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ABSTRACT

This study aimed to identify ocean- and land-based sources of nutrients to the coral reef communities surrounding the Southern Caribbean islands Aruba, Bonaire, and Curaçao (ABC islands). The composition of water masses around these islands were assessed to depths up to 300 m and three distinct overlying water masses were identified, separated by mixing zones. A fluctuating pycnocline separating surface from deeper (>~50 m) water indicated the presence of internal waves. Nutrient profiles were typical of tropical waters with oligotrophic waters occurring above the pycnocline and a deep chlorophyll-*a* maximum (DCM) just below it (~65 m). Concentrations of dissolved nutrients differed among islands. Inorganic nitrogen (DIN) and phosphate concentrations were respectively lowest around Bonaire and Curaçao. The spatial distribution of chlorophyll-*a* (indicative of phytoplankton biomass), rather than nutrient concentrations, suggested the presence of higher-than-average nutrient concentrations in islands with higher population densities and near urbanized/industrial areas.

1. Introduction

The Caribbean Sea is generally characterized by a distinct stratification of vertically separated water masses whose hydrodynamics, distribution, and composition influence the functioning and composition of nearby coral reef systems (e.g., De'ath and Fabricius, 2010; Fabricius, 2005; Szmant, 2002; Wiedenmann et al., 2013). The upper water layer is comprised of Caribbean Surface Water (CSW) and has a thickness of maximum 100 m and a salinity <35.5 (Casanova-Masjoan et al., 2018; Hernández-Guerra and Joyce, 2000). The CSW layer is well mixed across its depth range and consists of North Atlantic Surface Water mixed with rain and freshwater originating from the South American continent, including the Amazon and Orinoco rivers. Beneath this layer lies the North Atlantic Subtropical Under-Water (SUW) originating from the central tropical Atlantic. SUW is characterized by a vertical salinity maximum (exceeding 37) generally found between depths of 100 and 175 m depending on location in the Caribbean (Correa-Ramirez et al., 2019; Metcalf, 1976; Qu et al., 2016). CSW is generally characterized by lower nitrate concentrations than the SUW (CSW: <1.5 and SUW: 1–8 μmol/L, Cervantes-Díaz et al., 2022; Corredor and Morell, 2001). Both CSW and SUW, including the mixing zone between them, influence coastal marine organisms including calcifying corals that are abundant in shallow waters (<60 m) and of which some can occur to depths up to 150 m in Aruba, Bonaire, and Curaçao, i.e., the ABC islands (Frade et al., 2019). Below the SUW, water masses with Atlantic and Antarctic origins (e.g., western North Atlantic Central Water (wNACW), Antarctic Intermediate Water (AAIW)) are found that reach to the bottom and are characterized by specific salinities (35.6–36.7 and 33.8–34.5,

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respectively), temperatures (~8–19 and ~3–5 °C, respectively) and nutrient concentrations that are higher than those of the CSW and SUW (Cervantes-Díaz et al., 2022; Metcalf, 1976; Morrison and Nowlin, 1982).

In an area along the coast of South America roughly bounded by Trinidad in the East and Barranquilla (Colombia) in the West, seasonal upwelling often moves deep nutrient-rich waters towards the surface between December to March and in July (Astor et al., 2003; Castellanos et al., 2002; Correa-Ramirez et al., 2019; Rueda-Roa and Müller-Karger, 2013). Ekman transport causes these upwelled waters to move in a northern direction where they can reach the ABC islands, located <100 km from the South American continent (Bongaerts et al., 2015; Frade et al., 2019; Leichter et al., 2006). Such oceanic influences together with nutrient inputs of terrestrial origins (e.g., poorly, or non-treated domestic sewage, industrial waste) affect the biochemical composition of nearshore waters surrounding these Caribbean islands (DeGeorges et al., 2010; Suchley and Alvarez-Filip, 2018). Land-derived nutrients can also enter the islands' near-shore waters as direct discharge, run-off, and through submarine groundwater discharge (Lapointe et al., 1990; Moosdorf et al., 2015). Resulting nutrient influxes can occur as local and relatively short-lived (hours to days) events after heavy rains or as a more diffuse and chronic process when e.g., sewage infrastructure is permanently damaged (Häder et al., 2020; Wear and Thurber, 2015). Regardless of the mechanism, excess nutrients often alter the functioning of reef communities by benefitting fast-growing organisms such as fleshy algae that then outcompete slower growing organisms such as reef building corals (e.g., Adam et al., 2021; McCook, 1999; McManus and Polsenberg, 2004).

As on many other Caribbean islands, nutrient concentrations have been measured around the ABC islands at relatively shallow depths (<20 m, e.g., Den Haan et al., 2016; Gast et al., 1999; Lapointe and Mallin, 2011; Slijkerman et al., 2014; Van Duyl and Gast, 2001). However, little is known to what degree large-scale intra- and inter-island differences in water composition, including nutrient concentrations, exist, and whether they result from the influx of offshore waterbodies, upwelling and/or terrestrial sources. Such geographical differences in water chemistry composition likely account for some of the spatial differences in reef community composition. In short, it is currently not well known if and to what degree spatial differences in nutrient regimes exist in the ABC islands' offshore waters and, if present, if such spatial differences result from underlying natural (e.g., island mass effects, upwelling) or anthropogenic influences. This study strives to address this information gap by combining shipboard analyses of physical oceanographic parameters, nutrient concentrations, and isotopic signatures to describe the distribution and stratification of water masses surrounding the ABC islands.

2. Studied system and methods

2.1. Island characteristics

The Caribbean islands of Aruba (179 km^2, 600 persons km^{-2} on

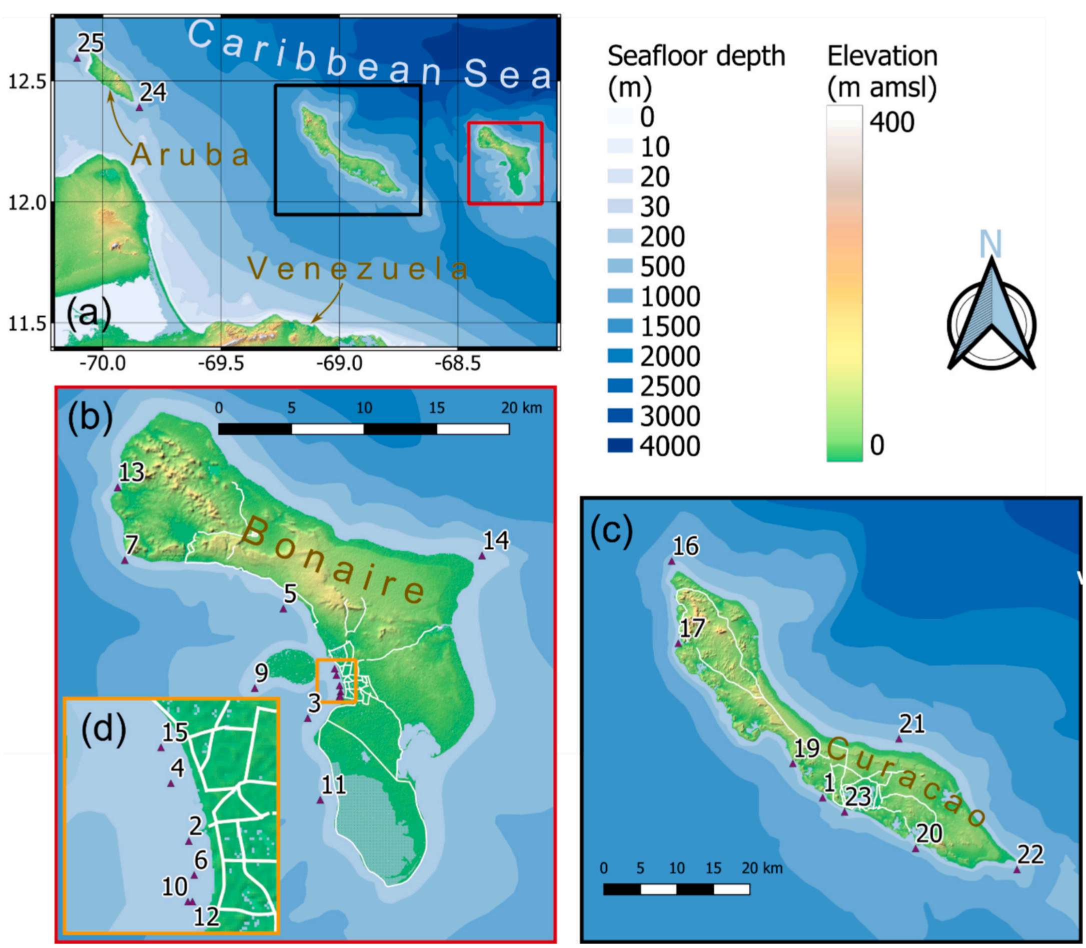

Fig. 1. (a) Location of the ABC Islands with sites surveyed in Aruba (a) and maps with sites surveyed at Curaçao (b), and Bonaire (c) with inset indicating stations in the Kralendijk urban area (d). Note that location 12 is not shown as it overlaps with location 8. Main roads are indicated by white lines, the Bonaire salt works are indicated by the light shaded area (data © OpenStreetMap contributors, www.openstreetmap.org). Elevations based on Shuttle Radar Topography Mission data (SRTM) available from the U.S. Geological Survey. AMSL stands for "above mean sea level".

average in 2022, (CBS-AU, 2022)), Bonaire (287 km^2, 72 persons km^{-2} on average in 2020, (CBS-NL, 2020)), and Curaçao (444 km^2, 335 persons km^{-2} on average in 2021, (CBS-CW, 2023)) are often referred to as the ABC Islands (Fig. 1). They are the three western-most islands of the Aruba-La Blanquila chain located 27 (Aruba) to 86 km (Bonaire) north of Venezuela. The ABC islands are generally hilly on their western side, but otherwise relatively flat with maximum elevations of 189 m (Aruba), 241 m (Bonaire), and 375 m (Curaçao). They harbor small beaches and inland bays that formed when former river valleys flooded during sea level rises during the Holocene. Sandy beaches are more pronounced in Aruba and in contrast to the other islands, Aruba's southwestern side is largely flanked by a lagoon.

The geology and hydrogeology of the ABC islands are somewhat comparable. Their coasts are to various degrees comprised of partially karstified, permeable limestone terraces bordering poorly permeable volcanic rock at the islands' centers (Westermann, 1949). Based on limited knowledge of the functioning of karstic aquifers in the ABC islands, groundwater discharge through conduits is expected along the islands' shores and seafloor (Abtmaier, 1978; Hummelinck, 1943; van Sambeek et al., 2000). Groundwater in all islands is slightly brackish due to high evapotranspiration, seawater intrusion due to tidal pumping, and sea spray (van Sambeek et al., 2000). Widespread contamination of groundwater has occurred, especially in built-up areas due to the presence of leaking septic tanks and cesspits (Arboleda and Peachey, 2016; van Sambeek et al., 2000).

2.2. Climate

Mean monthly sea water temperatures range between 27 °C in March and 29 °C in September/October (Skirving et al., 2020). Rainfall foremost occurs between September to January but is highly variable among years and across each island (DMA, 2019; MDC, 2023). Average annual rainfall is lowest in Aruba (470 mm) followed by Bonaire (490 mm), and Curaçao (550 mm, Schmutz et al., 2017). All islands experience sustained moderate easterly trade wind resulting in waves up to 3.5 m along the windward (northern and eastern) shores of the islands throughout the year, while the leeward (southern and western) shores of the islands experience wave heights of $<$1 m (Van Duyl, 1985). The ABC islands lie just outside the hurricane belt.

2.3. Local currents

Aruba is, contrary to Bonaire and Curaçao, not separated from the Venezuelan continent by the Bonaire Basin, and part of the Venezuelan continental flat (Van den Oever, 2000). The maximum water depth between Aruba and the Venezuelan peninsula is $<$190 m but around 1500 m for the oceanic islands Curaçao and Bonaire. The Caribbean Current, forced by the eastern trade winds, is the major ocean current influencing the ABC islands (Wüst, 1963). It transports Atlantic Ocean water through the Grenada, St. Vincent, and St. Lucia Passages in a westward direction along the coast of South America towards the Gulf Stream (Centurioni and Niiler, 2003). While moving westward along the South American continent, the Caribbean Current receives an influx of fresh water from various rivers, including the Amazon and the Orinoco (Chérubin and Richardson, 2007). While highly variable, the overall mean velocity of the Caribbean Current near the ABC islands is estimated at 70 cm/s with higher values reported up to 123 cm/s (Fratantoni, 2001; Gyory et al., 2009).

3. General data collection

All data were collected between January 25 and February 2, 2018 from the oceanographic research vessel *Pelagia* as part of the Netherlands Initiative Changing Oceans (NICO) expedition (Leg 3, expedition number 64PE430). The water column was sampled at 8 sites in Bonaire and Curaçao and 2 sites in Aruba to produce a biochemical and physical descriptions of water bodies located ~250 to 1500 m offshore (farther in Aruba due to shallow bathymetry) and across their entire depth range (range: 60–300 m; Fig. 1). The site near Bonaire's capital Kralendijk (Fig. 1d) encompassed a zone of ~2.5 km along shore where 6 additional stations were sampled either late afternoon (stations 6, 10) or at sunrise (stations 4, 8, 12, 15, note that station 8 and 12 are overlapping stations in Fig. 1). Given their proximity to one another, these additional stations were, together with station 2 (sampled late afternoon), considered as one "site" to investigate the presence of short-term changes in water quality and stratification between January 26 (3:20 pm, local time) to January 30 (6:43 am), 2018. The 6 additional stations were not used for inter-island comparisons in water column characteristics.

3.1. Physical characteristics of the water column

At each station the potential temperature, salinity, water density, light transmission, and chlorophyll-*a* fluorescence were measured across the entire water column by lowering a CTD package from the surface to a few meters above the seafloor. The CTD package comprised a Seabird CTD (SBE9plus), a SBE11plusV2 deck unit, a water sampler carousel (SBE32) connected to a pump (SBE5T), a thermometer (SBE3plus), a conductivity sensor (SBE4), a dissolved oxygen sensor (SBE43), a fluorometer (Chelsea Aquatracka MKIII), a transmissometer (Wetlabs C-Star, 25 cm path length, 650 nm), and an in water photosynthetic active radiation (PAR) sensor that was used in combination with a ship based PAR sensor (Satlantic logarithmic) to determine light extinction with increasing depth. pH was measured in water samples (see below) using a Schott Gerate CG840 pH meter and a Schott blue line 15 electrode that were calibrated using three buffer solutions of pH = 4.01, 7.00 and 10.00 (Certipur). The density of seawater was calculated using the TEOS-10 method (Pawlowicz, 2010).

3.2. Water characteristics

At each site, water samples from different depths were analyzed for nutrient concentrations (PO_4, NH_4, NO_2 and NO_x, i.e., NO_3 and NO_2 combined), ^{222}Rn (indicative of groundwater influx) and ^{18}O and ^2H (indicative of the water's geographic origin). Water samples were collected at depths between 3 and 59 to 280 m using a Rosette sampling frame with 24 twelve-liter Niskin sampling bottles (Ocean Test Equipment) that were mounted on the CTD package. Before taking each water sample, Niskin bottles were flushed at each sampling depth for at least 1 min to ensure a representative in-situ sample was collected.

To determine the concentration of ^{222}Rn isotopes, a sample was obtained by placing a glass bottle (597 mL) inside a larger glass container overflowing with water from the Niskin bottle containing seawater of a specific depth. The bottle was then capped underwater to prevent radon loss to the atmosphere. The sample was equilibrated with a known volume of air in a closed loop system for 30 min, followed by three measurement cycles lasting 30 min each. Radon activity was quantified using alpha-spectroscopy (SARAD EQF3220) capable of detecting radon concentrations $>$0.02 Bq/L (SARAD GmbH, 2007). Water samples to determine the concentration of stable water isotopes (^{18}O and ^2H) were collected separately in glass vials that were stored at 4 °C on board for analysis at BGR, Hannover, Germany using a cavity ring-down laser spectrometer (PICARRO L2120-i). Reported values represent the mean of at least four individual measurements from each sample. Raw data were checked for organic contamination using ChemCorrect and corrected for memory effects, drift, and normalized to the VSMOW/SLAP scale (Nelson, 2000). All values are given in delta notation per mil (‰) vs. V-SMOW (Vienna Standard Mean Ocean Water). Reproducibility, measured as the standard deviation of a quality control standard, was better than 0.8 ‰ and 0.20 ‰ for δ^2H and $\delta^{18}O$, respectively.

On board, subsamples from the Niskin bottles were collected for nutrient analyses using 60 ml HDPE syringes after three rinses with the sampled water. Nutrient samples were filtered (pore size: 0.8 followed by 0.2 μm) and filtrates were stored in three times pre-rinsed glass vials in the dark at 4 °C until they were analyzed on board within 12 h. Nutrient concentrations were determined using a Gas Segmented Continuous Flow Analyzer (QuAAtro) using individual channels for PO_4, NH_4, NO_2 and NO_x following the GO-SHIP protocol (Hydes et al., 2010). Stock-standards low nutrient seawater (LNSW from OSIL batch LNS 21) with the same salinity as the samples were diluted in filtered (0.2 μm) seawater and used for calibration prior to all measurements (Hydes et al., 2010). Detection limits for PO_4, NH_4, NO_3, and NO_2 were 0.02, 0.04, 0.015, and 0.001 μmol/L, respectively. Precision among repeated measurements on the same sample was high and variation among replicate samples ranged between 0.7 and 1.2 %. All nutrient analyses were conducted in a containerized temperature-controlled laboratory on board the RV Pelagia within 12 h after sampling. Average DIN: DIP ratios were calculated for each sample by dividing the concentration of dissolved inorganic nitrogen (DIN, i.e. NH_4 and NO_x) by the concentration of dissolved inorganic phosphate (DIP, i.e. PO_4). The salinity of the surface water (~3–5 m depth) was constantly measured while the Pelagia was in transit using a shipboard CTD (Aqua Flow system, Seabird SBE 21). Where relevant, nutrient concentrations and ratios are reported as means ± SD. SPSS 28 (IBM Corp., 2021) was used to assess potential differences among sampling locations and depths.

4. Results

4.1. General water column characteristics

Depth profiles for salinity (S), potential temperature (θ), and density (σ_θ) are shown in Fig. 2 for each island. On Bonaire and Curaçao (Fig. 2a, b), a well-mixed ~50 m thick surface layer was observed with S and θ values mostly typical of CSW during the rainy season, i.e., ~36 and 27 °C. This water layer appeared slightly less thick in Aruba, where only two sites were sampled (Fig. 2c). Below the CSW, a zone occurred where salinity concentrations increased with depth, indicating the presence of a halocline. This zone ended around 80 m on Bonaire and Curaçao, and at ~50 m depth in Aruba. Below these depths, water layer characteristics approached values typically reported for SUW, i.e., S = ~37 and θ = 22 °C. The depth of the top of the shallow pycnocline, i.e., the transition zone with the greatest density gradient between the well-mixed CSW and underlying SUW waters, defined as the depth where the density increases by >0.05 kg/m^3 over a 1 m depth interval, varied depending on sampling location and time. The pycnocline occurred between ~33 and 60 m depth in Bonaire, between ~43 and 68 m in Curaçao, and between ~21 and 45 m in Aruba (Fig. 2). The decline in S and θ with depth in the SUW layer suggests mechanical turbulent mixing with an underlying layer starting just below 300 m, most likely wNACW based on the physical definitions for these water masses from nearby Colombia (wNACW: ~36, ~13 °C, Correa-Ramirez et al., 2019).

Differences in the depth profiles of salinity, temperature, and density measured during our study appeared more pronounced among rather than within islands, with the exception of station 14, located on the northeastern side of Bonaire (Figs. 1, 2a). The salinity of the surface water at this station was relatively low (~35.45), and its halocline was characterized by relatively high temperatures (up to 28 °C, Fig. 2a). In the potential temperature-salinity diagram (Fig. 3) station 14 (the only sampled site on Bonaire's windward shore) deviated from all other stations in Bonaire and other islands whose water masses showed a comparable relationship between potential temperature and salinity. Stations at the exposed tips (16, 22, 24) and one exposed station along Bonaire's leeward coast (11) are also shown in Fig. 3 as open symbols (similar to station 14) to visualize potential differences between stations along the islands' wind- and leeward coasts. Somewhat similar to station 14, the average salinity in the surface layer (i.e., <50 m) in Aruba was higher (though the temperature lower) compared to the other two islands (Fig. 2). A general increase in surface water salinity from east (Bonaire) to west (Aruba) was also found from continuous shipboard measurements (~3–5 m depth, Fig. 4) and likely indicates a decreasing influence of freshwater input from South American rivers when moving in a westerly direction in the area under investigation.

4.2. Isotopes

No significant influxes of terrestrial groundwater were observed as the concentration of ^{222}Radon isotopes in water samples along Curaçao and Bonaire between 4 and 250 m depth were all below the detection limit. δ^2H and $\delta^{18}O$ values (Fig. 5) indicated depth specific differences in isotopic enrichment relative to V-SMOW ($\delta^2H = 0.0$ ‰; $\delta^{18}O = 0.0$ ‰). Increases in δ^2H and $\delta^{18}O$ coincided with increases in salinity (Fig. 5a, b) and are typical for tropical environments with high evaporation rates. Surface layer waters were characterized by salinities as low as 35.60 and by isotopic values of 5 ‰ < δ^2H < 7 ‰ and 0.6 ‰ < $\delta^{18}O$ < 1 ‰ (cf. Fig. 5a, b). With increasing depth surface water often became mixed with SUW resulting in salinities up to 36.95 and isotopic values of 6 ‰ < δ^2H < 8 ‰ and 0.8 ‰ < $\delta^{18}O$ < 1.1 ‰. SUW also mixed with an underlying water mass and based on extrapolation, this deeper water was characterized by salinities <35.85, and isotopic values of δ^2H < 3.5 ‰, and $\delta^{18}O$ < 0.55 ‰ suggesting mixing of SUW with deeper Atlantic waters (e.g., wNACW, Fig. 3).

For comparison, two known relationships between $\delta^{18}O$ and salinity from elsewhere in the Caribbean Sea have been plotted in Fig. 5b, one from Puerto Rico (Watanabe et al., 2001) and one from Venezuela (McConnell et al., 2009). Only the seawater in the mixed surface layer and near the halocline at station 12 deviated from the general patterns in Caribbean water stratification described for Puerto Rico, Venezuela, and all other stations included in this study. Station 12 was characterized by relatively low $\delta^{18}O$ values that showed no correlation with salinity, and its average δ^2H value was relatively high (Fig. 5). We are not aware of any process that would explain this observation, though this site was close to a man-made canal system that could have affected our observations at this station.

4.3. Nutrient concentrations

The distribution of nutrients showed a relatively consistent general pattern across depth among all sampled stations (Table 1, Fig. 6). Average NO_3 and PO_4 concentrations were lowest and relatively constant within the mixed surface layer (~0.15 and ~0.03 μmol/L, respectively). Below the mixed surface layer (i.e., >~50 m), NO_3 and PO_4 concentrations increased (linearly) with depth over the entire depth range sampled (Fig. 6). NH_4 concentrations were relatively stable across depth (Table 1, Fig. 6) though higher concentrations of NH_4 were observed locally in the mixed surface layer (i.e., station 7 in Bonaire, 0.479 μmol/L, not shown in Fig. 6a). NH_4 concentrations decreased slightly below ~70 m to average concentrations of ≤0.09 μmol/L (Fig. 6). NO_2 concentrations were low at the surface (~0.02 μmol/L) and increased with depth to 60–70 m (~0.08 μmol/L) after which they declined towards greater depths and became stable at depths greater than ~150 m (~0.01 μmol/L, Fig. 6). The increased abundance of NO_2 around 60–70 m was most pronounced in Bonaire. In the surface layer (<50 m), average PO_4 concentrations were lower in Curaçao compared to Bonaire (Dunn-Test, $p < 0.05$), NH_4 concentrations in Curaçao were lower compared to Bonaire and Aruba (Dunn-Test, $p < 0.01$), whereas NO_3 and NO_2 concentrations were higher in Aruba compared to Curaçao and Bonaire (Dunn-Test, $p < 0.01$, Table 1). Average DIN:DIP ratios in the islands' surface waters (<50 m depth) were lowest in Bonaire (8.1 ± 4.9), and different from those in Curaçao (21.3 ± 27.4) and Aruba (24.8 ± 10.3, Dunn-Test, $p < 0.05$). DIN:DIP ratios in Bonaire increased to values of ~18 with depth (to ~65 m), similar to values observed in shallower waters in Curaçao and Aruba. Below ~65 m DIN:DIP ratios were constant in all islands across the depth range sampled (i.e., in the

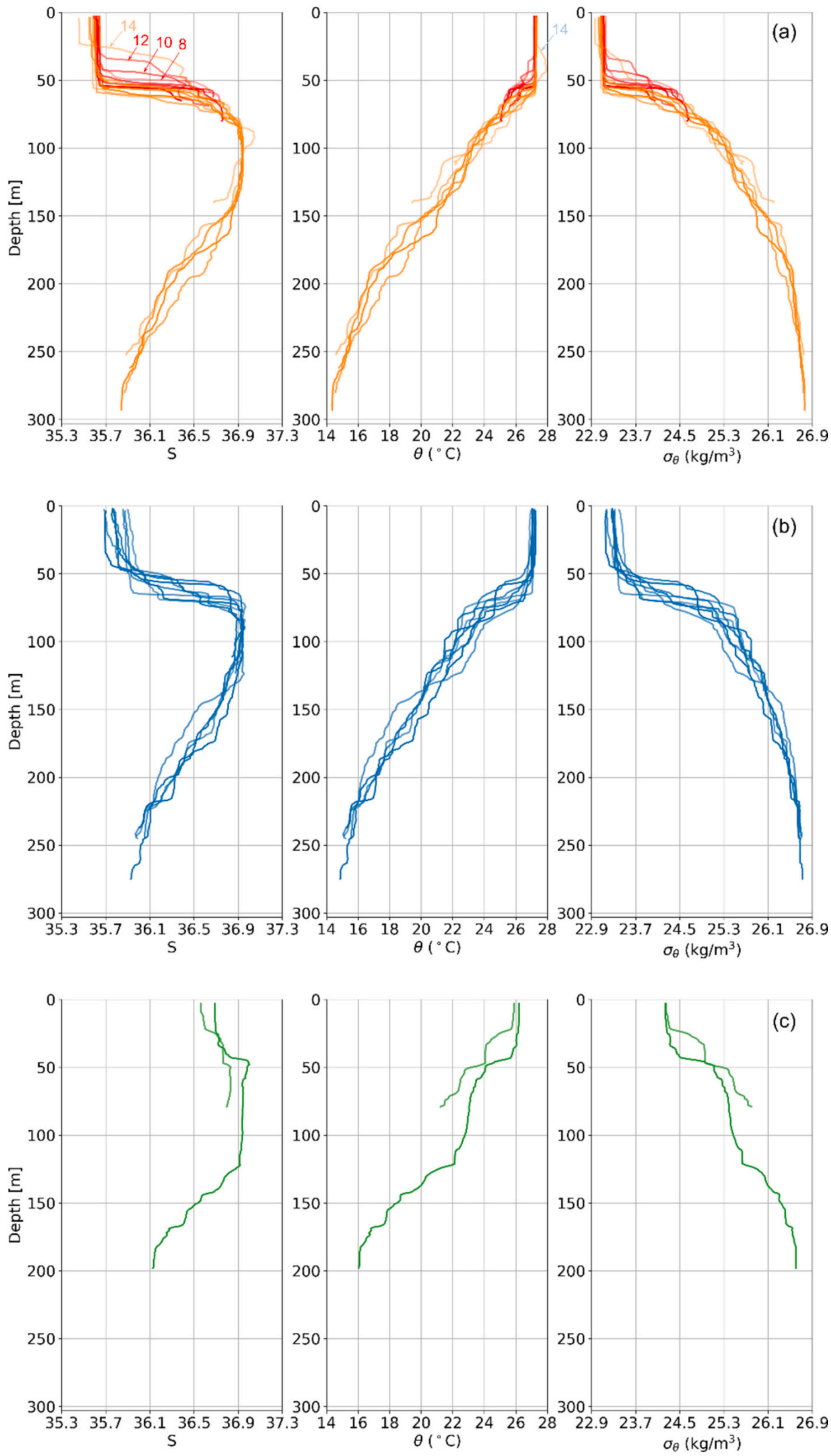

Fig. 2. Salinity (S), potential temperature (θ), and density ($\sigma\theta$) of water masses sampled using CTD casts at (a) Bonaire, (b) Curaçao, and (c) Aruba. Only the first 300 m are shown, values represent averages of 1 m depth intervals. The numbers of the stations that are discussed in the text are indicated in (a). Arrows with numbers point to the lines of the stations near Kralendijk (8, 10 and 12) that showed the largest vertical shift in the salinity profile and to station 14, which is discussed in detail in the main text.

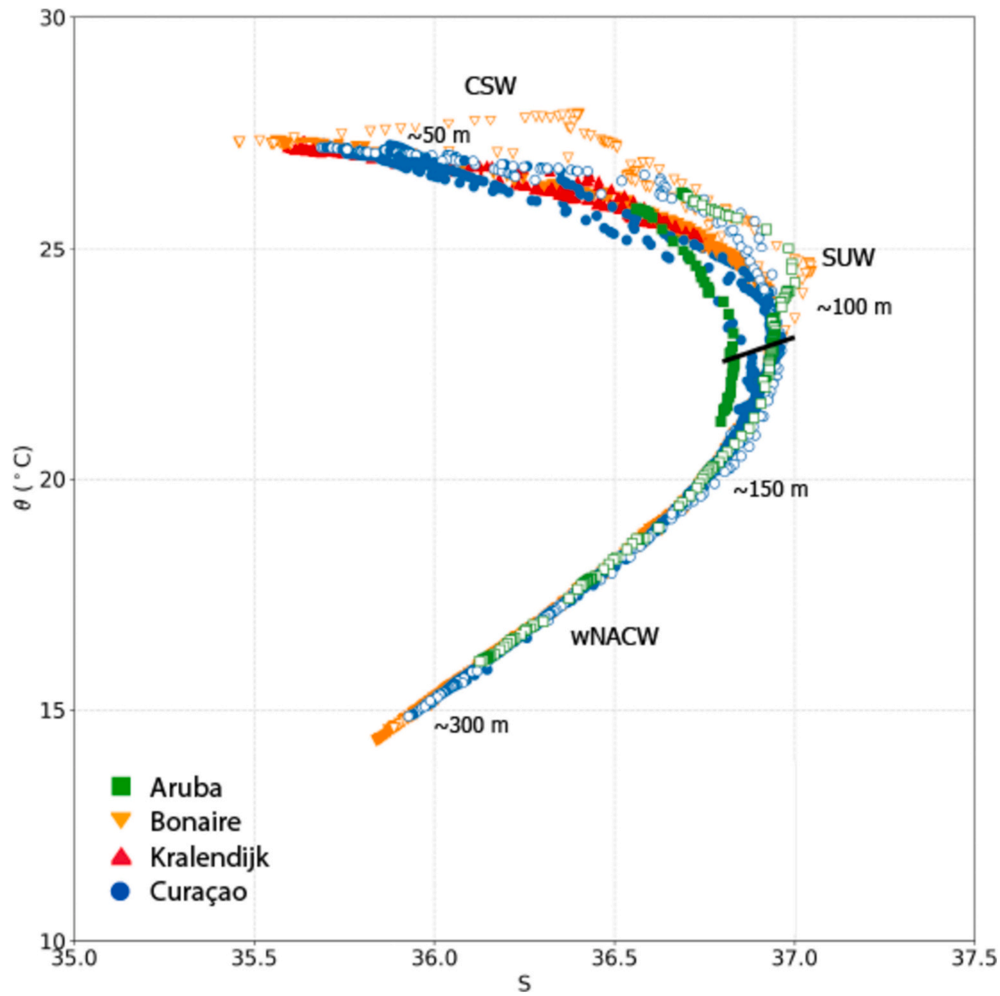

Fig. 3. Potential temperature (θ) versus salinity (S) diagram. Stations on the leeward side of the islands are shown as closed symbols and on the windward side and more exposed sites as open symbols. The presence of the Caribbean Surface Water (CSW), North Atlantic Subtropical Under-Water (SUW), and western North Atlantic Central Waters (wNACW) is indicated by their abbreviations. The black line is the $\sigma_\theta = 25.4$ kg/m^3 isopycnal between $36.8 \leq S \leq 37$ along which Subtropical Under Water sinks in deeper waters from the central Atlantic (Hernández-Guerra and Joyce, 2000).

SUW, Fig. 6). Across the entire dataset, NO_3 and PO_4 concentrations were highly correlated (Pearson's r: 0.99, $p < 0.01$, $n = 142$). Significant general correlations among other nutrient concentrations were negative and less pronounced (PO_4 – NH_4: Pearson's r: −0.32, $p < 0.01$, NO_3 – NH_4: Pearson's r: −0.26, $p < 0.01$, n = 142–144).

The average daytime DIN concentration in Bonaire (0.258 ± 0.207) was not different (Mann-Whitney *U* Test, $p = 0.77$) compared to that of the surface waters around the more densely populated island Curaçao (0.262 ± 0.187 μmol/L). The most densely populated island, Aruba, had the highest average DIN concentrations in its surface waters (Table 1, Dunn-Test, $p < 0.05$), whereas average PO_4 concentrations were lowest in Curaçao (Table 1, Dunn-Test, $p < 0.05$). When exposed stations, i.e., those exposed to the trade wind driven waves (stations 14, 16, 21, 22, 24), were compared to all other stations along the islands' leeward shores no differences in nutrient concentrations for the 3 depth zones (Table 1) could be detected (Mann-Whitney *U* Test, $p > 0.31$).

4.4. Chlorophyll-a

Chlorophyll-*a* (Chl-*a*) distributions across depth differed among islands (Fig. 7). In Bonaire, most Chl-*a* profiles showed a gradual increase with depth in the mixed surface layer followed by a steep increase below the top of the pycnocline, i.e., around ~60 m, representing the deep chlorophyll-*a* maximum (DCM, Fig. 7a). The DCM coincided with the highest concentrations of NO_2 across the depth range sampled (Fig. 6). Below the DCM, Chl-*a* concentrations decreased with depth, to <0.2 μg/L below 100 m depth (Fig. 7). Because the DCM occurred near the end of euphotic zone (around ~63 m), light limitation at depths greater than ~63 m likely caused the decrease in Chl-*a* concentrations below the DCM. Average Chl-*a* concentrations in the mixed surface layer are higher in Curaçao and Aruba compared to Bonaire (Dunn-Test, $p < 0.05$). This difference was foremost caused by a high abundance of Chl-*a* between depths of 0 to ~50 m at some of Curaçao's leeward side, e.g., stations 19 and 23 which correspond to respectively a watershed harboring the island's landfill and the opening of the Schottegat where Curaçao's capital, harbor, and refinery are located (Sandin et al., 2022). The DCM at these three sites was also less pronounced (Fig. 7b). The general high abundance of Chl-*a* measured at the 2 stations in Aruba (Fig. 7c) is likely the result of the island's thinner mixed surface layer (Fig. 2c), caused by the island's shallow bathymetry (Fig. 1) or its closer proximity to upwelling areas along the South American mainland (Rueda-Roa and Müller-Karger, 2013).

Chl-*a* concentrations are often used to identify areas experiencing nutrient pollution, i.e., eutrophication. While threshold values are often debated, we assumed a conservative eutrophication threshold of 0.2 μg/L for tropical marine ecosystems (following e.g., Bell et al., 2014) to assess whether signs of eutrophication were present at certain stations. Based on this assumption, widespread eutrophication of the mixed

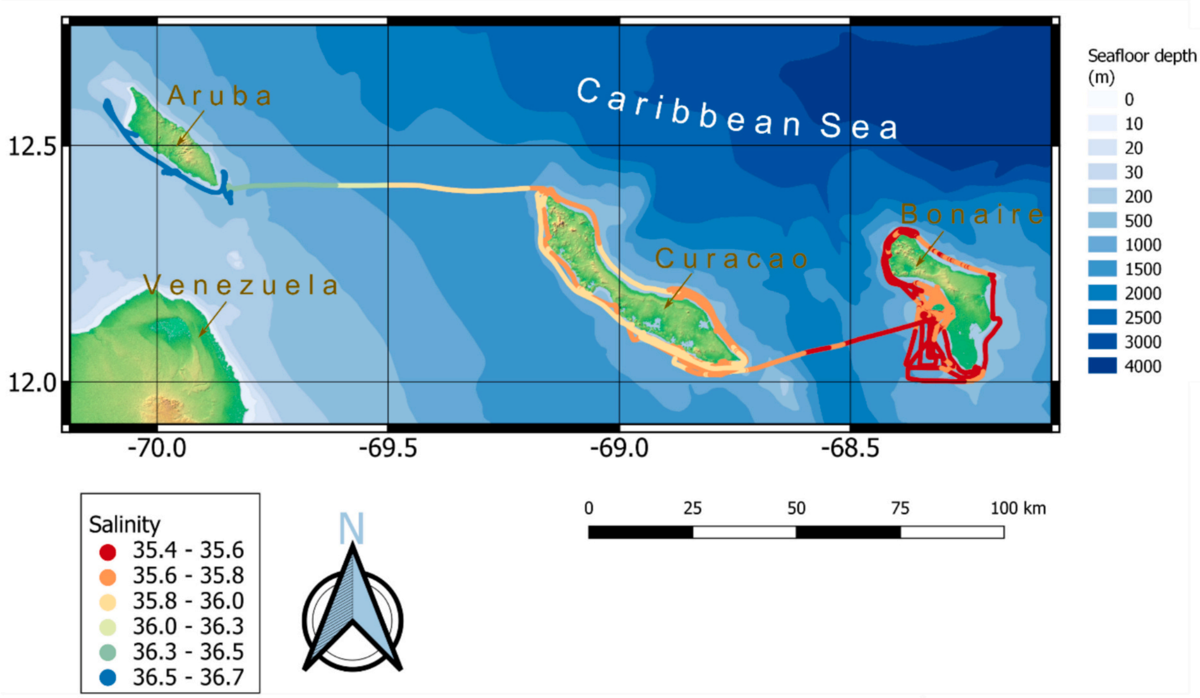

Fig. 4. Seawater salinity measured by the shipboard equipment of the R/V Pelagia between 28 January and 2 February 2018. Source of bathymetry data http://www.dcbd.nl/document/bathymetry-map-seas-surrounding-aruba-bonaire-and-Curaçao (accessed on 9 October 2018).

surface layer (CSW) was found, i.e., in Bonaire at stations 2, 3, 5, 6, 7, 10, 13 and 14, along the SW coast of Curaçao, from station 23 (outlet main harbor) downstream to stations 1, 19, 17, 16, and in Aruba (stations 24, 25, Fig. 7).

The limit of the photic zone, i.e., where sun light reaches 1 % of its value at the surface was on average deepest in Bonaire (63 m ± 8 SD) and decreased towards Curaçao (57 m ± 7 SD) and Aruba (47 m ± 11 SD) based on measurements taken during our cruise.

4.5. Spatio-temporal variation in water composition near Kralendijk

Based on repeated measurements taken in the mixed surface layer at nearby stations (all near Kralendijk, the capital of Bonaire, Fig. 1d), a simultaneous thinning of the mixed surface layer, upward movement of the thermocline and widening of the halocline was observed whereby the DCM followed the upward movement of the pycnocline (Fig. 8). The pycnocline rose from ~55 to ~34 m depth between January 26 (pm) and January 29 (am), followed by a drop of ~14 m on January 29 and 30 (Fig. 8). The upward movement of the pycnocline caused increases in Chl-*a* in shallower waters and likely also in nutrient concentrations as water from depths just below 50 m had higher nutrient concentrations (except NH_4^+) compared to shallower water masses at this location (Table 1).

5. Discussion

5.1. General water column characteristics around the ABC islands

The shallow waters (i.e., above the pycnocline) around the ABC islands had a relatively low salinity and high temperature (Fig. 2) typical of the westward flowing Caribbean current in this area (Johns et al., 2002). Beneath the surface layer, Subtropical Under-Water (SUW) was found, which was characterized as water with a salinity S > 37 along the 25.4 isopycnal in the θ-S diagram (Fig. 3). This pattern of stratification is consistent with observations for water of South Atlantic origin from the nearby coasts of Venezuela (Hernández-Guerra and Joyce, 2000) and Colombia (Correa-Ramirez et al., 2019). Spatial differences in water composition within and among islands were foremost evident in the surface layer (i.e., <~50 m) as data collected with CTD casts showed largely similar water for the SUW (e.g., the same θ-S pattern) around all islands. The presence of distinct mixing regimes based on the stable water isotope data (i.e., of surface water and SUW, and SUW and South Atlantic water, Fig. 5) was consistent with the presence of these three water types. While isotope studies to date have focused primarily on ^{18}O isotopes as a proxy for paleo-seawater conditions (Jentzen et al., 2018; McConnell et al., 2009), the clear depth dependent relationship between δ^2H and S (Fig. 5) suggests that ^2H could also be a suitable tracer for Atlantic waters in the Caribbean Sea in addition to other tracers like chlorinated fluorocarbons (Joyce et al., 2001).

5.2. Spatial variation in water mass composition and stratification

On the leeward side of Bonaire, the water column above the pycnocline was characterized by a uniform salinity and temperature (Fig. 2a). However, at the more exposed tips/sides of the island and particularly the windward, northern side, the surface waters, particularly station 14, showed an increased resemblance to the Caribbean Surface Water (CSW) found north of 13°N as indicated by the open symbols in the θ-S diagram (Fig. 3). To a lesser extent this was also the case for Curaçao suggesting that both islands are located near the southern boundary of the CSW. Locally higher salinities compared to typical values observed for CSW suggest that both islands are in close proximity to the Southern Caribbean Upwelling System (Torres et al., 2023). The systematic increase in salinity of the surface water towards the west around the islands confirms the presence of a salinity gradient in the southern Caribbean Sea caused by the decreasing influence of freshwater runoff from the South American continent, especially the resulting from the Orinoco River (Andrade and Barton, 2005; Chollett et al., 2012). This river's outflow is greatest near the end of the rainy season (Torres et al., 2023), i.e., during our cruise in January, and salinities increase is a westward direction due to horizontal and vertical mixing and by local air–sea fluxes (Jury, 2018; Müller-Karger et al.,

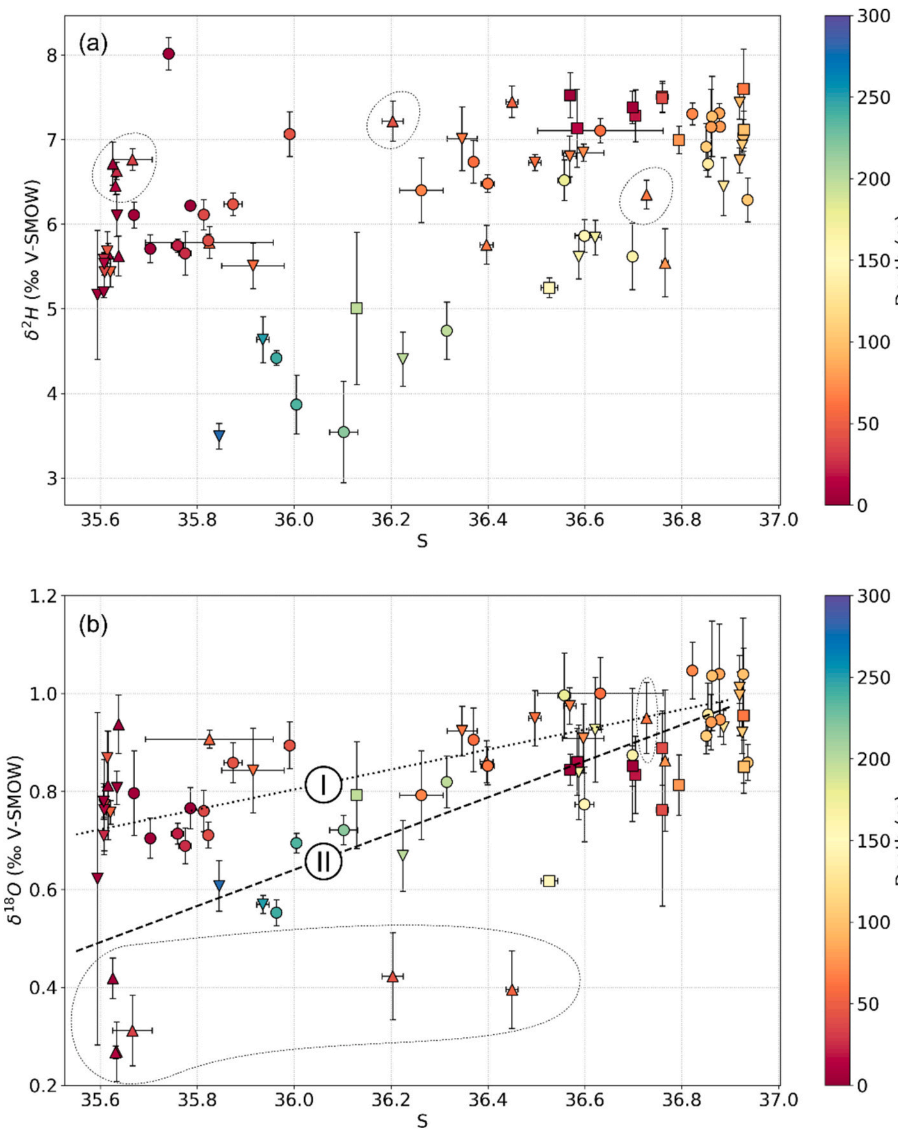

Fig. 5. (a) The relationship between δ^{2}H and (b) δ^{18}O values and seawater salinity. Salinity was derived from the CTD casts. Vertical error bars represent the standard deviation of the isotope measurement, horizontal error bars are the standard deviation of the salinity measurement (representing the variability encountered during the time it took to flush the Niskin bottles). The lines in (b) represent the regression line for (I) surface seawater water samples at Puerto Rico reported by Watanabe et al. (2001) and (II) samples up to 250 m depth in the Cariaco Basin (Venezuela) in February 2006 reported by McConnell et al. (2009). The values of station 12 are encircled by dotted lines. Symbols: ○ Curaçao; Δ Bonaire/Kralendijk; ▾ Bonaire other stations; □ Aruba.

Table 1
Water masses categorized by island and depth zone with characteristics of their nutrient concentrations.

Island	Depth zone	PO_4 (µmol/L)		NH_4 (µmol/L)		NO_2 (µmol/L)		NO_3 (µmol/L)		DIN:DIP	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Aruba	0–50 m	0.05	0.06	0.13	0.02	0.03	0.03	0.92	1.18	24.75	10.34
Aruba	51–100 m	0.30	0.08	0.11	0.01	0.03	0.01	5.74	1.19	20.08	1.24
Aruba	101–300 m	0.71	0.20	0.09	0.01	0.02	0.00	12.90	3.03	18.34	0.91
Bonaire	0–50 m	0.03	0.01	0.12	0.05	0.01	0.03	0.12	0.17	8.09	4.94
Bonaire	51–100 m	0.11	0.06	0.10	0.02	0.10	0.04	1.70	1.23	16.47	3.17
Bonaire	101–300 m	0.70	0.32	0.09	0.03	0.02	0.01	11.99	5.17	17.69	0.83
Curaçao	0–50 m	0.02	0.01	0.09	0.02	0.00	0.00	0.17	0.18	21.26	27.35
Curaçao	51–100 m	0.16	0.11	0.09	0.02	0.04	0.02	2.91	2.07	19.02	2.27
Curaçao	101–300 m	0.63	0.29	0.07	0.02	0.01	0.01	10.91	4.66	17.87	0.73

1989; Torres et al., 2023).

In Aruba, the surface water layer was not as clearly identifiable as along Bonaire and Curaçao, and SUW was already present at depths <60 m possibly. The shallower bathymetry separating Aruba from the South American continent likely promotes vertical mixing of water masses around the island relative to Curaçao and Bonaire that are surrounded by deep oceanic water (Fig. 1).

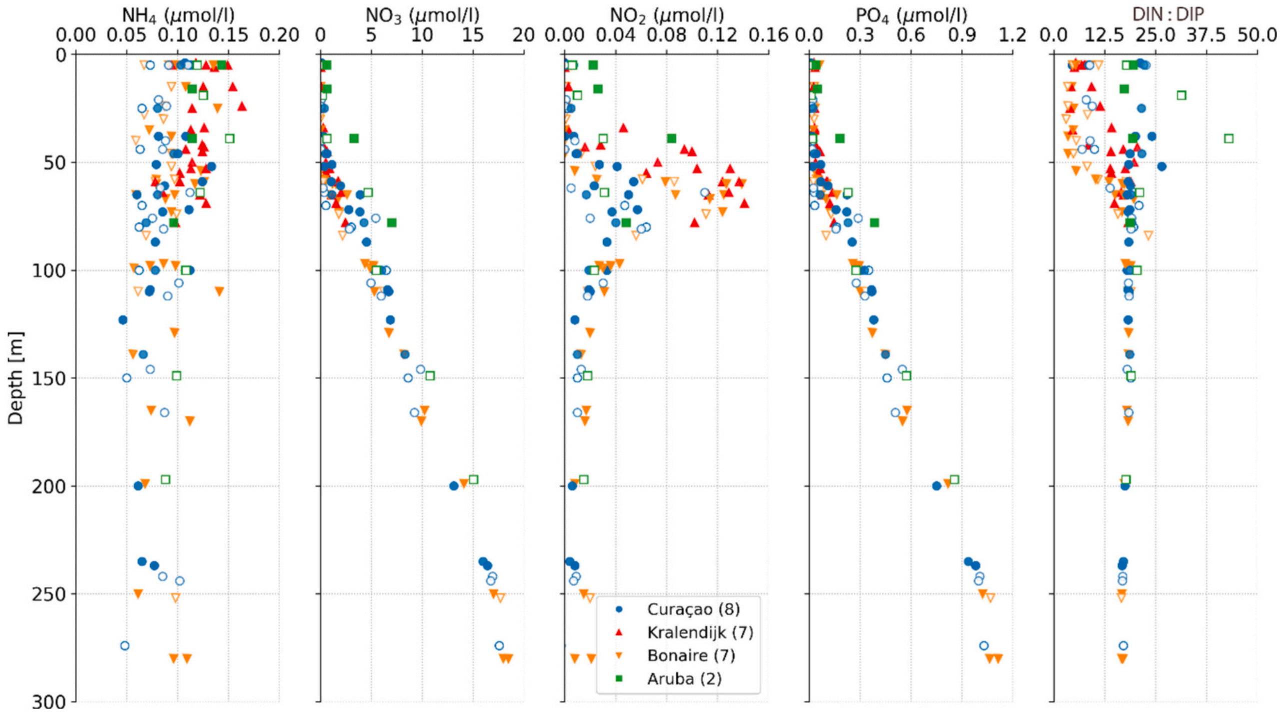

Fig. 6. Nutrient (NH_4, NO_3, NO_2, and PO_4) concentrations and DIN:DIP ratios (N:P) versus depth for all stations. The high concentration of NH_4 (0.479 μmol/L) at 5 m depth at station 7 is not shown. Colors denote the individual islands, with the samples taken offshore Kralendijk on Bonaire indicated separately. The number between parentheses in the legend indicates the number of stations per color category. Open symbols denote stations occurring in windward or exposed locations, whereas closed symbols are for stations located on the leeward side of the islands.

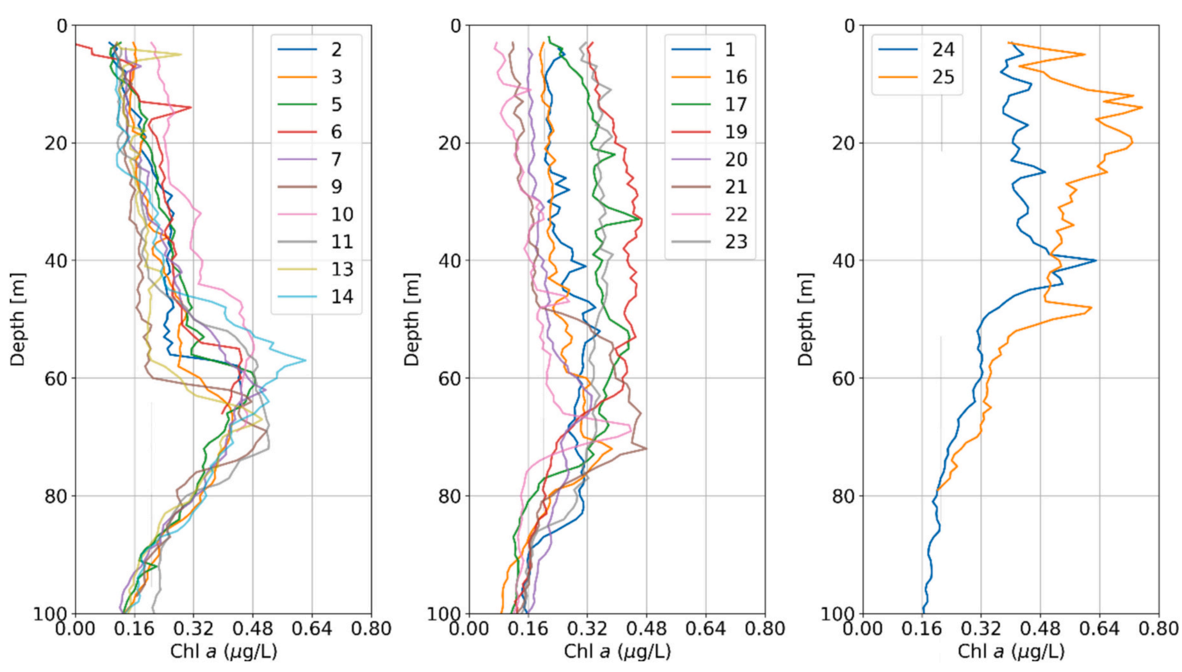

Fig. 7. Depth profiles of chlorophyll-*a* concentration on basis of daytime fluorescence measurements. (a) Bonaire (between 12:00 and 20:00 h LT), (b) Curaçao (between 7:00 and 19:00 h LT), and (c) Aruba (between 7:00–14:00 h LT). For the location of station numbers see Fig. 1. A thin vertical line indicates a Chl-a concentration of 0.2 μg/L used as an eutrophication threshold in this study.

5.3. Variations in stratification and undulations of the pycnocline

Haloclines, thermoclines, and pycnoclines were always found in the transition layer from the mixed surface layer (CSW) to the SUW, i.e., between depths of ~30 and 75 m depending on location and date of sampling. Variation in depths at which the composition of water in the first 100 m of the water column changes can be caused by local differences in bathymetry and oceanic processes such as internal waves (tidal waves, upwelling, Hernández-Guerra and Joyce, 2000; Leichter et al., 2006). The latter authors estimated the area's frequency of internal waves at ~0.5 cycles per day based on temperature time series data collected at Bonaire at a depth of 30 m. The internal wave that passed

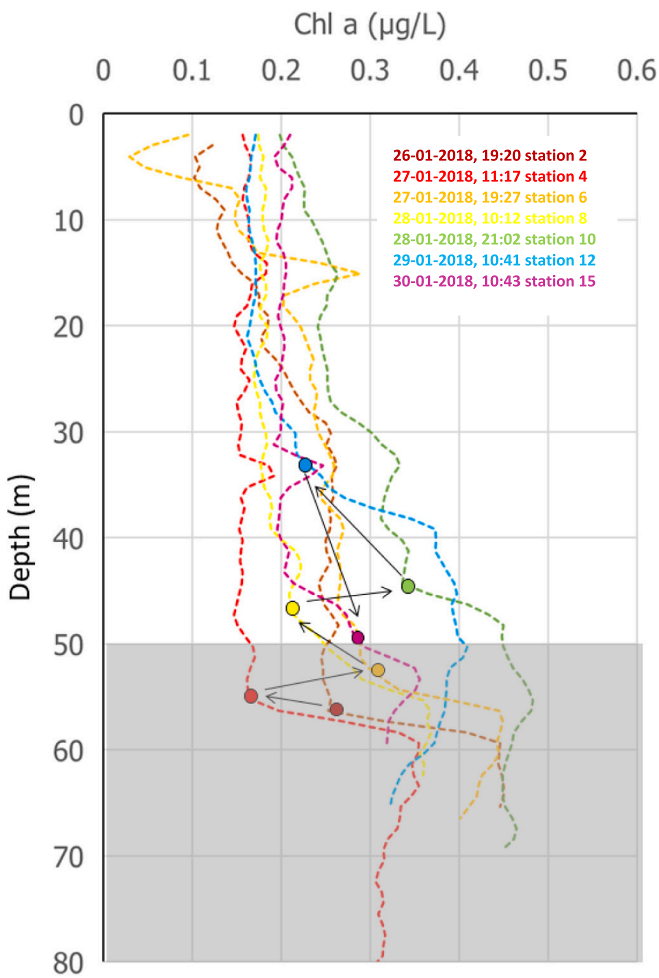

Fig. 8. Depth profiles for Chl-*a* concentrations near Kralendijk between January 26 and 30, 2018. The circles mark the depth of the top of the pycnocline. The area indicated in grey denotes the approximate depth below which certain nutrient concentrations at this site are elevated compared to shallower (<50 m) waters (see Table 1).

Kralendijk, Bonaire from 26 to 30 January (Fig. 8) undulated at an estimated ~0.2 cycles per day and moved the pycnocline from 55 to 34 m depth. These internal waves could underlie the reported short-lasting temperature drops of approximately 0.5–1 °C (and up to 3 °C) that occur year round at depths of around 50 m on reefs at the leeward side of Curaçao and Bonaire (Bak et al., 2005; Bongaerts et al., 2015; Gast et al., 1998; Leichter et al., 2006; Vermeij and Bak, 2003). With subsurface waves, the SUW also carries nutrient rich waters (Fig. 6) higher up into the photic zone supplying primary producers with NO_3 and PO_4, probably enhancing primary production in mixed surface water down to ~40–75 m depth (~1 % of surface irradiation/incident light). This structuring effect of upwelling on algal communities on coral reefs has also been reported from nearby Colombia (Diaz-Pulido and Garzon-Ferreira, 2002). In Bonaire and Curaçao, the shallower section of this depth range (around ~40 m depth) was historically locally dominated by dense communities of the brown algae *Lobophora* (Van den Hoek et al., 1978; Van den Hoek et al., 1975). The (historical) absence of this species in shallower reef sections could have been limited by the availability of nutrients brought up from deeper waters by upwelling and internal waves. If upward transport of nutrients does not occur, they appear to support a dense phytoplankton community at depths around ~70 m as evidenced by the occurrence of the DCM at these depths (Fig. 7).

5.4. Nutrients and chlorophyll-a

Nutrient profiles (particularly NO_3 and PO_4) around the ABC islands measured during our cruise were typical for (sub)tropical oligotrophic waters with nutrient limitation of primary producers in the mixed surface water layer and a DCM below the top of the pycnocline. Profiles at Aruba slightly differed from this general pattern in that nutrient and Chl-*a* concentrations were higher compared to Curaçao and Bonaire suggesting a more eutrophied status (Table 1, Figs. 6 and 7). From the pycnocline downwards nutrient concentrations of NO_3 and PO_4 increased around all islands. The increase in nitrite just below pycnocline (nitrite concentrations >0.04 μmol/L) most likely resulted from light limitation of phytoplankton in the DCM leading to a surplus of NH_4, (through mineralization), which is used by nitrifiers that oxidize NH_4 to NO_2 (Zakem et al., 2018).

5.5. Evidence for local eutrophication?

DIN and PO_4 concentrations in mixed surface waters (CSW) measured offshore remained below some commonly proposed threshold values of eutrophication (1.0 and 0.1 μmol/L respectively) (e.g., Bell et al., 2007). Nutrient measurements taken in shallower (<18 m) water closer to shore and above reef systems in the past often exceeded these same threshold values (e.g., Gast et al., 1999; Gast et al., 1998; Lapointe and Mallin, 2011). These authors reported DIN concentrations of ~1 μmol/L or more in 1994/1995 and from 2006 to 2008 along the leeward coasts of Curaçao and Bonaire, often close to areas with dense coastal development. From 2011 to 2013 Slijkerman et al. (2014) found DIN concentrations >1 μmol/L along the reef drop off (~5–17 m depth) in Bonaire often related to coastal-based pollution near the island's capital. In contrast, PO_4 concentrations in Curaçao and Bonaire have only exceeded eutrophication thresholds in a few sites in the past (e.g., Gast et al., 1999; Gast et al., 1998; Slijkerman et al., 2014). PO_4 concentrations along Bonaire were on average higher than along more densely populated Curaçao, similar to observations made in 2006–2008 by Lapointe and Mallin (2011).

General differences among the islands in reef condition could be related to differences in DIN/DIP ratios. DIN:DIP ratios were lowest (mean 6.3 ± 2.2) in Bonaire, the island with the highest average coral cover at 10 m depth, i.e., 21 % (de Bakker et al., 2019). Average DIN:DIP ratios were ~3 times higher on the other islands (range: 14–19) and exceeded values needed for productive coral growth (Wiedenmann et al., 2013). The mean abundance of corals on these islands is also lower than in Bonaire, i.e. 16 % for Curaçao (Sandin et al., 2022) and 6 % for Aruba (Vermeij et al., 2019). High DIN:DIP ratios in the CSW in Aruba and Curaçao suggest ineffective N sanitation (removal of inorganic N by nitrification and denitrification through sewage treatment) and/or more profound nitrogen influx via submarine groundwater discharge. In a comparison of groundwater composition among the ABC islands, van Sambeek et al. (2000) reported a considerably lower median NO_3 concentration at Bonaire than at Curaçao (74 vs. 494 μmol/L, respectively, data not available for Aruba). Possible occurrence of submarine groundwater discharge carrying less nitrate to coastal water bodies in Bonaire compared to Curaçao could explain the observed differences in DIN:DIP ratios between these islands, though P concentrations in the ground water of both islands remain presently unknown. In contrast to measurements taken closer to shore, and while our survey period was short and threshold values can be considered subjective, the fact that we did not encounter DIN concentrations exceeding aforementioned threshold values in the more offshore surface waters around the ABC islands (ranges: 0.104–0.762 and 0.002–0.039 μmol/L respectively) strongly suggests that nutrient enrichment (e.g., from terrestrial sources) foremost affects the waters (and organisms therein) close to shore and quickly dissipates as one moves farther offshore, either through usage by benthic and water column organisms or offshore advection.

Locations characterized by high DIN concentrations included locations with developed shorelines. Examples include station 7 (0.527 μmol/L, Wecua Point, Bonaire) located west of a large inland bay (Goto) and an oil transshipment terminal, stations 19 and 23 located respectively near the outlets of watershed harboring the island's landfill and a large, industrialized harbor located in the center of Curaçao's capital Willemstad (0.433 μmol/L, Sandin et al., 2022) and station 25 in Aruba located near beaches with dense tourist infrastructure (0.762 μmol/L, Vermeij et al., 2019).

5.6. Chl-a rather than nutrient concentrations indicate local eutrophication

While inorganic nutrient concentrations often remained below threshold values indicating eutrophication, Chl-*a* concentrations commonly exceeded the applied eutrophication threshold of 0.20 μg/L. Chl-*a* concentrations exceeding this threshold value were observed in the surface waters at stations in the vicinity and downstream of the main urbanized areas in Curaçao and Bonaire, near the oil transshipment terminal on Bonaire and in Aruba. Areas characterized by high Chl-*a* concentrations appear consistent through time as previous studies also found high Chl-*a* concentrations (>0.40 μg/L) near the same (urbanized) areas in 1994 (Van Duyl et al., 2002) and in 2006 and 2008 (Lapointe and Mallin, 2011). Combined, these and our study suggest that increases in phytoplankton (indicated by high Chl-*a* concentrations) can arise rapidly through local land-based processes. The rapid uptake by nutrients and subsequent increase in phytoplankton abundance has been confirmed for the main harbor entrance in Curaçao (Van Duyl et al., 2002) which shows that "eutrophication" should be cautiously defined (or measured) as "unnatural increases in nutrient concentrations" only as these concentrations can decrease when passing phytoplankton communities take up these nutrients to grow. Waterbodies with high phytoplankton abundance could of course move depending on local hydrodynamics and arrive in areas where the causes that led to their formation are no longer present. This would complicate the interpretation of the interaction between land-based forms of pollution (or lack thereof) and the composition of near shore water bodies in such places. Land-based forms of pollution commonly result in local increases in Chl-*a* concentrations that generally decrease with increasing distance from shore (e.g., Torregroza-Espinosa et al., 2021) including in Bonaire and Curaçao (Lapointe and Mallin, 2011). This would suggest that most excess nutrients entering the ocean through land-based forms of pollution in our study system are rapidly taken up by coastal phytoplankton and algae (Corredor, 1979; den Haan et al., 2016). Rather than by increases of their abundance in the water column, the higher than natural presence of nutrients therefore foremost appeared as increases in the abundance of their consumers, i.e., phytoplankton (using Chl-*a* abundance as a proxy), and fleshy algae that have increased in abundance in Curaçao and Bonaire over recent decades (Jackson et al., 2013).

The daytime increase in Chl-*a* abundance with depth in the mixed surface layer and its steep increase towards the DCM around 50 to 65 m depth and subsequent drop to <0.2 μg/L at 80–90 m depth (Fig. 7) can result from changes in phytoplankton physiology (e.g., fluorescence yield, photoadaptation) or net population growth, which includes grazing by zooplankton (Campbell and Vaulot, 1993; Marra, 1997; Moeller et al., 2019). Chlorophyll-*a* profiles based on in vivo fluorescence must therefore be interpreted with some caution, but it is interesting to note the temporal increase in Chl-*a* and nitrate concentrations in the mixed surface water in front of Kralendijk between January 26 and 30 (Fig. 8). The increased abundance of Chl-*a* and nitrate coincided with the passing of a large amplitude, low frequency internal wave, as suggested from the ~21 m upward movement of the pycnocline over a ~3-day period (Fig. 8). Shoaling of internal waves between Bonaire and a nearby small island (Klein Bonaire) and between Aruba and Venezuela are likely given the shallow depths of the water masses that separate them (i.e., ~90 and ~190 m depth, respectively). The passage of an internal wave can have increased the availability of nutrients in the photic zone, directly by nutrient enhanced upwelled water and/or the concentration of land-derived nutrients in a now thinner surface layer. Between Bonaire and Klein Bonaire smooth gently sloping sandy plains are present at depths where the DCM occurs. The seafloor here is covered by extensive and dense meadows of benthic cyanobacteria (Becking and Meesters, 2014) and on shallow reefs the supply of organic (algal) matter is known to stimulate the growth and extension of these cyanobacterial mats (Brocke et al., 2015; Ford et al., 2018). Analogously, the high abundance of organic material associated with the DCM could provide an explanation for the high abundance of cyanobacterial mats that are present at these sites. This example again illustrates how differences in water stratification in combination with local bathymetry can shape local benthic assemblages.

6. Conclusion

In this study, we described the vertical composition of the water masses surrounding the ABC islands in the Southern Caribbean to a depth of ~300 m. The general stratification of a ~50 m thick water layer of Caribbean Surface Water (CSW) on top of the North Atlantic Subtropical Under-Water with a mixing zone between depths of 50 and 80 m was observed. This confirmed a largely similar stratification of waters observed in nearby Venezuela and Colombia, but also elsewhere in the Caribbean, e.g., the US Virgin Islands. This general stratification can be affected by local bathymetry as for example the shallower bathymetry surrounding Aruba forces a thinning of the CSW around this island. Furthermore, local signs of eutrophication were observed near areas with extensive forms of coastal development (e.g., cities, harbors, dense tourism infrastructure). In such areas indications of eutrophication were foremost noticeable as increased abundances in phytoplankton (estimated as Chl-*a* abundance) instead of increases in nutrient concentrations.

CRediT authorship contribution statement

Fleur C. van Duyl: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Vincent E.A. Post:** Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Boris M. van Breukelen:** Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Victor Bense:** Writing – review & editing, Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Petra M. Visser:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Erik H. Meesters:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Paul Koeniger:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mark J.A. Vermeij:** Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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