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Seasonal variability of land-ocean groundwater nutrient fluxes from a tropical karstic region (southern Java, Indonesia)

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ABSTRACT

In tropical karstic regions, knowledge about the timing and quantity of land-ocean groundwater nutrient fluxes is important, as those nutrients may affect sensitive coastal ecosystems such as coral reefs. High permeability of karst aquifers, combined with high discharge during heavy rain events, lead to a close connectivity between groundwater in the hinterland and the coastal zone. Alteration between dry and wet periods can lead to a temporal variability of groundwater discharge volume and its associated nutrient fluxes. We studied the seasonal variability of land-ocean groundwater nutrient fluxes in the tropical karstic region of Gunung Kidul (southern Java, Indonesia) from November 2015 to December 2016. Satellite thermal infrared imagery revealed two major areas of direct submarine and coastal groundwater discharge. Nutrient fluxes were estimated at the largest coastal spring using a discharge dataset from a subsurface river dam and a monthly record of nutrient concentrations sampled from the spring. Nitrate fluxes ranged from 6×10^6–245×10^6 mol/day, dissolved silicon fluxes from 58×10^6–546×10^6 mol/day and phosphate fluxes from 17×10^3–1571×10^3 mol/day. Nutrient fluxes are mostly controlled by discharge and show a high variability through time. Extraordinarily high nitrate and phosphate fluxes were observed after a period of constant and heavy rain. Most likely a nutrient pool in the top soil in the hinterland from untreated sewage or fertilizer is flushed during rain events through the aquifer to the coast. In tropical karstic regions sudden inputs of large amounts of nutrients via groundwater discharge may affect coastal ecosystems such as coral reefs making them especially vulnerable during high discharge events.

1. Introduction

Groundwater discharge into the coastal ocean occurs along the worlds coastlines at the land-ocean interface and has been identified as an important source of nutrients to many coastal ecosystems (Szymczycha et al., 2012; Rodellas et al., 2015; Tamborski et al., 2017). Nutrients delivered to coastal ecosystem via groundwater discharge can lead to a shift in phytoplankton community structure, degradation of health of coral reefs and seagrass beds as reported in a number of locations all over the world (Lapointe, 1997; Lecher et al., 2015; Amato et al., 2016). In tropical karstic regions high groundwater discharge is expected, due to high aquifer permeability, coupled to a high recharge during the wet season and heavy rain events. Combined with high groundwater nutrient concentrations (e.g. transported from the unsaturated soil into the aquifer) and low retention times of nutrients in the aquifer, these conditions lead to high groundwater nutrient fluxes (Moosdorf et al., 2015). Nutrient inputs into groundwater from anthropogenic sources in the hinterland such as fertilizers or sewage may thus rapidly reach the coastal ocean (Tamborski et al., 2017). These conditions may further lead to temporal variations with high and low land-ocean groundwater nutrient fluxes (ArandaCirerol et al., 2006; Mallast et al., 2013). Sensitive coastal ecosystems along tropical karstic coasts (e.g. coral reefs) may thus be affected by sudden inputs of large amounts of nutrients via groundwater discharge.

Several studies describe the transport of nutrients via groundwater towards the ocean in tropical karstic regions as in northwest Yucatan (Mexico) (Hanshaw and Back, 1980; Herrera-Silveira, 1998; Young et al., 2008; Null et al., 2014), Bermuda (Lapointe and O'Connell, 1989; Simmons and Lyons, 1994), Barbados (Lewis, 1987) and Guam (Redding et al., 2013), while some studies investigated their temporal variability (Lewis, 1987; Lapointe et al., 1990; ArandaCirerol et al., 2006; Tapia González et al., 2008). Southeast Asia belongs to one of the

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regions with the strongest human modifications in the coastal zone (Elvidge et al., 1997) where significant groundwater nutrient fluxes to the coastal zone were observed in Bangkok, Manila and Jepara (Burnett et al., 2007; Taniguchi et al., 2008; Adyasari et al., 2018). However, a seasonal record of groundwater nutrient fluxes from a karstic region in Southeast Asia has not yet been investigated, even though one of the strongest impacts on coastal ecosystems can be expected in these regions. Hence, at the example of the tropical karstic coastal area of Gunung Kidul (southern Java, Indonesia) we investigated the seasonal behavior of groundwater nutrient fluxes to the ocean.

2. Study site

2.1. Climate, geology and land use

The karstic region of Gunung Kidul is located in southern central Java (Indonesia). The area has a tropical climate with a mean annual temperature of 27 °C (Haryono and Day, 2004), a high humidity of ~80% (Flathe and Pfeiffer, 1965), and an annual precipitation of up to 2000 mm (Brunsch et al., 2011). The amount of precipitation is controlled by the Australian-Indonesian Summer Monsoon (Brunsch et al., 2011). The wet season lasts from November until April with precipitation rates of 150–350 mm per month. During dry season (May until October) precipitation rates are much lower with 25–150 mm per month (Brunsch et al., 2011). The El Niño–southern oscillation (ENSO) has a considerable impact on the amount of annual rainfall (Aldrian and Dwi Susanto, 2003). While during El Niño years, the wet season starts later in the year and during the dry season precipitation is below average (Aldrian and Dwi Susanto, 2003), during La Niña the rainy season lasts longer with larger amounts of rainfall (Brunsch et al., 2011).

Three different geological sections can be distinguished in the study area. The north and north-east section comprise mountain ranges (Fig. 1) which mainly consist of sediments and volcanic deposits of Eocene and Miocene age. Further to the south the Miocene Wonosari formations represent the second section, which mainly consists of bedded lagoonal limestones (Sir MacDonald and Partners, 1984). The third section, the Gunung Sewu area, is morphologically known for its mature Kegelkarst hills. Common to all is the southward dipping towards the Indian Ocean. At the coast, cliffs with heights of 25–100 m are composed of strongly karstified massive coral reef-limestone, with intercalated clay and volcanic ash lenses (van Bemmelen, 1949; Flathe and Pfeiffer, 1965; Waltham et al., 1983; Haryono and Day, 2004).

The combination of low rainfall amounts during dry season and quick infiltration due to strong karstification leads to severe water scarcity mainly in the southern Kegelkarst area. Consequently, more than 250,000 people depend on onshore, coastal and submarine karstic springs, rain water cisterns, water trucks or subsurface rivers as water resource (Sir MacDonald and Partners, 1984; Matthies et al., 2016; Moosdorf and Oehler, 2017). This is one reason why the region is considered to be one of the poorest regions in Indonesia with a relatively low population density of 388 inhabitants per km^2 in the coastal area (Dittmann et al., 2011). At Bribin Sindon, the karst river is dammed up by a concrete barrage, which completely closed the elliptic cross section of the cave, creating an underground water storage which is managed by means of a hydropower-driven pumping system. This hydropower plant supplies water for more than 75,000 people in the area. More than 90% of the population depends on agriculture often with less than 0.3 ha land per family. Dry farming with soy, corn, peanuts and cassava is the dominant type of land use. Some families additionally have cattle to work on the fields and as source for manure. Artificial fertilizer is mainly applied in addition to cattle manure to balance the nutrient deficiency of the soils. Wastewater in Gunung Kidul is partly discharged directly into the subsurface or collected in unsealed septic tanks (Fach and Fuchs, 2010; Nayono et al., 2010). Additionally, solid waste enters into the underground river system via sinkholes (Nayono, 2014).

2.2. Subsurface hydrology

Perennial rivers are absent in the coastal area and scarce in the whole Gunung Kidul due to high karst permeability. Considerable surface runoff only takes place after major rain events. In the underground, however, a complex network of caves and conduits has developed due to karstification. Consequently, subsurface discharge dominates the area. Groundwater flow paths and discharge rates in the area were mapped in the recent years (Sir MacDonald and Partners, 1984; Eiche et al., 2012) (Fig. 1 and Electronic supplementary material). Also flow paths between subsurface rivers and coastal springs could be negotiated (Fig. 1, red dotted lines). The coastal freshwater spring at Pantai Baron is connected with the Wonosari-Bribin-Baron aquifer system in the hinterland, which is fed by different small rivers from the volcanic Panggung Masif in the north (Sir MacDonald and Partners, 1984). Discharge measured at the 25 km upstream located subsurface river dam Bribin Sindon reaches Pantai Baron with a travel time of 14 days during dry season (Sir MacDonald and Partners, 1984) and 4 days during wet season, as deduced from a tracer test (Eiche et al., 2012). In addition, several smaller tributaries feed the freshwater spring (see Electronic supplementary material). Discharge rates have been measured continuously every 10 min at the subsurface river dam Bribin Sindon since 2010 and discharge varies between $< 1\ m^3/s$ in the dry and up to $12\ m^3/s$ in the wet season (Oberle et al., 2016).

Groundwater in Gunung Kidul was classified as $Ca\text{-}HCO_3$ dominated, with varying hydrochemistry between the wet and the dry season (Eiche et al., 2016). During the dry season diffuse matrix-flow is dominant and assures a year-round flow of water. During wet season, matrix flow is regularly overprinted by piston flow and recharge occurs dominantly through larger cracks and sinkholes. These conditions are also reflected in the physio-chemistry of the groundwater with higher electrical conductivity (EC) values during matrix flow conditions and a rapid decline in EC as discharge increases (Eiche et al., 2016).

3. Material and methods

3.1. Investigation of groundwater discharge to the ocean

Groundwater discharge towards and into the ocean was investigated based on precipitation data, discharge measured at the subsurface river dam Bribin Sindon, remote sensing and by physio-chemistry (EC, T) of groundwater and coastal water.

Rainfall data was obtained from four climate stations (Fig. 1), operated by the Indonesian governmental agency BMKG on a daily interval from October 2015 until December 2016. Stations were chosen in a way that they most likely reflect the recharge area of the Wonosari-Bribin-Baron hydrogeological system. The first station ("Nglipar", Fig. 1) is located in the northern part of the Wonosari plateau at an elevation of 190 m above sea level. The second climate station "Ponjong" is located at an elevation of 242 m above sea level next to the subsurface river Gunung Kendil and close to the subsurface river dam Bribin Sindon (Fig. 1). The third station ("Semanu", Fig. 1) is located close to the subsurface river Kali Suci at an elevation of 198 m above sea level, while the fourth station "Tepus" is located closer to the coast at an elevation of 198 m above sea level.

Groundwater discharge was monitored at the subsurface river dam Bribin Sindon with 10 min intervals from October 2015 until December 2016. Discharge was monitored in a way that a defined flume was present and the water level behind the dam was measured.

Discharge areas into the coastal ocean were identified using a multi-temporal satellite-based thermal infrared approach and validated using in-situ offshore electrical conductivity measurements. The multi-temporal satellite-based thermal infrared approach exploits thermal radiance information of the sea-surface given in five Landsat TIRS scenes

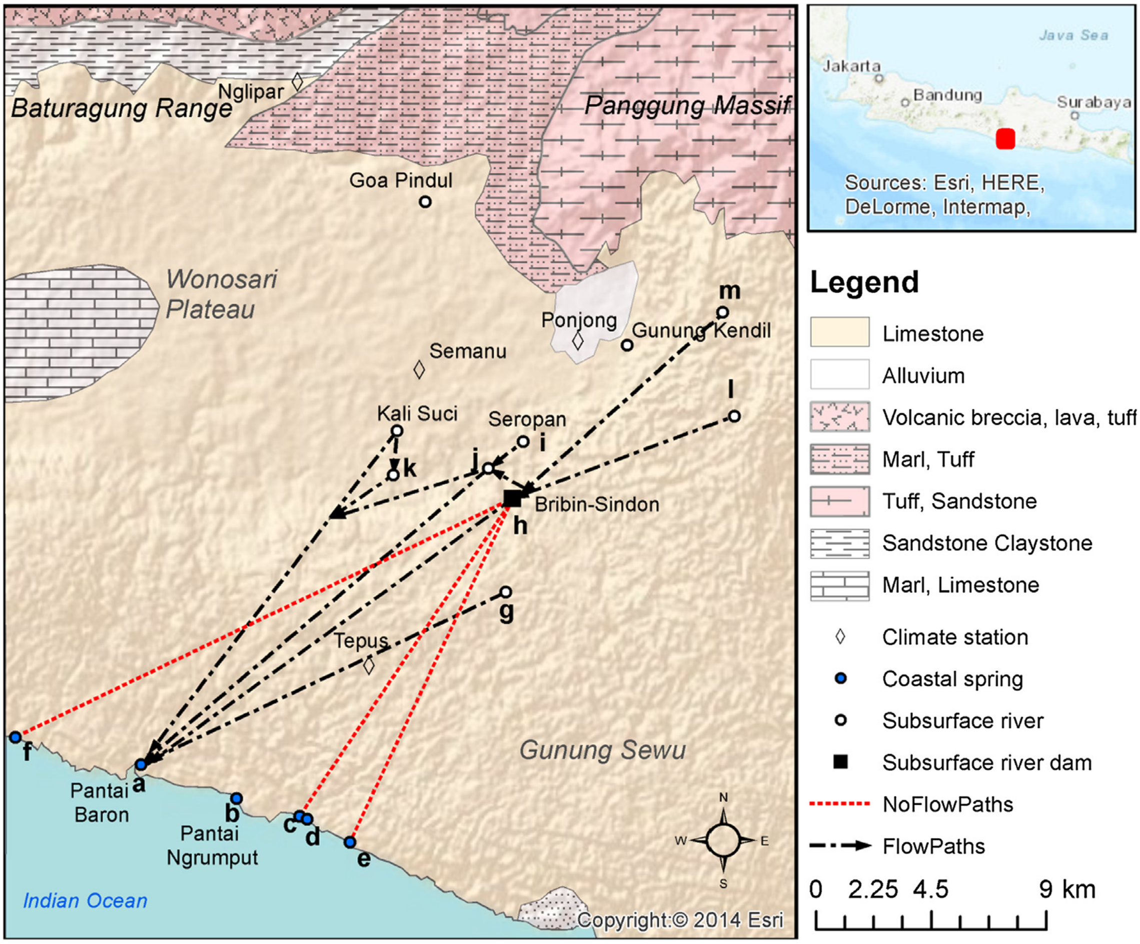

Fig. 1. A simplified geological map with the major geological units of Gunung Kidul, including the locations of the climate stations (diamond), and the subsurface rivers (white dots), the subsurface river dam Bribin Sindon (black square), and the coastal springs (blue dots). The letters refer to coastal springs (a–f) and subsurface rivers (g–m) whose names and discharge rates are listed in the electronic supplementary material. Connections of groundwater in the karstic aquifer are indicated by black lines, while red dotted lines indicate rejected connections. A detailed geological map can be found in Toha and Sudarno (1992). Geological profile charts can be found in Flathe and Pfeiffer (1965). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(WRS path/row 120/065). All applied scenes reflect the local wet season and represent low-tide status in the years 2013/2014. The pre-processing chain and the automatic and tide-based scene selection is described in Mallast et al. (2014). Given the assumption of sea surface temperature (SST) stabilization over time (small temporal variability) at groundwater discharge sites against a high temporal SST variability in areas which are not influenced by groundwater discharge (Siebert et al., 2014), we perform a variance analysis to detect potential groundwater discharge areas. It includes calculating the median of the absolute differences per pixel between each SST scene. This reduces influences of potential outliers evoked through e.g. thin clouds and represents an advancement described in Mallast et al. (2014). The final result is a SST variance image in which small variance values represent potential groundwater discharge areas (Fig. 2). These potential groundwater discharge areas were validated with in-situ offshore EC and temperature measurements. Measurements were taken on the 14th, 16th and 19th of November 2015 and on the 18th, 19th and 20th of April 2016 at a depth of 10 cm below water level with a WTW™ TetraCon 925-P conductivity probe from a small fishing boat.

3.2. Hydrochemical sampling

Hydrochemical samples were obtained from three subsurface rivers in the hinterland and from two coastal springs (Pantai Baron, Pantai Ngrumput) (Fig. 1) which were identified based on the remote sensing approach (Fig. 2). At most sites, samples were taken in November 2015 and on a nearly monthly interval from April 2016 until December 2016. The total number of samples amounts to 40 of which 10 were taken at Pantai Baron, 8 at Pantai Ngrumput, 9 at Goa Pindul, 5 at Gunung Kendil and 8 at Kali Suci (all listed in Table 1). EC, temperature, and dissolved oxygen were measured directly in the field using calibrated handheld probes: conductivity measuring cell (WTW™ TetraCon 925-P), dissolved oxygen (WTW™ FDO 925). Water samples for nutrient analyses were obtained with syringes and filtered (Whatman filters CA 0.45 µm) into 20 ml HDPE bottles. Samples were preserved either by freezing or by poisoning with 50 µl of saturated $HgCl_2$. In November 2015, April, May, June, July and December 2016 the water samples for nutrient analyses (nitrate, nitrite, ammonium, phosphate, dissolved silicon (DSi)) were transported to Germany and measured at the laboratory of the Leibniz Centre for Marine Tropical Research in Bremen using standard photometrical methods (Grasshoff et al., 2009) with an accuracy of ± 0.1 $\mu mol\,L^{-1}$ for phosphate, ± 2.4 $\mu mol\,L^{-1}$ for NOx, +0.02 $\mu mol\,L^{-1}$ for NO_2, ± 0.04 $\mu mol\,L^{-1}$ for NH_4 and ± 1.6 $\mu mol\,L^{-1}$ for DSi. In August 2016, September 2016, October 2016 and November 2016 nitrate was determined on fresh groundwater samples within a couple of days after sampling at the Geochemistry Laboratory, Dept. of Geological Engineering, Faculty of Engineering, UGM, Yogyakarta (Indonesia) using an ion chromatograph (MetroOhm IC-850) with an accuracy of 0.01 µM.

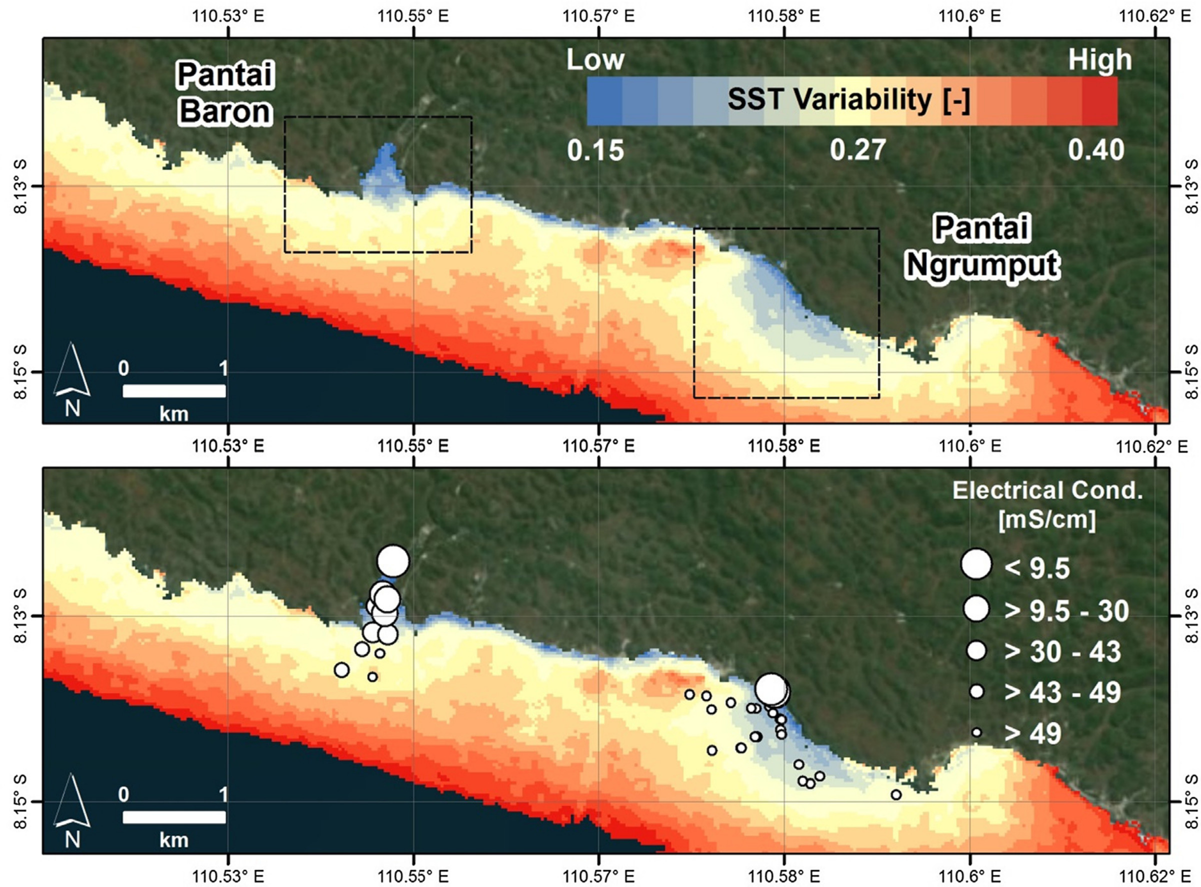

Fig. 2. The multi-temporal satellite-based thermal infrared image indicated two major sites at which groundwater discharges into the ocean.

3.3. Calculation of groundwater nutrient fluxes

In order to capture the temporal variability in groundwater nutrient fluxes, the temporal variability in groundwater nutrient concentrations and the temporal variability in groundwater discharge was considered. A range of a groundwater nutrient flux at the coastal spring Pantai Baron was calculated for each groundwater sampling event (in total 10 sampling events, see Table 1). A range of groundwater discharge at Pantai Baron was calculated with minimum (Q_{min}, Eq. (1)) and maximum (Q_{max}, Eq. (2)) discharge rates based on all known tributaries, marked as Qg, Qh, Qi and Qj (see Supplementary material), which feed the spring. Direct measurements were taken at Bribin Sindon, taking into account a travel time of 14 ± 2 days during matrix flow dominated conditions and 4 ± 2 days during piston flow dominated conditions. The type of flow was deduced from the physio-chemistry of the groundwater sampled at Pantai Baron, while a higher EC of more than 500 µS/cm was indicative for matrix flow conditions and a lower EC was typical for piston flow conditions (Eiche et al., 2016). Furthermore, smaller tributaries which feed Pantai Baron were included in the discharge estimate, including Buhputih-Baron (Fig. 1g) with 0.02 m^3/s in dry season, Seropan-Baron (Fig. 1i) with 0.4–0.5 m^3/s during dry season and 0.5 to < 3 m^3/s during wet season, Grubug-Baron (Fig. 1j) with 0.7–1 m^3/s during dry season and 2 m^3/s during rain season, and then the connection Ngreneng-Baron with < 0.1 m^3/s during dry season and 0.2 m^3/s during wet season.

$$Q_{min} = Q_{g-min} + Q_{h-min} + Q_{i-min} + Q_{j-min} \quad (1)$$

$$Q_{max} = Q_{g-max} + Q_{h-max} + Q_{i-max} + Q_{j-max} \quad (2)$$

A minimum and maximum groundwater nutrient flux for each respective sampling event was then calculated by multiplying the groundwater nutrient concentration which was measured at Pantai Baron at a time with the minimum (Q_{min}) and maximum (Q_{max}) estimated groundwater discharge rate.

4. Results

4.1. Identification of groundwater discharge into the ocean

Two sites with particularly high groundwater discharge potential were identified based on low SST variability values of < 0.24 (blue colors in Fig. 2). The first site was observed within an embayment and corresponds to the coastal karstic freshwater spring of Pantai Baron with EC values of 0.3–0.8 mS/cm at its outlet. Up to 500 m into the sea freshening was still detectable due to lower EC values. The second site matches the location of an intertidal spring located at Pantai Ngrumput (Fig. 2). The spring was accessible during low tide with brackish groundwater discharge into a backbarrier reef along the beach in the intertidal area. Groundwater EC values varied over the seasonal cycle with around 5.95–8.38 mS/cm in the wet season and 7.51–9.53 mS/cm during the dry season. Low SST variability was as well observed along the coast between Pantai Baron and Pantai Ngrumput. Due to steep cliffs, strong currents and heavy waves these sites were not accessible from land or from boat. The area may represent a site where discharge via multiple coastal springs or diffuse groundwater discharge through the coastal sediments occurs. They may also reflect longshore coastal currents which transport groundwater from Pantai Baron along the coast.

4.2. Seasonal variability of groundwater flow

A seasonal trend influenced by the ENSO in the year 2015/2016 was

Table 1
Hydrochemical and physical data obtained from different sampling sites. Piston flow conditions at Pantai Baron are marked in grey.

Event	Date	Season	DO (%)	Cond. (µS/cm)	Temp (°C)	NO_3 (µmol/L)	NO_2 (µmol/L)	NH_4 (µmol/L)	DSi (µmol/L)	PO_4 (µmol/L)
Pantai Baron-1	14-Nov-2015	Wet	83	557	27.9	170	0.0		408	0.1
Pantai Baron-2	19-Apr-2016	Wet	85	429	27.6	114	0.3	1.3	335	0.1
Pantai Baron-3	10-May-2016	Dry	88	521	28.0	90	0.2	0.6	458	0.1
Pantai Baron-4	24-May-2016	Dry	82	541	28.1	21	0.4	3.6	471	0.1
Pantai Baron-5	8-Jun-2016	Dry	82	525	28.0	78	0.3	2.4	436	0.1
Pantai Baron-6	21-Jun-2016	Dry	77	384	27.2	27	0.2	1.2	297	0.2
Pantai Baron-7	20-Aug-2016	Dry		640	27.8	271				
Pantai Baron-8	23-Sep-2016	Dry		820	28.4	115				
Pantai Baron-9	30-Nov-2016	Wet		260	23.0	52				
Pantai Baron-10	13-Dec-2016	Wet	92	429	27.6	140	0.4		312	0.9
Pantai Ngrumput-1	16-Nov-2015	Wet	75	8380	27.8	132	0.0		327	0.5
Pantai Ngrumput-2	19-Apr-2016	Wet	72	6300	28.4	30	0.1	7.9	350	0.1
Pantai Ngrumput-3	10-May-2016	Dry	83	9530	28.8	17	0.2	7.4	368	0.1
Pantai Ngrumput-4	21-Jun-2016	Dry	72	9450	28.4	7	0.4	5.1	391	0.1
Pantai Ngrumput-5	20-Aug-2016	Dry		7520	28.2					
Pantai Ngrumput-6	23-Sep-2016	Dry		7510	28.5					
Pantai Ngrumput-7	30-Nov-2016	Wet		8080	27.2					
Pantai Ngrumput-8	13-Dec-2016	Wet	67	5950	28.2	145	0.0		302	1.0
Gua Pindul-1	21-Apr-2016	Wet	92	533	28.6	94	0.6	1.9	320	0.1
Gua Pindul-2	11-May-2016	Dry	88	540	28.5	48	0.3	1.9	389	0.1
Gua Pindul-3	24-May-2016	Dry	87	567	27.9	72	0.3	1.4	413	0.1
Gua Pindul-4	8-Jun-2016	Dry	86	558	28.4	33	0.3	2.1	410	0.1
Gua Pindul-5	21-Jun-2016	Dry	86	413	27.3	34	0.4	3.3	303	0.1
Gua Pindul-6	20-Aug-2016	Dry		520	29.6	302				
Gua Pindul-7	23-Sep-2016	Dry		560	29.0	0				
Gua Pindul-8	30-Nov-2016	Wet		270	25.6	0				
Gua Pindul-9	12-Dec-2016	Wet	99	494	26.1	84	1.1		316	0.1
Gunung Kendil-1	17-Apr-2016	Wet	93	567	27.8	123	0.5	4.1	495	0.1
Gunung Kendil-2	11-May-2016	Dry	84	522	27.4	91	0.0	0.0	462	0.1
Gunung Kendil-3	24-May-2016	Dry	82	524	27.2	53	0.2	1.4	497	0.1
Gunung Kendil-4	8-Jun-2016	Dry	73	527	27.0	66	0.2	0.2	474	0.1
Gunung Kendil-5	21-Jun-2016	Dry	82	532	27.1	64	0.0	0.0	450	0.1
Kali Suci-1	21-Apr-2016	Wet	104	426	29.1	58	0.2	1.1	308	0.1
Kali Suci-2	10-May-2016	Dry	102	431	28.1	107	0.3	1.7	362	0.1
Kali Suci-3	24-May-2016	Dry	101	485	27.5	66	0.2	0.9	408	0.1
Kali Suci-4	8-Jun-2016	Dry	104	490	27.5	133	0.2	0.6	382	0.1
Kali Suci-5	21-Jun-2016	Dry	102	417	26.7	69	0.1	0.3	307	0.1
Kali Suci-6	20-Aug-2016	Dry		520	28.9	230				
Kali Suci-7	23-Sep-2016	Dry		490	29.2	0				
Kali Suci-8	30-Nov-2016	Wet		200	26.7	38				

= matrix flow at Pantai Baron
= piston flow at Pantai Baron

observed in rainfall and groundwater discharge data (Fig. 3). Typical for an El Niño year the wet season started delayed in 2015 with no rainfall in October 2015, low precipitation rates in November 2015, followed by an onset of higher precipitation rates in December 2015 which lasted until April 2016. The driest months were July 2016 and August 2016. As expected for a La Niña year, the wet season started early at the end of September 2016.

High precipitation rates during mid of April 2016 were followed by an increase in discharge rates at Bribin Sindon. A period with low precipitation and discharge rates was observed from end of April 2016 until the end of July 2016 (Fig. 3), which was followed by a sudden but then constant increase in discharge until October 2016. At the end of

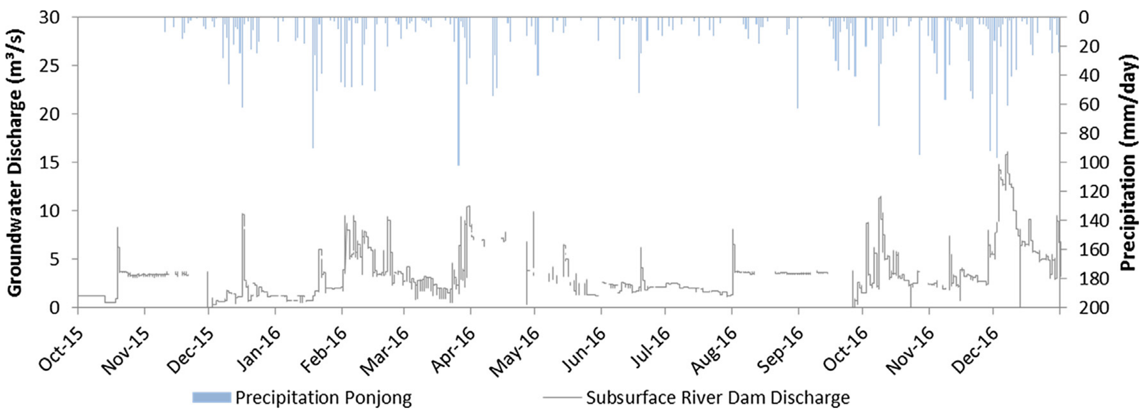

Fig. 3. Time series of precipitation (Station Ponjong, blue bars) and discharge data monitored at Bribin Sindon (grey line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

November 2016 discharge rates increased from 3.0 m^3/s to 8.0 m^3/s and then further increased by the beginning of December up to 16.1 m^3/s. During this time constant and high precipitation was observed at all climate stations Nglipar, Ponjong, Semanu and Tepus (Fig. 3, Electronic supplementary material).

On a shorter time scale of days, events with heavy rain and high discharge were observed which were in general also indicated by a lower groundwater temperature and EC at Pantai Baron, and partly in other subsurface rivers in the hinterland (Table 1). For example, on the 21st of June 2016 a short and heavy rain event was followed by an increase in discharge, which was also indicated by lower EC and temperature values. Similarly, on the 19th of April 2016, the 30th of November 2016 and the 13th of December 2016 events with higher precipitation and discharge rates were also indicated by a lower EC and temperature at Pantai Baron (Table 1).

4.3. Seasonal variability of nutrient concentrations and fluxes

A temporal variability of nutrient concentrations was observed in groundwater sampled in the hinterland and at coastal springs (Table 1). Dissolved inorganic nitrogen dominantly occurred in the form of nitrate which ranged from 0 to 300 µmol/L. At Pantai Baron, nitrate concentrations were high in the wet season 2015/2016 and in December 2016. Nitrate concentrations decreased at the beginning of the dry season from April until June 2016 at Pantai Baron, Pantai Ngrumput, Goa Pindul and Gunung Kendil. Highest nitrate concentrations were observed in August 2016 at Pantai Baron, Goa Pindul and Kali Suci, after the increase from a period of very low discharge to a period with a constantly higher discharge. Nitrate concentrations at the coastal spring Pantai Ngrumput followed the same pattern and were positively correlated with nitrate concentrations at Pantai Baron (Spearman correlation = 0.9). Phosphate concentrations were in general very low (0.1 µmol/L), with the only exception measured in December 2016, when concentrations increased to 0.9 µmol/L and 1 µmol/L at Pantai Baron and Pantai Ngrumput, respectively. DSi concentrations were in general lower when discharge was higher (Fig. 4, orange dots), indicating a dilution effect during periods with higher discharge (Fig. 4). An increase in DSi concentrations at Pantai Baron, Pantai Ngrumput, Goa Pindul and Kali Suci was observed at the transition from the wet season to the dry season from April 2016 until June 2016. Nitrate concentrations did not show any trend between concentration and discharge, while phosphate concentrations were only elevated during the highest discharge event.

The temporal variability of groundwater nutrient concentrations and discharge lead to the temporal variability of groundwater nutrient fluxes (Fig. 5). High nitrate concentrations coupled to high groundwater discharge rates lead to high fluxes in the wet season 2015/2016 with 63–74 × 10^6 mol/day and 94–129 × 10^6 mol/day in November

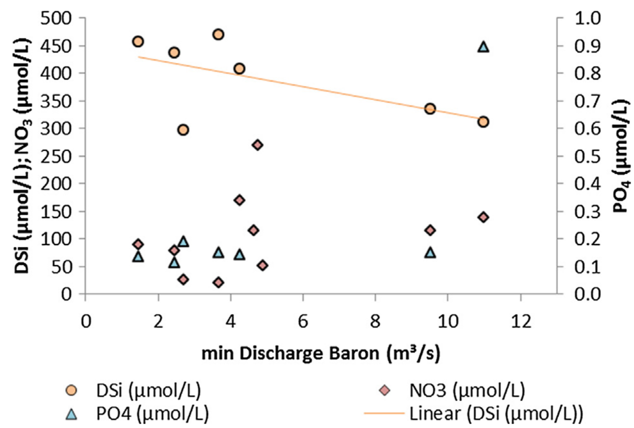

Fig. 4. Nutrient concentrations measured at Pantai Baron and the minimum groundwater discharge at Pantai Baron in m^3/s. DSi is presented in orange circles, PO_4 in blue triangles and NO_3 in red diamonds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2015 and April 2016, respectively. At the beginning of the dry season a lower discharge and lower nitrate concentrations lead to lower nitrate fluxes (e.g. 7–11 × 10^6 mol/day on the 24th of May 2016). During the dry season, a peak discharge event on the 21st of June 2016 did not lead to elevated nitrate fluxes due to low nitrate concentrations (Fig. 5). In August 2016 the increase in groundwater discharge and nitrate concentrations lead to a high nitrate flux of 111–123 × 10^6 mol/day, while the highest nitrate flux of 133–245 × 10^6 mol/day was observed in December 2016 after the period of heavy rain. During this time a high phosphate flux of 852–1571 × 10^3 mol/day was observed as well. DSi fluxes were higher during the wet season when compared to the dry season, but a temporal variability was not as pronounced as for nitrate fluxes.

5. Discussion

5.1. Seasonal variability of land-ocean groundwater nutrient fluxes

Correlating discharge rates at karstic springs with nutrient concentrations can help identifying and characterizing the flow behavior and the source of a nutrient. A negative correlation between discharge and nutrient concentration for example indicates a constant source of nutrients which is diluted during times of high discharge. A positive correlation between discharge rates and nutrient concentrations point towards a surface source of nutrients which is enriched during dry season and washed into the aquifer as a pulse in the rainy season.

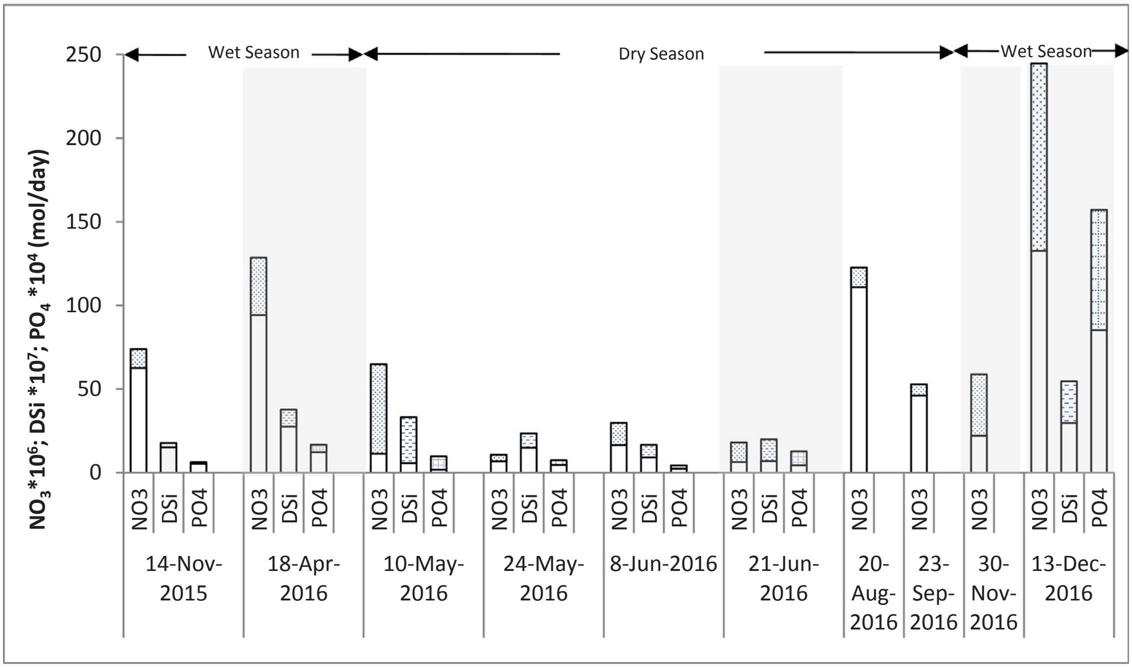

Fig. 5. Minimum and maximum nutrient fluxes from Pantai Baron. The minimum flux is indicated by the lower end of each shaded bar, the maximum flux by the upper end of each shaded bar. Grey shaded areas represent times of piston flow conditions. Wet season and dry season is indicated by the black arrows in the top of the graph.

In Gunung Kidul, higher groundwater EC and temperature indicate diffuse-matrix flow conditions in the subsurface aquifer system (Eiche et al., 2016), which was also reflected in higher DSi concentrations (Table 1). This was for example observed during the onset of the dry season from April 2016 until June 2016, when groundwater DSi concentrations increased both in some subsurface rivers in the hinterland as well as coastal springs. Lower DSi concentrations during times of higher discharge indicated a dilution effect in the aquifer during wet season due to piston flow conditions (Fig. 4), such as on the 21st of June 2016. However, total DSi fluxes were still higher during times of high groundwater discharge, thus a further source of DSi has to be present. This further DSi source might be volcanic material from the mountain ranges in the north (Fig. 1) and from agricultural fields nearby, which may be washed into the aquifer during heavy rain events. The transport of colloidal material in the karstic area during the wet season was also indicated by brownish water color during flash floods and can often be observed in the area after heavy rain events in surface and subsurface rivers (Eiche et al., 2016).

During wet season nutrient fluxes were mostly controlled by discharge. During some sampling events nutrient concentrations (e.g. phosphate, nitrate) sampled at subsurface rivers in the hinterland and at the coastal springs varied in a similar way with time. The variation indicated nutrient inputs into groundwater to occur in the hinterland, which are transported through the aquifer directly towards the coast. Especially nitrate fluxes were high during the wet season, which might be due to nitrogen leaching from a surface source like fertilizers, animal waste and general urban waste, which can also be observed in other karstic areas (Guo and Jiang, 2009). During wet season high groundwater nitrogen fluxes towards the coastal ocean were for example also observed in Florida Keys (Lapointe et al., 1990) and in Bermudas, possibly due to the use of fertilizers in the hinterland (Lewis, 1987). In Gunung Kidul major crops such as rice, corn and soy are mainly fertilized during wet season from October until March when water availability is high (Katam, 2017). In general three different types of fertilizer are used in the area of Gunung Kidul including urea, SP 36, as well as potassium chloride. Urea contains large amounts of nitrogen in the form of ammonium, which might be oxidized to nitrate in oxic groundwater within the aquifer (Table 1) and the soil (Heckmann, 2011). Furthermore large amounts of nutrients and contaminants may reach the subsurface aquifer system via direct infiltration and via sinkholes from sewage, due to a lack of wastewater treatment in the area (Heckmann, 2011; Nayono et al., 2016). In Gunung Kidul about 21% of the population (total population of 722,500 inhabitants (Badan Pusat Statistik Kabupaten Gunungkidul, 2017a) does not have access to wastewater treatment facilities (Badan Pusat Statistik Kabupaten Gunungkidul, 2017b). Septic tanks often leak, and sewage is often spilled uncontrolled into the environment (Heckmann, 2011; Nayono et al., 2016).

During dry season nutrient fluxes were, besides groundwater discharge also controlled by nutrient concentrations in the aquifer. Low nitrate fluxes, such as during the flood recession period from April to July 2016, may be attributed to a temporal depleted nitrate pool in the hinterland after the wet season (e.g. due to leaching of nitrate from the soil and sinkholes during the wet season). The peak discharge event on the 21st of June 2016 (Fig. 5) did not lead to elevated nitrate fluxes due to low groundwater nitrate concentrations. High nitrate fluxes in August followed an increase in discharge after an extended dry period in July, during which time a nutrient pool in the hinterland may have been build up. While fertilizers are not being used in the area during dry season, nutrients and pollutants may have accumulated in the top soil and in sinkholes from sewage (Heckmann, 2011; Nayono et al., 2016).

In general coastal managers and ecosystem studies should consider that during the wet season nutrient fluxes will in general be high due to a high groundwater discharge coupled to a nutrient source in the hinterland, while during dry season occasional events may occur during which nutrient fluxes can be temporarily high.

5.2. Effects on coastal ecosystems

Groundwater nutrient inputs into coastal waters may lead to severe effects on coastal ecosystems such as eutrophication (Adyasari et al., 2018) or the occurrence of harmful alga blooms (Lapointe et al., 2005). In tropical karstic regions, an increase in groundwater discharge (e.g. after heavy rain events) may suddenly transport large amounts of

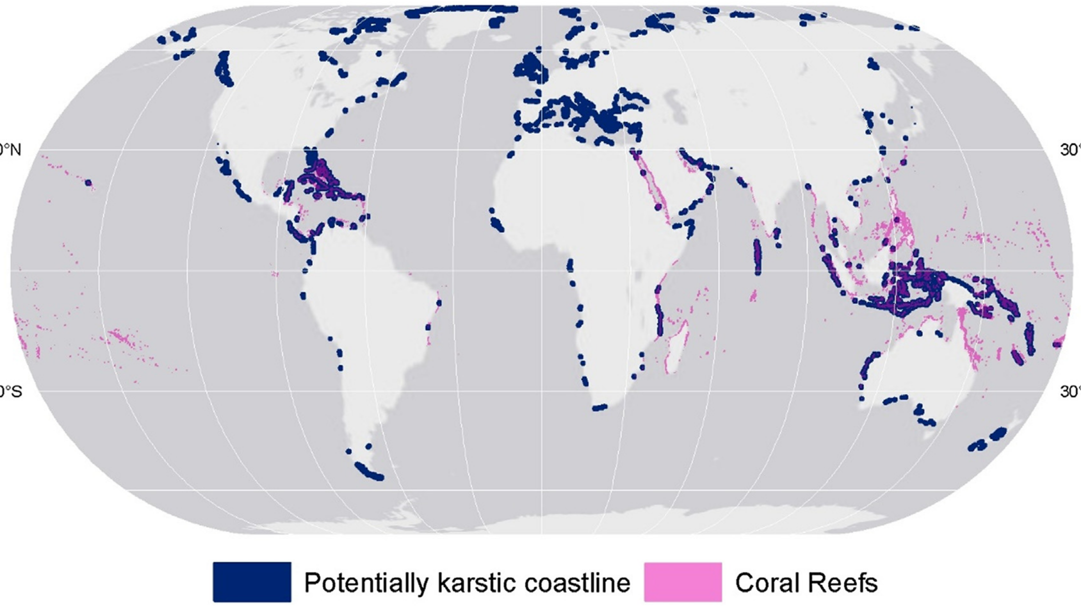

Fig. 6. Potentially karstic (defined as carbonate rocks mapped in Hartmann and Moosdorf (2012)) coastlines, and location of warm water coral reefs (UNEP-WCMC, WorldFish Centre, WRI, TNC, 2010). Areas in the map are not to scale because line thickness had to be increased to ensure visibility of the individual locations.

nutrients into sensitive coastal ecosystems. Along the coastline of Gunung Kidul, various barrier reefs and seagrass beds are situated in the vicinity of groundwater discharge sites. At Pantai Ngrumput groundwater directly discharges into a barrier reef which was only affected by high groundwater nitrate concentrations during the wet season in November 2015 and December 2016 (Table 1). Visually seagrass beds and macroalgae were observed within the reef which are likely affected by nutrient concentrations from groundwater. Furthermore large mats of macroalgae were observed along some of the beaches in the area. While the coastal ecosystems along the karstic coast of Gunung Kidul still need to be researched in more detail, our study indicates that significant terrestrial nutrient sources exist in the area. Especially sudden inputs of phosphate such as in December 2016 (Fig. 5, Table 1) may trigger algae blooms, as coastal waters around carbonates are often phosphate limiting, because calcium carbonate scavenges phosphate (Brand, 2002). Brackish groundwater discharge and associated phosphate fluxes from a karst aquifer in Florida bay was for example hypothesized explain the occurrence of alga blooms in the nearshore area (Blakey et al., 2015).

In many other tropical karstic regions groundwater discharge was identified as a major nutrient source for coastal ecosystems, with elevated groundwater nutrient concentrations often due to anthropogenic activities in the hinterland (Lapointe and O'Connell, 1989; ArandaCirerol et al., 2006; Tapia González et al., 2008; Amato et al., 2016). In the tropical karstic region of Yucatan groundwater is a dominant source of DSi and nitrate to lagoons (Herrera-Silveira, 1994), with high fresh groundwater inputs and high nutrient fluxes during wet season (Tapia González et al., 2008). Groundwater nitrate concentrations in Yucatan range from 2 to 300 µmol/L (ArandaCirerol et al., 2006) and thus vary in a similar way as in southern Java. In Barbados groundwater discharge into a coral reef was twice as high during wet season than during dry season (Lewis, 1987). Nutrients were only measured during wet season and nitrate was clearly elevated in fresh groundwater (Lewis, 1987). In Bermuda groundwater discharge associated anthropogenic nitrogen fluxes may support coastal alga blooms (Lapointe and O'Connell, 1989; Simmons and Lyons, 1994), but seasonal trends were not investigated. In Guam groundwater discharge was associated with anthropogenic nitrogen inputs into coastal waters, which lead to alga blooms (Marsh, 1977) and a decline in coral reef health (Redding et al., 2013). Salinity and NOx (concentrations from 75 to 144 µmol/L) in brackish beach seep water in Guam fluctuated after heavy rain events, with a lower salinity during the wet season (Matson, 1993).

The high nutrient fluxes with a high temporal variability found in the Gunung Kidul karst area highlight the importance of monitoring groundwater discharge and its associated nutrient fluxes from karst areas, particularly in the vicinity of sensitive ecosystems. Globally, coastal segments with a length of 0.27×10^6 km contain karstic areas (defined as carbonate rocks mapped in Hartmann and Moosdorf (2012)), following the approach of Chen et al. (2017) up to 500 m away from the coast. These areas are here named as potentially karstic coasts. This amounts to 14% of the total global coast length (coastal shapes according to (ISCIENCES L.L.C., 2009). Karstic coasts are particularly abundant in the Mediterranean, Carribean and in Southeast Asia (Fig. 6). Of the global potentially karstic coasts, 41% are situated in tropical areas. They are often in the immediate vicinity of coral reefs (Fig. 6), which in some locations have been shown to be impacted by groundwater discharge derived nutrient inputs (D'elia et al., 1981; Senal et al., 2011; Dadhich et al., 2017). The abundance of karstic coasts in tropical climatic regimes highlights that the here shown pathway deserves attention in order to understand its regional impacts on the sensitive ecology of tropical coasts. Climatic conditions, but also anthropogenic factors in areas as the one portrayed here in detail are different from better studied temperate regions. In order to understand the implications of groundwater discharge in these areas, more studies are needed that particularly recognize the strong temporal variability of nutriend fluxes demonstrated at the example of the Gunung Kidul area.

6. Conclusions

We studied the seasonal variability of groundwater nutrient fluxes into the coastal ocean in the tropical karstic region of Gunung Kidul, Indonesia. While in many porous coastal aquifers the transport of terrestrial groundwater towards the ocean is slow, in the karstic region of Gunung Kidul transport of groundwater can be fast with tens of kilometers from the hinterland within a few days and also highly variable throughout the year. During the wet season the variability of groundwater nitrate fluxes was mostly controlled by discharge, while during dry season nutrient concentrations in the aquifer also played a key role for groundwater nitrate fluxes. Extreme rain events lead to extraordinarily high nitrate fluxes, as well as to high phosphate fluxes which are otherwise low throughout the year. However, peak discharge events in the dry season did not lead to elevated nutrient fluxes due to dilution effect in the aquifer and a temporal exhaust of the surface nutrient pool (fertilizers, untreated sewage, and waste) in the hinterland. In developing countries such as Indonesia groundwater is often polluted with nutrients due to the lack of wastewater treatment facilities and the high population density, while large parts of the coastline consists of karst rocks and coral reefs. Coastal ecosystems along these coastlines may thus be affected by short and sudden pulses of high groundwater nutrient fluxes during times of high discharge which has to be considered by coastal managers and ecosystem studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jhydrol.2018.08.077.

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