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The use of stable isotopes of oxygen and hydrogen to identify water sources in two hypersaline estuaries with different hydrologic regimes

René M. Price[A,E], *Grzegorz Skrzypek*[B], *Pauline F. Grierson*[B], *Peter K. Swart*[C] and *James W. Fourqurean*[D]

[A]Department of Earth and Environment and Southeast Environmental Research Center, Florida International University, Miami, FL, USA.
[B]West Australian Biogeochemistry Centre and Ecosystems Research Group, School of Plant Biology, The University of Western Australia, Crawley, WA, Australia.
[C]Rosenstiel School of Marine and Atmospheric Sciences, Division of Marine Geology and Geophysics, University of Miami, Miami, FL, USA.
[D]Department of Biology and Southeast Environmental Research Center, Florida International University, Miami, FL, USA.
[E]Corresponding author. Email: pricer@fiu.edu

Abstract. Stable isotopes of oxygen and hydrogen are used here with salinity data in geochemical and mass-balance models to decipher the proportion of different sources of water in two hypersaline estuaries that vary in size and hydrologic condition. Shark Bay, located on the mid-western coast of Australia, is hypersaline year round and has an arid climate. Florida Bay, located in the south-eastern United States, is seasonally hypersaline and has a subtropical climate. The water budget in both bays can be explained by evaporation of seawater, with seasonal inputs of surface-water runoff and precipitation. In Shark Bay, discharge from the Wooramel River associated with a recent major flood was detected in the relationship between the stable isotopic composition and salinity of surface waters near the mouth of the river, despite the persistence of hypersalinity. The volume of water equal to one pool volume replenished Hamelin Pool (a hypersaline water body located at the southern end of eastern Shark Bay that supports living stromatolites) once every 6–12 months. The eastern portion of Florida Bay received a greater proportion of freshwater from overland flow (70–80%) than did the western portion where rainfall was the dominant source of freshwater.

Additional keywords: groundwater, precipitation, Shark Bay, surface water.

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Introduction

There is a long history of the use of stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) to identify fresh-water inputs to the ocean (Epstein and Mayeda 1953; Lloyd 1964; Martin and Letolle 1979; Bauch *et al*. 1995), continental shelf (Fairbanks 1982) and estuaries (Martin and Letolle 1979; Surge and Lohmann 2002; Stalker *et al*. 2009). However, the use of $\delta^{18}O$ and $\delta^{2}H$ in hypersaline estuaries is restricted to only a few studies (Swart and Price 2002; Corlis *et al*. 2003). The limited use of $\delta^{18}O$ and $\delta^{2}H$ in estimating freshwater inputs to hypersaline estuaries is understandable because evaporation exceeds freshwater inputs in these estuaries. Furthermore, evaporation affects salinity, $\delta^{18}O$ and $\delta^{2}H$, resulting in these three constituents often co-varying linearly (Epstein and Mayeda 1953). Despite these limitations, the freshwater sources of precipitation, surface-water runoff and groundwater discharge contain individual signatures of $\delta^{18}O$ and $\delta^{2}H$; therefore, these constituents should still be useful for identifying seasonal inputs of freshwater to hypersaline estuaries.

Although freshwater inputs to hypersaline estuaries may be small, they may be important contributors to chemical and nutrient budgets. For instance, precipitation tends to contain very low concentrations of major ions, but can be the dominant source of pollutants such as phosphorus (Rudnick *et al*. 1999) and mercury (Wängberg *et al*. 2007) to estuaries. Surface-water runoff can bring additional inputs of nitrogen and phosphorus from fertilisers as well as suspended sediment to an estuary (Logan and Cebulski 1970; Balls 1994). Groundwater always has higher concentrations of nutrients and ions than does the surface water, either from anthropogenic sources (Johannes and Hearn 1985; Valiela *et al*. 1999; Slomp and Van Cappellen 2004) or from subsurface biogeochemical reactions (Moore 1999). Quantification of the relative inputs of nutrients from different water sources into hypersaline estuaries would be

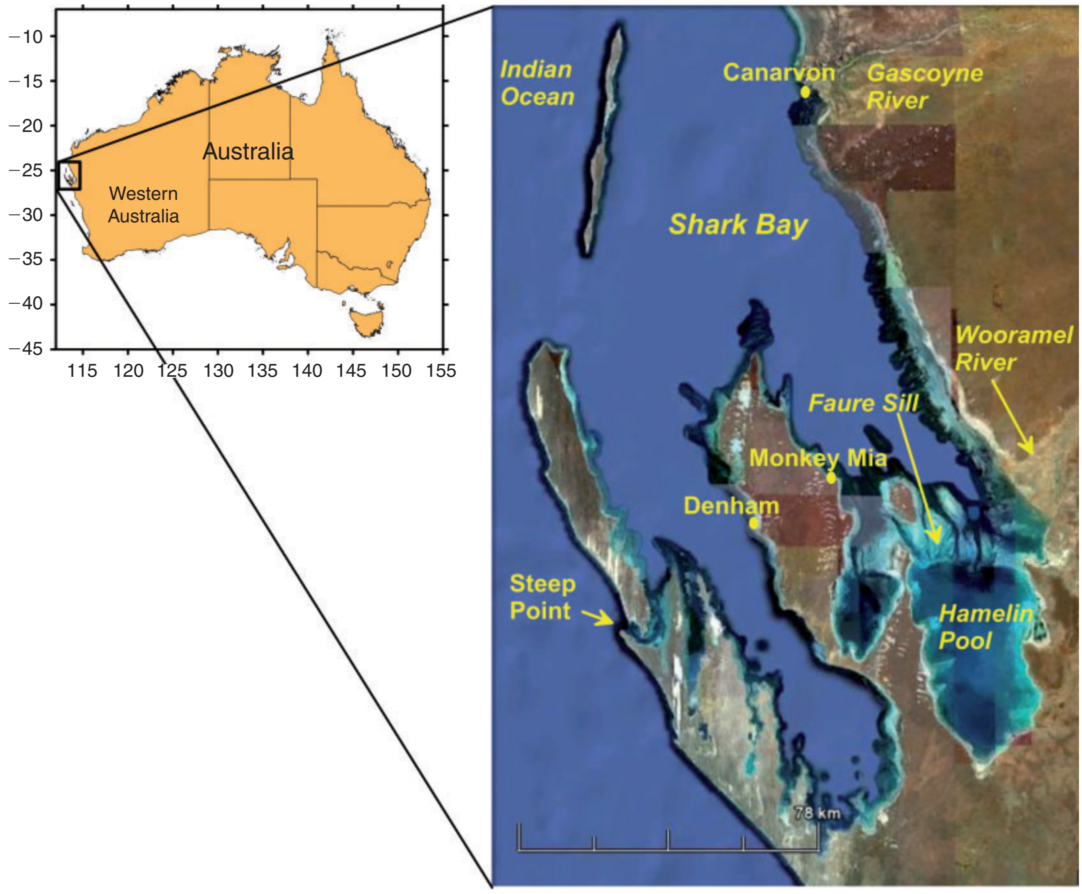

Fig. 1. Location map of Shark Bay, Australia.

greatly enhanced by improved capacity to distinguish between those sources.

Hypersaline estuaries are observed all over the world, including in North America (USA and Mexico), Europe, South Africa and Australia (Largier *et al*. 1997; Bianchi *et al*. 1999; Fourqurean and Robblee 1999; Lloret *et al*. 2005; Potter *et al*. 2010). Hypersaline estuaries, however, vary greatly in their geomorphology and physical relationships between their watersheds and the ocean (Potter *et al*. 2010; Elliott and Whitfield 2011). Two estuaries, Shark Bay and Florida Bay, were chosen for the research. These estuaries occur at the same latitude (~25°), but at opposite sides of the equator; Shark Bay is located in Western Australia (Fig. 1), whereas Florida Bay is located in North America (Fig. 2). The bays differ climatologically, with Shark Bay being characterised by a semiarid to arid climate, and Florida Bay as having a subtropical climate. With an area of ~13 000 km^2 and an average depth of 10 m, Shark Bay is more than six times larger and three times deeper than Florida Bay (Table 1). In both bays, tidal amplitude is small, being less than 1.5 m in Shark Bay (Burling *et al*. 2003) and less than 1 m in Florida Bay (Fourqurean and Robblee 1999). Stable-isotope and salinity data were used in evaporative and mixing models to characterise both evaporation and an influx of freshwater sources. In addition, geochemical and mass-balance models were applied to ecologically sensitive portions of Shark Bay, specifically the Faure Sill where seagrasses dominate the benthos, and Hamelin Pool (Fig. 1) where stromatolites dominate. Seagrasses and stromatolites are ecological features of special concern that in a large part led to the designation of Shark Bay as a World Heritage site (McCluskey 2008) and they are both sensitive to changes in water quality driven by either freshwater or seawater inputs (Playford 1980; Duarte 1995). The focus of the present paper is to demonstrate that $\delta^{18}O$ and $\delta^{2}H$, combined with salinity, can be useful in quantifying water input (freshwater and seawater) and output (evaporation) from two hypersaline estuaries with varying climatic and hydrological regimes.

Materials and methods

Study sites

(1) Shark Bay

Shark Bay is a W-shaped bay located along the extreme western coastline of Australia (Fig. 1). Shark Bay is open to the ocean at the north, whereas further south exchange of water with the ocean is limited because of the presence of several islands and submerged sills, particularly the Faure Sill, located in the eastern arm of the bay (Fig. 1). Water depth throughout Shark Bay is less than 20 m, with an average depth of 15 m in the north, decreasing to 0–4 m depth in the Faure Sill region to the south.

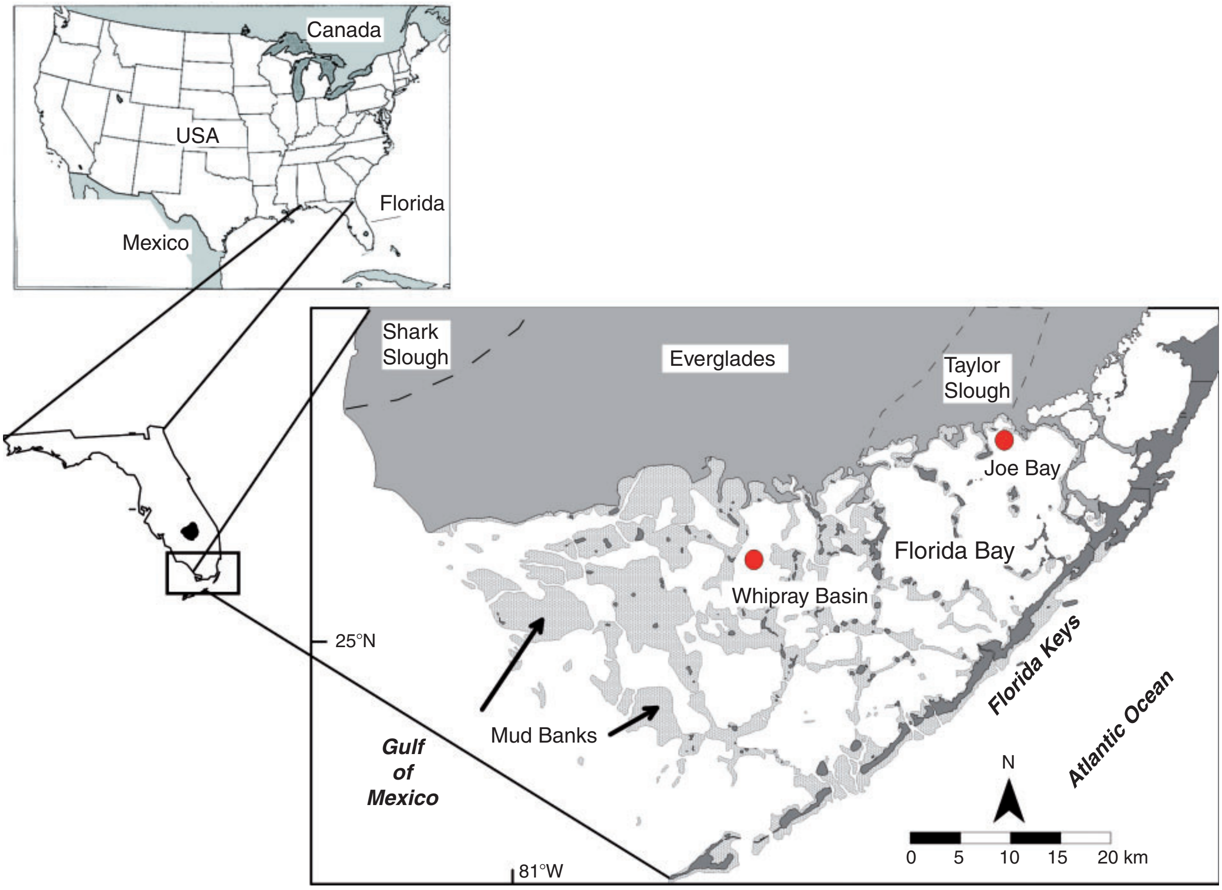

Fig. 2. Location map of Florida Bay, USA, showing study sites Joe Bay and Whipray Basin.

A few narrow channels with depths of up to 7 m cut across the Faure Sill into Hamelin Pool, which has an average depth of less than 10 m. Tidal fluctuations in Hamelin Pool are relatively low, with, on average, less than ~1-m difference between low and high water; however, the maximum difference over a year can be as high as ~2 m (Monkey Mia, Department of Transport, Western Australia, http://www.transport.wa.gov.au, accessed 16 December 2011) The shallow depth of the Faure Sill restricts water exchange between northern Shark Bay and Hamelin Pool, resulting in a north–south salinity distribution of 35 at its mouth and >60 at the southern end of Hamelin Pool that has been stable for at least the past 40 years (Logan and Cebulski 1970; Smith and Atkinson 1983). All salinity values in the present paper are based on the practical salinity scale of 1978 (Lewis 1980). Shark Bay waters north of the Faure Sill exhibit vertical stratification in the Austral winter (August), but not in the summer (February) (Burling *et al*. 1999). No vertical stratification in salinity has been observed across the shallows of the Faure Sill (Burling *et al*. 1999).

Holocene sediments within Shark Bay are predominantly marine carbonates formed locally and terrigenous sediments from the Wooramel River (Logan and Cebulski 1970). Geologically, Shark Bay is underlain by Pleistocene-age red sandstones (Peron sandstone) and white limestones (Tamala limestone) along its eastern shoreline (Logan *et al*. 1970). The younger units overlay much older Cretaceous and Tertiary Calcarenites that make up the Carnarvon Basin.

One intermittent river, the Wooramel, discharges into the eastern boundary of the bay. Another intermittent river, the Gascoyne, discharges near the mouth of Shark Bay, north of the study area. Typical for semiarid to arid climates, the mean annual rainfall of Shark Bay is extremely low (<250 mm), but also highly variable; evaporation rates are an order of magnitude greater than rainfall (Table 1). Most rainfall occurs in the Austral winter, between May and August. Summer months typically have no rain, although cyclones occasionally add ~300–500 mm rainfall to the area during those months (Australian Bureau of Meteorology; http://www.bom.gov.au, accessed 12 September 2011).

(2) Florida Bay

Florida Bay is a triangle-shaped bay located at the extreme south-eastern coastline of the United States (Fig. 2). Florida Bay is open to the ocean at the west, with limited ocean exchange to the south through passages between the Florida Keys. Numerous interconnecting, carbonate mud banks divide the bay into several shallow-water basins. The mud banks restrict water circulation in the bay, and as a result, salinity in the central and eastern portions of the bay can vary between 0 and 70 (Table 1; Fourqurean and Robblee 1999). In addition, salinities

Table 1. Physical and hydrological characteristics of Shark Bay, Western Australia, and Florida Bay, USA

Parameter	Shark Bay	Florida Bay
Latitude	24–27°S	24–25°N
Longitude	113–114°E	80–81°W
Area (km^2)	13 000	2000
Depth (m)	1–20	1–3
Tidal amplitude (m)	0.2–1.2[A]	0–0.8[B]
Climate	Semiarid to arid, winter wet season, summer cyclones	Subtropical, summer wet season and hurricanes
Mean rainfall (mm year^{-1})	221[H]	1060[C]
Rainfall range (mm year^{-1})	78–520	620–1520[C]
Mean evaporation (mm year^{-1})	2651[H]	1660[C]
Mean air temperature (°C)	22.4[H]	25.2[C]
Air-temperature range (°C)	14–43[D]	15–32[C]
Geology	Pleistocene limestones and sandstones	Pleistocene karstic limestones
Geomorphology	Carbonate sill	Carbonate mud banks
Salinity range[E]	35–60[F]	0–70[G]
Ecosystem	Seagrass, stromatolites	Seagrass, mangroves
Nutrients	Phosphorus limited	Phosphorus limited

[A]Burling *et al*. (2003).
[B]Nuttle *et al*. (2000).
[C]Price *et al*. (2007).
[D]http://www.eldersweather.com.au/wa/gascoyne/denham, accessed 12 September 2011.
[E]Practical salinity units.
[F]Smith and Atkinson (1983).
[G]Fourqurean and Robblee (1999).
[H]Means for 30-year period 1981–2010, Australian Bureau of Meteorology (http://www.bom.gov.au, accessed 12 September 2011, Carnarvon, site no. 006011).

on some of the islands reach values as high as 120 (Swart and Kramer 1997). Freshwater runoff from the Everglades occurs along the northern boundary of Florida Bay from Shark Slough and Taylor Slough, the two dominant drainage basins within the Everglades (Fig. 2). The quantity of flow from those drainages varies seasonally (Koch *et al*. 2012; Saha *et al*. 2012). Joe Bay and Whipray Basin (Fig. 2) are two sites in Florida Bay that represent extremes in salinity variations. Salinities of Joe Bay vary from essentially fresh to over 50, and Whipray Basin consistently has salinities in excess of 35, with extreme salinities of over 60 in drought years (Fig. 3). Florida Bay is underlain by the Pleistocene-age limestones of the Miami Oolite formation. The Florida Keys are made up of similar-age limestones of the Key Largo formation. Both limestones are karstic, with high porosity and permeability. The climate of Florida Bay is considered subtropical, with a mean rainfall two- to five-fold greater than at Shark Bay (1060 mm year^{-1} compared with 221 mm year^{-1}); however, evaporation still exceeds rainfall (Table 1). Seventy percent of the rainfall in Florida Bay occurs between May and November, which corresponds with the summer and hurricane seasons in the northern hemisphere.

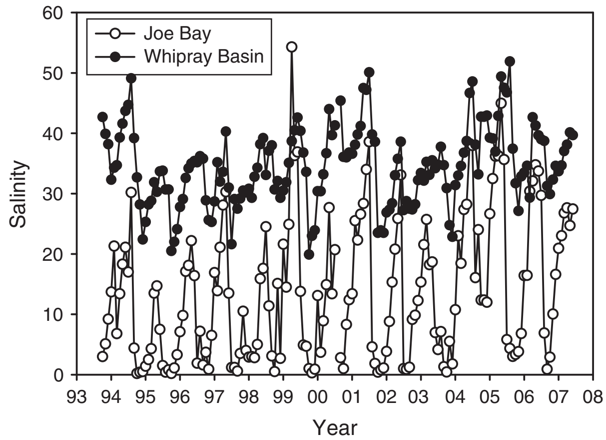

Fig. 3. Variations in salinity with time at two sites in Florida Bay. Joe Bay has variable salinity, whereas Whipray Basin tends be more consistently hypersaline. See Fig. 2 for site locations.

Sampling and water analyses

(1) Shark Bay

Surface water, groundwater and rainfall samples from Shark Bay were collected between March and September 2011. During the first week of March 2011, 43 surface-water samples were collected as grab samples from within 10 cm of the water surface, either from a boat or off the beach in Shark Bay (Fig. 4). An additional 17 surface water samples were collected in the western arm of Shark Bay between 29 March and 4 April, 2011. Staff from the Western Australia Department of Environment and Conservation (WA DEC) collected an additional five samples along the western side of Hamelin Pool in September 2011. Indian Ocean water was collected from Steep Point (Fig. 1). Surface-water samples were collected in 60-mL polycarbonate bottles that were rinsed three times before filling. Sample bottles were filled and capped below the surface of the water to minimise gas bubbles in the sample. Groundwater samples were collected from seven shallow (<2 m) wells located at Monkey Mia and two

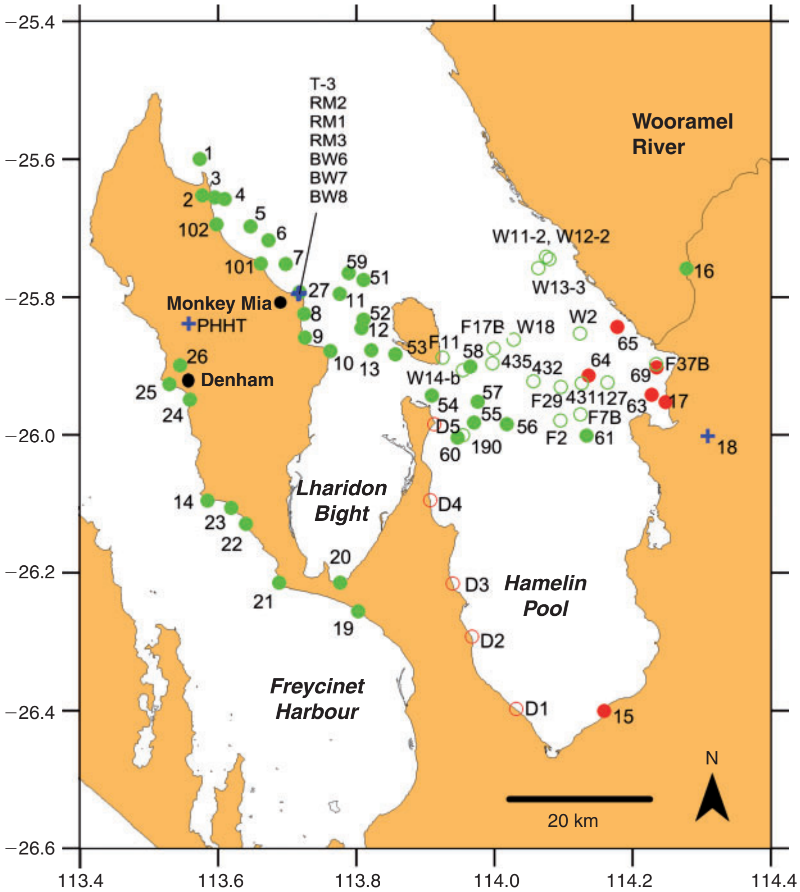

Fig. 4. Sampling locations in Shark Bay, Australia. Solid green and red dots are surface-water samples collected between 4 and 8 March 2011, whereas the open green dots are surface-water samples collected between 29 March and 4 April 2011. The open red dots are surface-water samples collected in September 2011 by the Western Australian Department of Environment and Conservation. The blue crosses represent the locations of bores sampled in this investigation.

deep (~400 m) wells from around the bay (Fig. 4). The shallow wells were sampled using a submersible pump. The well was purged for several minutes while the field parameters of temperature, specific conductance and pH were monitored in a flow-through chamber until readings were stable. The deep wells were artesian, and were sampled by opening a valve on the well and allowing the water to flow from the well for ~5 min before sampling. Groundwater samples were collected either from the pump discharge (shallow wells) or from the well discharge (deep wells) directly into 60-mL polycarbonate bottles, after rinsing three times. Bottles were overfilled and then capped to minimise air bubbles in the sample. Rainfall samples were collected from three events from both Monkey Mia and Denham in June and July 2011. Rain was collected in a 20-L bucket. Water in the bucket was subsampled directly into 10-mL glass vials with Teflon-lined caps, by first rinsing the vials three times, and then filling the vial under the water surface. Duplicate vials were collected for each rain event. After a sample was collected, the 20-L bucket was emptied so as to collect the next rain event.

The Wooramel River was sampled on 5 March 2011 near the last of the discharge from the tropical cyclones. Duplicate surface-water samples were collected from the Wooramel River at the bridge where Route 1 (North West Coastal Highway) crosses the river. Water samples from the river were collected in the same manner as the surface-water samples from Shark Bay. Discharge data for the Wooramel River from December 2010 through June 2011 was obtained from the Western Australia Department of Water (Fig. 5). Over that time, discharge from the Wooramel River was intermittent, flowing only from precipitation inputs within its catchment from two tropical lows (TL03U in December 2010; and TL06U in January 2011) and two tropical cyclones (Diane and Carlos, in February 2011).

Salinity of the surface-water and groundwater samples was determined either in the field using a YSI Model 85 S/C/T meter (YSI Incorporated, Yellow Springs, OH, USA) or in the laboratory using a refractometer. All samples were filtered through a 0.2-μm-size filter and then the stable hydrogen (δ^2H) and oxygen (δ^{18}O) isotope compositions of water samples were analysed using an Isotopic Liquid Water Analyzer L1102-i (Picarro, Santa Clara, California, USA) at the West Australian Biogeochemistry Centre, The University of Western Australia (UWA). In the present paper, the stable isotope compositions were expressed

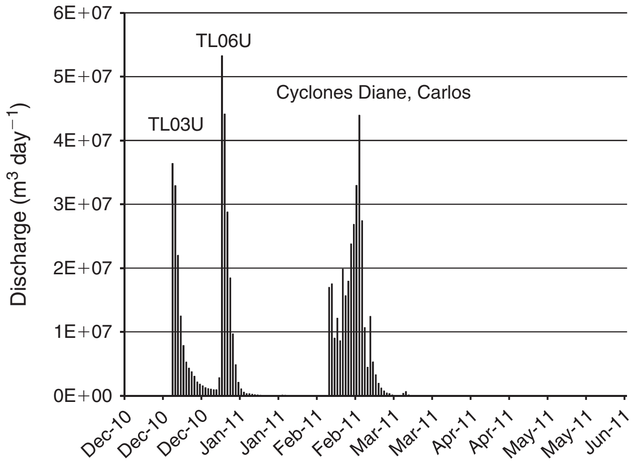

Fig. 5. Discharge (m^3 day^{-1}) of the Wooramel River between December 2010 and June 2011. High discharge events were attributed to the passage of two tropical lows (TL03U in December 2010; and TL06U in January 2011) and two tropical cyclones (Diane and Carlos, in February 2011). The Wooramel River was sampled in this investigation on March 5, 2011 near the tail end of the discharge from the tropical cyclones.

using the standard δ-notation (δ^2H and δ^{18}O) and were reported in per mil (‰) after normalisation to Vienna Standard Mean Ocean Water (VSMOW) scale. The normalisation was based on three laboratory standards, each replicated twice (Paul *et al.* 2007; Skrzypek *et al.* 2010). All laboratory standards were calibrated against international reference materials determining the VSMOW-SLAP scale (Coplen 1996). The long-term reproducibility, based on regularly measured laboratory standards, was better than 0.1‰ and 1.0‰ for δ^2H.

(2) Florida Bay

Surface-water samples were collected on a monthly basis from a network of stations in Florida Bay (Swart and Price 2002) between October 1993 and June 2007. Water samples were collected from near the surface of the water from the side of a boat into 1-L plastic bottles. Sample bottles were rinsed three times and capped under the water surface. Salinity measurements were made by Florida International University (FIU) at the time of sample collection, according to the methods described by Boyer *et al.* (1999). Of all of the stations sampled in Florida Bay, we include the data from only two sites, Joe Bay and Whipray Basin (Fig. 2), because they represent extremes in salinity variations in the Bay (Fig. 3). Rainfall was also collected at several locations in south Florida between 1995 and 2005 and analysed for δ^2H and δ^{18}O isotopic compositions (Swart and Price 2002; Price *et al.* 2008). Surface-water samples from six sites in Shark Slough and three sites in Taylor Slough (not shown on Fig. 2) were collected on an approximately monthly basis over the same period. All water samples were subsampled into 50-mL plastic bottles after filtering through a 0.2-μm filter. The δ^2H and δ^{18}O isotopic measurements were made in the Division of Marine Geology and Geophysics at the University of Miami. Both measurements were made using a water equilibration system (WEST) attached to an Europa GEO isotope ratio mass spectrometer (Swart 2000), using a method similar to that described by Epstein and Mayeda (1953) for δ^{18}O and Coplen *et al.* (1991) for δ^2H. The long-term reproducibility based on regularly measured laboratory standards was better than 0.1‰ for δ^{18}O and 1.5‰ for δ^2H. Both oxygen and hydrogen isotopic data were normalised to the international standards VSMOW-SLAP using laboratory standards calibrated against the primary reference material. Results are reported in conventional ‰ notation.

Modelling

A combination of geochemical and mass-balance models were used to assess the combined effects of evaporation with freshwater and seawater mixing in both Shark Bay and Florida Bay. An isotope evaporation model as developed by Craig and Gordon (1965) was used to describe the effects of evaporation on the δ^{18}O values of surface water in both Florida Bay (Whipray Basin) and Shark Bay. The dominant source(s) of freshwater to Shark Bay and Florida Bay were determined using linear mixing models between δ^{18}O and salinity. Florida Bay is a more data-rich environment and detailed water and salinity budgets have already been developed for the bay (Nuttle *et al.* 2000) and Whipray Basin (Lee *et al.* 2006). In contrast, hydrologic data for Shark Bay are scarce. Consequently, we applied two simplified mass-balance models to balance the contributions of freshwater and seawater with the loss of water as a result of evaporation in Shark Bay. Both δ^{18}O and δ^2H tend to exhibit similar behaviours when exposed to evaporation and mixing of different waters. Because similar conclusions would most likely be drawn from using both isotopes, only δ^{18}O data are presented here.

(1) Isotope model

The behaviour of oxygen and hydrogen isotopes has been succinctly described by the Craig–Gordon model of evaporation (Craig and Gordon 1965) and described and modified by others (Merlivat and Coantic 1975; Gonfiantini 1986). In these models, the δ^{18}O and δ^2H of the evaporating water body are controlled by the temperature of evaporation, the relative humidity of the atmosphere, the isotopic composition of the atmospheric water vapour and the salinity of the water body. As a result of these parameters, the pathway that the isotopic composition of water follows in an evaporating water body varies. In particular, the maximum isotopic value that a water body can attain is governed by a combination of the relative humidity and the isotopic composition of the atmosphere. Of all these parameters affecting the isotopic composition of evaporating water, the one that is least well known is the isotopic composition of the atmospheric water vapour, which is often assumed to be in equilibrium with the local rainfall. In the case of Shark Bay, a δ^{18}O of the atmospheric water vapour was assumed to be −12.83‰, which is a value estimated to be in equilibrium with the local rainfall value of $\delta^{18}O = -3.28$‰ (Table 2) at a mean air temperature 22.4°C, according to the equations by (Gonfiantini 1986). For Florida Bay, a slightly more positive atmospheric δ^{18}O value of about −11.8‰ was assumed to be in equilibrium with an annual mean δ^{18}O value for rainfall of −2.8‰ (Price *et al.* 2008) at a mean air temperature of 25°C (Price *et al.* 2007). The Craig–Gordon model as outlined by Gonfiantini (1986) was then utilised for both locations, assuming a mean annual relative humidity (RH) of 75% (Price *et al.* 2007; Carnarvon weather station Australian Bureau of Meteorology, http://www.bom.gov.au,

Table 2. Summary of temperature, salinity, $\delta^{18}O$ and $\delta^{2}H$ of groundwater samples collected near Shark Bay, Australia
VSMOW, Vienna Standard Mean Ocean Water

Sample	Site	Latitude	Longitude	Date	Temp. (°C)	Salinity	$\delta^{18}O$ (‰) VSMOW	$\delta^{2}H$ (‰) VSMOW
Shallow bores	T-3	25°47.601′S	113°43.080′E	3/8/2011	29.1	5	−8.00	−55.22
	RM2	25°47.606′S	113°43.065′E	3/8/2011	25.2	8	−4.56	−33.09
	RM1	25°47.645′S	113°43.041′E	3/8/2011	27.7	4.5	−5.83	−41.33
	RM3	25°47.637′S	113°43.048′E	3/8/2011	28.7	6	−6.13	−43.63
	BW6	25°47.683′S	113°43.058′E	3/8/2011	34.3	3.5	−5.65	−40.01
	BW7	25°47.685′S	113°43.087′E	3/8/2011	30.9	5	−6.03	−42.98
	BW8	25°47.740′S	113°42.931′E	3/8/2011	29.2	8.5	−8.31	−59.39
Deep bores	SB18	26°00.112′S	114°18.536′E	3/5/2011	31.7	3.2	−5.64	−39.96
	PHHT	25°47.641′S	113°43.049′E	3/9/2011	42.6	1.4	−5.60	−40.93
	PHHTD[A]	25°47.641′S	113°43.049′E	3/9/2011	42.6	1.4	−5.59	−40.68

[A]Duplicate sample.

accessed 12 September 2011, Site no. 006011 for 30-year period 1981–2010) and a starting salinity value of 25 for Whipray Basin (Florida Bay) and 35 for Shark Bay.

(2) Linear mixing model

The linear mixing model developed between $\delta^{18}O$ and salinity was used to estimate the dominant sources of freshwater to both Shark and Florida Bays. The linear mixing model consisted of plotting the $\delta^{18}O$ values of surface waters against salinity and then computing a best-fit linear regression through the data. The $\delta^{18}O$ value at the intercept of zero salinity was used to identify the dominant source(s) of freshwater to each bay. When applicable, a two-component mixing model was used to quantify the proportions of each of the freshwater components to both the salinity and $\delta^{18}O$ value of surface waters in each of the bays.

(3) Mass-balance models of Hamelin Pool

Two mass-balance models were developed to estimate the relative proportions of evaporative loss, with inputs of rain and seawater needed to maintain a constant water level in Hamelin Pool. One model, the simple math model (SMM), used a water-balance approach, whereas the other model, the simple isotope model (SIM), combined stable isotopes with the water-balance parameters to provide estimates of water exchange and water residence times. Steady-state conditions, implying a constant water level, were assumed for both models.

The area and volume of water in Hamelin Pool was estimated by first digitising 340 depth points from the Shark Bay nautical chart (Shark Bay, South Eastern Sheet Aus 784, Hydrographic Service, Royal Australian Navy, North Sydney, 1994). The northern border of Hamelin Pool was arbitrarily chosen along a line drawn approximately in the middle of the Faure Sill (25°57′S). By combining the Point Kriging with the Simpson's Rule algorithm in the software package Surfer 8.08 (Golden Software Inc., Golden, CO, USA). Hamelin Pool was determined to be relatively shallow ($<$10 m), with area of 1403 km^2 and the total volume of 7.05 km^3. Tidal fluctuations were not taken into account in this volume estimate. A cross-section across Faure Sill, the northern border of Hamelin Pool, was calculated from a three-dimensional model used for volume estimation, employing Surfer 8.08 and then Grapher 7.4 (Golden Software Inc.) programs. The cross-section was estimated to be 37.5 km wide, with water depths ranging between 0–4 m and up to 7 m in the narrow straights. The resulting cross-sectional area across Faure Sill was estimated to be relatively small at 0.08 km^2.

Assignment of the catchment area that could potentially supply fresh water to the Hamelin Pool was more challenging. Because of arid conditions, all creeks in the area are ephemeral and generally flow for a few days a year at most. Moreover, many of these pools lack well defined channels. The Wooramel River was not considered in the catchment for Hamelin Pool beause it enters Shark Bay north of the Faure Sill. The area of the Hamelin Pool catchment was estimated on the basis of the local topography and distribution of channels using satellite imagery (Google Earth, Scripts Institute of Oceanography (SIO), National Oceanic and Atmospheric Administration (NOAA), Unites States Navy (USN), National Geospatial-Intelligence Agency (NGA), General Bathymetric Chart of the Oceans (GEBCO) 2012), and was estimated to have a total area of 1614 km^2 (MapSource 6.16.3; Garmin Ltd, Olathe, KS, USA). Local climate data were obtained from the Carnarvon weather station run by the Australian Bureau of Meteorology (http://www.bom.gov.au, accessed 12 September 2011, Site no. 006011) for 1981–2010. Mean annual temperature was 22.4°C, relative humidity was 55%, rainfall was 221.4 mm and pan evaporation was 2651.9 mm.

The SMM utilised the following equations:

$$E_{\mathrm{total}}\ [\%] = (A_{\mathrm{pool}} \times PE_{\mathrm{pan}}) \times 100/V_{\mathrm{pool}}, \tag{1}$$

$$I_{\mathrm{rain}}\ [\%] = (0.5 \times A_{\mathrm{catch}} \times P_{\mathrm{rain}} + A_{\mathrm{pool}} \times P_{\mathrm{rain}}) \times 100/V_{\mathrm{pool}},\ \text{and} \tag{2}$$

$$I_{\mathrm{sea}}\ [\%] = E - I_{\mathrm{rain}}, \tag{3}$$

where E_{total} = total annual evaporation from the pool given as a percentage of the pool volume [%], A_{pool} = area of the pool [km^2], PE_{pan} = annual pan evaporation from the Australian Bureau of Meteorology [km], V_{pool} = pool volume [km^3], I_{rain} = annual amount of rain supplying the pool given as a percentage of the pool volume [%], A_{catch} = area of the catchment [km^2], P_{rain} = annual precipitation [km], I_{sea} = volume of water inflowing to the pool from the ocean to compensate evaporative loss, given as a percentage of the pool volume [%].

The SMM required the following assumptions: (1) loss of water from the Hamelin Pool was only due to evaporation; (2) gain of water from rainfall was either by direct inputs to Hamelin Pool or from runoff from the catchment (only 50% of precipitation falling on the adjacent catchment was included as runoff reaching the Pool, as the rest was assumed to be lost by evaporation from the ground surface); (3) seawater inputs were calculated as the difference between loss due to evaporation and gain from rain as required to maintain water levels; and (4) there were no groundwater inputs. A typical SMM would be applied to a lake that has an inflow and an outflow at different ends, experiencing a continual loss as a result of evaporation. Hamelin Pool differs from this type of steady-state model in that its inflow and outflow are at the same location, namely at the entrance across the Faure Sill, and are governed by tides. Given that the water level in Hamelin Pool more or less remains constant (subject to tides usually <1 m and evaporation), then steady-state conditions were assumed for both the SMM and SIM.

With the SIM, the ratio of evaporative loss to inputs (*E*/*I*) was calculated using the equation re-formulated by (Gibson and Reid 2010) for a steady-state model, as follows:

$$E/I = (\delta_L - \delta_P)/((\delta^* - \delta_L) \times m). \quad (4)$$

In Eqn 4, δ_L represents the $\delta^{18}O$ value of the surface water in Hamelin Pool, whereas δ_P is the $\delta^{18}O$ value of the source water for the pool (weighted mix of the seawater and rain water, as determined by the SMM). The δ^* value represents the local limiting isotope enrichment from evaporation and *m* reflects fractionation due to air temperature and humidity, as previously defined by Gat (1981). Refer to Gibson and Reid (2010) for a more detailed derivation of Eqn 4. The $\delta^{18}O$ value of the seawater entering Hamelin Pool was taken from nine sampling locations just north of the Faure Sill boundary and varied from +1.21‰ to +1.71‰, with a mean value +1.50 ± 0.14‰, which was used in the model. The stable isotope composition of the rainfall samples collected at Shark Bay was $\delta^{18}O = -3.28 \pm 0.75$‰. The $\delta^{18}O$ isotope composition of the mixture of seawater and rainwater contributing to the pool volume ($\delta^{18}O = +0.87$‰) was calculated on the basis of a mass balance according to the ratio between rain (13.1%) and ocean water (86.9%), as determined from the SMM. The $\delta^{18}O$ value for surface water in Hamelin Pool varied between +1.99‰ and +2.91‰ (SB60, SB61 SB190, SB15 and Sites D1 through D5), with a mean of +2.41 ± 0.14‰.

Results

Salinity and stable isotopes

(1) Shark Bay

All salinity and stable isotope values of surface-water samples collected from Shark Bay are available as Supplementary Material on the web. Surface-water salinity of Shark Bay ranged from 38 to 60, with the highest values observed in Hamelin Pool (Table 3). Salinity of the surface water from the Wooramel River sampled on 5 March 2011 was 0.2 (Table 3). Salinity of the shallow groundwater (<2 m) sampled at Monkey Mia ranged from 3.5 to 8.5, whereas the salinity of the two deep groundwater bores ranged from 1.4 to 3.2 (Table 2).

Table 3. Summary of salinity and stable isotope values of surface waters in and around Shark Bay, Western Australia, and Florida Bay, USA

VSMOW, Vienna Standard Mean Ocean Water

Location	Attribute	Salinity	$\delta^{18}O$ (‰) VSMOW	δ^2H (‰) VSMOW
Shark Bay				
Entire Bay	Mean	46.51	+1.42	+7.03
	Min	38.9	−1.31	−14.21
	Max	60.10	+2.91	+19.31
Hamelin Pool	Mean	56	+2.47	+15.43
	Min	49	+1.99	+6.96
	Max	56	+2.91	+19.31
Wooramel River	Mean	0.2	−4.65	−38.71
	Min	0.2	−4.52	−37.75
	Max	0.2	−4.77	−39.67
Florida Bay				
Joe Bay	Mean	13.8	+1.86	+12.23
	Min	0.20	−3.45	−27.21
	Max	54.3	+4.83	+35.94
Whipray Basin	Mean	34.5	+2.10	+14.27
	Min	19.9	−2.90	−25.22
	Max	51.9	+4.55	+35.16
Shark Slough	Mean	0	+0.86	+7.10
	Min	0	−2.98	−17.0
	Max	0	+3.65	+23.0
Taylor Slough	Mean	0	+0.16	+4.80
	Min	0	−2.25	−6.60
	Max	0	+1.55	+20.0

The few rainfall samples collected at Shark Bay had volume-weighted average values of $\delta^{18}O = -3.28$‰ and $\delta^2H = -9.03$‰ (Table 4) that plotted above the global meteoric water line (GMWL) (Fig. 6). Groundwater from both shallow and deep bores tended to be more depleted in ^{18}O and ^2H than was rainfall for the period sampled (Table 2). Values of $\delta^{18}O$ and δ^2H for the Wooramel River were similar to those obtained for the bores (Table 3). When plotted as $\delta^{18}O$ *v.* δ^2H, the Shark Bay surface-water samples fell along a best-fit line, with a slope of 6.6 ($R^2 = 0.89$, $P < 0.001$) (Fig. 6). The groundwater samples of both the deep and shallow bores also fell along this line, but closer to the GMWL.

The Shark Bay samples could be described by three linear relationships between $\delta^{18}O$ and salinity (Fig. 7). The $\delta^{18}O$ of most of the Shark Bay samples (Fig. 7, open and solid green circles) were linearly related to salinity, with a slope of 0.12 and an intercept of 4.12‰ ($R^2 = 0.83$, $P = <0.001$), and intersected the $\delta^{18}O$ and salinity values of the nearby Indian Ocean (Fig. 7, black square). Six of the Shark Bay samples (Fig. 7, shown in red) plotted away from the other Shark Bay samples with a slope of 0.15 and an intercept of −7.19‰ ($R^2 = 0.91$, $P = 0.0029$). Five of the six samples were located in the eastern arm of Shark Bay, close to the mouth of the Wooramel River, whereas the other sample was located at the southernmost end of Hamelin Pool from the boardwalk overlooking the stromatolites (Fig. 4).

Table 4. Summary of $\delta^{18}O$ and δ^2H of rainfall samples collected in Shark Bay, Australia
VSMOW, Vienna Standard Mean Ocean Water

Parameter	Date	Amount (mm)	$\delta^{18}O$ (‰) VSMOW	δ^2H (‰) VSMOW
Site				
Monkey Mia	14 June 2011	10	−1.15	9.71
Denham	14 June 2011	14	−3.32	−5.27
Denham	14 June 2011	14	−3.38	−5.29
Denham	5 June 2011	8	−2.88	−12.96
Monkey Mia	4 June 2011	4	−4.11	−20.90
Monkey Mia	4 June 2011	4	−4.03	−24.33
Monkey Mia	5 June 2011	2	−2.21	−5.98
Denham	28 July 2011	18.5	−4.28	−17.58
Weighted average			−3.28	−9.03

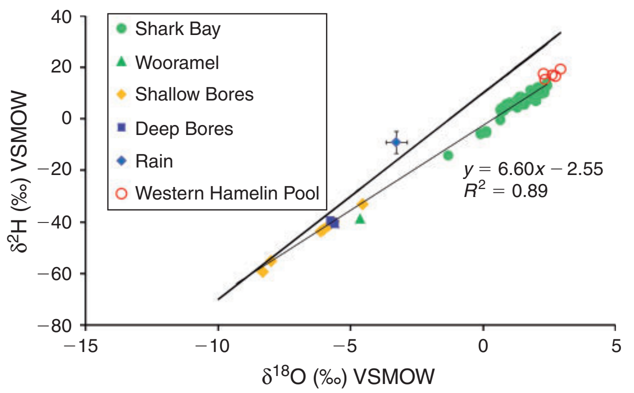

Fig. 6. Stable isotopic composition (δ^2H and $\delta^{18}O$) of surface waters in Shark Bay (solid green circles), western Hamelin Pool (open red circles) and the Wooramel River (green triangle). Also depicted are the δ^2H and $\delta^{18}O$ of shallow groundwater (gold diamonds), deep groundwater (blue squares) and rain (blue diamond) water collected around Shark Bay, Australia. The bold black line represents the global meteoric water line (GMWL), with a slope of +8 and an intercept of +10‰. The thin black line represents the best-fit line (equation given in figure) through the Shark Bay surface-water samples.

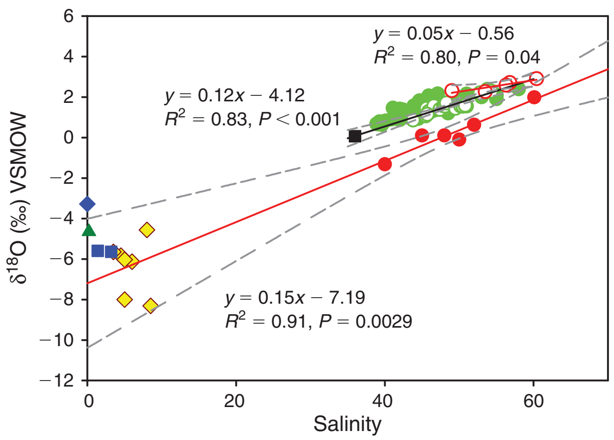

Fig. 7. The $\delta^{18}O$ versus salinity of Shark Bay surface water (solid and open green circles), shallow groundwater (yellow diamonds), deep groundwater (blue squares), rain (blue diamond), seawater (black square) and the Wooramel River (green triangle). The solid red dots represent surface water collected from the eastern Shark Bay Sites SB15 (stromatolites), SB17, SB63, SB64, SB65 and SB69 depicted in Fig. 4, whereas the open red dots represent five surface-water samples (D1–D5) collected from the western side of Hamelin Pool.

The intercept (−7.19‰) of those eastern-arm samples has a ranking of similarity (from most to least similar) with potential freshwater sources of shallow groundwater (−6.36‰), deep groundwater (−5.62‰), river water (−4.65‰) and rain water (−3.28‰). A linear regression line describing $\delta^{18}O$ and salinity for the points D1–D5 (Fig. 7, open circles) had a slope of 0.05 and an intercept of −0.56‰ ($\delta^{18}O = 0.05 \times$ salinity − 0.56). Following this relationship, the initial $\delta^{18}O$ of surface water entering the pool could be calculated. Solving this equation by using a salinity range from 35 to 40, representing values of open-ocean seawater and surface water near the Faure Sill, respectively, resulted in $\delta^{18}O$ values between +1.19‰ and +1.44 ‰. That calculated range in $\delta^{18}O$ values is similar to the range of values (+1.21‰ to +1.71‰) observed for nine surface-water samples collected over the Faure Sill at the entrance to Hamelin Pool.

(2) Florida Bay

The $\delta^{18}O$ and δ^2H values of the Florida Bay samples were correlated ($R^2 = 0.69$, $P < 0.001$), exhibiting a slope of 5.5, compared with a slope of 8 for the GMWL (Fig. 8). The $\delta^{18}O$ of precipitation measured between 1997 and 1999 ranged between −6.5‰ and 0‰, with a weighted-mean value of −2.83‰. The weighted-mean value of the δ^2H for the rainfall samples was −10.59‰. The mean $\delta^{18}O$ value of waters collected at Shark Slough was +0.86‰ ($\delta^2H = +7.1$‰) and ranged between −2.98 and +3.65‰ ($\delta^2H = -17$‰ to +23‰) (Fig. 8). In contrast, the mean value of $\delta^{18}O = +0.16$‰ ($\delta^2H = +4.8$‰) and the range from $\delta^{18}O = -2.25$ ‰ to $\delta^{18}O = +1.55$‰ ($\delta^2H = -6.6$‰ to +20‰) was obtained for three stations from Taylor Slough (Fig. 8). The mean isotopic values of both Shark Slough and Taylor Slough fell along the best-fit line of the Florida Bay samples, and were significantly more positive than the local rainfall (Fig. 8).

The mean monthly $\delta^{18}O$ values for Florida Bay were positively correlated with mean salinity (Fig. 9). For Whipray Basin, the linear relationship was defined by a slope of 0.12 and an intercept of −2.14‰ ($R^2 = 0.72$, $P < 0.001$), which was similar

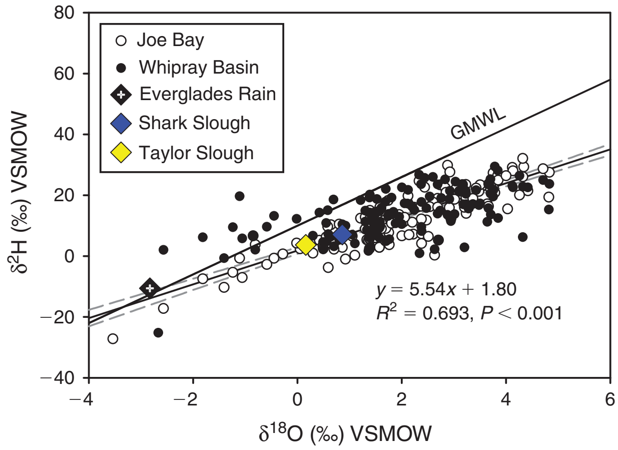

Fig. 8. Stable isotopic composition of surface waters collected in Joe Bay and Whipray Basin of Florida Bay, along with surface water from Shark Slough and Taylor Slough in the Everglades, as well as local rainfall. Best-fit linear line is through all of the Florida Bay data. Dashed grey lines represent the 95% confidence intervals around the line. GMWL = the global meteoric water line.

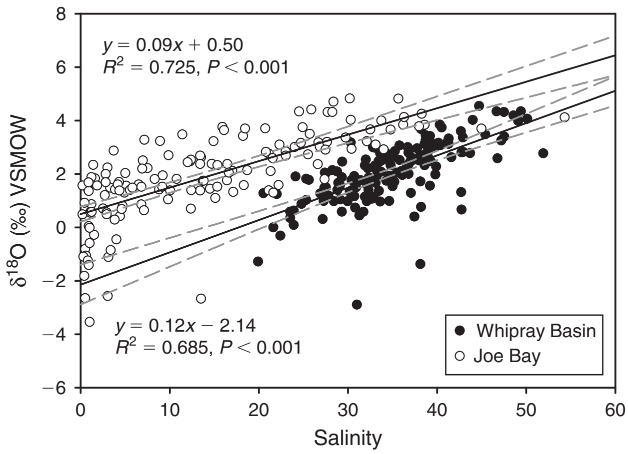

Fig. 9. Values of δ^{18}O and salinity were found to be correlated for samples collected from Joe Bay (open circles) and Whipray Basin (black dots) in Florida Bay.

to the rainfall isotope value of −2.83‰. The linear relationship for Joe Bay was defined by a slope of 0.09 and an intercept of +0.5‰ ($R^2 = 0.68$; $P < 0.001$), which was similar to the +0.16‰ value of the surface water in Taylor Slough.

Model results

The observed variations in δ^{18}O with salinity were well explained for both Shark Bay and Whipray Basin in Florida Bay by the Craig–Gordon (Craig and Gordon 1965) model of evaporation (Fig. 10). The maximum value of δ^{18}O predicted by the model at a salinity of 60 was near +2‰ for Shark Bay and near +4‰ for Florida Bay. In reality, there was a significant amount of mixing with water derived from other sources superimposed on the evaporation trends, accounting for the scatter at both locations. The evaporation model was not applicable for Joe Bay because the extreme salinity variations suggested a large influx of freshwater, which was not incorporated into the evaporation model.

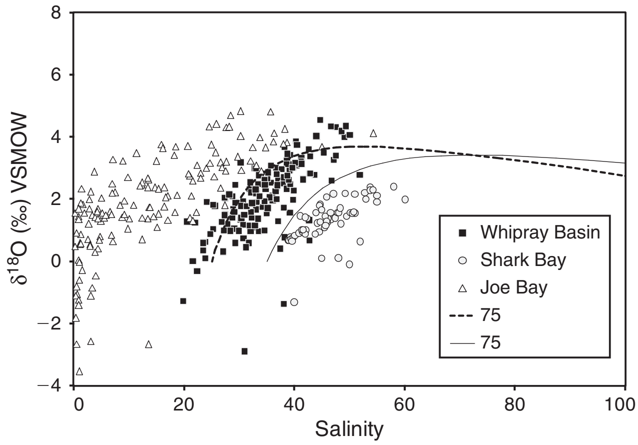

Fig. 10. Salinity and δ^{18}O data for two end-members from Florida Bay (Joe Bay and Whipray Basin) and Shark Bay. Shark Bay (solid 75 line) was assumed to have a starting salinity of 35, evaporating into an atmosphere with a relative humidity of 75% and an atmospheric δ^{18}O of −12.83‰. Whipray Basin (dashed 75 line) was assumed to have a starting salinity of 25, and atmospheric values of relative humidity and δ^{18}O of 75% and −11.8‰, respectively. Joe Bay was composed of mixtures of evaporated freshwater, precipitation and evaporated Bay water (as represented by Whipray Basin).

Using the SMM, the annual loss of water as a result of evaporation from Hamelin Pool calculated from the mean pan evaporation (2652 mm year^{-1}) and area (1403 km^2) was 3.72 km^3, or 52.79% of the total volume of the pool. Total annual inputs of rainfall were estimated as 0.49 km^3 or 6.94% of the pool volume. The resultant inflow of seawater, calculated as the difference between evaporation and precipitation, was 3.23 ± 0.18 km^3, or ~45.8 ± 2.5% of the total pool volume. Our estimates of uncertainty around the importance of seawater inflow are based on a range of calculated values, assuming a variation from a minimum of 0% of the rainfall falling in the catchment entering the pool as runoff to a maximum of 100% of the rainfall entering as runoff.

The percentage of the evaporative loss versus the inflow (E/I) was estimated from the SIM. Accordingly, before entering Hamelin Pool, ~12–20% (on average 16%) of the seawater inflowing from the distant open ocean through Shark Bay to Faure Sill was lost as a result of evaporation. This was reflected in the change of the average δ^{18}O value from 0.0‰ (open ocean) to +1.5‰ (Faure Sill). More substantial loss occurred in the shallow waters of Hamelin Pool, where an additional 14–40% (mean 23%) evaporated, resulting in a change of δ^{18}O value from 0.87‰ (mix of sea and rain water) to 2.4‰ (Hamelin) (Fig. 11).

Discussion

Freshwater sources

The hydrologic conditions of both Shark Bay and Florida Bay can be described by a combination of both mixing of isotopically distinct sources of freshwater with seawater and by fractionation during evaporation. Although the maximum

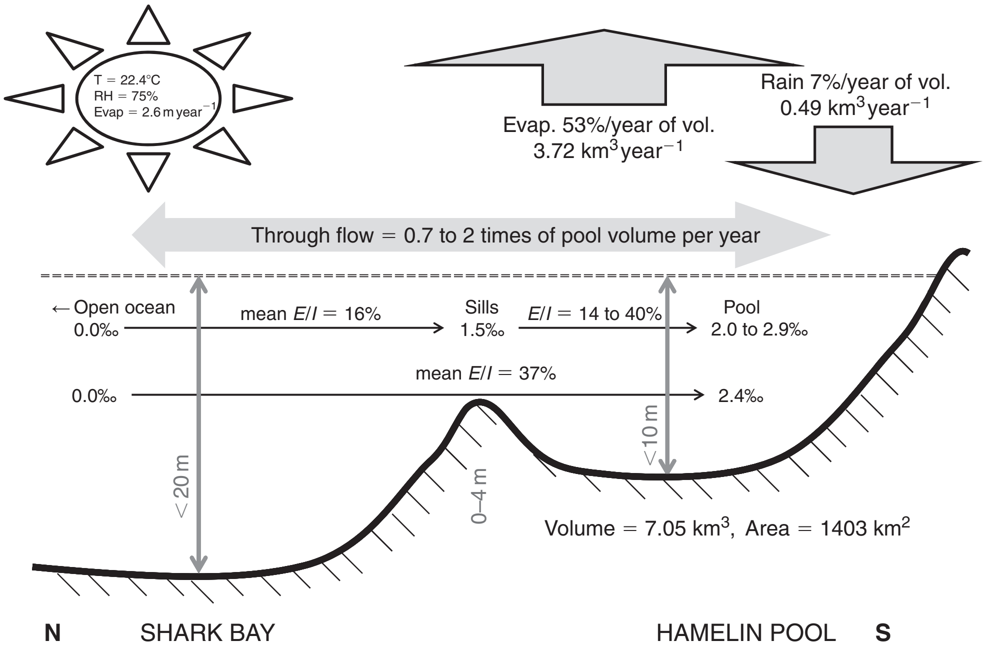

Fig. 11. Mass-balance model for Hamelin Pool, combining results of simple math model (SMM) and simple isotope model (SIM). All values are calculated per year. The values in per mil (‰) are given for measured $\delta^{18}O$ in water. *E/I* is given as evaporation–inflow ratio as calculated from SIM.

isotopic values of both Shark Bay and Whipray Basin in Florida Bay could be described well by an isotopic evaporation model (Fig. 10), linear relationships between $\delta^{18}O$ and salinity may also suggest inputs of different freshwater sources.

In the case of Shark Bay, the potential sources of freshwater include rain, surface-water runoff and groundwater discharge. The weighted-average value of the few rainfall samples collected at Shark Bay ($\delta^{18}O = -3.28$‰) was higher than the $\delta^{18}O$ values obtained for shallow groundwater (less than −6.36‰) and the Wooramel River (−4.65‰). The discrepancy between the $\delta^{18}O$ values of the rainfall and those of the Wooramel River and shallow groundwater may be a result of the limited period of rainfall collection. The samples collected in June and July 2011 from Shark Bay were from low-volume rain events typical in the winter season, as opposed to higher-rainfall events typically associated with summer-time cyclones. Low-volume rain events are often characterised by relatively positive $\delta^{18}O$ values that may not contribute substantially to surface runoff from catchments. For instance, in another study conducted inland of Shark Bay in the adjacent Pilbara region, runoff and groundwater recharge were found to be generated mainly by infrequent but large-volume rain events that tended to have more negative $\delta^{18}O$ values than did the smaller events (Dogramaci *et al.* 2012).

Most of the Shark Bay samples (Fig. 7, open and solid green symbols) exhibited a linear relationship between $\delta^{18}O$ and salinity, with an intercept value (−4.12‰) that was between the isotopic values of rainfall (−3.28‰) and the Wooramel River (−4.65‰). The linear relationship between $\delta^{18}O$ and salinity of those samples also intercepted the $\delta^{18}O$ and salinity values of the nearby Indian Ocean (Fig. 7, black square). Furthermore, not only were those samples hypersaline (salinity between 40 and 60), but their isotopic signature with salinity was well explained by the Craig–Gordon (1965) model of evaporation (Fig. 10). The simplest explanation for the chemical signature of most of the Shark Bay samples would be evaporation of Indian Ocean water, although mixing of freshwater sources of rainfall and/or river runoff cannot be dismissed. Although the western Hamelin Pool samples (Fig. 7, open red symbols) had a different linear relationship between $\delta^{18}O$ and salinity than did most of the other Shark Bay samples, their isotopic and salinity values overlapped with many of the Shark Bay samples.

Five of the Shark Bay samples collected in March 2011 from the eastern arm near the mouth of the Wooramel River had a significantly different linear relationship between $\delta^{18}O$ and salinity, with a much lower intercept value of −7.19‰ than for the other Shark Bay samples (Fig. 7). Given the location of those five samples near the mouth of the Wooramel River, then river discharge would be the most likely source; however, that source of water cannot be isotopically distinguished from either groundwater or rain. According to the records from the Western Australian Department of Water, the total discharge of the Wooramel River between December 2010 and June 2011 was 0.623 km^3, a volume approximately equivalent to 35% of the volume of water (1.8 km^3) overlying the Faure Sill (assuming a width of 22.5 km), but only 8.8% of the total volume of Hamelin Pool. Alternatively, the discharge from the Wooramel River equates to 3% of the volume of the Shark Bay waters north of Faure Sill, assuming that a total volume of 17.7 km^3 for that area (Smith and Atkinson 1983).

Although the five sample locations near the Wooramel River outlet demonstrated a change in the relationship between the stable isotopic values and salinity (Fig. 7), the samples remained hypersaline, with salinities ranging between 40 and 52. These results have demonstrated the potential power of combining stable isotope data with salinity values to distinguish sources of freshwater to hypersaline estuaries. Interestingly, the Shark Bay samples collected near the mouth of the Wooramel River during the second sample campaign (29 March to 4 April 2011) had stable isotope and salinity values more representative of evaporated seawater. Discharge from the Wooramel River was extremely low during that time, with values decreasing from 1000 m^3 day^{-1} to zero by 3 April 2011. We suggest that the Wooramel River, with some direct inputs of rainfall from the cyclones, may be more responsible for the isotopic shift in the water samples near its mouth than are groundwater inputs; this explanation is supported by the short-lived (3–4 weeks) response in the isotopic composition of the surface waters near its mouth. Presently, groundwater inputs to Shark Bay are unknown, but if they were significant, they would be expected to occur over a longer time period and thus be observable in more depleted isotopic values. The short residence time in the area at the mouth of the Wooramel River is consistent with an almost 1 m tidal amplitude reported for Monkey Mia (Department of Transport, Western Australia; http://www.transport.wa.gov.au, accessed 16 December 2011).

In the case of Florida Bay, the intercept $\delta^{18}O$ value of +0.5‰ at zero salinity for Joe Bay was similar to the average $\delta^{18}O$ value of +0.16‰ of the surface waters in Taylor Slough. The $\delta^{18}O$ intercept value for Whipray Basin was −2.14‰, close to the mean local rainfall $\delta^{18}O$ value of −2.83‰. In an earlier study, precipitation and surface-water runoff from the Everglades were found to be the dominant sources of freshwater into Florida Bay (Swart and Price 2002). The spatial distribution of the proportion of each of those freshwater sources was determined from linear relationships between $\delta^{18}O$ and salinity measurements taken monthly over 7 years (1993–1999) at 28 sites. In that investigation, the value of $\delta^{18}O$ at the intercept of zero salinity was used in a two-component mixing model to discern the proportion of each of the freshwater sources. The result was that in the eastern portion of the bay, such as Joe Bay, between 70% and 80% of the freshwater inputs were from Everglades runoff. Conversely, in the western portion of the bay, such as Whipray Basin, precipitation was the dominant freshwater input (70–80%). The linear relationship between $\delta^{18}O$ and salinity still holds for the longer time-series data of Joe Bay and Whipray Basin (Fig. 9). This approach of using the intercept of linear relationships between $\delta^{18}O$ and salinity to quantify sources of freshwater inputs was successfully applied to other estuaries in south Florida (Swart *et al*. 2001; Stalker *et al*. 2009). Groundwater is not considered a potential freshwater source to Florida Bay because seawater intrudes significantly into the Everglades, preventing the discharge of fresh groundwater directly into Florida Bay (Fitterman and Deszcz-Pan 1998). Furthermore, all of the groundwater sampled in Florida Bay was determined to be saline to hypersaline (R. M. Price, unpubl. data).

Hamelin Pool water budget

The results of the SMM suggest that evaporative loss is the largest component of the water budget (53%) of Hamelin Pool. This calculated evaporative loss is substantial, representing more than half of the total Pool volume lost each year, and is a consequence of the large surface area, shallow water depth and arid climate conditions. A loss of half of the Pool volume would also be expected, to maintain high salinities (60) in the Pool at nearly twice that of seawater. In addition, stable isotopic values of waters in the Pool have reached their maximum values ($\delta^{18}O > +2$‰) as predicted by the isotopic evaporation model (Fig. 10). Evaporative loss is also the largest component of the water budget in Florida Bay and, at 1660 mm $year^{-1}$, exceeds the combined freshwater inputs of rainfall (1060 mm $year^{-1}$) and runoff (100 mm $year^{-1}$) (Nuttle *et al*. 2000; Price *et al*. 2007). However, inputs of freshwater are seasonal and are offset in time from the evaporation, allowing for seasonal changes in salinity (Nuttle *et al*. 2000).

The large annual evaporative loss from Hamelin Pool would result in replacement of 99% of water in the pool within 7 years. However, a mean daily tidal amplitude of ±0.5 m in the Pool (Department of Transportation, Western Australia, http://www.transport.wa.gov.au for Monkey Mia, accessed 16 December 2011) would result in a volume oscillation of ~0.70 km^3 or ~10% of the Pool total volume per day. Assuming instantaneous mixing, this volume of water would result in replacement of 99% of the total volume of water in the Pool within 21 days. However, this simple estimate should be taken as a minimum retention time and most likely underestimates the true residence time for the following reasons: (1) restrictions in flow across the Faure Sill were not taken into account, (2) the assumption of instantaneous mixing and (3) a maximum value of evaporation (Pan evaporation) was used in the model. These estimates do not take into account any freshwater inputs from groundwater. The 21-day retention time calculated for Hamelin Pool was low compared with the >1-year retention time estimated for the entire eastern arm of Shark Bay by Smith and Atkinson (1983). However, the 21-day value is similar to the 3–4-week time interval that we observed for a change in the water chemistry at the mouth of the Wooramel River. These relatively short retention times suggest that the water-chemistry conditions in both the Faure Sill and Hamelin Pool could be susceptible to relatively small changes in water inputs, being either freshwater runoff from the catchment or seawater with an increase in sea-level rise.

The calculation of retention times based on evaporation only does not take into account flushing of the Pool by tides, whereas the calculation of retention times based on tidal fluctuations does not take into account restricted flow over the Faure Sill. However, the retention time for Hamelin Pool can be estimated by combining the results from both the SIM and SMM. The SMM does not consider inputs (I), but only evaporation (E), whereas the SIM model estimates E/I. Therefore, the input to the pool (I) can be calculated as I = SMM/SIM, using the results from both models: E/I = 14–40% (mean 23%) from the SIM, and E = ~53% from the SMM, with the estimated inflow (I) calculated to be 3.8–1.4 times higher than evaporation (E). From the SMM, 3.72 km^3 per year was determined to evaporate from the pool (E), therefore inflow to the Pool equals 4.9–14 km^3 $year^{-1}$. This implies that the volume of the pool is replaced between ~0.7 and two times each year, or between 6 and 12 months (Fig. 11). The longer flushing time (6–12 months) obtained by combining the SMM and SIM models than that obtained from the SMM alone (every 21 days) is considered to be more representative for Hamelin Pool, because of the assumption of the SMM. Across Florida Bay, water-residence

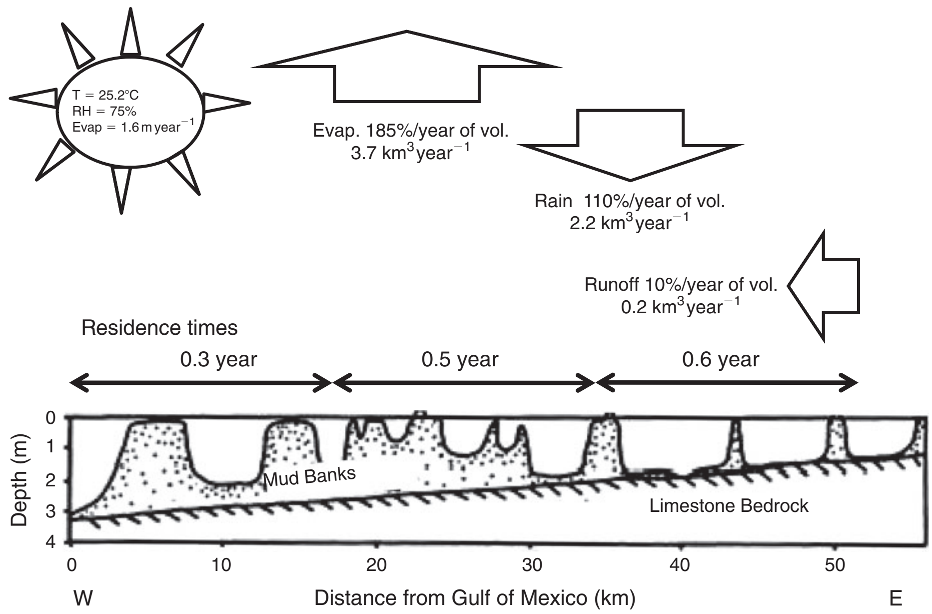

Fig. 12. Mass balance of water and water-residence times for Florida Bay based on the work of Nuttle *et al.* (2000) and Price *et al.* (2007). We assumed the volume of Florida Bay to be 2 km^3 (an area of 2000 km^2, with an average depth of 1 m to calculate annual fluxes as a fraction of the total volume. The bathymetry schematic is modified from Zieman *et al.* (1989).

times have been estimated to range between 2 and 6 months (Fig. 12), with the longer residence times occurring in the central portion of the bay where hypersaline conditions occur on a seasonal basis (Nuttle *et al.* 2000; Lee *et al.* 2006).

Salinity and the stable isotopes of oxygen and hydrogen in estuaries are influenced by their climate, tidal exchange, geomorphology and inputs of freshwater from their watersheds. In both Shark Bay and Florida Bay, hypersaline conditions occur as a result of shallow banks that physically restrict portions of those bays from the open ocean. With a wetter climate, smaller size and shallower depth, Florida Bay is more influenced by seasonal inputs of rainfall and runoff, as indicated by its wider range in salinity (0–70) than in Shark Bay (35–60; Table 1). The long-term (almost 14 years) set of data collected from Florida Bay allowed for a refinement in the approach of using a linear relationship between δ^{18}O and salinity, to distinguish between the freshwater sources and their relative contributions spatially across the bay. This geochemical approach has also proven useful in identifying the timing and spatial distribution of freshwater sources to smaller, brackish-water estuaries in the USA (Stalker *et al.* 2009) and Mexico (Stalker *et al.* 2011). The current paper presents the first attempt of using this method of combining stable isotopes and salinity in an estuary as large as Shark Bay. The significantly larger size of Shark Bay, greater depth, along with a drier climate and intermittent inputs of fresh water, result in more persistent hypersaline conditions, making identification of freshwater inputs unfeasible by salinity data alone. Although the data collection was limited in time, there was some indication of freshwater inputs to Shark Bay, when combining δ^{18}O data with salinity, despite the persistence of hypersaline conditions. The results of the present research suggest that this technique of combining stable isotopes with salinity may be useful in identifying freshwater inputs across a spectrum of estuary sizes and salinity ranges, including hypersaline estuaries.

Conclusions

This investigation determined that the stable isotopes of oxygen and hydrogen were useful in identifying potential sources of freshwater to two hypersaline estuaries. In Shark Bay, intermittent discharge from the Wooramel River may have been observed near the mouth of the Wooramel River from a combination of isotopic and salinity data, but only while the river was flowing. Limited sampling of the freshwater sources to Shark Bay prohibited a clear identification of the isotopic signature of those sources. Future attempts at collecting rainfall during cyclone events and river runoff during early and peak discharge may be needed to clearly identify the isotopic signatures of those freshwater sources. The influx of seawater to Shark Bay experiences a 16% loss as a result of evaporation on its way from the mouth to the Faure Sill. That water continues to evaporate, experiencing a further reduction of ~23% in volume on retention in Hamelin Pool. Significant restriction of the inflow to Hamelin Pool caused by Faure Sill results in relatively long retention time in the pool, where 70–200% of the volume is replaced every year because of combined tidal fluctuation and evaporation losses. In Florida Bay, freshwater runoff could account for as much as 80% of the inputs in the eastern part of the bay, whereas precipitation was the dominant source of freshwater in the western portion. The approach of combining stable isotopic and mass-balance models used herein could be used to assess current hydrologic conditions in other hypersaline estuaries or could be used in future studies of hypersaline estuaries where freshwater or seawater inputs would be expected to change because of either climate change and/or sea-level rise.

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References

Balls, P. W. (1994). Nutrient inputs to estuaries from nine Scottish east coast rivers; influence of estuarine processes on inputs to the North Sea. *Estuarine, Coastal and Shelf Science* **39**, 329–352. doi:10.1006/ECSS.1994.1068

Bauch, D., Schlosser, P., and Fairbanks, R. G. (1995). Freshwater balance and the sources of deep and bottom waters in the Arctic Ocean inferred from the distribution of $H_2^{18}O$. *Progress in Oceanography* **35**, 53–80. doi:10.1016/0079-6611(95)00005-2

Bianchi, T. S., Pennock, J. R., and Twilley, R. R. (Eds) (1999). 'Biogeochemistry of Gulf of Mexico Estuaries.' (John Wiley & Sons: New York.)

Boyer, J. N., Fourqurean, J. W., and Jones, R. D. (1999). Seasonal and long-term trends in the water quality of Florida Bay (1890–1997). *Estuaries* **22**, 417–430. doi:10.2307/1353208

Burling, M. C., Ivey, G. N., and Pattiaratchi, C. D. (1999). Convectively driven exchange in a shallow coastal embayment. *Continental Shelf Research* **19**, 1599–1616. doi:10.1016/S0278-4343(99)00034-5

Burling, M. C., Pattiaratchi, C. B., and Ivey, G. N. (2003). The tidal regime of Shark Bay, Western Australia. *Estuarine, Coastal and Shelf Science* **57**, 725–735. doi:10.1016/S0272-7714(02)00343-8

Coplen, T. B. (1996). New guidelines for reporting stable hydrogen, carbon, and oxygen isotope-ratio data. *Geochimica et Cosmochimica Acta* **60**, 3359–3360. doi:10.1016/0016-7037(96)00263-3

Coplen, T. B., Wildman, J. D., and Chen, J. (1991). Improvements in the gaseous hydrogen–water equilibration technique for hydrogen isotope ratio analysis. *Analytical Chemistry* **63**, 910–912. doi:10.1021/AC00009A014

Corlis, N. J., Herbert Veeh, H., Dighton, J. C., and Herczeg, A. L. (2003). Mixing and evaporation processes in an inverse estuary inferred from δ^2H and $\delta^{18}O$. *Continental Shelf Research* **23**, 835–846. doi:10.1016/S0278-4343(03)00029-3

Craig, H., and Gordon, L. I. (1965). Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In 'Proceedings of Stable Isotopes in Oceanographic Studies and Paleotemperatures Consiglio Nazionale delle Ricerche Laboratorio di Geologia. Nucleare, Pisa'. (Ed. E. Tongiorgi.)

Dogramaci, S., Skrzypek, G., Dodson, W., and Grierson, P. F. (2012). Stable isotope and hydrochemical evolution of groundwater in the semi-arid Hamersley Basin of sub-tropical northwest Australia. *Journal of Hydrogeology*. doi:10.1016/J.JHYDROL.2012.10.004

Duarte, C. M. (1995). Submerged aquatic vegetation in relation to different nutrient regimes. *Ophelia* **41**, 87–112.

Elliott, M., and Whitfield, A. K. (2011). Challenging paradigms in estuarine ecology and management. *Estuarine, Coastal and Shelf Science* **94**, 306–314. doi:10.1016/J.ECSS.2011.06.016

Epstein, S., and Mayeda, T. (1953). Variation of O^{18} content of waters from natural sources. *Geochimica et Cosmochimica Acta* **4**, 213–224. doi:10.1016/0016-7037(53)90051-9

Fairbanks, R. G. (1982). The origin of continental shelf and slope water in the New York Bight and Gulf of Maine: evidence from $H_2\,^{18}O/H_2\,^{16}O$ ratio measurements. *Journal of Geophysical Research* **87**, 5796–5808. doi:10.1029/JC087IC08P05796

Fitterman, D. V., and Deszcz-Pan, M. (1998). Helicopter EM mapping of saltwater intrusion in Everglades National Park. *Exploration Geophysics* **29**, 240–243. doi:10.1071/EG998240

Fourqurean, J. W., and Robblee, M. B. (1999). Florida Bay: a history of recent ecological changes. *Estuaries* **22**, 345–357. doi:10.2307/1353203

Gat, J. R. (1981). Groundwater in stable isotope hydrology: deuterium and oxygen-18 in the water cycle. Technical Report Series, Vol. 210 (Eds. J. R. Gat and R. Gonfiantini) pp. 223–240. International Atomic Energy Agency (Vienna, Austria).

Gibson, J. J., and Reid, R. (2010). Stable isotope fingerprint of open-water evaporation losses and effective drainage area fluctuations in a subarctic shield watershed. *Journal of Hydrology* **381**, 142–150. doi:10.1016/J.JHYDROL.2009.11.036

Gonfiantini, R. (1986). Environmental isotopes in lake studies. In 'Handbook of Environmental Isotopes Geochemistry, vol. 2'. (Eds P. Fritz and J. Fontes.) pp. 113–168. (Elsevier: Amsterdam.)

Johannes, R. E., and Hearn, C. J. (1985). The effect of submarine groundwater discharge on nutrient and salinity regimes in a coastal lagoon off Perth, Western Australia. *Estuarine, Coastal and Shelf Science* **21**, 789–800. doi:10.1016/0272-7714(85)90073-3

Koch, G. R., Childers, D. L., Staehr, P. A., Price, R. M., Davis, S. E., and Gaiser, E. E. (2012). Hydrological conditions control P loading and aquatic metabolism in an oligotrophic, subtropical estuary. *Estuaries and Coasts* **35**, 292–307. doi:10.1007/S12237-011-9431-5

Largier, J. L., Hollibaugh, J. T., and Smith, S. V. (1997). Seasonally hypersaline estuaries in Mediterranean-climate regions. *Estuarine, Coastal and Shelf Science* **45**, 789–797. doi:10.1006/ecss.1997.0279

Lee, T. N., Johns, E., Melo, N., Smith, R. H., Ortner, P., and Smith, D. (2006). On Florida Bay hydpersalinity and water exchange. *Bulletin of Marine Science* **79**, 301–327.

Lewis, E. L. (1980). The Practical Salinity Scale 1989 and Its Antecedents. *IEEE Journal of Oceanic Engineering* **OE-5**, 3–8.

Lloret, J., Marin, A., Marin-Guirao, L., and Velasco, J. (2005). Changes in macrophytes distribution in a hypersaline coastal lagoon associated with the development of intensively irrigated agriculture. *Ocean &Coastal Management* **48**, 828–842.

Lloyd, M. R. (1964). Variations in the oxygen and carbon isotope ratios of Florida Bay mollusks and their environmental significance. *The Journal of Geology* **72**, 84. doi:10.1086/626966

Logan, B. W., and Cebulski, D. E. (1970). Sedimentary environments of Shark Bay, Western Australia. *American Association of Petroleum Geologists Memoir* **13**, 1–37.

Logan, B. W., Read, J. F., and Davies, G. R. (1970). History of carbonate sedimentation, Quaternary Epoch, Shark Bay, Western Australia. *American Association of Petroleum Geologists Memoir* **13**, 38–84.

Martin, J. M., and Letolle, R. (1979). Oxygen 18 in estuaries. *Nature* **282**, 292–294. doi:10.1038/282292A0

McCluskey, P. (2008). Shark Bay world heritage property strategic plan 2008–2020. Department of Environment and Conservation, Perth, WA.

Merlivat, L., and Coantic, M. (1975). Study of mass-transfer at the air-water interface by an isotopic method. *Journal of Geophysical Research* **80**, 3455–3464. doi:10.1029/JC080I024P03455

Moore, W. S. (1999). The subterranean estuary: a reaction zone of ground water and sea water. *Marine Chemistry* **65**, 111–125. doi:10.1016/S0304-4203(99)00014-6

Nuttle, W. K., Fourqurean, J. W., Cosby, B. J., Zieman, J. C., and Robblee, M. B. (2000). Influence of net freshwater supply on salinity in Florida Bay. *Water Resources Research* **36**, 1805–1822. doi:10.1029/1999WR900352

Paul, D., Skrzypek, G., and Forizs, I. (2007). Normalization of measured stable isotope composition to isotope reference scale-a review. *Rapid*

Communications in Mass Spectrometry **21**, 3006–3014. doi:10.1002/RCM.3185

Playford, P. E. (1980). Australia's stromatolite stronghold. *Natural History* **89**, 58–59.

Potter, I. C., Chuwen, B. M., Hoeksema, S. D., and Elliott, M. (2010). The concept of an estuary: a definition that incorporates systems which can become closed to the ocean and hypersaline. *Estuarine, Coastal and Shelf Science* **87**, 497–500. doi:10.1016/J.ECSS.2010.01.021

Price, R. M., Nuttle, W. K., Cosby, B. J., and Swart, P. K. (2007). Variation and uncertainty in evaporation from a subtropical estuary: Florida Bay. *Estuaries and Coasts* **30**, 497–506. doi:10.1007/BF02819396

Price, R. M., Swart, P. K., and Willoughby, H. E. (2008). Seasonal and spatial variation in the stable isotopic composition of $\delta^{18}O$ an δD of precipitation in south Florida. *Journal of Hydrology* **358**, 193–205. doi:10.1016/J.JHYDROL.2008.06.003

Rudnick, D. T., Chen, Z., Childers, D. L., Boyer, J. N., and Fontaine III, T. D. (1999). Phosphorus and Nitrogen Inputs to Florida Bay: the importance of the Everglades Watershed. *Estuaries* **22**, 398–416. doi:10.2307/1353207

Saha, A.K., Moses, C.S., Price, R.M., Engel, V., Smith, T.J.I., and Anderson, G. (2012). A hydrological budget (2002–2008) for a large subtropical wetland ecosystem indicates marine groundwater discharge accompanies dimished freshwater flow. *Estuaries and Coasts* **35**, 459–474. doi:10.1007/S12237-011-9454-Y

Skrzypek, G., Sadler, R., and Paul, D. (2010). Error propagation in normalization of stable isotope data: a Monte Carlo analysis. *Rapid Communications in Mass Spectrometry* **24**, 2697–2705. doi:10.1002/RCM.4684

Slomp, C. P., and Van Cappellen, P. (2004). Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. *Journal of Hydrology* **295**, 64–86. doi:10.1016/J.JHYDROL.2004.02.018

Smith, S. V., and Atkinson, M. J. (1983). Mass balance of carbon and phosphorus in Shark Bay, Western Australia. *Limnology and Oceanography* **28**, 625–639. doi:10.4319/LO.1983.28.4.0625

Stalker, J. C., Price, R. M., and Swart, P. K. (2009). Determining spatial and temporal inputs of freshwater, including submarine groundwater discharge, to a subtropical estuary using geochemical tracers, Biscayne Bay, south Florida. *Estuaries and Coasts* **32**, 694–708. doi:10.1007/S12237-009-9155-Y

Stalker, J. C., Price, R. M., Rivera-Monroy, V., Herrera-Silveira, J., and Morales, S. (2011). Hydrologic dynamics of a subtropical estuary, using geochemical tracers, Celestun, Yucatan, Mexico. In 'Coastal Estuarine Research Federation (CERF) Societies, Estuaries and Coasts: Adapting to Change', 6–10 November, Daytona Beach, FL, p. 201.

Surge, D., and Lohmann, K. (2002). Temporal and spatial differences in salinity and water chemistry in SW Florida estuaries: effects of human-impacted watersheds. *Estuaries and Coasts* **25**, 393–408. doi:10.1007/BF02695982

Swart, P. K. (2000). The oxygen isotopic composition of interstitial waters: evidence for fluid flow and recrystallization in the margin of Great Bahama Bank. *Science Results* **166**, 91–98.

Swart, P. K., and Kramer, P. (1997) Geology of Mud Islands in Florida Bay. In 'Geology and Hydrogeology of Carbonate Islands, Developments in Sedimentology. Vol. 54'. (Eds H. L. Vacher and T. Quinn.) pp. 249–274. (Elsevier: Amsterdam.)

Swart, P. K., and Price, R. M. (2002). Origin of salinity variations in Florida Bay. *Limnology and Oceanography* **47**, 1234–1241. doi:10.4319/LO.2002.47.4.1234

Swart, P. K., Price, R. M., and Greer, L. (2001). The relationship between stable isopotic variations (O, H, and C) and salinity in waters and corals from environments in South Florida: implications for reading the paleoenvironmental record. *Bulletins of American Paleontology* **361**, 17–29.

Valiela, I., Costa, J., Foreman, K., Teal, J., Howes, B., and Aubrey, D. (1999). Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. *Biodegradation* **10**, 177–197. doi:10.1023/A:1008317906069

Wängberg, I., Munthe, J., Berg, T., Ebinghaus, R., Kock, H. H., Temme, C., Bieber, E., Spain, T. G., and Stolk, A. (2007). Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area. *Atmospheric Environment* **41**, 2612–2619. doi:10.1016/J.ATMOSENV.2006.11.024

Zieman, J. C., Fourqurean, J. W., and Iverson, R. L. (1989). Distribution, abundance and productivity of seagrasses and macroalgae in Florida Bay. *Bulletin of Marine Science* **44**, 292–311.