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Improving the knowledge of pesticide and nitrate transfer processes using age-dating tools (CFC, SF_6, ^3H) in a volcanic island (Martinique, French West Indies)

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ABSTRACT

Numerous successful examples of CFC and SF_6 groundwater dating applications were recently published. However the proposed CFC/SF_6 method needs various hydrodynamic parameters that are not always available. In order to predict groundwater-quality trends in areas where the hydrogeological context is poorly known, a dating method using tritium, CFC and SF_6 was successfully implemented in Martinique. Hydrogeological understanding is limited in this volcanic island where groundwater contamination by pesticides and nitrate has been recently proven in various areas. A negative correlation was observed between nitrate concentrations and groundwater ages while pesticide contamination showed a more complex schema. Consequently the presence of old groundwater clearly explained the absence or low pesticide and nitrate concentrations in some areas. However a possible degradation of the water quality is to be feared in the future. In view of the relatively long transfer times and the complexity of the remobilization processes of solutes, the expected effects of any modifications in the use of fertilizers, or of changes in pesticide-use legislation, would take a long time to become apparent.

1. Introduction

Enhanced monitoring of groundwater quality over several years has revealed a frequent nitrate and pesticide contamination of aquifers in North America and Europe (Barbash et al., 2001; EEA, 1999; IFEN, 2007), but also in countries less studied until now (Brena et al., 2005; Singh et al., 2005; Tariq et al., 2004; Thapinta and Hudak, 2003). The observed pesticide concentrations are locally greater than the drinking-water limit set in Europe, i.e. 0.1 µg L^{-1} per substance (except aldrin, dieldrin and heptachlor, 0.03 µg L^{-1}) and nitrate concentrations in unconfined aquifers of agricultural areas commonly exceed the international recommendations of 50 mg L^{-1} (Razowska-Jaworek and Sadurski, 2005). In 2004 in France, where drinking-water supply is mainly of aquifer origin, 25% of groundwater monitoring points indicated poor to very poor quality related to pesticides (IFEN, 2007) and 40% of the groundwater bodies is at risk of non-achievement of the acceptable status in 2015 due to pesticide- and nitrate contamination. Groundwater-quality monitoring for nitrate and pesticides is thus particularly pertinent. In Martinique, the knowledge of surface and groundwater contamination is limited as monitoring networks are recent; surveying of dissolved major- and trace elements and pesticides in groundwater started only in 2004 with two annual sampling campaigns on a limited numbers of points. However, contamination of some rivers, streams and groundwaters by pesticides is proven, and nitrate concentrations reach the recommended drinking-water limits at some points (Bocquené and Franco, 2005; IFEN, 2007).

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 in 2015". The Directive demands that Member States not only characterize their levels of groundwater contamination,

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but that they also study the evolutionary trends of their pollutant concentrations; they must be in a position to explain possible cases of non-achievement. The Member States have to identify and reverse any significant upward trend in the concentrations of pollutants. Specific measures thus have to be adopted for preventing and controlling groundwater pollution and for its evaluation.

Regarding pesticides, few published data exist concerning the evaluation of a trend based on intensive long-term monitoring and only a few studies have been published in which hydrogeological and hydrodynamic contexts have been taken into account (Lapworth and Gooddy, 2006). Taking hydrodynamics into consideration is, however, crucial to allow a correct interpretation of time-series. Using water age—also referred to as residence time—is one possible way to approach the hydrodynamics of systems. Water age determined from tritium concentrations allows to show spatial and temporal trends of pesticide- or nitrate concentrations in groundwater at both aquifer scale (Baran et al., 2007; Einsiedl and Mayer, 2006; MacDonald et al., 2003; Trojan et al., 2003) and regional scale (Kolpin et al., 2004; Mills et al., 2005).

The man-made atmospheric trace gases sulphur hexafluoride (SF_6) and chlorofluorocarbons (CFCs) constitute a more recently applied tool for dating young waters (up to 50 years old). The number of publications using this technique, mainly for the characterization of water-flow pathways in a restricted area, is increasing. However, few studies concern the relation between contamination due to diffuse pollution and the age of water (Ayraud et al., 2006; Tesoriero et al., 2007) and usually are related to a single aquifer system. Moreover, though numerous successful examples of CFC applications are published, CFC dating is quite complicated, notably due to gases comportment in the unsaturated zone, local contamination (Höhener et al., 2003; Oster et al., 1996), degradation processes under anoxic environment (Hinsby et al., 2007; Sebol et al., 2007) and the need for additional parameters such as the estimation of excess air which can be based on the N_2/Ar ratio or the determination of different noble gases (Aeschbach-Hertig et al., 2000; Beyerle et al., 1999; Gooddy et al., 2006; Heaton and Vogel, 1981).

The aims of our study were: to i) improve the knowledge of groundwater contamination by nitrate and pesticides at the scale of the island of Martinique, including different geological settings and land uses; ii) test the reliability of SF_6 and CFCs in a large-scale volcanic and tropical context and using limited available data and information; iii) link contamination and water age to obtain a better understanding of pollutant-transfer processes and to predict the probable evolution of groundwater quality with respect to diffuse agricultural pollution.

2. Materials and methods

2.1. Study area and hydrogeological context

Martinique, a tropical island bordered by the Atlantic Ocean and the Caribbean Sea, is one of the French overseas Departments (61° W, 14°40 N). Its surface area is about 1100 sq km, the coast being less than 12 km in any spot. The north side of the island is mountainous (maximum elevation 1397 m) and wet (annual precipitation from 3000 to 5000 mm), whereas the south side is lower (maximum elevation 500 m) and dryer (annual precipitation from 1000 to 1500 mm). The geological setting corresponds to volcanic formations including lavas (basalt, andesite and dacite), pyroclastites, hyaloclastites, conglomerates and lahar deposits. The conceptual hydrogeological model is not yet entirely understood, due to the complexity of the geological structure, the few boreholes and wells, and a general lack of local hydrogeological studies even if some areas are hydrogeologically well known thanks to recent drinking-water investigations.

In the absence of detailed studies and following Vittecoq et al. (2007), our study assumed the hydrogeological catchments to be equivalent to the topographic limits.

Water samples were taken from three springs and 16 pumping- and observation wells distributed throughout the island and corresponding to different hydrogeological settings. These sampling points correspond to the groundwater-quality monitoring points defining the monitoring network installed in the island (Fig. 1), following the recommendations of the Water Framework Directive (Vittecoq, 2006).

2.2. Sampling procedure and analytical methods

Sampling took place between 17 and 26 April 2007 during the dry season. The boreholes were sampled after pumping at least three purge volumes and the stabilization of the chemical groundwater parameters, such as pH and conductivity.

Samples for pesticide analysis were collected in 1 L precombusted brown-glass containers (except for glyphosate for which polyethylene bottles were used), kept on ice in coolers for transport to the laboratory and then stored at 4 °C until analysis. Analyses of 120 molecules were performed by liquid- or gas chromatography (GC/MS Saturn Varian®, GC/ECD Varian®, HPLC/UV-Varian®/MS with positive ACPI-Thermofinnigan®, HPLC/UV-Varian®/MS with negative ESI-Thermofinnigan®, HPLC/Fluo-Varian®) after liquid–liquid extractions (with dichloromethane or hexane) or extraction on solid cartridges (Oasis, Waters®) at neutral or acid pH. Pesticide quantification limits were at the most 0.1 $\mu g\ L^{-1}$ except for four molecules ($<0.2\ \mu g\ L^{-1}$) and thiabendazol ($0.7\ \mu g\ L^{-1}$ — Table 1).

Samples for chemical analysis were kept in polyethylene bottles after acidification with nitric acid for cation determinations. Anion analyses were done by ion chromatography (model DX120, Dionex®), cations by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; Ultima 2 model, Jobin Yvon®). The accuracy of both techniques is around 5–10% according to the concentration. Results on chemical data collected in April 2007 are discussed elsewhere (Brenot et al., 2008).

Samples for tritium activity measurements were collected in 1 L polyethylene bottles. Analyses were done by enriched liquid scintillation counting (AGH University of Science and Technology, Krakow, Poland). The detection limit is 1 TU (Tritium Unit with 1 TU equal to 1 tritium atom in 10^{18} hydrogen atoms) with an accuracy of 0.4 TU.

Samples for CFC and SF_6 were collected in 500 mL glass bottles. To avoid any air contamination, each bottle was kept in a water-filled metallic box. A simplified sample collection method described in IAEA (2006) was applied. The analyses were performed by gas chromatography with an electron-capture detector after pre-concentration using a purge-and-trap technique (Spurenstofflabor Oster, Wachenheim, Germany). The detection limit is close to 10^{-4} pmol, allowing the measurement