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Submarine Groundwater Discharge as a nitrogen source to the Ria Formosa studied with seepage meters

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Abstract Submarine Groundwater Discharge (SGD) has been frequently ignored as a nutrient source to marine ecosystems because it is difficult to identify and quantify. However, recent studies show its ubiquity and ecological importance to the coastal zone, particularly when associated with contaminated continental aquifers. The Ria Formosa is a coastal lagoon located in the south of Portugal and surrounded by an intensely farmed area. Following a 12-month field study using seepage meters, we identified groundwater discharge in the intertidal zone of the lagoon. The seeping fluid was a mixture of two water types: one with low salinity and high nitrate concentration and another similar to local seawater. Based on the integration of monthly seepage rate measurements throughout the year, we estimate the mean discharge of submarine groundwater into the lagoon to be 3.6 m^3 day^{-1} per linear meter of coastline with freshwater contributions (per volume) ranging from 10% to 50%. The results of this study suggest a continental origin for the freshwater component, thus linking the biogeochemical cycles in the lagoon to anthropogenic activities taking place in the neighboring coastal plain. We further identify SGD as an important nutrient source to the Ria Formosa, estimating annual loads of 36.2 mol (0.507 kg) of Nitrogen, 1.1 mol (0.034 kg) of Phosphorus and 18.6 mol (0.522 kg) of Silicon per meter of coastline. Based on these results, we suggest that SGD is a potential contributor to the observed nutrification status of the Ria Formosa lagoon.

Keywords Submarine Groundwater Discharge · Seepage meters · Nutrification · Permeable sediments · Ria Formosa · Nitrate

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Introduction

The increased human settlement of the continental fringe is promoting the contamination of water and sediments in the coastal zone, particularly in coastal lagoons. As the fraction of anthropogenic nutrients that is annually injected surpasses that originating from local ecological processes (Nausch et al. 1999;

García-Pintado et al. 2007), important changes in local biogeochemical cycles are observed (Smith and Atkinson 1994). Globally, nutrient loading into lagoons is thought to occur mainly through terrestrial runoff (in which rivers are included), atmospheric deposition and exchanges with the ocean (Smith and Atkinson 1994). However, growing evidence suggests that Submarine Groundwater Discharge (SGD) may also be an important source of nutrients to the coastal zone, particularly when originating from contaminated continental aquifers (Lee and Olsen 1985; Valiela and Costa 1988; Cable et al. 1997a; Chanton et al. 2003; Finkl and Krupa 2003; Ullman et al. 2003).

The term "Submarine Groundwater Discharge" has been used over the years with different meanings since some authors consider only freshwater discharge while others also include recirculated water seepage (Taniguchi and Iwakawa 2004). Nowadays, the most consensual definition is the one put forward by Burnett et al. (2003), in which "submarine groundwater discharge is any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of the fluid composition or driving force". SGD has been shown to occur every time a non-confined aquifer contacts the ocean and its hydraulic head is above sea level (Johannes 1980; Burnett et al. 2001). Because of its "invisibility" (Finkl and Krupa 2003) and unpredictability in time and space, its presence is often suggested only by its effects, i.e. nuisance algae blooms and massive fish mortality (Finkl and Krupa 2003; Verhoeven et al. 2006). These characteristics also hinder the quantification of the actual dimension and intensity of the discharge and, therefore, SGD is frequently ignored in local and regional nutrient mass balances (Burnett et al. 2003).

This study was conducted in the Ria Formosa, a coastal lagoon surrounded by a highly urbanized and intensively farmed area. The lagoon sustains high primary productivity during the whole year, but shows evidence of nutrient enrichment when compared to the adjacent coastal zone (Newton and Mudge 2005). During the past 15 years, some evidence of changes in its trophic status has surfaced in the literature, including decreasing bivalve harvests (Dinis 1992), the increase in the occurrence of algal blooms (Baptista 1993), the replacement of typical salt marsh vegetation by macro algae (Padinha et al. 2000) and increasing incidence of fish kills during summer months (Newton et al. 2003).

These changes may arguably be linked to nutrient enrichment, thus promoting research focused on nutrient loading pathways to the system. Until present, the major nutrient sources to the lagoon were considered to be urban effluents and agriculture-derived terrestrial surface runoff (Ferreira et al. 2003). Other suggested nutrient sources included atmospheric deposition, torrential runoff, imports from the adjacent coastal ocean and internal mineralization of excess organic loading (Falcão and Vale 1990, 1998; Newton et al. 2003; Newton and Mudge 2005). However, those potential contributions have never been properly quantified in-situ and major uncertainties remain, frequently leading to the presence of unidentified diffuse-source parameters in efforts to produce mass balances (Ferreira et al. 2003).

Here, for the first time, we identify SGD as an important internal source of nutrients into the lagoon and link the phenomenon to contaminated upland aquifers. Based on a complete year of sampling, we present preliminary estimates of the relative contribution of SGD to the internal nutrient loading by providing quantitative estimates of the seepage fluxes per meter of coastline.

Study area

The Ria Formosa is a coastal lagoon located in the south of Portugal (Fig. 1) and separated from the Atlantic Ocean by a chain of five barrier islands and two peninsulas (Salles 2001; Andrade et al. 2004). It is approximately 55 km in length, has an average depth of 2 m and a total area of 170 km^2, as well as an intertidal surface of more than 50 km^2 (Andrade et al. 2004). The contiguous coastal area has a semi-diurnal mesotidal regime with an amplitude range of 1.35–3 m for neap and spring tides, respectively (Salles 2001). The freshwater input to the lagoon is negligible, being reduced to the Gilão River, in Tavira. During spring tides, ~50% to 70% of the lagoon's internal water volume is renewed on a daily basis, thus supporting its high dilution capacity. Consequently, salinity inside the lagoon is similar to that of adjoining coastal waters and ranges between 35.5 and 36.9 psu (Ferreira et al. 2003).

The south of Portugal boasts a Mediterranean climate, with hot and dry summer months and dry moderate winters. The mean temperature is 16.3°C and the mean annual rainfall varies between 480 mm in

Faro and 580 mm in Tavira, on the eastern part of the lagoon (Stigter et al. 1998; Salles 2001). The main primary producers are the macrophytes *Zoostera noltii* and *Spartina maritima*, but periodic macro algae blooms of the genera Ulvae (Machás and Santos 1999; Salles 2001) occur in winter (Aníbal 2004).

Ferreira et al. (2003) estimated the annual nutrient load originating from urban and industrial effluents to be 421 ton (3.0×10^7 mol) of Nitrogen (N) and 83 ton (2.7×10^6 mol) of Phosphorus (P). However, according to the same authors these only represent part of the total supply which is estimated to be 1,028 ton (7.3×10^7 mol) and 164 ton (5.3×10^6 mol) of N and P, respectively. These numbers are based on the reported efficiency of local wastewater treatment plants and on population-based estimates of nutrient equivalents according to the World Bank. No precision estimates of these numbers are available in the literature.

The Ria Formosa supports a local economy based on tourism through natural resource harvesting and is thus strongly affected by human activities on the surrounding watershed. Two intensely farmed areas, Campina de Faro and Campina da Luz, are located north of the lagoon: both overlie nitrate-contaminated aquifers classified as Nitrate Vulnerable Zones (NVZ) according to the EU's Nitrate Directive. The aquifer's hydraulic head varies between 2 and 40 m above mean sea level (MSL) in the southern and northern limits respectively, and thus, preferential groundwater flow occurs from north to south (Stigter et al. 1998). From the hydrologists' point of view, these facts have already suggested that contamination of the lagoon might be possible (Stigter et al. 1998, 2006a, b) while Newton et al. (2003) have suggested the intensification of agriculture as a potential explanation for the perceived increase of the nutrient load to the Ria.

The study site is in the Ancão peninsula, located in the western part of the Ria Formosa, approximately 1.5 km southeast from the access bridge to the "ilha de Faro". Field sampling took place on the inner side of the peninsula, facing the major water channel leading to Faro—"Esteiro do Ramalhete" (Fig. 1). The beach profile at the site shows a moderate slope at the high and intermediate parts of the beach, which decreases at the lowest part, near low tide level (Fig. 2). The sampling profile is limited at the lower end by a major tidal channel running parallel to the beach.

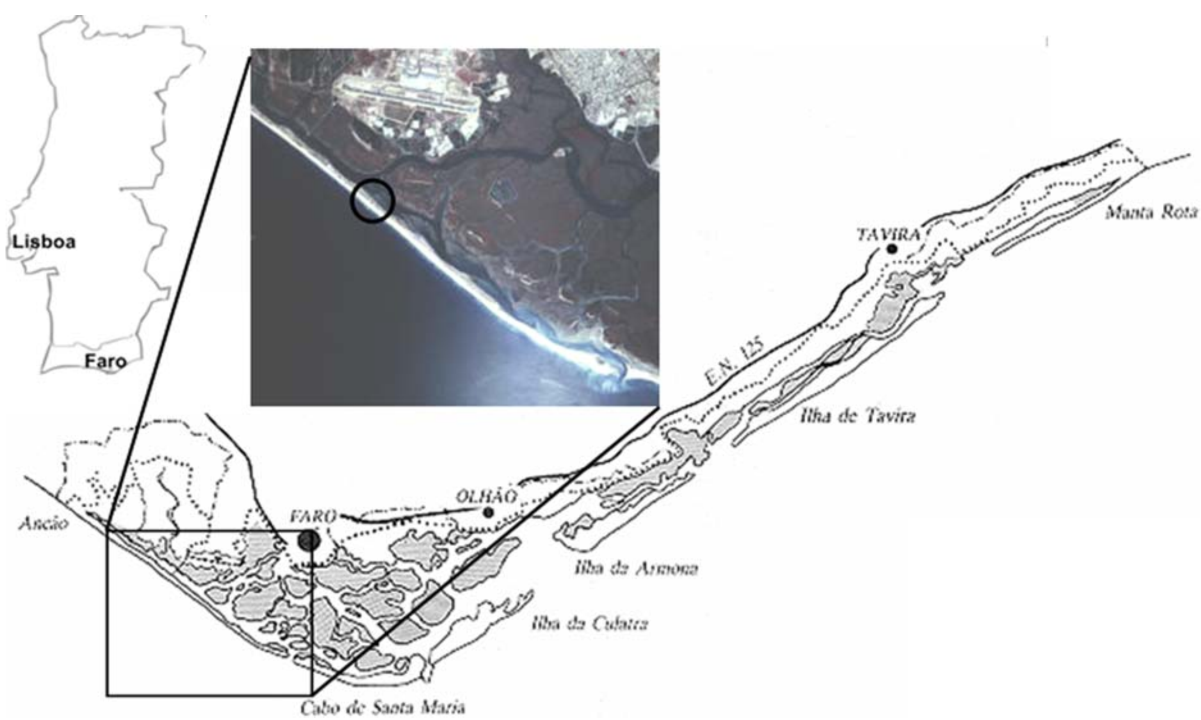

Fig. 1 Location of the Ria Formosa and the study site

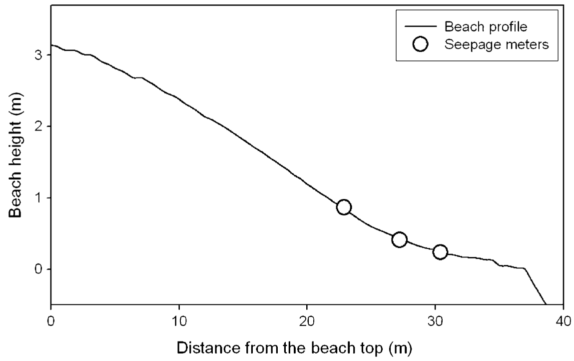

Fig. 2 Median beach profile at the study site

Methods

In order to identify seepage locations and quantify groundwater discharge, 12 monthly field trips were carried out, from January to December 2006. Field work was conducted during spring tides and 2 successive tidal cycles were sampled during each sampling trip, adding up to a total of 525 direct seepage measurements, complemented by water and sediment samples. Sampling focused on the intertidal area and was continuous during the ebb tide half period, the low tide and the flood tide half period. During each field trip, four to six Lee-type (Lee 1977) seepage meters (SM) connected to water collecting bags were deployed along the beach profile, with one meter placed slightly below the highest discharge boundary (SM 1), one or two positioned near the lowest low tide level (SM 4 and 4′), where the beach slope was less pronounced, and another two or three placed at an intermediate position (SM 2, 2′ and 3), as seen in Fig. 2. After the seepage meters were deployed, sampling was not carried out for the following half-tidal cycle to allow stabilization of the system.

The water collected from the meters was analyzed in situ with an YSI 600 multi-parameter probe (Yellowspring Instruments) for salinity, temperature, total dissolved solids, pH and redox potential. Water samples from the collecting bags were also taken with ultra-filtration membrane samplers (Rhizon SMS, Eijkelkamp Agriresearch Equipment) with a pore diameter of 0.1 μm, connected directly into vacuum tubes (BH Vaccutainer), for posterior nutrient analysis. The samples were stored at 4°C until analysis, carried out within 2 weeks at most. Nutrient concentrations were quantified following the spectrophotometric methods described in Grasshoff et al. (1983) for NO_2^-, NH_4^+, PO_4^{3-} and SiO_4, and according to Jones (1984) for NO_3^-.

Water and nutrient fluxes were integrated along the three beach profile levels in which seepage meters were located. Subsequently, a Gaussian peak curve was adjusted to the water fluxes, for each month, in order to obtain an estimate of the total discharge per meter of coastline. The beach nutrient fluxes were calculated by multiplying the integrated nutrient concentration in the area delimited by the seepage meters by the total discharge per meter of coastline. The numbers obtained were crossed-referenced with rainfall and public accessible water quality data available for continental boreholes (INAG—National Water Institute), aiming to establish annual patterns and potential relationships between field seepage observations and continental aquifer characteristics.

Results and discussion

Identification and behavior of SGD

Groundwater seepage occurred at the beach face throughout the 12-month sampling period. The discharge rate increased during ebb, peaked during low tide, and was significantly lower or absent during the high tide peak. Its temporal distribution strongly suggested that seepage rates depend on the tide (Fig. 3). The discharge intensity showed no great variations during the whole year with the exception of two discharge peaks in July and November and a minimum discharge in February (Fig. 4). The highest monthly discharge rates were measured at the intermediate and lower positions (SM 3 and SM 4), with values of 190.6 and 185.0 cm day^{-1}, in July and November, respectively. The lowest observed discharge was 1.7 cm day^{-1}, measured in February at the seepage meter placed the highest on the beach profile (SM 1).

Salinity and nutrient concentrations measured in the collected water evidenced some variation throughout the year (Table 1). The range of measured salinity was lower during summer, varying between 24.5 and 37 psu and showed a higher low limit, while during the rest of the year the range widened to fall between 16.8 and 37.7 psu. However, this seasonal pattern was more evident in the evolution of nutrient concentrations in the seepage meters. Nitrate, phosphate and

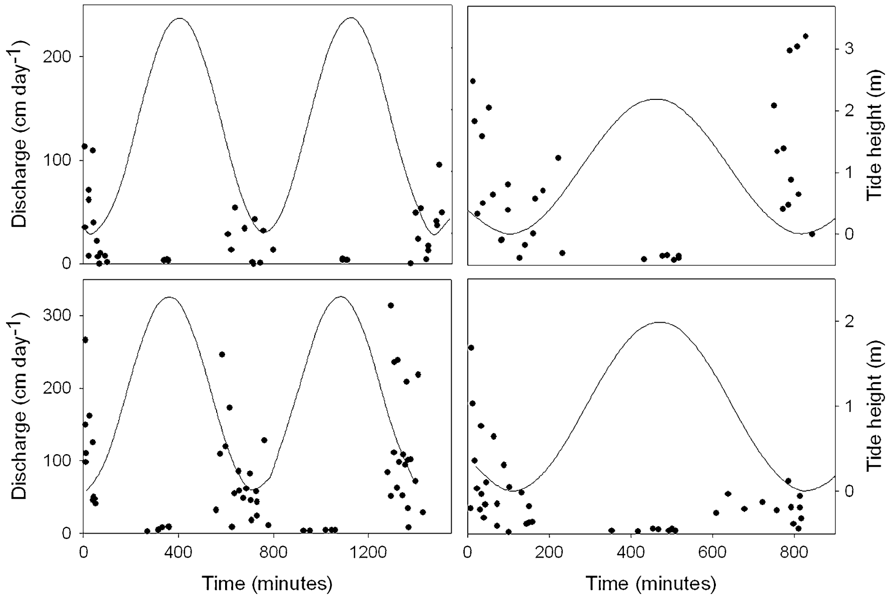

Fig. 3 Comparison between discharge and tide height in February and June (left-hand side) and September and December (right-hand side)

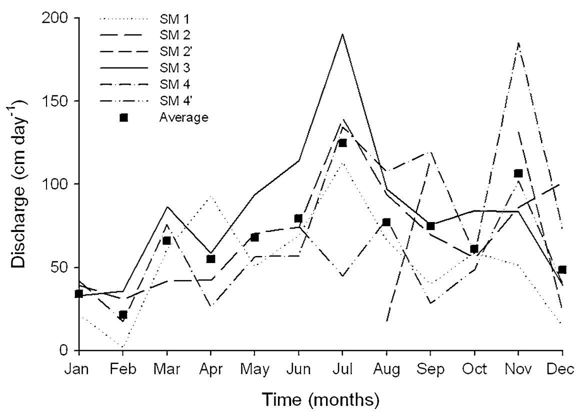

Fig. 4 Averaged discharge per seepage meter per month and monthly averaged discharge from January until December

silicate concentrations decreased in the early summer months of June and July, but increased during late summer (August and September). Ammonium was either absent or present at very low concentrations throughout the whole year, but levels also increased, albeit slightly, during early fall (September and October), although the apparent decrease during the summer months was not as clear as the pattern observed for the other nutrients.

For each sampling period, a significant decrease in salinity was observed as the tide ebbed, with peak lows measuring between 16.8 and 32.9 psu, while maximum values ranged between 36.2 and 37.7 psu, within typical levels for the Ria's water column. High temporal and spatial variability of the discharge was observed during the year. In some cases, the discharge measured at the same seepage meter was different for the two sampled low tide periods (albeit within the same range). On the other hand, two seepage meters placed next to each other (with a maximum distance of 2 m) also showed dissimilar discharge rates from time to time.

Presence of two water masses

The average discharge per meter of coastline was estimated to be 3.6 m^3 day^{-1}, which is within the range of literature values for SGD elsewhere: 2.0–4.2 m^3 day^{-1} m^{-1} (UNESCO 2004), 0.6–35.0 m^3 day^{-1} m^{-1} (Cable et al. 1997b), 4.5–23.0 m^3 day^{-1} m^{-1} (Boehm et al. 2006). The seepage meter method was adequate for the purposes of this study. Unlike other methods used to quantify SGD fluxes, seepage rates measured with Lee-type meters, if coupled with measurements of salinity in the outflowing water, allow for the separate quantification of freshwater discharge and recirculated seawater seepage (Oberdofer 2003), thus facilitating the establishment of correlations between salinity and nutrient levels. In fact, the differences in the characteristics of the discharged water revealed the presence of two distinct water masses (Fig. 5): one with high salinity and low nitrate concentration (water type 1) and another

Table 1 Salinity and nutrient concentration range for each month

Months	Salinity (psu)	NO_3^- (µM)	NH_4^+ (µM)	PO_4^{3-} (µM)	SiO_4^{2-} (µM)	Number samples
January	36.4–16.8	13.9–2.5	6.5–0.0	1.6–0.0	51.2–13.2	38
February	36.4–24.7	64.9–4.5	25.1–0.0	2.2–0.4	34.7–2.2	43
March	36.8–18.7	60.0–3.6	11.7–0.0	1.5–0.0	5.7–1.8	55
April	36.2–25.9	25.7–0.6	5.6–0.0	1.8–0.0	27.2–0.4	38
May	36.5–26.5	23.1–2.5	8.8–0.0	1.9–0.0	25.6–0.0	29
June	37.0–32.9	12.9–0.0	4.9–0.0	1.0–0.0	12.7–1.8	59
July	37.0–31.1	14.4–0.0	16.8–0.0	1.0–0.1	0.03–0.0	64
August	36.7–25.9	120.6–0.0	7.9–0.0	1.3–0.0	31.0–2.4	44
September	35.5–24.5	187.1–0.0	39.5–0.0	2.2–0.4	15.5–0.4	36
October	36.5–22.4	176.0–0.0	40.0–0.0	2.9–0.5	42.1–3.9	32
November	37.4–21.3	88.1–2.3	2.3–0.0	2.3–0.0	34.4–3.9	58
December	37.7–30.9	49.4–1.3	0.0–0.0	n.a.[a]	59.9–14.8	29

[a] n.a., not available

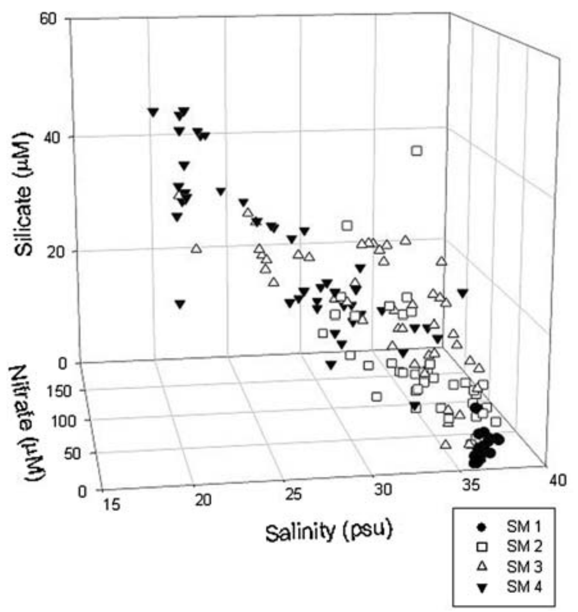

Fig. 5 Concentrations of nitrate, silicate and salinity in the discharged water during the months of February, March, April, August, October and November

with low salinity and high nitrate concentration (water type 2).

Spatial analysis of the data allowed us to separate the beach face into two distinct areas, according to the two types of discharged water. Water type 1 was associated with the highest part of the beach profile while water type 2 was found at the intermediate and lower parts of the beach. Considering its salinity, water type 1 originates from the drainage of infiltrated water *sensu* Horn (2002) during flooding and high tide (recirculated water). Water type 2, however, corresponds to brackish water, resulting from a mixture of infiltrated seawater and fresh groundwater seeping through the sediment.

Mixing curves (Fig. 6) show that nitrate concentrations were directly correlated to salinity. Good linear correlation, with coefficients varying between 0.5375 in February and 0.9910 in October, strongly suggests the presence of a freshwater nitrate source. The use of mixing plots also points to the existence of

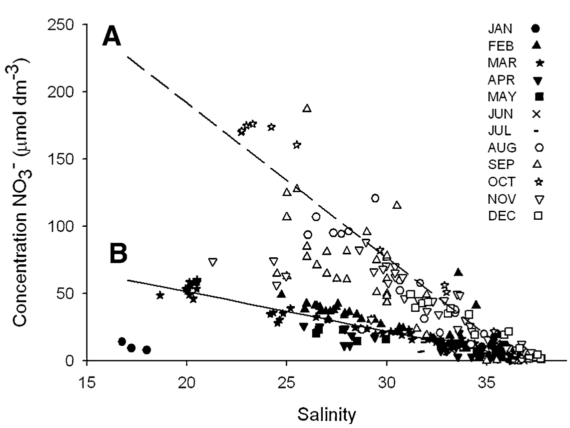

Fig. 6 Comparison between salinity and nitrate concentration with a mixing curve between seawater and brackish water: A) (from August to December) $y = -11.52x + 422.06$, $n = 55$, $p < 0.0001$ and B) (from January to July) $y = -2.94x + 110.08$, $n = 70$, $p < 0.0001$. Note periodic pattern on the nitrate concentration levels

an approximately semi-annual pattern in the nitrate concentration of the freshwater end-member, with lower levels of contamination present from January until July and higher contamination levels from August until December.

Freshwater origin and contribution

A comparison between the freshwater discharge rate at the beach and pluviometry in the drainage basin, on a monthly basis, suggests they are linked, with the higher discharge rates coinciding with the major rainfall peaks (Fig. 7). This suggests a continental origin for the freshwater, since the discharge appears to be directly related with rainfall that occurred over the drainage basin. The relative contribution of freshwater to the total discharged volume reached a maximum of 50%, but in general, varied between 10% and 30% of the total volume, as already noted elsewhere (Burnett and Dulaiova 2006; Moore 2003, 2006; Schiavo et al. 2006). By integrating the measured freshwater fluxes along the length of the beach profile, we estimate the average rate of freshwater discharge to be approximately 0.3 m^3 day^{-1} m^{-1}. Based on this figure, we extrapolate an annual freshwater discharge rate of 109.5 m^3 per linear meter of coastline.

Periodic pattern of water seepage rates and associated nutrient fluxes

Submarine groundwater discharge links soil use in the coastal plain to the nutrient status of the Ria Formosa. Based on our results, we estimate the annual nutrient input, per meter of coastline, to be ~1.1 mol phosphorus (P) and 18.6 mol silicon (Si). However, the most important contribution to the internal nutrient load is the total dissolved inorganic nitrogen (DIN), with an annual input of 36.2 mol N m^{-1}. Annually, the fraction of DIN discharged per meter of coastline as nitrate is 32.9 mol N, while ammonium and nitrite contribute only 2.2 and 0.7 mol N, respectively. Therefore, as seen on Fig. 8, nitrate is clearly the most abundant form of nitrogen, along the year, with ammonia representing 10% of the monthly load only in September and October. Just considering the freshwater source, the estimated annual N input in nitrate form by groundwater seepage is 28.6 mol m^{-1}. However, it is important to consider that these represent lower-limit estimates, since they are based on the extrapolation of the nutrient load to the perceived width of coastline with preconditions to host SGD (i.e. the area of sandy sediment exposed at low tide or located under a water column shallow enough to allow seepage while submerged).

High nitrate fluxes were observed from August until November, which is in tune with the variation of contamination levels calculated for the freshwater source (Fig. 6). This leads us to argue that the higher nutrient fluxes observed during the second semester are not exclusively related to the total discharged water volume, which depends on the hydraulic gradient, in turn controlled by the tide and aquifer recharge dynamics. Instead, this annual pattern may

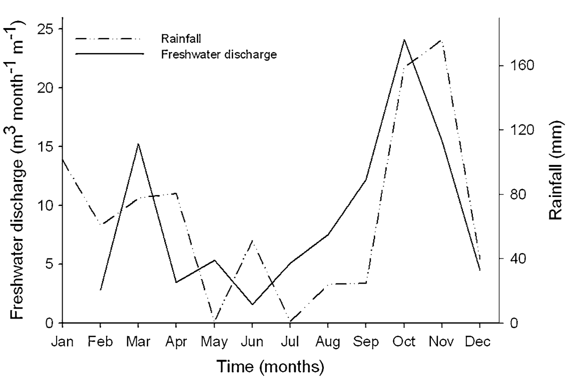

Fig. 7 Plot of monthly rainfall in S. Brás do Alportel according to data available from the Instituto Nacional da Água (INAG), compared to measured freshwater discharge at the sampling site

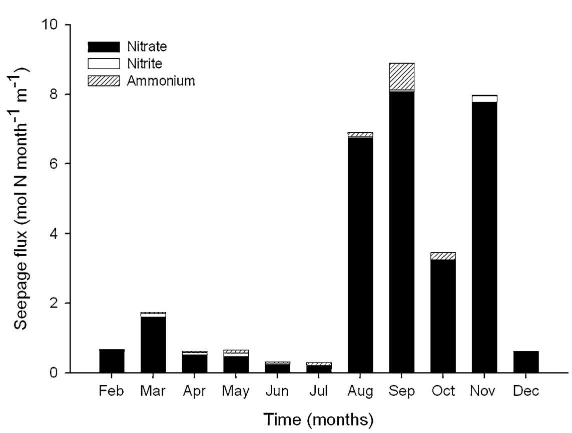

Fig. 8 Relative contribution of each measured N species to the total N monthly discharge

reflect the periodicity of agricultural practices in the surrounding watershed.

Implications and future research

The Ria Formosa is a highly productive ecosystem where signs of nutrification have been reported by several authors. Different hypotheses have been put forward to justify these signs, but major uncertainties remain concerning both the identification and quantification of the relevant sources.

The nutrient concentrations measured in the seepage water are in tune with the Ria's annual primary production cycle (Fig. 8). The spring/early summer bloom observed within the lagoon (Aníbal 2004) is in synch with the first peaks of groundwater-borne nutrient flux. A decrease in the nutrient concentration beginning in spring is followed by an increase in concentration during late summer, a fact that concurs with the decline of the benthic primary producer community and consequent enhanced remineralization rates (Aníbal 2004). Nitrogen concentrations also decline in early winter months, matching the behavior of macro algae blooms (*Ulva* sp. and *Enteromorpha* sp.) in the intertidal zone observed and described by Aníbal (2004). These parallelisms may indicate that SGD-borne nutrients are being consumed by primary producers during the seasonal algae blooms described by Aníbal (2004). Consequently, SGD might be an important modulator of local primary production, sustaining the occurrence of nuisance blooms during winter and eventually local benthic production during spring and summer. However, more evidence is needed to support this argument more fully.

When compared with the annual diffuse source for the whole Ria proposed by Ferreira et al. (2003) of $\sim 4.3 \times 10^7$ mol N, SGD-borne nutrients appear to be significant in terms of the lagoon's mass balance. Using our estimate of 36.2 mol N year^{-1} m^{-1} and a coastline length of 100 km, corresponding to the internal land water contact zone length, the nitrogen input justified by SGD is 3.6×10^6 mol N year^{-1}, or $\sim 10\%$ of the previous figure, which might be ecologically important, when considering the main discharge period. In truth, due to the very high tidal flux of the lagoon, the fact that the measured discharge is directly related to tide level leads to some important ecological implications. The higher seepage rates observed at the peak of low tide will, in effect, increase the residence time of the discharged nutrients, since most of the nutrient load will be naturally trapped within the lagoon by the incoming flood tide. The other anticipated nutrient sources will have lower residence times, since (1) Urban effluents are discharged by the waste-water works during peak high tide to unsure rapid dilution during ebb; (2) River load is only important during winter, and even then, most of the surface freshwater flow is torrential, the effect of which is negligible, when one looks at the annual salinity variation within the lagoon (max 1 psu) and finally (3) The average annual rainfall for the whole drainage basin, already corrected for evapotranspiration is just 1.2×10^6 m^3 (Salles 2001), and represents a very minor fraction of the tidal prism, which is 115×10^6 m^3 for mean tide periods (Ferreira et al. 2003).

However, our estimate is still very preliminary. One of the questions related to the accuracy of our numbers is that seepage meters are prone to measurement artifacts, sometimes leading to imprecise results (Taniguchi et al. 2003). The main one is the "Shaw-Prepas" effect, which refers to an anomalous increase observed in the seepage rates due to the mechanical properties of the collecting bags. This artifact may be controlled by pre-filling the bags with a known volume of reference water (Shaw and Prepas 1989). However, in this study, no bag pre-filling was performed, due to the need for fast and frequent sampling needed to comply with our sampling strategy. However, as shown by Shaw and Prepas (1989) the artifact is marginal when studying high seepage rates (above 0.5 l h^{-1} m^{-2}) and considering the high seepage rates observed in this area (the minimum was 0.7 l h^{-1} m^{-2}) we are confident that there was no substantial error associated with the procedure. Even so, the need for some kind of error estimate in these studies, obvious in general literature, is paramount.

Following the analysis of Bokuniewicz (1992), we considered that the discharge assumed the shape of a Gaussian curve, with a maximum discharge peak at the intermediate/lower beachface decreasing both in offshore and inland directions. Due to the steep depth increase resulting from the presence of the tidal channel, we assumed that the seepage became zero in the margins of the channel.

Concerning the nitrate concentration of the freshwater member, the year can be divided in two parts, with concentrations ranging between 110 μM, in the

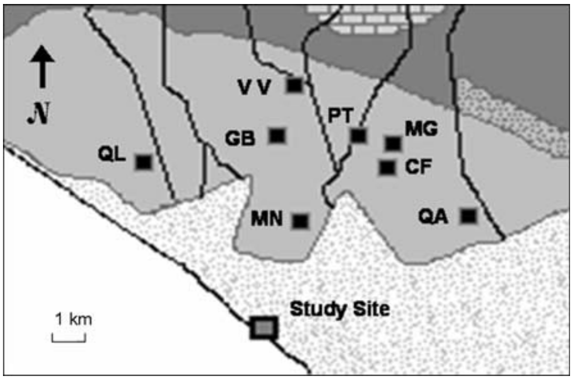

Fig. 9 Borehole location in the area surrounding the study site: QL—Quinta do Lago; MN—Montenegro; GB—Gambelas; VV—Vale da Venda; PT—Patacão; MG—Mar e Guerra; CF—Campina de Faro and QA—Quinta do Amendoal

first 7 months of the year (from January until July) and 420 μM, in the last 5 months (from August until December) (Fig. 6). These calculated concentrations are lower than the ones available at the INAG database for the study site's closest borehole, Montenegro. Moreover, other boreholes located close by like Mar e Guerra, Vale da Venda and Quinta do Amendoal, also show much higher concentrations than those we estimated for the freshwater source (Fig. 9 and Table 2). Apparently, since the lower nitrate concentrations measured at the beach are not the simple result of dilution with seawater, there must be some nitrogen removal at the beach and/or along the aquifer, evidencing the balancing task performed by wetlands and, especially, by sandy sediments. However, in spite of this apparent mitigation, when the nutrient input is too high, some unpleasant effects may occur in the ecosystem, including losses of biodiversity and greenhouse gas release (Verhoeven et al. 2006).

Table 2 Extrapolated nitrate concentration range in the freshwater source calculated from the study site and nitrate concentrations in several boreholes located in the surrounding area from 1995 until present

Location	Nitrate concentration (μM)
SGD "freshwater source"	483.0–12.9
Quinta do Lago	16.1–0.5
Gambelas	177.4–0.5
Montenegro	2274.2–361.8
Patacão	403.2–108.7
Mar e Guerra	2803.2–1164.0
Vale da Venda	1762.9–1209.7
Campina de Faro	3282.6–246.5
Quinta do Amendoal	5612.9–3902.6

Further studies are thus vital for a full understanding of the contribution of SGD to the Ria Formosa ecosystem. The priorities should be on determining the area of discharge, e.g. the contact area between upland aquifer systems and coastal sediments, the study and modeling of the mitigation capacity offered by sandy sediments and the determination of the fate of the discharged nitrogen inside the lagoon's system. The implementation of the European Water Framework and the establishment of new European rules concerning the maintenance and/or recovery of the environmental quality of coastal systems attribute high importance to research of coastal nutrient inputs and, therefore, future mass balance studies should take this potentially significant contribution into account.

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References

Andrade C, Freitas MC, Moreno J, Craveiro SC (2004) Stratigraphical evidence of Late Holocene barrier breaching and extreme storms in lagoonal sediments of Ria Formosa, Algarve, Portugal. Mar Geol 210:339–362

Aníbal J (2004) Processos ecológicos que controlam a dinâmica das macroalgas Ulvales (Chlorophyta) na Ria Formosa. Ph.D. Thesis, Universidade do Algarve, Portugal

Baptista TMC (1993) Microbiological observations in the Ria Formosa. M.Phil. Thesis, University of Wales, UK (unpublished)

Boehm A, Paytan A, Shellenbarger G, Davis K (2006) Composition and flux of groundwater from a California beach aquifer: implications for nutrient supply to the surf zone. Cont Shelf Res 26:269–282

Bokuniewicz HJ (1992) Analytical descriptions of subaqueous groundwater seepage. Estuaries 15(4):458–464

Burnett WC, Dulaiova H (2006) Radon as a tracer of submarine groundwater discharge into a boat basin in Donnalucata, Sicily. Cont Shelf Res 26:862–873

Burnett W, Taniguchi M, Oberdorfer J (2001) Measurement and significance of the direct discharge of groundwater into the coastal zone. J Sea Res 46:109–116

Burnett WC, Bokuniewicz H, Huettel M, Moore WS, Taniguchi M (2003) Groundwater and pore water inputs to the coastal zone. Biogeochemistry 66:3–33

Cable JE, Burnett WC, Chanton JP, Corbett DR, Cable PH (1997a) Field evaluation of seepage meters in the coastal marine environment. Estuar Coast Shelf Sci 45:367–375

Cable JE, Burnett WC, Chanton JP (1997b) Magnitudes and variations of groundwater seepage into shallow waters of the Gulf of Mexico. Biogeochemistry 38:189–205

Chanton JP, Burnett WC, Dulaiova H, Corbett DR, Taniguchi M (2003) Seepage rate variability in Florida Bay driven by Atlantic tidal height. Biogeochemistry 66:187–202

Dinis MT (1992) Situação da aquacultura no Algarve: perspectivas e condicionantes. In: Mesas redondas, Ponte International do Guadiana, Fev. 1992

Falcão M, Vale C (1990) Study of the Ria Formosa ecosystem: benthic nutrient remineralization and tidal variability of nutrients in the water. Hydrobiologia 207:137–146

Falcão M, Vale C (1998) Sediment-water exchanges of ammonium and phosphate in intertidal and subtidal areas of a mesotidal coastal lagoon (Ria Formosa). Hydrobiologia 373/374:193–201

Ferreira JG, Simas T, Nobre A, Silva MC, Shifferegger K, Lencart-Silva J (2003) Identification of sensitive areas and vulnerable zones in transitional and coastal Portuguese systems—application of the United States National Estuarine Eutrophication Assessment to the Minho, Lima, Douro, Ria de Aveiro, Mondego, Tagus, Sado, Mira, Ria Formosa and Guadiana systems. INAG and IMAR

Finkl CW, Krupa SL (2003) Environmental impacts of coastal-plain activities on sandy beach systems: hazards, perception and mitigation. J Coast Res 35:132–150

García-Pintado J, Martínez-Mena M, Barberá GG, Albaladejo J, Castillo VM (2007) Anthropogenic nutrient sources and loads from a Mediterranean catchment into a coastal lagoon: Mar Menor, Spain. Sci Total Environ 373:220–239

Grasshoff K, Ehrhadt M, Kremling K (1983) Methods of seawater analysis. Verlag Chemie, Weinheim

Horn DP (2002) Beach groundwater dynamics. Geomorphology 48:121–146

Johannes RE (1980) The ecological significance of the submarine discharge of groundwater. Mar Ecol Prog Ser 3:365–373

Jones MN (1984) Nitrate reduction by shaking with cadmium alternative to cadmium columns. Water Res 18:643–646

Lee DR (1977) A device for measuring seepage flux in lakes and estuaries. Limnol Oceanogr 22:140–147

Lee V, Olsen S (1985) Eutrophication and management initiatives for the control of nutrient inputs to Rhode Island coastal lagoons. Estuaries 8:191–202

Machás R, Santos R (1999) Sources of organic matter in Ria Formosa revealed by stable isotope analysis. Acta Oecol 20(4):463–469, Éditions scientifiques et médicales Elsevier Science

Moore WS (2003) Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. Biogeochemistry 66:75–93

Moore WS (2006) Radium isotopes as tracers of submarine groundwater discharge in Sicily. Cont Shelf Res 26:852–861

Nausch G, Nehring D, Aertebjerg G (1999) Anthropogenic nutrient load of the Baltic Sea. Limnologica 29:233–241

Newton A, Mudge S (2005) Lagoon-sea exchanges, nutrient dynamics and water quality management of the Ria Formosa (Portugal). Estuar Coast Shelf Sci 62:405–414

Newton A, Icely JD, Falcao M, Nobre A, Nunes JP, Ferreira JG, Vale C (2003) Evaluation of eutrophication in the Ria Formosa coastal lagoon, Portugal. Cont Shelf Res 23:1945–1961

Oberdofer JA (2003) Hydrogeologic modeling of submarine groundwater discharge: comparison to other quantitative methods. Biogeochemistry 66:159–169

Padinha C, Santos R, Brown MT (2000) Evaluating environmental contamination in Ria Formosa (Portugal) using stress indexes of *Spartina maritima*. Mar Environ Res 49:67–78

Salles P (2001) Hydrodinamic controls on multiple tidal inlet persistence. PhD thesis, Massachusetts Institute of Technology/Woods Hole Oceanographic Institution

Schiavo MA, Hauser S, Cusimona G, Gatto L (2006) Geochemical characterization of groundwater and submarine discharge in the south-eastern Sicily. Cont Shelf Res 26:826–834

Shaw RD, Prepas EE (1989) Anomalous, short-term influx of water into seepage meters. Limnol Oceanogr 34(7):1343–1351

Smith SV, Atkinson MJ (1994) Mass balance of nutrient fluxes in coastal lagoons. In: Bjerfve B (ed) Coastal lagoon processes. Elsevier Oceanography Series, vol 60. Elsevier, Amsterdam

Stigter TY, van Ooijen SPJ, Post VEA, Appelo CAJ, Carvalho Dill AMM (1998) A hydrogeological and hydrochemical explanation of the groundwater composition under irrigated land in a Mediterranean environment, Algarve, Portugal. J Hydrol 208:262–279

Stigter TY, Carvalho Dill AMM, Ribeiro L, Reis E (2006a) Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal. Agric Water Manage 85:121–132

Stigter TY, Ribeiro L, Carvalho Dill AMM (2006b) Application of a groundwater quality index as an assessment and communication tool in agro-environmental policies—two Portuguese case studies. J Hydrol 327:578–591

Taniguchi M, Iwakawa H (2004) Submarine groundwater discharge in Osaka Bay, Japan. Limnology 5:25–32. doi: 10.1007/s10201-003-0112-3

Taniguchi M, Burnett WC, Smith CF, Paulsen RJ, O'Rourke D, Krupa SL, Christoff JL (2003) Spatial and temporal distributions of submarine groundwater discharge rates obtained from various types of seepage meters at a site in the Northeastern Gulf of Mexico. Biogeochemistry 66:35–53

Ullman WJ, Chang B, Miller DC, Madsen JA (2003) Groundwater mixing, nutrient diagenesis and discharges across a sandy beachface, Cape Henlopen, Delaware (USA). Estuar Coast Shelf Sci 57:539–552

UNESCO (2004) Submarine groundwater discharge—management implications, measurements and effects, Scientific Committee on Oceanic Research (SCOR) and Land-Ocean Interactions in the Coastal Zone (LOICZ). Series on groundwater No. 5, IOC Manuals and guides No. 44

Valiela I, Costa JE (1988) Eutrophication of Buttermilk Bay, a Cape Cod coastal embayment: concentrations of nutrients and watershed nutrient budgets. Environ Manage 12:539–553

Verhoeven JTA, Arheimer B, Yin C, Hefting MM (2006) Regional and global concerns over wetlands and water quality. Trends Ecol Evol 21(2):96–103