Cemagref *Unité de recherche REBX*
Bordeaux, FRANCE

Dissipation of polar xenobiotics from pharmaceutical POCIS and suggestion of a performance reference compound

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Introduction

Evaluation of the water quality and its consequences on river biological organisms (WFD)

Effects of pesticides and metabolites on diatom communities

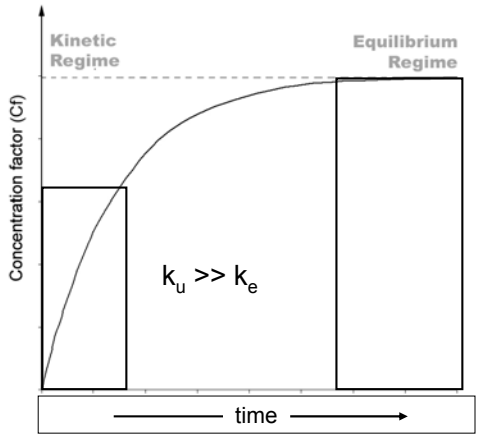
Time-weighted average concentration estimates :

✓ Classical grab sampling → **Representative ?**

✓ Automated/extensive sampling → **Time-consuming and expensive**

✓ Passive sampling → **Validity of quantitative results ?**

Introduction



$$Cf(t) = \frac{C_{POCIS}}{C_{water}} = \frac{k_u}{k_e}(1-e^{-k_e t})$$

Equilibrium regime

$$Cf = \frac{k_u}{k_e} = \mathbf{K_{sw}}$$

Linear uptake regime

$$Cf(t) = k_u \times t$$

Assumption of linear isotherms and isotropic exchanges

Aim and objectives

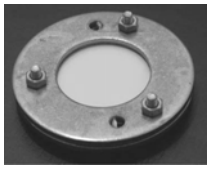
1. **Methodologies**
   Analytical techniques and analyte recoveries

2. **Calibration of pharmaceutical POCIS**
   Determination of k_u and R_s

3. **Study of analyte elimination rates**
   Suggestion of a potential PRC

Methodologies

Analyte recoveries

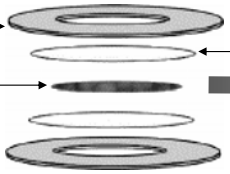


Columns packed with sorbents

Elution with MeOH

Compression holder washers

Sorbent



Polyethersulfone membranes

Methodologies

Herbicides analyzed

Large polarity range : -1.7 (Nicosulfuron) ≤ Log Kow ≤ 5.07 (trifluraline)

Different classes : Triazines, Phenylureas, Sulfonylureas, Diphenyl ethers, Chloroacetanilides, Dinitroanilines, Benzonitriles, Triketones

Triazines and Phenylureas metabolites

Analytical method

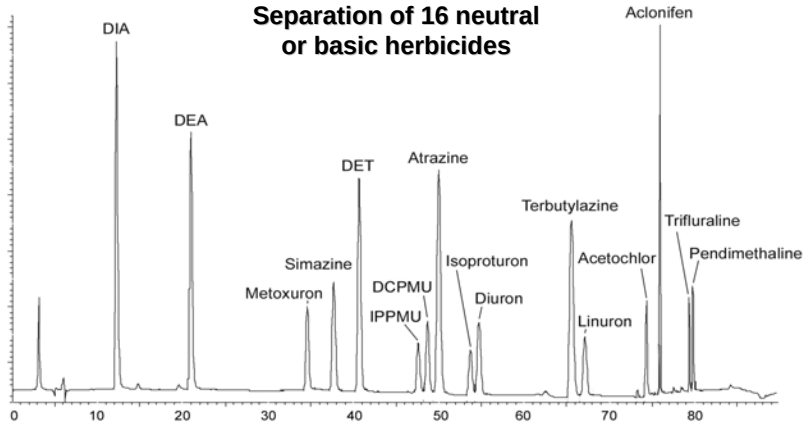
2 multiresidue methods :

HPLC-DAD technique

Reverse phase (ODS 2) and weakly anion-exchanger (polyamine) columns

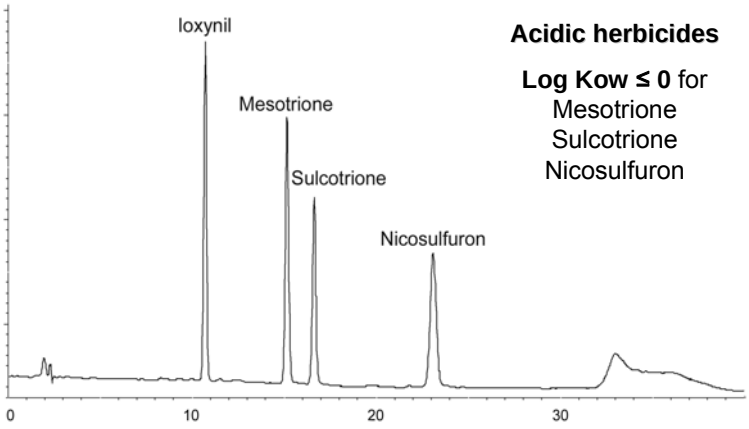
Methodologies

Analysis with an ODS 2 column



Methodologies

Analysis with a polyamine column

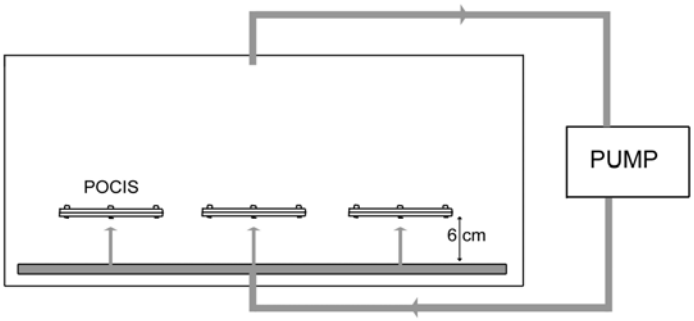


Acidic herbicides

Log Kow ≤ 0 for
Mesotrione
Sulcotrione
Nicosulfuron

Methodologies

Microcosm experimental design

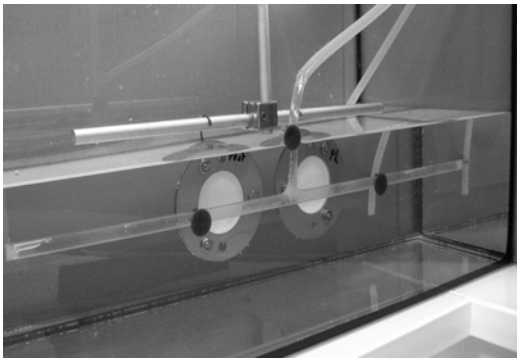


Constant temperature (17±1° C) and obscurity

Large volume (80 L)

Turbulent conditions : constant flow velocity 2-3 $cm.s^{-1}$

Calibration of POCIS



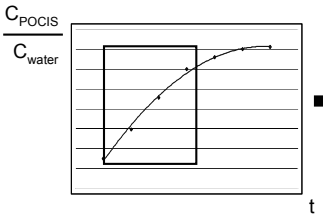
Microcosm experiment

Constant temperature and flow velocity, obscurity

Tap water

Constant concentrations over **21 days** of exposure

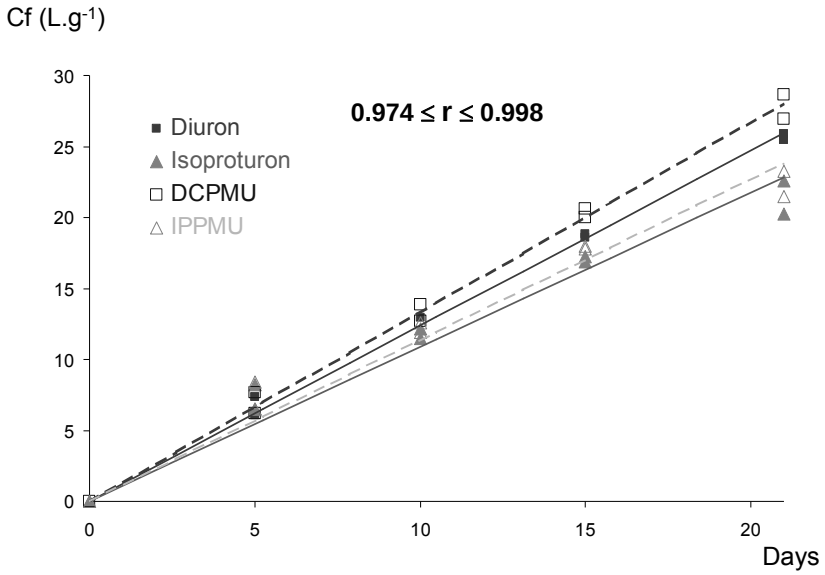
Duplicate analyses



1. Linearity and kinetic regimes

2. Sampling rates Rs

Calibration of POCIS

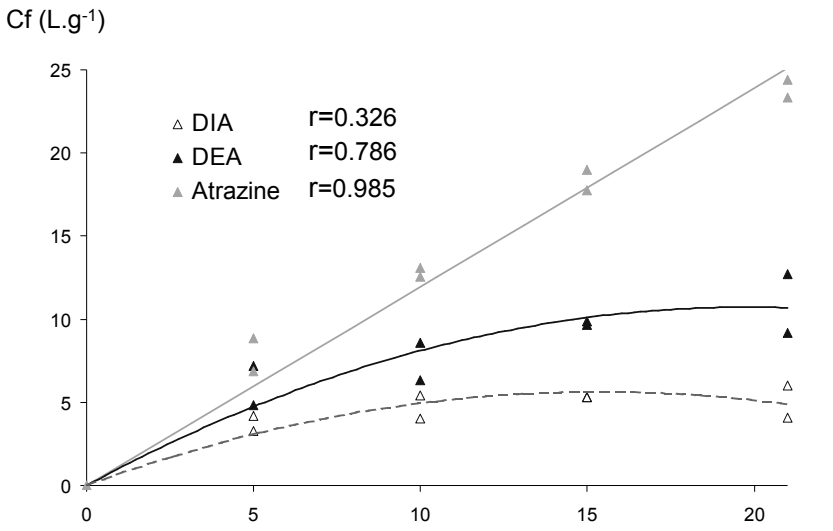


Calibration of POCIS

Sampling rates over 21 days

Herbicides	ku (mL g-1 d-1)	Rs (mL d-1)	% RSD	Linearity over 21 days
Nicosulfuron	219	43.9	3.5	0.910
Sulcotrione	146	29.3	23.8	0.806
Mesotrione	104	20.8	13.0	0.391
Ioxynil	884	176.8	6.2	0.971
DIA	318	63.6	16.5	0.326
DEA	608	121.5	16.5	0.786
Metoxuron	989	197.7	2.4	0.950
Simazine	1051	210.3	0.6	0.955
DET	1025	205.0	2.7	0.974
IPPMU	1135	226.9	3.4	0.981
DCPMU	1334	266.9	3.4	0.998
Atrazine	1195	239.0	3.4	0.985
Isoproturon	1088	217.6	4.7	0.977
Diuron	1236	247.3	0.1	0.998
Terbuthylazine	1253	250.7	3.8	0.994
Linuron	1179	235.9	0.4	0.996
Acetochlor	1126	225.2	7.2	0.989

Calibration of POCIS



Sorbent saturation or isotropic exchanges ?

Calibration of POCIS

Partial conclusion

Linear uptakes of 16 herbicides for 21 days

Curvilinear uptakes of **DIA** and 3 other polar herbicides :

- Assumption of isotropic exchanges for DIA
- Estimation of the elimination rate constant
- Use of DIA as PRC ?

Suggestion of a PRC

$$C_w = \frac{C_{POCIS} \times M_{POCIS}}{R_s \times t}$$

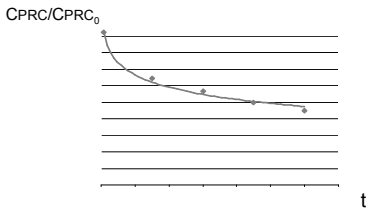
Rs depends on : Temperature
Turbulence
Biofouling

Performance Reference Compound

$$K_{SW} = \frac{ku}{ke}$$

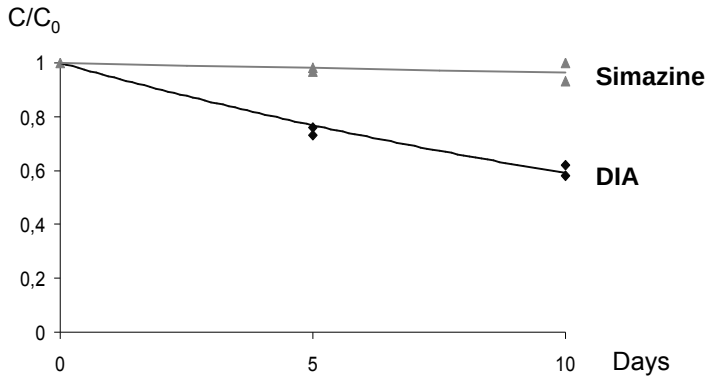
$$ke_{PRC} = \ln(C_{PRC_0}/C_{PRC})/t$$

$$Rs_{in\ situ} = (ke_{in\ situ}/ke_{cal}) \times Rs_{cal}$$



Suggestion of a PRC

Dissipation of DIA and simazine from pharmaceutical POCIS



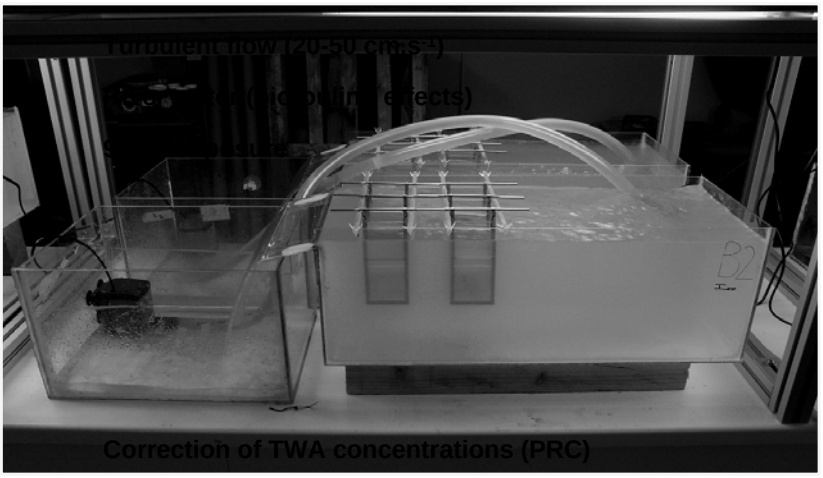
Elimination rate constant estimates :

k_e= **0.047 ± 0.005** d^{-1} (dissipation) and k_e= **0.08 ± 0.02** d^{-1} (uptake)

Isotropic exchanges might exist for DIA

Suggestion of a PRC

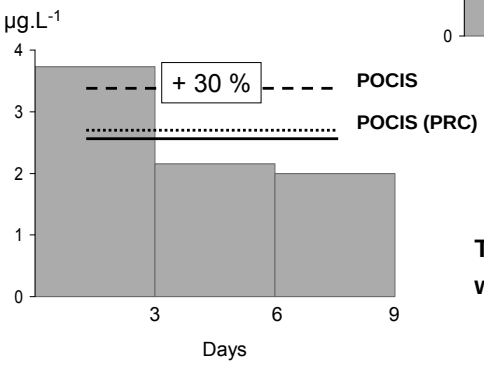
Microcosm experiment



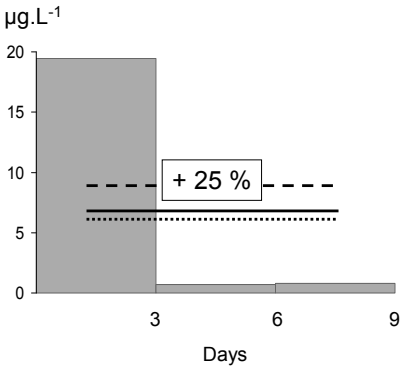
Suggestion of a PRC

Terbuthylazine

Average concentration



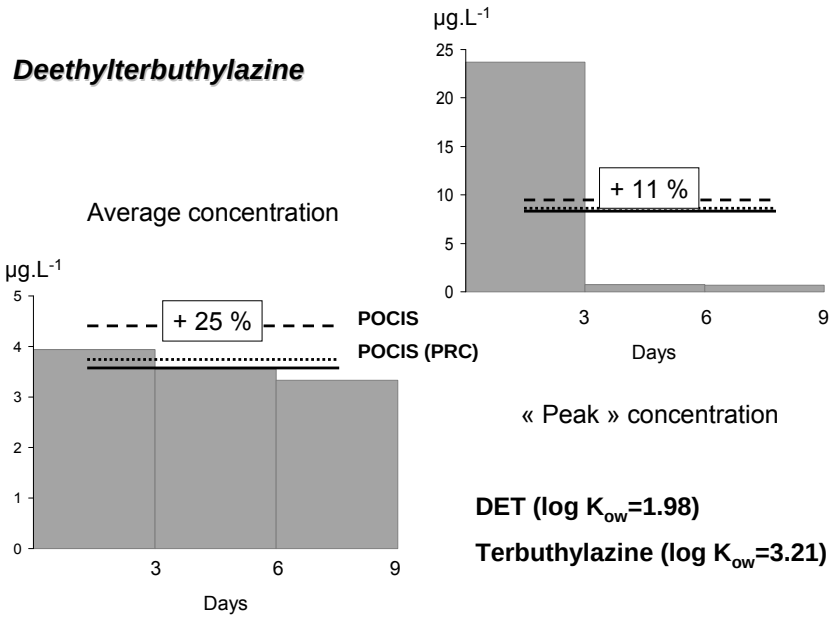
« Peak » concentration



The « peak » concentration was integrated during 9 days

Suggestion of a PRC

Deethylterbuthylazine



« Peak » concentration

DET (log K_{ow}=1.98)

Terbuthylazine (log K_{ow}=3.21)

Conclusions and further studies

Isotropic exchanges for DIA (first-order monophasic kinetic)

« Peak » concentrations are integrated for the 2 test chemicals

Correction of TWA concentration estimates for 9 days

Desorption of DIA and other herbicides for 28 days (biphasic kinetics)

Correction of TWA concentrations for 21-28 days

***In situ* validation with one or several PRCs**

Thank you for your attention !