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Experimental and numerical study of the relation between flow paths and fate of a pesticide in a riparian wetland

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SUMMARY

A field-scale pulse-injection experiment with the herbicide Isoproturon was conducted in a Danish riparian wetland. A non-reactive tracer (bromide) experiment was also carried out to characterize the physical transport system. Groundwater flow and reactive transport modelling was used to simulate flow paths, residence times, as well as bromide and Isoproturon distributions. The wetland can be characterized by two distinct riparian flow paths; one flow path discharges 2/3 of the incoming groundwater directly to the free water surface of the wetland near the foot of the hillslope with an average residence time of 205 days, and another flow path diffusively discharging the remaining 1/3 of the incoming groundwater to the stream with an average residence time of 425 days. The reactive transport simulations reveal that Isoproturon is retarded by a factor of 2–4, which is explained by the high organic content in the peat layer of the wetland. Isoproturon was found to be aerobically degraded with a half-life in the order of 12–80 days. Based on the quantification of flow paths, residence times and half-lives it is estimated that about 2/3 of the injected Isoproturon is removed in the wetland. Thus, close to 1/3 may find its way to the stream through overland flow. It is also possible that high concentrations of metabolites will reach the stream.

Introduction

Riparian wetlands are important buffer zones between groundwater and surface water as they often have a high potential for attenuating and even removing environmental pollutants. Wetlands intercept groundwater from upland areas. Removal of for example agricultural pollutants requires that there is a sufficient residence time for a reaction to complete within the wetland. Many studies have shown the importance of wetlands in removing nitrate (Brüsch and Nilsson, 1993; Blicher-Mathiesen and Hoffmann, 1999; Kehew et al., 1998; Vidon and Hill, 2004; Hoffmann et al., 2006), while there seems to have been no field-scale investigations of the fate of the pesticide Isoproturon in natural riparian wetlands. However, many studies have studied the fate of pesticides in constructed wetlands (e.g. Gregoire et al., 2009). The potential for pesticide mineralization has been demonstrated in the laboratory using sediment cores from natural wetlands. For example, Anderson et al. (2002) found that wetland sediments could remove 70–80% of Atrazine within one month. Larsen et al. (2001) showed that redox conditions and type of herbicide determined the degradability in cores from a Danish wetland. In situ removal of pesticides in natural wetlands can therefore be expected. Lorah and Olsen (1999) did find that wetlands can remove organic chemicals. In this case, the anaerobic conditions in the wetland favoured degradation of chlorinated organic compounds.

Riparian wetlands can therefore be considered as reaction compartments and their hydraulic characteristics need to be assessed along with the system's ability to remove pollutants. An increased understanding from field observations is needed in order to effectively manage, construct or restore wetlands. For example, a national scale programme in Denmark attempts to restore wetlands with the specific purpose of reducing nitrogen load to surface water bodies (Hoffmann and Baattrup-Pedersen, 2007). A good knowledge of the controlling factors is needed to efficiently implement such plans. A recent study by Dahl et al. (2007) proposed a groundwater–surface water interaction typology (GSI typology), which, as a hydrogeological conceptual model, can be applied on local scale to characterize flow paths and their respective attenuation capacities of e.g. agrochemicals through riparian areas. Dahl et al. (2007) defined four flow paths (riparian flow path types); diffuse flow through the riparian area with a long contact time and a

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large attenuation capacity, overland flow and drain flow with short or no contact time with riparian sediments, respectively, and therefore medium to small reaction capacity, and finally direct flow through the stream bottom from an aquifer below the stream with short or no-flow through the riparian aquifer and a corresponding small attenuation capacity. It is primarily the permeability contrast between the riparian aquifer and the contributing groundwater aquifer, and secondarily the hydrogeological setting, that determine the dominant flow path of a riparian area. Vidon and Hill (2004) developed a conceptual model that linked landscape hydrogeological characteristics to efficiency of riparian zones in removing nitrate. Generally, it is recognized that riparian zones or wetlands are so-called biogeochemical hot spots, where the geomorphologic setting, hydrology and redox chemistry determine how effective a wetland is as a reaction compartment (Mitchell and Branfireun, 2005).

Typologies and conceptual models need to be backed up by quantitative field studies of the flow and fate of pollutants in wetlands. Specifically, it is of interest to compare flow paths and associated residence times with rates of degradation, because overall this will determine the efficiency of a wetland in removing pollutants. Preferably, well-controlled field-scale tests designed specifically for this purpose should be carried out. In the past there have been some field studies on non-reactive transport of solutes. Knight et al. (1972) added tritiated water to five plots in a wetland and traced the plumes for 54 weeks. They found that drainage of the wetland explained the vertical movement, and differences in hydraulic gradients and peat hydraulic characteristics explained differences in lateral movement. Baird and Gaffney (2000) hydraulically isolated approximately 10 m^2 (8 m by 1.2 m) of a wetland and performed a tracer test using bromide. The tracer was monitored for about 6 days in a number of wells. Breakthrough curve analysis revealed that flow was more rapid than predicted from Darcy's law using slug-test hydraulic conductivity values determined at the site. They explained this as bypassing flow due to plot-scale heterogeneity. Such transport processes are of interest when dealing with reactions since the time allowed for reaction is greatly reduced in case of flow bypassing the matrix. Hoag and Price (1995) also found that the physical structure of the peat in a wetland controlled transport. They injected chloride and followed the tracer for 30 days over a distance of 70 m. Transport of chloride was primarily restricted to the upper part of the wetland because the hydraulic conductivity decreased vertically by six orders of magnitude over a little more than one meter. They found that the asymmetrical shape of the breakthrough curve could be explained by attenuation due to dual-porosity phenomena, where the solute diffuses into more stagnant zones of the peat. Parsons et al. (2004) investigated the flow behaviour beneath a small seasonal prairie wetland in Canada. These wetlands recharge the underlying aquifer during a short time period each year. During this time they mixed bromide into the standing surface water and, subsequently, traced the movement of the tracer beneath the small pond during wet and dry conditions. Furthermore, they sampled vegetation to measure bromide uptake. They found that a piston-type flow model could adequately describe the bulk infiltration, but also that preferential movement took place as some bromide was found at much greater depths than could be explained by the piston flow model. Tracer tests have been carried out in wetland systems in order to understand transport processes using natural tracers (Ronkanen and Kløve, 2007). Hunt et al. (1996) used stable isotopes and temperature to study flow of groundwater into natural sedge meadow and riparian and constructed wetlands. They found that the flow rates estimated from these two tracers gave higher values than using Darcy's law. A groundwater flow model indicated that use of Darcy's law resulted in too low values, caused by difficulties in accurately measuring hydraulic conductivities in a heterogeneous wetland system. This is definitely a major difficulty in assessing flow through wetlands. Application of Darcy's law is easy if reliable hydraulic parameters are available. Therefore, much research in the past has looked for field methods estimating hydraulic parameters (Surridge et al., 2005; Hogan et al., 2006; Quinton et al., 2008) or laboratory methods using undisturbed cores (Hoag and Price, 1997; Beckwith et al., 2003a,b).

There have been few examples of field tests with reactive tracers. One example is provided by Hedin et al. (1998), where biogeochemical processes at the soil–stream interface were studied using controlled experiments. Their site is perhaps not typical for a wetland, but still has some of the same characteristics, at least when it comes to the organic content of the soil and the occurrence of anaerobic conditions favourable for denitrification. They used a bromide tracer to account for dilution, and also injected dissolved organic carbon (DOC), which immediately induced increased rates of nitrate removal. They concluded that the flow paths delivering DOC to the system ultimately controlled denitrification.

Hunt et al. (1996) argued that a multi-tracer approach always is needed because each method of interpretation will be associated with uncertainties. Historically, flow nets and the use of Darcy's law have been applied, but box models and numerical models find more wide-spread use nowadays. Hunt et al. (1996) used a 2D horizontal model to compute water balance and flow rates. They assigned all nodes as specified heads based on an interpolation of observed heads and used the model to compute the flow rates. Reeve et al. (2000) used a 2D cross-sectional (synthetical) model to investigate the effects of regional landscape on vertical flows in peatlands. Beckwith et al. (2003a,b) concluded that geologic heterogeneity, rather than hydraulic conductivity anisotropy had the largest impact on flow patterns in a synthetic model of a wetland. Hoffmann et al. (2006) developed a simple 1D box model, where net removal of nitrate was computed based on information of hydraulic gradients, hydraulic conductivities and nitrate concentrations in the wetland. However, this simple model does not consider specific nitrate removal processes. There exist many models that can simulate the fate of pesticides in aquifers, but to date there appears to be very few model applications simulating the transport and fate of pesticides in natural wetlands.

The main objective of the present study has been to improve our understanding of how wetlands can attenuate pesticides. To our knowledge there have been no controlled field-scale injections of the herbicide Isoproturon studying its movement and degradation in riparian wetlands. We used a pulse-injection experiment to study the fate of Isoproturon (Dahl et al., 2000a,b; Nilsson et al., 2000; Christensen and Jensen, 1999) and subsequently modelled the transport to estimate rate of degradation. The experiment also involved bromide as a non-reactive tracer in order to quantify physical transport mechanisms. The controlled non-reactive/reactive tracer experiment and subsequent modelling allow us to relate Isoproturon degradation to riparian flow path type (Dahl et al., 2007) thus exemplifying the control that the distribution of flow paths and their associated residence times exert on attenuation capacities of riparian areas.

Site description and field installations

The wetland Mølgaarde (UTM32 623212; 550400) at Voldby Stream is located 25 km WNW of the city of Aarhus in Denmark (Fig. 1a). This region of Denmark is covered by clayey tills deposited during the last glacial advance (Weichsel) which ended 10,000 BP (Houmark-Nielsen, 1999). In the late Weichsel deep erosion valleys formed in the till during glacial drainage (Jørgensen