Hydrogeological processes and geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystem

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Deliverable 5.1

Atlas of hydrogeological settings of nitrate transport in the unsaturated zone

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The GeoERA-Groundwater HOVER (Hydrogeological processes and Geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems) project aims to gain an understanding of the controls on groundwater quality across Europe.

Within HOVER, Work Package 5 (WP5) aims to develop an improved understanding of the transport of nitrate (NO3) and pesticides (PST) from soil to groundwater receptors. The aim of the first task of WP5 (Task 5.1) is to characterise agrochemical travel times across Europe. This report and associated web atlas on the EGDI form the deliverable associated with this task.

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1 INTRODUCTION

1.1 Background to HOVER and WP5

The GeoERA-Groundwater HOVER (**H**ydrogeological processes and Geological settings **over** Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems) project aims to gain an understanding of the controls on groundwater quality across Europe.

Nitrate and pesticides remain ubiquitous groundwater contaminants in Europe, and are major concerns for public and private water supply and aquatic ecosystems. Within HOVER, Work Package 5 (WP5) aims to develop an improved understanding of the transport of nitrate (NO_3) and pesticides (PST) from soil to groundwater receptors.

1.2 Background to Task 5.1 and this report

There is now substantial evidence (Vero et al. 2018) that in some hydrogeological settings, time lags of decades or more can occur betweeen nitrate leaching from the base of the soil zone and the water table. Recently, this time lag and the associated store of nitrate has been quantified at the global scale (Ascott et al. 2017). However, the extent across Europe of hydrogeological settings in which time lags in the unsaturated zone are significant is poorly constrained.

The aim of the first task of WP5 (Task 5.1) is to characterise agrochemical travel times across Europe. This report and associated web atlas on the EGDI form the deliverable associated with this task. Here we present a series of common, evidence-based conceptual models for nitrate transport in the shallow subsurface, co-produced with HOVER WP5 partners. These conceptual models cover both aquifers in which there is the potential for significant travel times in the unsaturated zone, and aquifers with a limited unsaturated zone and unproductive, low permeability strata. These conceptual models are then mapped across the WP5 partners and presented here and in the EGDI. In conjunction with monitoring data in task 5.2, these conceptual models will be used to support the development and refinement of existing models of nitrate transport in the unsaturated and saturated zone (Ascott et al. 2017, Wang et al. 2016) in task 5.3.

It should be noted that it is beyond the scope of this report to provide a fully exhaustive account of the evidence base for each conceptual model. For each model, we provide an overview of the hydrogeological setting and provide references should the reader require further information. It should also be noted that for the purposes of this report, only unsaturated zone travel times are considered. Travel times for the saturated zone are considered in detail in HOVER WP6 Groundwater Age Distributions and in the other WP5 reports.

2 METHODOLOGY

2.1 Co-production of conceptual models

A co-production approach was used to develop simplified conceptual models for nitrate transport in the shallow subsurface across Europe. This is detailed as follows:

1. Initial conceptual models were developed by task leads based on the UK settings.
2. The initial conceptual models were reviewed by HOVER partners.
3. HOVER partners and the task leads worked iteratively to develop new conceptual models where the initial conceptualisations do not apply. This included references to “type sites” where conceptual models are supported by detailed studies and data.

For the purpose of this report, conceptual models are divided into those aquifers where there is the potential for significant travel times in the unsaturated zone, and aquifers with a limited unsaturated zone and non-aquifers.

Each conceptual model developed in section 2.1 was then mapped by WP5 partners in their country. These maps are presented in this report and in the EGDI.

3 CONCEPTUAL MODELS

3.1 Overview

In this section the conceptual models developed in this task and the evidence to support these models is given. The distribution of these conceptual models across the project partners is shown in Table 3.1.

Table 3.1 Distribution of conceptual models across participating HOVER WP5 Partners

Organisation	Country	Aquifers with unsaturated zones with potentially significant travel times						Aquifers with limited unsaturated zones and non-aquifers					
		Unconfined carbonates	Coarse-grained sandstone	Fine-grained sandstone	Karst	Hard rock/fracture flow	Multilayered aquifers	Mudstone	Aquifers overlain by low permeability superficial deposits	Shallow superficial aquifers	Quaternery sands and gravels	Karst aquifers with thin unsaturated zones	Had rock/fracture flow with thin unsaturated zones
BGS (NERC)	UK	X	X	X	X	X	X	X	X	X	X		
BRGM	France	X	X	X	X	X		X	X		X		
GSD	Cyprus	X			X	X	X				X		
GSI	Ireland			X					X		X	X	X
HGI-CGS	Croatia		X		X	X	X	X	X		X		
MTI	Malta						X						
GEUS	Denmark	X				X			X	X	X		
GeoZS	Slovenia		X		X	X	X						

3.2 Aquifers with unsaturated zones with potentially significant travel times

3.2.1 Unconfined carbonate aquifers

3.2.1.1 Lithology and transport mechanism

Unconfined carbonate aquifers consist of soft, white, fine grained limestones such as the Chalk of southeast England and the Paris basin. This conceptual model is shown in Figure 3.1. Whilst dual-domain transport occurs in the unsaturated zone of these aquifers, the majority of transport occurs within the matrix and more rapid bypass flow is ignored in this conceptual model as this does not result in significant travel times. The small poresize means that some water always retained in the matrix of the unsaturated zone.

3.2.1.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocity estimates were summarised by Chilton and Foster (1991) as 0.3-1.4 m/year. This is based on nitrate and tritium profiling from porewater in cores in Dorset and Norfolk, UK. A mean velocity of 0.8 to 0.9 m/year was reported. Similar velocities (c. 1 m/year) were reported by Chen et al. (2019) in Northern France and in Belgium (Brouyère et al. 2004). Moderate relief can lead to unsaturated thickness of over 100 m.

3.2.1.3 Location of case studies of the conceptual model

This conceptual model is present in the UK, France, Cyprus and Denmark. Chilton and Foster (1991) and Wang et al. (2012) provide more detail on the conceptual model for the English Chalk. Gourcy et al. (2017) provide information on the location of this conceptual model in France, principally in the Paris and Aquitaine basins. In Cyprus, carbonate aquifers are known as the Lefkara-Pakna aquifers. Unsaturated zone velocities are unknown in these aquifers but are reported to be extremely low. Unsaturated zone thicknesses in these aquifers may be > 100 m.

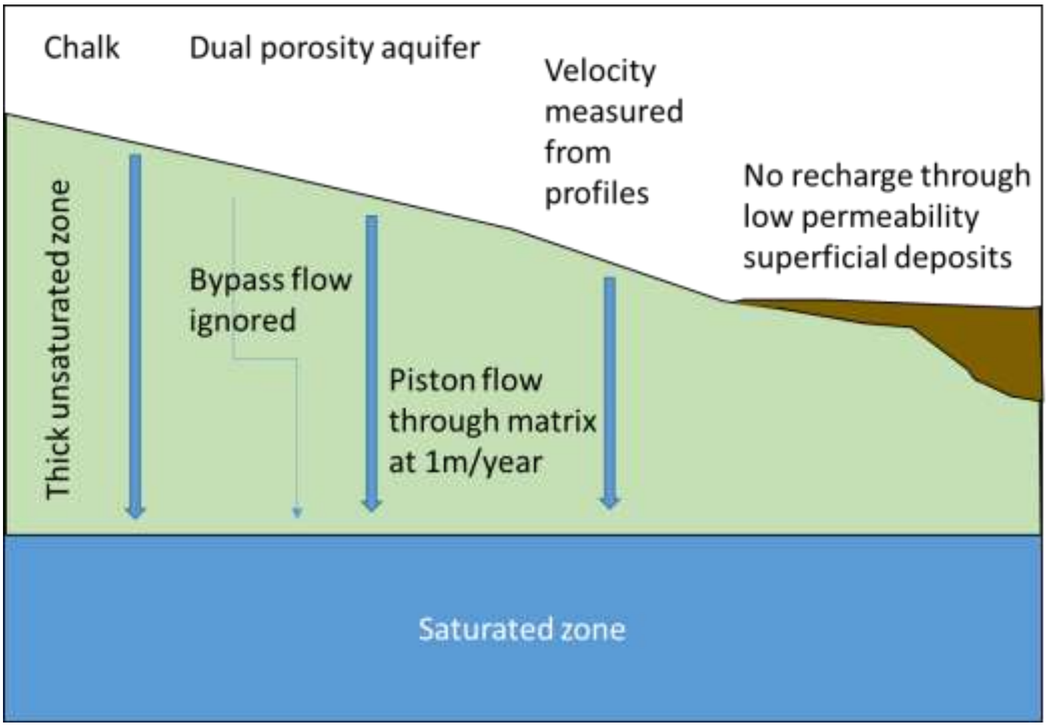

Figure 3.1 Conceptual model of unsaturated zone transport in unconfined chalk aquifers

3.2.2 Coarse-grained sandstone

3.2.2.1 Lithology and transport mechanism

Nitrate transport in coarse and medium-grained sandstones is dominated by the matrix. The large pore size in these formations results in a very low water content of the unsaturated matrix.

3.2.2.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Chilton and Foster (1991) summaried previous velocity estimates as 0.6-2.5 m/year from measurements in the Permo-Triassic sandstones of the Midlands and Yorkshire, UK, using profiling of nitrate in porewater from cores from shallow boreholes. In the UK, these deposits are relatively friable and do not form large areas of elevated ground and thus unsaturated zones are relatively thin.

3.2.2.3 Location of case studies of the conceptual model

This conceptual model applies to UK, France, Croatia and Slovenia (Geological Survey of Slovenia 2005, Mali and Korosa 2015). In the UK, research in the Permo-Triassic Sandstones have been reported by Chilton and Foster (1991), Foster et al. (1982) and Wang et al. (2012). In France, this conceptual model applies to coarse-grained sandstone at outcrop and permeable volcanic formations with hydrogeological characteristics similar to coarse-grained sandstone as reported by Gourcy et al. (2017). In Croatia, this conceptual model applies to Pliocene-Quaternary clastic deposits on the slopes of the mountains and quaternery low-permeability clastic deposits (Biondić and Brkić 2002, Biondić et al. 1996).

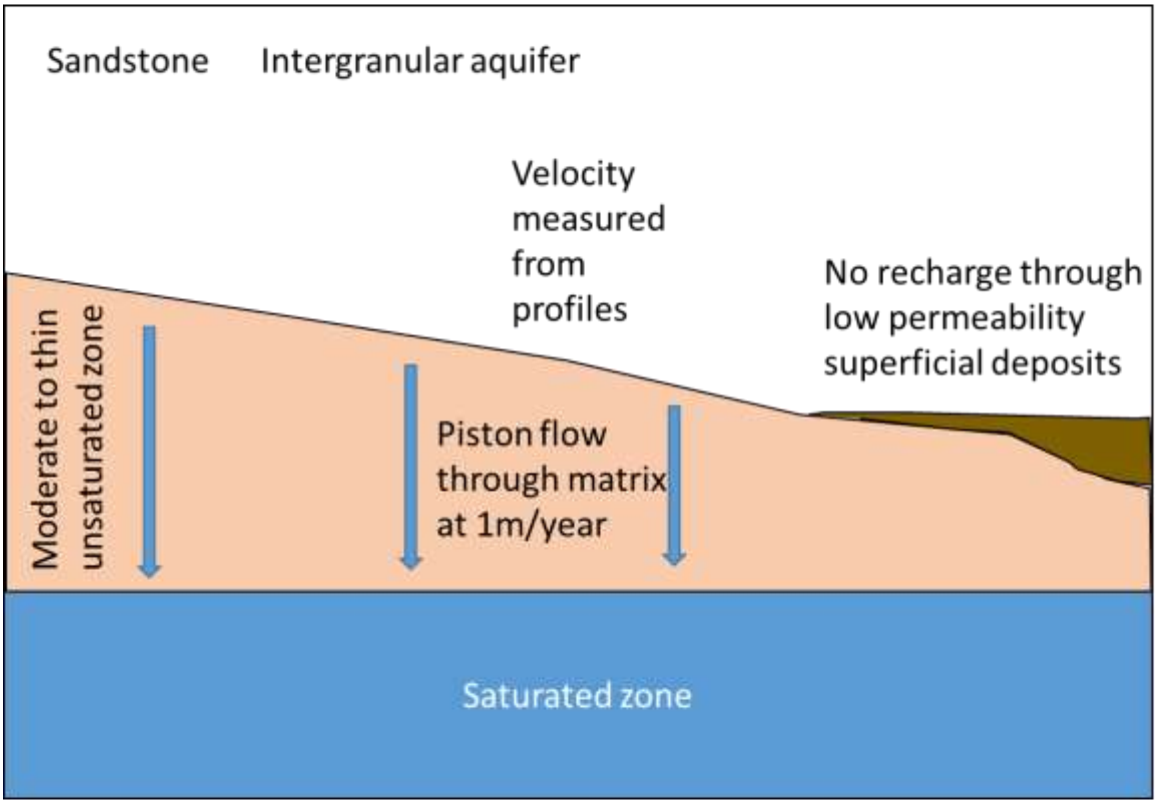

Figure 3.2 Conceptual model of unsaturated zone transport in coarse-grained sandstone aquifers

3.2.3 Fine-grained sandstone

3.2.3.1 Lithology and transport mechanism

Nitrate transport in fine-grained sandstones and silty sandstones is predominantly through the matrix. The water content of the unsaturated matrix is unknown but is likely to be low.

3.2.3.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities of 0.3 to 3m/year depending on ratio of sand to silt were measured by Chilton and M.J. (1994) and reported by Wang et al. (2012). Topography is likely to be variable, resulting in a range of unsaturated zone thicknesses.

3.2.3.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France and Ireland. In the UK, the model applies to Cretaceous sandstones and Lower Greensands as detailed by Allen et al. (1997), Jones et al. (2000) and Wang et al. (2012). In France this model applies to sandstones and sands in the sedimentary basins of Paris and Aquitaine (Gourcy et al. 2017). In Ireland this model applies to a very limited extent, to the Devonian Kiltorcan Formation (Daly 1988).

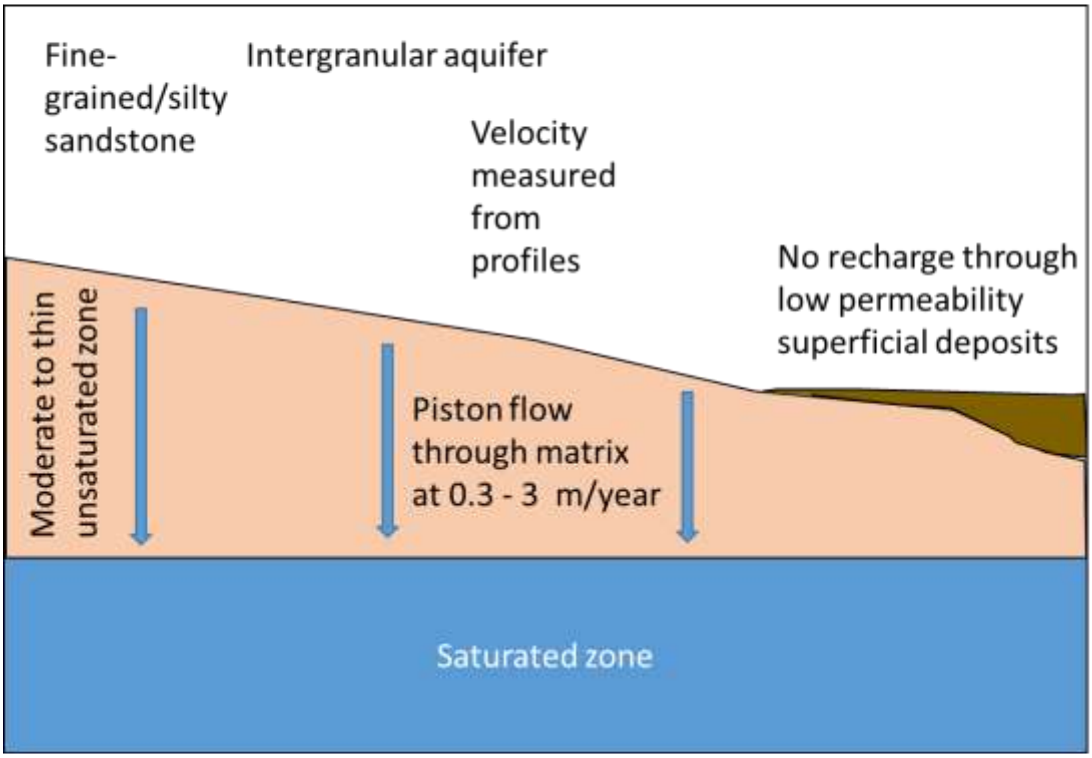

Figure 3.3 Conceptual model of unsaturated zone transport in fine-grained sandstone aquifers

3.2.4 Karst

3.2.4.1 Lithology and transport mechanism

Nitrate transport in karst limestones is through the fissure network. The water content of the unsaturated matrix is unknown but is likely to be insignificant.

3.2.4.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities of 10 m/year were estimated heuristically by Wang et al. (2012). Topography can to be significant, resulting in a large unsaturated zone thicknesses.

3.2.4.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France, Cyprus, Croatia and Slovenia. In the UK, the model applies to Carboniferous and Zechstein limestones, Durness (Cambro-Ordovician) and Dolomitic congolomerates (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012). In France this model applies to karst aquifers in southeast France (Gourcy et al. 2017). In Croatia, this model applies to the Žumberak, Ivančica, Papuk dolomite and limestone, the Dinaric karst (Biondić and Biondić 2014, Biondić and Brkić 2002, Biondić et al. 1996, Bonacci 1987, Brkić et al. 2018, Slišković 2014). In Cyprus, the karst conceptual model also applies to Koronia, Tera and Kyrenia range limestones and dolomites in gypsum pseudokarst (United Nations Development Programme 1970). In Slovenia, much of the centre and west of the country is underlain by this conceptual model (Cucchi et al. 2015).

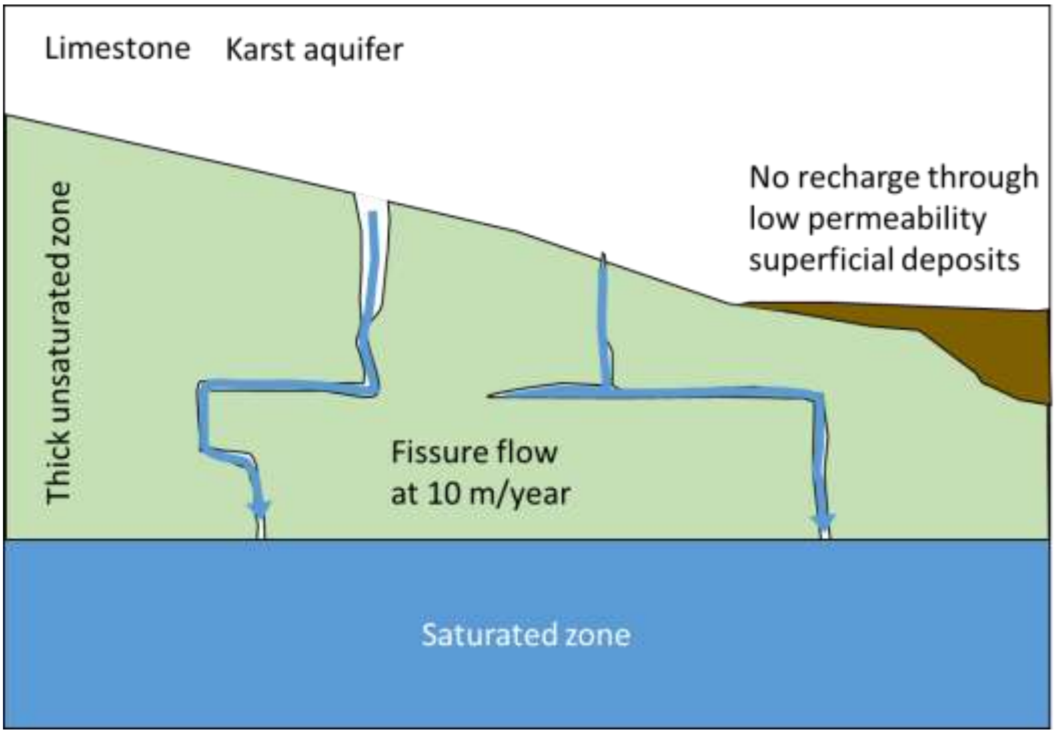

Figure 3.4 Conceptual model of unsaturated zone transport in karst aquifers

3.2.5 Hard rock/fracture flow

3.2.5.1 Lithology and transport mechanism

The hard rock/fracture flow conceptual model applies to granite and ophiolite formations and well consolidated sandstones (e.g. Carboniferous, Devonian). Nitrate transport is likely to be through the fissure network. The water content of the unsaturated matrix is unknown but is likely to be insignificant.

3.2.5.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities of 1 m/year were estimated heuristically by Wang et al. (2012) associated with poor fracture connectivity. Topography is likely to be significant, resulting in a large unsaturated zone thicknesses.

3.2.5.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France, Cyprus, Croatia and Slovenia (Geological Survey of Slovenia 2005). In the UK, the model applies to Carboniferous sandstone, Old Red Sandstone (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012), and indurated Silurian and igneous and metamorphic rocks. In France this model applies to crystalline basement, metamorphic and plutonic rocks (Gourcy et al. 2017). In Croatia, this model applies to Papuk, Mt. Moslavačka gora and Mt. Ivančica magmatic and low-grade metamorphic rocks; Paleozoic clastic rocks (Biondić and Brkić 2002, Biondić et al. 1996). In Cyprus, the conceptual model applies to the Troodos fractured aquifer (Afrodidis 1991, Boronina et al. 2003).

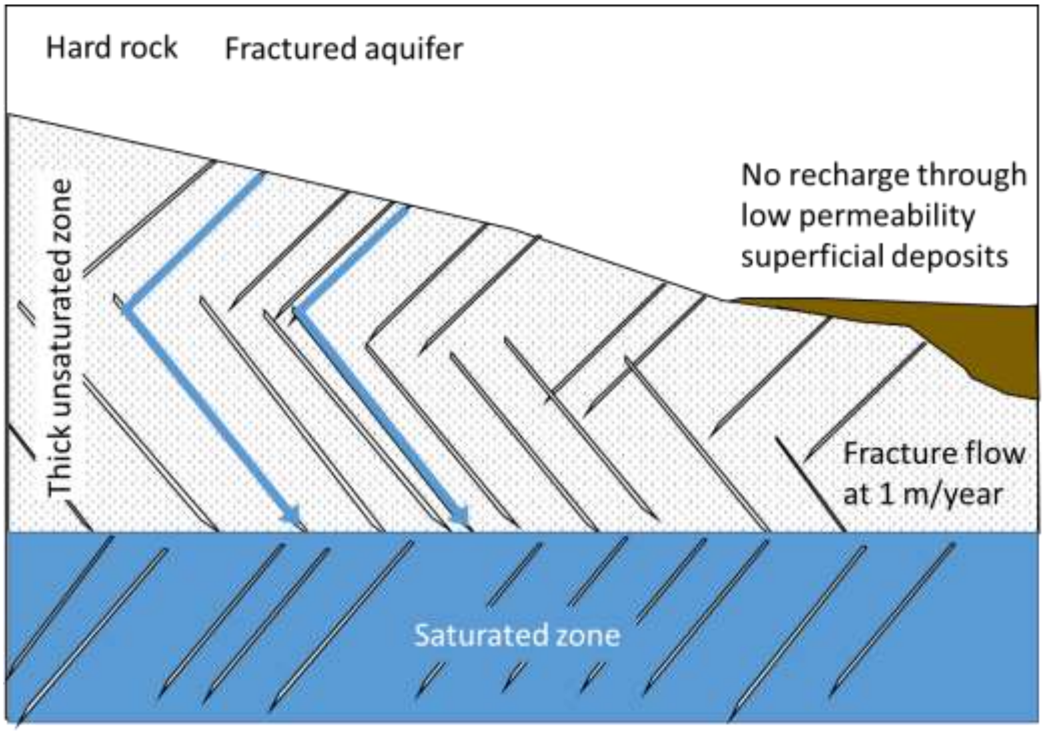

Figure 3.5 Conceptual model of unsaturated zone transport in hard rock fractured aquifers

3.2.6 Multilayered aquifers

3.2.6.1 Lithology and transport mechanism

The multilayered conceptual model applies to low permeability deposits with significant sandstone or limestone layers. Nitrate transport is likely to be through vertical matrix flow in permeable layers, and via shallow lateral flow where vertical flow is inhibited by low permeability strata. The water content of the unsaturated matrix is unknown.

3.2.6.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities of 1 m/year were estimated heuristically by Wang et al. (2012). Topography is likely to be limited resulted in small unsaturated zone thicknesses.

3.2.6.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, Croatia, Cyprus, Malta and Slovenia (Geological Survey of Slovenia 2005). In the UK, the model applies to Mercia Mudstone (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012). In Croatia, this model applies to the Istria flish (Biondić and Brkić 2002, Biondić et al. 1996). In Cyprus, this model represents the Mesaoria aquifer. This consists of high permeability deposits with significant unconsolidated gravel, sand, sandstone and/or silt layers. Deeper aquiferous, sand and sandstone layers, interlayered with lower permeability sandy marl, develop at places (Kitching et al. 1980, United Nations Development Programme 1970). In Malta, unsaturated zone flow in the mean sea level aquifer and Upper Coralline and intermediate Blue Clay conforms to this conceptual model (Stuart et al. 2008).

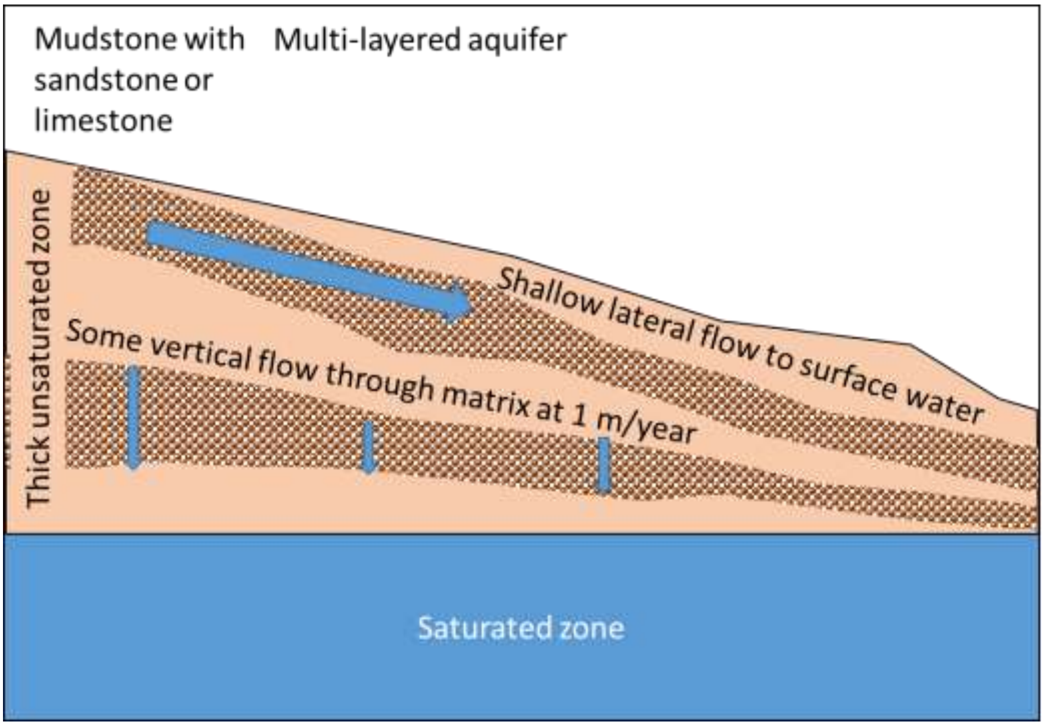

Figure 3.6 Conceptual model of unsaturated zone transport in complex multilayered aquifers

3.3 Aquifers with limited unsaturated zones and non-aquifers

3.3.1 Mudstone

3.3.1.1 Lithology and transport mechanism

The mudstone conceptual model applies to low permeability mudstones and clays. Vertical flow is likely to be inhibited and the mudstone is likely to act as an aquitard. The water content of the unsaturated matrix is likely to be high and potentially saturated.

3.3.1.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities of 0.1 m/year were measured by Smith et al. (1970) and used i modelling by Wang et al. (2012). Topography is likely to be limited resulted in small unsaturated zone thicknesses.

3.3.1.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France and Croatia. In the UK, the model applies to Jurassic clays (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012). In France, the model applies to mudstones, clays and marl deposits (Gourcy et al. 2017). In Croatia, this model applies to the Mt. Zrinska gora and Mt. Petrova gora Paleozoic clastic deposits (Biondić and Brkić 2002, Biondić et al. 1996).

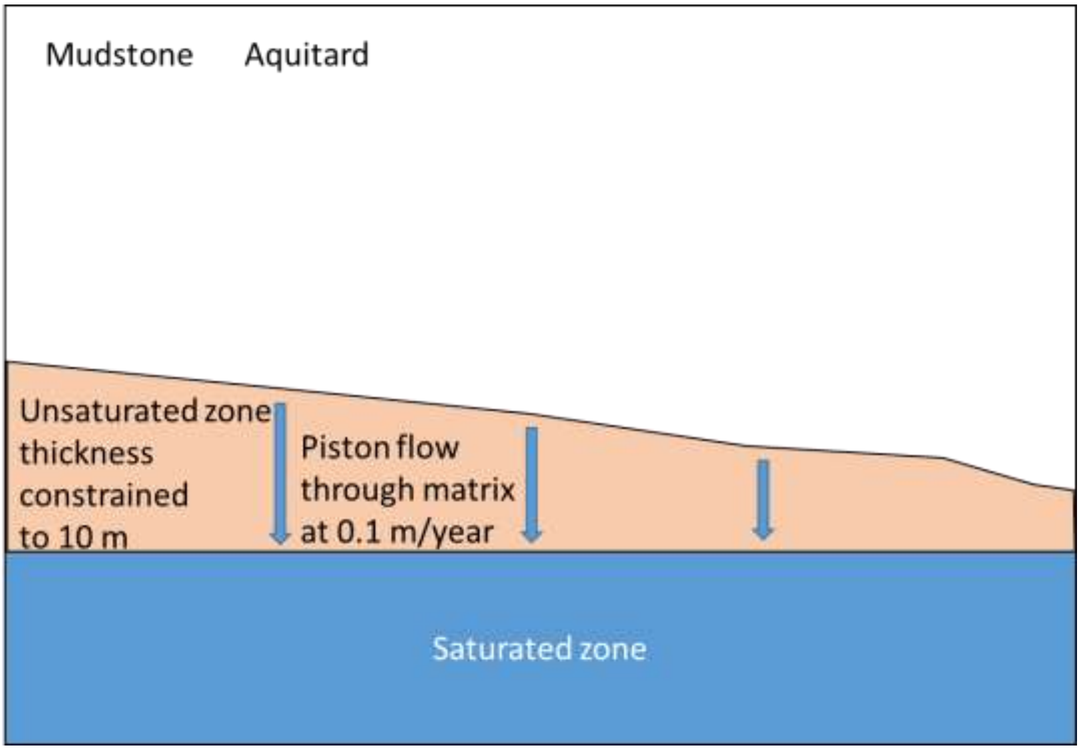

Figure 3.7 Conceptual model of shallow subsurface transport in mudstone aquitards

3.3.2 Aquifers overlain by low-permeability superficial deposits

3.3.2.1 Lithology and transport mechanism

In this conceptual model the aquifer is overlain by low permeability superficial deposits which may fully or partially confine (leaky) the aquifer. Where the aquifer is fully confined, no vertical flow occurs and there is no unsaturated zone. This conceptual model is shown in main aquifer models in section 3.2.

When the aquifer is semi-confined or unconfined some limited vertical flow may occur, depending on fracturing and permeability of the till layer. In some cases there may be limited vertical flow through microporous biopore flow (Rosenbom et al. 2008, Rosenbom et al. 2009). Low till matrix permeability results in a high degree of saturation.

3.3.2.2 Unsaturated zone velocity estimates and unsaturated thicknesses

There is unlikely to be any significant topography where this conceptual model applies. Where fully confined, no vertical flow occurs and there is no unsaturated zone.

When semiconfined or unconfined, there is likely to be either a very thin (< 5 m) unsaturated zone. Unsaturated zone flow velocities are likely to be highly variable dependent on the degree of till fracturing (1 mm/year > 10 m/year).

In fully, semiconfined and unconfined cases, there is likely to be limited unsaturated zone nitrate transport due to the thin unsaturated zone.

3.3.2.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France, Croatia, Denmark and Ireland. In the UK, the model applies to aquifers covered by till deposits in East Anglia (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012). In France, the model applies to confined aquifers of the Aquitaine Basin, which are overlain by Molasses (Gourcy et al. 2017).

In Croatia, the Sava and Drava alluvial aquifers are semi-confined by low permeability superficial deposits (Brkić et al. 2016, Brkić et al. 2013, Urumović et al. 2011) (Brkić et al. 2016; Brkić et al. 2013; Urumović et al. 2011), and the Savea is fully confined by a thick sequence of low permeabiltiy deposits is some areas (Biondić and Brkić 2002, Biondić et al. 1996).

In Denmark, the unconfined model applies to c. 40% of the surface of the country. Clayey till fields are underlain by fractured glacial till and either sand or fractured Chalk aquifers, as reported in the Danish Pesticide Leaching Assessment Programme (PLAP; http://pesticidvarsling.dk/areas_uk/index.html) and by Ernstsen et al. (2015), Rosenbom et al. (2015)

In Ireland this model applies to a limited extent in the north of Co Dublin, Tydavnet in Co Monaghan, Swan in Co Laois (Geological Survey of Ireland 2000) and consists of glacial tills of variable thickness overlying Precambrian to Upper Carboniferous deltaic sedimentary rocks.

3.3.3 Shallow superficial aquifers

3.3.3.1 Lithology and transport mechanism

The layered shallow aquifer conceptual model applies to clay layers with sand/gravel beds or lenses. Vertical flow is likely to be inhibited by clay layers and lateral flow to surface water is likely to be occurring.

3.3.3.2 Unsaturated zone velocity estimates and unsaturated thicknesses

No vertical flow is assumed. Topography is likely to be limited resulted in small unsaturated zone thicknesses.

3.3.3.3 Location of case studies of the conceptual model

This conceptual model applies in the UK to areas underlain by alluvium, alluvial fan, blown sand and marine, coastal and glacial lake deposits (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012).

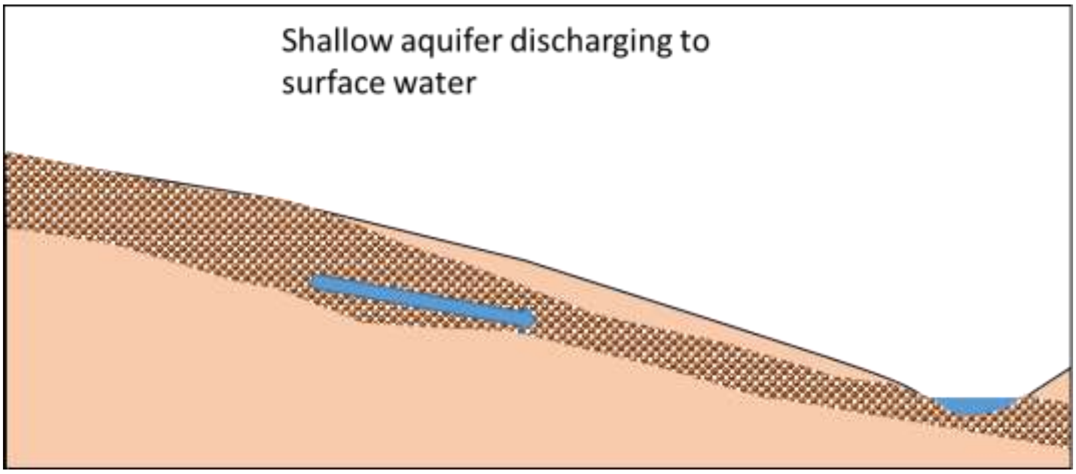

Figure 3.8 Conceptual model of shallow subsurface transport in shallow aquifers in layered deposits

3.3.4 Quaternary sands and river gravels

3.3.4.1 Lithology and transport mechanism

The Quaternary sands and gravels conceptual model applies to shallow gravel deposits where flow is through the matrix.

3.3.4.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities are unknown but are likely to be high. Topography is likely to be limited resulting in very small unsaturated zone thicknesses.

3.3.4.3 Location of case studies of the conceptual model

This conceptual model applies in the UK, France, Cyprus and Croatia. In the UK, the model applies to fluvio-glacial river gravels of the Thames basin (Allen et al. 1997, Jones et al. 2000, Wang et al. 2012). In France, the model applies to Quaternary alluvium and river deposits (Gourcy et al. 2017). In Croatia, this model applies to the Sava and Drava alluvial aquifers (Biondić and Brkić 2002, Biondić et al. 1996, Larva 2008, Patrčević 1995, Ružičić et al. 2016). In Cyprus, this model applies to the Pyrgos alluvial Aquifer (Food and Agriculture Organization of the United Nations 2002). Approximately 1.5% of Ireland is underlain by this conceptual model. Reporting is currently being finalised. Examples include The Curragh glacial sand and gravels and the Barrow and Nore river gravels.

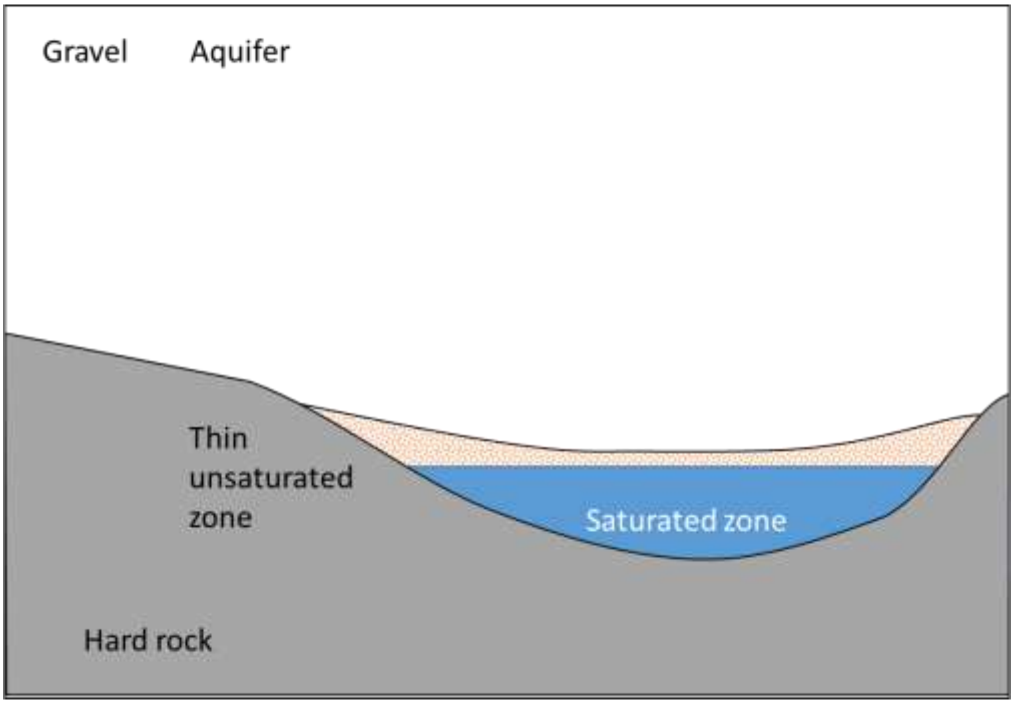

Figure 3.9 Conceptual model of shallow subsurface transport in quaternary gravel aquifers

3.3.5 Karst aquifers with thin unsaturated zones

3.3.5.1 Lithology and transport mechanism

Nitrate transport in karst limestones is through the fissure network. The water content of the unsaturated matrix is unknown but is likely to be insignificant. The epikarst is likely to be saturated in winter and during rainfall events but unsaturated at other times.

3.3.5.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Velocities > 200 m/day have been reported (Drew 2018). Topography is likely to be limited resulting in very small unsaturated zone thicknesses. This model is conceptually similar to the model presented in Figure 3.4 but with a shallow water table.

3.3.5.3 Location of case studies of the conceptual model

This conceptual model applies in Ireland, where the Mississippian (Tournaisian and Visean) Carboniferous Limestone covers c. 20% of the shallow subsurface by area. Most karstified Irish limestones are layered, with bedding typically 0.5-2m (check) thick. They may be separated by thin shales or chert bands at some intervals, and may be fossiliferous.

Upland and lowland karst with no/thin subsoil cover is present in the Burren, Co Clare and Gort Lowlands, Co Galway. Lowland karst with substantial medium permeability cover is also present, e.g. Kilkenny (Drew 2018).

3.3.6 Hard rock/fracture flow with thin unsaturated zones

3.3.6.1 Lithology and transport mechanism

The hard rock/fracture flow conceptual model applies to igneous, metamorphic and non-karstified sedimentary bedrock. Nitrate transport is likely to be through the fissure network. The water content of the unsaturated matrix is insignificant.

3.3.6.2 Unsaturated zone velocity estimates and unsaturated thicknesses

Unsaturated zone velocities are unknown but assumed to be close to the saturated bulk fracture permeability. Topography is likely to be limited resulting in very small unsaturated zone thicknesses. This model is conceptually similar to the model presented in Figure 3.5 but with a shallow water table.

3.3.6.3 Location of case studies of the conceptual model

This conceptual model applies in Ireland, and covers 80% of the subsurface by area. Examples include the Old Red Sandstone in Cork, Kerry and the Midlands, and Ordivican and Precambrian rocks in northeast and norhwest Ireland respectively (Comte et al. 2012).

4 MAPS OF CONCEPTUAL MODELS

4.1 Overview

This section presents overview maps of the locations of these conceptual models for all contributing partners to HOVER WP5 Task 5.1. These are also presented on the EGDI.

Figure 4.1 shows the distribution of HOVER WP5 partners contributing to D5.1. Figure 4.2 to Figure 4.9 show the distribution of the conceptual models for each partner country. It must be noted that some formations reported in Table 3.1 are not mapped in the figures below where they are insignificant at the national scale (for example, fine grained sandstone aquifers in Ireland). It should also be noted that the mapping of conceptual models in Denmark is primarily derived from sites used in the Pesticide Leaching Assessment Programme (PLAP, Rosenbom et al. (2015)), and thus the maps presented are not continuous at the national scale.

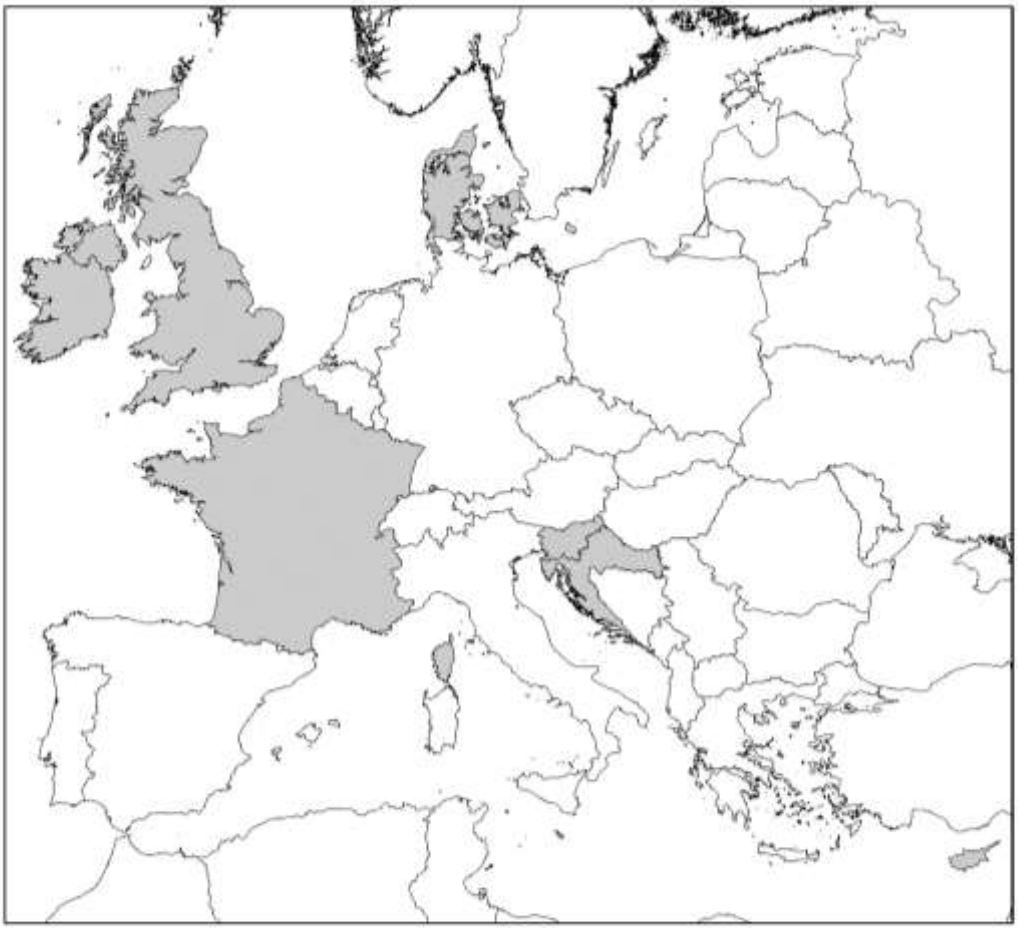

Figure 4.1 Countries participating in HOVER D5.1. Contains linework © EuroGeographics.

4.2 UK

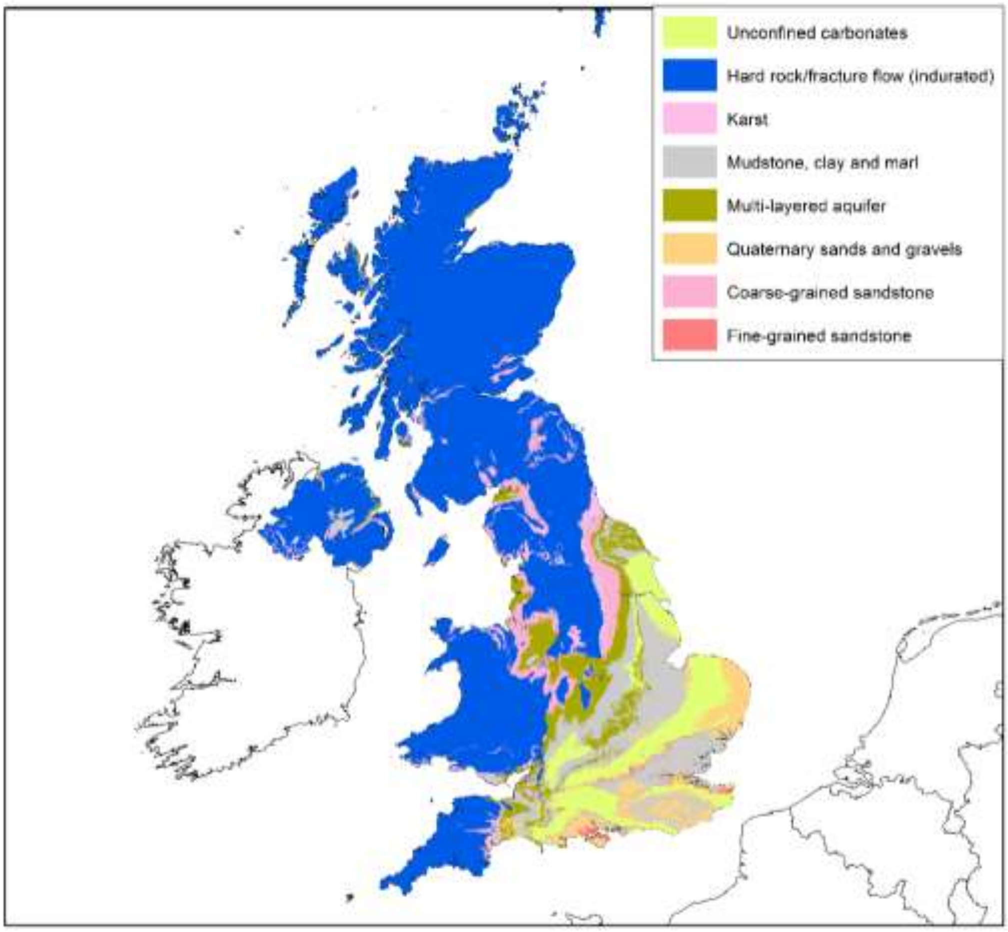

Figure 4.2 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the UK. Contains linework © EuroGeographics. Contains BGS hydrogeological mapping data © UKRI 2019.

4.3 Ireland

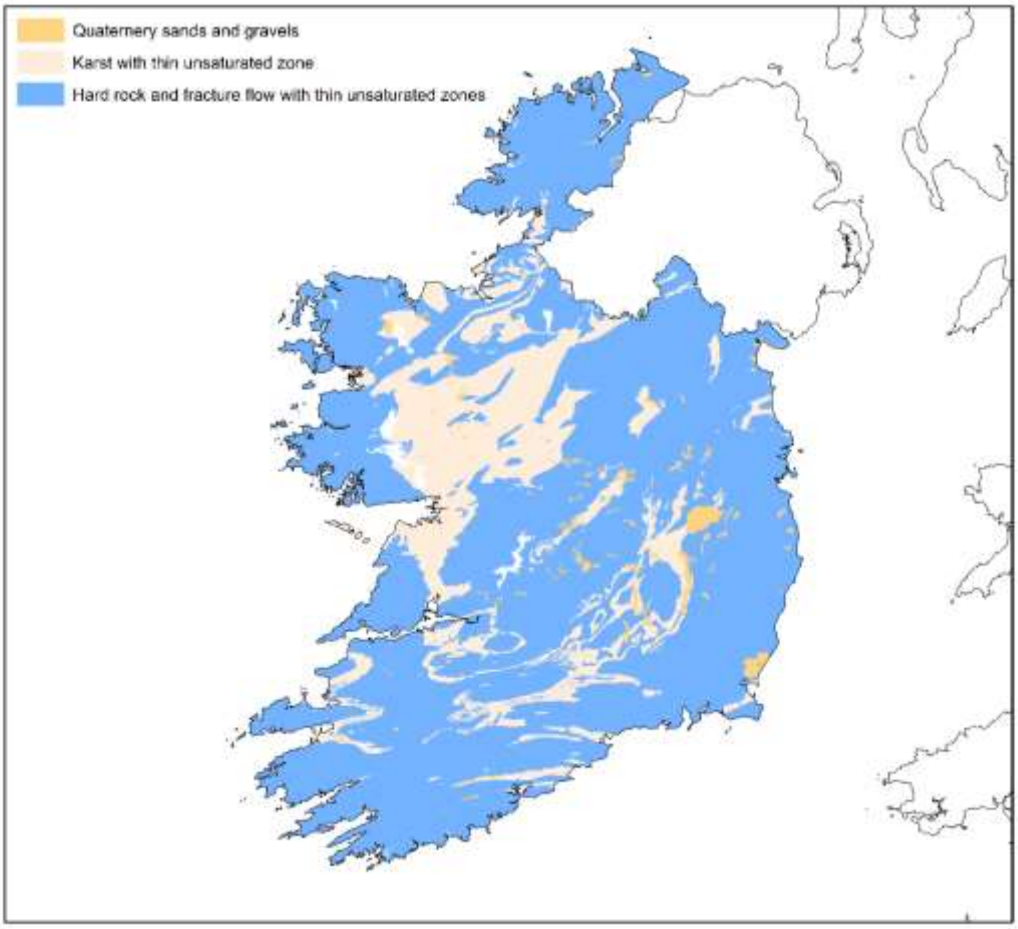

Figure 4.3 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Ireland. Contains linework © EuroGeographics. Contains data provided courtesy of the Geological Survey Ireland.

4.4 France

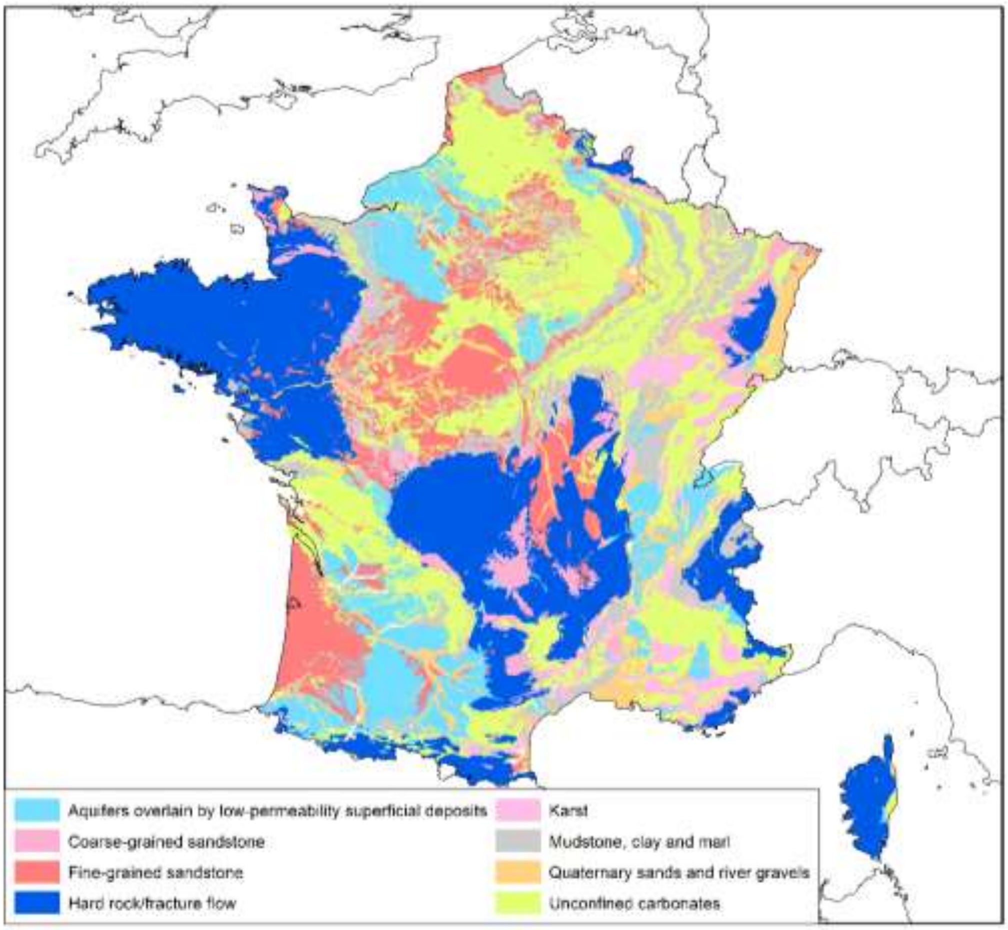

Figure 4.4 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the France. Contains linework © EuroGeographics. Contains data provided courtesy of the French Geological Survey.

4.5 Denmark

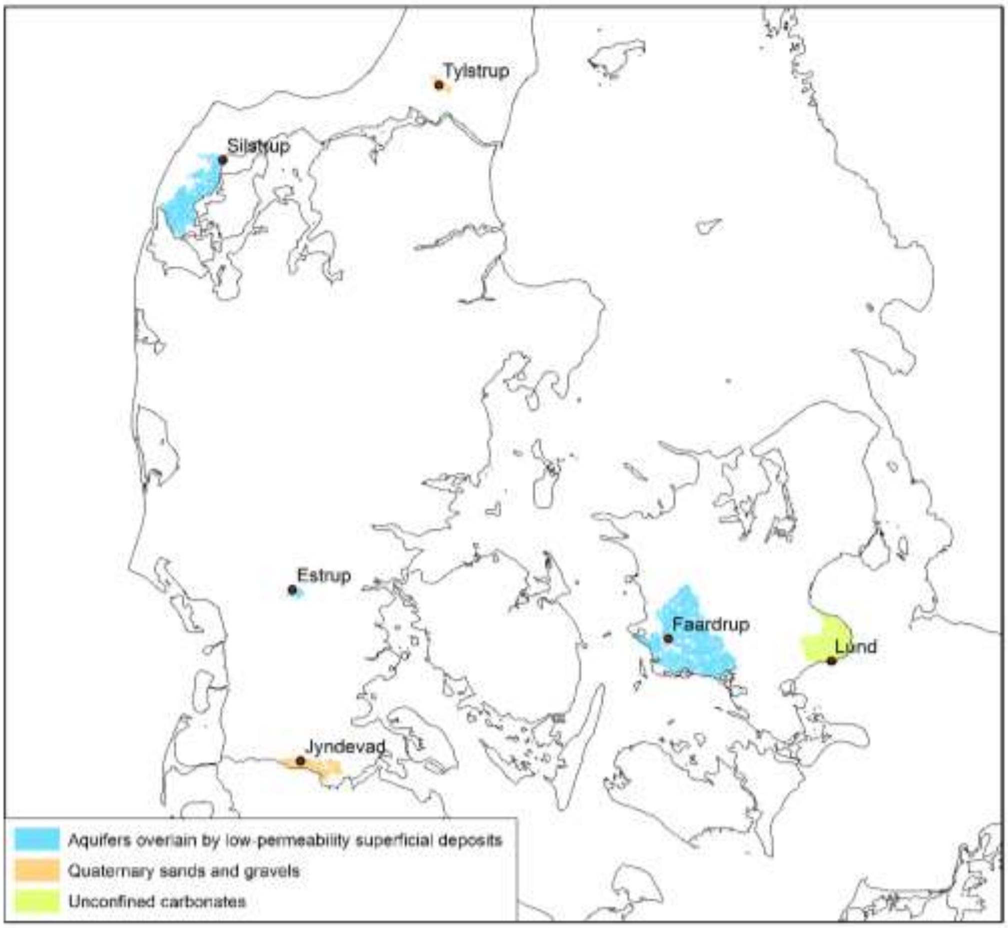

Figure 4.5 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Denmark. Locations of the PLAP sites are shown (Rosenbom et al. 2015). Contains linework © EuroGeographics. Contains data provided courtesy of the Geological Survey of Denmark and Greenland.

4.6 Croatia

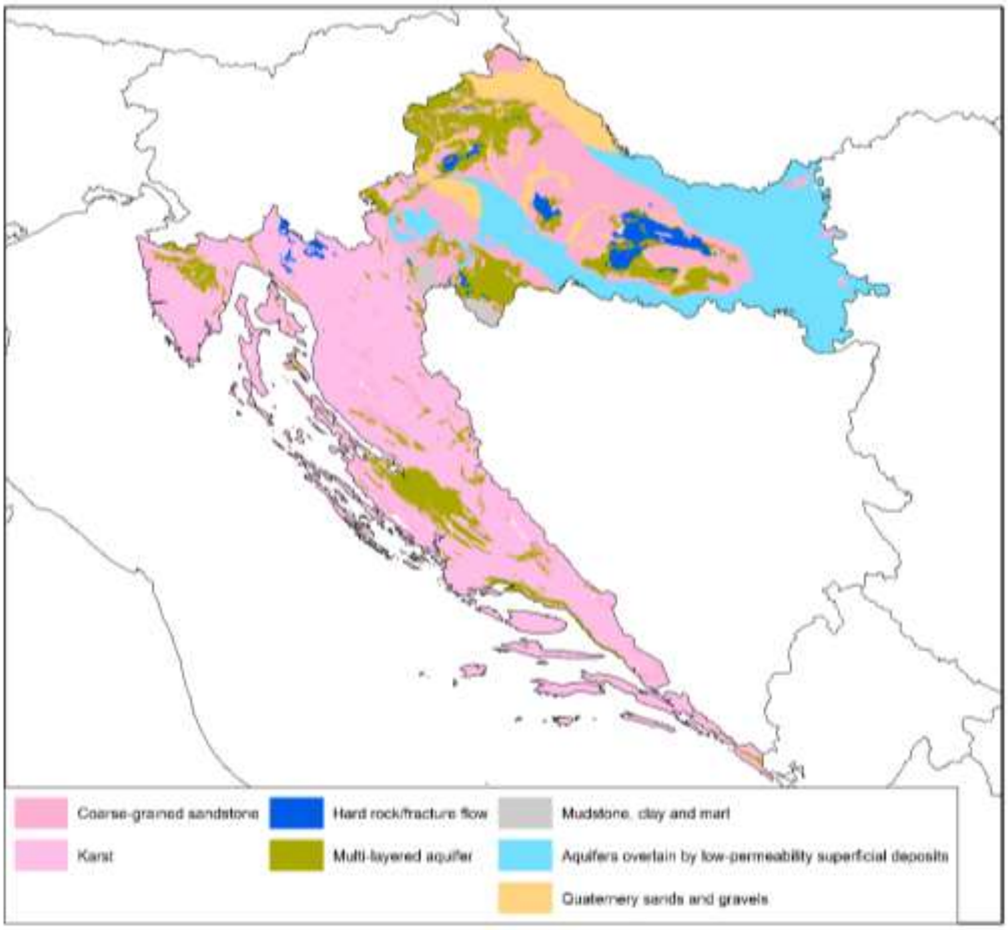

Figure 4.6 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Croatia. Contains linework © EuroGeographics. Contains data provided courtesy of the Croatian Geological Survey.

4.7 Slovenia

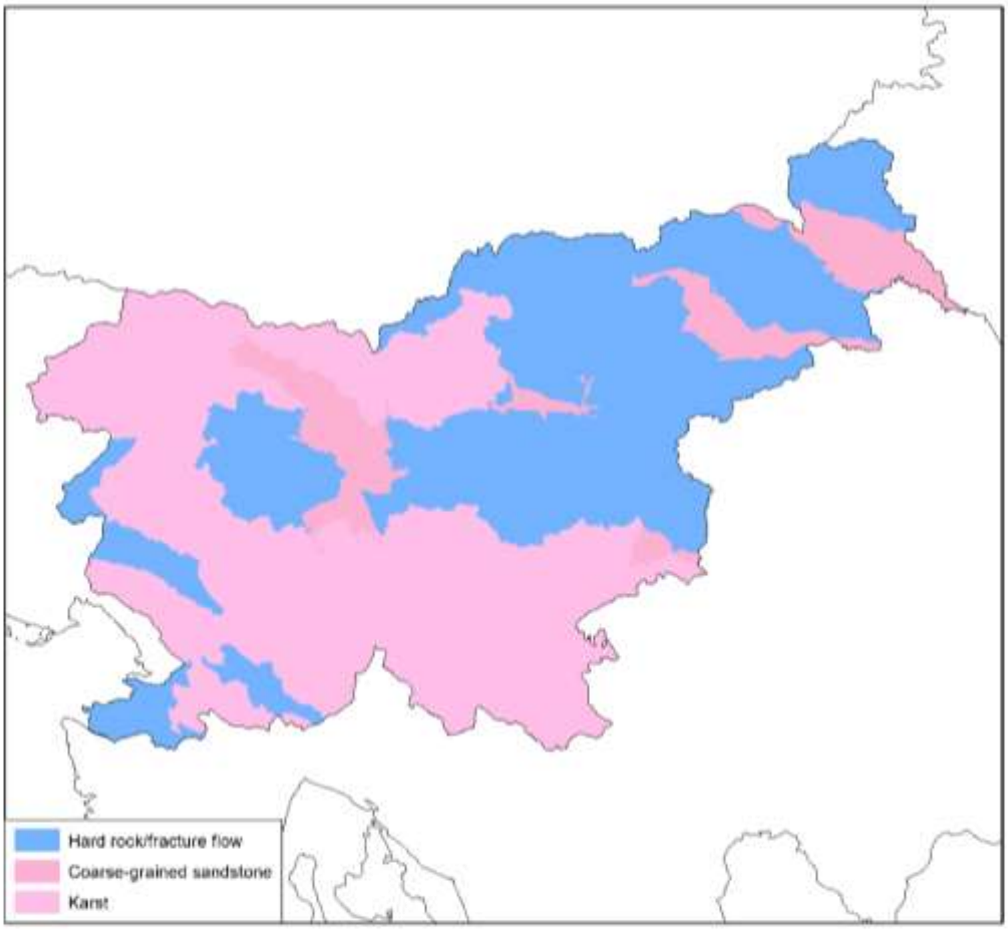

Figure 4.7 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Slovenia. Contains linework © EuroGeographics. Contains data provided courtesy of the Geological Survey of Slovenia.

4.8 Cyprus

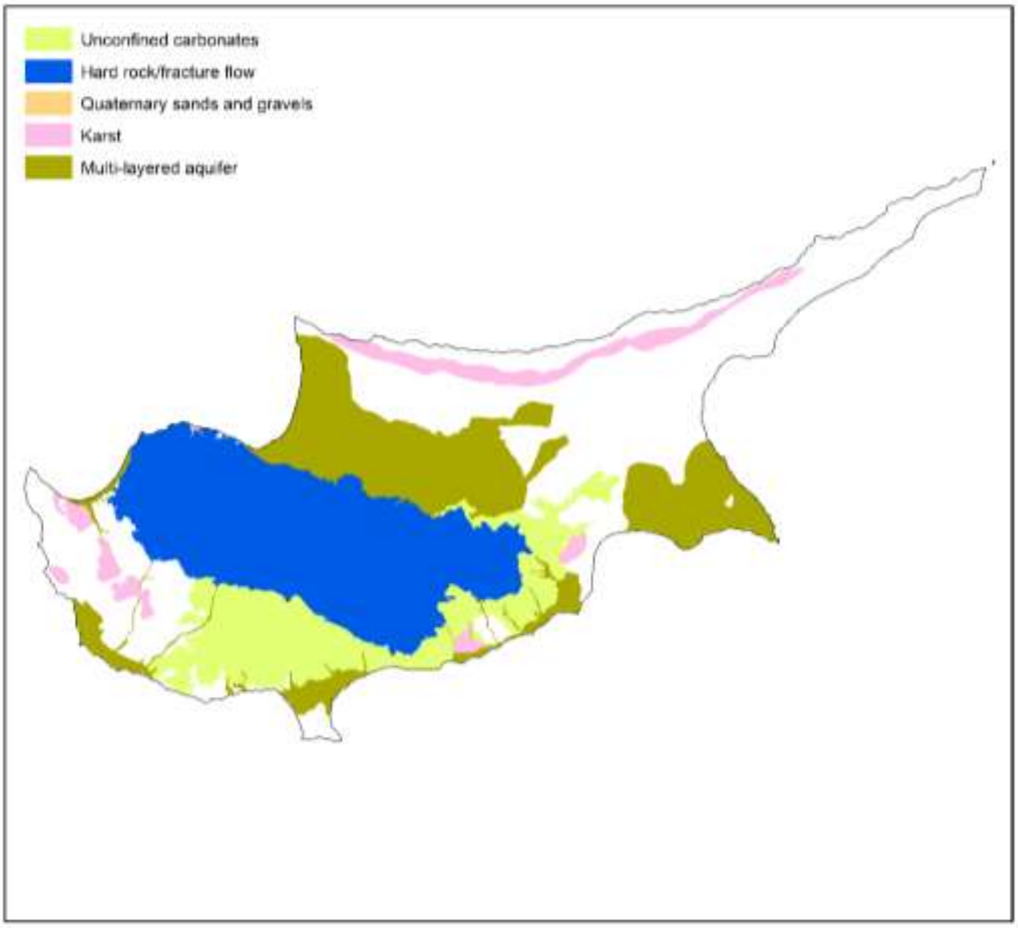

Figure 4.8 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Cyprus. Contains linework © EuroGeographics. Contains data provided courtesy of the Ministry of Agriculture, Natural Resources and Environment of Cyprus – Geological Survey Department.

4.9 Malta

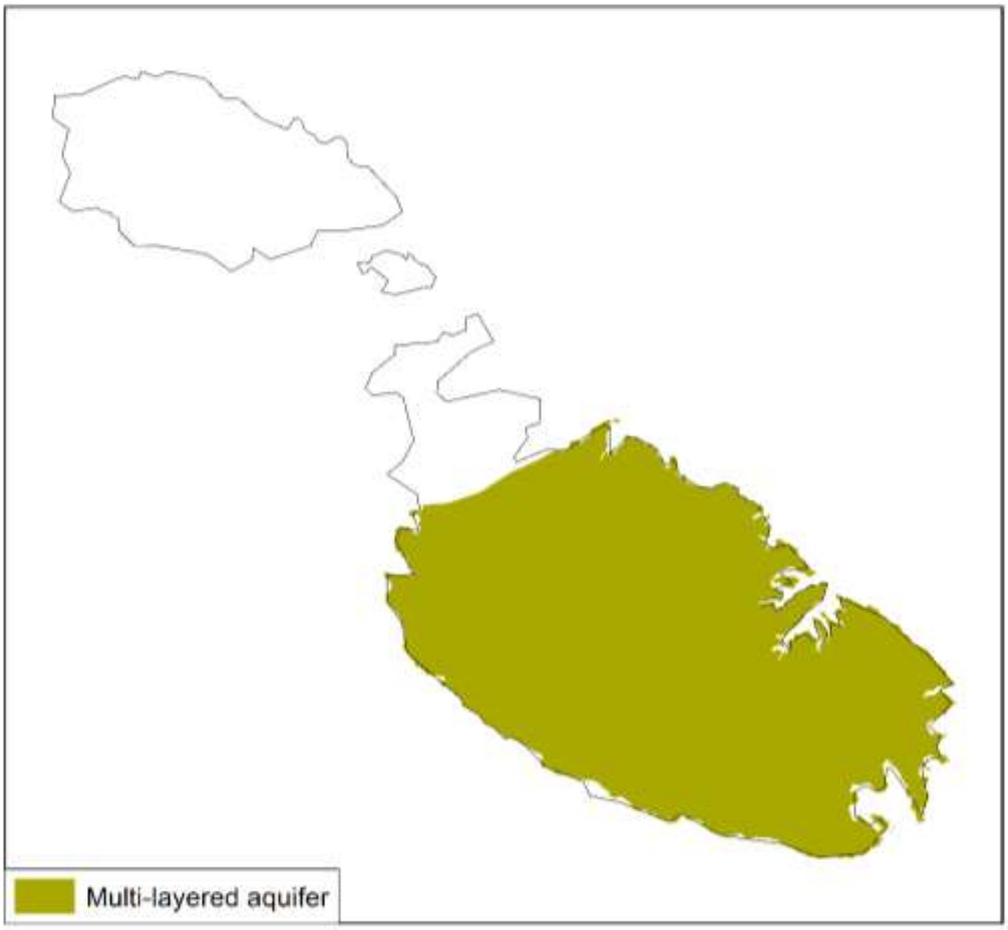

Figure 4.9 Distribution of conceptual models of nitrate transport in the unsaturated zone and shallow subsurface in the Malta. Contains linework © EuroGeographics. Contains data provided courtesy of the Ministry for Transport and Infrastructure, Malta.

5 CONCLUSIONS

Work Package 5 (WP5) of HOVER aims to develop an improved understanding of the transport of nitrate (NO_3) and pesticides (PST) from soil to groundwater receptors. The aim of the first task of WP5 (Task 5.1) is to characterise agrochemical travel times across Europe.

This report and associated web atlas form deliverable 5.1 associated with Task 5.1. A series of evidence based conceptual models of nitrate transport in the unsaturated zone and shallow subsurface have been developed with HOVER partners. These conceptual models have then been mapped across partner countries and presented in this report and in the EGDI.

Together with the analysis of monitoring data undertaken in Task 5.2, the outputs of Task 5.1 will be used to further develop existing numerical models of nitrate transport in Task 5.3.

6 REFERENCES

Afrodidis, S. (1991) Groundwater Exploration of the Igneous Rocks of the Troodos Ophiolite Complex, Cyprus Assosiation of Geologist and Mining Engineers, Nicosia, Cyprus.

Allen, D., Brewerton, L., Coleby, L., Gibbs, B., Lewis, M., MacDonald, A., Wagstaff, S. and Williams, A. (1997) The physical properties of major aquifers in England and Wales, p. 333, British Geological Survey, Keyworth, UK.

Ascott, M.J., Gooddy, D.C., Wang, L., Stuart, M.E., Lewis, M.A., Ward, R.S. and Binley, A.M. (2017) Global patterns of nitrate storage in the vadose zone. Nature Communications 8(1), 1416.

Biondić, B. and Biondić, R. (2014) Hydrogeology of the Dinaric Karst in Croatia. Mesec, J. (ed), University of Zagreb, Faculty of Geotechnical Engineering, Varaždin, Croatia.

Biondić, B. and Brkić, Ž. (2002) Water management base document of the Republic of Croatia. Groundwater Croatian Geological survey, Croatia.

Biondić, B., Brkić, Ž., Biondić, R. and Singer, D. (1996) Water management base document of the Republic of Croatia: Hydrogeology (Phase 1), Croatian Geological survey, Croatia.

Bonacci, O. (1987) Karst Hydrology, Springer-Verlag, Berlin.

Boronina, A., Renard, P., Balderer, W. and Christodoulides, A. (2003) Groundwater resources in the Kouris catchment (Cyprus): data analysis and numerical modelling. Journal of Hydrology 271(1), 130-149.

Brkić, Ž., Briški, M. and Marković, T. (2016) Use of hydrochemistry and isotopes for improving the knowledge of groundwater flow in a semiconfined aquifer system of the Eastern Slavonia (Croatia). CATENA 142, 153-165.

Brkić, Ž., Kuhta, M. and Hunjak, T. (2018) Groundwater flow mechanism in the well-developed karst aquifer system in the western Croatia: Insights from spring discharge and water isotopes. CATENA 161, 14-26.

Brkić, Ž., Urumović, K. and Briški, M. (2013) Post Audit Analysis of a Groundwater Level Prediction Model in Developed Semiconfined Aquifer System. Water Resources Management 27(9), 3349-3363.

Brouyère, S., Dassargues, A. and Hallet, V. (2004) Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. Journal of Contaminant Hydrology 72(1), 135-164.

Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M. and Ribstein, P. (2019) Water, nitrate and atrazine transfer through the unsaturated zone of the Chalk aquifer in northern France. Science of the Total Environment 652, 927-938.

Chilton, P. and Foster, S. (1991) Nitrate Contamination, pp. 333-347, Springer.

Chilton, P.J. and M.J., B. (1994) Nitrate in Jersey's groundwater: results of unsaturated zone profiling, British Geological Survey, Keyworth, UK.

Comte, J.-C., Cassidy, R., Nitsche, J., Ofterdinger, U., Pilatova, K. and Flynn, R. (2012) The typology of Irish hard-rock aquifers based on an integrated hydrogeological and geophysical approach. Hydrogeology Journal 20(8), 1569-1588.

Cucchi, F., Zini, L. and Calligaris, C. (2015) Le acque del Carso Classico, Progetto Hydrokarst, p. 179, Edizioni Universita di Trieste, Trieste, Italy.

Daly, D. (1988) The Kiltorcan Sandstone Aquifer, IAH (Irish Group).

Drew, D. (2018) Karst of Ireland: Landscape, Hydrogeology and Methods, Geological Survey of Ireland, Dublin.

Ernstsen, V., Olsen, P. and Rosenbom, A.E. (2015) Long-term monitoring of nitrate transport to drainage from three agricultural clayey till fields. Hydrol. Earth Syst. Sci. 19(8), 3475-3488.
Food and Agriculture Organization of the United Nations (2002) Reassessment of the Island's Water Resources and Demand, Cyprus. Volume i: Water resources, Nicosia, Cyprus.
Foster, S.S.D., Cripps, A.C. and Smith-Carington, A. (1982) Nitrate Leaching to Groundwater. Philosophical Transactions of the Royal Society, B: Biological Sciences 296(1082), 477-489.
Geological Survey of Ireland (2000) Swan Water Supply Scheme: Groundwater Source Protection Zones, p. 20, Geological Survey of Ireland, Dublin.
Geological Survey of Slovenia (2005) Methodology for groundwater bodies determination in Republic of Slovenia, p. 61, Geological Survey of Slovenia, Ljubljana, Slovenia.
Gourcy, L., Pinson, S. and Surdyk, N. (2017) Description de la méthode appliquée à l'échelle nationale pour l'analyse pression–impact du nitrate sur les eaux souterraines, p. 106, BRGM.
Jones, H.K., Morris, B., Cheney, C.S., Brewerton, L., Merrin, P.D., Lewis, M.A., MacDonald, A.M., L.M., C., Talbot, J.C., McKenzie, A.A., M.J., B., Cunningham, J.E. and Robinson, V. (2000) The physical properties of minor aquifers in England and Wales, p. 234, British Geological Survey.
Kitching, R., Edmunds, W.M., Shearer, T.R., Walton, N.R.G. and Jacovides, J. (1980) Assessment of recharge to aquifers / Evaluation de recharge d'aquifères. Hydrological Sciences Bulletin 25(3), 217-235.
Larva, O. (2008) Aquifer vulnerability at catchment area of Varaždin pumping sites, University of Zagreb.
Mali, N. and Korosa, A. (2015) Assessment of nitrate transport in the unsaturated (coarse gravel) zone by means of tracing experiment (Selniška dobrava, Slovenia). Geologija, 183-194.
Patrčević, V. (1995) Hydrological analysis of vertical water balance of groundwater at the area of river alluvium, University of Zagreb.
Rosenbom, A.E., Ernstsen, V., Flühler, H., Jensen, K.H., Refsgaard, J.C. and Wydler, H. (2008) Fluorescence Imaging Applied to Tracer Distributions in Variably Saturated Fractured Clayey Till. Journal of Environmental Quality 37(2), 448-458.
Rosenbom, A.E., Olsen, P., Plauborg, F., Grant, R., Juhler, R.K., Brüsch, W. and Kjær, J. (2015) Pesticide leaching through sandy and loamy fields – Long-term lessons learnt from the Danish Pesticide Leaching Assessment Programme. Environmental Pollution 201, 75-90.
Rosenbom, A.E., Therrien, R., Refsgaard, J.C., Jensen, K.H., Ernstsen, V. and Klint, K.E.S. (2009) Numerical analysis of water and solute transport in variably-saturated fractured clayey till. Journal of Contaminant Hydrology 104(1), 137-152.
Ružičić, S., Mileusnić, M., Posavec, K., Nakić, Z., Durn, G. and Filipović, V. (2016) Water flow and solute transport model of potentially toxic elements through unsaturated zone at regional wellfield Kosnica. Hydrological Processes 30(22), 4113-4124.
Slišković, I. (2014) Water in karst catchments of the rivers Neretva and Cetina. Miklin, Ž. (ed), Croatian Geological Survey, Zagreb, Croatia.
Smith, D.B., Wearn, P.L., Richards, H.J. and Rowe, P.C. (1970) Water Movement in the Unsaturated Zone of High and Low Permeability Strata by Measuring Natural Tritium, IAEA, International Atomic Energy Agency (IAEA).
Stuart, M.E., Heaton, T.H.E., Maurice, L., Chilton, P.J. and Williams, P.J. (2008) A preliminary study on the identification of the sources of nitrate contamination in groundwater in Malta: Results and interpretation, p. 126, British Geological Survey.

United Nations Development Programme (1970) Survey of groundwater and mineral resources-Cyprus, United Nations, New York, USA.
Urumović, K., Duić, Ž. and Hlevnjak, B. (2011) Impact of rainfall infiltration on groundwater recharge of a deep quaternary aquifer. Geologia Croatica 64(1), 17-30.
Vero, S.E., Basu, N.B., Van Meter, K., Richards, K.G., Mellander, P.-E., Healy, M.G. and Fenton, O. (2018) Review: the environmental status and implications of the nitrate time lag in Europe and North America. Hydrogeology Journal 26(1), 7-22.
Wang, L., Stuart, M.E., Bloomfield, J.P., Butcher, A.S., Gooddy, D.C., McKenzie, A.A., Lewis, M.A. and Williams, A.T. (2012) Prediction of the arrival of peak nitrate concentrations at the water table at the regional scale in Great Britain. Hydrological Processes 26(2), 226-239.
Wang, L., Stuart, M.E., Lewis, M.A., Ward, R.S., Skirvin, D., Naden, P.S., Collins, A.L. and Ascott, M.J. (2016) The changing trend in nitrate concentrations in major aquifers due to historical nitrate loading from agricultural land across England and Wales from 1925 to 2150. Science of the Total Environment 542, 694-705.