

Models and statistical analysis of organic micropollutants in groundwater-based drinking water resources

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Models and statistical analysis of organic micropollutants in groundwater-based drinking water resources



Flavio Malaguerra

Models and statistical analysis of organic micropollutants in groundwater-based drinking water resources

Flavio Malaguerra

PhD Thesis
September 2011

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Flavio Malaguerra

**Models and statistical analysis of organic micropollutants in
groundwater-based drinking water resources**

PhD Thesis, September 2011

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Preface

The work reported in this PhD thesis, entitled "Models and statistical analysis of organic micropollutants in groundwater-based drinking water resources", was conducted at the Department of Environmental Engineering (Technical University of Denmark), under the supervision of Professor Philip Binning and Professor Hans-Jørgen Albrechtsen. The PhD project ran from June 2008 to June 2011 and was funded by the Technical University of Denmark, Copenhagen Energi and the Danish Agency for Science Technology and Innovation funded project *RiskPoint - Assessing the risks posed by point source contamination to groundwater and surface water resources*. The study included an external stay of one month at the Leibniz-Institute of freshwater ecology and inland fisheries in October 2010.

The PhD thesis consists of a synopsis and 3 papers prepared for scientific journals. In the synopsis, the papers are referred to by roman numbers:

- I.** Malaguerra, F., Chambon, J. C., Bjerg, P. L., Scheutz, C. and Binning P. J. Development and sensitivity analysis of a fully-kinetic model of sequential reductive dechlorination in groundwater, submitted to *Environmental Science & Technology*.
- II.** Malaguerra, F., Albrechtsen, H-J. and Binning P. J. Contamination of drinking water supply wells by pesticides from surface water resources, submitted to *Journal of Hydrology*.
- III.** Malaguerra, F., Albrechtsen, H-J., Thorling, L. and Binning P. J. Pesticides in water supply wells in Zealand, Denmark: a statistical analysis, submitted to *Science of the Total Environment*.

The papers are not included in this www-version, but can be obtained from the Library at DTU Environment

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Bertrand Russel wrote once that *the good life is one inspired by love and guided by knowledge*. Many are the people who inspired me: my friends, scattered around the world, my family, which always believed in me and *mon Amour* to who I owe almost everything. I'm also sincerely grateful to the persons that guided me in the last three years: my supervisors, my co-authors and all my colleagues.

Thank you all of you for making my life a good life!

Flavio Malaguerra
June 2011

Summary

The access to safe drinking water is essential for the well being of the population. The spread of micropollutant contamination jeopardise many freshwater reservoirs, and is a serious threat for human health, especially because of its long-term effects. To asses the threat of contamination, models are required to study the main contamination pathways, and to make predictions of pollution fluxes. Groundwater is used as drinking water in many countries because subsurface processes can mitigate pollution and purify the water by removing xenobiotic compounds. However, groundwater often interacts with surface water, which is more vulnerable to contamination, and can transfer pollution to groundwater.

The fate of micropollutants in aquifers is influenced by many factors: sorption, degradation and dilution are processes that can interact together and create very complex systems, which are difficult to model. The identification of dominant processes is an essential step in the understanding of system behaviour, because it enables the development of simplified models that can approximate the fate of contaminants with the best trade-off between model complexity and reliability of results. In this thesis, global sensitivity analysis techniques are used to assess detailed models in order to identify the main processes involved in the degradation of chlorinated solvents in the subsurface, and in the transport of pesticides from surface water into nearby wells in confined aquifers. Statistical techniques are also employed to identify large-scale contamination processes by examining observations of contamination in drinking water wells in Zealand, Denmark.

Results show that persistent compounds in surface water can leach into nearby pumping wells even if an impermeable clay layer overlies the well screen. Thus aquitards may not provide adequate protection against contamination by micropollutants in surface water, as generally thought. Results also show that the fermentation of organic compounds and the sulphate concentration in groundwater govern the success of sequential reductive dechlorination in aquifers, and that the simulation of chlorinated aliphatic hydrocarbon degradation cannot be approximated by simple models without losing the ability to simulate important system behaviour. The statistical analysis of contaminant concentrations in Danish drinking water wells demonstrates that drinking water well contamination by BAM, a pesticide metabolite, is mainly a problem in urban areas, and that in Zealand, wells close to surface water are generally more vulnerable to pesticide contamination.

Dansk sammenfatning

Adgang til sikkert drikkevand er essentielt for befolkningens sundhed. Spredning af organiske forureninger truer mange ferskvandsreservoir og udgør en alvorlig helbredstrussel, ikke mindst på grund af deres langtidseffekter. For at imødegå sådanne trusler er der behov for at udvikle modeller til at studere de væsentligste forureningsveje og til at beregne forureningsbelastningen. I mange lande benyttes grundvand til drikkevand, da en række processer under grundvandsdannelsen kan reducere forureningen og rense vandet ved at fjerne de organiske forureninger. Overfladevand forurenes derimod lettere og i det omfang der er kontakt mellem overfladevand og grundvand, kan dette føre til grundvandsforurening.

Skæbnen af de organiske forureninger i grundvandsmagasiner er påvirket af mange faktorer: sorption, nedbrydning og fortynding er variable processer, der kan påvirke hinanden og skabe et meget komplekst system, som er vanskeligt at modellere. Således er identifikation af de dominerende processer et centralt trin i forståelsen af systemets opførsel, da det muliggør udvikling af forsimplede modeller, som kan estimere de organiske forurenings opførsel med den bedste balance mellem modellens kompleksitet og resultaternes pålidelighed. I dette PhD-arbejde er detaljerede modeller koblet med "global sensitivity analysis"-teknikker for at identificere hovedprocesserne i nedbrydning af klorerede opløsningsmidler i undergrunden og i transport af pesticider fra overfladevand til nærliggende borer i grundvandsmagasiner under lerlag. Ved at undersøge data over forureninger i drikkevandsboringer på Sjælland med statistiske teknikker blev der identificeret stor-skala forureningsprocesser.

Disse analyser viste, at svært nedbrydelige forureninger i overfladevand kan trænge ned til nærtliggende produktionsboringer - selv om de er dækket med lerlag. På denne måde ser det ud til, at vandstandsende lag ikke, som hidtil antaget, altid yder tilstrækkelig beskyttelse mod forurening med organiske stoffer. Etablering af sekventiel reduktiv deklorering er styret af fermentering af organiske stoffer og sulfatkoncentrationen i grundvandet, og simulering af nedbrydning af klorerede alifater er meget vanskelig at beskrive med simple modeller uden at miste evnen til at simulere systemets opførsel. Statistiske analyser af forureningen af danske drikkevandsboringer viste, at koncentrationen af BAM, et pesticidnedbrydningsprodukt, navnlig er et problem i bymæssige områder og at på Sjælland er borer tæt på overfladevand generelt mere følsomme over for pesticid forurening.

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1 Introduction

In the past, mankind has been plagued by countless epidemics of water-transmitted diseases caused by the failure of water treatment systems. Even today, pathogenic contamination of drinking water still poses the most significant health risk to humans. About one fifth of human population does not have access to safe water, and pathogens in water still cause more than 2 millions deaths every year in the poorest parts of the World (WHO, 2011).

In developed countries, microbiological contamination of drinking water is still sporadically encountered (Furtado et al., 1998; Szewzyk et al., 2000; Lahti, 1995), but the major threat to drinking water safety is now contamination by micropollutants (Schwarzenbach et al., 2006) such as: pesticides, pharmaceuticals, detergents, hormones, petrochemicals and industrial solvents (Schipper et al., 2008; Kolpin et al., 2002; Doong and Lin, 2004; Rivett et al., 1990). Some of these substances are known to be carcinogenic, teratogenic or behave as endocrine disruptors, and many of them provoke adverse effects to humans even at very low concentrations (ng/L) (Cantor, 1997; Leeuwen, 2000; Kilburn, 2002; Westerhoff et al., 2005).

To protect consumers against these threats, many countries have enacted laws and promoted monitoring campaigns to ensure that micropollutant concentrations in drinking water remain below safety thresholds (e.g. European Union directive 98/83/EC (EC, 1998)). Over the last few decades, it has become evident that investing and legislating for the protection of water bodies against pollution is more effective than complex treatment of water sources after pollution had occurred (Chave, 2001). With this in mind the European Union has introduced the EU Water Framework Directive (EC, 2000), which requires governments to conduct comprehensive risk management, from the water source to the end of the water pipe.

In order to assess the risk of contamination of drinking water resources, models must be developed to predict pollution fluxes into water bodies and contaminant concentrations in drinking water. But modelling the fate of micropollutants in the environment is challenging, since natural systems are usually too complex to be effectively described by mathematical equations. Moreover, the description of the processes affecting contaminant fate requires competences in various scientific disciplines (hydrogeology, chemistry, microbiology), which are sometimes difficult to unify. An effective way to deal with such a high level of complexity is to develop

models at different scales, and identify dominant processes at several levels that can be coupled to provide comprehensive models.

Degradation of organic pollutants in groundwater is often studied at the small scale because is dominated by microbiological processes occurring in the pore space of sediments (Thullner et al., 2005). Detailed models simulating the degradation of pesticides (Sniegowski et al., 2009; Wilde et al., 2009), chlorinated solvents (Becker, 2006; Duhamel and Edwards, 2007; Kouznetsova et al., 2010) and other organic compounds (Watson et al., 2003; Rolle et al., 2008) exist, but they are usually very complex, attempting to describe the many biogeochemical interactions (Matott and Rabideau, 2008). These models therefore require simplification (Hunter et al., 1998; Hu and Huang, 2002).

Scaling is a major issue in model construction. Sources of contamination and drinking water wells are often separated by distances ranging from few meters to kilometres (Bauer et al., 2004; Trolborg et al., 2008; Kohfahl et al., 2009), and therefore transport models of contaminants in aquifers have to be considered at these scales. However, the simulation of mechanisms leading to contaminant attenuation (e.g. sorption, degradation, mixing) can be computationally prohibitive (Robinson et al., 2000). So, the dominant processes must be identified and incorporated in simpler models, which run faster and are easier to calibrate.

Upscaling of transport models to predict contamination at large scale (>10 km) is often not feasible because of computational limitations and aquifer heterogeneities (Quinlan et al., 1996; Robinson et al., 2000). Deterministic models can therefore not be used, and different tools are required to simulate dominant processes at the large-scale. A statistical analysis of contaminant observations can reveal relationships between measurable parameters (e.g. aquifer characteristics (Worrall and Kolpin, 2004; Rowe et al., 2007), contaminant properties (Worrall and Thomsen, 2004), agriculture types (Nolan et al., 2002; Shomar et al., 2006)) and pollutant concentrations in drinking water wells, and provide insights on the mechanisms of contamination.

Mathematical procedures such as Global Sensitivity Analysis and regression analysis, can identify dominant processes in complex deterministic models (Saltelli et al., 2000; Campolongo et al., 2007) or in extensive observation datasets (Kleinbaum and Klein, 2010; Weisberg, 2005), and can provide new insight on process understanding (Kitano, 2002).

Although these techniques have been used in many scientific disciplines (Fieberg and Jenkins, 2005; Chu et al., 2007; Kontoravdi et al., 2008), they are usually not employed in models simulating micropollutant transport and degradation in groundwater, which are often limited to model calibration to laboratory or field observations.

1.1 Objectives

The aim of this PhD study is to develop models to describe the processes leading to the contamination of drinking water wells, and to identify dominant processes of micropollutant contamination at different scales using sensitivity analysis techniques and statistical analysis. The goal is to improve the understanding of contamination pathways of selected compounds and to provide guidance on how to limit the contamination of drinking water wells. Specific objectives have been:

- Understand how the success of chlorinated solvent degradation is linked to the biogeochemical processes in groundwater (e.g. redox zonation).
- Evaluate the possibility of simplification of a complex model of chlorinated aliphatic hydrocarbon degradation using Global Sensitivity Analysis.
- Identify the geological conditions and drinking water well characteristics which can lead to micropollutant leaching from surface water to groundwater, thereby jeopardizing drinking water quality.
- Identify large-scale contamination patterns of drinking water wells by pesticides on the Zealand island, Denmark, and suggest processes responsible for contaminant spread.
- Provide probabilistic estimates of drinking water well contamination by pesticides in the Zealand island, Denmark, and propose possible explanations of contamination mechanisms.

The thesis develops models and applies statistical analysis at several scales to identify the dominant processes affecting micropollutant contamination of drinking water supplies. Paper **I** deals with microbial processes involved in reductive dechlorination of chlorinated solvents occurring at the pore scale (<1 cm), Paper **II** considers interactions between surface water and groundwater at the field scale (0.5-2 km), and Paper **III** study contamination of drinking water wells by pesticides at the regional scale (>10 km).

1.2 Contaminant considered

The study focuses on contamination by pesticides and chlorinated solvents, since they are the most frequent cause of groundwater pollution in developed countries (Pankow and Cherry, 1995; Gilliom et al., 1999) and because of their ubiquity, mobility and toxicity (Abelson, 1990; Arias-Estevez et al., 2008).

Pesticides are chemical products that are applied to kill a more or less broad spectrum of organisms. Herbicides, which aim to control weeds growth, are the most common pesticides in several countries (EUROSTAT, 2007). Herbicides are mainly used in agriculture, but are also employed for domestic purposes and to manage recreational areas (golf courses, parks, sports fields, etc.) (Grube et al., 2011).

Unlike pesticides, chlorinated solvents are used in industry and not purposefully released into the environment. Tetrachloroethene (PCE) and trichloroethene (TCE) are the most important chlorinated solvents being extensively used since the 1950s as solvents in dry cleaning facilities and as degreasing agents in industry (Pankow and Cherry, 1995; Jackson, 2004). These compounds occur in groundwater due to leakage from underground storage tanks (Häggblom and Bossert, 2004). Chlorinated solvents are denser than water, and so they can easily reach the deepest parts of the aquifers and jeopardize drinking water safety.

1.3 Structure of the thesis

The structure of the thesis is as follows. Chapter 2 focuses on the pathways of drinking water well contamination and provides an overview of the processes affecting pollutants transport and degradation. Chapter 3 presents the methods used to identify dominant processes affecting drinking water contamination, and the techniques used to i) model the fate of contaminants in aquifers, ii) investigate model behaviour using Global Sensitivity Analysis, and iii) determine contamination trends using statistical tools. Chapter 4 concludes the thesis and discuss further research needs.

2 Pathways of contamination

The major pathways of contamination of drinking water wells are shown in Figure 2.1. When the source of contamination is limited to a small area (e.g. landfills, machine shops, dry cleaning facilities, etc.), then it is defined as a point source. In this case the contamination appears as a plume of high contaminant concentration, which can pass through the unsaturated zone and reach the water table (Christensen et al., 2001). Depending on the local hydrogeological settings, the plume can travel in groundwater and eventually contaminate a drinking well (Figure 2.1-A) (Trolborg et al., 2010), or a surface water body (Figure 2.1-B) (Conant et al., 2004).

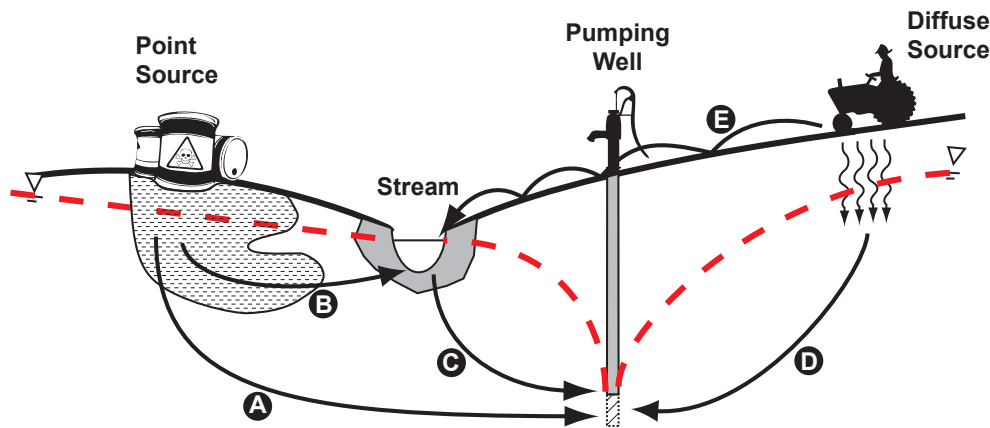


Figure 2.1: Pathways of drinking water well contamination: (A) transport from point source to DWW, (B) transport from point source to surface water, (C) infiltration from surface water and leaching into DWW, (D) transport from diffuse source to DWW, and (E) transport from diffuse source to surface water via water runoff.

Pesticides, are purposefully released on the soil surface over large areas. Degradation processes can occur in the topsoil due to the presence of oxygen and intense microbial activity (Rodriguez-Cruz et al., 2006). However, some pesticides can leach into groundwater (Figure 2.1-D) (Flury, 1996) or can be directly transported to the closest surface water body by surface runoff during precipitation events (Figure 2.1-E) (Kreuger, 1998). Drinking water wells are often placed near surface water, since streams and rivers often overly more permeable sediments and because the water table is close to the surface, and so pumping cost are reduced. However, the lowering of the water table by pumping wells can invert the natural flow from the groundwater to the stream, inducing infiltration of surface water and contaminants to groundwater and consequently to the well (Figure 2.1-C) (Winter et al., 1998).

Point sources, diffuse sources, surface water and drinking water wells are often very close to each other (Figure 2.2). Thus, the pathways in Figure 2.1 can coexist in a small area.

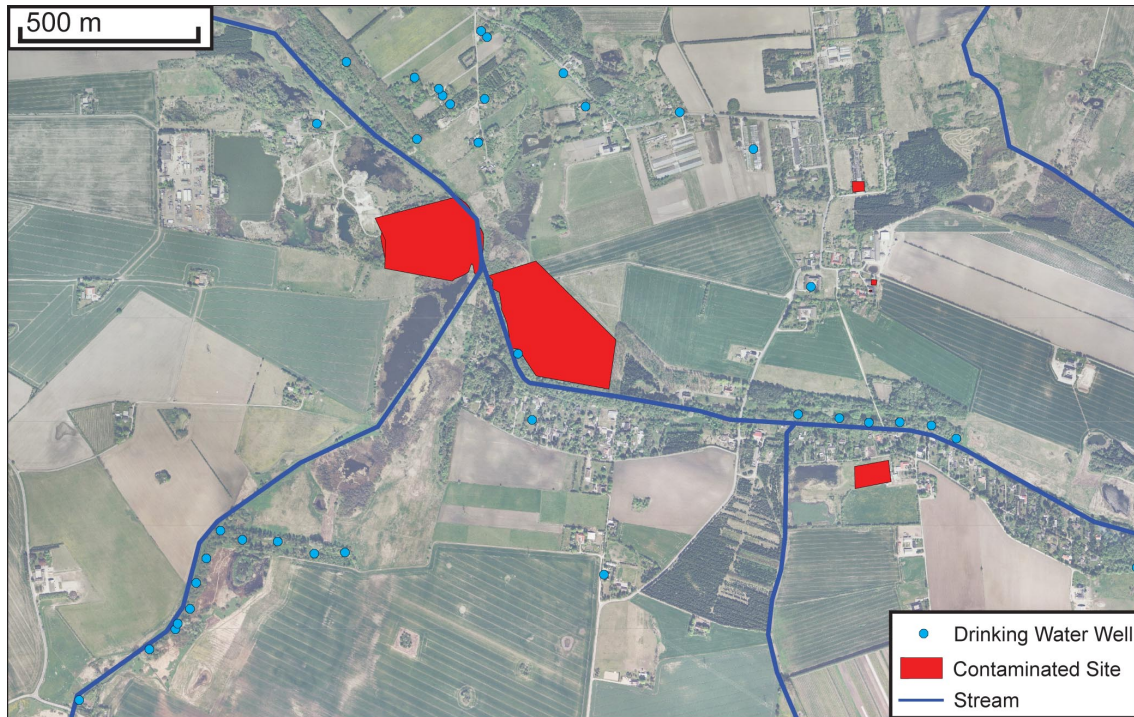


Figure 2.2: Example of the concomitant presence of point sources of pollution (red areas), surface water (dark blue lines), drinking water wells (light blue points) and diffuse sources (the agricultural fields are visible in the aerial photo), in Zeeland, Denmark.

In the next subsection, we will review the processes governing the transport of contaminants i) from the source to surface water, ii) from surface water to nearby drinking water wells, and iii) from the source directly into water wells.

2.1 From contaminant source to surface water

Surface water bodies are linked to groundwater flow systems, and the flux between surface water and groundwater is dominated by the landscape type and the climate. In lowland regions the water flows most often from groundwater to streams (Dahl et al., 2007). Contaminants in groundwater are thereby transported into surface water.

The organic matter content of riparian areas, the zones in proximity of streams and rivers, is often higher than elsewhere, due to the deposition of particulate organic matter during floods (Baker et al., 2000), delivery of carbon by plants roots and litter (Bowden et al., 1993), and deposition of stream algal production (Jones et al., 1995). In addition, the water table is usually close to the surface in these areas, and organic matter mineralization may be slow (Leisman, 1953). Organic matter in riparian zones can be oxidized by several electron acceptors, which can be present in-situ or provided by the groundwater flow, such as oxygen (O_2), nitrate (NO_3^-), ferric iron (Fe(III)), manganic manganese (Mn(IV)), sulfate (SO_4^{2-}) and carbon dioxide (CO_2) (Dahm et al., 1998). Hence, strong redox gradients and intense microbial activity commonly occur at the groundwater-surface water interface.

It is widely recognized that riparian areas can mitigate the release of nitrate and ammonium from groundwater into surface water, because of high denitrification rates and ammonium nitrification during seasonal sediments dry-down (Barling and Moore, 1994). Moreover, the presence of organic matter increases soil sorption capacity for pollutants such as pesticides, soluble metals and phosphorous (Lowrance et al., 1984; Vidon et al., 2010; Krutz et al., 2006). However, riparian zones are physically and chemically heterogeneous (Valett et al., 1997; Doppler et al., 2007; Kalbus et al., 2009; Schornberg et al., 2010). The degradation of contaminants is unevenly distributed at the groundwater-surface water interface due to the variability in redox conditions and spatial heterogeneity of water seepage (Conant et al., 2004).

In rivers and streams, the water flow through bank sediments creates a mixing zone where groundwater is brought in contact with freshly infiltrated surface water. This region of mixing is called the hyporheic zone and hosts intensified biogeochemical activity (Sophocleous, 2002), which creates a barrier against pollution leaching from upper aquifers (Lewandowski et al., 2011).

Although many organic compounds are better mineralized under aerobic conditions (e.g. BTEX (Lu et al., 1999), MTBE (Schmidt et al., 2004), phenols (Broholm and Arvin, 2000), and some pesticides (Larsen and Aamand, 2001)), many highly halogenated molecules need anaerobic conditions to be degraded (Fetzner, 1998), since they are metabolized as electron acceptors (Holliger and Schumacher, 1994). The presence of high level of organic matter is therefore necessary to produce enough molecular hydrogen (H_2) via fermentation, which is subsequently

used by dehalogenating bacteria to break the bond between carbon and the halogen (Wiegel and Wu, 2000; Heimann et al., 2007). Nevertheless, poorly halogenated compounds, which are commonly produced by the degradation of more halogenated compounds, are usually more easily degraded under aerobic conditions (Fetzner, 1998). Thus, the succession of anaerobic and aerobic environments close to surface water can facilitate the complete degradation of halogenated compounds. Vinyl chloride, for instance, is a highly toxic degradation product resulting from the sequential anaerobic dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE), is not very degradable under anaerobic conditions since only few bacterial strains are able to extract the remaining chlorine atom (Holliger et al., 1998), whereas it is quickly oxidized in the presence of oxygen (Tiehm et al., 2008).

Paper I aims to model TCE degradation under the complex geochemical conditions found in riparian areas, where reduced conditions prevail and electron donors are in ready supply. The study employs this complex model to identify the main processes influencing dechlorination of TCE and discuss the possibilities of model simplification.

Another mechanism of surface water contamination is the transport of contaminants by runoff water during precipitation events. Pollutants deposited on the soil surface can be quickly transported into nearby streams by Hortonian flow, thus, contaminants are not infiltrating in subsurface and microbial degradation cannot occur. This process is particularly important for the transport of phosphate (Mc-dowell and Sharpley, 2001) and agrochemicals (Kreuger, 1998), especially those which are highly sorbed and degraded in subsurface (e.g. glyphosate) (Borggaard and Gimsing, 2008).

2.2 From surface water to pumping wells

Water filtration has been known to occur through riverbanks for many years (Eckert and Irmscher, 2006), and artificial recharge of groundwater by surface water is a major part of drinking water production in many countries (e.g. Netherlands, Germany, Hungary, Finland, France and Switzerland (Tufenkji et al., 2002)). In the metropolitan area of Berlin, Germany, approximately 70 % of drinking water is sourced from bank filtrate (Heberer et al., 2004), and interest in riverbank filtration is increasing all over the world because of its ability to provide safe drinking water at a relatively low cost.

Bank filtration can effectively remove pathogens (Havelaar et al., 1995; Dash et al., 2008), nitrate (Grischek, 1998), and attenuate contamination due to pesticides (Verstraeten et al., 2002) and pharmaceutical residues (Greskowiak et al., 2006).

Many processes attenuate contaminant levels when water is transported from surface water to groundwater and drinking water wells. Suspended solids are eliminated by mechanical filtering in the riverbed (Schubert, 2002). Sorption and degradation of contaminants can occur in the hyporheic layer due to the presence of organic deposits, high microbial activity and the constant supply of oxygen from surface water (Tufenkji et al., 2002; Kohfahl et al., 2009). Moreover, sorption and mixing processes taking place in the zone between the surface water bodies and water wells can diminish the impact of surface water contamination on drinking water (Hiscock and Grischek, 2002). The main processes taking place during bank filtration are presented in Figure 2.3.

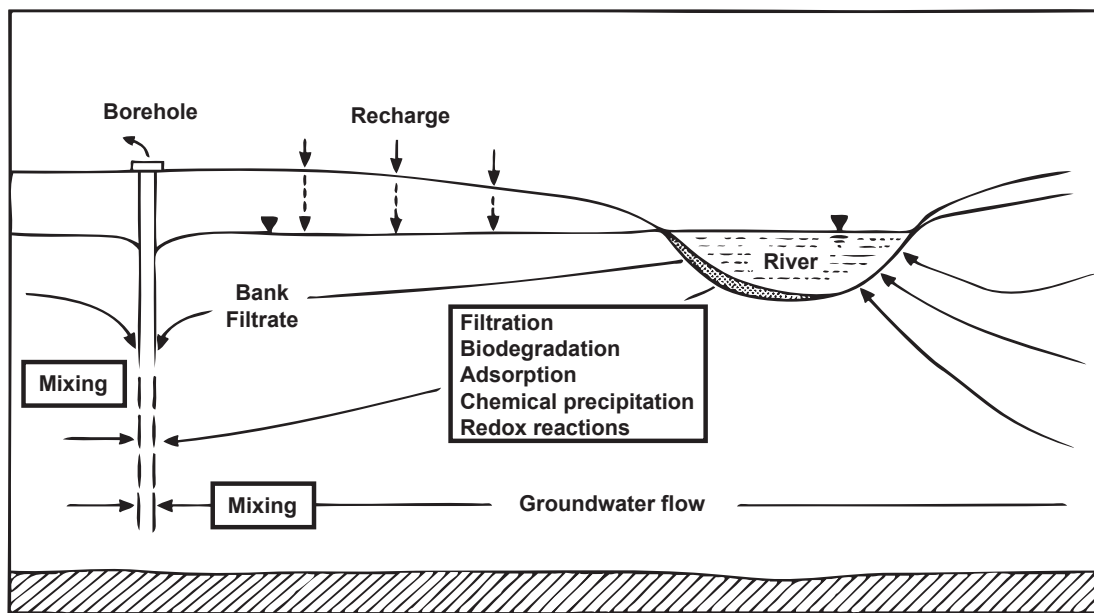


Figure 2.3: Processes acting during bank filtration. Modified from Hiscock and Grischek (2002)

However, contaminant attenuation by bank filtration is not sufficient to ensure safe drinking water if the contaminants are poorly degradable or if the water travel time between surface water bodies and the well is too short (Schwarzenbach et al., 1983; Tufenkji et al., 2002), e.g. during flood events (Mauclaire and Gibert, 1998).

The change in redox conditions induced by surface water infiltration can also negatively impact drinking water quality, for example by increasing hardness and am-

monium concentrations, or by producing smelly sulphurous compounds, and leading to high levels of dissolved iron and manganese (Hiscock and Grischek, 2002; Farnsworth and Hering, 2011). Therefore secondary treatment of abstracted water is sometimes necessary.

Surface water can be a substantial component of the water abstracted from a drinking water well, even when infiltration from surface water resources is unwanted because of its poor quality, or other water resources are available (Hunt et al., 2005). Contamination by polluted surface water has been documented in deep confined aquifers (Borchardt et al., 2007; Hunt et al., 2010), even though they are widely assumed to be a source of safe water due to their disconnection from the surface. Thus, contamination of persistent compounds in surface water can seriously threaten all types of groundwater-based drinking water resources.

These recent findings motivate the investigation of the connection between surface water and drinking water wells in confined aquifers (Paper II). Some pesticides regularly found in surface water are known to be extremely persistent and mobile in groundwater. Therefore, if the bank filtration processes are insufficient to prevent their infiltration into groundwater, and if there is an hydraulic connection between surface water and drinking water wells, then pesticides in surface water can jeopardize drinking water quality even in confined aquifers.

2.3 Direct contamination

In many cases, the groundwater abstracted from drinking water wells has not been in contact with surface water, but is directly infiltrated from precipitation. Thus, contaminants at the surface (spills from underground tanks, leaching landfills, spread of agrochemicals, etc.) can travel through the vadose zone, reach the water table, and subsequently be transported into drinking water wells.

The water travel time between the surface and the well, and therefore the risk of well contamination, is often linked to the depth of the well and the geology. In fact, water in well-confined or deep aquifers is usually safe because it is very old water that has not been contaminated.

However, preferential flow paths caused by fractures in confining layers (Harrison et al., 1992; Ross and Lu, 1999), or hydraulic short-circuits in defective borehole seals (Avci, 1992; Landon et al., 2010), may allow fast contaminant transport from

the surface into drinking water wells. Leaching and infiltration of contaminants is also strongly climate-related, because the climate affects recharge (Giambelluca et al., 1996) and dry climate extremes can lead to cracks and macro fissures which facilitate preferential flow processes (Bergström, 1995).

Contaminants can be degraded as they are transported to drinking water wells (Christensen et al., 1994), but degradation rates in groundwater can be very low due to the lack of electron donors or acceptors (Phelps et al., 1994). The most energetic electron acceptors (O_2 , NO_3) are often depleted in shallow aquifers (Postma and Jakobsen, 1996), while deeper aquifers are often dominated by sulphate reducing or methanogenic conditions (Lovley and Chapelle, 1995). Thus, the energy available for contaminant oxidation is small (Stumm and Morgan, 1996) and pollution degradation rates can be slow (Christensen et al., 2001).

Some strongly sorbed compounds are immobilized in topsoils for a long time (Clausen et al., 2004) and can then pose a threat to groundwater many years after their use. For example BAM, a degradation product of the pesticide dichlobenil: BAM is the most common contaminant of Danish drinking water (Thorling et al., 2010), even though dichlobenil has been banned since 1997.

In Paper **III**, statistical methods are applied to study large-scale patterns of contamination, in order to identify the processes dominating the spread and attenuation of some key contaminants. The study determines whether the contaminants in drinking water wells are due to direct contamination (Figure 2.1-D) or surface water intrusion (Figure 2.1-C).

3 Identification of dominant processes

Numerical modelling is an essential tool for the prediction of contamination spread and for quantifying pollution concentrations in aquifers (Barry et al., 2002). The pathways described in the previous chapter can be modelled in various ways and with different levels of complexity. The aim of this chapter is to provide an overview of the tools that can be used to simulate the fate of contaminants in aquifers, and to provide insights on how to identify the most important processes involved in drinking water well contamination.

3.1 Modelling the fate of contaminants in aquifers

Since contaminants in saturated sediments are transported by water, the first step to predict pollutants migration is to determine the water velocity field. In the presence of a pumping well, the natural flow of water in the aquifer is strongly disturbed, and the complexity of the flow field increases. Moreover, inconstant abstraction rates induce rapid changes of the water velocity field, which represent an additional challenge in groundwater flow modelling. The flow of groundwater in a confined aquifer can be described by the equation:

$$S_s \frac{\partial H}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla H) - W \quad (3.1)$$

Where H is the hydraulic head, S_s is the specific storage (representing the elastic storage of the system), \mathbf{K} is the hydraulic conductivity tensor and W is a term including sinks and sources. Analytical solutions to predict water streamlines and particle pathways in groundwater exists (Bear, 1972), but usually require strong assumptions, which are rarely met in real cases. Numerical solutions based on finite differences (McDonald and Harbaugh, 1988) or finite element schemes (Kolditz et al., 1998) are much more flexible, allow groundwater flow fields to be modelled for any aquifer geometry, and can easily handle spatial heterogeneities of hydraulic conductivity. Nevertheless, the flexibility comes at a computational cost, which can be a barrier when constructing very detailed models.

Solutes in groundwater are transported by advection (movement of the solute along with water), and dispersion (spreading of the solute due to diffusion and hydrodynamic water-soil interactions), and are affected by sorption (chemical interaction with the soil matrix, e.g. adsorption, ion exchange) and degradation.

Mathematically, the transport of an aqueous component is described by the advection-dispersion equation:

$$R \frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v}C) - \nabla \cdot (\mathbf{D} \nabla C) = -\kappa C \quad (3.2)$$

Where \mathbf{v} is the pore water velocity, \mathbf{D} is the dispersion tensor, R is the retardation factor and κ is a term describing the form of the degradation process. The advection-dispersion equation is usually solved using numerical methods and many computer codes have been developed for this purpose (Zheng and Wang, 1999; Kipp, 1997).

Depending on the solute and the sediments matrix, sorption can be described in different ways and the retardation factor R can assume various forms. Linear, Freundlich, Langmuir and Toth isotherms are the most used sorption models (Barry et al., 2002). For the simplest model, the linear isotherm, the retardation factor is given by:

$$R = 1 + \frac{\rho_b}{n} K_d \quad (3.3)$$

Where K_d is the sorption coefficient, ρ_b is the sediments bulk density and n is the soil porosity. Similar relationships can be established for the other isotherms, but it should be noted that the sorption model can affect the performance of the numerical solution (Sheng and Smith, 1999).

Organic chemicals in aqueous systems can be degraded by abiotic or biotic processes. However, biologically mediated transformations are usually several orders of magnitude faster than chemical reactions (Barry et al., 2002). Biogeochemical processes involved in compound degradation (e.g. mineralization) can be modelled either as equilibrium reactions or using kinetic rate laws.

Biodegradation can be modelled as being at equilibrium if changes in solute and bacterial populations are faster than changes due to water flow, or if sources and sinks of the compound occur at stable rates (Postma and Jakobsen, 1996). If a system is at equilibrium, the law of mass action states that the distribution of solutes in water depends on an equilibrium constant, which is linked to the thermodynamics of the reaction considered (Barry et al., 2002). Thus, the solute concentration is obtained by the solution of a system of multiple equilibrium equations which can easily be solved numerically (Parkhurst and Appelo, 1999).

However, many groundwater systems are not at the equilibrium and therefore another modelling approach is needed. Moreover, equilibrium models do not provide information on system dynamics and so degradation times cannot be estimated. Kinetic modelling of organic degradation requires equations describing transformation rates, which reflect the dynamic behaviour of microbial colonies.

If the only factor affecting the biodegradation rate is the concentration of a substrate, then the factor κ in Equation 3.2 is a constant and degradation can be described by a first-order kinetic model. However, it is known that degradation rates are slower for low substrate concentrations, and so Michaelis-Menten models (Michaelis and Menten, 1913), which were developed for the study of enzyme-substrate reactions, are commonly used. In this case, the factor κ in Equation 3.2 is given by:

$$\kappa = \frac{k_{max}}{K_s + C} \quad (3.4)$$

Where C is the substrate concentration, k_{max} is the maximum rate of substrate transformation and K_s is the half saturation constant. The Michaelis-Menten formulation can be extended to take in account other limiting factors (Watson et al., 2003), inhibiting species (Schäfer et al., 1998), and substrate competition (Mösche and Jördening, 1999).

The solution of the differential equations describing solute degradation can be numerically challenging, especially when many species are considered and when solute concentrations range over several orders of magnitude. Thus, reactive transport models need much more computational power than conventional groundwater flow and transport models. Computer power can be a serious limitation when considering three-dimensional domains or during model calibration.

Several models have been developed to simulate the fate of contaminants during batch (Watson et al., 2003; Kouznetsova et al., 2010) and column (1D) experiments (Horner et al., 2007; Haest et al., 2010). Reactive transport models have been also applied to simulate the migration of contaminant plumes in two-dimensional (Christ and Abriola, 2007; Chambon et al., 2010) and three-dimensional (Prommer et al., 2006; Mao et al., 2006) domains.

In Paper II a three-dimensional reactive transport model is used to simulate the fate of three pesticides being transported from surface water into a nearby drinking water well. In Paper I a reactive model of TCE degradation based on Michaelis-Menten kinetic has been developed.

3.2 Global Sensitivity Analysis

Sensitivity analysis is an essential step in the model building process, since it allows the quantification of the relative influence of input variables on the designed output variables (Archer et al., 1997). Sensitivity analysis is usually employed to quantify the effect of parameters uncertainty on the output uncertainty, in order to determine which factors must be better determined (Saltelli et al., 2004).

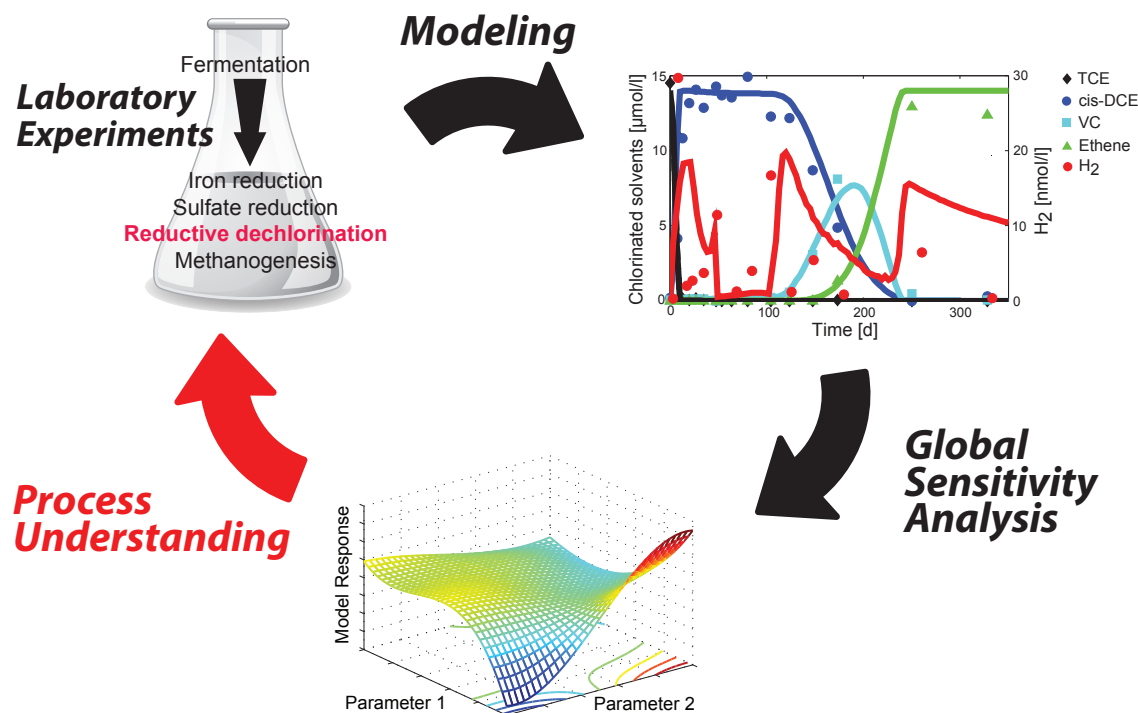


Figure 3.1: Models are used to describe processes observed in laboratory experiments. Then, Global Sensitivity Analysis is applied to study the relative importance of the model parameters and to identify parameter interactions. Finally, information on model behaviour is used to improve the process understanding. The schema refers to the study presented in Paper I.

However, sensitivity analysis can also be used to improve conceptual system understanding and to identify the essential mechanisms determining a given model output (Kitano, 2002) (Figure 3.1). It can be used to assess the relative importance of mechanisms controlling a system and to discover interactions among processes (e.g. Fieberg and Jenkins (2005); Chu et al. (2007); Kontoravdi et al. (2008); Holstein and Wirtz (2009); Sivakumar (2008); Kitano (2002); Fishtik et al. (2000); Turányi (1990); Tuljapurkar (1982)). Such a sensitivity analysis is applied here in Papers I and II.

Mathematically, sensitivity is a measure of the response surface of a model vari-

able. The model space includes all the possible values of a variable, and the model response is the ensemble of model evaluations for the model space. Figure 3.2 shows an example of a response surface for a 2-parameter model.

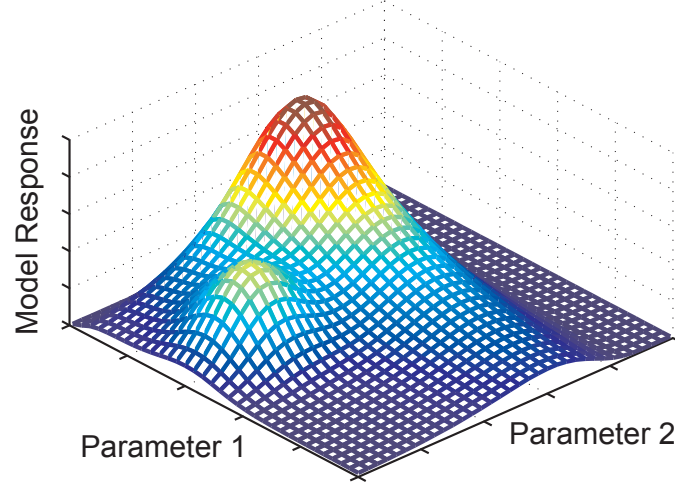


Figure 3.2: Example of a model response for a two parameter model. The response surface is created evaluating the model for every parameter couple.

At any point of the model space, one measure of sensitivity of a variable is defined by the gradient of the response surface and the sensitivity measure can be obtained by a simple derivative (Saltelli et al., 2004):

$$SI_i = \frac{\partial Y}{\partial X_i} \quad (3.5)$$

Where Y is the output of interest and X_i is an input factor.

However, Equation 3.5 is a point measure, which can be inappropriate to describe the behavior of a model over its entire input space, since the model response for a particular parameter or input variable might vary (sometimes rapidly and discontinuously) within the model space (Beven, 2009). Global Sensitivity Analysis (GSA) tools address this limitation and provide a better description of the model over the full extent of the model space.

The simplest way to globally assess model sensitivity is to perform a *factor screening*, which aims to identify the most influential factors in a model, without providing quantitative information about the uncertainty propagation. Each input factors can be ranked in order of importance, but it is not possible to quantify how much a given factor is more important than another (Saltelli et al., 2000). These meth-

ods are able to provide important information at a very limited computational cost, and they are usually employed in the assessment of models whose evaluation is computatioonnally expensive.

Many screening methods exist (e.g. (Box and Hunter, 1957; Cotter, 1979; Andres, 1997; Bettonvil and Kleijnen, 1997)), but the Morris method (Morris, 1991; Campolongo et al., 2007) is by far the most popular (Francos, 2003; Brockmann and Morgenroth, 2007; Pappenberger et al., 2008; Haest et al., 2010).

In the Morris method, a regular n-dimensional grid is constructed over the model space, where n is the number of parameters (Figure 3.3), and the *elementary effect* d_i associated to each input factor is then defined as:

$$d_i(\mathbf{x}) = \frac{[y(x_1, x_2, \dots, x_{i-1}, x_i + \Delta, x_{i+1}, \dots, x_k) - y(x)]}{\Delta} \quad (3.6)$$

for $i = 1, 2, \dots, n$ and Δ being a multiple of the grid step size. The mean of the distribution of elementary effects for each input factor is then used to define the importance of each factor and allows the ranking the parameters according to their importance.

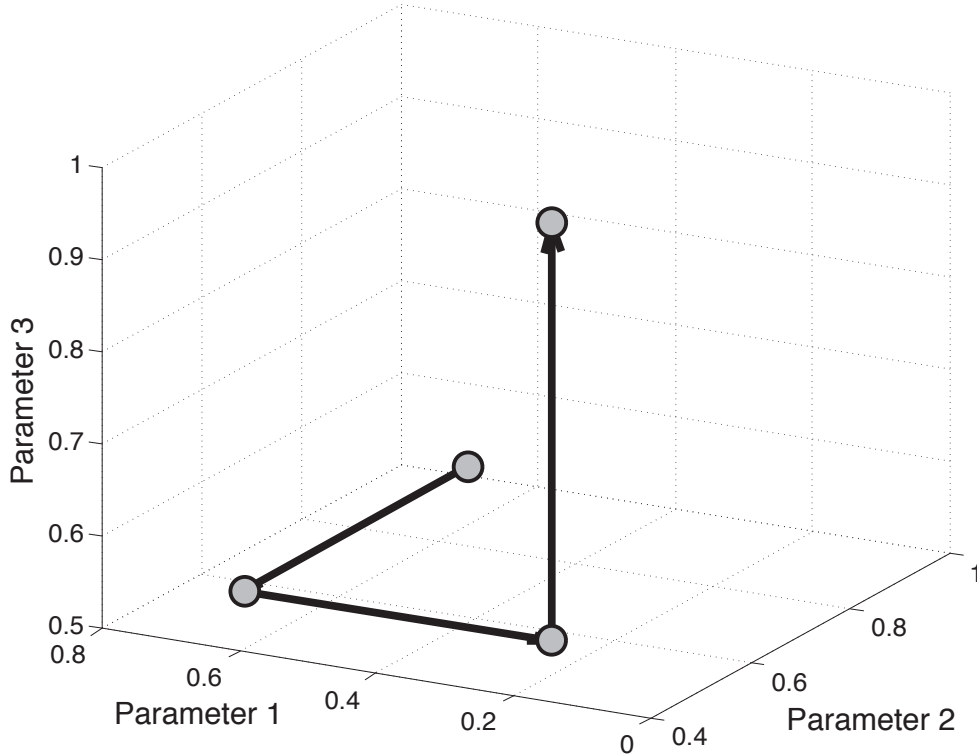


Figure 3.3: Example of a screening path using the Morris method for a model with 3 parameters.

GSA methods that are able to provide quantitative uncertainty estimates are most often based on Monte Carlo techniques employing a variety of sampling strategies and sensitivity measures (Saltelli et al., 2004). Random sampling has the advantage of producing unbiased estimates of the mean and standard deviation of the output, but the use of stratified sampling (e.g. the latin hypercube sampling (Stein, 1987) or the quasi-random sampling (Sobol, 1990)) can provide a better coverage of the space of the model inputs (Saltelli et al., 2000).

Variance-based GSA methods provide the most interesting sensitivity measures because they can determine the part of the total model variance that is due to each input factor, i.e. they can quantify how much model uncertainty is attributable to each parameter. In fact, the aim of variance-based methods is to decompose the variance of the model output Y as follows (Saltelli et al., 2004):

$$Var(Y) = Var(E(Y | X_i)) + E(Var(Y | X_i)) \quad (3.7)$$

Where X_i is a parameter, $Var(E(Y | X_i))$ is the expected reduction of model output variance if parameter X_i is known (also called the main effect of X_i) and $E(Var(Y | X_i))$ is the expected remaining model output variance if X_i is known. The first order sensitivity index S_i is then defined as:

$$S_i = \frac{Var(E(Y | X_i))}{Var(Y)} \quad (3.8)$$

Equation 3.7 can be extended to take in account the variance induced by parameter interactions (Saltelli et al., 2000).

Two main variance-based methods are currently used: the Fourier amplitude sensitivity test (FAST) (Cukier et al., 1973, 1975), and the Sobol sensitivity indexes (Sobol, 2001). The main difference between the two methods is the technique used to solve a multidimensional integral needed to provide the sensitivity indexes: the FAST approach uses a Fourier transform approximation, while the Sobol method solves the integral with a Monte Carlo method. The calculation of sensitivity indices can be very computationally demanding, since the number of samples needed to approximate a multivariate function grows exponentially with the number of parameters. However, this issue can be solved using High Dimensional Model Representations (Rabitz and Aliş, 1999; Aliş and Rabitz, 2001; Ziehn and Tomlin, 2009), which approximate the model output by polynomials and do not consider high-order interactions.

Knowledge of the amount of model variance that is attributable to each parameter can be used to identify the parameters that can be fixed in a model, thereby simplifying the model and making it easier to run and to calibrate, without losing important model behavior. Moreover, sensitivity analysis can be used to determine and prioritize which parameters must be better estimated (for example by field measurements or laboratory experiments) to achieve a lower level of model output uncertainty.

3.3 Statistical analysis

The identification of dominant processes using global sensitivity analysis can be assimilated to an *inductive* process: the model is first built by assembling well-established mathematical equations. Then, after having tested its validity against data, the model is used in conjunction with sensitivity analysis techniques to draw conclusions about the importance of the parameters, and therefore of the processes underlying them. This is a bottom-up approach, where model complexity is built up by joining simple model components.

Another way to investigate which processes are the most influential in a given system is by performing a statistical analysis of observed data. Statistical tools can be used to identify hidden in the observation data. This kind of analysis represents a more *deductive* approach because it tries to reduce observed complexity by establishing significant relationships.

Statistical analysis cannot directly identify the processes involved, but can be used to limit the number of possible explanations responsible for a certain observation. Experience is needed to construct hypothesis about the relationships between observations, which can then be tested to find those most consistent with the data. A fundamental limitation of statistical approaches is that *correlation does not imply causation*: it may be that a cause-and-effect relationship is present between two correlated variables, but the presence of correlation cannot exclude the possibility that another process is responsible for such a link (or that there is no link at all).

Correlation analysis is widely used to investigate factor dependencies (Hamby, 1994), because it provides descriptive statistical measures of the degree of association between two or more variables. Correlation coefficients are usually employed with inferential statistical tests to test the hypotheses concerning the correlation coefficient (for example statistical significance). Many correlation coefficients have

been developed, and their use depends on the type of relationship expected and on the statistical distribution of the data. The Pearson correlation coefficient determines the degree to which a linear relationship exists between variables (Sheskin, 2000), and assumes that the data are normally distributed. The Spearman (Spearman, 1904) and Kendall (Kendall, 1938) correlation coefficients do not require data normality and are able to identify non-linear relationships, provided they are monotonic. Both methods are based on calculating correlation coefficients on the variable ranks instead of on their values.

Statistical tests can be applied to draw inferences (i.e. derive conclusions) on particular data characteristics. A binomial test, for instance, can be used to test if the occurrence of an event (e.g. the frequency of contamination) in two datasets is significantly different (Paper III). T-tests and Mann-Whitney U-tests will be used to determine if the means of two distributions (e.g. mean pollution concentrations) are different and if one is significantly higher than the other, while Siegel-Tukey tests and F-tests can be used to compare the variance (e.g. pollution variability) between two datasets. Inference tests can also be employed to assess the goodness of fit of regression models dealing with probabilities (Hosmer and Lemeshow, 2000; Sheskin, 2000), where standard measures (e.g. Root Mean Squares) cannot be applied.

In many cases it is desired to use existing data to predict the value of the response for a given set of variables. Regression analysis investigates relationships between variables and provides a mathematical model to use for predictions. The aim of the regression analysis is to find a function f :

$$Y \approx f(\mathbf{X}, \beta) \quad (3.9)$$

where Y is the output of interest (the dependent variables), \mathbf{X} are the independent (explanatory) variables and β are parameters that have to be estimated. For example, for drinking water well contamination, the concentration of pollutants at the well or the probability of contamination are possible dependent variables, and the well characteristics (well depth, well age, distance to surface water, . . .) are potential independent variables.

The choice of the function f depends on the purpose of the model and on the nature of the process explaining the dependence. Linear regression, where Y is a linear combination of \mathbf{X} and β , is the most popular type of regression. But when Y

is a probability estimate, logistic regression is usually used (Walker and Duncan, 1967). The mathematical formulation of the logistic model is:

$$Y = \frac{1}{1 + e^{-(\beta_o + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_p X_p)}} \quad (3.10)$$

Where X_1, X_2, \dots, X_p are the explanatory variables, β_o is the model intercept and $\beta_1, \beta_2, \dots, \beta_p$ are parameters. The advantage of a logistic model of probability is that it provides only values between 0 and 1, which is not always true for other possible models (Kleinbaum and Klein, 2010).

Regression techniques have been used to assess contamination by pathogens (Howard, 2003; Bargellini et al., 2011), Volatile Organic Compounds (Squillace et al., 2004; Wu et al., 2009), nutrients (Bruningfann et al., 1994; Goss et al., 1998), heavy metals (Pekey et al., 2004; Twarakavi and Kaluarachchi, 2005) and pesticides (Worrall and Kolpin, 2004; Frans, 2008).

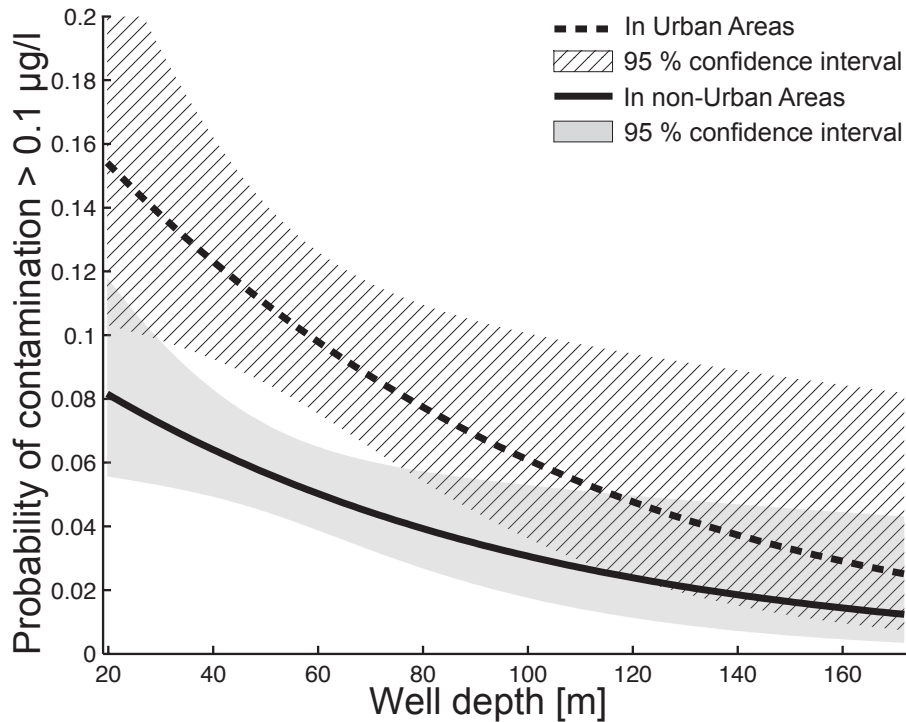


Figure 3.4: Logistic models to predict the probability that a drinking water well is contaminated by BAM in Zealand depending on the well depth and on the landuse. The curves describe the probability of contamination of a hypothetical well located 500 m to surface water and with a clay layer 20 m thick.

In Paper **III**, logistic regression is used to estimate the risk of contamination of drinking water wells by pesticides with concentrations above the detection limit ($0.01 \mu\text{g/L}$), and above the maximum allowable concentration ($0.1 \mu\text{g/L}$) (Figure 3.4). The explanatory variables in the logistic model were: the well depth, the thicknesses of clay, sand and chalk layers overlying the well screen, the distance between the wells and surface water, the distance between the wells and the contaminated sites, and the landuse.

4 Conclusion and perspectives

Contamination of groundwater-based drinking water resources is a serious issue in many countries. Mathematical models can be used to understand contamination processes and to provide predictions for water resources management. The processes governing the fate of contaminants in the subsurface are complex and it is important to identify the dominant factors in order to provide good system approximations.

This study employed statistical tools and global sensitivity analysis techniques to investigate the transport of pesticides in surface water into drinking water wells in confined aquifers, the degradation of chlorinated aliphatic hydrocarbon in a complex geochemical environment, and the main paths of drinking water well contamination by pesticides in Zealand, Denmark.

The following key findings have been made:

- The fermentation of organic compounds and sulphate concentration govern the success of sequential reductive dechlorination in anaerobic aquifers.
- Simple models cannot describe chlorinated aliphatic hydrocarbon degradation without losing important system behaviours.
- Reductive dechlorination cannot occur in the presence of readily biodegradable iron, while dehalogenating bacteria can outcompete iron reducing bacteria as the iron bioavailability decreases.
- Persistent compounds in streams can leach into nearby pumping wells even if an impermeable clay layer overlies the well screen. Thus aquitards may not provide adequate protection against contamination by micropollutants in surface water, as generally thought.
- Drinking water well contamination by BAM, the most frequent contaminant in Danish groundwater, is higher in wells located in urban areas.
- In Zealand, wells close to surface water are generally more vulnerable to pesticide contamination, possibly because of contamination leaching from surface water bodies.
- Sandy layers can provide better protection against the leaching of oxidizable pesticide than clay aquitards, because more likely to host aerobic conditions.

4.1 Perspectives

The work carried out in this PhD thesis has identified some further research needs to achieve a better understanding of the pathways involved in drinking water well contamination by micropollutants:

The transport of micropollutants from streams into drinking water wells in confined aquifers could be verified experimentally using a transect of monitoring wells between the stream and the pumping well. Comparison of the time series of stream water quality with observed groundwater levels should enable the risk of pesticide leaching from surface water to be identified. The major issue in this experiment will be the time needed to observe contaminant breakthrough, since the travel time through the clay layer will be long.

The dechlorination model is very sensitive to the fermentation process, because the fermentation of organic compounds is governing the rate of hydrogen production. A great deal of research is currently being carried out on the production of hydrogen in bioreactors, but few studies have investigated the production of molecular hydrogen in natural environments from different fermentable compounds. A better description of the fermenting processes would improve the reliability of sequential dechlorination models in aquifers.

The logistic models developed in this study are based on an actual database. It would be interesting to extend these models to make them time-dependent. In future, for instance, BAM contamination will reach deeper aquifers, while the stock in the topsoil will be gradually depleted. Thus, future models could indicate that shallow wells are less vulnerable to contamination.

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6 Papers

- I.** Malaguerra, F., Chambon, J. C., Bjerg, P. L., Scheutz, C. and Binning P. J. Development and sensitivity analysis of a fully-kinetic model of sequential reductive dechlorination in groundwater, submitted to *Environmental Science & Technology*.
- II.** Malaguerra, F., Albrechtsen, H-J. and Binning P. J. Contamination of drinking water supply wells by pesticides from surface water resources, submitted to *Journal of Hydrology*.
- III.** Malaguerra, F., Albrechtsen, H-J., Thorling, L. and Binning P. J. Pesticides in water supply wells in Zealand, Denmark: a statistical analysis, submitted to *Science of the Total Environment*.

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