Submarine groundwater discharge within a landslide scar at the French Mediterranean coast

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1. Introduction

Submarine groundwater discharge (SGD) refers to any water mass discharging from the seabed to the ocean, including terrestrial fresh and recirculated saline water (Burnett et al., 2003). SGD is driven by a variety of factors including tides, waves, bottom currents, and/or density driven transport processes (Burnett et al., 2006; Santos et al., 2009). The mixing of freshwater and seawater leads to a variety of chemical reactions in the “subterranean estuary” (STE) (Moore, 1999).

The distribution of inert and reactive solutes within marine sediments can elucidate transport and reaction processes within the STE. Chloride, a chemically inert species, can be used as a tracer to study the distribution of fresh groundwater and seawater within marine sediments. The pore water concentration profile of chloride may be used to model advective and diffusive freshwater discharge from marine sediments into the sea (Berner, 1980; Schlüter et al., 2004). Reactive solutes may also be used to trace the distribution of seawater within the STE. However, they may be subject to biogeochemical alterations according to the sedimentary redox dynamics. For example, ammonium is typically released during the degradation of organic matter but may be oxidized during nitrification in the presence of oxygen (Froelich et al., 1979; Mogollon et al., 2016). Likewise, barium can be released into the pore water from the dissolution of minerals (e.g. barite, Mn oxides), or desorption from particles when fresh groundwater and seawater are mixed (Froelich et al., 1979; Charette and Sholkovitz, 2006; Santos et al., 2011; Russak et al., 2016) and has been associated with SGD occurrence e.g. in the Ganges-Brahmaputra delta (Moore, 1997).
SGD, in the form of submarine springs, is a common feature of the Mediterranean coast (Fleury et al., 2007), including locations in Turkey (Elhatip, 2003), Greece (Tsabaris et al., 2011), Italy (Povinec et al., 2006), France (Dorflinger, 2003), and Spain (Garcia-Solsona et al., 2010b). These springs have been used as freshwater source for at least 2000 years and some are still used today (Gilli, 2015). SGD was shown to transport substantial amounts of nutrients to the Mediterranean (Rodellas et al., 2015), which could lead to eutrophication in coastal ecosystems. Most of the studies of submarine groundwater discharge in the Mediterranean have focused on submarine springs from karstic aquifers, but SGD from sediments could also have a strong effect on coastal environments.

In 1979 a submarine landslide was triggered south of the airport of Nice (France), which exposed freshwater-charged sediments to seawater (Kopf et al., 2010) and thus created an ideal research location for SGD. The landslide was hypothesized to be triggered by groundwater charging into weak, clay-mineral rich layers in the alluvial fan, which had been gradually destabilized by anthropogenic activity on the shelf (Stegmann et al., 2011). This study investigates the current status of SGD within the Nice airport landslide scar by evaluating 13 profiles taken from an STE located in water depths of down to 44 m.

2. Study area

The study area is located in the Ligurian Sea (French Mediterranean coast), close to the Var river mouth and the Nice Côte d’Azur airport (Fig. 1). At the Mediterranean coastline most of the porous

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**Fig. 1.** (A) Bathymetric map of the study area south of the Nice airport. Gravity cores recovered from outside of the landslide scar (yellow) were only affected by seawater, while cores inside of the landslide scar (blue) were affected by submarine fresh groundwater. (B) Schematic cross section through the study area. The location is indicated in (A) by the white dotted line. Two aquifers systems, a lower confined and an upper unconfined aquifer which is examined in this study are known (modified after Dubar and Anthony (1995) and Kopf et al. (2016)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
coastal aquifers are located in Plio-Quaternary deposits (Lofi et al., 2012). The history of these aquifers is closely linked to the Messinian Salinity Crisis, which exposed the margin of the Mediterranean Sea to subaerial erosion (Lofi et al., 2005) and created deep valleys, which were subsequently filled with Plioene-Quaternary deposits (Lofi et al., 2003).

In the Var Paleo-Valley, conglomerates and marls were deposited at the base of the Pliocene, overlain by a 100 m thick wedge of Holocene alluvial sediments (Sultan et al., 2004). Two aquifer systems, recharged by the river Var and subsurface infiltration formed in this sediment succession (Guglielmi and Mudry, 1996; Anthony and Julian, 1997). The upper delta sediments of mixed grain sizes form an unconfined aquifer, which we examine in this study. The basal, coarse-grained Pliocene conglomerate (so called Puddingstones) constitutes a second aquifer, confined below a thick wedge of shallow marine deltaic mud. A hydrological model and a hydrochemical investigation indicates that the second aquifer layer drains seawards along permeable gently southward-dipping beds at various depths down to ~ 140 m (Guglielmi, 1993; Guglielmi and Mudry, 1996; Anthony and Julian, 1997). Fresh submarine groundwater discharge seems to occur within a distance of less than 1.5 km off the coast (Guglielmi and Prieur, 1997) and has been shown to be linked to high discharge (flooding) at the river Var and flow through the aquifer (Stegmann et al., 2011).

A detailed hydrochemical characterization of surface and groundwater in the Var Valley was conducted by Potot et al. (2012). Groundwater chemistry in the aquifers is mainly affected by water/rock interaction (Potot et al., 2012). Surface and alluvial groundwater are dominated by Ca and SO4. Barium concentrations range from 0.2 to 0.3 μM and ammonium concentrations are below detection in Var river water and alluvial groundwater (Potot et al., 2012). The mean oxygen isotopic signature of the Var river is −10.0‰ VSMOW (−11.4 to −8.5‰ VSMOW) and alluvial groundwater range from −10.3 to −6.3‰ VSMOW (Potot et al., 2012).

Currently, the Var river basin is increasingly affected by anthropogenic activities such as urbanization. In the 1970s a deepening of the river Var channel led to salt water intrusion and increased risk of flood damage (Anthony and Julian, 1997). In 1979 a landslide occurred at the pro-delta of the Nice slope, which was likely caused by a combination of creep in sensitive clay sediments, loading by landfill material and embankment construction, and a pore pressure rise owing to precipitation (Dan et al., 2007). The landslide exposed freshwater charged sediments to seawater (Kopf et al., 2010) and its scar has been showing freshened pore waters on a number of repeated cruises over the past decade (Kopf et al., 2007, 2009).

3. Methods

3.1. Pore water and sediment sampling

For sediment and pore water analyses, 13 gravity cores were collected within the area of the airport landslide scar (Fig. 1) using the research vessels RV Meteor in summer 2007 and RV Poseidon in summer 2009. In the shallow waters off Nice 6 m long gravity cores were taken to prohibit the core from super penetration and losing surface sediments. This strategy proved to be successful since the most recent deposits were cored on all occasions (for details see Kopf et al. (2016)). All gravity cores were taken in plastic liners and cut into 1 m segments on deck. To prevent a warming of the sediments on board, the cores were immediately stored at a temperature of about 4 °C. The wet sediment was exposed by cutting a small ‘window’ in the plastic liner at an interval of 25 cm. Eh and pH were measured directly in the sediment using punch-in electrodes. Pore water was extracted with rhizons ( pore size 0.1 μm) (Seебerg-Elverfeldt et al., 2005). Depending on the sediment porosity, the amount of pore water recovered ranged from 4 to 20 mL. Electric conductivity was measured using a conductivity probe. Ammonium was measured on board using a conductivity method (modified after Hall and Aller, 1992). Aliquots of the remaining pore water samples were diluted 1:10 and acidified with ultrapure HNO3 for laboratory analyses at the University of Bremen. There, cation (Ca, Mg, Sr, K, Ba, S, Mn, Si, B, Li) concentrations were determined by ICP-OES, chloride and sulfate were measured with an ion chromatograph following established procedures (Price et al., 2007). Oxygen and hydrogen isotopes were measured using a “Liquid-Water Isotope Analyser” (Los GatosSM). δ18O and δD are reported as deviations in permil (%) from the Vienna Standard Mean Ocean Water (VSMOW).

Solid-phase samples of most cores were taken for total diagenetic, sequential extractions and mineralogical analyses at 25 cm intervals, and kept at 4 °C in gastight glass and heavy plastic bottles under an argon atmosphere.

The saturation index (SI) calculation for certain mineral phases (e.g. barite) was performed using the software PHREEQC (version: Phreeqc Interactive 3.2.0—9820) and the database llnl.dat (Lawrence Livermore National Laboratories) (Parkhurst and Appelo, 1999) for each depth interval in each core. The ion activity product and the solubility of all pore water species which are related to a certain mineral phase were considered. A negative SI (under saturation) indicates that, based on thermodynamic considerations, a given mineral should dissolve. Positive SI (over saturation) values indicate that a given mineral should precipitate within the pore water.

3.2. Pore water modelling

Assuming constant temperatures and porosities (in both time and depth), the distribution of chloride in sediment pore water is controlled by dispersion and advection according to the following equation (Bern er, 1980).

$$\frac{\partial C}{\partial t} = \nu \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} + \frac{\partial q v}{\partial x}$$

(1)

where C is the concentration of chloride, t is the time passed since the landslide occurred, x is the depth below the seawater mixed sediment, v is the advection rate, and D is the chloride (hydrodynamic) dispersion coefficient. The D term (in cm2 s−1, Eq (2)) is composed of two parts. The chloride diffusion (first term in right hand side of Eq. (2)) was calculated for an average bottom water temperature (Tb) of 17 °C and corrected for tortuosity according to Boudeau (1997) as it acts within a sediment matrix (as represented by the denominator term). The second term on the right hand side represents the mechanical dispersion coefficient, which scales to pore-water velocity:

$$D_s = \frac{\left(9.6 + 0.438T_c \right)10^{-6}}{1 - 2ln(\phi)}$$

(2)

where $\alpha$ is the dispersivity coefficient (= 10.0 cm), $T_c$ is the temperature in Celsius (=17 °C), and $\phi$ is the porosity. Values obtained for $D_s$ are dominated by molecular diffusion and range from 209 to 345 cm2 yr−1 for the various porosity values. Eq. (1) has the following analytical solution (van Genuchten and Alves 1982).
\[ C = (C_i + (C_0 - C_i)) \left( \frac{0.5 \text{erfc} \left( \frac{x - vt}{2\sqrt{D_s t}} \right)}{C_{18}} + 0.5 \exp \left( \frac{\nu x}{D_s} \right) \text{erfc} \left( \frac{x + vt}{2\sqrt{D_s t}} \right) \right) \]  

where \( C_i \) is the initial chloride concentration in the freshwater portion of the sediment, and \( C_0 \) is the concentration at the top of the freshwater layer. In equation (1) the advection rate with respect to a fixed sediment layer (\( \nu \)) is the remaining unknown, as the diffusion coefficient in sediments is well constrained. Thus, \( \nu \) can be obtained by comparing modeled chloride profiles with measured data and minimizing the sum of the least squares. A sensitivity analysis for the porosity, temperature and advective velocity is shown in supplementary materials.

4. Results

The gravity cores could generally be divided into two groups based on their position in the area of the Nice airport landslide scar. The first group refers to gravity cores recovered from adjacent areas of the 1979 landslide scar on the stable shelf/plateau (Fig. 1 marked in yellow). The second group consists of gravity cores taken in the 1979 landslide scar (Fig. 1 marked in blue).

4.1. Gravity cores outside the landslide scar

The most common deposit on the Nice Slope outside the 1979 landslide scar was a slightly plastic to medium plastic silty clay, mainly derived from the suspension load of the river Var (Kopf et al., 2016). The clays were often deformed by creep and flow processes or slump folding. In the fairly homogeneous package, thin (mm-to cm-thick) layers of silt or fine sand were also present.

The pore water composition of gravity cores collected outside of the landslide scar was dominated by seawater as indicated by major ion concentrations similar to Mediterranean Seawater (e.g. around 600 mM for chloride) (Figs. 2A and 2B). Sulfate concentrations decreased in each core from typical seawater concentrations in the range of 29 mM (Grasshoff et al., 2009) in the top section, to values below the detection limit (<1 μM) with depth. A zone with elevated pore water barium concentrations was observed in the deepest section of each core (about 3–4 m), which coincided with a zone where barite was under saturated, i.e., SI < 0. Pore water in the upper sections of the cores was over saturated with respect to barite, as indicated by a positive saturation index of barite (Figs. 2A and 2B).

![Fig. 2A. Pore water profiles (Cl, SO_4, NH_4, Mn, Ba and the saturation index of barite) of gravity cores which were collected outside of the landslide scar and were only affected by seawater. The water depth of each station is shown in brackets behind each station name.](image-url)
4.2. Gravity cores inside the landslide scar

In cores from inside the landslide scar, mass wasting deposits, such as alluvial gravel and other coarse particles amalgamated into the clays of the Nice slope were common (Kopf et al., 2016). In places we found deposits that consist of the landslide debrite (e.g. core 13929), a deposit from the tsunami following the landslide (e.g. core 13953), and deposits out of a suspension cloud either from the tsunami or Var river discharge (e.g. core 13939).

Most pore water profiles from within the landslide scar can be divided into two zones. In the upper first meter of the sediment we observed a seawater dominated zone as indicated by comparatively high chloride concentrations. Below, we observed a second fresh to brackish groundwater affected zone indicated by lower chloride concentrations (Figs. 3A and 3B). Within this second brackish to freshwater affected zone, chloride concentrations decreased with sediment depth either in form of a concave shaped pore water profile (e.g. 13925, 13929, 13934, 13940, 12042) or a linear pore water profile (13939). Porewater profiles of other major ions of seawater (e.g. Li, Mg, K, Ca, Sr, Na) and $\delta^{18}O$ and $\delta^D$ followed the chloride profile in a similar way (see electronic supplementary material).

Barium pore water concentrations were depleted within the upper seawater dominated zone (Figs. 3A and 3B). In most cores barium pore water concentrations of more than 15 $\mu$M were observed within a brackish water mixing zone directly below the seawater dominated zone. In the lower fresh groundwater dominated zone, barium pore water concentrations decreased with sediment depth down to concentrations of 0.3–1 $\mu$M in cores with a concave shaped chloride profile. Core 13939, which was dominated by a linear chloride profile (Fig. 3B), showed comparably higher pore water barium concentrations of 5 $\mu$M in the deeper part of the core.

Oxygen ($\delta^{18}O$) and hydrogen ($\delta^D$) isotopes of pore waters from cores inside of the landslide scar are shown in Fig. 4. The most depleted values were $-9.4\%$ for $\delta^{18}O$ and $-64\%$ for $\delta^D$. Values for seawater were in a positive range of up to $+1.7\%$ for $\delta^{18}O$ and $+6.9\%$ for $\delta^D$, which is a typical value for Mediterranean seawater (Schmidt et al., 1999). The isotopes indicated linear mixing between meteoric water and seawater, which was mostly below the local meteoric water line (LMWL) (Fig. 4) and the global meteoric water line (GMWL) (Fig. 4). Endmember values of oxygen isotopes were calculated by applying a linear regression of pore water $\delta^{18}O$ values against pore water chloride concentrations for each respective core inside the landslide scar. Endmember values were in the range of $-8.1$ to $-9.4\%$ for $\delta^{18}O$ (Table 1(D)), which was in a range similar to alluvial groundwater and Var river water sampled in the vicinity of the Var river mouth (Potot et al., 2012).

5. Discussion

5.1. Barium cycling in the subterranean estuary

Within the coastal area of the Nice airport, we observed a STE (after Moore, 1999) inside of the landslide scar, which most likely evolved after the landslide exposed fresh groundwater charged sediments to seawater (e.g. within 30 years prior to sampling). Outside of the landslide scar pore waters were only affected by seawater. We can thus directly compare barium cycling in pore waters which were affected and which were not affected by sub-marine fresh groundwater.

In sites which were only affected by seawater, the zone in which barium was released into the pore water coincided with a zone which was depleted in sulfate pore water concentrations and which was under saturated with respect to barite (Figs. 2A and 2B). In these sites, barium might be released into the pore water due to the dissolution of barite, forced by the depletion of sulfate within the zone of sulfate reduction (Henkel et al., 2012).
In fresh groundwater dominated sites, barium was released into the pore water within the brackish mixing zone, which was over-saturated with respect to barite (Figs. 3A and 3B). Barite dissolution as a source of barium seems unlikely, as solid phase barium concentrations did not show any significant variations with sediment depth (see electronic supplementary material). Similarly, because Mn pore water concentrations were depleted within the brackish water zone (Figs. 3A and 3B), a release of barium related to the dissolution Mn oxides (Charette and Sholkovitz, 2006) also appears unlikely. A remaining source of barium could be related to cation exchange reactions within the brackish water zone (Russak et al., 2016). This latter source is corroborated by pore water ammonium profiles, which are also strongly affected by cation exchange reactions (Russak et al., 2015) and closely follow the barium profile trends.

In most cores, barium freshwater endmembers in the deeper part of the core still exceeded those of Var river water or alluvial groundwater. If fresh groundwater in the landslide scar was derived from Var river water or alluvial groundwater as indicated by δ¹⁸O values, a further barium source in the deeper part of the sediment must exist.

5.2. Submarine groundwater discharge within the landslide scar

The rate of vertical pore water advection within the sediments of the landslide scar can be calculated by modeling the pore water chloride profile (Fig. 5), assuming that before the landslide fresh groundwater was located in the deeper part of the sediment. If only
diffusion affected the mixing of groundwater with seawater, a curvature similar to the red dotted line, indicated in Fig. 5, would have developed after 30 years. Therefore, an upper mixed seawater zone, followed by a concave shaped chloride profile indicated either advective transport of freshwater from below or a change in chloride concentrations from above. A change in chloride concentrations from above could have been due to rapid sedimentation and burial, e.g. from the mass wasting after the 1979 landslide or sediment suspension of the Var river (Berner, 1980; Kopf et al., 2016) or due to seawater intrusion forced by differences in the hydraulic heads between land and sea, density driven transport and/or bottom water currents (Burnett et al., 2006; Santos et al., 2009).

Most of the modelled pore water profiles indicated an upward flow of freshwater (Table 1), which coincided with an upward migration of barium and ammonium poor fresh groundwater in cores with concave shaped chloride profiles (Figs. 3A and 3B). In one core (13939) seawater intrusion was indicated by the pore water model (Table 1), which coincided with comparatively high ammonium and barium concentrations in the deeper part of the core and thus no dilution by freshwater from below (Fig. 3B). While in most cores, fresh groundwater seemed to flow upwards it did not replace the upper seawater dominated layer, possibly because seawater was recirculating through the upper, in general less compacted sediment layer. Intensive mixing processes from density driven seawater recirculation, rapid sediment deposition and resuspension, coupled to horizontal bottom-water currents penetrating (and possibly scouring) into this upper sediment layer might help to maintain near seawater concentrations. This mixing seems to be sufficiently strong to overcome the vertical fresh groundwater advection occurring within the landslide scar.

The 1-D advection-diffusion pore water model (eq. (1)) was applied to the concave and linear shaped part of the pore water profile. Calculated pore water velocities based on the advection-diffusion model yielded upward flow velocities of about +2.3 to +8.8 cm yr\(^{-1}\) with an average upward flow velocity of +4.8 cm yr\(^{-1}\). A volumetric discharge can be calculated by multiplying the pore water velocity with the porosity in each core, respectively. The volumetric discharge was in a range of 0.0124 m\(^3\) m\(^{-2}\) yr\(^{-1}\) to 0.053 m\(^3\) m\(^{-2}\) yr\(^{-1}\) with an average volumetric discharge of 0.026 m\(^3\) m\(^{-2}\) yr\(^{-1}\).

SGD fluxes into the Mediterranean sea were mostly studied in karstic aquifers and are reported to be in the range of 37.6 m\(^3\) m\(^{-2}\) yr\(^{-1}\) on the island of Majorca (Spain) (Basterretxea et al., 2010), 29.2 m\(^3\) m\(^{-2}\) yr\(^{-1}\) total SGD and 18.2 m\(^3\) m\(^{-2}\) yr\(^{-1}\) fresh SGD in Dor Bay (Israel) (Weinstein et al., 2007), 9.1 m\(^3\) m\(^{-2}\) yr\(^{-1}\) fresh SGD in the Alcalfar cove on Minorca (Spain) (Garcia-Solsona et al., 2010a), 1.6–10 m\(^3\) m\(^{-2}\) yr\(^{-1}\) total SGD in the Messiniakos Gulf (SE Ionian Sea) (Pavlidou et al., 2014). SGD fluxes in the sediments of the landslide scar were about 2–3 orders of magnitude lower.

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**Fig. 3B.** Pore water profiles (Cl, SO\(_4\), NH\(_4\), Mn, Ba and the saturation index of barite) of gravity cores which were collected inside the landslide scar. The water depth of each station is shown in brackets behind each station name. Also note the comparatively large amount of freshwater in core 13934 and core 13939 in top core sediments and the comparatively short penetration depth of core 13934 and 13930.
compared to these fluxes, which might be attributed to slower groundwater seepage in sediments when compared to a karstic aquifer. Furthermore, the pore water model only considers the vertical component of SGD, whereas a large part of the pore water migration within the sediment may be horizontally. This is supported by the frequent silt bands and layers interbedded with the fine-grained muds (see Kopf et al., 2016), which may act as “conduits” for groundwater discharge.

6. Conclusions

In 1979, a submarine landslide next to the Nice airport (western Mediterranean Sea) exposed freshwater charged sediments to seawater. The distribution of dissolved chemical species (e.g. Cl, Ba, Mn, NH₄) in the pore water of the mixing zone between fresh groundwater and seawater indicated transport processes and reactions in the sediment. A 1-D advection-diffusion model estimated...
average vertical pore water velocities of 4.8 cm yr\(^{-1}\) towards the sediment surface. In the Mediterranean Sea, it was recently shown that SGD derived nutrient fluxes can be on the same order of magnitude than river derived nutrient inputs (Rodellas et al., 2015), but submarine groundwater discharge has been studied mostly on karstic springs (Fleury et al., 2007; Bakalowicz, 2014). Our study indicates that submarine groundwater discharges also from sediments as deep as 44 m water depth. This might be an overlooked part of SGD especially along the French Mediterranean coastline.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ecss.2017.09.006.


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