Water monitoring of emerging pesticides in France: organization of a screening study from prioritization to measurements

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Monitoring data availability for surface water

Routine monitoring of chemicals in surface waters has been effective in France for decades. French Water Agencies regularly monitor diverse chemicals such as, e.g. chemicals, pesticides, biocides and pharmaceuticals.

- LQ > PNEC
- Not good matrix: water vs sediment
- Not enough investigated (< of 30% of stations)

In order to develop the appropriate management measures, the French Ministry in charge of Ecology has launched a national plan for the 2010-2013 period. In this context, exceptional monitoring campaign was scheduled for surface water in 2012.

- Improve information about less investigated substances
- Prepare future revision of RB specific pollutants list (WFD)
## A R&D method for surface water screening

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<td>Regional – RB Coordination</td>
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<td>Sampling Material different Regional courier</td>
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Pesticides Behaviour in soils, water and air – York (UK), 2-4 September 2013
1) New approach for identifying new priority pesticides

- Establish a list of approved pesticides for France in 2011
- Prioritize the substances to be analyzed in water and sediment
- Bibliometric research based on number of publication to identify laboratories
- Organize a screening study (2012)
- Improve analytical tools and ecotoxicological studies
Prioritisation of emerging substances: NORMAN scheme

2316 candidates subst.
(700 already part of national monitoring)

Substances were prioritized using several criteria including occurrence, hazards to the human health and the environment, including suspected endocrine disruption activity and PBT-like properties.

TOP PRIORITY subst.: 221 water and 370 in sediment

Investigation done by AQUAREF on French Laboratory capabilities and analytical performances

Screening study
Choice substances with LQ < PNEC

Improvement of analytical performance (Next years)

Dulio and Andres, French Prioritization methodology, 2013
Substances included in the screening study

INSECTICIDES

- Organophosphonates: Phoxime, etc.
- Pyrethroid ester: Deltamethrin, etc.

FUNGICIDES

- Dicarboximides: Procymidon, etc.
- Substitute pyrimidine: Fenarimol, etc.

HERBICIDES

- Chlorotriazines: Propazine, etc.
- Dinitroaniline: Profluralin, etc.
2) Point selection criteria and sampling strategy

The sampling sites were selected by Water Agencies and selection criteria for surface water were defined by the INERIS at national level.

**SURFACE WATER**

- **RIVER**
  - 139 sampling points
  - 3 times / water matrix
  - 1 time / sediment

- **LAKES**
  - 19 sampling points
  - 1 time / water matrix
  - 1 time / sediment

- **COASTAL (IFREMER)**
  - 40 sampling points
  - 1 time / passive samplers
  - 1 time / sediment
Different type of sampling point

Reference

Identify potential contamination of no pressure areas

<table>
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<tr>
<th>Agricultural</th>
<th>Urban</th>
<th>Industrial</th>
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<tr>
<td>![Agricultural Image]</td>
<td>![Urban Image]</td>
<td>![Industrial Image]</td>
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In case of multi-use of pesticides or pharmaceuticals, understand the specific origins

Bad ecological status

Identify a potential link between emerging substances and bad biological status
Water and sediment sampling in all rivers and lakes (grab sampling)

Passive samplers (POCIS) in 20 rivers and in all 40 coastal sampling stations

Bioassays and biomarkers in 20 surface water sampling points

Sampling strategy

A multiple sampling strategy in order to:

- Establish the occurrence of a substance in the water / sediment compartment
  - Test new tools for the future surveillance
  - Determine the relative strength of a substance by comparing its effect on a test organism
3) Data quality control (55000 data)

Same material for all the screening study, no material impact on analytical results

Material

Sampling quality control

Data transfer to databases

Analyses

Transport control

National experts committee (15 experts) supervised the analytical process

Informatics tool to detect anomalies in data + expert analyses of each sample data before the transfer to a database

Guide on best sampling practices established by AQUAREF

Water samples sampled and shipped directly for analysis by fast courier (24 hours) in thermostated boxes (4°C). More than 800 samples arrived from overseas territories by fast courier, all of them under 48 hours.

5 research laboratories for analytical measurements, performed by LC-MS/MS or GC MS/MS for pesticides.
Preliminary results of emerging substances

26 substances quantified on water (76% of investigated pesticides)
22 substances quantified on sediment (51% of investigated pesticides)

19 pesticides never found
(>500 samples)
Ex.
- Dicofol
- Spinosad
- Benfluralin,
- Pyriproxyfen
- Spinosad
- Flubenzimine

And
18 oversea specific pesticides never found
(>70 samples)

Pesticides quantified at frequency higher than 10% in water (>400 samples)

Acetochlor [Conc] > PNEC in ~15% of cases = Risk
Information concerning sources...

Concentration (µg/L)

- Bad ecological status (n=57)
- Agricultural pressure (n=78)
- Industrial Pressure (n=52)
- Urban Pressure (n=77)
- No expected pressure (n=66)

ESA Metolachor (Degradate, herbicide)
Information concerning persistence and sources...

Carbofuran (insecticide, forbidden use in France)

Concentration (µg/L)

Bad ecological status (n=57)
Agricultural pressure (n = 78)
Industrial Pressure (n =52)
Urban Pressure (n =77)
No expected pressure (n =66)
Information concerning concentration variability

Concentration (µg/L)

- September-October (n = 111)
- November-December (n = 112)
- April-May (n = 108)

Carbendazim
(forbidden use in France as PPP but used as biocide)
Conclusions

- Application of a unique **prioritization** scheme (NORMAN NETWORK) at national level for substance and site selection

- Overall, in 2 years, more than **20000** robust analytical data were collected on more than **90 pesticides/biocides**, in different areas (Urban, Agricultural) and different contexts (Mediterranean, Oceanic, Tropical).

- Information on **occurrence**, **source** and **variability** of emerging pesticides

- Compared to previous monitoring surveys previously performed in France, this survey was performed with an innovative improved approach with analysis of all samples for a **substance** always performed by the **same laboratory**

- **Quality data control** : unique data collection template, fast data validation method and easy access to metadata (access to all dataset for water managers 4 months after last sampling)
Thank you for your attention!

Courtesy of BRGM Guiana