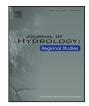
## **ARTICLE IN PRESS**

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## Groundwater-derived nutrient and trace element transport to a nearshore Kona coral ecosystem: Experimental mixing model results

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*Study region:* The groundwater influenced coastal waters along the arid Kona coast of the Big Island, Hawai'i.

*Study focus:* A salinity-and phase partitioning-based mixing experiment was constructed using contrasting groundwater endmembers along the arid Konacoast of the Big Island, Hawai'i and local open seawater to better understand biogeochemical and physicochemical processes that influence the fate of submarine groundwater discharge (SGD)-derived nutrients and trace elements.

New Hydrological Insights for the Region: Treated wastewater effluent was the main source for nutrient enrichment downstream at the Honokōhau Harbor site. Conservative mixing for some constituents, such as nitrate + nitrite, illustrate the effectiveness of physical mixing to maintain oceanic concentrations in the colloid ( $0.02-0.45 \,\mu$ m) and truly dissolved (< $0.02 \,\mu$ m) forms. In contrast, the nonconservative behavior of phosphate highlights the importance of surface complexation reactions that can lead to higher concentrations based on conservative mixing alone. Results from this physiochemical mixing experiment demonstrate how relative availability of P can shift with adsorption behavior, affecting the mobility of phosphate in the environment. With a proposed 8-hectare wastewater treatment facility (WWTF) to be constructed upslope of the Kaloko-Honokōhau National Historical Park (NHP), treated effluent is projected to add additional nutrients. Combined with high permeability, rapid discharge, and increased nutrient loading SGD will likely continue to serve as a persistent source of nutrients and potential contaminant to coral ecosystems.

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### 1. Introduction

Along the arid west coast of the island of Hawai'i submarine groundwater discharge (SGD) is the dominant waterborne transport vector for nutrients and trace elements to the coastal ocean (e.g., Bienfang, 1980; Johnson et al., 2008; Parsons et al., 2008; Street et al., 2008; Peterson et al., 2009; Knee et al., 2010). Chemical export of trace elements is an

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important source to the coastal ocean (Shaw et al., 1998; Basu et al., 2001; Moore et al., 2006; Beck et al., 2007; Bone et al., 2007; Moore, 2010; Santos et al., 2011; Beck and Cochran, 2013; Gonneea et al., 2013) suggesting that "subterranean estuaries" alter nearshore trace element concentrations (Moore, 1996; Santos et al., 2008; Swarzenski and Izbicki, 2009). As a result, discharge of groundwater can impact marine biotic communities by delivering heightened nutrient and trace metal loads that may lead to eutrophication, harmful algal blooms (Anderson et al., 2002), decreased coral abundance and diversity, and increased macroalgal abundance (Fabricius, 2005; Lapointe et al., 2005). In particular, eutrophication caused by nitrogen and phosphorous pollution from land-based sources (e.g., septic leachate, fertilizers), can alter ecosystem function and structure by shifting reefs dominated by corals to algae (Howarth et al., 2000; Andrefouet et al., 2002; Hughes et al., 2007), and increase vulnerability of reefs to coral disease (Bruno et al., 2003; Redding et al., 2013). Therefore, coral reefs directly influenced by SGD are particularly sensitive to land-based activities that can alter groundwater quantity and quality.

The coral reef complex of Honokōhau Bay within Kaloko-Honokōhau National Historical Park (NHP) on the central, leeward coast of Hawai'i provides critical structure (e.g., habitat) for the area's coastal ecosystems. Freshened surface water plumes derived from SGD are prevalent in most areas of the Park within 5-m water depth (Johnson et al., 2008). The influence of SGD in this region was also noted by Parsons et al. (2008) reporting salinities at nearshore reef sites commonly below open ocean values. Elevated nutrient loads observed in coastal groundwater have been attributed to recent land-use changes upslope (e.g., residential subdivisions, golf courses, unsewered suburban and commercial developments, agriculture) as well as the establishment of the Kealakehe Wastewater Treatment Facility (WWTF) (Johnson et al., 2008; Knee et al., 2010; Hunt, 2014). The WWTF discharges effluent into an excavated pit approximately 1 km up gradient from the Honokōhau Harbor at a rate of 4921– 6435 m<sup>3</sup> day<sup>-1</sup> (Parsons et al., 2008), acting as a point-source for nutrients to the oligotrophic seawater of this region.

The primary aim of this process-level study was to investigate the delivery and transformations of trace elements and nutrients, including the role of colloids in nutrient and metal fluctuations in a subterranean estuary by conducting a series of mixing experiments using two contrasting groundwater endmembers collected from the Kona coast. This experimental mixing approach cannot account for the full spectrum of conditions within a subterranean estuary (e.g., redox conditions, physicochemical properties of the aquifer substrate, and spatial or temporal changes in solution composition within the aquifer) however, results from the mixing model can provide insight on fundamental reactions inherent to the FW-SW mixing zone. For example, along an estuarine salinity gradient, surface complexation models (SCMs) predict that phosphate will desorbs from metal oxyhydroxides as pH increases (e.g., Gao and Mucci, 2001; Gao and Mucci, 2003). Determining the patterns and processes that influence the fate of SGD mixing with nearshore waters is important for effective management of coastal resources where population growth and resulting land development projects may lead to increased stressors to nearshore coral ecosystems on the island of Hawai'i.

### 2. Methods

### 2.1. Study site

The island of Hawai'i is the largest of the Hawaijan Islands and lies between 154°48'W and 156°04'W and between latitude 18°54'N and 20°17'N (Fig. 1). The island is composed of five shield volcanoes: Kohala, Mauna Kea, Hualālai, Mauna Loa, and Kilauea (Langenheim and Clague, 2015; Clague, 1987). The study site is on the Kona Coast on the leeward, west side, bounded on the east by the south-southeast rift zone of Hualālai Volcano and the southwest rift zone of Mauna Loa Volcano, and on the west and south by the Pacific Ocean. The upland area of the of Kaloko-Honokohau NHP region is composed of three Holocene basalt flows that originated from the Hualālai Volcano (altitude of 2.5 km) and range in age from 10ka to 1.5ka (Wolfe and Morris, 1996). The Hualālai volcanics are dominated by alkali basalt with tholeiitic basalt present in submarine samples from dredges (Clague, 1987; Langenheim and Clague, 2015). Thin basalt flows, ranging in thickness from less than a meter to several meters, form aquifers characterized by thin freshwater lenses with high permeability and rapid discharge, with the best developed aquifers in volcanic rocks that formed during the main shield volcano building stage (Gingerich and Oki, 2000). Groundwater flows rapidly from the mountains to the sea, with recharge occurring through infiltration, primarily via precipitation, and inflow from higher groundwater systems (Oki, 1999; Bauer, 2003). Sources of freshwater include recharge up gradient, infiltration of rainfall and fog drip, and irrigation water. The area of highest recharge is at altitudes greater than 600 m. Rainfall is less than 64 cm year<sup>-1</sup> on the coast but over 250 cm vear<sup>-1</sup> on the mountain slope (Giambelluca et al., 2013). The development of soil is minimal due to the young age of the basalt and low rainfall, therefore rainfall percolates downward, contributing to groundwater rather than overland flow. Hydraulic conductivity within the Park was estimated at 2.3 km day<sup>-1</sup> and between 0.15 to 10 km day<sup>-1</sup> north of the Park (Oki, 1999). Groundwater in the Kona area is characterized by a coastal unconfined groundwater system in the form of a freshwater lens, as water impounded to high levels within the inland part of the aquifer with lower overall permeability, and as a coastal confined-groundwater system beneath the coastal freshwater-lens system (Oki et al., 1999; Tillman et al., 2014). Permeability is high within the coastal aquifer and is enhanced by the presence of lava tubes.

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