# NATIONAL GROUNDWATER MONITORING AS HIGHER TIER ASSESSMENT FOR PESTICIDES AND THEIR METABOLITES


Ferrari F. [1]
Zighetti C. [1]
Ferrari T. [1]
Ballerini N. [1]
Botteri L. [1]
Rossi R. [1]
Fragkoulis G. [1]
Medini L. [3]
Bruzzone D. [3]
Venzano S. [3]
Suciu N. [4]
Isacco L. [4]

[1]Aeiforia srl, Piacenza (PC), Italy.
Contact: federico.ferrari@aeiforia.it

[2]CeRSAA, Centro di Sperimentazione e Assistenza Agricola – CCIAA Savona (SV)- Italy

[3]Labcam srl, Albenga (SV) - Italy

[4]Università Cattolica del Sacro Cuore, Piacenza (PC) Italy


## Introduction

In the framework of Plant Protection Product (PPP) risk assessment under EU Reg. 1107/2009, groundwater (GW) monitoring programs can be carried out and assessed as refined risk assessment in the tiered approach defined by the FOCUS GW group (SANCO, 2010) and EFSA (2013). However, specific indications of methodologies on how to conduct the studies and about the possible use of the monitoring results have not been proposed by the EU authorities so far. The SETAC group EMAG-Pest/groundwater, is developing scientific bases to recommend harmonised guidance for groundwater monitoring.
At the Italian level, a national provision requires that companies perform monitoring plans for toxicologically non-relevant metabolites whose PECgw exceeds 0.75 µg/L in the Italian relevant scenarios (CCPF, 2009) calculated with standard FOCUS GW models (Min. Salute, 2012). In the last years, AEIFORIA has implemented a specific network of more than 250 wells for field leaching and groundwater monitoring (of which more than 130 new installed piezometers) distributed in relevant agricultural national areas, useful also to accomplish this requirement.

## Objectives

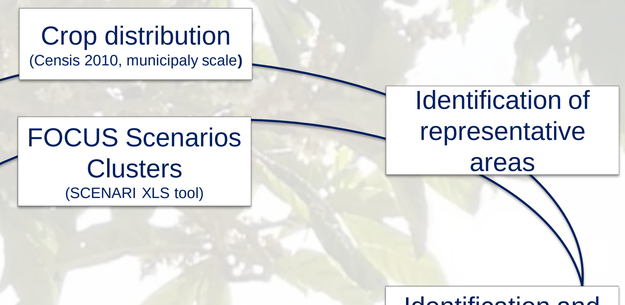
- **To establish a robust methodology at national and EU level for the identification of sites vulnerable to leaching based on the indication of GW FOCUS modelling;**
- **To characterize the extent of occurrence of active substance or its metabolites in wells by retrospective monitoring.**

## Materials and methods

• REPRESENTATIVE AREAS IDENTIFICATION: identification of areas checking shallow GW, crop data, sales data, vulnerability, potential vulnerable layer, weather data and agronomical aspects.
• SITE IDENTIFICATION AND CHARACTERIZATION: identification and characterization through direct interviews with farm owners and farmers, characterization of PPP usage, Cone penetration test and litho-stratigraphic assessment.

• SITE SET-UP: selection of existing suitable wells or installation of new piezometers, also taking in consideration the preliminary indication from EMAG-Pest.
• MONITORING: starting of sampling schedule, carried out in the best way possible in order to preserve samples from degradation, photo degradation and to avoid cross-contamination of GW.

• ANALYSIS: samples are analyzed using the most appropriate analytical methods in terms of specificity and sensitivity. The most common analytical technique is performed by reversed-phase HPLC with triple quadrupole mass spectrometric detection (LC-MS/MS). At least two daughter ions of characteristic transitions of each analyte are monitored.







| | |
|---|---|
| | Unconfined well |
| | Partialy confined Well |
| | Confined well |
| | Unconfined piezometer |
| | Partially confined piezometer |

## Results

| Study | Molecule | Total sampling points | Total analized samples | Total planned samples | N° of metabolites researched | Parent compound detections | | | Metabolites detections | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | <LOQ | >LOQ <0,1 µg/L | >0,1 µg/L | <LOQ | >LOQ <0,75 µg/L | >0,75 µg/L <10 µg/L | >10 µg/L |
| Study 1 | H/FUM | 24 | 24 | 24 | 1 | N.A. | N.A. | N.A. | 24 | 0 | 0 | 0 |
| Study 2 | M/HER-1 | 30 | 120 | 120 | 3 | N.A. | N.A. | N.A. | 120 | 0 | 0 | 0 |
| Study 3 | R/HER-1 | 14 | 28 | 28 | 0 | 28 | 0 | 0 | N.A. | N.A. | N.A. | N.A. |
| Study 4 | M/HER-2 | 20 | 360 | 360 | 6 | 280 | 0 | 0 | 347 | **13** | 0 | 0 |
| Study 5 | W/HER-1 | 36 | 36 | 36 | 2 | N.A. | N.A. | N.A. | 30 | **1** | **4** | **1** |
| Study 6 | R/HER-2 | 12 | 12 | 12 | 0 | 12 | 0 | 0 | N.A. | N.A. | N.A. | N.A. |
| Study 7 | W/HER-2 | 35 | 188 | 306 | 2 | N.A. | N.A. | N.A. | 172 | **9** | **7** | 0 |
| Study 8 | M/HER-3 | 20 | 160 | 200 | 4 | N.A. | N.A. | N.A. | 153 | **7** | 0 | 0 |
| Study 9 | R/HER-3 | 7 | 14 | 14 | 0 | 12 | 0 | **2** | N.A. | N.A. | N.A. | N.A. |
| Study 10 | H-W/FUN | 20 | 120 | 180 | 1 | 59 | 0 | **1** | 101 | **3** | **16** | 0 |
| Study 11 | H-O/FUN | 18 | 108 | 234 | 3 | N.A. | N.A. | N.A. | 84 | **21** | **3** | 0 |
| Study 12 | O/FUN | 8 | 32 | 72 | 2 | N.A. | N.A. | N.A. | 28 | **2** | **2** | 0 |
| Study 13 | M/HER-4 | 20 | 140 | 240 | 4 | 60 | 0 | 0 | 128 | **12** | 0 | 0 |
| Study 14 | W-B/FUN | 20 | - | 80 | 1 | N.A. | N.A. | N.A. | - | - | - | - |
| Study 15 | R/HER-4 | 10 | 20 | 20 | 0 | 18 | **1** | **1** | N.A. | N.A. | N.A. | N.A. |
| Study 16 | R/HER-5 | 10 | 0 | 20 | 0 | - | - | - | N.A. | N.A. | N.A. | N.A. |
| Study 17 | O-V/INS | 10 | 0 | 30 | 4 | NA | NA | NA | - | - | - | - |

N.A.: Not Analysed

| MOLECULE | | |
|---|---|---|
| H: horticultural crops | TARGET CULTURE | FUM: fumigant |
| M: maize | | HER: herbicide |
| R: rice | | FUN: fungicide |
| W: wheat | | INS: insetticide |
| O: orchard | | USAGE |
| V: vineyard | | |

**From 2018 to 2019 four new studies about herbicide and fungicide will start.**

Table 1: The GW monitoring studies implemented in recent years.

## Monitoring Vs Modelling (Molecule W/HER-1)

| Crop | | Mean annual rainfall (mm) | Mean annual temperature (°C) | Soil texture | Organic matter content of topsoil | Cluster | PECgw METABOLITE 1 µg/L | | | PECgw METABOLITE 2 µg/L | | | Sampling site monitored | Higher value observed |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DURUM WHEAT | | 640 | 16,3 | Medium | 1% | Cluster 1 | 52.23 | | | 8.668 | | | 1 sampling site | 0.136 (METABOLITE 2) |
| | | | | | 2% | | 33.33 | | | 7.622 | | | | |
| | | | | Medium fine | 1% | | 46.37 | | | 6.634 | | | | |
| | | | | | 2% | | 28.02 | | | 5.375 | | | | |
| | | 690 | 16,6 | Medium | 1% | Cluster 2 | 51.68 | | | 8.548 | | | 0 sampling sites | - |
| | | | | | 2% | | 32.56 | | | 7.498 | | | | |
| | | | | Medium fine | 1% | | 45.89 | | | 6.545 | | | | |
| | | | | | 2% | | 27.66 | | | 5.289 | | | | |
| | BARLEY | 800 | 15,2 | Medium | 1% | Cluster 3 | 49.96 | | 49.96 | 8.351 | | 8.351 | 14 sampling sites | 0.109 (METABOLITE 2) |
| | | | | | 2% | | 32.47 | | 32.47 | 7.491 | | 7.491 | | |
| | | | | Medium fine | 1% | | 45.06 | | 45.06 | 6.457 | | 6.457 | | |
| | | | | | 2% | | 28.40 | | 28.40 | 5.671 | | 5.671 | | |
| COMMON WHEAT | | 900 | 13,2 | Medium | 1% | Cluster 5 | | 37.71 | 37.71 | | 10.41 | 10.41 | 2 sampling sites | - |
| | | | | | 2% | | | 28.33 | 28.33 | | 10.26 | 10.26 | | |
| | | | | Medium fine | 1% | | | 38.56 | 38.56 | | 9.947 | 9.947 | | |
| | | | | | 2% | | | 28.68 | 28.68 | | 9.54 | 9.54 | | |
| | | 668 | 14,2 | Medium | 1% | Cluster 6 | | 61.23 | | | 10.31 | | 5 sampling sites | 0.336 (METABOLITE 2) |
| | | | | | 2% | | | 42.64 | | | 9.51 | | | |
| | | | | Medium fine | 1% | | | 56.44 | | | 8.50 | | | |
| | | | | | 2% | | | 38.58 | | | 7.91 | | | |
| | BARLEY | 880 | 13,6 | Medium | 1% | Cluster 7 | | 41.56 | 41.56 | | 9.03 | 9.03 | 7 sampling sites | - |
| | | | | | 2% | | | 32.38 | 32.38 | | 8.63 | 8.63 | | |
| | | | | Medium fine | 1% | | | 43.25 | 43.25 | | 7.49 | 7.49 | | |
| | | | | | 2% | | | 32.21 | 32.21 | | 7.12 | 7.12 | | |
| | | 890 | 13,2 | Medium | 1% | Cluster 8 | | 45.60 | | | 10.94 | | 0 sampling sites | - |
| | | | | | 2% | | | 34.89 | | | 10.81 | | | |
| | | | | Medium fine | 1% | | | 49.07 | | | 9.22 | | | |
| | | | | | 2% | | | 35.02 | | | 8.746 | | | |

Table 2: modelling results VS monitoring results

## Discussion

- The identified monitoring areas mostly correspond to the sites monitored by the national Italian authority for environmental monitoring (ARPA) and to the most intensively cultivated areas;
- Results obtained until now indicate that population of concentrations exceeding the limit of 0.1 µg/L for a.i. and relevant metabolites, and the threshold of 0.75 µg/L for toxicologically non-relevant metabolites is near to 1% of the whole dataset. Values above 10 µg/L have not been observed until now;
- As additional model exercise, for W/HER-1, a scenario selection for the higher tier assessment was based on the Italian Clusters identified with the application excel model SCENARIOS.xls and the process of the GIS maps (crop cover, topsoil OC, climatic rainfall and temperature and topsoil soil texture) that became available from JRC and EFSA. Eight environmental clusters have been identified as representative of Italian territory and 7 of them are representative for the intended uses of W/HER-1. Higher tier simulations have been carried out 4 times for each relevant environmental cluster in combination of different texture and OC content.

## Conclusion

- The sampling data obtained until now indicate that the potential GW contamination does not occur in the identified vulnerable sites under realistic conditions. Thus, GW monitoring programs can constitute a valid higher tier for the pre-registration assessment of PPPs;
- Development and implementation of an official EU guidance on GW monitoring would be helpful to share common methodologies for the identification of national vulnerable scenarios. Moreover, it would facilitate the processes of PPP risk assessment and management, also in the post–authorization phase;
- Through the use of "scenari xls" tool (ICPS, 2007), already employed to evaluate the representativeness of FOCUS step 1 scenarios for the national territory, the representativeness of the sampling results could be extended to large areas in Italy. Monitoring results could be indeed considered valid for similar agro-climatic conditions, thereby reducing efforts and costs of monitoring programmes and simplifying the work both for industry and authorities.

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