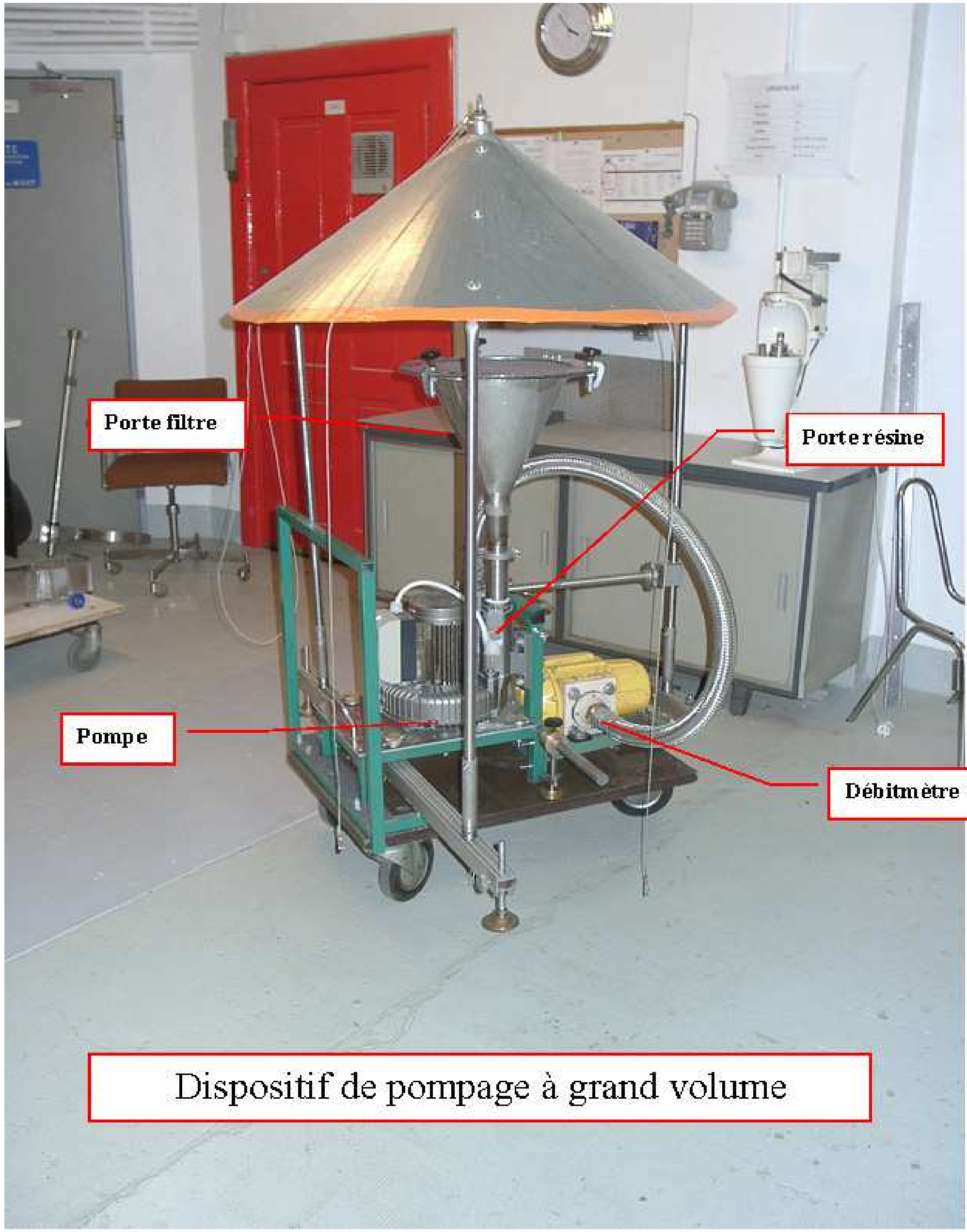
Profile correlated with application



➢ detected during all the year

➢ No urban - rural profile

➢ high concentration until 1310 $ng.L^{-1}$

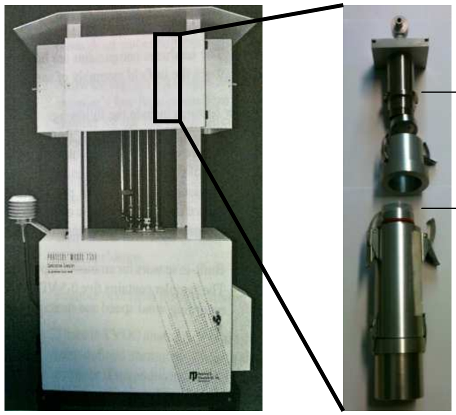


Dispositif de pompage à grand volume

Analytical development.

Application to outdoor / indoor air

Experimental protocol



Air samples

↓

ASE Extraction
100% ACN / 3 statics of 15 min

150°C
1500 psi

↓

45°C
220 mbar

Concentration to 1 mL
Rotary evaporator

↓

SPME solution
1mL extract in 10 mL water (pH3, 1.5 % NaCl)

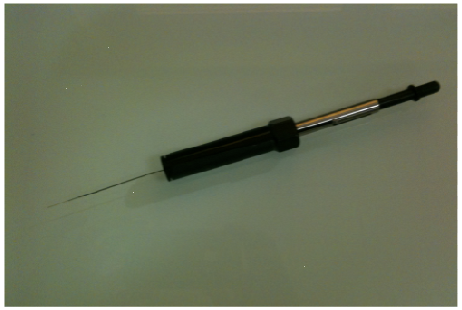
← Internal standards

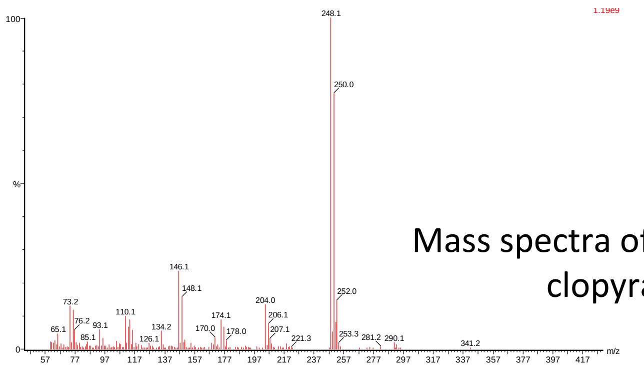
↓

← 2 µL MtBSTFA

SPME-GC-MS

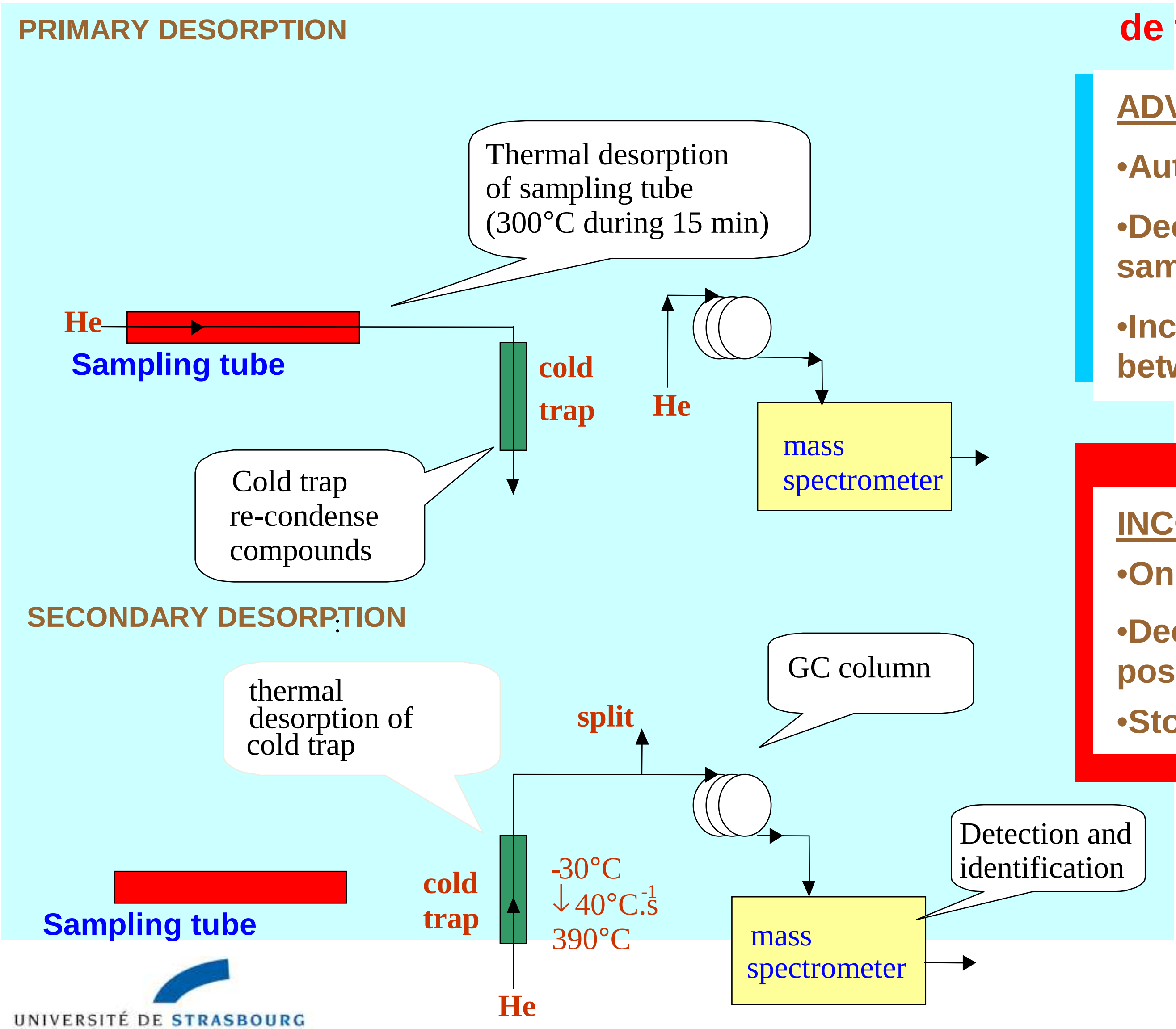
Accelerated Solvent Extractor
(Dionex – ASE®300)





Mass spectra of derivatised clopyralid

Principle of thermal desorption :



Advantages et inconvénients de this technique :

ADVANTAGES

- Automatisation
- Decrease of manipulations of samples
- Increase of sensitivity (no step between sampling and analysis

INCONVENIENTS

- Only one injection !!
- Decomposition of compound possible with temperature
- Storage stability

UNIVERSITÉ DE STRASBOURG

cnrs

UNIVERSITÉ DE STRASBOURG

Development and validation of passive samplers for the measurement of airborne pesticides.

Application to exposure assessment of general population

cnrs

Objective

« better evaluation of the exposition by airborne pesticides »

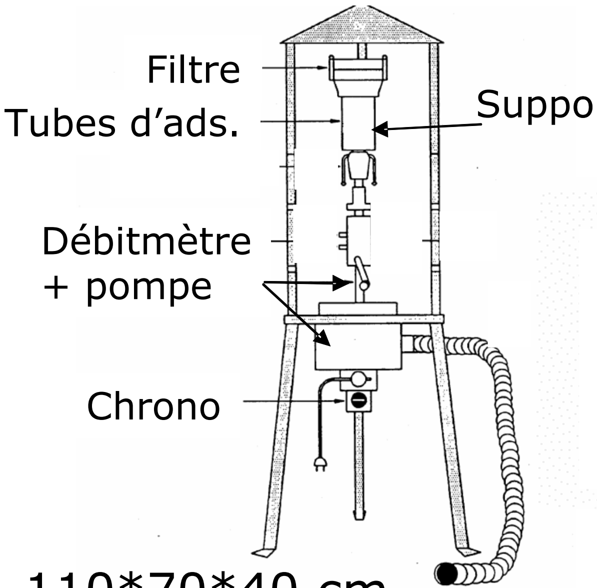
Identification of available systems and development of new ones

Evaluation of their potential in laboratory protocols

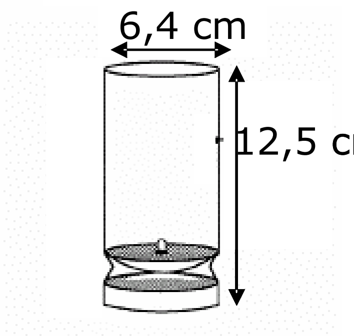
Field studies for applicability

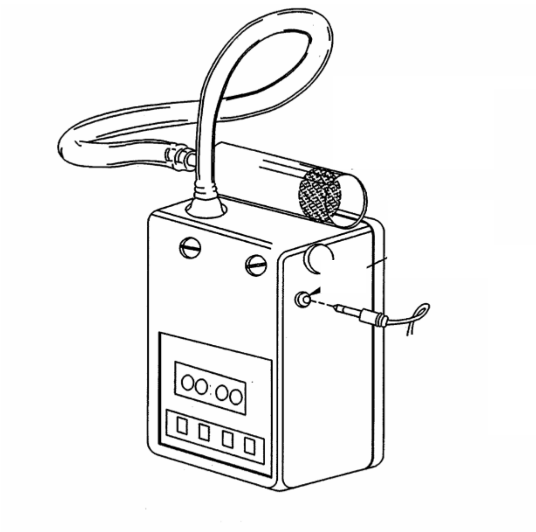
Usual techniques

Mousse polyuréthane, XAD, tenax, chromosorb, charbon actif

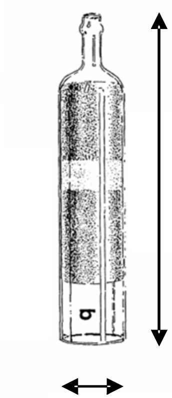


110*70*40 cm





14*8*6 cm



0,6-2 cm

Energie	110-230V	110-230V / batterie
Air échantillon	<100-1000 m^3	<0,1-5 m^3
Prélèvement	200-300 L.min^{-1}	<0,5-5 L.min^{-1}

Passive sampling

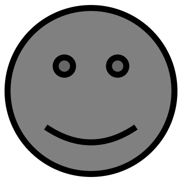
$$C_{air} = \frac{m}{DE * t}$$

C_{air} : concentration in air ($\mu g/m^3$)

m : mass of pesticides in sampler (μg)

t : sampling duration (j)

SR :sampling rate(m3/j)



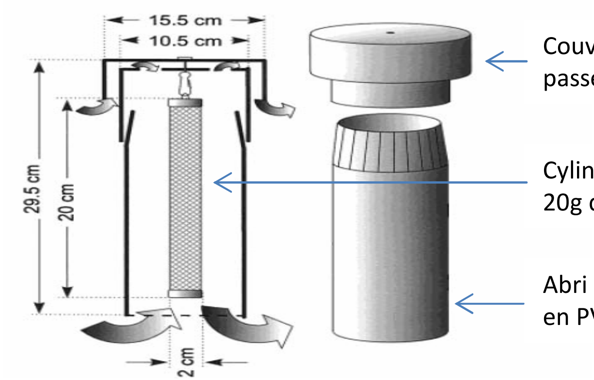
- No pump (no energy use)
- No noise
- Easy to use
- Low costs
- Sampling duration very variables

- Calibration not easy

Development of a laboratory system

UNIVERSITÉ DE STRASBOURG

✓ Air sampling: Passive sampler



Couvercle laissant passer l’air

Cylindre maillé contenant 20g de résine XAD®-2

Abri cylindrique en PVC

Wania and al. 2003. Environ. Sci.Technol. 37, 1352-1359

Passive sampler- Resin Amberlite® XAD®-2

✓ Theoretical aspects *(Shoeib and Harner, Environ. Sci. Technol. 2002, 36,4142-4151)* :

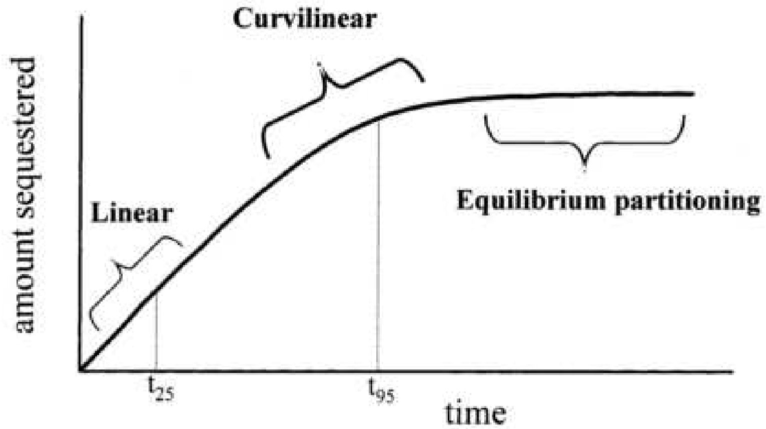
➔ Free movements of molecules to sampler

$$V_{PSM}\frac{dC_{PSM}}{dt} = k_{air}A_{PSM}\left(C_{air} - \frac{C_{PSM}}{K_{PSM/air}}\right)$$

C_{PSM} : concentration dans le capteur passif (ng.cm^{-3})
C_{air} : concentration dans l’air (ng.cm^{-3})
k_{air} : coefficient de transfert de masse dans l’air (cm.s^{-1})
k_{PS} : coefficient de transfert de masse dans le capteur passif (cm.s^{-1})
$K_{PSM/A}$: coefficient de partition capteur passif/air
V_{PSM} : volume du capteur passif (cm^3)
A_{PSM} : section du capteur passif (cm^2)

✓ Theretical aspecrt: 3 régimes

$$V_{PSM}\frac{dC_{PSM}}{dt}=k_{air}A_{PSM}\left(C_{air}-\frac{C_{PSM}}{K_{PSM/air}}\right)$$



C_{PSM} : concentration dans le capteur passif ($ng.cm^{-3}$)
C_{air} : concentration dans l'air ($ng.cm^{-3}$)
k_{air} : coefficient de transfert de masse dans l'air ($cm.s^{-1}$)
k_{PS} : coefficient de transfert de masse dans le capteur passif ($cm.s^{-1}$)
$K_{PSM/A}$: coefficient de partition capteur passif/air
V_{PSM} : volume du capteur passif (cm^3)
A_{PSM} : section du capteur passif (cm^2)
M : quantité piégée dans le capteur (ng)

Linear zone➔ $\frac{C_{PSM}}{K_{PSM/air}}$ small

$$\frac{dC_{PSM}}{dt}=k_{air}\frac{A_{PSM}}{V_{PSM}}C_{air} \rightarrow M=k_{air}A_{PSM}C_{air}\Delta t$$

Conditions d'utilisation du capteur

Where sampling rate is $$R=\frac{k_{air}}{A_{PSM}}=\frac{M}{C_{air}\Delta t}$$

Curviliear zone

$\frac{C_{PSM}}{K_{PSM/air}}\nearrow$ Non négligeable

Equilibrium

$\frac{C_{PSM}}{K_{PSM/air}}=C_{air}$ constant

Shoeib and Harner, Environ. Sci. Technol. 2002, 36,4142-4151

Passive sampler calibration

✓ Why active sampling ?

$$R = \frac{k_{air}}{A_{PSM}} = \frac{M}{C_{air}\Delta t}$$

1 equation
2 unknowns parameters

Calculation of C_{air} with active sampler

Quantité into dans filtre and resin

Air volume sampled

Calibration : Calculation of the sampling rate R relative to each compound

Phase particulaire : Filtre en fibres de verre

Phase gazeuse : Cylindre contenant 20g de résine XAD®-2

Compteur volumétrique

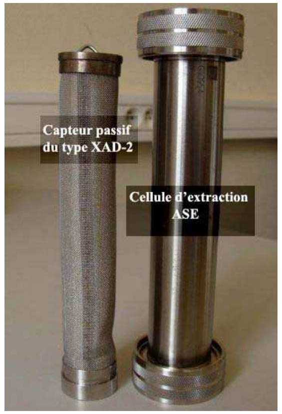
➔ Exposure of passive samplers : M

➔ Utilisation of R for detemination of C_{air}

Passive samplers « Ambient air »

Passive samplers « Ambient air »

Experimental protocol



Cellule d'ASE et capteur passif

Echantillons d'air

↓

150 °C
1500 psi

Extraction ASE
100% AcN / 3 statiques de 15 min

↓

45 °C
220 mbar

Concentration à 1 mL
Evaporateur rotatif

↓

Analyse

Accelerated Solvent Extractor (Dionex – ASE®300)

Etalonnage interne

HPLC-fluorescence
Chromatographie Liquide Haute Performance
Détection : fluorimétrie
HAP

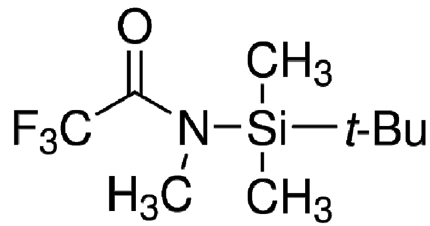
SPME-GC-2 ECD
Micro-extraction sur Phase Solide
Chromatographie Gazeuse
Détection : capture d'électrons
PCB et Pesticides Organochlorés

SPME- GC-MS/MS
Micro-extraction sur Phase Solide
Chromatographie Gazeuse
Détection : spectrométrie de masse en tandem
Pesticides

Pesticides analysis

- ✓ 43 pesticides / 4 methods : SPME-GC-MS/MS
- ✓ Pré-concentration / purification par SPME

Température d'extraction	Durée d'extraction	Fibre
40 °C	50 min	PDMS-DVD 65 µm
60 °C	30 min	
80 °C	40 min	
60 °C	50 min	PA 85 µm



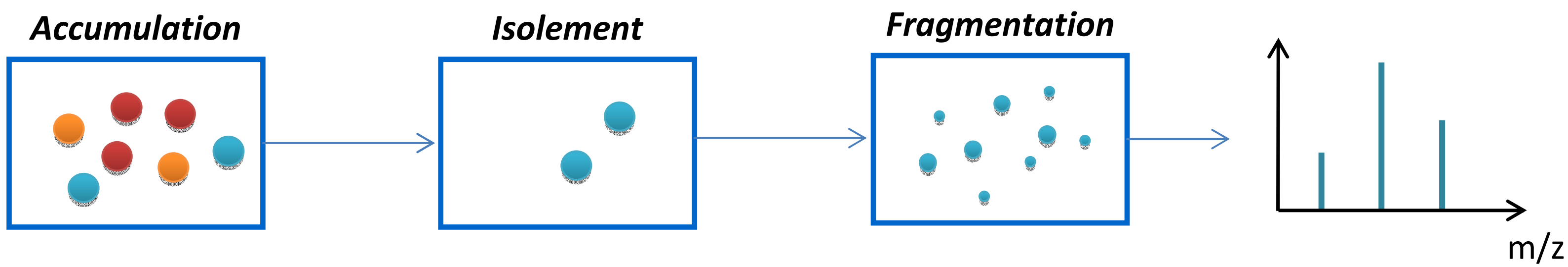
→ Derivatisation step : M*t*BSTFA

Paramètres optimisés :

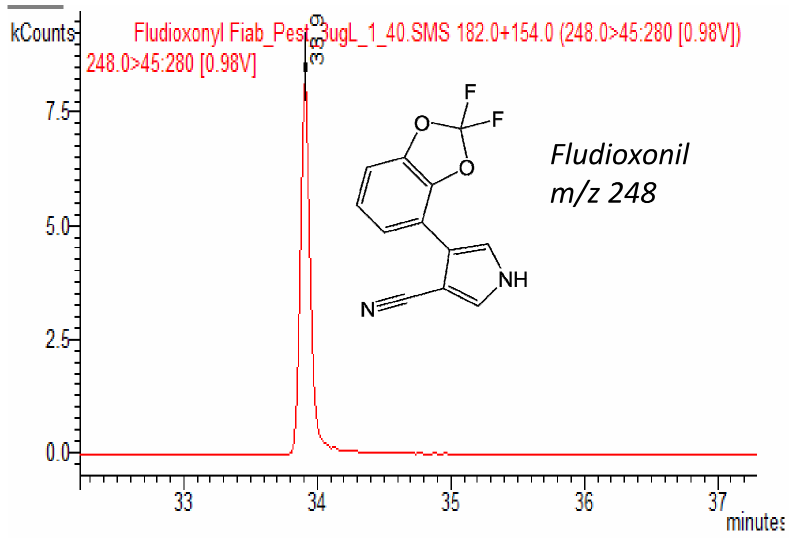
- ➔ Choix de la fibre
- ➔ Mode d'extraction : *immersion totale*
- ➔ Température d'extraction
- ➔ Durée d'extraction
- ➔ Salinité du milieu : *eau à 1,5% saturation en NaCl, pH=3*
- ➔ Temps de désorption de la fibre dans injecteur

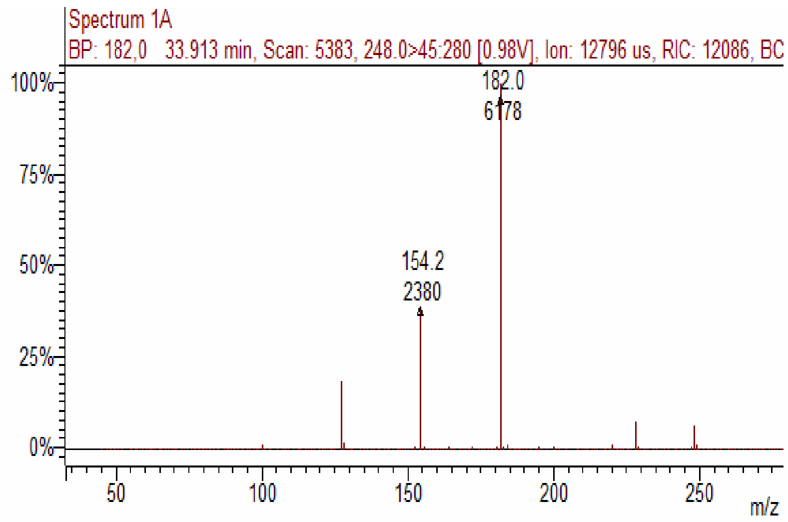
Analyse des pesticides

- ✓ Chromatographie Gazeuse couplée à la spectrométrie de masse en tandem (ion trap)



MS/MS mode parent





Alsace campaign

✓ 2 sampling location➔ one rural and one urban

- **JBS** : Jardin Botanique / Observatoire de Strasbourg – **milieu urbain de fon**
- **SND** : Sand, proche Benfeld / Erstein - **milieu rural de proximit**

✓ Duration 1 year : 21 november 2011 au 17 december 2012

✓Reference site: Jardin Botanique de Strasbourg

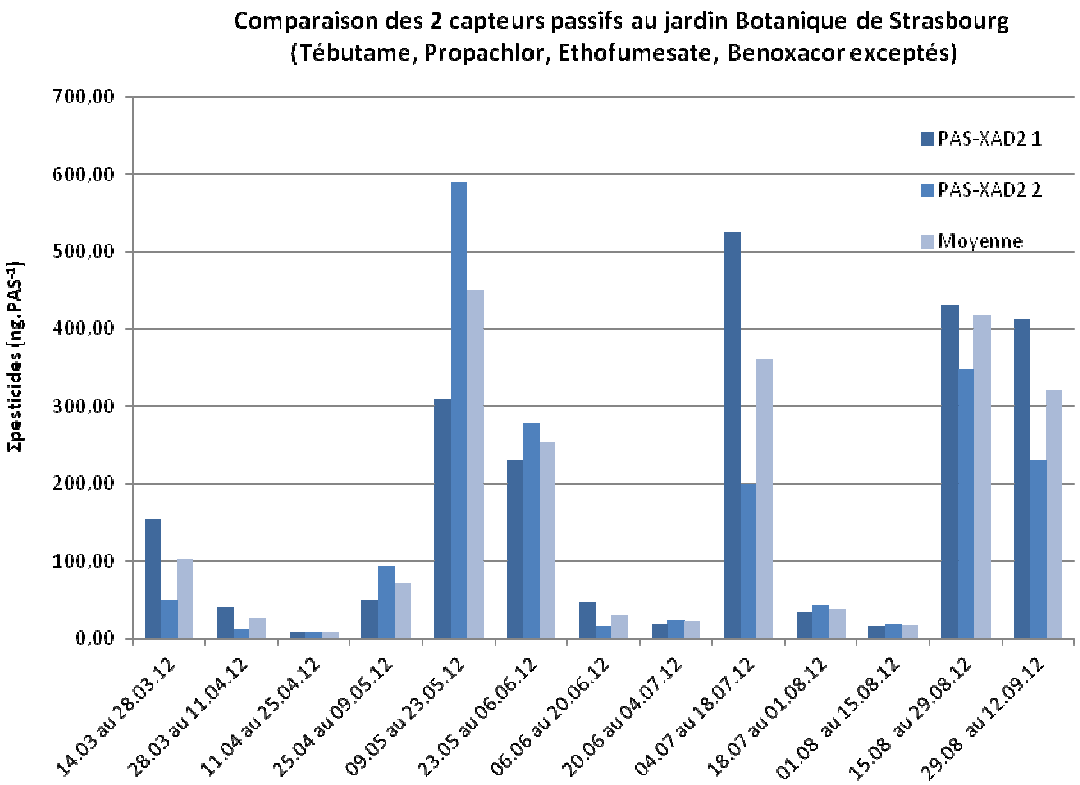
 +  x 2 → Calibration

2 weeks exposition of PAS
Changing of filter and resin each week

✓ Field blanks

Pesticides results

✓ Campaign from 14 March 2012 to 12 September 2012



➔ **Value globally equivalent between two PAS exposed simultaneously**

Pesticides results

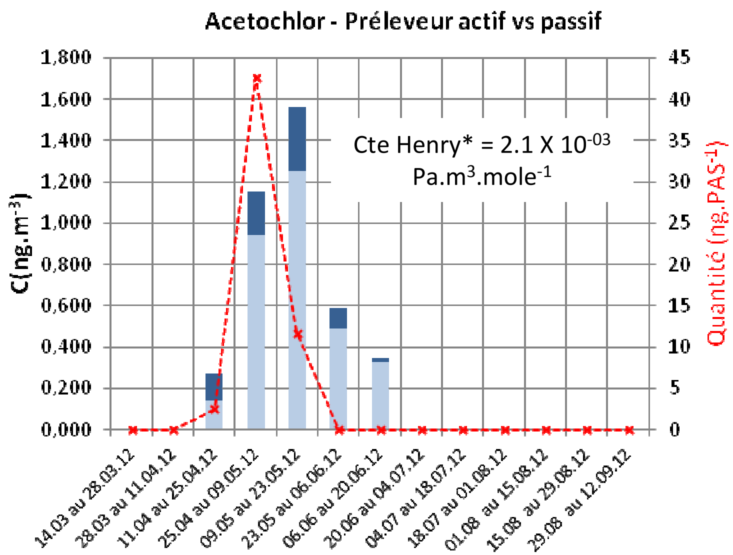
✓ Active sampling

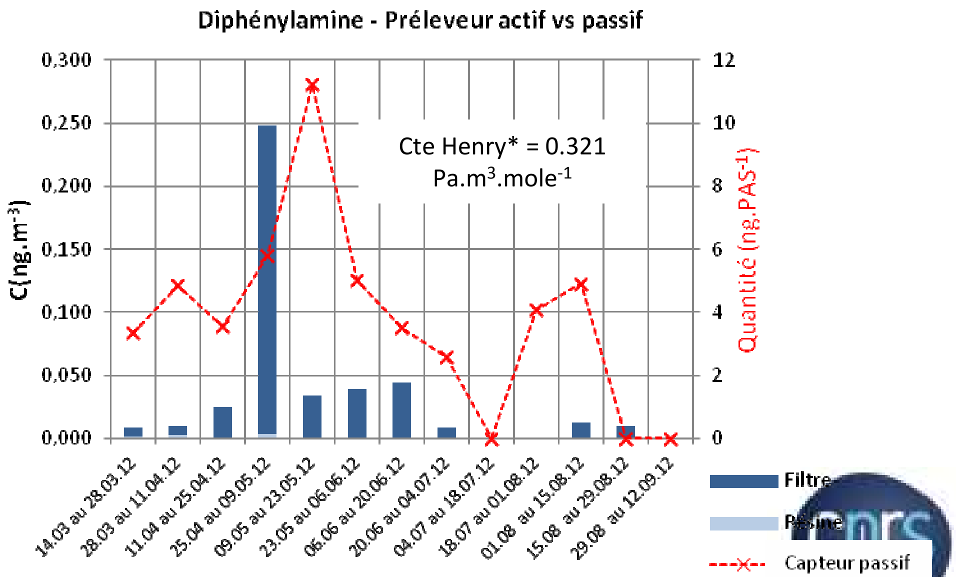
➔ Repartition of pesticides between filtre and resin
➔ Validity passive sampler
➔ Low volatiles : **Particle phase**
➔ Volatiles : **Gas phase**

➔ Détection ponctuelle en fonction de la période
➔ Question débit pompe?

Produits volatiles

Constante de Henry >> 1 Pa.m³.mole⁻¹

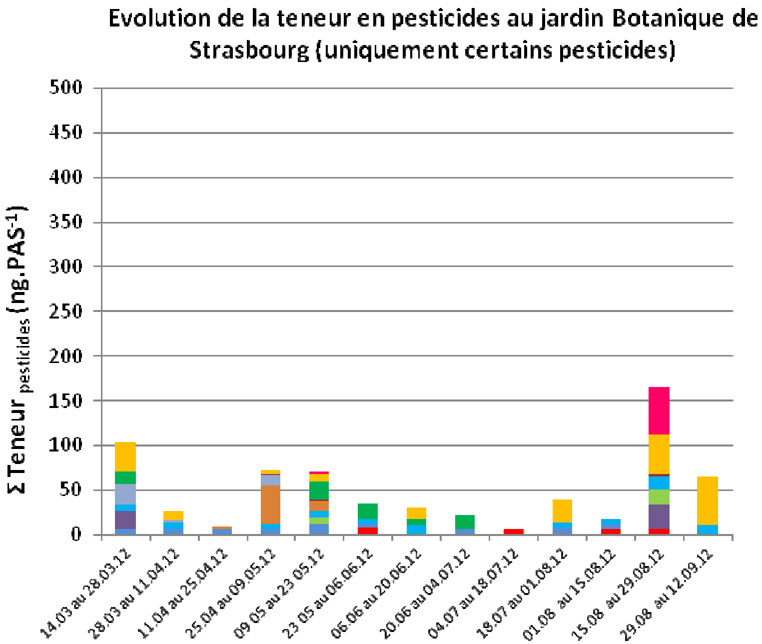


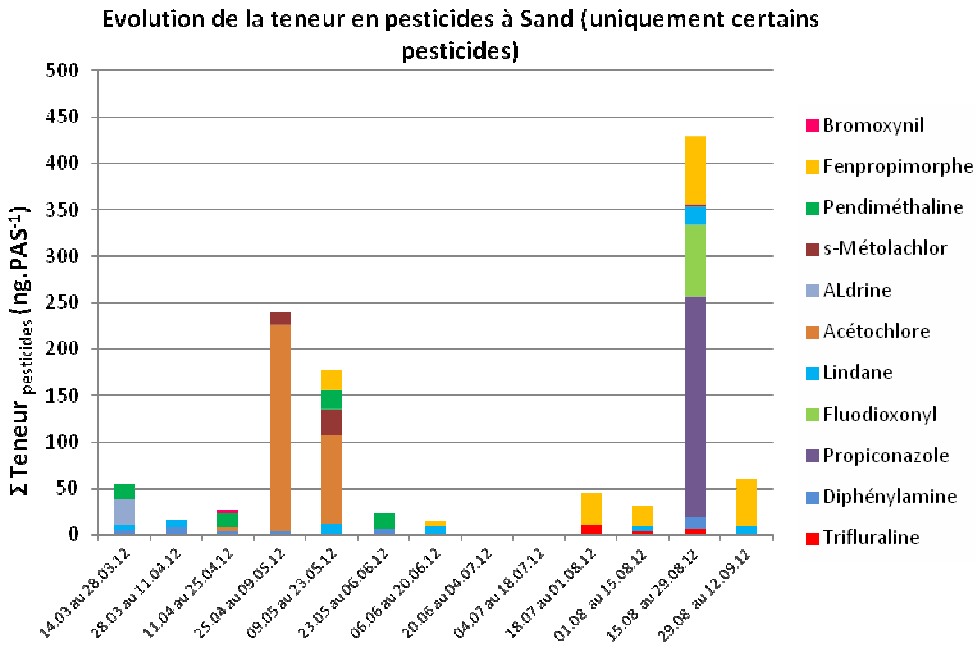


**PPDB: Pesticide Properties DataBase*

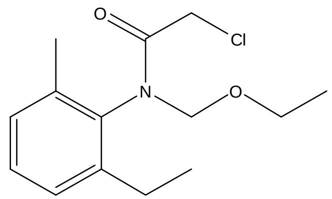
Pesticides results

✓ Comparaison urban / rural

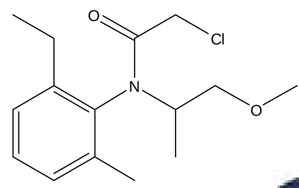




➔ **Strasbourg lower pollution than Sand**
➔ **Same pesticides**
➔ **Acetochlor / s-metolachlor**



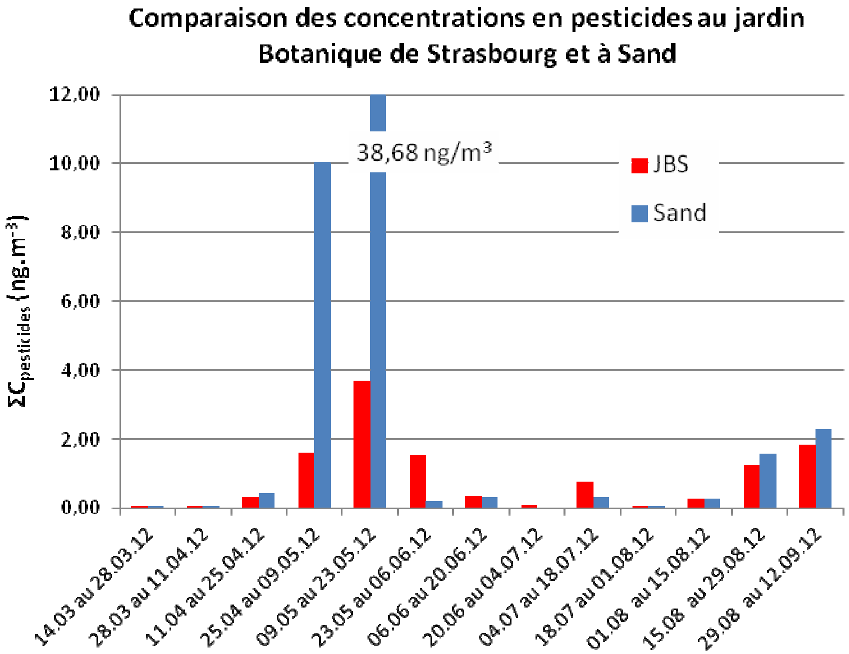
Acetochlor

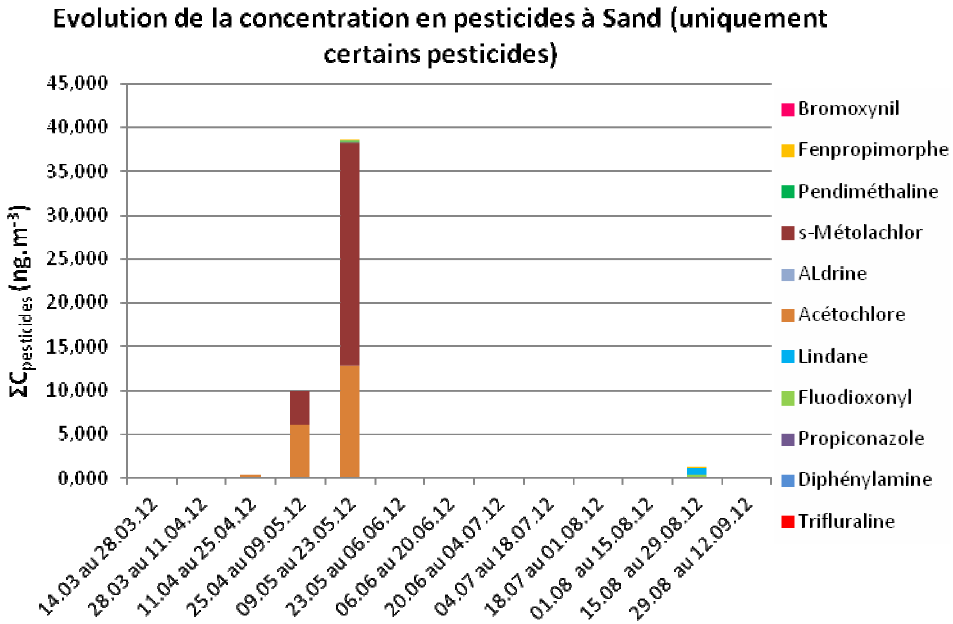


S-Metolachlor

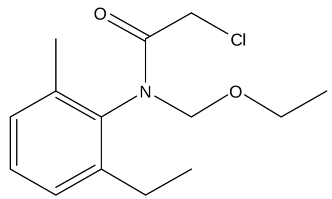
Pesticides results

✓ **Utilisation de R** : comparaison urban / rural

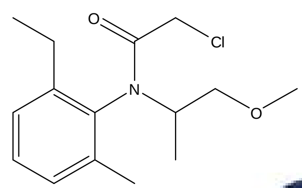




➔Same observations
➔Calibration only for some pesticides
➔Pesticides used on maize



Acetochlor



S-Metolachlor

UNIVERSITÉ DE STRASBOURG

Research on non agricultural pesticides and indoor air

2,4 D	deltamethrin	mecoprop-p
MCPA	dicamba	myclobutanil
alphacypermethrin	dichlobenil	oryzalin
bifenthrin	dichlorprop	oxadiazon
bromoxynil	diflufenicanil	picloram
buprofezin	diuron	tau-fluvalinate
carbaryl	fenoxaprop	tebuconazole
carbofuran	flazasulfuron	triclopyr
clopyralid	fluroxypyr	trifluralin
cymoxanil	ioxynil	trinexapac-ethyl
cyprodinil	isoxaben	

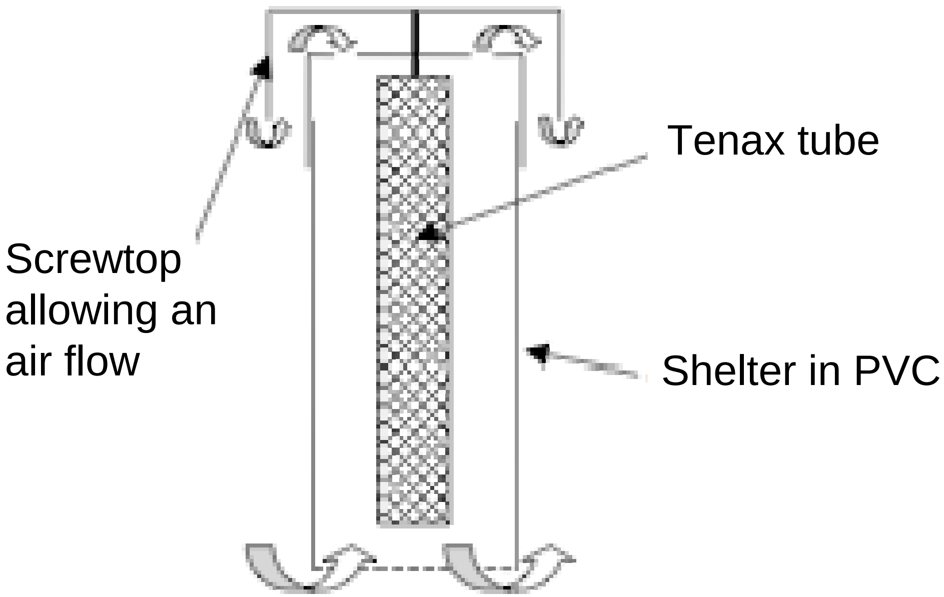
cnrs

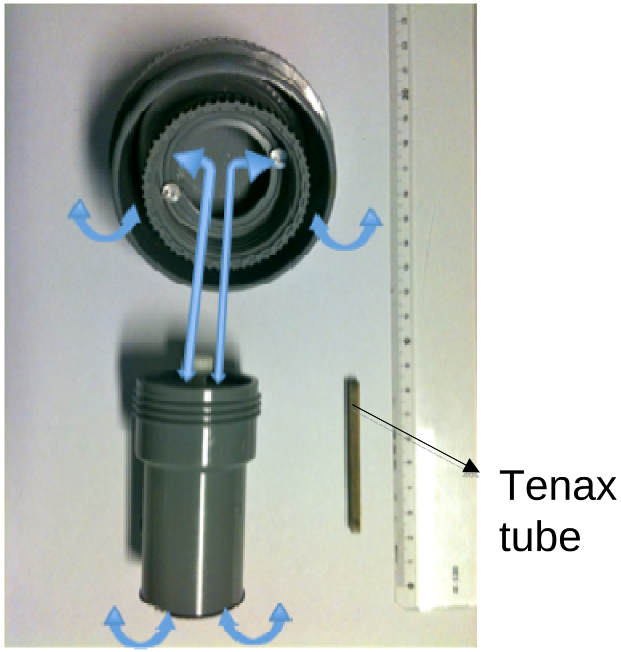
UNIVERSITÉ DE STRASBOURG

Passive air samplers (PAS)

- Tenax tube protected by a plastic shelter
- Method easy to carry out, adapted for large scale sampling and cost-efficient

Scheme of a PAS





From Wania and al. 2003 Development and calibration of a resin-based passive sampling system for monitoring persistent organic pollutants in the atmsophere. Environ. Sci.Technol. 37, 1352-1359

cnrs

Analytical method

- Multi-residue analyse
- Extraction by thermal desorption (time and sensibility saving)
- Coupled with a GC-MS in electron impact ionisation mode
- Derivatisation step during the thermal desorption process with MtBSTFA
- Internal calibration: 4-Nitrophenol d4, Trifluralin d14

Derivatisation reaction

X = O, COO, N, NH

UNIVERSITÉ DE STRASBOURG

✓ Professional Applications: weeding
Oil pumping station Scheibenhard (France)

- Active substances: 1. 2,4 D, Triclpoyr

  2. 2,4 D, Picloram, Diflufenican
- Sampling period : 1. October- November 2009

  2. June 2010
- Samples: outdoor and indoor (office)

cnrs

UNIVERSITÉ DE STRASBOURG

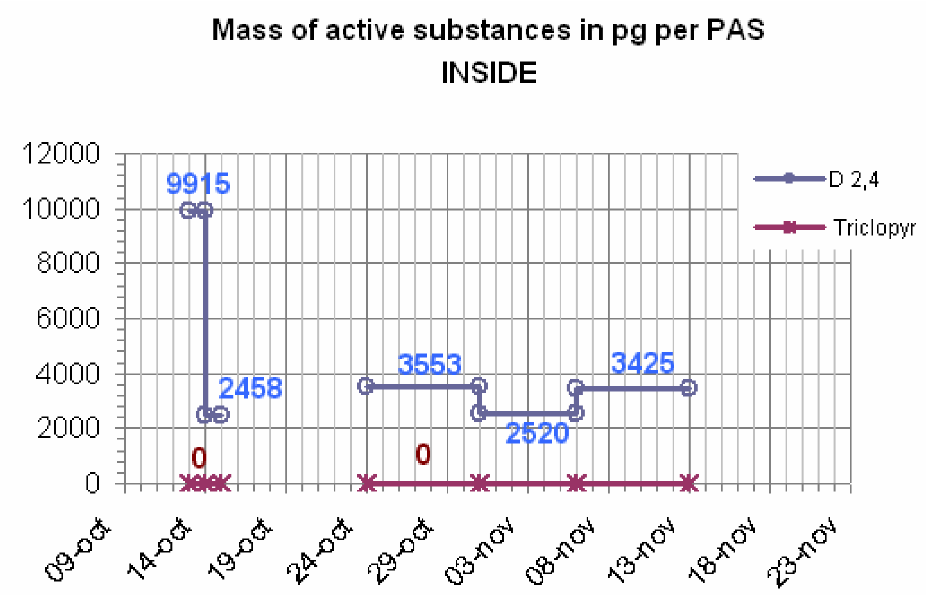
✓ Professional Applications: weeding
Oil pumping station Scheibenhard (France)

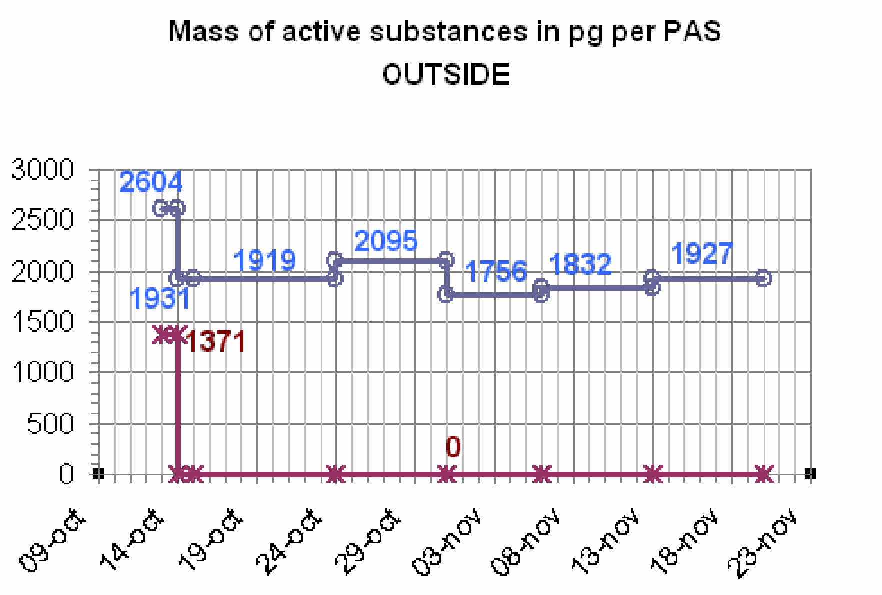
<u>1st application</u>: 2,4 D, Triclpoyr

- Most important quantities observed on the application day (excepted for Triclopyr inside the office)

- Triclopyr only observed on the application day outside suggesting no volatilisation process

- 2,4 D observed during all the sampling period: volatilisation, contamination by another source ?





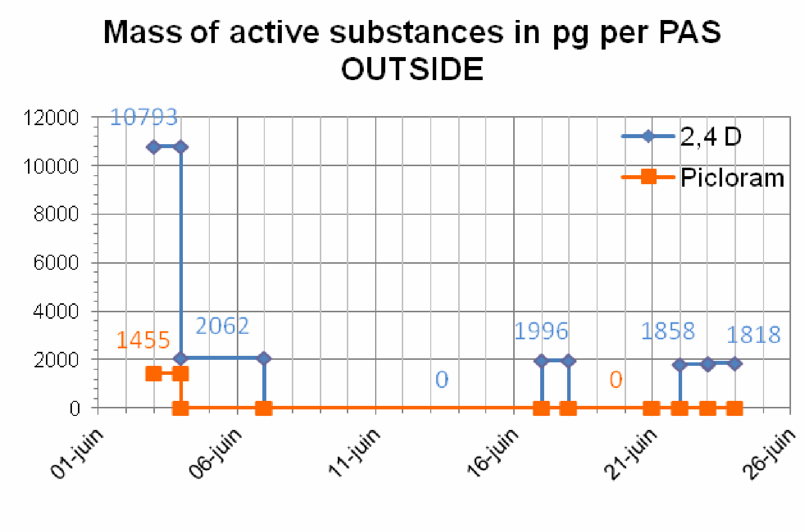
✓ Professional Applications: weeding
Oil pumping station Scheibenhard (France)

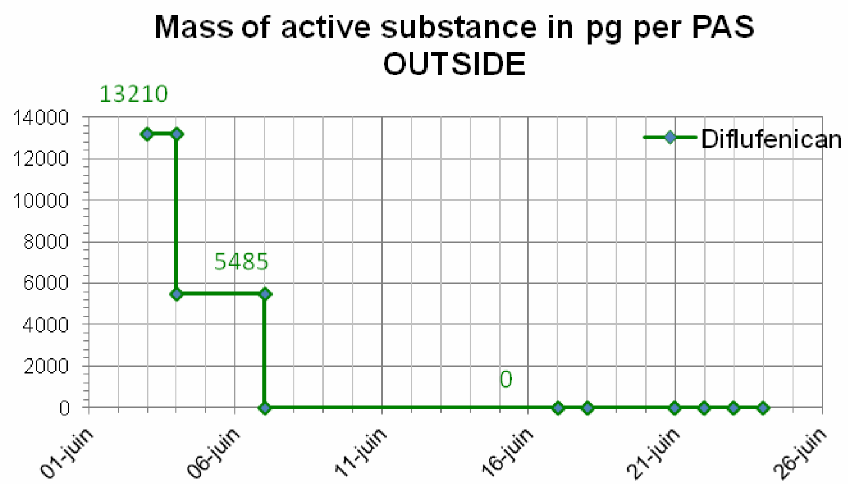
<u>2nd application</u>: 2,4 D, Picloram, Diflufenican

- Most important quantities observed on the application day

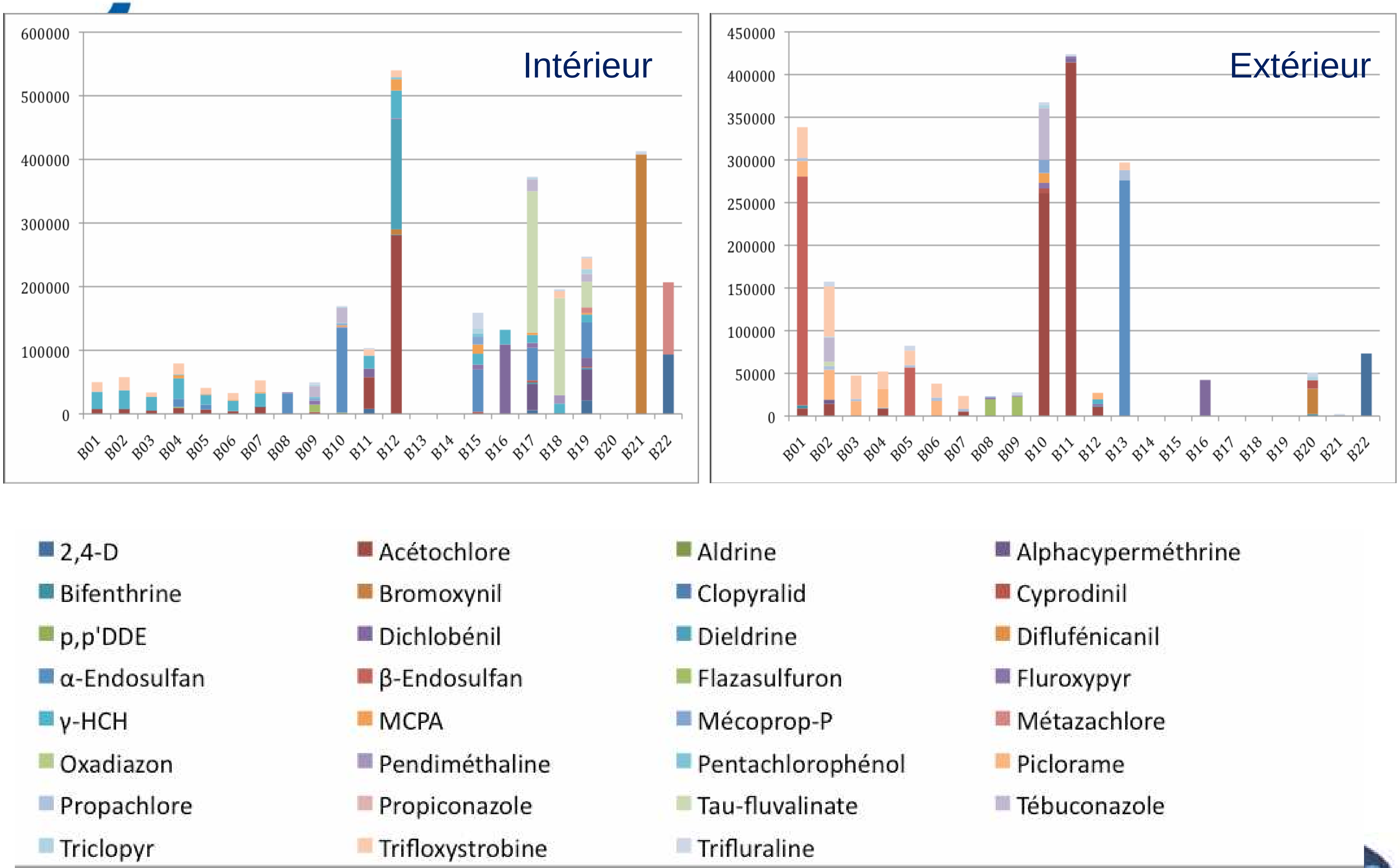
- Picloram only observed on the application day outside suggesting no volatilisation process

- 2,4 D and Diflufenican: volatilisation, contamination by another source ?





UNIVERSITÉ DE STRASBOURG



Biomonitoring

Potentiel des végétaux en tant que biomoniteurs de l'air ambiant

- ✓ Echantillons : aiguilles de pins (genre *Pinus)*
  - Large zone de répartition
  - Représentation importante du genre

- ✓ Les aiguilles de pin
  - Surface recouverte de cire épicuticulaire
  - Persistance sur plusieurs années

<u>Échantillons étudiés:</u>

Zone urbaine de Strasbourg

Objectifs :

Extraction des aiguilles de pin

Fractionnement des 3 classes de composés par une seule méthode de purification

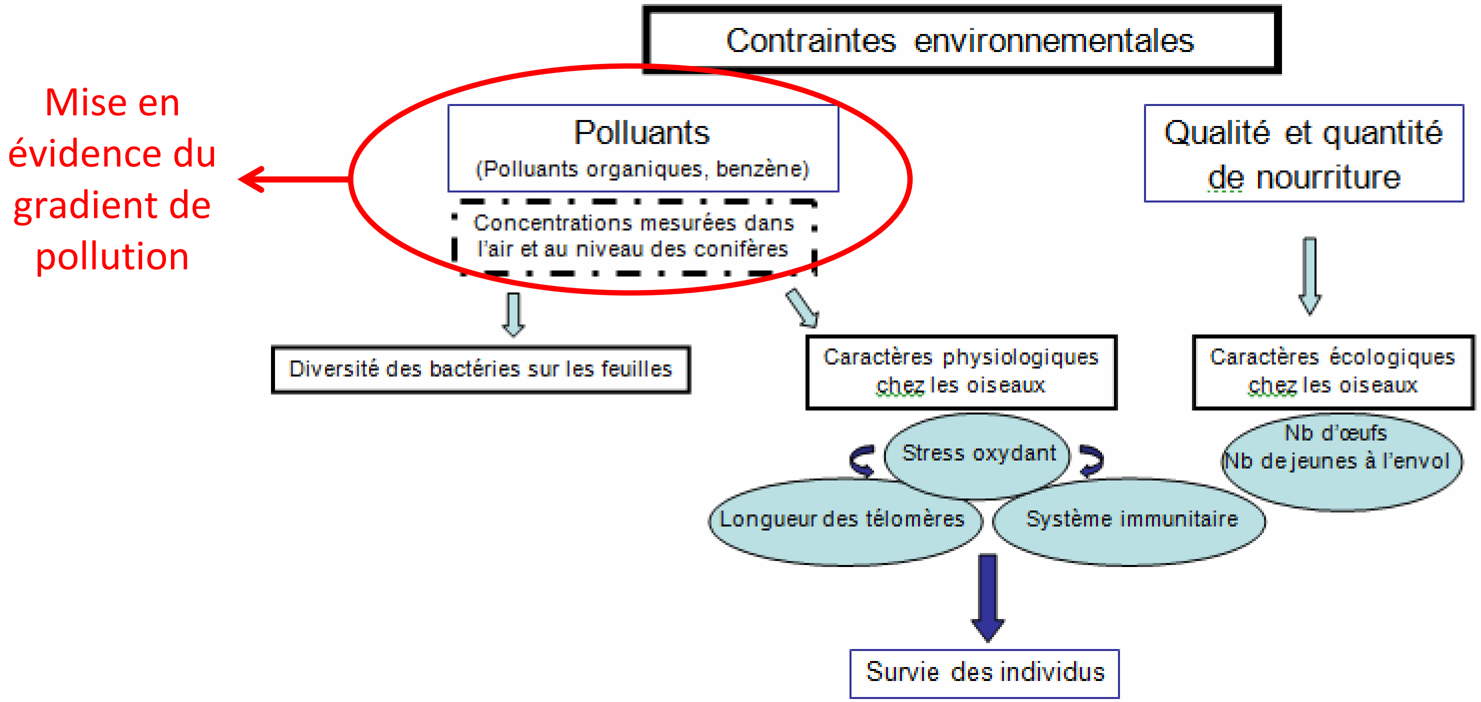
Chromatographie flash envisagée

Large gamme de polarité

Projet oiseaux - ZAEU

✓ Exemple d'application (en projet):

Objectifs : Evaluer l'effet d'un gradient de polluants sur la physiologie d'une espèce aviaire et exploration d'un bioindicateur microbien associé aux végétaux



Laboratoires : *DEPE-IPHC CNRS ; GMGM UMR 7156 CNRS ; LPCA-LMSPC UMR 7515 CNRS*