Investigating Water Quality and Ecological Health within Kempen-Broek, Natuurmonumenten

Assessment of the physicochemical characteristics of surface waters and the relationship to ecological health in the Kempen-Broek nature reserve.

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Abstract.

Kempen-Broek is one of many cross-border wetlands. These wetlands provide important economic and ecological value. However, in the Netherlands, many surface waters have been determined to have pooper surface water quality according to WFD parameters (Fraters, et al., 2017), which will affect the wetlands biological functions and diminish their value. The Surface-water quality in Kempen-Broek, in particular, may be contaminated due to its proximity to an industrial zone, surrounding agricultural, urban land and unique land-use change. However, there is no existing in-depth water analysis within the Kempen-Broek area to demine if this area may be under threat of pollutants. Therefore, it would be essential to identify the current water quality and have an indication of potential point sources and diffuse sources of pollutants. This, in turn, will help identify if Kempen-Broek has deteriorated surface water quality that may impact ecosystem health.

The aim of this study is to have a better understanding of the surface water quality in the Kempen-Broek area. In this way, this study aims to identify key point sources and diffuse sources of pollutants and identify key impacted areas together with mitigating strategies. Surface water samples were collected and investigated for nutrients (N and P), Major ions (Al, B, Ba, Be, Fe K, Fl, Cl, Br, Si, So4, Na, and Mg) and Heavy metal (Ca, Cd, Ni, Cr, Co, Zn, Zr, Sr, Mo, and Mn). In addition, indicator species and biodiversity were investigated to determine relationships between water quality and ecological health.

Following the investigations, Kempen-Broek's surface waters, generally, show to be good in terms of ecological health. There is evidence that surrounding land uses have impacted surface water quality. There is a concern in a few sample sites that have higher Fe, F^- and Zn^{++} concentrations. Fe may be contributed to alterations in stream flows contributing to higher oxidations rates. F- and Zn contributions are suggested to reflect the surrounding industrial land use. There are no immediate mitigation strategies required. Further studies are suggested as higher F^- and Zn^{++}can have an impact on insects and plant function.

From this study, it has been recommended that Natuurmonumenten continues monitoring. The on-going cost of monitoring can be minimised by focussing on those sites that can be expected to show signs of change first and limiting measures to those of higher risk. This study can be used as a baseline and expanded to show trends over time to provide early warning of negative change. The ideal would be to include seasonal impact, so potentially two sets of samples per annum: summer and winter one year than spring and autumn the following and so on. Limit the samples to E.C., F^-, Zn^{++}, P and N.

Keywords: Water Quality, Ecological Health, Wetland, Kempen-Broek

Contents

1. Introduction.

1.1. Wetland and its Importance.

Wetlands are among the world's most crucial environmental resources, but at the same time, they are the most threatened (Best et al, 1993). Wetlands are not exclusively land or water environments, they may include both environments simultaneously, and wetlands can be seasonally aquatic or terrestrial (European Commission, 2007). In 2012, 127 governments in line with the Ramsar convention indicated that the status of wetlands had declined in recent years (Bridgewater, 2021). In the Netherlands alone, 16% of its territory is regarded as an internationally important wetland (European Commission, 2007). The wetlands in the Netherlands mainly consist of coastal ecosystems, freshwater systems, and large riverine systems (European Commission, 2007).

Wetlands bring value, not only environmental value but economical too. Regarding environmental value, wetlands increase habitat as they sustain some of Europe's most important birds, invertebrates, amphibians, and plant species (Tiéga, 2013). In addition, they contribute to key water-related and water-dependent ecosystem services such as carbon sequestration, nitrogen regulation and erosion control (Tiéga, 2013).

Regarding economic value, wetlands play an essential role in flood mitigation, particularly in the Netherlands. Flood mitigation potential depends on the geographic situation of the wetland itself, the interaction of the wetland area with other flood defences, the potential floodwaters, and what the alternative land uses could have been (Rouquette et al., 2011). With climate change, increasing sea levels, and the frequency of extreme weather events, these wetlands increase in value. Wetlands can be regarded as the 'kidney' of the landscape in their role in surface water pollution mitigation. Due to the close interaction of terrestrial and aquatic environments, wetlands are abundant with microbial and plant life that transforms and displace nutrients and pollutants. Wetlands are five times more efficient at reducing riverine nutrient concentrations than most nitrogen mitigation strategies (Hansen et al., 2018), making them more and more interesting for filtering of areas with high nitrogen output, such as wastewater treatment facilities and agricultural runoff sites. The estimated costs for nitrogen removal of 1.7 – 5 Euro/kg (Cost-Effective Nitrogen Removal, 2021), so wetlands could be viewed as more elegant, cost-effective solutions to industrial removal strategies with the addition that they are often characterised by beautiful landscapes with rich biodiversity. Thereby providing important aesthetic, educational and recreational ecosystem services that contribute to overall wellbeing and the economy (Tiéga, 2013).

1.2. Kempen-Broek.

Kempen-Broek is a multi-managed wetland, as it is located on the Netherlands/Belgian border, South-East of Weert. The Nature Reserve covers the Dutch municipalities of Cranendonck, Neder Weert and the Flemish municipalities Bocholt, Bree, Kinrooi and Maas oak. Due to the cross-border nature, the reserve is managed by Natuurmonumenten (Netherlands side) and Natuurpunt (Belgium side) and located on the edge of the Kempisch Plateau and west of the Meuse valley. The Kempisch Plateau is a geological unit formed by parent materials from the Ardennes, which were deposited by the Meuse during the Ice Ages. The eastern part mainly consists of these fluvial gravels, while in the western part, especially coarse sands (Runhaar, et al,.2018). Consequently, the narrow valley streams flow west-east parallel with the Meuse Valley, with the larger streams: Wijffelterbroek, Tungelroysche beek and De Raam that would have a larger influence of transporting pollutants. The canals surrounding Kempen-Broek act like an impermeable layer towards surface waters that prevents streams from Bree and further south from entering the wetlands. However, these canals are a major waterway within themselves that transports pollutants across the muse basin. Seepage from the canals may deliver NO_3 and Cl to the surface water system (Runhaar, et al,.2018). The nature reserve is sculpted from a range of natural and anthropogenic interventions over the years that have brought about a mosaic of landscapes, including a variety of brook valleys, agricultural areas, drift-sands, heathlands, forests, and wetlands. Additionally, Kempen-Broek is surrounded by densely populated urban regions between Eindhoven, Venlo, Maastricht and Hasselt (Runhaar et al,.2018).

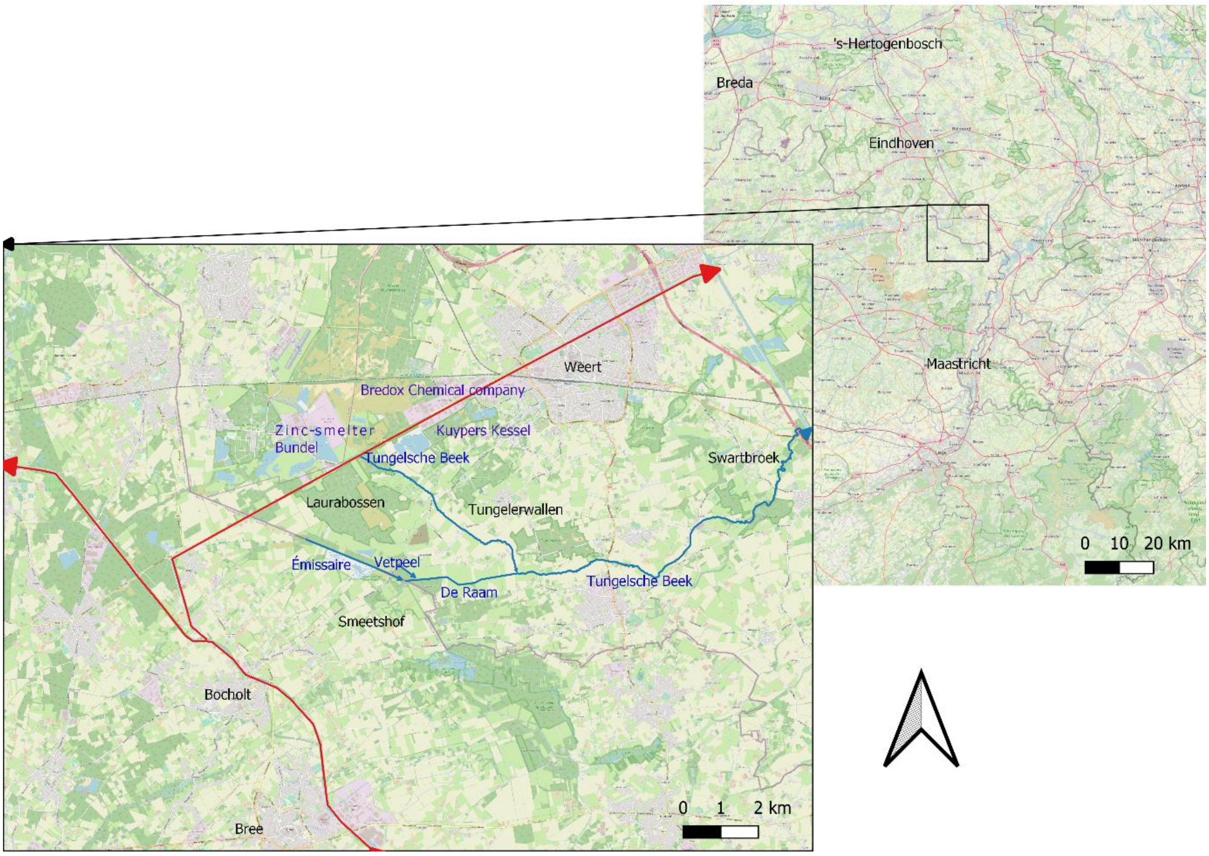
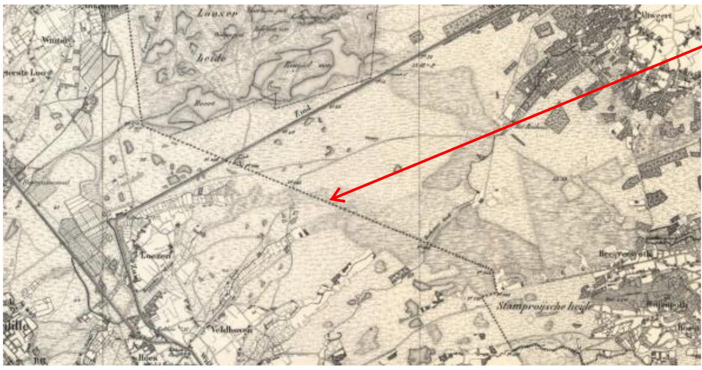


Figure 1. An overview of major streams in Kempen-Broek blue lines names are streams; red lines are canals, black labels are names of places, and purple is industrial sites.

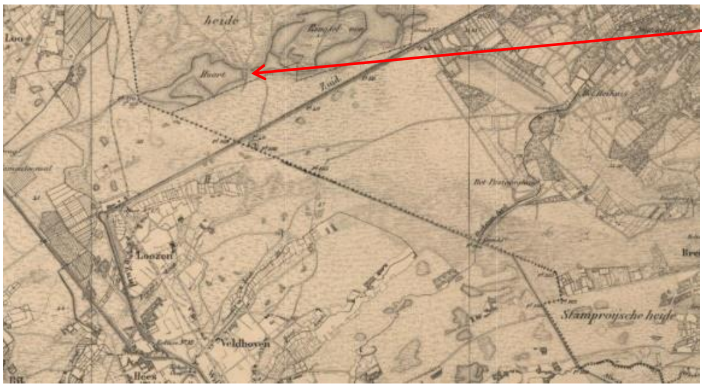
1.2.1 Historic changes to Topography.

In 1870, Belgium wanted to improve the drainage from the Bocholterbroek to the south of the Wijffelterbroek in this way to be able to develop the area, see Figure 2. Because the Netherlands did not want to cooperate in improving drainage, a drainage ditch was dug along the Belgian border via the Wijffelterbroek, sometimes referred to as Emissaries or Lossing (Runhaar et al,.2018). As a result, during World War II, 1500 hectares of an extensive marsh system was drained to increase food production within the Kempen area. The area drained has remained in agricultural production ever since (Jepson et al, 2018). Watercourse systems were constructed along the east of the nature reserve, which not only provides deep drainage of the area but also allows water seepage to be captured and removed from its area. This, in turn, made larger areas of the reserve less wet due to the strong draining effect of the various waterways. In 1892 a zinc smelter was founded in Budel, seen in Figure 2. On a remote site near Kempen-Broek and further developments of industrial sites north, along Kempenweg. Additionally, ditches were dug through the majority of the swamp area, and the peat was extracted. The reclamation of wetlands to enable urbanisation and agriculture severely changed the hydrological, chemical, and ecological environment of these areas. Lowland delta areas become more vulnerable to water quality deterioration by processes like salinisation and eutrophication, which can be amplified by climate change and land subsidence (Hoeksema et al, 2006).

In 2003, an extensive nature development project was carried out over the area. The main goal of creating a climate buffer was to counteract the drying effect and the negative influences of agriculture. Climate buffers are a nature-based solution to limit the effects of climate change, and additionally, in the case of Kempen-Broek, it provides a natural water retention measure for buffering inland flooding or water shortage situations. But, also, to improve water quality for multifunctional purposes. This is done through the nutrient uptake from plants and organisms in the wetlands (Hansen, et al 2018.). This climate buffer is in the lowest part of the area, near the border with the Netherlands (see Figure 2). Areas of older agricultural plots were restored into natural areas. In 2000, Natuurmonumenten had the adjacent Chain Dyke area: a former agricultural and production forest area of 125 ha located in the northern part of the central valley and not only directly adjacent to the Smeetshof, but also to the further East to Wijffelterbroek and further North. In more recent years, the ARK foundation has purchased important land in the vicinity of the nature reserve, and the foundation also wants to purchase and manage more areas here in the future. The new developments influenced land on both Dutch and Belgian territory as pollutants are more easily accumulated due to changes in the natural environment, as most streams and ditches have been directed to flow through the same path. As a consequence, there can be an Increase in volume and velocity, peak flows within the streams and may be many times greater than in more natural streams.



Year 1870: Development of the canal to help drainage (Emissaries).



Year 1892: Development of the Budel zinc smelter and industrial Zone.

Year 2003: Development of the climate buffers.

Figure 2. Graphics highlighting Kempen-Broek's key historical land-use changes Great historical province atlas, (Topotijdreis: 200 jaar topografische kaarten, 2021)

1.2.2 Current Topography.

The geology of an area will affect runoff and the movement of surface waters. In the case of Kempen-Broek, a valley-shaped depression changes into the upper reaches of the Tungelrooijse brook. This allows for most of the streams and surface waters to flow Eastwards. The former Bocholterbroek flows into several streams from Belgium. These waters drain into the Émissaire, which ends up at De Raam. The old discharge, which in the past drained the water from Belgium to the southwest. As a consequence, Émissaire lost its function as the main drain and is now used as local drainage towards De Raam. The Vetpeel drains water from the Laurabossen. The Vetpeel joins De Raam on the north side of the Wijffelterbroek. These smaller rivers eventually drain into the Meuse River further east (Runhaar, et al,.2018).

From the hydrological study of Wiffelterbroek en Vetpeel (Runhaar, et al,.2018), their research suggests that the Marsh areas in Kempen-Borek can release fresh groundwater water to the environment, and this limits drought damage in agriculture. This is due to shallow ground waters that can well up in the marsh areas. From the nature of the land, most marsh areas lay above the streams so that ground water can seep into the streams. Lewandowski et al. (2020) found that groundwater discharge can contributed up to 50% of the overall external P load in wetland areas.

All land-disturbing activities may result in the addition of sediment to streams. Lenat et al (1994) suggested that construction activities cause the highest erosion rates. Agriculture is the most common source of sediments because agricultural land is the most common use, and that is true for Kempen-Broek too. Sediment inputs degrade habitat quality for both fish and invertebrates (Lenat,et al.,1994).

1.3. Problem Statement.

In 2017 the National Institute for public health and the environment published a study of water quality and ecological status in the Netherlands. (Fraters, et al., 2017). In summary, the study concluded that that the ecological status of many surface waters had been degraded and were poor according to WFD water quality standards. From their findings, this is due to relatively high discharges of nitrogen and phosphorus from agriculture, industry, and wastewater treatment plants. Agriculture is suggested to be a predominant source, as discharges from industry and wastewater treatment plants have declined over the years. Within the total surface area in The Netherlands, 60% is covered by agricultural land, and a dense network of ditches, streams and lakes provide water to most of this land. This suggests most of the surface waters in the Netherlands would have higher nutrients from agricultural runoff (Fraters, et al., 2017). Aside from sediment problems, agricultural and urban runoff may cause a variety of other water quality problems. Both land-uses can cause enrichment through the addition of nutrients (Swartjes, et al 2012) Urban streams also can contain a wide variety of toxic contaminants (Swartjes, et al 2012), as well as elevated concentrations of nutrients and organics.

In the Netherlands, significant efforts have been made to combat heavy metals in surface waters during the last decade. However, many surface water still exceeds WFD parameters (Schipper et al., 2008; Bonten, 2008). Rozemeijer (2014) highlighted that the leaching of metals alone could be enough to push water quality through the threshold of good ecological status. Additionally, Rozemeijer (2014) mentions that the highest leaching rates could be expected from the wet peat areas and in agricultural regions with intensive horizontal drainage systems. The contribution of leaching of heavy metals (Zn, Cd, Pb and Ni) to total surface water loads are calculated at 20 to 50% on a national scale (Rozemeijer et al., 2014).

Heavy metal contamination from stormwater runoff can result in both acute and chronic impairment of receiving water bodies. The studies investigating heavy metals focused on the build-up and wash off from roofs (Walker, et al,2002.) and road surfaces. Metal's concentration in roof runoff from this study was also affected by climatic conditions. Metals such as manganese and Pb derived primarily from the resuspension of roadside soil by wind, while traffic was the primary source of Cu, Zn, and Cr. On roads, the metal build-up of Cu, Zn, Pb, Ca, Cr, and Ni because of the degree of traffic congestion and road roughness, and less on traffic volume.

Further investigated build-up and wash-off of heavy metals on pavement surfaces and identified pavement type, peak intensity, rain duration, and rain depth were related to heavy metal concentrations (Campisano et al., 2017). Urban runoff can be toxic to stream invertebrates during storms events (Medeiros et al., 1983). Many studies have shown that streams draining urban watersheds have elevated levels of metals in surface waters (Lenat et al. 1994), Particularly for wetlands adjacent to urban areas as wetlands act as a natural sink for many pollutants (Inglett et al., 2011).

Budel's zinc smelter could potentially influence heavy metal concentrations as combustion gases were released during the desulphurisation of the zinc blend. These gases contain cadmium dust, among other things, which is filtered out and then processed into metallic cadmium. A major route of distribution of the heavy metals released in the past from industrial zinc production is via the atmosphere. The metals, especially Zn and Cd, were emitted as particles in the combustion gases and then carried along by the wind. This has allowed pollution to spread over a large area. These heavy metals cannot be broken down by bacteria, and they can immobilise biological processes if they accumulate in food chains. The metals can be absorbed in sediments or bioaccumulate in benthic fauna, at times up to toxic levels (Kahlon et al., 2018). The most contaminated zinc sites were remediated in the 1980s. Here and the zinc ashes remained there, including on the edges of the sand drift, along the railway verges and in the old industrial estates. Anthropogenic activities, namely Zn smelting activities, represented the most critical sources of Pb, Cd, Cu, Zn, and Mn (Chen et al., 2020).

Other industries such as Bredox Chemical company and Kuypers Kessel (that specialise in the excavation of sand and gravel) are in close proximity to Kempen-Broek (north of Kempen-Broek). Dry deposition from the excavation can contribute to the ion make-up of surface waters, and in turn, influence the hardness of the water. Parent materials include calcite, dolomite, gypsum, fluorite and others in the Kempisch Plateau (Runhaar, et al,.2018). Additionally, the historic changes to natural stream flows and velocities may also influence the surface water make-up, increase in volume and velocity, peak flows within the streams and may be many times greater than in more natural streams (Walker et al., 2002.).

There is currently no in-depth quantification of the surface water quality in Kempen-Broek, compounding the question if this water exceeds levels of nutrients and heavy metals deemed suitable for a healthy wetland. They are potentially jeopardising the sustainability and economic potential of the wetland.

2. Aim.

The aim of this study is to have a better understanding of the surface water quality in the Kempen-Broek area. This study intends to map surface waters of different characters (streams, canals, ditches, ponds, and standing water in this wetland) their connections and provide a first overview of dissolved solids in surface water. Furthermore, several plant species will be mapped as indicators for Kempen-Broek ecological health. In this way, this study aims to identify key point sources and diffuse sources of pollutants and identifies key impacted areas (if any) and provide a suggestion for more in-depth studies for pollutant mitigation.

2.1. Research Question.

Main research question: What is the surface water quality in Kempen-Broek, and is there concern for ecological health?
<u>Sub questions</u>

Sub-question 1: How is the surface water system physically structured?
Sub-question 2: What spatial patterns in E.C. exist, and how are they related to the physical structure of the system?
Sub-question 3: Which potential point sources and diffuse sources of pollutants exist in the Kempen-Broek nature reserve?
Sub-question 4: What influence do these pollutant sources have on the concentration of pollutants in surface water within Kempen-Broek.
Sub-question 5: What relationships exist between water quality and indicator plant species?
Sub-question 6: To what extent has current and previous land use impacted the water quality of the Kempen-Broek nature reserve?
Sub-question 7: What are the pollutant mitigation suggestions for Kempen-Broek?

3. Theory.

3.1. Water Quality for Ecological Health.

The Water Framework Directive (WFD) is an essential piece of environmental policy which aims to improve European water quality and secure ecological health. It applies to rivers, lakes, groundwater, estuaries, and coastal waters. The Water Framework Directive was agreed upon by all individual E.U. member states in 2000 and implemented in October of the same year. The WFD states that 'for good ecological status, nutrient and pollutant concentrations should not exceed biological quality elements that support the aquatic biology (The E.U. Water Framework Directive 2000/60/E.C., 23 October 2000). The framework sets up a common way of assessing water quality across the E.U. so that members can monitor improvements in quality. While this assessment has a range of statuses (bad, poor, to good) the chemical status is defined as either: 'Good' or 'Failing to achieve Good.' This paper uses Poor to define anything not good.

For this study, Kempen-Broek is regarded as inland water. The average nutrient levels (river thresholds) used by the WFD across Europe are N= 2.5 mg/l and P=100 µg/l (Phillips et al, 2018). However, as discussed by Phillips et al (2018), especially for rivers and inland waters, some variation is expected due to natural variation of parameters. So, the use of some parameters will not directly apply to all wetlands. There was much less evidence of type-specific differences for threshold concentrations wetlands within the Netherlands. To represent water qualities of unimpacted wetlands, this study uses parameters with a lower threshold N<1.1 mg/l, P <80 (µg/l) to try to give a comparable parameter.

Within the WFD, only priority substances are given parameters, and these parameters are mainly for nutrients and pesticides. However, this study covers a wide range of elements that are not listed in the WFD. So, this study uses the FOREGS baseline for major ions and heavy metals parameters to compare the Kempen-Broek water quality. FOREGS was initiated to provide high quality environmental geochemical baseline data for Europe. The data was based on samples of stream water collected from all over Europe using standardised sampling and analytical procedures. (See Annex II). As there are no existing water quality measurements in Kempen-Broek, the FORGES baseline is easier to compare against.

3.2. Measuring for Surface Water Quality.

The quality of surface waters is impacted by anthropogenic influences (urban, industrial, and agricultural activities, increasing consumption of water resources) as well as natural processes (changes in precipitation inputs, erosion, weathering of crustal materials) (Ranalli, A.J., 2004).

Measuring electric conductivity (E.C.):
Given that anthropogenic activity and natural processes influence surface water quality, the total mineralisation comprises a wide range of elements, which can be investigated in different ways, such as using individual ions, total dissolved salts (TDS), and electric conductivity (E.C.). Measured dissolved ions depend on various factors like watershed geology, the watershed's size in relation to the wetland, wastewater from point sources, runoff from nonpoint sources, atmospheric inputs,

evaporation rates, and some types of bacterial metabolism (Atkinson et al, 2006). While this information is beneficial, the number and cost of analysis is limiting TDS measurements are time-consuming and energy-intensive. Higher E.C. concentrations potentially indicate the occurrence of pollutants and other ions; Higher E.C. concentrations potentially indicate the occurrence of pollutants and other ions; the measure is a cost-effective way of achieving a map of potential issues which can be further investigated. General guidelines for aquatic ecosystems (Palmer et al, 2004) do not treat high E.C as a toxicant but instead recommend that the surface waters need investigation. From natural freshwater systems E.C. will typically range from 40 to 3000 µs/cm (Palmer et al, 2004).

Measuring for nutrients (N and P):
Nutrient loading to waterways from point and nonpoint sources is an ecological concern and represents one of the most significant water quality issues in surface waters. Nutrients are essential to the survival of aquatic organisms, but excess nutrient loading to water bodies can impact water through eutrophication. Both natural and anthropogenic sources contribute to nutrient enrichment in surface waters. Nutrient loading to receiving waters can be dependent on numerous factors: source output and location, speciation and concentration, seasonal variation, mode of loading (continuous vs sporadic) and bioavailability. Nutrient loading is possible through atmospheric deposition, wet and dry (Carpenter et al,1998).

Measuring for major ions, anions and Heavy metals (Major ions: Al, B, Ba, Be, Fe K, Cl, Si, SO4, Na, Mg. Major anions are Cl, F-, Br, SO4, PO4 and Heavy metals: Ca, Cd, Ni, Cr, Co, Cu, Pb, Zn, Zr, Sr, Mo, Mn). Regarding Major ions, the ionic composition of surface water plays an important role in assessing the quality of water. In unpolluted systems, major ions in surface waters are provided by weathering of rocks. Water quality is related to several factors such as geology, weathering regime, quality and quantity of runoff, and water-rock interaction. Whereas in more polluted systems, industrialisation, urbanisation, and activities such as agriculture can increase the concentration of several ions and trace elements in groundwater, which results in the deterioration of the water (Mora et al, 2017). Major anions are Cl, F-, Br, SO4 and PO4. Although few, these ions determine aspects of water quality that are essential for all aquatic organisms. Na+, K and Cl are vital minerals for plant and animal function. Ca, Mg and Br alkalinity is also vital for the biota and are the principal components of water “softness” and “hardness” (Sutcliffe et al 1998.).

Regarding Heavy metals, traces of metal ions have important roles in a broad spectrum of functions of life. Heavy metals in natural freshwater systems are usually not dangerous for the environment because they are present only in minimal quantities. Heavy metals are pollutants in the environment only if it’s present in large quantities (this fact is usually attributed to industrial activities) Some of these metals may become toxic at high concentrations, such as Fe, Pb, Ni that affects the central nervous system of fauna (Voica, et al, 2012). Significant sources of anthropogenic Zn discharges include electroplating, smelting, ore processing, drainage from Industrial zones, domestic and industrial sewage, road surface runoff, corrosion of Zn alloys or galvanised surfaces, and erosion of agricultural soils (Olaifa, et al 2017). Heavy metals in soils in rural areas have accumulated for decades due to the application of manure (containing Zn and Cu), phosphate fertiliser (containing Cd), and atmospheric deposition (Pb, Ni from cars). In time, these accumulated metals will leach to the surface or can be taken up by vegetation (Rômkens et al,2002).

3.3. Measuring for Ecological Health.

In a wetland environment, two of the most important local factors affecting plant community composition are water quantity and quality (Brinson 1993). All these studies found significant relationships between water chemistry (most often pH, E.C., or alkalinity) and plant community composition. This link between wetland plants and the water in which they live make it possible to use plants as indicators of wetland water quality. In addition, plant species distribution is determined primarily by the environmental characteristics of a site. In a wetland, water chemistry is one of the most important of these environmental characteristics (Goslee et al, 1997). Both are functions of water source. This study will investigate ecological health with plant indicators. Plants are particularly useful for monitoring pollutants in wetlands owing to their stationary nature, making them ideal as bioindicators and can provide a cost-effective approach for monitoring pollutants and ecological Health (Phillips et al, 2015). In a wetland environment, two essential local factors affecting plant composition are water quantity and quality (Goslee, et al,.1997). The local level plant distribution is primarily determined by local environmental factors. Using indicator species has limitations when the quality of the environment is to be quantified. In an ideal monitor, there is a linear relationship between the concentration in the environment and vegetation. The indicator species that are investigated are Urtica dioica, Rubus fruticosus, Pteridium aquilinum, Phragmites australis and Iris pseudacorus.

Table 1. An overview of the indicator species selected.

Indicator species	Indicator parameter
Urtica dioica	Urtica dioica (stinging nettle) is a tall, rhizomatous herb that produces a dense, rapidly ascending canopy in summer that often precludes the growth of other plants. Higher abundance rates are in habitats within a soil pH range of 5.0– 8.0. (Hipps et al, 2005). Urtica dioica grows as a weed in neglected places, such as along roads and river valleys and near settlements. Nettle can grow in higher nutrient concentrations (Rorison, et al., 1968.) This species was used as an indicator of high nutrients and disturbance.
Rubus fruticosus	Rubus fruticosus (bramble) is a polymorphic species grouping numerous taxa that are difficult to differentiate. It is a cosmopolitan species that will grow on a wide variety of soil types (with a preference for acid soils), (Balandier et al., 2012), (Oleskevich, et al, 1996). Bramble species are adapted to higher ecological stress. Rubus fruticosus is more adapted to heavy metal accumulation than other vegetation, particularly Cd and Zn). This species was used as an indicator of heavy metals (Zn and Cd) (Vlad et al 2019).
Pteridium aquilinum	Pteridium aquilinum (fern) restricts the growth of trees (Senyanzobe, Mulei, Bizuru and Nsengumuremyi, 2021). This species is an indicator of higher heavy metals accumulation (Senyanzobe, 2020) as they can accumulate very high concentrations of metals in their tissues without showing signs of toxicity (Cu, Fe and Zn).
Phragmites australisis	Phragmites australisis (common reed) can grow in and around a variety of waters which include freshwater, brackish, and alkaline water types. They grow along a gradient from deep water (> 2 m) to terrestrial (< 1 m below substrate) conditions. It often dominates the area it occupies to form dense stands in floodplains, shallow lowland lakes and along natural river channels (Poulin, Davranche and Lefebvre, 2010).

	Phragmites australisis is moderately tolerant to Fe, showing marked signs of iron toxicity at high Fe concentrations (Saaltink,et al, 2017). This species was used as an indicator of indication high pH, high E.C and high Fe.
Iris pseudacorus	Iris pseudacorus (flat reed) has a low ecological tolerance. Surface water is a factor affecting the distribution of this plant species. Since the plant prefers areas besides freshwater, it may be an indicator of fresh or salty water. It has been determined that the species prefers sandy and loamy soils. Also is commonly distributed over calcareous soils, which included a low or medium level of $CaCO_3$ and preferred neutral or low alkaline soils. In high E.C. concentration, Iris pseudacorus populations are found to be very low. (Sutherland, 1990; Engin, et al, 1998.) This species was used as an indicator of good environmental conditions.

However, a major limitation is many plants are accumulators. Plants store substances at high accumulation factors, especially at low environmental concentrations (major ions and heavy metals); plants may not show effects concentrations. At high environmental concentrations, the accumulation factor decreases plants more considerably (Goslee et al,.1997). Ions seldom reach solution concentrations sufficient to cause osmotic disturbances in plants without previous symptoms of lethal toxicity (Rucińska-Sobkowiak et al,2016).

So, in this study, not only process limited species are monitored but also biodiversity. This, in turn, will give an additional perspective on ecological health. A low species diversity suggests a lower number of successful species and poorer ecosystem health (Yadav., 2013). I.e. high biodiversity is an indication of good ecological health.

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4. Methodology.

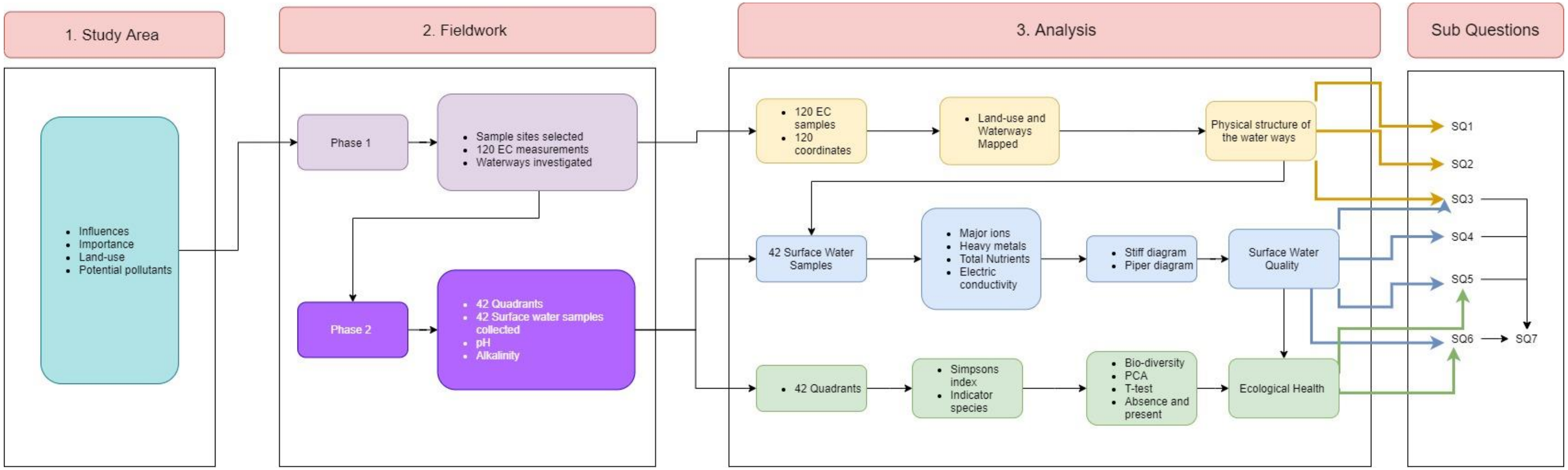

Figure 3. A flow diagram representing an overview of the methodology.

This study used a three-step approach to investigate the surface water quality and ecological health to help address the research sub-questions. First, the study area. This step is identifying the study area. Because the area in question is very large, this study needed to refine the scope. So, an area was selected under expert opinion to include major streams, rivers, and potential influences. Secondly, fieldwork was conducted to address how the surface water system is physically structured, the spatial patterns of E.C. that exist, and how are they related to the physical structure of the system (phase 1). These factors were taken assessed. Then further fieldwork was conducted (phase 2). 42 samples sites were selected, and an in-depth investigation was conducted on surfaces waters and plant indicators. Lastly, data analysis was conducted to determine The chemical make-up of Surface water quality, The implications of pollutants on ecological health and the extent to land use impacted the water quality of the Kempen-Broek nature reserve.

4.1. Study Area.

4.1.1. Selection of the study area.

The selection of the study area takes under consideration variables that would influence the chemical make-up of Surface water quality. Starting with potential pollutant sources, as mentioned in the problem statement, Kempen-Broek is in close proximity to industrial, agriculture, and urban land uses, as seen in Figure 4. Five land use types were distinguished from the use of google earth imagery and, in conjunction with historical land-use change highlighted by great historical province atlas (Topotijdreis: 200 jaar topografische kaarten, 2021), to note, the climate buffer constructed in 2003 was considered as natural land use as it showed to have established vegetation. In addition, streams that enter Kempen-Broek flow from or are influenced by the land-uses will be covered to establish pollution flow entering and exiting the nature reserve. Additionally, in alignment with the management authorities (both Netherlands and Belgium), all major surface waters within the reserve were investigated to give a complete perspective of the streams, ponds and standing waters. Finally, using an expert opinion (Prof. dr. M. Wassen, 2021, personal communication), the study area was established, as seen in Figure 5.

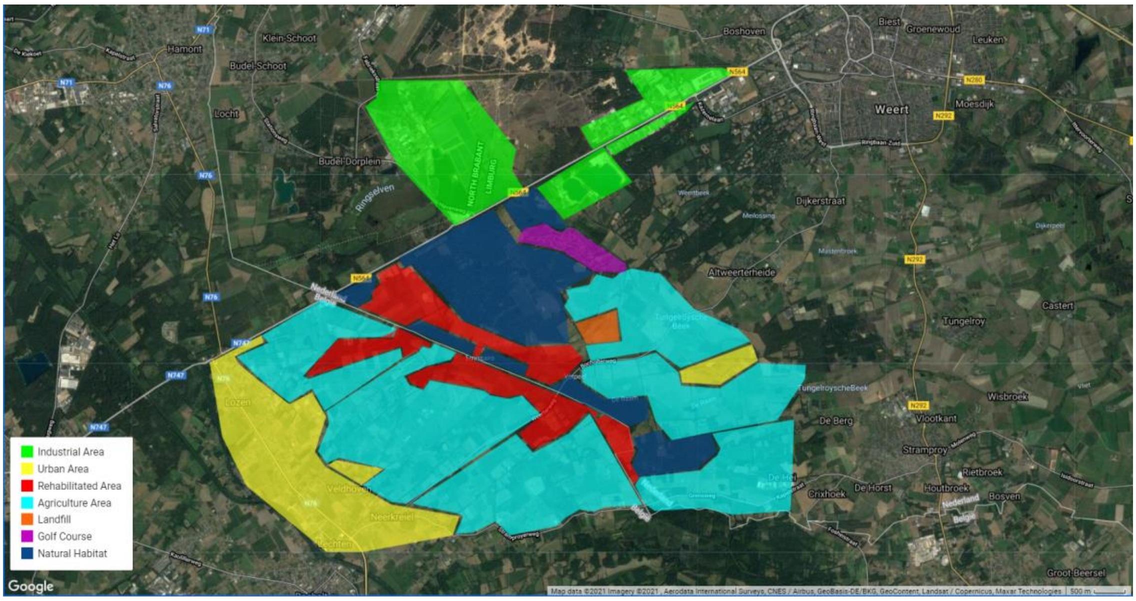

Figure 4. Land use map in the study site and surrounding area, created with google earth engine. Note the landfill and golf course were not included in this study

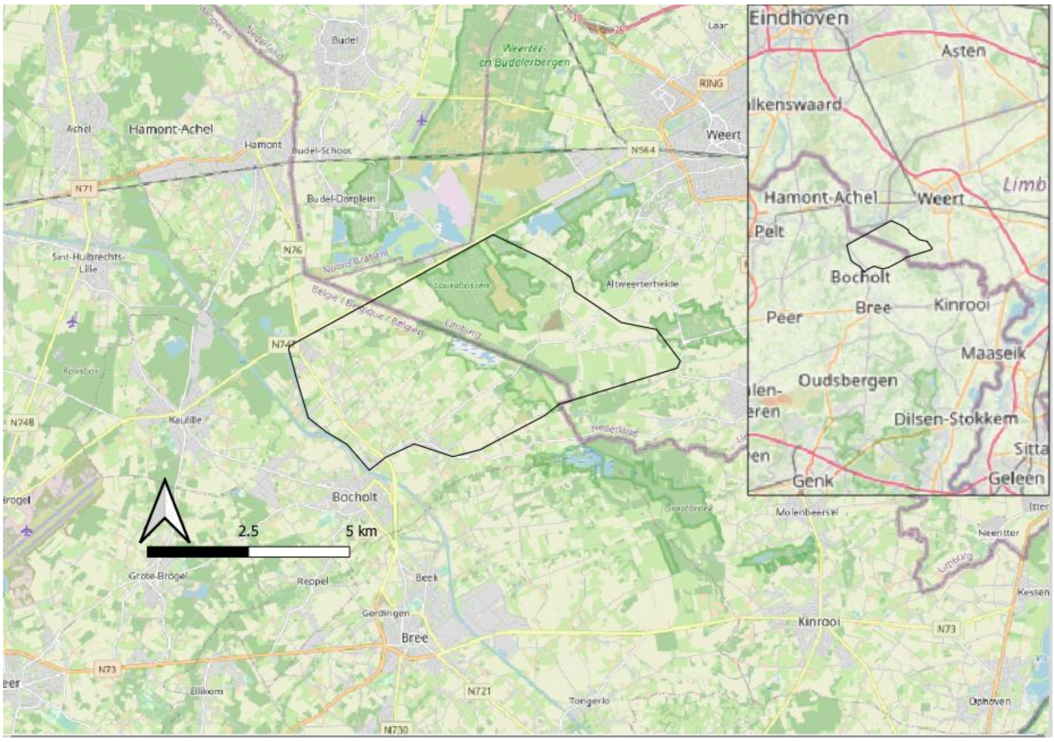

Figure 5. The study area of Kempen-Broek (60 km2), used to investigate the physicochemical characteristics of surface waters and the relationship to ecological health in the Kempen-Broek nature reserve.

4.2. Fieldwork.

4.2.1. Phase 1.

Surface water was investigated, March 26th to March 31st (2021) during the end of winter. During phase one, E.C. measurements were conducted at every surface water site, at the same site recordings of the characteristics of water. The characteristics included: flow/ no-flow, the direction of flow, estimated flow strength (fast, medium or slow). Other observations were recorded, like interesting features, litter, water colours. A detailed waterways map was made to identify the main physical structures, flow paths and observations that would influence the chemical make-up of surface waters. Since the sample locations were used for future monitoring (phase 2), a precise GPS instrument (+/- 5 m) was used. This, in turn, gave a distribution of E.C. measurements for Kempen-Broek. QGIS was used to map Surface waterways, QGIS 2.18.21. The QGIS is a Free Open-Source Geographic Information System licensed under the GNU General Public License.

4.2.2. Phase 2.

42 sample sites were selected during phase 2 (see Figure 6). The sample sites included four land use types: agriculture area, natural habitat, urban area, and rehabilitated area, as seen in Figure 4. Ten sample sites were selected for their E.C. values (5 maximum E.C. values and five minimum values). Water bodies with interesting observations, such as colour, were included. Additionally, a representative of all surface water was included (agricultural drain, road ditch, marsh, stream,

pond). Finally, to ensure spatial coverage of the study site, selecting sample sites close together was avoided.

Table 2. A table showing the criteria for each site selection.

ample site	Description	Criteria	Location
1	Marsh	Low EC value	51°12'44.5"N 5°36'27.8"E
2	Large stream	Minimum EC value	51°12'35.5"N 5°35'43.0"E
3	Large stream	Low EC Value	51°12'32.7"N 5°35'02.8"E
4	Agricultural ditch	Low EC value	51°12'46.2"N 5°34'57.6"E
5	Ditch	In Urban land use	51°12'07.9"N 5°34'16.5"E
6	Stream	Near urban land use	51°12'02.2"N 5°35'31.2"E
7	Agricultural ditch	Agriculture Land use	51°12'09.2"N 5°36'24.9"E
8	Connector	Connecting agricultural streams	51°12'20.3"N 5°36'47.1"E
9	Lake	Unique surface water body	51°12'15.9"N 5°37'24.7"E
10	Large stream	Ensure Spatial coverage	51°11'52.9"N 5°36'55.7"E
11	Agricultural ditch	Ensure Spatial coverage	51°12'05.0"N 5°38'06.4"E
12	Marsh	Low EC value	51°12'10.5"N 5°38'23.4"E
13	Road drainage	Unique surface water body	51°12'15.3"N 5°38'16.2"E
14	Marsh	Natural land use	51°12'24.5"N 5°37'31.9"E
15	Drainage pit	Unique surface water body	51°13'09.2"N 5°36'23.3"E
16	Marsh	Natural land use	51°13'12.2"N 5°35'55.2"E
17	Agricultural ditch	Agricultural land use	51°12'57.7"N 5°35'05.7"E
18	Agricultural ditch	High EC value	51°13'33.9"N 5°36'48.3"E
19	Lake/ large stream	Maximum EC value	51°13'48.8"N 5°37'32.9"E
20	Marsh	Natural land use	51°13'43.7"N 5°37'40.7"E
21	Stream	High EC value	51°13'22.1"N 5°38'57.3"E
22	Stream	High EC value	51°12'48.6"N 5°39'49.0"E
23	Connector	Connecting wetland flows are observed	51°12'16.4"N 5°38'25.5"E
24	Lake	Unique surface water body	51°12'09.1"N 5°40'49.0"E
25	Wiffelterbroek	Exiting surface waters	51°12'10.3"N 5°41'33.0"E
26	Stream	Red colours observed	51°11'31.7"N 5°39'03.6"E
27	Stream	Ensure Spatial coverage	51°11'19.0"N 5°37'26.2"E
28	Ditch	Urban land use	51°11'16.1"N 5°35'31.2"E
29	Ditch	Unique surface water body	51°12'40.7"N 5°37'46.7"E
30	Agricultural ditch	Ensure Spatial coverage	51°12'31.2"N 5°38'35.6"E
31	Marsh	Natural land use	51°12'14.4"N 5°38'27.0"E
32	Road drainage	Unique surface water body	51°12'10.5"N 5°38'23.4"E
33	De Raam	Major surface water	51°12'04.5"N 5°38'36.9"E
34	Connector	Diverging wetland streams	51°12'03.3"N 5°38'34.0"E
35	Stream	Red colours observed	51°11'59.6"N 5°38'47.7"E
36	Essimire	Major surface water	51°12'27.3"N 5°37'02.6"E
37	Small stream	Red colours observed	51°11'53.8"N 5°38'23.6"E
38	Vetpeel	Major surface water	51°12'16.1"N 5°39'03.9"E
39	Pond	Unique surface water body	51°13'03.6"N 5°37'55.5"E
40	Marsh	Natural land use	51°12'32.0"N 5°36'56.0"E
41	Tungelsche beek	High EC value	51°12'38.2"N 5°40'13.5"E
42	Marsh	Natural land use	51°13'00.8"N 5°38'09.5"E

*Connector is multiple streams or ditches connecting or diverging in the same area.

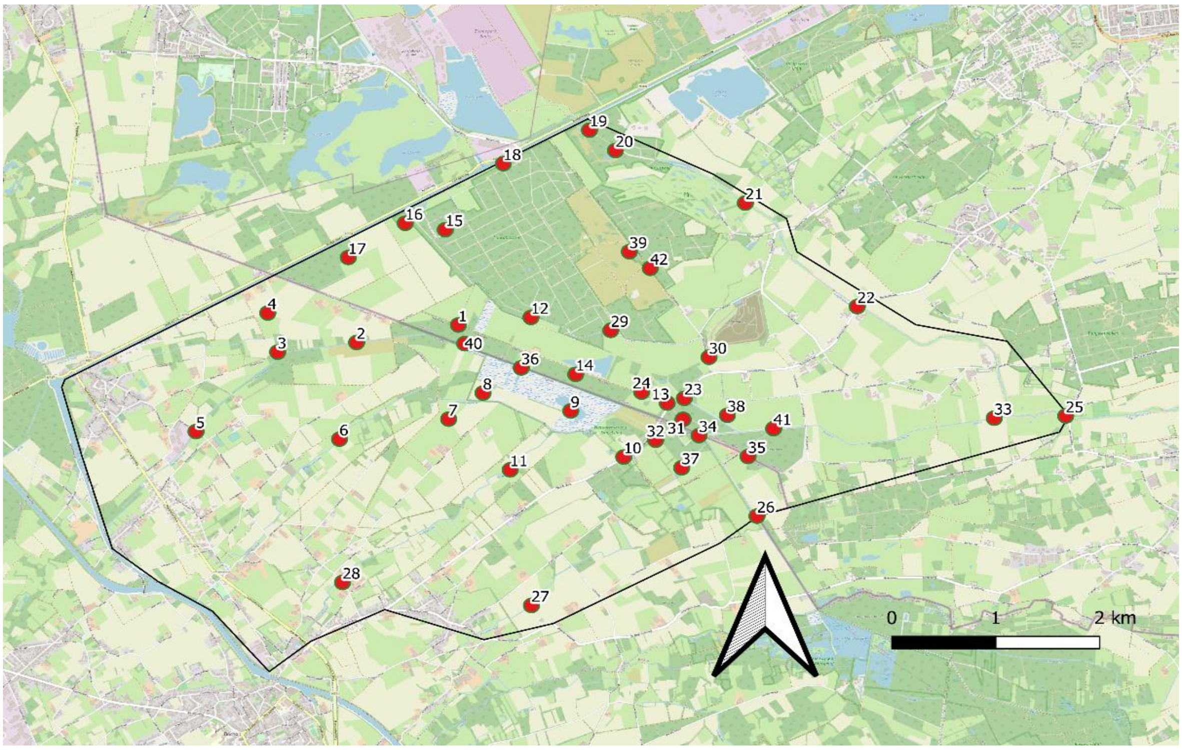

Figure 6. 42 samples sites that were selected during phase 2.

Phase 2 investigations were conducted during April 29th to May 8th (2021), At the early stages of spring. During the investigations, In-depth surface water sampling during phase 2. From the 42 sample sites, 84 surface water samples were collected. These samples were then analysed for major ions, heavy metals, and nutrients at Utrecht University laboratories. Additionally, a selection of 42 quadrants was conducted.

- 42 x 100 ml sample tubes filtered water for Nitrogen, Phosphorous, major ions, and I.C. ion analysis (ion chromatography)
- 42 x 100 ml sample tubes filtered water for ICP-OES. These samples need to have a constant pH of 5 to 7. To account for this, samples were mixed with 0.1 moles of hydrochloric acid.

All Surface water samples were immediately filtered through 0.45-µm nitrocellulose filters and were stored in a dark, cool place. Alkalinity and pH were measured in the field soon after extraction. All measurements were recorded (seen in Annex I). pH was measured with compact pH 3110 precision pH meter, whereas alkalinity was measuring with Alkalinity Test Kit (Model AL-AP, mg/L), a titration method was used with a Drop count titration of Sulfuric acid.

Alkalinity means the ability of water to neutralise the acid. It is defined as the number of ions, such as $CO_3{}^{2-}$, $HCO_3{}^{-}$, O.H. $^{-}$, $HSiO^{3\,-}$, $H_2BO_3{}^{-}$, $HPO_4{}^{2-}$ and $H_2PO_4{}^{-}$, in water that will neutralise hydrogen ions. However, in most waters, $HCO_3{}^{-}$ is the dominant Ion between pH 4.5 and 8.3. The alkalinity is often expressed as mg/l of $CaCO_3$. The determination of alkalinity is made by titrating the known amount of water with acid (sulphuric acid) to pH 4.5. At this point, all the ions which neutralise and the colour of the indicator (bromcresol green) will change.

$$\textbf{Alkalinity (as CaCO3)} = \textbf{20} * \textbf{drops of sulphuric acid}.$$

Equation 2, Alkalinity (mg/l $CaCO_3$) measurements from the titration method. Where drops of sulphur acid are the volume of 0.16 N H2 SO4 (ml) used in the titration.

Apart from surface water samples, vegetation was counted (Simpson's Index and species indicators), this was done in Quadrants. Allows establishing a link between these sample water qualities and the vegetation indicator species diversity using Simpson's Index. Selection of Quadrants: At each site, plots of 1 m^2 quadrants were selected as close to each sample point as possible while still including all riparian vegetation. As Changes in water quality can affect the riparian communities, measuring the biodiversity will give an indication of the health of riparian communities. Biodiversity was measured. This was done by counting the vegetation taxa in each quadrant using the Simpsons diversity index: species richness is the measure of individuals of each species present (Yadav, 2013). Simpson's index is a measure of diversity (Equation 1), which considers the evenness of abundance among the species present and species richness. In principle, it measures the probability that two individuals randomly selected from an area will belong to the same species. A higher Simpson's index represents higher biodiversity, and in turn, higher ecological health. Conversely, a lower Simpsons index represents lower biodiversity and thus a pooper ecological health. Note: grass species were not included in vegetation taxa.

$$\boldsymbol{D} = \frac{\sum \boldsymbol{ni}\,(\boldsymbol{ni}-\mathbf{1})}{\boldsymbol{N}(\boldsymbol{N}-\mathbf{1})}$$

Equation 1, Where *ni stands for the total number of organisms of each individual species.*
And N is the total number of species.

Additionally, counting indicator species: firstly, identifying indicator plant species: within the 42 quadrants. This was done by identifying process-limited species: species sensitive ecological parameters. The species that are investigated are Urtica dioica, Rubus fruticosus, Pteridium aquilinum, Phragmites australis and Iris pseudacorus. Indicators of plant species are counted in same quadrants as the Simpson index. Plant species will vary across the study site as a function of variations in site soil character, hydrology, hydrochemistry, and pollutants where this impacts the plant growth (Yadav, 2013). So, it can be an effective indicator showing a relationship between the effective plants and pollutant concentrations within the study area and, therefore, mapped (absence and presence mapping) to determine the extent to which pollutants: heavy metal accumulation, high nutrients and disturbance affects ecological function within the study area.

The first four indicator species Urtica dioica, Rubus fruticosus, Pteridium aquilinum and Phragmites australis were selected to highlight poor ecological conditions. If these species are abundant in particular sample sites across Kempen-Broek, it may be an indication of 'poor' environmental conditions. These locations will have further investigations to determine if there are relationships between plant species and the nutrient loads throughout the reserve. The last species Iris pseudacorus was selected to show 'good' ecological health of wetlands. If these species are predominat throughout the sample sites, it will reflect in more favourable environmental conditions for plant growth.

4.3. Data Analysis.

4.3.1. Physical structure of the surface water system.

To help tackle the sub questions 1, 2 and 3, the mapping of the spatial distribution of indicators and physicochemical parameters were needed. Geographical information system (GIS) was applied. QGIS 3.18.2 ‘was used to map the results. The QGIS is a Free Open-Source Geographic Information System licensed under the GNU General Public License. By using observations together with GIS to distinguish flow patterns, physical barriers. Flow speeds were observed during phase 1 and chartered between no flow, slow flow, medium flow, and fast flow. Additional features that were observed that might influence the surface water quality were included on the map.

4.3.2. Surface Water Quality.

Samples were collected in the field then processed at Utrecht university laboratories. The method and parameters assessed were:

- Discrete Analyser for NO_3 and NO_2.
- Photometer for P.
- ICPOES for: Al, B, Ba, Be, Fe K, Fl, Cl, Br, Si, S (as SO_4), Na, Ca, Cd, Ni, Cr, Co, Pb, Cu, Zn, Zr, Sr, Mo, and Mn.
- I.C. for anions Cl and SO_4 and PO_4.

To measure N, this study used a discrete analyser. Samples were given to Utrecht university laboratories, which measures the concentration of organic and inorganic compounds in a solution by determining the absorbance of wavelengths of light. The nitrogen in the solution can react with the phenol and hypochlorite to a larger molecule that has a blue colour, and this colour is what is measured.

To measure P, this study used the Phosphorous colourimetric method. Within the solution, phosphate is dissolved. Furthermore, the chemical reaction between phosphate and the ammonium molybdate that is added will create ammonium pentamolybdate. Ammonium pentamolybdate can create a kegging structure that can enclose phosphorous boron and silicon. This autonomy will have a bright blue structure when reduced by ascorbic acid. This is what can be measured in a photometer at 880nm.

The measurements for heavy Metals and major ions used an ion chromatography method was used. Samples were given to Utrecht university laboratories for the use of optical emission spectrometry (ICP-OES). It can measure for Major ions (Al, B, Ba, Be, Fe K, Fl, Br, Si,), Na, and Mg. Heavy metal (Ca, Cd, Ni, Cr, Co, Pb, Cu, Zn, Zr, Sr, Mo, and Mn)

To measure for major anions an I.C., Samples were given to Utrecht university laboratories for the use of Ion chromatography. It can measure for Cl and SO4 and PO4. This method separates ions based on their ionic strength, with a concentration of eluent over a column. It uses a column that partly binds the ions so that ions flow at their given speed. Weak binding ions flow first were as strong bindings flow last, and according to their flow speed. Conductivity measures the peaks at the time the solutions leave the column. To determine the Ion and its concentration, the samples need to be filtered and have a pH between 5 to 9 and not too high in alkalinity; otherwise, the column may not perform optimally. Additionally, samples must contain minimum amounts of oxygen. To account for this, samples were mixed with 0.1 moles of hydrochloric acid.

To help address the sub-question 3, 4, 5 and 6, stiff diagrams were used to analyse large changes within the surface water profiles and distinguish key characteristics in surface water chemistry. Stiff diagrams were made using Geochemist's work bench community (edition 15.0). Furthermore, distribution maps of all elements were made with QGIS. This, in turn, will help identify sample sites with concentrations above the WFD or FOREGS parameters and highlight high concentration distributions.

4.3.3. Ecological Health.

To help address the sub-question 4 and 5; Biodiversity and indicator species were used. To do so, the Simpsons index was mapped through QGIS, in turn highlighting the sample sites of high or low biodiversity.

Additionally, the indicator species are mapped into a present and absent map (done with QGIS). Using the map comparison to each sample sites, surface water chemical make-up is investigated to highlight any relationships between surface water quality and the indicator species.

A Principal components analysis (PCA) was conducted. A PCA will highlight the relationship between indicator species, summarise the information contained in data tables that can be more easily visualised and analysed. The statistical relationships between indicator species will help identify species growth patterns to other indicators.

To identify relationships between indicator species and water quality, a t-Test was used to show if there are any statical relationships between parameters and the presence of indicator species. Significant differences were tested at the $P < 0.05$ for the presence of nutrition dependent indicators (Urtica dioica) and the N and P concentrations.

5. Results.

5.1. Physical structure of the surface water system.

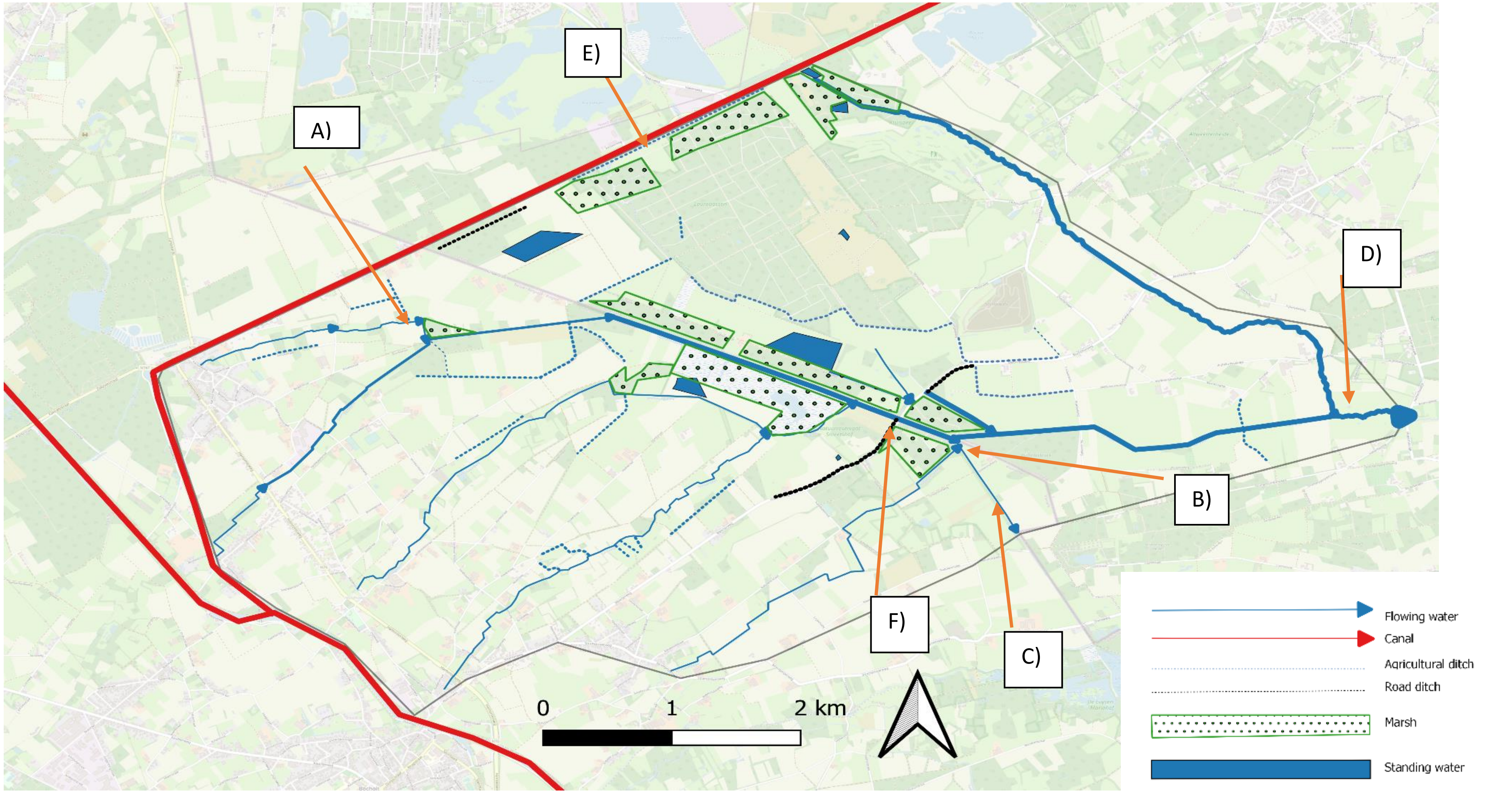

Figure 7. Surface waterways area map.

In general, as on the Kempen plain, most streams flow eastward. On the Belgium side of the reserve, streams flow from Urban areas into agricultural, and then through the natural areas. Whereas the Netherlands side, there are fewer streams, and the majority of flowing surface waters are diverted into De Raam or Tungelroysche beek. Regarding agricultural ditches, most of them are perpendicular to a stream with little or no flow. Interesting features include:

A) Large flow channel that directs streams towards Essimire. A series of ditches and streams that flow through agricultural land are channelled through here.
B) The Essimire gets diverted into De raam, the remainder of the Essimire flows along the border, however, at a substantially lower flow.
C) The river majority flow has been diverted at point B), making the flow slow and, at some points, standing. Additionally, in this stream, rubbish and reddish water are visible.
D) Connection of Tungelroysche beek and de Raam, where fast flows were visible. Additionally, this is surrounded by agricultural land, mainly cattle. This stream connects to Wijffelterbroek.
E) An interesting feature, as relatively close proximity to the Bundle zinc smelter, but also alongside a road. Standing water is visibly discoloured as red.
F) Main border crossing, where cars are frequent. Additionally, there was a road ditch, other than this road; Within the reserve, few major roads are present, other than walking/cycling trails

Agricultural areas on the Belgium side are mostly open fields, with a few horses in the occasional field. The main vegetation varies, between grasses, shorter shrubs on Belgium side whereas the Netherlands side, a large established pine forest was present in Laurabossen. Established thicker vegetation was present on either side of Essimire. Rehabilitated areas showed mixed vegetation, some areas still resigning to large fields with grasses and shrubs, whereas other areas showed to be more dense riparian vegetation.

- High flow streams include: De raam, and Tungelroysche beek.
- Medium to low flow streams includes Vetpeel and Essimire.
- No flow was indicated by dashed lines, and these mainly consisted of drainage ditches from agricultural lands or roads.

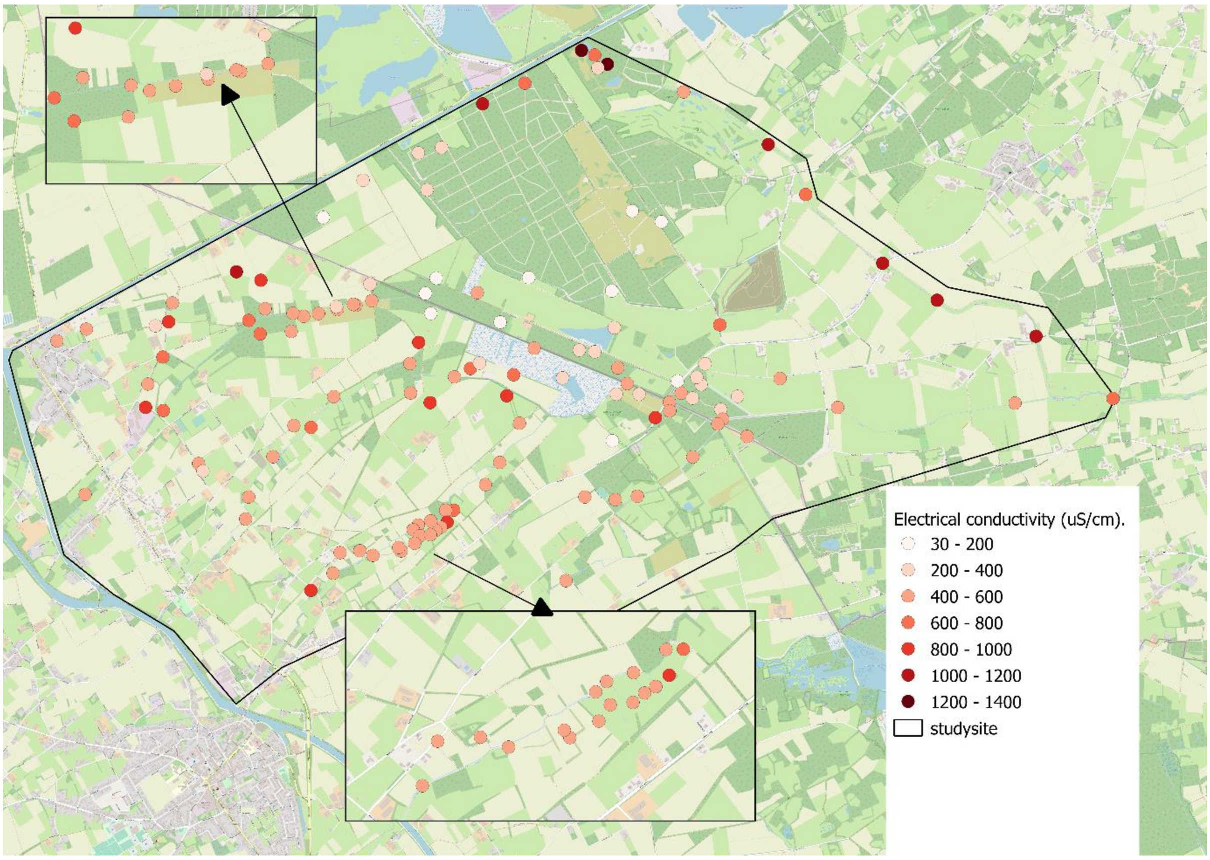

Figure 8. 120 EC measurements of surface waters.

In general, most steams flow eastwards that eventually flow into the Wiffelterbroek. Note E.C. values within the Tungelroysche beek, North of the study site, are consistently high in relationship to the rest of the study area, ranging between 1000 to 1400 (µS/cm) with the exceptions of a few sample sites. This river flows alongside the reserve, and it's one of the few rivers that do not flow through the central marsh system. A potential cause for the higher E.C. readings is the closer proximity to the industrial land use and direct imports of water from the canal.

As a consequence of the mosaic landcover types, there are a lot of agricultural/road ditches to promote drainage. Most of these ditches do not contain flowing water, most notable on the Belgium side. These ditches can have isolated waters that can have a unique chemical make-up that will not directly flow across the nature reserve. Whereas, Lower E.C. values are probably related to rainwater collected in ponds and ditches, more seen on the Netherlands side.

It is important to note, the majority of the streams flow through the central marsh system. Some of the lower E.C. values can also be observed in the marsh. Shallow ground water seepage, which perhaps influences the water chemistry as indicated with lower E.C. values within the marshes. Additionally, the vegetation and micro-organisms will influence the E.C., as they are absorbing minerals. However, to the extent, minerals absorption is not know until the chemical make-up is investigated.

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5.2. Surface Water Quality.

Table 3. The chemical make-up of Surface water quality. The Sample sites are grouped into land-use where n=42. Average values in (mg/l) unless otherwise specified. Only elements above the detection limit are represented.

Parameter	Agriculture Area	Natural Habitat	Urban Area	Rehabilitated Area	Averages	Standard Deviation	FOREGS Mean baseline (mg/l)	FOREGS Maximum baseline (mg/l), Geochemical Baseline Database FOREGS	WFD Parameters for inland waters (Phillips et al., 2018)
Number of sample sites	13	17	4	8	42	42			
Nutrients									
Phosphorus (µg/l),	24.63	30.24	66.47	7.90	27.70	33.30			80
Nitrate (mg/l)	0.16	0.04	0.38	0.07	0.11	0.20			1.1
Major ions and Dissolved metals (mg/l)									
Aluminium (Al)	0.03	0.52	0.03	0.32	0.50	0.51	0.08	3.37	
Barium (Ba)	0.03	0.03	0.03	0.03	0.01	0.01	0.04	0.44	
Calcium (Ca)	49.50	30.31	53.46	22.46	22.32	22.86	55.20	592.00	
Iron (Fe)	2.38	3.45	0.29	1.89	2.68	2.74	0.27	4.82	
Potassium (K)	8.84	5.33	8.75	5.36	3.98	4.08	3.07	182.00	
Magnesium (Mg)	8.37	4.79	9.27	4.34	3.53	3.62	11.5	230.00	
Manganese (Mn)	0.46	0.39	0.29	0.18	0.38	0.39	0.05	3.01	
Sodium (Na)	49.88	31.12	47.28	17.23	37.48	38.39	23.10	4030.00	
Sulphate (SO_4^{2-})	24.50	16.67	24.38	12.08	16.79	17.20	52.10	2420.00	
Silicon (Si)	3.70	4.97	2.54	3.93	2.66	2.72	9.10	72.00	
Strontium (Sr)	0.17	0.10	0.20	0.09	0.08	0.07	0.33	13.60	
Zinc (Zn)	0.03	0.20	0.04	0.05	0.19	0.20	0.01	0.31	
Fluoride (F^-)	0.07	0.27	0.12	0.06	0.3	0.31	0.13	1.55	
Chloride ($Cl^{-)}$)	20.25	21.78	13.34	10.92	14.46	14.80	33.30	4560.00	
Bromide (Br^-)	0.08	0.10	0.06	0.03	0.14	0.15	N/A	N/A	
Suspended sediments									
pH	7.0	6.9	7.0	7.1	6.97	0.89			
E.C. (µS/cm)	451.00	406.30	475.80	491.60	442.97	199.15			
Alkalinity (as $CaCO_3$ mg/l)	72.30	74.11	75.00	85.00	75.71	39.19			

Note: B, Ba, Be, Cd, Ni, Cr, Cu, Co, Pb, and Mo are below the detection limit.

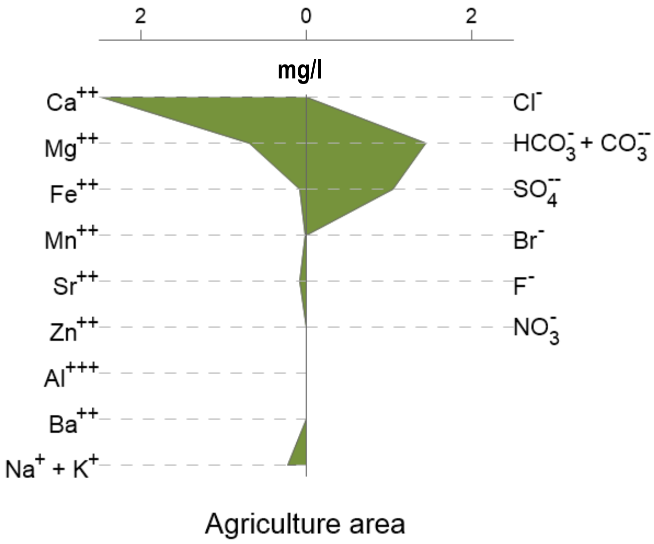


Figure 9. A legend to show elements of a stiff diagram.

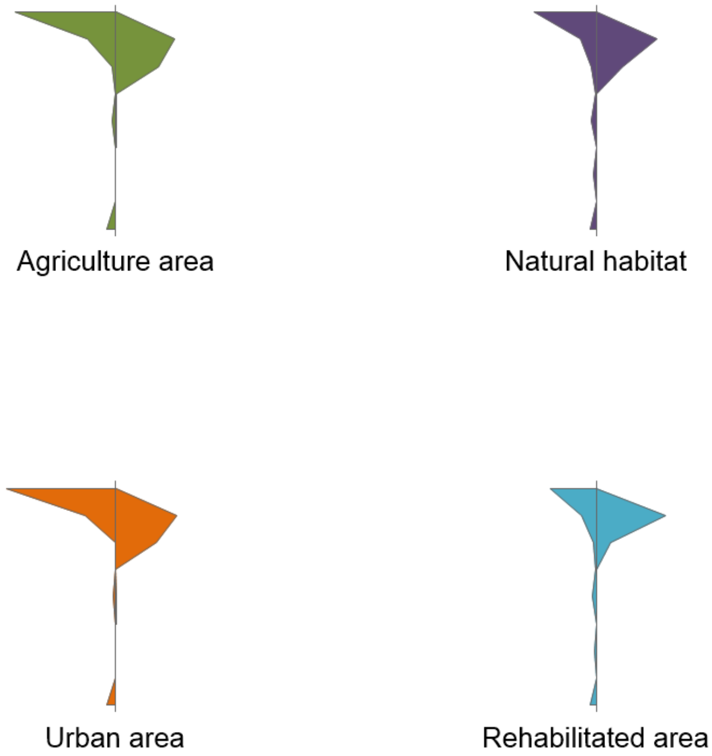


Figure 10. Stiff diagrams of the different land use types.

Note measurements are in mg/l, and only elements above the detection limit are represented. The land use type shares similar profiles across all land uses. However, the larger distinction is the larger Ca^{++} concentrations in the agricultural and Urban areas. Ca is an important determinant of water harness, and it also functions as a pH stabiliser because of its buffering qualities. Ca is naturally present in water but is also an indication of ground water seepage. The alkalised groundwater increases the alkalinity of the surface water, which is indicated by the high correlation, surface water HCO_3, and with Ca^{++} in surface water. Alkalinity distributions (Annex II) show high values on the Belgium side, sharing similarities in distribution. Distributions also show low concentrations of Alkalinity and Ca within the marsh area.

pH distribution (Annex II) shows to be constant, ranging between a pH of 6-8, with the exception of suspected rainwater ponds within Laurabossen. Two sample sites showed high pH, sample site 17 (pH of 9.1) and sample site 18 (pH of 8.2).

Further nutrient trends can be observed in distribution maps. Higher nutrient levels (Nitrates of 0.3-0.9 mg/l and Phosphate of 50-175 mg/l) are found mainly on the Belgium side. As seen in Figure 11, These levels are within the nutrient parameters.

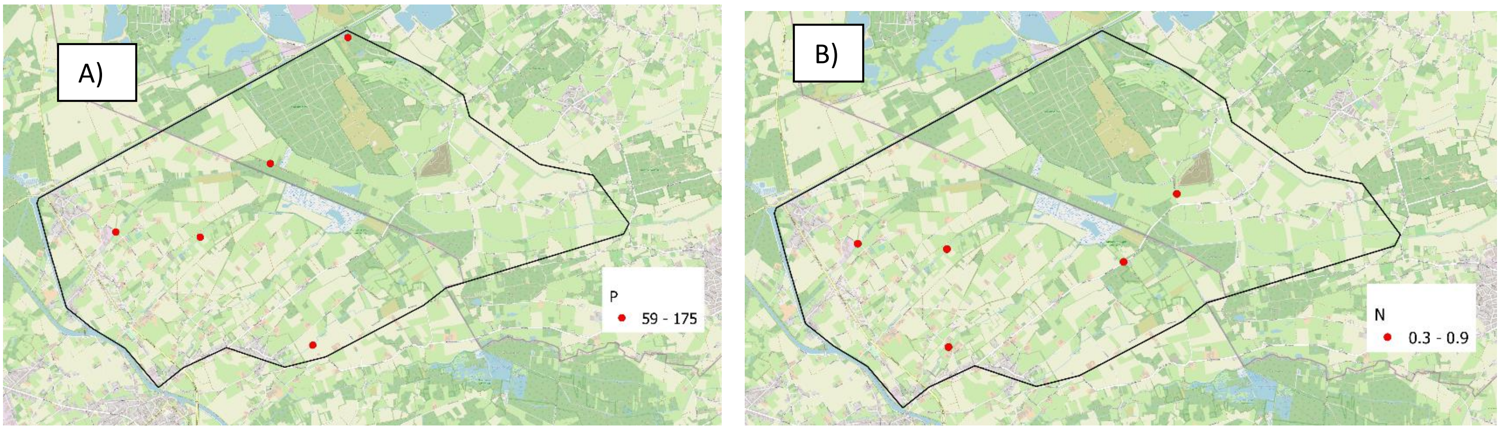


Figure 11. Nutrient distribution of the highest nitrate and phosphate levels within the 42 sample sites.

Nutrient distributions show A) Phosphate levels show an equal distribution, so do B) Nitrates. Additionally, two sample sites (5 and 6) share high nitrate and phosphate levels. These sample sites are within the urban land-use Area. The majority of higher concentrations are found on the Belgium side, within Urban and agricultural land uses. This suggests the Belgium streams have a larger influence on nutrient loading. Sample sites 5 and 6 also suggests that the agricultural area on the Belgium side has the most significant contribution to nutrient levels within Kempen-Broek.

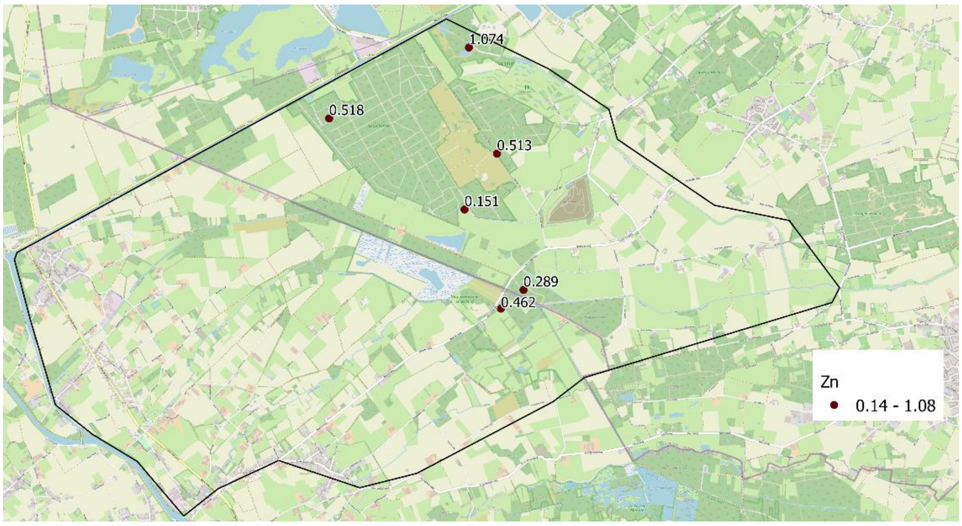


Figure 12. Zn^{++} distribution of higher concentrations. FOREGS baseline, Zn had a maximum value of 0.31 mg/l.

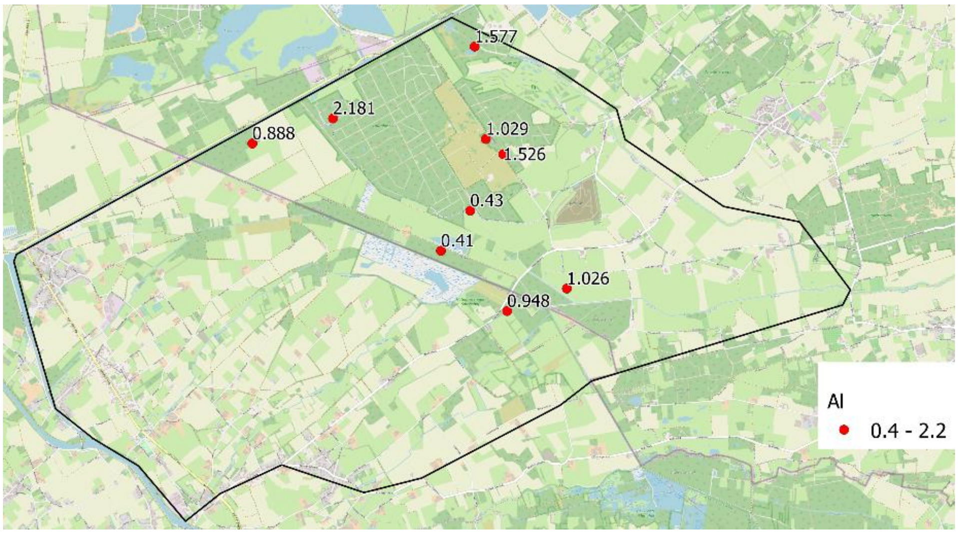


Figure 13. Al distribution of higher concentration. FOREGS baseline, Al had a maximum value of 3.37 mg/l.

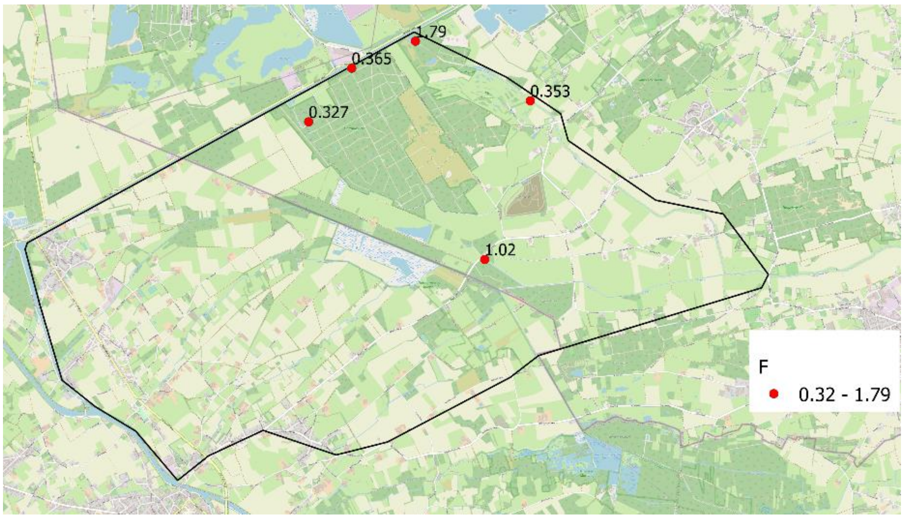


Figure 14. F^- distribution of higher concentration. FOREGS baseline, F^- has a maximum value of 0.31 mg/l.

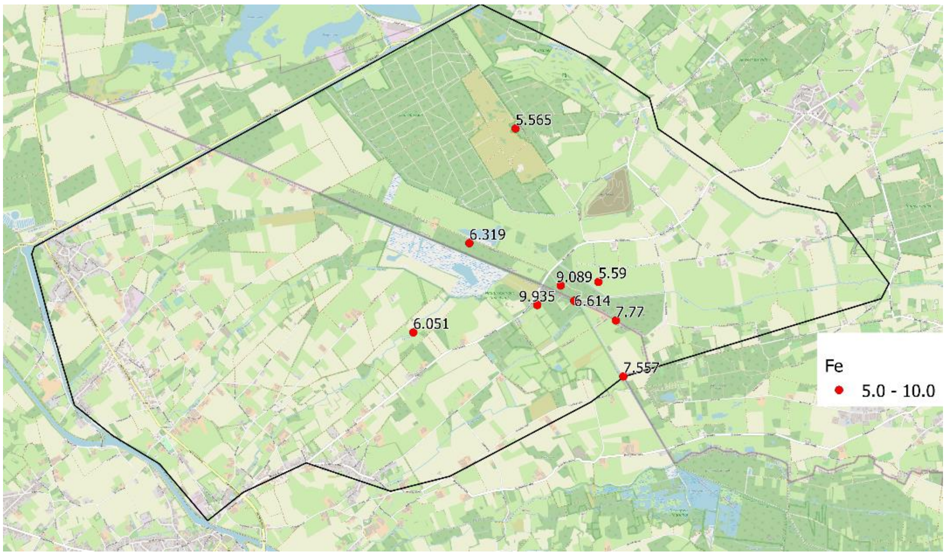


Figure 15. Fe distribution of higher concentration. FOREGS baseline, Fe^- has a maximum value of 4.82 mg/l.

Figures 12, 13, 14 and 15 represent the distribution of higher average concentration elements or elements that show interesting patterns across Kempen-Broek. All other elements distributions can be seen in Annex II.

Zn: from Figure 12, The average concentration of Zn in surface waters is 0.19 mg/l, which is under the FOREGS baseline, but a few sample sites showed higher concentrations. The water sample sites 20: 1.07 mg/l, sample site 15 of 0.52 mg/l, sample site 39 of 0.51 and sample site 32 of 0.46 mg/l. All these sample sites are over the maximum parameter. Mainly on the Netherland's side of the border, around Laurabossen.

F^-: From Figure 14, The average concentration of F- in surface waters is 0.30 mg/l, which is under the FOREGS baseline of 0.31 mg/l. Sample site 19: 1.97 mg/l. sample site 21 of 0.353, sample site 23 of 1.02 mg/l, sample site 15 of 0.327 mg/l and sample site 18 of 0.365 mg/l. These samples sites are all over the maximum parameters. In addition, F- shares a similar distribution pattern with high concentration Zn (Figure 12) around Laurabossen.

Fe: From Figure 15, The average concentration of Fe in surface waters is 2.68 mg/l, which is less than the FORGES baseline of 4.82 mg/l. Nine sample sites surpass the maximum parameter. These sites include sample site 32 of 9.93 mg/l; sample site 31 of 9.09 mg/l, sample site 35 of 7.77 mg/l, sample site 26 of 7.56 mg/l, sample site 34 of 6.61 mg/l, sample site 14 of 6.31 mg/l, sample site 11 of 6.05 mg/l, sample site 38 of 5.59 mg/l and sample site 39 of 5.56 mg/l. The majority of sample sites are within natural areas.

Al: Figure 13 shows the higher concentrations of Al found in surface waters. The average concentration of Al in surface waters across Kempen-Broek is 0.50 mg/l, with Al has a higher concentration range of values ranging between 0.4 and 2.2 mg/l. These values are under the FOREGS maximum value of 3.37 mg/l. A.L. shares a distribution pattern with Fe.

Other distribution patterns that share similarities are Br, Cl, Mn and Si (Annex II), a collection of higher concentrations of major ions found in the wetlands. Wetlands acting like a sink

5.3. Ecological Health.

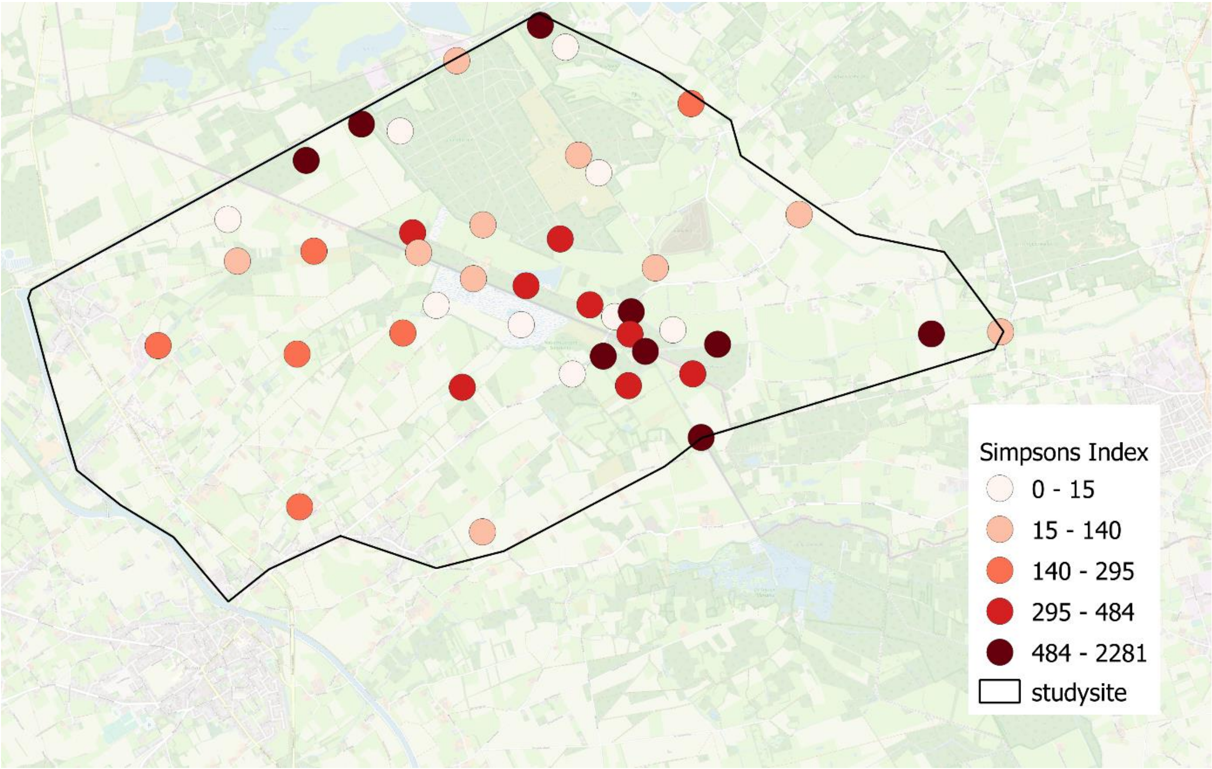
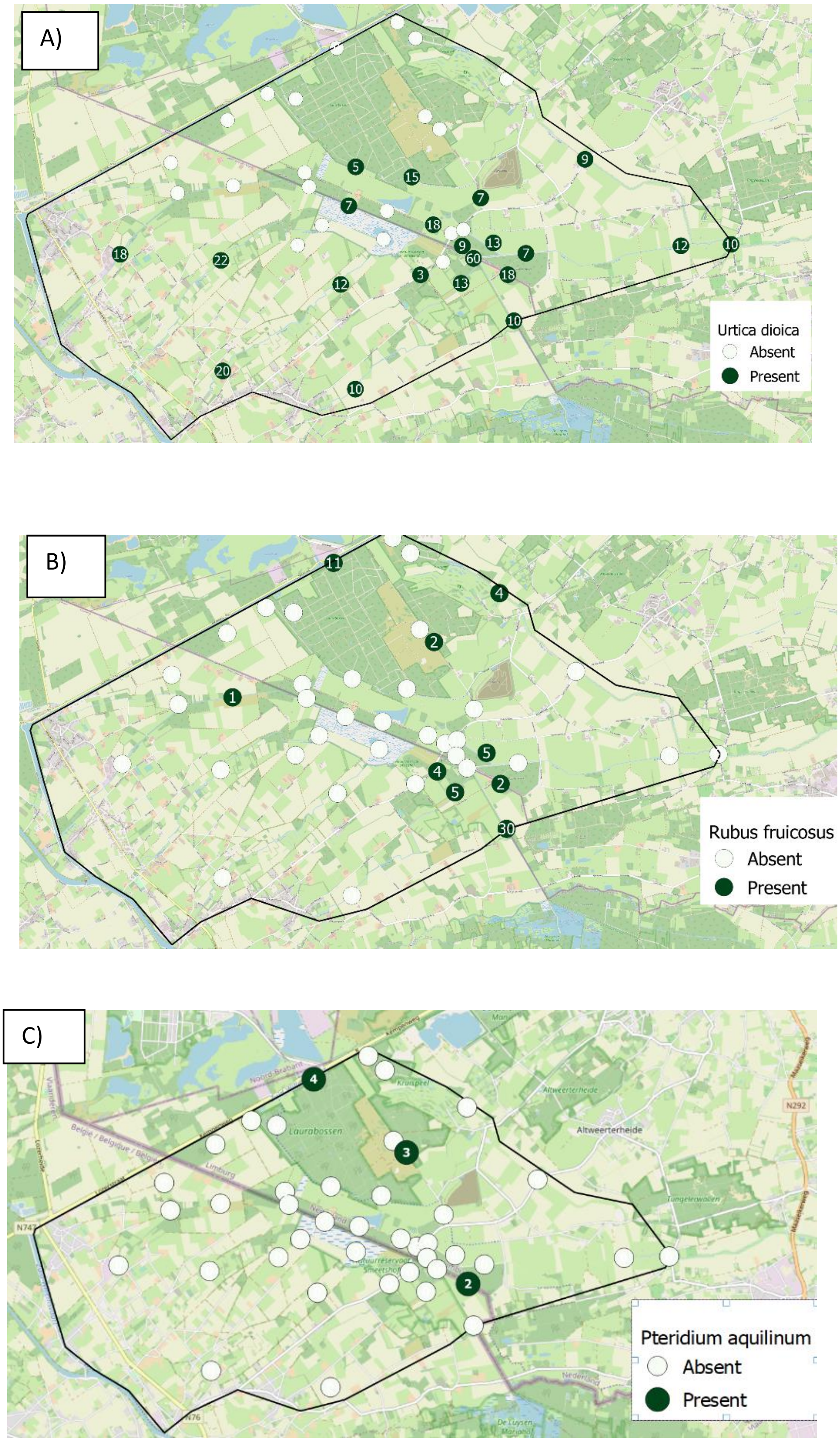


Figure 16. Biodiversity in 42 sample sites was measured with the Simpson index.

The darker the red circles, the higher Simpsons index, thus a higher degree of biodiversity, whereas the lighter red show smaller Simpson index values, thus pooper biodiversity. The legend is divided into 5 equal count quartiles following the 42 sample sites.

From figure 15, there is no clear pattern of biodiversity. However, places that showed to have the highest Simpsons index are sample sites 26, 41, 34, 32, 23, 17, 16, 33 and 19. The lowest biodiversity sample sites are 15, 20, 42, 38, 9, 10, 8, 4. Sample site 32 was an abnormality with a high Simpson's index of 2281. This site was alongside a road (main border crossing), as seen in Figure 7 (point F).


A)
Urtica dioica
Absent
Present
B)
Rubus fruicosus
Absent
Present
C)
Pteridium aquilinum
Absent
Present

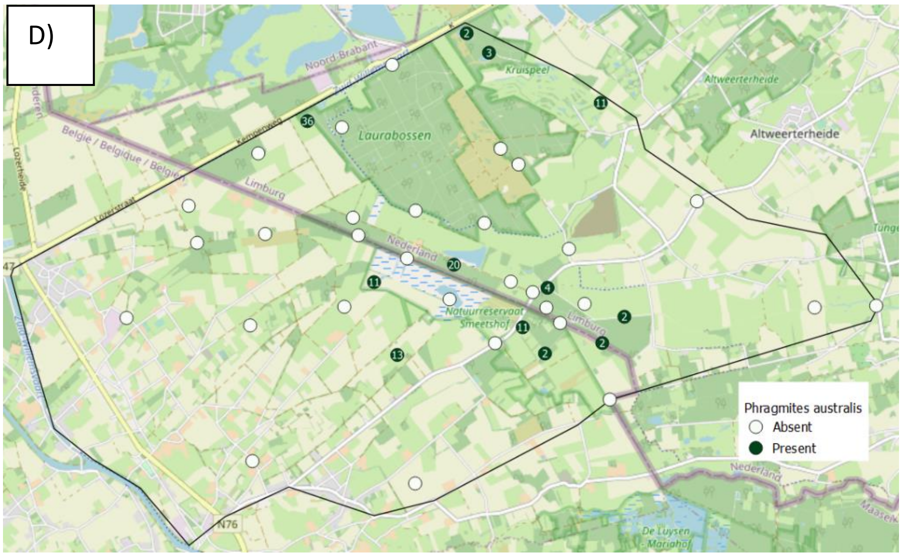


Figure 17. Four absence and presence maps indicator species for more inferior water quality, A) Urtica dioica B) Rubus fruticosus C) Pteridium aquilinum D) Phragmites australis. White dots are areas where species are not present, green dots are where species are present. The green dot also includes the number of individual species present in the sample site.

A) Urtica dioica was the most abundant across all sample sites as an indicator of higher nutrient concentrations and disturbance. This shows that the wetland has favourable conditions for Urtica dioica growth. Sample site 34 showed a very high species count with 60 species present. Notably, this sample site showed some level of disturbance on the ground (turned up ground). B) Rubus fruticosus showed to be less dominant than Urtica dioica. Additionally, their species count was also much lower. Sample site 26 showed to have the most species present, with 30 species present. Growth patterns mainly reside within natural areas. C) Pteridium aquilinum was the least common species, with only 9 species present. D) Phragmites australis shows to grow mainly within natural areas.

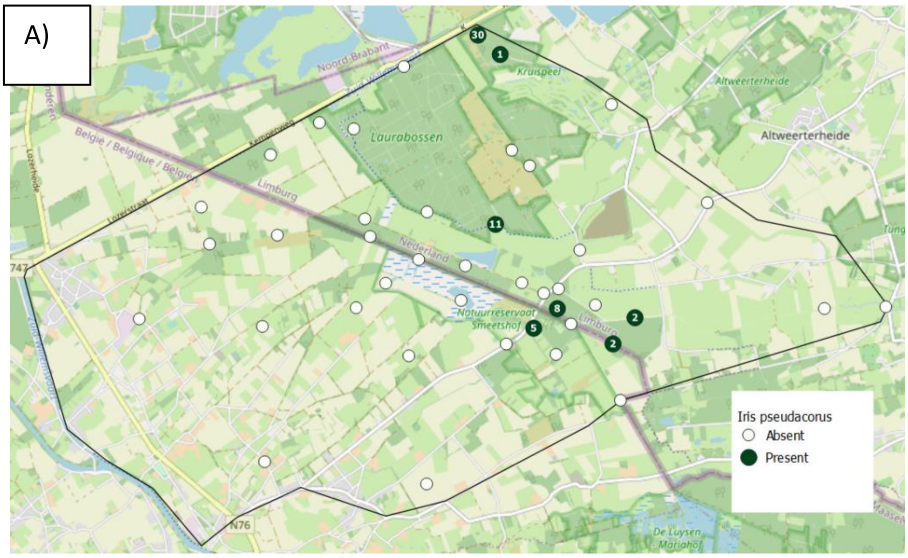


Figure 18. Absence and presence maps indicator species for Wetland Health. A) Iris pseudacorus.

A) Iris pseudacorus, growth is predominantly only found in marsh areas. The presence is an indicator of good ecological health, so surprisingly sample site 19, which showed higher E.C. values, also had the greatest number of species present with 30 individuals.

Table 4. Principal components analysis (PCA) of the five indicator species.

Components	Variance	Proportion	Cumulative proportion		
1	1.30	0.26	0.26		
2	1.18	0.24	0.50		
3	1.01	0.20	0.70		
4	0.81	0.16	0.86		
5	0.70	0.14	1.00		
Coefficients	Components				
	1	2	3	4	5
Urtica dioica	-0.14	0.73	-0.12	-0.40	0.49
Rubus fruicosus	-0.93	-0.21	0.02	-0.64	-0.39
Pteridium aquilinum	-0.63	-0.30	0.17	0.34	0.61
Phragmites australis	0.37	-0.58	-0.33	-0.46	0.45
Iris pseudacorus	0.24	0.01	0.91	-0.31	0.16

*Note: Red colours show a strong negative relationship, whereas blue colours show a strong positive relationship

To determine if the indicator species have relationships with each other, a PCA was conducted. All the components explain a reasonable amount of variance. Its evenly distributed, so it is possible to interpret most of the components. From the co-efficient, Component 1 is shown to be negatively associated with Rubus Fruicosus and Pteridium aquilimum. So, these two species are often absent or present in the same sample sites, independently from Urtica dioica, Phragmites australis and Iris pseudacorus. The second component shows that Urtica dioica has a strong component of 0.73, whereas Phragmites australis shows the opposite with a lower -0.58. This means that these species are excluding each other. In sites where there is Urtica dioica there will be no or few Phragmites australis presents (vice versa). The third component is associated with Iris pseudacorus. So, Iris pseudacorus shows to be independent of the other species. The fourth component shows that all species are shown to be negative, and relationships are unclear. The fifth component shows that Pteridium aquilinum and Phragmites australis shares a somewhat strong relationship. Iris pseudacorus is completely independent of the rest. With a bit of speculation, if the Urtica dioica is present, the Phragmites australis will not be, so using Urtica dioica as a flagship indicator, creating a t-test between sites with the indicator species Urtica dioica and sites without the presence of the species. By testing high nutrients and the presence of the indicator species, we can determine if there is a relationship between higher nutrients areas and Urtica dioica. If there are positive relations, we can assume with relative certainty that these areas are dominated by Urtica dioica because of the phytochemical make-up of surface waters. This will impact the ecological Health of Kempen-Broek as Urtica dioica are more dominate over other species (Negatively affecting biodiversity).

Table 5. t-Test: P relationship to the presence of Urtica dioica.

t-Test: Two-Sample Assuming Unequal Variances		
	P (mg/l) *values without Urtica dioica*	*P* (mg/l) *values with Urtica dioica*
Mean	2.74	2.81
Variance	9.20	14.65
Observations	21	21
Hypothesized Mean Difference	0.07	
P(T<=t) one-tail	0.45	

Table 6.t-Test: N relationship to the presence of Urtica dioica.

t-Test: Two-Sample Assuming Unequal Variances		
	N values with Urtica dioica	*N values without Urtica dioica*
Mean	175.29	46.47
Variance	67517.77	6772.16
Observations	21	21
Hypothesized Mean Difference	175.29	
P(T<=t) one-tail	0.22	

P-value of 0.45, so p>> 0.005. There is no statistically significant relationship between N measurements and the presents of *Urtica dioica.* Additionally, the same goes for P concentrations and the presence of *Urtica dioica.* P-value of 0.44, p>> 0.005. therefore, there is no relationship between Urtica dioica and Phosphate concentrations.

As Rubus Fruicosus and Pteridium aquilimum showed to be independent but dependent on each other, further T-tests were conducted to determine if there is a relationship between nutrients and Rubus Fruicosus. (Pteridium aquilinum would reflect similar findings as the PCA showed that these species shared similar characteristics in growth patterns)

Table 7.t-Test: P relationship to the presence of Rubus Fruicosus.

t-Test: Two-Sample Assuming Unequal Variances	*N without Rubus Fruicosus*	*N with Rubus Fruicosus*
Mean	124.285	61.76
Variance	49787.40	4902.47
Observations	33	9
Hypothesized Mean Difference	62	
P(T<=t) one-tail	0.49	

Table 8. t-Test: P relationship to the presence of Rubus Fruicosus.

t-Test: Two-Sample Assuming Unequal Variances	*P* (mg/l) *without Rubus Fruicosus*	*P* (mg/l) *with Rubus Fruicosus*
Mean	2.92	2.22
Variance	14.33	1.88
Observations	33	9
Hypothesized Mean Difference	0.7	
P(T<=t) one-tail	0.49	

Table 9. t-Test.: Zn relationship to the presence of Rubus Fruicosus.

t-Test: Two-Sample Assuming Unequal Variances	*Zn* (mg/l) *concentrations without Rubus Fruicosus*	*Zn* (mg/l) *concentration with Rubus Fruicosus*
Mean	0.12	0.04
Variance	0.05	0.01
Observations	33	9
Hypothesized Mean Difference	0.08	
P(T<=t) one-tail	0.49	

t-Test shows no statistical relationship to nutrients (P and N) and the Rubus Fruicosus presence; As Rubus Fruicosus was listed as an indicator that showed tolerance heavy metal accumulations, a further t-Test was conducted to investigate a relationship between Rubus Fruicosus presence and Zn concentrations. The results showed that with a p-valve of 0.08 (> 0.05), there was no statistical relationship. Pteridium aquilinum would reflect the same relationship as table 3. Showed that Pteridium aquilinum and Rubus Fruicosus shared sample sites.

Table 10. t-Test.: E.C. relationship to the presence of Phragmites australisis.

t-Test: Two-Sample Assuming Unequal Variances		
	E.C. concentration (µS/cm) *without Phragmites australisis*	*E.C. concentration* (µS/cm) *with Phragmites australisis*
Mean	411.39	532
Variance	58241.9	132812.6
Observations	31	11
P(T<=t) one-tail	0.03	

Table 11. t-Test.: Fe relationship to the presence of Phragmites australisis.

t-Test: Two-Sample Assuming Unequal Variances		
	Fe concentrations (mg/l) *without Phragmites australisis*	*Fe concentration*(mg/l) *with Phragmites australisis*
Mean	2.14	3.59
Variance	5.85	11.63
Observations	31	11
P(T<=t) one-tail	0.01	

Table 12. t-Test.: pH relationship to the presence of Phragmites australisis.

t-Test: Two-Sample Assuming Unequal Variances		
	pH without Phragmites australisis	*pH concentration with Phragmites australisis*
Mean	2.098	4.69
Variance	3.62	31.37
Observations	31	11
P(T<=t) one-tail	0.006	

Tables 10,11, and 12 show that the presence of Phragmites australisis has no statistical relationship towards E.C., Fe and pH parameters within Kempen-Broek. All p-vales show to be larger than 0.005.

6. Discussion.

6.1. Summary of findings.

The sub-questions have been specifically developed to give a broad structured view of the water quality within Kempen-Broek and its impact on ecological health; these are discussed in turn before addressing the primary question in the conclusion.

The first sub-question of this thesis was: “How is the surface water system physically structured?”

There is a general flow of water towards the east. Most of the streams flowing from Belgium are directed through the Kempen-Broek natural areas. Steams entering the wetland are influenced by urban and agricultural areas on the Belgium side, except for Tungelroysche beek. Consequently, there are many ditches and non-flowing channels dug, separating the agricultural, urban, and natural land uses. This promotes drainage; however, it has led to isolated surface waters differing in water quality. A distinction of flow speeds is noticeable, with the majority of streams diverted towards De Raam and Wijffelterbroek., older streams have lost flow intensity. Within these slower flows, reddish water colours were observed. Regarding vegetation, large marsh areas are present. Within these areas, dense vegetation is established; additionally, groundwater seepage is present. On the Belgium side there are large fields of grasses and riparian vegetation, whereas the Netherlands side host a large pine forest on Laurabossen.

The second sub-question was: “What spatial patterns in E.C. exist, and how are they related to the physical structure of the system?”

There is no clear pattern of E.C. measurements. However, there are some distinguishing sample sites of lower or higher E.C. levels. The area that reflected high E.C. measurements is in the Northwest of Kempen-Broek, particularly sample sites 18, 19, 20 and 21. Noticeably this area is also closest in relation to the industrial area. Some of the lower E.C. values can be seen in the marsh or natural areas of Laurabossen. Some isolated ponds on the Netherlands side. Measured E.C. values are low enough to suggest this was rainwater collected. E.C. values range between 30-1400 (µS/cm) for inland waters, and natural freshwater systems typically range from 40-3000 µs/cm (Palmer et al, 2004). This indicates that the surface waters in Kempen-Broek do not have many dissolved elements.

The third sub-question was: “Which potential point sources and diffuse sources of pollutants exist in the Kempen-Broek nature reserve?”

Regarding the chemical make-up of surface waters for Kempen-Broek (Table 3), generally, most land-uses show pollutants to have low or normal concentrations in comparison to the ‘FOREGS’ parameters. However, closer inspection of nutrients, heavy metal and major Ion distributions, there are some sample sites that have higher concentrations than the maximum parameters.

Regarding Zn^{++} and F^{-} distribution maps (Figure 12 and Figure 14), Most sites close to the industrial zone show higher concentrations. Re-enforcing the claim that the industrial zone influences the chemical make-up of surface waters in Kempen-Broek. The absence of Pb, Ni, and Cu suggest the Zn high concentrations are mainly from the smelter rather than road runoff or dry deposition from vehicles.

The Belgian agricultural and urban land use is suggested to have the largest impact of nutrient loading on surface waters, as sample site distributions for N and P (Figure 12) suggest that Belgium contributes to the majority of the nutrient loading. Additionally, the stiff diagram's profiles of Ca^{++} shows the largest difference between land uses. It is considered unlikely to be a consequence of urban or agricultural activity and more likely a consequence of ground water seepage. Ca++ and Alkalinity distributions (Annex II) show similar high trends on the Belgian side.

Further influence from the canals into Tungelroysche beek can be observed. Sample sites 19, 21 and 25 are consistently high in E.C concentrations. Interestingly, the majority of Na and Cl concentrations were found along or near the Tungelroysche beek. These concentrations are below FOREGS index, so there should be no need for concern.

High Fe concentrations are predominantly in the natural areas, particularly in the climate buffer constructed in 2003.

The fourth sub-question was: "What influence do these pollutant sources have on the concentration of pollutants in surface water within Kempen-Broek?"

Generally, the concentrations are within the threshold of the WFD and FOREGS. However, some sample sites show higher than the FOREGS maximum baseline. Industrial land use has been attributed to the high influence of Zn and F^- concentrations across Kempen-Broek.

- Zn: Sample site 15 of 0.518 mg/l, sample site 20 of 1.074 mg/l, sample site 32 of 0.462 mg/l and sample site 39 of 0.513.
- F^-: Sample site 15 of 0.327 mg/l, sample site 18 of 0.365 mg/l, sample site 19: 1.97 mg/l, sample site 21 of 0.353, and sample site 23 of 1.02 mg/l.

These sample sites are summarised in the figure below,

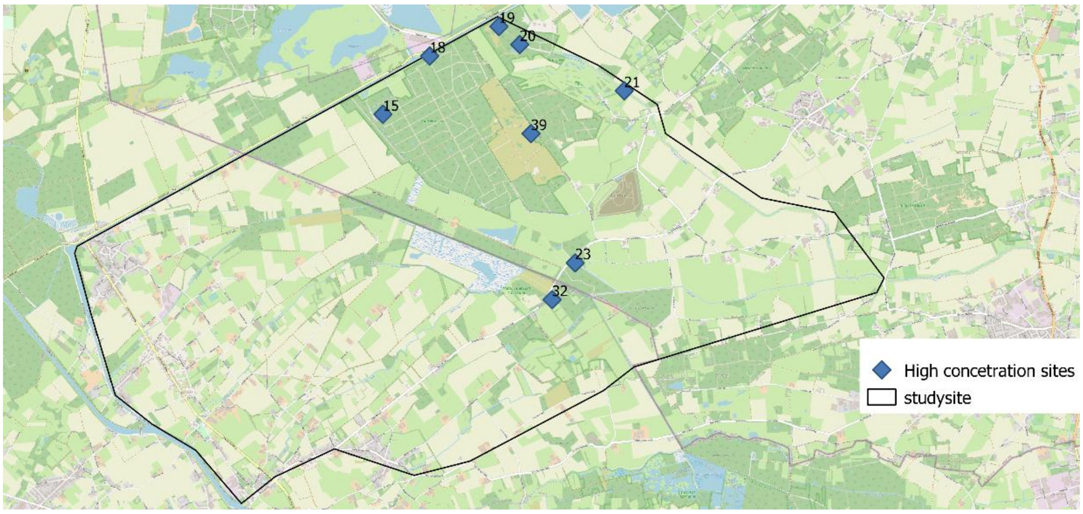


Figure 19. Sample sites reflecting concentrations over the FOREGS parameters, for Zn or F^-.

- Fe: Sample site 11 of 6.05 mg/l, sample site 14 of 6.31 mg/l, sample site 26 of 7.56 mg/l, sample site 31 of 9.09 mg/l, 32 of 9.93 mg/l, sample site 34 of 6.61 mg/l sample site 35 of 7.77 mg/l, sample site 38 of 5.59 mg/l and sample site 39 of 5.56 mg/l.

High Fe concentrations may be linked to slower stream flows resulting from land use change. Observations in sample sites with lower flow are shown to have reddish colours (particularly sample site 26). Slower flow conditions allow for a better oxidising condition to interact with soil layers. To support this, Si and Fe share similar distribution patterns (Annex II), given that Fe and Si are enriched at similar soil depths (Björnerås, et al, 2017).

Regarding nutrient levels: within the Kempen-Broek study site, nutrient levels are shown to be within the WFD parameters. The areas that show higher nutrient levels are within the urban and agricultural land areas.

The fifth sub-question was: ": What are the implications of pollutants on ecological health?"

There seem to be no limitations to growth driven by the pollutants. This is best illustrated by the fact that Iris pseudacorus was found growing in the sample sites 19 and 20, and these sites have high E.C., F and Zn. These sample sites were highlighted with higher E.C., F and Zn concentrations. Iris pseudacorus was selected due to its sensitive ecological nature, so these sample sites show no chemical limitations to growth. Furthermore, high Fe, F and Zn concentrations samples sites show high biodiversity through the Simpsons index. They are indicating that these are good conditions for vegetation growth.

Nutrient concentrations, regarding the T-test between indicator species *Urtica dioica*, t no statistical relationship is shown between N, P or E.C. concentrations and plant growth.

As Rubus fruicosus and Pteridium aquilimum showed to be independent of *Urtica dioica*, the same t-test was done, which concluded that growth is shown to have no statistical relationship between N and P. Furth more as Rubus Fruicosus is an indicator of higher heavy metal accumulations (particularly Zn), A t-test was conducted for Rubus Fruicosus and Zn concentrations, which was found to have no statistical relationship.

Overall indicating that the surface water quality in Kempen-Broek does not limit vegetation growth and can be regarded as having 'good' ecological heath. Regarding the higher concentration of F^- in the surface waters, this is very unlikely to impact drinking waters for human consumption, as the higher concentrations are isolated, and dilution will be a factor. However, flora and fauna close to these contaminated sites may be affected.

Fe can be toxic to vegetation at high concentrations, Phragmites australisis was used as an indication of high Fe concentrations. Table 11 shows that the presence of Fe has no statistical relationship in Phragmites australisis growth. Additional sample sites 14, 26, 25, 31 and 34 are shown to have high concentrations in Fe and shown to have higher Simpson's index. Suggesting that the concentration of Fe in Kempen-Broek are not high enough to have an effect on vegetation growth.

The surface waters leaving the study site (sample site 25) Annex II, showed no abnormality in its surface water profile to figure 7, a stiff diagram representing the average surface water concentrations in agricultural land use. Apart from a higher concentration of Na, assumed to be derived from the Tungelroysche beek. So, there should be no concern for Kempen-Broek's surface water affecting ecological health downstream.

The sixth sub-question was: ": To what extent has current and previous land use impacted the water quality of the Kempen-Broek nature reserve?"

The development of the climate buffer has influenced the level of nutrients concentrations from urban areas and agricultural farms on the Belgium side of the border, as flows show nutrient and E.C. concentrations are reduced. Noting most of the streams have been diverted to flow through the marsh areas. However, a collection of higher concentrations of major ions can be found in the wetlands, notably Fe distribution in Figure 15. The majority of higher Fe concentrations are found in the marsh. This is the same for Al, Br, Cl, Mn and Si.

Changes in hydrologic regime can be seen, as some rivers and ditches are diverted towards Tungelroysche beek or de Raam, this leaves other rivers with little to no flow or, in some cases, become entirely isolated. Additionally, the development of the surrounding farms has created a maze of ditches. The isolated surface waters may differ in water quality and during larger storm events may affect surrounding waters. Particularly for the Netherlands side, with many high concentrations of Zn and F.

The seventh sub-question was: “What are the pollutant mitigation suggestions for Kempen-Broek?”

There are no immediate mitigation strategies suggested. However, it would be in Natuurmonumenten and Natuurpunt best interest to continue monitoring and perhaps conduct further studies into the heavy metal and major ion concentrations in the soil. Especially for the few sample sites that exceed the FOREGS water quality baseline and are exposed to higher risk from change in climate, agricultural, industrial or urban activity.

The removal of F^- in surface waters is most commonly achieved by ion-exchange methods. These methods would be complex and expensive. Following this study, it is not immediately apparent that F^- concentrations are a risk to human or ecological health. Similarly, it may be interesting to do this study focussed on the aquatic environment. If required, cheaper methods such as clay pots can remove around 80 mg F/l (Edmunds et al, 2013).

Regarding higher Fe concentrations, they do have an impact on ecological health. If authorities would like to reduce Fe concentrations, cheaper and easier strategies are to increase stream flow, particularly at sample site 26.

Regarding Zn, according to WHO drinking water standards (1989), Zn standards in drinking water is 3.0 mg/l (with the highest Zn level found in Kempen-Broek at 1.1 mg/l) given the WHO guidelines, coupled with findings of no impact of water quality of ecological health, there is no need for further Zn mitigation strategies.

Regarding nutrients, there is no need to undergo mitigation strategies. However, to establish successful management of the wetland, it is necessary to establish the stakeholders responsible for the majority nutrient loading, in the case of Kempen-Broek: farmers and residents in Belgium. With successful policy, authorities can safeguard the sustainability of the wetland. However, the socio-economic impacts of such measures on rural and urban communities need to be considered

6.2. Limitations.

Regarding the study area for Kempen-Broek, the area of interest is extensive (roughly 60 km^2), and most of the samples were only accessible by foot in dense vegetation. As a consequence, some surface waters may have been missed within potentially contaminated sites. Either they were not easily visible, or they were behind fences and private property. Additionally, a GPS instrument (+/- 5 m) was used during the fieldwork. Following phase one, the locations were then revisited using Google maps with marked sample locations. Some locations can have a few meters difference from the actual sample location. Between google maps and the GPS, the pin may vary in accuracy. This will cause some accuracy errors in the area maps.

The time of data collection was between April to May 2021 during early spring, as ion concentrations would be influenced by the time of year with less rain, so the time of data collection results would slightly differ in the wet seasons as surface waters are influenced by low rainwater concentrations of major ions and lowering pH values (Wassen et al, 1992). Additionally, this would influence indicator species. As Rubus fruticosus had not fruited yet, so it was harder to identify, but Urtica dioica seemed to be dominant during early spring. This study does not account for seasonal variation, as nutrient levels may change in different seasons. Not only due to rain but due to farming seasons when crops need to be sprayed with more nutrients.

This study only used five species indicators. This will give a limited reflection of the site Siddig et al., (2016) suggest using more taxa a cross-taxa index as indicators, particularly insects and plants, as they will give more holistic and conclusive results. Even though in this study the use of indicator species could reflect ecological health, there are limitations in addressing environmental changes, assess the efficiency of management and provide early warning signs for ecological shifts. A more direct link may have been determined if aquatic species were selected.

Due to covid-19, data analysis for heavy metals and major ions was delayed. Utrecht university laboratories were busy and had limited space; this means samples for the ICP-OES were slow to be processed (over three weeks). This may affect the quality of results.

7. Conclusion.

In conclusion and the primary question of the study: “What is the surface water quality in Kempen-Broek, and is there concern for ecological health?”

Generally, the surface water chemical characteristics do not exceed critical nutrients levels. According to the WFD definition of good ecological Health, Kempen-Broek has good ecological status. However, some sample sites show high concentrations of heavy metals and major ions, as seen in heavy metal distributions, particularly Zn^{++}, Fe, F^- distributions.

There should be no immediate concern for authorities as these levels have little to no implications for ecological or human health. There does not seem to be an influence of water quality towards ecological health, concluding that the surface water pollutants should not hinder any ecological function. However, the concentration effect of Zn and especially F^- in plant matter local to contaminated sites is still unknown, especially in the aquatic environment, and further studies are recommended.

7.1. Recommendations.

On-going change driven by climate, agricultural, industrial, and human development is inevitable, but with timely mitigating action, the sustainability of this wetland can be guaranteed. Considering the economic and environmental value of this wetland, it is essential to the region, and so it is recommended to continue monitoring the water quality. The on-going cost of monitoring can be minimised by focussing on those sites that can be expected to show signs of change first and limiting measures to those of higher risk seen in table 13. This study can be used as a baseline and expand to show trends over time to provide an early warning with time to plan and implement appropriate mitigating action. The ideal would be to include seasonal impact, so potentially two sets of samples per annum: summer and winter one year than spring and autumn the following and so on. Limit the samples to E.C., F^-, Zn^{++}, Fe, P and N.

Table 13. List of suggested sample sites to focus on for future monitoring.

Sample Site	x-coordinate	y-coordinate	Motivation
5	167961.1	356935.5	High P, N concentrations. Influenced by Belgium Agricultural and urban land use.
19	171747.2	360115.8	High F, Zn concentrations. Proxy to Industry zone
21	173246.6	359346.1	High Zn, F concentrations. These surface waterways bypass the marsh.
23	172659.6	357285.3	High Zn, F. Sample sites are within natural land use.
32	172383.4	356844.3	High Fe concentrations, samples are within the marsh

Information on the state of ecosystems is fundamental for assessing their capacity to deliver ecosystem services. It is also important to explore possible ecological thresholds where ecosystem functions can be irreversibly lost. On-going monitoring with indicators plays an important role in informing the public and creating policies. They report on the overall status, trends of ecosystems and their value, thereby helping to identify the most urgent environmental problems to address while also helping to set up the policy priorities. In addition, to monitoring, it is key to start target setting, policy, and instrument design and evaluation, linked to the WFD so that this wetland can be benchmarked against others in the country and Europe so on-going work can be prioritised. There are no immediate mitigation strategies required; methods would be complex and expensive, and returns relatively low. Following this study, it is not immediately apparent that F- concentrations are a risk to human or ecological health. However, the impact on insect life and aquatic life close to contaminated sites is unknown and maybe an issue worth investigating.

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Investigating Water Quality and Ecological Health within Kempen-Broek, Natuurmonumenten

Assessment of the physicochemical characteristics of surface waters and the relationship to ecological health in the Kempen-Broek nature reserve.

This, is a master thesis project written by lee johnstone (l.johnstone@students.uu.nl) for the master track: Water science and management.

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Contents

Annex I

This document is Annex I, obtained from data during phase 1, 2 and data analysis

Phase 1.

Table 1.this includes all samples sites investigated in phase one (120) with an additional 4 sites investigated later during phase 2. This incorporates an overview of the location of the sample sites.

Sample number	GPS cordinates	Discription	Flow	Direction	Ec measurmetns (us/cm)	temperature(° c)	Notes
1	51°12'42.6"N 5°35'56.6"E	small stream	slow	S	266	8.6	
2	51°12'37.7"N 5°35'58.5"E	large stream	medium	W	506	9.6	
3	51°12'36.2"N 5°35'51.6"E	Marsh	no flow		401	8.8	
4	51°12'37.0"N 5°35'50.5"E	Large stream	medium	W	518	10.1	
5	51°12'35.5"N 5°35'43.0"E	large stream	medium	W	517	9.9	connected to the northern stream
6	51°12'36.3"N 5°35'42.7"E	Marsh	no flow		400	10.1	
7	51°12'34.4"N 5°35'34.7"E	small stream	slow	N	402	9.9	Very red, suspicion of high iorn
8	51°12'33.5"N 5°35'27.9"E	Agricultural ditch	slow	NW	541	9	Very red, suspicion of high iorn
9	51°12'34.5"N 5°35'23.5"E	large stream	fast	W	421	10.3	connected to an Agricultural ditch
10	51°12'29.4"N 5°35'22.7"E	Agricultural ditch	fast	E	422	9.5	
11	51°12'28.7"N 5°35'08.1"E	Marsh	no flow		625	11.6	
12	51°12'32.7"N 5°35'02.8"E	large stream	medium	E	647	11.6	connected between two larger streams

13	51°12'35.7"N 5°35'10.6"E	Marsh	no flow		503	10.2	
14	51°12'43.9"N 5°35'08.6"E	Agricultural ditch	no flow		909	9.9	
15	51°12'46.2"N 5°34'57.6"E	Agricultural ditch	no flow		1176	9.4	
16	51°12'37.3"N 5°34'28.6"E	Agricultural ditch	no flow		453	8.9	
17	51°12'32.2"N 5°34'26.9"E	Agricultural ditch	slow	E	904	11.1	Very red, suspicion of high iorn
18	51°12'30.9"N 5°34'21.1"E	Agricultural ditch	no flow		336	8.9	surrounded by horse and live stock
19	51°12'21.7"N 5°34'24.6"E	Agricultural ditch	no flow		759	9.1	near industrial waste
20	51°12'14.6"N 5°34'17.8"E	large stream	mediu m	NE	510	9.1	
21	51°12'07.9"N 5°34'16.5"E	Agricultural ditch	no flow		997	8.9	
22	51°12'06.9"N 5°34'24.5"E	Agricultural ditch	no flow		692	10	
23	51°11'52.0"N 5°34'40.4"E	Agricultural ditch	no flow		492	11.5	
24	51°11'49.9"N 5°34'42.5"E	drainage	no flow		293	8.8	large drainage area
25	51°12'02.7"N 5°35'23.5"E	large stream	fast	NE	494	8.6	agricultural land (maze)
26	51°12'02.2"N 5°35'31.2"E	stream	fast	NE	619	11.1	
27	51°12'10.9"N 5°35'41.4"E	Agricultural ditch	no flow		425	11	

28	51°12'20.1"N 5°36'15.7"E	Agricultural ditch	no flow		585	11.2	
29	51°12'26.2"N 5°36'19.8"E	Agricultural ditch	no flow		870	8.7	
30	51°12'11.9"N 5°36'16.1"E	large stream	fast	E	556	12.4	
31	51°12'09.2"N 5°36'24.9"E	Agricultural ditch	no flow		974	12	
32	51°12'16.4"N 5°36'36.2"E	stream	fast	E	587	11.2	inflow from high Ec ditch
33	51°12'18.8"N 5°36'42.8"E	Marsh	no flow		627	10.5	marsh between march and lake is connected
34	51°12'20.3"N 5°36'47.1"E	lake	no flow		368	12.1	
35	51°12'17.1"N 5°37'02.8"E	Marsh	no flow		731	11.2	
36	51°12'11.2"N 5°36'59.3"E	Agricultural ditch	no flow		936	9.4	surrounded by agricultural fields
37	51°11'59.7"N 5°37'09.4"E	Agricultural ditch	no flow		543	11.2	between road (somwhat busy) and fields
38	51°11'52.9"N 5°36'55.7"E	large stream	fast	N	550	11.3	shallow fast stream
39	51°11'46.0"N 5°36'50.0"E	large stream	slow	N	431	12.2	connected to stream '38'
40	51°11'38.8"N 5°36'35.5"E	Agricultural ditch	no flow		665	11.7	connected to stream '38'
41	51°11'38.8"N 5°36'31.8"E	stream	mediu m	N	567	10.9	
42	51°11'35.4"N 5°36'32.6"E	Agricultural ditch	no flow		891	10.2	connected to stream '38'

43	51°11'33.9"N 5°36'29.7"E	stream	mediu m	N	568	11.5	
44	51°11'34.4"N 5°36'19.4"E	Agricultural ditch	no flow		571	9.6	
45	51°11'24.6"N 5°36'04.7"E	Agricultural ditch	no flow		571	10	
46	51°11'31.7"N 5°36'20.1"E	Agricultural ditch	no flow		568	9.8	
47	51°11'29.4"N 5°36'17.9"E	Agricultural ditch	no flow		555	10.3	
48	51°11'27.3"N 5°36'11.9"E	Agricultural ditch	no flow		584	10.5	
49	51°11'25.6"N 5°35'59.0"E	stream	mediu m	NE	591	10	
50	51°11'27.3"N 5°35'53.3"E	small stream	mediu m	NE	582	10.6	
51	51°11'26.8"N 5°35'44.3"E	Agricultural ditch	no flow		593	10	
58	51°11'16.1"N 5°35'31.2"E	Agricultural ditch	no flow		807	9	near chicken farm and urban area
59	51°12'05.0"N 5°38'06.4"E	Agricultural ditch	no flow		968	10.3	marsh connected to It, near a busy raod betweetn netherlands and belguim
60	51°12'09.3"N 5°38'12.7"E	large stream	mediu m	E	516	8.3	
61	51°12'19.1"N 5°37'49.5"E	Marsh	no flow		449	9.8	large marsh system
62	51°12'19.1"N 5°37'49.5"E	boarder stream	mediu m	E	511	11.2	
63	51°12'11.7"N 5°37'59.0"E	Marsh	no flow		362	11	

64	51°12'11.7"N 5°37'48.4"E	Marsh	no flow		400	10.5	
65	51°12'24.5"N 5°37'31.9"E	Marsh	no flow		354	10	
66	51°12'24.5"N 5°37'11.9"E	boarder stream	mediu m	E	473	9.4	
67	51°13'09.2"N 5°36'23.3"E	drainage pit	no flow		243	9.6	large drainage area
68	51°13'19.7"N 5°36'19.3"E	stream	mediu m	E	270	9.5	
69	51°13'21.4"N 5°36'29.8"E	stream	mediu m	E	281	8	
70	51°13'33.9"N 5°36'48.3"E	Agricultural ditch	no flow		1092	8.6	large drange ditch along the marsh
71	51°13'39.9"N 5°37'07.4"E	Marsh	no flow		734	8.8	
72	51°13'48.8"N 5°37'32.9"E	lake/ large stream	mediu m	E	1236	12.5	
73	51°13'54.0"N 5°37'52.6"E	Marsh	no flow		636	10.1	
74	51°13'44.9"N 5°37'44.8"E	stream	mediu m	E	1224	13.3	
75	51°13'43.7"N 5°37'40.7"E	Marsh	no flow		239	10.4	
76	51°13'37.0"N 5°38'19.4"E	stream	mediu m	E	487	11.3	drainage from golf course
77	51°13'22.1"N 5°38'57.3"E	stream	mediu m		1173	12.4	between gold course and farm
78	51°12'48.6"N 5°39'49.0"E	stream	mediu m	E	1133	12.4	

79	51°12'38.2"N 5°40'13.5"E	Tungelsche beek	mediu m	E	1108	12.9	surrounded by farms
80	51°12'10.3"N 5°41'33.0"E	stream	mediu m	E	679	11.8	
81	51°12'09.1"N 5°40'49.0"E	De raam	mediu m	E	447	10.9	
82	51°12'28.1"N 5°40'58.3"E	stream	mediu m	E	1017	11.5	
83	51°12'16.1"N 5°39'03.9"E	Agricultural ditch	no flow		463	15	
84	51°12'11.0"N 5°38'43.5"E	Agricultural ditch	no flow		303	12	
86	51°12'31.2"N 5°38'35.6"E	Agricultural ditch	no flow		653	12	near rubbish dump
87	51°12'19.9"N 5°38'28.9"E	stream	mediu m	E	369	12.8	
88	51°12'14.4"N 5°38'27.0"E	Marsh	no flow		202	11.2	Very red, suspicion of high iorn
89	51°12'11.9"N 5°38'18.4"E	Marsh	no flow		421	12.3	
90	51°11'42.7"N 5°37'58.1"E	stream	mediu m	NE	590	11	
91	51°11'53.8"N 5°38'23.6"E	small stream	mediu m	E	540	8.9	
92	51°11'41.7"N 5°37'48.0"E	stream	mediu m	NE	541	13.1	
93	51°11'19.0"N 5°37'26.2"E	stream	mediu m	NE	564	11.6	
94	51°11'18.5"N 5°38'45.3"E	stream	mediu m	E	530	16.6	

95	51°11'31.7"N 5°39'03.6"E	stream	mediu m	E	291	12.2	a lot of litter in stream and very red
96	51°13'00.8"N 5°38'09.5"E	Marsh	no flow		70.4	11	
97	51°13'03.6"N 5°37'55.5"E	pond	no flow		29.5	13.3	
98	51°12'44.4"N 5°37'09.4"E	Marsh	no flow		83.3	17.2	drainage from the marsh ?
99	51°12'40.7"N 5°37'46.7"E	canal/ road graingae	no flow		117.8	16.2	large marsh system
100	51°12'30.4"N 5°37'48.3"E	lake	no flow		244	16.2	
101	51°12'44.5"N 5°36'27.8"E	Marsh	no flow		65.5	12.6	
102	51°12'39.9"N 5°36'22.7"E	Marsh	no flow		65.5	13	
103	51°12'34.6"N 5°36'25.8"E	Marsh	no flow		54.7	13.3	
104	51°12'40.4"N 5°36'46.1"E	Agricultural ditch	no flow		471	10.1	
105	51°12'23.7"N 5°37'39.3"E	Agricultural ditch	no flow		250	10.5	
106	51°12'15.3"N 5°38'16.2"E	stream	mediu m	E	188.2	13.5	stream at the head of the lake
107	51°12'10.5"N 5°38'23.4"E	Marsh	no flow		230	12.2	
108	51°12'07.2"N 5°38'35.7"E	Marsh	no flow		396	11	
109	51°12'04.5"N 5°38'36.9"E	De raam	mediu m	E	499	11.7	

110	51°11'59.6"N 5°38'47.7"E	stream	slow	E	444	10.7	
111	51°12'03.3"N 5°38'34.0"E	stream	slow	E	432	11.5	
112	51°12'07.1"N 5°38'13.0"E	Marsh	no flow		528	10.5	
113	51°11'27.3"N 5°36'11.7"E	Agricultural ditch	no flow		580	9.8	
114	51°12'25.2"N 5°33'32.1"E	stream	slow	N	432	7.8	surrounded urban area
115	51°12'30.0"N 5°33'49.6"E	Agricultural ditch/ road drainage	no flow		532	10	in urban area
116	51°13'08.0"N 5°39'14.3"E	stream	mediu m	E	720	9.3	
117	51°11'44.7"N 5°33'48.6"E	Agricultural ditch	no flow		554	11.4	
118	51°12'15.9"N 5°37'24.7"E	lake	no flow		301	8.6	
119	51°11'36.4"N 5°35'02.1"E	stream	slow	N	490	9	
120	51°11'42.6"N 5°37'34.5"E	stream	slow	N	423	8.7	

Phase 2

Table 2.42 sample sites: this sheet includes all sample investigated during phase 2. Investigations expand on alkalinity, biodiversity measured with the Simpson Index.

GPS cordinates	Sample Site	Discription	pH	EC (us/cm)	Alkalinity (as CaCO3 mg/l)	Biodiversity (Simpsons index)
51°12'44.5"N 5°36'27.8"E	1	Marsh	6.801	155.5	60	465

51°12'35.5"N 5°35'43.0"E	2	large stream	6.985	472	80	152
51°12'32.7"N 5°35'02.8"E	3	large stream	7.175	521	80	36
51°12'46.2"N 5°34'57.6"E	4	Agricultural ditch	7.508	540	140	0
51°12'07.9"N 5°34'16.5"E	5	Agricultural ditch	7.162	524	80	264
51°12'02.2"N 5°35'31.2"E	6	stream	7.343	369	80	253
51°12'09.2"N 5°36'24.9"E	7	Agricultural ditch	7.914	794	80	276
51°12'20.3"N 5°36'47.1"E	8	lake	8.029	492	60	3
51°12'15.9"N 5°37'24.7"E	9	lake	7.556	349	60	0
51°11'52.9"N 5°36'55.7"E	10	large stream	6.966	466	60	6
51°12'05.0"N 5°38'06.4"E	11	Agricultural ditch	6.864	733	120	433
51°12'10.5"N 5°38'23.4"E	12	Marsh	6.064	156	20	73
51°12'15.3"N 5°38'16.2"E	13	stream	7.271	213	40	0
51°12'24.5"N 5°37'31.9"E	14	Marsh	6.608	205	60	380
51°13'09.2"N 5°36'23.3"E	15	drainage pit	6.113	165.3	40	6
51°13'12.2"N 5°35'55.2"E	16	wetland (at entrance)	6.454	308	40	937

51°12'57.7"N 5°35'05.7"E	17	Essimire	9.72	157.7	60	1081
51°13'33.9"N 5°36'48.3"E	18	Agricultural ditch	7.364	923	100	140
51°13'48.8"N 5°37'32.9"E	19	lake/ large stream	8.175	1301	200	704
51°13'43.7"N 5°37'40.7"E	20	Marsh	4.717	336	40	13
51°13'22.1"N 5°38'57.3"E	21	stream	7.771	1090	140	204
51°12'48.6"N 5°39'49.0"E	22	stream	7.964	850	140	73
51°12'16.4"N 5°38'25.5"E	23		6.418	206	40	698
51°12'09.1"N 5°40'49.0"E	24	De raam	7.228	425	60	308
51°12'10.3"N 5°41'33.0"E	25	stream	7.311	478	80	140
51°11'31.7"N 5°39'03.6"E	26	stream	6.632	309	60	1419
51°11'19.0"N 5°37'26.2"E	27	stream	7.878	566	120	60
51°11'16.1"N 5°35'31.2"E	28	Agricultural ditch	7.096	539	80	210
51°12'40.7"N 5°37'46.7"E	29	canal/ road drainage	5.955	177.5	40	468
51°12'31.2"N 5°38'35.6"E	30	Agricultural ditch	7.017	665	100	140
51°12'14.4"N 5°38'27.0"E	31	Marsh	6.582	233	40	315

51°12'10.5"N 5°38'23.4"E	32		5.887	267	40	2281
51°12'04.5"N 5°38'36.9"E	33	De raam	6.897	449	60	527
51°12'03.3"N 5°38'34.0"E	34	stream	7.001	460	140	1830
51°11'59.6"N 5°38'47.7"E	35	stream	6.994	465	120	442
51°12'27.3"N 5°37'02.6"E	36		6.917	436	60	99
51°11'53.8"N 5°38'23.6"E	37	small stream	7.612	449	80	315
51°12'16.1"N 5°39'03.9"E	38	Agricultural ditch	6.178	197.4	40	488
51°13'03.6"N 5°37'55.5"E	39	pond	6.222	43.8	20	1
51°12'32.0"N 5°36'56.0"E	40		5.834	152	40	106
51°12'38.2"N 5°40'13.5"E	41	Tungelsche beek	7.802	889	140	20
51°13'00.8"N 5°38'09.5"E	42	Marsh	4.575	77.7	40	4

Table 3.Surface water chemical make-up: The final sheet is an overview of chemical characteristics of the surface waters found in Kempen-Broek. Only values above detection limit are present

Site number	Al (mg/l)	Ba (mg /l)	Ca (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	Na (mg/l)	S (mg/l)	Si (mg/l)	Sr (mg/l)	Zn (mg/l)	F (mg/l)	Cl (mg/l)	Br (mg/l)	pH	EC (us/cm)	P (mg/l)	N (µM)	Alkalinity (as CaCO3 mg/l)
1	0.13	0.02	16.57	3.57	11.77	3.29	0.35	1.67	1.81	1.67	0.04	0.07	0.21	15.10	0.05	8.18	1301.00	12.05	0.65	200.00
2	0.01	0.04	42.80	2.15	7.15	7.50	0.28	27.58	21.45	5.71	0.17	0.06	0.22	14.90	0.04	7.77	1090.00	1.32	195.57	140.00

3	-0.01	0.04	47.42	2.12	8.79	8.18	0.26	31.52	20.53	5.10	0.18	0.05	0.00	<0.09	<0.02	7.36	923.00	5.73	244.21	100.00
4	-0.01	0.04	58.14	0.55	4.69	7.70	0.26	33.73	15.26	4.63	0.19	0.01	0.01	<0.09	<0.02	7.80	889.00	1.03	40.06	140.00
5	0.01	0.04	42.46	0.56	13.04	7.98	0.20	30.46	19.05	4.29	0.18	0.06	0.07	11.40	0.04	7.96	850.00	17.48	663.97	140.00
6	0.00	0.01	26.76	0.15	9.91	4.35	0.11	28.32	10.34	3.04	0.11	0.05	0.01	<0.09	<0.02	7.91	794.00	7.49	301.49	80.00
7	0.01	0.01	69.06	1.77	15.31	17.10	1.20	52.06	49.43	0.57	0.23	0.02	0.06	34.60	0.05	6.86	733.00	0.44	10.68	120.00
8	0.06	0.01	32.51	0.14	13.64	6.04	0.09	42.73	14.22	2.86	0.12	0.02	0.01	<0.09	<0.02	7.02	665.00	3.08	264.97	100.00
9	0.01	0.02	32.08	0.53	5.37	4.23	0.26	22.60	16.33	3.11	0.12	0.01	0.03	12.60	0.04	7.88	566.00	0.73	19.72	120.00
10	0.02	0.05	40.50	0.98	7.17	8.90	0.41	26.76	25.62	3.82	0.17	0.05	0.03	12.50	0.04	7.51	540.00	0.73	289.38	140.00
11	0.05	0.05	57.45	6.05	4.13	7.08	0.41	74.08	16.32	5.83	0.18	0.01	0.07	64.50	0.11	7.10	539.00	1.47	1.30	80.00
12	0.07	0.01	10.80	2.13	0.99	2.13	0.11	9.87	7.96	6.70	0.04	0.00	0.01	<0.09	<0.02	7.16	524.00	1.32	0.68	80.00
13	0.10	0.02	20.66	1.72	3.30	4.14	0.10	19.03	7.88	0.80	0.08	0.02	0.05	9.83	0.02	7.18	521.00	0.29	0.45	80.00
14	0.41	0.03	28.22	6.32	3.37	4.46	0.34	20.88	8.03	10.96	0.10	0.02	0.05	5.29	0.02	8.03	492.00	2.50	0.83	60.00
15	2.18	0.02	11.57	2.37	4.36	2.32	0.21	16.99	1.68	4.45	0.03	0.52	0.33	18.50	0.04	7.31	478.00	1.76	0.77	80.00
16	0.31	0.02	23.64	1.32	5.31	4.99	0.25	24.96	12.71	0.52	0.07	0.01	0.13	21.80	0.04	6.99	472.00	0.44	0.21	80.00
17	0.89	0.02	8.81	0.36	14.23	2.57	0.04	7.77	4.61	0.23	0.02	0.02	0.03	7.58	0.02	6.97	466.00	0.73	0.52	60.00
18	0.03	0.03	110.34	0.33	4.77	11.34	0.10	51.86	65.33	3.92	0.30	0.12	0.37	43.60	0.11	6.99	465.00	1.47	0.18	120.00
19	0.04	0.03	65.24	0.03	5.94	12.04	1.75	194.79	75.08	4.52	0.26	0.03	1.79	60.70	0.77	7.00	460.00	9.11	1.20	140.00
20	1.58	0.04	25.40	3.15	10.79	5.06	0.41	17.59	24.16	3.12	0.08	1.07	0.14	16.10	0.04	6.90	449.00	0.73	0.57	60.00
21	0.09	0.03	62.58	0.77	5.91	11.18	1.30	150.32	59.53	3.47	0.24	0.03	0.35	14.10	0.18	7.61	449.00	5.14	144.21	80.00
22	0.06	0.02	57.20	0.19	5.58	10.16	0.64	100.95	42.39	2.16	0.21	0.03	0.26	11.50	0.11	6.92	436.00	2.35	156.46	60.00
23	0.14	0.01	17.20	3.03	1.77	3.07	0.16	15.48	7.65	5.51	0.06	0.03	1.02	43.20	0.43	7.23	425.00	1.91	87.46	60.00
24	0.02	0.03	37.16	0.96	7.00	6.16	0.23	25.96	17.24	3.30	0.14	0.03	0.06	18.40	0.04	7.34	369.00	1.18	41.08	80.00
25	0.00	0.03	40.16	0.97	6.85	6.77	0.30	37.58	21.25	3.26	0.15	0.03	0.15	20.80	0.08	7.56	349.00	1.32	15.64	60.00

26	0.07	0.03	14.82	7.56	15.35	3.56	0.11	24.26	12.88	6.48	0.06	0.05	0.03	4.61	0.03	4.72	336.00	1.32	68.75	40.00
27	0.02	0.02	62.98	0.27	7.55	8.01	0.11	28.29	16.51	0.98	0.19	0.00	0.06	9.14	0.03	6.63	309.00	6.02	120.18	60.00
28	0.03	0.04	51.21	0.13	8.83	10.93	0.23	29.43	19.59	2.75	0.22	0.05	0.09	21.30	0.04	6.45	308.00	0.73	584.61	40.00
29	0.43	0.02	4.80	1.20	1.45	1.10	0.04	10.87	4.08	1.22	0.02	0.15	0.05	10.80	0.03	5.89	267.00	0.44	2.16	40.00
30	0.02	0.10	81.59	0.45	12.39	13.17	0.25	18.11	28.55	0.89	0.29	0.03	0.05	14.60	<0.02	6.58	233.00	0.29	985.59	40.00
31	0.14	0.02	23.29	9.09	1.34	3.38	0.21	11.33	5.59	7.27	0.08	0.29	0.08	15.00	0.02	7.27	213.00	4.11	3.97	40.00
32	0.95	0.04	22.77	9.93	2.66	3.49	1.43	18.51	4.21	9.90	0.08	0.46	0.11	33.00	0.11	6.42	206.00	3.08	0.73	40.00
33	0.03	0.03	37.66	1.48	8.02	6.54	0.26	28.64	17.93	4.22	0.14	0.04	0.07	28.10	0.06	6.61	205.00	1.47	164.46	60.00
34	0.01	0.02	44.04	6.61	5.90	5.89	0.49	34.55	10.25	7.03	0.12	0.01	0.08	13.80	0.06	6.18	197.40	2.50	10.83	40.00
35	0.05	0.02	47.71	7.77	7.08	6.55	0.61	35.17	10.64	7.10	0.14	0.03	0.08	13.60	0.08	5.96	177.50	2.50	3.97	40.00
36	0.03	0.03	36.45	1.42	7.95	6.53	0.24	28.41	18.54	4.48	0.14	0.05	0.01	<0.09	<0.02	6.11	165.30	1.32	190.52	40.00
37	-0.01	0.02	44.88	0.98	10.36	6.27	0.19	23.40	13.03	1.12	0.14	0.03	0.04	3.72	<0.02	9.72	157.70	1.62	117.99	60.00
38	0.29	0.02	10.42	4.84	2.60	2.40	0.14	9.42	8.14	3.74	0.04	0.07	0.05	15.90	0.04	6.06	156.00	2.94	51.50	20.00
39	1.03	0.03	14.15	5.59	1.57	2.24	0.22	9.97	7.78	9.64	0.05	0.08	0.03	2.42	<0.02	6.80	155.50	0.29	0.76	60.00
40	1.03	0.03	14.19	5.56	1.55	2.23	0.22	9.96	7.86	9.59	0.05	0.08	0.07	3.73	<0.02	5.83	152.00	3.08	1.56	40.00
41	0.04	0.02	55.21	0.29	6.17	10.41	0.77	111.34	42.77	2.35	0.21	0.02	0.03	3.89	<0.02	4.58	77.70	2.20	4.61	40.00
42	1.53	0.04	1.40	0.45	1.58	0.64	0.03	7.32	1.88	1.89	0.01	0.51	0.08	8.42	0.06	6.22	43.80	0.59	1.06	20.00
Averages	0.28	0.03	36.96	2.52	6.75	6.24	0.36	35.82	18.95	4.15	0.13	0.10	0.15	18.31	0.09	6.97	442.97	2.77	114.18	75.71
Standard divation	0.50	0.01	22.32	2.68	3.98	3.53	0.38	37.48	16.79	2.66	0.08	0.19	0.30	14.46	0.14	0.89	272.52	3.33	199.15	39.19

Table 4.The chemical make-up of Surface water quality. The Sample sites are grouped into land-use where n=42. Average values in (mg/l) unless otherwise specified. Only elements above the detection limit are represented.

parameter	Agriculture area	Natural habitat	Urban area	Rehabilitated area	Averages	Standard divation	FOREGS Mean baseline (mg/l)	FOREGS Maximum baseline (µg/l), Geochemical Baseline Database FOREGS	WFD establised levels, Phillips et al., 2018

Number of sample sites	13.0	17	4	8	42	42			
Nutrients (mg/l)									
Phosphate	24.6	30.24	66.47	7.90	27.70	33.30			80
Nitrate	0.2	0.04	0.38	0.07	0.11	0.20			1.1
Major ions and Dissolved metals (mg/l)									
Aluminium (Al)	0.0	0.52	0.03	0.32	0.28	0.50	0.08	3.37	
Barium (Ba)	0.0	0.03	0.03	0.03	0.03	0.01	0.04	0.44	
Calcium (Ca)	49.5	30.31	53.46	22.46	36.96	22.32	55.20	592.00	
Iron (Fe)	2.4	3.45	0.29	1.89	2.52	2.68	0.27	4.82	
Potassium (K)	8.8	5.33	8.75	5.36	6.75	3.98	3.07	182.00	
Magnesium (Mg)	8.4	4.79	9.27	4.34	6.24	3.53	0.01	0.23	
Manganese (Mn)	0.5	0.39	0.29	0.18	0.36	0.38	0.06	3.01	
Sodium	49.9	31.12	47.28	17.23	35.82	37.48	23.10	4030.00	
Sulfate (SO4-2)	24.5	16.67	24.38	12.08	18.95	16.79	52.10	2.42	
Silicon (Si)	3.7	4.97	2.54	3.93	4.15	2.66	9.10	72.00	
Strontium (Sr)	0.2	0.10	0.20	0.09	0.13	0.08	0.33	13.60	
Zinc (Zn)	0.0	0.20	0.04	0.05	0.10	0.19	0.01	0.31	
Fluoride (F-)	0.1	0.27	0.12	0.06	0.15	0.30	0.13	1.55	
Chloride (Cl-)	20.3	21.78	13.34	10.92	18.31	14.46	33.30	4560.00	
Bromide (Br-)	0.1	0.130	0.057	0.033	0.09	0.14	N/A	N/A	
Suspended sediments									
pH	7.0	6.92	6.99	7.08	6.97	0.89			
EC	451.0	406.26	475.75	491.56	442.97	199.15			
Alkalinity	72.3	74.12	75.00	85.00	75.71	39.19			

Note: Agriculture land use: sample sites = 4 ,6, 7, 11, 21, 25, 26, 30, 33, 35, 37, and 41
Natural land use sample sites = 1, 8, 9, 14, 15, 16, 18, 20, 23, 31, 32, 34, 36, 38, 40, and 42
Rehabilitated land use sample sites = 2, 10, 13, 17, 24, 29, and 39

Urban land use sample sites= 22, 27, and 28

Table 5.Ecological health expands on indicator species. The species investigated are: Urtica dioica (nettle),Rubus fruicosus (bramble), Pteridium aquilinum(fern), Phragmites australis(common reed), Iris pseudacorus (flat reed).

wkt_geom	sample site	xcoord	ycoord	Biodiversity (as the simpsons Index)	Urtica dioica individual species count	Rubus fruicosus individual species count	Pteridium aquilinum individual species count	Phragmites australis individual species count	Iris pseudacorus individual species count
Point (170485.83102253152173944 358059.37210853211581707)	1	170485.831	358059.3721	465	0	0	0	0	0
Point (169506.35614708749926649 357874.80010017356835306)	2	169506.3561	357874.8001	151.6666667	0	1	0	0	0
Point (168746.58192465986940078 357773.46204574953299016)	3	168746.5819	357773.462	36	0	0	0	0	0
Point (168651.71382502687629312 358186.21478568471502513)	4	168651.7138	358186.2148	0	0	0	0	0	0

Point (167961.11546778399497271 356935.49115400976734236)	5	167961.1155	356935.4912	263.5	18	0	0	0	0
Point (169341.86654599790927023 356855.58380696212407202)	6	169341.8665	356855.5838	253	22	0	0	0	0
Point (170391.77467539062490687 357066.62896750774234533)	7	170391.7747	357066.629	276	0	0	0	0	0
Point (170722.79984059321577661 357341.81856267643161118)	8	170722.7998	357341.8186	3	0	0	0	11	0
Point (171566.98048277670750394 357153.04115922731580213)	9	171566.9805	357153.0412	0	0	0	0	0	0
Point (172076.24699480543495156 356666.88107274600770324)	10	172076.247	356666.8811	6	3	0	0	0	0

Point (170984.03054325308767147 356531.53808801341801882)	11	170984.0305	356531.5381	433.3333333	12	0	0	13	0
Point (171183.91830942826345563 358139.67518426169408485)	12	171183.9183	358139.6752	73.33333333	5	0	0	0	0
Point (172494.76252341590588912 357235.80958969163475558)	13	172494.7625	357235.8096	0	0	0	0	0	0
Point (171614.36104068197892047 357538.54470162023790181)	14	171614.361	357538.5447	379.5	0	0	0	20	0
Point (170359.46569038089364767 359064.84725511912256479)	15	170359.4657	359064.8473	6	0	0	0	0	0
Point (169974.24729711754480377 359133.14556089253164828)	16	169974.2473	359133.1456	937.3333333	0	0	0	36	0

Point (169426.90913749160245061 358772.03379422781290486)	17	169426.9091	358772.0338	1081	0	0	0	0	0
Point (170918.172805617476115 359762.19850181264337152)	18	170918.1728	359762.1985	140	0	11	4	0	0
Point (171747.16414085758151487 360115.81287336553214118)	19	171747.1641	360115.8129	704	0	0	0	2	30
Point (171997.15459550535888411 359900.48345158196752891)	20	171997.1546	359900.4835	13.33333333	0	0	0	3	1
Point (173246.56809621269349009 359346.08651659800671041)	21	173246.5681	359346.0865	204	0	4	0	11	0
Point (174323.39479597427998669 358254.17418595246272162)	22	174323.3948	358254.1742	73.33333333	9	0	0	0	0

Point (172659.62388168403413147 357285.28218284988543019)	23	172659.6239	357285.2822	697.5	0	0	0	4	0
Point (172248.99211603723233566 357351.44395615899702534)	24	172248.9921	357351.444	308	18	0	0	0	0
Point (176328.88760457214084454 357099.3732455016579479)	25	176328.8876	357099.3732	140	10	0	0	0	0
Point (173358.63278277881909162 356043.05171639524633065)	26	173358.6328	356043.0517	1419	10	30	0	0	0
Point (171188.63661646479158662 355100.73855868203099817)	27	171188.6366	355100.7386	60	10	0	0	0	0
Point (169371.1772766403737478 355343.54537957563297823)	28	169371.1773	355343.5454	210	20	0	0	0	0

Point (171951.91846791046555154 358003.0788022544584237)	29	171951.9185	358003.0788	468	15	0	0	0	11
Point (172896.88567275073728524 357719.5030587303917855)	30	172896.8857	357719.5031	140	7	0	0	0	0
Point (172647.63263195235049352 357063.84607287374092266)	31	172647.6326	357063.8461	315	9	0	0	0	8
Point (172383.38802060327725485 356844.27654372103279456)	32	172383.388	356844.2765	2281.333333	0	4	0	11	5
Point (175641.59158987857517786 357076.77661363134393468)	33	175641.5916	357076.7766	526.5	12	0	0	0	0
Point (172801.18280344936647452 356893.23477121035102755)	34	172801.1828	356893.2348	1830	60	0	0	0	0

Point (173272.60876857180846855 356672.15844242338789627)	35	173272.6088	356672.1584	441.6	18	2	2	2	2
Point (171090.8195957524003461 357607.46447989443549886)	36	171090.8196	357607.4645	99	7	0	0	0	0
Point (172633.983727819257183 356552.91012210299959406)	37	172633.9837	356552.9101	315	13	5	0	2	0
Point (173518.46863381084403954 356965.789472128264606)	38	173518.4686	356965.7895	487.5	7	0	0	2	2
Point (173073.76036761637078598 357107.1280657445313409)	38	173073.7604	357107.1281	1	13	5	0	0	0
Point (172130.85159953110269271 358832.49432630173396319)	39	172130.8516	358832.4943	105.6	0	0	0	0	0

Point (170545.77918271190719679 357863.45252811803948134)	40	170545.7792	357863.4525	20	0	0	0	0	0
Point (172331.46143912951811217 358658.1507424729061313)	42	172331.4614	358658.1507	4	0	2	3	0	0

T-tests

Table 6. T-test to address if there is a statistical relationship between Urtica dioica and N

t-Test: Two-Sample Assuming Unequal Variances		
	N values with Urtica dioica	*N values without Urtica dioica*
Mean	175.2956418	46.47523443
Variance	67517.77289	6772.164299
Observations	21	21
Hypothesized Mean Difference	175.29	
df	24	
t Stat	-0.781292252	
P(T<=t) one-tail	0.221134992	
t Critical one-tail	1.71088208	
P(T<=t) two-tail	0.442269984	
t Critical two-tail	2.063898562	

Table 7. T-test to address if there is a statistical relationship between Urtica dioica and P

t-Test: Two-Sample Assuming Unequal Variances		
	P values without Urtica dioica	*P values with Urtica dioica*
Mean	2.735138095	2.805090476
Variance	9.200415343	14.65234967
Observations	21	21
Hypothesized Mean Difference	0.07	
df	38	
t Stat	-0.131316886	
P(T<=t) one-tail	0.448108714	
t Critical one-tail	1.68595446	
P(T<=t) two-tail	0.896217428	
t Critical two-tail	2.024394164	

Table 8.The T-test to address if there is a statistical relationship between Rubus Fruicosus and EC.

t-Test: Two-Sample Assuming Unequal Variances		
	EC without Rubus Fruicosus	*EC with Rubus Fruicosus*
Mean	434.9939394	521.55
Variance	71822.50996	101465.7914
Observations	33	8
Hypothesized Mean Difference	86	
df	10	
t Stat	-1.415551676	
P(T<=t) one-tail	0.093644086	
t Critical one-tail	1.812461123	
P(T<=t) two-tail	0.187288173	
t Critical two-tail	2.228138852	

Table 9. The T-test to address if there is a statistical relationship between Rubus Fruicosus and Nutreiants

t-Test: Two-Sample Assuming Unequal Variances		
	N without Rubus Fruicosus	*N with Rubus Fruicosus*
Mean	124.2791895	61.77501622
Variance	49787.40079	4902.472968
Observations	33	9
Hypothesized Mean Difference	62	
df	39	
t Stat	0.011126026	
P(T<=t) one-tail	0.49558981	
t Critical one-tail	1.684875122	
P(T<=t) two-tail	0.99117962	
t Critical two-tail	2.02269092	

t-Test: Two-Sample Assuming Unequal Variances		
	P without Rubus Fruicosus	P with Rubus Fruicosus
Mean	2.920193939	2.219822222
Variance	14.3298828	1.885218707
Observations	33	9
Hypothesized Mean Difference	0.7	
df	36	
t Stat	0.000463306	
P(T<=t) one-tail	0.499816446	
t Critical one-tail	1.688297714	
P(T<=t) two-tail	0.999632893	
t Critical two-tail	2.028094001	

Table 10. The T-test to address if there is a statistical relationship between Rubus Fruicosus and Zn.

t-Test: Two-Sample Assuming Unequal Variances		
	Zn concentrations without Rubus Fruicosus	*Zn concentration with Rubus Fruicosus*
Mean	0.12036039	0.040289092
Variance	0.049330176	0.000589476
Observations	33	9
Hypothesized Mean Difference	0.08	
df	35	
t Stat	0.001804957	
P(T<=t) one-tail	0.499285051	
t Critical one-tail	1.689572458	
P(T<=t) two-tail	0.998570103	
t Critical two-tail	2.030107928	

Table 11.The T-test to address if there is a statistical relationship between Phragmites australisis presence and EC

t-Test: Two-Sample Assuming Unequal Variances		
	EC concentration without Phragmites australisis	*EC ceoncentration with Phragmites australisis*
Mean	411.383871	532
Variance	58241.90006	132812.6
Observations	31	11
Hypothesized Mean Difference	121	
df	13	
t Stat	-2.045491458	
P(T<=t) one-tail	0.03079762	

t Critical one-tail	1.770933396
P(T<=t) two-tail	0.06159524
t Critical two-tail	2.160368656

Table 12. The T-test to address if there is a statistical relationship between Phragmites australisis presence and Fe

t-Test: Two-Sample Assuming Unequal Variances		
	Fe concentration without Phragmites australisis	*Fe concentration with Phragmites australisis*
Mean	2.140872581	3.588901001
Variance	5.846009122	11.62997371
Observations	31	11
Hypothesized Mean Difference	1.45	
df	14	
t Stat	-2.596387678	
P(T<=t) one-tail	0.010562658	
t Critical one-tail	1.761310136	
P(T<=t) two-tail	0.021125315	
t Critical two-tail	2.144786688	

Table 13. The T-test to address if there is a statistical relationship between Phragmites australisis presence pH.

t-Test: Two-Sample Assuming Unequal Variances		
	pH without Phragmites australisis	*pH concentration with Phragmites australisis*
Mean	2.089770968	4.687445455
Variance	3.620640888	31.37008288
Observations	31	11
Hypothesized Mean Difference	2.6	
df	11	
t Stat	-3.016697271	

P(T<=t) one-tail	0.005862352
t Critical one-tail	1.795884819
P(T<=t) two-tail	0.011724704
t Critical two-tail	2.20098516

Annex II

Annex II, obtained in the data from Annex I (excluding the FOREGS parameters). The assessment of the physicochemical characteristics of surface waters and the relationship to ecological health in the Kempen-Broek nature reserve.

1. FOREGS Baseline parameters.

Table 14: Baseline parameters of Europe, Geochemical Baseline Database FOREGS (http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php) that provides water chemistry in surface waters in unimpacted areas across Europe.

Parameter	unit	count	minimum	median	Mean	standard deviation	percentile 90	maximum
Al	µg/l	807	0.7	17.7	75.5	180	209	3370
As	µg/l	807	<0.01	0.63	1.24	2.25	2.45	27.3
B	µg/l	807	0.1	15.6	45.2	137	94.5	3030
Ba	µg/l	807	0.2	24.9	35.4	39.6	76.8	436
Be	µg/l	807	<0.005	0.009	0.028	0.109	0.056	2.72
Bi	µg/l	807	<0.002	0.002	0.004	0.01	0.007	0.16
DOC	mg/l	803	<0.5	4.99	7.76	8.48	17	71.9
Ca	mg/l	808	0.226	40.2	55.2	61.7	119	592
Cd	µg/l	807	<0.002	0.01	0.026	0.081	0.053	1.25
Ce	µg/l	807	<0.002	0.055	0.401	1.59	0.936	36
Cl	mg/l	808	0.14	8.81	33.3	191	43.6	4560
Co	µg/l	807	0.01	0.16	0.333	1.01	0.582	15.7

Cr	µg/l	806	<0.01	0.38	0.792	2.47	1.4	43
Cs	µg/l	802	<0.002	0.006	0.07	0.903	0.052	24.3
Cu	µg/l	808	0.08	0.88	1.23	1.31	2.45	14.6
Dy	µg/l	807	<0.002	0.008	0.036	0.141	0.084	3.43
EC	mS/m	768	<0.5	30	44.6	83.9	90	1710
Er	µg/l	807	<0.002	0.006	0.023	0.086	0.05	2.08
Eu	µg/l	807	<0.002	0.005	0.01	0.034	0.021	0.87
F-	mg/l	808	<0.05	0.1	0.134	0.144	0.28	1.55
Fe	µg/l	807	<1.0	67	268	531	744	4820
Ga	µg/l	807	<0.002	0.011	0.017	0.02	0.036	0.17
Gd	µg/l	807	<0.002	0.01	0.045	0.177	0.11	4.32
Ge	µg/l	807	<0.005	0.009	0.012	0.023	0.022	0.44
HCO_3^-	mg/L	808	<1.0	126	154	147	339	1800
Hf	µg/l	807	<0.002	0.004	0.006	0.009	0.015	0.12
Ho	µg/l	807	<0.002	0.002	0.008	0.029	0.017	0.71
I	µg/l	807	<0.01	0.33	1.83	7.88	2.83	104
K	mg/l	808	<0.01	1.6	3.07	7.35	6.83	182
La	µg/l	807	<0.002	0.034	0.221	0.772	0.502	16
Li	µg/l	807	<0.005	2.1	6.67	24.4	11	356
Lu	µg/l	807	<0.002	<0.002			0.008	0.3
Mg	mg/l	808	0.048	6.02	11.5	19.3	27.3	230
Mn	µg/l	804	<0.05	15.9	56.7	155	132	3010
Mo	µg/l	807	<0.002	0.22	0.495	1.02	1.07	16
Na	mg/l	808	0.231	6.58	23.1	158	25.7	4030
Nb	µg/l	807	<0.002	0.004	0.009	0.017	0.02	0.34
Nd	µg/l	807	<0.005	0.04	0.228	0.861	0.53	19.8
Ni	µg/l	807	0.03	1.91	2.43	2.49	4.72	24.6
NO_3^-	mg/l	808	<0.04	2.82	9.07	13.5	28.2	107
Pb	µg/l	807	<0.005	0.093	0.224	0.588	0.43	10.6

pH	-	800	2.2	7.7	7.5	0.8	8.3	9.8
Pr	µg/l	807	<0.002	0.009	0.057	0.212	0.13	4.7
Rb	µg/l	807	0.09	1.32	2.41	6.61	4.25	112
Sb	µg/l	807	<0.002	0.07	0.109	0.177	0.21	2.91
Se	µg/l	807	<0.01	0.34	0.566	0.974	1.1	15
SiO_2	mg/l	808	0.1	8.03	9.1	6.6	16	72
Sm	µg/l	807	<0.002	0.009	0.044	0.164	0.11	3.82
SO_4^{2-}	mg/l	808	<0.3	16.1	52.1	153	103	2420
Sr	mg/l	808	0.001	0.11	0.327	1.01	0.494	13.6
Tb	µg/l	807	<0.002	0.002	0.007	0.024	0.015	0.59
Te	µg/l	807	<0.005	<0.005			0.011	0.11
Th	µg/l	807	<0.002	0.009	0.025	0.039	0.066	0.37
Ti	µg/l	807	<0.01	0.9	1.48	1.94	3	16.8
Tl	µg/l	807	<0.002	0.005	0.009	0.016	0.016	0.22
Tm	µg/l	807	<0.002	<0.002			0.007	0.28
U	µg/l	807	<0.002	0.32	0.889	1.69	2.43	21.4
V	µg/l	807	<0.05	0.46	0.829	1.46	1.66	19.5
W	µg/l	807	<0.002	0.007	0.034	0.2	0.035	3.47
Y	µg/l	807	0.003	0.064	0.247	1.05	0.522	26.6
Yb	µg/l	807	<0.002	0.006	0.022	0.076	0.048	1.79
Zn	µg/l	807	0.09	2.68	6.01	16.7	10.2	310
Zr	µg/l	807	<0.002	0.053	0.125	0.201	0.35	2.41

2. Major ion and heavy metal distributions.

Only elements above the detection limit are represented. All units are mg/l.

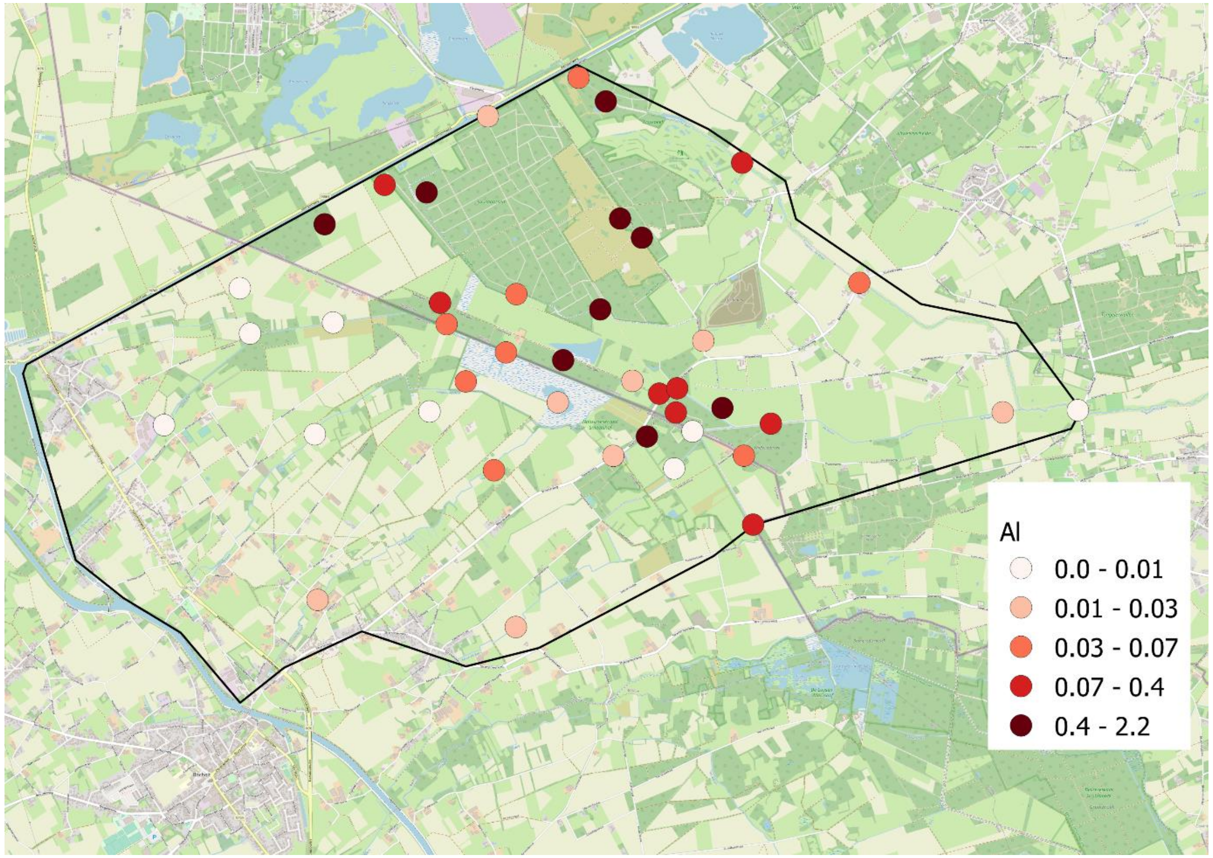

Figure 1. Al distribution.

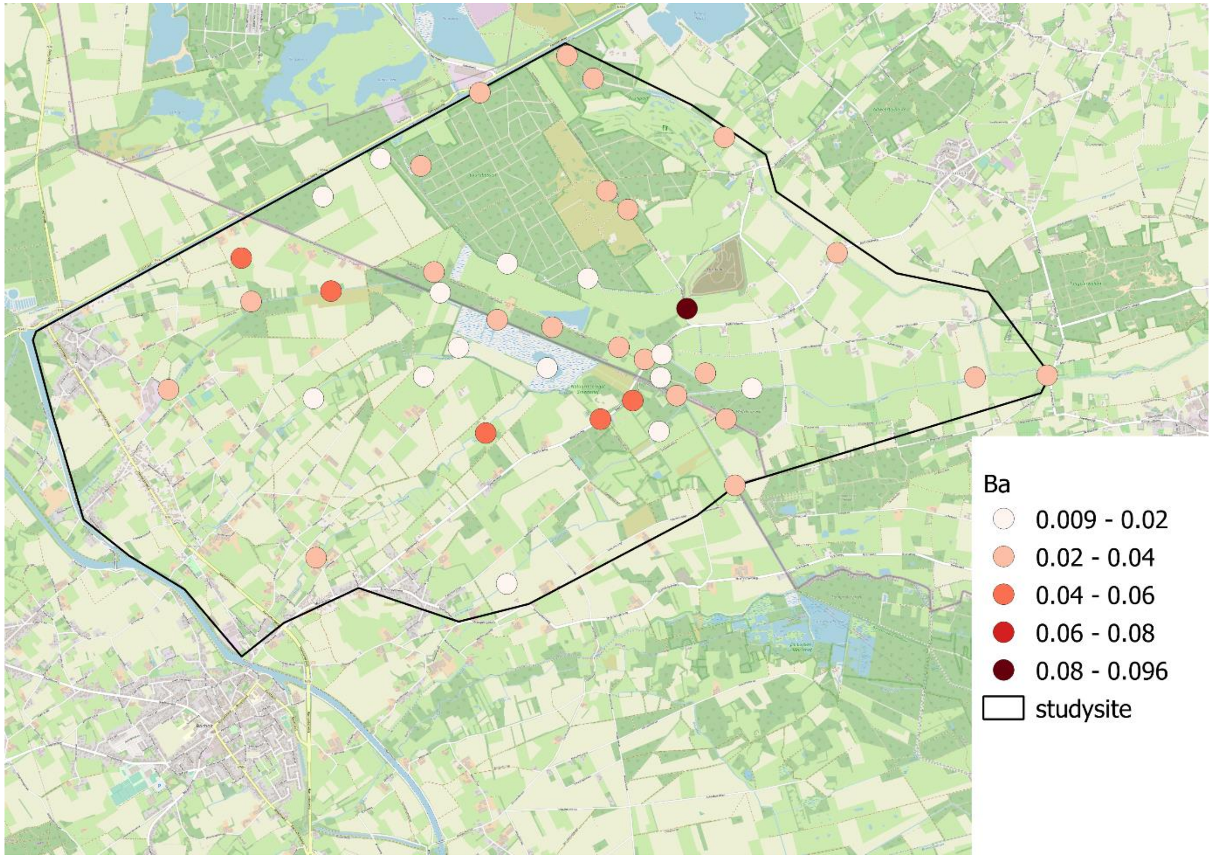

Figure 2. Ba distribution.

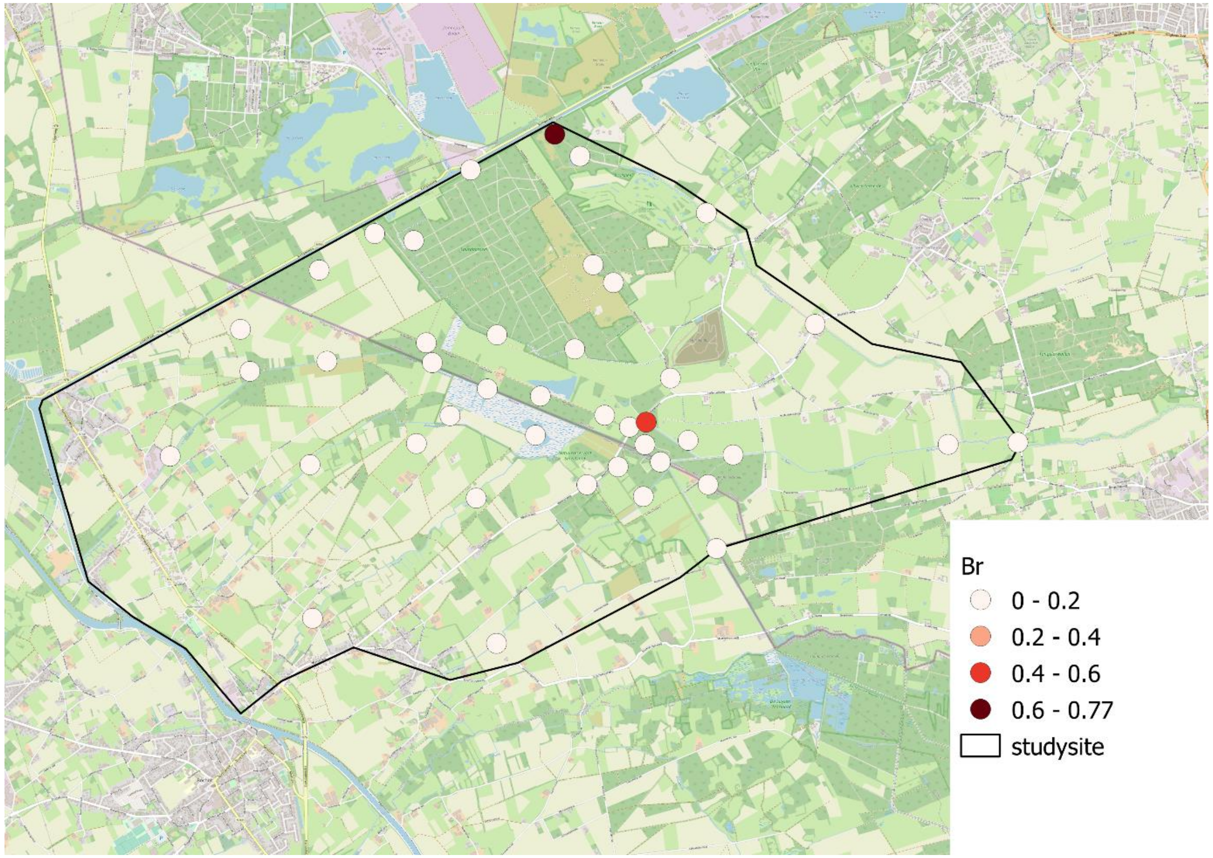

Figure 3. Br distribution.

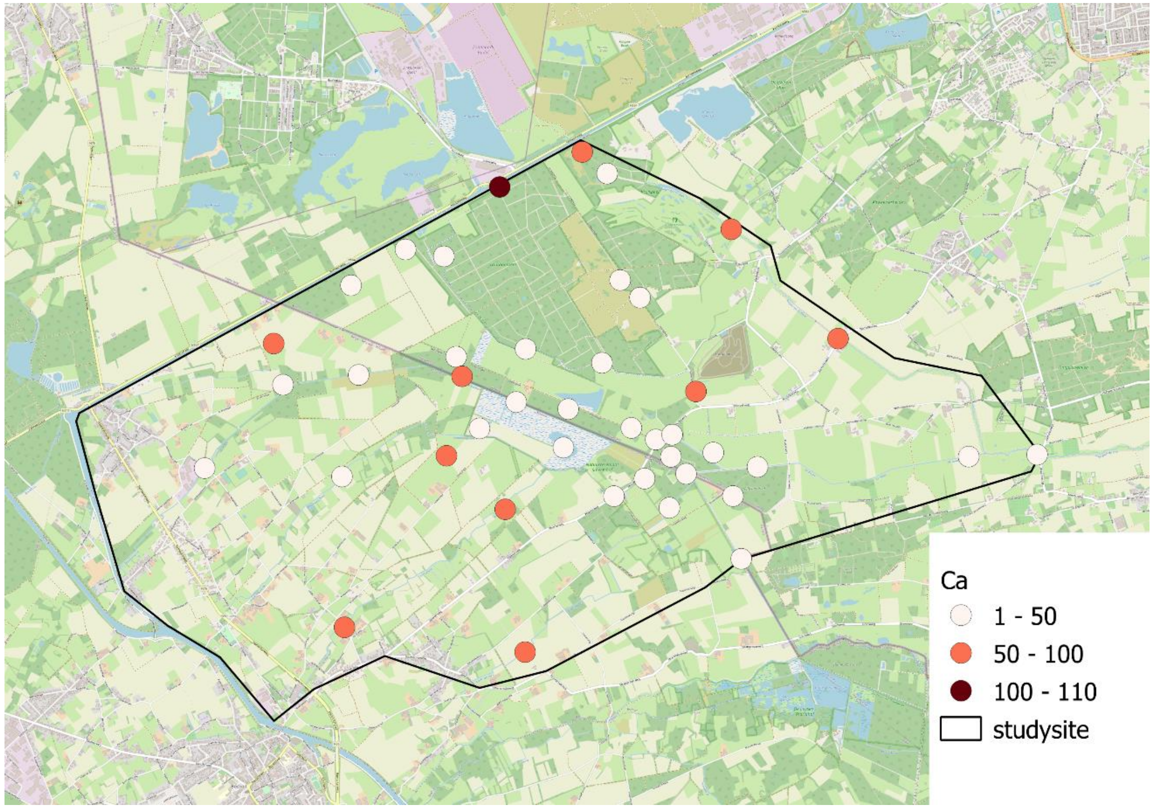

Figure 4. Ca distribution.

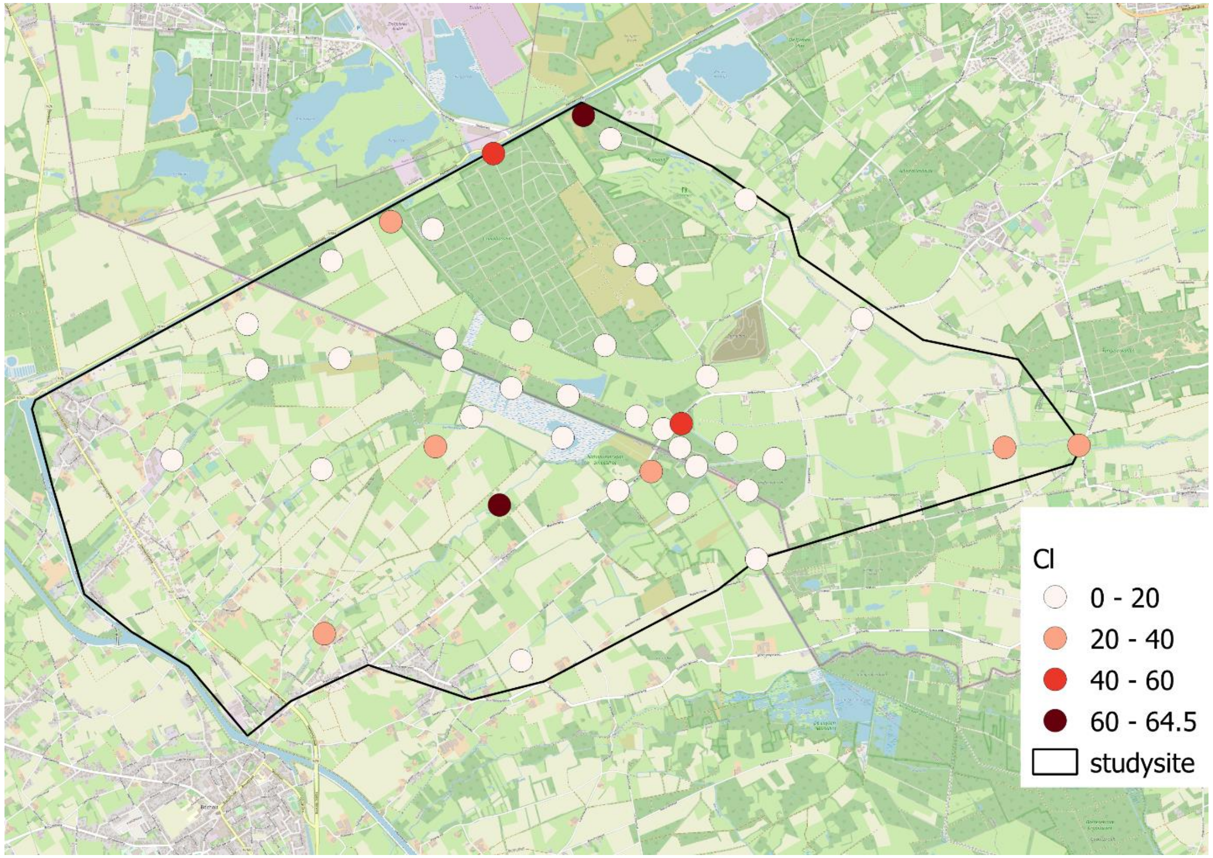

Figure 5. Cl distribution.

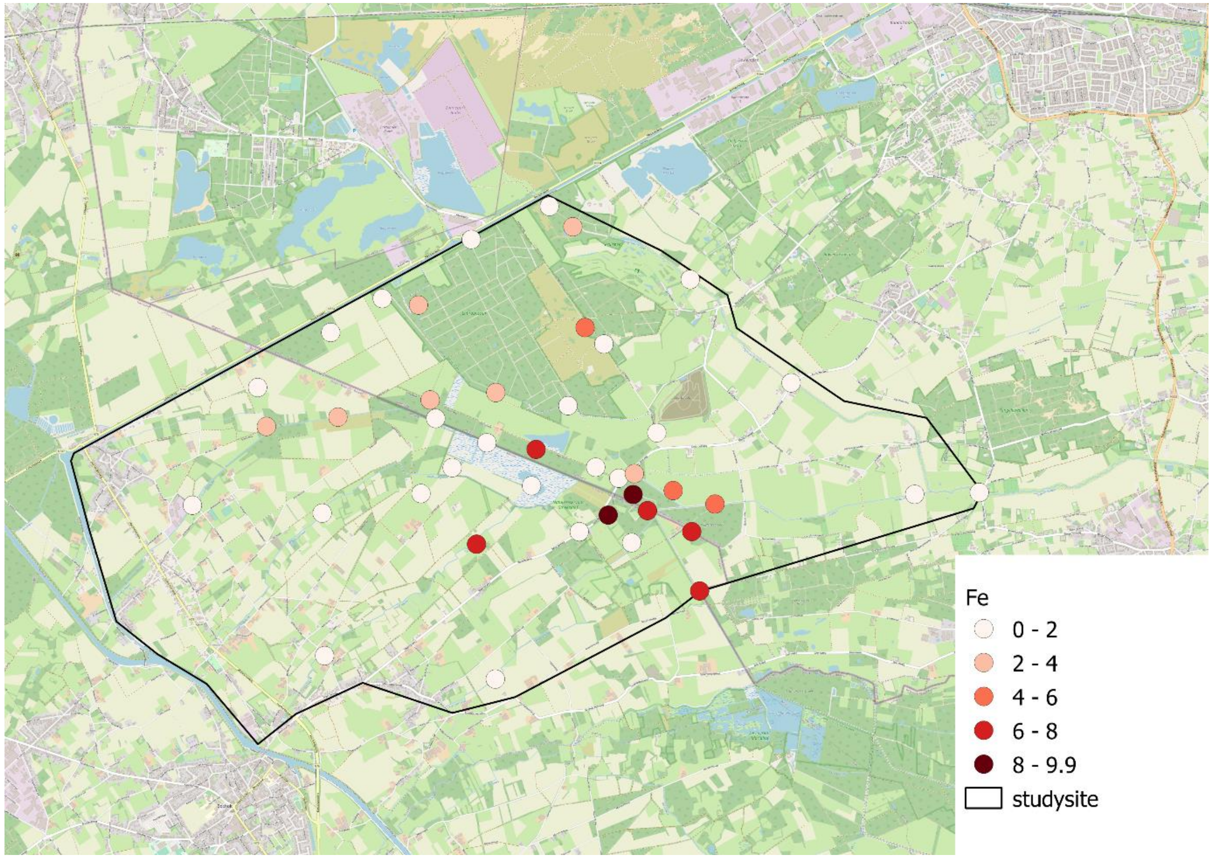

Figure 6. Fe distribution.

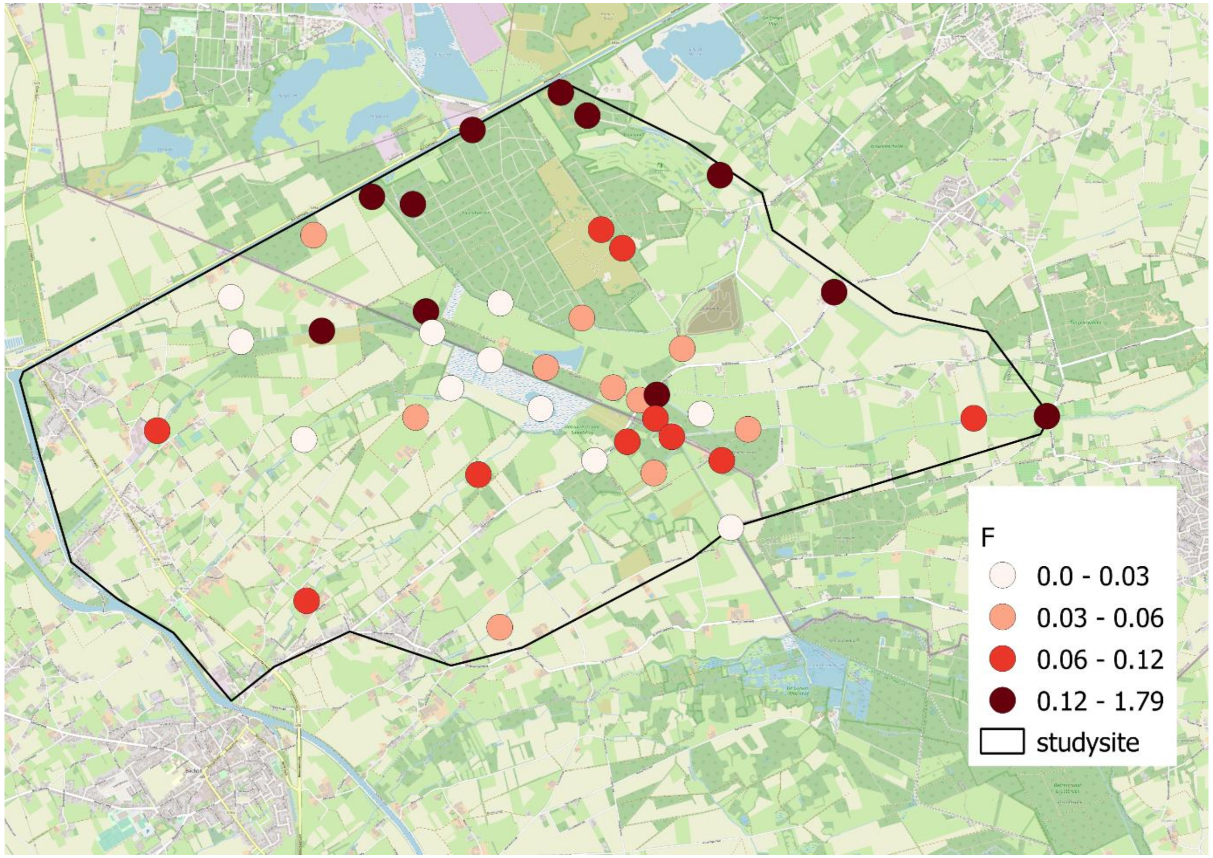

Figure 7.F distribution.

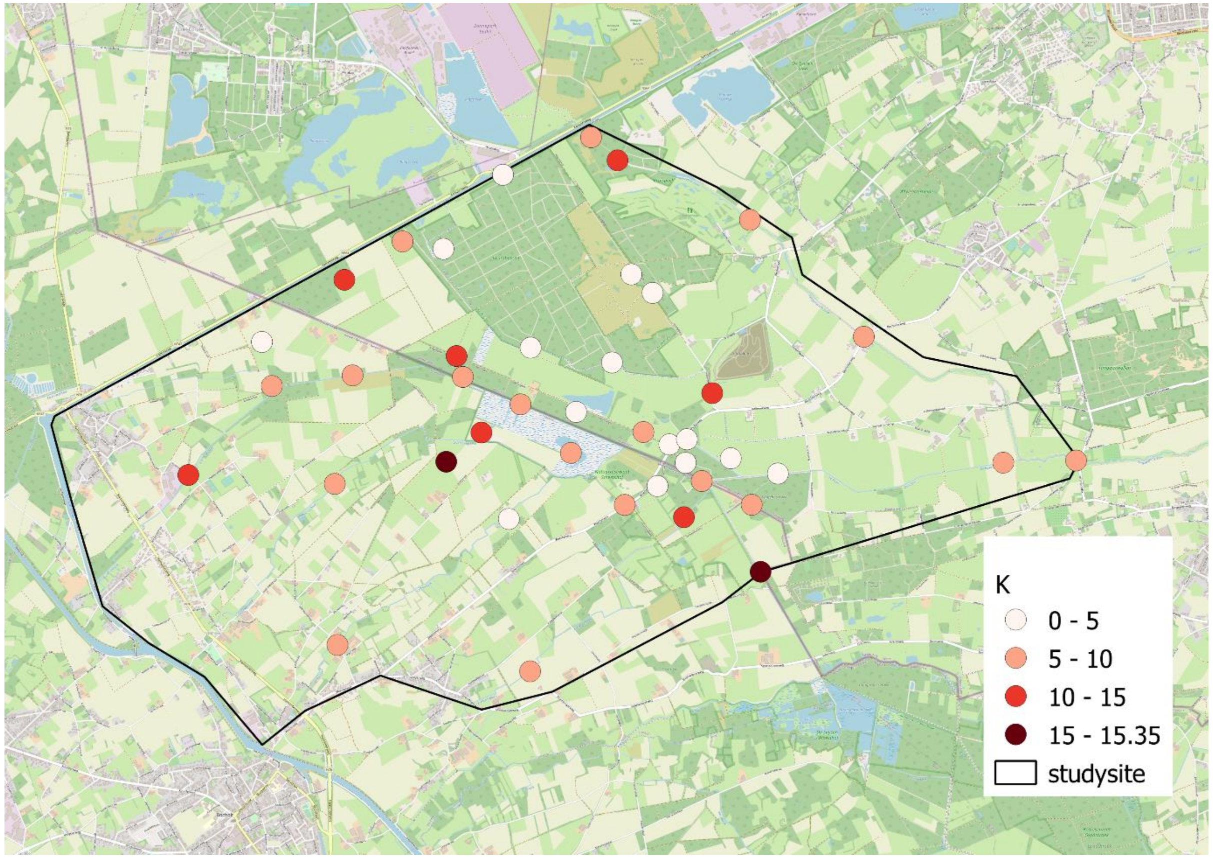

Figure 8. K distribution

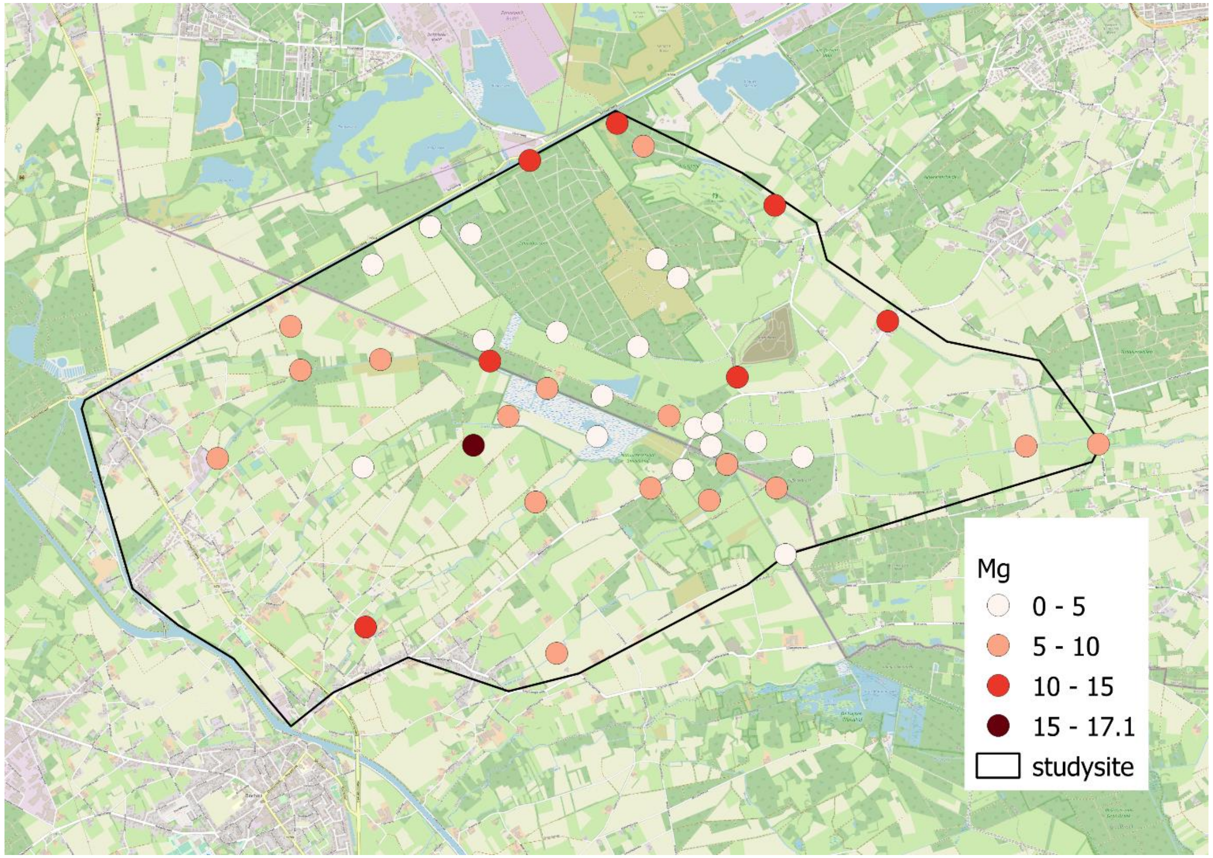

Figure 9. Mg distribution.

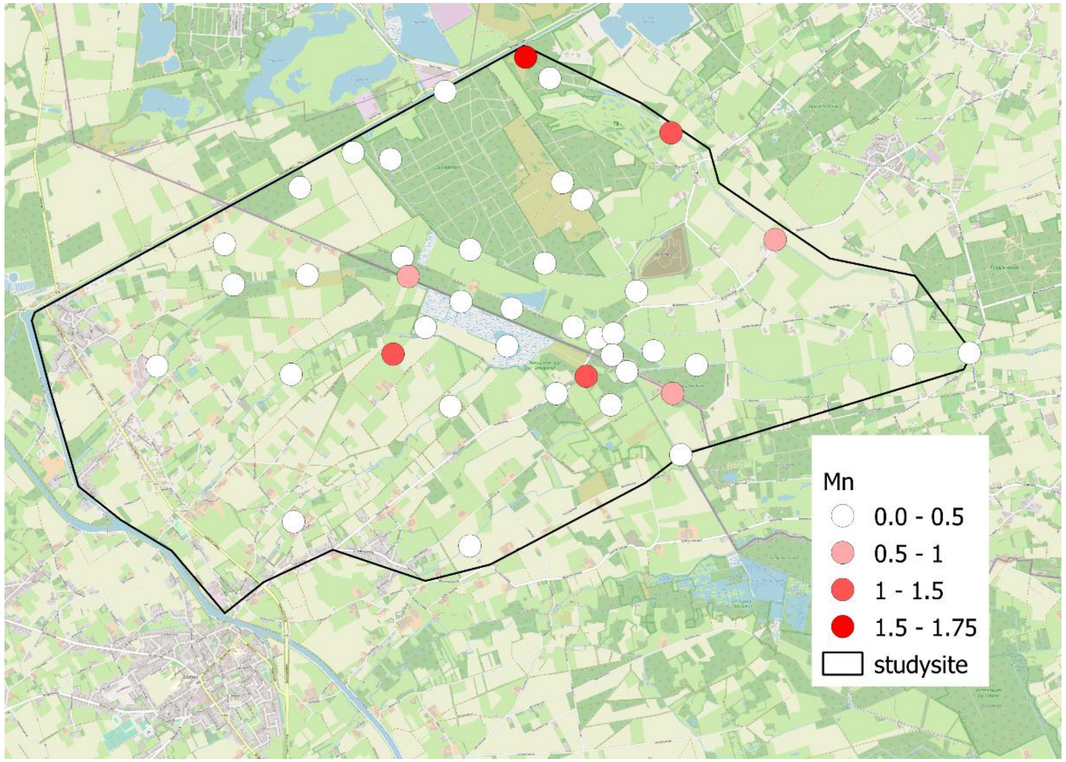

Figure 10. Mn distribution.

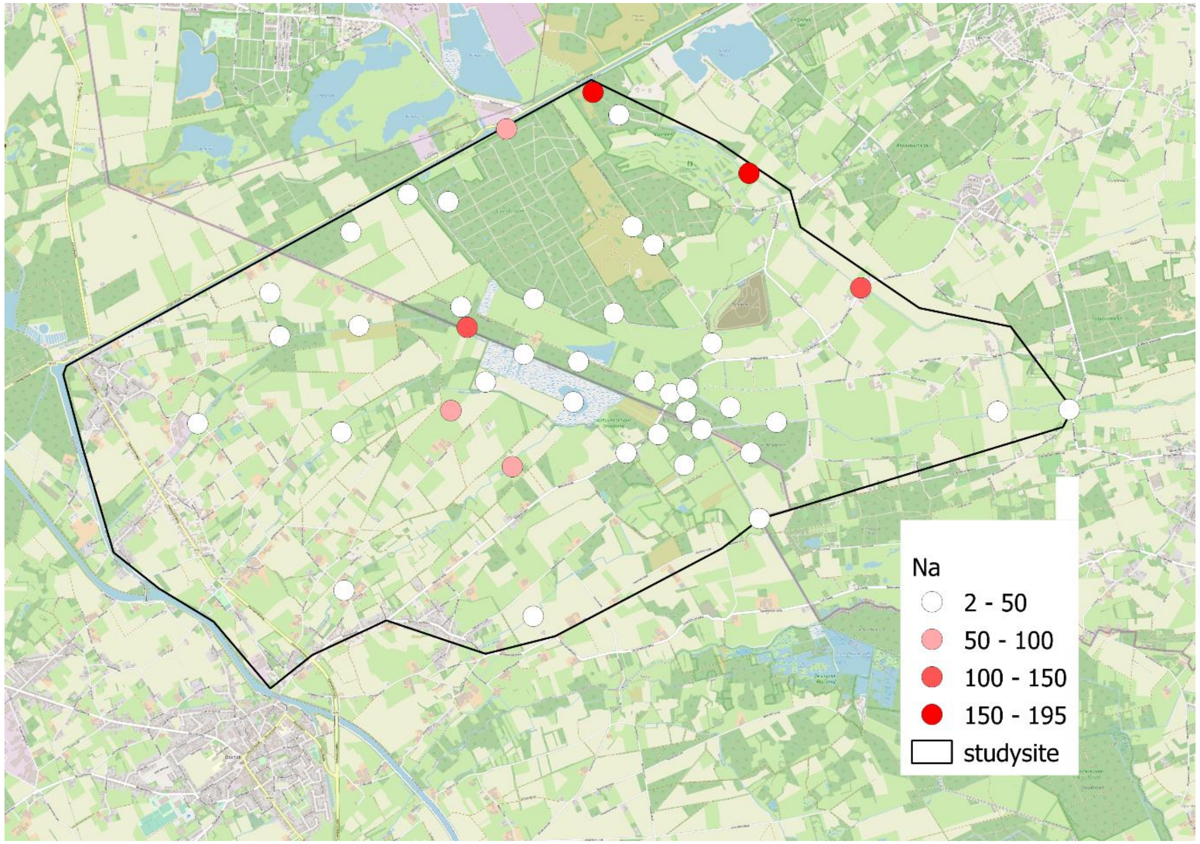

Figure 11. Na distribtuion.

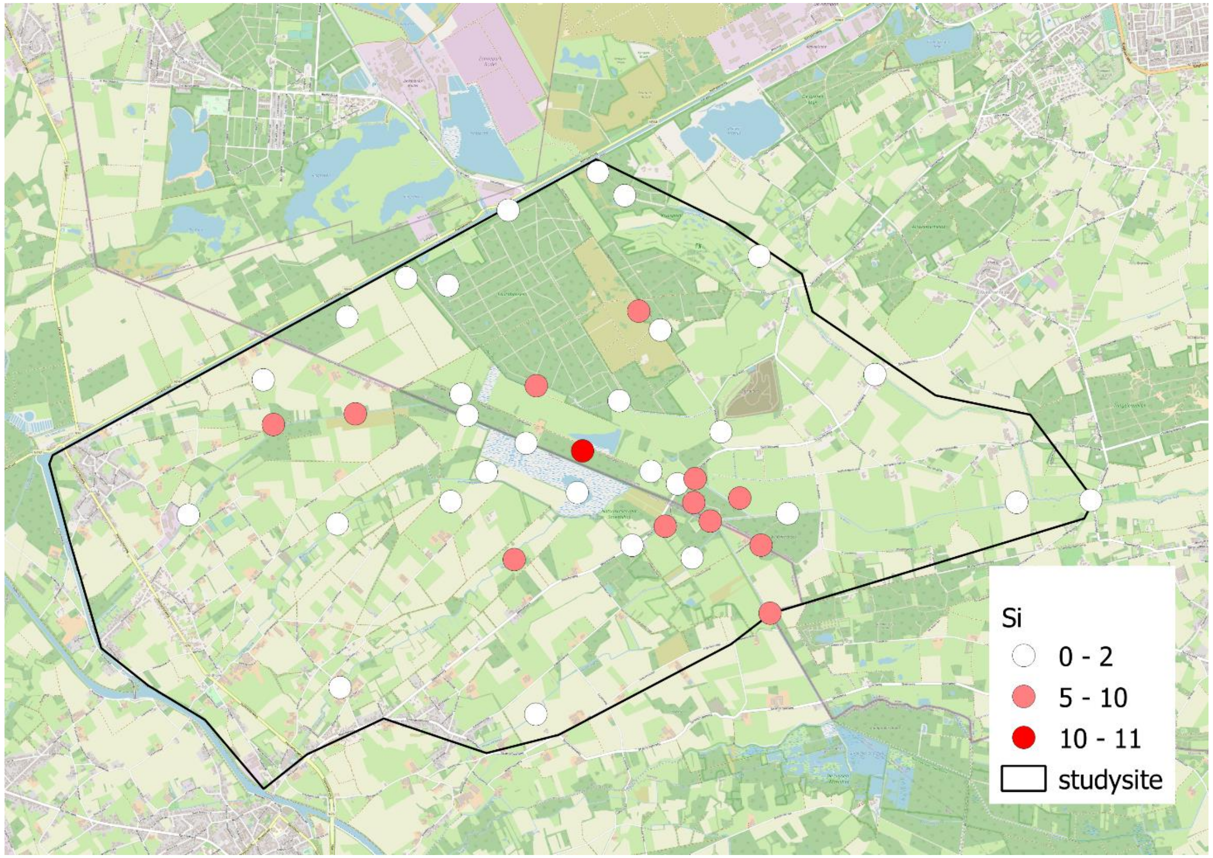

Figure 12. Si distribution.

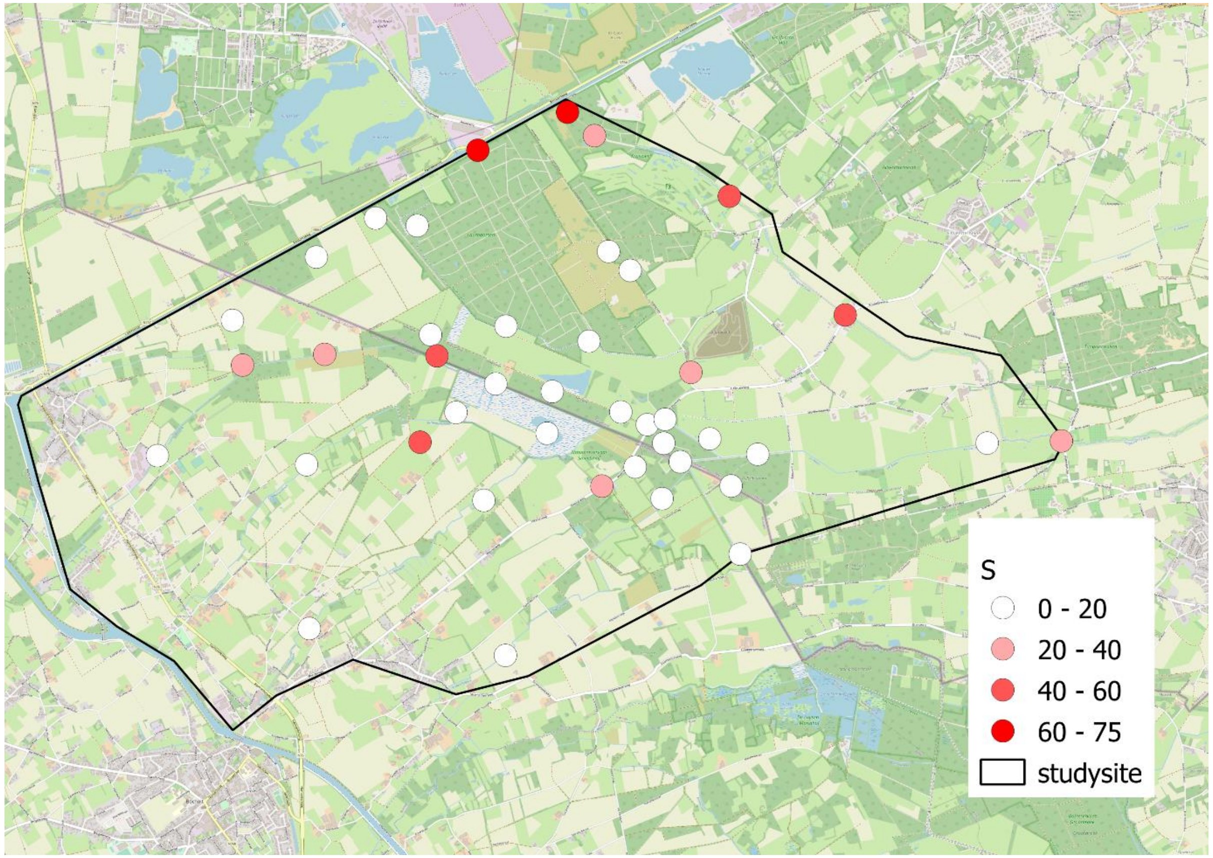

Figure 13. S distribution, Note: S as (SO4.)

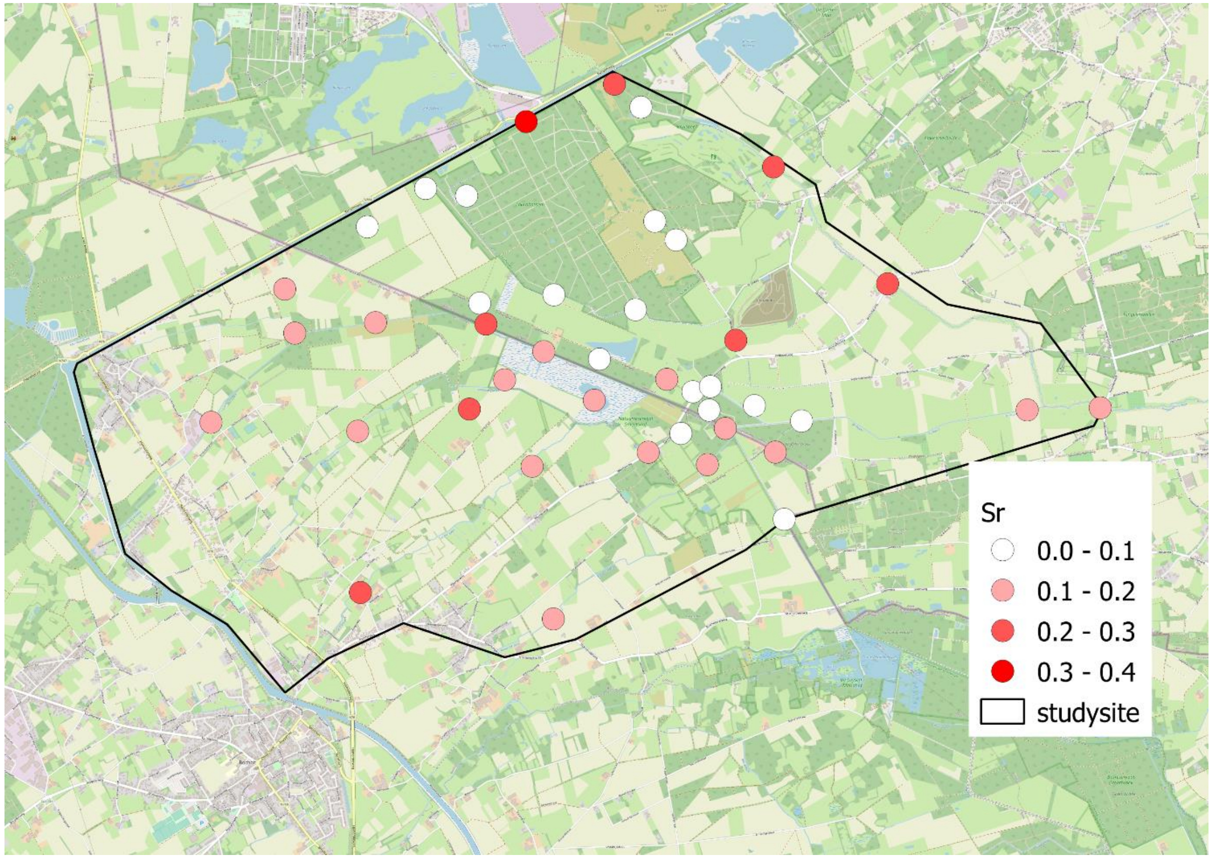

Figure 14. Sr distribution

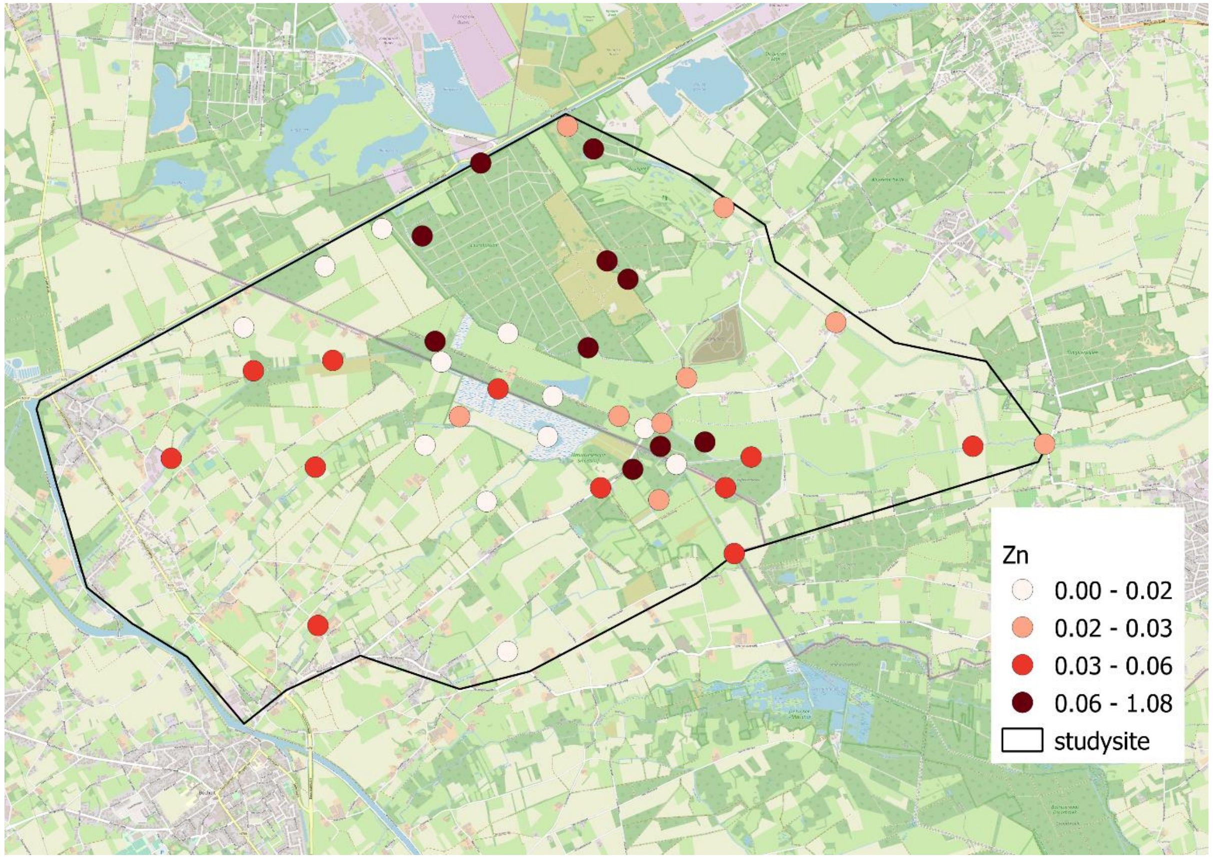

Figure 15. Zn distribution.

3. Nutrient Distribution.

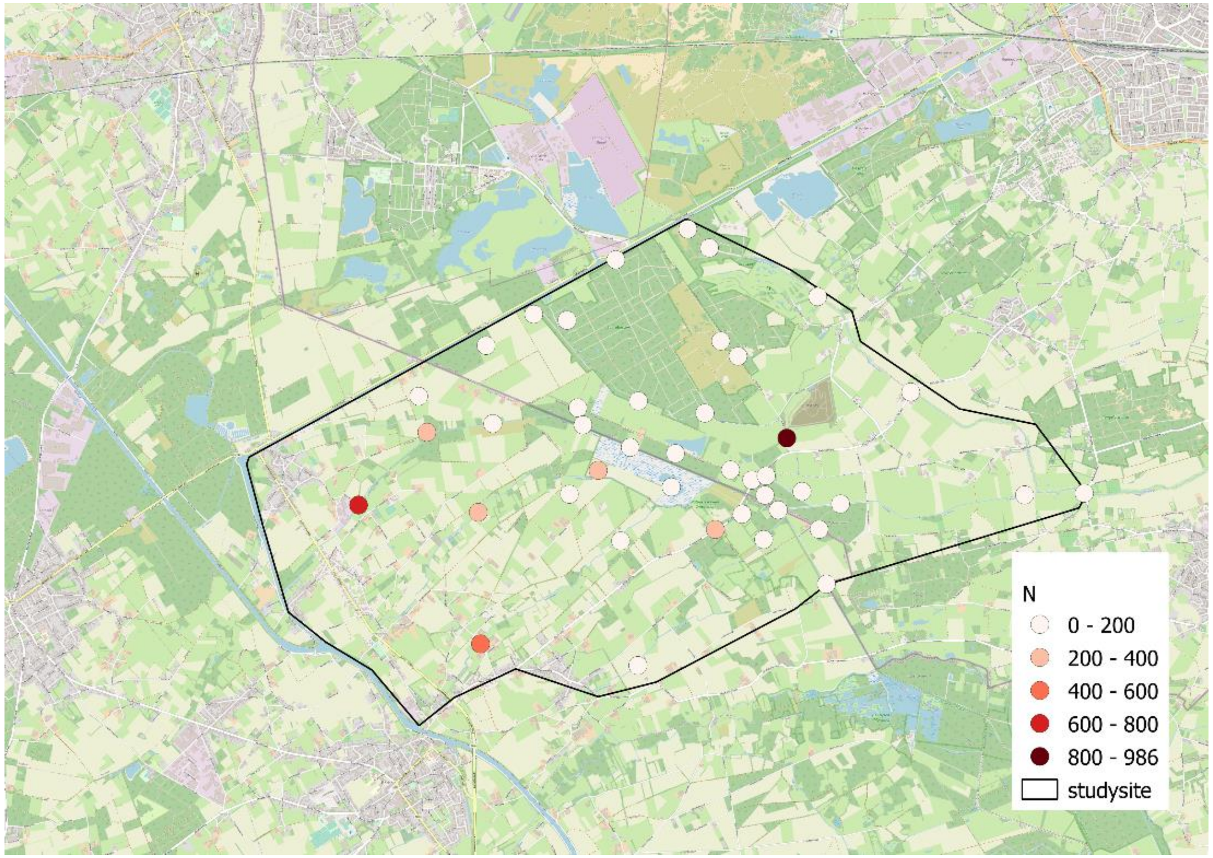

Figure 16. N distribution in µg/l.

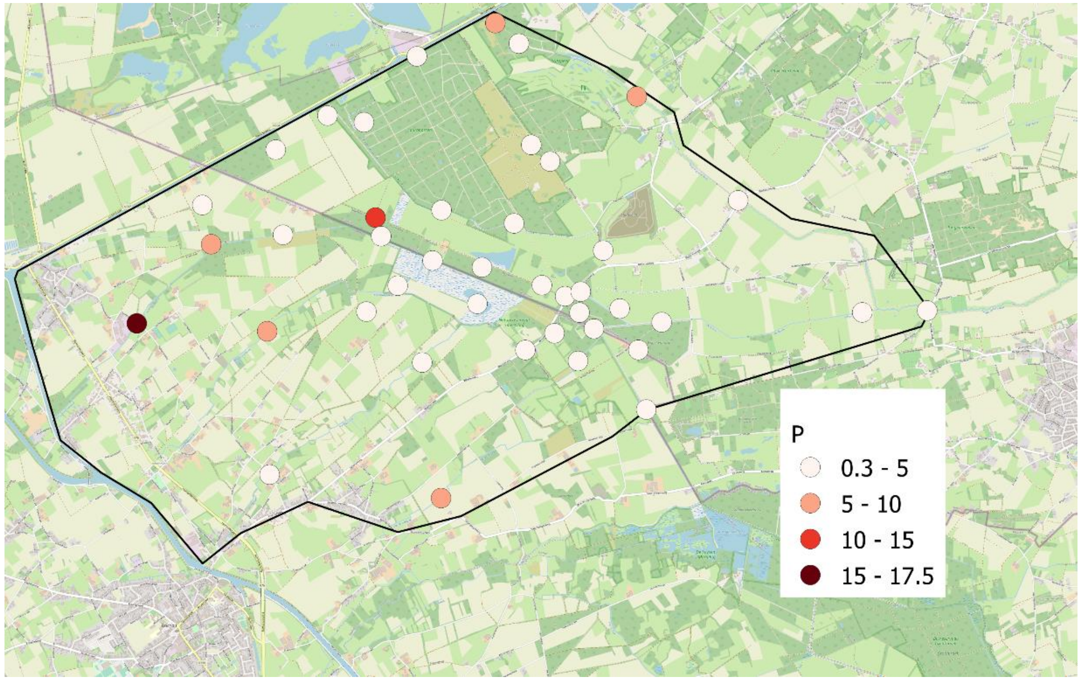

Figure 17. P distribution

4. Alkalinity and pH Distribution.

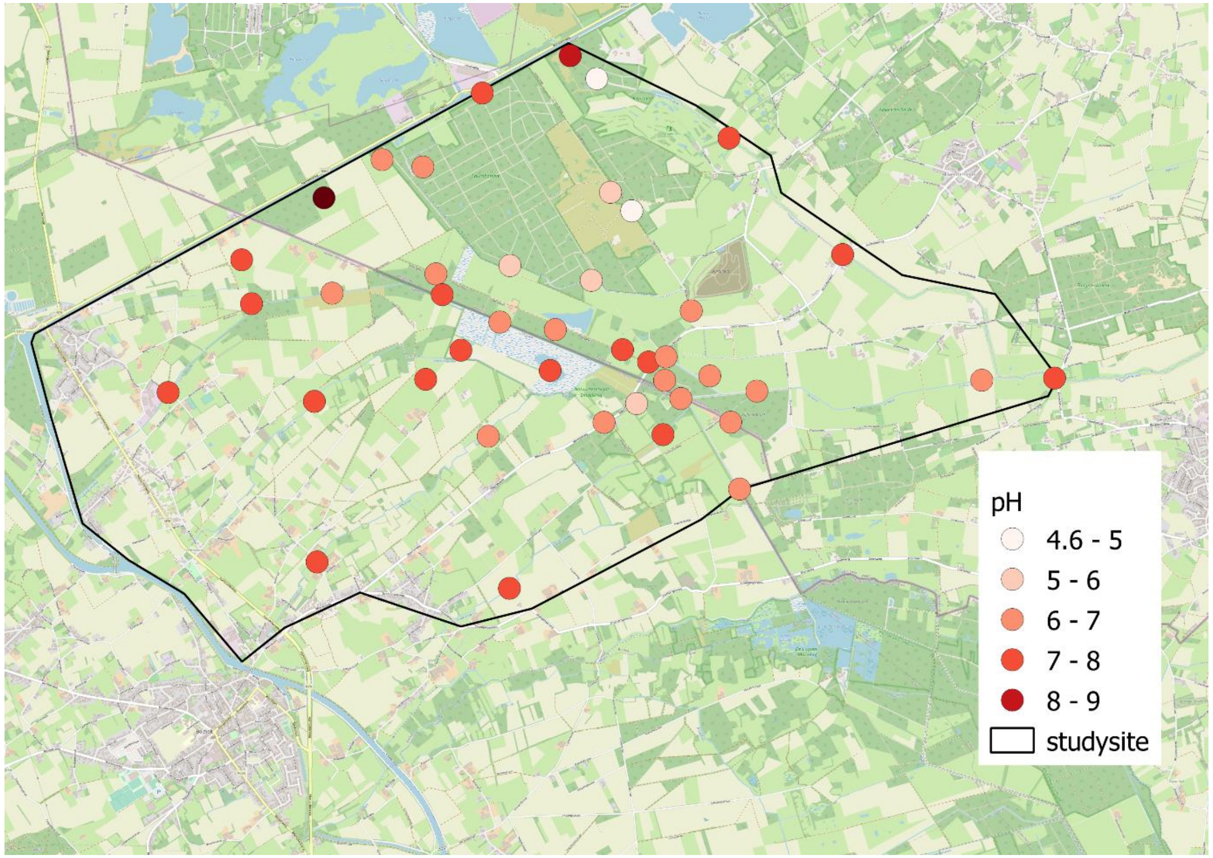

Figure 18. pH distribution

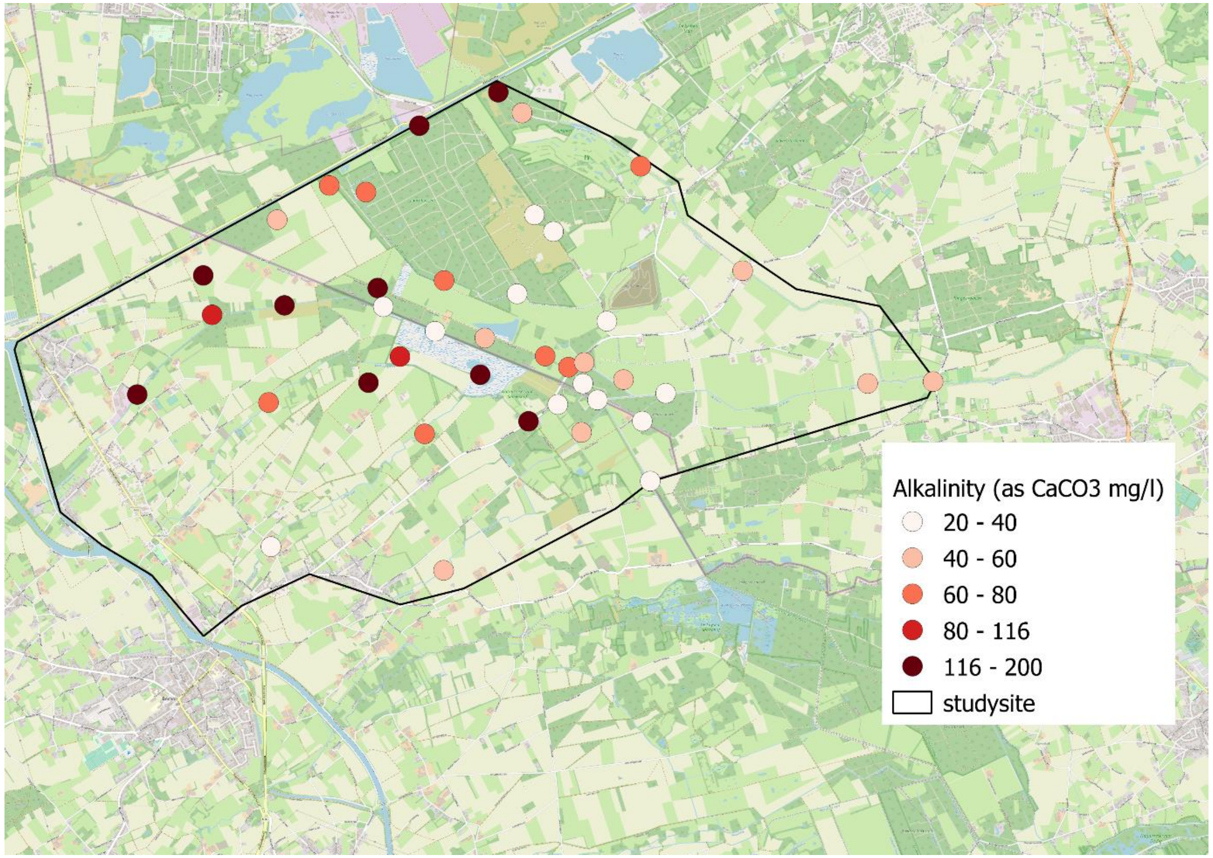

Figure 19. Alkalinity distribution.

5. Stiff diagrams for each sample site.

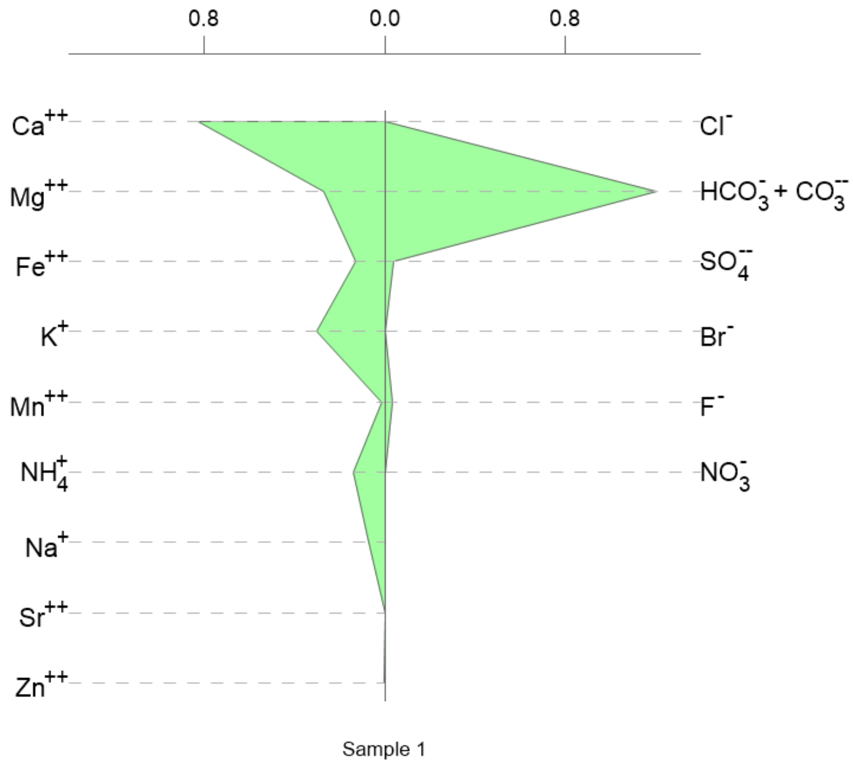

Figure 20. Stiff diagram of sample 1. mg/l.

Note: all stiff diagrams share the labels with sample 1. Additionally, they are all in mg/l.

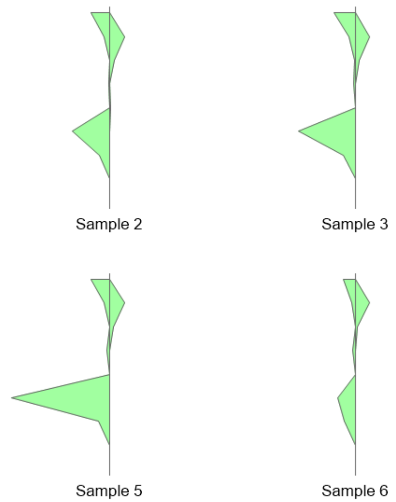

Figure 21. stiff diagrams of sample site 1-6.

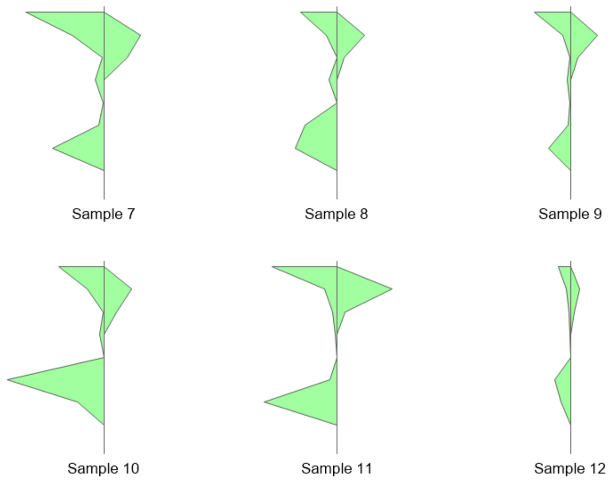

Figure 22. stiff diagrams of sample site 7-12.

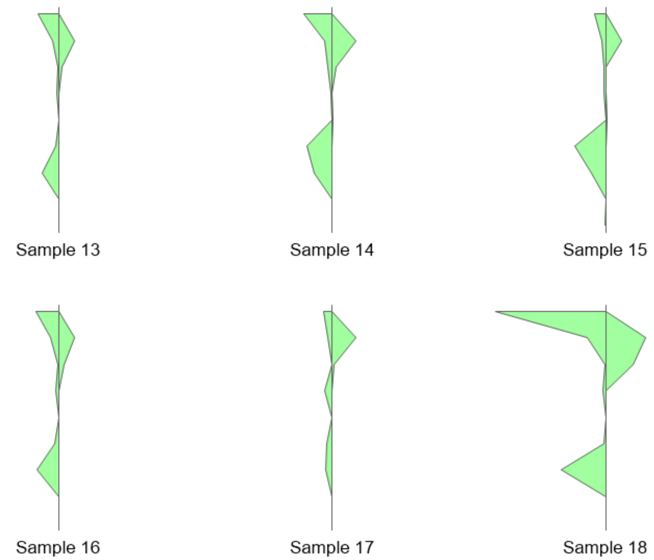

Figure 23. stiff diagrams of sample site 13-18.

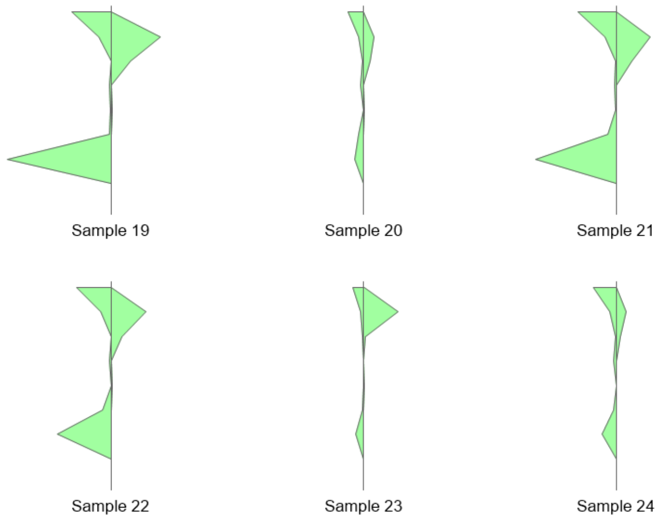

Figure 24. stiff diagrams of sample site 19-24.

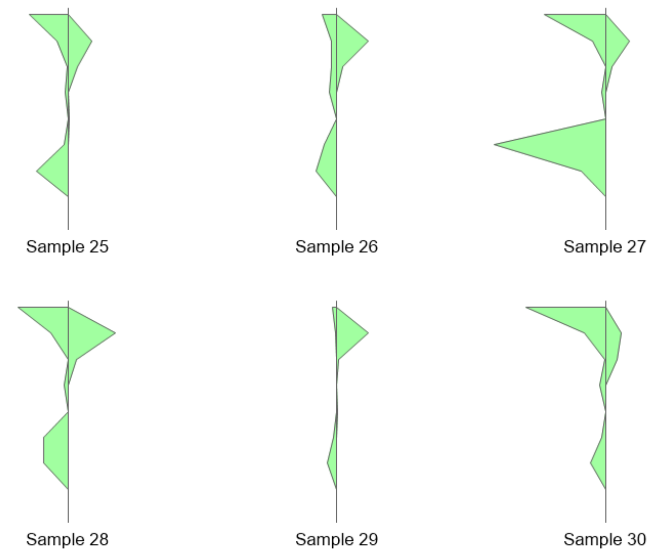

Figure 25. stiff diagrams of sample site 25-30.

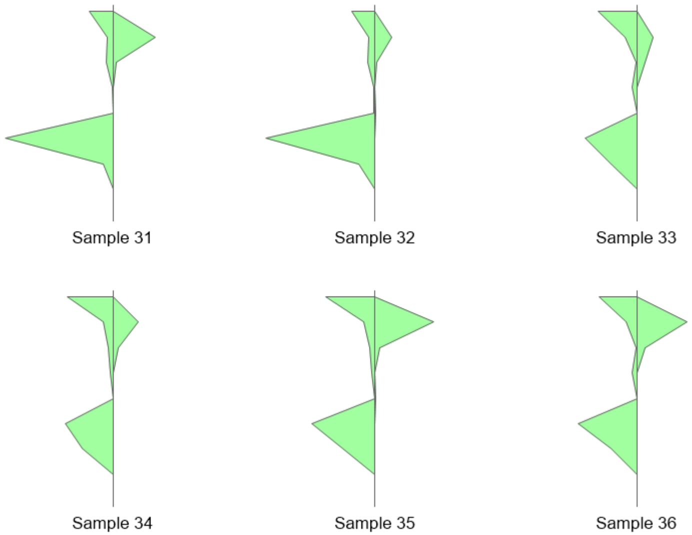

Figure 26. stiff diagrams of sample site 31-36.

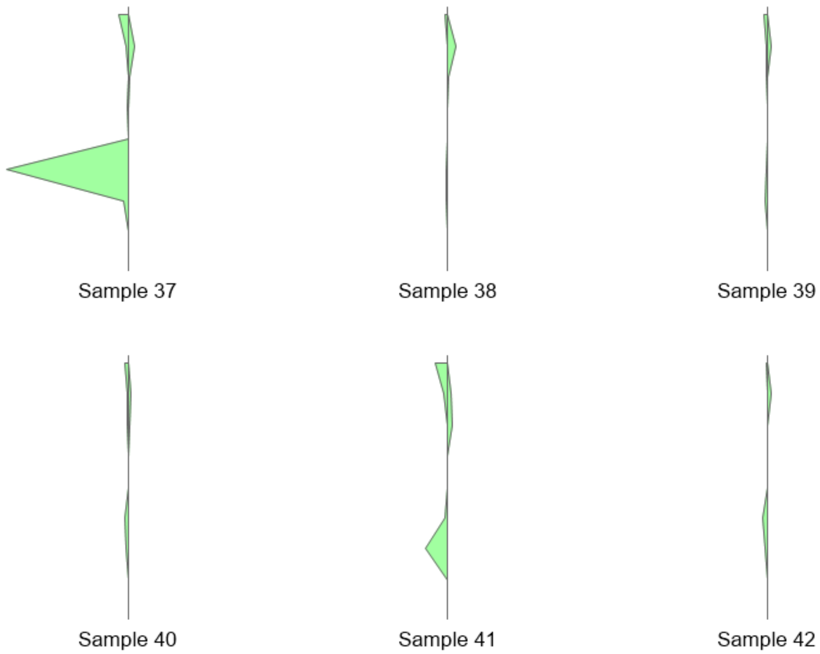

Figure 27. stiff diagrams of sample site 37-42.