The influence of flow-through saline gravel pit lakes on the hydrologic budget and hydrochemistry of a Mediterranean drainage basin

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Abstract

Flow-through brackish gravel pit lakes near the Adriatic Coast of Emilia Romagna (Italy) in the Mediterranean have a large influence on the hydrologic budget of the watershed. Strong evaporation in combination with intense drainage of the low lying basins enhances groundwater inflow into the lake. Precipitation falling on the lakes is mixed with brackish/saline lake water causing the loss of freshwater. The gravel pit lakes are characterized by a high salinity (TDS = 4.6–12.3 g L^{-1}) and high pH (8.5). Stable isotope data show that gravel pit lake water is fed by groundwater which is a mix of Apennine River water and (Holocene) Adriatic Seawater, subsequently enriched by evaporation. The slope of the local evaporation line is 5.4. Conservative tracer and water budget modeling shows that the final Cl concentration depends strongly on the ratio of evaporation to total inflow. Increasing drainage to compensate for sea level rise, subsidence or intense precipitation would enhance ground water flow into the lake and decrease Cl concentration while increasing evaporation would increase Cl concentration. Groundwater rich in dissolved trace elements flows into the gravel pit lakes that contains water with a higher pH and dissolved oxygen. Pit lake water remains enriched in some elements (e.g., Ba, Mo, Sb) and depleted in others (e.g., Fe, Ca, Zn, SO4) with respect to groundwater composition. The gravel pit lakes show limited eutrophication but the water quality should be monitored for trace elements (e.g., As) if they are to be used for recreational purposes.

Our modern society uses an enormous amount of sand and gravel to construct buildings, highways and anything made of concrete. According to the USGS (2011) the main producers of sand and gravel extract a total of $10^8 \times 10^6$ metric tons per year, and Italy is the top gravel and sand producer after the United States with 14×10^6 metric tons per year. There are 5592 active and 16,045 abandoned quarries in Italy of which 62.5% are for the extraction of sand and gravel (Legambiente 2014). Gravel typically is produced from natural gravel deposits such as streambeds, beach deposits, or alluvial fans. Where the gravel pits are excavated below the water table, they fill up with groundwater and become artificial lakes. These lakes change the hydrology and chemistry of the surrounding sediments, the soil, surface- and groundwater. Changes in hydraulic gradient may cause

groundwater to flow towards, away or through these gravel pit lake lakes, in the latter case making them so called flow-through lakes (e.g., Kidmose et al. 2011). Gravel pit lakes may have a positive effect on water quality when for example phosphates and nitrates are depleted biochemically by residence of groundwater in gravel pit lakes (Weilhartner et al. 2012; Muellegger et al. 2013). They may however also have a negative effect on water quality by allowing the mobilization of soil-bound compounds like arsenic, the growth of harmful algae and bacteria in response to accumulation of nutrients (phosphorus and nitrogen) and availability of light (Downing et al. 2001; Smith 2011). These processes are not instantaneous and may occur long after the gravel pit lake formed. Small lakes such as gravel pit lakes cover a much greater portion of the Earth's land surface (~3%) than previously believed (Seekell et al. 2013). Gravel pit lakes are a relatively new environmental phenomenon. The hydrology and hydrochemistry of gravel pit lakes depends on their particular setting. The lakes studied for this paper are in a coastal setting and the groundwater that fills the lake is brackish.

A flow-through gravel pit lake lacks natural inflow and outflow by rivers and may become a sink for carbon different from the carbon cycle in natural lakes (e.g., Massicotte and Frenette 2013) or a sink for metals (Mollema et al. 2015).

The hydrochemistry of ground and surface water in coastal areas is affected by processes such as conservative mixing of fresh- and seawater, and water-rock interaction processes such as cation exchange, calcite and gypsum dissolution or precipitation and redox reactions alone or in combination with organic matter degradation (Stuyfzand 1999; Andersen et al. 2005; Appelo and Postma 2005). The presence of gravel pit lakes in such a coastal environment complicates the hydrochemistry even more.

Salt water intrusion is a worldwide problem (e.g., Werner et al. 2013). We know from previous studies that many processes have affected the salinity distribution in the coastal aquifer near Ravenna including salt water intrusion enhanced by drainage, evapotranspiration, lack of natural recharge, seepage of saline water and land subsidence (e.g., Antonellini et al. 2008; Mollema and Antonellini 2013; Mollema et al. 2013b). These processes have affected the natural areas along with agriculture (Greggio et al. 2012). The gravel pit lakes are close to the protected natural areas of the Regional Park of the Po Delta, which is part of the Mediterranean biodiversity hotspot (Myers et al. 2000). Vegetation species richness in the area is threatened by increasing groundwater salinity as shown by Antonellini and Mollema (2010). In this context and in relationship to soil degradation for agriculture it is important to better understand the hydrochemistry of the gravel pit lakes and the interaction with groundwater. Gravel pit lakes offer a wide variety of post excavation uses including swimming, canoeing, fishing and other aquatic sports, creation of a nature reserve or even the possibility for building waterfront houses. They have been used or considered for use as a place to dispose of wastewater- or dredging sludge and gravel pit lakes may be used for artificial recharge and recovery of drinking water (Fang et al. 2009; Mollema et al. 2015). It is important to understand the hydrology and hydro- and biochemistry of the aquifers and lakes to effectively and safely manage gravel pit lakes after their creation.

We studied the brackish gravel pit lakes near the coast of the southern Po plane in Italy to establish the potential role of gravel pit lakes in influencing (1) the water budget of the brackish-coastal aquifer in this Mediterranean setting with particular emphasis on the surface water evaporation and groundwater flow, (2) the salinity of lakes and groundwater, and (3) the hydrochemistry of groundwater flowing into the lake including the concentration of nutrients, arsenic and other (trace) elements. We seek a better general understanding of the hydrological and hydrochemical interaction between surface and groundwater, of the hydrology and hydrochemistry of coastal zones and how to use gravel pit lakes safely after excavation.

## Hydrogeological and hydrochemical setting

Hydrogeological setting

The gravel pit lakes of this study are concentrated in a 2.5 km wide zone parallel to the coast of the Adriatic Sea at
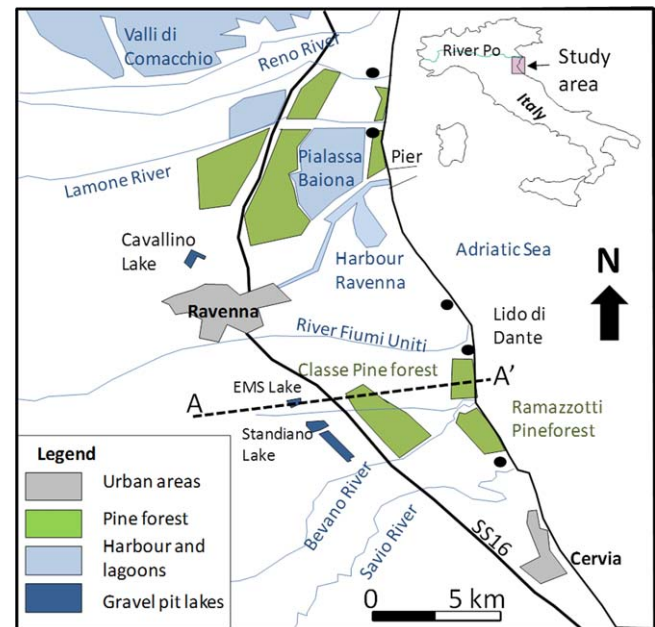
Fig. 1. Index map of the study area with location of the gravel pit lakes. AA′ is the trace of the cross sections in Figs. 3, 4.

a distance of 7 km from the shore, south and west to northwest of Ravenna, Italy (Figs. 1–3). A large part of the study area is below sea level and hydraulic gradients are typically directed inland due to pumping stations located 5–8 km from the sea, that drain excess water from a network of ditches (Antonellini et al. 2008; Mollema et al. 2013a). The minimum water table elevation within the aquifer is −4.0 m.a.s.l. and the maximum +0.2 m.a.s.l (Fig. 2). The gravel pit lakes were excavated into the upper shallow coastal aquifer near Ravenna. The sedimentary composition of the southern Po plain is determined by Alpine and Apennine river sediments, and by sediments deposited through long shore currents. Two transgression periods can be recognized above the base of the Pleistocene. The upper shallow coastal aquifer formed during the most recent transgression period during the late Dryas and Holocene (12 ka to present; Amorosi et al. 2002), when a barrier-lagoon-estuary system was moving eastwards with the receding sea. As a result, the aquifer consists of a wedge-shaped dune and beach sand body pinching out in westerly and northern direction, which is sealed at the bottom and top by clays and peat formed in lagoons, marshes, and alluvial plains (Fig. 3a). The Flandrian continental silt-clay basement is at a depth varying from −20 m in the west to −30 m.a.s.l. at the present shoreline (Amorosi et al. 2004). At the inland tip of the aquifer wedge, there are the beach gravel deposits. The oldest gravel pits were excavated at gravel exposures at the surface. Later gravel pits were and are excavated by digging through the
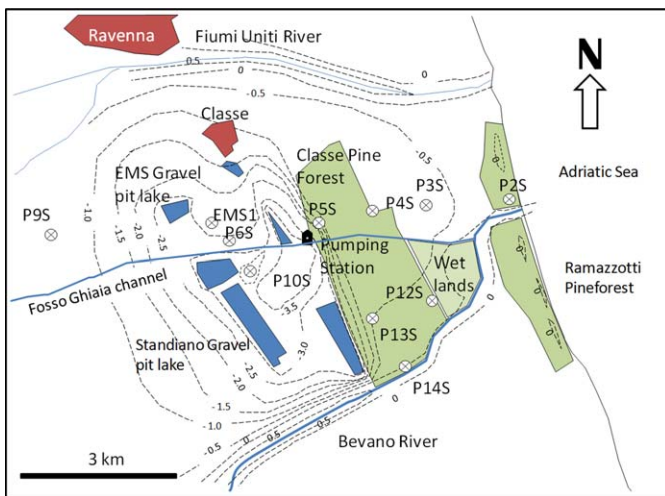
Fig. 2. Map with location of gravel pit lakes Standiano and EMS in "Quinto" watershed. Water table elevation contours show that lake surfaces are below sea level, and that there is a strong hydraulic gradient towards the pumping station both from the lakes more inland and from the dunes more seaward. Note that there is a drainage system of ditches in which the flow direction may be different from the groundwater flow direction. The locations of the wells from which the water table measurements were used, are indicated.

clay layer on top of the gravel deposits. Subsidence rates of 1 m in the period 1950–1990 and the continuing subsidence rates of up to 1 cm yr^{-1} are mostly due to water and gas exploitation while natural subsidence rates are 0.5 mm yr^{-1} due to compaction of the sediments (Teatini et al. 2006).

The gravel pit lakes are brackish-saline lakes and are much deeper (up to 13 m deep) than typical natural saline lakes such as coastal lagoons or sabkahs (e.g., Van Dam et al. 2009). The gravel pit lakes do not have natural inlets or outlets, but they do have a constant water level, which is regulated by the surrounding drainage network and the pumping station Fosse Ghiaia (Figs. 1, 2). The pumping station starts to pump water into the Fosse Ghiaia drainage channel when the water level reaches a certain level. The Fosso Ghiaia channel brings the drained water to the Adriatic Sea (Fig. 1). The first quarry activity in the area started in the 1930s. The oldest quarries are now abandoned and form lakes up to 13 m deep. The saline gravel pit lakes are best classified as warm polymictic lakes: no seasonal ice cover and stratification for more than a few hours to weeks a year (Lewis 1983). The lakes are probably mixed in winter by density differences caused by cooling of the lake surface and in summer by density differences caused by evaporation (Lewis 1983; Imboden 2004) and all year round by the flow through the lake caused by the strong drainage towards the pumping station. Some of the abandoned gravel pit lakes are used for recreational activities such as swimming, canoeing, fishing and boating. In the watershed between the Fiumi Uniti River and the Bevano River, the gravel pit lakes cover 684 hectares or

7% of the land surface (Mollema et al. 2012). The three gravel pit lakes that were studied in detail are the *Cavallino* Lake, the *EMS* Lake, and the *Standiano* lake (Figs. 1, 2). See Table 1 for an overview of their characteristics.

General aquifer and gravel pit lake hydrochemistry

A large scale hydrochemical study of the area by Mollema et al. (2013b) showed that throughout the whole shallow aquifer the most common water type is brackish to saline water with Na as major cation and Cl as major anion. The Cl concentration ranges between 300 mg L^{-1} and 20,000 mg L^{-1} and most samples have a negative Base Exchange Index (BEX). BEX is indicative of cation-exchange reactions caused by water-rock interactions during the infiltration of saline water in a freshwater aquifer (Stuyfzand 1999). Calcium-dominated freshwater is found only in the rivers, in the irrigation and drainage channels, and in a few groundwater samples. The analysis of stable isotopes and tracer ratios SO_4^{2-}/Cl^- and $\delta^{18}O/Cl$ ratios indicated that the various processes of evaporation, mixing of fresh and saline water, cation exchange, oxidation of organic matter and sulfate reduction, migration and seepage of (hyper) saline contribute in different amounts in the various coastal environments resulting in distinct different hydrochemistry in each coastal environment (Mollema et al. 2013b). The migration and upward seepage of (hyper) saline water driven by the hydraulic gradients induced by the drainage system cause the aquifer to become more saline over time, also to the north of the study area (Giambastiani et al. 2013; Mollema et al. 2013b).

Climate and water balance

The climate of the study area is Mediterranean with generally warm summers and mild winters (Giorgi and Lionello 2008).

The mean annual precipitation over the period 1991–2008, averaged over four nearby weatherstations is 635 ± 116 mm. Average winter precipitation (October through March) is 292 ± 66 mm and average summer precipitation (April through September) is 343 ± 51 mm (Mollema et al. 2012). The average maximum temperature is 19°C and the average minimum temperature is 8°C with July and August the warmest and December and January the coldest months of the year. The gravel pit lakes are ice-free year round. Open water evaporation from surface waters in the area was calculated by Mollema et al. (2012) using the Penman (1948) equation described in Maidment (1992) that describes how the available energy from the sun is used for water evaporation. The average annual open water evaporation for the period 1988–2008 is 1529 mm per year (Mollema et al. 2012) of which 348 mm evaporates in winter (October through March) and 1181 mm in summer (April through September). Mean annual wind speed averaged over four weather stations is 1.9 ± 0.6 m/s (Mollema et al. 2012). A very large quantity of water is drained from the area by a network of mostly east–west oriented ditches and several
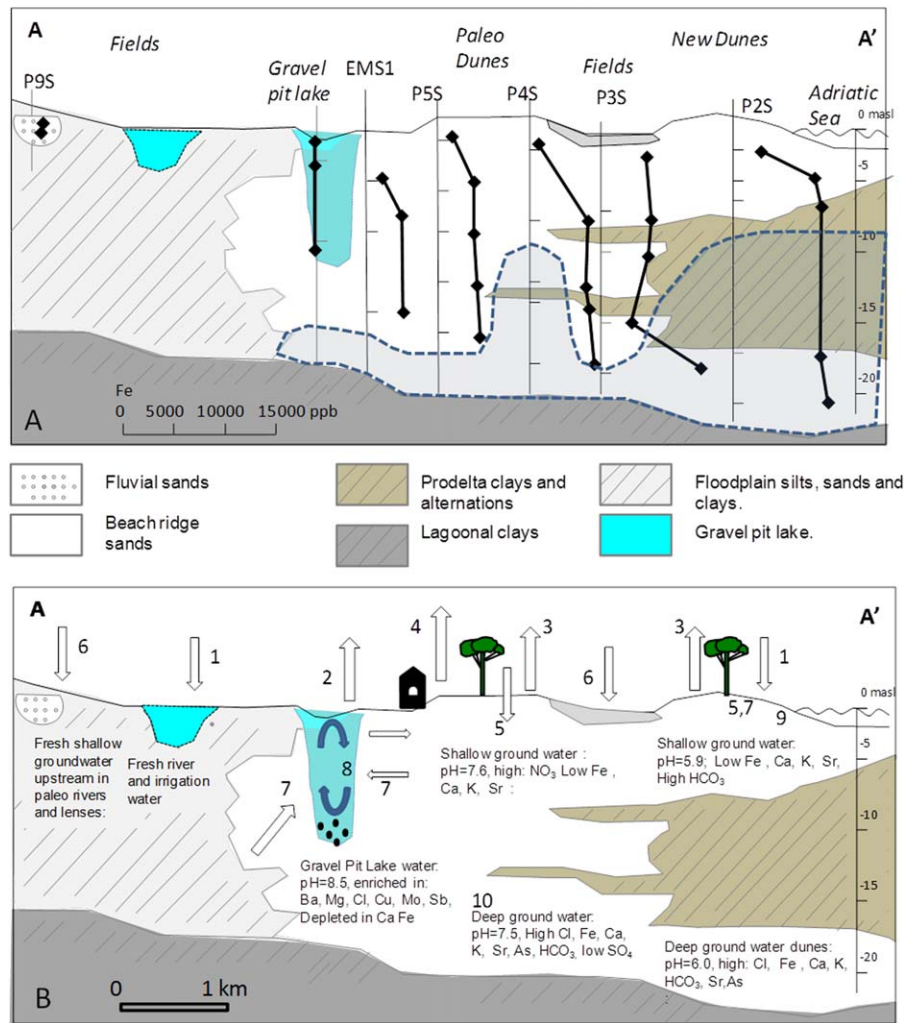
Fig. 3. (a) Profile through the aquifer and across gravel pit lake EMS from well P9S to the Adriatic Sea. Vertical concentration profiles of Fe are shown in interconnected bold black dots along well trace to illustrate the increase in concentration of Fe as many other elements towards the Adriatic Sea, depletion of shallow groundwater with respect to deeper groundwater and typically a relative depletion or enrichment in the gravel pit lake. Location of wells and sampling points are shown, (b) summary of hydrochemistry and hydrochemical processes occurring in and around the coastal gravel pit lake. Arrows indicate direction of water flow. Numbers correspond to the following processes: (1) precipitation and natural recharge of the gravel pit lake and aquifer, land upstream and dunes downstream. (2) Evaporation from lake surface. (3) Transpiration by pine trees. (4) Drainage of water seawards. (5) Groundwater table fluctuation exposing sediments to oxygen. (6) Fertilization of soil brings PO_4 and NO_3 in groundwater. (7) Redox reactions involving Fe(hydr)oxides or Pyrite, then Fe, and As (among others) are released into groundwater. (7) Groundwater exfiltrates into lake. (8) Groundwater rich in dissolved metals comes into contact with basic lake water enriched in oxygen; metal oxides and $CaCO_3$ precipitate. (9) Cation exchange, Fe-oxides precipitation and carbonate dissolution. (10) Sulfate reduction.

pumping stations. For the watershed (Quinto basin), in which Standiano and EMS Lake are situated, the estimated amount of water that is annually drained is 20 million m³.

Methods

Sampling and chemical and stable isotope analyses

As part of a larger monitoring campaign (Mollema et al. 2013b) 31 groundwater samples were taken in December 2010 from monitoring wells P2S, P3S, P4S, P5S, EMS1, and P9S aligned on a profile perpendicular to the coast, the 2.5

inch diameter wells were constructed without gravel pack and fully screened and the levels to be sampled were shut off by straddle packers. The volume of water present in the chamber between the two straddle packers (that isolate an effective screen length of 30 cm) was flushed five times. Surface water samples were taken from different water bodies: from gravel pit lakes (4), one from the Adriatic Sea sampled 400 m from the coast on the pier north of Ravenna (Fig. 1), three from the rivers Savio, Bevano and Fiumi Uniti and one from the river Po, sampled in the irrigation channel Canale Emilia Romagna (CER). All water samples were filtered in the

Table 1. Properties of the three gravel pit lakes studied.

	Lake Standiano	Lake EMS	Lake Cavallino	Notes
Location	281039 m E 4913129 m N	279227 m E 4915599 m N	272009 m E 4927081 m N	Google Earth Coordinates in Zone 33T
Surface area at time of monitoring [ha]	113.3	20.7	5.2	Surface area determined with google earth on images acquired at 30 Oct 2012
Shape	Rectangular 2.3 × 0.5 km	Rectangular 0.6 × 0.4 km	Rectangular 0.3 × 0.2 km	
Orientation	Parallel to coast—length direction north west	Long side perpendicular to coast (not final geometry)	Long side perpendicular to coast (not final geometry)	
Distance to coastline [km]	6	7	11	The gravel deposits (and so the gravel pit lakes) north of Ravenna are further from the coast than South of Ravenna
Distance to nearest fresh surface waters	To Bevano River 1 km, and to Fosso Ghiaia (Drainage channel) 0.8 km	4 km to Fiumi Uniti River and 0.5 km to Fosso Ghiaia	To Montone river 5 km	
Depth range [m]	7–9	12–13	4–13	
Average depth [m]	8	12	9	
Water volume [m^3]	9.2×10^6	2.9×10^6	0.5×10^6	
Residence time [yr]	1.0	1.6	1.2	The ratio of lake volume to outflow as a first approximation of the residence time of lake water (Ambrosetti et al. 2003)
Maximum TDS [g L^{-1}]	12.3	7.7	7.7	
Excavation	1972–1998	2003–present	2009–present	

field through a 0.45 μm filter. The samples for anion determination were analyzed within 24 h in the laboratory. The other samples were acidified with HNO_3. The water was stored in pre-cleaned HDPE plastic bottles. Electrical conductivity (EC), pH, DO and Eh and temperature were measured with a multiparameter device XS PCD650 1 located in a flow cell. The samples were analyzed for major and trace elements by ACME Labs in Vancouver (Canada) with the ICP-MS analysis and VU laboratories using analytical methods (ICP-OES on acidified subsamples, IC for anions). Quality control was carried out by including a sample of deionized water, duplicate samples and a sample of multi standard as well as blanks and standards by ACME Laboratories. The major ion chemistry are presented in Mollema et al. (2013b).

Samples for isotope analysis were collected in 100 mL glass bottles. Stable O and H isotopes (δ^2H, δ^{18}O) were determined by the stable isotope laboratory of VU University Amsterdam using a Thermo Finnigan Delta XP mass spectrometer equipped with a TC-EA pyrolysis furnace. Calculated averages of triplicate analyses of each sample result in a reproducibility of better than 1.5‰ (1 SD) for δ^2H and 0.15‰ (1 SD) for δ^{18}O. Values are reported relative to V-SMOW (Gonfiantini et al. 1995) but it is recognized that other standards are available (Coleman and Meier-Augenstein 2014). The samples have been measured in triplicates interspaced between a set of standards with values ranging from 156‰ to 6.5‰ for H and 21.2‰ and 1.1‰ for O. The stable isotope data have been published before by

Mollema et al. (2013b) but the results of 55 samples are presented also here to be used for the first time to quantify the waterbudget of the gravel pit lakes. See Table 1 and Supporting Information for results.

Temperature and electrical conductivity logs in the gravel pit lakes

Multi-Parameter Groundwater Monitoring Dataloggers (AquaTroll™ probe and Divers) were used to log temperature and Electrical Conductivity (EC) changes with depth in the gravel pit lakes. The Diver records water pressure, which is converted to hydraulic head during data elaboration including a correction for barometric pressure. Temperature and salinity logs were measured in three gravel pit lakes and surrounding piezometers in different periods of the year. The EC and temperature data were used to calculate TDS with the method described by Maidment (1992).

Water budget calculations, stable isotopes and conservative tracer modeling

Local evaporation line and E/I ratio

To calculate the slope of the Local Evaporation Line (LEL) and the ratio of evaporation to total inflow (*E/I*), we used the excel spreadsheet from Skrzypek et al. (2015). The spreadsheet uses the stable isotope composition of precipitation, ground- and lake water, as well as temperature and relative humidity of the ambient air to estimate the isotope composition of ambient air, the LEL and the *E/I* ratio. The gravel pit lakes are considered in steady-state condition, where the water body is constantly replenished by inflowing water and the water level remains constant as the evaporative losses from the pool are compensated by inflow that equals or exceeds evaporation. In our case the inflowing water is groundwater. The ratio of evaporation over inflow *(E/I)* can be calculated using the following reformulated equation (e.g., Horita and Wesolowski 1994; Gibson and Edwards 2002; Mayr et al. 2007). *E/I* is the fraction of inflowing water evaporated from a lake (Eq. 10 in Skrzypek et al. 2015):

$$\frac{E}{I} = \left[\frac{(\delta_L - \delta_P)}{(\delta^* - \delta_L) \times m} \right] \qquad (1)$$

where δ_P represents inflowing water and δ_L represents water discharged from the lake, δ^* is the limiting isotope enrichment factor as given above and *m* is a factor defined by (Eq. 11 in Skrzypek et al. 2015)

$$m = \frac{h - \frac{\varepsilon}{1000}}{1 - h + \frac{\varepsilon_k}{1000}} \qquad (2)$$

where *h* is the relative humidity (in fraction) of the ambient air, ε is the total isotopic separation factor including both equilibrium ε^* and kinetic ε_K components (see also Supporting Information S3 for further equations and input parameters).

A low value of *E/I* suggests that the evaporation is relatively low compared to the water inflow. The results depend strongly on the humidity and temperature of the ambient temperature therefore the *E/I* ratios are calculated for various combinations of T and h characteristic of the climate in the study area (Table 2). See Supporting Information S3 for an overview of input parameters and output for one particular combination of T and h.

Conservative tracer modeling and evapoconcentration

We used Cl as a conservative solute and calculated the Cl concentration in the gravel pit lakes based on an annual mass balance equation. We studied the sensitivity to (1) the rate of annual evaporation from the lake surface, (2) the ratio of evaporation to total inflow (*E/I*), (3) the Cl concentration of the inflowing groundwater and (4) the effect of the replacement of material excavated from the gravel pits by brackish/saline groundwater.

The initial Cl concentration of the gravel pit lake water was varied in the models between 1 g L^{-1} and 3 g L^{-1} based on the observations that the aquifer is brackish/saline throughout and probably was never completely filled with fresh water (Mollema et al. 2013b; Vandenbohede et al. 2014). Since the gravel is typically stored on the soil close to the pits during excavation, part of the mined water may

Table 2. Evaporation over inflow rate as calculated with the spreadsheet by Skrzypek et al. (2015). *E/I* ratios are listed for several *T* and *h* combinations that are characteristic of the climate of Ravenna taken from (Mollema et al. 2012). Annual mean isotope composition of ambient air is based on the isotope composition of rainfall on Commachio a coastal town nearby Ravenna (Longinelli and Selmo 2003) while mean winter and summer isotope composition of ambient air is calculated with an algorithm developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003) and Bowen et al. (2005) for Ravenna with lat. 44.4184, long. 12.2035 and alt. 3 m. See Supporting Information S3 for the formulas and other parameters used.

T	*h*	δ^2H$_{Rain}$	δ^{18}O$_{Rain}$	*E/I* based on δ^2H	*E/I* based on δ^{18}O	LEL calculated	Notes
13.7	0.77	−42.40	−6.75	0.3	0.2	5.4	Annual mean *T* and *h* and δ_{Rain}
7.7	0.71	−50.8	−7.8	0.3	0.2	5.5	Mean winter *T*, *h* and δ_{Rain} (October–March)
19.8	0.83	−32.5	−5.3	0.2	0.2	5.6	Mean summer *T*, *h* and δ_{Rain} (April–September)

infiltrate back into the soil and into the lake and affect the Cl concentration of the lake water. This is difficult to quantify but to get an idea of the influence of the replacement of mined water we varied f, the fraction of the lake volume that is taken out by mining water and gravel together and replaced by brackish/saline groundwater. See Supporting Information S5 for derivation of the mass balance equation and results and discussion for the outcome of the calculations.

Calculation of saturation index

The saturation indices (SI) of anhydrite, barite, calcite, dolomite, gypsum, and halite were calculated for gravel pit lake water and selected groundwater samples along the profile of Fig. 3 using the PHREEQC software (Parkhurst and Appelo 1999).

Results

Water budget calculations, stable isotopes and conservative tracer modeling

The delta values of the stable water isotopes of the samples with respect to VSMOW range from -9.0 to $+0.2‰$ for $\delta^{18}O$ and from -68.4 to $-5.5‰$ for $\delta^{2}H$. Most samples have an isotope composition that falls between the isotope ratios of water from Apennine rivers ($\delta^{18}O = -8.22$, $\delta^{2}H = -54.01$) and that of the coastal Adriatic Seawater ($\delta^{18}O = -2.8$, $\delta^{2}H = -18.2$; Fig. 4). Open Adriatic Sea water has a composition of $+1.29‰$ for $\delta^{18}O$ and $+8.4$ $\delta^{2}H$ (Gattacceca et al. 2009) but our samples were taken closer to the coast and is a mixture of Po and Apennine river water and seawater and possibly groundwater. Three groundwater samples fall below the estuarine mixing line. These samples were taken close to a ditch that is filled with

Fig. 4. (a) $\delta^{18}O$ and $\delta^{2}H$ values of groundwater and surface water samples of the Quinto Bacino drainage basin. The estuarine mixing line between fresh river water and Adriatic Seawater is a dashed line. The calculated LEL (slope = 5.4) and the Local Meteoric water line are indicated (NIMWL) as well as precipitation from Comacchio along the coast and from the Apennines and Alps from Longinelli and Selmo (2003).
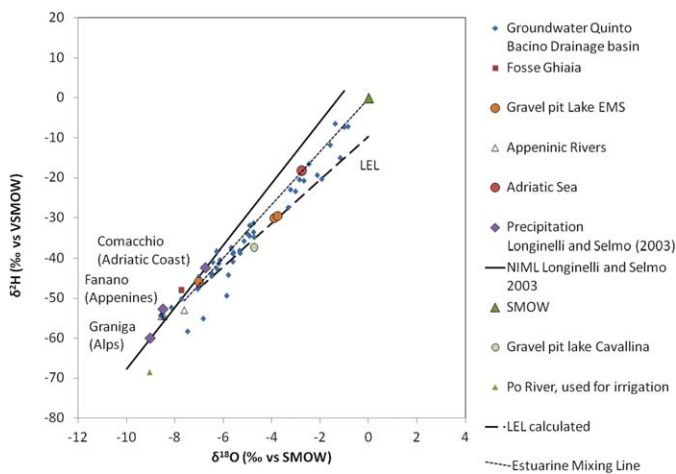
water from the Po River, used for irrigation in summer and the isotope signature reflects this different origin. For comparison we show also the northern Italian Meteoric Water Line (NIMWL, Longinelli and Selmo 2003) and the LEL based on annual average T and h data and $\delta^{18}O$.

The results of the modeled water budget and increasing Cl concentration over time for varying evaporation rate (E), concentration of Cl of inflowing groundwater ($C_{GW\text{-}in}$) and E/I ratio are shown in Fig. 5a–c. The graphs show that for the first 5–25 yr after start of excavation, the Cl concentration increases rapidly and almost linearly over time after which the rate of increase becomes smaller until a constant concentration is reached. For a E/I of 0.2, it takes less than 5 yr for the Cl concentration to become stable. The initial Cl concentration in the lake has a large influence on the Cl concentration in the first 5–25 yr but does not influence the final Cl concentration which is determined by the salinity of the inflowing groundwater (Fig. 5c) and the E/I ratio (Fig. 5d). The evaporation rate does not have a large influence on the chloride concentration if the E/I ratio is kept constant. In other words, the relative contribution of groundwater flow is more important than the absolute magnitude of evaporation.
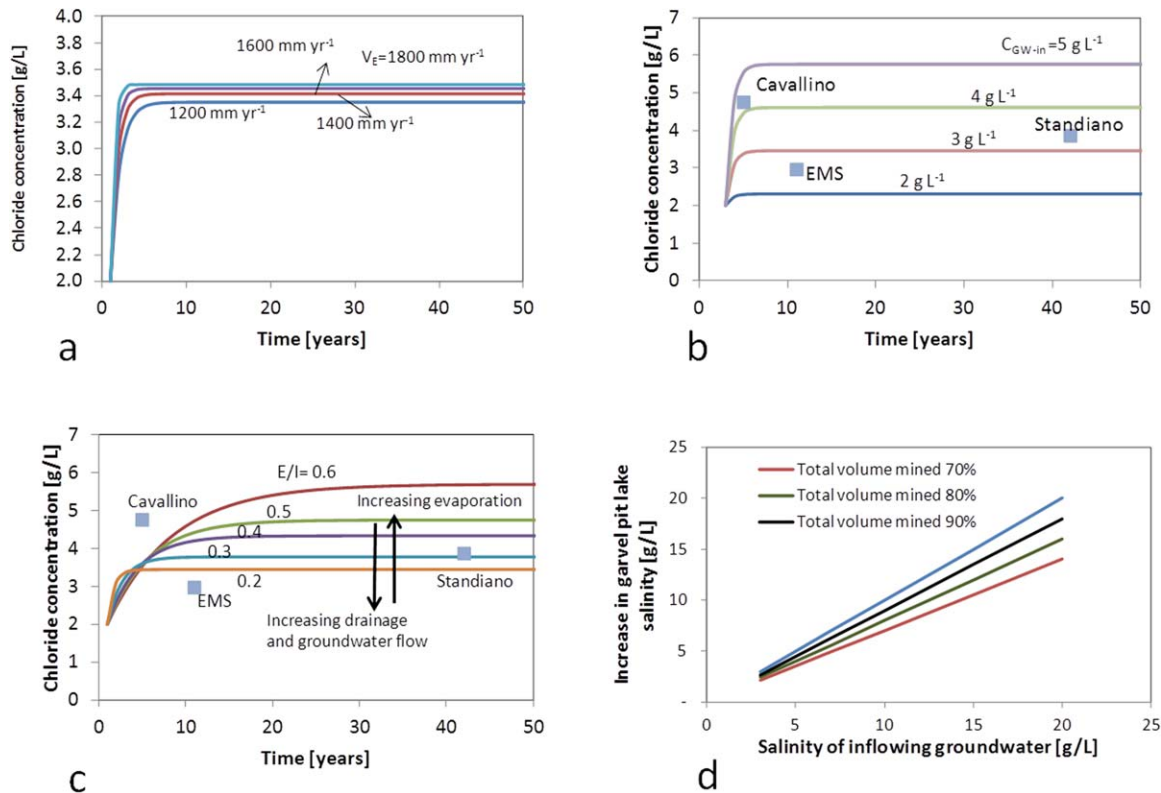
Hydrochemistry

The mean pH of the gravel pit lakes is 8.5 ± 0.4 and this is higher than the pH of the nearby groundwater (7.4), seawater (8.3) or river water (8.4). In general, the imported Po river water and the Apennine Rivers have the lowest concentration of dissolved elements compared to groundwater, gravel pit lake water, and seawater. The Po water has lower concentrations of all elements with respect to the Apennine river water except for Fe and Ni (Table 3). Conversely sea water, contains the highest concentrations of most elements and ions except for HCO_3, Bi, Co, Cr, Fe, Mn, Ni, P, Sn, and Zn, which show the highest concentrations in groundwater. The gravel pit lakes show high concentrations of Ba, Bi, Ga, La, Mo, Sb and low concentration of SO_4, Ca, Fe, Mn, Ni, P, and Zn compared to the average groundwater composition.

A hydrochemical profile perpendicular to the coast and through the EMS gravel pit lake compares the chemical composition of groundwater with surface waters. Well P9S is in fresh groundwater of a buried paleo alluvial sand channel furthest from the coast whereas the other wells are in the brackish saline aquifer encasing the gravel pit lakes. In general, the concentration of most elements increases towards the coast (Figs. 3a,b, 6). The concentrations of many elements and ions such as Fe, Ca, K, and Sr are lower in the gravel pit lake and in the upper 7 m of groundwater than in the deep groundwater (below 7 m depth). The shallow groundwater below the paleo and coastal dunes is depleted in many elements with respect to the deep groundwater (illustrated for Fe in Fig. 3a). NO_3 occurs in small amounts

Fig. 5. Modeled chloride concentration over time in water of the gravel pit lakes calculated with the mass balance equation. (a) As a function of evaporation where the *E/I* ratio is kept constant at 0.2, and the chloride concentration of inflowing groundwater at 3 g L^{-1}. (b) As a function of Cl concentration of the inflowing groundwater C$_{gw\_in}$. The ratio *E/I* is kept constant at 0.2 and evaporation at 1529 mm yr^{-1}. (c) As a function of *E/I* ratio where C$_{gw\_in}$ is kept constant at 3 g L^{-1} and evaporation at 1529 mm yr^{-1}. (d) The effect of the replacement of excavated material with brackish groundwater.

in the Apennine rivers and in well EMS1. Only in P5S is there a high concentration of NO$_3$ (56 mg L^{-1}).

The SI values of anhydrite, gypsum and halite are negative for all samples indicating sub saturation whereas the SI values for barite, calcite and dolomite, are positive in all samples indicating super saturation (Supporting Information Table S2).

Temperature and salinity and dissolved oxygen (DO) in gravel pit lakes and groundwater

The distribution of temperature with depth varies among the three gravel pit lakes. Summer and winter water temperatures were fairly constant and homogeneous with depth in Lake Standiano (Fig. 7a). The summer temperature log in Lake EMS (Fig. 7c) had a temperature of 21°C up to 4 m depth and below 4 m the temperature gradually decreased to 12°C. Winter water temperature of Lake EMS slightly increased with depth from 5°C to 7.4°C. The salinity was almost constant with depth in all three gravel pit lakes and there was little variation between summer and winter (Fig. 7b,d,f). Lake Standiano was the most saline with a TDS of

12.3 g L^{-1} in summer and 11.3 g L^{-1} in winter. EMS Lake had a slight decrease in salinity with depth from 5.1 g L^{-1} at the top to 4.6 g L^{-1} at 13 m depth and an increase in salinity (up to 7.7 g L^{-1}) in the deepest part of the lake. All surface waters together had a DO concentration of 9.9 ± 1.6 mg L^{-1}. The DO of Lake EMS was constant with depth at 10.0 ± 0.2 mg L^{-1} while Lake Cavallina was 5.7 mg L^{-1}. The mean DO of the ground water samples is 3.5 ± 1.7 mg L^{-1}. Wells P4S and P5S east of the gravel pit lakes in the Paleo dunes have especially low DO (<2 mg L^{-1}) at all but the shallowest of depths. The Eh (redox potential) ranged from 28 mV to 186 mV for groundwater samples and from 211 mV to 400 mV for surface water samples including the ones of the gravel pit lake. The Eh in EMS Lake increased with depth from 211 mV at the lake's surface to 206 mV at the lake bottom.

Discussion

Digging gravel pit lakes in areas with aquifers can lead to changes in groundwater flow and hydrochemistry, especially if there are many gravel pit lakes in close proximity to one

Table 3. Concentration of major and selected trace elements in samples of various ground and surface waters in the study area. NO_3, SO_4, HCO_3, stable isotopes $\delta^{18}O$ and δ^2H from Mollema et al. (2013b). Adriatic Seawater from Tankere and Statham (1996), Apennine River water (Fiumi Uniti River, Bevano River and Savio River); Po River water sampled in the Channel of Emilia Romagna (CER) this study and for comparison River Po water from Tankere et al. (2000). "n" indicates the number of samples included in the average value. See the electronic supplement for a complete list of data for all samples and all elements analyzed.

	pH	EC	Na [mg/L]	K [mg/L]	Ca [mg/L]	Mg [mg/L]	Fe [µg/L]	Mn [µg/L]	Cl [mg/L]	SO$_4$ [mg/L]	HCO$_3$ [mg/L]	NO$_3$ [mg/L]	Al [µg/L]	As [µg/L]	B [µg/L]	Ba [µg/L]	Bi [µg/L]
Fresh groundwater (well P9S) (n=2)	8.6	1421	104	27.6	162.4	56.2	766	1155	107	138	656	<1.25	14	1.8	428	221	0.1
Gravel pit lakes (n=4)	8.5	16736	2405	75.6	78.0	321.5	118	77	3420	285	775	<1.25	23	12.3	1925	1026	3.8
Groundwater all samples (n=31)	7.4	24855	4726	154.9	260.6	660.5	5228	755	7637	1137	759	3.3	34	23.6	2856	229	0.4
Adriatic Seawater (n=1)	8.3	52485	7368	272.8	318.0	889.5	300	15	12400	2022	242	3.6	75	37.5	2725	31	0.0
Adriatic Seawater Tankere et al. (1996)																	
Average Appenine river water (n=3) Fiumi Uniti, Bevano and Savio Rivers	8.4	1216	66	8.3	110.3	39.9	11	34	80	130	366	13.1	8	0.9	154	75	<0.1
River Po water (CER) (n=1)	8.4	440	19	2.9	49.1	15.8	41	4	37	45	188	3.8	6	0.9	48	35	<0.1
River Po water (Average Tankere et al. 2000)							2	2									

	Br [µg/L]	Co [µg/L]	Cu [µg/L]	Li [µg/L]	Mo [µg/L]	Ni [µg/L]	P [µg/L]	Pb [µg/L]	Rb [µg/L]	Si [µg/L]	Sn [µg/L]	Sr [µg/L]	U [µg/L]	W [µg/L]	Zn [µg/L]
P9S fresh groundwater (n=2)	303	4.5	3.5	30.8	1.4	29.7	76	1.0 / 1.5	3017	0.06	1787	3.1	0.1	117.5	−6.19
Gravel pit lakes (n=4)	12430	0.8	11.3	45.8	13.0	6.5	570	1.8 / 14.0	1608	0.6	1288	3.4	0.2	31.3	−4.86
Groundwater all samples (n=31)	25813	1.4	11.4	63.3	3.5	16.8	1681	1.3 / 24.9	6629	0.1	4533	2.4	0.0	154.4	−4.57
Adriatic Seawater (n=1)	40325	0,5	30.0	160.0	7.5	7.5	0.0	7.5 / 78.3	2175	2.3	5243	2.8	0.0	107.5	−2.77
Adriatic Seawater Tankere 1996*			0.45	19.83		0.53								0.24	
Average Appenine river water (n=3) Fiumi Uniti, Bevano and Savio Rivers.		0.3	3.9		1.4	2.4	355	0.3 / 2.8	3970	0.0	1374	2.1	0.2	26.2	−8.22
River Po water (CER) (n=1)	108	0.2	2.5	3.4	1	3.4	87	0.1 / 2.01	1367	0.0	366	1.1	0.0	14.5	−9.05
River Po water (Average Tankere et al. 2000)			3			2.9		0.3						5.2	

another. The area of the gravel pit lakes is not protected by a top soil layer and an unsaturated zone, which leads to direct interaction of groundwater with the atmosphere. The lakes in our study area cover a large surface (7% of the Quinto Basin watershed; Mollema et al. 2012). The precipitation that falls is mixed with the brackish surface water as the salinity with depth profiles show and does not contribute to aquifer recharge. Natural aquifer recharge is very limited in the local coastal watersheds in this climate (Mollema and Antonellini 2013; Vandenbohede et al. 2014), and the presence of the lakes further reduces the infiltration of freshwater.

Water sources, water budget and evapoconcentration

The stable isotope data of the groundwater samples indicate a mixing between fresh water from the Apennine Rivers and Adriatic seawater, which is a typical mixing for an estuary (Mook 2001; Fig. 4). Currently the area is not a natural estuary where mixing between seawater and fresh river water occurs freely, as the rivers are controlled with dykes and the gravel pit lakes are not connected with any river or the sea. However, during the maximum Holocene transgression, 6000 yr ago, the Adriatic coastline was 20–30 km inland from its current position. During subsequent regression of the sea, the morphology of the Po plain around Ravenna was a free moving barrier lagoon system with small fresh water environments (Amorosi et al. 2004). Flushing of saline water from a coastal aquifer by natural recharge is a slow process and it is, therefore, very likely that not all Holocene transgression water was flushed from the aquifer. This is the case in similar settings (e.g., Edmunds and Milne 2001; Kooi, 2008) where modern groundwater is partly a mix of fresh and salt water from a Holocene estuary. The most saline water is at the bottom of the aquifer as indicated by the Cl concentration contour of 10,000 mg L^{-1} in Fig. 3A and seeps upwards under the paleo dunes in the Classe pine forest.

A comparison of the δ^{18}O- the δ^2H and the δ^{18}O—Cl ratios of ground and surface waters in a large area near the gravel pit lakes (Mollema et al. 2013b) showed that despite the high evaporation rates in this Mediterranean setting no very strong evaporation concentration of Cl or stable isotope enrichment occurs in the gravel pit lakes as in the lagoons north and east of Ravenna. The isotope signature of the samples from the gravel pit lakes however falls below the estuarine mixing line, indicating that evaporation has influenced the isotope composition. The E/I ratio, which is the ratio of evaporation to total inflow, (i.e., the sum of precipitation and groundwater inflow) ranged between 0.2 and 0.3 for the various combinations of T and h (Table 2). A value of 0.2 is thought to be most representative since it is based on δ^{18}O. The calculated E/I based on δ^2H is less reliable since it is shown that δ^2H enrichment is strongly affected by the salinity of the liquid phase (Horita et al. 1995) and the salinity is, and always was, high in our study area. An E/I ratio of 0.2

means that 20% of the inflowing groundwater evaporates. Since the models show that the Cl concentration in the gravel pit lakes is not very sensitive to variations in the evaporation rate (Fig. 5a), we kept the evaporation rate constant at 1529 mm yr^{-1} as previously estimated with the Penman Monteith method (Mollema et al. 2012) and vary the groundwater inflow (Fig. 5b,c) to maintain a constant E/I ratio of 0.2.

The chloride concentration in the gravel pit lakes stabilizes because water leaving the lake through the ground water flow driven by the drainage system removes part of the Cl accumulating in the lake due to evapoconcentration. These observations may help to elucidate the effect of future changes due to for example global warming. Whether annual evaporation rates will actually increase or decrease will depend on the exact combination of changes in solar net radiation, air temperature, humidity, and wind velocity (e.g., Van Heerwaarden et al. 2010). An increasing evaporation rate would lead to a higher E/I ratio and to a higher Cl concentration but the models show that the Cl concentration is not very sensitive to reasonable changes in Evaporation (Fig. 5a). Instead sea level rise would increase the hydraulic gradients towards land and this would result in the need for more drainage as in other low lying deltas with land reclamation (Oude Essink et al. 2010). Continuing subsidence of the land as well as increasing precipitation would also result in an increasing need for drainage which all would enhance groundwater flow through the lake. The resulting E/I ratio would be smaller than the current ratio and consequently the steady state Cl concentration of the lakes would become less than the current Cl concentration, see trend arrows in Fig. 5d.

The Cl concentration of Cavallino Lake is higher than that of the other lakes despite its young age. This suggests that the salinity of the groundwater flowing into this lake is higher (Fig. 5b). This is consistent with Cl concentration data collected north of Ravenna that shows that overall the salinity of the groundwater in that area is higher than south of Ravenna (Mollema et al. 2013b).

During excavation of the pit lakes, the gravel and sand was replaced by brackish/saline groundwater. This also contributes to the salinity of the gravel pit lake. For f = 0.7, the fraction of mined gravel and water, in-flowing groundwater with a Cl concentration of 1–5 g L^{-1} will increase the overall salinity of the gravel pit lake by 0.7–3.5 g L^{-1} (Fig. 5d). In the (hypothetical) extreme case that all mined lake water and gravel was replaced by groundwater (f = 1.0), then the additional Cl concentration would be equal to the salinity of the in-flowing groundwater.

Hydrochemistry

The high concentration of major exchangeable ions and trace elements such as Na, Ca, K, Mg, Sr, Br, Cl, Mg, Na, V, Sr, Rb, Li, P, and a high EC indicate the presence of seawater

in the gravel pit lakes, in agreement also with the stable isotope data. Both the appearance and the disappearance of chemical elements along groundwater flow lines are likely indicative of redox processes (Stuyfzand 1999; Appelo and Postma 2005). The high concentrations of metals such as Fe, Cr, As in the groundwater seawards from gravel pit lake EMS (Figs. 3, 6a–c) are typical for redox reactions. The presence of high dissolved Fe in a water with a pH > 7 suggests that microbial reduction of Fe-oxides occurred releasing trace elements (e.g., Appelo and Postma 2005 or Smedley and Kinniburgh 2002).These types of redox reactions are in general well known to occur in coastal aquifers (e.g., Du Laing et al. 2009) including the coastal aquifer of Ravenna (Marconi et al. 2011). The current data does not allow for us to document the exact redox reactions that have occurred in the past or are presently occurring now in the aquifer but our observations show that the concentrations of dissolved metals (Fe, Mn, Ni, Zn) in the gravel pit lake EMS are much lower than in groundwater (Figs. 3, 6a–c). This is in agreement with observations on other gravel pit lakes (Marques et al. 2008; Mollema et al. 2015) and natural lakes (Stumm 2004) and is in part related to the typically high pH and dissolved oxygen concentration of gravel pit and natural lakes that reduces the solubility of many metals (Stumm 2004; Appelo and Postma 2005). This agrees also with the observation that the Eh is higher in lake water than in groundwater. The most important sources of dissolved metals in natural lakes are by wet or dry atmospheric deposition and by inflow of rivers (Stumm 2004). In gravel pit lakes that are not connected to a river, the most important source is atmospheric deposition and inflow of groundwater. Once the dissolved metals exfiltrate with groundwater into a gravel pit lake, they encounter oxygen-rich water with a high pH that favors the precipitation of Fe or Mn (hydr)oxides. The relatively low Al concentration of lake water is instead possibly related to aggregation and settling of Al-hydroxide colloids. In this way metal may accumulate in bottom sediments of gravel pit lakes as seen elsewhere (Mollema et al. 2015). Precipitation of Al, Fe or Mn (hydr)oxides usually involves scavenging of other trace metals and elements such as Cr, Co, Cu, Ni and Zn. Cationic trace metals adsorb strongly onto Fe-oxides at pH's between 7 and 9 (Appelo and Postma 2005), so this process explains the low concentration of Mn, Ni, Zn in lake water as well. Although As also adsorbs at these pH's, it may be out-competed for sorption sites by the other cationic trace metals. A few metal ions (Mo, Sb and Sn), instead showed higher concentrations in the gravel pit lake compared to the surrounding groundwater. This can be explained for oxyanions Mo and Sb as they are more soluble under high pH (Harita et al. 2005; Helz et al. 2011) and in water with a high Ca concentration (Brookins 1988; Salminen 2005). Mo (Algeo and Lyons 2006) and Sb (Willis et al. 2011) are more abundant in TOC rich sediments where iron sulfides are important host phases for Mo in modern
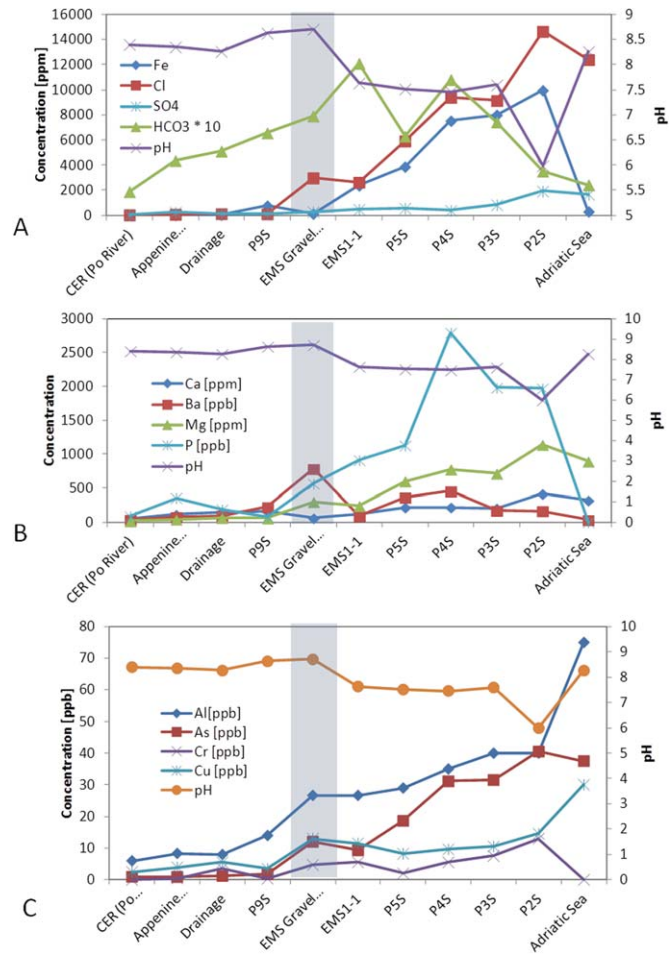
Fig. 6. (A) Fe, Cl, HCO₃ and SO₄ concentrations and pH of water samples, averaged for each observation well and for the gravel pit lake, along a profile perpendicular to the coast. Note that the horizontal axis is not to scale. Concentration in water from the river Po (CER), Apennine Rivers and drainage are shown for comparison but the locations of these surface waters are not necessarily exactly located along the profile. Blue shaded vertical area is position of the gravel pit lake. (B) Idem for Ca, Ba, Mg, P and pH and (C) Idem for Al, As, Cr, Cu and pH.

sediments and peats (e.g., Dellwig et al. 2002). The sediments of the study area were formed in swamp like condition: i.e., anoxic with high Total Organic Carbon (TOC) likely to be enriched in Mo. Therefore Mo and Sb may have been released in the sediment pore water accompanying sulfate reduction (e.g., Polack et al. 2009), and may be diffusing up into the lake partly explaining the higher Mo concentration in lake water than in groundwater. H₂S is one factor, along with pH and availability of reactive Fe that controls Mo deposition in euxinic basins (Fig. 8 of Helz et al. 2011). The dissolved Fe concentration is very low suggesting that there is also no further Fe available in the lake water for precipitation with Mo (Helz et al. 2011). Under high pH conditions pH > 7 Sb is stable in various species (Polack et al. 2009).
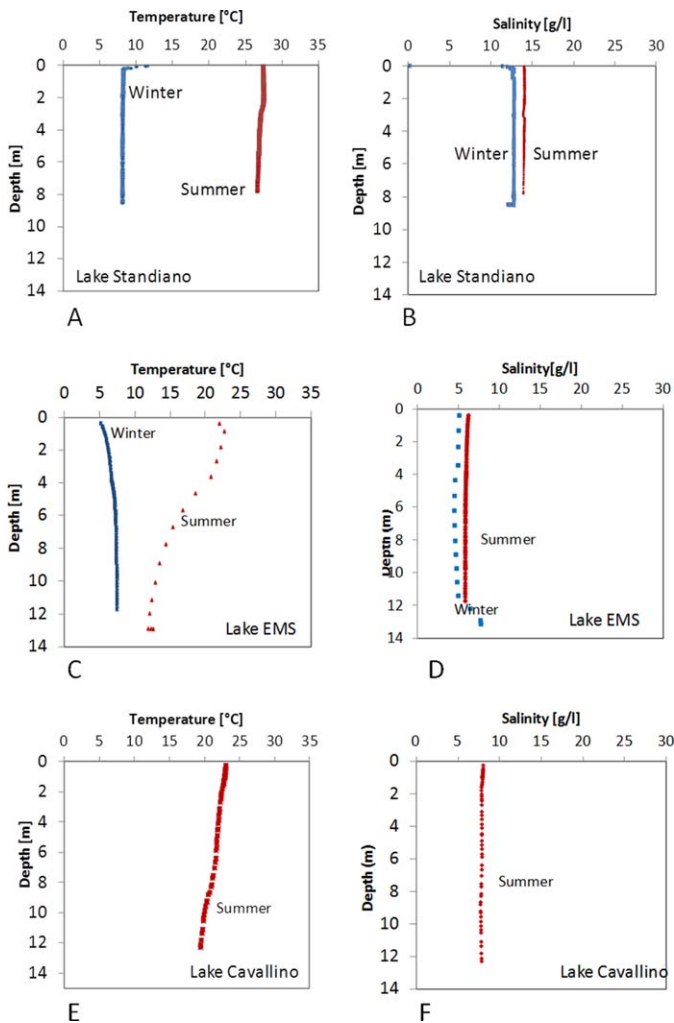
Fig. 7. Salinity (TDS) and temperature logs in the gravel pit lakes. (A) and (B) Lake Standiano, (C) and (D) Lake EMS, (E) and (F) Lake Cavallino.

The gravel pit lake water contains less Ca than groundwater suggesting that $CaCO_3$ has precipitated.

Ba occurs in relatively high concentration in groundwater underneath the Paleo dunes and in the gravel pit lake. Since the gravels were deposited along the paleo-shoreline in the tidal zone (Amorosi et al. 2002, 2004), it may be that part of the Ba enrichment occurred at the time of deposition or shortly thereafter in coastal processes (Moore and Shaw 2008; Gonneea et al. 2013). Water-soluble barium compounds are poisonous and may affect muscles and the human nervous system (Pradyot 2003) and cause hypertension (WHO 2011).

Arsenic concentrations measured in the ground and surface water samples are fairly high: 20.2 ± 15.2 μg/L on average for all samples, 12.3 ± 0.5 μg L^{-1} for the gravel pit lake samples, and 26 ± 14 μg L^{-1} for the average groundwater

concentration in the profile near the gravel pit lakes. The As concentration of the Adriatic Seawater sample is very high 37.5 μg L^{-1} but this sample was taken relatively close to the coast where exchange with groundwater may occur and also close to the harbor channel of Ravenna which is known to exchange water with the Pialasse Lagoon that is extremely rich in heavy and trace metals and not representative of average Adriatic Sea water (Donnini et al. 2007; Franzellitti et al. 2010). The As values are all exceeding the drinking water norm recommended by the World Health Organization (WHO 2011) of 10 μg L^{-1}, a value also adopted by the European Union and Italian regulatory office (ARPAV 2009). The northern part of the Po plain is known to be an As-rich province (ARPAV 2009) and the setting of the Po plain is very similar to the setting of other high As aquifers such as those in Bangladesh (Smedley and Kinniburgh 2002) or in the Netherlands (Stuyfzand et al. 2008) with Holocene alluvial/deltaic sediments, abundance of solid organic matter, strongly negative Eh, neutral pH, high alkalinity and slowly moving groundwater (Mollema et al. 2013b). The As concentration in the gravel pit lakes is less than that of the average groundwater, which could be explained by precipitation of metal oxides (e.g., Fe, Mn) on the lake bottom and scavenging of trace metals such as As (Weiske et al. 2013; Mollema et al. 2015). It is known that As accumulates in the fishes of the Adriatic Sea (together with Cd and Hg, Ghidini et al. 2003) and in the mussels of the Venice Lagoon (Argese et al. 2005). This is important to monitor since some of the gravel pit lakes in the area are used as fishing ponds.

The water of the gravel pit lakes of this study appears very transparent and clean. Even though a particular strain of a harmful Alga species (*Fibrocapsa japonica*) of the class Rapidophyceae has caused regular blooms in the coastal waters of the northern Adriatic Sea since 1997 (Cucchiari et al. 2008), the salinity in the gravel pit lakes ranges from 5 g L^{-1} to 12 g L^{-1} and very few species can thrive within that salinity range as shown by a study on species richness by Bleich et al. (2011). They showed species richness to be lowest in water with a salinity of 5–8 g L^{-1}—relatively high above 15 g L^{-1} with a maximum richness at 35 g L^{-1}. The gravel pit lakes are too brackish for the saline species and too saline for the freshwater species which is similar to what was found for plant species richness in the area (Antonellini and Mollema 2010). Another limiting factor for algae growth could be the amount of nitrogen and/or phosphorus in the lake water. The Redfield Ratio defined as the molar ratio of N to P in the elemental composition of marine plankton and dissolved nutrients in the ocean interior (Geider and La Roche 2002), ranged from 0.6 to 3.4 in the gravel pit lakes which is below any of the *N/P* ratios observed for marine algae or cyanobacterial cultures in other studies (Geider and La Roche 2002; Martiny et al. 2013 and references in both) suggesting that the nutrient

concentration is far from optimum. With little primary production, there will be less accumulation of organic material on the lake bottom to fix metals to the bottom sediments (Weiske et al. 2013; Mollema et al. 2015). The fact that dissolved Fe concentration is low in the gravel pit lakes, which are mainly fed by Fe-rich groundwater, suggests that most of the iron precipitated to the bottom. The rather elevated dissolved metal concentrations (e.g., As) may indicate the presence of competing ions like PO_4, or the lack of sufficient binding material (e.g., organic) for the metals to precipitate with Fe.

Whether or not the metal and other trace concentrations are important depends on the use of the gravel pit lake after excavation. For example one gravel pit lake is used for swimming and scuba diving because the water seems so clean and indeed it is very clear water without algae as usually there are in the Adriatic Sea.

The brackish gravel pit lakes along the Adriatic Coast offer many recreational opportunities but the amount of groundwater flowing into the lake is very large due to high drainage and evaporation rates which leads to the inflow of groundwater metals and trace elements flow into the lake. Here pH, dissolved oxygen and interaction with the atmosphere causes the precipitation of certain elements but other elements such as As may remain in concentrated solution. Therefore the water quality needs to be monitored to be able to use the lake safely.

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