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Water and (bio)chemical cycling in gravel pit lakes: A review and outlook

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ABSTRACT

The world produces 1.7×10^8 metric tons of gravel and sand per year (USGS, 2015) creating many gravel pit lakes that change the morphology and drainage pattern of catchments. Gravel pit lakes abruptly intersect the geologic layering creating an environment where surface and groundwater will interact and where elaborate food webs can develop. Here we preview previous work on gravel pit lakes and compiled a comprehensive hydrochemical database to compare the chemistry of gravel pit lake water with other types of surface and groundwater. Water budget calculations confirm that gravel pit lakes cause freshwater loss in temperate and Mediterranean climates where surface water evaporation is larger than the actual evapotranspiration of vegetated land that was replaced by the gravel pit lakes. Groundwater fed gravel pit lakes where evaporated water is replaced by groundwater are especially sensitive to climate change.

The gravel pit lakes included in this review have a relatively low acidity and high alkalinity most likely caused by weathering and leaching of carbonates in the catchment. The inflow of groundwater is a key process in gravel pit lakes with important consequences. The creation or presence of the gravel pit lakes may induce fluctuation of the up stream water table which enhances groundwater flow and redox reactions in the soil. Groundwater rich in dissolved elements typically meets more alkaline water in gravel pit lakes enhancing the precipitation of metal oxides, calcite and other composite minerals including phosphorus (P), calcium (Ca) and carbon (C). Gravel pit lakes provide many different ecological habitats increasing the biodiversity in typically an agricultural or urban setting. Plant and animal species observed in gravel pit lakes consists of phytoplankton, zooplankton, micro plankton, macrophytes, fish and birds similar to natural lakes but the fact that gravel pit lakes may be only groundwater fed, or instead in open contact with rivers causes large variations between the ecosystem of different lakes. Plants and animal species take part in the chemical cycling of gravel pit lakes by, among others, uptake of atmospheric carbon dioxide (CO_2) and nitrogen (N_2), of dissolved compounds including bicarbonate (HCO_3^-), iron (Fe) and manganese (Mn); of elements including phosphate (P) and Fe from lake sediments, and carbon mineralization and burial. Gravel pit lakes may contribute to denitrification of groundwater as N is consumed by plankton, but they may also enhance the mobilization of soil bound compounds like potentially toxic (trace) metals released from aquifer sediments. The creation of gravel pit lakes provides more available sites for carbon burial but once deposited on the lake bottom, metals and other elements may be released again due to redox cycling, influenced by climatic or land use change. Gravel pit lakes are water bodies of recent formation and so far only a few different settings have been studied in detail compared to other types of natural and man made lakes. From this review it is evident that gravel pit lakes are hydrochemically most similar to so called 'marl lakes' or 'nutrient rich' lakes. Key areas for further research include the study of gravel pit lakes in other settings to better separate the similarities and differences between natural and gravel pit lakes. Also the feedback mechanisms between change in land use and climate, ground and lake water chemistry ecological functioning and use of the gravel pit lakes need to be addressed.

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1. Introduction

Our modern society uses an enormous amount of sand and gravel to construct buildings, highways and anything made of concrete. According to the USGS (2015a, b) the world produces a total of 1.65×10^8 metric tons of sand and gravel per year (Table 1) with the USA, Italy, and Germany as the three main producers. Gravel is produced from natural gravel deposits such as streambeds, beach deposits or alluvial fans. Where the gravel pits are excavated at or below the water table, they fill up with groundwater and become artificial lakes. Since gravel pit lakes follow geologic layers, there are often many gravel pit lakes close to one another significantly influencing the landscape and hydrology of a region. For example in Maine USA, 34 active and former gravel pits cover 26% of the aquifer surface (Peckenham et al., 2009). In the Netherlands, 500 gravel pit lakes give this country the highest production of gravel and sand per surface area of 108 t per km² (Table 1). In Italy, the gravel pit lakes along the coast near Ravenna increased the open water surface in the catchment by 6% from 1972 to 2012 and the excavation is not yet finished (Mollema et al., 2012). In these two examples, as in many other areas, freshwater is a limited resource due to a limited amount of precipitation, or an irregular distribution of precipitation throughout the year. Drainage towards the sea to prevent flooding in low lying areas such as polders and coastal zones may furthermore limit the amount of freshwater, as does salt water intrusion. In densely populated areas there may also

be a lack of storage space for fresh water. Over the next decades, these pressures are expected to increase due to climate change and sea level rise (e.g. Oude Essink et al., 2010). Gravel pit lakes play a role in the hydrological cycling of these above mentioned areas, letting freshwater disappear into the atmosphere by evaporation (E), but they may also form a possible storage place for freshwater (Mollema et al., 2015a). McDonald et al. (2012); Seekell et al. (2013), and Verpoorter et al. (2014) showed that lakes, including small ones, cover a much greater portion of the Earth's land surface (~3.7%) than previously believed. This has an influence on all chemical and hydrological budgets: lakes store substantial amounts of carbon (C) in their sediments and greenhouse gas (carbon dioxide (CO₂) and methane (CH₄) emissions from lakes may almost completely offset the terrestrial carbon sink (e.g., Bastviken et al., 2011; Tranvik et al., 2009; Wetzel and Likens, 1991). Lakes play an important role in the (trace) metal cycles of soils in the catchment (Mollema et al., 2015a; Mollema 2016). Research demonstrates the sensitivity of lakes to climate and showing that physical, chemical, and biological lake properties respond rapidly to climate related changes (ACIA, 2004; Rosenzweig et al., 2007). Lakes are therefore called 'sentinels' of current climate change (Adrian et al., 2009) but it also means that lake sediments form valuable historical archives for natural and anthropogenic environmental changes. Fossil diatom assemblages may indicate changes in the input of nutrient rich water (Sayer and Roberts, 2001; Sayer et al., 2010a) and C isotopes in Daphnia in sediments may reflect methane

Table 1
Sand and gravel production data from the highest producing countries as reported in *, USGS, 2015a, b. ** CBS, PBL, Wageningen UR, 2016. Surface area of countries from <http://data.worldbank.org/indicator/AG.SRF.TOTL.K2>, consulted on 16/07/2014.

	Mine production in 2012 [thousand tonnes]*	Mine production in 2013 [thousand tonnes]*	Mine production in 2014 [thousand tonnes]*	Production per land surface area (2014) [thousand tonnes per km ²]
USA	49,500	62,100	75,000	0.008
Italy	19,800	16,400	16,400	0.054
Germany	7770	7500	7500	0.021
Australia	5600	5500	5500	0.001
France	5000	6290	6300	0.011
United Kingdom	3800	3760	3800	0.016
The Netherlands	4500**	4600**		0.108
World (rounded)	140,000	152,000	165,000	0.001

availability in lake water (Schilder et al., 2015). The relative abundance of C and nitrogen (N) and their isotopes points to the source of organic matter in the form of algae and vegetation while particular organic molecules of sterol and stanol reveal the presence of sewage and distinguishing that from vegetation sourced organic matter (Vane et al., 2010). Lakes in general, however, are not mentioned in the latest reports on climate change (IPCC, 2013) and gravel pit lakes do not (yet) appear in databases of lakes (ILEC, 2014). Although in some areas (e.g. River Trent, Attenborough lakes, UK), the extraction of gravel from river beds has occurred almost continuously since Roman times, most gravel pit lakes that formed due to gravel extraction are less than hundred years old, young compared to most natural lakes (Bridgland et al., 2014; Mollema, 2016; Muellegger et al., 2013). Gravel pit lakes are therefore a relatively new environmental phenomenon, and little work has been done to investigate long term environmental concerns (Fang et al., 2009, 2010; Miller et al., 1996; Shevenell et al. 1999). Although the recycling of concrete has become common (CMRA, 2014), new gravel pits are still being created. Because of new uses for gravel and sand, for example as proppant in hydraulic fracturing, the demand in the USA for sand has increased more than 50% between 2012 and 2014 (Table 1, USGS, 2015a; 2015b).

After excavation activities have ceased, gravel pit lakes can be used for canoeing, fishing (Zhao et al., 2015) and other aquatic sports, such as long distance swimming (Standiano Lake, Ravenna, lastour, 2014). However many older gravel pit lakes are unsafe to use in this way because of the steep edges, irregular bottom topography and upwelling of deep cold water causing people to drown (e.g. Neilson, 2013). Eutrophication can affect water quality in gravel pit lakes in a negative way with blooms of cyanobacteria (Codd, 2000). In the tropics, open water bodies often are places where diseases are transmitted, for example schistosomiasis (also called bilharzia, snail fever, or Katayama fever) which have part of their lifecycle in water; or malaria which is transmitted by water related vectors (WHO, 2014). Creating lakes where there used to be an aquifer may increase the risk of occurrence of these water borne illnesses. Gravel pit lakes offer many ecosystem services especially but not only if they become a nature reserve as the Attenborough Nature Reserve in Nottinghamshire, Derbyshire, UK that received the designation of a Site of Special Scientific Interest (SSSI) but that was also listed as one of the top ten eco destinations in the world (Andrews and Kinsman, 1990; BBC, 2007). Where many gravel pit lakes occur in the same area with replication of size, depth, geological setting and more, they can be useful for ecosystem scale research and comparisons (e.g. Cross et al., 2014; Jones et al., 2016; Vane et al., 2010). The artificial lakes offer also the possibility for building waterfront houses as for example in the Cotswold Waterpark, Gloucestershire, UK (Waterpark, 2014). Gravel pits have been used or considered for use as a place to dispose of wastewater or dredging sludge (in Michigan, Blener, 1979; Switzerland, Lemann, 2008; The Netherlands, Deskundigencommissie zandwinputten, 2009; Implementatieteam besluit Bodemkwaliteit, 2010; Delleur, 2010) or debris from land clearing and even salt (Peckenham et al., 2009). Gravel pit lakes may be used for artificial recharge and recovery of drinking water as has been done in The Netherlands (Mollema et al., 2015a) and is being considered in the USA (Fang et al., 2009, 2010). They may also serve as flood retention areas where particulate matter settles (Cross et al., 2014). With the fast technological development of alternative energy sources such as solar energy, the need for (seasonal) storage of heat is rising and gravel pit lakes may be one of the places to consider for heat storage (Novo et al., 2010).

In this review, we present a synthesis of past research on the role of gravel pit lakes and discuss current perspectives for new research in this field. Sometimes this same type of lake is referred to in the literature as 'urban', 'shallow', 'hypertrophic' or 'nutrient rich' without referring to their origin. In this paper however we use the term 'gravel pit lakes' to indicate artificial lakes that formed due to excavation of gravel or coarse sand. We evaluate the effect of climate and land use change on the water budget and specific hydrochemical processes occurring in gravel pit lakes. We give examples of values for hydrological cycling of gravel pit lake systems in temperate and Mediterranean climate zones,

obtained from a case study in the Netherlands (Mollema et al., 2015a) and in Italy (Mollema et al., 2015b). We compare the hydrochemical characteristics of gravel pit lakes with published hydrochemistry data of different types of natural lakes and other types of surface waters. The fact that hydrochemical studies are published in an enormous spread of scientific journals in the fields of hydrology, environmental sciences, geochemistry, hydrogeology, ecology, and biology and the fact that many different units of measurements are used to express concentration of chemical elements makes it time consuming to compare the hydrochemistry of gravel pit lakes to natural lakes or other types of water. By means of this review we hope to contribute to an understanding of the hydrological, and (bio)chemical cycling in gravel pit lakes, their ecological functioning as well as the effect of multiple gravel pit lakes on a catchment.

2. Geological settings

2.1. Gravel pit lakes versus natural lakes

An important difference with natural lakes is that gravel pit lakes abruptly dissect the geological layering. Natural lakes form typically along particular geologic layers or by tectonic causes. Gravel and sand deposits are very permeable and so gravel pit lakes permit significant exchange of surface water with groundwater. Gravel pit lakes may be relatively shallow with a depth of 2 to 3 m (Cross, 2009) or 7 to 12 m (Mollema et al., 2015b) but they can be as deep as 40 m (Mollema et al., 2015a). Natural lakes can have a depth of up to hundreds of meters and they typically have a relative depth to surface area less than 5%, whereas gravel pit lakes commonly have relative depths to surface area ranging between 10 and 40% (Wetzel and Likens, 1991; Doyle and Runnells, 1997). As a consequence gravel pit lakes have relatively a larger surface area across which interaction occurs with groundwater and/or river water.

The most common annual bottom sedimentation rates in natural lakes range from 1 to 5 mm/year. Thus natural lakes with a depth between 10 and 500 m can be expected to possess a life span between 10^4 and 10^5 years (Löffler, 2003) and are filled up by sand, clay and gravel brought in by rivers, atmospheric deposition and transport of chemicals with groundwater and organic detritus depositing on the bottom. Reservoirs tend to fill up by sediments that are trapped behind dams with rates that typically vary from 0.03 to 1 mm year⁻¹ (e.g. De Vente et al., 2005; Minear and Kondolf, 2009).

Many gravel pit lakes are isolated from rivers and may fill up by atmospheric deposition and influx of minerals in groundwater, and precipitation of organic material and metal oxides on the bottom and occasional slumping of steep edges. Often gravel pit lakes are in relatively flat floodplains, so there is limited inwash of water and material compared to natural lakes with steeper catchments. The inflow of metals in gravel pit lakes with groundwater can be up to 1000s of kg year⁻¹ (Mollema et al., 2015a) but this results in sedimentation rates of only 2×10^{-9} mm year⁻¹. All this suggests that the sedimentation rate into isolated gravel pit lakes is relatively small and these types of gravel pit lakes are likely to last at least a few thousand years.

2.2. Depositional environment

Alluvial fans are one type of geologic deposit that is mined for its gravel and sand. They consist of a fan or cone shaped deposit of sediment built up by streams (Boggs, 1987). Because of the steep topographic gradients in current alluvial fans, lakes typically do not form when the gravel is mined. Instead gravel in current fluvial deposits occurs in different morphological parts of rivers (Boggs, 1987). When these are mined, they often form gravel pit lakes (Fig. 1a). Fluvial streambeds, stream terraces and floodplains all contain gravel that can be mined (e.g. along the Meuse, Netherlands; Mollema et al., 2015a; along Donau River, Weilhartner et al., 2012). In north Europe (Van

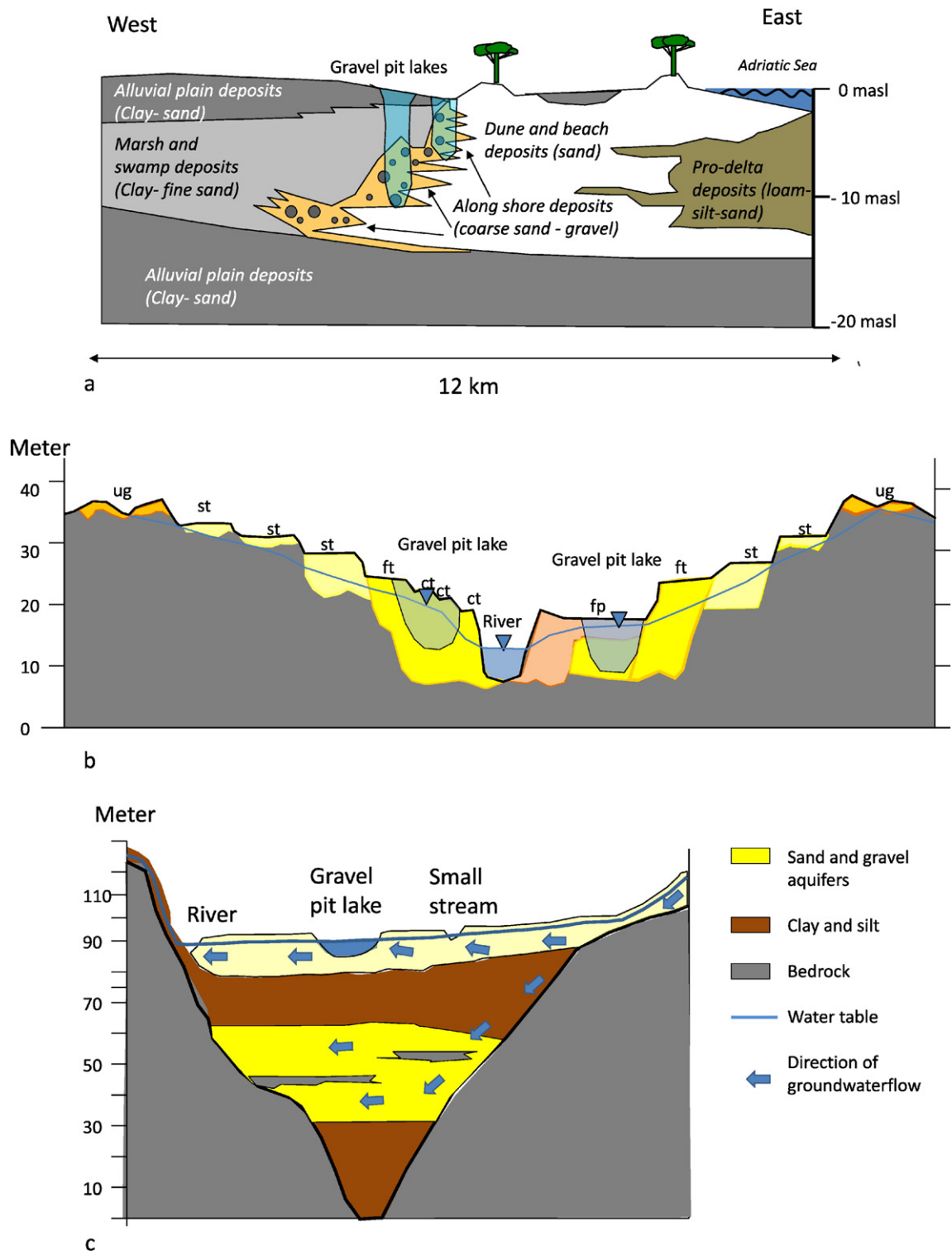


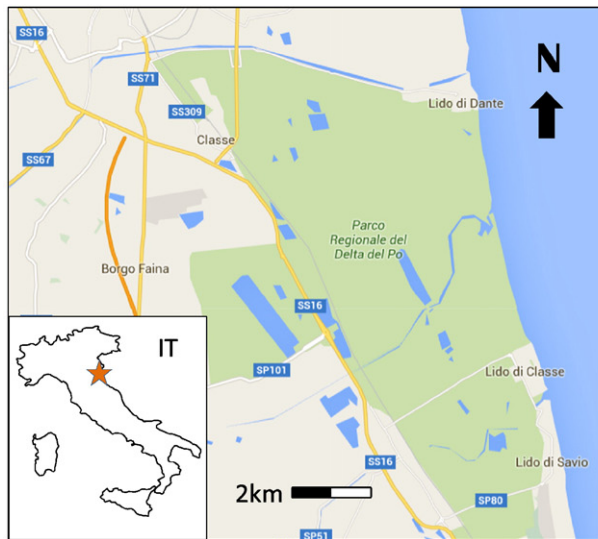
Fig. 1. a. Valley cross-section illustrating a complex sequence of terraces and deposits (upland gravels). The location of gravel pit lakes that would form if the gravel is excavated is indicated in blue. Only the original water table is indicated. Note ct = cut terraces, ft = fill terraces, fp = active floodplain, st = strath terrace, and ug = upland gravels. b. Example of a gravel pit lake excavated in a glacier deposits in a bedrock-valley. c. Holocene beach gravel deposits near Ravenna, Italy, deposited by along-shore now excavated to form gravel pit lakes, about 7 km from the current shoreline.

Balen and Busschers, 2010; Waterpark, 2014), North America (Maine, Peckenham et al., 2009), and Canada (Stephenson et al., 1988) thick accumulations of sand and gravel were deposited in front of advancing glaciers during the ice ages (Boulton, 1986). The gravel was or still is being accumulated in glacial terraces, outwash plains, eskers, and kame terraces (Boulton, 1986) that may form gravel pit lakes when

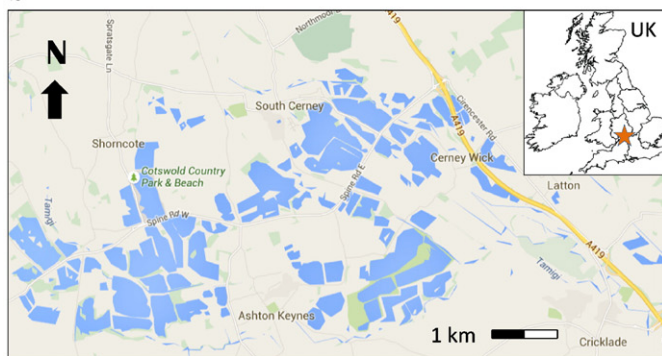
excavated (Fig. 1b). Also currently new gravel deposits are being formed at the margins of glaciers (e.g. Shugar and Clague, 2011) but these deposits are usually above the water table. Both current and fossil (raised) beach deposits may contain gravel (Bluck, 2011) and are mined with gravel pits for example along the coast of the north Adriatic in Italy (Fig. 1c, Mollema et al., 2013a, 2015b). Weathered bedrock is found to



a



b



c

Fig. 2. a Google map of part of the Meuse Valley, south Netherlands that contains about 70 gravel pit lakes (lat 31 U 703349m long E5672291). The inset shows approximate location in the Netherlands (NL). The following types of lakes are indicated: 1. Flow-through gravel pit lake, separated from river 2. Gravel pit lakes in active and abandoned meanders. 3. Gravel pit lake in open connection to a river. b. Google map of gravel pit lakes along the Adriatic coast (Italy lat. 33°28'1595, long. E49°15'220). The lakes are aligned along ancient beach deposits parallel to the current coast line, 5–7 km inland. The inset shows location in Italy (IT). c. Google map image of gravel pit lakes in glacier deposits with new housing developments. The inset shows approximate location in the United Kingdom (UK; Gloucestershire; Cotswold Waterpark lat 30 U 573671, long E57°23'155).

be a source of sand and gravel in Australia (Stubbs and Smith, 1997). Gravel deposits are also found and mined offshore (Cattaneo and Steel, 2003; Kubicki et al., 2007).

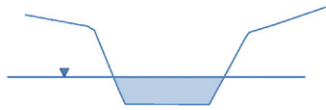
3. Hydrology of gravel pit lakes

3.1. Drainage pattern and residence time

Gravel mining along the streambed of rivers disrupts the continuity of sediment transport by rivers and changes the river morphology by creating local areas of deposition and erosion (Kondolf, 1997) and changing the natural morphology into an anthropocene landscape with different incision rates (e.g. Florsheim et al., 2013). The presence of gravel pit lakes changes the hydraulic gradients in the surrounding aquifer, especially if the lakes are created in a sloping area or in a low lying plain. The lakes themselves are by definition a surface of equipotential head. Because the drainage pattern of the area changes (Figs. 2 and 3), a gravel pit lake may cause the rise or the lowering of the water table over a large area (Mas Plaa et al., 1999). If the gravel pit lakes are in a low lying coastal plain, they will enhance the need for drainage. This can enhance salt water intrusion up to several kilometers inland as observed by Mas Plaa et al. (1999) and confirmed by modeling studies (Mollema et al. 2010; Werner et al., 2013) especially if sea level is rising.

Gravel pit lakes may abruptly intersect geologic formations such as a confining clay layer or buried paleo channels. This will enhance the transport of water and its solutes and may disrupt the original stratification of groundwater types (Mollema et al., 2013a; Stuyfzand, 1999). The residence time of water in natural lakes varies from 1343 years for a large lake as Titicaca (850 km³) while it is only 0.4 year for a small pond (0.013 km³) (Löffler, 2003). The residence time of water in gravel pit lakes documented so far, ranges from 0.03 to 0.04 year for river connected gravel pit lakes (Cross et al., 2014) and 0.1 to 2 years for ground water fed or flow through gravel pit lakes (Löffler, 2003; Mollema et al., 2015a, b; Weihartner et al., 2012). The residence time of water in gravel pit lakes may increase with time as the permeability of its banks changes due to clogging. The (enhanced) groundwater flow transports chemical elements into the lake that in part may precipitate and clog the bottom or the downstream bank of the lake by accumulation of suspended solids, precipitates, the formation of gas bubbles and sediment compaction (Baveye et al., 1998). Besides the physical and chemical clogging mechanisms, nutrient inflow leads to the accumulation of biomass and this may cause biological clogging as observed in Austrian gravel pit lakes (Weihartner et al. 2012). The clogging is a highly temporal and spatial variable process that will vary from lake to lake but the deposition of particulate matter (organic and inorganic) is observed to contribute up to one third of the organic matter internally produced in the upper sediment layer (e.g. macrophyte rhizomes, microalgae, biofilms; Hoffmann and Gunkel, 2011). The occurrence of redox reactions in the aquifer system downstream of gravel pit lakes trigger a chemical clogging process when (sub)oxic lake water and anoxic groundwater mix (Bustos Medina et al., 2013; De la Loma Gonzalez et al., 2013) as it does in regular river bank filtration (Hiscock and Grischek, 2002; Schlieker et al., 2001). In contrast to river bank and bed sediments, periodic resuspension due to floods does not occur naturally in lowland lakes and flow regulated lowland rivers (Hoffmann and Gunkel, 2011) or gravel pit lakes, so the clogging in banks of gravel pit lakes may be permanent.

We can distinguish several types of gravel pit lakes depending on the hydrogeologic setting (Figs. 2 and 3). In a river basin, there may be excavations that create a lake in contact with the river (Bayram and Önsoy, 2015; Cross et al., 2014; Kondolf, 1997), in a meander, or an old gravel bar (Fig. 2). A lake may have formed in an abandoned meander (Fig. 3d). Gravel pit lakes may be topographically higher than the stream and not directly connected to the river (Mollema et al., 2015a; Weihartner et al., 2012; Fig. 3c). If groundwater infiltrates on one side of such a lake and flows out of the lake on the other side, we call it a



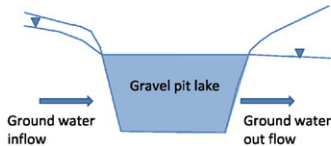
Gravel pit lake is to all effects an 'outcrop' of the water table. Gravel pit lake formed where the floor of the pit lies below the water table on groundwater divide or in impervious rock. There is no lateral flow.

a



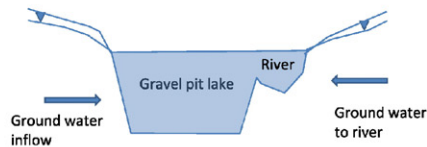
Terminal gravel pit lake: water flows from all sides into the gravel pit lake

b



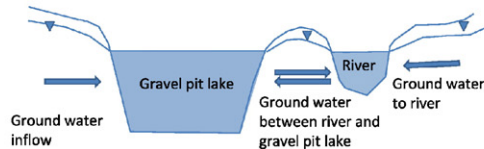
Drainage into and out of a gravel pit lake by lateral groundwater flow, flow through lake.

c



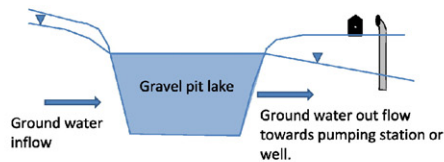
Drainage into gravel pit lake and river, open connection between gravel pit lake and river.

d



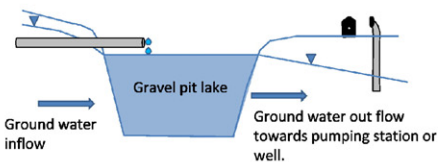
Drainage into gravel pit lake and river, flow between gravel pit lake and river. Gravel pit lake could be an oxbow lake.

e



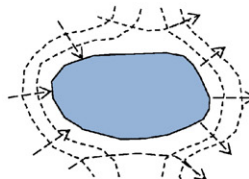
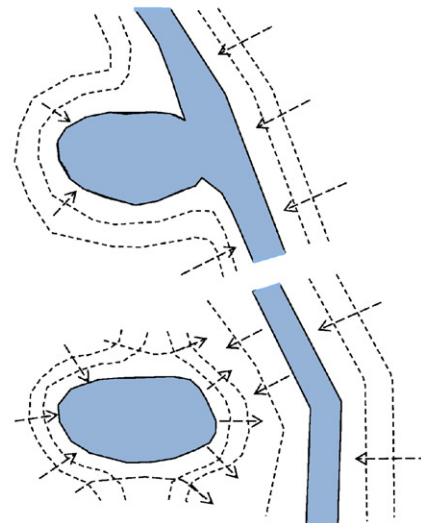
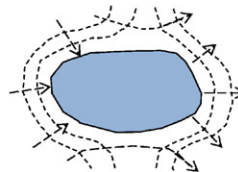
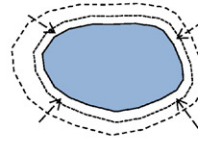
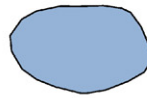
Drainage into and out of a gravel pit lake by lateral groundwater flow, flow through lake driven by artificial drainage or pumping.

f

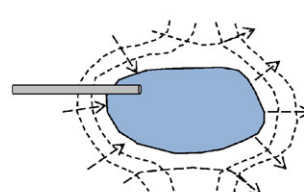


Drainage into and out of a gravel pit lake by lateral groundwater flow, artificial recharge through pipe system, flow through lake driven by artificial drainage or pumping.

g



- Pumping wells or Drainage system
-
-
-



- Pumping wells or Drainage system
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“flow through lake”. A flow through lake may also form under the influence of an artificial drainage network as is the case in the gravel pit lakes excavated along the coast of the Adriatic Sea (Mollema et al., 2015b). Whether or not gravel pit lakes are isolated or connected to a river influences the chemical composition of the lake water, including the nutrient supply and therefore the ecosystem (Cross et al., 2014 and see Section 5).

3.2. Water budget

Gravel pit lakes increase the extent of surface water in a catchment, and therefore the area from which direct evaporation can occur (Fig. 4). Evaporation (E) depends on many different climate variables: wind velocity, the relative humidity of air, and vapor pressure deficit, (e.g. Mohamed et al., 2012; Van Heerwaarden et al. 2010 a, b) while the actual evapotranspiration (ET_a) from a vegetated piece of land also depends on the physiologic characteristics of the vegetation (radiation properties and physical resistances in the plant's internal pathway), the proportion of the area covered by vegetation and by bare soil as well as the soil water potential in the root zone (Mohamed et al., 2012). In most climate settings E is larger than ET_a of a piece of vegetated land since the resistance to E is smaller without vegetation or soil (Maidment, 1992; Mohamed et al., 2012; Penman, 1948). Emergent aquatic vegetation of wetlands that is present in many (shallow) gravel pit lakes is thought by some to have a larger ET_a than E in particular circumstances such as in a (sub)tropical and temperate winter climate, especially at low wind speeds (Mohamed et al., 2012) but this issue is controversial (e.g. Maltby and Barker, 2009; Mohamed et al., 2012). In groundwater fed gravel pit lakes, typically only the available energy of the sun limits evaporation since inflowing groundwater replaces the evaporated water.

4. Chemical cycling

4.1. Chemistry of gravel pit lake water versus other types of surface and ground water

To try to understand whether the hydrochemistry of gravel pit lakes is different from natural lakes and other waters, we compared the water quality of Dutch and Italian gravel pit lakes studied by Mollema et al. (2015a, b), of Austrian gravel pit lakes studied by Muellegger et al. (2013) and Weilharter et al. (2012), and additional data on British gravel pit lakes (Cross et al., 2014), with water quality of rivers, various types of natural lakes (marl lakes, alpine lakes, nutrient rich lakes and more), groundwater and seawater (Table 2). We discuss the processes that are responsible for the hydrochemical differences between gravel pit lake and other water types. Precipitation contains less dissolved elements than gravel pit lake water (Table 2). River water contains more dissolved substances than precipitation but usually less than gravel pit lake water. The strongest enrichment of water occurs usually as groundwater due to water rock interactions especially in coastal settings. These include the area of groundwater discharge into the sea, the so called subterranean estuary, where seawater with high concentration of solutes has a large influence (Fig. 6 and Table 2). When groundwater exfiltrates into surface water of a different chemical composition, acidity and alkalinity, chemical reactions occur that include but are not limited to the precipitation and dissolution of minerals on the lake bottom. Gravel pit lakes are an unnatural type of surface water that interrupts the natural flow of solutes towards the rivers, lakes or the sea and in some cases this may result in a relative

enrichment of certain elements, in other cases a relative depletion of certain elements. Fig. 5a and b illustrate this for two particular case studies where gravel pit lake water is depleted in Iron (Fe) and Ca compared to groundwater.

Lake water chemistry is variable and changes with the particular setting of a lake. We have therefore indicated the type of lakes and the number of lakes involved as described in the original publications (Table 2). The range of pH values observed in gravel pit lakes (pH 7.2–10.4) is slightly different and smaller than the range of pH of the reviewed natural lakes (pH 5.0–9.0) (Fig. 6a, Table 2). The pH of gravel pit lakes is higher than that of typical alpine or boreal natural lakes but similar to natural ‘marl’ lakes. A much larger range in Ca concentration is (so far) observed in natural lakes than in gravel pit lakes, which may be explained by the fact that natural lake studies include high alpine, boreal or arctic settings as well as unconsolidated sediments with hard water or ‘marl’ lakes. The gravel pit lakes included in this comparison by definition are in unconsolidated sediments and they are located in lithologies that include carbonate grains which causes the high alkalinity of ground and lake water. The alkalinity of the gravel pit lakes is high compared to that of natural lakes except for that of hard water (marl) lakes (e.g. Wiik et al., 2013). In coastal saline gravel pit lakes we observed the highest HCO_3^- values (727–812 $mg\ L^{-1}$; Table 2). High HCO_3^- concentrations in this setting are caused by current and past redox reactions and Calcium carbonate ($CaCO_3$) dissolution (Mollema et al., 2015a, b; 2013a, b). Also in a non coastal setting, the HCO_3^- concentration of gravel pit lakes is high (103–147 $mg\ L^{-1}$). The gravel pit lake and natural lake studies included in this review show that lake water typically has a low concentration in dissolved metals. The maximum Fe concentration observed so far in natural lakes is higher and the minimum Zinc (Zn) concentration is lower in gravel pit lakes compared to natural lakes (Fig. 6e and f, Table 2). Instead groundwater in certain circumstances may have very high concentrations in dissolved metals (Table 2). Seawater contains typically high concentrations of solutes such as chloride (Cl^-) and sulfate (SO_4^{2-}) but metals and other trace elements tend to disappear from the water column.

If we compare three systems of gravel pit lakes with one another (low alpine river deposits, Muellegger et al., 2013; lowland river deposits Mollema et al., 2015a; coastal plain beach deposits Mollema et al., 2015b), we find that the pH is fairly high in all three lake systems 7.2–8.7 (Table 2), the largest nitrate (NO_3^-) and Fe concentrations are observed in the alpine lake setting and the highest dissolved Ni concentration in the Italian coastal gravel pit lakes. Cross et al. (2014) found that gravel pit lakes connected to a river have higher NO_3^- and Total P concentrations than isolated gravel pit lakes in line with the general observation that NO_3^- in river water may show higher concentrations of nutrients than isolated gravel pit lakes (Table 2).

Stable oxygen and hydrogen isotopes of lake water reflect the isotopic composition of the precipitation and groundwater flowing into the lakes, and the evaporation rate which causes a relative enrichment in heavy isotopes (Table 2). Therefore it is difficult to quantify how gravel pit lakes influence the stable oxygen and hydrogen isotopes of water differently from natural lakes. So far there have been carried out more studies on natural lakes in a larger range of climate and geographical locations and therefore the observed and published range in stable water isotope values is larger in natural lakes than in gravel pit lakes (Table 2).

4.2. Nutrient cycling

The nutrient cycle in a gravel pit lake includes the addition of P and N by atmospheric deposition, fertilization of the surrounding soil, sewage

Fig. 3. a. Cross sectional and map view of different types of gravel pit lakes with groundwater flow indicated by arrows. a. Gravel pit lake intersects the water table. b. Terminal pit lake (uncommon for gravel pits) c. Flow-through gravel pit lake. d. In stream gravel pit lake. e. Gravel pit lake in valley bottom. f. Gravel pit lake in an artificially drained basin. g. Artificially recharged gravel pit lake in artificially drained basin. Modified in part from Gammons et al. (2009); Gandy et al. (2004); Mollema et al. (2015a) and Younger and Robins (2002).

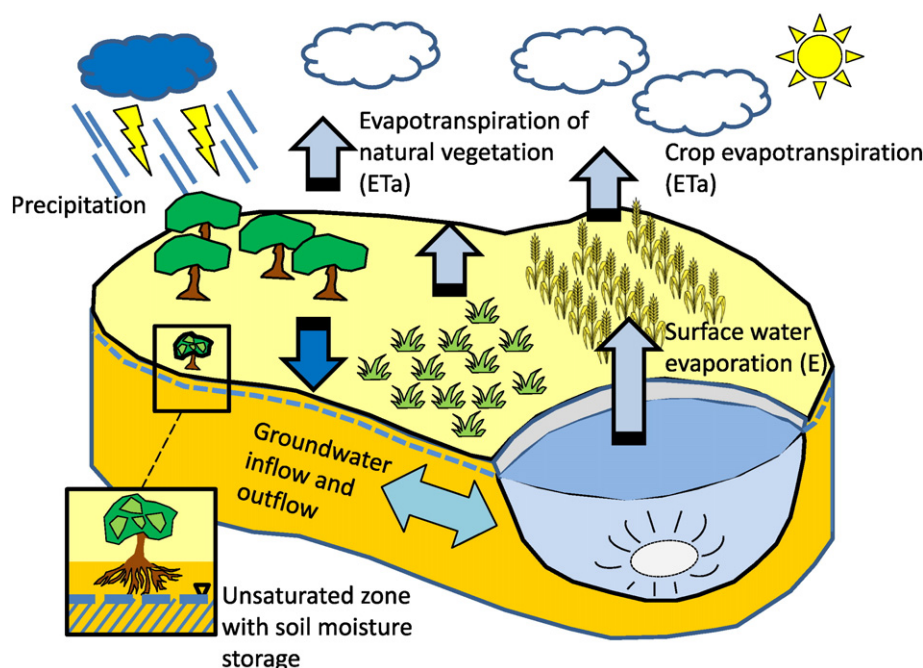


Fig. 4. Components of the water cycle for an area with a gravel pit lake. The water cycle of forest, grassland, and wetland include evapotranspiration while the water budget of a gravel pit lake includes surface water evaporation, which is usually larger than the original evapotranspiration.

pollution and subsequent surface runoff, transport by rivers and/or groundwater (Fig. 7; Alvarez Cobelas et al., 1992; Vane et al., 2010). The resulting measured NO_3 concentrations in gravel pit lakes range from 0.1 to 18 mg L^{-1} (Table 2), which is not as high as the amount that has been observed in fresh or brackish groundwater (up to 58 mg L^{-1} ; Table 2) or in river water (up to 372 mg L^{-1} ; Table 2). The NO_3 concentration is higher than that of natural lakes not affected by land use (up to 0.7 mg L^{-1} Table 2; Sickman et al., 2003), which is logical since most gravel pit lakes are in an urban or agricultural setting and are indeed affected by land use. The presence of the gravel pit lake affects the amount of N and P in groundwater downstream, typically reducing the concentration as they turn into biomass (Alvarez Cobelas et al., 1990; Garnier and Billen, 1994; Helmer and Labroue, 1993; Weilhartner et al., 2012; Muellegger et al., 2013; Mollema et al., 2015a). The inflow and accumulation of nutrients into the gravel pit lakes may cause eutrophication with nuisance algal blooms (Section 5) and interferes with metal cycling, see Section 4.4. Organic matter in sediment strongly affects PO_4 adsorption as observed in pit lakes in a former lignite mine (Herzprung et al., 2010), with the light fraction organic matter (LFOM) playing a key role in nutrient cycling. The chemistry and kinetics may change over time: if LFOM is removed, PO_4 adsorption decreases (Wang and Mulligan, 2006). Sulfide may take the place of P bound to iron in sediments during reduction processes (Lamers et al., 2002, 2013; Smolders and Roelofs, 1996).

4.3. Carbon and Ca cycling

Inland waters including gravel pit lakes play an important role in the carbon cycle since they are extremely active sites for transport, transformation, and storage of considerable amounts of carbon received from the terrestrial environment despite a limited surface area (Nöges et al., 2016; McDonald et al., 2013; Marcé et al., 2015; Tranvik et al., 2009). Many processes are recognized to play a role in carbonate bicarbonate equilibrium of natural lakes (e.g. Cole et al., 2007; Kortelainen et al., 2007) that also will play a role in gravel pit lakes although no specific studies on all components of the carbon budget in gravel pit lakes have yet been carried out (Fig. 8): uptake of atmospheric CO_2 in water, release of CO_2 to the atmosphere (e.g. Raymond et al., 2015),

carbonate (CaCO_3) dissolution by CO_2 and H_2O , weathering of silicate minerals (Liu et al., 2010), the photosynthetic uptake of dissolved inorganic carbon (DIC) by aquatic organisms and assimilation of C, Ca and Silicon (Si) by organisms including plankton, diatoms and molluscs and deposition on the lake bottom (Einsele et al., 2001; Iglesias Rodriguez et al., 2008); anaerobic degradation of organic matter by specialized methanogenic microbes and subsequent partial methane (CH_4) oxidation by methanotrophic bacteria in oxic surface sediments or in the water column (Bastviken et al., 2011; Bles et al., 2015; Weilhartner et al., 2012) as well as biological methane production in lake waters (e.g. Bles et al., 2015).

The relative contribution of various fluxes to the carbon cycle of lakes varies with latitude, type of bedrock and whether or not the lake is a reservoir (Marcé et al., 2015; Tranvik et al., 2009) and with salinity, and pH of lake water (Duarte et al., 2008). The gravel pit lakes reviewed in this paper are most similar to hard water lakes or reservoirs in a temperate climate and so the largest components in their C cycle are most likely the in and outflow of DIC with groundwater and the storage in the lake bottom sediment (Marcé et al., 2015; Tranvik et al., 2009). The more so since the amount of groundwater flow into gravel pit lakes can be very large compared to the other water fluxes (Mollema et al., 2015a, b; Weilhartner et al., 2012).

Einsele et al. (2001) found that although the area of lake basins is only about 0.8% of the ocean surface or 2% of the land surface, a surprisingly high amount of atmospheric carbon is buried in lake sediments, which amounts to 0.07×10^{15} g of C per year, more than one fourth of the annual atmospheric carbon burial in the modern oceans. This burial is mainly accomplished by rapid accumulation of lacustrine sediments and a very high preservation factor, which is on average 50 times higher than that in the oceans (Einsele et al., 2001). Comparing among different types of natural lakes and a (agricultural) water reservoir, Tranvik et al. (2009) found that the carbon stored in the lake sediments was higher in the reservoir than in natural lakes. In this sense, the creation of gravel pit lakes provides more available sites for carbon burial. Many lakes and reservoirs are supersaturated with CO_2 which has been attributed partly to the accumulation of inorganic carbon where respiration exceeds photosynthesis (Duarte and Prairie, 2005) and to carbonate weathering in the catchment (when lake water alkalinity is

Table 2

Range of concentrations of selected (trace) elements, cations, anions, and pH in different types of water. Values converted to mg L⁻¹ for major components and to µg L⁻¹ for trace elements. The number of lakes included in the studies is written between square brackets; [rev] means the quoted paper is a compilation of multiple studies on different types of lakes; types of lakes are copied from articles.

	Precipitation	River	Groundwater fresh	Natural lakes	Gravel pit lakes	Coastal brackish groundwater	Sea/ocean
pH	4.1–6.3 ¹ 4.5–7.6 ¹⁷	5.5–8.4 ⁷	5.0–7.6 ⁴ 7.1–7.8 ³ 4.4–6.5 ²⁰	5.3–7.9 (alpine lakes) ⁴¹ [57] 4.5–7.2 ¹¹ [>23 rev] 5.7 (boreal lakes) ³⁰ [>36] 7.5–9.0 ('marl lakes') ³⁹ [rev] 4.7–7.8 (contaminated lakes) ²⁹ [15] 7.04–8.84 (nutrient rich lakes) ⁴⁰ [37]	7.2–8.6 ³ [5] 7.5–8.6 ⁴ [3] 7.9–8.7 ³ [2] 7.2–10.4 ³⁸ [6] 8.27 ³² [1]	6.0–7.7 ⁵	8.1 ¹⁰
TDS [mg L ⁻¹]		4–1000 (surface waters together) ⁶ 99.6 (unpolluted)–110.1 ¹¹					20,000–40,000 ⁶
Al [µg L ⁻¹]	13.2 ¹⁴	13.2 ¹³	0.7–1842 ⁴ 0–8094 ²¹ (max values in acid soils)	270–1349 (acidified lakes) ²⁶ [4] 0–33 (soft water lake) ²⁷ [1]	0.7–19.5 ⁴ [3] 10–30 ⁵ [2]	0–100 ⁵	0.08–1.05 (mean about 0.05) ²
As [µg L ⁻¹]	0.025 ¹⁴	0.15–45 (high for polluted rivers) up to 21,800 for rivers fed by As rich groundwater ¹⁰	0.5–10 baseline 10–5000 As rich ¹⁰	0.06–9.2 ¹⁰ [rev]	0.3–4.3 ⁴ [3] 12–13 L ⁵ [2]	0–48 ⁵ 0.7–3.8 ¹⁰	1.4–1.8 ² 1–3.7 ¹⁰
Ba [µg L ⁻¹]		4–17 ⁸	16 ⁹ 26–154 ²⁴		748–1768 ⁵ [2]	51–640 ⁵	4–20 (mean 15) ²
Ca [mg L ⁻¹]	0.1–0.4 ¹⁶ 0.1–5.3 ¹⁷	13–3727 (median 401) ⁷	4–60 (unsaturated soil) ¹ 2–96 (saturated soil) ¹ 8.3–89.5 ⁴	1.4–2.3 (boreal lakes) ³⁰ [36] >30 (marl lakes) ³¹ [rev]	29.1–56.3 ⁴ [3] 56.6–136 ³ [2]	104.1–436.5 ⁵	416 ¹⁰
Fe [µg L ⁻¹]	20.1 ¹⁴	53.9 ¹³	0–27,925 ¹ 100–18,200 ⁴	>11–1117 (glacier formed lake) ¹⁸ [1] 2.2–10.1 (soft water lake) ²⁷	5–138 ³ [5] 2–76 ⁴ [3] 72–77 ⁵ [2] 38.1–45.8 ⁴ [3] 2920–4760 ³ [2]	335–13,500 ⁵	0.001–0.11 (mean 0.03) ²
Cl [mg L ⁻¹]	0.2–9.8 ¹	0–16.9 (mean = 0.1) ⁷	6.3–55.6 ⁴	0.4–9.9 ¹¹ [>23 rev]	103–147 ⁴ [3] 727–812 ⁵ [2] 0.7–6.4 ³ [5] 1.2–7.2 ⁴ [3] 4–13 ³ [2] <1.25 ⁵ [2]	465–16,500 ⁵	1888 ³
HCO ₃ [mg L ⁻¹]	0.5–1.5 ¹	17.9–183.0 ¹¹ 188–435 ⁵	0–305.1 ¹ 5–198.8 ⁴	10.5–140.1 ¹¹ [>23 rev] 54.9–85.4 (glacier formed lake) ¹⁸ [1]	0.01–0.03 (PO ₄) ⁴ [3] 0.5–0.6 (total P) ⁵ [2]	291–1468 ⁵	109.0 ¹⁰
Ni [µg L ⁻¹]	0.1 ¹⁴	2.4 ¹³	0.1–71.1 ⁴ 0–20.5 ²⁰	0–117 (contaminated lakes) ²⁹ [15]	0.7–6.4 ³ [5] 1.2–7.2 ⁴ [3] 4–13 ³ [2] <1.25 ⁵ [2]	>0.2–80 ⁴	0.1–0.7 ²
NO ₃ [mg L ⁻¹]	0.3–3.9 ¹ 0–0.8 mg L ⁻¹ (N) ¹⁵ 0–2 ¹⁶	0.6–31.0 (pristine rivers) ⁷ 0.6–372 (present-day rivers) ⁷ 2.1–2.5 ¹² (European rivers)	0.1–12.4 ¹ 0.1–58.1 ⁴ 17–21 ¹²	0–0.7 (alpine lakes) ²⁵ [28] 0.02–1.8 (nutrient rich lakes; total N: 0.76–3.02) ⁴⁰ [37] 0.03–3.6 (annual average; man-made/peat lakes) ⁴² [39] 0.025–0.03 ¹² [rev] 0.004–1.24 (soluble reactive P) 0.055–1.59 (Total P) ⁴⁰ [37] 0.031–0.49 (annual average total P; man-made/peat lakes) ⁴² [39] 1.8–45.4 ¹¹ [>23 rev]	0.1–6.8 (infiltrated river water) ⁴ [1] 1.0–4.3 (groundwater fed only) ⁴ [2] 1.5–18.0 (approximate range) ³ [5] 9.35 ³² [1] 0.01–0.03 (PO ₄) ⁴ [3] 0.5–0.6 (total P) ⁵ [2]	<1.25–56 ⁵	0–2.7 (mean 1.8) ²
PO ₄ [mg L ⁻¹]	0.005–0.41 ³⁷	0.03–0.9 (median 0.5) pristine – human impacted up to 15.8 ⁷	0.02–2.1 ⁴	0.025–0.03 ¹² [rev] 0.004–1.24 (soluble reactive P) 0.055–1.59 (Total P) ⁴⁰ [37] 0.031–0.49 (annual average total P; man-made/peat lakes) ⁴² [39] 1.8–45.4 ¹¹ [>23 rev]	0.01–0.03 (PO ₄) ⁴ [3] 0.5–0.6 (total P) ⁵ [2]	0.4–4.1 ⁵	0.01–0.07 (mean, open ocean) ¹⁹
SO ₄ [mg L ⁻¹]	0.4–8.4 ¹ 0–2.5 ¹⁶	33–239 ⁵	1.0–480.3 ¹ 0.2–105.8 ⁴	0.6–3.9 ¹¹ [>23 rev]	16.1–78.5 ⁴ [3] 218–290 ⁵ [2] 4.7–16.4 ⁴ [3] <0.1–13.3 ³ [5] 31.64 ^{4**} [2] 35.65 ⁵ [2]	231–2183 ⁵	2743 ¹⁰
Zn [µg L ⁻¹]	6.3 ¹⁴	10.3 ¹³	8.3–1607.8 ⁴	0.6–3.9 ¹¹ [>23 rev]	4.7–16.4 ⁴ [3] <0.1–13.3 ³ [5] 31.64 ^{4**} [2] 35.65 ⁵ [2]	30–463 ⁴	0.003–0.6 ²
δ ² H (‰ vs VSMOW)	46.78 ⁴ 56.00 ³⁴ 114.8 min–20.4 max ³⁶	44.56 ⁴ 52.04 ³³	47.44 ^{4*}	97.04 ³⁵ [100 rev] 88.44 (peri alpine lake) ³⁶ [1]	31.64 ^{4**} [2] 35.65 ⁵ [2]	38.19 ^{33*}	0.00 SMOW 18.20 (coastal Adriatic Sea) ³³
δ ¹⁸ O (‰ vs VSMOW)	7.00 ⁴ –8.2 ³⁴ –15.4 min–3.2 max ³⁶	6.00 ⁴ –8.16 ³³	7.26 ^{4*}	11.45 ³⁵ [100 rev] 12.31 (peri alpine lake) ³⁶ [1]	4.25 ^{4**} [2] 4.86 ⁵ [2] 7.5 to 0.5 ⁴³ [9]	5.54 ^{33*}	0.00 2.77 (coastal Adriatic Sea) ³³

1. Appelo and Postma (2005) and references therein. 2. Bruland and Lohan (2003). 3. Muellegger et al. (2013). 4. Mollema et al., 2015a *Only groundwater upstream from gravel pit lakes, **Not included the gravel pit lake used for water infiltration, ***Precipitation Beek 94–2009. 5. Mollema et al., 2015b. 6. Gibbs (1970). 7. Meybeck (1995, 2003). 8. Moore and Shaw (2008). 9. Gonnea et al. (2008). 10. Smedley and Kinniburgh (2002) and references therein. 11. Stumm (2004) with reported values of Meybeck, 1995; Berner and Berner (1996) and Garrels and Mackenzie (1971). 12. Waterbase Europe, from 2004 to 2010. 13. Longterm average for Meuse River (NL) by RIVA 2013 as reported by Mollema et al., 2015a. 14. RIVM (2011). 15. Vet et al., 2014. 16. Nilles and Conley, 2001. 17. Liu et al. (2010). 18. Balistrieri et al. (1992). 19. Conkright et al. (2000). 20. Antonov et al. (2010). 21. Kjoller et al. (2004). 22. Giovanoli et al. (1988) as reported in 11. 23. LaZerte and Dillon (1984). 24. Mollema, 2016. 25. Sickman et al. (2003). 26. Veselý et al. (2003). 27. Hamilton-Taylor and Willis (1990). 28. Kopacek et al., 2011. 29. Ponton and Hare, 2009. 30. Jeziorski et al., 2008. 31. Katz and Nishri, 2013. 32. Alvarez Cobelaset al. 1990. 33. Mollema et al., 2013a *Groundwater underneath paleodunes Classe. 34. Longinelli et al., 2006. 35. Henderson and Shuman, 2010, Mean values large number of lakes in USA. 36. Halder et al., 2013. 37. Migon and Sandroni, 1999. 38. Cross et al., 2014. 39. Wiik et al., 2013. 40. Fisher et al., 2009. 41. Sommaruga-Wögrath et al., 2013. 42. Sayer et al., 2010b; 43. Jones et al., 2016.

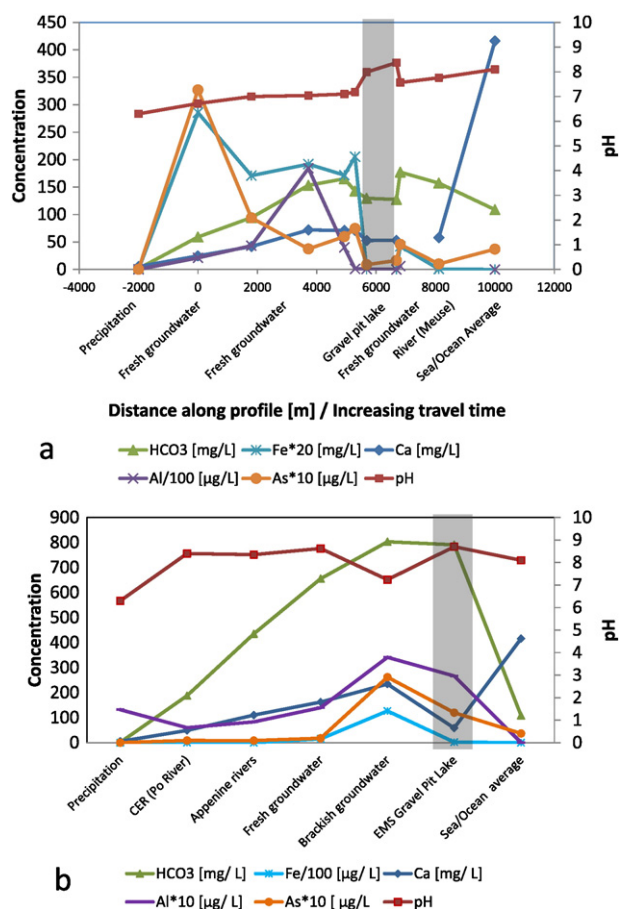


Fig. 5. Examples of relative enrichment and depletion in selected dissolved elements and components and pH in gravel pit lakes. Precipitation and seawater data are taken from the literature and ground and surface water data are averages over multiple samples. See Table 2 and Mollema et al. (2015a, b) for original data. Read from left to right along the horizontal axis. Precipitation contains very little amounts of anions, cations and dissolved metals. River water usually has a higher concentration of solutes; strong enrichment occurs in groundwater due to water-rock interactions especially in coastal zones. When groundwater exfiltrates into surface water bodies such as (gravel) pit lakes, rivers or sea, strong changes in concentration in certain elements occur. A. Example from a freshwater fluvial system (The Netherlands, where freshwater flows through the gravel pit lake (data from Mollema et al., 2013a) and from Appelo and Postma (2005) and references therein, Seawater data from Bruland and Lohan (2003); Meybeck (1995, 2003), Precipitation data from RIVM (2011); Liu et al. (2010), see Table 2. The horizontal axis represents the realistic distance along the profile except for the location of precipitation and seawater. B. Example from a coastal brackish-saline groundwater and gravel pit lake system (Italy).

higher than 1 meq L^{-1} or HCO_3^- of 61 mg L^{-1} ; Marcé et al., 2015). The exact relation between the particular source of C input (DIC, organic carbon (OC), primary production, etc.) and its fate in lakes in general and gravel pit lakes in particular are still unclear (Hanson et al., 2015). The gravel pit lakes of this review have a pH that varies between 7.2 and 10.4 (Table 2) and the HCO_3^- concentrations range from 103 to 147 mg L^{-1} in freshwater gravel pit lakes and from 727 to 812 mg L^{-1} in saline gravel pit lakes (Table 2 and Fig. 6). The alkalinity exceeds the threshold of 1 meq L^{-1} (Marcé et al., 2015) suggesting that the alkalinity is caused by weathering and leaching of carbonates in the catchment rather than in situ production by photosynthesis. In coastal zones, saline lakes surrounded by a brackish aquifer are affected also by cation exchange as the infiltration of saline water in a fresh aquifer or freshwater into a brackish aquifer promotes the exchange of cations including Ca and Na (e.g. Andersen et al., 2005; Appelo and Postma, 2005). The Ca cycle is related to the carbon cycle in biochemical processes as CaCO_3 is incorporated into the skeleton or shell of many organisms.

Previous studies on other types of lakes showed that calcite precipitation occurs in pulses during phases of high primary production of phytoplankton between May and October (peri alpine Lake Zurich: Kelts and Hsu, 1978; Naeher et al., 2013; Sigg et al., 1987; Marl lakes: Wiik et al., 2013) also on macrophytes (Bloesch, 2004). Observed dissolved Ca concentration in gravel pit lakes ranges between 29 and 56 mg L^{-1} in freshwater and between 57 and 136 mg L^{-1} in saline gravel pit lakes (Table 2). The Ca depletion of gravel pit lake water with respect to upstream groundwater (Fig. 5; Mollema et al., 2014, Mollema et al., 2015a, b; Muellegger et al., 2013) indicates that CaCO_3 precipitation on the lake bottom plays a role in gravel pit lakes in a freshwater fluvial setting as well as in a brackish coastal setting (Fig. 5). Gravel pit lakes are potentially very efficient in CaCO_3 precipitation since high epilimnic water temperatures and high pH in combination with high primary production and intensive CO_2 assimilation leads to reduced CaCO_3 solubility (Walpersdorf et al., 2004). A very important side effect of natural calcite precipitation is the removal of particulate and dissolved P from the water column as well as metals as Fe and Mn (Walpersdorf et al., 2004; see Section 4.4).

4.4. Metal and trace element cycling

Introducing gravel pit lakes where previously there was an aquifer changes the metal budget of a catchment (Fig. 9). Redox reactions occur generally in all types of aquifer sediments (Appelo and Postma, 2005) including those upstream and downstream of gravel pit lakes (e.g. Mollema et al., 2015a, b). The redox reactions are triggered for example by natural acidification of the soil or anthropic acidification due to atmospheric acid deposition, fluctuating water tables and with the introduction of acid due to mining activities or fertilizers (Gandy and Younger, 2008; Marques et al. 2008; Mollema et al., 2015a; Weiske et al., 2013). The excavation of the gravel pit lakes themselves or nearby water ways can be the cause for water table fluctuations that trigger redox reactions (Mollema et al., 2015a). Well known redox reactions are denitrification mediated by pyrite or other Fe compounds (Appelo and Postma, 2005; Choi et al., 2011 and references in both). Pyrite-oxidation may also occur by nitrate or oxygen rich groundwater (Appelo and Postma, 2005). This reaction produces H^+ which may then contributes to the nitrate reduction of pyrite and ferrous iron (Appelo and Postma, 2005). Pyrite normally contains trace elements (As, Cobalt (Co), Nickel (Ni), Zn) that can be released upon pyrite oxidation. As a result of the redox reactions in the aquifer, Fe, As, Ni and Zn concentrations (among others) can be very high in fresh and brackish groundwater upstream from gravel pit lakes as observed so far in Dutch and Italian case studies (Fig. 6; Table 2; Mollema et al., 2015a, b). Arsenic remains more in solution in groundwater with a high pH while on the contrary Co, Ni and Zn remain in solution in water with a lower pH (<6). When metals dissolved in (acid) groundwater flow into a gravel pit lake, they come into contact with less acidic and usually better oxygenated water. These are conditions under which Fe, and Manganese (Mn) hydr(oxides) precipitate, binding also to organic matter, P and Ca removing these elements (temporarily) from the water column. Zn, Cu and Ni and other metals may adsorb on and co-precipitate with Fe and Mn oxyhydroxides eliminating also those elements from the lake water column (Appelo and Postma, 2005; Tessier et al., 1985). The metals precipitated to the bottom of natural lakes are known to participate in cycling redox processes (e.g. Naeher et al., 2013 and Stumm, 2004 and references in both). Our literature review (Table 2) reveals dissolved Al concentration up to 8094 $\mu\text{g L}^{-1}$ in acid soils and the highest concentrations in natural lakes is up to 1349 $\mu\text{g L}^{-1}$ whereas Al concentrations observed so far in gravel pit lakes do not exceed 30 $\mu\text{g L}^{-1}$. Remobilization of (heavy) metals in floodplains may also contribute to metal deposition in gravel pit lakes, especially downstream of mines (Du Laing et al., 2009; Zhao and Marriott, 2013).

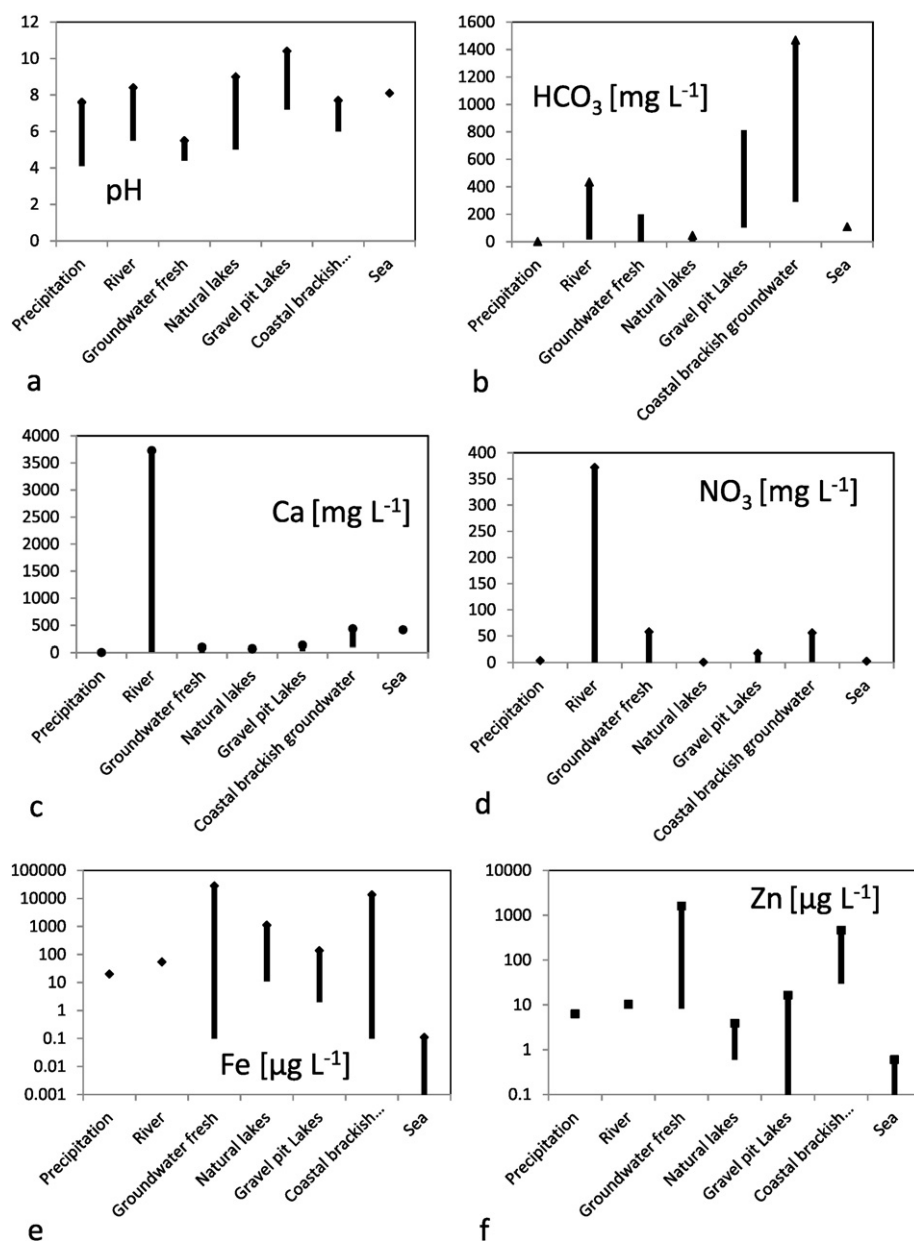


Fig. 6. Range of observed values for selected parameters and elements in various types of surface and groundwater indicating enrichment and depletion in different types of water from precipitation on the left of the horizontal axis via river, lake and groundwater to seawater on the right hand side of the horizontal axis (see for values and references in Table 2). Symbols indicate maximum observed value as documented in the reviewed literature. a. pH, b. HCO_3^- , c. Ca, d. NO_3^- , e. Fe, f. Zn.

In some cases, the metal concentration in lake bottom sediments may exceed legal norms (Mollema et al., 2015a). This could become a practical problem as cleaning lakes of their sediments is not an easy endeavor and the very process of cleaning may reduce water quality. In stead high dissolved metal concentration in lake water may occur if there is a lack of binding material such as organic matter or H_2S , and CaCO_3 (Walpersdorf et al., 2004) that help fix metals to lake bottom sediments. The sulfide ion has a strong affinity for many heavy metals and so will precipitate as metal sulfides (Manahan, 2013).

5. Ecological functioning

The creation of gravel pit lakes typically increases the diversity of aquatic habitats in a catchment (Fig. 10). Some species of flora and fauna do thrive in groundwater (e.g. Danielopol et al., 2000) but gravel pit lakes, especially in an urban setting, increase biodiversity (e.g. Santoul et al., 2009). The direct interaction of a lake surface with the

atmosphere and the infiltration of sunlight make it possible for primary producers (e.g. algae) to convert inorganic carbon from atmospheric CO_2 or from dissolved HCO_3^- into organic carbon through photosynthesis, forming the base of a large food web. This section gives a brief overview of the types of biological communities that are observed in lakes in general and in gravel pit lakes in particular with emphasis on the inter action with the chemical cycles described in Section 4. For a more detailed description of species and biological functioning, the reader is referred to the bibliography.

Phytoplankton are single celled organisms of lakes, streams and oceans that make their own food from sunlight through photosynthesis. They include green algae, diatoms, cyanobacteria, dinoflagellates and coccolithophores (Padišák, 2004). Besides inorganic carbon, phyto plankton needs at least 20 other chemical elements to survive of which P, N Si and Fe are thought to be the most important. Generally, the lack of one of these elements determines the growth of phytoplankton (Padišák, 2004; Reynolds, 2004; Weilhartner et al., 2012). The

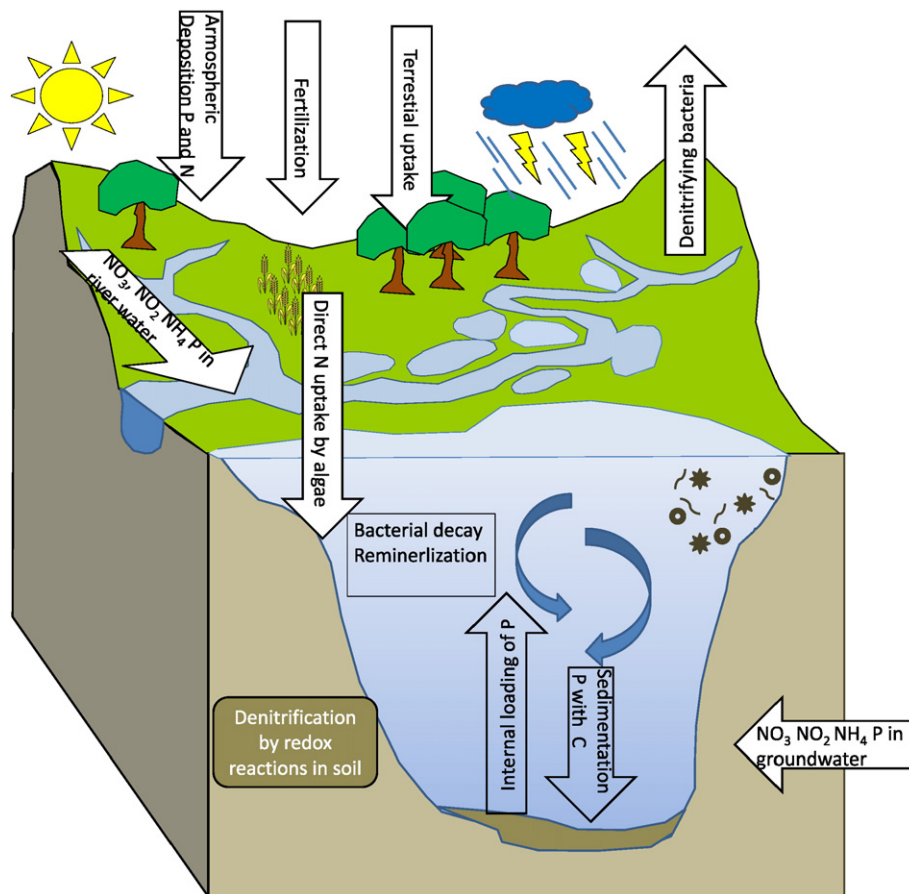


Fig. 7. Diagram illustrating the nutrient (P and N) cycles in a catchment containing multiple gravel pit lakes. Atmospheric deposition and fertilization add nutrients to the catchment; N is fixed by vegetation on land and algae in the surface water. P becomes part of lake sediments in chemical compounds that include organic matter (plankton). Adapted from Tranvik et al. (2009).

gravel pit lakes reviewed here are HCO_3^- rich (Table 2), so there will be probably no lack of inorganic carbon dissolved in water. As discussed in paragraph 4.2, P, N, Si and Fe may come in with river water in connected gravel pit lakes (Cross et al., 2014) or with groundwater into isolated gravel pit lakes (Weilhartner et al., 2012; Mollema et al., 2015a, b), so there is unlikely to be a shortage of these elements in gravel pit lakes. The life cycle of phytoplankton in gravel pit lakes contributes to denitrification of lake water which may improve water quality (Fig. 10; Helmer and Labroue, 1993; Muellegger et al., 2012; Weilhartner et al., 2012). Phytoplankton species richness in gravel pit lakes may be large (Arauzo et al., 1996; Cross, 2009; Garnier and Billen, 1994; Hindak and Hindakova, 2003; Padisák et al., 2003; Sayer and Roberts, 2001; Tremel, 1996) but varies from season to season and with water salinity (Chapman et al., 1997) and the input of river water during floods (Cross, 2009). Cyanobacteria that can take up N_2 directly from the atmosphere also occur in gravel pit lakes (Cross, 2009; Hindak and Hindakova, 2003; Rojo and Alvarez Cobelas, 1994). Microbial (bacterial) and fungal plankton (mycoplankton) live on detritus and play an important role in remineralising organic material down the water column and in nutrient cycling (Weisse, 2004). Zooplankton, also called grazers or herbivores, includes small protozoans or metazoans that feed mostly on phytoplankton, bacteria and detritus. In the spring, there is typically a strong increase in phytoplankton in temperate regions that leads to an increase in the zooplankton biomass and this is followed in many instances by a depletion of edible phytoplankton and a significant clearing of the water, often called 'clear water phase' (Lewis, 1980; Sommer et al., 1986). Aquatic macrophytes (water plants which can be viewed without a microscope) include vascular plants, mosses and the larger filamentous algae (e.g. Pokorný and Květ, 2004). They provide habitat

and food for zooplankton and zoobenthos, concentrate nutrients, and release oxygen during photosynthesis (Fig. 10). The rooting systems of macrophytes provide access to nutrients in the underlying littoral sediment and its interstitial water (e.g. Mo, Fe). Macrophytes may concentrate certain elements like P, K and Mn, which may reach 1000 and over 10,000 fold higher concentrations than the surrounding water (Dykyjova et al., 1998). They also play a role in the Ca cycle as photosynthetic uptake of free carbon dioxide and bicarbonate often leads to precipitation of calcium carbonate on the surface of water macrophytes (Pokorný and Květ, 2004) reducing thus the dissolved Ca concentration in lake water. Macrophytes enhance the rate of nutrient cycling as vegetated sediments showed significantly higher rates of N cycling than bare sediments (Vila Costa et al., 2016). Last but not least macrophytes together with phytoplankton and periphyton are also important determinants of the oxygen regime of the lake.

In older gravel pit lakes, the slopes may be too steep for all habitat types to be present. For example, the macrophyte zone (Fig. 10) may be very small or non-existent due to the lack of a shallow lake edge. The growth of submerged plants is related strongly to light availability, hence the importance of lake bed topography. On the other hand, in shallow gravel pit lakes the macrophyte zone may be relatively large while the pelagic zone may be small or missing. The macrophyte community may also change over time after extraction of gravel stopped (Lambert Servien et al., 2006). The topography of the lake bottom influences not only the macrophyte community but also other parts of the food chain as shown by Jeppesen et al. (1997) who found an inverse relationship between the relative contribution to secondary production of zoobenthos and lake depth. In smaller lakes the relative influence of the watershed increases with more rapid hydrological renewal, larger

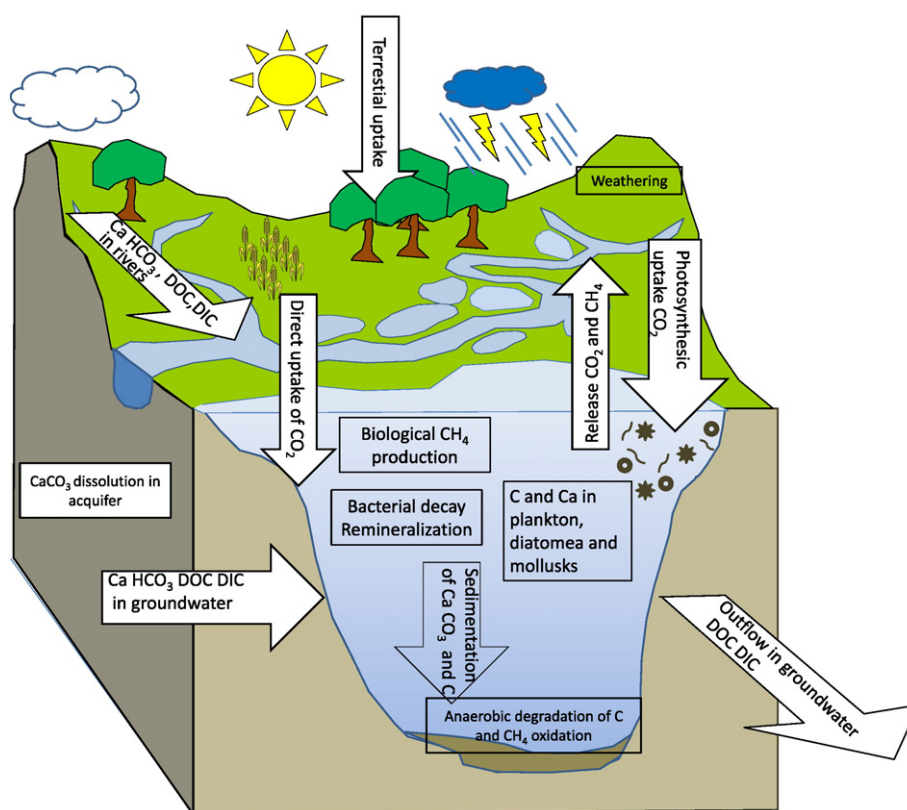


Fig. 8. Diagram illustrating the carbon cycle in a catchment containing multiple gravel pit lakes. Carbon dioxide is fixed by photosynthesis, bacterial decay and mineralization releases carbon dioxide, precipitation and deposition locks away the carbon in lake sediments. CaCO_3 is dissolved in the aquifer upstream from the gravel pit lake and transported to the gravel pit lakes. See text for further explanation.

nutrient imports and enhanced cycling. Most gravel pit lakes are in a suburban setting influenced by agricultural activities and as a consequence are eutrophic to hypertrophic with possibly algal blooms (Alvarez Cobelas et al., 1992; Cross et al. 2014). Deeper gravel pit lakes (Mollema et al., 2015a) or brackish gravel pit lakes (Chapman et al., 1997; Mollema et al., 2015b) may not have this problem so much. In coastal gravel pit lakes the unnatural salinity range ($5\text{--}12\text{ g L}^{-1}$) may limit species richness (Mollema et al., 2015a, b; Bleich et al., 2011). Fish and birds inhabit gravel pit lakes either naturally or artificially introduced (e.g. Giles, 1994; Santoul et al., 2009), and it is the subtle interaction between all levels of the food web, the influx of nutrients and other chemical elements as well as the climate that determine the stability and quality of gravel pit lake water (see Section 7).

6. Effects of climate change on hydrological aspects of gravel pit lakes

The changes foreseen by the IPCC (2013) due to anthropogenic emissions of greenhouse gasses include increasing air temperature over the time span of decades as well as changes in the seasonal variability of periods of droughts and rainstorms and sea level rise. In this section the influence of these changes on the hydrology of gravel pit lakes is discussed.

6.1. Changes in E and ET_a

We use data from two case studies to compare the water budget of gravel pit lakes. One case is the Meuse Lakes (The Netherlands) with a temperate climate. The Meuse Lakes or *Maasplassen* in Dutch are the collective name for 71 lakes that formed during gravel and sand excavation along the river Meuse in the southern Netherlands and North Belgium (Electronic supplement A). Today, they are mostly used for recreation

except one that is used for drinking water production (Mollema et al., 2015a). The total surface area of the 71 lakes between Swalmen (Netherlands) and Maaseik (Belgium) is 18 km^2 . For the Meuse Lakes we used the historical climate data of Maastricht (Netherlands, average 1981–2010) and future climate scenarios for the year 2050 and for the year 2085 as published by KNMI (2014), see Electronic supplement B for details.

The other study area is along the Adriatic Coast, (North Italy) with a Mediterranean Climate.

The brackish saline coastal gravel pit lakes near Ravenna, Italy occupy more than 6% of the surface in this catchment and are used mostly for recreation (Mollema et al., 2015b). We used the historical climate data for Ravenna for the reference period 1989–2008 from Mollema et al. (2012), and IPCC (2013) scenarios for the period 2046–2065, and for the period 2081–2100 (Electronic supplement C). To quantify the effect of these gravel pit lakes on the water budget of their respective catchments, we calculated the surface water E with the Penman Monteith equation as described in Maidment (1992) under current climate and future climate scenarios. We compared E with ET_a of a similar surface covered with grassland, under the same climatic conditions, calculated with Cropwat (Allen et al., 1998; Smith, 1992), a model based on the Penman Monteith (1948) equation and a soil water budget. The Cropwat model takes into account the difference between available water in the soil column and potential grass evapotranspiration, calculating thus the *actual* grass evapotranspiration.

The seasonal accumulative E and ET_a are shown in Fig. 11a (Meuse Lakes, NL) and Fig. 11c (Ravenna, It) while Fig. 11b and d show the precipitation for the reference period and future climate scenarios for respectively the Dutch and Italian site.

The calculations show that E of both the Dutch and the Italian gravel pit lakes will increase under all climate scenarios. The largest increase for the Dutch lakes is predicted under the Wh scenario for the year 2085: 38 mm (10%) in spring and 96 mm (17%) in summer with respect

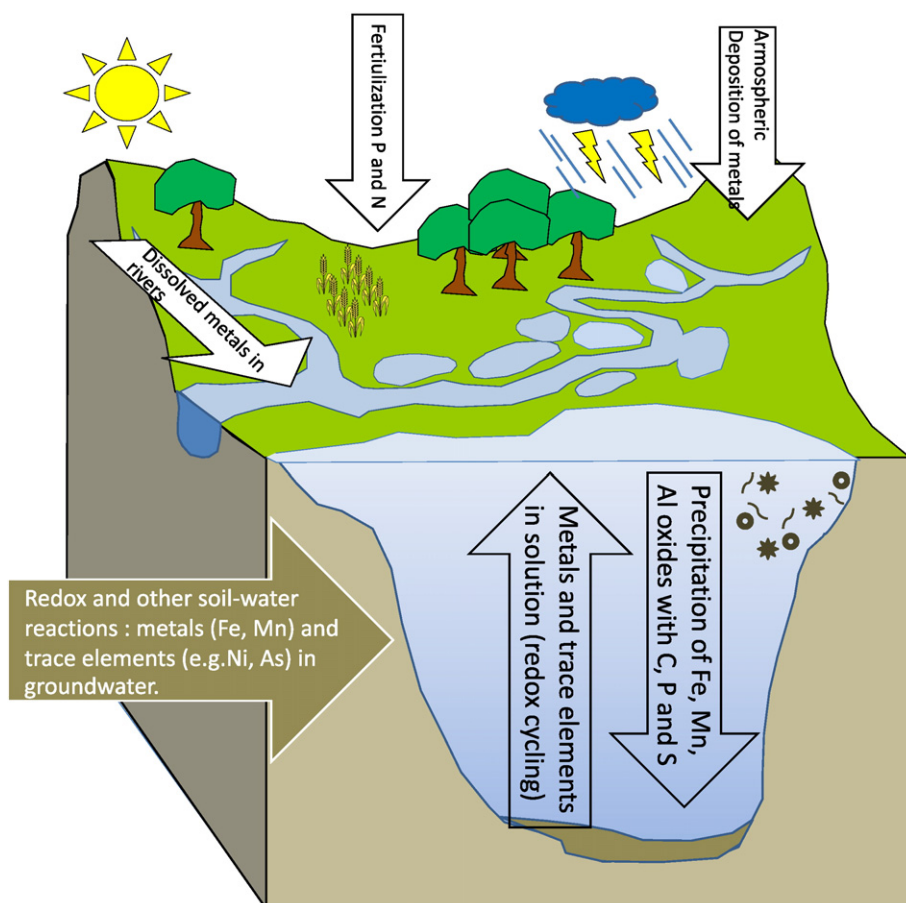


Fig. 9. Diagram illustrating the metal cycle in a catchment containing multiple gravel pit lakes. The metal cycle is related closely to the nutrient cycle. Hydrochemical processes include atmospheric deposition of metals and nutrients, redox reactions taking place in the soil up-stream of the gravel pit lakes whereby metal ions are dissolved in groundwater and transported towards the lakes. Oxidation of metal ions in lake water. Deposition of metal oxides (and sometime sulfides) and other components including P, C and Ca on bottom of lake.

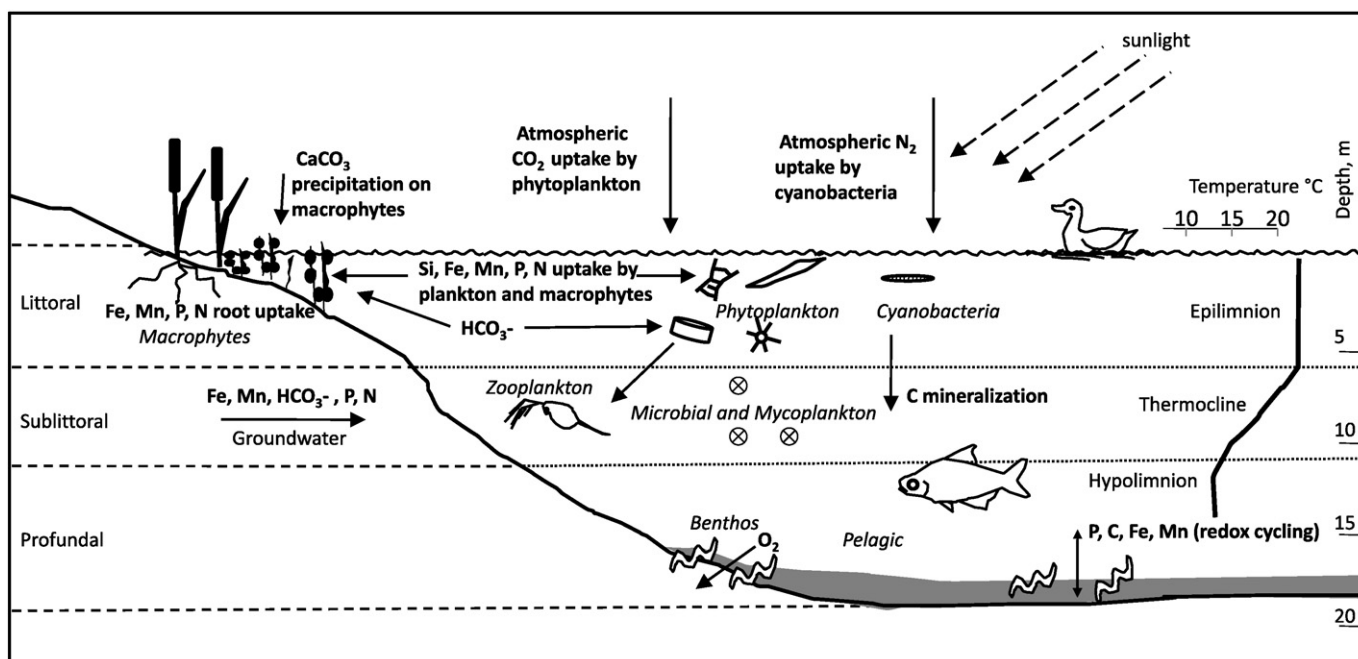


Fig. 10. Ecological communities in a gravel pit lake and interaction with the chemical cycles.

to the period 1981–2010 (Fig. 11a). The E rate in the Mediterranean climate is already high but there is an increase to be expected by the end of the century: in spring by 35 mm (8%) and in summer by 56 mm (14%). The increase is caused by the increase in maximum and minimum temperature and solar radiation and in the Netherlands, also by a decrease of the relative humidity (KNMI, 2014). ET_a near the Dutch gravel pit lakes during spring will increase in 2050 by 6 mm and in 2085 by 26 mm under the Wh scenario. Summer ET_a will increase in 2050 by 15 mm (8%) under the Gl scenario but will decrease by 50 mm (28%) under the 2085 Wh scenario (Fig. 11a). The decrease can be explained by the fact that precipitation under the Wh scenario will decrease considerably during the growth season, so that there will be less soil moisture available for transpiration even though the sun will provide enough energy.

ET_a in Ravenna will increase in summer but will decrease in spring since there will be less precipitation in that season (Fig. 12). The historical ET_a for Ravenna is similar to the future ET_a rate for the Netherlands by the end of the century (Compare Fig. 11a and c): ET_a is higher in spring than in summer because there is more soil moisture available.

In summary, under these climate scenarios, catchments with gravel pit lakes in a temperate and Mediterranean climate, where evaporated gravel pit lake water is replaced immediately with inflowing ground or river water, will lose more freshwater due to E than a catchment without gravel pit lakes would lose due to ET_a . This confirms a world wide trend of increase in water withdrawal due to evaporation from artificial lakes and reservoirs: from the year 1900 to 2010 evaporation from artificial lakes and reservoirs increased from practically 0 to 333 km³ year⁻¹ and now amounts to 8% of total global water withdrawal (FAO, 2015). The increasing numbers of gravel pit lakes excavated in this period contributes to this process.

The Meuse Lakes cover a total surface area of 18 km² (Electronic supplement A). Much more water (12.4×10^6 m³ by 2050 and 15.3×10^6 m³ by 2085) will evaporate during future summers than if the catchment had consisted of the original grassland. A change of land use from forest to grassland is often incorporated in basin wide

water balance models (e.g. Ward et al., 2008) but similarly the change from grassland to surface water (i.e. gravel pit lakes) should be taken into account or these models may underestimate the amount of water leaving the watershed by E and ET_a .

6.2. Hydrological and meteorological extremes

Besides the more or less gradual changes in average climatic parameters, also more sudden changes will affect gravel pit lakes such as droughts and floods caused by concentration of storms in shorter periods foreseen by IPCC (2013). Cross et al. (2014) found that under such extreme hydrological conditions British gravel pit lakes connected to the River Erewash were affected differently than those isolated from the river. In particular, the isolated lakes had longer water residence (retention) times, smaller influx of nutrients and higher extent of internal nutrient recycling than the lakes connected to the river (Cross et al., 2014; see Section 7.2 for the ecological consequences of these processes). During droughts or floods, lake levels could fall or rise but whether this will happen depends on the changes in the river flow for lakes that are fed by river water and on groundwater levels for flow through lakes. Changes in natural or artificial drainage required by climate and land use change will affect the water budgets of gravel pit lakes. For example in a low lying coastal plain setting, a rising sea level would require enhanced drainage of the low lying land which would augment the groundwater flow into the gravel pit lakes (Mollema et al., 2015b). If the Cl concentration of groundwater is lower than that of lake water, the resulting Cl concentration of the lake will decrease under enhanced drainage while increasing evaporation will instead increase Cl concentration. Periods of droughts and rainstorms however could dilute or concentrate lake water in a short period.

6.3. Lake and groundwater temperature

Shallow (2 to 3 m) gravel pit lakes typically show a weak temperature stratification only during summer (Cross, 2009). However, gravel

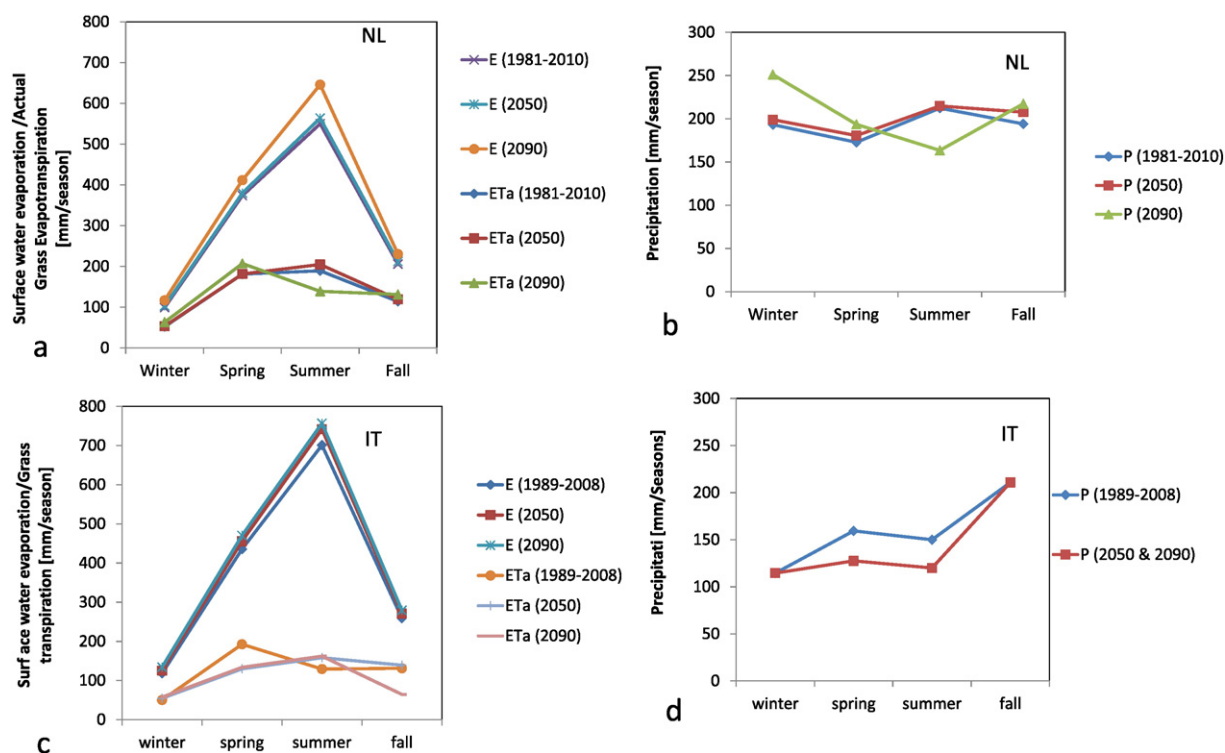


Fig. 11. a. E and ET_a for the Dutch case study for the period 1981–2010 and for future climate scenarios for the year 2050 and 2090. b. Precipitation (P) for the Dutch case study for the period 1981–2010, for the period 2050 (scenario Gl) and for 2085 (Wh). c. E and ET_a for the gravel pit lakes near Ravenna (Italy) in the period 1989–2008 and 2050 and 2090 based on scenarios by IPCC (2013). d. P for Ravenna (Italy) for the period 1989–2008 and for 2050 and 2090 based on scenarios by IPCC (2013).

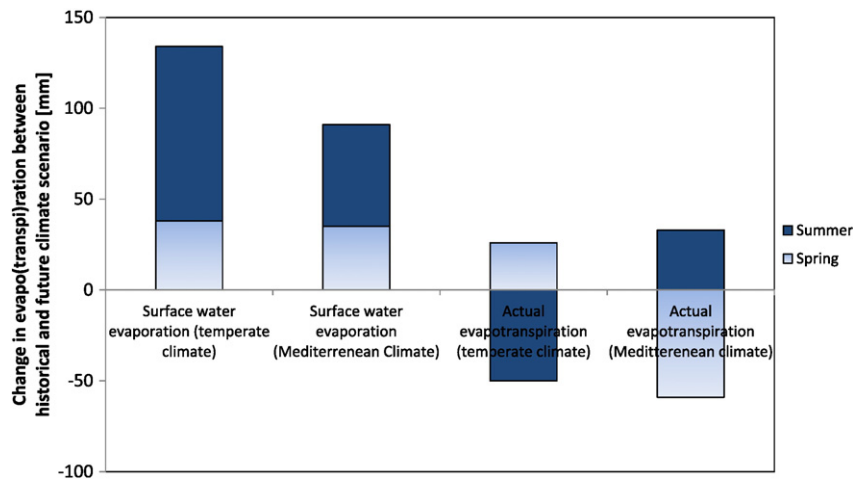


Fig. 12. Histogram showing the change in E and ETa for temperate and Mediterranean climate calculated with historical data and with a climate change scenario for the end of the century. A positive change means that the evaporation rate will increase.

pit lakes, if they are deep enough, may be thermally stratified with a distinct epilimnion, thermocline and hypolimnion as observed in the Boschmolen lake (The Netherlands) that is 30 to 40 m deep (Figs. 10, 13), similar to natural lakes (Imboden and Wuest, 1995; Imboden, 2004). De stratification by air pumps may occur in gravel pit lakes used for drinking water production (Mollema et al., 2015a).

As far as we know, no observations on changing water temperatures over time for gravel pit lakes have been published but Scheffer (2001) reported increasing shallow lake water temperatures in the Netherlands, Schneider and Hook (2010) observed rapid surface warming of all inland water bodies since 1985 and Schmidt et al. (2014) found that the lake surface equilibrium temperatures are predicted to increase by 70 to 85% of the increase in air temperatures as a response to climate change. The maximum difference between surface and bottom water temperatures in stratified lakes is projected to increase by 1 to 2 °C with a local maximum of 3.2 °C due to climate warming (Fang and Stefan, 2009). Climate change may force more prolonged stratification in deep lakes or temporary stratification in shallow lakes and increase average annual lake stability affecting ecological functioning of the lake (Section 7; Jensen and Andersen, 1992; Sahoo et al., 2015; Søndergaard et al., 2003). Higher lake temperatures also change the solubility of minerals, their reaction kinetics and the resulting chemical profiles (Fang and Stefan, 2009; Löffler, 2003; Yu et al., 2010).

Increasing air temperatures as predicted by climate change will affect groundwater. Many gravel pit lakes are flow through lakes fed by

groundwater. As a result, a change in temperature of in flowing groundwater will affect the gravel pit lake water. However changes in groundwater temperature due to changes in air temperature are much smaller than changes in direct warming of surface water, so that their effect on hydrochemical processes is likely to go unnoticed (Bonte et al., 2013).

7. Implications of land-use and climate change on chemical and ecological aspects of gravel pit lakes

The consequences of climatic change will be felt in all functions of gravel pit lakes including the chemical cycles and the ecological functioning. In reality, changes in hydrology, water chemistry and ecological functioning are strongly related. A change in water chemistry will change lake ecology and vice versa, a change in the ecology will influence the chemical cycles. The separation into distinct paragraphs below on changes in nutrient, carbon, metal cycling and in ecological functioning are therefore only to facilitate reading. Where links exist between the changes in different functions of gravel pit lakes, they are indicated.

7.1. Nutrient cycling under climate and land use change

There are several possible effects of climate change on the nutrient cycle of gravel pit lake systems. In case of enhanced average annual amount of precipitation, for example, the flux of nutrients in cultivated areas from groundwater into gravel pit lakes could increase as foreseen for other surface waters in North Europe, enhancing eutrophication and risk of algal bloom (Andersen et al., 2005; Jeppesen et al., 2009, 2012; Smith and Schindler, 2009; Trolle et al., 2015). On the other hand, a future decrease in average annual precipitation could limit the influx of nutrients into surface water as predicted for the Netherlands (Visser et al., 2012) and also observed in some gravel pit lakes along the river Meuse (Boschmolen plas and Anna's Beemd, Mollema et al., 2015a). Better management practices and policy guidelines that aim to reduce the nutrient load into groundwater may also lead to a long term (years decades) reduction in nutrient load (Weiske et al., 2013). It has been difficult until now to separate the effect of changes in climate from changes in land use on nutrient concentration in ground and surface water (Jeppesen et al., 2014). Climate change itself induces a land use change: more forests will grow and terrestrial production will increase in areas receiving sufficient precipitation, whereas the opposite will happen under drier conditions (Hessen et al., 2009). On a long term scale (decades to centuries) changes in catchment properties will regulate the flux and fate of C, N, P, in catchments, while on a

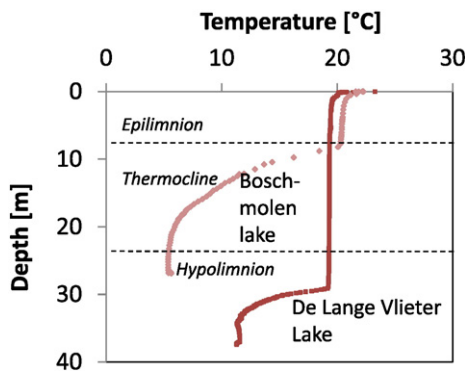


Fig. 13. Summer temperature profiles in gravel pit lake De Lange Vlieter (The Netherlands) with river water infiltration, and air blowers and no stratification and in the Boschmolen lake without artificial mixing, and stratification into epilimnion, thermocline and hypolimnion.

Modified from Mollema et al., 2015a.

shorter time scale (seasonal e.g. Søndergaard et al., 2005; years to decades) changes in anthropogenic effects on the N cycle, temperature, precipitation patterns, and soil or root processes will be dominant. Regardless of a load reduction into gravel pit lakes, the P concentration may still remain high, particularly in shallow eutrophic (gravel pit) lakes, due to a high natural internal load within the lake sediments (Cross et al., 2014; Fisher et al., 2009; Jeppesen et al., 2014; Ozen et al., 2010). See Section 7.4 for relationship between nutrients, ecological functioning and seasonal changes.

7.2. Carbon and Ca cycling under climate and land use change

The effects of acid rain in the first part of the 20th century and of climate change in its latter part confuses the analysis of changes in pH and temperature that influence the carbonate equilibrium and carbon cycle in surface waters. No studies on gravel pit lakes in particular are available but some studies on natural lakes give insight into changes that may occur in gravel pit lakes. The average long term Dissolved organic carbon (DOC) of lake water may increase due to enhanced annual average precipitation, runoff, and groundwater inflow related to changes in terrestrial vegetation cover, wetlands and ice melting (Liu et al., 2010; Tranvik et al., 2009). Instead average annual runoff and DOC may decrease over the next few decades in the Mediterranean region where as much as a 25–30% decrease in freshwater runoff is expected by 2040–61 (Giorgi and Lionello, 2008). Boreal lakes are known to change from being a source of CO₂ to sequestering CO₂ (Finlay et al., 2015), explained by accumulating CO₂ under ice in winter. On the other hand, the carbon efflux in form of CO₂ emission from lakes could instead increase in response to elevated temperatures and increased hydrological delivery of mineralizable dissolved organic matter (Tranvik et al., 2009). The amount of organic carbon in lake sediments could diminish as mineralization of organic carbon in lake sediments exhibits a strongly positive relationship with temperature (Gudas et al., 2010). A decrease in organic content of lake bottom sediments over a period of 10 years was observed in a gravel pit lake in the Netherlands (Mollema et al., 2015a) but it is difficult to separate the effect of the use of the lake for artificial recharge from other processes. The solubility of CaCO₃ could decrease due to higher epilimnetic water temperatures and higher pH that change the carbonate buffering conditions in lakes (Walpersdorf et al., 2004) as observed in boreal lakes (Jezierski et al., 2008) and alpine lakes (Psenner and Schmidt, 1992), and in rivers (Meybeck, 2003). Analysis of alkalinity trends in rivers of the USA (Stets et al., 2014) and of small head water systems (Chen and Lin, 2009) relates an alkalinity increase over years and decades to recovery from acidification and lime use in agriculture. Although changes in nitrate leaching over years to decades to gravel pit lakes and reservoirs has been observed (Mollema et al., 2015a, b; Weiske et al., 2013) the relationship to the carbon and calcium cycle has not been documented yet.

7.3. Metal and trace element cycling under climate and land use change

The metal cycles of a catchment and its gravel pit lakes are closely related to the acidity and redox potential of ground and surface water in the catchment and to input of NO₃ and PO₄. If one of these parameters changes, also the amount of dissolved metals in the gravel pit lakes and the amount or type of metal oxides deposited on the lake bottom may change. An increase of dissolved As concentration in a reservoir was thus correlated to a decrease in agricultural fertilizer use, explained by a release of As from reservoir bottom sediments (Weiske et al., 2013). In the future, because of reduced application of fertilizers, the NO₃ concentration is expected to decrease. This could lead to less available oxygen (either as DO or NO₃) that influences biochemical cycles (e.g. P release from sediments). The average lake water pH may change over a period of years to decades as a consequence of climate change, recovery from acid rain or a change in land use (less fertilizers) as observed for other types of lakes and rivers. With changes in pH,

alkalinity or NO₃, the reactions that caused the deposition of the metals and trace elements on the lake bottom may be reversed and metals and trace elements may go again into solution. This could possibly create a toxic environment for plants, animals and humans. A change in ground water and lake temperature has an effect on the solubility of metals as was observed for Al by Veselý et al., 2003: higher temperature caused lower Al mobilization in soil horizons and/or enhanced precipitation of Al in natural lakes. Given enough time, all (trace) metals and organic material will be leached from aquifers upstream to gravel pit lakes. This will require hundreds or thousands of years at the current natural recharge rates since many pore volumes of water flushing the aquifer are needed to leach only small parts of the solid rock matrix (Antoniou et al., 2013). Climate change may affect those recharge rates and consequently aquifer and lake hydrochemistry including metal mobilization. For example, Visser et al. (2012) predicted that reduced groundwater flow associated with droughts would reduce the leaching of heavy metals to surface waters in a Dutch catchment.

7.4. Ecological functioning under climate and land use change

Biodiversity, ecosystem services and the benefits to society that flow from them are increasingly threatened by habitat loss and fragmentation and climate change, among others. This holds true also for gravel pit lakes although few specific studies have been done so far on these particular types of lakes. Species will respond differently to climate change and thus new communities of species will form with unknown consequences for ecosystem functioning (e.g. Walker and Steffen, 1997). Many gravel pit lakes are isolated and as such form a fragmented ecosystem, from which species cannot easily move away to other habitats (e.g. Malcolm et al., 2002). Certain 'niche' parameters may not change in the same way or at the same rate as certain climate parameters, resulting in the appearance of new habitats in gravel pit lakes. Changing interactions between different species are difficult to predict as each species reacts differently to climate change (e.g. Lavergne et al., 2010). Furthermore, invasion of alien species is already a worldwide problem and will also affect gravel pit lakes.

Gradual changes in temperature (Scheffer, 2001) with depth in lakes as well as changes in water residence time (Reynolds, 2004) will affect the timing and presence of the clear water phase: warm winter and spring conditions can lead to an earlier and longer lasting clear water phase than in cold winters, owing to earlier life cycle development of zooplankton and longer periods of zooplankton survival (Straile, 2000). In addition to gradual changes, hydrological extremes can suddenly alter the properties of lake ecosystems (Cross et al., 2014). Longer water residence times, for example, may lead to phytoplankton blooms which can significantly deplete the in lake concentrations of NO₃ N and SiO₂ (Cross et al., 2014; Reynolds, 2004). Deeper lakes respond differently to changes than shallow lakes, the latter showing a positive trend in total N and total P loss with increasing temperature, most likely related to macrophyte growth (Coppens et al., 2015).

Increasing nutrient load in combination with higher water temperatures and more intense and longer stratification as well as the fact that cyanobacteria have a large tolerance for water temperature and salinity ranges may lead to a dominance of these toxic bacteria (Paerl and Paul, 2012; Wagner and Adrian, 2009 and references therein). In some natural lakes, the changes in hydrology and input of N from the catchment have a larger influence on the N budget of lakes than climatic effects related to temperature, salinity and water level (Olsen et al., 2015). Hydrochemical or physical changes in lake water will most likely alter species and ecosystems. However, Craig et al. (2015) found that for shallow temperate lakes the availability of a well oxygenated habitat can compensate for lack of DOC or light limitation of benthic primary production. Temperature increases and heat waves have been shown to affect the submerged macrophytes, which showed adaptive changes in growth and asexual reproduction (Cao et al., 2015).

In the Mediterranean and other arid and semi arid regions, the warmer temperatures may enhance evaporation and evapotranspiration that can lead to increased salinity in gravel pit lakes and other surface waters (Williams, 2001; Mollema et al., 2015b), with negative effects on the diversity of phytoplankton, zooplankton, macro invertebrates and fishes (Cucchiari et al., 2008; Jeppesen et al., 2014; Brucet et al., 2012) as well as on vegetation (Antonellini and Mollema, 2010). The reduction in the size and abundance of zooplankton grazers due to enhanced salinity may further negatively affect the resilience of lakes to enhanced nutrient loading (Brucet et al., 2012).

8. Future research directions

8.1. Water budget measurements

The water budget of gravel pit lakes includes two components that are not easy to measure directly or quantify: surface water evaporation and groundwater inflow. Direct measurement of surface water evaporation in lakes is notoriously time consuming and complicated although floating evaporation pans have been developed and successfully tested (Masoner et al., 2008, 2007; Masoner and Stannard, 2010). Placing evaporation pans close to but not on the lake water surface is more practical but less representative. Pan evaporation trends, however, show decreasing surface water evaporation despite global warming indicating that the interplay between climate variables on evaporation needs more fundamental physical research (Fu et al., 2009). Most methods for determining surface water evaporation (or evapotranspiration) are based on formulae developed for example by Penman Monteith or Thornthwaite that use climate data. It is known, however, that small lakes have different surface evaporation rates than large lakes (e.g. Maidment, 1992; Winter et al., 1995) and it is even more difficult to measure evaporation rates over multiple gravel pit lakes. Remote sensing data is increasingly used to quantify components of the water budget over large areas, in particular of soil moisture (see Seneviratne et al., 2010 for a review) and changes in groundwater storage (Green et al., 2011; Yeh et al., 2006) or vegetation and evapotranspiration (e.g. Pôças et al., 2013). This type of study could be helpful in large catchments with gravel pit lakes. If the amount of surface evaporation and the stable isotope composition of the so called evaporation end member ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are known, a mass balance equation (e.g. Skrzypek et al., 2015) can be used to determine the amount of groundwater flowing into gravel pit lakes, as demonstrated for natural lakes (e.g. Gibson et al., 1993, 2008; Mayr et al., 2007) and applied to gravel pit lakes by Jones et al. (2016) and Mollema et al. (2015a, b). Better understanding of the fractionation of stable isotopes in various parts of a catchment, on small lakes and in particular in gravel pit lakes under various climatic conditions is needed. Tracer studies using other environmental (natural) tracers than stable H or O isotopes in combination with modeling may help to understand flow paths and residence time of water in gravel pit lakes. These include tracers that have a known rate of decay or fractionation (e.g. ^{39}Ar , ^{14}C , ^{36}Cl) or are non reactive while in the subsurface (e.g. noble gas isotopes) or those that accumulate over the time spent in the subsurface (e.g. ^{36}Cl , ^3He , ^4He ; see for an overview Turnadge and Smerdon, 2014). Another type of tracer is heat as used in groundwater flow (Anderson, 2005).

Groundwater flow into gravel pit lakes could be measured by seepage meters as used in studies of submarine groundwater discharge (e.g. Taniguchi et al., 2006) or by geophysical measurements as done in natural lakes (Nyquist et al., 2009). In combination with all these methods, hydrological modeling including watershed modeling will help reduce uncertainties in water budgets (e.g. Kauffeldt et al., 2016). The effect of lakes themselves on changes in climate is not yet completely understood and (small) lakes need to eventually be incorporated in weather prediction and climate models as sources for atmospheric moisture (Mironov et al., 2010).

8.2. Hydrochemistry, ecological functioning and biomanipulation

So far, few detailed hydrochemical studies of gravel pit lakes have been published. With time, more data will become available and the more subtle differences between the hydrochemistry of gravel pit lakes in different hydrogeologic settings (glacier, fluvial, coastal setting) may become clear (e.g. Stephenson et al., 1988). Long term monitoring over years and decades of lake water and groundwater quality as well as the ecology will help to better understand and separate the effects of land use change upstream from gravel pit lakes from those caused by climate change, including extreme climate change (Trolle et al., 2015). It is important to consider many aspects of the catchment containing gravel pit lakes including climate, and river, groundwater and surface water quality. To this end, both water fluxes and water quality need to be monitored. In particular, it is important to be able to take groundwater samples from specific depths without mixing shallow and deep groundwater, for example by constructing multilevel samples with minifilters (e.g. Pickens et al., 1978; Butler et al., 1999; Einarson and Cherry, 2002). This monitoring methodology will also help to better map the heterogeneities in aquifer material with the role of specific organic layers associated with particular metals (for example Al) becoming more apparent. In some situations, groundwater flows in and out of one gravel pit lake and then into another gravel pit lake. As far as we know, it is currently unknown how the multiple transit of groundwater through lakes affects ground and lake water properties. Most hydrochemical studies of gravel pit lakes now focus on nutrients, eutrophication, the foodweb, major ion chemistry or (trace) metals. There are many other chemical elements that need to be researched for their environmental impact, for their possible use as tracers of flow paths or to determine the hydrochemical processes that occur both in the aquifer and in gravel pit lakes. These include organic contaminants, pathogens, pesticides, and pharmaceutical compounds. Another challenge in studying gravel pit lakes is the collection of water or sediment from the lake bottom or below as it is expensive and time consuming and not always routinely done, especially if the lakes are deep (>20 m). This would, however, help to increase our knowledge of redox cycling and the speciation of metal oxides and other compounds including P, C, trace elements and metals that are deposited on gravel pit lake bottoms, and to follow changes in their concentration over time.

The hydrological and hydrochemical changes need to be studied in relation to ecosystem changes, especially with regards to the effects of extreme variations in water level and salinity in lakes due to extreme climate events (Jeppesen et al., 2015). For example, drought related reacidification effects on water chemistry is thought to have important effects on algal communities in acid sensitive lakes with modest wet land coverage (Faulkenham et al., 2003).

To better understand the ecological response to changes in climate or land use and the explicit links between species evolution, species assemblages, and ecosystem functioning, the study of evolutionary biology and community ecology needs to be combined (see Lavergne et al., 2010 and references for a review) with (hydro)chemical (e.g. Appelo and Postma, 2005) and ecological (Turner et al., 2016) modeling. The genetic alteration or adaptation of one particular species to (climatic) changes will affect the whole ecosystem and complicated feedbacks are recognized to exist (Lavergne et al., 2010). For example, stratification in lakes in temperate areas may persist over longer periods of the year (Sahoo et al., 2015), extending the reproductive season of plankton with consequences for the whole food web. Because gravel pit lakes are typically in densely populated and agricultural countries, nutrient levels and eutrophication (Muellegger et al., 2013), in particular with toxic cyanobacteria (Cross et al., 2014), are a reason for concern. Possible management strategies to cope with external or internal nutrient loading are, for example, chemical treatment of the water to precipitate phosphorus and to reduce internal phosphorus loading and thus phytoplankton growth. Another possibility restricted to (summer) stratified lakes is to add oxidizers to an otherwise anoxic hypolimnion, for

example with air pumps that introduce oxygen. Alternatively nitrate may be used as an oxidizer but caution is needed to avoid eutrophication and (toxic) algal blooms. Often these chemical methods are applied together with biomanipulation that generally includes eliminating or introducing certain plant or animal species (Jeppesen et al., 2012; Smolders et al., 2006). This has been done in gravel pit lakes (Giles, 1994; Jeppesen et al., 2012; Søndergaard et al., 1990). While this approach has worked well in many cases in northern and temperate lakes where there is a period of low or no reproduction, it has proven more complicated in Mediterranean or (sub)tropical lakes where biomass, biodiversity and species richness tends to be larger and the ecosystems more complicated and where reproduction occurs (almost) year round (Jeppesen et al., 2012). In natural lakes, phytoplankton is controlled by removal of zooplankton or benthic omnivorous fish, and stocking of predatory or pelagic herbivorous fish (see review in Jeppesen et al., 2012). Macrophyte transplantation to offer habitat for zooplankton or instead introduction of herbivorous fish to control the growth of macrophytes is another method to control phytoplankton (see Jeppesen et al., 2012 and references for an overview). Whether macrophytes are successful in a lake depends among others on whether the lake sediments have sufficient organic content and limited toxic substances (e.g. Smolders and Roelofs, 1996).

Besides biomanipulation there are hydrologic interventions that may help to maintain water quality and ecosystem stability. These include water table management and hydrological connectivity to the river system of fluvial gravel pit lakes. In addition, adding Fe or other chemical elements which naturally bind to phosphate may help control lake water quality and ecosystem functioning (Geurts et al., 2008; Immers et al., 2015; Smolders et al., 2006).

Controlling nutrient concentrations and eutrophication while at the same time making gravel pit lakes suitable for specific ends may be difficult. For example, the artificial recharge with nutrient rich river water of a Dutch gravel pit lake leads to high NO_3 concentrations so that air blowers are needed to prevent eutrophication and degraded water quality. Another possible conflict may arise between recreational users and nature conservation of gravel pit lakes. For example, macrophytes will help to restore shallow lakes and to clear the water but if plants become abundant they will cause nuisance to boating and swimming and obstruct water flow (van Nes et al., 2002). Vice versa recreational activities may disturb certain species such as birds (Pochard; Fox et al., 1994). Possibly different uses of gravel pit lakes, for example the storage of heat (Novo et al., 2010), will present new challenges as it affects the hydrochemistry as well as the ecology in as yet unknown ways. All this will be controlled by policy guidelines as for example those of the Water Framework Directive (WFD; European Commission, 2000) with special elaboration for groundwater (European Commission, 2006a) and on discharges of certain dangerous substances (European Commission, 2006b) as well as on the technical specifications for chemical analysis and monitoring of ground and surface water status (European Commission, 2009). Gravel pit lakes are not mentioned as a separate type of environment to monitor but they fall under inland surface waters, groundwater, transitional waters and coastal waters.

Eventually we should be able to better understand the effect of a system of multiple (tens of) gravel pit lakes not only on the catchment near the lakes but also on the chemical budget downstream in the estuary and its offshore area. For example, one gravel pit lake is estimated to 'trap' the following quantities of metals in its bottom sediments: Ni 113 kg year^{-1} , Zn $1439 \text{ kg year}^{-1}$ and Fe $16,676 \text{ kg year}^{-1}$ (Mollema et al., 2015a). Assuming these values are representative for the catchment then the 71 gravel pit lakes present in the catchment together prevent 1.3 million kg of metal to reach the (submarine) estuaries and shore downstream. The transport of other metals is also likely to be significantly affected. Dissolved metals and other solutes play an important role in coastal ground water and submarine estuaries and changing the budgets of these solutes upstream affects the ecosystem along the coast (Moore and Shaw, 2008 and references therein).

9. Summary and conclusions

Gravel pit lakes are excavated in gravel deposits along rivers, in glacial valleys and in old beach gravel deposits to fulfill the need for building materials. In some cases, many (tens) of these lakes have formed close to one another creating, in aggregate form, a large new open water surface. The gravel pit lakes change the environment in many ways concerning landscape, land use, the hydrology, hydrochemistry, biochemistry and ecology and may exist for thousands of years. The drainage pattern of a catchment changes in presence of gravel pit lakes possibly causing changes of the water table over a large area. If occurring in a coastal zone, these fluctuations and the presence of the gravel pit lakes will enhance salt water intrusion. Gravel pit lakes can be flow through lakes where groundwater moves through the lake downstream towards a river or other draining feature. Water budget calculations show that catchments with many gravel pit lakes in temperate and Mediterranean areas are much more sensitive to changes in evaporative losses caused by climate change than they would be without gravel pit lakes. Gravel pit lakes studied in great detail so far occur in fluvial and coastal settings and are relatively alkalinity and Ca rich, most similar to 'marl' lakes or 'nutrient rich' lakes. When groundwater flows into gravel pit lakes, the concentration of many dissolved elements changes due to redox, precipitation and dissolution reactions. Gravel pit lake water therefore is typically enriched or depleted in specific chemical components with respect to the inflowing ground water. Gravel pit lake water shows (on the basis of the reviewed studies) a smaller variation than natural lakes in pH and concentration in HCO_3 and metals (e.g. Fe, Ni). Gravel pit lakes influence the nutrient cycle of a catchment by incorporating N and P that flows into the lake with groundwater or atmospheric deposition in biomass and bottom sediments. The nutrient cycle is related to the carbon and metal chemical cycles as fertilization upstream from the lakes mobilizes metals in groundwater that eventually are incorporated into bottom lake sediments. In this way, gravel pit lakes may contribute to denitrification of groundwater but they may also enhance the mobilization of soil bound compounds like metals. Gravel pit lakes offer space for many different ecological habitats increasing the biodiversity in an agricultural or an urban setting. Plants and animal species including phytoplankton, zoobenthos and macrophytes, fish and birds take part in the chemical cycling of gravel pit lakes among others, by uptake of atmospheric CO_2 and N_2 , uptake of dissolved compounds including HCO_3 , Fe and Mn; by uptake of elements including P, Fe from lake sediments and by carbon mineralization and burial. Gravel pit lakes typically receive nutrient rich water from rivers or groundwater which may cause eutrophication. The (bio)chemical cycles may change over time since gravel pit lakes have formed only recently and land use and climatic change play a role in their future evolution. Therefore key areas for further research include the study of gravel pit lakes in other settings to better separate the similarities and differences between natural and gravel pit lakes as well as the feedback mechanisms between change in land use, climate and water quality and ecosystem functioning. Understanding these feedback mechanisms as well as the effects of chemical changes or biomanipulation, will help society to use gravel pit lakes efficiently and contemporaneously for multiple uses including ecosystem services, storing water and recreational areas. The planning of new gravel pit lake excavations should include an evaluation of possible freshwater loss by evaporation, chemical processes such as metal accumulation in lake bottoms, and ecological functioning in relation to eutrophication and nutrient fluxes.

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Appendix A. List of symbols

Symbol (alphabetical order)	Name
Al	Aluminum
As	Arsenic
Ba	Barium
C	Carbon
Ca	Calcium
CaCO ₃	Calcium carbonate
CH ₄	Methane
Cl	Chlorine
Cl	Chloride ion
Co	Cobalt
CO ₂	Carbon dioxide
δ ² H (‰ vs VSMOW)	Hydrogen 'heavy' isotope, delta notation
δ ¹⁸ O (‰ vs VSMOW)	Oxygen 'heavy' isotope, delta notation
DIC	Dissolved inorganic carbon
DLV	De Lange Vlieter (gravel pit lake in NL)
DOC	Dissolved organic carbon
E ET _a	Evaporation
Fe	Actual evapotranspiration
H ₂ S	Iron
HCO ₃	Hydrogen sulfide
N Ni	Bicarbonate
NO ₃	Nitrogen
OC P	Nickel
PO ₄	Nitrate
pH Si	Organic carbon
SO ₄	Phosphorus
TD\$	Phosphate
Zn	Acidity
	Silicon
2	Sulfate
	Total dissolved solids
	Zinc

Appendix B. Supplementary data

Supplementary data associated with this article can be found in on line version, at <http://dx.doi.org/10.1016/j.earscirev.2016.05.006>. These data include the Google map of the most important areas described in this article.

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