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A Municipal Management Plan for Urban Groundwater Investigation and Remediation

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Abstract: The project MAGPlan, funded by the European Commission under the program LIFE+2008, aims to develop and implement an optimal strategy for integral groundwater investigation and efficient remediation of key sources of pollution for the whole inner city area. The first investigations included descriptions of the complex hydro-geological system of the eight aquifers, drilling of monitoring wells and set up of the conceptual contaminant model. A conceptual contaminant model was developed to describe the status quo of the present contaminant distribution, as well as the basic processes controlling contaminant migration within the observed aquifers. This included the characterization of redox conditions and natural chlorinated hydrocarbons degradation processes, as well as age dating, forensic interpretations with respect to the contaminant origin, and determination of radioactive and stable isotopes. Further on, a numerical unsteady groundwater flow and contaminant transport model were developed, which enabled a quantitative description of the mass balance within the project area. The unsteady numerical model provided detection of migration paths in the valley of Stuttgart and identification of key sources of pollution.

Key words: Chlorinated hydrocarbons, hydro-geology, natural degradation, forensic methods, conceptual model, 3D numerical contaminant transport model.

1. Introduction

For decades groundwater in Stuttgart has been impacted by the infiltration of volatile CHC (chlorinated hydrocarbons). Low level concentrations have been detected even in Stuttgart's local mineral water springs with a capacity of 500 L/s, used for spa activities. Although tremendous efforts have been taken to improve the situation by remediating single sites, the mineral springs are still affected by tetrachloroethene and trichloroethene. Pathways of contaminants on their way to the mineral springs are largely unknown [4]. Geologic setting in the project area of 26 km² within the city centre is extremely complex with eight aquifers, a multitude of tectonic faults as well as extensive karst and subrosion processes. To cope with this complex situation, the project MAGPlan (http://www.MAGPlan-life.eu/) has selected a targeted strategy based on an integral approach, already developed in preceding projects like INCORE and MAGIC and now further expanded and improved to cope with project size and demands.

2. Conceptual Contaminant Model

A comprehensive data collection and exploring archives of more than 25 years municipal site investigation showed that tremendous amount of data was available for evaluation and interpretation.

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However, there were still some knowledge gaps and targeted investigations in selected areas were performed. Drilling and installation of 12 groundwater monitoring wells (Fig. 1) were specifically placed in zones with lack of knowledge about (1) the level of groundwater contamination, (2) flow directions, and (3) contamination dispersion. Some of the drillings reached a depth of 90 m up to the karst aquifer, which discharged the mineral springs with a rate of 500 L/s [10]. Additionally, 96 h immission pumping tests were carried out simultaneously in pairs of wells. The results showed crucial insights into the migration of contaminants within deeper aquifers and especially within the zones characterised by particularly complex hydraulic conditions [8].

The geology of the MAGPlan project area is mostly characterized by heterogeneities, extremely complex vertical interactions between the eight groundwater

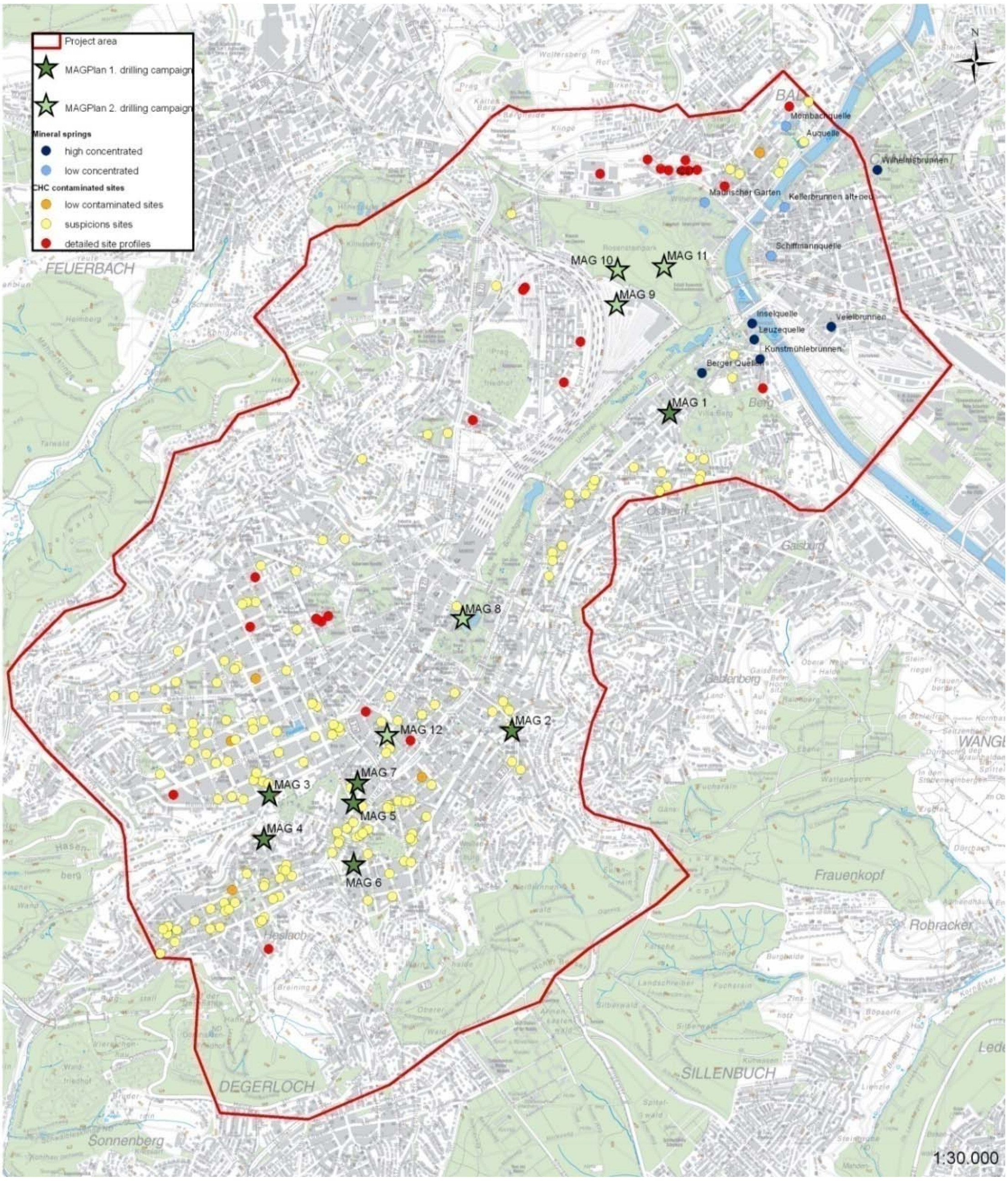

Fig. 1 Project area MAGPlan within Stuttgart city, drilling wells, mineral springs and contaminated sites.

aquifers, many tectonic faults and extensive karst characteristics. The vertical structuring of aquifers within the project area can be described by the strata shown in Fig. 2.

The hydraulic system of the subjected area is very complex. Vertical dislocations of about 10 m appear at the faults indicating high heterogeneity and high permeability contrasts. Moreover, the hydraulic data in deeper aquifers are more unreliable due to generally less deep drillings and lower density of geological data. In order to estimate hydraulic permeability of the aquifers, all existing analysis of pumping tests and hydraulic tests were complied, verified and re-evaluated. Altogether, more than 1,600 sets of experimental data were obtained. It can be concluded that the estimated hydraulic permeabilities vary considerably, even more than 10 orders of magnitude (10 E-2 to 10 E-10).

A conceptual contaminant model was developed to describe the state of the present contaminant distribution within the observed aquifers. Furthermore, the basic processes controlling contaminant discharge were determined. This includes the following:

(1) The characterization of hydrochemistry and redox conditions (oxygen, nitrate, sulfate, chloride and methane were chosen and plotted on maps for each aquifer).

(2) Volatile CHC were measured in monitoring wells, whereas the segmentation of the pie chart, showed in Fig. 3, is based on the molar percentage of the total concentration and shows the proportion of the four chloroethenes: PCE (tetrachloroethene, red), TCE, blue (trichloroethene), cis-1, 2-DCE (dichloroethene, green) and VC (vinyl chloride, yellow). The Fig. 3 shows the dominance of PCE in the contaminated sites in the centre of Stuttgart as red hot spots. By contrast, the north-eastern part of the project area (outlet of the project area) is dominated by the less chlorinated CHC metabolites TCE (blue) and DCE (green) with sporadic VC (yellow) occurrence. The area around the city centre (middle of the project area) shows considerably lower CHC concentrations.

(3) Natural CHC degradation processes can occur under several different conditions. By reductive dechlorination, which is so far the best known

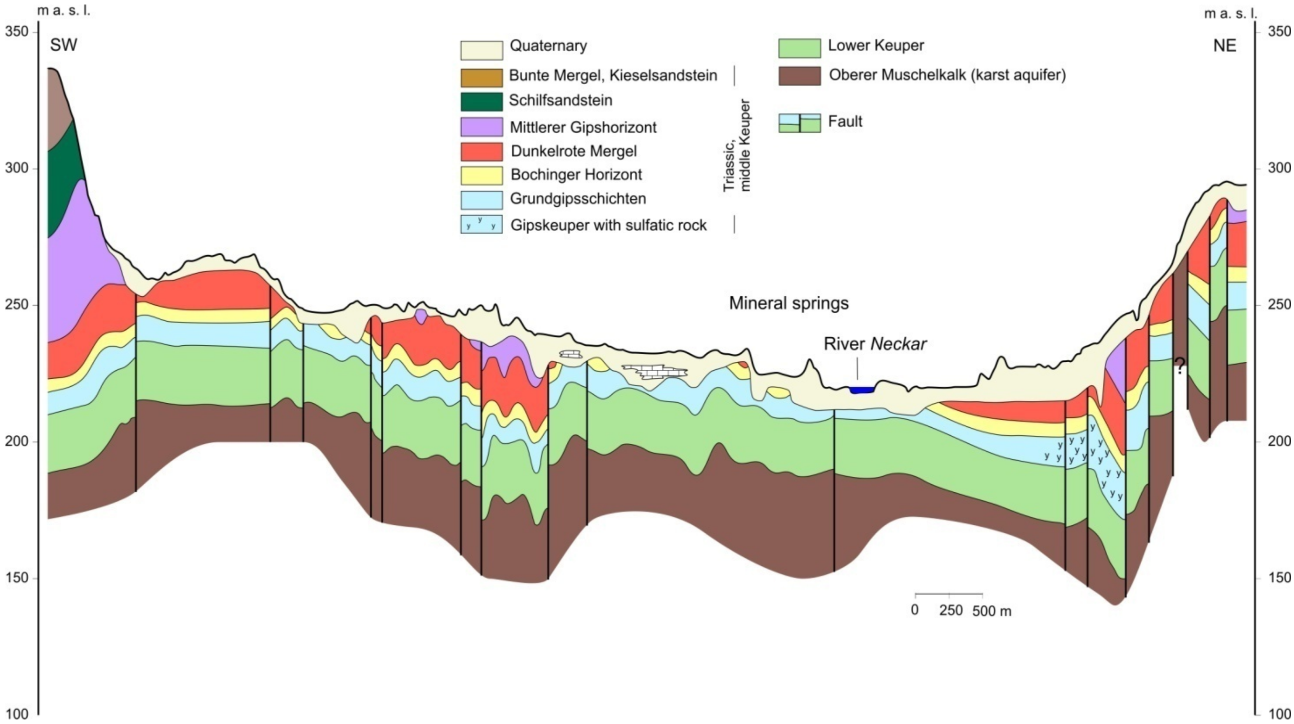

Fig. 2 Geological structuring of aquifers.

degradation process, one chlorine atom successively gets exchanged with one hydrogen atom in the order from PCE to TCE to DCE (most often cDCE and tDCE) to VC and finally to ethane [1]. Ethene is then partly mineralized by an intermediate step to ethane before being further mineralized to the end products, water and CO_2. The process of reductive dechlorination requires a sufficient supply of hydrogen as an electron donor. Hydrogen gets released during the fermentation of easily degradable organic substances which is why reductive dechlorination is dependent on a sufficient supply of organic matter (like acetate, lactate, glucose or ethanol, toluene, etc.). Fermentation though requires the presence of suitable microorganisms. According to current knowledge no aerobic degradation of PCE occurs in groundwater. The initial degradation step to break down PCE occurs only under anaerobic conditions [1].

Within the project area several examples of different biodegradation cases were observed. In western part of the city former dry cleaning company contaminated the groundwater with PCE (Fig. 3) up to 92.000 µg/L. Almost no changes in the pollution spectrum have been observed, neither temporal nor spatial. Due to aerobic conditions no metabolites of reductive dechlorination occurred.

In the northern part of the city on the place of former junkyard and mineral oil storage, the CHC concentrations reached maximum 3.435 µg/L, consisting mainly of low chlorinated metabolites DCE and VC, as shown in Fig. 4. It was assumed that the petroleum hydrocarbons, which were also to be found in the groundwater at this site, initiated reductive dechlorination.

Aerobic degradation was assumed at several monitoring wells, for example in mineral spring with low mineral content "auquelle". Groundwater is aerobic and the decline in TCE was observed, while PCE concentrations remained constant, which indicated selective aerobic degradation.

In several cases, temporal varying conditions were observed as well as no reductive dechlorination despite anaerobic conditions.

(4) Anthropogenic trace substances, SF6 (sulfur hexafluoride) and CFC (chlorofluorocarbon), were analyzed in the monitoring wells. Freon F12 was preferred for use in fridges [11], F113 was used for textile cleaning purposes, and Freon 11 was widely used as a propellant and as a cleaning agent [7]. Contaminated sites can be differentiated by their characteristic CFC signature, while usually one of the three analyzed freons dominates. In this way, the migration paths of each CFC plume originating from the marked contaminated sites were determined.

The anthropogenic trace gas SF6 has been increasingly emitted into the atmosphere since the 1960's. Due to its stability and persistency the amount of SF6 within the atmosphere is constantly rising [2]. The age of groundwater is feasible if the quantity of SF6 input into the groundwater via precipitation is known [6]. In this way, all available SF6 data from the project area were evaluated and assembled into distribution maps of the layers. The results showed that the oldest groundwater of more than 40 years appear in the area surrounding the mineral springs, as well as south of the springs.

Based on all gained information and performed analysis, with the aim to characterize the key sources of pollution within the project area, detailed site profiles were complied. The project area comprised more than 800 contaminated sites and areas suspected to be contaminated. By reduction of sites which are not relevant regarding CHC contamination, 186 sites remained. A distinction was made between sites which are not yet technically examined with likely CHC contaminations (156, shown in Fig. 1 as suspicions sites) and sites which are technically investigated with high CHC contamination (30, shown in Fig. 1 as low concentrated sites). By connecting the adjacent contaminated sites within the project area, 20 key sites of pollution were defined to be examined in detail. These site profiles characterize the contaminated key

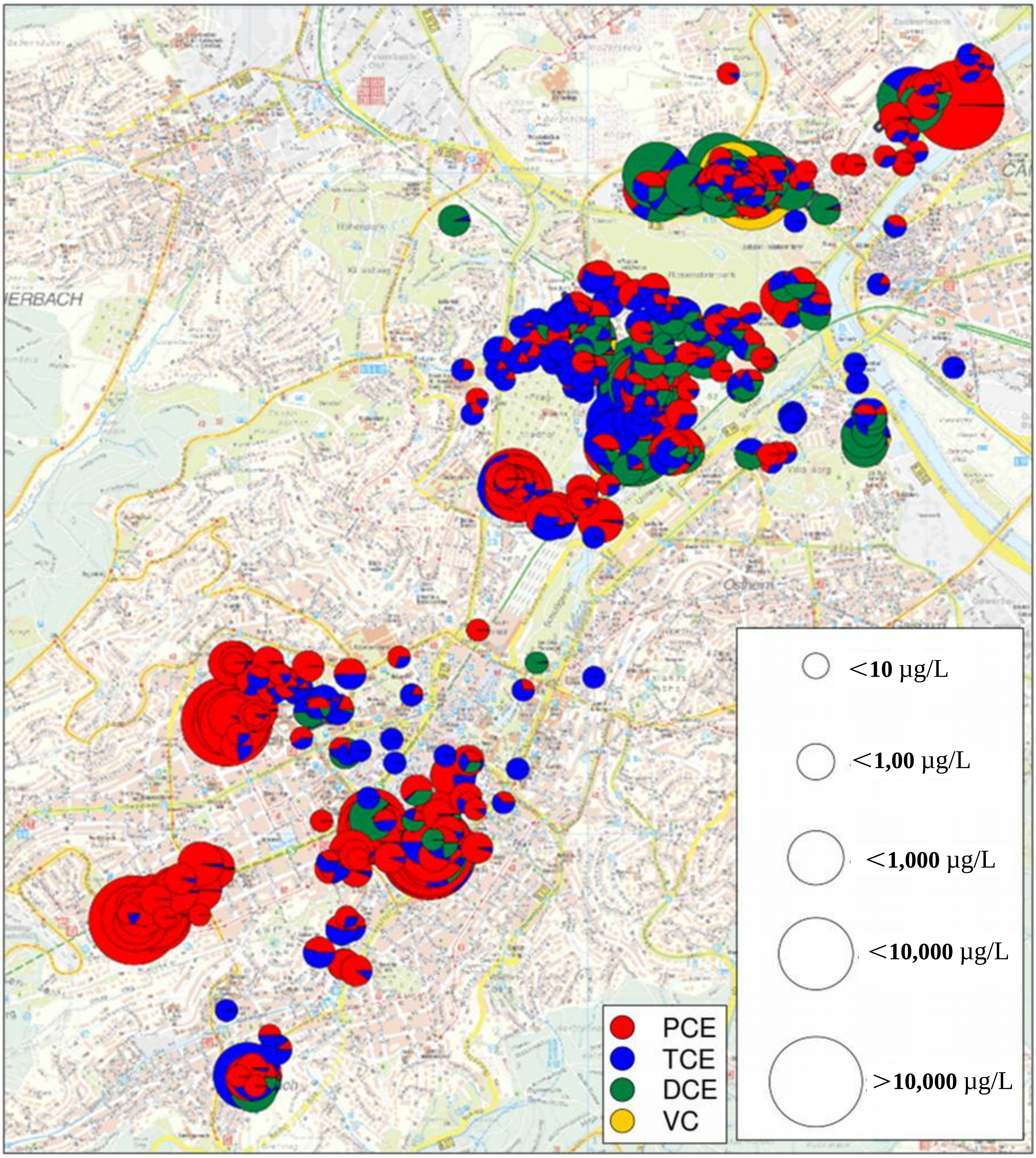

Fig. 3 CHC distribution within the project area (µg/L).

sites according to: their pollution history, contaminant potential, the presence of individual CHC components, temporal CHC patterns and spatial distribution. Additionally, degradation processes and redox conditions, and information about previous removal of contamination by remediation are included as well. Even though the hydrogeology is complex, the site profiles allow a good overview of the respective contaminant situation and support the data transfer to the numerical model.

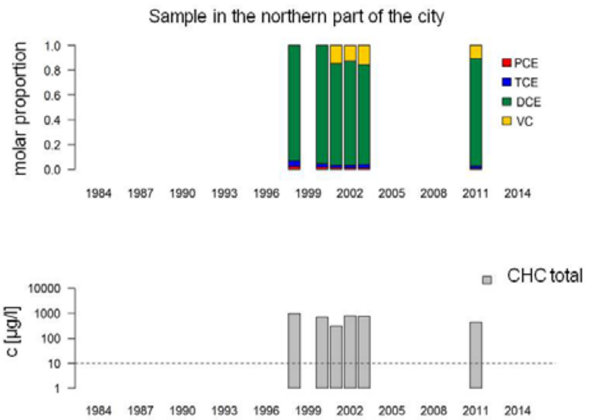

Fig. 4 Molar proportions of CHC of the sample taken in the northern part of the city.

3. Numerical Model

The groundwater flow and contaminant transport were simulated by the finite-difference 3D MODFLOW software, developed by United States Geological Survey [3]. Model development was carried out according to the hydro-geological conceptual model. It considered all relevant information for the hydro-geological structure and for the flow conditions which are proven by numerous groundwater observation wells and by long time series of groundwater levels and spring discharges [5].

The numerical concept has required a layer-based model structure, where different geological units were assigned to at least one model layer. Some of the geological strata were divided into more model layers by considering the: (1) separation between higher permeable layer and the lower permeable parts; (2) separation due to vertical leaching that has enabled a vertical differentiation of partly leached sections. Based on this concept, 17 model layers were defined for eight geological strata.

A horizontal model discretisation of 10 m by 10 m was applied for the central part of the modelled area, whereas model cells with 50 m cell lengths were applied for the marginal areas. Model boundaries were defined according to natural boundary conditions. The flow model calibration was performed for steady state conditions for two parameters: hydraulic conductivities and leakage coefficients at mineral springs and River Neckar. The calculated values of piezometer heads and spring discharges were compared to the measured ones in order to achieve the best fit (Fig. 5). Moreover, the water mass balance of karst aquifer was compiled.

Based on the numerical groundwater flow model a contaminant transport model was developed to firstly validate the groundwater flow model using transport information from tritium, SF6 and results from tracer tests. The second step comprised the extension of the contaminant transport model to represent the CHC contamination within the project area of MAGPlan.

To achieve this, the sum of all CHC components was considered first. The simulation was done based on the equivalent PCE concentrations which result from the stoichiometric ratio of the involved CHC components. The aim of the simulation was to identify the main CHC input areas by varying the input rates within the key sites (for which site profiles were compiled) within a calibration process. CHC data of wells within the MAGPlan area since 2008 were available to use as reference values. Altogether, there were 748 measurements from all aquifers representing snapshots in time. Additionally, 108 hydrographs of CHC concentrations from the project area (since 1985) were used to model temporal developing. Again, this data

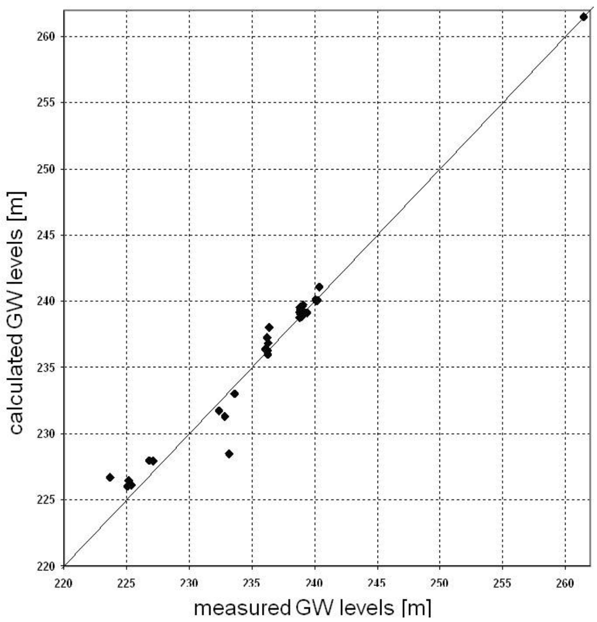

Fig. 5 Calibration results of piezometer heads (m a.s.l.) in karst aquifr.

were compared to the calculated CHC concentrations and were especially useful for the determination of the temporal development of the CHC inputs at the contaminated sites.

The input of CHC's was defined by detailed site profiles compiled for the key contaminated sites and was quantified by a calibration process. Thus, the results of the calibration process are the CHC release rate differentiated by each site and the identification of possible further CHC input sites (with regard to the about 160 potential CHC contaminated sites within the project area, see Fig. 1).

During the calibration process the flow field within the project area was refined by adjusting the conductivity distribution locally. The result was that the flow field (1) matched the measured distribution of contaminants; (2) corresponded to the exchange within hydro-geological units; (3) correlated with the synoptic map of CHC plumes.

The unsteady CHC transport simulation for the equivalent PCE concentrations comprised the period from 1960 to today. In this simulation, mineralisation of CHC's was excluded. A comparison between measured and calculated CHC concentrations enabled the identification of those areas in which the calculated CHC values downstream of the input site are significantly higher than those actually measured. That gave evidence for ongoing degradation processes which resulted in a reduction of the entered CHC mass.

The comparison of measured versus calculated CHC concentrations showed that fundamental transport processes were already covered by the current transport model. The model described the temporal dynamics corresponding to the measured hydrographs and displayed the distinct differences between the maximum CHC concentrations within the observed aquifers. The results showed medium to maximum concentrations within the middle keuper aquifers range between 1,000 µg/L and 50,000 µg/L, within the lower keuper between 100 µg/L and 10,000 µg/L and within the upper Muschelkalk of upper karst aquifer less than 100 µg/L. As an example, numerical results of one detailed site profile for middle keuper aquifer are shown in Fig. 6. Calculated CHC concentration distribution at one contaminated site indicated the plume spreading within the city area.

The model yielded an adequate reproduction of the measured CHC concentrations as well as a mass balance of the CHC transport within the observed aquifer system since 1960. It became apparent that in

Fig. 6 Calculated CHC concentration distribution.

total about 11 to 13 t PCE equivalent has been entered into the aquifer since 1960. Furthermore, the modelling process has shown that an input of 300 kg to 400 kg CHC per year during the 1980's (before remediation started) can be assumed. Currently 50 kg to 100 kg of CHC per year is discharged. The remaining difference of 200 kg/a to 350 kg/a can be ascribed to the removal by on-going remediation within the aquifer. This calculated amount of removal by remediation corresponds to the average measured removal by remediation since 1988 of 268 kg CHC per year.

The total removal by remediation since 1988 was measured to be 4.243 kg with removal by the model calculated at about 4,000 kg to 4,500 kg. Likewise, the calculated removal masses generally are matched when looking at individual remediation sites, thus, enabling a plausibility check and validation of the simulated results. Greater variances arose where CHC phase exists because the removal of CHC phase was considerably higher than the removal of dissolved CHC as assumed by the model [9].

4. Conclusions

The project MAGPlan "management plan to prevent threats from point sources on the good chemical status of groundwater in urban areas", funded by the European Commission under the program LIFE+2008, is running from 2010 to 2015. In this paper, the main findings and results of the project are presented.

With the aim to characterize the hydraulic properties of the aquifer system in Stuttgart, both, classical methods (data evaluation, drillings, pumping tests, reference measurements at certain dates) and innovative methods (anthropogenic tracers, isotopic fingerprinting, etc.) were applied. With help of the conceptual contaminant model, the fundamentals of contaminant migration within the project area were established. The findings are documented in a conceptual model, which is ongoing updated, and was incorporated into a numerical groundwater model.

Several hundred CHC analyses were evaluated by plotting them onto distribution maps for each aquifer. Additionally the time series of each well were evaluated. The illustration as molar weighted pie charts allowed a quick overview of the involved CHC single components and potential spatial relationships. In contrast, bar graphs of mean annual values show temporal shifts and therefore possible changes in redox conditions. In order to characterise hydro-chemical and redox conditions, the CHC biodegradation potential, groundwater age and hydraulic connections anorganic parameters, redox indicators, isotopes and anthropogenic trace substances were used.

From a variety of more than 800 potentially contaminated sites within the project area less than 200 sites were screened as potential and relevant CHC input sites. Out of these 200, the 20 most CHC contaminated sites were examined more in detail and site profiles giving a compact overview of the contamination situation of these key sites were made. The site profiles have proved to be a valuable instrument in the development and calibration of the numerical transport model because these sites are responsible for the main CHC input into the aquifer system of the project area. The potential contribution of the remaining 160 sites not yet technically examined will be proved in more detail by the numerical transport model and thus other potential CHC input sites within the project area will be identified.

By means of the numerical transport model the CHC release rates of the most CHC contaminated sites could be determined. Afterwards, the further migration of contaminants was simulated. The model has given new insights into contaminant input into the aquifer system which in the last 50 years totals about 12 t of CHC. So far, groundwater remediation has removed about 4 t CHC out of the system.

The graphic presentation of hydro-geological, redox and chemical information together with the modelled results of the project area enabled, for the first time, a closed spatial picture of the whole inner city of Stuttgart. However, it also raised new issues. The high degree of complexity of the regarded aquifer system (fractured and karst aquifer properties, hydraulically relevant tectonics), the size of the project area, and the fact that for the deepest and most important aquifer, the fewest dataset is available, imply a challenge for further investigation and modelling.

In the next step, evaluation of the microbial degradation potential, laboratory tests to prove the microbial proportion on the decrease in concentrations of selected CHC plumes, and in-depth evaluation of carbon isotope analysis of the CHC-moleculethe will be performed. Furthermore, combined tracer test within the karst aquifer in the immediate inflow area to the mineral springs will be performed in order to eliminate uncertainties of the pressure head distribution and verify the inflow directions in this area.

The transport model will be extended to a reactive multi-species-model which will allow the consideration of transport relevant processes like biodegradation and adsorption. This tool will enable a more precise assessment of the contamination input sites, additional to the known CHC hot spots (site profiles) and subsequently, the possible polluters will be identified.

Acknowledgments

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