HOVER
GeoERA GROUNDWATER

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

Linking aquifer microbial ecology and diversity to contaminant transforming processes at European groundwater-surface water transition zones. Characterization of field sites based on existing and measured data

Deliverable 4.1

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1 INTRODUCTION

The main objective of WP4 is to increase our understanding of how groundwater ecology and microbial diversity determine contaminant-transforming processes at European groundwater-surface water (GW-SW) transition zones. In order to do this, three field sites have been selected in Denmark, France and Latvia. Common for the three sites is a solid knowledge regarding hydraulic heads and hydraulic conductivities and to some extent previous knowledge of existing pollutants in the areas. The two sites in France and Latvia are impacted by agriculture whereas the site in Denmark is located near a landfill. Both cases are relevant in order to increase our knowledge on the degradation of pesticides in areas impacted by agricultural as well as other xenobiotic compounds that may have influenced the surrounding environment from the landfill.

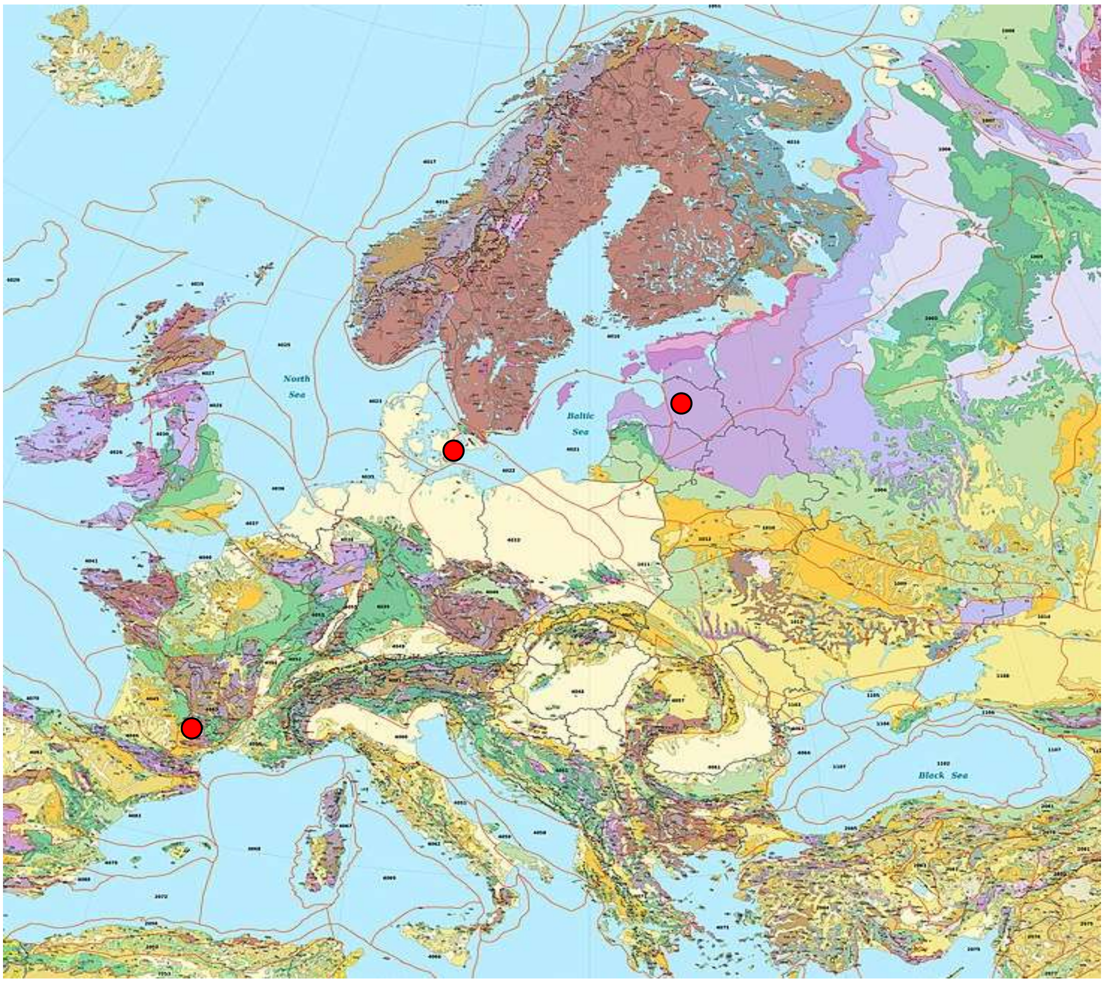


Figure 1. European map with surficial geology. The three locations are marked by red circles. (https://commons.wikimedia.org/w/index.php?curid=11171117)

2 DENMARK

2.1 Background

Risby Landfill is located west of Copenhagen and was actively used from 1959 to 1981. There were no liners or leachate collection systems installed at the landfill, and the site still remains this way. It contains a mixture of municipal waste, demolition waste, fly ashes and some chemical waste although no exact records exist. It covers an area of 6.5 ha and contains a total of 500,000 m3 of waste. During the 60' it is expected to have been a place of an uncontrolled waste deposition. (Thomsen *et al.*, 2012)

2.2 Geology and hydrogeology

Leachate from the landfill that enters the stream has been established in previous work to be concentrated along a 20 m long discharge zone. This includes potential pollution hot spots and potential transport routes to the stream.
Risby Landfill is located close to surface waters in a heterogeneous geological setting. The Landfill is placed on clay till with interbedded sand lenses, bulk sand deposits and peat deposits in the former wetland part of the area (Thomsen *et al.*, 2012). This type of soil often consist of a low permeable clayey matrix intersected by preferential flow paths, such as vertical fractures.

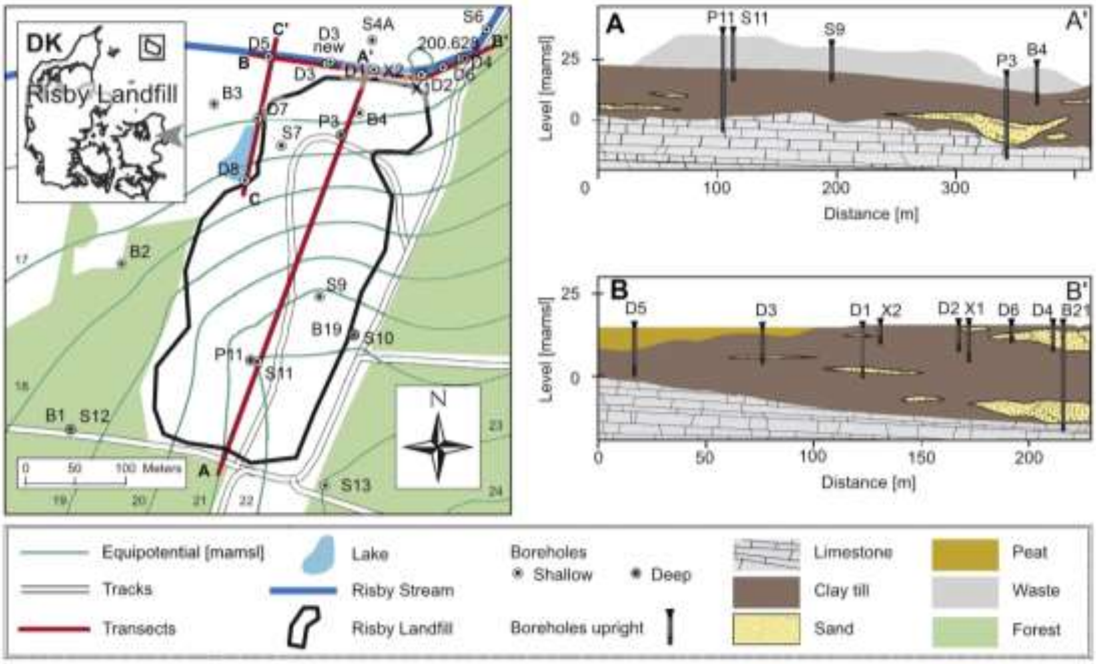


Figure 2. General geology and hydrology at the Risby landfill site. Plan view and geologic transects at the site show horizontal and vertical heterogeneity of geologic settings (clay till, sand, and peat) in the upper layer, groundwater flow direction going from the landfill towards the stream, and leachate delineation transects placed between the landfill and the stream. (Milosevic *et al.*, 2012)

The original terrain below the landfill consists of coarse and medium clay tills with sand and peat deposits underlain by clay till in its northern part along Risby stream. Geological transect A-Á shows Quaternary clay till with sand lenses down to 15-30 m below surface (m.b.s.) i.e. 15-0 m above sea level and a Tertiary limestone below.
The flow field at the landfill scale is derived from hydraulic heads in drilled and driven wells (Thomsen *et al.*, 2012). The groundwater flow direction from the landfill is towards the stream, as seen in Figure 3.

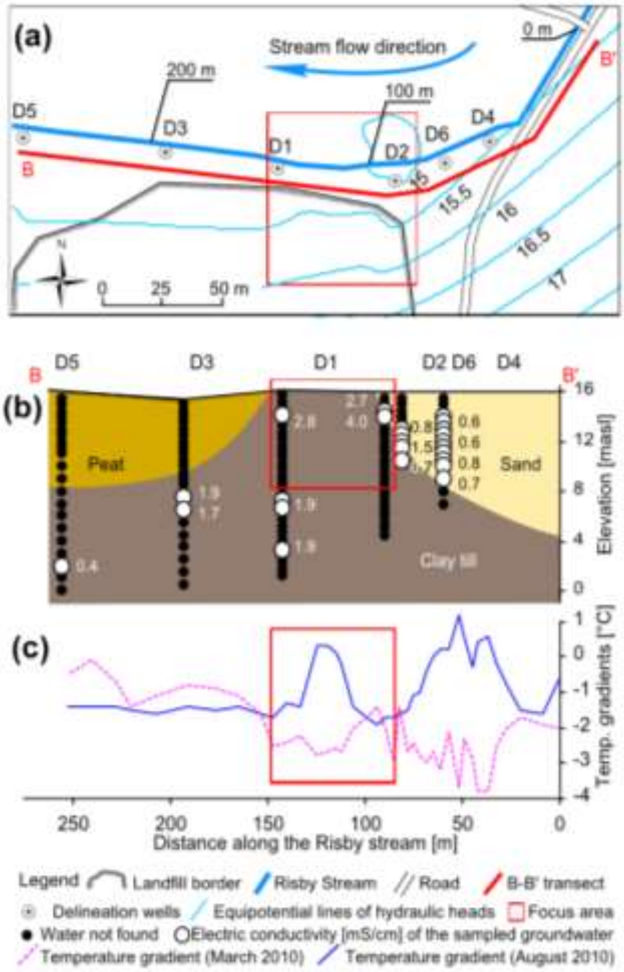


Figure 3. Identified focus area is shown on the plan view. Temperature gradients between the streambed and stream water were used to locate the groundwater discharge. (Milosevic *et al.*, 2012)

2.4 Previous data

There has been a few studies that have looked at the degradation of pesticides at the GW-SW interface at the Risby Landfill site. (Batıoğlu-Pazarbaşı *et al.*, 2013) looked at the mineralization of four pesticides at three seepage meters (SM1, SM2 and SM3) that varied by groundwater discharge and pesticide concentration. The highest mineralization was seen at SM3, which also received the highest pesticide mass discharge. In general there was seen a mineralization in the range of 20-40 % of MCPA, MCPP, 2,4-D and 2,4-DP.

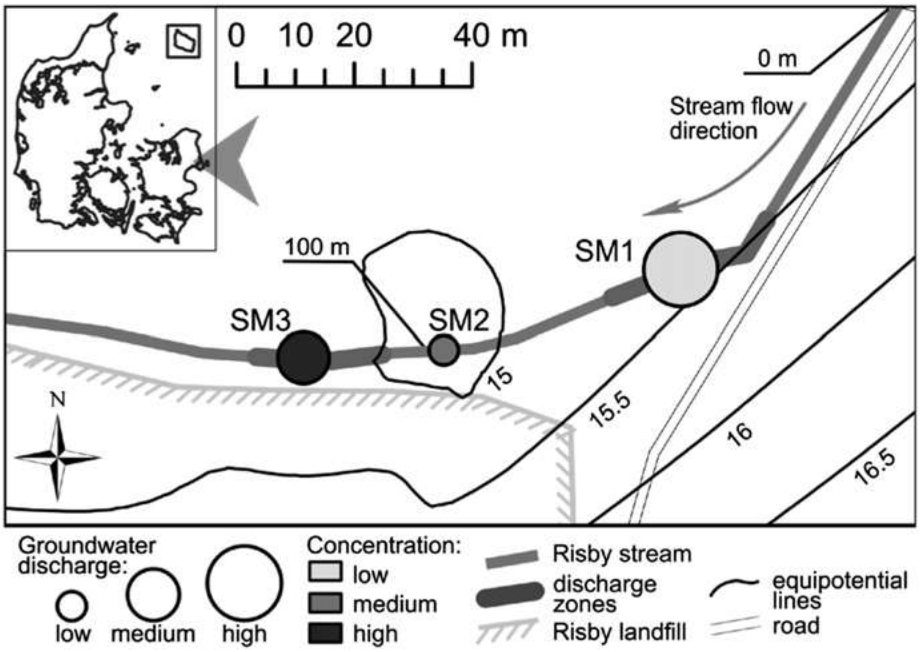


Figure 4. Sampling location of the Risby Landfill and the groundwater discharge zones. Groundwater was collected from the three seepage meters (SM1, SM2, SM3) and streambed sediments were collected in the vicinity of the SM. Sampled discharge zones have different pesticide mass discharges due to variations in the groundwater discharge or pesticide concentration (Batıoğlu-Pazarbaşı *et al.*, 2013).

2.5 Sampling strategy

At the Risby site we will sample within the 20 m discharge zone in the river, where we will expect that the microbial community has been influenced by the highest concentration of xenobiotics as shown in figure 4. These sediment samples will be compared to upstream sediment samples as well as groundwater samples from SM1, SM2 and SM3.

3 FRANCE

3.1 Background

The study site in France is located in the alluvial plain of the Ariège River Basin, on the Crieu River. The alluvium was deposited in five distinct terraces of rather similar composition. The aquifer is unconfined and the unsaturated zone is generally <10m thick. The alluvial plain is mostly cultivated farmland, mainly corn. This basin has been previously studied which has enabled us to choose two spots along the river Crieu that are of great interest for the HOVER project.

The main pesticides found in the groundwater along this river basin are (S-)metolachlor and to a lesser extent atrazine despite its withdrawal from the market in 2003. Besides active substances, metabolites of pesticides (notably chloroacetanilides) show high occurrence in groundwater (Amalric *et al.*, 2013).

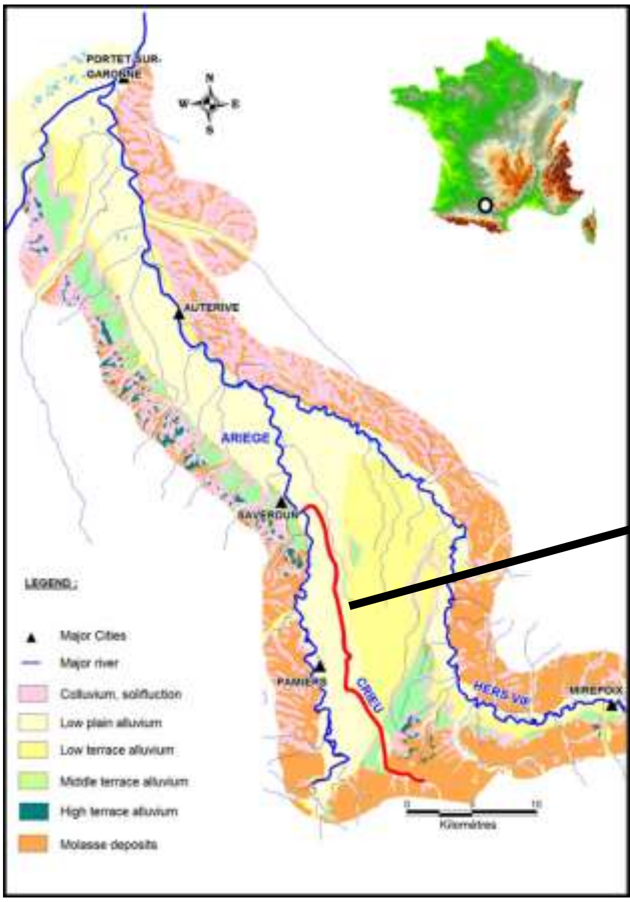
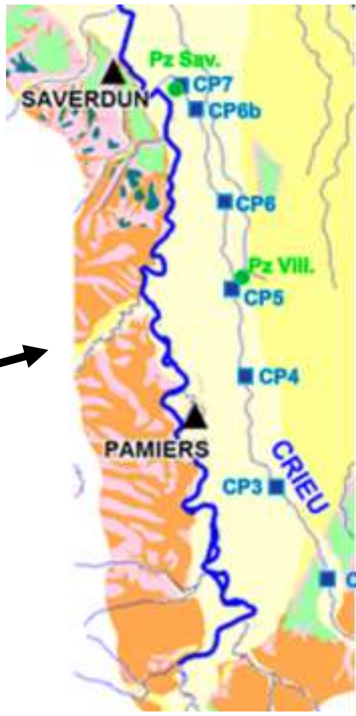


Figure 5. Localization of the Crieu River and the sampling spots identified for HOVER (Pz Sav & Pz Vill)



3.2 Geology and hydrogeology

The study points identified for the HOVER project are located in the middle and downstream stretches of the Crieu River. The first, Villeneuve du Paréage (Pz Vill) is characterized by the infiltration of river water into the aquifer below (Fig 6) whereas the downstream site, Saverdun (Pz Sav) is characterized by a resurgence of groundwater towards the river (Fig 6).

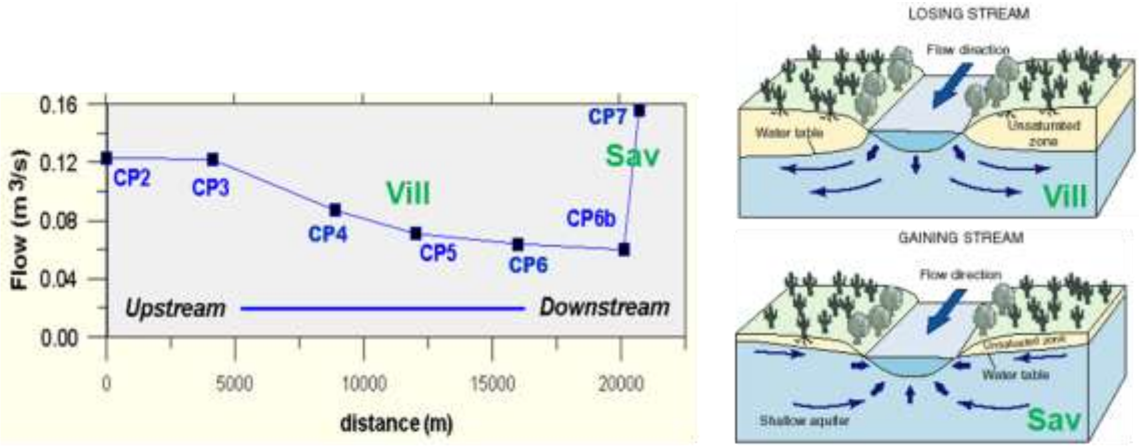


Figure 6. Water flow along the Crieu river and illustration of the phenomena taking place at Villeuneuve de Paréage and Saverdun.

3.3 Previous data

During the ELISE project (funding BRGM and Adour-Garonne Water Agency N°2010/6774) the site was extensively monitored to elucidate the relations between river-aquifer-river along a 20 km river section. The project measured river discharge and piezometric levels as well as chemical parameters to highlight complex relations and Sr isotopes to confirm the exchanges and help to constrain the reservoirs involved (Baran *et al.*, 2015). The project also enabled to identify the impact of groundwater on the surface water quality which can be degraded by the addition of metabolites typical of groundwater and by active substances specific to groundwater.
Understanding surface water – groundwater relations is the only way to explain the occurrence of contaminants and take appropriate measures to reduce the contamination. The work on this site in the HOVER project will enable to pursue our understanding of these interactions by focusing on the groundwater/surface water transition zones. It will base the sampling and analyses on the data acquired during the ELISE project, in particular the chemistry data on nitrate, pesticides and other geochemical and microbial data (Baran *et al.*, 2015; Imfeld *et al.*, 2018; Mauffret *et al.*, 2017).

3.4 Sampling strategy

Sampling was initially programed late September 2019 however due to the very dry weather conditions in France this year the campaign has been set back to November 2019 (the river ran dry at Villeneuve). At the two sites (Saverdun and Villeneuve) water will be sampled in the river and in the nested piezometers set either along or perpendicular to the river (Fig. 7).
Samples will be collected for pesticide degradation assays, chemistry, isotope Sr measurements and DNA collection. In situ parameters will be measured during the sampling. Measurement of river flow before and after each of the 2 sites is also planned.

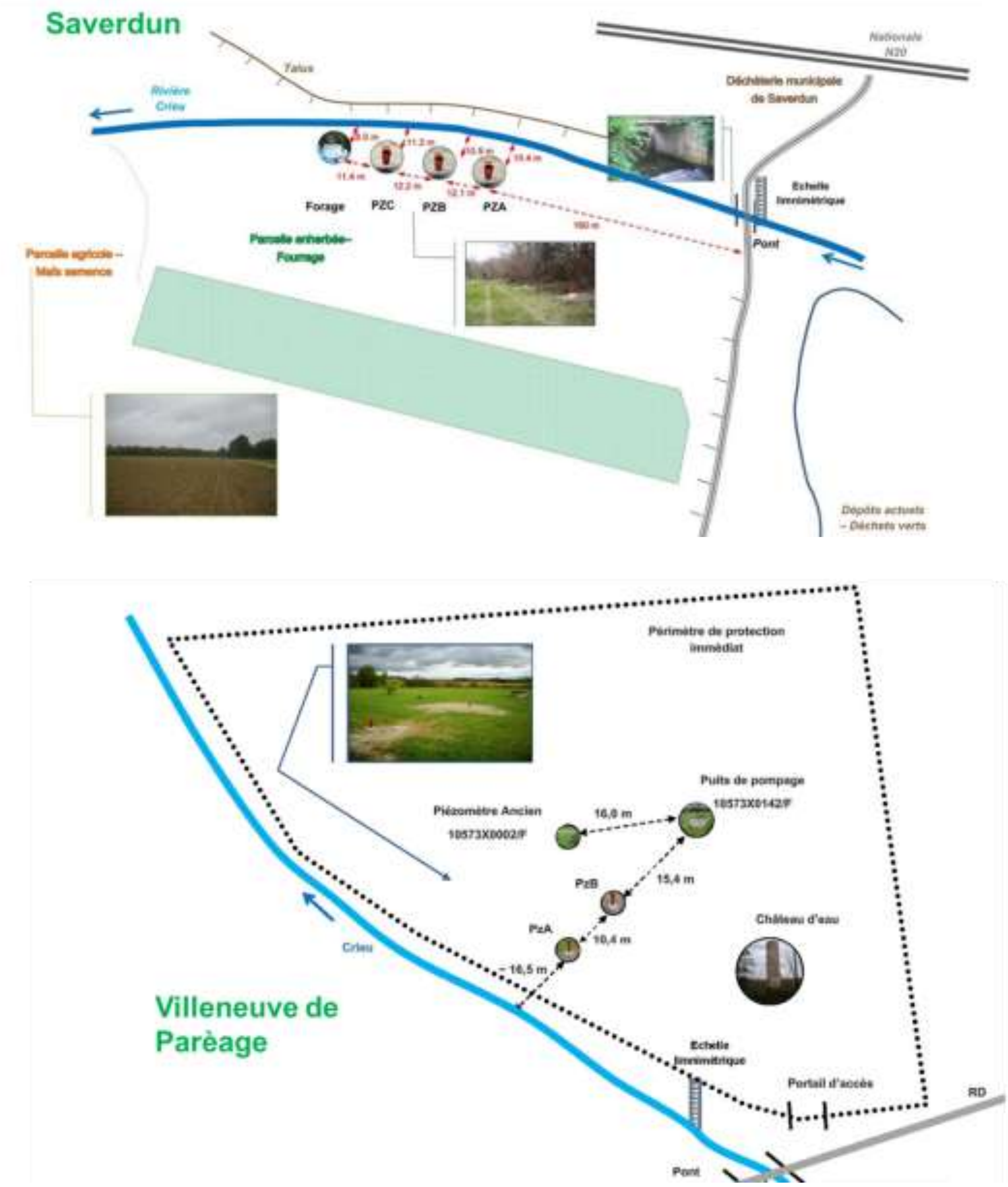


Figure 7. Piezometer implantations in Saverdun and Villeneuve de Paréage.

4 LATVIA

4.1 Background

Gypsum is mainly found in the Salaspils formation of Upper Devonian, but limestone is more typical for the Upper Permian formations. Karst processes are observed in carbonate and sulphate rocks in the central and southern part of Latvia, but in some areas surface features of the karst such as sinkholes and land subsidence are found (Fig. 8).

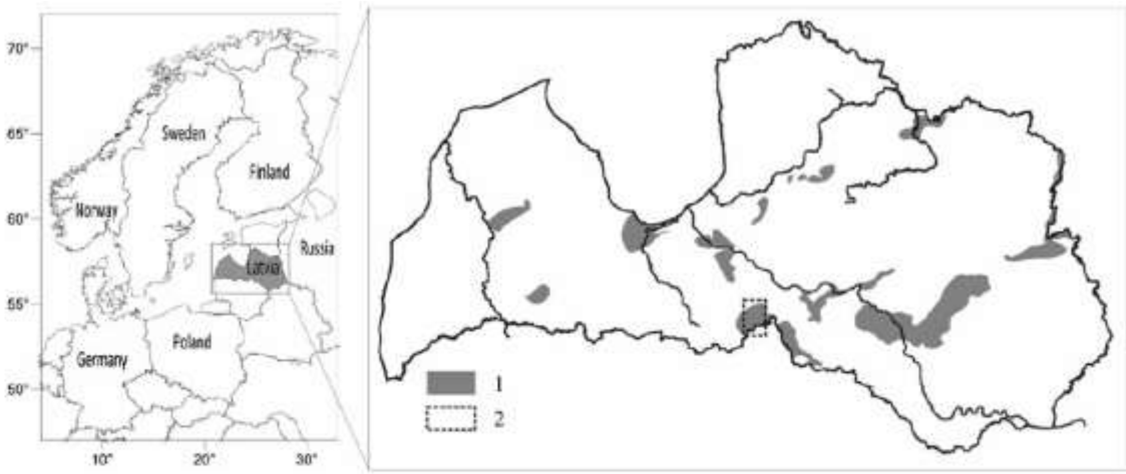


Figure 8. Distribution of surface karst features in Latvia (Levins and Buzajevs, 1999). 1 – carbonate and sulphate karst distribution areas; 2 – study area at the Skaistkalne vicinity (Delina et al., 2012).

The Skaistkalne area in Latvia is one of the places where karst processes in gypsum strata occurs. The Iecava and Memele rivers border the area with extensive surface karst features such as sinkholes and karst lakes. There is a known surface-groundwater interaction in the karstic environment (Delina et al., 2012).

4.2 Geology and Hydrogeology

The study area is located in the Upmale hillock plain of the Middle Latvia lowland. The land surface is slightly undulated, gently sloping from east–northeast to west–southwest and its altitude is 40–50 m a.s.l. (Fig. 9), but the relative height of the hills is from 2–5 to 8–10 m. Several rivers cross the Upmale hillock plain, and the main ones are the Iecava and Memele rivers (Delina et al., 2012).

The Iecava river flows along the northern border of the study area, and the Memele river along its southern border (Fig. 9). The Iecava river valley is 2–3 m deep, mainly cut in the Quaternary deposits, but sediments of Upper Devonian Salaspils. Formation are found at the river bottom in places. The Iecava river flows from northeast to southwest, the mean WL changes from 25.5 to 43.1 m a.s.l. and the flow gradient is 0.5 m/km on average, and in the study area it is 0.46 m/km (Delina et al., 2012).

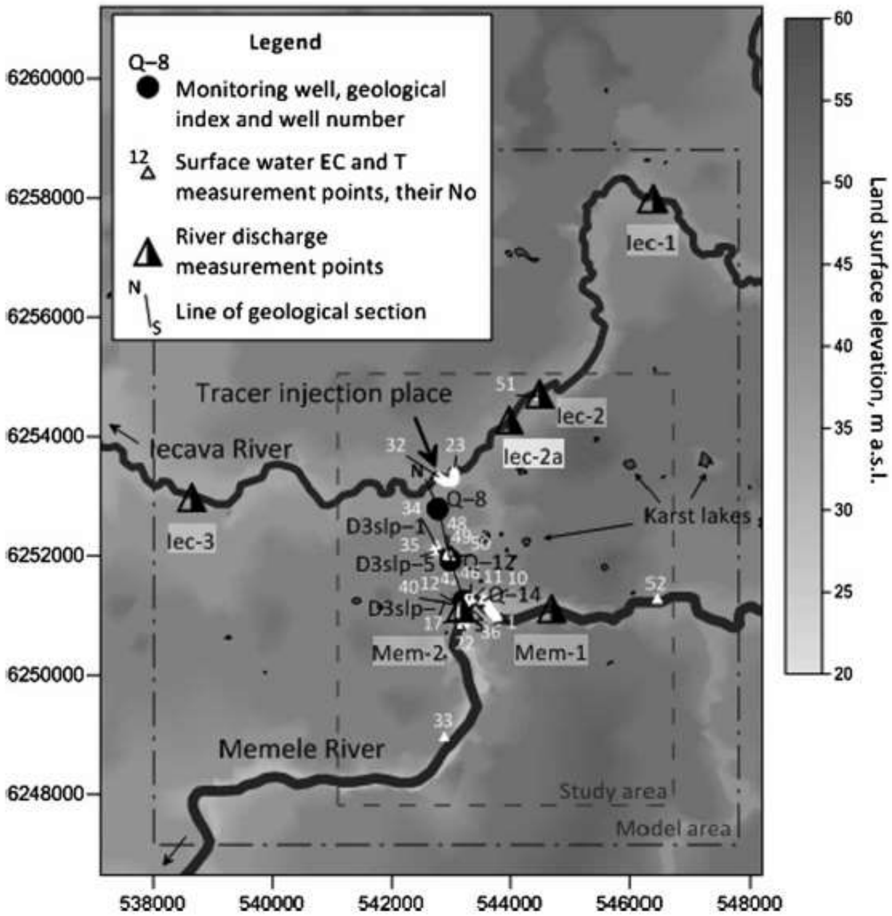


Figure 9. Location of investigation points (Delina et al., 2012)

The Memele river is the largest river in the study area and it flows in the deep valley, which is cut in Quaternary and Devonian sediments (Fig. 10). The river valley depth varies from 2–5 to 10–12 m, and outcrops of the Devonian carbonate and sulphate rocks are found in the deepest stretches of the valley. The Memele river flows from northeast to southwest, the mean WL changes from 21.2 to 46.6 m a.s.l., flow gradient in the study area is 0.5 m/km on average, and in the study area it is 0.17 m/km. The mean annual WL change in both rivers is 1–1.5 m, rarely reaching 2 m (Pastors 1987).

The high WL is typical for spring and late autumn, and the low WL is in late summer and winter. There is a difference in WL altitude in both rivers; the WL altitude in the Iecava river is constantly 5–7 m higher than in the Memele river, causing a hydraulic head difference in the Salaspils Formation (Delina et al., 2012).

Quaternary and Devonian sediments form the upper part of the geological section in the study area (Fig. 10). The thickness of the Quaternary sediments varies from a few metres in the river valleys and around Skaistkalne town west of the study area to 10–15 m in the study area. Quaternary cover formed during the Late Weichselian glaciation and in post-glacial time, and consists of glaciolacustrine deposits (lgQ3ltv) – sand, fine and silty, thickness 0–5 m and clay, silty clay and sandy clay, thickness 0–5 m, which were deposited in the glacial lake environment. The sand and silt sediments are found on the ground surface in almost the whole study area, apart from some islets where underlying glacigene till (moraine) outcrops. The base of the Quaternary cover was formed during the Late Weichselian glaciation and consists of glacigene deposits (gQ3ltv) – till loam with gravel and pebbles, the thickness of the till deposits varies from a few to about 10 m (Delina et al., 2012).

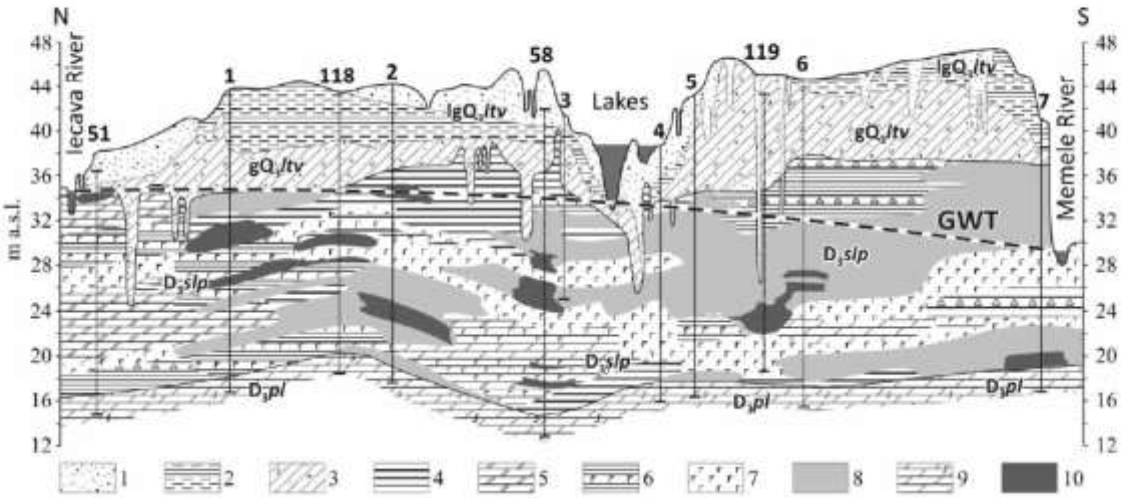


Figure 10. Geological section of the study area along the line of sampled wells, the length of the section is 2.6km (Tracevska et al., 1986). 1 – sand, 2 – silt, clayey silt, 3 – till loam, 4 – carbonate clay, 5 – marl, dolomite marl, 6 – clayey gypsum, 7 – gypsum, 8 – dissolved gypsum strata with clay and dolomite flour, 9 – dolomite, fractured dolomite, 10 – karst cavities, partially filled with dolomite flour; GWT – groundwater table; lgQ3ltv – glaciolacustrine sediments, gQ3ltv – glacigene till deposits, D3slp – Upper Devonian Frasnian stage Salaspils Formation sediments, D3pl – Upper Devonian Frasnian stage Plavinas Formation (Delina et al., 2012).

Devonian sediments lie below the Quaternary deposits, the surface of the pre-Quaternary rocks is gently sloping to northwest, the absolute height of the pre-Quaternary sediments surface changes from 42 to 45 m a.s.l. in the centre of the study area to 34–36 m a.s.l. in the periphery. The pre-Quaternary surface is dissected by a number of sinkholes up to 8–10 m deep filled with Quaternary deposits. Some of the sinkholes are filled with water forming small karst lakes. These lakes are recharged from precipitation and confined groundwater, the recharge type can be identified based on the chemical composition of water in the lakes; there are significantly higher values of electric conductivity (EC) and sulphates content in the lakes where confined groundwater discharges (Delina et al., 2012).

The Upper Devonian Frasnian stage Salaspils Formation (D3slp) sediments lay below the Quaternary deposits within the study area (Figure 10), and only in the periphery they are covered with the dolomites of Upper Devonian Frasnian stage Daugava Formation (D3dg), the Daugava Formation deposits are eroded at the study area. The thickness of Daugava Formation dolomites varies from 0.2–0.5 m near the distribution border to 3–5 m further from it. Salaspils Formation sediments formed during the regression stage of the sedimentary basin, when lagoon conditions prevailed, facilitating sedimentation of evaporites such as gypsum (Birger et al. 1979). Three substrata are divided in the Salaspils Formation: (1) carboniferous clay layer, 0.5–3.5 m thick, lay in the bottom of the formation; (2) the middle strata consists of carbonate and sulphate rocks – dolomite, gypsum, dolomite marl and dolomite flour, the total thickness of this strata is from a few metres to 10–12 m in areas where gypsum layers are present, the thickness of the gypsum beds is 3–9 m; and (3) the upper layer is mainly carboniferous clay with 1–1.5 m thick interbeddings of dolomites, the thickness of the layer is 5–8 m (Delina et al., 2012).

The karst processes are bound to the gypsum-containing strata, but sinkholes, caverns and fractures have also formed in the layers above due to the dissolution of gypsum layers and collapse of the overlaying strata. Upper Devonian Frasnian stage Plavinas Formation (D3pl) fractured dolomites lays below the Salaspils Formation, their thickness is 20–23 m (Delina et al., 2012).

Hydrogeologically, the geological section is divided in three aquifers separated by the aquitards: (1) water table aquifer, bound to the Quaternary sand deposits; (2) Salaspils semi–confined aquifer, bound to the middle part of the formation, is the karst aquifer where groundwater flow occurs along the karst conduits; and (3) Plavinas confined aquifer bound to the fractured dolomites. Groundwater recharges from precipitation and discharges in the deeper river valleys. However, it was found (Narbutas et al. 2001) that there is a water loss of about 15% (compared with the river discharge upstream from the karst area) in the Iecava river showing that groundwater recharge from the rivers occurs. The groundwater table in the unconfined Quaternary aquifer is 0.5–2 m below the ground surface and 4.5– 18 m below the ground surface in the semi-confined Salaspils aquifer. Hydraulic conductivity of the Salaspils aquifer sediments is 30–100 m/day in the areas of intensive karst (Tracevska et al.1986).

4.3 Previous data

Earlier investigations suggested a hydraulic connection between the Iecava and Memele rivers exists via the karst conduits due to the water level (WL) difference in the rivers (Narbutas et al., 2001).

A set of methods was performed to study the possible connection: dye tracer was applied in the Iecava river and its occurrence was visually observed at the karst lakes and Memele river; the current velocity was measured and discharge of rivers calculated at several profiles; surface water and groundwater composition was studied involving in situ measurements of water pH and electrical conductivity, water sampling and chemical analysis of the water samples on the content of sulphates, calcium and magnesium ions. A numerical finite element 3D groundwater flow model was developed to assess the impact of WL changes in rivers to groundwater flow. A tracer test proved that there is underground hydraulic connection between the Iecava and Memele rivers. The Iecava river discharge loses 10–25% from the river discharge upstream karts area, but the Memele river discharge increases by 200% compared with the upstream discharge due to the flow from the Iecava river and massive groundwater inflow, characterised by the increased sulphate values in the river's water. Huge difference between calculated (10–30 m/d) and observed (800–1,300 m/d) water flow velocity shows that large karst conduits should be developed in the Iecava–Memele water divide area. The numerical model shows that groundwater discharge to the Memele river should vary by seasons. Little discharge is characteristic for high season and intensive discharge for low season. (Delina et al., 2012).

Attempts were made to distinguish groundwater residence time of multiple components of water applying CFC and tritium dating techniques supplied by tracer test and numerical model of the study area. Complex investigations lead to conclude that three different sources of groundwater occur characterized by different flow velocities, recharge age and chemical composition. Although CFC's has been degraded, it is possible to use the results to distinguish different groundwater components and even to estimate groundwater flow velocity because of near located recharge and discharge areas. Tritium results doesn't show considerable variations along flow path with 6 TU in average confirming conclusions based on CFC's. Tracer test approve very high groundwater velocity zones in study area that supposedly doesn't mix with groundwater in matrix (Bikshe et al., 2014).

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