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# Coastal groundwater discharge – an additional source of phosphorus for the oligotrophic wetlands of the Everglades

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# 1 **Abstract**

2 In this manuscript we define a new term we call Coastal Groundwater Discharge (CGD), 3 which is related to submarine groundwater discharge (SGD), but occurs when seawater intrudes 4 inland to force brackish groundwater to discharge to the coastal wetlands. A hydrologic and 5 geochemical investigation of both the groundwater and surface water in the southern Everglades 6 was conducted to investigate the occurrence of CGD associated with seawater intrusion. During 7 the wet season , the surface water chemistry remained fresh. Enhanced chloride, sodium, and 8 calcium concentrations, indicative of brackish groundwater discharge, were observed in the 9 surface water during the dry season. Brackish groundwaters of the southern Everglades contain 10 1 to 2.3 µM concentrations of total phosphorus (TP). These concentrations exceed the expected 11 values predicted by conservative mixing of local fresh groundwater and intruding seawater, 12 which both have TP < 1 µM. The additional source of TP may be from seawater sediments or 13 from the aquifer matrix as a result of water-rock interactions (such as carbonate mineral 14 dissolution and ion exchange reactions) induced by mixing fresh groundwater with intruding 15 seawater. We hypothesize that CGD maybe an additional source of phosphorus (a limiting 16 nutrient) to the coastal wetlands of the southern Everglades.

# 1 **Introduction**

2 All coastal aquifers with a hydraulic connection to the sea are susceptible to seawater 3 intrusion (Bear et al., 1999). The interface between freshwater and seawater in coastal aquifers 4 was first identified by (Du Commun, 1828), half a century earlier than the more widely cited 5 Ghyben-Herzberg principle (Ghyben, 1888;Herzberg, 1901). A systematic study of seawater 6 intrusion in the 1950s in south Florida formed a set of benchmark papers on the subject (Cooper, 7 1959; Kohout, 1960; 1964). The most significant finding of these studies was the recognition 8 that the freshwater-seawater interface was not sharp as described by the Ghyben-Herzberg 9 principle, but formed a zone of mixed water composition termed by many in the field as a 10 'mixing zone' (Fig. 1a; Back et al., 1986; Price & Herman, 1991). Brackish water in this mixing 11 zone is circulated along with the freshwater to the sea (Cooper, 1959). If the groundwater 12 discharge occurs beneath overlying marine or estuarine waters it is termed submarine 13 groundwater discharge (SGD; Younger, 1996; Fig 1a). However, the position and extent of the 14 mixing zone and the flux of its associated brackish groundwater discharge is governed by many 15 factors such as rainfall, groundwater withdrawals, irrigation and evapotranspiration on the 16 freshwater side, with tides, waves, and changes in sea level on the seawater side (Kohout, 1960; 17 Bear et al., 1999). Along many of the worlds developed coastlines, the combined effects of 18 increased groundwater withdrawals and sealevel rise results in enhanced seawater intrusion into 19 the freshwater coastal aquifers (Konikow & Reilly, 1999), thereby shifting the discharge of 20 brackish groundwater inland (Fig. 1b). We wish to define a new term, coastal groundwater 21 discharge (CGD) to describe the discharge of brackish to saline groundwater to coastal areas 22 including coastal wetlands and streams (Fig. 1b).

1 The discharge of this brackish groundwater can have a significant impact on the ecology 2 of dominantly freshwater coastal wetlands and streams. CGD has the potential to alter the 3 salinity of wetland soils and surface waters, to be a source of water, and to deliver dissolved 4 constituents like nutrients and dissolved toxins. Such discharge also can be an important 5 determinant of the productivity of coastal systems, as they are often nutrient limited and 6 groundwater tends to be enriched in nitrogen and phosphorus compared to oligotrophic surface 7 waters.

8 The potential for brackish groundwater discharge to the surface water of the Everglades 9 as evidenced by a comparison of groundwater and surface water levels was presented earlier 10 (Price et al., 2003). The objective of this paper is to provide geochemical evidence of the 11 discharge of brackish groundwater to the overlying surface water of the coastal Everglades. 12 Furthermore, this paper demonstrates that the brackish groundwater contains elevated 13 concentrations of phosphorus (P). Phosphorus limits primary producer biomass, animal biomass, 14 the structure of the primary producer community, the structure of the microbial community and 15 the structure of animal community of the coastal Everglades (Armitage et al., 2005; Armitage et 16 al., this issue; Gil et al., this issue). We propose that the enhanced productivity of the freshwater-17 marine ecotone of the coastal Everglades as compared to either freshwater or marine end-18 members maybe fueled by the P delivered by CGD.

19

# 20 **Site Description**

21 The Everglades occupies most of the south Florida peninsula and discharges into Florida 22 Bay and the Gulf of Mexico (Fig. 2). The topography across the Everglades is extremely flat, 23 and contributes to an exceptionally low hydraulic gradient  $(5 \times 10^{-5})$  and poorly defined



1 Okeechobee and the Everglades to the ocean. Construction of additional canals combined with 2 periodic drought conditions resulted in increasing the extent of seawater intrusion in the 3 Biscayne Aquifer from 1904 to 1990 (Parker et al., 1955; Klein & Waller, 1985; Sonenshein & 4 Koszalka, 1996). No significant increase in seawater intrusion occurred in the area between 5 1990 and 1995 (Sonenshein, 1997). An aerial resistivity survey of shallow groundwater 6 conditions confirmed that seawater intrusion into the Biscayne Aquifer occurs along the entire 7 southern and western coastlines of the southern Everglades (Fitterman et al., 1999).

8

#### 9 **Methods**

# 10 *Geochemical Investigation*

11 Data presented in this paper was compiled from two investigations, one conducted 12 between 1997 and 1999, and the other conducted during the summer of 2003. Between 1997 and 13 1999, a total of 45 groundwater wells (Fig. 3) were sampled on an approximately monthly basis. 14 These wells were organized into clusters of 1 to 4 wells with finished depths ranging from 2 to 15 60 m within the SAS and were completed by either the USGS (Fish and Stewart, 1991; 16 Fitterman, 1999) or the National Park Service. Most of the wells completed by the USGS 17 contained and some wells completed just for this investigation by the National Park Service 18 consisted of PVC pipe that was 2.5 to 5.0 cm in diameter with the bottom 2 m or less screened 19 for water collection. To prevent the exchange of surface water into the groundwater well, the 20 annulus surrounding the PVC pipe was sealed at the land surface with a bentonite/cement 21 mixture, and then the PVC pipe was capped. Pre-existing wells completed by the National Park 22 Service contained a 7 cm to 15 cm diameter metal surface casing that was between 1 to 2 meters

1 long, with the remainder of the well left as an open borehole. More detailed description of the 2 wells and their locations can be found in Price (2001).

3 Prior to sampling, all wells were purged of at least three well volumes. Surface water 4 was collected at 23 sites in conjunction with the groundwater wells or from the canals that border 5 ENP (Fig. 3). Both groundwater and surface water samples were filtered in the field and stored 6 at  $4^0$ C until analyzed. Bottles collected for cations were acidified to a pH of less than 2. The 7 pH, specific conductance and/or salinity, and temperature were recorded at the time of sample 8 collection using an Orion pH, and S/C/T meter, respectively. Major cations (calcium, 9 magnesium, sodium and potassium) and anions (chloride and sulfate) were determined by ion 10 chromatography on a Dionex 120. Total alkalinity was determined by acid titration according to 11 the Gram method. A total of 1685 water samples were analyzed. A detailed description of the 12 methods for this investigation can be found in Price (2001).

13 During the summer of 2003, 14 of the groundwater wells and 9 surface water samples 14 were sampled across the seawater-freshwater mixing zone in the southern Everglades for TP 15 (Table 1). To reduce the exposure of anoxic groundwater to oxygen during sampling, 16 groundwater samples were collected directly into acid-washed, evacuated blood collection tubes 17 that were first flushed with nitrogen gas. Samples were processed for TP using colorimetery 18 following dry-oxidation/acid hydrolysis methods (Solorzano & Sharp, 1980) within 1 to 5 days 19 of sample collection. A total of 23 water samples were analyzed for TP (Table 1).

20

# 21 *Water Chemistry*

22 Specific conductance measured in all of the water samples varied from 100 and 36,900 23  $\mu$ S cm<sup>-1</sup> while salinity varied from 0 to 27.4 psu, with both specific conductance and salinity

1 increasing towards the coastline. During most times of the year, surface water salinities in 2 southern Taylor Slough and the C-111 basin were below 1 psu, but increased above a value of 1 3 during three times during the study period, in March and April 1997, in July 1998, and again in 4 April and May 1999 (Fig. 4). Surface water salinity was most variable in the southern reaches of 5 Shark Slough, particularly at Tarpon Bay and Canepatch (Fig. 4). For most groundwater wells, 6 there was no discernable trend in salinity between 1997 and 1999 (Fig. 5). Goundwater salinity 7 in the C-111 basin well EP8A was the most variable (Fig. 5).

8 A Piper diagram provided geochemical evidence of brackish groundwater discharge to 9 the surface water (Fig. 6). Surface water of the Everglades is most often characterized as a 10 calcium-bicarbonate type water, typical for water in contact with limestone. The underlying 11 groundwater, at site EP8A located within the mixing zone in the C-111 basin had salinity of 13.7 12 psu at a depth of 7.6 m and was dominated by sodium and chloride ions (Fig. 6). During four 13 sampling events in the dry-season, surface water at EP8A had elevated concentrations of sodium 14 and chloride relative to the other ions and these samples plot along a mixing line between the 15 freshwater and the underlying brackish groundwater. Enhanced sodium and chloride signatures 16 were also observed in the surface waters at sites E146 in Taylor Slough at RB-1 in Shark Slough 17 during the dry-season.

18 The mean concentrations of the cations and anions in the water samples were plotted 19 against their percent seawater composition (assuming chloride to be conservative) and compared 20 to a seawater mixing line. Calcium was enriched relative to the seawater dilution line in all 21 groundwaters containing greater than 5% seawater (Fig. 7). Surface waters collected from 22 Canepatch and Tarpon Bay fall along the seawater dilution line, while calcium concentrations of 23 some surface waters collected at E146, EP8A, and RB-1 are enriched in calcium compared to the



1 seawater intrusion extends the farthest inland in Shark Slough (25 to 28 km ) most likely due to 2 tidal action in the Gulf of Mexico. The Gulf of Mexico experiences a mixed semi-diurnal tide 3 with a maximum tidal range of 2.28 m at the mouth of the Shark River. Tidal forces aid in the 4 dispersion of salts along the interface of a seawater intrusion (Moore, 1999).

5 Seawater intrusion in the C-111 basin was found to extend 6 to 10 km landward from the 6 coastline, approximately coincident with the placement of the C-111 canal. Variations in 7 shallow groundwater salinity in wells located south of the C-111 canal indicate that the extent of 8 seawater intrusion in this area can vary on a monthly to seasonally basis. Tidal forces in 9 northeast Florida Bay are weak due to a dampening of the Gulf of Mexico tides by the many 10 shallow mud banks across Florida Bay. However, passing storm fronts and changes in wind 11 direction can result in changes in water levels up to 30 cm (Fourqurean & Robblee, 1999). Low 12 water levels caused by dry season conditions and southerly winds can drive seawater from 13 Florida Bay into the southern creeks of the C-111 Basin (Hittle et al., 2001). Salinity increases 14 in the surface waters of the C-111 canal and southern marshes during the end of the dry seasons 15 in 1997 and 1999 (Fig. 4) are most likely in response to lowered water levels. In 1997, the 16 groundwater salinity in wells EP8A increased markedly from near 1 to above 10, and remained 17 high throughout 1998 and into 1999. This increase in groundwater salinity followed a spike in 18 the surface water salinity occurring at the end of the dry season in 1997 and is most likely in 19 response to lowered water levels during that time. The subsequent year long increase in 20 groundwater salinity of the C-111 basin suggests that landward advancement of seawater 21 intrusion within the SAS is slow compared to that observed in the surface water. The drops in 22 salinity of the groundwater in EP8A in May and July 1999 may signify a slight seaward retreat 23 of the seawater intrusion in the SAS within the C-111 basin. The landward extent of seawater

1 intrusion in Taylor Slough is about 10 to 14 km inland (Fig. 3), intermediate between that of the 2 C-111 basin and Shark Slough. The salinity of groundwater in the E-146 wells did not vary 3 markedly throughout the study period (Fig. 5), suggesting that the position of the seawater 4 intrusion front in Taylor Slough may be more stable than observed in the C-111 basin.

5

7

# 6 *Evidence of CGD*

8 During times of low water levels, the surface water at EP8A (as well as at E146 and RB-9 1) exhibited a brackish signature (Fig. 6). There are two potential sources for the observed 10 seawater mixture at these surface water sites: 1) surface seawater from Florida Bay or the Gulf of 11 Mexico moving inland with the lowering of water levels, or 2) the discharge of brackish 12 groundwater. That these sites are approximately 6 to 25 km inland of the coastline and 13 coincident with the position of the seawater intrusion in the shallow portion of the SAS (Fig. 3) 14 suggests that brackish groundwater is the source of the seawater signature. 15 Elevated concentrations of calcium in the surface waters also suggest a brackish

16 groundwater source as opposed to surface seawater from Florida Bay or the Gulf of Mexico 17 moving inland in response to the lowering of water levels (Fig. 8). If surface seawater flowing 18 inland from the marine bays was the source of the brackish signatures in the surface waters, then 19 the surface water concentrations of calcium would fall along a seawater dilution line produced 20 from mixing of fresh Everglades waters and surface seawater. In fact, mean calcium 21 concentrations of surface waters from Tarpon Bay and Canepatch fall along a seawater mixing 22 line indicating that surface waters at these sites do receive surface seawater from the Gulf of 23 Mexico (Fig. 7). This result is expected since surface water levels at these sites are tidally 24 influenced.

2 from the surface water at sites E146, EP8A, and RB-1 reveal elevated concentrations of calcium 3 relative to the seawater dilution line in samples containing greater than 1 percent seawater (Fig. 4 8). The elevated calcium concentrations in the surface waters is a result of mixing with the 5 underlying brackish groundwater that also has elevated calcium levels as compared to seawater 6 mixing. The excess calcium in the brackish groundwaters relative to the seawater mixing line is 7 as high as 9 mM with an average of  $4.1 \pm 3.5$  mM. The excess calcium concentrations are most 8 likely the result of dissolution of calcium carbonate minerals from the aquifer matrix.

1 Close inspection of calcium concentrations of individual surface water samples collected

9

# 10 *Phosphorus*

11 Ambient surface water TP concentrations in the fresh waters of the Everglades range 12 from 0.15 to 0.45 µM (Table 1). Median TP concentrations in marine surface waters of 13 northeastern Florida Bay and the Gulf of Mexico are 0.25  $\mu$ M and 0.58  $\mu$ M, respectively (Boyer 14 et al., 1999). Concentrations of TP in the groundwater underlying the coastal wetlands of the 15 Everglades range from 0.5 to 2.3 µM and are consistently higher than either surface freshwater or 16 surface seawater; TP also shows a direct relationship with salinity (Fig 9). Fresh groundwater 17 TP concentrations tend to be less than 1  $\mu$ M (Table 1). Conservative mixing of fresh 18 groundwater having TP concentrations of less than 1 µM with surface seawater from Florida Bay 19 and/or the Gulf of Mexico also having TP concentrations of less than 1  $\mu$ M can not produce the 1 20 to 2.3 µM concentrations of TP observed in the brackish groundwater. An additional source of 21 phosphorus is needed.

22 Given that the seawater intrusion from Florida Bay must first pass through the underlying 23 sediments before entering the aquifer, then the sediments could be a source of phosphorus for

1 saline groundwaters. Phosphorus concentrations in the sediment porewaters in the region are 2 orders of magnitude higher than the concentrations of phosphorus in the overlying surface waters 3 because of the remineralization of organic matter in the sediments and the trapping of inorganic 4 phosphorus by sorption on calcium carbonate particles. The solid aquifer matrix can also be a 5 source of phosphorus. Phosphorous may exist either as phosphorus minerals (such as apatite) 6 within the aquifer material, or may be adsorbed onto the particle surfaces. Areas of seawater 7 intrusion are known geochemically active regions particularly in carbonate aquifers, where 8 carbonate mineral dissolution (Back et al., 1986) and ion exchange (Sivan et al., 2005) are 9 important. Both of these processes can lead to a release of phosphorus from the aquifer matrix to 10 the groundwater. The excess calcium concentrations observed in the brackish groundwaters (Fig. 11 7) indicates that carbonate mineral dissolution is occurring within the saltwater intrusion zone of 12 the southern Everglades. Millero et al. (2001) have determined that phosphate adsorption onto 13 carbonate minerals decreases as salinity increases and attributed their results to the presence of 14 sulfate and bicarbonate ions. These anions may be competing with the phosphate ion for 15 exchange sites and may explain the nonconservative nature of sulfate upon mixing fresh 16 groundwater and surface seawater. The linear increase in TP concentration with salinity in the 17 brackish groundwaters suggests phosphorus may be desorbed from the aquifer materials with the 18 intruding seawater (Fig.8).

19 Groundwater discharge in the southern Everglades appears to be seasonal, occurring 20 dominantly during the dry season when excess sodium, chloride, and calcium is observed in 21 receiving surface waters. This seasonality in groundwater discharge was observed by others 22 (Top et al., 2001; Sutula et al., 2001) , and is due to higher surface water levels in both the 23 Everglades and in Florida Bay in the summer wet season. The higher surface water levels result

1 in either reducing groundwater discharge to near zero or even reversing the direction so that the 2 surface water recharges the groundwater. For instance, groundwater discharge in the regions of 3 Taylor Slough and C-111 basin have been estimated at 48 cm/yr during the dry season, but 4 during the wet season the groundwater was recharged between 25 to 35 cm/yr, resulting in a 5 mean annual discharge of 8 cm/yr (Sutula et al., 2001). This groundwater discharge value is 6 similar to the rate of 2 to 12 cm/yr estimated for groundwater recharge in the upland regions of 7 ENP (Price & Swart, In press).

8 Assuming an average TP value in the CGD of 1.5  $\mu$ M, a CGD of 8 cm/yr results in a 9 discharge flux of 0.12 mM P  $m^{-2}yr^{-1}$ . This value is twice as high as earlier estimates of 10 groundwater input of 0.06 mM P  $m^2yr^{-1}$  along Taylor Slough and the C-111 basin (Sutula et al., 11 2001), however, those estimates were made without groundwater P data. Assuming an extent of 12 seawater intrusion of 10 km inland along 75 km length of coastline extending from the C-111 13 basin to the western edge of Shark Slough, results in a CGD zone of  $750 \text{ km}^2$ , and a flux of 2.8 14 metric tons of P to the surface water annually. This amount of P is equivalent to the amount of 15 phosphorus delivered by Taylor Slough (<2.6 metric tons/yr) to Florida Bay. This amount of P, 16 however, is considerably less than the estimated 14 metric tons/yr of P delivered to the the 750 17 km<sup>2</sup> coastal zone via atmospheric inputs (Rudnick et al., 1999).

18 Despite the high concentrations of TP in the brackish groundwaters, only low TP values 19 (<0.5µM) are detected in the overlying surface waters. These results suggest that the phosphorus 20 transported with the CGD is either removed from the surface water column quickly by biotic 21 processes (Gaiser et al., 2004) or is retained in the Everglades soils by sorption, particularly to 22 calcium carbonate particles (De Kanel & Morse, 1978), clays (Zhou & Li, 2001) and iron-oxides 23 (Chambers et al., 2001). Soils within the mangrove zone are indeed a sink for phosphorus as

1 indicated by higher concentrations of phosphorus measured in shallow sediments (2.5 cm) within 2 the mangrove zone as opposed to freshwater upland sites (Chen & Twilley, 1999). The high 3 concentrations of TP in the groundwater along with any sorbed to the soils is then available for 4 plant root uptake by the coastal mangroves. 5 The Everglades and Florida Bay are oligotrophic systems and extremely sensitive to 6 exogenous inputs of nutrients, particularly phosphorus (Fourqurean et al., 1992; Gaiser et al., 7 2004). Phosphorus inputs from canals that drain the surrounding agricultural landscape have 8 been implicated as major drivers of biotic change of the Everglades ecosystem (Davis, 1994; 9 Noe et al., 2003). Along the southern margin of the Florida peninsula, the freshwater, 10 oligotrophic Everglades and the marine oligotrophic Florida Bay ecosystems are separated by an 11 often lush mangrove forest. The highly productive mangrove forest separating the two nutrient-12 limited ecosystems seems to require a phosphorus source that is independent of the mixing of 13 Everglades surface water and the marine waters of Florida Bay. We hypothesis that the high 14 productivity of the mangrove forest along the coastal Everglades maybe supported by P 15 delivered by CGD.

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# 1 **References:**











<b>Site Name</b>	<b>Sampling</b>	Depth	Temp.		<b>Salinity</b>	<b>Total P</b>
(SW=Surface water)	<b>Date</b>	(m)	$(^{\circ}C)$	pH	(psu)	(uM)
SH-1 SW	20-Jun-03		31.1	7.35	0.0	0.31
LO1 SW	18-Jul-03		30.6	7.53	0.0	0.21
CH1 SW	18-Jul-03		35.5	7.38	0.0	0.45
<b>UPPER TAYLOR RIVER SW</b>	$12-Aug-03$		30.2	7.46	0.2	0.27
E-146 SW	15-Aug-03		28.3	7.32	0.0	0.21
RB-1 SW	19-Aug-03		28.4	7.00	0.0	0.33
<b>CANEPATCH SW</b>	19-Aug-03		29.3	7.02	0.0	0.16
<b>TARPON BAY SW</b>	19-Aug-03		30.6	7.30	0.6	0.22
E-130 SW	25-Nov-03		24.9	7.30	0.0	0.15
(GW=Groundwater)						
SH-1 GW	20-Jun-03	2.5	25.9	6.37	0.06	0.88
G-3302A	$1-Aug-03$	4.3	26.5	7.06	0.0	0.75
E-130 SHALLOW	25-Nov-03	3	26.2	7.01	0.0	0.12
E-130 DEEP	25-Nov-03	15.2	25.9	6.96	0.0	0.22
CH1 GW	$18$ -Jul-03	2.5	26.6	6.81	29.9	2.34
<b>UTR DEEP GW</b>	$12$ -Aug-03	6.7	27.4	6.54	28.1	1.45
UTR SHALLOW GW	$12-Aug-03$	0.6	28.7	6.54	27.5	2.12
E-146 SHALLOW GW	$15-Aug-03$	4.6	26.2	6.65	10.6	0.5
E-146 DEEP GW	$15$ -Aug-03	7.6	25.9	6.68	12.6	0.63
E-146-27 GW	$15-Aug-03$	8.4	25.8	6.58	16.3	0.75
RB-1 GW	19-Aug-03	6.7	25.1	6.67	3.4	0.37
<b>CANEPATCH GW</b>	19-Aug-03	15.5	25.4	6.84	15.2	1.9
<b>TARPON BAY GW</b>	19-Aug-03	19.8	26.1	6.8	20.8	2.25
LO1 GW	18-Jul-03	3	27.7	6.57	7.6	0.97

**Table 1. Summary of phosphorus concentrations in groundwater and surface water.** 







 $\frac{1}{2}$ Price et al. Fig. 1



 $\frac{17}{18}$ Price et al. Fig 2



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 $\frac{16}{17}$ Price et al. Fig. 6



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- $\frac{20}{21}$
- Price et al. Fig. 7



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 $\frac{17}{18}$ Price et al. Fig. 8

