



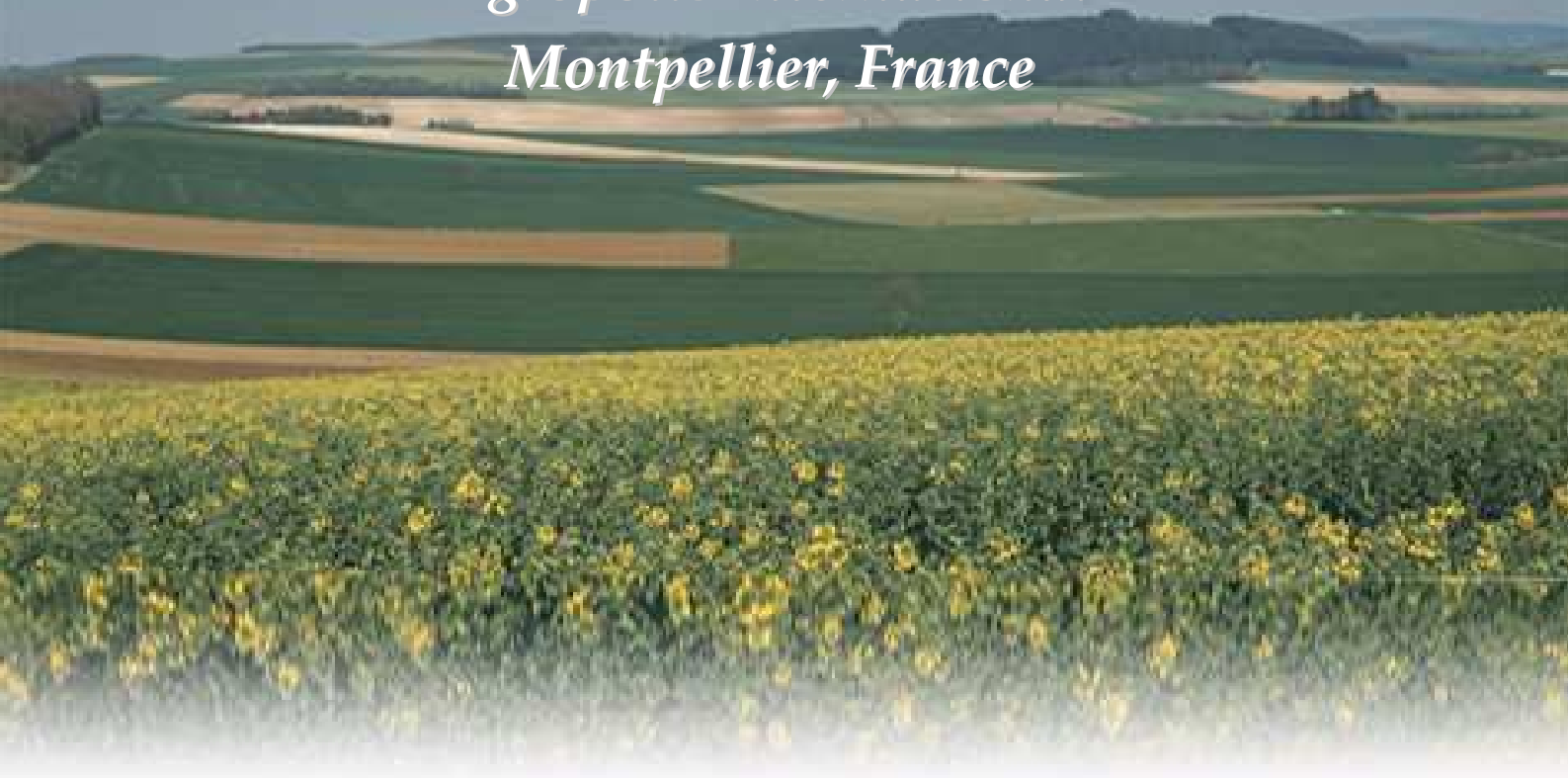
**Innovative approaches for the
management of environmental
risks from plant protection
products**

*A joint EurAqua-PEER Scientific
Conference*

October 26-28, 2011

Agropolis International

Montpellier, France



SCIENTIFIC COMMITTEE

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SCIENTIFIC PROGRAM

Day1: October 26th

Opening speeches: E. Vindimian (Cemagref, Regional director) - JP Torterotot (Cemagref, Deputy-director of of Strategy and Research)

| Session 1: Ecological Risk Assessment | | | Chair |
|--|--|-------|---------------------------------|
| (keynote) | Could the concept of ecosystem services help to improve ecological risk assessments of pesticides? (unconfirmed title) | 11:00 | |
| Lagadic L. (INRA, F) | Structural and functional effects of conventional and low pesticide input wheat and oilseed rape crop protection programmes in outdoor aquatic mesocosms | 11:45 | M. GRUNG, A. DOMANGE |
| Ippolito A. (Milano Univ., I) | Site-specific ERA: new trends in PPP risk evaluation | 12:05 | |
| Lunch | | 12:25 | |
| Ateyyat M. (Al-Balqa' University, J) | Toxicity of five medicinal plant oils to woolly apple aphid, <i>Eriosoma lanigerum</i> (Homoptera: Aphididae) | 14:00 | |
| Stenrod M. (Bioforsk, N) | Soil microbial diversity as an indicator of ecotoxicological effects of single pesticides and mixtures; case study with picoxystrobin and nonylphenol... | 14:20 | |
| Pesce S. (Cemagref, F) | Combining polar organic chemical integrative samplers (POCIS) with toxicity testing to evaluate pesticide mixture effects on natural phototrophic biofilms | 14:40 | M. GRUNG, A. DOMANGE |
| Rasmussen, J. (Aarhus Univ., DK) | Microbial litter degradation in Danish streams is reduced with increased pesticide contamination during storm flow | 15:00 | |
| Arts G. (Alterra/WUR, NL) | Aquatic macrophyte risk assessment for pesticides: current status and future challenges | 15:20 | |
| Discussion | | 15:40 | |
| Coffee Break | | | |
| Session 2: Trends, effects of global changes and of other drivers | | | |
| El Hassan W. (WRMRI, E) | Effect of climate change on reference evapotranspiration and water risk management in Nile Delta | 16:30 | |
| Herrero-Hernades E. (IRNASA-CSIC, SP) | Determination of multi-class pesticides in surface and ground water from La Rioja (Spain) by solid-phase extraction and GC-MS | 16:50 | M. BABUT |
| Li Z. (Montpellier Univ., F) | Leaching behavior of emerging contaminants from wastewater irrigation in agricultural soil | 17:10 | |
| Discussion | | 17:30 | |
| End of day 1 | | 18:00 | |
| Day 2: October 27th | | | |
| Session 3: Fate, monitoring & trends | | | |
| Roex, E. (Deltares, NL) | The advantages of passive sampling with respect to monitoring of Plant Protection Products | 09:00 | |
| Mazzella N. (Cemagref, F) | Evaluation of chemical and biological quality of rivers: relevance and validity of a range of in situ sampling method | 09:20 | A. BARRA-CARRACIOLO, E. ROEX |
| Margoum, C. (Cemagref, F) | Use of PDMS coated stir bars for the passive sampling of agricultural pesticides in surface waters: calibration and determination of lag times | 09:40 | |
| Coffee break and poster session | | 10:00 | |

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|--|--|-------|--------------------------------|
| Barra-Carraciolo A. (IRSA-CNR, I) | Environmental fate of the herbicide terbuthylazine: study cases from Italian agricultural areas | 10:45 | |
| Martin-Laurent F. (INRA, F) | Evidence for filtering capabilities of grass buffer strips: key parameters favoring natural attenuation of pesticides in vineyard area | 11:05 | A. BARRA-CARRACIOLO E. ROEX |
| Siimes K. (SYKE, F) | Pesticide monitoring in Finnish surface waters - Monitoring results 2007-2011 | 11:25 | |
| Stenrod M. (Bioforsk, N) | Trends of pesticides in Norwegian streams and rivers 1995-2010 | 11:45 | |
| <i>Discussion</i> | | 12:05 | |
| <i>Lunch and posters</i> | | 12:30 | |
| Session 4: Indicators and models | | | |
| de Werd R. (Alterra/WUR, NL) | Proposed methodology for listing problematic plant protection products in surface water, causal analysis and emission reduction integrated in registration holders' 'Product Stewardship' and the authorisation procedure in the Netherlands | 14:00 | |
| Carluer N. (Cemagref, F) | Building risk indicators of surface water contamination by pesticides at the small catchment scale. Taking into account spatial and temporal dimensions. Support for risk assessment and risk management: MIRIPHYQUE project | 14:20 | |
| Vernier F. (Cemagref, F) | EIS pesticide: an innovative Environmental Information System to calculate agro-environmental indicators | 14:40 | V. GOUY |
| Miralles A. (Cemagref, F) | EIS Pesticides: An information system for data and knowledge capitalization and analysis | 15:00 | |
| Sinfort C. (Cemagref, F) | Pesticide drift impact at the level of a watershed : a geo-referenced approach | 15:20 | |
| Reichenberger S. (Footways, F) | A web-based risk assessment platform to reduce water contamination by pesticides in catchments in France and across the EU | 15:40 | |
| <i>Discussion</i> | | 16:00 | |
| <i>End of day 2 - Scientific committee meeting</i> | | 16:20 | |
| Day 3: October 28th | | | |
| Session 5 : Risk Management | | | |
| M. Röttele (keynote) | Mitigation of Plant Protection Products losses to surface water from agricultural uses | 9:00 | |
| Tournebize J. (Cemagref, F) | Efficiency of two constructed wetlands (in- and off-stream) to mitigate pesticide contamination in drained agricultural watershed | 9:45 | B. REAL |
| Vindimian E. (Cemagref, F) | Assessing and reducing environmental risks linked with the use of pesticides: a French research program to support public decision | 10:05 | |
| Conclusive discussion | | 10:25 | |
| End | | 11:25 | |

Structural and functional effects of conventional and low pesticide input wheat and oilseed rape crop protection programmes in outdoor aquatic mesocosms

Auber Arnaud¹, Roucaute Marc¹, Caquet Thierry¹, Réal Benoît², Surdyk Nicolas³, Dubus Igor⁴, Togola Anne³, Azam Didier⁵, Quemeneur Alphonse⁵, Lagadic Laurent¹

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This study was designed to evaluate the benefits to aquatic ecosystems of reducing pesticide inputs in crop protection programmes. Models of pesticide transfer (Ganzelmeier curves for drift; MACRO for drainage; PRZM for runoff) were used to estimate fluxes and dates of transfer for each substance under conditions of hydromorphic soils of Northern France. Two contrasted pedoclimatic conditions were considered, which correspond to drained soils of north-western France (Jaillièrè) and of the north-east of the Parisian Basin (Brie). Each condition was associated to two wheat and oilseed rape crop protection programmes (thereafter named 'Conventional' and 'Low pesticide inputs' which include product substitution and application rate reduction) representative of actual agricultural practices. Model estimates of the concentrations and dates at which pesticide mixtures enter water bodies were used to contaminate outdoor pond mesocosms (9 m³). Three mesocosms were used for each treatment and four ponds were kept as controls. Treatments were performed with commercial products for inputs corresponding to drift whereas active ingredients were used for inputs resulting from drainage and runoff. Water concentrations and effects of pesticide mixtures were followed from November 2008 to October 2010. They concerned water physicochemistry, microalgae (phytoplankton and periphyton), zooplankton (zpk) and benthic macroinvertebrates (bmi). Alder litter breakdown rate (litter-bag method) was used as a descriptor of ecosystem functioning. The results of this two-year survey clearly showed that both 'Conventional' and 'Low pesticide inputs' programmes significantly altered the structure of zpk and bmi communities over the long-term, and agropedoclimatic conditions had no influence on those effects. A transient recovery of bmi was observed only in the pond receiving the pesticide mixtures from the 'Conventional' programme. For both programmes, reduction in the abundance of shredders resulted in a significant decrease of alder litter breakdown rate, observed in Autumn and Spring. The effects of the two crop protection programmes were mainly associated with the exposure to potent insecticides (pyrethroids) and some fungicides (e.g., cyprodynil). These compounds were transferred to the aquatic environment at critical periods resulting in altered structure-function relationships. This should be taken into account for improving the management of environmental risks from plant protection products.

Site-specific ERA: new trends in PPP risk evaluation

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Plant protection products (PPPs) loads in rivers are well known to be a potentially major stress for freshwater ecosystems. Current methods for Ecological Risk Assessment of PPPs are referred to generic environmental scenarios. Indeed, the level of alteration in response to the same level of exposure can vary greatly among different ecosystems. This is one of the reasons for which site-specific assessments are gaining importance both in environmental policies and in ecotoxicological research. Site-specific risk assessment is particularly relevant for the management of water bodies according to the European Water Framework Directive. In this view, the focus of the protection is shifted from a generic scenario to a real ecological system, with all its peculiarities that make it more or less vulnerable toward a certain stressor. The study of the ecological vulnerability is a developing discipline within the field of ecotoxicology, and is a clear example of how risk assessment, as becoming site-specific, needs more ecological knowledge. An important change of view is required, especially for what concern the endpoint to be measured. First of all, at individual level, it is necessary to remember that each organism is strongly conditioned by a huge number of interactions with other components (biotic and abiotic) of the ecosystem. The usual endpoints of standard (lethal or sub-lethal) toxicity tests may be insufficient to assess the alterations induced by the exposure to a chemical on natural populations or on structure and functions of ecosystems. Thus, ecological risk assessment procedures should consider more ecologically relevant endpoints, focusing even on higher level of organisation (i.e. community, ecosystems), to achieve a better ecological realism. This requires again a development of new endpoints, which should be representative of the whole biological community (or even ecosystem) and give a safe indication of the chemical-induced alteration. It is very important that these endpoints should be able to detect a stressor-specific alteration, without being disturbed by any other natural or anthropogenic confounding factor. New methods and concepts concerning site-specific risk assessment for PPPs will be presented, discussing insights and limitations, with a specific focus on their future applicability.

Toxicity of five medicinal plant oils to woolly apple aphid, *Eriosoma lanigerum* (Homoptera: aphididae)

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The toxicity of oil extracts of five medicinal plants was evaluated against the woolly apple aphid, *Eriosoma lanigerum*, (Homoptera: Aphididae). Oils were extracted from *Achillea santolina*, *Artemisia seiberi*, *Salvia officinalis*, *Thymus Vulgaris* and *Senecio vernalis*. Each oil extract was used at three concentrations, 100 ppm, 1000 ppm and 100,000 ppm. Mortalities were corrected using Abbott's formula and TableCurve fitting program (Jandel Scientific®) was used to predict the LC50 of each extract. Results revealed that LC50 after 24 hr post treatment is 7011, 6161, 6667, 9090 and 9034 ppm for *A. santolina*, *A. seiberi*, *S. officinalis*, *T. Vulgaris* and *S. vernalis*, respectively. As time response, LC50 was obtained at <1, <1, 37, <1 and 14 hr of using *A. santolina*, *A. seiberi*, *S. officinalis*, *T. Vulgaris* and *S. vernalis* oils, respectively at a concentration of 10,000 ppm. At 1000 ppm, LC50 was obtained at 66, 61, 62,75 and 71 hr post treatment of *A. santolina*, *A. seiberi*, *S. officinalis*, *T. Vulgaris* and *S. vernalis* oils, respectively. LC50 was achieved at 73, 78, 75, 68 and 95 hr post treatment of 100 ppm of oil extracts of *A. santolina*, *A. seiberi*, *S. officinalis*, *T. Vulgaris* and *S. vernalis*, respectively. Finally, *A. seiberi* oil extract was the most toxic to woolly apple aphid in terms of dose and time responses compared with other tested oil extracts, but it was not as toxic as the imidacloprid insecticide that gave LC50 at 0.056 of recommended rate of application (0.25 mL L⁻¹). Nevertheless, oil extract of *A. seiberi* provides valuable mortality rates for the woolly apple aphid and can be used as botanical insecticides as part of the integrated pest management programs of this insect pest.

Soil microbial diversity as an indicator of ecotoxicological effects of single pesticides and mixtures; case study with picoxystrobin and nonylphenol

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Current risk assessment procedures for contaminated land and for pesticides often fail to properly characterize the risk of chemicals for environment or human health and provide only a rough estimate of the potential risk of chemicals. Chemicals often occur in mixtures in the environment, while regulatory agencies often use a chemical-by-chemical approach, focusing on a single media, a single source, and a single toxic endpoint. Further, the importance of soil microbes and their activity in the functioning of soils impose a need to include microorganisms in soil quality assessments including terrestrial ecotoxicological studies.

Numerous papers have been published on the effects of different contaminants on soil microbes, establishing changes in soil microbial diversity as an indicator of soil pollution. However, only a limited number of molecular studies focus on changes in fungal species when investigating soil microbial diversity. The main objective of the study presented here, is to assess the applicability of changes in soil microbial diversity and activity levels as indicators of ecologically relevant effects of chemicals contamination. We will achieve this through studies of effects of the fungicide picoxystrobin and the chemical 4-n-nonylphenol on the microbial biodiversity in a Norwegian sandy loam, with focus both on prokaryotes and the fungal species.

Laboratory incubation experiments at 20°C with soil samples treated with the single chemicals or mixtures, with continuous monitoring of respiration activity as well as occasional destructive sampling for extraction of soil DNA, RNA, and chemical residues, was performed through a 70 d period. Results from amplification of soil bacterial and fungal DNA followed by T-RFLP (terminal restriction fragment length) analyses to assess chemicals effects on soil microbial diversity, indicate significant effects of the studied chemicals on soil microbial community structure. To identify specific bacterial or fungal groups that are affected, an assessment of the effects of the chemicals on the soil microbial metagenome by high throughput shot-gun sequencing (454 sequencing) is in progress

This work is part of the research project 'Bioavailability and biological effects of chemicals - Novel tools in risk assessment of mixtures in agricultural and contaminated soils' funded by the Norwegian research council.

Combining polar organic chemical integrative samplers (POCIS) with toxicity testing to evaluate pesticide mixture effects on natural phototrophic biofilms.

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Polar organic chemical integrative samplers (POCIS) are valuable tools in passive sampling methods for monitoring polar organic pesticides in freshwaters. Moreover, the combination of passive samplers and bioassays offers a simple and cost-effective method to determine potential acute impacts of contaminant mixtures in various aquatic environments. One original feature of our approach is the use of natural stream biofilms to investigate the toxicity of POCIS extracts to phototrophic microbial communities.

In a first study, biofilms collected at two sampling stations located along a French stream (Ruiné River) were exposed for 24 h and 48 h to various dilutions of an extract from POCIS immersed for two weeks in this stream. The POCIS extract was mainly composed of triazines and metabolites. The highest mixture concentrations impacted chlorophyll a concentrations, photosynthesis activity and phototrophic community structure. Nevertheless, the range of microbial responses differed according to origin of the biofilms tested, revealing spatial variations in the sensitivity of natural communities in the studied stream. These results thus suggested that such an approach could offer promising perspectives for evaluate pesticide effects on aquatic ecosystems, especially in the view of implementing pollution induced community tolerance (PICT) assessment for mixtures.

Accordingly, a second study was performed in a stream characterized by a marked increase in pesticide concentrations from upstream to downstream (Morcille River). Using the same procedure with POCIS immersed in the contaminated section, we showed that downstream communities, which were pre-exposed to high pesticide concentrations in the field, were about 4-fold more tolerant to the tested mixture than the upstream communities. This observation was in accordance with the PICT concept.

Our works reveal that passive samplers can easily be combined with community-level toxicity testing, offering new perspectives for ecological risk assessment. Indeed, the use of multiple passive samplers (e.g. Diffusive Gradients in Thin-film, Semipermeable, Membrane Device or silicone rods) to screen a large variety of inorganic and organic contaminants combined with toxicity testing on biological communities should be a possible alternative for evaluating contaminant mixture effects on aquatic ecosystems.

Microbial litter degradation in Danish streams is reduced with increased pesticide contamination during storm flow

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Stream ecosystems are impacted by numerous anthropogenic stressors, and they remain some of the most impaired ecosystems on earth. This emphasizes the importance of a yet unresolved question – whether these ecosystems are able to maintain their ecological functions. In consequence, it is highly important to address and characterize relations between stream functions and anthropogenic stress. In streams, fungi and bacteria are key organism groups in the decomposition and conversion of riparian plant litter into more palatable food resources for macroinvertebrate shredders and collectors.

We measured mass loss in beech leaves (*Fagus sylvatica*) using net bags (mesh size < 500 µm) in 14 Danish streams draining catchments with different agricultural activity. In each stream 30 leaf bags were mounted to the stream bed. Fifteen were positioned at sites characterized by low flow and fine particulate substratum and the other fifteen at sites characterized by turbulent flow and coarse substratum. Leaves were submerged in the streams from April to July. Concurrently, water samples were collected during storm flow events using event triggered samplers and analysed for 31 pesticide compounds.

Breakdown coefficients (k) were reduced by a factor 3-8 in agricultural streams compared to reference streams. Breakdown coefficients were, furthermore, significantly lower for leaf packs that were positioned at sites with low flow compared to sites with turbulent flow. Moreover, we calculated Toxic Units (TU) for all pesticides in each sample by weighing the toxic contribution of each compound against its toxicity for aquatic fungi. Of all measured physical and chemical stream properties and catchment properties the TUFungi was the parameter most strongly correlated to breakdown coefficients.

Our study is the first to evaluate effects of pesticides on microbial litter degradation in the field. The results clearly emphasize the importance of considering microbial litter breakdown as endpoint when evaluating the effects of anthropogenic stressors in streams. Agricultural pesticides could have the potential to alter the entire flux of energy through ecosystems – an effect that is further enhanced when physical conditions in streams are poor. In addition, our study shows that TUFungi is applicable for predicting effects of agricultural pesticides on microbial communities.

Aquatic Macrophyte Risk Assessment: current status and future challenges

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Aquatic macrophytes fulfill critical functions in ecosystems, contributing to structure and function. Aside from the floating, non-sediment rooting duckweed species (*Lemna* spp.), other aquatic macrophytes are not routinely considered in standard risk assessments for chemicals in Europe yet. In the pesticide regulation (1107/2009/EC) *Lemna* spp. are the Tier 1 test species. However, they differ from rooted and submerged macrophytes, most markedly in their short generation time and free-floating growth form. The concern, that risk assessments based on endpoints derived from tests with *Lemna* may not be protective for other macrophyte species, was a driving reason for the workshop "Aquatic Macrophyte Risk Assessment for Pesticides" (AMRAP) in 2008. The participants concluded that the risk assessment based on data obtained from *Lemna* studies may not be sufficiently protective in certain cases. Additional triggers for further testing were defined including the specific mode of action of pesticides and the possible exposure of macrophytes via sediment. Therefore, an additional Tier 1 test with a rooted dicotyledonous macrophyte, *Myriophyllum* spp., was proposed. Test protocols for *Myriophyllum* sp. are currently being ring-tested in order to become a standardized OECD test. If concern over the safety of a pesticide is still present after Tier 1 testing and risk evaluation, higher-tier assessments may be performed through e.g. the generation of further macrophyte species data for use in species sensitivity distributions (SSDs), or by conducting multi-species tests or microcosm and mesocosm studies. Species Sensitivity Distribution analyses on 14 compounds performed by a working group with Aquatic Macrophyte Ecotoxicology Group (or AMEG, which emerged out of the AMRAP workshop) found that effects on *L. gibba* and the four algal species required for US pesticide registration are in most cases protective for rooted and submerged macrophyte species. Exceptions can generally be predicted based on the mode of action of the chemical. In European pesticide regulation (1107/2009/EC) *Myriophyllum* spp. and *Glyceria maxima* have recently been proposed as additional test species. Other regulatory frameworks include the Water Framework Directive (WFD) which aims to achieve a 'good' ecological and chemical status for all surface waters in the EU. Attainment of this status requires that chemical concentrations meet Environmental Quality Standards based on ecotoxicological data. The integration of climate change and how it can modify our understanding of ecosystems and effects in the field for risk evaluation poses additional challenges for aquatic macrophyte risk assessment. For example, modeling tools are needed to predict the effects of changing water temperature on plant growth and development and changing hydrological regimens might change exposure. While the potential effects and manner in which climate change might be manifest in freshwater ecosystems are still being discussed and quantified, the integration of these aspects into risk assessments is missing. Working on these concepts and translating patterns into robust aquatic macrophyte risk assessments is one of the challenging topics for future research.

Effect of climate change on reference evapotranspiration and water management in Nile Delta

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The objective of this study was to identify the effect of climate change within last 30 years on reference crop evapotranspiration (ET_o) and to predict its future trend in the northern coastal areas of Egypt. Correct estimating of ET_o is important to determine the exact quantity of irrigated water needed for specific crop. The overuse of water for irrigation has resulted in eliminating the water resources in the whole country. Estimating ET_o, which is the main input for water balance simulations, using Hargreaves, Penman Monteith, FAO Penman Monteith, Penman (Modified) and Penman Open Water models was through DAILYET version 3.0 model. The determination of ET_o using simulation models, for irrigation purposes will be used as a vital tool for supporting the decision-making process in the future management of water resources and on the other hand will have a positive effect on the rest of limited water resources of Egypt. It was observed the over the last 30 years, air temperature has risen by 2 degree Celsius in the study area. However, this change in air temperature did not affect the ET_o estimates by using different models. Among the different methods tested, Pan Evaporation Rate method behaved the best and appeared as a simple method for accurate ET_o daily estimations. Also, maximum and minimum air temperatures among the climate parameters have the most effect on ET_o.

Determination of multi-class pesticides in surface and ground water from La Rioja (Spain) by solid-phase extraction and GC-MS

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A multi-residue method for the trace determination of more widely used pesticides in La Rioja has been developed for screening, quantification and confirmation of 37 compounds, which included 16 herbicides, 12 fungicides, 5 insecticides and 4 of their degradation products. Pesticide consumption in La Rioja region (Spain) is very high, especially in vineyard areas, and data are scarce regarding the concentration of these compounds in surface and ground water.

The proposed method is based on solid phase extraction (SPE), which combines isolation of the pesticides and sample clean-up in a single step, and by gas chromatography coupled to mass spectrometry with electron impact ionisation in SIM and SCAN mode. In the SPE pre-concentration step, different types of sorbent were studied: carbon, C18 on silica and polymeric sorbents (Oasis HLB, Strata STX and LiChrolut EN), the best results were obtained with the polyvinyl pyrrolidone cartridge. Parameters that might influence the extraction efficiency such as the sample volume and the nature of the eluent were studied. Optimized procedure implies pre-concentration of a sample volume of 500 mL, elution of the cartridge with acetone and acetonitrile, evaporation and later reconstruction with 500 μ L of methanol. The experimental results showed a good linearity in the range of concentrations studied and precisions < 15 % with detection limits lower than 0.1 μ g L⁻¹, which is the limit established by current EU legislation for the determination of pesticides in drinking water.

The proposed method was used to evaluate the presence of selected pesticides and their degradation products in samples of surface and ground waters from La Rioja. The analysis of 95 samples taken in September 2010 showed the presence of several herbicides (alachlor, metalachlor, ethofumesate and fluometuron) together some triazines like terbutylazine, atrazine and propazine and some of their major degradation products like deethyl-terbutylazine, deisopropil- and deethyl-atrazine. Several fungicides were found like metalaxyl and one of its main degradation products, pyrimethanil, cyprodinil, tebuconazole, penconazole, kresoxim-methyl, etc. The insecticide diazinon was also found.

Leaching behavior of emerging contaminants (pharmaceuticals) from wastewater irrigation in agricultural soil

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Irrigation of agricultural soils by treated wastewater is of concern in recent years. Penury of water supply and conflict in water use between irrigation and drinking water make reuse of treated wastewater for irrigation a good alternative in the future, especially in arid and semiarid regions such as Mediterranean basin. However, treated municipal wastewater still contains some organic pollutants such as pharmaceutical products (PPs), and can introduce these compounds in soil even in ground water. Environmental fate of PPs is of interest because of potential ecological risk due to their biological activities. In addition, their pseudo persistence due to daily release by municipal wastewater makes them ideal tracers for anthropic pollution in soil. By now, there are few studies of their environmental fate in soil.

In this work, we study the leaching behavior of some pharmaceuticals in laboratory conditions in columns packed with two Mediterranean soils, which are likely to receive treated wastewater. Three non ionic and ionic pharmaceuticals (carbamazepine, venlafaxine and zolpidem) in environmental pH and their human metabolites are chosen because they are usually detected in the environment. Soils are sandy loam and sandy clay loam with low organic matter content (<2%). The leaching of contaminants is carried out with solutions of different pH or ionic strength under a saturated flow regime and breakthrough curves are obtained at flow rate of 1 mL/min. The influence of surfactants, present in both water solution or soil, in the leaching of these compounds is also studied because surfactants can reach the soil from different sources. The results obtained show leaching of compounds is depending on their chemical structure. Different mechanisms can be involved in the adsorption of organic compound and modify the leaching process. Adsorption of non ionic compound is dominated by hydrophobic affinity while adsorption of cationic compounds is based on cationic exchange. The leaching behavior of organic contaminants in soil is of crucial importance for ecological risk assessment. Following the persistence of compounds in soil, the most retained represent ecological risk for terrestrial environment. And the most mobile pollutants could be leached in groundwater and represent sanitary risk by entering in drinking water facilities.

The advantages of passive sampling with respect to monitoring of Plant Protection Products

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Monitoring is an essential part of the risk assessment cycle. It is essential in checking compliance with set environmental quality standards (EQS), and consequently if, and which risk reducing measures should be taken. However, adequate monitoring of plant protection products is often hampered by two important aspects of these substances:

1. Their emission to the receiving environment can easily be missed by classic grab sampling, because of their intermittent use pattern.
2. Compliance check with environmental quality standards may fail because of their high toxicity in relation to their Limit Of Quantification (LOQ). Regularly, the LOQ is higher than the EQS.

In several sampling campaigns in which Deltares has participated recently, we were able to demonstrate the advantages of silicone passive samplers with respect to PPPs. Passive sampling may overcome the above mentioned problems. Passive samplers absorb compounds from their receiving environment as a consequence of the difference in chemical activity between the passive sampler and the environment. Because of their long sampling time in the surface water, lasting up to several months, all compounds released into the environment and passing the passive sampler are adsorbed by and accumulated on the passive sampler, depending on the chemical properties of the compounds. By determining the release of Performance Reference Compounds (PRC) during the sampling period the sampling rate is calculated. Consequently, sampler concentrations can be transferred into water concentrations. By using passive sampling, regulators will get a more realistic overview of the PPPs that are used in the vicinity of surface waters, and are able to perform a monitoring program more fit to purpose.

Evaluation of chemical and biological quality of rivers: relevance and validity of a range of in situ sampling methods

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This work has mainly targeted the study of various sampling strategies to assess water quality of rivers in relation to agricultural diffuse pollution. For that purpose, a panel of methodologies was implemented to provide additional knowledge on the dynamics of pesticide concentrations in several small rivers. One of our objectives was to compare the results obtained from spot sampling, automated integrated weekly sampling and passive sampling to evaluate the exposure of biofilms to various pesticides.

These methods have involved the development of innovative, more reliable and less expensive sampling techniques for in situ estimates of the time-weighted average concentrations of pesticides. Several types of passive samplers were tested: Polar Organic Chemical Integrative Samplers (POCIS) for hydrophilic organic pesticides, Stir Bar Sorptive Extraction (SBSE) for hydrophobic organic pesticides and Diffusion Gradient in Thin-Film (DGT) for metals.

First, the implementation of POCIS and SBSE required analytical developments and laboratory calibrations. Then, the three types of tools were deployed in 2009 and 2010 on several sampling sites on the Morcille and Ardières rivers (Beaujolais area near Lyon), as well as in the Ruiné creek, a sub-basin of the Charente River. These sites are characterized by different agricultural, hydrological, physicochemical and geological contexts, which allowed to study the performances and limitations of the different sampling techniques under various conditions.

Furthermore, analytical methods for measuring pesticides and metals accumulated in the river biofilms were developed. Hence, we were able to evaluate the bioaccumulated contaminants and their likely impacts on the periphyton and to compare results with the exposure estimates derived from the different sampling techniques.

Use of PDMS coated stir bars for the passive sampling of agricultural pesticides in surface waters: calibration and determination of lag times

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Passive sampling has recently been developed as an alternative to grab or average automated sampling, in order to obtain at lower cost, more realistic estimates of the average concentrations of contaminants in surface waters. This technique allows the accumulation of chemicals from large amounts of water, resulting in ultratrace level detection and smoothed integrative sampling over periods ranging from days to weeks. The lag time is the time required for a compound to reach a steady state flux in the receiving phase. Although it represents relevant information in case of short temporal variations of the organic pollutant concentrations in the aquatic medium, it has been rarely investigated.

Passive samplers can monitor a broad range of micropollutants with various physicochemical properties, from polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyl congeners (PCB) to pharmaceuticals compounds and hydrophilic pesticides (1-3). Nevertheless, the integrative sampling of hydrophobic pesticides has been poorly reported in the literature.

Stir Bar Sorptive Extraction (SBSE) is a solvent free sample preparation technique dedicated to the analysis of moderately hydrophobic compounds in aqueous samples (4). The in situ application of this technique has been reported in the literature only for PAH (5).

The aim of this study was to develop and calibrate the in situ SBSE as a passive sampling technique for the monitoring of 20 agricultural pesticides in surface waters. A laboratory calibration of the stir bars was realised under controlled temperature and flow velocity conditions in order to determine the sampling rates of the target compounds. In this study, we paid particular attention to the determination of the lag time for each compound, which enabled to assess the minimum duration for a concentration peak of pesticides in surface waters to be efficiently integrated by the stir bars. In addition, desorption kinetics of one deuterium labelled insecticide was monitored under laboratory conditions. The corresponding elimination rate constant was calculated, and the isotropic exchange on the stir bar was demonstrated for the chemical. These results allowed the authors to consider the insecticide as a possible PRC and the in situ SBSE as a technique for the determination of time-weighted average pesticide concentrations in surface waters.

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Environmental fate of the herbicide terbuthylazine: study cases from Italian agricultural areas

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The herbicide terbuthylazine is widely used, primarily in maize producing regions, both in Italy and worldwide. Monitoring data from Italy and other countries indicate that a significant proportion of monitored surface and groundwater is contaminated by s-triazines, mainly terbuthylazine and its main metabolite desethyl-terbuthylazine (DET). In several cases the concentration of these contaminants is found to be above the Maximum Allowable Concentrations established for pesticides in the EC and national drinking water regulations (0.1-0.5 µg/L for single and total pesticides, respectively).

Terbuthylazine degradation depends on both abiotic and, especially, biotic processes, which are responsible for its complete degradation. Biodegradation and mineralization of s-triazines have been shown to be carried out by bacterial consortia and by strains isolated from contaminated sites.

Owing to their occurrence in water bodies and to their biological properties, terbuthylazine and DET may pose environmental and health problems for man and aquatic organisms. The widespread presence of terbuthylazine and DET in water bodies may be traced back not only to the high amounts of parent compound used in agriculture, but also to agricultural practices, improper pesticide handling (e.g. accidental spills, uncontrolled disposals, equipment washing water, etc.) and the specific climatic and hydrogeological characteristics of the receiving environment.

In this context, we show the results of several degradation experiments performed in different Italian agricultural areas. The overall results confirm that terbuthylazine degradation depends mainly on bacterial activity and that abiotic factors (soil depth, pH, temperature, water content, presence of exogenous nitrogen, organic matter content, etc.) can directly or indirectly influence the degradation rate. The latter in fact varies quite considerably between different soils and assuming that abiotic factors (i.e. water content, temperature, pH and so on) are the same, the intrinsic characteristics of the soil, such as texture and mineralogy, seem to be key factor in the degradation. The different persistence (DT50s ranging from 20 to more than 100 days) of terbuthylazine in the different soils studied suggest that for the prediction of its actual environmental fate both the intrinsic specific soil characteristics and climatic and hydrogeological traits of the receiving ecosystem have to be taken into consideration. The use of the herbicide terbuthylazine is therefore advised against in areas where its persistence is high and the aquifer beneath is vulnerable.

Evidence for filtering capabilities of grass buffer strips: key parameters favoring natural attenuation of pesticides in vineyard area.

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Vineyard is among the crops the most heavily treated with pesticides. In the context of the new EU policy for the protection of water resources, vineyard area will account as one of the major contributor to water contamination. Grass buffer strips have recently been developed as a solution for reducing pesticide transfer by surface runoff from vineyard parcels to adjacent streams. Although pesticide interception by grass strips has generally been proven effective, little is known about the fate of intercepted pesticides. In order to tackle this question we worked since several years at the scale of a small watershed located in the Beaujolais vineyard (France). The ability of the soil microflora to degrade diuron, an herbicide belonging to phenyl-urea family, was addressed by radiorespirometric analyses showing that the grass buffer strip could develop efficient degrading ability if regularly exposed to the contaminant (1). Interestingly, we revealed the presence of bacterial populations able to rapidly mineralize this herbicide in the grass buffer strips. We also showed that their genetic potential (*puhA* and *puhB* genes) could be transferred by erosion to the sediment of the river adjacent to the grass buffer strip (2). With the aim to promote natural attenuation of pesticides in the grass buffer strip, bioaugmentation experiments with diuron-degrading bacterial populations are ongoing. All these data seem to indicate that the development of a second generation of engineered grass buffer strip acting as an 'in field bioreactor' favoring pesticide biodegradation could represent an interesting tool to protect water resources in the vineyard area.

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Pesticide monitoring in Finnish surface waters 2007-2011

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Pesticide occurrence in Finnish surface waters have been studied in a few screening studies (Oct 1975, 1985-87, 1991-92, 2004-6) before the continuing monitoring started in 2007. In addition to the results of screening, a reason for monitoring was the obligations of Water Framework Directive.

Annually around 85 (+10 parallel) water samples have been taken from rivers and tributaries. In 2009 a lake was also sampled. In the first year, water samples were taken monthly all year round. Because pesticides were not found during winter months, sampling was decided to focus to the period from May to September. Since 2008 samples have been collected twice a month in most of the sites. The concentrations of over 150 compounds in water samples have been analyzed using liquid and gas chromatography methods. In addition to these multi-residue methods, compound specific analyses for glyphosate, tribenuron methyl and ethylethiourea were carried out for certain samples.

By May 2011, 58 compounds have been detected in water samples. The most frequently found compounds have been widely used phenoxy herbicides: MCPA being detected in over half of the samples. Concentrations have mainly been low and so far only three compounds have caused concern. Because of single high concentrations of alfa-endosulfan (0.07 µg/L) and hexazinone (0.52 µg/L) calculated mean concentrations exceeded environmental quality standard (EQS) of endosulfan in Porvoonjoki and predicted no effect concentration of hexazinone in Kokemäenjoki. The use of endosulfan and hexazinon has been banned years ago. The concentration of diuron, which has never been accepted for agricultural use in Finland, has increased since 2007 in Vantaanjoki. In 2010 the mean concentration was 0.18 µg/L (EQS 0.20 µg/L). Diuron is currently used e.g. as paint additives and plastic stabilizers. The source of diuron to Vantaanjoki has been investigated in 2010 and 2011.

The current monitoring has been financed by the Ministry of Agriculture and Forestry and organised (statutory) by Finnish Environment Institute. The local authorities have collected samples and collaborating laboratory has analyzed pesticide concentrations. In future, monitoring may undergo changes due to the new (2011) national action plan related to sustainable pesticide use (see 2009/128/EC).

Trends of pesticides in Norwegian streams and rivers 1995-2010

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Pesticides in Norwegian streams and rivers have been monitored since 1995 through JOVA - the Norwegian Agricultural Environmental Monitoring Program. During these years the regulatory authorities have implemented measures to minimize the risk for pesticides entering the water bodies.

Streams and rivers in selected agricultural drainage basins in intensively cropped areas have been sampled (volume proportional mixed samples and/or point samples) through the period without soil frost and analysed for pesticide residues. Trend analyses of the monitoring data have been done to establish whether there have been reductions in the retrieval of pesticides. The indicators used include: (1) Frequency of pesticides detection, (2) Sum concentration of all individual pesticides in each sample, (3) Environmental risk by weighing the concentration of each pesticide against the environmental maximum residue limits (MRL). Monitoring results and trend analyses for the time period 1995-2010 will be presented at the conference.

Preliminary interpretations of the results indicate that developments in streams and rivers show both positive and negative trends regarding the different parameters studied. Through the monitoring period there have been shifts in the trends in some of the drainage basins, from an initial positive trend to a slightly negative trend. None of the study areas do however show an increase in pesticide loads to rivers and streams, which is good considering the increase in number of pesticides analysed for and the reduction in detection levels. In total, the monitoring results indicate reduced pesticide loads, but variations in climatic conditions govern the use and retrieval of pesticides.

Proposed methodology for listing problematic plant protection products in surface water, causal analysis and emission reduction integrated in registration holders ' Product Stewardship' and the authorisation procedure in the Netherlands.

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To meet the requirements of the European Water Framework Directive (WFD), exceedances of environmental quality standards (EQS) for plant protection products (PPP) in surface water, need to be reduced.

A procedure is being developed for the feedback of monitoring results to registration holders and the Dutch board of authorisation of plant protection products. At the moment, this procedure is tested with the stakeholders involved. It consists of three main steps: 1) identification and ranking of problematic substances, 2) analysis of plausible causes, 3) and feedback to the authorisation of plant protection products and finally the setup of an emission reduction plan.

Substances exceeding the EQS in so called WFD water bodies are extracted from the Dutch Pesticides' Atlas, in which monitoring data of PPP in surface water are processed. WFD priority substances are ranked highest. The other substances are ranked, based on type of water body, number and percentage of locations with exceedance and degree of exceedance.

Next, for a number of problematic substances, a causal analysis is requested. The goal of the causal analysis, is to reveal plausible relations between specific applications and emission routes for a PPP. It combines the use of 'standard' national information sources like national PPP use questionnaires, substance information from the authorisation dossier, the Dutch Environmental Risk Indicator and Pesticides' Atlas on the one hand, with the consultation of a wide range of experts and collection of more specific (e.g. regional) information on the other hand. The outcome of the causal analysis is used by the authorisation holder(s) to set up a substance specific emission reduction plan. An emission reduction plan consists of guidance for a sustainable use of the PPP and/or restrictions in the authorised uses. The proposed methodology describes that each year a causal analysis and emission reduction plan will be initiated for a number of EQS exceeding substances, as part of the dossier requirements for (re-)authorisation.

Building risk indicators of surface water contamination by pesticides at the small catchment scale. Taking into account spatial and temporal dimensions. Support for risk assessment and management: MIRIPHYQUE project.

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In order to reach the "good status" requested by the European Water Framework, it seems necessary to develop tools making it possible to link agricultural practices (including pesticides uses) on a catchment and water contamination or biological status at its outlet. In this context, several teams joined to propose a project whose main objective is to design a method in order to assess the potential of surface water contamination by pesticides at the small catchment scale. The originality of this project is to aim at developing a method allowing taking into account spatial distribution of plots and processes, as well as processes temporal dynamics, without being as complex as a full physically based model. The final "indicator" will result in concentration-duration-frequency curves, useful to assess pesticides impact on biological organisms. The strong point is to aggregate at the catchment scale results coming from pesticides behaviour mathematical simulations at the plot scale. The project is structured in three interconnected axes: 1/ modelling at the different relevant scales ; 2/ organizing simulated time series in spatio-temporal data warehouses (see companion paper by Miralles et al) ; 3/ aggregating the modelling results –in a way which allows to represent water main trajectories on the catchment- , implementing a sensitivity analysis of the global approach and comparing the results with existing data (chemical and biological).

The method will be developed on two small experimental catchments, where large data set are available (Brittany in the west of France, and Beaujolais vineyard, near Lyon). This will allow assessing the ability of the developed tool to represent inter-annual contamination variations in two contrasted agro-pedo-climatical contexts. The sensitivity analysis will give insights into the possibility to transpose this method to various contexts.

This method will make it possible to assess ex ante the contamination and risk reduction that can be expected after a management plan has been implemented on a catchment, as well as to improve a priori risk assessment before a new molecule is introduced on the market.

EIS pesticide: an innovative Environmental Information System to calculate agro-environmental indicators.

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The European Parliament recently approved a new EU pesticides legislation. Member States must adopt National Action Plans for reducing the "risks and impacts" of pesticide use and take measures to protect the water resources. The French program "Ecophyto 2018" targets a 50% reduction in pesticides use. The funding available for these mitigation measures have to be used in the most cost-effective way. As the characteristics of agricultural production differ across a catchment, policy instruments can lead to various results in terms of environmental effectiveness and implementation costs. Therefore defining policy priorities requires appropriate tools with results about ecological and social features of agricultural practices. The evaluation "ex-ante" of scenarios using agro-environmental indicators (AEI) and/or agro-hydrological models needs to implement an effective information system, able to take into account the characteristics of the ecosystem and of agricultural activities at embedded spatial scales. The "trans-time-plot" scale, a homogeneous part of watershed for agricultural practices through the time, is used for the calculation of indicators for small agricultural catchments. At a larger watershed scale, other spatially designed entities are used regarding typologies of farming systems and natural conditions, or areas of mitigation measures.

The produced data model allows describing in the same database the agricultural practices at these embedded scales as well as a range of data relating to river basin characteristics. The agricultural practices (crop rotation, crop management, irrigation, fertilization, pesticides use) are described at the farm level for homogeneous plots or from a typology of farming systems built using surveys and institutional data. A dictionary gives detailed information about all the concepts used. The EIS system generated automatically from the business models offers tools for analysis. It has been tested with a data set collected on the Charente watershed and its sub-basins. Several axes of analyses have been defined (time, amount of pesticides sprayed, spatial aggregation). The tools implemented allow new possibilities for the analysis of data and the calculation of spatial indicators (AEI). The EIS system allows calculating a simple indicator of pesticide pressure. It is expected to implement the calculation of an institutional indicator at two embedded spatial scales.

EIS Pesticides: An information system for data and knowledge capitalization and analysis

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Within the framework of the French governmental plan Ecophyto 2018 whose objective is to reduce by 50% the use of pesticides in France, if possible, several teams of Cemagref have been carrying out researches dealing with pesticides: evaluation ex-ante of change in agricultural practices, sprayers and green equipments, pesticides behavior in the environment and their impact on applicators health and ecosystems, etc. All these teams produce knowledge and data related to pesticides in different formats and supports which are, then, are very difficult to share and analysis in a comprehensive approach.

In order to improve the capitalization as well as the organization of knowledge and data, the Cemagref project entitled Environmental Information System for Pesticides was conceived 3 years ago.

In this project, computer scientists of Cemagref worked in very strong synergy with the thematic teams involved into the project (hydrologists, agronomists, etc.). The thematic scientists objectives were to produce knowledge as well as designing methods, indicators and mathematical models to improve the diagnosis and quantification of pesticide transfer and to better evaluate associated impacts on the aquatic ecosystems. The computer scientists' objectives were to structure the knowledge produced by conceiving an information system improving the access to professional knowledge relative to pesticides in order to facilitate their later re-analysis.

Computer scientists implemented new methods and new tools in order to capture the thematic knowledge and mobilized the most recent research works in data-processing architecture to structure data.

Relating to the technical choices, Unified Modeling Language (UML) was used to capitalize the thematic knowledge and to formalize the concepts relative to the field of activity of each research team. The produced information models made it possible to generate automatically the databases. The data warehouse principles were applied to separate the primary data obtained by field measurements or surveys, from the indicators calculated from the former. To do this, the computer scientists had to define new methodologies in order to model and to implement the databases and the data warehouses.

Pesticide drift impact at the level of a watershed : a geo-referenced approach

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Pesticide drift impact is usually analysed at the level of the sprayed plot. Nevertheless, when considering environmental impacts, one should consider the cumulative effects, both on space and time, of the spraying of the plots of a given watershed. This study aims at providing such cumulative results, to evaluate if measured concentrations could result from drift during applications and to evaluate the potential of some mitigation measures.

The selected watershed is the Gibault-Delisle (19 km²), located in the South-West region of the St Lawrence river, in Quebec (Canada). It is mainly occupied by horticultural crops. To reach our objectives, a geo-referenced approach was proposed. Plots and streams of the watershed were digitized and their geometrical features measured on maps and, for some of them, on fields. Where crops on the plots were unknown, Landsat 5 Thematic Mapper-7 bands images were analysed through supervised classification methods. Spraying operations were known for some crops (onions, potatoes). Output flowrate and wind data were available and statistics could be extracted. Drift was then simulated for each plot of the watershed and concentrations in streams were computed at the level of the plot. Then chemical transport in streams was computed giving chronologies of concentrations.

The simulation of conditions registered during 2007 show that concentrations in water are of the same order of magnitude than measurements so drift could be a main contributor to river contamination. . Improving sprayer setup to limit drift decreases concentrations by a factor of 10 while implementing systematic 5m buffer zones yielded a 30% reduction. . Monte-Carlo simulations based on a probabilistic description of the input factors of the model was performed for a sensitivity analysis and showed that the river flowrate is the main factor influencing the results.

A web-based risk assessment platform to reduce water contamination by pesticides in catchments in France and across the EU

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FOOTWAYS Pro is an online platform for pesticide risk assessment and management connecting a web portal with a high-performance computing cluster fully dedicated to pesticide fate modelling. MACRO and PRZM results are newly and specifically generated in each assessment ("modelling on demand"), which ensures high flexibility in model input and parameterisation.

A FOOTWAYS Pro assessment consists of three major steps: 1. Assessment setup by the user through the web portal, 2. Modelling activities on the cluster; 3. Visualisation of outputs on the web portal (maps, CDFs, individual time series, and the new water quality management indicators PITSA). On the web input interface, the user can choose between a number of pesticide application programmes with different levels of plant protection intensity and different combinations of applied products, or define new programmes. With the results provided on the web output interface, the user can i) compare the environmental performance of the various programmes for a given crop, ii) compare the risks to ground- and surface water between crops, iii) identify problematic areas and iv) explore the effect of mitigation measures.

A real-world application of FOOTWAYS Pro has been recently implemented in France for the Fosse de Melun basin (800 km²), an area under intensive agricultural use which is also a major drinking water source. Local input data were used to set up the agro-environmental scenarios for the study area. Roughly 10000 MACRO 5.2 and PRZM simulations each were performed, postprocessed and aggregated to different levels and output types.

The results of the Fosse de Melun study show that a reduction of pesticide use (in terms of the treatment frequency index TFI) does not necessarily lead to a reduction of pesticide inputs into water resources and the associated impacts. It is therefore vital to integrate pesticide fate and transport in the elaboration of new "low-use" pesticide application programmes. The Fosse de Melun study has a pilot character for the implementation of the Sustainable Use Directive, the ÉCOPHYTO 2018 action plan in France and the WFD. The methodology employed by Footways and the PITSA indicators are generic and can be applied throughout the EU.

Mitigation of Plant Protection Products losses to surface water from agricultural uses

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As the main user of Plant Protection Products (PPP), agriculture is in the main focus to mitigate losses of PPP to water. Although recent studies have suggested that other use areas like urban uses, turf and amenity and emissions from greenhouses may add a relatively higher amount of PPP losses to water compared to the rather lower volumes used in these areas. In about 75 % of the currently evaluated EU-River Basin Management Plans, PPP emissions from agriculture are mentioned as an issue. These plans do not very consistently distinguish between the two main emission routes point and diffuse sources. Point sources originate mainly from handling of PPP on the farm (e.g. filling, cleaning sprayers), diffuse sources are directly related to the application in the field (e.g. run off, drift). A clear distinction and a common understanding on the significance of these emission routes are necessary, because it has direct implications on the mitigation measures. Perception studies with stakeholders and farmers showed that the perceived significance of entry routes and the reality often do not match. Problems and their solutions only exist in the minds of people and the first mitigation measure is to create a common understanding on the risks and their significance. Point sources have long been underestimated and the different diffuse sources were not discussed according to their significance (Bach et.al. 2001). Best Management Practices (BMP) recommendations to mitigate point source pollution can be addressed in a general way to each user of PPP. Respective recommendations to mitigate diffuse sources are more complex and specific to a catchment or a field. Factors like weather conditions cannot be directly controlled but may have a significant impact on diffuse losses

BMP recommendations are a widely accepted approach to advice and educate operators and advisors on the correct use of PPP. Surveys in the TOPPS project indicated that BMPs on water protection are not everywhere available across EU. An important aspect is to have consistent and implementable measures and BMPs across the EU in order to have a good acceptance and implementation by the operators and the advisers. Beside the aspect of informing and educating operators on the correct use of PPP also further risk mitigation measures provided through optimized spray equipment and infrastructure need to be evaluated and recommended. An innovative and efficient risk mitigation concept able to largely reduce PPP losses to water needs to focus on the PPP user, the equipment and appropriate infrastructure in a catchment.

Efficiency of two constructed wetlands (in- and off-stream) to mitigate pesticide contamination in drained agricultural watershed.

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In agricultural landscapes, pesticides can be transported by surface or tile-drained waters to aquatic ecosystems. To dampen pesticide transfer fluxes, vegetative filter strips have been widely implemented. However, in sub-surface tile-drained watersheds, vegetative buffer strips are short-circuited leading to a drastic reduction of their efficiencies. In such situations, constructed wetlands, directly connected to drainage pipe outlets, are suitable and efficient pesticide pollution remediation tools. Constructed wetland implementation and design largely depend on land availability which is particularly critical in Europe where land is scarce. Consequently, off- and in-stream configurations have been developed to collect and treat either a portion (off-stream, in parallel), or all water volumes (in-stream, in a series) generated by a watershed. Other design features also impact constructed wetland efficiency like wetland surface area, water storage capacity, vegetation density, hydraulic berms, dry-out/fill-in alternations...

Two field experiments were carried out in France to compare pesticide dissipation efficiency of two kinds of constructed wetlands located at the outlet of subsurface tile-drained catchments. The two agricultural catchments were cultivated for similar crops (winter wheat, barley, rape or winter wheat, carrot, sugar beet) on waterlogged tile-drained soils.

The Aulnoy constructed wetland was situated in-stream whereas the Bray wetland was constructed off-stream, in parallel to the main agricultural ditch.

Inlet and outlet discharges and pesticide concentrations were continuously monitored and helped characterize pesticide exportation seasonality and constructed wetland efficiency.

Both constructed wetlands showed positive impacts on water quality despite being attributable to distinct governing dissipation processes. In the Aulnoy in-stream wetland, outlet pesticide concentrations were frequently below analytical limits of quantifications. It results that dilution effects hid possible degradation or retention processes but led to improved water quality. Conversely, the Bray constructed wetland appeared to enhance pesticide adsorption, desorption and degradation. It was observed that efficiency was related to pesticide properties. Indeed, strongly sorbing molecules, and those presenting the lowest applied doses in the catchment, were associated with the highest removal rates. In the Bray configuration, despite only a portion of outlet volumes crossed the wetland, 35 % of pesticide masses at the catchment outlet was eliminated.

Assessing and reducing environmental risks linked with the use of pesticides: a French research program to support public decision.

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Using pesticides has enabled a significant rise of production during the past years. However, their dispersion in the environment and their ecological impacts are now current issues. In France, this has led to the Environment Round Table (Grenelle de l'Environnement) and the Ecophyto 2018 plan, aiming to reduce the nationwide use of pesticides by 50% until 2018. In this context, developing researches on the assessment of pesticide-related risks and on the development of systems allowing to reduce the use of pesticides is of major interest.

As early as 1999, anticipating these issues, the French Ministry for Ecology, sustainable Development, Transports and Housing set up the research program "Assessing and reducing risks linked with the use of pesticides", aiming to promote research on this subject so as to support decision-making. Key issues are defined following environment managers' and public decision makers' needs while the scientific excellence is guaranteed by an independent Scientific Council.

The research program first focused on acquiring knowledge on the fate and the environmental effects of pesticides. Then the necessity of understanding and influencing current agricultural practices and their social and economic determinants have additionally been taken into account. A particular attention is paid to the dissemination of results towards stakeholders.

This communication aims to give an overview of the program, its aims and its functioning. Some major results and productions on the fate of pesticides in the environment, on monitoring tools, on risk assessment and on new approaches to reduce pesticide use will be highlighted. Reflections about research needs related to risks related to the use of pesticides will be presented.

Evaluation of pesticide accumulation in biofilm: method development and accumulation kinetics

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The contamination of aquatic systems by pesticides in agricultural watersheds can directly or indirectly impact the structure and functioning of algal and microbial communities. In small rivers, these microorganisms are organised in biofilm that can be considered as an indicator of ecosystem impairments. The correct assessment of exposure to pesticides involves the implementation of their quantification in the biofilm. We have then developed and validated an analytical method for the extraction and determination by LC-MS-MS of 15 pesticides in the biofilm. In a second step a laboratory experiment was conducted to evaluate the accumulation kinetics of pesticides in the biofilm. To better understand the response to such an exposure, a measure of the effects associated was established.

The analytical development was performed by means of experimental design. This methodology allowed to identify main factors affecting performances of the method, then to efficiently optimize analytical recoveries. Pesticides were extracted from dried biofilm with acetone under pressurized liquid extraction (ASE® 200, Dionex), followed by purification on solid-phase extraction (Chromabond HRX®, 3mL, 200mg, Macherey Nagel). The organic extract was then analyzed by ESI(+)-LC-MS-MS. Method performances have been characterized according to the French standards NF T90-210 (2009) and XP T90-220 (2003). Quantification limits varied between 15 and 100 ng/g dry weight for 12 of the 15 pesticides. Recoveries ranged from 52 to 120% and uncertainties from 10 to 35%.

Accumulation kinetics in biofilm were evaluated under controlled hydrodynamic conditions. The biofilm developed in the laboratory on glass cylinders was put in contact with water contaminated with pesticides and was collected after different contact times (0-24 hours). Diuron, azoxystrobin, dimetomorph and tebuconazole were adsorbed after 15 minutes only. Moreover, it may be noted that the accumulation of pesticides on the biofilm is in relation with their hydrophobicity, except for diuron. We observe that norflurazon has not been quantified in the biofilm, indicating that it was probably not accumulated, these results are consistent with the photosynthetic activity. Indeed, whatever the duration of exposure to this herbicide, no inhibition of the activity measured is observed. In contrast, exposure to diuron causes a fall of 40% of photosynthetic activity in less than 2 hours.

Drift mitigation techniques for surface water protection: another French paradox ?

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Since the publication of the French Arretee 2006, Sept 12th , surface water is to be protected from aerial drift issued from spraying applications. Among practical measures, crop free buffer zones including vegetation strips were created along permanent and non permanent water courses (including ditches); spraying operation traceability was mandatory and drift mitigation techniques were to be implemented when chemicals spray free buzzer zone equals 20 to 50 m. When these 3 conditions are satisfied, the spray free buffer zone of chemicals can be reduced to 5 m.

The accreditation of drift mitigation techniques is then subjected to a minimum reduction of drift values of 66 % compared to a reference's spraying technique (drift mitigation ratio of 3 at 5 m and beyond). Cemagref testing hall - ReducPol - located in Montpellier, was in charge of the accreditation scheme, through wind tunnel measurements. One hundred references of nozzles (used for field crop sprayers) are accredited.

The situation nowadays faces new scientific challenges as spraying practices are evolving (e.g. increasing forward speed, boom height & flow pressure) and potentially lead to increase in drift. On the other hand, drift mitigation techniques are accredited when a threshold of 66 % drift reduction is achieved but the effective drift reduction ratio is not taken into account. The combination of those two aspects induces a paradoxical situation.

This paper first introduces examples of drift values based on field tests as well as wind tunnel measurements with an emphasis to the impact of new spraying practices. Second, a focus on real drift mitigation performances of accredited nozzles is presented.

The discussion focuses on environmental impact of pesticides application techniques that induces new technical but also political issues regarding the present regulation scheme.

Pesticide atomization: Modelling and experimental approaches

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Limiting losses of plant protection products during their application depends in particular on droplet size and velocity at nozzle exit. Small droplets lead to an optimal coverage but may contribute to drift contaminating air, water and soils. Large droplets are less prone to drift but may stream down. The droplets having a significant kinetic energy will tend to rebound off the leaves. However, the size and the velocity of the droplets depend mainly on the nozzle itself and injection characteristics.

In this study, an Eulerian model is developed to model a liquid sheet atomization. The model calculates the flow inside and outside a hollow cone nozzle in order to estimate droplet size and velocity close to the nozzle exit (up to 5 cm from the exit). The model considers a single phase of liquid-gas mixture to represent the turbulent mixing of the liquid sheet with the ambient air. As the flow is highly swirled and highly anisotropic, the Reynolds stress model is used for turbulence. The turbulent flux of liquid mass fraction is modelled taking into account density variation effect. The mean liquid-gas interface density balance equation is solved to get the Sauter Mean Diameter of droplets. One term appearing in this equation involves surface tension coefficient. Surfactant influence can therefore be taken into account in the model.

Experimental data have been carried out using Phase Doppler Anemometry. Atomization characteristics such as the axial velocity and droplet Sauter Mean Diameter are compared to modelling results. Agreement between predictions and measurements is reasonably good. The modelling approach is a cost-effective way to get spray characteristics and study factor influence.

Combined effects of surfactants and nozzle types on hollow cone sprays

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Transfers of plant protection products (PPP) in air, water and soils depend partially on physical characteristics of product droplets. Slow and/or small droplets may be more prone to spray drift, whereas droplets with high kinetic energy may rebound off the leaves and fall off. In orchards and vineyards, hollow cone nozzles are usually used. Most of the time, water-soluble pesticides contain surfactants, either formulated into the original concentrate or added later by the operator. Surfactants are used to minimize emissions of PPP during and after application.

This study aims at investigating coupling between hollow cone nozzles and surfactants. Three surfactants (Break Thru, Elton and Heliosol) added to water were evaluated for their spray performance through two different nozzles: a classical hollow cone nozzle and an air-induced hollow cone nozzle. Droplet diameter and velocity have been measured by Phase Doppler Particle Anemometry. Radial profiles of mean diameter and mean velocity have been carried out at 5 and 10 cm from the nozzle exit. For each nozzle, surfactants added to water sprays were compared to water spray. Spray angle values and droplet proportion in number in several points have also been compared for different surfactants solutions and both nozzles.

Results have shown that effect of each surfactant addition depends on the nozzle type. For instance, using the classical hollow cone nozzle, spray angle of Elton and Heliosol solutions was reduced compared to water spray angle. On the contrary, using the air-induced hollow cone nozzle, spray angle was unchanged by any surfactant. Moreover, Break-Thru surfactant did not play a role compared with water when sprayed through the classical nozzle; however Break-Thru led to the more pronounced increased of sheet droplet mean diameter (around 30%) compared to water, when sprayed through the air induced nozzle. Spray characteristics are influenced by surfactant addition. Therefore, evaluate nozzle drift potential with water could appear inadequate.

Simulation of aerial exposition of pesticides in a vine crop watershed

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During crop spraying, sensible amounts of pesticide are emitted to the air and then transported within the atmospheric boundary layer on rather large distances. Some measurements evidenced air contamination nearby sprayed plots but such measurements cannot be used to compute population exposition because there are too much molecules to analyse and no sampling method is currently available. Such exposition is suspected to be rather important in the vine crops area, where large amounts of pesticides are used and spraying machines involve air assistance which facilitates pesticide departure to the air. This study aims at simulating pesticide transport from sprayed crops in a watershed where all spraying operations were registered into a database during two years (2007 and 2008) and to analyse the influence of the main variables.

The database was built during the European Life project "Aware" (<http://www.lifeaware.org/>). Registered data included wind conditions and the database was analysed to define several "standard" spraying conditions in the area. Simulations used the DriftX software developed by Montpellier University and Cemagref. This software computes pesticide emission from a sprayed plot and gaussian dispersion considering wind velocity field.

When reproducing standard conditions, it is shown that the population of the nearby village is exposed in 20% of the cases. These results can be used to define acceptable conditions for spraying in the area. Simulations were also used to show the points of major concentrations and identify the points where measurements should be done either to validate the simulation results or for a supervising approach.

How embedded NICT tools can help to improve treatment quality and reduce the amount of pesticide used.

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This study aims to provide the results of LIFE AWARE & TICSAD projects and to show how embedded NICT tools can help to improve quality treatments of vine and reduce the environmental impact. We will discuss how the data measured during application allow to detect sprayer's and farmer's work dysfunctions and to find the ways to correct positively the methods.

The main objective of these projects is to enable farmers to completely control every day the operations and their working tools. It is undeniable that the quality of application of the products is undoubtedly the first means with which the wine grower can reduce the use of pesticides. A good adjustment of the sprayer makes it possible to limit losses in air and in soil, drifts and avoid the over and under proportioning.

Embedded NICT tools gives operators the means to control pesticides application and to reduce significantly soil and air losses thereby to mitigate surface and groundwater pollution and atmospheric contamination. The objective to reduce the amount of pesticides used can be achieved in a short time frame, without compromising the quality of the protection necessary to achieve high yields and good quality products.

The information recorded are the GPS sprayer's positioning, left and right flow rates, volume of mixture tank residues and weather conditions (temperature, hygrometry, wind speed and direction). The Information related the each plot is extracted from each treatment event using a Geographical Information System (GIS). Cross-referenced analysis of the data is performed to derive essential criteria to assist decision-making.

The farmer can check and correct sprayer parameters daily. Geo-referenced inter-plot traceability of treatments provides an objective assessment of application quality, which allows the winegrower analyzing and the correction of operations. The embedded NICT tools enable the automatic generation of reliable data, automatic feedback on current practices and real traceability on spraying and pesticide product usage. Analyse of these data, which involves the different stakeholders, enables detection of malfunctions and provides mean to improve equipments and practices. The most important hydraulic parameters involved in sprayer functioning can be visualized and, if needed, easily corrected.



EurAqua is the European Network of Freshwater Research Organisations. The aim of EurAqua is to contribute substantially to the development of European freshwater science and its dissemination on a European scale, thus having a significant input on the development of the scientific basis of European water management. is to contribute substantially to the development of European freshwater science and its dissemination on a European scale, thus having a significant input on the development of the scientific basis of European water management.

More at <http://www.euraqua.org/2.4a4d22a41128e56161b800011923.html>



PEER is a partnership of seven of the largest European environmental centres founded in 2001 with the aim of combining forces to follow a joint strategy in environmental sciences and to enhance research on ecological sustainability. PEER member centres carry out basic and applied research combining different disciplines from natural and social sciences. Research covers all fields of the environment, particularly addressing the interaction between man and nature.

More at <http://www.peer.eu/index.php>

PEER and EurAqua have several fields of interest in common. There also are close institutional links between the two networks: five of the seven PEER members are also member of EurAqua.

PEER and EurAqua decided in 2009 to intensify their collaboration in order to further benefit from the potential synergies and complementarities. This is essential especially for the relations with the European Commission, DG Research, DG Environment, JRC, EEA and other international bodies in the field of Environment.

This conference was implemented in application of the collaboration agreement signed between EurAqua and PEER in 2009.