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Conceptual model for groundwater status and risk assessment – case study of the Zagreb aquifer system

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ABSTRACT

This paper presents a conceptual model of the Zagreb aquifer system. The conceptual model can be applied to groundwater status risk assessment and pollution risk assessment at the local scale, thus satisfying both environmental and preventative/limitation objectives of the Water Framework Directive (WFD) and Groundwater Directive (GWD). Its main purpose is to apply a risk assessment procedure, according to the WFD requirements, and to serve as a foundation for setting up a numerical model of flow in both the saturated and unsaturated zones in order to identify pressure and impact effects on groundwater quality. The model is divided into two parts, taking into account the WFD requirement to assess a risk for a wide range of source-pathway-receptor relationships. The *Global Conceptual Model* (GCM) provides insight into the processes and pressures at the level of the groundwater system. It contains the geological and hydrogeological characterization of the Zagreb aquifer system and the description of the most significant point and diffuse sources and pathways of pollution and processes influencing pollutant behaviour in saturated and unsaturated zone of the groundwater system. The main pollutants of the Zagreb aquifer system are potentially toxic metals, nitrates, pesticides, pharmaceuticals and chlorinated aliphatics. A *Local Conceptual Model* (LCM) supports parameterization of the whole groundwater system through the description of heterogeneities and flow and solute parameters of the system components at two sites representing local conditions in the saturated (Stara Loza) and unsaturated (Kosnica) zones. This concept can be regarded as an effective tool for groundwater management of the groundwater system and its compartments and for communicating the conditions in complex groundwater systems with experts, policy makers and general public in an understandable way.

Keywords: Global conceptual model (GCM), Local conceptual model (LCM), risk and status assessment, groundwater quality, Zagreb aquifer system

1. INTRODUCTION

Groundwater is the only source of potable water for the City of Zagreb. The Zagreb aquifer system, where groundwater is naturally stored, is currently under threat due to decreasing water quantity and increasing concentrations of pollutants. Groundwater levels in the aquifer have particularly decreased over the last 40 years reaching such minimal levels as to cause problems to the City's water supply during periods of drought (POSAVEC, 2006). Industrial developments and fast growth of the City of Zagreb have considerably affected the quality of groundwater in this area (NAKIĆ et al., 2001, BAČANI et al., 2002), with increasingly progressive groundwater pollution being observed over the last twenty-five years. High concentrations of pollutants including atrazine, potentially toxic metals and chlorinated hydrocarbons confirm the impact of pollution sources on groundwater quality (NAKIĆ et al., 2010).

In order to identify a coherent approach to mitigation of the impacts of different pressures, (point and non-point source

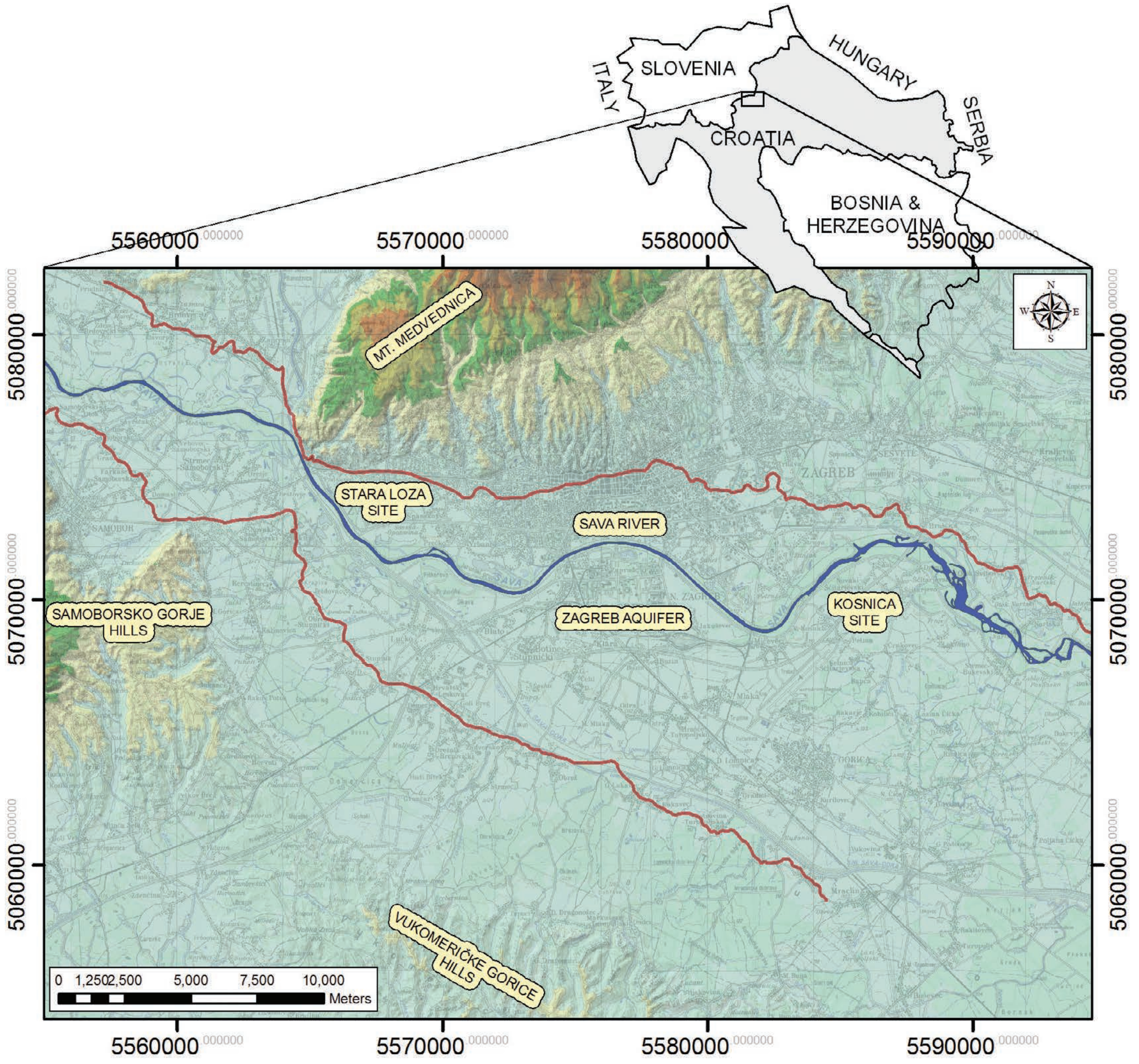

Figure 1: Geographical location of the Zagreb aquifer system and locations of small scale experiment sites.

of pollution with respect to groundwater quality and overexploitation of the groundwater), a risk assessment was applied, as defined in CIS document No. 26 (COMMISSION OF THE EUROPEAN COMMUNITIES, 2010). Risk assessment tries to draw a causal chain linking the origin of a hazard or pressure (e.g. an identified or estimated loading of polluting substance) along an environmental pathway to consequences for human health or the environment. This is generally known as a source-pathway-receptor (SPR) paradigm (COMMISSION OF THE EUROPEAN COMMUNITIES, 2010). In the context of this paper, pollution risk is related to achieving the environmental objectives of the Water Framework Directive (WFD, 2000/60/EC) and not in the perspective of risk to human health. In order to assess the risk of not reaching the goal of good groundwater quality in the Zagreb aquifer system, the Driver, Pressure, State, Impact, Response (DPSIR) analytical framework has to be followed, according to recommendations from the *Analysis of Pressures and Impacts – Guidance Document No 3* (COMMISSION OF THE EUROPEAN COMMUNITIES, 2003). According to this approach, Driver is an anthropogenic activity that can affect the environment; Pressure is the direct effect of a driver, and Impact is an environmental effect of a Pressure. State is the environmental condition resulting from the Pressure and Responses are the measures taken for improving the State.

To apply this analytical framework, a conceptual model is needed in the form of simplified representations, or working descriptions, of the groundwater system under investigation, in this case the Zagreb aquifer system. A new Groundwater Directive (GWD, 2006/118/EC) recognized the significance of the conceptual model in the groundwater risk and status assessment, which represents, by definition, the current understanding of the groundwater system based on the knowledge of its natural characteristics (GRATH et al., 2007). The aim of building a conceptual model is to gain an adequate understanding of the groundwater system in order to identify pressures on the system and the relevant physical processes within it. According to the CIS guidance No. 17 (COMMISSION OF THE EUROPEAN COMMUNITIES, 2007a), a conceptual model should describe the relevant geological characteristics, groundwater and surface water flow conditions, hydrogeochemical (including terrestrial and aquatic ecosystems) processes, anthropogenic activities (relevant land uses) and their interactions. The accuracy and complexity of the models increases with the amount of, and confidence in, the available environmental information, so they become more effective and reliable descriptions of the system (BALDERACCHI et al., 2011).

The main focus of this paper is to describe a conceptual model that can be applied according to the WFD requirements in assessing pollution risk caused by point and non-point pollution sources with respect to groundwater quality in the Zagreb aquifer system at different scales, ranging from the scale of the groundwater system down to a single site, representing local conditions in the saturated (Stara Loza site) and unsaturated zones (Kosnica site).

The philosophy behind this approach is to start developing adequate groundwater management of the whole Zagreb aquifer system based on available knowledge of the system, and then to gain new information where needed to improve such understanding and the effectiveness of the measures applied for mitigating the risk of not achieving the environmental objectives of the WFD and GWD. In this respect, a number of iterations are expected, until the improved conceptual model can describe the measured data in a consistent way and with sufficient accuracy. The goal is to obtain a hydrogeological conceptual model of the Zagreb aquifer system which will be used not only for describing, but also for quantifying the relevant geological and hydrogeological characteristics, flow and boundary conditions, hydrogeochemical processes, including natural groundwater quality and processes influencing contaminant behaviour in the unsaturated and saturated zones.

2. RESEARCH AREA

2.1. Geographical position and climate

The study area (extent of the Zagreb aquifer system) is situated in northwest Croatia (Fig. 1) and includes the City of Zagreb and its surroundings, covering an area of 350 km^2.

The broader region is characterized by highly variable lithology, pedological features and land use. The study area consists of a large alluvial plain bordered to the north by the Mt Medvednica mountain chain. The alluvial plain has two marked geomorphological features: the raised sealed terrace of the Sava River (varying in width down the rivers length), and a Holocene terrace. Numerous meanders of the Sava River inundated fluvial cones and numerous bowl-shaped depressions abound in the alluvial plain.

The climate of the City of Zagreb is classified as a moderately continental climate (Cfwbx in the Köppen climate classification system) with four separate seasons. Summers are warm, and winters are cold, without a discernible dry season. The average temperature in winter is −0.5 °C and the average temperature in summer is 22.0°C. The average rainfall on the basis of ten years observations (1998–2008) is 928 mm year^{-1} (CROATIAN METEOROLOGICAL AND HYDROLOGICAL SERVICE).

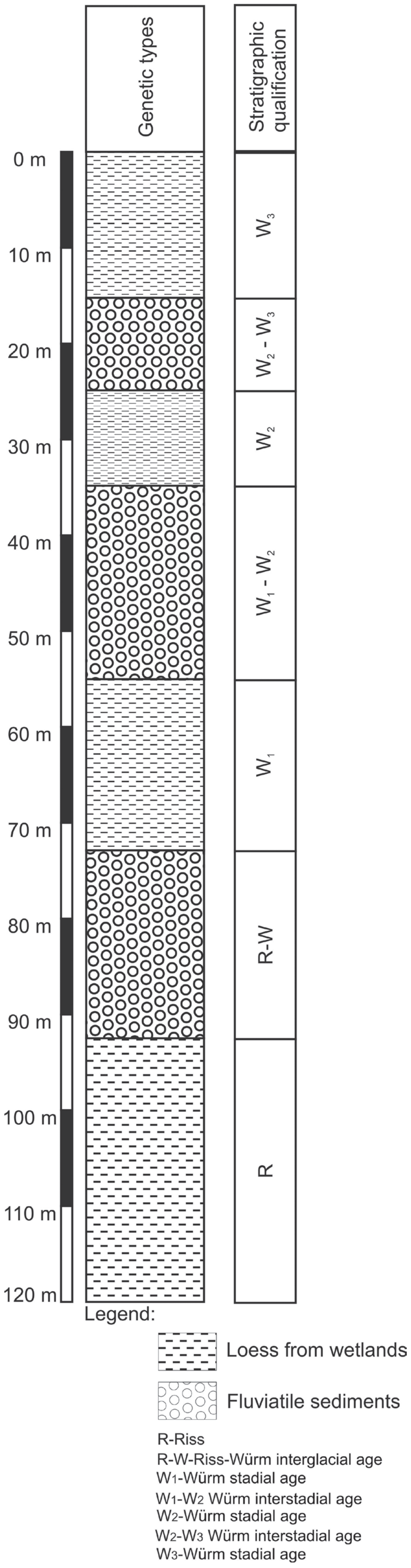

Figure 2: Simplified exploration core according to ŠIMUNIĆ & BASCH (1975).

A small scale experiment site in the unsaturated zone is located near the village of Velika Kosnica, about eight hundred metres from the right bank of the Sava river (45°46’ N; 16°05’ E) (Fig. 1). The location is close (straight line distances) to Zagreb airport (3.5 km), the Zagreb bypass (250 m) and the largest Croatian landfill site Jakuševec (4.5 km).

A small scale saturated zone experiment site is located in the area of the abandoned water abstraction site at Stara Loza on the left bank of the Sava river (45° 47’ 37’’ N, 15° 52’ 33’’ E) (Fig. 1).

2.2. Geological setting

The geology of the studied area is described in the explanatory notes for Basic Geological Map of SFRY 1:100 000 (BASCH, 1983; ŠIKIĆ et al., 1979; PIKIJA, 1987).

The Zagreb aquifer system is composed mainly of Quaternary sediments, which have been studied in detail by ŠIMUNIĆ & BASCH (1975). Four horizons of marshy-loess and three horizons of fluviatile deposits were recognised in a 120 m long exploration core (Fig. 2).

ŠIKIĆ el al. (1979) and ŠIKIĆ & BASCH (1975) consider that detailed division of the Pleistocene deposits of the western part of the Zagreb environs is difficult, apart from division into genetic types, which are pondy-loess, continental loess without carbonates, alluvial deposits of the third Sava river terrace and cave-fillings. Lower Pleistocene deposits are predominantly composed of yellowish-red, yellowish-orange and yellowish-brown, clayey silts/silty clays with sporadic lenses and interbeds of gravelly-sands, up to a few decimetres in thickness. Highly variable coefficients of sorting, compared to the average values, possibly indicate that loess, mixed with local materials (loessoid) has contributed to the sediment composition (VELIĆ & DURN, 1993).

The Middle Pleistocene unit is relatively uniform in composition. While the lower and middle part is predominantly composed of grey coloured sands, the upper part comprises grey coloured or red to yellowish-brown mottled silt and clay sized material. During warmer periods, the top of these sediments were exposed to pedogenic processes (VELIĆ & DURN, 1993; VELIĆ & SAFTIĆ, 1996).

The Upper Pleistocene unit is characterized by frequent lateral changes of gravels, sands, silts and clays. In the upper part, varves are recognized, as alternating, millimetre thick light coloured, fine-grained sands and dark grey to black silts. The Holocene is composed of pale, yellowish- grey coloured gravels and sands in which limestone cobbles prevail.

Both small scale experiment sites are situated in the Holocene sediments.

2.3. Pedological settings

The large heterogeneity of the parent material, combined with the climate and geomorphology, has caused the development of a wide variety of soil types. The floodplain soils, formed in materials eroded from sediments present in the catchment basin, are represented by specific mineralogical, chemical and textural characteristics.

The investigated area of the Zagreb aquifer system encompasses predominantly three pedologic units: Fluvisols, Stagnic Podzoluvisols (Pseudogley) and Eutric Cambisols, developed on Holocene deposits (BOGUNOVIĆ et al., 1998).

Fluvisols (AC profile) are found on alluvial plains, river fans and valleys (FAO, 1998). This type of soil is characterized by weak horizon differentiation, although a distinct Ah-horizon may be present. The texture of these soils is mainly loam, rarely clayey loam, while the structure is crumb to blocky (ROMIĆ et al., 2005)[1].

Stagnic Podzoluvisols (Ap-BA-Bwr-Cr profile) is a hydromorphic soil which belongs to the Stagnosol class. Stagnosols occur on flat to gently sloping land in cool temperate to subtropical regions with humid to perhumid climate conditions (FAO, 2007). In the study area, this type of soil developed from Luvisols, i.e. it is secondary in origin, with a silty-clay-loam texture and a granular and very unstable structure (ROMIĆ et al., 2005)[1].

Eutric Cambisols (A-Bv-R profile) belong to the cambic class of soils, characterized by a cambic horizon. Cambisols are characterized by slight or moderate weathering of the parent material and by the absence of appreciable quantities of illuviated clay, organic matter, Al and/or Fe compounds (FAO, 2007). In the study area, this type of soil has a humus-accumulative horizon which is mainly mollic and noncalcareous, developed by pedogenc processes from rendzine on marls and Holocene deposits. The texture of this soil is silty-clay to clay-loam (mainly loamy), developed on marls and Holocene deposits, respectively (ROMIĆ et al., 2005)[1].

The Fluvisol type of soil is developed at small scale Kosnica and Stara Loza experiment sites, and is texturally mainly loamy, in some parts clayey with loam. Structure of this type of soils is mainly granular. In some parts, soil horizons are red to black in colour, due to Fe and Mn oxides enrichments.

3. CONCEPTUAL MODEL DEVELOPMENT

The primary purpose in developing the conceptual model of the Zagreb aquifer system was to serve as a foundation for setting up a numerical model of flow and transport in the saturated and unsaturated zones, in order to identify pressure and impact effects on groundwater quantity and quality. However, over time, its purpose has been extended and it can now be regarded as a tool for communication with experts, policy makers, or the general public, and can provide the basis for the derivation of measures for groundwater protection. With relation to the WFD objectives, the conceptual

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[1] ROMIĆ, D., ROMIĆ, M., DOLANJSKI, D., STRIČEVIĆ, I., ONDRAŠEK, G., MAUROVIĆ, N., KONDRES, N., HUSNJAK, S. & HENGL, T. (2005): Održivost agro-ekosustava na području Grada Zagreba s obzirom na onečišćenost teškim metalima. [The sustainability of agro-ecosystems of City of Zagreb with respect to potentially toxic metals contamination -in Croatian] Unpubl. report. Faculty of Agriculture, University of Zagreb, Zagreb.

model of the Zagreb aquifer system is intended to assess the risk of failing to achieve good groundwater status.

In setting up the conceptual model, separate components have been taken into account. Firstly, subsurface characteristics and dominant processes in the saturated and unsaturated zones of the Zagreb aquifer system have been addressed and incorporated in the model. Then, hydrogeological parameters are quantified and variables are introduced that quantify the exchange of fluxes between different compartments, e.g. exchange of water between the shallow aquifer and the Sava River. The current stage of construction focuses on qualifying the significance of point and non-point pollution sources on groundwater deterioration. It is recognized that in evaluating the anthropogenic activities and their interactions, anthropogenic and non- anthropogenic effects need to be clearly distinguished. Hence, relevant natural occurring substances in the groundwater system are identified and the importance of the natural background load assessment is highlighted. It is also recognized that, in relation to the objectives set, there is a knowledge gap in understanding the behaviour of the groundwater system at small and medium scales, with regard to its heterogeneity and the determination of groundwater pathways and mixing rates.

According to the WFD requirements, risks need to be assessed for a wide range of source-pathway-receptor relationships, at scales from the very local through the medium scale, (for example, impact on individual abstraction boreholes or terrestrial ecosystems) to whole groundwater bodies (COMMISSION OF THE EUROPEAN COMMUNITIES, 2010). Hence, further improvement of the conceptual model of the Zagreb aquifer system is made according to the recommendation of CIS guidance No. 15 (COMMISSION OF THE EUROPEAN COMMUNITIES, 2007b). The model is divided into two parts: a) *Global Conceptual Model* (GCM), which provides an insight into the processes at the level of groundwater system and b) *Local Conceptual Model* (LCM), which supports parameterization of the groundwater system through small scale experiments conducted at two sites: Kosnica, which provides an insight into the behaviour of contaminants in the unsaturated zone and Stara Loza, which provides an insight into small scale heterogeneity.

The development of both types of conceptual models and the current understanding of the groundwater system and its compartments are presented here. This paper further investigates the sources of contamination and contaminants in the urban water cycle that are directly linked to the deterioration of groundwater status in the area of the City of Zagreb. Due to multiple pollution sources and the wide range of potential hazards in this highly urbanized region, it is quite difficult to estimate exactly the risks of not meeting the WFD objectives. However, risks can be managed to some extent by using information about the sources of contamination and contaminant behaviour in the subsurface.

3.1. Concept of groundwater status and risk assessment

Conceptual models are considered as a vital tool to support the implementation of all aspects of groundwater requirements of the WFD and GWD (COMMISSION OF THE EUROPEAN COMMUNITIES, 2009). It is clear that both the groundwater status and risk assessment should be based on a well developed conceptual model of a groundwater system.

In the status assessment, a clear understanding of the behaviour of pollutants which characterize bodies of groundwater as being at risk of not meeting the WFD objectives is needed, which is also linked to the pressure and impact analysis (risk assessment), in relation to the validation of article 5 of the WFD. If the water body fails to meet its objectives, or is at risk of failing to meet its objectives, then the cause of the failure (i.e. the pressure or combination of pressures) must be investigated (COMMISSION OF THE EUROPEAN COMMUNITIES, 2003).

The potential benefit of the conceptual model of the Zagreb aquifer system is not only in using it to assess the risk of failing to achieve good groundwater status of the system (groundwater bodies within the aquifer system), but also to estimate the risk of pollution at a local scale, thus satisfying the prevent/limit objectives in the WFD and GWD. However, in case of such localized pollution it is necessary to use the conceptual model to assess the overall risk for the groundwater system/body and to take measures to limit the pollution. This approach is followed in estimating the vulnerability of the Zagreb aquifer system to potentially toxic metal pollution at the Kosnica site. The idea is to estimate the leakage potential of the potentially toxic metal pollution load through the unsaturated zone at a local scale and to use risk assessment procedures to estimate the concentration range of selected potentially toxic metals in the soil and the unsaturated zone, which may be considered as an acceptable addition of human influence to the natural background concentration load that doesn't represent a threat to the relevant receptor, (in this case groundwater itself). By using numerical modelling of transport through the unsaturated zone, the potential of this zone to retard potentially toxic metals may be assessed, as a basis for subsequent calculation of background concentrations in the unsaturated zone. This approach is in line with the concept of REIMANN & GARRETT (2005), who proposed the introduction of *ambient background concentration*, which occurs under slightly altered conditions, when elevated levels of element concentrations in soil or water result from long-term human impact such as agriculture, industry, and urbanization and are no longer natural.

3.2. Global conceptual model (GCM)

A *Global Conceptual Model* (GCM) of the Zagreb aquifer system provides an overview of the processes which occur at the level of the groundwater system. It contains the geological and hydrogeological characterization of the aquifer system, including the definition of boundary conditions and conclusions of the sensitivity analysis of the factors influencing groundwater recharge. To distinguish between natural and man-made concentrations, the natural background loads of selected inorganic parameters in the groundwater are identified, reflecting natural processes unaffected by human activities. The concept of the risk assessment implies

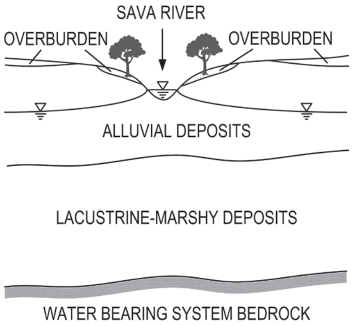


Figure 3: Schematic hydrogeological cross-section of the Zagreb aquifer system.

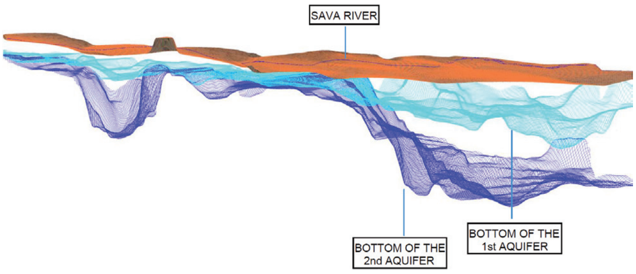


Figure 4: 3D geological model of the Zagreb aquifer system.

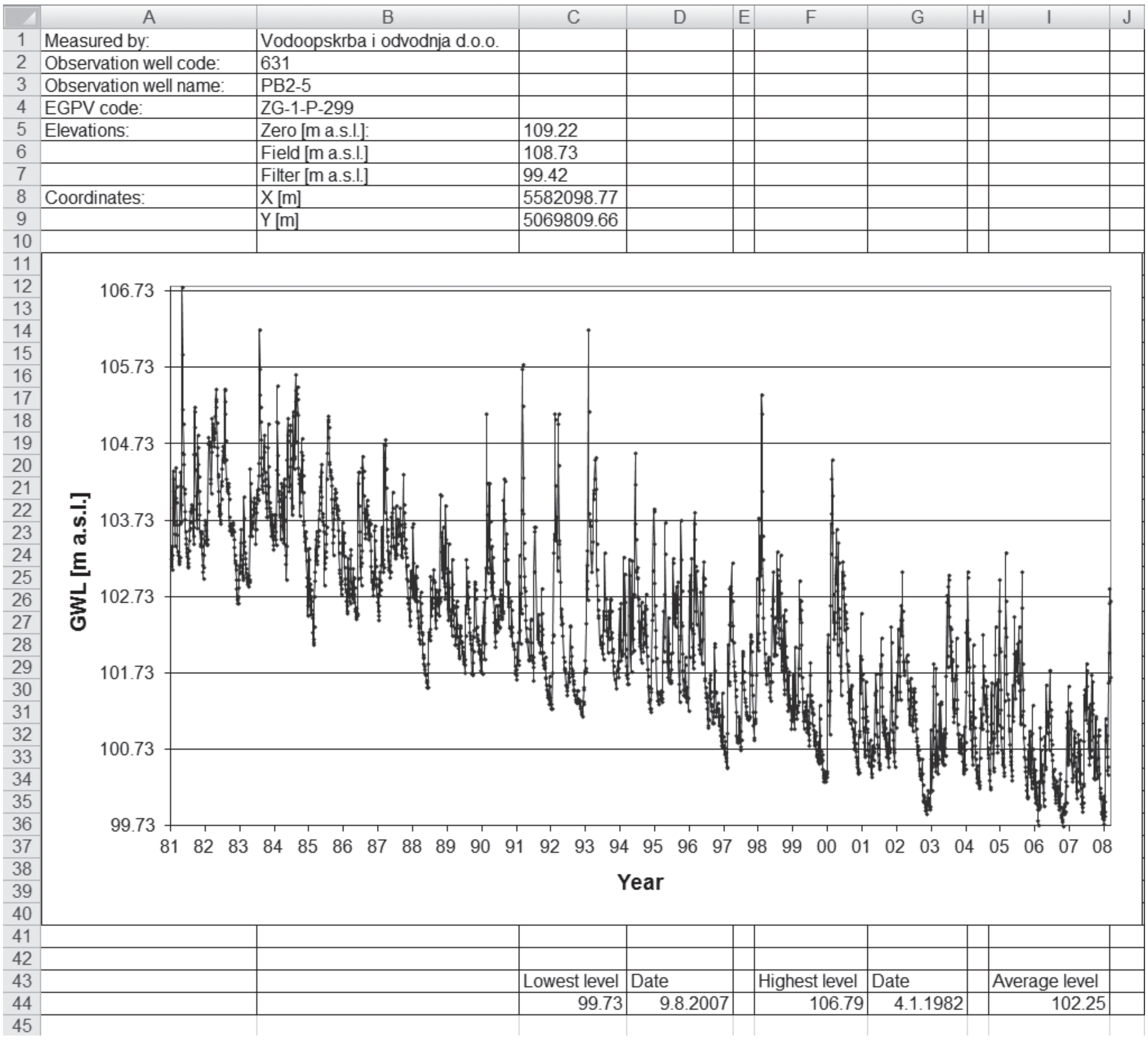
that the impact of human activity on the groundwater system should be defined, specifically those impacts that threaten the achievement of the objectives of the WFD. To that end, the most significant sources and pathways of pollution and processes influencing pollutant behaviour in saturated and unsaturated zone of the Zagreb aquifer system are identified and specifically outlined here.

3.2.1. Geological model of alluvial aquifer system

The aquifer system comprises two Quaternary aquifers (Figs. 3 and 4). Hydrogeologically, the Quaternary deposits are divided into three basic units: the overburden of clay and silt; a shallow Holocene aquifer of medium-grain gravel mixed with sands; and deeper aquifers from the Middle and Upper Pleistocene, with frequent lateral and vertical alterations of gravel, sand and clay.

3.2.2. Hydrogeological characterization

The Zagreb aquifer system (Fig. 1) is an alluvial unconfined aquifer with a water table connected to the Sava River (Fig. 3). Sava River represents the main source of recharge. The general groundwater flow direction is from west to east, or south-east. Although recharge also occurs from precipita-



	A	B	C	D	E	F	G	H	I	J
1	Measured by:	Vodoopskrba i odvodnja d.o.o.								
2	Observation well code:	631								
3	Observation well name:	PB2-5								
4	EGPV code:	ZG-1-P-299								
5	Elevations:	Zero [m a.s.l.]:	109.22							
6		Field [m a.s.l.]	108.73							
7		Filter [m a.s.l.]	99.42							
8	Coordinates:	X [m]	5582098.77							
9		Y [m]	5069809.66							
43			Lowest level	Date		Highest level	Date		Average level	
44			99.73	9.8.2007		106.79	4.1.1982		102.25	

Figure 5: Negative trends of groundwater levels.

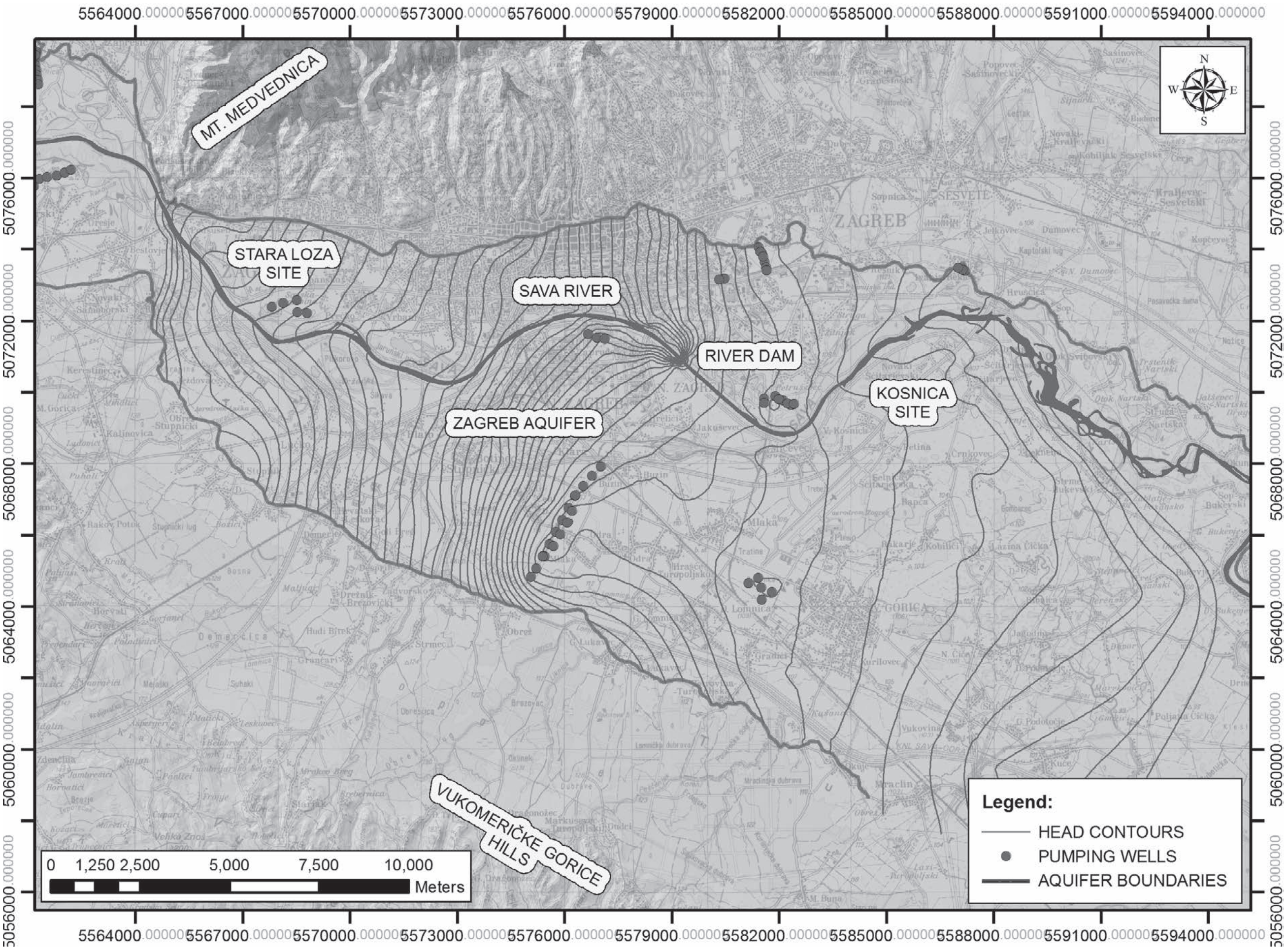


Figure 6: River dam location and head contour maps showing the impact of the dam on groundwater flow direction in its near vicinity.

tion, alteration in the Sava river water levels dominantly influence the changes in groundwater levels across the whole aquifer.

The quantity of groundwater is diminishing continuously (Fig. 5). The main reasons for lowering of groundwater levels are (1) extensive riverbed erosion due to upstream Sava river regulation in the Republic of Slovenia and gravel exploitation from the river; (2) embankment of the Sava river which stopped occasional flooding of the area and potential infiltration to groundwater; (3) excessive abstraction for municipal and industrial needs; and (4) prolonged periods of drought. Groundwater levels have already reached minimum levels (defined as the upper elevations of the well screens) on some well fields, causing water scarcity during droughts (POSAVEC, 2006).

Analysis of the water quantity data of the Zagreb aquifer system showed that groundwater levels are declining on average at 1–2 m every 10 years (BAČANI et al., 2010).

The total annual abstraction from the Zagreb well fields exceeds the annual renewable groundwater reserves (which from 1997 – 2007 averaged about 107×10^6 m^3 per year), while pumping in the same period averaged about 125×10^6 m^3 per year. Groundwater abstraction rates which exceed renewable groundwater reserves are recovered from the permanent groundwater reserves. The volume of permanent groundwater reserves in 1977 was 1.81×10^9 m^3 and by 2007 was 1.68×10^9 m^3, which is a decrease in permanent groundwater reserves of 7% (BAČANI et al., 2010).

The Sava River, which is the largest river in Croatia, divides the Zagreb aquifer system into two parts. The river, (which is the main source of groundwater recharge within the aquifer system), is in direct hydraulic connection with the shallow aquifer, which has extremely high values of hydraulic conductivity (up to 3000 m/day).

Head contour map analysis (POSAVEC, 2006) showed that during high Sava river water levels, infiltration to groundwater occurs over all parts of the flow while during medium and low water levels the river drains groundwater on some parts of the flow.

Groundwater levels are also strongly affected by the small river dam. An average drop of the Sava river water level amounts to 0,4 m/km, while the drop of the water level downstream from the dam can be up to 6 m over a rather small distance of tens of metres. This strongly affects the aquifer flow directions and groundwater levels in near vicinity of the river dam (Fig. 6).

The thickness of the unsaturated zone of the Zagreb aquifer system varies from 8 metres in the NW part to 2 metres

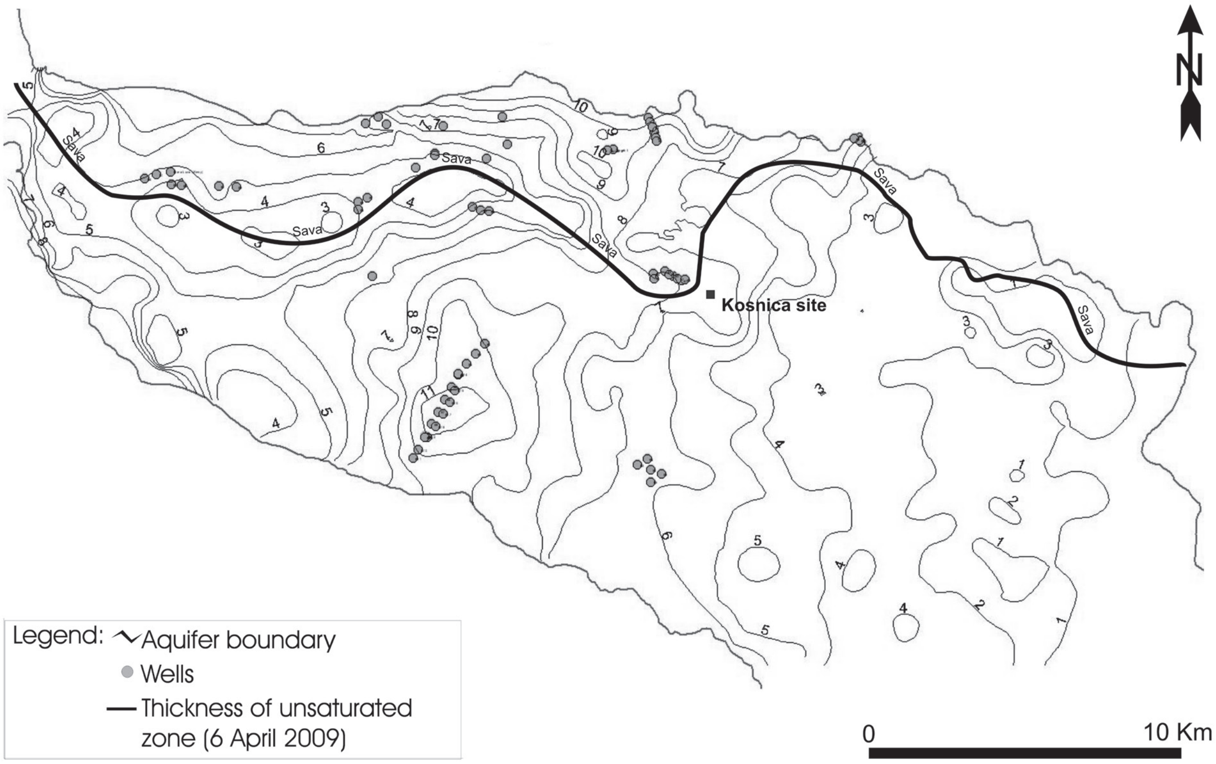


Figure 7: Isopach map of the unsaturated zone according to RUŽIČIĆ et al. (2011).

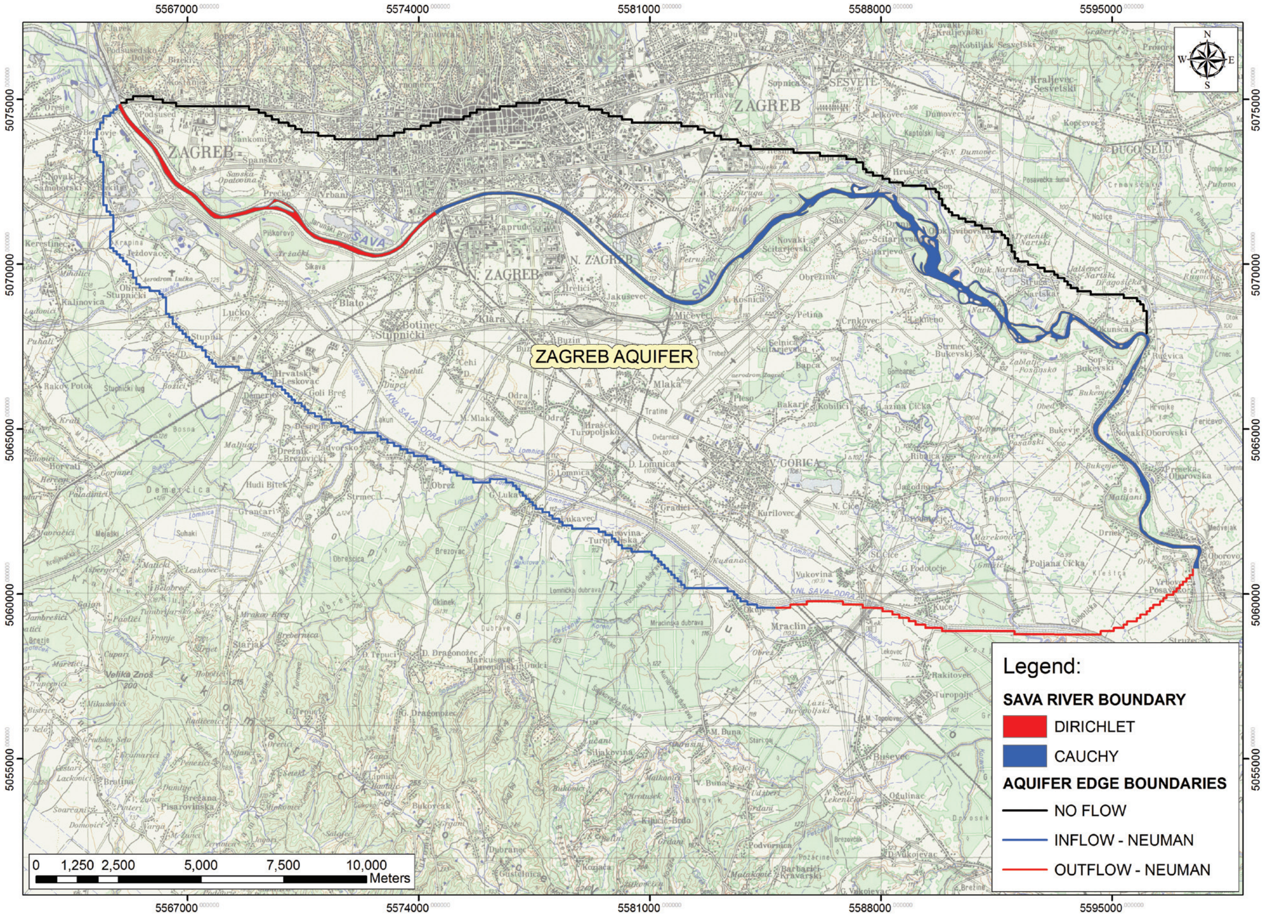


Figure 8: Boundary conditions of the Zagreb aquifer system.

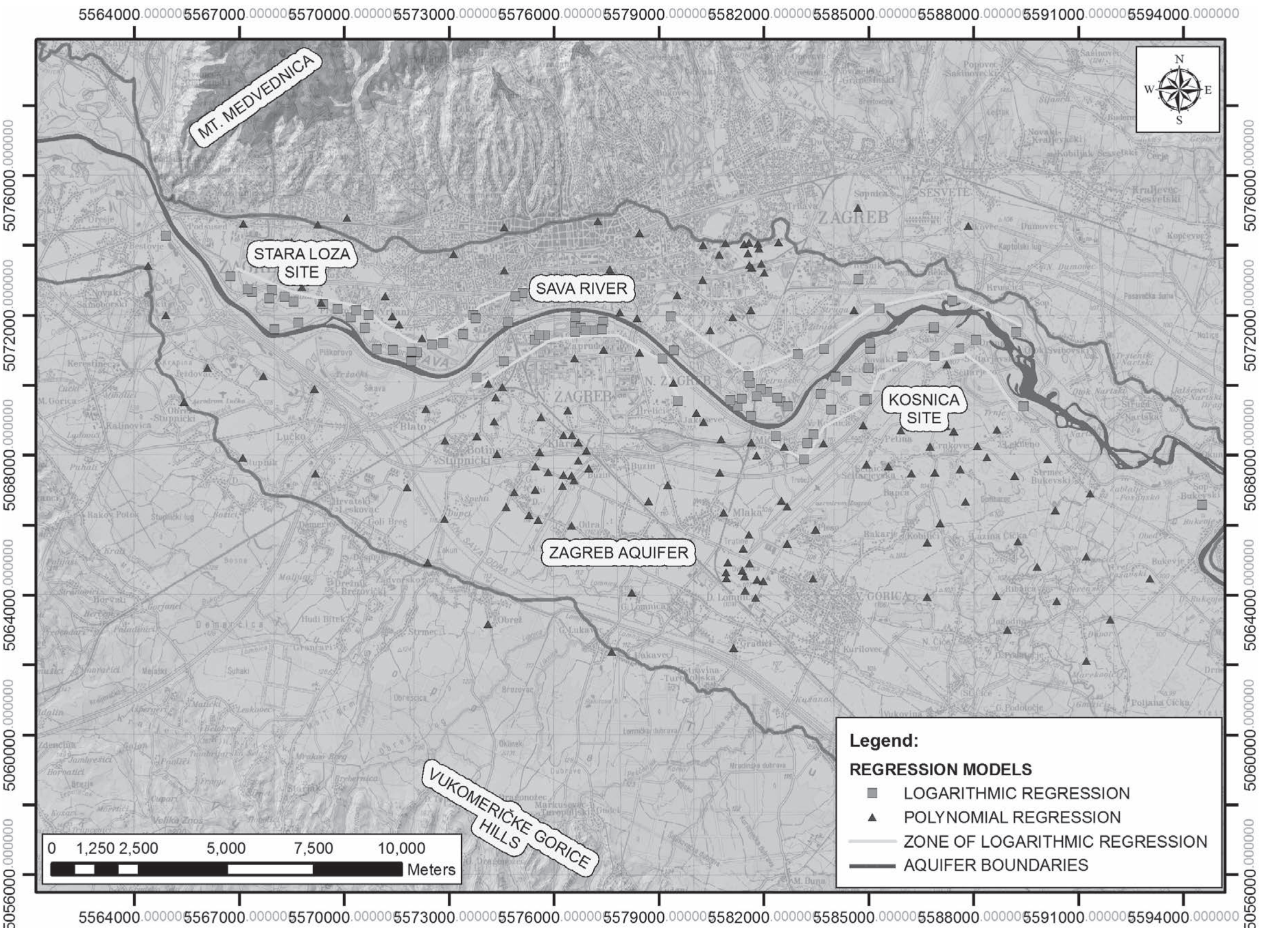


Figure 9: Regression models showing zones of higher impact of the Sava River.

in the SE part (Fig. 7). An isopach map of the unsaturated zone is derived from differences of groundwater level and terrain elevations. Groundwater level data were collected from 406 wells by the State Meteorological and Hydrological Service and Water Supply and Drainage Company. The zone consists predominantly of gravels and sands, with sporadic clays. The upper part is dominated by silty to sandy material, with the lower part being mostly gravel. In some parts this material is interbedded with clay layers.

Hydraulic conductivity of the unsaturated zone of the Zagreb aquifer system varies from 1.26 m/day in the upper part to 1015 m/day in the lower part. This zone is predominantly composed of quartz, calcite, dolomite and plagioclase in the upper part, while clay minerals represent the dominant mineral phases in the lower part.

3.2.3. Boundary conditions

The Zagreb aquifer is an aquifer with no flow boundary to the north, an inflow boundary to the west and south and an outflow boundary to the east (Fig. 8). The Dirichlet boundary condition specifies the value of the head at the boundary. The Neumann boundary condition specifies the flux normal to the boundary and the Cauchy boundary condition specifies the head and the flux normal to the boundary. Determination of inflow/outflow/no flow boundaries was based on analysis of head contour maps for high, medium and low groundwater levels (POSAVEC, 2006). The results showed that there is no significant inflow or outflow through the northern aquifer boundary, possibly due to the mainly impermeable deposits of Mt. Medvednica which results in predominantly surface flow.

Inflow quantification through the southern boundary is rather difficult due to lack of data and observation wells. Based on head contour map analysis and water balance analysis it can be assumed that some inflow through southern boundary does exist but with rather different fluxes across the region. Boundaries within the aquifer are represented by the Sava River which is the dominant boundary condition (Fig. 8).

In order to identify and quantify the relevance of the impact of land-use and climate effects on groundwater flow in general, sensitivity analysis of the recharge boundary condition, i.e. infiltration from precipitation, was carried out on existing numerical groundwater flow model of the Zagreb aquifer. For simulation of groundwater flow, a numerical method, i.e. MODFLOW code was identified and used as an appropriate simulation model according to defined goals. A numerical model for groundwater flow was established, calibrated and validated for the whole of the Zagreb aquifer.

Sensitivity analysis of the recharge boundary condition, i.e. infiltration from precipitation, carried out on an existing numerical groundwater flow model of the Zagreb aquifer, has shown that recharge from precipitation does not present the relevant boundary condition. The Sava River was defined as the dominant and the most relevant boundary condition.

Spatial zonation of areas where the Sava River has a higher impact on groundwater levels was analyzed using recession curve models. The analysis of groundwater level time series using recession curve models was performed with the Master Recession Curve Tool (POSAVEC et al., 2006). In total, 278 master recession curves were obtained for the 278 observation wells analysed.

Analysis of the spatial distribution of the selected regression model showed that logarithmic regression prevails in parts of the aquifer near the river Sava, while polynomial regression prevails in other parts of the aquifer (Fig. 9). These results are logical and reasonable with respect to the changes in groundwater levels which occur faster in the vicinity of the Sava River. In other parts of the aquifer where such strong boundaries do not exist, groundwater level changes occur less rapidly.

Principal component analysis (PCA) – following the procedure by WINTER et al. (2000) – can be used to define hydrodynamic zones within the regional groundwater system with identical groundwater table changes or fluctuation patterns in time. This procedure was implemented in the Zagreb case study, as part of the sensitivity analysis, pointing to aquifer recharging conditions and enabling conclusions on prevalent groundwater flow conditions in parts of the Zagreb aquifer system to be drawn.

Results of the PCA, implemented in the Zagreb case study example (NAKIĆ, 2005), enabled characterization of the groundwater fluctuation pattern at the locations of observation wells, revealing diversity of hydrodynamic characteristics in different parts of the groundwater system (Fig. 10).

On the right bank of the Sava River the groundwater fluctuation pattern is similar for the shallow and deeper layers, and it mainly reflects the impacts of the regional groundwater flow from the west towards the east. At the edge of the aquifer system, the impact of the Sava River is less and the water wave propagation is significantly lagging in time, while in the zone located immediately next to the Sava River, intensive fluctuations in the groundwater tables reflect the rapid and intensive impacts of changes in river water levels on the groundwater tables.

Further evidence of the Sava River – groundwater interaction has been provided by NAKIĆ et al., (2004), who delineated hydrogeochemically homogenous areas within the Zagreb aquifer system, using the PHREEQC groundwater modelling tool (PARKHURST et al, 1980) and Cluster analysis, more specifically the Ward method of hierarchical tree clustering. They revealed the very similar or identical macro chemical composition of groundwater in the area bordering

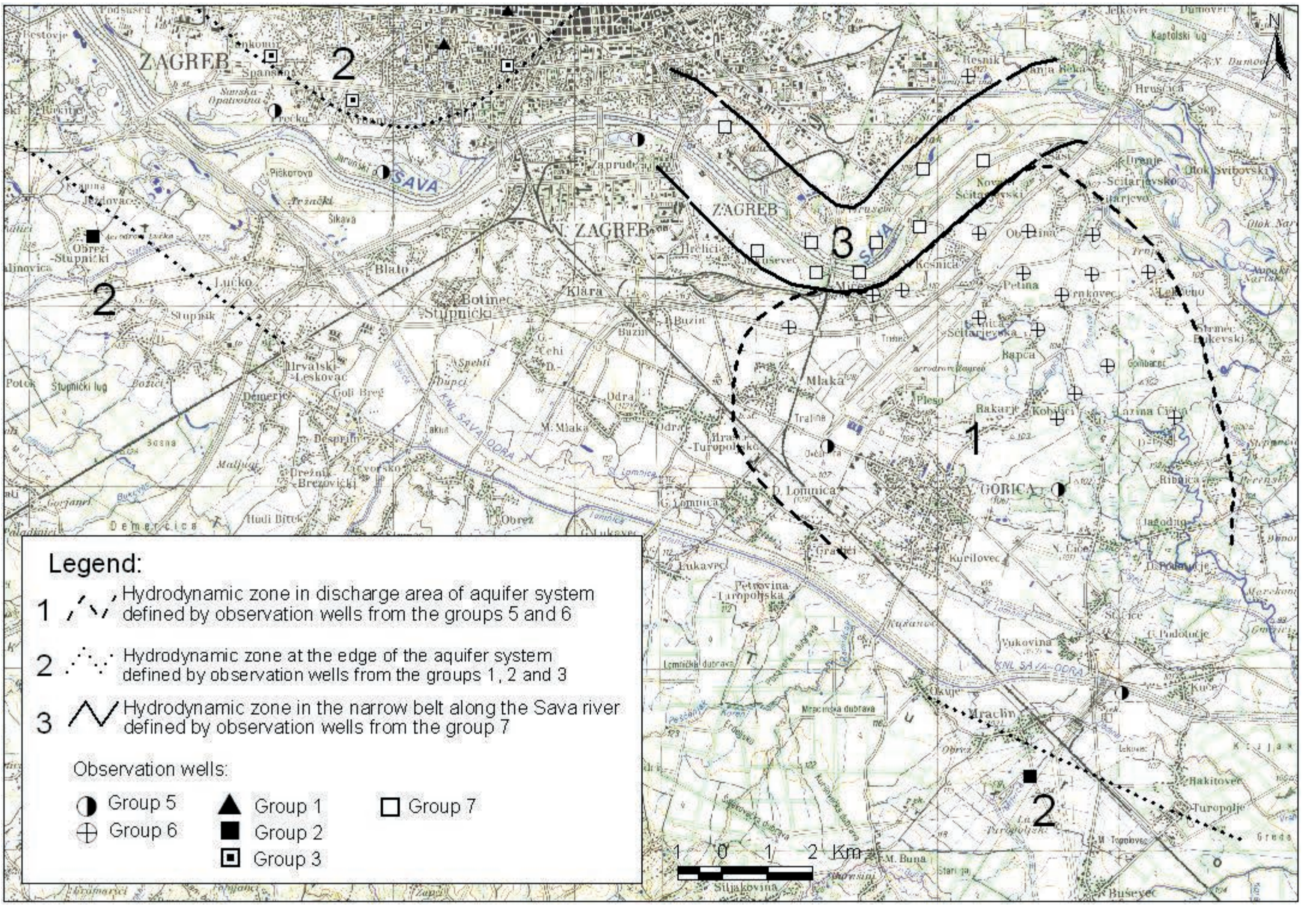


Figure 10: Hydrodynamic zones within the Zagreb aquifer system according to NAKIĆ (2005).

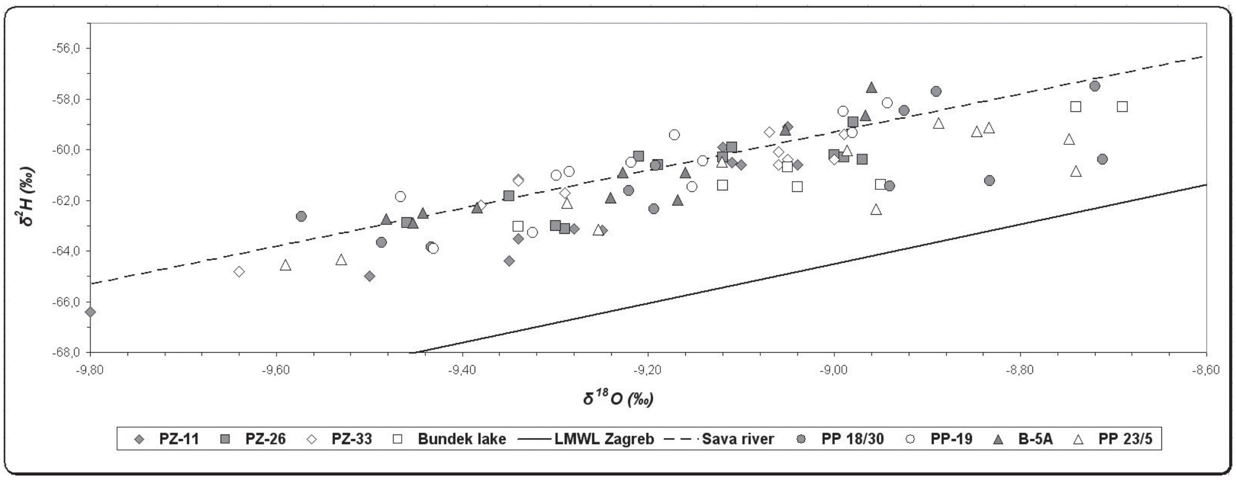


Figure 11: Relationships between δ^2H and δ^{18}O in the waters of the Zagreb area.

the river, which supports the evidence of strong impacts of the Sava River water levels on the groundwater levels adjacent to the river. These results were confirmed by hydrogeochemical investigations, conducted by VLAHOVIĆ et al. (2009). It was proven that the direct exchange between the Sava River and the aquifer weakens with distance away from the river, while the difference in hydrogeochemical characteristics between the Sava River water and groundwater increases.

To identify the pattern of groundwater – Sava River water interaction, comprehensive investigations of isotopic composition in precipitation, groundwater and river water were carried out. HORVATINČIĆ et al., (2011) and PARLOV et al. (2012) used measurements of stable isotopes of oxygen and hydrogen in precipitation, surface waters and groundwater in order to determine the relative contributions of the Sava River and precipitation on groundwater recharge along the left (HORVATINČIĆ et al., 2011) and right (PARLOV et al. 2012) banks of the Sava river respectively.

The results of these investigations are combined in Figure 11, which indicates the relationship between δ^2H and δ^{18}O in: the Sava River and groundwater at the left bank of the Sava River in 2010 (HORVATINČIĆ et al., 2011); groundwater and Bundek lake at the right bank of the Sava River in 2011 (PARLOV et al., 2012). For illustration purposes, long term records of Zagreb precipitation (1980–2003) and the Local Meteoric Water Line (LMWL) (VREČA et al., 2006) are also included (Fig. 11).

It can be seen that all groundwater values lay very close to the correlation line of the Sava River showing its direct influence on the groundwater. Differences between particular piezometers indicate the temporal and spatial variability in groundwater-surface water (Sava River) interactions. Accordingly, mixing of water from the Sava River and groundwater is occurring in the near vicinity of the Sava River and it weakens further away.

Analyses of the recharge boundary condition presented here show that recharge from precipitation does not represent an important boundary condition in the Zagreb aquifer system. Due to the identified high impact of the Sava River levels on groundwater levels, the Sava River is defined as the dominant and the most relevant boundary condition in the numerical model. Changes in the Sava River levels are naturally related to climate scenarios, but primarily in the upper parts of the flow where the Sava River is fed by surface runoff and by groundwater drainage. Since the course of the Sava River through the Zagreb area is characteristic of the valley river, it doesn't drain the whole Zagreb aquifer, yet it controls the processes of recharge and drainage. Therefore in the case of the Zagreb aquifer, (i.e. an alluvial aquifer with high hydraulic conductivity and a water table connected to the stream with significant oscillation in water levels due to lack of regulation), the stream i.e. the Sava River represents the dominant boundary condition.

3.2.4. Natural groundwater quality and ambient background values

Development of industry and the fast growth of the City of Zagreb during the last three decades have considerably affected the quality of the groundwater in the Zagreb aquifer system. The Zagreb area accommodates an extremely high number of diverse diffuse and point pollution sources causing degradation of groundwater quality and posing a particular threat for its future use.

Although human activity may lead to water compositions which exceed drinking water standards, water quality limits may be also breached for elements such as F, As and Fe by entirely natural processes, the result of geochemical conditions existing in aquifer or due to the specific geology in the area (EDMUNDS & SHAND, 2008). Groundwater pollution is most easily recognised by the presence of artificial organic compounds, but it is difficult to recognise incipient pollution in most groundwaters.

In order to be sure that pollution is occurring, natural spatial and temporal characteristics and trends of the chemical substances must be ascertained. Under such conditions, it is particularly important to make a clear distinction between geogenic and anthropogenic influences in groundwater quality. This is aided by determination of the geochemi-

Table 1: Geochemical topsoil data for the City of Zagreb and surrounding area from different studies (data from geochemical atlases and maximal permissible concentrations from Croatian legislation are for comparison).

Element	Official GAZETTE (2010)			NAMJESNIK (1994)		SOLLITO et al. (2010)			Geochemical Atlas of the Republic of Croatia (HALAMIĆ & MIKO, 2009)					
	Croatia			Zagreb		Zagreb county			Central Croatia			Croatia		
	maximal permissible concentration			Min	Max	Min	Max	Med	Min	Max	Med	Min	Max	Med
	*	**	***											
Cd (mg/kg)	0.5	1.0	2.0	0.01	22.5	0.02	4.94	0.31	0.2	9.4	0.2	0.2	15.5	0.4
Cr (mg/kg)	40	80	120	9	161	11.5	400	51.2	28	524	74	18	524	88.2
Cu (mg/kg)	60	90	120	–	–	3.64	1335	23.5	3	248	19	3	429	25.4
Hg (µg/kg)	500	1000	1500	18	1938	–	–	–	5	4535	50	5	4535	60
Ni (mg/kg)	30	50	75	4	651	0.7	488	29.7	12	427	33	9.2	427	47.5
Pb (mg/kg)	50	100	150	5	546	1	216	19.6	14	217	27	10	699	33
Zn (mg/kg)	60	150	200	12	1250	27.1	479	70.7	28	477	73	23	1432	88

*Legend: * – sandy soil; ** – silty-loamy soil; *** – clayey soil.*

cal background of naturally occurring substances which reflect natural processes unaffected by human activities. The new GWD (2006/118/EC), which introduces the term background level, as: „the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions" particularly recognises this.

Although the term geochemical background was introduced much earlier in the scientific terminology by HAWKES & WEBB (1962), who defined it as the normal abundance of an element in barren earth material, human influences on the planet as a whole have been so pervasive for such a long time that it may be pointless to attempt to determine pre-settlement background values, because concentrations from presumed pristine areas in these locations are likely to have also been affected (KELLY & PANNO, 2008). An option is to define *ambient background values* under slightly altered conditions, when elevated levels of element concentrations in soil or water result from long-term human impact, such as agriculture, industry and urbanization, and are no longer natural (REIMANN & GARRETT, 2005).

The geochemical background is a response to variable recharge rates, rainfall composition, water-gas interactions in soil and the unsaturated zone, as well as the processes (mineral dissolution, redox reactions, ion-exchange reactions and mixing) that have taken place along flow paths. Under natural conditions, groundwater quality is determined by the sum of soil-modified atmospheric inputs plus water-rock interactions taking place at the soil-bedrock interface and from longer-term reactions taking place in the saturated zone. In order to fully understand the evolution of groundwater chemistry along a flow path, in depth knowledge of the background and pollution loads in soils and unsaturated zone is needed.

Research into soil geochemistry in the area of the Zagreb aquifer system was carried out in different professional and scientific projects at different scales. For the „Geochemical Atlas of the Republic of Croatia", a total of 640 topsoil (0–25 cm) samples were collected in the Central Croatian region using systematic sampling on a 5km grid (HALAMIĆ & MIKO, 2009). Numerous studies of metal contamination of soils have been made in the area of Zagreb and Zagreb County (NAMJESNIK, 1994; MIKO et al., 2001; ROMIĆ, 2002; ROMIĆ & ROMIĆ, 2003; ROMIĆ et al., 2004[5]; HALAMIĆ & MIKO, 2009; SOLLITTO et al., 2010). A total of 420 topsoil (0–15 cm) samples were collected, using systematic sampling on a 2km grid, with sampling density increasing to 1 km near the urban part of Zagreb (NAMJESNIK, 1994). SOLLITTO et al. (2010) collected 916 topsoil (0–20 cm) samples in the Zagreb County. Compendious results for potentially toxic metals in soils from these studies, together with maximum permissible concentrations in agricultural soils defined by Croatian government regulation (OG, 2010) are presented in Table 1. It is evident that in some areas of Zagreb concentrations of cadmium, chromium, cooper, mercury, nickel, lead and zinc in soil exceed maximum permissible concentrations.

The vertical distribution of trace elements in soil profiles has been extensively studied, mainly in order to define the mobility of certain contaminants from soil to groundwater. About 70 vertical profiles of soil were studied in the area of Zagreb and Zagreb County. The Department of Field Crops, Forage and Grassland from the Faculty of Agriculture carried out agricultural soil trace element contamination studies in the framework of several projects (ROMIĆ et al., 2003[6]; ROMIĆ et al., 2004[5]; ROMIĆ et al., 2005[1]). ROMIĆ (2002) investigated twelve profiles of the most abundant soil types. Profile depths and thicknesses of layers from which the samples were taken vary, depending on soil type and morphological features. The results of the aforementioned investigations show that cadmium, iron, manganese and nickel have increased concentrations with depth, while concentrations of lead, zinc, chromium and copper vary.

Table 2: Local ambient background values of selected chemical parameters in groundwater of the Zagreb aquifer system.

Chemical Parameters	Normal range of ambient background values	Upper limits of ambient background values	Method of calculation	Source
Nitrate (mg N/l)	0.0 – 4.80	4.8	iterative 2-σ technique	NAKIĆ et al., 2007
	0.0 – 5.9	5.9	calculated distribution function	
Dissolved oxygen (mg/l O_2)	1.4 – 8.4	1.4*	iterative 2-σ technique	NAKIĆ et al., 2008
Sulphate (mg/l SO4)	14.2 – 47.6	47.6	iterative 2-σ technique	NAKIĆ et al., 2008
Chloride (mg/l Cl)	1.7 – 35.3	35.3	iterative 2-σ technique	NAKIĆ et al., 2008
Iron (mg/l Fe)	0.0 – 11.4	11.4	iterative 2-σ technique	NAKIĆ et al., 2008
Manganese (mg/l Mn)	0.0 – 0.5	0.5	iterative 2-σ technique	NAKIĆ et al., 2008

* For dissolved oxygen a lower limit of ambient background value is applicable to determine the outliers below background fluctuation (low values of dissolved oxygen as indicators of extreme oxygen consumption)

Since the WFD (2000/60/EC) came into force, several hydrogeochemical investigations of the Zagreb aquifer system have been undertaken with the aim of characterising the dominant geochemical processes and sources influencing natural groundwater chemistry. NAKIĆ (2001) and BAČANI et al. (2002) used statistical methods, trend analysis and multivariate statistical analyses, in order to discriminate between natural and man-made concentrations on a qualitative basis. BRKIĆ et al. (2003) studied the intrinsic vulnerability of the Zagreb aquifer system, while NAKIĆ et al. (2004) outlined hydrogeochemically homogenous areas within the Zagreb aquifer system by multivariate statistical analyses and geochemical modelling tools, showing that it is possible to differentiate a shallow Holocene alluvial aquifer from the deeper Middle/Upper Pleistocene lacustrine-marsh aquifers.

In order to distinguish between geogenic and anthropogenic influences in groundwater quality of the Zagreb aquifer system, background levels of inorganic substances were calculated on several occasions (Table 2), using model-based objective statistical methods (NAKIĆ et al., 2007; NAKIĆ et al., 2008). Pre-settlement background values of elements were not determined due to the extensive temporal impact of human activity in the Zagreb area. An option used was to define *ambient background values* under altered conditions, according to the concept set out by REIMANN & GARRETT (2005). For this purpose, the Visual Basic macro BACKGROUND, created by NAKIĆ et al. (2007) was applied as it uses algorithms that incorporate model-based objective statistical methods (*the iterative 2-σ technique* and the *calculated distribution function*), as defined by MATSCHULLAT et al. (2000).

Overall, the ranges of ambient background values for the selected chemical substances reflects local geological and geochemical conditions in the aquifer system as well as the slight impact of anthropogenic sources, e.g. agricultural activities or atmospheric inputs due to emissions from the burning of fossil fuels. With respect to NO_3, *ambient background* includes sources such as soil organic matter from the residue of fertilized and unfertilized crops, products of combustion, and evaporation of ammonia (NH_3) from synthetic and organic N fertilizer and livestock waste, in addition to naturally derived NO_3.

At first glance, it seems that ranges of ambient background values for particular chemicals, e.g. for sulphate are wide, however comparison to the range of estimated background values from European aquifers (see e.g. SHAND & EDMUNDS, 2008), suggests that values reflect the specific groundwater chemistry in the Zagreb aquifer system.

Similar evidence can be provided for the other elements and compounds under consideration. Variable ambient background ranges of iron and manganese are due to rapidly changing concentrations of these elements across redox boundaries in the Zagreb aquifer system. As a consequence, concentrations may vary over four to five orders of magnitude across the shallow and deeper aquifers.

3.2.5. Sources and pathways of pollution, pollutants and their behaviour

Groundwater of the Zagreb aquifer system is facing increasing pressure from human activities and there is a threat of contamination by diffuse and point sources. Pathways from sources to receptors are outlined in Figure 12.

The main point pollution sources in the area of the Zagreb aquifer system include the Jakuševec city landfill site, marshalling yard, wastewater treatment plant, septic tanks, illegal waste depositories, gravel pits, industrial facilities, Zagreb airport, fuel stations and domestic households. The main diffuse pollution sources are traffic, leaky sewage pipes and agriculture (use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides). These sources can generally be divided into active (permanent and temporary) and potential sources of pollution. The permanent sources of pollution include the location of wastewater discharges, wastewater treatment plant, septic tanks, leaky sewage system, semi-legal disposal of municipal and industrial waste, abandoned gravel pits covered with municipal and construction waste. Temporary sources of pollution include storm water discharge locations, tailings disposal in open pit mines, manure and other waste materials dumps from farms, storm drainage system wastewater, and other agricultural activity (BAČANI et al., 2010)[2]. Potential sources of pollution can occur due to failures, malfunctions or negligence (e.g. active and abandoned gravel pits).

Pollutants, causing regional or local pollution which, depending on soil properties and hydrogeological conditions,

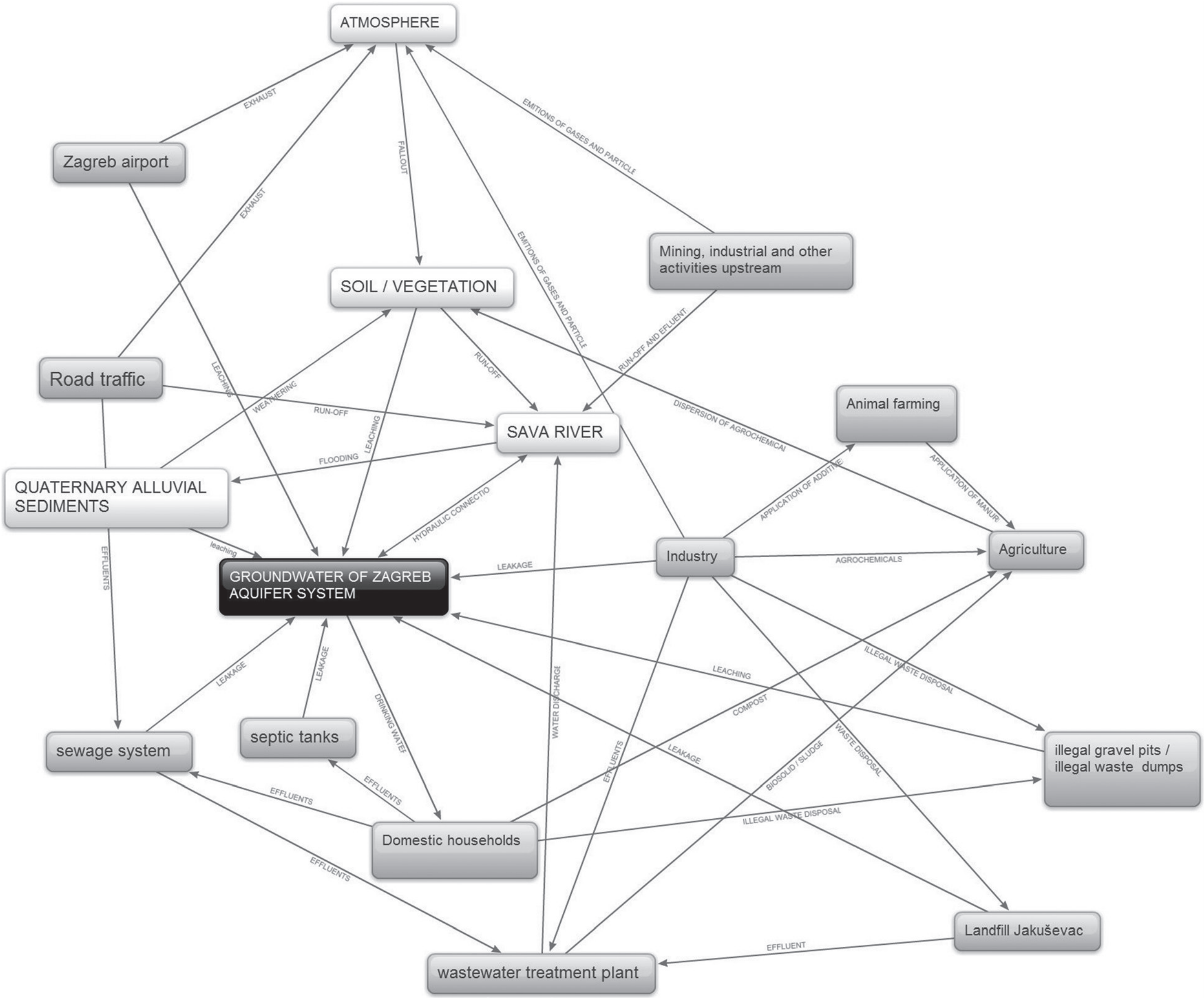


Figure 12: The most significant anthropogenic sources (grey boxes), pathways (arrows) and receptors (white and black boxes) of pollution in the area of the Zagreb aquifer system.

may reach groundwater, can be divided into ***natural substances***: (1) potentially toxic metals; (2) radionuclides; (3) road salt; (4) nutrients (mainly nitrogen); and ***synthetic substances***: (1) pesticides; (2) chlorinated aliphatics and petroleum hydrocarbon contaminants; (3) organic wastewater contaminants (BALDERACCHI et al., 2011). Potentially toxic metals, nitrates, pesticides, pharmaceuticals and chlorinated aliphatics are the main pollutants of the Zagreb aquifer system.

Pathways of pollutants from the sources of pollution to the environmental receptors (atmosphere, soil, vegetation, Sava River, Quaternary alluvial sediments) ending in the groundwater of the Zagreb aquifer system are shown in Fig. 12. They include: fallout from the atmosphere onto vegetation, soils, sediments and surface waters; runoff from the soil/sediment surfaces and other urban surfaces to the Sava river and other surface waters; flooding of the Sava river onto the Zagreb floodplain; weathering of rocks and sediments; leaching from point sources (e.g. Jakuševec landfill) and polluted soils and sediments.

Potentially toxic metals

Groundwater concentrations of lead exceed the maximum permitted concentrations in some locations though the overall trend is one of decreasing levels as a consequence of a reduction in the use of leaded petrol. In some wells, the concentration of manganese is extremely high (BAČANI et al., 2007)[3]. The occurrence and concentration of Mn in groundwater is controlled by many factors, the main ones being rock geochemistry, water chemistry and microbiological activity. Water chemistry, in particular pH, redox potential (Eh), dissolved oxygen (DO), and dissolved organic carbon (DOC) influence mobilisation of Mn and control its speciation and concentration in the water environment. Micro-organisms can play an important role in Mn mobilisation in the environment and can both enhance or inhibit concentrations in groundwater. The impact of microbiological activity on Mn behaviour in water is frequently evident in the accumulation of Mn oxides on pipe surfaces.

There is also the threat of potentially toxic metals leaching from point sources and polluted soils and sediments to the groundwater. NAKIĆ et al. (2007), in their study of groundwater quality at the Jakuševec landfill indicated such leaching of potentially toxic metals into both soil and groundwater. Different studies of soils and sediments in Zagreb aquifer area indicated elevated concentrations of following trace elements: Cu, Hg, Zn, Pb, Cd, Ni, As. HALAMIĆ et al. (2003) showed that the spatial distribution of Cu in topsoils of the Zagreb area was mostly related to the winegrowing areas, i.e. to the anthropogenic input of this metal into the topsoil. They also assumed that anomalous values of As and Cd are mainly of natural origin (mineralization). Greater amounts of Hg in topsoil of Zagreb area were probably caused by fossil fuel combustion and airborne pollution from industrial plants (NAMJESNIK et al., 1992). ALJINOVIĆ et al. (1995)[4] highlighted higher concentrations of lead in the topsoil of Kosnica and assumed traffic to be the source. Elevated concentrations of Zn, Pb and Cd in topsoils of the Zagreb aquifer system are a consequence of the atmospheric deposition of particles from urban sources such are industrial emissions, traffic, waste disposal, heating plants, etc. (ROMIĆ et al., 2004)[5]. Higher concentrations of Hg, Cd and Ni as observed in the vertical profile of soils in water protected areas of the Zagreb aquifer system (ROMIĆ et al., 2005)[1] are probably related to airborne deposition and traffic. Anomalous concentrations of nickel in the vicinity of the highway and the airport result from anthropogenic influences due to fuel combustion (ROMIĆ & ROMIĆ, 2003). High nickel concentrations are probably partly connected to the morphogenetic characteristics of the wider region, primarily basic and ultrabasic magmatic rocks of the surrounding mountain range.

Nitrates

Sporadically high concentrations of nitrates are registered in the groundwater beneath the City of Zagreb, especially at the Mala Mlaka well field. It was confirmed that periodically high nitrate concentrations are a consequence of agricultural production (NAKIĆ et al., 2001; PETOŠIĆ et al., 2012). Nitrogen is present in soils as the nitrate ion (NO^{3-}), ammonium ion (NH^{4+}) and as a component of soil organic matter. Nitrate leaching from soil depends on the amount, frequency and intensity of precipitation, soil properties, crop type and crop development stage, evaporation, soil tillage practices, and nitrogen fertilization regime (VIDAČEK et al., 1996, 1999; NEMETH, 2006; JOSIPOVIC et al., 2006; NEMČIĆ et al., 2007). ROMIĆ et al. (2003)[6] found that high concentrations of nitrates result from flushing of previously unsaturated layers during periods of high rainfall. Soil solution in arable soil contains 20–40 mg NO_3-N/l, rising more than tenfold after fertilization (ROMIĆ et al, 2003)[6]. As nitrates are very soluble in water, leaching to groundwater is highest when precipitation exceeds evapotranspiration and for irrigated land at the beginning of the vegetation growing period.

Although intensive agriculture (nitrogen and organic fertilizer) is the main potential nitrate pollution source in the Zagreb area, other sources include leakage from septic tanks and the sewage system, atmospheric deposition and other urban waste, as well as accident situations.

Pesticides

Pesticides present in the groundwater of the Zagreb aquifer system originate mainly from agricultural use and can be dispersed in the environment by diffuse and point sources. Diffuse pesticide pathways into groundwater are mainly leaching through the soil and the unsaturated zone. Point sources mainly concern farmyard runoff, septic tank leakage, accidental spills, plumes from landfills and poor handling of pesticides. GOJMERAC et al. (2006) found high concentrations of atrazine in the groundwater of the Velika Gorica well field. Groundwater samples from observation wells during 2000–2010 showed that atrazine occasionally exceeded the maximum permissible concentration beneath agricultural areas (BAČANI & POSAVEC, 2011)[7]. Soils with high pesticide concentrations occurred at Kosnica (ROMIĆ et al., 1995)[8]. This contamination resulted from infiltration through the unsaturated zone which has a high filtration coefficient favouring the undisturbed transport of contaminants. The continued presence of these pollutants over time reflects the persistence of atrazine and other pesticides.

Agricultural pesticide inputs into the soil and groundwater are dependent on various factors. At the field scale, inputs into soil depend on spraying, crop interception and wash-off, losses through spray drift or volatilization processes (BALDERACCHI et al., 2011). Pesticide pathways to groundwater mostly depend on: (1) sorption processes, which control the amount of pesticide available for leaching into the soil and aquifer, and (2) on transport processes through the soil and the unsaturated zone (JARVIS, 2007; KOHNE et al., 2009b). Such processes are strongly dependent on the physical, physicochemical and biological properties of soils. Atrazine for example, can be detected in groundwater several years after the last application (BARAN et al., 2008; MORVAN et al., 2006; TAPPE et al., 2002) because it has slow remobilization from the soil and the unsaturated zone.

Chlorinated aliphatics

Chlorinated aliphatics are some of the most widespread groundwater contaminants in the industrialised world (KÄSTNER, 1991; WILSON, 1996). Because of spills and accidents, these hydrocarbons have become important contaminants in both soil and groundwater (SCHAERLAEKENS et al., 1999). The contamination associated with chlorinated aliphatics and petroleum hydrocarbon compounds is typically of a point source such as: landfill with municipal and industrial wastes; leaky sewage collecting leachate from small industrial activities (e.g. Dry-cleaning; metal degreasing); petrochemical activities; leakage of underground storage tanks. Some of them are primary compounds in industrial processes, some are by-products of degradation. Many are recalcitrant, but under favourable conditions (especially anaerobic) they can be transformed and degraded through microbially mediated processes which include reductive dechlorination, dehydrochlorination and dichloroelimination (FERGUSON & PIETARI, 2000).

Tetrachlorethylene (PCE) concentration in all wells within the Zagreb aquifer system is relatively high, and in some cases

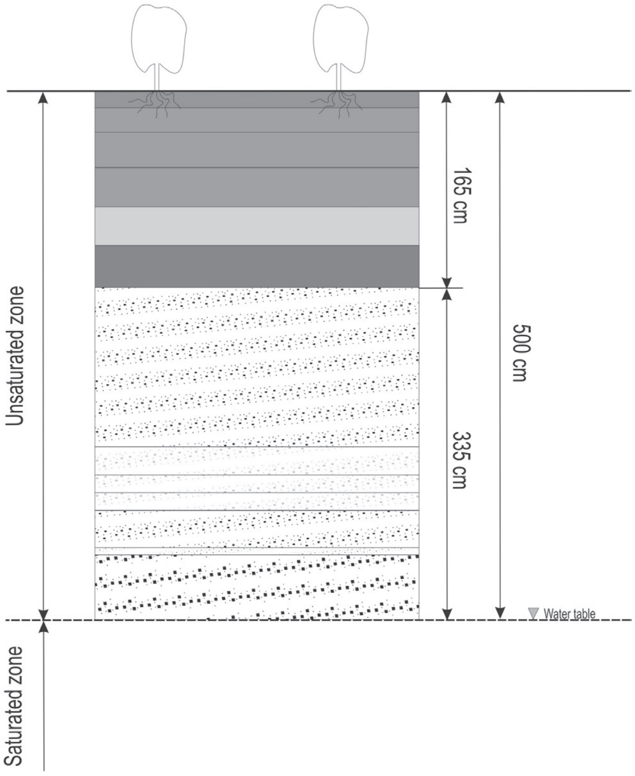


Figure 13: Sketch of the unsaturated zone profile at Kosnica.

exceeding the maximum permitted concentrations (BAČANI et al., 2007)[3]. Mobility of tetrachlorethylene (PCE), a dense non-aqueous phase liquid (DNAPL), is described as moderate (FETTER, 1988). In the presence of water, PCE will form a separate phase. The half-life degradation rate in groundwater is estimated to be between 1 – 2 years, based on aqueous aerobic biodegradation (HOWARD et al., 1991), but may be considerably longer under certain conditions.

Organic wastewater contaminants

Recent research, carried out in the Zagreb area, within the framework of the implementation of EU directives, is partly related to the determination of the qualitative status of the groundwater (BAČANI & POSAVEC, 2011)[7], and it confirmed that part of the aquifer system is endangered from organic pollutants. Organic wastewater contaminants include pharmaceuticals, surfactants, flame retardants, plasticizers and sterols. Pharmaceuticals represent the most studied class and are a diverse group of chemicals used as medicinal products for both humans and animals (HEBERER, 2002), as well as bioactive food supplements, cosmetics, fragrances, sunscreen agents, insect repellent and antiseptics (ELLIS, 2006). After application at hospitals or households, pharmaceuticals are excreted either in their parent form or as metabolites, and enter the aquatic systems via various pathways (FENT et al., 2006). The main sources of contamination are sewage-system leaching, sewage sludge, septic tanks, re-use of reclaimed domestic wastewater for irrigation and manure, contaminated landfill and accidental release. Most of them are not eliminated during wastewater treatment (JONES et al., 2005). Due to the polar structure of most pharmaceutical compounds they are not significantly adsorbed in the subsoil and may leach into the groundwater aquifers from contaminated surface water (HEBERER et al., 1997).

Sediment samples from Gorjak Creek (a small watercourse), were analysed by TERZIĆ et al. (2011) in order to identify organic contaminants present in the polar fraction of freshwater sediment. A number of different contaminants were successfully identified including various pharmaceuticals (chlorthalidone, warfarin, terbinafine, torsemide, zolpidem, azithromycin, desmethylazitromycin, erythromycin and dehydrated erythromycin).

AHEL & JELIČIĆ (2000) showed that solid waste in the Jakuševec landfill contains significant amounts of phenazone and propylphenazone. The attenuation of phenazone concentrations in the unsaturated zone and in groundwater seems to be much faster than the attenuation of propylphenazone. It can be assumed that the retention of phenazone compounds by aquifer sediments is low due to their high solubility in water which indicates that abiotic and/or biotic transformations are involved.

Radionuclides

Although the manufacturing, application and disposal of man-made radionuclides are under strict regulatory control and under normal conditions only minute amounts of radioactivity are released to the environment, nuclear accidents can cause large scale radioactive pollution. HORVATINČIĆ et al. (2011) reported significant increase of tritium activity in the Sava River in June 2010, as well as in groundwater (wells in the area of Petruševec) with a delay for 3–5 months related to the Sava River. This increase was explained by the release of tritiated water from the Krško Nuclear Power Plant 30 km upstream of Zagreb. Low level radioactive waste in a slag dump near the TETO thermal plant, as well as low radioactive waste from hospitals, also presents potential threats to groundwater.

Salts

The main anthropogenic source of chloride is NaCl used on roads to remove ice at temperatures around 0°C. Other anthropogenic sources of chloride can be dust-binding on roads, storage of salt, snow dumps, leakage from sewage and waste deposits, fertilizers and chemicals used at water and sewage treatment plants (LUNDMARK, 2003). Since chloride is a mobile compound, it will be transported to groundwater. Chloride stored in the unsaturated zone will, during snowmelt, be flushed into groundwater and so increase its chloride concentration (NYSTÉN, 1998).

3.3. Local conceptual model (LCM) – supporting GCM parameterization

Local Conceptual Model (LCM) supports development of the *Global Conceptual Model* (GCM) through characterization of two sites representing local conditions in the saturated (Stara Loza) and unsaturated (Kosnica) zones. As previously stated, the main goal is to estimate the risk of pollution on a local scale through the description of heterogeneities of the groundwater system and through identification of the relevant flow and solute parameters in both the unsaturated and saturated zones.

Only the design of site experiments is presented here together with an outline of the main results, since both experiments are still in progress.

3.3.1. Case studies

3.3.1.1. Experiments in the unsaturated zone

The aim of the unsaturated zone experiment is the identification of solute transport parameters, necessary for modelling the behaviour of potentially toxic metals. The catchment area of the Kosnica well field was chosen for the experiment because of its accessibility and results of previous investigations (ROMIĆ et al, 1995[8], 2004[5]; ALJINOVIĆ et al. (1995)[4]. A solute transport model will be the basis for the risk assessment of pollution with potentially toxic metals at a local scale. A prediction transport model of potentially toxic metals through the unsaturated zone is based on results of field and laboratory experiments.

Detail characterization of the unsaturated zone profile (5 m) at Kosnica, together with sedimentological, chemical and mineralogical analyses of soil and sediment samples were the basis for the experimental setup. The lower part of the profile consists of gravels with a sand component, while the upper part is dominated by gravels with silty to sandy material (Fig. 13). Fluvisols are developed on the top of the unsaturated zone profile. The texture of this type of soil is mainly loamy, in some parts clayey with loam, while the structure is mainly granular. Soil pH increases while electrical conductivity generally decreases with depth. The mineral composition of the profile samples includes quartz, calcite, dolomite and plagioclase in the lower part and clay minerals mainly in the upper part. Both the longitudinal dispersion coefficient (D_L) and the distribution coefficient (Kd) are the main parameters needed for modelling dispersion and sorption processes, respectively. These processes are obtained from laboratory results and will be verified by field and laboratory experiments.

In order to obtain the sorption parameters (distribution coefficient, Kd) of Cd, Pb and Zn, a laboratory batch experiment was performed on different soil samples taken from a pedological burrow. Multi element solutions of different concentrations were prepared from $Pb(NO_3)_2$, $ZnCl_2$ and $CdCl_2$. Current results from the sorption experiment showed that Pb had a slightly higher affinity for sorption on these soil textures than Cd and Zn (RUŽIČIĆ et al., 2012).

To obtain transport parameters and confirm this experiment, a field dispersion coefficient determination will be set up. Calcium chloride solution will be used because of its relatively low sorption potential and its suitability (SEUNTJENS et al., 2001; AKHTAR M.S. et al., 2003; DIŞLI, E., 2010).

Monitoring of parameters such as water content, electrical conductivity, soil water tension and concentrations of chlorides in percolating water is necessary for the calibration of models. Therefore, field measurement instruments are installed in a pedological burrow located in the proximity of the profile. Water content is measured using Time domain reflectrometry (TDR) equipment; electrical conductivity (EC) using EC-probes (Fig. 14a) and soil water tension using tensiometers (Fig. 14b).

The soil column laboratory experiment will also be used for determination of both the longitudinal dispersion coefficient (D_L) and the distribution coefficient (Kd). The longitudinal dispersion coefficient will be determined using breakthrough curves of chloride concentration. After the dispersion experiment, soil columns will be irrigated by metal solutions

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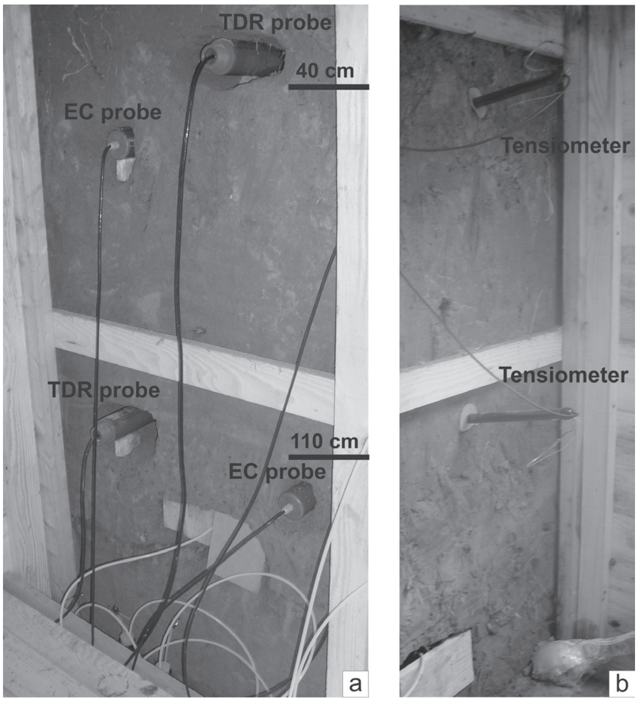

Figure 14: Pedological barrow: a) installed TDR and EC probes; b) installed tensiometers.

prepared from $Pb(NO_3)_2$, $ZnCl_2$ and $CdCl_2$ for determination of the distribution coefficients (Kd).

Transport of potentially toxic metals is modelled using HYDRUS 1D (ŠIMŮNEK et al., 1998). Figure 15 represents development of the solute transport prediction model using parameters obtained by laboratory and field experiments. Models 2 and 3 will be compared to evaluate the validity of soil column experiments in modelling solute transport for the field scale.

It should be stated that the experiment at Kosnica can support the parameterization of the soil and unsaturated zone of a large part of the groundwater system. About 88% of the area is covered by fluvisol which is also developed at Kosnica. Thus, field and laboratory experiments of fluvisol at Kosnica will provide the basis for a risk assessment of pollution with potentially toxic metals not only at the local scale, but also on a groundwater system scale.

3.3.1.2. Experiments in the saturated zone

The Stara Loza site is a well field previously used for Croatia's capital (Zagreb) public water supply (Fig. 16). It has not operated since 1997. The well field has 5 pumping wells distanced approximately 500 – 1000 m from the Sava River. 15 head observation wells (11 operating) and 7 concentration observation wells (4 operating) are concentrated in the surrounding area and are still in use for monitoring of ground water levels and quality.

Tracer experiments in the saturated zone at Stara Loza were conducted in order to determine longitudinal and transversal dispersion parameters as well as the effective (seepage) velocity. The obtained parameters would then be used as the input for the prediction models of contaminant transport in the Zagreb aquifer. The experiment was designed as a natural gradient tracer test, with one injection and fourteen observation wells, setup in two rows 25 and 50 m from the injection well, perpendicular to the ground water flow direction. Due to the expected transverse dispersivities of 0.25 – 1.25 m and associated transverse spread of 7.0 – 15.0 m for the first row and 10.0 – 22.0 m for the second row of observation wells, the distance between wells in the first and second rows was set to 1.5 m and 3.0 m, respectively. The artificial tracer used in the experiment was Uranine (Na-fluorescein) which was chosen because of its good sorption behaviour and small mass (LEIBUNDGUT et al., 2009). The mass of the tracer was calculated with respect to water volume and the detection limit of the tracer and the sampling frequency were calculated with respect to expected breakthrough times. For the first row of observation wells 25 m from the injection well, the sampling started 6 hours after tracer injection, and 12 hrs for the second row. The sampling campaign lasted

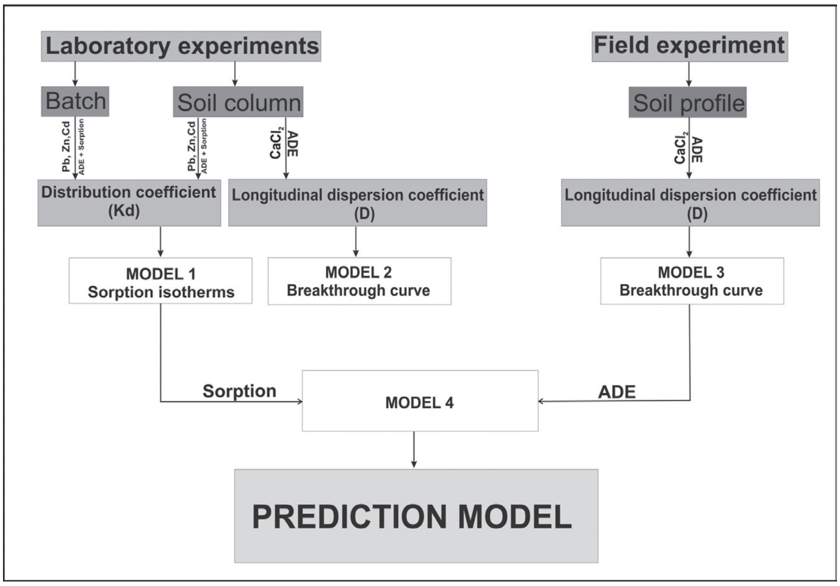

Figure 15: A scheme representing development of the solute transport prediction model, using parameters obtained by laboratory and field experiments.

for 40 days, during which 1598 groundwater samples were taken.

Analysis of the tracer experiment results have shown that a major part of the Uranine tracer bypassed the first row of wells possibly through small palaeomeanders or palaeochannels, but appeared in the second row of observation wells. This clearly suggests pronounced local scale heterogeneity of the aquifer and preferential flow paths, but there is a lack of scientific evidence to further support such an interpretation. Therefore further research including geophysics will be conducted. 2D and 3D electrical tomography, which is generally applied in geophysical research of aquifers (ŠUMANOVAC, 2007), is planned in order to gain a better understanding of lateral changes in lithological composition and hopefully detect preferential flow paths or palaeomeanders i.e. palaeochannels, which would give further insight into probable tracer migration paths.

4. CONCLUSIONS

The main purpose of developing a conceptual model of the Zagreb aquifer system is to apply a risk assessment procedure through linking the origin of pollution sources along environmental pathways to consequences for the status of groundwater dependent ecosystems (GDE) and groundwater itself. This will provide a baseline for achieving the environmental objectives, according to the WFD requirements. To that end, the conceptual model is intended to assess the risk of failing to achieve good groundwater and GDE status through qualitative and quantitative description of real system behaviour. At the current state of knowledge and understanding of the Zagreb aquifer system, it is evident that a number of iterations in the development of the conceptual model will be needed in order to accurately describe all the relevant processes within the groundwater system and pressures on it. This is particularly recognized in attempts to describe the heterogeneities of the groundwater system components at different scales and to quantify the significance and effects of point and diffuse pollution sources on the system.

Taking into consideration knowledge gaps in the understanding of groundwater systems, a coherent approach to assess a risk for a wide range of source-pathways-receptor relationships at different scales is applied by dividing the conceptual model in two parts: a) *Global Conceptual Model* (GCM), which gives an insight into the processes and pressures at the level of the groundwater system and b) *Local Conceptual Model* (LCM), which supports parameterization of the whole groundwater system through the description of heterogeneities of the system components at a site scale and through identification of the relevant flow and solute parameters in both the unsaturated and saturated zones. The reasoning behind this approach is to use the conceptual model not only to assess the risk of failing to achieve good status of the groundwater and GDE bodies within the Zagreb aquifer system, but also to satisfy the preventative/limitation objectives in the WFD and GWD, by estimating the risk of pollution at a local scale. Furthermore, this concept helps to extend the primary purpose of the conceptual model by developing an effective tool for groundwater management of the Zagreb aquifer system, particularly through creation of the basis for delineation of groundwater protection measures

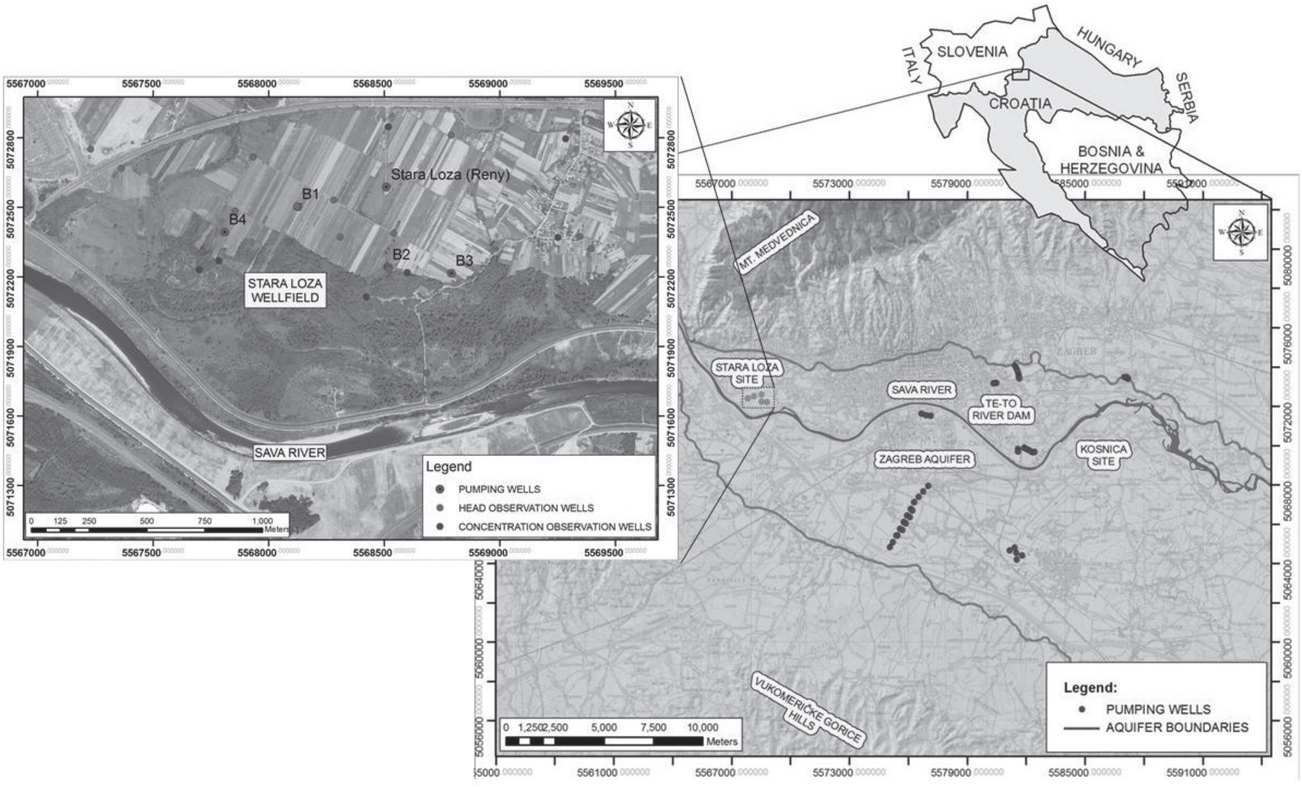

Figure 16: Stara Loza site.

at different scales and through communicating conditions in complex groundwater systems with experts, policy makers and the general public in an understandable way.

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