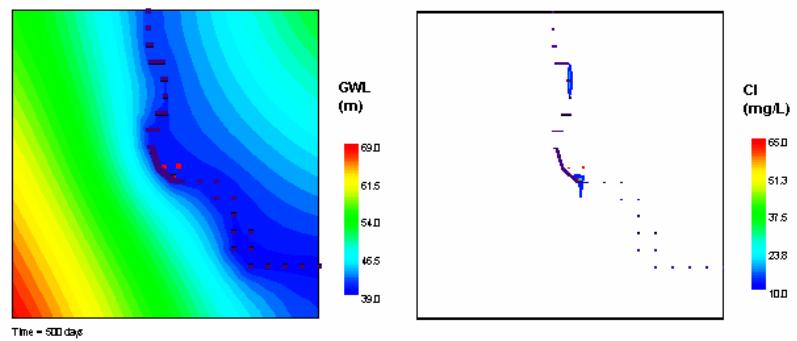




Development of a geochemical transport model for the Gatehampton abstraction site using PHAST

Groundwater Resources Programme

Open Report OR/09/005



Development of a geochemical transport model for the Gatehampton abstraction site using PHAST

The National Grid and other Ordnance Survey data are used with the permission of the Controller of Her Majesty's Stationery Office.
Licence No:100017897/2009.

Keywords

Report; groundwater; geochemical transport; PHAST; Gatehampton; Chalk.

Front cover

Simulated distributions of groundwater heads and chloride concentrations visualised in Modelviewer

Bibliographical reference

C ABESSER. 2009. Development of a geochemical transport model for the Gatehampton abstraction site using PHAST. *British Geological Survey Open Report*, OR/09/005. 53pp.

Copyright in materials derived from the British Geological Survey's work is owned by the Natural Environment Research Council (NERC) and/or the authority that commissioned the work. You may not copy or adapt this publication without first obtaining permission. Contact the BGS Intellectual Property Rights Section, British Geological Survey, Keyworth, e-mail ipr@bgs.ac.uk. You may quote extracts of a reasonable length without prior permission, provided a full acknowledgement is given of the source of the extract.

Maps and diagrams in this book use topography based on Ordnance Survey mapping.

BRITISH GEOLOGICAL SURVEY

The full range of our publications is available from BGS shops at Nottingham, Edinburgh, London and Cardiff (Welsh publications only) see contact details below or shop online at www.geologyshop.com

The London Information Office also maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

British Geological Survey offices

BGS Central Enquiries Desk

☎ 0115 936 3143 Fax 0115 936 3276
email enquires@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

☎ 0115 936 3241 Fax 0115 936 3488
email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131 667 1000 Fax 0131 668 2683
email scotsales@bgs.ac.uk

London Information Office, Natural History Museum, Cromwell Road, London SW7 5BD SW7 2DE

☎ 020 7589 4090 Fax 020 7584 8270
☎ 020 7942 5344/45 email bgslondon@bgs.ac.uk

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

☎ 029 2052 1962 Fax 029 2052 1963

Forde House, Park Five Business Centre, Harrier Way, Sowton EX2 7HU

☎ 01392 445271 Fax 01392 445371

Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

☎ 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

☎ 028 9038 8462 Fax 028 9038 8461
www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

☎ 01793 411500 Fax 01793 411501
www.nerc.ac.uk

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

Acknowledgements

The author would like to thank Andrew Hughes and Chris Jackson (BGS) for their help during the development of the model and Chris for providing the data for the flow model. Other members of the BGS modelling group are thanked for their comments and support during project meetings. I also thank Majdi Mansour (BGS, project leader) and the BGS science budget programme for providing the time and resources that allowed this work to be carried out. Finally, thanks to the creators of PHAST (incl. Model Viewer) and PHREEQC, for making their software freely available and for helping with problems and questions.

Contents

Acknowledgements	i
Contents	ii
Summary	iv
1 Introduction	1
2 The PHAST flow model	2
2.1 Formulation of the conceptual model	2
2.2 Model definition	4
2.3 Development of the flow model	10
2.4 Summary and discussion of results from flow and transport modelling	23
3 The geochemical model	25
3.1 Underlying assumptions	25
3.2 Data availability and end-member selection	25
3.3 PHREEQC modelling	26
3.4 PHAST modelling	28
3.5 Summary and discussion of results from Geochemical modelling	29
4 Conclusions and recommendations	32
4.1 The reactive transport model	32
4.2 PHAST as a modelling tool	33
Appendix 1 PHAST model code for MOD4 (.trans.dat file)	35
Appendix 2 PHREEQC input file for inverse modelling	40
Appendix 3 Chemistry input file for MOD4	41
Appendix 4 Geochemical output from PHAST model MOD4	43
References	44

FIGURES

Figure 1	Location of Gatehampton model area and the Gatehampton abstraction site....	3
Figure 2	Conceptual model of the study area and parameter values applied during model development and in the final model (arrows indicate good connectivity)	3
Figure 3	Discretization of model area in PHAST (node-centred mesh) (after Neumann and Kinniburgh, 2004)	4
Figure 4	Model grid of numerical model including boundary conditions (green square marks area of grid refinement)	5
Figure 5	Spatial discretization and parameterization of models developed during step 1	11

Figure 6	Spatial discretization and parameterization of MOD2b and MOD2c developed during step 2.....	13
Figure 7	Spatial discretization and parameterization of MOD3 developed during step 3	15
Figure 8	Zones of gravel coverage along the river valley as defined in MOD4	20

TABLES

Table 1	Solution composition during development of the flow model (*Ca concentrations are used to achieve charge balance of the solution).....	9
Table 2	Well properties	9
Table 3	Comparison of model output from model development step 1	12
Table 4	Comparison of model output from model development step 2	14
Table 5	Simulation results with adjusted borehole screen depths.....	15
Table 6	Results from modelling scenarios 1 to 3 of model develop step 3 (MOD3)... <td>17</td>	17
Table 7	Coordinates for gravel zone definition in MOD4	19
Table 8	Model outputs from MOD4 Scenario 1 and 2 (natural flow without/with recharge).....	21
Table 9	Model outputs from MOD4 Scenario 3 and 4 (different pump rates + recharge).....	22
Table 10	Proportion of river water in the abstraction boreholes at different pump rates calculated from simulated Cl concentrations	23
Table 11	Composition of the precipitation, river and groundwater end members (before accounting for soil processes)	26
Table 12	Model solutions calculated by inverse model (using two end members)	28
Table 13	Comparison of results from the PHAST simulation with measured groundwater chemistry (EM = end member)	29

BOXES

Box 1	Definition of Leaky boundary conditions in PHAST.....	7
Box 2	Definition of flux boundary conditions in PHAST	8
Box 3	Definition of river nodes in PHAST	8
Box 4	Definition of wells in PHAST	9
Box 5	Definition of initial conditions in PHAST	10

Summary

This report describes the development of a coupled geochemical transport model for the Gatehampton abstraction site. The work was undertaken as part of the BGS science budget programme and represents an addition to the detailed groundwater flow modelling of the area around Gatehampton undertaken by (Hughes et al., 2005; Jackson et al., 2006a; 2006b). The model was created in PHAST with the aim to provide a tool for identifying the water sources at the Gatehampton abstraction boreholes and for investigating aquifer-river interactions at the site. At the same time, the ability of PHAST to simulate such site-scale problems was tested and this is the focus of this report. The resulting model is very simple, compared to the complexity of the simulated system, but it is able to reproduce the changes in groundwater chemistry that were observed between the abstraction site and borehole located upstream of the site at Wood Farm. Additional simulations, using an inverse mass balance modelling approach were included in the model development to help the identification of potential water sources. The results suggest that additional sources (e.g., anthropogenic/agricultural inputs) influence the groundwater chemistry and need to be considered in future simulations. However, these results are only preliminary and a number of steps need to be implemented to improve the model and to test the validity of the underlying model assumptions.

1 Introduction

The work presented in this report is an addition to the detailed groundwater flow modelling of the area around the Gatehampton groundwater source (Hughes et al., 2005; Jackson et al., 2006b). The groundwater abstraction site at Gatehampton, operated by Thames Water, is one of the largest, if not the largest Chalk abstractions in the UK. The site consists of seven boreholes drilled into the Chalk situated on the banks of the River Thames in the Goring Gap. Detailed modelling of groundwater flow at the site and the surrounding area has been carried out by Hughes et al.(2005) and Jackson et al.(2006b). This work has identified a number of possible sources of water at Gatehampton, including

1. River water from the Thames
2. Gravel groundwater from upstream of the abstraction site
3. Chalk groundwaters (originated from either the west or the east of the Thames).

Determining how these sources contribute to the abstraction at the Gatehampton boreholes is important to enable a better understanding of how the groundwater system operates within the vicinity of these abstraction boreholes and to predict how the system responds to pumping.

The work described here makes use of existing geochemical data to infer the sources of groundwater at the abstraction boreholes. It integrates geochemical with flow modelling through the development of a coupled geochemical transport model of the abstraction site using the modelling package PHAST. PHAST is one of the first three-dimensional models that is able to simulate complex geochemical interactions in a three-dimensional flow field. It allows the simulation of geochemical interactions between the water and the aquifer and therefore can consider changes in source water composition along the flow path.

In addition to providing a tool for identifying the source(s) of the groundwater at the abstraction boreholes and investigating the interactions between the river and the groundwater at the abstraction site, this study also assesses the suitability of PHAST for modelling site-specific problems such as this.

The work is presented in four parts. The first part gives an introduction to the project and the context of the work. The second part describes the development of the flow model in PHAST and presents the preliminary results. The third part describes the geochemical modelling. It includes a description of the inverse mass balance modelling in PHREEQC that was carried out to help identifying water sources at Gatehampton. It further describes the development of the reactive transport/geochemical model in PHAST and presents the preliminary results. The final part discusses the results of the flow and geochemical modelling. It summarises the limitation of the model and outlines steps for the further development and improvement of the model. Finally, the performance of the PHAST model is assessed with regards to its suitability for modelling site-specific problems such as the one presented here.

2 The PHAST flow model

PHAST is a three-dimensional groundwater-flow and solute-transport simulator with capabilities to model a wide range of equilibrium and kinetic geochemical reactions. The flow and transport calculations are based on a modified version of the HST3D model (Kipp, 1987) that is restricted to constant fluid density and constant temperature. The geochemical reactions are simulated with the geochemical model PHREEQC (Parkhurst and Appelo, 1999), which is embedded in PHAST.

The combined flow, transport and geochemical processes are simulated by three sequential calculations for each time step. First, the flow velocities are calculated, followed by the transport of all chemical components and lastly, the calculation of the geochemical reactions.

PHAST is a node-centred finite-difference model. It is restricted to saturated groundwater flow. The numerical implementation of the equations used for flow and transport calculations in PHAST is detailed in Parkhurst et al. (2004) along with the equations used for calculating the chemistry.

A wide range of geochemical reactions can be coupled to the transport calculations, including 1) aqueous complexation, 2) mineral equilibrium, 3) surface complexation, 4) ion exchange, 5) solid-solution equilibrium, 6) gas phase equilibration and 7) general kinetic reactions. Essentially, any modelling capability available in PHREEQC can be employed in PHAST, with the exception that geochemical simulations in PHAST are restricted to constant temperature and constant density systems and cannot account for density-dependent flow. A detailed description of PHREEQC's modelling capabilities and relevant equations are given in Parkhurst and Appelo (1999).

2.1 FORMULATION OF THE CONCEPTUAL MODEL

A simple hydrogeological model was developed for the area at and around the Gatehampton study site (Figure 1). The model is based on findings from Jackson et al. (2006a) to whom the reader is referred to for a detailed descriptions of the geological and hydrogeological settings at the study site.. The model is illustrated in Figure 1 and consists of three hydrogeological units: (1) the lower Chalk, (2) the fractured (upper) Chalk and (3) gravels. The gravel aquifer is limited to the river valleys, covering about 500m either side of the river with a maximum thickness of 10 metres at the Gatehampton site (Jackson et al., 2006a).

The conceptual model assumes a good hydraulic connection between all three aquifer units. It also assumes a good connection between the river and the underlying gravel aquifer, although Jackson et al. (2006a) suggest that this connection may vary spatially as well temporally. The hydrogeological properties of the three aquifer units are included in Figure 2 and are based on values given in Jackson et al. (2006b) and Allen et al. (1997).

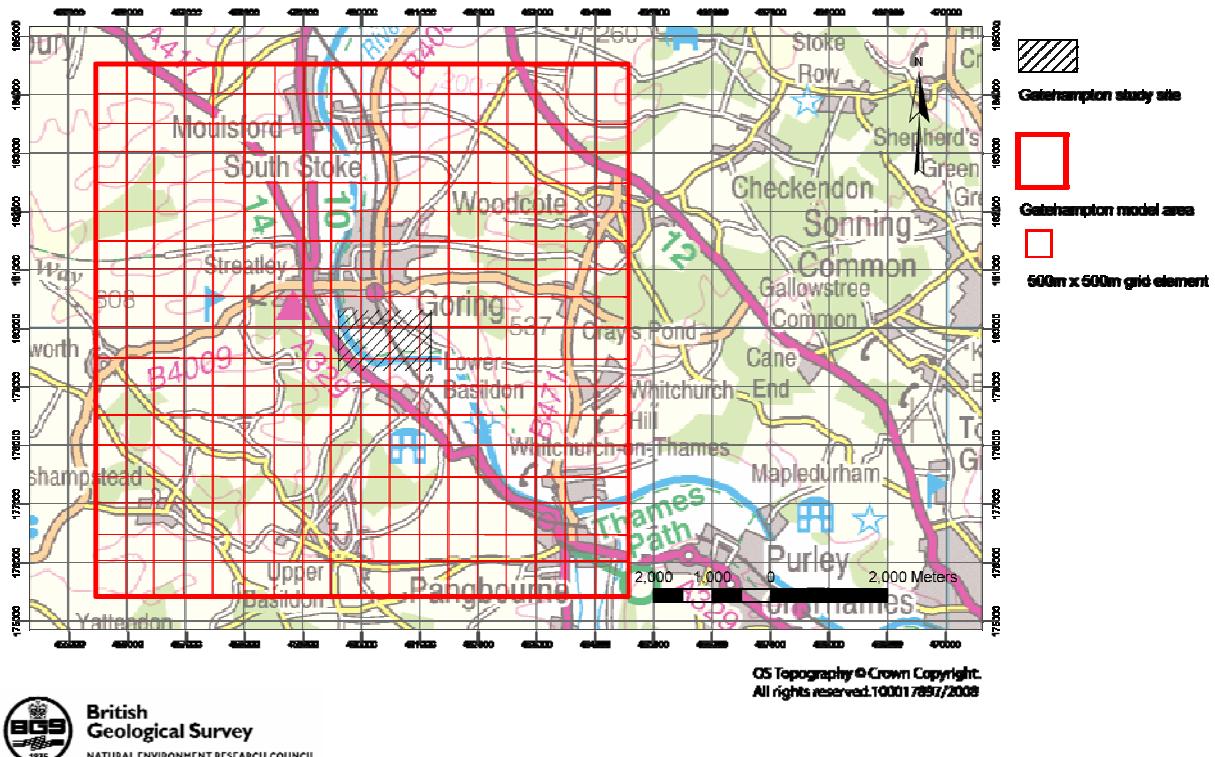


Figure 1

Location of Gatehampton model area and the Gatehampton abstraction site

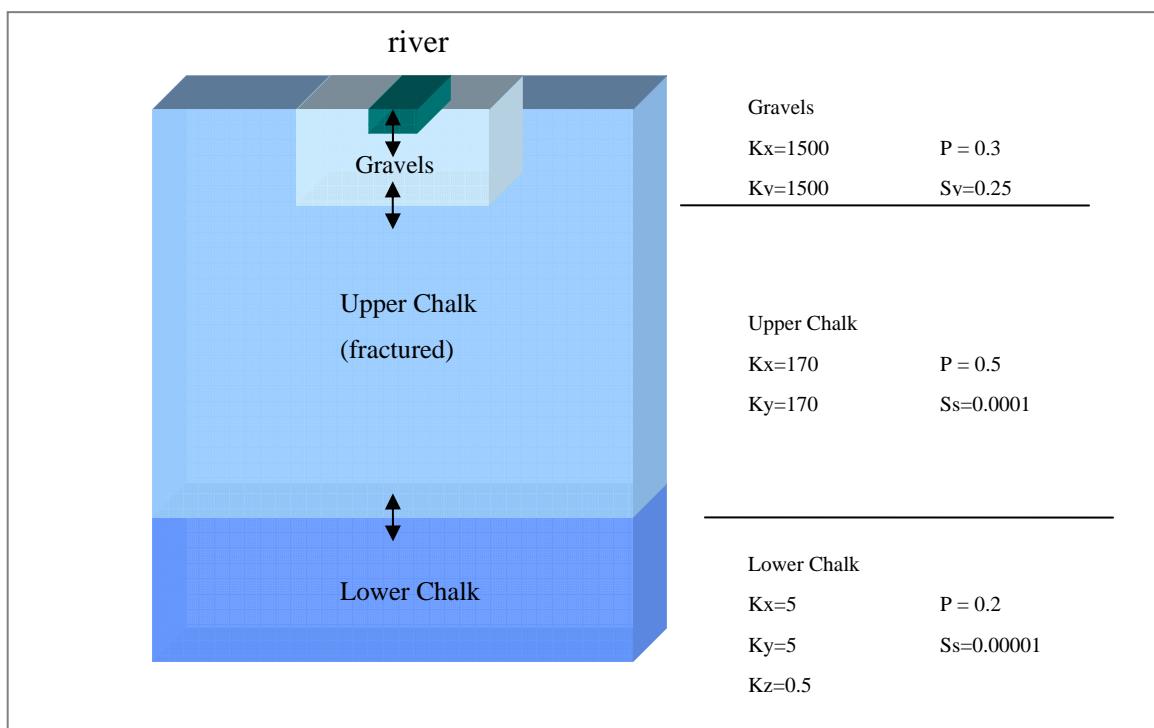


Figure 2

Conceptual model of the study area and parameter values applied during model development and in the final model (arrows indicate good connectivity)

2.2 MODEL DEFINITION

In order to investigate flow pattern around the Gatehampton abstraction site and to assess the performance of the PHAST model, a staged modelling approach was chosen. All models were three-dimensional but varied in complexity. Starting with a simple one-layered model, complexity was increased with each development step until the final three-layer model as conceptualised in Figure 1 was implemented.

2.2.1 Model discretization

PHAST is a node-centred (point-distributed), finite-difference model. The model area is discretized using a uniform nodal spacing to create a grid-centred mesh (Figure 3). This is different to modelling packages such as MODFLOW which uses a block-centred mesh. The model area given in Appendix 1, therefore, illustrates the border of the grid elements and the relationship between grid cell, elements and nodes in PHAST is illustrated in Figure 3.

All spatial data including porous media properties, initial and boundary conditions for the grid area are defined by zones, which are rectangular volumes. Zones allow the distribution of identical property values to large areas of the grid or to the entire grid region. Additional zones can then be defined to overlay different property values in different parts of the grid region. The order in which grid properties are defined in PHAST is very important as the last property value defined for a node will be the one used in the simulation.

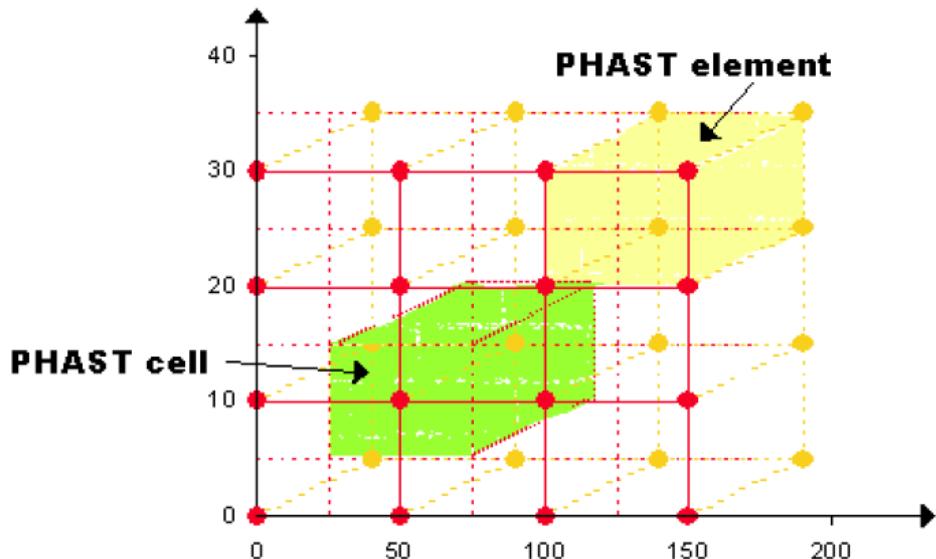


Figure 3 Discretization of model area in PHAST (node-centred mesh) (after Neumann and Kinniburgh, 2004)

In this modelling exercise, aquifer properties are assigned from the base of the model upwards, i.e. properties of the deepest aquifer are defined first. These properties are assigned to the entire grid region prior to defining the properties of the overlying aquifer units. This way, it is ensured that each aquifer unit is defined correctly and that the definition of the spatial distribution of the aquifer properties is complete.

The horizontal extend of the model area is represented by a 9 km by 9 km grid, defined by 19 nodes in both x- and y-direction and a node spacing of 500m (Figure 4). The resulting grid consists of 18x18 elements and 19x19 cells (see Figure 3). The model resolution is refined around the Gatehampton abstraction site by overlaying a 1 km by 1 km grid with 20m node

spacing. The spatial discretization of the numerical model in x-y- direction is illustrated in Figure 4.

Vertical discretization (z-direction) varies between the different models and details are provided at each development step.

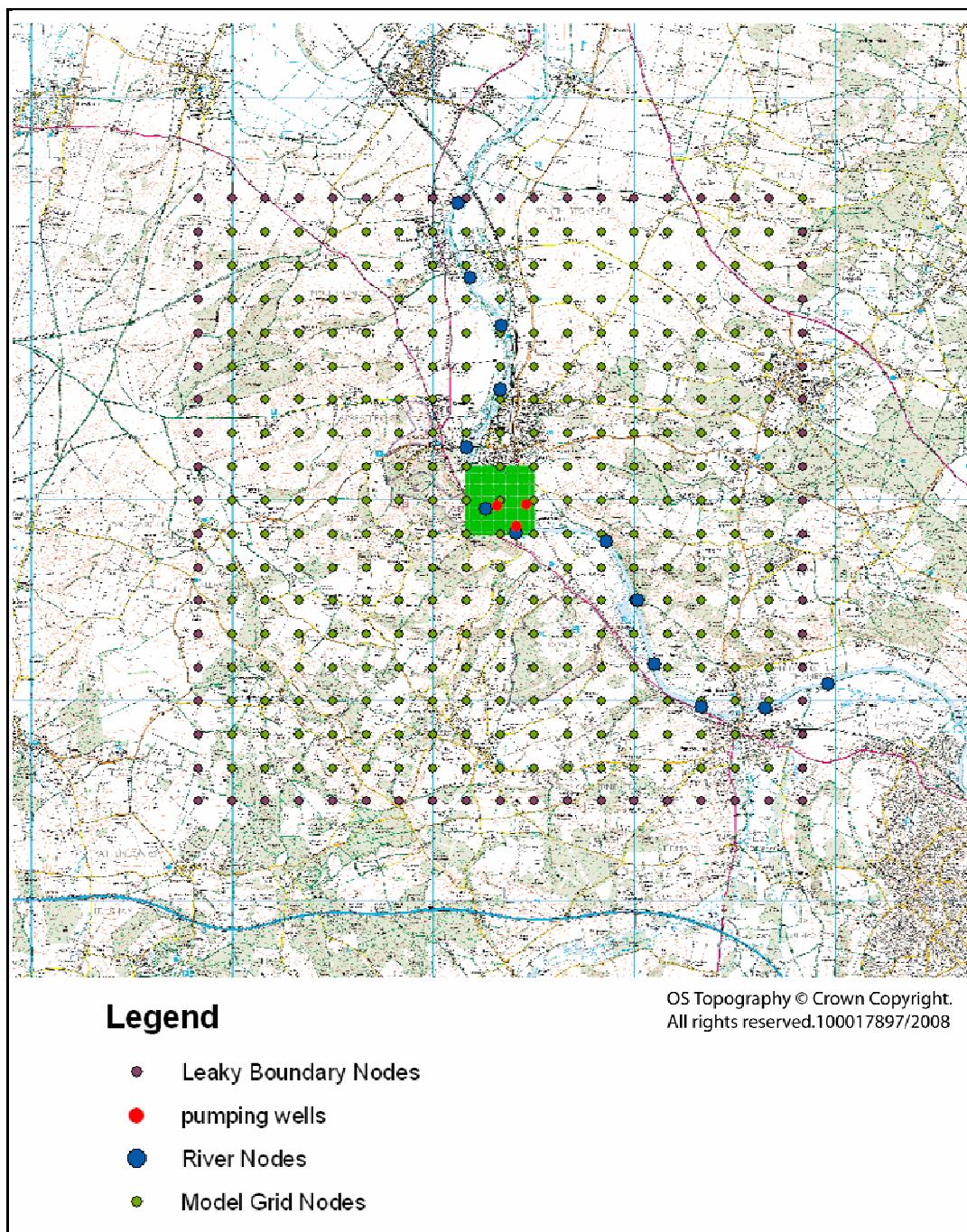


Figure 4 Model grid of numerical model including boundary conditions (green square marks area of grid refinement)

All models were run as transient simulations (STEADY_FLOW false) for, initially, 2000 days with a time step length of 50 days. However, boundary conditions and fluxes (e.g. recharge, abstraction, river stage) were kept constant (time-invariant), so that simulations represented a quasi-steady state. Steady state conditions were usually achieved after 300 days and simulation times were later adjusted to 500 days with a time step length of 50 days.

Parameter values for aquifer properties applied during model development are specified at the individual development steps and were derived from values given in Jackson et al. (2006b) and Allen et al. (1997).

The hydraulic conductivity of the river bed was set to be large (10000 m d^{-1}) to simulate good hydraulic connection to the underlying aquifer and to force the head in the aquifer to be similar to the head in the river for each cell that contains the river. This value is several magnitudes higher than the actual river bed conductivity which at the study site is about 0.13 m d^{-1} (Jackson et al., 2006b).

Longitudinal dispersivity (20m) and horizontal and vertical transverse dispersivities (0.5) were set arbitrary to be less than the node spacing of the refined grid.

2.2.2 Boundary Conditions

Boundary conditions and initial conditions were kept constant during all development steps, with the exception of the Flux boundary condition (=recharge) which was only included in the final model (MOD4).

LEAKY_BC

The section of the PHAST input file relating to leaky boundary conditions is shown in Box 1. Specified head conditions are defined along all four boundaries of the active grid to allow groundwater flow into and out of the region. The thickness of the boundary layer is defined as 200m and its hydraulic conductivity is 170m/d.

Groundwater heads are defined for the corner nodes of the grid region and in the north and east also for the river nodes that intersect these boundaries. Spatially distributed groundwater heads are then assigned along the boundaries by interpolating between these head values. Groundwater heads for these points were provided by Chris Jackson (BGS) and were derived from outputs from the ZOOM model.

The head distribution along the ‘leaky’ boundaries is such that the resulting flow pattern simulates groundwater inflow from the north/northwest and outflow in the south/southeast. The inflowing groundwater has the same chemical composition (defined as solution 1 in the PHAST input files) as groundwater within the active grid. Groundwater composition in the final model was defined from field data collected on 25 April 2006 at Woods Farm borehole and is chosen to represent the Chalk end member composition. Composition of all solutions used in the final model, including groundwater, river water and recharge, are given in Table 11.

FREE_SURFACE_BC

The aquifer was defined as being unconfined across the entire simulation region.

LEAKY_BC

```

-zone 455500 175500 -25 455500 184500 45      # east
    -head          0      Y      69.6532 175500 55.7336 184500
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

-zone 456000 175500 -25 464000 175500 45      # south
    -head          0      X      67.9122 456000 41.4168 464000
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

-zone 464500 177000 -25 464500 184500 45      # west -north of river
    -head          0      Y      39.5018 177000 54.2195 184500
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

-zone 464500 175500 -25 464500 176500 45      # west -south of river
    -head          0      Y      41.2837 175500 39.8282 176500
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

-zone 456000 184500 -25 459500 184500 45      # north -east of river
    -head          0      X      54.1718 456000 41.3089 459500
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

-zone 460000 184500 -25 464500 184500 45      # north -west of river
    -head          0      X      41.8982 460000 52.3476 464000
    -associated_solution           0      1
    -hydraulic_conductivity       170
    -thickness                   200

```

Box 1 Definition of Leaky boundary conditions in PHAST

FLUX_BC

Recharge inputs were initially added as spatially-distributed, time-invariant (constant) flux across the entire grid region (z-direction). The recharge grid for the region was provided by Chris Jackson, but could only be used for simulations that excluded the grid refinement around the study site. In the final model, the spatially-distributed recharge was therefore replaced by an average recharge value of 0.5075 mm d^{-1} (calculated from the grid data) that was applied across the entire study region. Recharge chemical composition was defined from average precipitation composition at the ECN monitoring site at Wytham measured between

May 1993 and April 2005. It was assumed to be concentrated by evapotranspiration¹ resulting in the composition as shown in Table 11 (solution 3). The relevant part of the input file is shown in Box 2.

```
FLUX_BC
-zone          455500 175500 45 464500 184500 45
-flux          0      -0.5705 #average recharge for region calculated from recharge.dat
#-flux    0     file      recharge.dat
-face          z
-associated_solution 0      3
```

Box 2 Definition of flux boundary conditions in PHAST

RIVER

River leakage was defined as constant-head (spatially-distributed, time-independent) boundary and the leakage term is calculated by the model from river head, river widths and river-bed-leakage parameters. These properties are explicitly defined for each river point as illustrated in Box 3. The river is defined as being 10m wide with a depth of 2m and river heads are spatially-distributed along the river ranging from 41.3 maOD in the north to 39.4 maOD in the east. The river bed is assumed to have a thickness of 2m and is hydraulically connected to the aquifer with a hydraulic conductivity of the river bed of 10000m/d (the high value was chosen to represent full connectivity). River chemical composition during model development was defined by solution 2 (Table 1). The high Cl concentrations were used as a tracer for river water leakage into and movement within the aquifer. For the geochemical transport modelling, a more realistic river water composition was assigned to solution 2 (in Table 11) based on field measurements taken on 4 April 2006. River solution chemistry within the model is time-invariant and hence does not reflect the temporal changes in the river composition.

```
RIVER 1 Thames River
-point        464885  177252
-head         0      39.43
-width        10
-bed_hydraulic_conductivity   10000
-bed_thickness 2
-depth        2
-solution     0      2
```

Box 3 Definition of river nodes in PHAST

¹ Evapotranspiration is assumed to result in a threefold concentration under prevailing climatic conditions (Appelo and Postma, 1993)

Table 1 Solution composition during development of the flow model (*Ca concentrations are used to achieve charge balance of the solution)

Component	Groundwater	River	Precipitation
Solution no	1	2	3
pH	7	7	7
T	25	25	25
Cl (mg/L)	10	100	0
Ca (mg/L)	5 *	5 *	5*

WELL

Three abstraction wells are included in the model representing boreholes GH1, GH4 and GH6 at the Gatehampton abstraction site. Well locations and properties are given in Table 2 and the input file for well GH1 is shown in Box 4, as example. The model was run with a range of pump rates, including $0.001\text{m}^3 \text{d}^{-1}$ (no abstraction), $15,000 \text{ m}^3 \text{d}^{-1}$ and $35,000 \text{ m}^3 \text{d}^{-1}$. Abstraction rates for the operational use of the Gatehampton boreholes were not available. Therefore, the abstraction rates for these simulations were based on results from a pump test carried out by Thames Water in 1986 (Robinson and Banks, 1987). The rates were selected to simulate (1) natural flow conditions (no abstraction), (2) maximum pump rates at individual boreholes and (3) maximum total (site-wide) abstraction rate ($105,000 \text{ m}^3 \text{d}^{-1}$) licensed for the Gatehampton source (peak licence).

WELL 1 Abstraction Well 1 - GH1
459960 179920
-pumping_rate
0 day 35000 #m3/day
-diameter 750
-land_surface_datum 40.77
-depth 15 30

Box 4 Definition of wells in PHAST

Table 2 Well properties

Well ID	Easting	Northing	Datum (maOD)	Well diameter (mm)	Screening depth (mbd)
GH1	459960	179920	40.77	750	15-30
GH4	460250	179620	41.05	740	15-30
GH6	460390	179940	44.27	750	16.4-31.4

2.2.3 Initial conditions

Initial conditions were the same for all development steps and were defined such that the groundwater heads throughout the region are 60 m aOD (Box 5). Groundwater chemical composition is defined as solution 3 (Table 1). During model development, only the conservative solute Cl was included in the simulation as a tracer of river water infiltration into the aquifer. For the geochemical transport modelling, a more realistic groundwater composition was assigned to solution 3 (see Table 11) which represents the Chalk groundwater at the Woods Farm borehole PS No2 [NGR 45823 17954] measured on 25 April 2006.

```
HEAD_IC
-zone 455500 175500 -25 464500 184500 45
-head 60

CHEMISTRY_IC
-zone 455500 175500 -25 464500 184500 45
-solution 3 # gw at Gatehampton
```

Box 5 Definition of initial conditions in PHAST

2.3 DEVELOPMENT OF THE FLOW MODEL

The flow model was developed in four steps which are described below. Geochemical processes were not considered during this stage. However, a solution was assigned to each component (Table 1) with the aim of using the conservative solute chloride (Cl) as a tracer of river water infiltration and mixing in the aquifer.

2.3.1 Development step 1

Three models were developed consisting of one, three and 12 layers as shown in Figure 5. Model parameterisation was based on parameter values for the gravel aquifer. Parameter values are identical for all three models as well as for all layers within each model. Therefore, the results from all three models should be identical.

Initial and boundary conditions are defined as detailed in Section 2.2, with the exception that recharge is not included in these models. Furthermore, groundwater abstraction rates are set to 35,000 m³/day at all three boreholes.

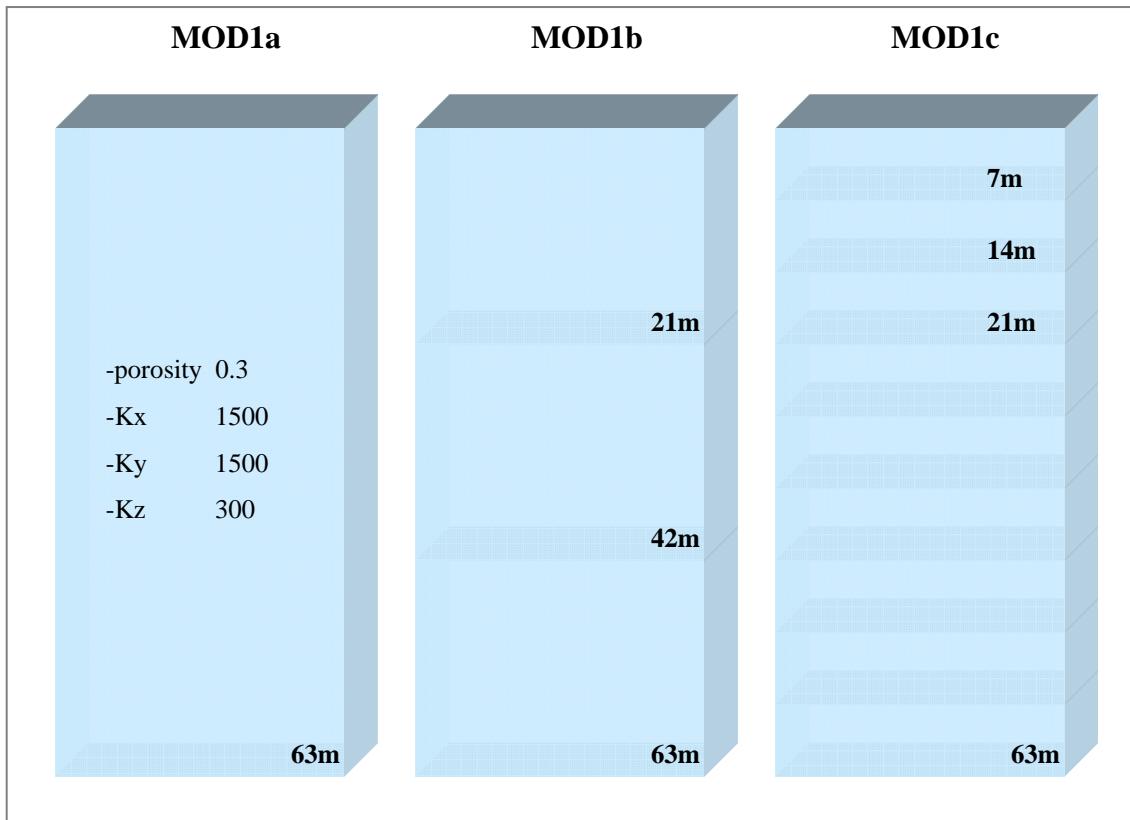


Figure 5 Spatial discretization and parameterization of models developed during step 1

PROBLEMS

A problem was experienced with running model MOD1b, which did not converge when run with study area discretization using the iterative solver². The problem was solved by changing the SOLUTION_METHOD to use the direct solver³ which is more efficient in solving small problems of a few hundred to a thousand nodes (Parkhurst et al., 2004).

RESULTS

Model outputs including maps of the groundwater head distribution (black) and distribution of Cl concentrations (red) as well as mass balances for all three models are given in Table 3. The three models display good agreement in simulating groundwater heads. Chloride concentrations do not exceed 10 mg L⁻¹ (concentrations in the groundwater) indicating that river leakage does not occur at this pump rate. Water mass balances of the models also compare well and show low fractional imbalances. There is a slight increase in mass flows with increasing vertical discretization.

² restarted generalized conjugate-gradient (ORTHOMIN) iterative solver

³ D4 Gaussian elimination direct solver

Table 3

Comparison of model output from model development step 1

MOD1a	Mod 1b	MOD1c
GWL in 0.5 m intervals Pumping rate 35,000m ³ d ⁻¹		
Global water mass balance		
Cumulative specified head b.c. fluid net inflow 0.000000E+00 (kg)	Cumulative specified head b.c. fluid net inflow 0.000000E+00 (kg)	Cumulative specified head b.c. fluid net inflow 0.000000E+00 (kg)
Cumulative flux b.c. fluid net inflow 0.000000E+00 (kg)	Cumulative flux b.c. fluid net inflow 0.000000E+00 (kg)	Cumulative flux b.c. fluid net inflow 0.000000E+00 (kg)
Cumulative leakage b.c. fluid net inflow 2.653550E+12 (kg)	Cumulative leakage b.c. fluid net inflow 2.678790E+12 (kg)	Cumulative leakage b.c. fluid net inflow 2.773893E+12 (kg)
Cumulative river leakage b.c. fluid net inflow -2.903994E+12 (kg)	Cumulative river leakage b.c. fluid net inflow -2.925392E+12 (kg)	Cumulative river leakage b.c. fluid net inflow -3.014813E+12 (kg)
Cumulative well fluid net inflow -5.250000E+10 (kg)	Cumulative well fluid net inflow -5.250000E+10 (kg)	Cumulative well fluid net inflow -5.250000E+10 (kg)
Cumulative Fluid inflow..... 2.678993E+12 (kg)	Cumulative Fluid inflow 2.710134E+12 (kg)	Cumulative Fluid inflow 2.816715E+12 (kg)
Cumulative Fluid outflow... 2.981938E+12 (kg)	Cumulative Fluid outflow ... 3.009236E+12 (kg)	Cumulative Fluid outflow ... 3.110135E+12 (kg)
Cumulative Change in fluid in region -3.029445E+11 (kg)	Cumulative Change in fluid in region -2.991020E+11 (kg)	Cumulative Change in fluid in region -2.933719E+11 (kg)
Current Fluid in region 1.592455E+12 (kg)	Current Fluid in region..... 1.596298E+12 (kg)	Current Fluid in region 1.602028E+12 (kg)
Current Fluid volume in region 1.592455E+09 (m ^3)	Current Fluid volume in region 1.596298E+09 (m ^3)	Current Fluid volume in region 1.602028E+09 (m ^3)
Residual imbalance..... 5.991211E-01 (kg)	Residual imbalance..... 5.317383E-01 (kg)	Residual imbalance..... 4.794099E+07 (kg)
Fractional imbalance 0.0000	Fractional imbalance..... 0.0000	Fractional imbalance 0.0000

2.3.2 Development step 2

Based on MOD1b and MOD1c, two models are developed consisting of three and 9 layers as shown in Figure 6Figure 6. Model parameterisation in both models is identical and such that it represents an aquifer consisting of 21 m of gravels underlain by 21 m of fractured (Upper) Chalk underlain by 21 m of Lower Chalk. As in step 1, the model results should be identical.

Initial and boundary conditions are defined as detailed in Section 2.2, with the exception that recharge is not included in these models. The model was run with a pump rate of $35,000 \text{ m}^3 \text{ d}^{-1}$ at all three wells.

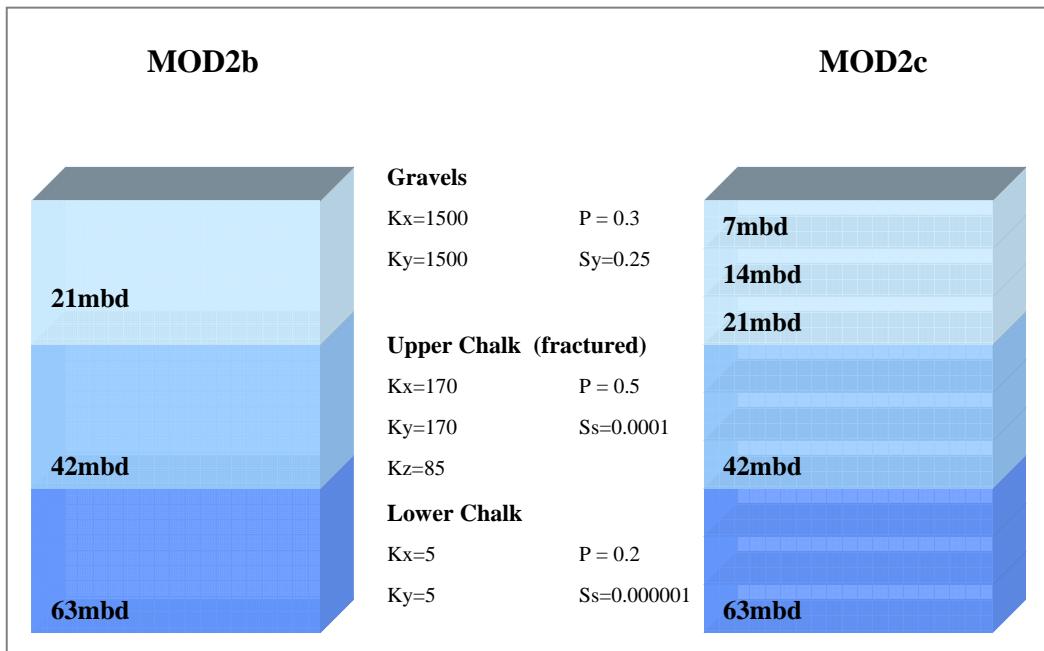


Figure 6 Spatial discretization and parameterization of MOD2b and MOD2c developed during step 2.

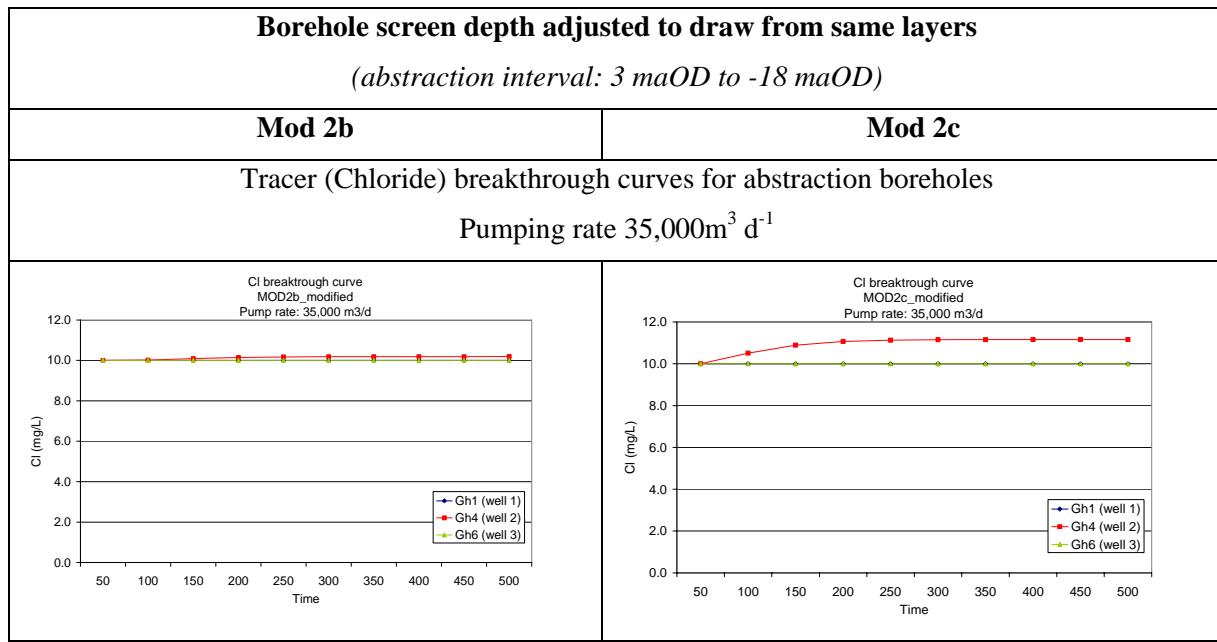
RESULTS

The results for simulating an abstraction rate of $35,000 \text{ m}^3 \text{ d}^{-1}$ per well are given in Table 4. The maps show that the models produced similar distributions in groundwater heads and chloride concentrations. There are some differences in the mass balances of the two models with fluid and solute mass fluxes being higher in MOD2c. These higher fluxes also cause higher Cl concentrations at well GH4 in the MOD2c simulation and are probably the cause for the higher residual imbalance. Initially, these differences in well Cl concentrations were attributed to the positioning of the well-screen in relation to layer nodes, cell boundaries and geology which differed slightly in the two models due to the different number of z-layers. However, adjusting the well-screen depths to ensure identical proportional representation of the different geological layers in the abstraction wells of both models had no effect on the results (Table 5). It is, therefore, suggested that the discrepancy is related to model convergence but this needs further investigation.

Table 4 Comparison of model output from model development step 2

MOD2b	MOD2c
Pumping rate $35,000\text{m}^3 \text{d}^{-1}$	
GWL in 0.5m intervals, Cl in 1mg/L intervals	
Tracer (Chloride) breakthrough curves for abstraction boreholes	
Global water mass balance	
Cumulative specified head b.c. fluid net inflow 0.000000E+00 (kg) Cumulative flux b.c. fluid net inflow 0.000000E+00 (kg) Cumulative leakage b.c. fluid net inflow 1.186081E+12 (kg) Cumulative river leakage b.c. fluid net inflow -1.408467E+12 (kg) Cumulative well fluid net inflow -5.250000E+10 (kg) Cumulative Fluid inflow 1.259642E+12 (kg) Cumulative Fluid outflow 1.534527E+12 (kg) Cumulative Change in fluid in region -2.748855E+11 (kg) Current Fluid in region 1.790615E+12 (kg) Current Fluid volume in region 1.790615E+09 (m ^3) Residual imbalance 5.869141E-01 (kg) Fractional imbalance 0.0000	Cumulative specified head b.c. fluid net inflow 0.000000E+00 (kg) Cumulative flux b.c. fluid net inflow 0.000000E+00 (kg) Cumulative leakage b.c. fluid net inflow 1.203761E+12 (kg) Cumulative river leakage b.c. fluid net inflow -1.422647E+12 (kg) Cumulative well fluid net inflow -5.250000E+10 (kg) Cumulative Fluid inflow 1.288239E+12 (kg) Cumulative Fluid outflow 1.559625E+12 (kg) Cumulative Change in fluid in region -2.713655E+11 (kg) Current Fluid in region 1.794134E+12 (kg) Current Fluid volume in region 1.794134E+09 (m ^3) Residual imbalance 2.039594E+07 (kg) Fractional imbalance 0.0000

Table 5 Simulation results with adjusted borehole screen depths



2.3.3 Development step 3

The model developed in this step is based on MOD2c. The model block is discretized into 9 layers but the thickness of the individual aquifer units (defined as zones) is adjusted to more realistic values (Figure 7). The gravel aquifer extends is assumed to have a total thickness of 10m. It is underlain by 50 m of Upper Chalk followed by 30 m Lower Chalk. The horizontal discretization was kept the same as in the previous models, but maintaining the 10-node vertical discretization from MOD2c resulted in a 9-layer model with a layer thickness of 7.8 m. Note that zones in PHAST (i.e., aquifer units) are defined independently from the layers and that the layer boundaries in this model do not coincides with the zone boundaries.

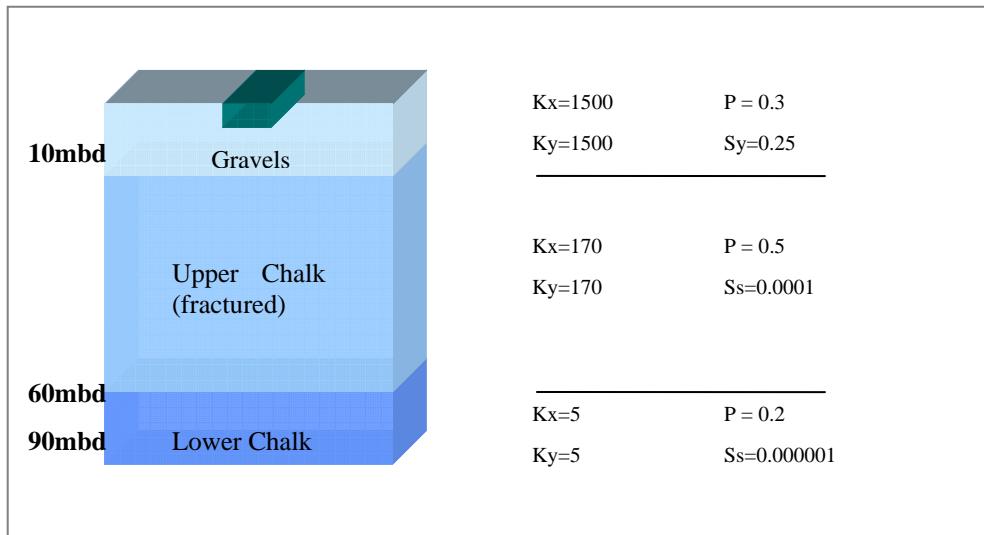


Figure 7 Spatial discretization and parameterization of MOD3 developed during step 3

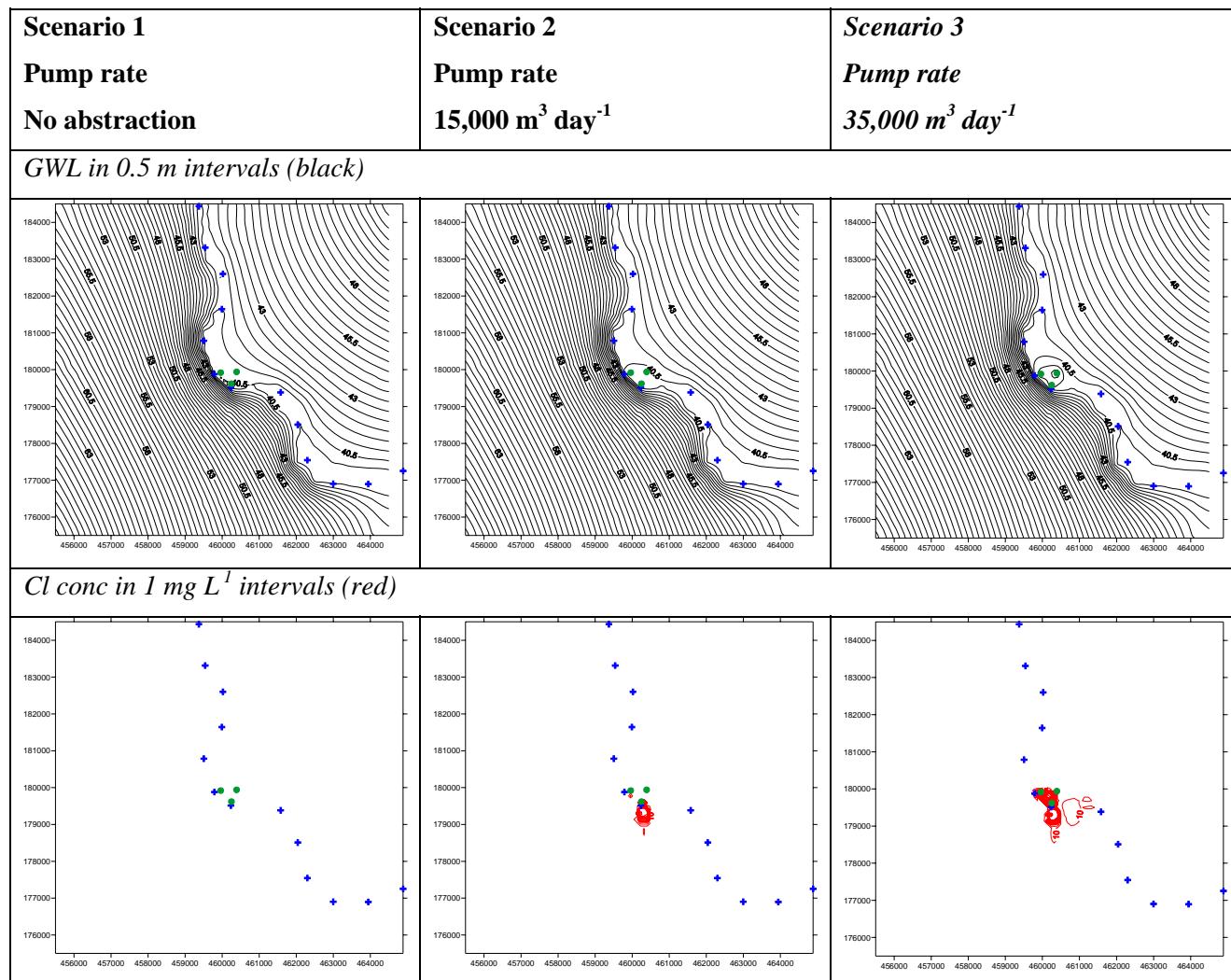
The model was run for three different abstraction scenarios:

1. no abstraction (pump rate: $0.001\text{m}^3 \text{ day}^{-1}$ per well)
2. pumping individual wells at their maximum pump rate of $15,000 \text{ m}^3 \text{ day}^{-1}$
3. pumping each well at a rate of $35,000 \text{ m}^3 \text{ day}^{-1}$ to simulate abstraction at peak rate of $105,000\text{m}^3 \text{ d}^{-1}$ licensed for the Gatehampton source

RESULTS

The results from all three simulations are displayed in Table 6. The data show that at natural flow conditions (no pumping), there is no leakage of river water into the gravels or the Chalk. Pumping at $15,000 \text{ m}^3 \text{ d}^{-1}$ causes river water infiltration into the underlying aquifer at both sides of the river. However, north of the river, river water-groundwater mixing (delineated by the 10-mg L^{-1} -contour) is limited to near-river areas and the river water signature (represented by $\text{Cl} > 10 \text{ mg L}^{-1}$) is only observed in well GH 4. With increasing pump rates, river water infiltration increases and the zone of river water-groundwater mixing extends northwards. At the pump rate of $35,000 \text{ m}^3 \text{ d}^{-1}$, the river water component is present in all three wells. River water inputs are largest in well GH1, as indicated by the highest Cl concentrations and not in well GH4 as was the case at the lower pump rate.

Table 6 Results from modelling scenarios 1 to 3 of model develop step 3 (MOD3)



Scenario 1	Scenario 2	Scenario 3
<i>Breakthrough curves for Cl</i>		
<p>Cl breakthrough curve MOD3 Pump rate: 0.001m³/d</p>	<p>Cl breakthrough curve MOD3 Pump rate: 15.000 m³/d</p>	<p>Cl breakthrough curve MOD3 Pump rate: 35.000 m³/d</p>
Cumulative Fluid inflow... 7.502721E+11 (kg) Cumulative Fluid outflow 1.005312E+12 (kg) Cumulative Change in fluid in region -2.555163E+11 (kg) Current Fluid in region 2.061984E+12 (kg) Current Fluid volume in region 2.061984E+09 (m ^3) Residual imbalance..... -4.764266E+08 (kg) Fractional imbalance -0.0005	Cumulative Fluid inflow....7.516717E+11 (kg) Cumulative Fluid outflow 1.006927E+12 (kg) Cumulative Change in fluid in region -2.557423E+11 (kg) Current Fluid in region ... 2.061758E+12 (kg) Current Fluid volume in region 2.061758E+09 (m ^3) Residual imbalance -4.867391E+08 (kg) Fractional imbalance -0.0005	Cumulative Fluid inflow ... 7.616600E+11 (kg) Cumulative Fluid outflow 1.017210E+12 (kg) Cumulative Change in fluid in region -2.560542E+11 (kg) Current Fluid in region. 2.061446E+12 (kg) Current Fluid volume in region 2.061446E+09 (m ^3) Residual imbalance -5.043443E+08 (kg) Fractional imbalance..... -0.0005

2.3.4 Development step 4

Based on MOD3, the final flow model of the study area was created. The complete PHAST input file for this model is given in Appendix 1 and represents the numerical implementation of the conceptual model presented in Figure 2. In this model, the gravel deposits are limited to the river valley and each aquifer unit is presented in its actual thickness. The conceptual model, as given in Jackson et al. (2006a), suggests that gravel deposits at the Gatehampton site are between 5 to 15 m thick and cover an area of approximately 1 km within the valley. In PHAST, aquifer (media) properties can be defined either by assigning a value for each element within the zone definition or by assigning a single value to the zone containing the elements (in this case only the corner coordinates of the zone and a media value for the zone are required). The former method is useful for defining small-scale variations in media properties. However, it is very time-consuming and requires that element properties are redefined each time the spatial discretization of the grid changes. Therefore, the latter method was used here to delineate the spatial distribution of the gravels in the river valley by defining a number of zones along the path of the river. The number of zones determined how well the numerical model matched the conceptual model which assumes approximately 500 m of gravels on either side of the river. Six zones were defined as detailed in Table 7 and illustrated in Figure 8. The gravel thickness is assumed to be 10m.

Unlike in the previous models, the upper Chalk in this model is only confined in the river valley where it is overlain by gravels but it is unconfined elsewhere. Therefore, specific yield values are used in this model rather than specific storage values. This will only be important in transient simulations (as opposed to quasi-steady state simulations undertaken here) where groundwater heads/water table elevations in the aquifer vary over time. The specific yield value for the upper Chalk as given in Jackson et al. (2006b) is $Sy = 0.25$.

The model was run for four different scenarios: Scenario 1 and 2 simulated natural flow conditions (no abstraction, pump rate $0.001 \text{ m}^3 \text{ day}^{-1}$ per well) without (scenario 1) and with (scenario 2) recharge inputs. Scenarios 3 and 4 included a constant recharge flux and simulated abstraction rates of $15,000 \text{ m}^3 \text{ day}^{-1}$ and $35,000 \text{ m}^3 \text{ day}^{-1}$, respectively.

Table 7 Coordinates for gravel zone definition in MOD4

Zone no	Left (x_1)	Front (y_1)	Lower (z_1)	Right (x_2)	Back (y_2)	Upper (z_2)
1	459000	183000	35	460000	184500	45
2	459500	181000	35	460500	183000	45
3	459000	179500	35	460000	181500	45
4	459500	179000	35	462000	180000	45
5	461500	177500	35	462500	179000	45
6	462000	176500	35	464500	177500	45

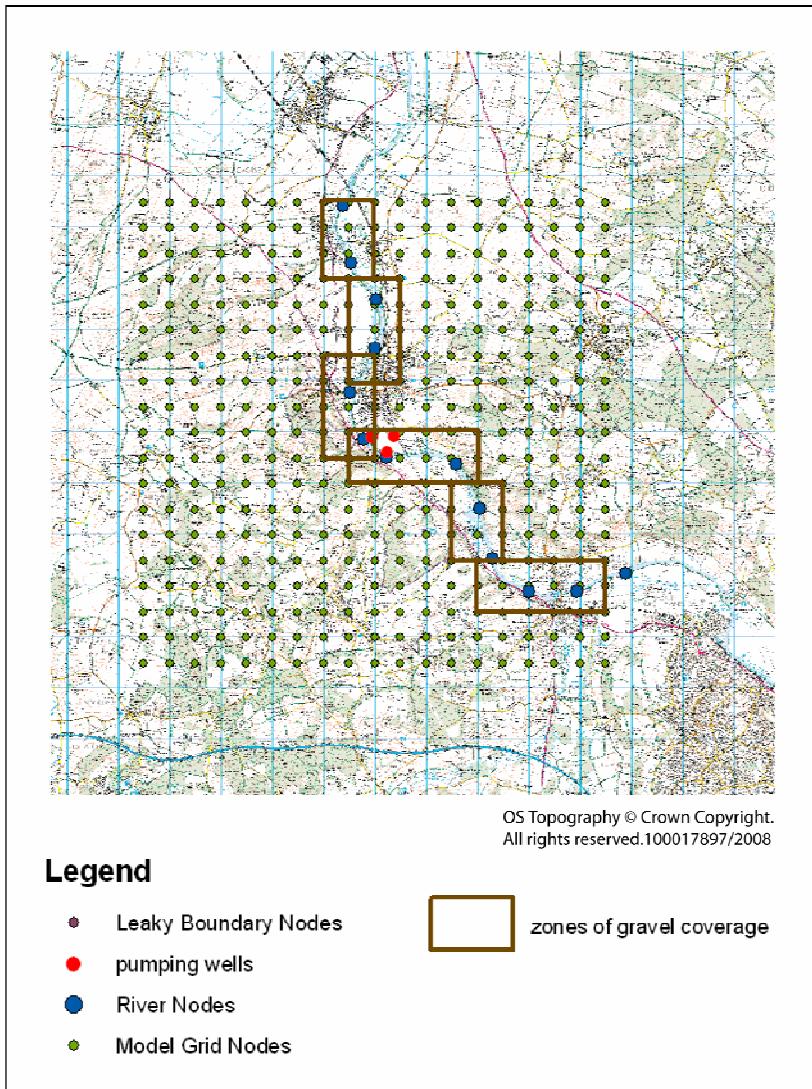


Figure 8 Zones of gravel coverage along the river valley as defined in MOD4

RESULTS

Table 8 displays the results for simulations 1 and 2. It shows that recharge inputs have little effect on the distribution of groundwater heads in the study area, but affect groundwater Cl concentrations. This is because the recharge component (as defined by solution 3 in Table 1) does not contain chloride ($\text{Cl} = 0 \text{ mg L}^{-1}$), so that adding recharge to the groundwater results in the dilution of the initial groundwater Cl concentrations of 10 mg L^{-1} .

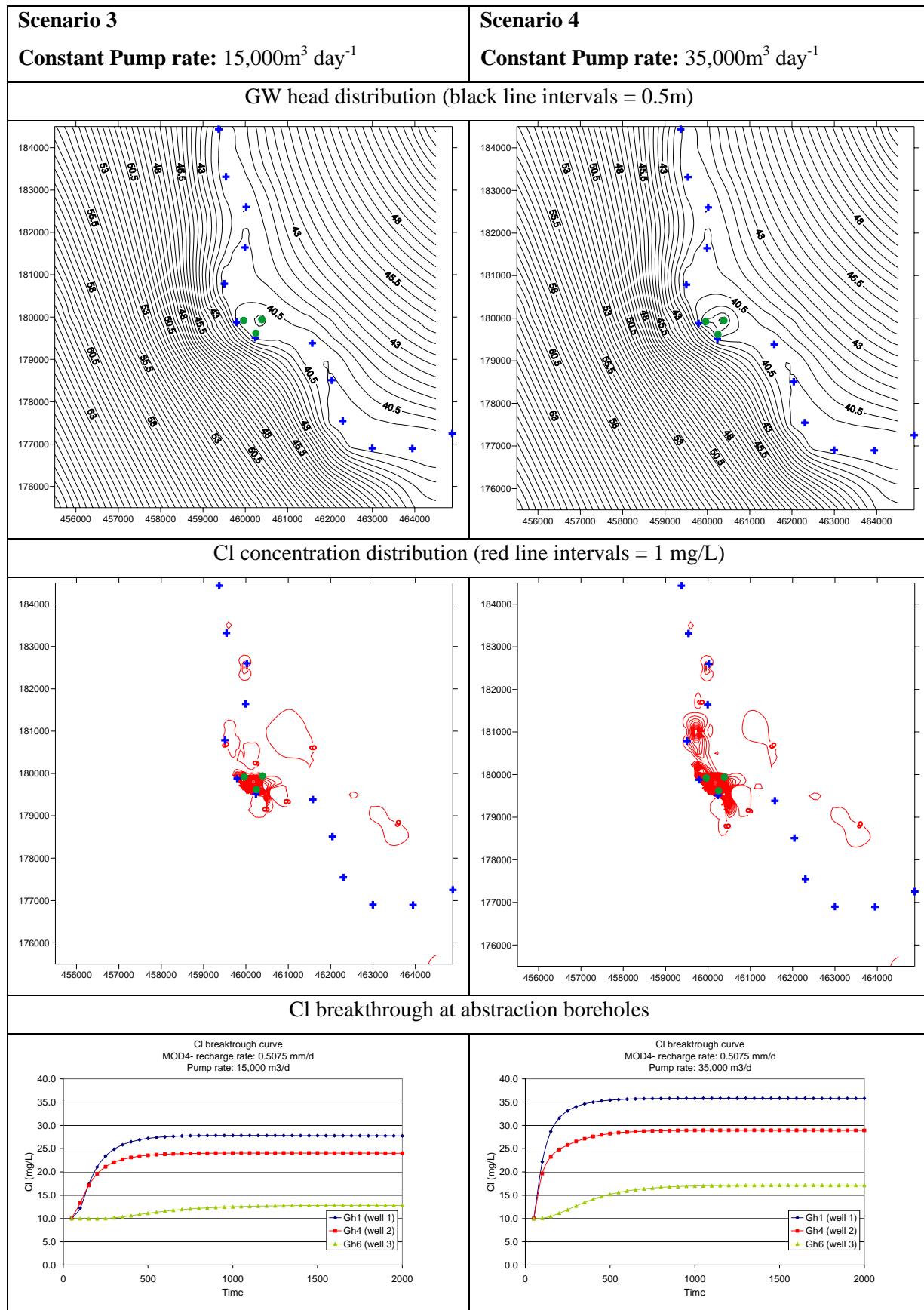
Results for scenario 3 and 4 are displayed in Table 9. The maps of Cl distribution show that river water infiltration due to pumping occurs mostly on the northern/eastern side of the river (where the abstraction boreholes are located). The river water signature (represented by $\text{Cl} > 10 \text{ mg L}^{-1}$) is observed at all three abstraction wells, even at the lower abstraction rate of $15,000 \text{ m}^3 \text{ day}^{-1}$. Chloride concentrations are highest in well GH1 at both pump rates. This implies that GH1 receives the highest inputs from the river, despite GH4 being closest to the river. Ignoring recharge inputs and assuming that only two end-members, namely river water ($100 \text{ mg L}^{-1} \text{ Cl}$) and groundwater ($10 \text{ mg L}^{-1} \text{ Cl}$), contribute to the well chemistry, the

proportion of river water in each borehole were estimated from the data and the results are given in Table 10.

Table 8 Model outputs from MOD4 Scenario 1 and 2 (natural flow without/with recharge)

No abstraction (pump rate: 0.001 m³ day⁻¹) Upper Chalk = unconfined	
Scenario 1: No recharge	Scenario 2: Recharge: 0.5705 mm/d over entire area
GW head distribution (black line intervals = 0.5m)	
Cl concentration distribution (red line intervals = 0.5 mg/L)	
Global water mass balance	
Cumulative Fluid inflow 1.102661E+12 (kg) Cumulative Fluid outflow 1.520811E+12 (kg) Cumulative Change in fluid in region -4.185194E+11 (kg) Current Fluid in region 2.221286E+12 (kg) Current Fluid volume in region 2.221286E+09 (m ³) Residual imbalance -3.693048E+08 (kg) Fractional imbalance -0.0002	Cumulative Fluid inflow 1.157756E+12 (kg) Cumulative Fluid outflow 1.573015E+12 (kg) Cumulative Change in fluid in region -4.156253E+11 (kg) Current Fluid in region 2.224180E+12 (kg) Current Fluid volume in region 2.224180E+09 (m ³) Residual imbalance -3.664757E+08 (kg) Fractional imbalance -0.0002

Table 9 Model outputs from MOD4 Scenario 3 and 4 (different pump rates + recharge)



Global water mass balance	
Cumulative Fluid inflow	1.187739E+12 (kg)
Cumulative Fluid outflow	1.603316E+12 (kg)
Cumulative Change in fluid in region	-4.159495E+11 (kg)
Current Fluid in region	2.223856E+12 (kg)
Current Fluid volume in region	2.223856E+09 (m ³)
Residual imbalance	-3.724905E+08 (kg)
Fractional imbalance	-0.0002
Cumulative Fluid inflow	1.257103E+12 (kg)
Cumulative Fluid outflow	1.673116E+12 (kg)
Cumulative Change in fluid in region	-4.163925E+11 (kg)
Current Fluid in region	2.223413E+12 (kg)
Current Fluid volume in region	2.223413E+09 (m ³)
Residual imbalance	-3.789925E+08 (kg)
Fractional imbalance	-0.0002

Table 10 Proportion of river water in the abstraction boreholes at different pump rates calculated from simulated Cl concentrations

Pump rate per well	Well GH1	Well Gh4	Well Gh6
15,000m ³ d ⁻¹	20%	16%	3%
35,000m ³ d ⁻¹	29%	21%	8%

2.4 SUMMARY AND DISCUSSION OF RESULTS FROM FLOW AND TRANSPORT MODELLING

A simple flow model of the Gatehampton abstraction site was developed using the modelling code PHAST. The final model (MOD4) represents the three-layer aquifer system consisting of lower Chalk (bottom), overlain by fractured (upper) Chalk and gravels in the river valleys.

Model development was carried out in four steps, starting with a simple one-layer model and increasing complexity with each step. In the process, some small discrepancies in model outputs were identified in step 2 for two models that were identical except for the vertical discretization. Differences in results were most obvious in the simulated Cl concentrations but were also seen in the global mass balances. To further investigate the causes of the observed differences, grid convergence tests need to be carried out with the aim to better understand the effects of (vertical) grid discretization on the model outputs.

Comparing the results from development step 3 (MOD3) and step 4 (MOD4) shows that the distribution of the gravels in the study area is an important factor in determining how river water – aquifer interactions are simulated by the model. Results from MOD3 (gravels cover the entire study area), for example, suggests that groundwater abstraction at the Gatehampton site (located at the northern/eastern side of the river) causes significant river water leakage on the opposite side of the river. At lower pump rates, the model predicts that river water leakage is more important on the southern/western side of the river with very little river leakage on the side of the actual abstraction.

Results from MOD4 (gravels limited to the river valley) appear to be more realistic in predicting the response of the river-aquifer system to pumping. Simulation results suggest that abstraction at a total rate of 45,000 m³ day⁻¹ (15,000 m³ day⁻¹ per well) induces river water infiltration on the northern/eastern side of the river (where the abstraction wells are located) but has little effect on the opposite side. Even at the peak abstraction rate of 105,000 m³ day⁻¹, leakage on the southern/western side is minimal compared to that at the abstraction site. At both pump rates, the river water signature is observed in all three abstraction wells. River inputs are highest at well GH1 (20-29%), intermediate at GH4 (16-21%) and lowest at GH6 (3-8%). These values are consistent with findings from Jackson et al. (2006a), who used different geochemical approaches to estimate the proportions of river water in the Gatehampton boreholes. The methods gave poor agreement for GH6, but the value calculated here falls within the lower end of the estimated range of river water proportions of 5% - 45%.

Comparison between the data from this geochemical study and the results presented here is difficult since it is not known at what pump rate the wells were operating at the time of the geochemical sampling.

The model assumes a good hydraulic connection between all parts of the aquifer system including the river and the underlying gravel aquifer. However, results from a recent modelling study that simulated groundwater flow at the Gatehampton site under different hydrogeological settings suggest that this connection may vary spatially as well temporally (Jackson et al., 2006a). This needs to be considered in future simulations, which should include scenarios of locally restricted/spatially discontinuous connectivity between the river and the underlying aquifer. The above study has also confirmed the presence of an old river channel that is running across the abstraction site. This low permeability feature may partially separate the gravels and hence, affect the interaction of individual wells with the river. Thus, a low permeability zone needs to be included in the model to better simulate groundwater flow path and river-aquifer interactions at the Gatehampton abstraction site.

The model has not been calibrated per se, but model outputs were assessed during each development step and, where necessary, input parameters were adjusted to give meaningful results. Nevertheless, a comparison of the model results with observed head measurements and/or pumping test data is necessary in order to validate model outputs and to assess model performance. Alternatively, model calibration and validation could be tied to outputs from the existing ZOOM model that was developed for the Gatehampton abstraction site (Jackson et al., 2006b).

3 The geochemical model

Geochemical modelling was carried out with the aims of (1) determining the sources of water at the Gatehampton abstraction boreholes and (2) investigating how inputs from the different sources change under different water abstraction regimes and how this affects the geochemical composition of the abstracted groundwater.

Constraints on time and data availability have limited this part of the modelling effort. The models presented below are only the first step in the development of the geochemical transport model and all results should be regarded as preliminary. This section concentrates on outlining the modelling strategy and underlying assumptions. It discusses the model's limitation as well as problems that were identified during this initial development phase and proposes future development steps.

3.1 UNDERLYING ASSUMPTIONS

This modelling application hinges on a number of assumptions which are discussed below. Firstly, it is assumed that the groundwater at the Gatehampton study site originates from four potential sources:

1. Chalk groundwaters
2. River water from the Thames
3. Locally recharged precipitation
4. Gravel groundwater from upstream of the abstraction site.

It is further assumed that the gravels act as mixing zone for river water, Chalk groundwater and local recharge, implying that gravel groundwaters themselves present a mixture of waters from these three sources.

Following from that, it is assumed that the groundwater geochemistry at the study site can be represented by three end-members: recent recharge, Chalk groundwater and river water. Further assuming that (1) the end-member compositions can be identified from the available precipitation, groundwater and river chemical data and (2) that they are sufficiently different from one another to allow distinction between the end-members, it should be possible to identify the sources of the groundwater at the abstraction boreholes from their geochemical composition.

3.2 DATA AVAILABILITY AND END-MEMBER SELECTION

Groundwater chemistry data were available for the abstraction boreholes No 1, 3, 4, 5, 6 and 7 at the Gatehampton study site as well as for borehole PS No2 at Wood Farm (NGR 45823 17954) and the Cleeves boreholes PS No 4 (NGR 46076 18169) and 5 (NGR 46076 18169). Groundwater samples were collected between 04 March and 04 April 2006 at the Gatehampton site and on 25 April 2006 at Cleeve and Wood Farm. Chemistry data for the River Thames at Gatehampton were also available from a survey carried out on 04 April 2006.

Direct measurements of precipitation and/or recharge chemistry were not available for this modelling exercise. Instead, measurements of precipitation chemistry collected at the ECN terrestrial site at Wytham Woods (near Oxford) between March 1993 and April 2005 (<http://www.ecn.ac.uk/index.html>) were used to simulate the composition of recharge inputs at the Gatehampton site. To represent the recharge end-member, the original data were

modified to account for (1) evapotranspiration and (2) soil processes. This was done by multiplying the initial elemental concentrations by a factor of three⁴ and equilibrating the resulting solution with soil CO₂. Other reactions of infiltrating precipitation with soil minerals were ignored as information on the mineralogical composition of the alluvial and soil deposits at the Gatehampton site were not available at the time of modelling. Similarly, the river-water end-member was derived by equilibrating the river component with soil CO₂.

For the definition of the groundwater end-members for the model, chemistry data from boreholes located at some distance from the river were considered. They initially included data from the Gatehampton borehole No 7 and from the Wood Farm borehole PS No 2. However, only the Wood Farm data were included in the simulations as chemistry and tracer studies suggest that this borehole contains mostly locally recharged groundwater while the Gatehampton borehole No 7 may also contain up to 40% river water (Jackson et al., 2006a, BGS unpublished data).

The end-member compositions used for geochemical modelling are given in Table 11. The table displays uncorrected data, except for the precipitation analysis which has been multiplied by a factor of three to account for evapotranspiration processes.

Table 11 Composition of the precipitation, river and groundwater end members (before accounting for soil processes)

Component Solution no	Precipitation ¹	River ²	Groundwater ³
	1	2	3
pH	5.03	7.99	7.05
Ca (mg/L)	2.89	119	109
Mg	0.40	5.48	1.53
Na	3.12	22.7	7.5
K	0.22	5.87	1.72
Si	0	4.19	9.16
Cl (mg/L)	6.04	36.5	15.8
SO ₄	2.21	59.7	8.36
Alkalinity	as	245	273
HCO ₃			
NO ₃ -N	1.40	7.71	7.49

¹ Precipitation (*3) at Wytham ECN Terrestrial site (calculated from monthly average data from May 1993-April 2005)

² River Thames at Gatehampton (04 April 2006)

³ Groundwater at Wood Farm PS No2 (25 April 06)

3.3 PHREEQC MODELLING

The first part of the geochemical modelling was carried out in PHREEQC (Parkhurst and Appelo, 1999). The program can simulate the equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers and sorption surfaces and also includes a capability for inverse geochemical calculations. Inverse mass balance modelling allows the identification of water sources for observed water compositions under consideration of the reactions that occurred along flow lines. The applicability of inverse mass balance modelling is based on a number of assumptions, including

⁴ Evapotranspiration is assumed to result in a threefold concentration under prevailing climatic conditions (Appelo and Postma, 1993).

1. “initial” and “final” solutions represent packets of water that flow along the same path
2. dispersion and diffusion do not significantly affect the solution chemistry
3. chemical steady state prevails during the time considered
4. mineral phases used in the calculation are/were present in the aquifer.

The relevance of these assumptions varies for different types of problems and scales as well as for different hydrogeological settings as is discussed by Zhu and Anderson (2002).

In this study, inverse mass balance modelling was used to investigate the sources of the groundwater at the Gatehampton abstraction boreholes. This was done by defining the compositions of the three potential end-members (=initial solutions)

1. precipitation (equilibrated with partial pressure of soil CO₂)
2. river water (equilibrated with partial pressure of soil CO₂) and
3. Chalk groundwater (at Wood Farm borehole PS No2)

as well as the final water composition (final solution composition was defined from measurements from the Gatehampton borehole GH1). The composition of the three end-members is given in Table 11 and the model code is displayed in Appendix 2. Concentrations of K and NO₃-N were not included in the inverse mass balance modelling.

The mineral phases calcite and quartz/amorphous silica were defined to be available for reaction with the groundwater along the flow line. Elements that cannot be derived from any of these minerals were defined separately. These included the elements Cl, Na, Mg and SO₄. Uncertainty values for all solutions and elements were initially set to 0.1 (representing a 10% uncertainty in element concentrations in the solutions), but these had to be adjusted for Cl, Na, Mg and SO₄. Enhanced concentrations of these elements in the groundwater of the study area are likely to originate from (point and/or diffuse) agricultural inputs. Since such sources are not considered in this first modelling step, the uncertainty limits of these elements were increased to 0.5 to allow a model solution to be found.

3.3.1 Results

Running of the model with three end-members did not produce a model solution, despite varying the uncertainty values as described above and/or changing the phase assembly. The model was therefore reduced to two end members: the river water and the Chalk groundwater end-members, the rationale being that the precipitation end-member carries the highest uncertainty in terms of its chemical composition.

Running of the inverse model with two end members: river water and Chalk groundwater for GH1 produced two model solutions (Table 12): Model 1 suggests that the groundwater at GH1 is a mixture of 62% Chalk groundwater and 38% river water. It has evolved by dissolving 0.17 mmol/L calcite and 0.05 mmol/L amorphous silica, removing about 1.0 mmol/L of CO₂(g) from the water. Model 2 suggests that the groundwater at GH1 does not contain any Chalk groundwater but has evolved from river water by dissolving 0.31 mmol calcite and 0.1 mmol/L amorphous silica. Conceptually, this model seems unlikely considering that the borehole abstracts directly from the Chalk aquifer. The sum of residuals and the uncertainty limits (Table 12) indicate that the extent to which the analytical data were adjusted for this model is relatively high compared to model 1. The maximum uncertainty in element concentrations of 50% is also very high, although the somewhat lower value of 38 % in model 1 still makes a meaningful interpretation of the results debatable.

Table 12 Model solutions calculated by inverse model (using two end members)

	Model 1	Model 2
Chalk groundwater fraction	0.62	0
River water fraction	0.38	1
Phase mole transfer (moles/L):		
CO ₂ (g)	-9.668e-04	-1.229e-03
Calcite	1.656e-04	3.068e-04
SiO ₂ (a)	4.982e-05	1.008e-04
Sum of residuals	1.767	4.545
Sum of uncertainty limit	3.080	4.573
Maximum fractional error in element concentration	0.38	0.50

3.4 PHAST MODELLING

The geochemical transport modelling was carried out in PHAST using the flow model (MOD4). The development of this model and parameterisation has been described in the previous sections and the model code is provided in Appendix 1. The model was run for 2000 days with a time step length of 50 days. The pump rate at each abstraction borehole was set to 15,000 m³ d⁻¹, providing a combined abstraction rate of 45,000 m³ d⁻¹.

In the chemistry input file (.chem.dat), as detailed in Appendix 3, precipitation, river water and groundwater composition were defined according to Table 11. Precipitation and river water were allowed to equilibrate with CO₂ partial pressure in the unsaturated zone. A pure-phase assemblage containing calcite was defined for the aquifer and allowed to react with the groundwater until the saturation index of 0.5 (as observed in the groundwater at GH1) was reached. Other minerals (e.g., quartz, clay minerals) and processes (e.g. surface adsorption, ion exchange) that may influence the groundwater composition were not considered in this initial simulation.

3.4.1 Results:

The distribution of groundwater heads and selected geochemical parameters as simulated by the PHAST model are displayed in Appendix 4. The simulated groundwater composition at the Gatehampton boreholes is summarised in Table 13 together with end-member compositions and measured groundwater composition at the three boreholes. The data show that the general trends in groundwater chemistry changes between Wood Farm and Gatehampton are captured by the simulated data for almost all elements even though the absolute concentrations are somewhat different. For example, the relative increase in Mg, K, Na and SO₄ at the Gatehampton site compared to Wood Farm is currently underestimated by the model. This could be due to the simulated pump rates being too low, resulting in a lower proportion of river water in the boreholes. However, this would be expected to affect the Cl concentrations, which in this simulation were overestimated by the model. Therefore, it seems more likely that these elements are derived from additional processes/sources that are not considered by the model. Magnesium, K, Na and Si, for example, can be derived from silicate weathering. Including these processes in future simulation is also likely to improve the prediction of the groundwater alkalinity which at present is overestimated by the model. The high SO₄ concentrations are more likely to be associated with agricultural inputs from point and diffuse sources. Such sources often also contain high concentrations of Mn, K and Na.

Table 13 Comparison of results from the PHAST simulation with measured groundwater chemistry (EM = end member)

	Precipitation EM	River EM	Ground water EM	measured			simulated		
Element	ECN site Wytham Woods	River at Gate-hampton	Woods Fm PS No 2	GH1	GH4	GH6	GH1	GH4	GH6
Ca (mg L⁻¹)	2.89	119	109	109	125	65.7	116	81	128
Cl (mg L⁻¹)	6.04	36.5	15.8	23.3	26.5	22.5	31.2	23.6	27.1
HCO₃(mg L⁻¹)	10.8	245	273	280	300	225	324	316	345
K (mg L⁻¹)	0.22	5.87	1.72	3.08	2.67	2.15	2.44	1.91	1.84
Mg (mg L⁻¹)	0.4	5.48	1.53	3.46	2.71	2.15	2.23	1.75	1.65
Na (mg L⁻¹)	3.12	22.7	7.5	22.1	16.2	17.9	10.0	7.8	7.9
NO₃-N (mg L⁻¹)	1.4	7.71	7.49	6.36	6.96	6.82	6.70	4.72	7.18
pH (mg L⁻¹)	5.03	7.99	7.05	7.83	7.34	7.15	7.15	7.09	7.36
Si (mg L⁻¹)	0	4.19	9.16	10.2	8.93	8.51	7.05	4.71	8.54
SO₄ (mg L⁻¹)	2.21	59.7	8.36	27.5	28.8	23.5	18.7	15.6	10.4

3.5 SUMMARY AND DISCUSSION OF RESULTS FROM GEOCHEMICAL MODELLING

Inverse mass balance modelling in PHREEQC predicted that groundwater abstracted at GH1 contains 38% river water. This value is similar to the river water proportion estimated by Jackson et al. using different hydrogeochemical approaches. They estimated that river water proportions at well GH1 lie between 20% and 30%. These estimates were based on an average river composition with concentrations of Na=32.9 mg L⁻¹ and Cl=49 mg L⁻¹. The spot sample used here (Table 11) has somewhat lower Na (22.7 mg L⁻¹) and Cl (36.5 mg L⁻¹) concentrations, which explains why a higher river proportion was estimated for GH1.

Inverse mass balance modelling did not find a model solution for wells GH4 and GH6. This could be due to the following reasons:

1. high uncertainty in the input data
2. inputs from additional sources that are not accounted for in the model
3. incomplete definition of mineral phases and reactions.

As a result, some of the underlying assumptions were probably not fully satisfied. The steady state assumption, for example, requires that the chemical composition at the source (initial solution) does not change with time. This is probably true for the Chalk end member, but is unlikely to be the case for the river water or precipitation composition. In fact, Jackson et al. (2006a, b) illustrated the importance of using averages from long-term water quality data rather than spot samples when river waters are being considered. Uncertainty in river water composition is also an issue for the two-end-member simulation. In this simulation, it was set to 10%, but it is likely to be higher. To better define the uncertainty limit in future simulations, long-term time series data of river chemistry are needed to provide a representative average of river water chemistry. Uncertainty in precipitation composition is mostly due to the fact that it was measured at some distance from the study site but also due to different rates of evapotranspiration. For calculating recharge composition, it was assumed that evapotranspiration results in a threefold solute concentration. This is an average value calculated for the prevailing climatic conditions (Appelo and Postma, 1993), but the

concentration factor is likely to be higher for recharge beneath woodlands and other densely-vegetated surfaces.

Hydrodynamic dispersion and matrix diffusion may account for some of the imbalances in the mass transfer between initial and final solution, in particular where much of the water travels through the fractured Chalk. To test this assumption, a sensitivity analysis needs to be carried out by running the PHAST flow model with a range of longitudinal (=dispersion) and transverse (=diffusion) dispersivity values. However, inputs from sources that are not accounted for in the model (e.g., diffuse and point source inputs) are far more likely to be the reason for discrepancies in the mass/solute balance, in particular for elements like Cl, Na and SO₄. A recent study in the Lambourn catchment near Newbury, for example, has found that the groundwater chemistry at the study site could not be represented by simple 3-component mixing (recharge-river-groundwater) since the groundwater chemistry was strongly affected by point source inputs from a nearby farm which added high concentrations of Na, K, SO₄ and Cl to the groundwater (Abesser et al., 2008).

The validity of the mass balance models also depends on the definition of appropriate mineral phases that are present within the aquifer. In this simulation, only calcite and quartz/silica were included in the phase definition. Other phases, such as clay minerals, which are also present in the aquifer, were ignored. These need to be included in future simulations to achieve more realistic model solutions.

The simple reactive transport model created in PHAST was able to reproduce the observed trends in groundwater chemistry between Wood Farm and the Gatehampton abstraction site for most elements. However, absolute concentrations were underestimated for some elements (Mg, K, Na and SO₄) and overestimated for others (Cl, alkalinity). This may be due to:

1. the end-member composition not being representative
2. an insufficient number of end members being defined
3. the definition of aquifer mineralogy (phases) and geochemical processes (reactions) being incomplete
4. poor performance of the flow model.

As previously discussed, uncertainty in the input data limits the ability of the model to make reliable predictions; even if all other aspects of the model are correctly defined. Therefore, selecting a representative end-member composition is a crucial part of the modelling process. For (quasi) steady-state simulations, as run in this study, the end-members definition should be based on long-term observations rather than spot samples. This is particularly important for end-members with transient compositions, such as river water and precipitation. To improve model performance and increase confidence in the results, it is recommended that future simulations use long-term averages of river water chemistry, groundwater chemistry and precipitation chemistry to define end-member compositions.

Underestimation of solute concentrations by the PHAST model suggests that other end-members or processes influence the groundwater chemical composition/evolution but are not accounted for by the model. Similar conclusions were drawn from the inverse mass balance modelling in PHREEQC. However, it is unknown what these end-members/processes are. The most-affected elements are Mg, K, Na, Si and SO₄ which suggests an agricultural/anthropogenic contribution. Conversely, many of these elements can be derived from silicate weathering. Such processes are likely to be important in the gravel aquifer but also in the Chalk as both contain varying amounts of clay minerals as well as quartz (Woods et al., 2004; Jeans, 2006). In order to separate end-members from processes, it is

recommended that additional elements are included in future simulations. These should be reasonably conservative (if possible) and indicative of anthropogenic inputs (e.g., B, Li, Cr) derived from effluent and/or agricultural sources. Elements derived from agrochemicals (e.g., NO₃), however, are less suited as they enter the groundwater diffusely via the recharge and are also present in the runoff from the river. Once the missing end-members and/or geochemical processes have been identified these need to be added to the model in order to improve model performance.

Furthermore, the validity of the other model assumptions needs to be re-assessed, in particular the assumption that the gravel waters represent a mix of Chalk groundwater and river water. This assessment should include the analysis of shallow gravel water chemistry and the comparison of the results to Chalk groundwater and river water compositions.

A sensitivity study on the effects of dispersion and diffusion on solute transport, as suggested above, would help to estimate to what extent these processes affect the solute mass balances. However, since PHAST does not discriminate between different chemical components when simulating dispersion and diffusion processes the effect should be similar for all elements and cannot be the reason for the observed discrepancy between measured and simulated concentrations.

Finally, implementing the changes suggested for improving the performance of the PHAST flow model (Section 2.4) is likely to also improve the geochemical predictions. In particular, the addition of the low permeability palaeo-channel to the model may help to reproduce field measurements at the wells that are likely to be affected by the channel (e.g., GH6). The model can then be used as an investigative (hypothesis testing) tool to test why the boreholes located at a distance from the river contain a higher proportion of river water compared to those located next to it – as was found by Jackson et al. (2006a).

4 Conclusions and recommendations

4.1 THE REACTIVE TRANSPORT MODEL

The model created here represents a regional flow and transport model of the Goring Gap area with local grid-refinement around the Gatehampton study site. The model was created in PHAST with the aim to simulate reactive transport at the study site in order to help identifying the water sources at the Gatehampton abstraction boreholes and to investigate aquifer-river interactions at the site. The PHAST model consists of two input files containing the flow model (*prefix.trans.dat*) and the geochemical model (*prefix.chem.dat*). Additional files were defined to specify spatially-distributed initial and boundary conditions.

The groundwater flow model was set up before the transport/geochemical model was defined. Simulations using the final model (MOD4.trans.dat) produced plausible results with regards to the distribution of groundwater heads and Cl concentrations (included as conservative tracer for river water leakage into the aquifer). However, these are only preliminary results and a number of steps are necessary before the model is fully implemented. These include:

1. Defining spatially discontinuous connectivity between the river and the underlying aquifer as suggested by Jackson et al. (2006a)
2. Including a low permeability feature that represents the paeleo-channel identified by Jackson et al. (2006a)
3. Calibrating the model and validating the simulation results based on observed groundwater head data and/or using outputs from the existing ZOOM model that was developed for the Gatehampton abstraction site (Jackson et al., 2006b).

The geochemical component was developed separately but run in conjunction with the transport component (MOD4.trans.dat). The resulting model was very simple, compared to the complexity of the simulated system, but it was able to reproduce the general changes in groundwater chemistry that were observed between Wood Farm and the Gatehampton abstraction site. However, a number of problems with the underlying model assumptions as well as with the model input data were identified and these need to be addressed in future modelling efforts:

1. Use long-term averages of river water chemistry, groundwater chemistry and precipitation chemistry (rather than spot samples) to define end-member compositions
2. Better define the aquifer mineralogy (phases) as well as expected groundwater-aquifer interactions (reactions) within the model , e.g. include weathering of clay minerals and silicates
3. Identify unaccounted end-members (e.g., pollution sources) that contribute to the groundwater signature at the abstraction boreholes and include in future simulations
4. Re-assess the assumption that gravel groundwater can be regarded as mixture of the river water and the Chalk groundwater end member

Finally, it is recommended that the model is run at a range of abstraction scenarios in order to assess its performance.

As part of the geochemical modelling, inverse mass balance modelling was carried out in PHREEQC with the aim to aid identification of potential sources of groundwater at the abstraction wells. The model only found a solution for well GH1 but not for wells GH4 and

GH6. A number of recommendations are included here to reduce the uncertainty in model inputs and outputs and to help finding realistic model solutions:

1. Use long-term averages to define end-member compositions
2. Include an end-member that represents agricultural/anthropogenic inputs
3. Include clay minerals in mineral phase definition (as available for dissolution)
4. Include isotope data as additional constraints to the model to help eliminate unrealistic solutions
5. Carry out sensitivity study in PHAST to asses influence of (longitudinal and transverse) dispersivity on the solute concentrations at the abstraction boreholes.

4.2 PHAST AS A MODELLING TOOL

The flow and transport component of PHAST is a modified version of HST3D which has been restricted in its functionality in order to accommodate its reactive transport capability. For example, the PHAST simulator has been restricted to constant density and viscosity, and a number of simplifying assumptions have been made to determine its constitutive equation set (Parkhurst et al., 2004). Therefore, PHAST may not be able to simulate very complex flow models as was found by Neumann and Kinniburgh (2004). However, the strength of PHAST does not lie in its capacity to model complex groundwater flow systems but in providing a tool that allows the simulation of complex chemical processes along groundwater flow paths. With this in mind, the suitability of PHAST for modelling site-specific problems such as the Gatehampton abstraction site was assessed.

The model definition in PHAST is straightforward and the structure of the input files is clear and concise. However, a number of limitations in running the model and processing the data were encountered during the development process:

1. PHAST can only handle a limited number of river points. In this model, the number of river nodes had to be reduced to 13 for the model to run. For simulations that focus on site-scale processes, a smaller but more detailed model of the actual study site may be more suitable than a regional-scale model with grid-refinement.
2. The vertical discretization was found to control the simulated solute concentrations and their distributions, i.e. a 3-layer model (4-node discretization) produced a different solute distribution than an equivalent 4-layer model (5-node discretization). The reason for this needs further investigation, and it is recommended that grid convergence tests are carried out.
3. Observing groundwater levels at a given position within the modelling grid (e.g., observation well) is difficult in PHAST. Output files for wells only include temporal changes in well chemistry, but not for groundwater heads. Obtaining groundwater heads for a defined location requires post-processing of the output matrix (*prefix.xyz.head.dat*). In this study, an R-routine has been written that allows the extraction of groundwater head data from the *prefix.xyz.head.dat*-file for all time steps and any specified location within the modelling grid.
4. Spatial distributions and temporal changes in groundwater heads and concentrations can be visualized in PHAST using a three-dimensional visualisation software called Model Viewer. Unfortunately, there are occasional problems with running the software on Windows XP or Vista (Paul Hsieh, personal communication). There is no

fix for this problem at the moment; hence alternative visualisation packages such as Surfer must be used.

However, points (3) and (4) are mere inconveniences rather than serious limitations.

The results obtained from preliminary simulations gave realistic results for groundwater head distributions as well as for groundwater chemistry. This suggests that the model performed well (although validation of the results with actual measurements is still to be done) and was suitable for modelling the Gatehampton site (as defined so far). However, the model is still under development and a number of changes need to be made before the model is fully implemented. These are outlined above and it remains to be seen how PHAST performs when these more complicated hydrogeological settings and features (e.g limited connectivity between the river and the aquifer, presence of a low permeability zone across the site) have been included in the model.

Appendix 1 PHAST model code for MOD4 (.trans.dat file)

```

TITLE
Gatehampton 3 layer model (MOD4)

UNITS
-time d
-horizontal_grid m
-vertical_grid m
-head m
-hydraulic_conductivity m/d
-specific_storage 1/m
-dispersivity m
-flux mm/d
-river_bed_hydraulic_conductivity m/d
-river_bed_thickness m
-well_diameter mm
-well_flow_rate m3/day
-leaky_k m/d
-leaky_thickness m

GRID
-uniform x 455500 464500 19
-overlay_uniform x 459500 460500 51
-uniform y 175500 184500 19
-overlay_uniform y 179500 180500 51
-uniform z -25 45 10 # 9 layers of 7.8m
-print_orientation XZ

SOLUTE_TRANSPORT true

STEADY_FLOW false

MEDIA
# zones are defined such that largest is defined first for entire area (Lower Chalk)
# then overlain with fractured Chalk, then with gravels

#Lower Chalk (20m)
-zone 455500 175500 -25 464500 184500 45
    -porosity 0.2
    -Kx 5
    -Ky 5
    -Kz 0.5
    -horizontal_dispersivity 0.5
    -vertical_dispersivity 0.5
    -long_dispersivity 20
    -specific_storage 0.000001

#Fractured Chalk (40m)
-zone 455500 175500 5 464500 184500 45
    -porosity 0.5
    -Kx 170
    -Ky 170
    -Kz 300
    -horizontal_dispersivity 0.5
    -vertical_dispersivity 0.5
    -long_dispersivity 20
    -specific_storage 0.25

#Gravels zone 1(10m)
-zone 459000 183000 35 460000 184500 45
    -porosity 0.3
    -Kx 1500
    -Ky 1500
    -Kz 300
    -horizontal_dispersivity 0.5
    -vertical_dispersivity 0.5
    -long_dispersivity 20
    -specific_storage 0.25

#Gravels zone 2 (10m)
-zone 459500 181000 35 460500 183000 45

```

```

-porosity          0.3
-Kx                1500
-Ky                1500
-Kz                300
-horizontal_dispersivity 0.5
-vertical_dispersivity 0.5
-long_dispersivity   20
-specific_storage    0.25
#Gravels zone 3(10m)
-zone 459000 179500 35 460000 181500 45
-porosity          0.3
-Kx                1500
-Ky                1500
-Kz                300
-horizontal_dispersivity 0.5
-vertical_dispersivity 0.5
-long_dispersivity   20
-specific_storage    0.25
#Gravels zone 4(10m)
-zone 459500 179500 35 462000 180000 45
-porosity          0.3
-Kx                1500
-Ky                1500
-Kz                300
-horizontal_dispersivity 0.5
-vertical_dispersivity 0.5
-long_dispersivity   20
-specific_storage    0.25
#Gravels zone 5(10m)
-zone 461500 177500 35 462500 179000 45
-porosity          0.3
-Kx                1500
-Ky                1500
-Kz                300
-horizontal_dispersivity 0.5
-vertical_dispersivity 0.5
-long_dispersivity   20
-specific_storage    0.25
#Gravels zone 6(10m)
-zone 462000 176500 35 464500 177500 45
-porosity          0.3
-Kx                1500
-Ky                1500
-Kz                300
-horizontal_dispersivity 0.5
-vertical_dispersivity 0.5
-long_dispersivity   20
-specific_storage    0.25
#####
LEAKY_BC
-zone 455500 175500 -25 455500 184500 45      # east
  -head            0      Y     69.6532  175500  55.7336  184500
  -associated_solution 0      1
  -hydraulic_conductivity 170
  -thickness        200
-zone 456000 175500 -25 464000 175500 45      # south
  -head            0      X     67.9122  456000  41.4168  464000
  -associated_solution 0      1
  -hydraulic_conductivity 170
  -thickness        200
-zone 464500 177000 -25 464500 184500 45      # west -north of river
  -head            0      Y     39.5018  177000  54.2195  184500
  -associated_solution 0      1
  -hydraulic_conductivity 170
  -thickness        200
-zone 464500 175500 -25 464500 176500 45      # west -south of river
  -head            0      Y     41.2837  175500  39.8282  176500
  -associated_solution 0      1
  -hydraulic_conductivity 170
  -thickness        200
-zone 456000 184500 -25 459500 184500 45      # north -east of river
  -head            0      X     54.1718  456000  41.3089  459500
  -associated_solution 0      1
  -hydraulic_conductivity 170
  -thickness        200

```

```

-zone 460000 184500 -25 464000 184500 45      # north -west of river
      -head          0           X        41.8982  460000  52.3476  464000
      -associated_solution 0           1
      -hydraulic_conductivity    170
      -thickness         200

```

FLUX_BC

```

-zone      455500 175500 45 464500 184500 45
-flux      0       -0.5705  #average of recharge values for region taken from recharge.dat
#-flux     0       file   recharge.dat
#use only without study area discretization
-face      z
-associated_solution 0           3

```

RIVER 1 Thames River

```

-point      464885  177252
-head0      39.43
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      463945  176896
-head0      39.54
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      462998  176902
-head0      39.6
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      462301  177546
-head0      39.78
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      462042  178509
-head0      39.95
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      461580  179384
-head0      40.13
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      460236  179513
-head0      40.37
-width       10
-bed_hydraulic_conductivity      10000
-bed_thickness 2
-depth       2
-solution    0       2

-point      459792  179880
-head0      40.48
-width       10
-bed_hydraulic_conductivity      10000

```

```

-bed_thickness 2
-depth 2
-solution 0 2

-point 459505 180787
-head0 40.65
-width 10
-bed_hydraulic_conductivity 10000
-bed_thickness 2
-depth 2
-solution 0 2

-point 459993 181643
-head0 40.83
-width 10
-bed_hydraulic_conductivity 10000
-bed_thickness 2
-depth 2
-solution 0 2

-point 460021 182601
-head0 40.98
-width 10
-bed_hydraulic_conductivity 10000
-bed_thickness 2
-depth 2
-solution 0 2

-point 459542 183314
-head0 41.1
-width 10
-bed_hydraulic_conductivity 10000
-bed_thickness 2
-depth 2
-solution 0 2

-point 459372 184436
-head0 41.29
-width 10
-bed_hydraulic_conductivity 10000
-bed_thickness 2
-depth 2
-solution 0 2

```

WELL 1 Abstraction Well 1 - GH1

```

459960 179920
-pumping_rate
    0      day      15000 #m3/day
-diameter
    750
-land_surface_datum 40.77
-depth
    15      30

```

WELL 2 Abstraction Well 2 - GH4

```

460250 179620
-pumping_rate
    0      day      15000 #m3/day
-diameter
    740
-land_surface_datum 41.05
-depth
    15      30

```

WELL 3 Abstration Well 3 - GH6

```

460390 179940
-pumping_rate
    0      day      15000 #m3/day
-diameter
    750
-land_surface_datum 44.27
-depth
    16.4     31.4

```

FREE_SURFACE_BC true

```
#####
HEAD_IC
-zone 455500 175500 -25 464500 184500 45
-head 60
```

```
CHEMISTRY_IC
-zone 455500 175500 -25 464500 184500 45
```

```

-solution 1          # gw at Gatehampton
#####
SOLUTION_METHOD
-iterative_solver    false
-tolerance           1e-6
-save_directions     10
-maximum_iterations  800
-time_differencing   1

TIME_CONTROL
-time_step           0      50
-time_end            2000 days

PRINT_INITIAL
-HDF_heads           false
-HDF_chemistry        false
-xyz_heads            false
-xyz_chemistry        false
-xyz_wells            false

PRINT_FREQUENCY
0 days
-xyz_wells           1 step # writes to prefix.xyz.wel
-xyz_chemistry        40 step
-HDF_chemistry        1 step # writes to prefix.h5
-HDF_heads            1 step # writes to prefix.h5
-save_final_heads     # creates prefix.head.dat

-progress_statistics  40 step
-boundary_conditions 40 step
-bc_flow_rates        40 step
-flow_balance         40 step

END

```

Appendix 2 PHREEQC input file for inverse modelling

```
TITLE Inverse Modelling: Gatehampton Groundwater source
SOLUTION 1 Groundwater Wood Farm : Chalk EM
    units mg/L
    pH 7.05
    temp 10.0
    Alkalinity 273 as HCO3
    Ca 109 charge
    Cl 15.8
    Mg 1.53
    Na 7.5
    S(6) 8.36 as SO4
    Si 9.16
    END

SOLUTION 2 River Water EM
    units mg/L
    pH 7.99
    temp 10
    Alkalinity 245 as HCO3
    Ca 119 charge
    Mg 5.48
    Na 22.7
    Cl 36.5
    S(6) 59.7 as SO4
    Si 4.19
    END
# equilibrate infiltrating river water with CO2 partial pressure in vadose zone
USE solution 2
EQUILIBRIUM_PHASES 2
    CO2(g) -1.5 100
SAVE solution 2
END

SOLUTION 4 Groundwater at GH1
    units mg/L
    pH 7.83
    temp 10.0
    Ca 109 charge
    Mg 3.46
    Na 22.1
    Cl 23.3
    S(6) 27.5 as SO4
    Alkalinity 280 as HCO3
    Si 10.2
    END

INVERSE_MODELING
-solutions 1 2 4
-uncertainty 0.1
-phases
    CO2(g)
    Calcite
    SiO2(a)
#
    quartz
-balances
    Na 0.5
    Cl 0.5
    S(6) 0.5
    Mg 0.5
    H(O) 0.1
    - uncertainty_water 0.55 # moles (~1%)
END
```

Appendix 3 Chemistry input file for MOD4

```
TITLE Gatehampton model

SOLUTION 1 groundwater EM at Wood Farm PS No 2
    Units          mg/L
    pH            7.05
    temp          10
    Ca             109
    Mg             1.53
    Na             7.5
    K              1.72
    Si             9.16
    Cl             15.8      charge
    S(6)           8.36
    N(+5)          7.49
    Alkalinity 273 as HCO3
END

# equilibrate groundwater with calcite (quartz / amorphous silica)
USE solution 1
EQUILIBRIUM_PHASES 1
Calcite          0.5          SI at GH4
#SiO2(a)        - 0.9
#quartz         0.4
SAVE solution 1

SELECTED_OUTPUT
    -file Phreeqc.dat
    -reset false
    -solution
    -pH

USER_PUNCH
# output in mg/L
    -headings Ca Mg Na K Si Cl SO4 NO3 Alkalinity SI_calcite
    -start
    10 PUNCH MOL ("Ca+2")*40.08*1000, MOL("Mg+2")*24.312*1000, MOL("Na+")*22.9898*1000
    20 PUNCH MOL ("K+")*39.102*1000, TOT("Si")*60.0843*1000, MOL("Cl-")*35.453*1000
    30 PUNCH MOL("SO4-2")*96.0616*1000, MOL("NO3-")*14.0067*1000, MOL("HCO3-")*61.016*1000
    40 PUNCH SI("Calcite")
    -end
END

SOLUTION 2      River EM measured at Gatehampton 04/04/06
    Units          mg/L
    pH            7.99
    temp          10
    Ca             119
    Mg             5.48
    Na             22.7
    K              5.87
    Si             4.19
    Cl             36.5      charge
    S(6)           59.7
    N(+5)          7.71
    Alkalinity 245 as HCO3
END

#equilibrate infiltrating river water with partial CO2 pressure of vadose zone
USE solution 2
EQUILIBRIUM_PHASES 2
CO2(g) -1.5      100
SAVE solution 2
END

SOLUTION 3 Precipitation (*3) from monthly averages at Wytham ECN monitoring site
    Units          mg/L
    pH            5.03
    temp          10
    Ca             2.89
```

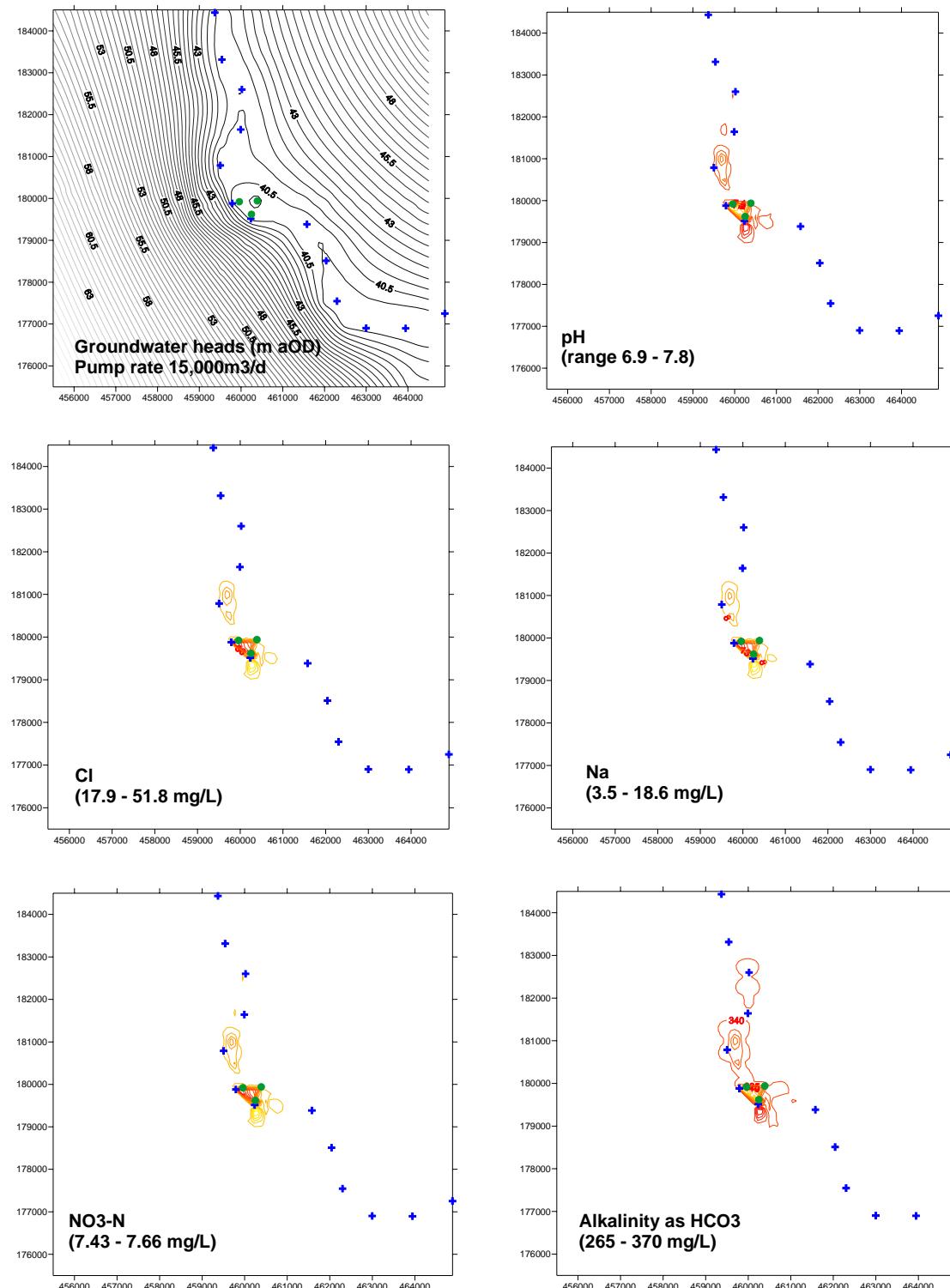
```
Mg          0.4
Na         3.12
K          0.22
Si          0
Cl          6.04      charge
S(6)       2.21
N(+5)      1.4
Alkalinity 1.4 as HCO3
END

# equilibrate infiltrating precipitation (x3) with partial CO2 pressure of vadose zone
USE solution 3
EQUILIBRIUM_PHASES 3
CO2(g) -1.5      100
SAVE solution 3
END

END
```

Appendix 4 Geochemical output from PHAST model MOD4

(Pump rate: 15,000 m³ d⁻¹, concentration ranges as displayed: yellow = low concentrations, red = high concentrations)



References

- ABESSER, C, SHAND, P, GOODDY, D C, and PEACH, D. 2008. The role of alluvial valley deposits in groundwater-surface water exchange in a Chalk river. in *Groundwater-surface water interactions: Process understanding, conceptualisation and modelling*. ABESSER, C, WAGENER, T, and NUETZMANN, G (editors). *IAHS Publications*, 320. (Wallingford: IAHS Press.)
- ALLEN, D J, BREWERTON, L J, COLEBY, L M, GIBBS, B R, LEWIS, M A, MACDONALD, A M, WAGSTAFF, S J, and WILLIAMS, A T. 1997. The physical properties of major aquifers in England and Wales. *British Geological Survey Research Report WD/97/34*.
- APPELO, C A J, and POSTMA, D. 1993. *Geochemistry, Groundwater and Pollution* (1 edition). (Rotterdam: Balkema.)
- HUGHES, A G, BLOOMFIELD, J P, MANSOUR, M M, JACKSON, C R, and PEACH, D W. 2005. Review of conceptual and numerical models in the Goring Gap area. *British Geological Survey Commissioned report*, CR/05/085C.
- JACKSON, C R, BLOOMFIELD, J P, BUCKLEY, D K, CHAMBERS, J E, DARLING, W G, HUGHES, A G, MANSOUR, M M, NEWELL, A J, PEACH, D W, and RAINES, M G. 2006a. Conceptualisation of groundwater flow in the Chalk aquifer around Gatehampton. *British Geological Survey Commissioned Report*, CR/06/206C.
- JACKSON, C R, HUGHES, A G, MANSOUR, M M, and PEACH, D W. 2006b. Numerical modelling of groundwater flow to Gatehampton. *British Geological Survey Commissioned Report*, CR/06/205C.
- JEANS, C V. 2006. Clay mineralogy of the Cretaceous strata of the British Isles. *Clay Minerals*, Vol. 41, 47-150.
- KIPP, K L, JR.,. 1987. HST3D: A computer code for simulation of heat and solute transport in three-dimensional ground-water flow system. *U.S. Geological Survey*, Water-Resources Investigations Report 86-4095.
- NEUMANN, I, and KINNIBURGH, D. 2004. Applying MODFLOW/MT3D and PHAST on vertical slice models developed for the Bangladesh aquifer. *British Geological Survey Internal Report*, IR/04/102.
- PARKHURST, D L, and APPELO, C A J. 1999. User's guide to PHREEQC (version 2)— A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geological Survey*, Water-Resources Investigation Report 99-4259.
- PARKHURST, D L, KIPP, K L, ENGESGAARD, P, and CHARLTON, S R. 2004. PHAST-A program for simulating ground-water flow and multi-component geochemical reactions. *U.S. Geological Survey*, Techniques and Methods 6-A8.

ROBINSON, V K, and BANKS, D. 1987. Hydrogeological investigation of the Gatehampton groundwater source. 1984 to 1986. *Thames Water Authority Regulation and Monitoring Report*.

WOODS, M A, ALLEN, D J, FORSTER, A, PHAROAH, T C, and KING, C. 2004. Geology of London. *British Geological Survey*, Sheets 256 (North London), 257 (Romford), 270 (South London) and 271 (Dartford) (England and Wales).

ZHU, C, and ANDERSON, G. 2002. *Environmental Applications of Geochemical Modelling*. (Cambridge: Cambridge University Press.)