Assessing the recharge of peat bogs in Northern Germany using various methods

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Abstract

Most peatlands in Northern Germany suffer from increasing water balance deficits and decreasing groundwater levels. According to recent studies, this is not only a local trend but is observed throughout the Northern Hemisphere. Ombrotrophic bogs function as natural lysimeters and are solely rain-fed, therefore the assessment of their groundwater recharge can be a great option for the water balance evaluation of their region. From the difference between their climatic and modelled water balance, deductions about external anthropogenic effects and climate change can be drawn. This study uses environmental tracers: isotopes and major ions for the estimation of the groundwater recharge. The tracers were analysed from groundwater samples from different depths, taken from two peat bogs in Schleswig Holstein with different characteristics. The water balance can be inferred from the groundwater recharge of recent years, estimated from the depth profile of environmental tracers. Different models were applied to simulate the recharge from 2018 to 2023, based on measured and collected data: a groundwater balance method based on climatic variables estimated a 193 mm/year recharge. The modelling by Hydrus 1D estimated 420 mm/year, the cumulative method estimated 240 and 280 millimetres for the two study areas, while the isotope model estimated 162 and 173 mm/year based on the concentrations of Oxygen-18 and deuterium. However, problems with the sampling can be inferred from the results, therefore conclusions must be drawn with caution.

Keywords

Peatland, hydrology, groundwater, water balance, recharge, ion-chromatography.

Észak-németországi tőzeglápok vízutánpótlásának értékelése különböző módszerekkel

Kivonat

Az észak-németországi tőzeglápok többségénél a talajvízszint csökkenése tapasztalható a növekvő vízháztartási hiány miatt, ami a legújabb kutatások szerint az északi félteke egészére jellemző tendencia. Az ombrotróf tőzeglápok természetes liziméterként működnek, vízutánpótlásuk pedig kizárólag a csapadékból származik, ezért a talajvíz utánpótlásuk értékelése kiváló lehetőség lehet a régiójuk vízmérlegének vizsgálatára. Az éghajlati jellemzőkből számított és a modellezett vízmérlegük különbségéből antropogén hatásokra és klímaváltozás okozta változásokra lehet következtetni. Jelen vizsgálat természetes nyomjelzőket: izotópokat és főbb ionokat vizsgál a felszín alatti víz utánpótlásának becslésére. A nyomjelzők Schleswig-Holstein tartomány két tőzeglápjának különböző mélységekből vett vízmintáiból kerültek elemzésre. A felszín alatti víz utánpótlását a természetes nyomjelzők mélység menti koncentráció változásából lehet megbecsülni a csapadék izotóp és ion koncentrációinak, illetve a talajt és a transzport folyamatokat jellemző különböző paraméterek ismeretében. A mért és becsült paraméterek felhasználásával így különböző modellekkel szimulálásra került a felszín alatti víz utánpótlása 2018 és 2023 között. Egy éghajlati változókra alapozott talajvízmérleg-módszer 193 mm/év vízutánpótlást becsült, a Hydrus 1D modellezése 420 mm/év értéket adott, a kumulatív módszer 240 és 280 millimétert becsült a két vizsgálati területre, míg az izotóp modell az oxigén-18 és deutérium koncentrációi alapján 162 és 173 mm/év értékeket adott. Az eredményekből azonban mintavételi problémákra lehet következtetni, így megállapításokat csak kellő körültekintéssel lehet tenni.

Kulcsszavak

Tőzegláp, hidrológia, talajvíz, vízháztartás, feltöltődés, ionkromatográfia.

INTRODUCTION

Wetlands are complex ecosystems, performing significant environmental and economic functions, providing numerous ecosystem services (*EPA 2003)*. They can store, filter and purify water, while they are modulating the atmospheric concentrations of some of the most dominant greenhouse gases (*Salimi et al. 2021*). Around 20 to 30% of the world's carbon pool is comprised in wetlands, making them a terrestrial ecosystem that has the highest carbon density (*Salimi et al. 2021*). If the layer of organic soil, built up from plant remains is thick enough (more than around 40 centimetres), then the wetland is called a peatland (*Price et al. 2023*). Ombrotrophic mires (bogs) are those peatlands that only receive water from precipitation and are therefore poor in solutes compared to minerotrophic mires (fens) that have groundwater and/ or surface water inflows as well (*Koster 2005*).

While wetlands, including peatlands are vitally important during climate change, they are among the most threatened ecosystems globally due to the rapid changes in climate and human activities, such as peat mining, land reclamation, the unsustainable degree of irrigation, agriculture, urbanization, drainage, and pollution. Although in general they are highly resilient to change – as they are fluctuating hydrologically between an aquatic and a terrestrial state every year – their ecosystem and functions are not flexible enough to adapt to all the additional changes and disturbances (*Salimi et al. 2021*). The altered hydrology and biogeochemistry of peatlands can lead to a higher rate of decomposition, carbon dioxide and methane emissions, and the release of nutrients instead of water purification (*Gutierrez Pacheco et al. 2021*). To mitigate the negative impacts on wetlands, monitoring and restoration projects are essential to assess their current state, identify the main threats, and implement management strategies to restore and conserve them. The first step is to quantify the recharge of groundwater and the sustainable yield with a high accuracy, which can provide a strong basis for sustainable groundwater management plans (*Sajil Kumar et al. 2021*). Recharge should be estimated with a method, which can be frequently updated, that is economical and easily feasible. A straightforward method for understanding groundwater flow is by tracing the movement of a dissolved substance through the groundwater. Environmental tracers, like major ions and isotopes are naturally present in groundwater, therefore the application of ion and isotope profile methods can be a great option for the estimation of point recharge (*Cook 2020*). The stable isotope and ionic composition of precipitation shows clear seasonal variations, which can be tracked through the groundwater column (*Yao et al. 2024*). This method can give a more accurate estimation than the groundwater balance method (*Sajil Kumar et al. 2021*), where the recharge is essentially the difference of total precipitation, groundwater inflow and outflow and potential evapotranspiration. This tracer technique was applied in the current study as well, following the example of several researchers, who have investigated solute and isotope concentrations to assess recharge mechanisms in different geological settings (*He et al. 2012, Joshi et al. 2018, Sreedevi et al. 2022*).

The aim of this study was to present an easily feasible method for the estimation of the yearly groundwater recharge in Northern Germany and to better understand the groundwater recharge of peat bogs in the area. Water rights are granted on the basis of outdated recharge estimations in the region, while there is already a huge pressure on groundwater and due to the increasing rate of evapotranspiration, the overall groundwater recharge is decreasing (*Wunsch et al. 2022*). The calculation of groundwater recharge in ombrotrophic (rain-fed) bogs can be a good proxy for regional groundwater recharge, because these bogs rely exclusively on atmospheric inputs (precipitation) and are largely insulated from direct groundwater contributions due to their perched, waterlogged nature. This allows them to act as natural rain gauges, capturing long-term precipitation patterns and evapotranspiration losses, which are primary components in estimating recharge (*Rydin and Jeglum 2013*). If the amount of yearly precipitation is higher than the evapotranspiration in the area of these bogs and their net recharge is positive, but their groundwater level is gradually decreasing, it can be inferred that the amount of water extractions from the connected aquifer is unsustainable. Therefore, two ombrotrophic bogs were chosen as study areas in the vicinity of Lübeck. The bog close to the municipality of Horst is located on a clearing of a forested area, far from roads, urbanisation or agricultural activities. The second sampling location on the other hand is located on the edge of Krummesser Moor, which is part of a water logging initiative by the city of Lübeck, focusing on raising the groundwater level to its original level to restore the once species-rich wetland, reduce greenhouse gas emissions, and support native biodiversity (*Lübeck.de 2022*). Over the past 20 years, measures such as closing inland ditches, and installing adjustable dams have been implemented to regulate water flow and improve habitat conditions, but further rewetting is still necessary. The area has now become a valuable ecological site and popular recreation destination, attracting bird enthusiasts (*Lübeck.de 2022*).

MATERIALS AND METHODS

The recharge of groundwater was calculated and modelled based on four different methods depicted in *Figure 1,* in order to reach more validated scientific conclusions on the basis of concordant data. It was important to choose models that describe the system and its representative factors well, that are based on the appropriate concept of tracer transport, and are calculating the behaviour of the tracer in the system correctly (*Leibundgut et al. 2009*). To model the transport of environmental tracers, a known or measured input and output of the same parameters (e.g. volume, concentration) is necessary as a function of space and time. Concentration time-series of solute and isotope concentration in precipitation was obtained from the weather stations at St. Jürgen and Wasserpfad, next to the Lübeck University of Applied Sciences (TH Lübeck). It was important to use several tracers, so that the possibility of the wrong understanding of the hydrological system - because of limitations or errors of a particular tracer or method - can be excluded (*Leibundgut et al. 2009*).

Sampling was carried out at Krummesser Moor and at a peat bog close to the municipality of Horst. Samples were analysed in the laboratory of the TH Lübeck (for solute concentrations) and at the laboratory of Hydroisotop in Schweitenkirchen (for isotopes). Input data for the recharge estimations were measured, collected and estimated based on literature and expert opinion or acquired from online databases. The flowchart of the study is depicted in *Figure 1.*

The study areas

The climate in the investigated region of Northern Germany is classified as temperate oceanic, with relatively mild temperatures (the average annual temperature is around 9 °C) and high precipitation levels (around 640 mm/year) throughout the year (*Climate 2024*). Two ombrotrophic bogs were chosen as the study areas of the study, located 18 kilometres from each other in Schleswig Holstein, which is the Northernmost state of Germany. A significant characteristic of these bogs is that they are perched above the local water table and rely entirely on precipitation for their hydrological needs, with no significant groundwater inflow (*Gajewski et al. 2001*). One of the study areas was at Krummesser Moor (*Figure 2/a*), to the South from Lübeck and to the Northwest from the lake of Ratzeburg, in an area surrounded by a larger (120-hectare) wetland. The second successful sampling was carried out close to the municipality of Horst (around 500 meters from Pinnsee) at a small peat bog in a clearing of a forested area, around 2 to 3 meters from a small lake (*Figure 2/b*).

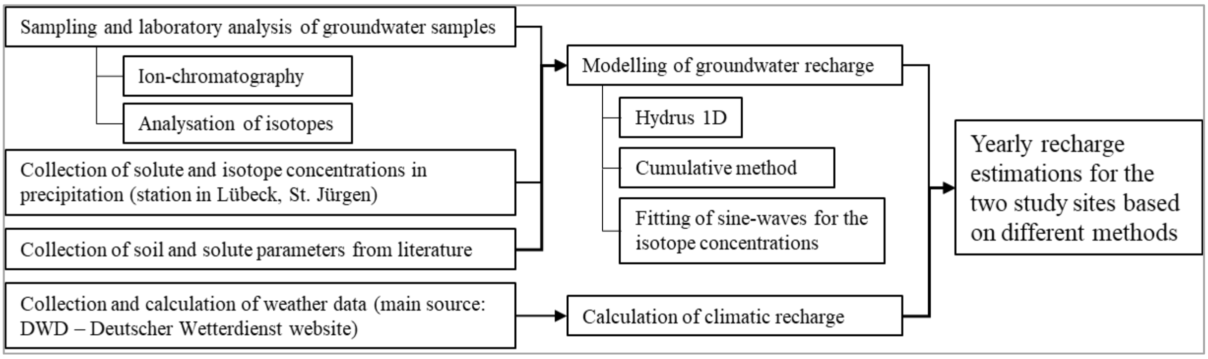


Figure 1. Steps of the groundwater recharge assessment of the study
1. ábra. A talajvíz-utánpótlási vizsgálat lépései

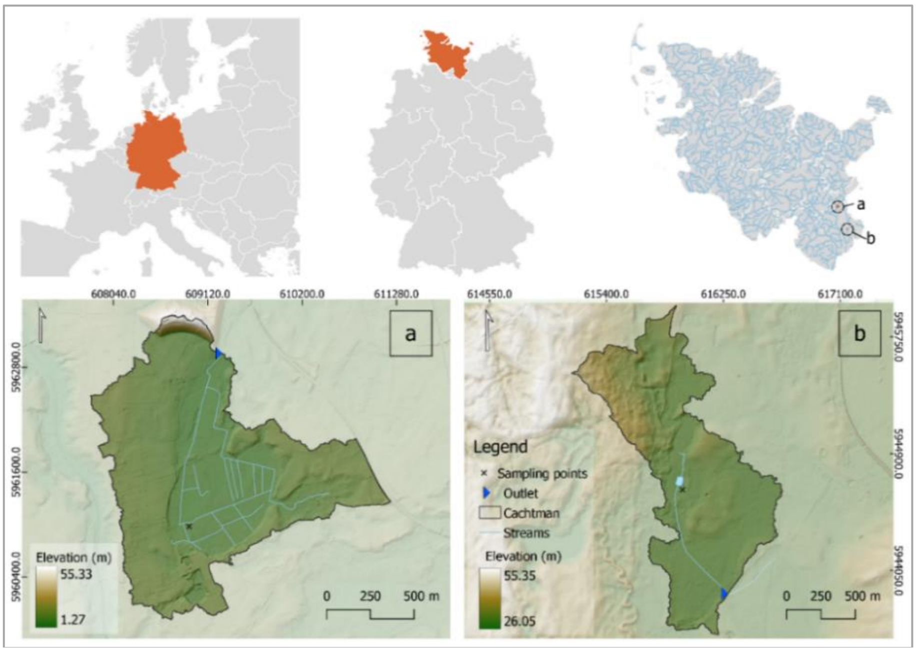


Figure 2. Map of the two study areas: Krummesser Moor (a) and the peatland near Horst (b)
2. ábra. A vizsgált területek térképei: Krummesser Moor (a) és a tőzegláp Horst közelében (b)

The soil in the study areas is primarily composed of peat, which is rich in organic matter and has a high water-bearing capacity. The vegetation of both study areas is predominantly composed of sphagnum moss. The topography of Schleswig-Holstein is characterized by a predominantly flat terrain, with low hills and occasional depressions. Glacial deposits, deformed by salt structures of the rising Permian and Upper Triassic are characterising the near-surface geology of Northern Germany. The “Lübecker Basin” was mainly formed during the Weichselian (Würm) Glaciation and its main inflow water stream is the Trave (*Grube and Lotz 2004*).

Around a quarter of the area of Northern Germany is affected by inland salinity, originating mainly from the upcoming of deep-seated salt waters from the pre-Tetriary sub-ground. Salty water reaches the shallow aquifer system at several locations in Schleswig-Holstein, thus salty springs and seashore salt grass also emerge across the region (*Magri et al. 2009*). *Grube and Lotz (2004)* investigated the distribution pattern and the origin of salinized water (>250 mg Cl/l) in the region. Intensive pumping in the 1970s resulted in the widespread drop of groundwater potential in the region, some depressions reaching 10 m below sea level. The decrease in the level of the groundwater table resulted in the mobilization of seawater and several pumping wells had to be abandoned. Since then, the situation has improved thanks to regulations, but in some parts the salinization is still increasing. It is important to note, that *Grube and Lotz (2004)* investigated a West-East cross section of geological layers between the Segeberg salt diapir and the Baltic Sea, which crosses 4.8 km north from Krummesser Moor. The thickness of the geological layers is very thin below the area and the salt diapir is less than 150 meters from the surface, which can potentially have an influence on the solute concentrations of groundwater at Krummesser Moor.

The investigated peat bog near Horst is in the watershed of Pinnsee. The lake does not have any in- or outflows above ground, it is purely fed by the precipitation in the catchment area and has a slowly decreasing water level (*Roehl 2023*). The interaction between the lake and the groundwater was investigated with the application of analytical element models by *Roehl (2023)*. Although the Pinnsee has no outflows on the surface, the calculated water balance indicated the presence of an outflow, prompting an investigation into the possibility of groundwater discharge. A surface water body, corresponding with the watershed was found, at the very location of the peat bog investigated in this study, near Horst. Therefore, there is a through flow, i.e. a lateral component in the groundwater flow at the peat bog, but it is much (around 50 times) smaller than the vertical gradient.

Sampling

The sampling equipment was a two-meter-long copper rod with small 1.5-millimetre openings on the last 5 centimetres and with a sharpened, closed ending. Inside the copper rod, there was a plastic tube (diameter: 0.5 cm), which was connected to a pump. The rod was inserted into the ground until the desired depth, after which the pump was turned on and a sample was collected when the pumped water turned visibly clear. After the collection of a sample (of 200 ml), the rod was pushed to the next desired depth, where the method was repeated after waiting for two minutes, to make sure that the water is no longer mixed, and it is coming from the desired depth. Due to the soil composition and the sponge-like behaviour of peat, the rod was easily pushed– and pulled - by hand until the desired depth. The sampling interval was 10 centimetres, and samples were collected from a 1-meter-deep column at Krummesser Moor (on the 3rd of May, 2023) and from 1.5 meters at Horst (on the 25th of June, 2023). The samples were taken to the laboratory and after filtration solute concentrations were measured by ion-chromatography. Samples from Horst were also sent to a laboratory for the analysis of isotopes.

As for Krummesser Moor, water temperature (10.7-15 °C), pH (decreasing from 6.6 to 5.8), electric conductivity (541-618 µS/cm), oxygen concentration (0.51-0.8 mg/l, 4.7-8.0%) and redox potential (175-200 mV) were measured on the field using a multimeter. From the fluctuations of the measured values between higher and lower peaks, it can be assumed that two years of recharge can be seen in the 1-meter-deep profile, as three lower and two higher peaks were observed, representing winter and summer concentrations. At the second sampling close to Horst, after the copper tube was completely pulled out, the tip of the rod was missing, thus the tube was open at its end. This gives a reason to treat the collected samples and the later acquired data with caution, as the depth where the tip has separated is not known and it is possible that the pump was not only sucking the water from the desired horizontal layer, but from a mixed water column below as well.

While the measured pH is similar to the measured values at Krummesser Moor, its range is considerably smaller (5.16 to 5.33). The electric conductivity was five times smaller compared to Krummesser Moor (91 to 112 µS/cm) and it was almost constant (excluding the first two samples). This could mean that the pumped groundwater was mixed indeed, but it cannot be unequivocally concluded simply from these values.

Laboratory analysis

Environmental tracers are powerful tools for understanding groundwater systems, offering insights into the origin, age, and recharge processes of groundwater. Unlike artificial tracers, which are less effective for slow or large-scale systems, environmental tracers - which are naturally integrated into the groundwater - provide a more accurate picture of the movement and aging of water (*Cook 2020*).

The transport of solutes through peat is controlled by the complex combination of physical factors and biogeochemical conditions. The latter is governed by the reactivity of organic matter and the presence of chemical species that are sensitive for redox reactions, like nitrate and sulphate (*Price et al. 2023*). As peat is a dual porosity medium, it has both mobile and immobile porosity. Solutes can get into the smaller pores with immobile porosity via diffusion from the solute flowing in the mobile region. The amount of these smaller pores is increasing with depth (*Price et al. 2023*). Tracers must be chosen carefully, considering the high complexity of peat. An ideal tracer for groundwater recharge assessments is soluble, mobile, relatively non-reactive, and easy to measure. Environmental tracer analysis typically assumes that their transport is primarily governed by advection, where substances move with the bulk flow of groundwater, rather than by diffusion or dispersion. In a relatively homogeneous aquifer, this results in the tracer progressively aging with increasing depth (*Cook 2020*).

Major anions (fluoride, chloride, nitrate, nitrite, sulphate), and cations (lithium, sodium, ammonium, potassium, calcium, magnesium) were measured from the groundwater samples by ion-chromatography (IC). While most of the anions are not sorbed and are not reacting with other molecules or the organic matter in the peat, cations usually are. Therefore, while the concentrations and depth-profiles were assessed for all measured ions, not all were further investigated and modelled. The only pre-treatment needed for the samples for the IC measurements was for the removal of particulates with filtration through a 0.45 µm filter (*Jackson 2000*). Oxygen-18 (^{18}O), which is an isotope of oxygen and deuterium (^{2}H) – an isotope of hydrogen – are commonly used as environmental tracers (*Cook 2020*) and these were measured in this study as well. Concentrations of both environmental isotopes show an observable pattern in precipitation, which can be approximated by sine waves. This seasonal isotopic signal can be used to evaluate the mean transit time of soil water (*DeWalle et al. 1997*).

At Krummesser Moor, most of the solute concentrations were unexpectedly high, which led to the assumption that the peat bog has an external input source, possibly a stream originating from the salt depositions close to the surface. As for the peat bog near Horst, the assumed small vertical gradient in the inflow can result in a slightly distorted profile of the investigated solute concentrations. This also means that the water might have been in contact with the aquifer before and it could have picked up some salts. The samples from the peat bog near Horst were analysed for isotopes as well, for oxygen-18 and deuterium. The range of the isotope ratios– measured by a dual-inlet stable isotope ratio mass spectrometer – was surprisingly small (-7.44 to -7.07‰ for $\delta^{18}O$ and -50.8 to -48.6‰ for $\delta^{2}H$). The isotope concentrations were stated in delta per mil notation (δ‰), with respect to the internationally accepted standard Vienna Standard Mean Ocean Water (V-SMOW) (*Wit et al. 2007*).

Collection of weather parameters

While rainfall can be measured in a reliable way, evapotranspiration depends on a great number of factors. Daily precipitation data was downloaded from the Deutscher Wetterdienst (DWD) website (*Wetter Und Klima 2023*) for the station of Grambek (station ID: 01736) 8 kilometres to the south-west from Horst, and Lübeck-Blankensee (station ID: 03086), 3 kilometres to the east from Krummesser Moor. The time series of precipitation was calculated for the sampling locations from the two station's data series based on their distance from the study sites. Yearly rainfall ranged from 490 to 870 millimetres per year in the 20-year period from 2003 and it shows a slightly decreasing trend. Calculations and modelling were carried out using five years of precipitation data from 2018. The time-series of daily evapotranspiration was calculated on the basis of the FAO Penman-Monteith equation (1), which requires several climatological and physical parameters (*Allen et al. 1998*):

$$ET_0 = \frac{0{,}408\Delta(R_n - G) + \gamma\frac{900}{T+273}u_2(e_s - e_a)}{\Delta + \gamma(1 + 0{,}34u_2)} \tag{1}$$

Where: ET_0 = Reference evapotranspiration [mm/day], R_n = Net radiation at the crop surface [MJ/m^2 d], G = Soil heat flux density [MJ/m^2 d], T = Mean daily air temperature at 2 m height [°C], u_2 = Wind speed at 2 m height [m/s], e_s = Saturation vapour pressure [kPa], e_a = Actual vapour pressure [kPa], e_s-e_a = Saturation vapour pressure deficit [kPa], Δ = Slope vapour pressure curve [kPa/°C], γ = Psychrometric constant [kPa/°C].

These parameters were either measured at weather stations or they were calculated by empirical relationships from measured data. Relevant weather data was downloaded from the website of DWD (*Wetter Und Klima 2023*) and calculations were carried out on the basis of the guidelines of FAO (*Allen et al. 1998*). Potential evapotranspiration defines the amount of water that could be evaporated and transpired by plants if sufficient water is available (*Allen et al. 1998*). Since the investigated peat bogs are wet all year-round and their vegetation cover is not significantly fluctuating during the year, actual evapotranspiration is close to potential. One of the most straightforward methods to calculate recharge is based on the groundwater balance method and equation (2) (*Sajil Kumar et al. 2021*):

$$(P + G_{in}) - (Q + ET + G_{out}) = \Delta S \tag{2}$$

Where P = precipitation, G_{in} = groundwater inflow, Q = discharge, ET = evapotranspiration, G_{out} = groundwater outflow, and ΔS = change is storage. Due to the ombrotrophic nature of the bogs, groundwater inflow and discharge can be neglected. Since the sought parameter is the recharge (R) and not the change in storage, the equation can be simplified (*Hendrickx 1992*):

$$R = P - ET_p \tag{3}$$

An important input function for the physical models was the time series of isotope and solute concentrations in precipitation. Time series of concentration were provided for chloride, ammonium, phosphate, sulphate, sodium, potassium, calcium and magnesium in two-weekly intervals from a weather station in Lübeck, St. Jürgen (7 kilometres from Krummesser Moor and 23 kilometres from Horst). Monthly average concentrations were calculated, which can be seen in *Figure 4*, arranged according to the pattern of their seasonal fluctuations. The concentrations of phosphate were below the detection limit in the precipitation, thus these ions were excluded from further calculations. Data about the concentration of isotopes in precipitation were based on measurements that were carried out at the TH Lübeck station (Wasserpfad) between November 2017 and October 2022. These measured concentrations are depicted in *Figure 3.*

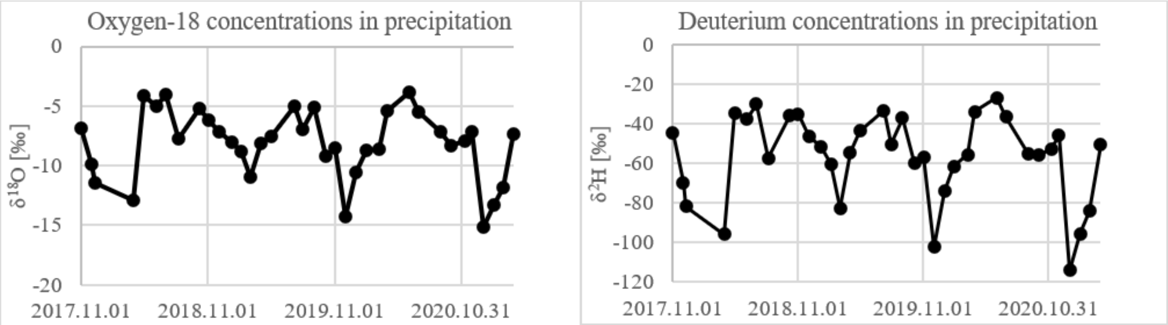


Figure 3. Concentration time series of the investigated isotopes, measured at the TH Lübeck station
3. ábra. A vizsgált izotópok csapadékban mért koncentrációjának idősorai a TH Lübeck állomáson

Sodium, chloride and magnesium appear with a high concentration in the precipitation in Northern Germany generally in the colder part of the year, possibly due to marine enrichment, the higher amount of storms and subsequently the elevated levels of sea spray in the air (*Keresztesi et al. 2019*). During the summer months, their concentration decreases almost to zero, as seen in *Figure 4*. These solutes might not be perfect tracers, since their concentration is high during the same period, when the evapotranspiration and thus the enrichment is low. Therefore, peak concentrations originating from higher winter concentrations might be neutralized by elevated concentrations due to enrichment. Calcium and ammonium behave in the opposite way, since their concentration is depleted in the precipitation during winter, and they appear with high concentrations during summer. These higher concentrations can be attributed to anthropogenic activities, such as industrial emissions, the use of fertilisers in agriculture, wind-blown soil dust or the presence of open quarries (*Keresztesi et al. 2019*). Ammonium could be a good tracer, as it appears with higher concentrations in the precipitation during summer, and it is also enriched at the same time due to the higher rate of evapotranspiration. However, it is a highly reactive compound, and it is converted in the water. Sulphate and potassium have three, less elevated peaks in a year. As *Figure 4* shows, they appear with higher concentrations during December and January in the winter, around April and May in the spring and around September in the autumn.

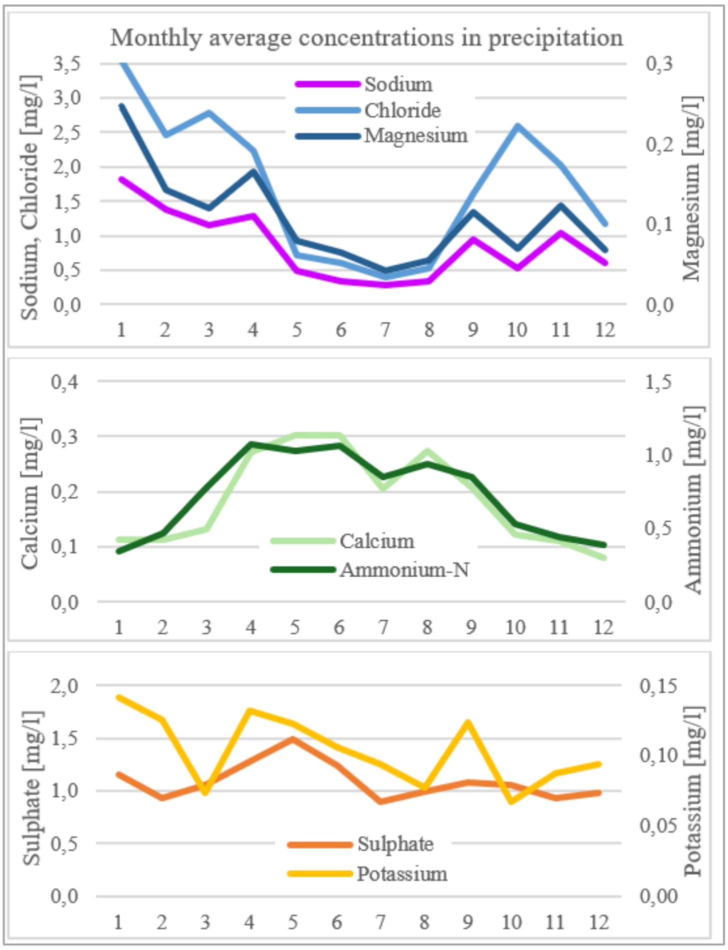
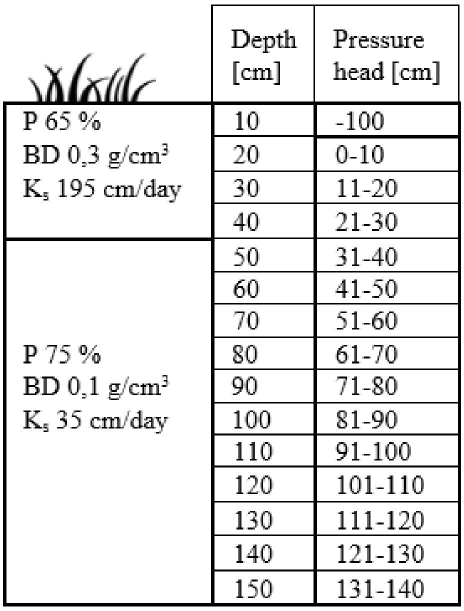


Figure 4. Monthly average concentrations of the investigated ions in precipitation
4. ábra. A vizsgált ionok csapadékban mért havi átlagos koncentrációja

Modelling with Hydrus 1D

A one-dimensional approach can be sufficient to represent the vertical flow and transport in peat bogs with variably saturated conditions in the profile. Hydrus 1D has the advantage that it is widely available, relatively simple and has a limited computational demand. It is commonly applied for the estimation of groundwater recharge in soils and for the evaluation of near-surface water balance (*Leterme et al. 2012*). With the available data, Hydrus 1D, version 4.17 (*Simunek et al. 2013*) was the best option to model the recharge and the movement of solutes.

In a simplistic manner, peat bodies can be divided into two parts vertically that have considerable differences in function and physical properties: the acrotelm and the catotelm. Consisting of moss and litter, the acrotelm is usually 30-50 centimetres deep and is the variably saturated upper layer of peat, where the rate of energy and matter exchange is considerably higher. Below it lies the saturated, generally more homogenous catotelm (*Whittington et al. 2021*). With the increased decomposition and compression and decreased pore size, the hydraulic properties of peat are also changing with the depth (*Price et al. 2023*). Two soil materials were defined in the simulated 150 cm deep soil profile, representing these two layers of the peat, which can be seen in *Figure 5*, together with the pressure head (which was set at the initial condition) along the modelled peat column. The depth of the acrotelm was defined on the basis of observations during the sampling process as 40 centimetres. It was not possible to pump water from the upper 10-20 centimetres of the peat, meaning that there was no water with free pressure in this layer. Therefore, this top zone was considered as an unsaturated layer with negative pressures, while in the saturated layer the pressure is increasing with depth.



	Depth [cm]	Pressure head [cm]
P 65 % BD 0,3 g/cm³ K_s 195 cm/day	10	-100
	20	0-10
	30	11-20
	40	21-30
P 75 % BD 0,1 g/cm³ K_s 35 cm/day	50	31-40
	60	41-50
	70	51-60
	80	61-70
	90	71-80
	100	81-90
	110	91-100
	120	101-110
	130	111-120
	140	121-130
	150	131-140

Figure 5. Main soil parameters and the pressure head of the modelled peat column
5. ábra. A tőzegláp paraméterei és nyomásmagassága a modellezett talajoszlop mentén

To understand and model the hydrological functioning of a peat bog, its hydraulic properties need to be known. Hydrological models like Hydrus require the parameters from the soil water retention curve (SWRC) and also the hydraulic conductivity function for the modelling of the water and solute transport under unsaturated conditions (*Menberu et al. 2021*). Values for the necessary parameters were chosen carefully in order to represent the study sites the best, based on literature, the site visits and expert opinion. In Hydrus 1D, the Richards's equation (4) is used to model the movement of water through soil:

$$\frac{\delta\theta}{\delta t} = -\frac{\delta q}{\delta z} = \frac{\delta}{\delta z}\left[K(h)\frac{\delta h}{\delta z} - K(h)\right] - S \tag{4}$$

Where: θ = Volumetric water content - estimated based on literature (*Price et al. 2023, Whittington et al. 2021*), z = Vertical coordinate, q = Water flux, t = Time (time passed from the start of the modelling in days), S = Sink term representing root water uptake, $K(h)$ = Soil hydraulic conductivity function (depending on the pressure head "h") - estimated based on literature (*Price et al. 2023*) and expert opinion

The relationship between soil moisture and hydraulic conductivity is described by the Van Genuchten equations (5; 6) (*Van Genuchten 1980*):

$$\theta(h) = \begin{cases} \theta_r + \frac{\theta_s-\theta_r}{[1+|\alpha\cdot h|^n]^m},\ h < 0 \\ \theta_s,\ h \geq 0 \end{cases} \tag{5}$$

$$K_r(h) = \frac{\left[1-(\alpha\cdot h)^{n-1}\cdot[1+(\alpha\cdot h)^n]^m\right]^2}{[1+(\alpha\cdot h)^n]^{\frac{m}{2}}} \tag{6}$$

Where = θ_s: Saturated water content [-] - estimated based on literature (*Price et al. 2023*) and expert opinion, θ_r = Residual water content [-] - estimated based on literature (*Price et al. 2023*) and expert opinion, α, m, n = Empirical parameters [1/L], [-], [-] - defined based on literature (*Menberu et al. 2021*), S_e = Effective water content [-] - calculated based on the water content, K_s = Saturated hydraulic conductivity [L/T] - defined based on literature (*Menberu et al. 2021*), K_r = Relative hydraulic conductivity [-] estimated based on literature (*Price et al. 2023*) and expert opinion, $K_k(h_k)$ = Unsaturated hydraulic conductivity at pressure head h_k [L/T]

Some further parameters had to be defined for the modelling of solute transport: l = Tortuosity parameter in the conductivity function [-] - a dimensionless parameter, defined based on literature (*Gharedaghloo et al. 2018, Weber et al. 2017)*, ω = Mass transfer coefficient for peat [-], defined based on literature (*Rezanezhad et al. 2016*), BD = Bulk density [-] (the quotient of the dry mass and the total volume) - defined based on expert opinion, D_L = Longitudinal dispersivity [cm] - As its rate was not known, it was a calibration parameter, $Fract$ = Fraction of adsorption sites in contact with mobile water [-] - defined based on expert opinion, D_W = Molecular diffusion coefficient in free water [m^2/s] - defined based on water temperature and literature (*Holz et al. 2000*), α = Mass transfer coefficient for solute exchange between mobile and immobile liquid regions [1/day] - defined based on literature (*Genuchten and Wierenga 1976*).

The chosen and defined values for the parameters are listed below in *Table 1*.

Table 1. Calculated or chosen water flow and solute transport parameters
1. táblázat. A vízáramlást és az oldott anyag transzportot leíró számított és választott paraméterek

Water flow parameters		**θ_r [-]**	**θ_s [-]**	**α [1/cm]**	**n [-]**	**K_s [cm/day]**	**l [-]**	**$\theta_{im,r}$ [-]**	**$\theta_{im,s}$ [-]**	**ω_W**
Depth [m]	0-0.4	0.3	0.65	0.05	1.39	195	0.8	0.4	0.7	0.6
	0.4-1.5	0.25	0.75	0.02	1.42	35	2	0.35	0.75	0.6
Solute transport parameters		**BD**	**D_L [cm]**	**initial conc, (mobile)**		**initial conc, (immobile)**		**Fract [-]**	**D_W [m^2/s]**	**α [1/day]**
Depth [m]	0-0.4	0.3	0.5	listed in *Table 2*		listed in *Table 2*		0.3	$1.607 \cdot 10^{-9}$	0.4
	0.4-1.5	0.1	0.5	listed in *Table 2*		listed in *Table 2*		0.25		

2001 days were simulated from the 1st of January 2018 until the second successful sampling date (25th of June 2023). The 'Dual-porosity (mobile – immobile, water content mass transfer)' model was chosen as the hydraulic model. Therefore, the Van Genuchten parameters were defined for the mobile and immobile regions as well, together with an exchange factor, as listed in *Table 1*. The hysteresis option – which describes the difference between wetting and drying – was not chosen, since the investigated peat bogs are wet all year round and there is a considerable impact only in case the peat becomes dry (*Simunek et al. 2013*). Boundary conditions had to be chosen that represent the modelled 5-year- long period well. The upper boundary condition was set to the 'Atmospheric Boundary Condition with Surface Layer' option, where the time-series of daily precipitation and the calculated evapotranspiration had to be provided. Since the aim was to model a situation, where the rainwater either evaporates or percolates (so there is no significant runoff), ponding was defined as zero. The lower boundary condition was set to 'Constant Pressure Head'. Longitudinal dispersivity (D_L) was a calibration parameter during the modelling, since its rate was not known. The best fit of the modelled concentrations to the measured ones was reached with it being defined as 0.5 cm.

The upper boundary condition for the solute transport was set as a 'Concentration Flux', which was the time-series of the concentration of major ions in precipitation. The lower boundary was set as 'Zero Concentration Gradient'. The initial conditions were set in the liquid phase concentrations for every modelled ion, which describes the amount of the solute's mass per the volume of water. Observation points were set at every 10 centimetres of the modelled peat column. After running the model, the most recent results for the observation points were taken for the peat bog near Horst, while for Krummesser Moor results for the 1948th modelled day (the day of the sampling: 3rd of May 2023) were considered.

Cumulative Method

A simple model was built in Excel to model the movement of major ions from the precipitation through the peat columns. Since the tracer – in this case the ions – is entering the peat perpendicular to the flow direction throughout the whole cross-section of the column, dispersion can be neglected (*Leibundgut et al. 2009*). The x-axis is the flow direction, while the concentration gradients in the y and z directions equal zero. Assuming that the tracer enters the column at x = 0, the solution to the transport equation of *Leibundgut et al. (2009)* is the following:

$$C(x,t) = \frac{M}{Q} \cdot \frac{x}{\sqrt{4\pi D_L t^3}} exp\left[-\frac{(x-vt)^2}{4D_L t}\right] \tag{7}$$

Where: M = The mass of the injected tracer [g], Q = Volumetric flow rate through the column [m^3/year], x = Distance travelled by the tracer (depth) [m], D_L = Longitudinal dispersivity [m], t = Transit time [days], v = Velocity [m/year].

The mass of the injected tracer can be calculated from the amount of precipitation and the ionic concentrations in precipitation. Calculations were carried out in monthly intervals up until four years before the sampling dates. Effective porosity (which directly influences velocity) and longitudinal dispersivity functioned as calibration parameters and were being changed – in a range based on expert opinion, taking all the properties of the sampled peat into account – to find the best fit between the measured and modelled profile. The range was between 0.65 to 0.80 for porosity, based on literature about sphagnum peat (*Price et al. 2023*) and the observations during the sampling. In the calibration process the dispersion parameter (P_D) was used instead of D_L, which is calculated by equation (8):

$$P_D = \frac{D_L}{vx} = \frac{\alpha_L}{x} \tag{8}$$

Evaporation causes the enrichment of solutes in the soil during rainfall and after infiltration in shallow groundwater (*Sreedevi et al. 2022*). Due to evapotranspiration, recharge is around 2.5 to 3.5 times lower than the amount of precipitation in the area, which results in the enrichment of ions in the infiltrated water. In the top layer the rate of enrichment varies due to the fluctuation of the evapotranspiration between the summer and winter period. To include the process of enrichment in the modelling, a factor was introduced. The cumulated calculated concentrations at each depth were multiplied by an enrichment factor. At the bottom of the modelled peat column, the factor was calculated by the equation (9) from the yearly precipitation and evapotranspiration (*Leibundgut et al. 2009*):

$$Enrichment_{bottom} = \frac{1}{\frac{P_{yeraly} - ET_{yearly}}{P_{yearly}}} + Factor \tag{9}$$

A factor could be added to the calculated enrichment, so that the amount of enrichment can be increased for those ions, where it plays a bigger role. At the surface, it was possible to add an enrichment factor or leave it at zero. From the surface until the bottom of the column, the rate of the enrichment was interpolated between the two given factors. While the rate of the enrichment is almost constant below one meter, on the surface its factor can vary between one and five. While ions get enriched due to evapotranspiration, isotopes are quasi-insensitive to evaporation. Therefore, the concentration of isotopes in the investigated peat column was calculated with a different model.

Modelling for isotopes

Małoszewski et al. (1983) applied a sine-curve analysis for the seasonal variations in precipitation and subsurface sources of the concentrations of isotopes. From this analysis, a model is described to determine subsurface water transit times. The sine-curve theory can also be used to describe soil hydraulic diffusivities (*DeWalle et al. 1997*).

A seasonal sine-curve model was fitted to the measured oxygen-18 and deuterium concentration fluctuations by using periodic regression analysis:

$$\delta(z) = \delta_A \cdot e^{z/d} \cdot sin(\omega \cdot z + \varphi_0) + \delta_{00} \tag{10}$$

$$f(z) = f \cdot e^{z/dv} \tag{11}$$

Where: δ_A = Amplitude, z = Depth of the sample [m], d = Attenuation factor, δ_{00} = A quasi-constant isotopic value, f = Frequency corresponding to the seepage velocity, ω = Angular frequency (ω=2πf), φ_0 = Variable, describing the phase shift, calculated as:

$$\varphi_0 = arcsin\big((\delta_0 - \delta_{00}) \,/\, \delta_A\big) \tag{12}$$

Where: δ_0 = the isotope value at t=0, δ_A, f, d, δ_0, δ_{00} and d_v can be fitted either manually or via several standard optimizing methods.

RESULTS AND DISCUSSION

In this section, the results of the climatic recharge calculation, the modelling by the cumulative method, by Hydrus and by the isotope model are described.

Groundwater Balance Method

From the time-series of precipitation and the calculated evapotranspiration, monthly rates of recharge were derived. The average yearly rainfall in the investigated period between January 2018 and June 2023 was 621 millimetres, while the evapotranspiration was 428 millimetres. The yearly recharge ranged between 36 millimetres (in 2018) and 317 millimetres (2021), with an average of 193 mm/year in the investigated period. The fluctuation of the monthly precipitation and evapotranspiration is depicted in *Figure 6*. The periods when evapotranspiration exceeds precipitation are in the growing season, which results in the lowering of groundwater tables.

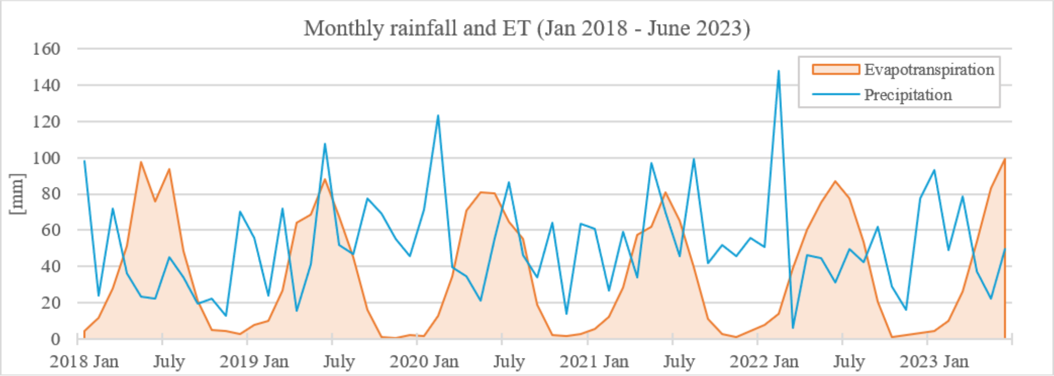


Figure 6. Monthly rainfall and evapotranspiration (ET) of the study area for the climatic water balance
6. ábra. Havi csapadékmennyiség és evapotranspiráció (ET) a vizsgált területen

Modelling with Hydrus 1D

Initially, the goal of the modelling with Hydrus was to reproduce the measured concentration profiles and determine the soil and solute parameters and the recharge. However, since there was a problem with the sampling at the peat bog near Horst (which was either the mixing of the sampled water column due to the dislocation of the tip of the sampling tube, or the not fine enough sampling resolution – or both), the aim of the modelling changed. It is also possible, that the solute concentrations in the peat are influenced by a lateral groundwater flow. As for Krummesser Moor there must be an external stream and/or groundwater inflow indicated by the high level of the measured concentrations. Therefore, the following modelled concentration profiles demonstrate how does the concentration change in the peat column based on the precipitation, the calculated evapotranspiration and the ionic concentration inputs from the rainfall with the chosen soil and solute parameters. The results show how would an ombrotrophic bog's depth profile look like with the defined characteristics.

The modelling results were the most sensitive to the initial concentration and to the longitudinal dispersivity (D_L). The initial concentrations had to be set for every ion, which are listed for the mobile region (which equal the average measured concentration for every ion) and immobile region as well in *Table 2* for the peat bog near Horst. As for the dispersivity, different values were tried. *Figure 7* depicts how does the modelled chloride concentration start to deviate from the given initial concentration and how does it start to show the actual concentrations by depth, while applying the dispersivity that gave the best fit for the modelled concentration depth profile. The modelled concentrations are reliable for every depth from around two years after the start date of the modelling (1st of January 2018).

Table 2. Initial concentration of solutes for the modelling
2. táblázat. Az oldott anyagok kezdeti koncentrációja a modellezéshez

Horst	**Initial concentration (mobile) [mg/l]**	**Initial concentration (immobile) [mg/l]**
Chloride	6.5	6
Sulphate	0.3	0.28
Ammonium	2.9	2.5
Sodium	4.7	4.5
Potassium	2.2	2
Calcium	11.8	11.5
Magnesium	2.3	2.5

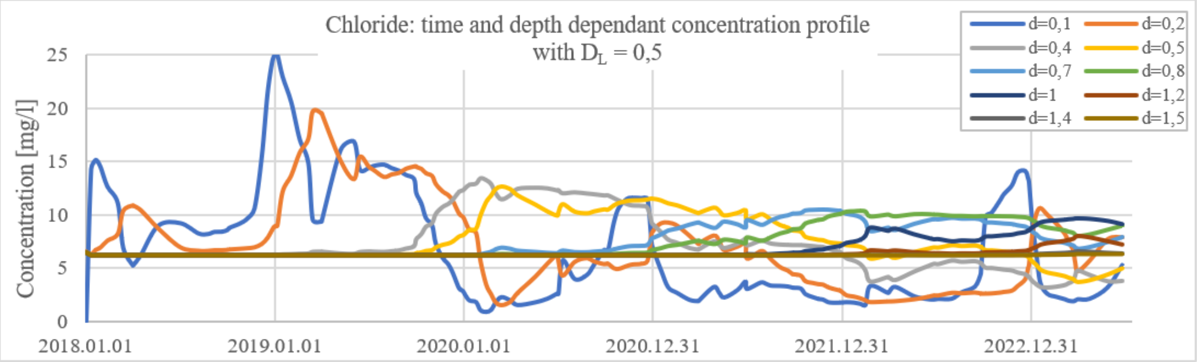


Figure 7. Concentration time series of chloride in the groundwater at the observation points of the investigated soil column at Horst. 'D_L' [cm] is the longitudinal dispersivity and 'd' [m] is the depth below the surface.
7. ábra. A horsti talajvíz megfigyelési pontokon modellezett kloridion koncentrációinak idősorai. A 'D_L' [cm] a hosszirányú diszperzivitás, 'd' [m] pedig a felszín alatti mélység

Figure 8 depicts the modelled chloride concentrations based on the different longitudinal dispersivities. While the modelled concentrations are around the measured ones, the modelled results have a much wider range. The Root Mean Square Error (RMSE) for the measured and modelled concentrations is 1.44. The most likely reason for this is the error during the sampling process and the mixing of the sampled groundwater column. On the other hand, the modelled concentration profile depicts the seasonal variation of chloride well. Based on the fluctuations, the modelled 1.5-meter-deep peat column contains 2.5 years of recharge assumed on the basis of the 3 positive and 3 negative peaks. This would indicate a yearly recharge of around 420 millimetres if the porosity is considered as 70%. The modelled concentration profiles of the other ions also show the same number of peaks.

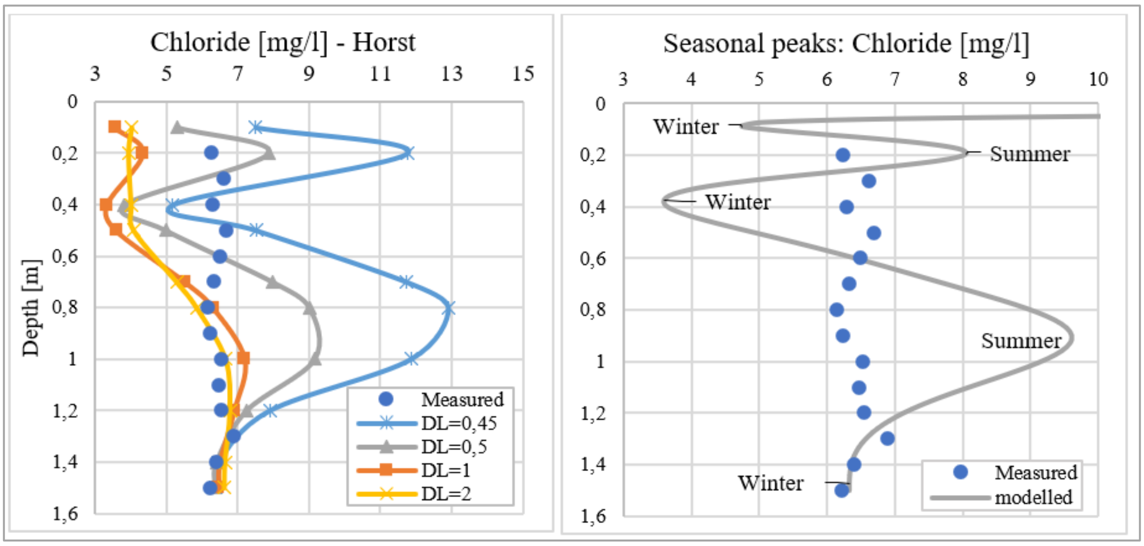


Figure 8. Modelled concentration profile of chloride at Horst with different dispersivity parameters
8. ábra. A kloridion modellezett koncentrációprofilja Horstnál különböző diszperzivitás paraméterekkel

Similarly to the results of the cumulative method, the reduction of sulphate can be assumed from the modelled concentration profile with Hydrus. On the bottom of the modelled column, the modelled concentrations approach the measured ones, but this is only due to the lower boundary conditions and the initial concentration. Since chemical reactions that could represent the reduction of solutes were not applied in the model, the modelled sulphate concentration in the peat and groundwater column are occasionally more than 10 times higher than the measured, reduced ones and they change based on the input concentrations from the rainfall and the set soil and solute transfer parameters.

Ammonium and sodium behave in a similar way to chloride in the model. While the range of the modelled concentrations is significantly wider than of the measured ones, they provide an estimate of the fluctuations of the measured profile well. The longitudinal dispersivities that give the best estimate are D_L=0.45 and D_L=0.5, which can be seen in *Figure 9*. The difference in the range is most probably due to problem with the sampling device during the sampling, where the samples belonging to certain depths got mixed with water pumped up vertically. However, the fact that the model was run based on the presumption of a continuous input of solute concentrations from the precipitation, and it stayed around the average of the measured concentrations after modelling 5 and a half years of recharge proved that the bog near Hort is indeed ombrotrophic and it does not have any significant secondary groundwater input sources.

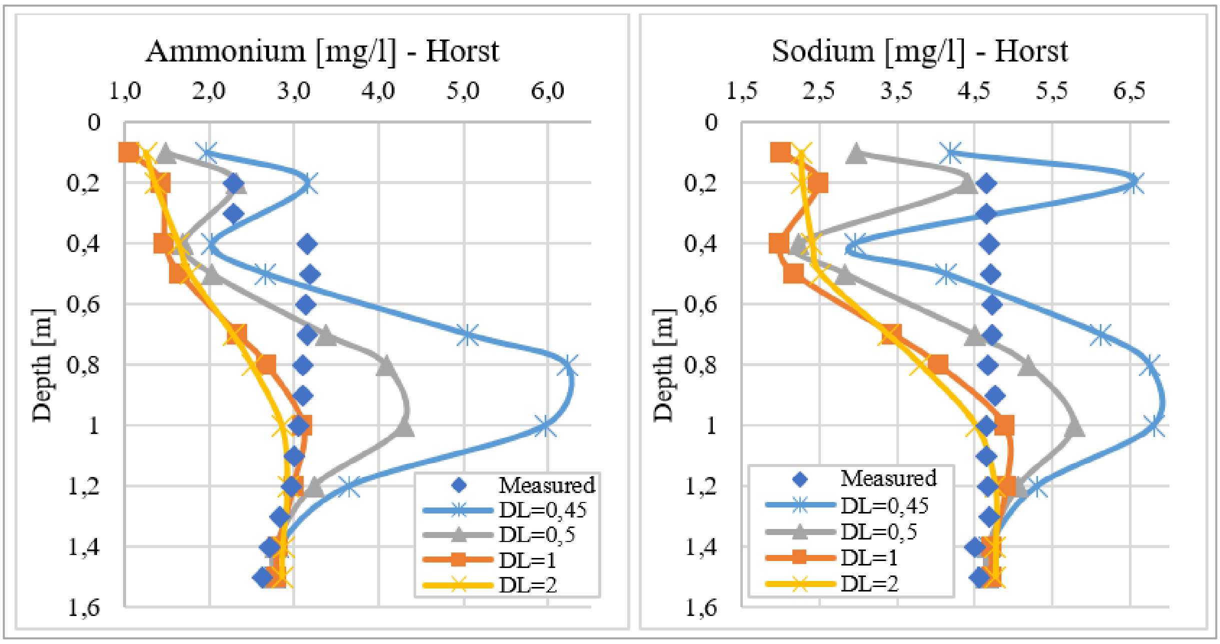


Figure 9. Modelled and measured concentration profile of ammonium and sodium at Horst with different longitudinal dispersivity (D_L) parameters

9. ábra. Ammónium és nátrium modellezett és mért koncentrációprofilja Horstnál különböző longitudinális diszperzivitás (D_L) paraméterek mellett

Potassium, calcium and magnesium profiles are underestimated by the model. These are the same ions which were not estimated well with the cumulative method. Cations are not as good tracers as anions in general, as they react with the organic material content of the peat and with other compounds more frequently. However, it is more likely, that the real explanation for the discrepancy is that these cations also have an additional input source aside from the rainfall.

The amount of yearly recharge was evaluated based on the propagation of the modelled concentration profile. However, this method would only be reliable if the modelled concentration profile would provide a good estimate of the real concentrations of the peat and the measured values – which was not the case in this study. These results would indicate a recharge of 250 to 300 millimetres per year.

While the modelled concentrations were in the range of the measured values in the case of the samples from Horst, for Krummesser Moor it was not possible to reach the range of the measured solute concentrations. As mentioned before, this is because the peat bog at Krummesser Moor has an additional inflow aside from the precipitation. By simply using the precipitation and the ionic concentrations in the precipitation as an input, the range of the modelled concentrations is 5 to 10 or even more times lower than the measured concentrations, even if the initial concentration is set as the average of the measured values.

Cumulative Method

As a result of the calibration process, the velocity – and thus recharge – was 240 mm/year for Krummesser Moor which is 320 mm/year when porosity is considered (which was considered as 0.75). As for Horst, the velocity (and recharge) was 280 mm/year, which is 370 mm/year taken the porosity of 0.76 into consideration. The calculated velocity, which takes the porosity into account visualises the recharge that belongs to one year in the soil column.

The dispersion parameter and the two enrichment factors (on the surface and at the bottom of the peat column) were changed for each ionic compound separately. The surface enrichment should have been between 1 and 5, and around 2.5-3.5 in the bottom. To match the range of the measured concentrations with the modelled ones, the factor of enrichment had to be out of this range for some of the ions, mostly for the cations. In these cases, the enrichment factor only conceals the discrepancy between the measured and modelled concentrations. A high enrichment factor therefore mostly implies an external source and means that the solute does not only originate from precipitation.

The results of the model prove that there must be an external input (stream or groundwater) at Krummeser Moor. Ionic concentrations are ten times higher in some cases than at the peat bog near Horst and the results of the simulation do not correlate with the measured concentrations. Therefore, it was only possible to match the range of the measured concentrations with the model by adding a factor with a high value. The factor – which was originally meant to represent the enrichment – was only in a reasonable range for ammonium and potassium. Assumptions can be made that groundwater indeed comes to the surface from a layer with salt depositions around Krummesser Moor.

As for the peat bog near Horst, the modelling results matched the range of the measured concentrations for chloride (RMSE: 0.50), sulphate (RMSE:1.77), ammonium (RMSE: 0.25) and sodium (RMSE: 0.34). The factor had to be increased for potassium (RMSE: 0.27), calcium (RMSE: 0.83) and magnesium (RMSE: 0.35) to a degree which cannot be explained with the enrichment from evapotranspiration (the calculations of the RMSE were carried out using the modelled calculations with these high enrichment factors). Therefore, it can be assumed that these cations have an additional, external input source, possibly from the direction of Pinnsee.

Chloride concentrations in the rainfall are mostly between 0 and 2 mg/l and they increase up to 6-8 mg/l around 2-3 times during the colder part of the year. Two additional concentration peaks were observed during the period of 2016-2022 with 20 and 14 mg/l (these peaks cannot be observed from *Figure 4*, only from the full time-series of chloride concentrations in the precipitations, since the figure only shows the average monthly concentrations). The range of the concentration of chloride at the peat bog near Horst matches this interval when the enrichment by evapotranspiration is considered, therefore the factors chosen to represent it are also in a reasonable range. As for Krummesser Moor, the measured values in the top layer could be explained by enrichment, which is also shown by the chosen surface enrichment with the value of 4, but deeper in the ground it increases in a way that a factor that is 5 times higher than the expected enrichment had to be chosen to fit the measured concentrations. This implies an external source for chloride at Krummesser Moor. Since the measured concentrations at Horst are in a very small range, it was only possible to estimate them with a high P_D value. Therefore, the modelled concentrations don't show the small variations that the measured values do. The factor of enrichment and the chosen calibration parameters for chloride are listed in *Table 3* and the measured and modelled depth-profile of the solute is depicted in *Figure 10*.

Table 3. Chosen calibration parameters for chloride

3. táblázat. A kloridion koncentrációjának modellezéséhez használt kalibrációs paraméterek

Calibration variables	**Chloride**	
	Krummesser Moor	**Horst**
v [m/year]	0.24	0.28
Porosity [-]	0.75	0.76
v_p [m/year]	0.32	0.37
P_d	0.1	0.15
Enrichment: surface	4.0	0.9
Enrichment: bottom	15.52	2.75

Peat is a highly reducing environment, where sulphate is also reduced and converted into hydrogen sulphide. This chemical process cannot be modelled on the basis of solute transport. In case of Krummesser Moor, sulphate levels are completely reduced below 60 centimetres below the surface, while the model keeps an elevated concentration. In the case of Horst, sulphate is reduced throughout the whole sampled column, thus the modelled results overestimate the concentrations. Sulphate concentrations in the rainfall (mostly between 0.5 and 2.0 mg/l) are also significantly lower than in groundwater (*Scheytt 1997*), which can give an additional explanation for the difference in the multitude of the sulphate levels at the two different study sites, since Krummesser Moor has an external groundwater and/ or stream input according to the assumptions made on the basis of the data. Furthermore, sulphate commonly has dry depositions and it can be enriched by fertilizers, thus results of models that only use the concentrations in precipitation as an input are not necessarily reliable for the anion, even if they include chemical reactions (*Scheytt 1997*).

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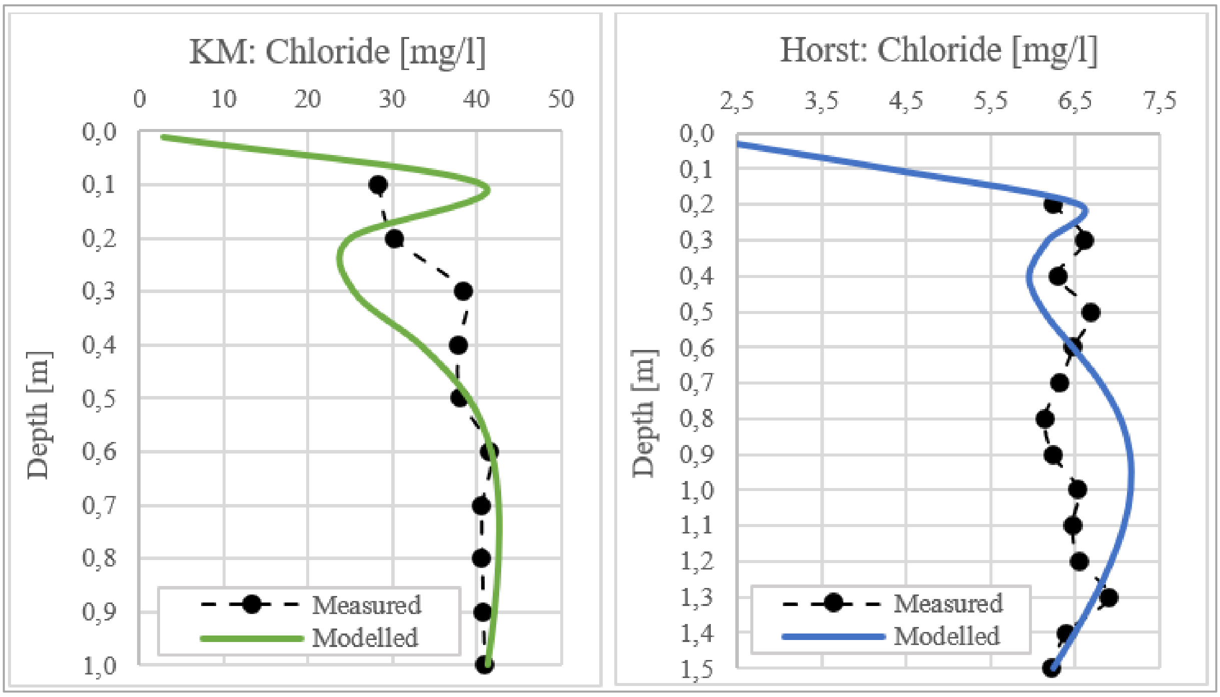

Figure 10. Measured and modelled concentration profile of chloride at Krummesser Moor (KM) and at the peatland near Horst with the cumulative modelling method

10. ábra. A kloridion mért és modellezett koncentrációprofilja Krummesser Moor-nál (KM) és a Horst melletti tőzeges területen, a kumulatív modellezési módszerrel

As for the concentration of ammonium, the upper 30-40 centimetres in the soil are still controlled by atmospheric processes, therefore the model can approximate the measured concentrations well. Below this top layer, reactions start to happen and the model deviates. In the case of Krummesser Moor, a high ammonium concentration is maintained based on the model, but in reality – and also according to the samples – the concentration is lowered due to the degassing of ammonium, but as the process of nitrification decreases with depth due to the reduction of oxygen availability (this process was measured during sampling as well), it reverts to an elevated level where conditions are favourable for the accumulation of ammonium. Since the model does not include chemical reactions, the concentration stays high. Aside from the lowered concentration in the transition zone, the model gives a good estimate of the concentration profile of ammonium, with reasonable enrichment factors. The first two peaks in the top layer are also matched with the model. As for Horst, the model gives a good estimate for the measured concentrations and the calibrated enrichment factors are also reasonable.

The chosen calibration parameters for ammonium are listed in *Table 4* and the measured and modelled depth-profile of the solute is depicted in *Figure 11*.

Table 4. Chosen calibration parameters for ammonium

4. táblázat. Az ammónium modellezéséhez választott kalibrációs paraméterek

Calibration variables	**Ammonium**	
	Krummesser Moor	**Horst**
v [m/year]	0.24	0.28
Porosity [-]	0.75	0.76
v_p [m/year]	0.32	0.37
P_d	0.01	0.08
Enrichment: surface	2.4	1.5
Enrichment: bottom	3.02	2.75

Sodium concentrations are around 10 times lower in precipitation, then in groundwater in the region (*Scheytt 1997*), which explains why the enrichment factor had to be increased significantly for Krummesser Moor to match the measured concentrations, with the assumption of the external input source. At Horst, the model matched the range of the measured concentrations and the chosen enrichment factors are also reasonable.

High potassium concentrations (>3.0 mg/l) can be an indicator for anthropogenic effects (mainly agricultural use and fertilizers), as its level is naturally very low both in precipitation and in groundwater (*Arbačauskas et al. 2023*). This explains why the factor had to be slightly increased above the expected enrichment in the case of both sites to be able to match the range of measured potassium concentrations. This also means, that in the case of this solute, the factor does not indicate a high enrichment by evapotranspiration, but a moderately high additional input.

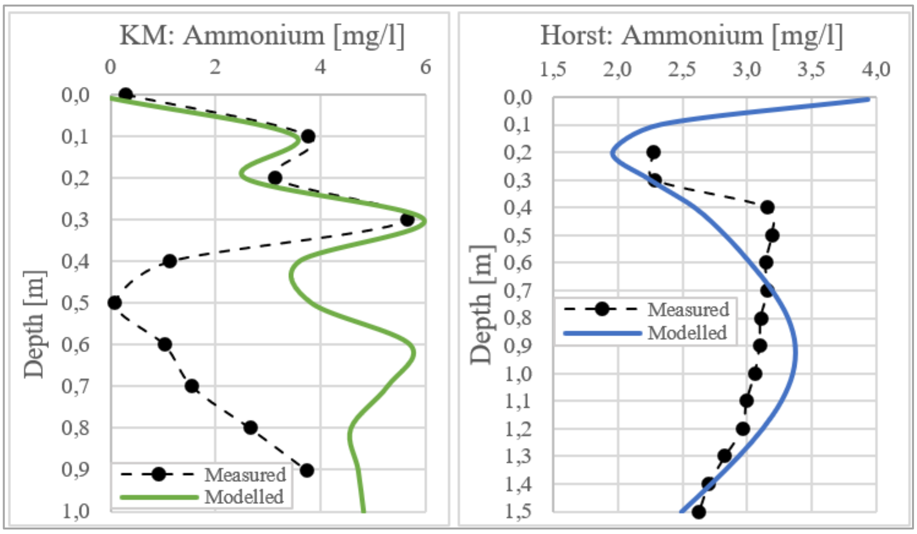

Figure 11. Measured and modelled concentration profile of ammonium at Krummesser Moor and at the peatland near Horst
11. ábra. Az ammónium mért és modellezett koncentrációprofilja Krummesser Moor-nál (KM) és a Horst melletti tőzeges területen, a kumulatív modellezési módszerrel

Calcium concentrations are also significantly lower in precipitation (around 0.1 to 0.4 mg/l), than in groundwater and it can have high agricultural inputs (*Scheytt 1997*). This explains why the factors had to be increased for both study sites. It again leads to the conclusion that Krummesser Moor must have an external input source, but in this case the peat bog near Horst also must have an input of calcium from somewhere else as well, probably from the groundwater from the direction of Pinnsee.

The case and behaviour of magnesium is similar to calcium, but the extent of the external input is presumably smaller, as the factors are 2 to 4 times smaller. The magnesium concentration of the precipitation is also similar to calcium, ranging between 0.1 and 0.3 mg/l.

The extent of the concentration peaks of the measured values does not show a general increasing or decreasing pattern with depth. However, the modelled concentration profile does, as the extent of both the positive and negative peaks are decreasing with depth. This is probably due to the dual porosity in peat, which is not considered in this model. In reality, smaller pores hold onto groundwater like a sponge and the main flow is only through the bigger macropores.

Isotopes

For oxygen-18, the recharge is 162.54 mm/year with an RMSE of 0.048, while for deuterium the result is 172.79 mm/year with an RMSE of 0.376. The fitted sine-curves can be seen in *Figure 12* for both isotopes.

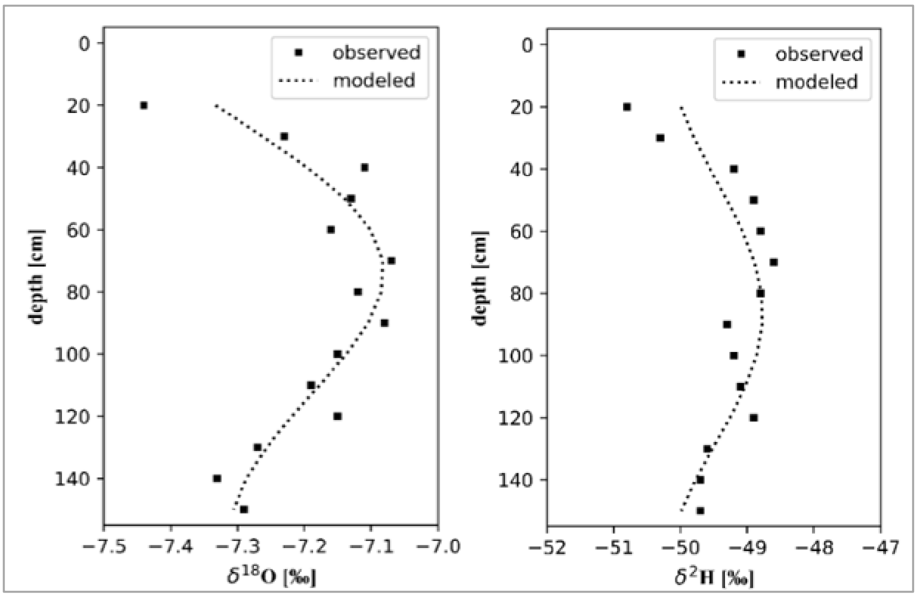

Figure 12. Fitted sine-waves for the measured oxygen-18 and deuterium concentrations
12. ábra. Illesztett szinuszhullámok a mért oxigén-18 és deutérium koncentrációkhoz

Discussion

The estimates of groundwater recharge gained with the different methods varied greatly. Results are summarized in *Table 5*. The calculated climatic water balance must be treated with caution as well, as the calculated evapotranspiration depends on many factors. These factors are either measured or estimated, therefore the margins of error can superimpose upon each other. While the values of soil parameters were chosen with great care, the reliability of recharge estimates could be improved by defining the necessary parameters based on the analysis of peat samples from the investigated locations. Ideally at least those parameters should be measured to which the model results are sensitive: the ratio between mobile and immobile pores, their respective water content and porosity. Dual porosity can influence the flow and the spreading of water and solutes and therefore also the estimate of recharge made with these methods to a high extent. While its effect was considered in Hydrus and its required additional parameters were set, they were only estimated on the basis of observations.

Table 5. Final estimations of groundwater recharge based on different methods
5. táblázat. A különböző módszerekkel becsült felszín alatti víz utánpótlás értékei

Study site	Recharge estimations [mm/year]					
	Calculated	Modelled				
	Climatic recharge	Cumulative method	Hydrus		Isotopic model	
			Method I	Method II	O18	Deuterium
Krummesser Moor	193	240	-	-	-	-
Peatland near Horst		280	420	250-300	162.54	172.79

CONCLUSIONS

While the inaccurate or not precise parameterisation of the soil and solute can result in inaccurate recharge estimates, the main problem in this study was with the sampling method and the sampling locations. Due to the shortage of time, samplings could not be repeated. Results of the modelling were greatly underestimating the measured concentrations at Krummesser Moor, which means that the peat bog must have an external input source. This posed a problem to this study, because only those peat bogs are representative for the regional recharge from precipitation that are ombrotrophic. Moreover, it was found from literature that around the site there is a layer with salt depositions close to the surface, which can potentially influence solute concentrations. As for Horst, the area seemed suitable, although according to ongoing research there might be lateral groundwater inflow in the direction of the investigated peat bog from Pinnsee (*Roehl 2023*). However, results of the modelling by Hydrus 1D do prove that the bog is ombrotrophic, and that the extent of this lateral inflow component is probably negligible.

It is also possible, that the chosen sampling resolution was not fine enough. If a porosity of 75% and a yearly recharge of 200 mm is assumed, then one meter of peat would hold four years of recharge, thus a full yearly cycle of winter and summer peaks would have had to be found in a 250 mm thick layer. The sequence of peaks in this case is very small, therefore a much smaller sampling resolution would be required: 2 to 2.5 centimetres, instead of the applied 10 centimetres, to have a more reliable estimate of every seasonal peak by at least 5 points.

To make estimates of groundwater recharge would be vitally important for sustainable groundwater management and for the calculation of sustainable yield, as a base for the provision of water rights. Ion and isotope profile methods are indeed promising options, but the acquirement of their input data – the sampling process – must be optimized and executed precisely and sampling locations must be chosen with greater care.

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