



Diffuse pollution (pesticides and nitrate) at catchment scale on two contrasted sites: mass balances and characterization of the temporal variability of groundwater quality.

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Enhanced monitoring of groundwater quality over several years has revealed a nitrate and /or pesticide contamination of aquifers in North America and Europe (Gilliom et al., 2006; Ifen, 2004). In many countries (France, United Kingdom, Denmark, Switzerland), drinking water is partly or dominantly supplied by groundwater. Assessing the extent of nitrate or pesticide contamination in aquifer and understanding the transport of the solutes to groundwater is, therefore, of major importance for the management of groundwater resources. Besides, the objective set by the European Water Framework Directive (WFD - 2000/60/EC, OJEC 2000) is for "all groundwater bodies to achieve the good quantitative and chemical status ... at the latest by 2015". The Directive demands that European Union Member States not only characterize their levels of groundwater contamination, but also that they study the evolutionary trends of their pollutant concentrations. Monitoring groundwater quality for nitrate and pesticide is thus particularly relevant as well as the characterization of the transfer of solutes to and in groundwater is essential for effective water resource management.

Several countries have approached the stage of characterization of their groundwater bodies either by using data derived from various measurement networks, as in France or by establishing specific sampling and analysis protocols (NAQUA network in Switzerland; NAWQA network in the United States). Pesticide monitoring networks, where they exist, are often less than 10 years old with a fairly low measurement frequency (1 to 4 analyses per year). Chemical status and trend interpretations are thus difficult and limited. Characterizing an entire groundwater body from observations limited in time and space remains a challenge. Little published data exists concerning intensive monitoring over several years, whether at the catchment outlet or at observation points spread over a basin, that would allow these characterizations.

Notable changes in the use of pesticides generally result from the evolution of regulations. In Europe, the herbicides atrazine and isoproturon have been classified as priority substances (2455/2001/EC, OJEC 2001). The use of atrazine was forbidden in France since September 2003 following restrictions already in force since 1991. In January 2004 the maximum permitted application of isoproturon was reduced from 2500 to 1800 g ha⁻¹.

In France, two contrasted hydrogeological systems located in agricultural contexts were intensively monitored for at least a decade in order to i) characterize the spatial and temporal variability of groundwater contamination by different pesticides with varied physical and chemical characteristics (atrazine, isoproturon and their metabolites and chloroacetanilides used as atrazine substitutes) and nitrate, ii) calculate annual pesticide mass balances for a long period including years with contrasted climatic conditions and to iii) identify the different mechanisms influencing water and solute transfer.

Although both sites (Brévilles and 3 Fontaines) have very different hydrogeological characteristics (4 vs. 50 sq km, sandy vs. chalky saturated zone, non karstic vs. karstic, ...) the monitoring of the major springs representing the outlet of the catchments revealed similarities. For example, atrazine and its metabolite deethylatrazine have been both systematically quantified at the outlet springs despite the stop of atrazine use on the Brévilles and 3 Fontaines catchments since April 1999 and September 2003, respectively. For both sites, the mass balances (comparison of inputs and outfluxes) indicated that only few percents of the applied quantity of atrazine reached

the spring but led to concentrations higher than the allowed limit for drinkable water. At the opposite, isoproturon which is the pesticide applied with the highest quantities for the last decade on both sites, is detected in a very limited number of samples.

The different tools used on these sites complementarily to the monitoring (modelling, isotope and classical geochemistry approaches, dating) enabled a better understanding of the hydrodynamic of the hydrogeological systems and gave explanation on the observed temporal variability of groundwater quality and the time transfer of solutes. These intensive monitoring gave also insight on the representativeness of a sample (location in the catchment, date of sampling, depth of the aquifer sampled, ...). The results of these studies also raise questions on how efficient and how fast will the positive impact of product substitution or environmental regulations be. Taking into consideration these aspects is of primary importance to conform to the requirements of the European Water Framework Directive regarding good status assessment of groundwater bodies.

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