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Hydrocarbons in a coral reef ecosystem subjected to anthropogenic pressures (La Réunion Island, Indian Ocean)

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Abstract. The La Saline fringing reef, which is the most important coral reef complex of La Réunion Island, (south-western Indian Ocean), is subjected to anthropogenic pressures through river and groundwater inputs. Salinity and biogeochemical parameters (silicates, nitrates, dissolved organic carbon, chlorophyll-*a*), as well as aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs) were analysed in particulate and dissolved material from groundwaters, rivers, harbour, back reef, fore reef and oceanic waters in the La Saline reef area during the rainy season (February–March 2012). Particulate and dissolved AH concentration ranges were 0.07–144 and 0.06–0.58 $\mu\text{g L}^{-1}$ respectively. Particulate and dissolved PAH concentrations ranges were 4.3–326 and 28–350 ng L^{-1} respectively. AHs, dominated by *n*C₁₅, *n*C₁₇, *n*C₁₈ compounds or *n*C₂₆, *n*C₂₇, *n*C₂₉, *n*C₃₁ compounds, were mainly of biogenic origin (phytoplankton, bacteria, higher-plant debris) although some anthropogenic (petroleum inputs) signatures were recorded in the dissolved phase from the harbour and fore reef areas. PAHs, dominated by two- to three-ring compounds and their alkylated homologues, reflected unburned petroleum inputs, but probably also biogenic sources. From the distribution of salinity, biogeochemical parameters and hydrocarbons, we found that inland waters flowed mainly in the surface and in the southern part of reef waters and that particulate PAHs allowed tracking these inland water intrusions in fore reef waters. Finally, this pilot study highlights the uncoupling between the dynamics of AHs and PAHs in tropical environments.

Additional keywords: aliphatic hydrocarbons, groundwaters, La Saline fringing reef, polycyclic aromatic hydrocarbons, tropical environment.

Introduction

Currently, 60% of the world population lives in coastal zones (within 100 km of the sea), and this number is expected to reach 75% in 2050 according to the United Nations Environment Programme (UNEP).^[1] Population growth and intensification of urban activities will exacerbate the anthropisation of coastal areas in the coming years.^[1,2] Although a great deal of attention has been given to the effect of inorganic nutrients, much less study has been dedicated to the potential effects of organic pollutants in the coastal environment.^[3,4] Hydrocarbons, including aliphatic hydrocarbons (AHs) and polycyclic aromatic hydrocarbons (PAHs), are among the most widespread organic pollutants

found in the marine environment. Some of them are harmful to living organisms with reprotoxic, carcinogenic and mutagenic effects.^[5,6] Therefore, they have been recognised for a long time as high-priority contaminants by various international organisations: eight PAHs were included in the list of the 45 priority regulated substances by the European Union (Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regard priority substances in the field of water policy) and 16 PAHs were included in the list of 126 priority regulated substances by the US Environmental Protection Agency (US EPA, 40 CFR Part 423, Appendix A to Part 423).

Hydrocarbons are introduced into coastal marine waters mainly through atmospheric deposition, rivers, municipal-industrial effluents and surface runoff.^[7–9] Although AHs and PAHs may be both of biogenic or anthropogenic origin, the sources, transport and removal processes affecting these two hydrocarbon classes are uncoupled.^[10–12] Indeed, AHs are generally used to assess the relative abundance of biogenic (marine and terrestrial) inputs compared with petroleum-related residues whereas PAHs (whose natural origin is less widespread) are rather sensitive indicators of petrogenic (uncombusted petroleum) and pyrogenic (incomplete combustion residues) sources.^[13,14] In addition, AHs tend to be linked to particles whereas PAHs can be more abundant in the dissolved phase, especially in areas with a low suspended-matter load.^[15] Finally, even though both low-molecular-weight (LMW) AHs (compounds $< n\text{-C}_{24}$) and PAHs (two- to three-ring compounds) are subject to biodegradation, LMW PAHs alone are highly sensitive to photodegradation.^[16–18] Thus, knowledge about both AH and PAH pools in dissolved and particulate phases of the water column is essential for the comprehensive assessment of diverse inputs, especially in estuarine and coastal regions where multiple hydrocarbon sources are involved. Although hydrocarbons, especially PAHs, have been investigated in various temperate coastal waters including estuaries, bays and harbours, there is a lack of data concerning their distribution in coral reef tropical ecosystems.

La Saline fringing reef is the most important coral reef complex of La Réunion Island, a French volcanic island in the south-western Indian Ocean. This coral reef ecosystem is subjected to anthropogenic pressures through river inputs^[19] and submarine groundwater discharge (SGD).^[20,21] Actually, SGD is the main source of freshwater and nutrients (mainly nitrates) to the reef,^[22–26] except during heavy rains.^[19] This excessive nutrient load is responsible for large shifts in community structure,^[27,28] with a continuous decrease in the mean living coral cover. Currently, $\sim 50\%$ of the La Saline fringing reef area is considered to be degraded.^[29] In relation to these eutrophication and degradation issues, several biogeochemical parameters have been extensively studied in the La Saline area, such as oxygen, carbon, calcium carbonate, nutrients and fluorescent dissolved organic matter.^[20,21,30–32] However, although some authors stressed that chronic, sublethal hydrocarbon concentrations could have a variety of detrimental effects on coral reef communities,^[33] to our knowledge, the hydrocarbon composition and distribution have never been examined in this ecosystem.

The objectives of the present study are (i) to characterise the hydrocarbon content (AHs and PAHs) in the dissolved and particulate phases of water samples collected in different environments of the La Saline fringing reef ecosystem, including SGD, rivers, harbours, reef waters and oceanic waters; (ii) to determine the origin of AHs and PAHs (natural *v.* anthropogenic, marine *v.* terrestrial, petrogenic *v.* pyrogenic) in some of these water bodies; and (iii) to identify inland-water intrusions in reef waters and to assess the relevance of using hydrocarbons as tracers of these freshwater inputs.

Material and methods

Study area

La Réunion is a young volcanic island, located in the south-western part of the Indian Ocean ($21^{\circ}07'S$, $55^{\circ}32'E$), 800 km east of Madagascar (Fig. 1). Coral formations are mostly limited

to small and discontinuous fringing coral reefs along the dry western coast. Intense short bursts of orographic events during the rainy season can deliver terrestrial or anthropogenic material to the reefs on time scales of hours to days.^[19] The La Saline fringing reef is part of the most extensive coral reef complex of the island (9 km long, up to 500 m wide, 1 to 1.5 m deep) (Fig. 1). Groundwater is conspicuous along most of the shoreline.^[23,26] In the south part of the reef, there are highly permeable volcanic (basaltic) formation outcrops, which enable groundwater issuing from an agriculture-dominated catchment area to flow onto the reef at low tide. Impermeable sedimentary formations, lying over the volcanic aquifer, increase northwards, which leads to groundwater discharge beyond the reef front. Some discontinuities in the sedimentary formations allow limited groundwater recharge^[22] but because the corresponding coastal area is often flooded and heavily urbanised, this shallow groundwater body is likely to be affected by anthropogenic inputs from septic tanks and cesspools. Moreover, the effluent from a sewage treatment plant overflows into the Hermitage River (H-R; Fig. 1). Physical processes on the La Saline fringing reef were described by Cordier.^[34] Briefly, wave-breaking near the reef crest drives a cross-shore flow across the shallow reef flat and into the back reef zone, after which water moves along the shoreline either towards the Hermitage pass (H-pass), or towards the Trois-Bassins pass. Water residence time is ~ 10.5 h in the back reef area. Recently, agriculture, including sugarcane and market gardening production, was developed on both sides of the Hermitage River. Regarding living organisms, the general trend on the La Saline reef is a continuous decrease in mean live coral cover on the reef slope. Increased macroalgal cover and benthic productivity are attributed to nutrients derived from SGD.^[20,21,30]

Sampling

The samples were collected from 22 February to 9 March 2012 in the morning during the summer season, which is usually characterised by high seawater temperatures and strong rainfall (Table 1; Fig. 1). Groundwater samples from the volcanic aquifer (basaltic layer groundwater, BLG) were obtained from three piezometers (BLG-P 1–3) and a natural well formed by the collapse of a lava tunnel (BLG-TE). Groundwater from the sedimentary formations (sand layer groundwater, SLG) was collected from two piezometers (SLG 1–2) located north of the Hermitage River. To collect groundwater from the piezometers and well in 4-L Nalgene polycarbonate bottles (Fisher Scientific, Illkirch, France), we employed a peristaltic pump with silicone tubing. Samples from the Saint Gilles River (SG-R) were taken close to a collection site for drinking water, samples from the Hermitage River (H-R) were collected downstream from the sewage treatment plant, and those from Trois-Bassins River (3B-R) were taken few hundred metres upstream from the beach. Back reef waters (LG 1–4) were sampled along the beach between the Hermitage River (H-R, northwards) and the volcanic aquifer (BLG-TE, southwards). River and back reef waters were taken at ~ 0.1 -m depth using 4-L Nalgene polycarbonate bottles. The bottles were opened below the water surface to avoid sampling of the surface microlayer. Saint Gilles harbour (SG-HD, close to the dock), off harbour (SG-OH), fore reef (FR 1–9), Hermitage pass (H-pass) and oceanic reference (OR 1–3) waters were taken at ~ 0.1 -m depth from the R/V *Explorer* using a 5-L Niskin bottle equipped with silicone ribbons and Viton o-rings (Maritech, Grimaud, France). FR 1–9

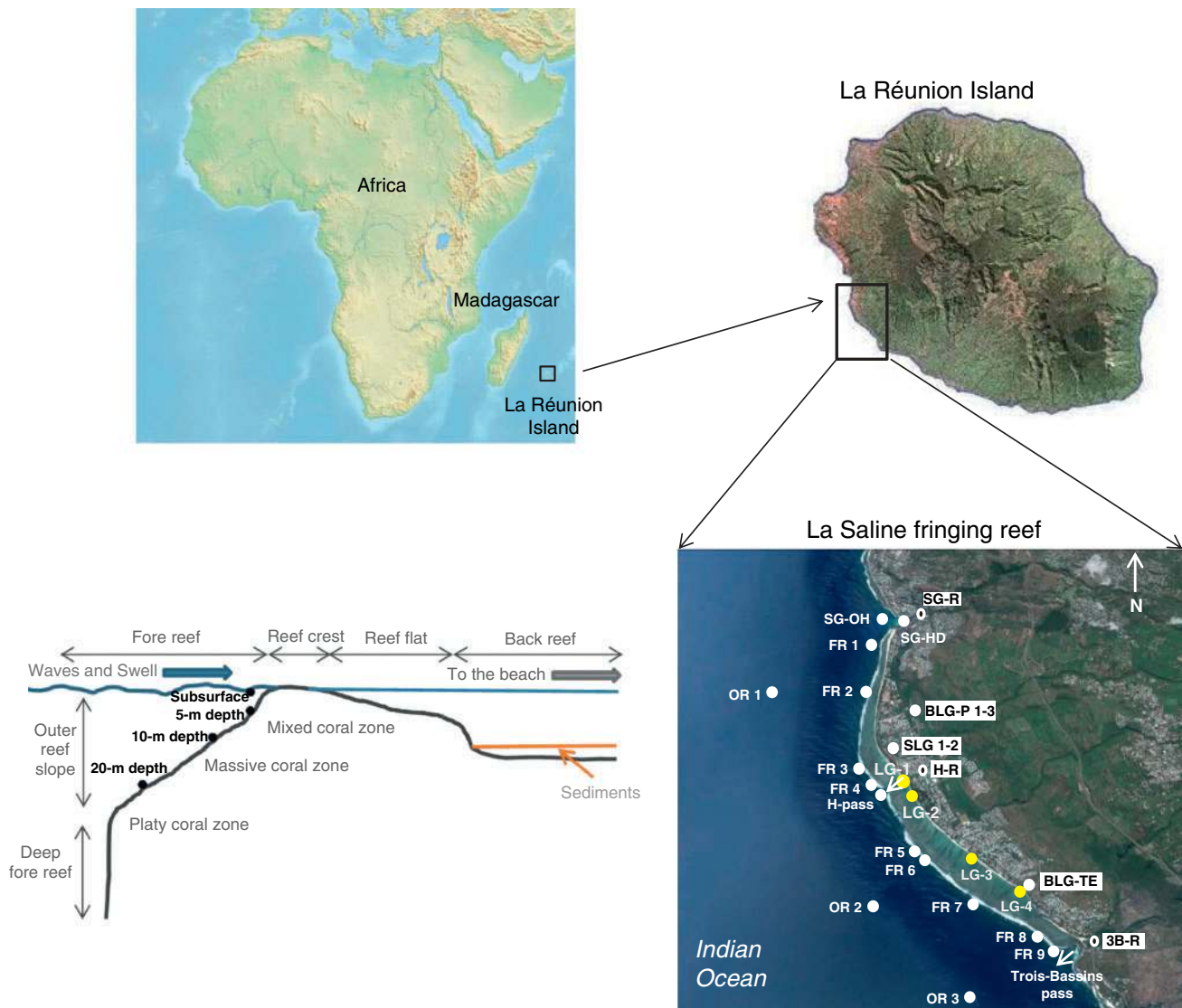


Fig. 1. Location of the study sites in the La Saline fringing reef environment (La Réunion Island, south-western Indian Ocean). The detailed characteristics of these sites are provided in Table 1.

waters were also collected along the outer reef slope at 5-, 10- and 20-m depth, the subsurface (0.1-m depth) being sampled vertically above the 5-m-depth slope point (Fig. 1). The locations of FR 1–9 were chosen according to a preliminary cruise conducted in 2011 that carried out hydrological measurements for detecting freshwater (groundwater) intrusions in the outer-reef-slope seawater. To sample water as close as possible to the reef, the Niskin bottle was operated by divers. All the samples were transferred into 4-L Nalgene polycarbonate bottles. Silicone tubing and 4-L Nalgene polycarbonate bottles were extensively washed with 1 M HCl and ultrapure water (i.e. Milli-Q water from a Millipore system, final resistivity: $18.2 \text{ M}\Omega \text{ cm}^{-1}$) before use. The bottles were rinsed three times with the respective sample before filling, and placed in the cold and in the dark after collection.

Filtration of samples

Back in the laboratory, samples were immediately filtered under low vacuum ($<6.7 \text{ kPa}$) through precombusted (500°C , 4 h) GF/F ($\sim 0.7 \mu\text{m}$) glass fibre filters (47-mm diameter, Whatman, Fisher

Scientific) using 2-L Schott glass bottles equipped with polysulfone filtering systems (Fisher Scientific) for hydrocarbons (AHs and PAHs) and all-glassware systems for hydrological and biogeochemical parameters, i.e. salinity, silicates (Si), nitrates (NO_3^-), dissolved organic carbon (DOC) and chlorophyll-*a* (Chl-*a*). The material that passes through GF/F filters consists of truly dissolved and colloidal matters, which can be each subjected to specific processes.^[35] However, because it is difficult to separate these two fractions operationally and in spite of the resulting bias, most environmental studies (including the present one) consider the material present in GF/F-filtered water simply as the ‘dissolved matter’. It is worth noting that hydrocarbon concentrations in the truly dissolved phase would be lower than those reported below. Filtered samples for dissolved hydrocarbon analyses were stored in 2-L Schott glass bottles with 50 mL of dichloromethane (CH_2Cl_2) at 4°C in the dark before solvent extraction (within 24 h). Filtered samples for Si, NO_3^- and DOC as well as filters for Chl-*a* and particulate hydrocarbon analyses were stored frozen until analysis. During the experiments and analyses, gloves were worn and care was taken to avoid contamination. All the glassware was washed with

Table 1. Characteristics of the study sites located in the La Saline fringing reef environment (La Réunion Island, south-western Indian Ocean) and sampled from 22 February 2012 to 9 March 2012

Name	Abbreviation	Water type	Position	Date of sampling	Sampling depth
Basaltic layer piezometer	BLG-P 1	Groundwater	21°04.48'N, 55°13.84'E	29-Feb-2012	Unknown
	BLG-P 2	Groundwater	21°04.38'N, 55°13.76'E	29-Feb-2012	Unknown
	BLG-P 3	Groundwater	21°04.37'N, 55°13.68'E	29-Feb-2012	Unknown
Basaltic layer well	BLG-TE	Groundwater	21°06.03'N, 55°14.67'E	5-Mar-2012	Unknown
Sand layer piezometer	SLG 1	Groundwater	21°04.71'N, 55°13.37'E	5-Mar-2012	Unknown
	SLG 2	Groundwater	21°04.71'N, 55°13.33'E	9-Mar-2012	Unknown
Saint Gilles river	SG-R	River water	21°03.18'N, 55°13.66'E	22-Feb, 01-Mar-2012	0.1 m
Hermitage River	H-R	River water	21°05.04'N, 55°13.62'E	22-Feb, 01-Mar-2012	0.1 m
Trois-Bassins River	3B-R	River water	21°06.55'N, 55°15.40'E	22-Feb, 29-Feb, 01-Mar-2012	0.1 m
Saint Gilles harbour dock	SG-HD	Harbour water	21°03.26'N, 55°13.48'E	29-Feb-2012	0.1 m
Off Saint Gilles harbour	SG-OH	Harbour water	21°03.25'N, 55°13.21'E	29-Feb-2012	0.1 m
Back reef	LG 1	Back reef water	21°05.06'N, 55°13.56'E	1-Mar-2012	0.1 m
	LG 2	Back reef water	21°05.20'N, 55°13.64'E	1-Mar-2012	0.1 m
	LG 3	Back reef water	21°05.85'N, 55°14.28'E	1-Mar-2012	0.1 m
	LG 4	Back reef water	21°06.15'N, 55°14.73'E	1-Mar-2012	0.1 m
Fore reef	FR 1	Fore reef water	21°03.63'N, 55°13.17'E	2-Mar-2012	0.1 m and along the outer reef slope (5-, 10- and 20-m depth)
	FR 2	Fore reef water	21°04.17'N, 55°13.06'E	23-Feb-2012	
	FR 3	Fore reef water	21°04.89'N, 55°13.06'E	7-Mar-2012	
	FR 4	Fore reef water	21°05.12'N, 55°13.23'E	2-Mar-2012	
	FR 5	Fore reef water	21°05.61'N, 55°13.53'E	2-Mar-2012	
	FR 6	Fore reef water	21°05.91'N, 55°13.82'E	7-Mar-2012	
	FR 7	Fore reef water	21°06.29'N, 55°14.33'E	24-Feb-2012	
	FR 8	Fore reef water	21°06.53'N, 55°14.79'E	7-Mar-2012	
	FR 9	Fore reef water	21°06.94'N, 55°14.95'E	23-Feb-2012	
Hermitage pass	H-pass	Oceanic water	21°05.20'N, 55°13.27'E	23-Feb-2012	0.1 m
Oceanic reference	OR 1	Oceanic water	21°04.33'N, 55°11.83'E	2-Mar-2012	0.1 m
	OR 2	Oceanic water	21°06.40'N, 55°13.12'E	2-Mar-2012	0.1 m
	OR 3	Oceanic water	21°07.12'N, 55°14.52'E	2-Mar-2012	0.1 m

1 M HCl and ultrapure water and combusted at 500 °C for 4 h. All the materials that could not be baked were washed with 1 M HCl and ultrapure water and dried at room temperature. Chl-*a* was not measured in all groundwater samples (dark environment) and particulate hydrocarbons were not analysed in SLG 1–2 because of the presence of large numbers of ants in the samples.

Hydrocarbon extraction and purification

Dissolved hydrocarbons present in the fraction <0.7 µm were extracted from water by liquid–liquid extraction with CH₂Cl₂ (2 × 60 mL L⁻¹). Particulate hydrocarbons present on the filters were extracted according to the method of Bligh and Dyer.^[36] Each filter was ground in a monophasic solvent mixture (CH₂Cl₂/methanol (CH₃OH)/H₂O, 1 : 2 : 0.8 v/v/v) and sonicated for 15 min. The mixture was then filtered and CH₂Cl₂ (1 v) and H₂O (1 v) were added to produce a biphasic mixture in such a way that hydrophobic compounds were released into the organic phase. The latter phase was removed and extraction of the aqueous phase was performed once again. Then, the analytical steps were similar for both dissolved and particulate hydrocarbon extracts. Organic phases were combined and evaporated with a rotary evaporator until a few hundred microlitres of CH₂Cl₂ remained. To avoid risk of contamination with unnecessary manipulations, only rich-organic-matter samples (i.e. river samples) were purified. Prior to purification, the remaining CH₂Cl₂ was changed to *n*-hexane. Hexane-solubilised extracts were then purified to separate AHs and PAHs (hydrocarbon fraction) from more polar compounds. Extracts were fractionated on a 500-mg silica column. Silica gel

(extra-pure, Merck) was activated at 500 °C for 4 h followed by partial deactivation with 4 % water by weight. The hydrocarbon fraction was eluted with 3 mL *n*-hexane/CH₂Cl₂ (3 : 1 v/v). All solvents were of organic trace-analysis quality (Rathburn Chemicals Ltd, Walkburn, Scotland, purchased from Interchim, France).

Analysis of hydrocarbons by gas chromatography

Extracts (purified or not) were concentrated under a gentle stream of nitrogen and analysed by gas chromatograph–mass spectrometer (GC-MS) (TraceISQ, ThermoElectron, Waltham, MA, USA) operating at an ionisation energy of 70 eV for a range of *m/z* 50–600 (full-scan and selected-ion monitoring (SIM) modes processed simultaneously), using helium as carrier gas at a flow rate of 1.2 mL min⁻¹. The GC-MS was equipped with a DB-5 MS column (30 m × 0.25 mm × 0.25 µm, J&W Scientific, Agilent Technologies, Santa Clara, CA, USA). The injector (used in splitless mode) and detector temperatures were 250 and 320 °C respectively. The initial column temperature was held for 3 min at 70 °C, then ramped at 15 °C min⁻¹ (ramp 1) to 150 °C and then at 7 °C min⁻¹ (ramp 2) to a final temperature of 320 °C, which was held for 10 min. PAHs and AHs were identified and quantified in SIM mode.^[12]

Determination of hydrocarbon indices

For AHs, we determined the concentrations of the resolved *n*-alkane series from *n*-C₁₅ to *n*-C₃₆ (R) with two isoprenoids, pristane (Pr) and phytane (Phy). We also determined unresolved complex mixture (UCM) concentrations by integrating the

hump (when present) using the mean response factor of the resolved compounds (relationship between the area of the peak and the mass of each AH). The UCM hump corresponds to a mixture of many structurally complex isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by capillary GC columns.^[10] Its relative importance, expressed as the ratio of unresolved to resolved compounds (UCM/R), is commonly used as diagnostic criterion of pollutant inputs.^[37]

Concerning PAHs, we determined the concentrations of 18 parent PAHs, namely naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), dibenzothiophene (DBT), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), perylene (Per), dibenz[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BP) and indeno[1,2,3-*cd*]pyrene (IndP), as well as the concentrations of alkylated homologues (methyl = C₁, dimethyl = C₂, trimethyl = C₃) of the five target compounds Naph, Flu, Phe, Pyr and Chr, which leads to a total of 33 PAHs. Naph and its alkylated homologues are two-ring compounds. Acy, Ace, Flu, DBT, Phe, Ant and alkylated homologues of Flu and Phe are three-ring compounds. Flt, Pyr, BaA, Chr and alkylated homologues of Pyr and Chr are four-ring compounds. BbF, BkF, BaP, Per, DBA, BP and IndP are five- to six-ring compounds.^[38]

Quality assurance and quality control

Deuterated standard mixtures (C₁₆-*d*₃₄, C₂₄-*d*₅₀, C₃₆-*d*₇₄ for AHs, and Naph-*d*₈, Phe-*d*₁₀, Per-*d*₁₂ for PAHs) were introduced into samples before extraction, as well as a supplementary deuterated standard before injection, and used as surrogates to assess the recoveries of analytical procedures and to determine quantitation accuracy. The C₁₆-*d*₃₄, C₂₄-*d*₅₀ and C₃₆-*d*₇₄ average recoveries were respectively 30, 63 and 85 %, whereas Naph-*d*₈, Phe-*d*₁₀, Per-*d*₁₂ average recoveries were 38, 74 and 88 %. Precautions were taken during evaporation under nitrogen because dryness could lead to the total loss of the more volatile compounds. In addition, blanks were run for the whole procedure including the use of the Nalgene polycarbonate bottles, extraction, solvent concentration and purification. These whole-procedure blanks were 0.014 ± 0.008 µg L⁻¹ for total dissolved AHs (from *n*-C₁₅ to *n*-C₃₆) and of 0.87 ± 0.72 ng L⁻¹ for total dissolved PAHs (∑33 PAHs), representing between 2.4 and 23.8 % of total dissolved AH concentrations and between 0.25 and 3.8 % of total dissolved PAH concentrations measured in our samples. All concentration values were blank- and recovery-corrected. These recoveries, which include extraction, evaporation and purification processes, do not take into account potential losses of high molecular weight (HMW) dissolved hydrocarbons by sorption onto the polycarbonate bottles. These losses are indeed very difficult to quantify in natural samples owing to the number of physicochemical factors affecting the sorption of organic compounds.^[39] Detection limits of the method for individual compounds varied from 1 to 30 pg L⁻¹ in water. Compounds were identified and quantified by reference to the analysis of standard mixtures (04071, Fluka, and 47543-U, Supelco, among others, purchased from Sigma-Aldrich, Saint Louis, MO, USA). Calibration curves were constructed for all target compounds analysed except for the alkylated homologues, which were quantified with their parent-compound calibration curves. Calibration was performed in SIM mode. The correlation coefficients (*r*) were >0.99 for all the compounds.

Salinity and biogeochemical analysis

Salinity was determined using a Kal Mark IV salinometer (Yeo-Kal Electronics Pty Ltd, Sydney, Australia). Si and NO₃⁻ were measured using a Bran + Luebbe Autoanalyser II and standard analysis methods. Chl-*a* was analysed by the fluorescence method following a methanol extraction.^[40] DOC was measured on two replicates, previously spiked with ultrapure orthophosphoric acid (Sigma-Aldrich) and bubbled for 10 min with CO₂-free air to purge inorganic carbon, by high-temperature catalytic oxidation using a Shimadzu TOC 5000 Total Carbon Analyser (Kyoto, Japan).^[41]

Statistics

Mann-Whitney non-parametric tests (U-tests) were used for the comparison of two independent data groups because of the non-normal distribution of some variables (normality assessed with the Kolmogorov-Smirnov test) and the low number of samples for some groups. U-tests were carried out using *StatView 5.0* (Abacus Corporation, Baltimore, MD, USA). Spearman's rank-order correlations were preferred to Pearson's correlations because of the high amplitudes of some variables and their non-normal distribution.^[42] Spearman's correlation matrices were performed using *XLSTAT 2010.2* (Microsoft Excel add-on program). For the different analyses and tests, the significance threshold was set at *P* < 0.05.

Results

Salinity and biogeochemical parameters

Salinity and biogeochemical parameter data are reported in Table 2 and Fig. 2. All groundwater samples were characterised by low salinity (0.24–6.01) and high Si values (582–1251 µM) (Table 2). Groundwater samples from the basaltic aquifer (BLG-P 1–3 and BLG-TE) exhibited high NO₃⁻ (289–797 µM) and very low DOC concentrations (27–43 µM) whereas groundwater samples from sedimentary formations (SLG) showed the opposite pattern, with 0.08–1.5 µM for NO₃⁻ and 245–309 µM for DOC. In rivers, both SG-R and H-R displayed low salinity (0.09–0.83) along with high Si and NO₃⁻ concentrations (695–749 and 63–123 µM respectively). However, SG-R showed low DOC and Chl-*a* concentrations (58–62 µM and 0.34–1.3 µg L⁻¹ respectively) whereas H-R displayed the highest values of the data set (393–396 µM and 16.6–19.4 µg L⁻¹ respectively) for these two parameters. In comparison with the two rivers mentioned previously, 3B-R presented higher salinity values (25.98–27.87) and lower Si and NO₃⁻ concentrations (126–149 and 5.6–15.7 µM respectively) associated with high DOC and Chl-*a* concentrations (266–338 µM and 9.0–17.1 µg L⁻¹ respectively). At the harbour site SG-HD, salinity, Si, NO₃⁻, DOC and Chl-*a* concentrations were 18.12, 342 µM, 60 µM, 104 µM and 0.82 µg L⁻¹ respectively. Seaward (at SG-OH), salinity increased (35.28) and biogeochemical parameters decreased (7.8 µM, 1.3 µM, 86 µM and 0.27 µg L⁻¹ respectively). In back-reef waters (LG 1–4), salinity and biogeochemical parameters were quite variable (28.48–34.36, 45–162 µM, 4.0–20 µM, 74–142 µM, 0.3–3.9 µg L⁻¹ respectively). Compared with the latter, in the fore reef (FR 1–9), H-pass and oceanic reference waters (OR 1–3), salinity increased (35.32–35.61) whereas biogeochemical parameters decreased (2.04–7.50 µM, 0.03–1.18 µM, 63–98 µM, 0.02–0.34 µg L⁻¹ respectively) (Table 2).

Fig. 2 shows the variability of salinity, Si, NO₃⁻, DOC and Chl-*a* concentrations in the La Saline fringing reef with regard to

Table 2. Salinity, biogeochemical parameters and hydrocarbon (AHs and PAHs) concentrations

Si, silicates; NO₃⁻, nitrates; DOC, dissolved organic carbon; Chl-*a*, chlorophyll-*a*; AHs, sum of *n*-alkanes from C₁₅ to C₃₆ with two isoprenoids, pristane and phytane; PAHs, sum of 18 parents and 15 alkylated homologue polycyclic aromatic hydrocarbons; nd, not determined. *n*, number of samples taken at each site. Fore reef waters sampled at 0.1-, 5-, 10- and 20-m depth on the outer reef slope (Fig. 1)

Site	<i>n</i>	Salinity and biogeochemical parameters					Hydrocarbons				
		Salinity	Si (μM)	NO ₃ ⁻ (μM)	DOC (μM)	Chl- <i>a</i> (μg L ⁻¹)	AHs (μg L ⁻¹)		PAHs (ng L ⁻¹)		
							Particulate	Dissolved	Particulate	Dissolved	
Groundwaters	BLG-P 1-3	1	0.24-0.33	940-1251	289-797	27-43	nd	0.07-0.29	0.09-0.13	Nov-13	112-133
	BLG-TE	1	0.67	951	477	43	nd	0.08	0.3	8.2	129
	SLG 1-2	1	5.74-6.01	582-614	0.08-1.5	245-309	nd	nd	0.13	nd	119-165
Rivers	SG-R	2	0.09-0.15	695-700	116-123	58-62	0.34-1.3	0.20-0.42	0.11-0.21	17-96	28-78
	H-R	2	0.63-0.83	729-749	63-100	393-396	16.6-19.4	1.22	0.46-0.58	106-124	188-350
	3B-R	3	25.98-27.87	126-149	5.6-15.7	266-338	9.0-17.1	49-144	0.19-0.43	71-326	72-96
Harbours	SG-HD	1	18.12	342	60	104	0.82	0.46	0.28	32	47
	SG-OH	1	35.28	7.8	1.3	86	0.27	0.07	0.42	17	76
Back reef	LG 1-4	1	28.48-34.36	45-162	4.0-20	74-142	0.3-3.9	0.10-36	0.06-0.58	6.8-17	30-72
Fore reef	FR 1	4	35.58-35.60	2.04-2.27	0.03-0.51	70-79	0.05-0.10	0.11-0.18	0.07-0.15	6-9.3	49-125
	FR 2	4	35.50-35.59	2.13-3.49	0.16-0.91	69-73	0.11-0.23	0.19-0.32	0.11-0.23 ^A	14-17	61-114
	FR 3	4	35.55-35.60	2.10-2.29	0.12-0.44	68-72	0.06-0.13	0.18-0.24	0.11-0.19	4.3-7.5	125-227
	FR 4	4	35.53-35.61	2.42-3.29	0.21-0.71	63-68	0.04-0.09	0.07-0.15	0.12-0.13	5.5-8.9	75-119
	FR 5	4	35.54-35.58	2.10-2.15	0.14-0.39	73-79	0.03-0.09	0.13-0.20	0.13-0.16	5.1-7.7	100-162
	FR 6	4	35.41-35.52	2.27-2.50	0.24-0.49	73-75	0.18-0.34	0.13-0.28	0.06-0.13	Oct-15	53-77
	FR 7	4	35.48-35.57	2.24-3.63	0.27-0.87	77-98	0.14-0.21	0.13-0.18	0.12-0.14	Nov-21	74-102
	FR 8	4	35.46-35.53	2.5-3.6	0.26-0.60	68-73	0.15-0.19	0.14-0.24	0.10-0.17	5.7-11	133-236
	FR 9	4	35.32-35.55	2.15-7.50	0.07-1.18	72-87	0.09-0.33	0.13-0.25	0.08-0.11	16-26	59-88
Pass	H-pass	1	35.56	2.84	0.77	73	0.16	0.08	0.11	6.2	128
Oceanic reference	OR 1-3	1	35.57-35.58	2.07-2.24	0.03-0.10	88-94	0.02-0.10	0.20-0.25	0.09-0.11	9.7-11.5	45-51

^AUnresolved complex mixture (UCM) was found at FR-2 10-m depth.

the coast–open sea gradient, the depth of the outer-reef slope (0.1, 5, 10, 20 m) and the north–south gradient in fore reef waters. The main trend for the coast–open sea transect was an increase in salinity associated with a decrease in the concentration of biogeochemical parameters. Actually, significantly higher salinity values and significantly lower Si, NO₃⁻, and Chl-*a* concentrations were recorded in marine sites (back and fore reef, harbour, Hermitage pass and oceanic waters) compared with inland waters (groundwaters and rivers) (U-test, $P = 0.0001$, $n = 7-46$). Fore reef surface waters (0.1-m depth), except FR-5 and FR-6, exhibited significantly lower salinities along with significantly higher Si and NO₃⁻ concentrations compared with fore reef waters collected at 10- or 20-m depth (U-test, $P = 0.005-0.04$, $n = 7-9$). Finally, we observed significantly lower salinity values associated with significantly higher Si, DOC and Chl-*a* concentrations in fore reef waters sampled in the south of the study area compared with those sampled in the northern part (U-test, $P = 0.0001-0.03$, $n = 16-20$) (Fig. 2).

Hydrocarbon concentrations

Total AH and PAH concentrations are reported in Table 2 and Fig. 3. Total particulate AH concentrations ranged from 0.07 to 0.29 μg L⁻¹ in groundwaters, from 0.07 to 144 μg L⁻¹ in rivers and harbours, from 0.10 to 0.36 μg L⁻¹ in the back reef, and from 0.07 to 0.32 μg L⁻¹ in the fore reef, Hermitage pass and oceanic reference waters (Table 2). Total dissolved AH concentrations ranged from 0.09 to 0.30 μg L⁻¹ in groundwaters, from 0.11 to 0.58 μg L⁻¹ in rivers and harbours, from 0.06 to 0.58 μg L⁻¹ in back reef, and from 0.06 to 0.23 μg L⁻¹ in fore reef, Hermitage pass and oceanic reference waters. Concerning PAHs, total

particulate concentrations varied from 8.2 to 13 ng L⁻¹ in groundwaters, from 17 to 326 ng L⁻¹ in rivers and harbours, from 6.8 to 17 ng L⁻¹ in the back reef, and from 4.3 to 26 ng L⁻¹ in the fore reef, Hermitage pass and oceanic reference waters. Total dissolved PAH concentrations ranged from 112 to 165 ng L⁻¹ in groundwaters, from 28 to 350 ng L⁻¹ in rivers and harbours, from 30 to 72 ng L⁻¹ in the back reef, from 49 to 236 ng L⁻¹ in the fore reef and Hermitage pass, and from 45 to 51 ng L⁻¹ in oceanic reference waters (Table 2).

Fig. 3 displays the variability of concentrations in total particulate and dissolved AHs and PAHs in the La Saline fringing reef with regard to the coast–open sea gradient, the depth of the outer reef slope (0.1, 5, 10, 20 m) and the north–south gradient in fore reef waters. Total dissolved AH and particulate PAH concentrations were significantly higher in inland waters (groundwaters and rivers) than in marine waters (U-test, $P = 0.0006-0.01$, $n = 11-46$). Also, although not statistically different (because of high standard deviations for inland samples), with regard to Fig. 3a, we may reasonably consider that total particulate AH concentrations were higher in groundwaters and rivers than in marine waters. In addition, only particulate AH concentrations displayed differences with depth along the outer reef slope: they were significantly lower in surface water (0.16 ± 0.06 μg L⁻¹) than at 20-m depth (0.22 ± 0.05 μg L⁻¹) (U-test, $P = 0.03$, $n = 9$), where they were similar to those of oceanic reference waters (0.23 ± 0.03 μg L⁻¹). Moreover, total dissolved AH concentrations were significantly higher in fore reef waters from the north of the coral reef, whereas total particulate PAH concentrations were significantly higher in the southern part (U-test, $P = 0.002-0.05$, $n = 16-20$) (Fig. 3).

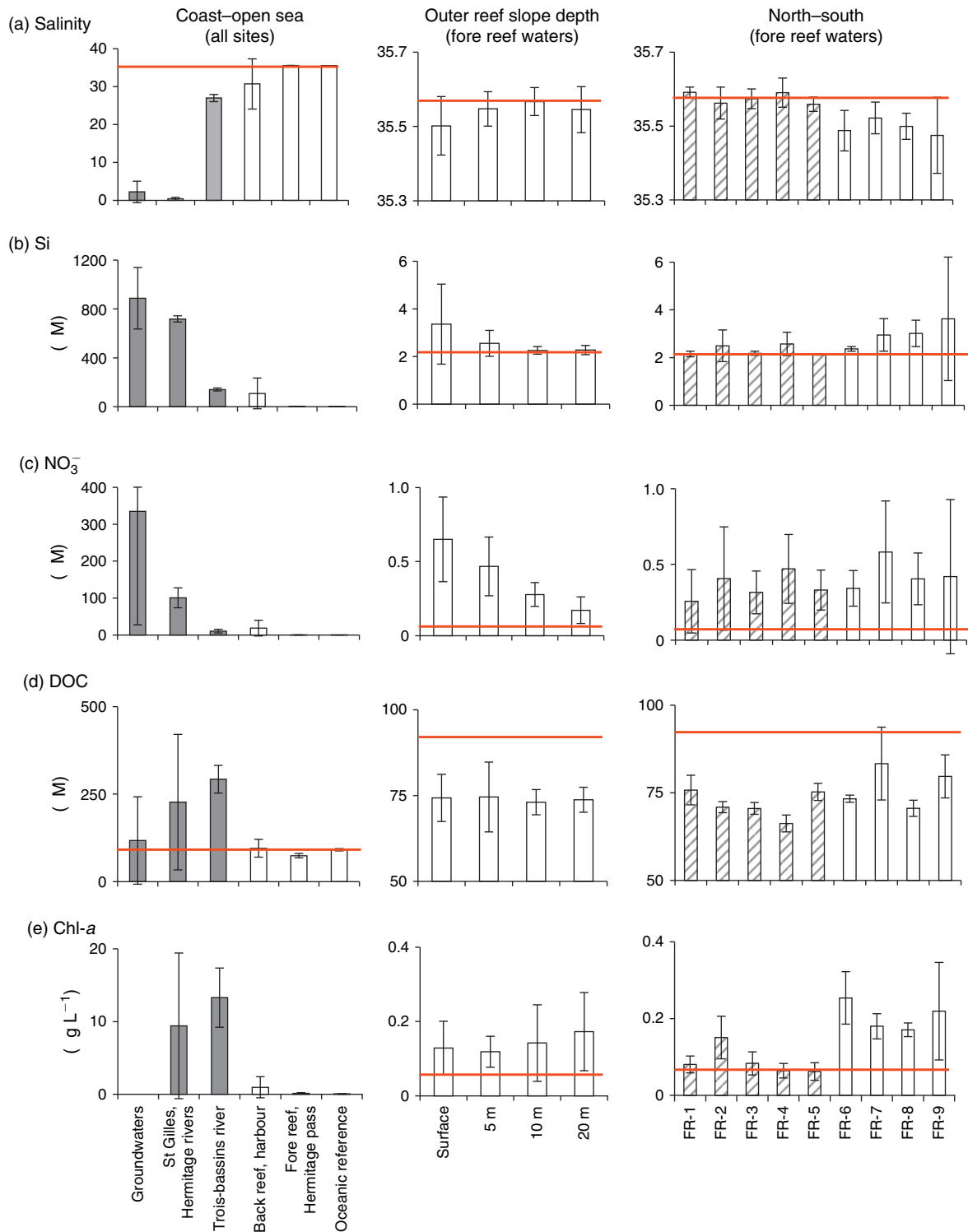


Fig. 2. Spatial variability of salinity, silicates (Si), nitrates (NO_3^-), dissolved organic carbon (DOC) and chlorophyll-*a* (Chl-*a*) concentrations in the La Saline fringing reef. The red line represents, where possible, the values of oceanic reference waters. In the left column, inland waters (groundwaters and rivers) are drawn in grey and marine sites are in white. In the right column, the fore reef waters located in the northern part of the study area (FR 1–5) are hatched and those located in the southern part (FR 6–9) are in white.

Correlations between salinity, biogeochemical parameters and hydrocarbons

Table 3 shows Spearman's correlation matrices for three groups of samples: (i) rivers, harbour, back reef, fore reef, oceanic waters ($n=50$); (ii) harbour, back reef, fore reef, oceanic waters ($n=43$); and (iii) fore reef and oceanic waters ($n=38$).

We found significant negative correlations between salinity and Si concentration ($r = -0.58$ to -0.82 , $P = 0.001$, $n = 38-50$), even when considering solely fore reef and oceanic waters. This underlined the intrusions of freshwater into the back reef waters but also into the fore reef waters. These freshwaters were enriched in NO_3^- (significant positive correlations between Si and

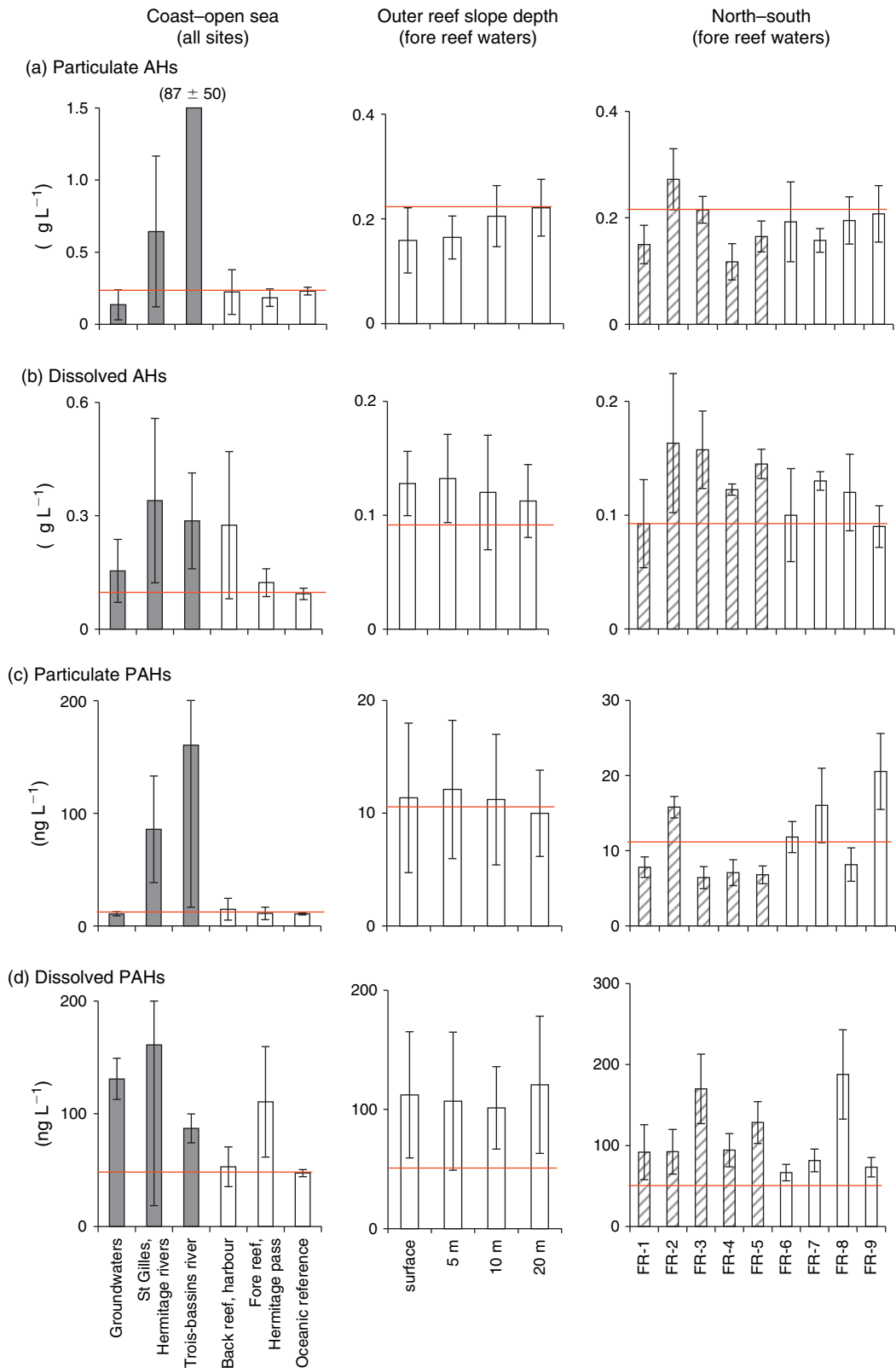


Fig. 3. Spatial variability of concentrations in total particulate and dissolved aliphatic hydrocarbons (AHs) (a, b); and in total particulate and dissolved polycyclic aromatic hydrocarbons (PAHs) (c, d) in the La Saline fringing reef. The red line represents, where possible, the values of oceanic reference waters. In the left column, inland waters (groundwaters and rivers) are drawn in grey whereas marine sites are in white. In the right column, the fore reef waters located in the northern part of the study area (FR 1–5) are hatched and those located in the southern part (FR 6–9) are in white.

Table 3. Spearman's correlation matrices for (a) rivers, harbour, back reef, fore reef, oceanic waters ($n = 50$); (b) harbour, back reef, fore reef, oceanic waters ($n = 43$); and (c) only fore reef and oceanic waters ($n = 38$)

AHs part., total particulate AHs; AHs diss., total dissolved AHs; PAHs part., total particulate PAHs; PAHs diss., total dissolved PAHs. Ground waters, for which Chl-*a* concentrations were not determined, are not included in these matrices. Significant correlations ($P < 0.05$) are in bold. Correlations that are significant in all three matrices are underlined

	Si	NO ₃ ⁻	DOC	Chl- <i>a</i>	AHs part.	AHs diss.	PAHs part.	PAHs diss.
(a)								
Salinity	<u>-0.82</u>	-0.67	-0.38	<u>-0.77</u>	-0.34	-0.27	-0.57	0.31
Si		<u>0.82</u>	0.26	<u>0.71</u>	0.15	0.27	0.5	-0.23
NO ₃ ⁻			0.14	0.53	-0.01	0.51	0.34	-0.13
DOC				0.36	0.28	0.15	<u>0.43</u>	<u>-0.29</u>
Chl- <i>a</i>					0.42	0.31	<u>0.63</u>	<u>-0.32</u>
Part. AHs						0.16	0.48	-0.03
Diss. AHs							0.17	0.16
Part. PAHs								<u>-0.39</u>
(b)								
Salinity	<u>-0.71</u>	-0.48	-0.39	<u>-0.66</u>	-0.03	0	-0.34	0.32
Si		<u>0.72</u>	0.19	<u>0.55</u>	-0.25	-0.01	0.23	-0.22
NO ₃ ⁻			0.02	0.28	-0.48	0.36	0.01	-0.07
DOC				0.27	0.11	-0.12	<u>0.39</u>	<u>-0.49</u>
Chl- <i>a</i>					0.13	0.02	<u>0.45</u>	<u>-0.37</u>
Part. AHs						-0.18	0.23	-0.03
Diss. AHs							-0.18	0.19
Part. PAHs								<u>-0.49</u>
(c)								
Salinity	<u>-0.58</u>	-0.25	-0.25	<u>-0.54</u>	-0.12	0.2	-0.44	0.12
Si		<u>0.6</u>	-0.04	<u>0.41</u>	-0.25	-0.2	0.3	0.01
NO ₃ ⁻			-0.25	0.03	-0.57	0.3	0	0.2
DOC				0.13	0.15	-0.29	0.38	<u>-0.4</u>
Chl- <i>a</i>					0.18	-0.15	<u>0.53</u>	-0.22
Part. AHs						-0.28		-0.08
Diss. AHs							-0.35	0.34
Part. PAHs								<u>-0.62</u>

NO₃⁻ concentrations; $r = 0.60-0.82$, $P = 0.001$, $n = 38-50$) and induced an increase in Chl-*a* concentration (significant negative correlations between salinity and Chl-*a* and significant positive correlations between Si and Chl-*a*; $r = -0.54$ to -0.77 and 0.41 to 0.71 respectively, $P = 0.001$, $n = 38-50$). Moreover, the freshwaters were enriched in particulate PAHs (significant negative correlations between salinity and particulate PAH concentrations; $r = -0.34$ to -0.57 , $P = 0.001-0.02$, $n = 38-50$). Particulate PAHs were significantly positively correlated with Chl-*a* and DOC concentrations ($r = 0.38-0.63$, $P = 0.001-0.02$, $n = 38-50$) and negatively correlated with dissolved PAHs ($r = -0.39$ to -0.62 , $P = 0.001-0.005$, $n = 38-50$). These results clearly showed that the back reef and fore reef waters were affected by intrusions of inland waters enriched in Si, NO₃⁻ and particulate PAHs, leading to an increase in Chl-*a* concentrations, and that these inputs affected mainly surface waters and the southern part of the reef (Table 3; Figs 2, 3).

Hydrocarbon molecular profiles

Particulate and dissolved AH molecular profiles are presented in Figs 4 and 5 respectively. Particulate AH molecular profiles displayed bi- or monomodal distributions (Fig. 4). On one hand, groundwater samples from the basaltic aquifer (BLG-P 1-3 and BLG-TE), rivers (except 3B-R) and harbour dock (SG-HD) showed bimodal distributions rather centred on n -C₁₇ for the light compounds ($<n$ -C₂₀) and on n -C₂₆ or n -C₂₉ for the heavy ones ($>n$ -C₂₀). On the other hand, 3B-R, fore reef (FR 1-9) and oceanic reference (OR) waters displayed monomodal distributions with a maximum at n -C₁₅ reaching up to $\sim 100\%$ and

almost completely masking the $>n$ -C₁₈ compounds. Interestingly, particulate AH molecular profiles in fore reef waters showed significant differences with depth (Fig. 6). The two most abundant compounds, n -C₁₅ and n -C₁₇, represented $54 \pm 15\%$ and $19 \pm 6\%$ of total particulate AHs in surface water, whereas they reached $77 \pm 9\%$ and $9.7 \pm 5.5\%$ of the total pool at 20-m depth (U-test, $P = 0.0009-0.0023$, $n = 9$) where their contributions were similar to that of OR waters ($79 \pm 11\%$ and $9.3 \pm 1.7\%$ respectively). Then, SG-OH, back reef (LG 1-4) and H-pass displayed intermediate distribution with a rather monomodal pattern and a clear dominance of n -C₁₅ or n -C₁₇ but a quite visible signature of the heavy compounds, illustrating the mixing between inland and oceanic waters previously highlighted by salinity values (Fig. 4).

Dissolved AH molecular profiles displayed a bimodal distribution (Fig. 5). The n -C₁₅- n -C₂₀ distributions were centred on n -C₁₈, except at H-R and 3B-R, which exhibited a maximum at n -C₁₅. In addition, the n -C₂₁- n -C₃₆ distributions were centred on n -C₂₄ and n -C₂₆ and could display a slight even over odd carbon-number predominance. A single UCM was found at FR 2 10-m depth (UCM = $43 \mu\text{g L}^{-1}$, UCM/R = 189).

Particulate and dissolved PAH molecular profiles are presented in Fig. 7. Molecular profiles were similar between sites and very similar for dissolved and particulate compounds. In both phases, relative abundances were 60 ± 7 , 38 ± 6 and $2 \pm 1\%$ for two-, three- and four-ring PAHs respectively. The five- to six-ring compounds were always below the detection limit in the dissolved phase although they represented on average 0.2% of total PAHs in the particulate phase, reaching

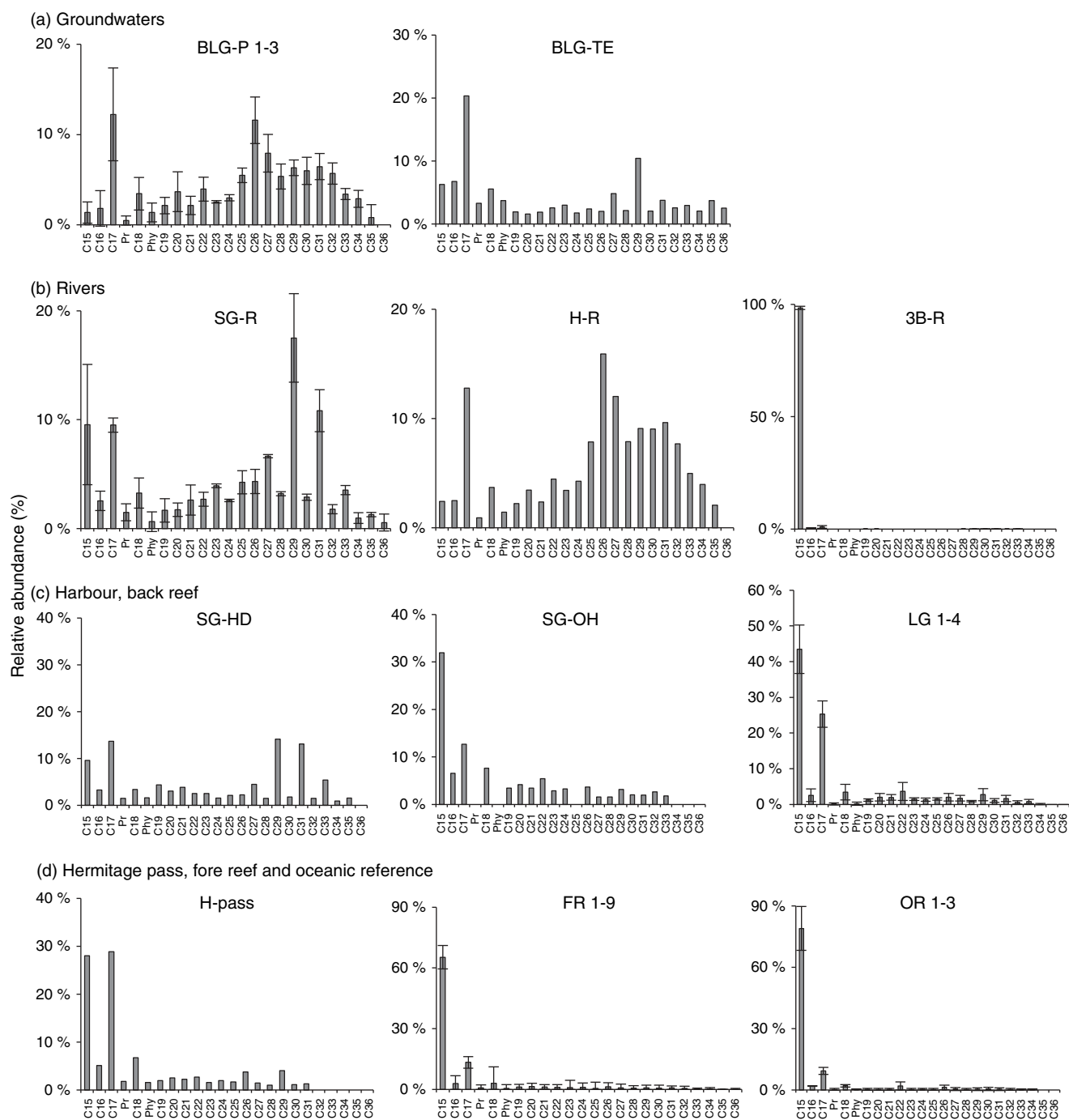


Fig. 4. Molecular profiles of particulate aliphatic hydrocarbons (AHs) (%) at all sites. Pr, pristane; Phy, phytane.

up to 4% in harbour (SG-HD), back reef (LG 1–4) and fore reef waters (FR-2 all depths) (Fig. 7).

For AHs and PAHs, when plotting their octanol–water partition coefficients ($\log K_{ow}$) against the organic-carbon-normalised partition coefficient between the particulate and the dissolved phases (calculated as $C_{part}/C_{diss}[\text{DOC}]$), we did not find any linear correlation. This absence of correlation along with the molecular profiles observed attests of a discrepancy between the hydrophobic character of AHs and PAHs and their partition between the dissolved and particulate phases of water in the La Saline reef ecosystem. This discrepancy could be due to a difference in the composition or origin of organic matter between the two phases and to the biogenic origin of the

hydrocarbons (demonstrated for AHs, strongly suspected for PAHs, see below).

Discussion

Characteristics of water bodies and freshwater inputs in La Saline reef waters

Basaltic (BLG) and sedimentary (SDG) groundwaters clearly differed in terms of composition (Table 2). BLG were enriched in NO_3^- very likely derived from anthropogenic activities, especially agriculture, located upstream on both sides of the Hermitage River.^[23,24,26] High concentrations of DOC measured in the sedimentary aquifer were due to large inputs of

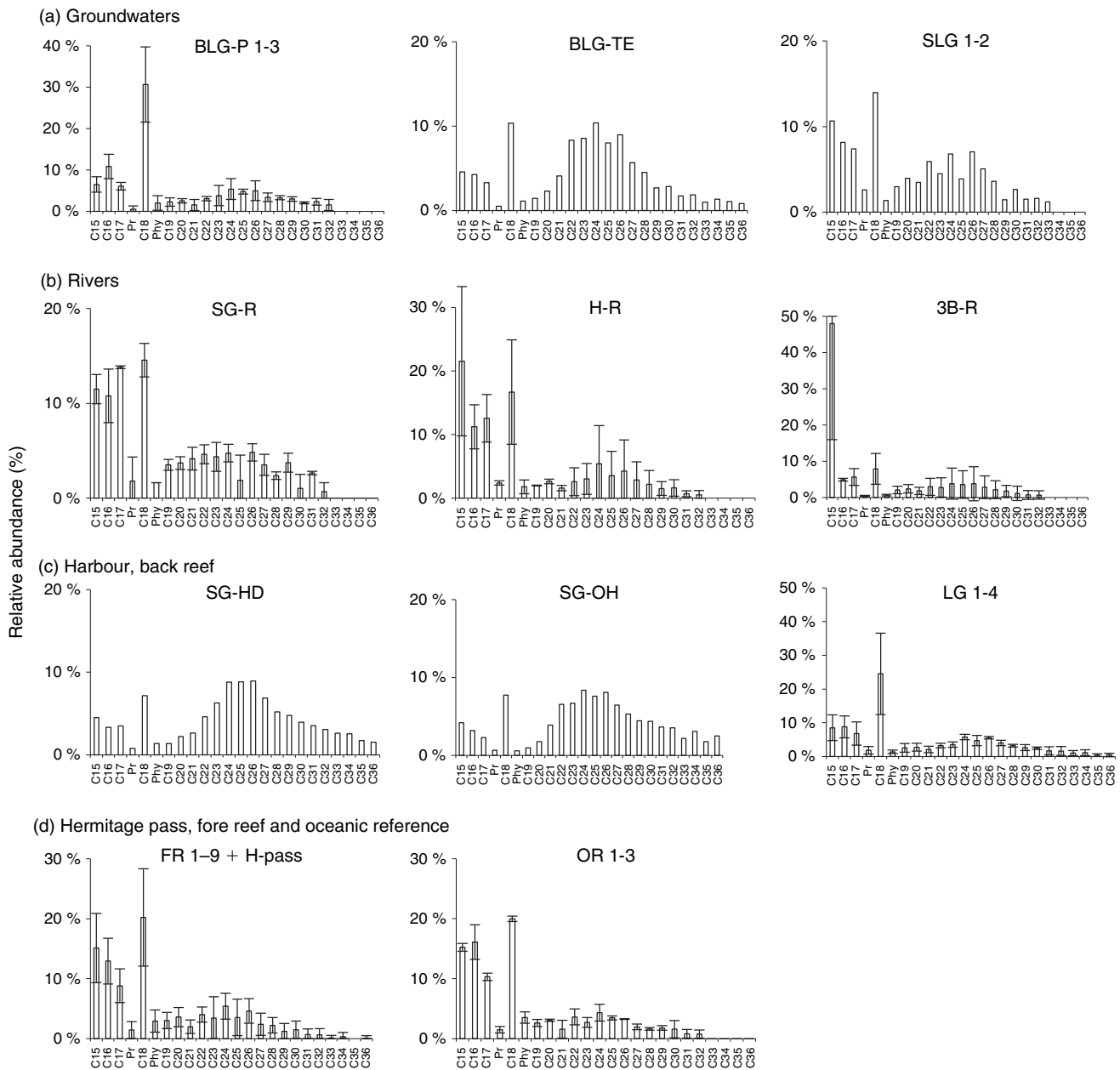


Fig. 5. Molecular profiles of dissolved aliphatic hydrocarbons (AHs) (%) at all sites. Pr, pristane; Phy, phytane.

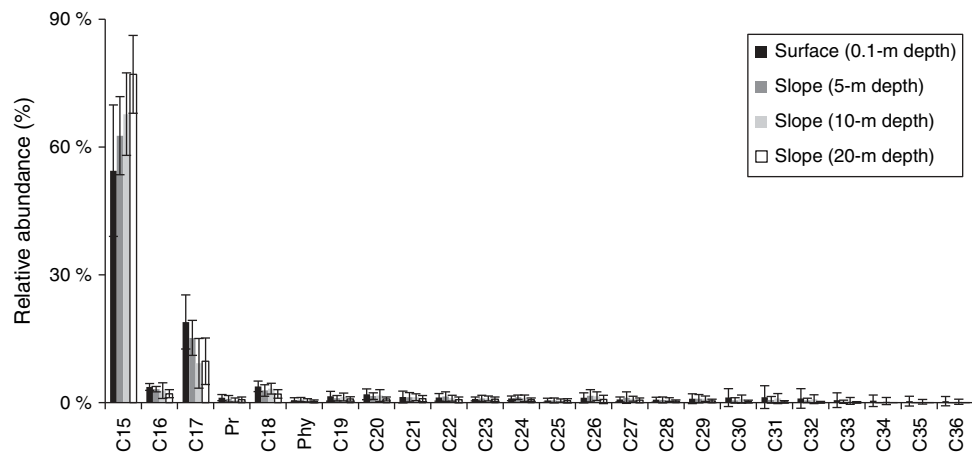


Fig. 6. Molecular profiles of particulate aliphatic hydrocarbons (AHs) (%) in fore reef waters at 0.1-, 5-, 10- and 20-m depth of the outer reef slope. Pr, pristane; Phy, phytane.

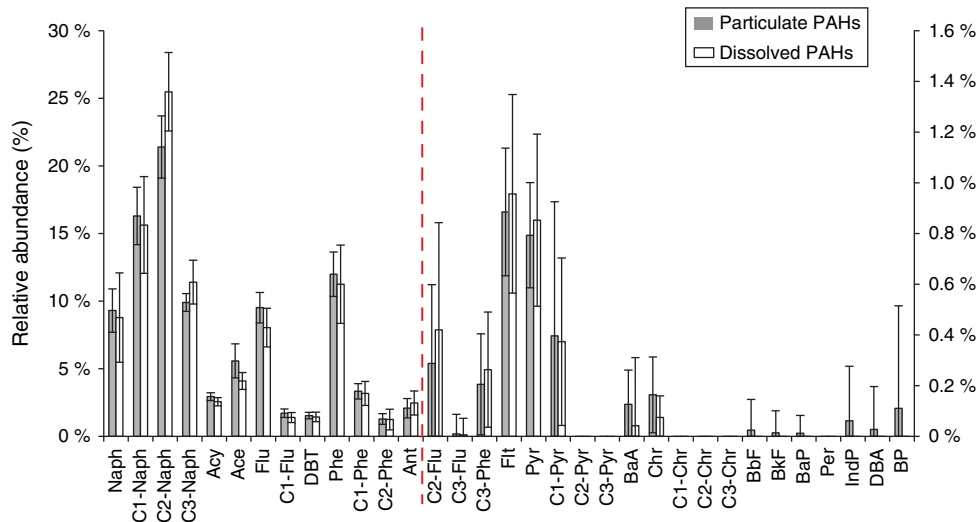


Fig. 7. Molecular profiles of particulate and dissolved polycyclic aromatic hydrocarbons (PAHs) (%) at all sites. Naph, naphthalene; C₁-Naph, methylnaphthalenes; C₂-Naph, dimethylnaphthalenes; C₃-Naph, trimethylnaphthalenes; Acy, Acenaphthylene; Ace, Acenaphthene; Flu, Fluorene; C₁-Flu, methylfluorenes; C₂-Flu, dimethylfluorenes; C₃-Flu, trimethylfluorenes; DBT, dibenzothiophene; Phe, phenanthrene; C₁-Phe, methylphenanthrenes; C₂-Phe, dimethylphenanthrenes; C₃-Phe, trimethylphenanthrenes; Ant, anthracene; Flt, fluoranthene; Pyr, pyrene; C₁-Pyr, methylpyrene; C₂-Pyr, dimethylpyrene; C₃-Pyr, trimethylpyrene; BaA, benz[*a*]anthracene; Chr, chrysene; C₁-Chr, methylchrysene; C₂-Chr, dimethylchrysene; C₃-Chr, trimethylchrysene; BbF, benzo[*b*]fluoranthene; BkF, benzo[*k*]fluoranthene; BaP, benzo[*a*]pyrene; Per, perylene; IndP, indeno[1,2,3-*cd*]pyrene; DBA, dibenz[*a,h*]anthracene; BP, benzo[*g,h,i*]perylene. The second axis on the right is for the compounds from C₂-Flu to BP.

plant-derived organic matter (OM). During the rainy season (study period), the Hermitage coastal plain is regularly flooded and the sedimentary aquifer collects waters highly loaded in plant material infiltrating from the surface. Thus, during this season, the sedimentary groundwater is supplied by water from above (rain and soil waters) in addition to being supplied by water from below (basaltic aquifer). Surprisingly, sedimentary groundwater was not affected by NO₃⁻ contamination whereas the basaltic aquifer, in spite of its numerous fissures, received not as much plant-derived OM as reported by Tedetti et al.^[32]

Rivers also displayed great differences (Table 2). The Hermitage River (H-R), which contained high concentrations of Si, NO₃⁻, DOC and Chl-*a*, received high amounts of plant and soil-derived OM and was subjected to strong anthropogenic pressures through direct inputs from a sewage treatment plant and various wastewaters from agricultural activities set up on both sides of the river. The Saint Gilles River (SG-R) presented higher NO₃⁻ concentrations but a much lower content of DOC and Chl-*a*. The Trois-Bassins River (3B-R) is known to be supplied by the basaltic aquifer. However, samples collected in the present study at 3B-R were brackish and presented high salinity values and low Si and NO₃⁻ concentrations because intrusions of marine waters occurred during swell events. Besides, as for the Hermitage River, the Trois-Bassins River was enriched in terrigenous organic matter.

With regard to their salinity values, Si and NO₃⁻ concentrations, back reef waters (LG 1–4) were clearly affected by freshwaters (Tables 2, 3; Fig. 2). This is consistent with previous work that demonstrated that the back reef waters were affected by basaltic groundwater in the south part of the reef and by other freshwater bodies (Hermitage River or sedimentary groundwater) in the northern part.^[22,23,32] Interestingly, we found in the present study that fore reef waters were also subject to intrusions of freshwaters, and that these intrusions were not exclusively located in front of passes but occurred mainly in surface waters

(0.1-m depth) and in the southern part of the reef (i.e. from FR 6 to FR 9) (Tables 2, 3; Figs 2, 3). Cuet et al.^[43] have shown that inland waters entering the back reef may be dispersed in the fore reef zone from passes by tidal currents or may directly reach the fore reef zone thanks to swell and tidal phenomena. Therefore, it is very likely that freshwaters affecting the fore reef in the southern area were basaltic groundwaters. These intrusions of freshwater are known to be responsible for the degradation and eutropication of reef waters. However, despite the evidence found in the present work of a spatial variability in inland water intrusions in fore reef waters (with depth and north to south), no spatial differences were observed in the degradation of the coral formations along La Saline reef (P. Cuet, L. Bigot and J. Turquet, unpubl. data). This is probably due to a bias in the observation scale: the degradation of coral reef formations took place over several years whereas the present study focussed only on 3 weeks and took place during the rainy season.

Hydrocarbon concentration levels and PAH indicators of freshwater inputs

Data on hydrocarbon (AHs and PAHs) concentrations in waters from tropical coral reef ecosystems and from the Indian Ocean are very scarce in the literature.^[44,45] Total dissolved + particulate AH concentrations measured in marine waters (back reef, harbour, fore reef and oceanic waters; $0.33 \pm 0.14 \mu\text{g L}^{-1}$) were comparable with those found in the Great Barrier Reef area (Australia) ($0.19 \pm 0.08 \mu\text{g L}^{-1}$ and $0.29 \pm 0.16 \mu\text{g L}^{-1}$ ^[44]) as well as with those recorded from Antarctic regions ($0.25 \pm 0.16 \mu\text{g L}^{-1}$ and $0.45 \pm 0.10 \mu\text{g L}^{-1}$).^[46,47] They were lower, up to one order of magnitude, than those found in the Marseilles coastal area.^[15] Concerning PAHs, when taking into account only the compounds in common (i.e. 14 parent PAHs), particulate PAH concentrations in marine waters ($2.90 \pm 1.34 \text{ ng L}^{-1}$) were of the same order of magnitude as in Antarctic pristine waters ($3.97 \pm 2.03 \text{ ng L}^{-1}$ and $3.60 \pm 0.81 \text{ ng L}^{-1}$),

whereas dissolved PAH concentrations ($20.70 \pm 8.56 \text{ ng L}^{-1}$) were one order of magnitude higher than in Antarctic waters ($1.70 \pm 0.63 \text{ ng L}^{-1}$ and $2.42 \pm 0.27 \text{ ng L}^{-1}$).^[46,47] Further, when considering all PAH compounds (parents + alkylated homologues), particulate and dissolved PAH concentrations found here in marine waters were of the same order of magnitude as those recorded in the Marseille coastal area, which is considered at a global scale as moderately to highly contaminated by hydrocarbons.^[12,15] Hence, hydrocarbon concentrations measured here in the La Saline reef ecosystem, especially PAH concentrations, reached higher values than those found in pristine areas, stressing the anthropogenic impact in this tropical ecosystem.

In the present work, we found that dissolved AHs and particulate PAHs were significantly higher in inland waters than in marine waters and that they were significantly higher in the southern part (particulate PAHs) or in the northern part (dissolved AHs) of the fore reef (Table 2; Fig. 3). This highlights the uncoupling of the dynamics between these two hydrocarbon classes. Further, particulate PAHs were positively correlated with DOC concentrations (especially in rivers), which is in line with the results of Zheng et al.,^[48] who revealed that soil organic carbon content is closely linked to soil-bound PAH transport during rainfall runoff events. In addition, they were negatively correlated with salinity (Table 3), which implied quite conservative behaviour of the particulate PAHs from inland to marine waters. Therefore, in the present study, the spatial distribution of particulate PAHs allowed tracking of inland intrusions in fore reef waters.

Biogenic v. anthropogenic hydrocarbon signatures

The simultaneous analysis of AH and PAH molecular profiles may reveal complementary information for a better comprehensive assessment of various natural and anthropogenic inputs.^[10,12] In the present study, particulate AHs were mainly of biogenic origin. The short *n*-alkanes with odd numbers of carbons (*n*-C₁₅–*n*-C₁₇) are indicative of planktonic contributions and high in situ primary production^[49,50] whereas the heavy odd-numbered ones (*n*-C₂₇–*n*-C₃₁) are indicative of higher plant waxes from continental inputs^[51]; *n*-C₂₆ is more related with bacteria.^[52] In addition, the significant positive correlation between particulate AH and Chl-*a* concentrations (shown in Table 3a) associated with the substantial biogenic signatures of AH molecular profiles underscored the high primary production (or phytoplanktonic biomass) taking place in these sites. Nevertheless, it is worth noting that the high particulate AH concentrations recorded especially at H-R and 3B-R attested of the eutrophication of inland waters, which are supplied in nutrients derived from agricultural activities.^[20] Further, we observed marked differences in particulate AH molecular profiles between inland waters (rather bimodal distribution enriched in *n*-C₁₇ and *n*-C₂₉) and oceanic reference waters (monomodal distribution enriched in *n*-C₁₅). Consequently, the intermediate distributions found in brackish SG-OH, LG 1–4 and H-pass sites clearly originated from the mixing of these two water bodies, whose proportions were reflected by salinity values. The situation with 3B-R was singular because it was also a brackish environment but contained particulate AH concentrations that were excessively high and dominated by *n*-C₁₅, as in oceanic reference waters. One can make the assumption that (i) the Trois-Bassins River and the reef flat are not subject to the same dynamics in terms of water-body renewal and that opportunistic brackish-water-adapted

phytoplankton species enriched in *n*-C₁₅ could proliferate; or (ii) the marine phytoplankton can adapt to salinity fluctuations.^[53] However, complementary studies are required to clarify the phytoplankton taxonomic composition and distribution in this ecosystem. Concerning the fore reef area, inland water intrusions at the surface, revealed by the strong relationship between salinity and Si, was supported by the significant shift in particulate AH concentrations and molecular profiles from 0.1- to 20-m depth (Fig. 6). The concentration and relative abundance of *n*-C₁₅ (dominant in marine waters) increased with depth whereas the relative abundance of *n*-C₁₇ (dominant in inland waters) decreased. One can assume that freshwater-adapted phytoplankton could die when arriving in the seawater (salt) matrix.^[54]

Dissolved AHs originated from both biogenic and anthropogenic inputs. On one hand, *n*-C₁₈ and *n*-C₂₁–*n*-C₃₆ even-carbon-numbered *n*-alkanes predominance came from direct microorganism contribution (bacteria, fungi, yeast) and from their action on algal detritus.^[55] In addition, the predominance of *n*-C₁₅ recorded in some dissolved samples, especially at 3B-R, may come from phytoplankton lysis (with regard to the corresponding particulate profiles) or the presence of small-sized phytoplankton cells (picophytoplankton), which would support the hypothesis of a particular phytoplankton taxonomic composition at this site. On the other hand, the high relative abundance percentages in the *n*-C₂₁–*n*-C₃₆ range along with a lack of even- or odd-*n*-alkane predominance, especially in basaltic groundwater and harbour areas (BLG-TE, SG-HD, SG-OH), stressed petroleum inputs^[10,56] probably originated from harbour and agricultural activities. An additional fingerprint of degraded petroleum, UCM, was evident in the fore reef (FR-2 10 m).^[37]

Concerning PAH molecular profiles, the main feature was the dominance of two to three-ring compounds, with a high proportion of alkylated homologues in both the dissolved and particulate phases as well as in the different water bodies (including oceanic waters) (Fig. 7). This homogeneity between the dissolved and particulate phases revealed a partitioning equilibrium of the distribution like that which occurs in natural waters.^[57] This partitioning was illustrated by the significant negative correlations between dissolved and particulate PAHs (Table 3). Moreover, the molecular homogeneity between the different water bodies emphasised that all sites were affected by inputs of the same nature. These two- to three-ring PAHs and their alkylated derivatives may be of anthropogenic origin but also of biogenic origin. Considering their anthropogenic nature, they would reflect unburned fossil fuel inputs (i.e. petrogenic origin^[58]) from agricultural activities, shipping traffic and vehicle exhausts, and transported in the marine environment through atmospheric deposition and run-off (strong rainfall events occurred during the study period). Nevertheless, this petroleum residue signature was only present in a few AH molecular profiles (basaltic groundwater, harbour areas, fore reef FR-2). Therefore, a biogenic source for these LMW PAHs may be also hypothesised. Indeed, several works have shown that PAHs (including LMW compounds) are biologically produced in soils, especially tropical ones, from woody plants, termites or microbial transformation of organic matter.^[59–63] These biological PAHs could then enter the marine waters via the atmosphere, runoff, rivers or groundwaters.^[63] The soils of La Reunion are typically tropical and contain a large number of termites,^[64] which would favour a soil-derived biological source of PAHs in this ecosystem. In addition, the positive correlation between particulate PAHs and Chl-*a* concentrations

may support the hypothesis of an in situ aquatic biological source of PAHs, as already demonstrated by Andelman and Suess^[65] and suggested by Nizzetto et al.^[63]

Albeit not dominant, HMW particulate PAHs were mainly present in the samples in which we observed a petroleum residue signature in the AH molecular profiles (basaltic groundwater or back reef, harbour areas, fore reef FR-2). The presence of these HMW PAHs associated with AH petroleum residue signatures is a sign of anthropogenic inputs of hydrocarbons derived from combustion processes (pyrogenic origin).

Conclusions

The present study allowed the characterisation of salinity, biogeochemical parameter and hydrocarbon (AHs and PAHs) content of groundwaters, rivers, back reef, reef flat and oceanic waters from the La Saline fringing reef environment during the rainy period. Results underscored that anthropised freshwaters from inland sites flowed mainly in surface waters and in the southern part of the fore reef area. The La Saline fringing reef ecosystem was moderately to highly contaminated with hydrocarbons. We found that particulate AHs were of biogenic (plankton and bacteria) origin although concentrations recorded in the Hermitage River and Trois-Bassins River attested of the eutrophication of inland waters from human activities. Dissolved AHs displayed both biogenic and petroleum residue signatures. PAHs, however, could be of anthropogenic origin, essentially derived from petrogenic inputs associated with organic matter and probably coming from runoff. The biogenic origin of PAHs can reasonably be assumed, in particular a biological production of LMW compound in soils that could be introduced in inland and marine waters. Clear spatial variabilities were observed among particulate and dissolved AH and PAH concentrations, particulate PAHs proving to be an indicator of inland water intrusions in fore reef waters. Nevertheless, because no significant spatial differences were identified in the degradation of coral formations in reef waters (P. Cuet, L. Bigot and J. Turquet, unpubl. data), the ecological state of the reef failed to be linked with the hydrocarbon content. The latter may contribute, however, to this degradation because hydrocarbon-related anthropogenic pressure was recorded in the northern part (dissolved AHs profiles, presence of UCM) and in the southern part of the reef (higher particulate PAH concentrations than those recorded in the northern part).

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