WP1: Innovative methodologies for measuring fluxes of agricultural chemicals in the subsurface

In the last five decades, there has been a huge population growth which reflected in an exponential demand in food consumption. The demand for higher productivity rates was satisfied by an extensive use of phosphorus and nitrogen fertilisers, which subsequently led to an extensive contamination of the aquifers. The impact of agricultural sources carrying excess phosphorus and nitrogen that ends up in the surface water still remains obscure even after implementation of strict regulations codifying fertilizer inputs to control the “surface” runoff. Therefore, focus is now slowly drifting towards exploration of the “sub-surface” pathways. Apart from run-off, excessive fertilizer input can also result in soil leaching causing percolation of phosphorus and nitrogen from soil into groundwater.

Currently, optimization of resource usage and its sustainable management is of utmost importance. Hence, monitoring of water quality is very important,since it can provide information on the status of the aquifers and prevent or address more effectively possible contamination phenomena. The subsurface of our Earth acts as a sink for all the materials used on its surface during human and natural activities, including the fertilizers and pesticides consumed for agricultural purposes. There is evidence showing that the groundwater is highly susceptible to pollutants. Contamination at the subsurface level is much more challenging than surface level due to its difficult to getting detected, the slow movement and its physical constraints.

However, technological advancements in the environmental sector have recently enabled monitoring of nutrient contamination using various old and new sampling techniques. Work Package 1 focuses on groundwater monitoring using both passive sampling and continuous sampling techniques by introducing two different research projects dealing with phosphorus and nitrogen contamination in the subsurface.

ESR 2 Priyanka Banerjee: Quantifying the phosphorus flux leaching from field to groundwater and surface water using innovative techniques

In past, phosphorus was envisaged to be “immobile” in groundwater, but with time, the soil-groundwater-surface water linkage has started getting more evident. Only recently P leaching started being recognized as a dominant P loss pathway (Heathwaite et al., 2005; van der Salm et al., 2011), but this field needs more scientific attention and development. Studies mostly have focused on P mobility and behaviour in soil and surface water, but not on the P transport via leaching from soil via groundwater to surface water. This is because groundwater lacks proper characterization of its solute contaminants (like nitrogen, P, Volatile Organic Contaminants). This knowledge gap can be attributed to three main factors: (1) “hidden” quotient of groundwater that makes monitoring its contamination still a big challenge, (2) complex chemistry of phosphorus at soil-water interface, (3) methods used for flux calculations. Hence, proper characterisation and quantification of P fluxes in groundwater is essential to assess its leaching losses via the groundwater pathway.

Erroneous estimation of phosphorus in groundwater arises from simulations based on phosphorus concentration measurements and estimated Darcy water-flux values. Consequently, this research will focus on application of direct flux measurements. The measurement and interpretation of mass fluxes in favour of concentrations is gaining more and more interest, especially within the framework of characterization and management of groundwater contamination (Annable et al., 2005; Basu et al., 2006; Verreydt et al., 2010). Conventional methods of estimating contaminant fluxes involve individual measurements of the contaminant concentrations and calculations of the Darcy water fluxes (Michel, 2013; Verreydt et al., 2010).

Verreydt (2012) points out the three main problems with existing contaminant flux calculations. (1) First, groundwater is sampled from the monitoring wells and then analysed in the lab in terms of concentration of contaminants. Hence, these measurements still needs to be combined with groundwater water flux estimations (back calculated) in order to finally calculate the contaminant mass flux and mass discharge. This makes contaminant flux calculations with this method very highly uncertain. (2) Secondly, a huge problem is that the concentration measurements don’t take into account the variations in groundwater flow and contaminant concentrations as they are “snapshot” measurements. (3) Soil heterogeneities exist which is why the correlation between concentration measurements and water flux is very difficult to make. All of this explains the existence of huge uncertainties in flux calculations used for current groundwater remediation measures resulting in failures.

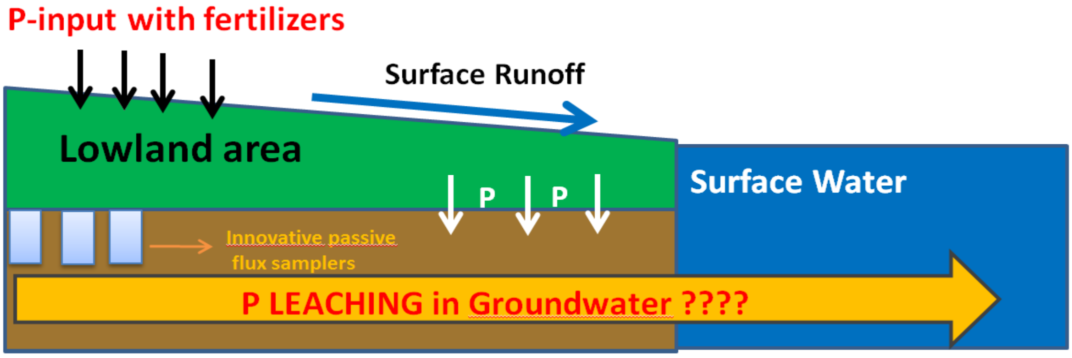

Figure 1: Passive flux samplers to monitor phosphorus fluxes in groundwater

Figure 1 show passive sampling techniques with time-integrated groundwater and solute flux measurements is considered to be an innovative way of measuring contaminant fluxes. The passive flux samplers are in-situ devices consisting of permeable cartridges filled with parameter selective sorbents and resident tracers for groundwater flux calculations. When placed in a monitoring well, the samplers intercept the groundwater flow by calculating time-averaged data which is used for both phosphorus and groundwater flux calculations. The residence time of these samplers depend on expected phosphorus concentrations and the groundwater velocity.

In this PhD study, ESR1 attempts to set up a methodological framework to predict the impact and efficiency of innovative passive sampling techniques and to evaluate the efficiency of each of them against other passive samplers in different field conditions (low P, high P, high iron, low iron).

ESR 2, Polyxeni Damala, Geolys SPRL: Development of a sensor for monitoring nitrate in groundwater

Nitrate is a ubiquitous pollutant of surface water and groundwater. It originates from several sources, which might be either the result of human intervention or not. Among them, agriculture plays a major role in nitrate contamination, owing to the extensive use of fertilizers which are applied for the increase of crop productivity. When the nutrients originating from the nitrogen fertilizers are not taken up by the plants, they end up in the groundwater, enriching the subsurface with considerable amounts of nitrate.

Increased levels of nitrate lead to the nutrient enrichment of water bodies and the potential spreading of algal blooms. An important concern related to the algal growth is the depletion of the oxygen levels in the water bodies. This depletion is attributed to the activity of bacteria, which use the oxygen in order to decompose the algae when they die. The resulting oxygen deficiency affects the rest of the living organisms, which consequently die (Addiscott, 2005).

Following the nitrate levels in the subsurface is essential for preserving our water resources. The main objective of this research project is to develop a method for the continuous and in-situ monitoring of nitrate in water, overcoming the limitations of the current sensors that prevent their use in specific applications. The idea behind this project lies on the use of specific compounds which are able to reversibly trap the nitrate ions found in water. These nitrate-selective compounds will be incorporated into suitable matrices which can then be used either for optical or electrochemical sensing of nitrate. Testing different experimental conditions, types of matrices, sensing mechanisms and other auxiliary compounds that are necessary for the enhancement of the sensor response, are among the different steps that will be implemented. Since the focus is shifted on groundwater nitrate contamination, different ions which are commonly found in the subsurface might interfere on the sensor response. Hence, examining the influence of those ions on the performance of the sensor will be another important aspect of this study.

For this project, both theoretical and experimental (laboratory-based) work is under progress. The output of this research aims not only to overcome the limitations of the existing real-time sensors, but also to demonstrate a new method for monitoring nitrate and other ions of interest found in the water. In addition to this, the measurement of nitrate fluxes will also be feasible through the combination of the nitrate concentration data obtained by the sensor with the groundwater fluxes. For this purpose, a method that can be used to monitor the variations of groundwater fluxes has already been developed and tested by the Hydrogeology and Environmental Geology group of Liège University (Brouyère, 2008).

References:

Addiscott, T. M. (2005) Nitrate, agriculture and the environment. CABI Publishing. Oxfordshire, UK

Annable, M.D., Hatfield, K., Cho, J., Klammler, H. , Parker, B.L., Cherry, J.A. and Rao, P.S.C. (2005). Field-scale evaluation of the passive flux meter for simultaneous measurement of groundwater and contaminant fluxes. *Environmental Science and Technology*, 39, 7194–7201

Basu, N.B., Rao, P.S.C., Poyer, I.C., Annable, M.D. and Hatfield. K. (2006). Flux-based assessment at a manufacturing site contaminated with trichloroethylene. *Journal of Contaminant Hydrology*, 86, 105-127

Brouyère S. (2008) A new tracer technique for monitoring groundwater fluxes: The Finite Volume Point Dilution Method. *J. of Cont. Hydrol.*, 95 (3-4), 121-140

Heathwaite, A. L., Dils, R. M., Liu, S., Carvalho, L., Brazier, R. E., Pope, L., Hughes, M., Phillips, G. and May, L. (2005). A tiered risk-based approach for predicting diffuse and point source phosphorus losses in agricultural areas. *Science of the total environment*, 344, 225-239

Michel J. (2013). Groundwater quality measurement with passive samplers – Code of best practices. *Citychlor project*, 65 pages

van der Salm, C., Dupas, R., Grant, R., Heckrath, G., Iversen, B. V., Kronvang, B., Levi, C., Rubaek, G. H. and Schoumans, O. F. (2011). Predicting Phosphorus Losses with the PLEASE Model on a Local Scale in Denmark and the Netherlands. *Journal of Environmental Quality*, 40, 1617-1626

Verreydt G., Bronders J., Van Keer van I., Diels, D. and Vanderauwera P. (2010). Passive Samplers for Monitoring VOCs in Groundwater and the Prospects Related to Mass Flux Measurements. *Ground Water Monitoring and Remediation*, 30(2), 114-126

Verreydt G. (2012). New approaches of groundwater management using contaminant mass flux measurement. *PhD dissertation*, University of Antwerp, 147 pages