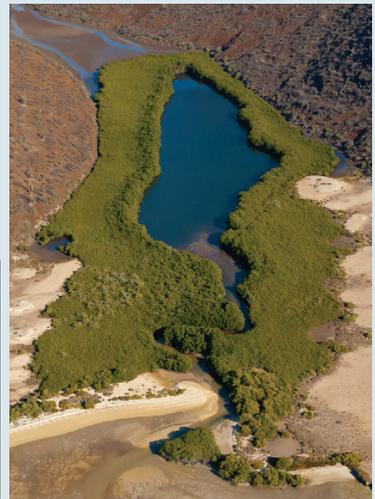




# CONSERVATION SCIENCE IN MEXICO'S NORTHWEST

ECOSYSTEM STATUS AND TRENDS IN THE GULF OF CALIFORNIA



Elisabet V. Wehncke, José Rubén Lara-Lara,  
Saúl Álvarez-Borrego, and Exequiel Ezcurra  
EDITORS



# NEW PHYTOPLANKTON PRODUCTION AND BIOGENIC SILICA AS TOOLS TO ESTIMATE NUTRIENTS AND DISSOLVED INORGANIC CARBON EXCHANGE BETWEEN THE GULF OF CALIFORNIA AND THE PACIFIC OCEAN

Saúl Álvarez-Borrego\*

Water exchange between the Gulf of California and the Pacific Ocean (PO) has a significant vertical component (VCWE). Surface (0-200 m) Gulf water flows out to the PO, and deep (200-600 m) water flows into the Gulf. The objective of this chapter is to review biogeochemical methods to estimate the VCWE assuming that the concentration of nutrients in the Gulf are in steady state, and using the necessary net annual input of nutrients from the PO to balance the dissolved Si needed to support the production of opal (mainly diatoms) preserved in the Gulf's sediments, and to balance the nitrate needed to support new phytoplankton production in the whole Gulf ( $P_{NEW}$ ). Opal accumulation [ $(273.3 \pm 6.8) \times 10^9$  moles  $\text{SiO}_2 \text{ year}^{-1}$ ], and  $P_{NEW}$  [ $(2586.7 \pm 131.7) \times 10^9$  moles C  $\text{year}^{-1}$ ], were deduced from the literature. Annual averages for  $\text{H}_4\text{SiO}_4$  and  $\text{NO}_3^-$ , for the Gulf's mouth and for the depth intervals 0-200 m and 200-600 m, were used to independently calculate the VCWE needed to balance the opal accumulation and  $P_{NEW}$ . The results are  $0.23 \pm 0.02$  Sv in the first case, and  $(0.67 \pm 0.10)$  Sv in the second ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ). These relatively low values are only ~3% and ~7% of the whole average water exchange. Thus, most of the exchange between the Gulf and the PO consists of the horizontal component. These VCWE values were used to estimate the net input of dissolved inorganic carbon from the PO into the Gulf ( $\text{DIC}_{NET INPUT}$ ). After comparing  $\text{DIC}_{NET INPUT}$  with  $P_{NEW}$  in both scenarios the results are that the Gulf is a source of  $\text{CO}_2$  to the atmosphere, with an average out-gassing of  $(7.66 \pm 2.65) \times 10^{12}$  and  $(18.16 \pm 6.14) \times 10^{12}$  grams of carbon in the form of  $\text{CO}_2$ , in the first and second scenarios, respectively. These values are equivalent to an average of  $52.1 \pm 18.0$  and  $123.5 \pm 41.8$  grams C  $\text{m}^{-2} \text{ year}^{-1}$ , respectively. The value for the second scenario is higher than the highest value for the eastern equatorial Pacific as reported in the literature ( $\sim 108$  grams C  $\text{m}^{-2} \text{ year}^{-1}$ ), which indicates that the value for the first scenario is closer to reality.

Keywords: Gulf of California, Pacific Ocean, water exchange, net input of nutrients, new primary production, CO<sub>2</sub> water-to-air flux.

## 1. INTRODUCTION

The Gulf of California (GC) is the only evaporative basin of the Pacific Ocean (PO) (Roden 1964). Despite the strong evaporative forcing, the Gulf differs markedly from the Mediterranean and Red seas, which are the primary evaporative basins of the Atlantic and Indian oceans. Fundamental differences between the GC and the Mediterranean and Red sea may be attributed to a net heat gain from the atmosphere in the former, compared to a net heat loss to the atmosphere in the other two (Bray 1988, Lavín and Organista 1988). In the GC there is an annual average net surface heat flux into the sea of  $\sim 118 \text{ W m}^{-2}$  (Castro *et al.* 1994). This heat has to be exported to the PO somehow; otherwise the Gulf's temperature would be increasing (Lavín *et al.* 1997). The Gibraltar strait, connecting the Mediterranean with the Atlantic, and the strait of Bab-el-Mandeb, connecting the Red sea with the Indian Ocean, has only 14 and 28 km width, respectively. A large entrance to the GC ( $>200$  km wide, and  $>2500$  m deep) allows for a complex circulation to and from the PO (*i.e.*, Roden 1972), including eddies spanning much of the entrance (Emilsson and Alatorre 1997), and that is another significant difference from the Mediterranean and Red sea.

Water exchange between the GC and the PO exhibits spatial and temporal variability, it has a large horizontal component with inflow occurring mostly at the center and eastern side of the Gulf's entrance, and outflow mostly at the western side, but sometimes showing alternating cores of flow into and out of the Gulf (Roden 1972, Castro *et al.* 2006). Integrated transport across the Gulf ( $T_{\text{INTz}}$   $\text{m}^2 \text{ s}^{-1}$ ) is the sum of velocities at each depth. When dealing with the average water exchange for a long period (*i.e.*, a year average), most of the inflow at a certain depth is balanced by the outflow; if there is a difference it has to be balanced by flow in the opposite direction at another depth and this constitutes the vertical component of water exchange (VCWE). Notice that it does not imply a vertical component of advection. When integrating velocity across the Gulf's mouth for each depth the horizontal component of water exchange is eliminated. The VCWE may be defined as the integration of  $T_{\text{INTz}}$  with depth, for layers between depths with zero  $T_{\text{INTz}}$ . This VCWE between the GC and the PO consists of less dense, warmer, saltier, and nutrient and dissolved inorganic carbon (DIC) poor surface and near surface water flowing out from the Gulf into the PO, and to balance this flow, relatively deep, denser, colder, fresher,

and nutrient and DIC rich water flows into the Gulf. Marinone (2003) used a three-dimensional model to conclude that heat and salt flow out of the Gulf in the top 200 m, and into the Gulf at 200–600 m, and most of the heat budget of the Gulf is defined in the upper 350 m. The average net heat flux is an export of  $17 \times 10^{12}$  W to the PO.

Roden (1958) was the first to estimate the total net water exchange at the mouth of the Gulf by use of salt and water budget considerations. He estimated the inflow as 1.19 Sv ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ), and the outflow as 1.17 Sv. Roden and Groves (1959) again estimated the water exchange by means of the salt budget computation. The resulting inflow and outflow were each 3.5 Sv. Warsh and Warsh (1971) estimated the water exchange based on geostrophic flow at the mouth of the Gulf for July 1967, to be at least 3.25 Sv and possibly 3.65 Sv in each direction; and their estimate was between 2.57 and 3.5 Sv for February 1957 and May 1959, respectively. Roden (1972) sampled hydrostations with closed spacing (9 km) across the entrance to the Gulf and produced another estimate to be between 10 Sv (inflow) and 12 Sv (outflow), for early December 1969. More recent geostrophic computations and direct measurements of currents confirm that water exchange at the Gulf's entrance is in the order of several Sv (up to >8 Sv) (Lavín *et al.* 2009). But, as indicated by Bray (1988), there is no estimate on how much of this flow includes eddies or frontal meanders which do not contribute to exchange with the PO. Bray (1988) has produced the only estimate of the VCWE but between the northern and central Gulf. She used geostrophic calculations and then integrated transport across the Gulf for each depth, and integrating this with depth water flux was  $0.4 \pm 0.05$  Sv, southward between 0–250 m and northward at 250–500 m. However, her value for  $T_{\text{INT}_2}$  was not zero at 500 m, suggesting a significant vertical component of transport below this depth.

The VCWE between the Gulf and the PO has a very important ecological implication because it is a natural fertilization mechanism for the Gulf. Nutrient concentrations have very weak horizontal gradients across the Gulf (Álvarez-Borrego *et al.* 1978), but it is very well known that they have strong vertical gradients with values increasing with depth (Calvert 1966). We are interested in the VCWE because it causes net input of nutrients from the PO into the GC, and also input of other chemical properties increasing with depth, like trace metals and DIC.

Álvarez-Borrego (2012) and Álvarez-Borrego and Giles-Guzmán (2012) proposed new and independent methods to estimate this VCWE assuming, as a first approximation, that the concentration of nutrients in the Gulf are in steady state, and using the necessary net annual average input of nutrients from the PO to balance the nitrate needed to support new phytoplankton production in the whole GC, and

to balance the dissolved Si (because of the pH range of sea water, dissolved Si is in the form of  $\text{Si}(\text{OH})_4$ ) needed to support the production of biogenic particles (opal, mostly diatom frustules and radiolarians) that are preserved in the Gulf's sediments. The objective of this chapter is to review Álvarez-Borrego's (2012) and Álvarez-Borrego and Giles-Guzmán's (2012) results, and to analyze Rodríguez-Ibáñez *et al.*'s (2013) application of these results to infer that the Gulf is a source of  $\text{CO}_2$  to the atmosphere.

## 2. NEW PHYTOPLANKTON PRODUCTION AS A TOOL TO ESTIMATE THE VERTICAL COMPONENT OF WATER EXCHANGE BETWEEN THE GULF OF CALIFORNIA AND THE PACIFIC OCEAN

New production is the fraction of total phytoplankton production supported by the input of nitrate from outside the euphotic zone (Dugdale and Goering 1967), mainly from below the thermocline by vertical eddy diffusion and upwelling. Phytoplankton cells use nutrients recycled within the euphotic zone for regenerated production ( $P_R$ ). Total production is equal to the sum of both new and regenerated production ( $P_T = P_{\text{NEW}} + P_R$ ). Álvarez-Borrego (2012) proposed a biogeochemical method to estimate the VCWE between the GC and the PO which is based on using the annual average net input of nitrate needed to support new phytoplankton production in the whole Gulf of California ( $P_{\text{NEW}}$  moles C year<sup>-1</sup>). This latter author explored the possibility of other sources of nutrients, besides the input from the PO, and concluded that usable forms of nitrogen input by rivers, agricultural runoff, and  $\text{N}_2$  fixation by diazotrophs might add to only ~1.5% of the input of nitrate from the PO.

Hidalgo-González and Álvarez-Borrego (2004) used satellite ocean color data to estimate  $P_T$  and  $P_{\text{NEW}}$  for the Gulf of California. From their data, Álvarez-Borrego (2012) estimated a  $P_{\text{NEW}}$  annual average of  $(31.04 \pm 1.58)10^9$  kg C for the whole Gulf, for non-El Niño years (in this and all following cases the number after  $\pm$  is one standard error,  $s n^{-0.5}$ ). This is equivalent to  $(2586.7 \pm 131.7)10^9$  moles C year<sup>-1</sup>, for the whole Gulf. This  $P_{\text{NEW}}$  annual average value has to be supported by the annual average net nitrate input from the PO. Redfield *et al.* (1963) proposed a nitrogen to carbon ratio (N:C) for phytoplankton photosynthesis equal to 16:106 when they are expressed in moles. Based on chemical data from isopycnal surfaces, Takahashi *et al.* (1985) proposed a "new Redfield" N:C ratio of 16:122 = 0.131. The formula of the hypothetical mean organic molecule corresponding to this ratio is  $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ , which takes into account that marine phytoplankton often contain considerable

quantities of lipid materials such as triglycerides and waxes (Pilson 1998). Thus, the nitrate needed to support the annual average  $P_{NEW}$  for the whole Gulf is  $(2586.7 \pm 131.7)10^9(0.131) = (339 \pm 17)10^9$  moles year<sup>-1</sup>.

An inference may be done on the average vertical component of water fluxes needed for the net annual nitrate input from the PO into the Gulf to sustain  $P_{NEW}$  for the whole Gulf. One way to estimate the net input of nitrate, from the PO into the Gulf, is to calculate the transport out of the Gulf in the surface water layer (0-200 m), and into the Gulf in the deep layer (200-600 m), and calculate the difference. These depth limits were chosen based on Marinone's (2003) results, as mentioned above. Proper averages of nitrate concentration ( $NO_3$ ) for each layer (0-200 and 200-600 m), for the Gulf's mouth, are needed. These  $NO_3$  averages have to be weighted means, where the weighting factor is  $T_{INTz}$  at each depth. Álvarez-Borrego (2012) used a similar shape to that of the average of Bray's (1988) integrated transport profiles ( $m^2 s^{-1}$ ), and Marinone's (2003) results to generate an  $T_{INTz}$  profile with relative values ( $T_{INT(z)}$ ) for 0-600 m, with zero relative integrated transport at 200 and 600 m (see Figure 1). Notice that a depth with zero horizontally integrated velocity ( $T_{INTz}$ ) is not necessarily without motion; it is a depth with equal input and output of water. Álvarez-Borrego (2012) generated an average  $NO_3$  vertical profile for the mouth of the Gulf and for the 0-600 m depth interval (see Figure 2) and combined it with the  $T_{INT(z)}$  profile to generate weighted averages for nitrate concentrations for the depth intervals 0-200 m, and 200-600 m, respectively:  $NO_{3(0-200)} = \sum(NO_{3(z)} * T_{INT(z)}) / \sum(T_{INT(z)})$ , with z changing from 0 to 200 m, and similarly for 200-600 m. The annual  $NO_3$  averages for the mouth of the Gulf are  $(14.37 \pm 1.13)10^{-3}$ , and  $(30.45 \pm 0.50)10^{-3}$  moles nitrate  $m^{-3}$ , for 0-200 m and 200-600 m, respectively (Álvarez-Borrego 2012).

If the annual average net water flux in and out of the Gulf is represented by  $X Sv$ , then the average flux of nitrate out of the Gulf in the surface layer (0-200 m) is  $(14.37 \pm 1.13)10^{-3}$  moles  $m^{-3}(10^6 X m^3 s^{-1}) = (14.37 \pm 1.13)(10^3 X)$  moles  $s^{-1}$ , equivalent to  $(453.2 \pm 35.6)(10^9 X)$  moles year<sup>-1</sup>. Similarly, the average annual flux of nitrate into the Gulf in the deep layer (200-600 m) is  $(960.3 \pm 15.8)(10^9 X)$  moles year<sup>-1</sup>. The difference is the average annual net input of nitrate from the PO into the Gulf, and it is equal to  $((960.3 \pm 15.8) - (453.2 \pm 35.6))(10^9 X) = (507.1 \pm 51.4)(10^9 X)$  moles year<sup>-1</sup>. Making this net input of nitrate equal to the one required to support the  $P_{NEW}$  annual average in the whole GC:  $(507.1 \pm 51.4)(10^9)X = (339 \pm 17)(10^9)$ ; then  $X = VCWE = (0.67 \pm 0.10) Sv$  (Álvarez-Borrego 2012).

Beman *et al.* (2005) studied the discharge of nutrients from the Yaqui Valley to the Gulf and proposed that agricultural runoff may be fueling large phytoplankton blooms in the Gulf of California. However, Ahrens *et al.*'s (2008) largest estimate of

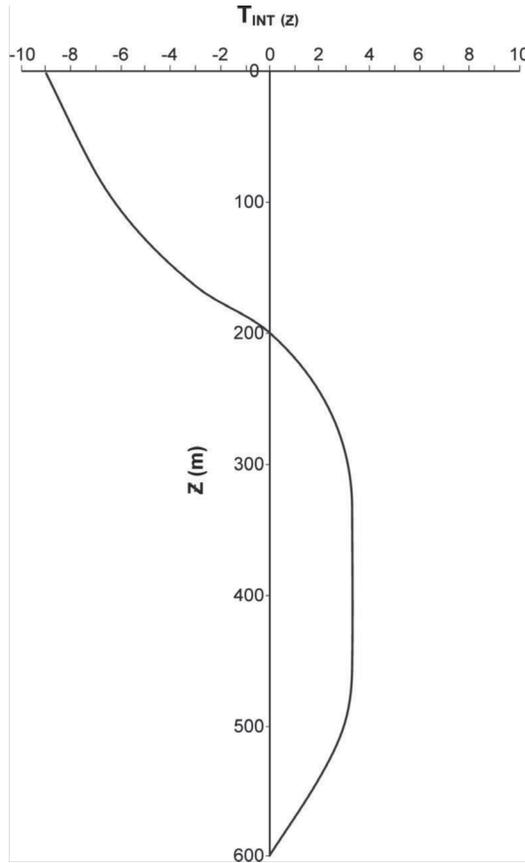


FIGURE 1. Shape of the annual average of the vertical distribution of water transport integrated across the mouth of the Gulf of California, with relative values (taken from Álvarez-Borrego and Giles-Guzmán 2012).

annual dissolved inorganic nitrogen coastal loading from the Yaqui Valley was only  $(1.93)10^6$  kg of N (equivalent to  $(137.9)10^6$  moles N, mostly in reduced forms), which is only  $\sim 0.04\%$  of the net annual input of nitrate from the PO to the GC. Even if Ahrens *et al.*'s (2008) figure is multiplied by five, considering the input of inorganic nitrogen from other agricultural valleys like those of the rivers Mayo, Culiacán, and other smaller ones, the total annual inorganic N input from agricultural runoff to the Gulf is only about  $\sim 0.2\%$  of the input from the PO. Agricultural runoff may have an important impact on coastal lagoons and estuaries, but the Gulf's oceanic primary productivity is mainly driven by the input of nutrients from the PO into the GC. On

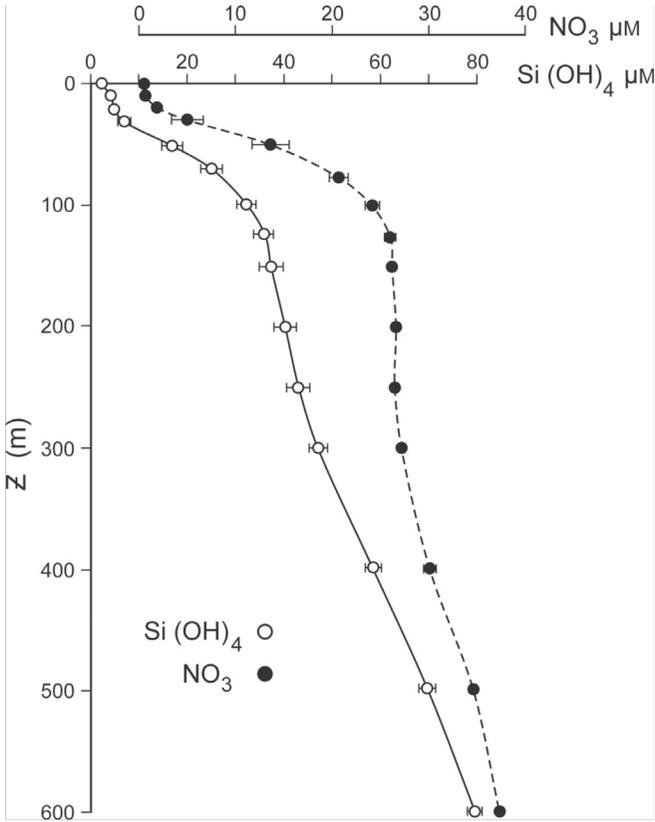


FIGURE 2. Annual averages of the vertical distributions of  $H_4SiO_4$  and  $NO_3$  for the mouth of the Gulf of California. Horizontal bars represent  $\pm$  one standard error ( $s n^{-0.5}$ ) and where it does not show it is smaller than the symbols (taken from Álvarez-Borrego and Giles-Guzmán 2012).

the other hand, White *et al.* (2007) studied  $N_2$  fixation in the central and southern Gulf during summer. They concluded that phytoplankton “blooms” ( $0.68-0.79$  mg chlorophyll a  $m^{-3}$ , compared to a regional summer mean of  $0.38$  mg  $m^{-3}$ ) due to  $N_2$  fixation are very patchy and episodic, and they only occur throughout the central to eastern Gulf south of the midriff islands, away from upwelling off the western coast and from the mixed waters closed to the midriff islands. Nitrogen fixation supported blooms occur regionally in  $\sim 3.7\%$  of the cloud-free satellite data record for summer periods. These presumed  $N_2$  fixation supported blooms may result in an approximately twofold increase in chlorophyll a concentrations and primary productivity, above the regional summer means (White *et al.* 2007). Combining White *et al.*'s (2007) results with those of Hidalgo-González and Álvarez-Borrego (2004) for total

primary production in the central and southern Gulf during summer,  $\sim 0.09(10^9)$  kg C for  $N_2$  fixation supported primary production is calculated, and it is only  $\sim 0.3\%$  of the above estimate for  $P_{NEW}$  ( $(31.04 \pm 1.58)10^9$  kg C year $^{-1}$ ).  $N_2$  fixation supported primary production is very significant ecologically, but in terms of its contribution to annual  $P_{NEW}$  for the whole Gulf it is negligible (Álvarez-Borrego 2012).

### 3. BIOGENIC SILICA (OPAL) PRESERVED IN THE SEDIMENTS AS A TOOL TO ESTIMATE THE VERTICAL COMPONENT OF WATER EXCHANGE BETWEEN THE GULF AND THE PACIFIC OCEAN

In the Gulf of California, at intermediate depths (500 to 1100 m), the concentration of oxygen in some places is undetectable by the Winkler method. Laminated, diatomaceous sediments are formed where the basin slopes intersect the oxygen minimum in the water column (Calvert 1966). Burrowing organisms do not live in this poorly oxygenated zone, and the absence of biogenic disturbance allows the laminations to become finely developed. The opal content of the sediments of the Gulf and the formation of alternating light and dark millimeter-scale laminae have been studied extensively since the 1939 EW Scripps cruise (*i.e.*, Revelle 1939, 1950, Calvert 1966, DeMaster 1979, Thunell *et al.* 1994). Most of the biogenic silica is preserved in the basins of the central Gulf, but diatoms and radiolarians are also preserved in bio-disturbed sediments throughout the Gulf (Calvert 1966).

DeMaster (1979) sampled six sediment cores and found agreement with Calvert's (1966) data. This latter author studied 150 sediment cores. Thunell *et al.* (1994) sampled two sediment cores and calculated biogenic silica accumulation rates, and they expressed that their estimates were very similar to the average opal accumulation rate of  $0.34 \text{ g m}^{-2} \text{ day}^{-1}$  determined by DeMaster (1979) for the entire GC. Multiplying DeMaster's (1979) figure by the area of the whole GC:  $(0.34(10^{-3}) \text{ kg m}^{-2} \text{ day}^{-1})(147 \times 10^9 \text{ m}^2)(365 \text{ days year}^{-1}) = 18.24 \times 10^9 \text{ kg opal year}^{-1}$ . Since diatom frustules have 10% water (Calvert 1966) the total amount of accumulated silica is  $16.42 \times 10^9 \text{ kg SiO}_2 \text{ year}^{-1}$ , and transforming it to grams and dividing by the molecular weight of  $\text{SiO}_2$  it is equivalent to  $273.3(10^9)$  moles  $\text{SiO}_2 \text{ year}^{-1}$ .

Considering a minimum value for the standard error of this average value equal to  $\pm 2.5\%$  (Calvert 1966), its absolute value is  $\pm 6.8(10^9)$  moles  $\text{SiO}_2 \text{ year}^{-1}$ . This annual average of preserved silica has to be supported by the dissolved Si annual input from the PO to the Gulf (Álvarez-Borrego and Giles-Guzmán 2012).

Álvarez-Borrego and Giles-Guzmán (2012) used the average net annual input of dissolved Si needed to support the production of biogenic silica particles that are preserved in the Gulf's sediments to make an independent estimate of the VCWE,

in a similar manner as the one done by Álvarez-Borrego (2012) using the balance between the net input of dissolved nitrate and  $P_{NEW}$ . Álvarez-Borrego and Giles-Guzmán (2012) discussed the possibility of other sources of Si, besides the input from the PO to the Gulf, with the conclusion that dissolved Si input from rivers and hydrothermal vents might add to only ~3% of the input from the PO.

Again, one way to estimate the annual average net input of dissolved Si, from the PO into the Gulf, is to calculate the transport out of the Gulf in the surface water layer (0-200 m), and into the Gulf in the deep layer (200-600 m), and calculate the difference. Álvarez-Borrego and Giles-Guzmán (2012) generated an average dissolved Si vertical profile for the mouth of the Gulf and for the 0-600 m depth interval (see Figure 2), and combined it with Álvarez-Borrego's (2012)  $T_{INT(Z)}$  profile (see Figure 1) to calculate weighted averages for dissolved Si concentrations for the depth intervals 0-200 m, and 200-600 m, respectively:  $H_4SiO_{4(0-200)} = \Sigma(H_4SiO_{4(Z)} T_{INT(Z)}) / \Sigma(T_{INT(Z)})$ , with z changing from 0 to 200 m, and similarly for 200-600 m. The annual averages of  $H_4SiO_4$  for the mouth of the Gulf, weighted by  $T_{INT(Z)}$ , are  $(20.23 \pm 1.47)10^{-3}$ , and  $(57.70 \pm 1.48)10^{-3}$  moles Si  $m^{-3}$ , for 0-200 m and 200-600 m, respectively.

If the annual average water flux in and out of the Gulf is represented by X Sv, then the average flux of dissolved Si out of the Gulf in the surface layer (0-200 m) is  $((20.23 \pm 1.47)10^{-3} \text{ moles } m^{-3})(10^6 X \text{ m}^3 \text{ s}^{-1}) = (20.23 \pm 1.47)(10^3 X) \text{ moles } s^{-1}$ , equivalent to  $(640.2 \pm 46.4)(10^9 X) \text{ moles Si year}^{-1}$ . Similarly, the average annual flux of dissolved Si into the Gulf in the deep layer (200-600 m) is  $(1819.6 \pm 46.7)(10^9 X) \text{ moles Si year}^{-1}$ . The difference is the average annual net input of dissolved Si from the PO into the GC, and it is equal to  $((1819.6 \pm 46.7) - (640.2 \pm 46.4))(10^9 X) = (1179.4 \pm 93.1)(10^9 X) \text{ moles Si year}^{-1}$ . Making this net input of dissolved Si equal to the average total annual opal accumulated in the sediments of the whole Gulf:  $(1179.4 \pm 93.1)(10^9)X = (273.3 \pm 6.8)(10^9)$ ;  $X = VCWE = 0.23 \pm 0.02 \text{ Sv}$  (Álvarez-Borrego and Giles-Guzmán, 2012).

At the beginning of the 20th century, before the construction of dams, the dissolved Si input from rivers to the Gulf was  $9.15 \times 10^9$  moles Si  $year^{-1}$  (Calvert 1966), which was only ~3.3% of the amount needed to support the production of preserved biogenic silica in the sediments of the Gulf. At present the input of dissolved Si by rivers is much smaller because of the large amount of dams. Another possible source of dissolved Si to the Gulf is the fluids from hydrothermal vents like those of Guaymas basin. Álvarez-Borrego and Giles-Guzmán (2012) used data from the literature (Von Damm *et al.* 1985, Campbell and Gieskes 1984) to estimate that hydrothermal vents contribute a maximum of ~2% of the Si needed to support the production of preserved biogenic silica in the Gulf. Furthermore, this input of hydrothermal Si is

confined to deep waters closed to the bottom and do not reach the euphotic zone to be utilized by plankton. Thus, the VCWE between the Gulf and the PO remains by far the main source of dissolved Si for the production of biogenic silica particles accumulated in the sediments of the Gulf.

Using their VCWE value, Álvarez-Borrego and Giles-Guzmán (2012) estimated the average net annual input of nitrate from the PO to the GC, and then transformed it to a  $P_{\text{NEW}}$  value for the whole Gulf. The nitrate export to the Pacific in the 0-200 m layer is  $((14.37 \pm 1.13)10^{-3} \text{ moles m}^{-3})((0.23 \pm 0.02)10^6 \text{ m}^3 \text{ s}^{-1})(86400 \text{ s}^1 \text{ day}^{-1})(365 \text{ days year}^{-1}) = (104.2 \pm 17.2)10^9 \text{ moles year}^{-1}$ ; and the input in the deep layer is  $(220.8 \pm 22.8)10^9 \text{ moles year}^{-1}$ , with a net input into the Gulf of  $(116.6 \pm 40.0)10^9 \text{ moles year}^{-1}$ . Thus, applying Takahashi *et al.*'s (1985) Redfield C:N ratio,  $P_{\text{NEW}}$  for the whole Gulf is  $7.625(116.6 \pm 40.0)10^9 \text{ moles C year}^{-1} = (10.67 \pm 3.66)10^{12} \text{ g C year}^{-1}$  (Álvarez-Borrego and Giles-Guzmán 2012).

#### 4. COMPARISON OF THE NET INPUT OF DISSOLVED INORGANIC CARBON FROM THE PACIFIC OCEAN INTO THE GULF WITH $P_{\text{NEW}}$ TO INFER IF THE GULF IS A SINK OR SOURCE OF $\text{CO}_2$ TO THE ATMOSPHERE

The oceans have been considered to be a major sink for  $\text{CO}_2$ . Hence the improved knowledge of the net transport flux across the air-sea interface is important for understanding the fate of this important greenhouse gas emitted into the earth's atmosphere (Callendar 1938, Siegenthaler and Sarmiento 1993). On the basis of the global distribution of  $\Delta p\text{CO}_2$  values ( $\Delta p\text{CO}_2 = \text{surface water } \text{CO}_2 \text{ partial pressure minus air } \text{CO}_2 \text{ partial pressure} = p\text{CO}_{2w} - p\text{CO}_{2\text{air}}$ ), a global net ocean uptake flux for anthropogenic  $\text{CO}_2$  emissions of  $2.0 \pm 1.0 \text{ PgC yr}^{-1}$  was estimated in a reference year 2000 (one PgC is  $10^{15}$  grams of C in the form of  $\text{CO}_2$ ) (Takahashi *et al.* 2009). Among the four ocean basins, the Atlantic Ocean (north of  $50^\circ\text{S}$ ) is the strongest sink providing about 60% of the total global ocean uptake, whereas the Pacific (north of  $50^\circ\text{S}$ ) is nearly neutral. The Indian and Southern Oceans contribute about 20% each to the global uptake flux (Takahashi *et al.* 2002). However, the coastal ocean has been largely ignored in global carbon budgeting efforts, even if the related flows of carbon and nutrients are disproportionately high in comparison with its surface area (Chen-Tung *et al.* 2003).

The wind field over the Gulf of California is essentially monsoonal in nature, from the NW during "winter" and from the SE during "summer". Upwelling occurs off the eastern coast with northwesterly winds ("winter" conditions from December through May), and off the Baja California coast with southeasterly winds ("summer"

conditions from July through October), with June and November as transition periods (Roden 1964). Coastal upwelling areas are known to show oversaturation of CO<sub>2</sub> with respect to atmospheric equilibrium because of the input of DIC-rich deep waters (Borges 2005). Besides, the northern Gulf exhibits spectacular tidal phenomena, and in spite of relatively strong stratification during summer, tidal mixing in the midriff islands region produces a vigorous stirring of the water column down to >500 m depth, with the net effect of carrying colder, nutrient-rich water to the surface (Simpson *et al.* 1994) and creating an ecological situation similar to constant upwelling (Álvarez-Borrego 2002). This also has the effect of making the areas around the midriff islands a strong source of CO<sub>2</sub> to the atmosphere (Zirino *et al.* 1997, Hidalgo-González *et al.* 1997).

Rodríguez-Ibáñez *et al.* (2013) used Álvarez-Borrego's (2012) and Álvarez-Borrego and Giles-Guzmán's (2012) VCWE values to calculate the net annual average inputs of dissolved inorganic carbon ( $DIC_{NET\ INPUT} = DIC_{INPUT} - DIC_{OUTPUT}$ ). Rodríguez-Ibáñez *et al.* (2013) compared  $DIC_{NET\ INPUT}$  values with the  $P_{NEW}$  annual averages to infer if the Gulf acts as a sink or source of CO<sub>2</sub> to the atmosphere.

Rodríguez-Ibáñez *et al.* (2013) considered the entrance to the Gulf a place where DIC is input from the Pacific Ocean into the Gulf, and from there it is transported throughout the Gulf. Steady state of DIC profiles throughout the Gulf was assumed at the scale of annual averages. Their method only requires an annual average DIC profile for the entrance to the Gulf. The Gulf is considered as a box open to the Pacific for water and dissolved components exchange, and also open to the atmosphere for gas exchange (see Figure 3). In order to achieve steady state, once inside the Gulf  $DIC_{NET\ INPUT}$  has to be balanced by consumption by new phytoplankton production and water-air CO<sub>2</sub> exchange:

$$DIC_{NET\ INPUT} - P_{NEW} - CO_{2EXCHANGE} = 0,$$

$$CO_{2EXCHANGE} = DIC_{NET\ INPUT} - P_{NEW}$$

If  $CO_{2EXCHANGE}$  is positive there is an excess of  $DIC_{NET\ INPUT}$  after nitrate has been exhausted by new phytoplankton production, and carbon dioxide flows from the water to the atmosphere; if  $CO_{2EXCHANGE}$  is negative there is a deficit of  $DIC_{NET\ INPUT}$  and carbon dioxide flows from the atmosphere to the water. This occurs regardless of the particular characteristics of DIC profiles in different regions of the Gulf. Gas exchange occurs with different intensities at different regions of the Gulf according to their particular physical dynamics (mixing and upwelling). Rodríguez-Ibáñez *et al.*'s (2013) objective was to produce an average  $CO_{2EXCHANGE}$  estimate for the whole Gulf.

Rodríguez-Ibáñez *et al.* (2013) generated an average DIC profile for the mouth of the Gulf and combined it with Álvarez-Borrego's (2012) average  $T_{INT(Z)}$  profile (see

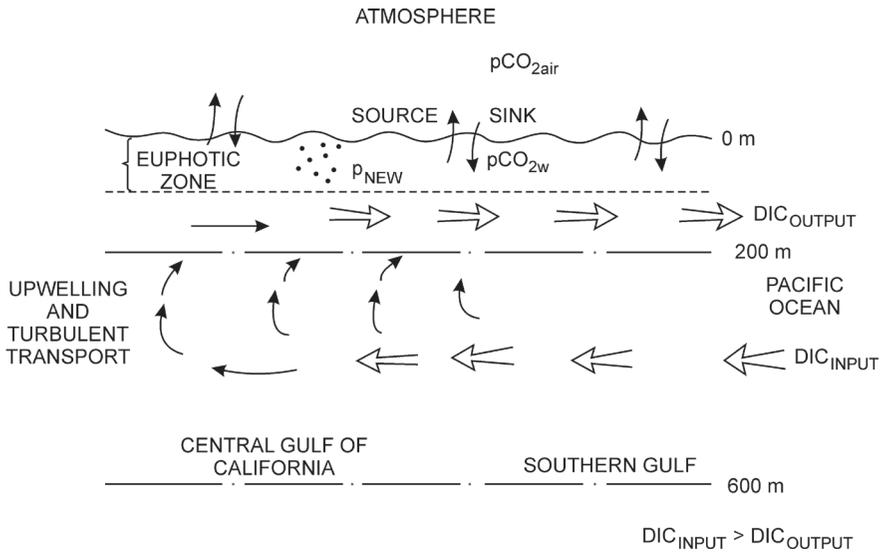


FIGURE 3. A simplified diagram showing the net input of dissolved inorganic carbon ( $DIC_{NET\ INPUT}$ ) and how it could be compared with new phytoplankton production ( $P_{NEW}$ ) to infer if the Gulf is a sink or source of  $CO_2$  to the atmosphere.  $DIC_{NET\ INPUT} = DIC_{INPUT} - DIC_{OUTPUT}$ . When  $P_{NEW} > DIC_{NET\ INPUT}$  the Gulf is a sink of  $CO_2$ ; when  $P_{NEW} < DIC_{NET\ INPUT}$  the Gulf is a source of  $CO_2$  (taken from Rodríguez-Ibáñez *et al.* 2013).

Figs. 1 and 4) to calculate weighted averages for DIC for each layer, 0-200 m and 200-600 m:  $DIC_{(0-200)} = \frac{\sum (DIC_{(z)} \cdot T_{INT(z)})}{\sum (T_{INT(z)})}$ , with z changing from 0 to 200 m; and similarly for 200-600 m. The average DIC for the first 200 m ( $DIC_{(0-200)}$ ), weighted by  $T_{INT(z)}$ , is  $2.100 \pm 0.012$  moles  $m^{-3}$ ; and the respective average for 200-600 m is  $2.294 \pm 0.006$  moles  $m^{-3}$ .

The average DIC output from the Gulf to the PO in the 0-200 m layer was calculated multiplying  $DIC_{(0-200)}$  (moles  $m^{-3}$ ) by the water transport ( $10^6 \times VCWE$   $m^3 s^{-1}$ ); and similarly for the average DIC input from the PO into the Gulf in the 200-600 m layer. Each of the two results was transformed into an annual DIC flux:

$$DIC_{OUTPUT} = (DIC_{(0-200)} \text{ moles } m^{-3})(10^6 \times VCWE \text{ } m^3 \text{ } s^{-1})(86400 \text{ s } day^{-1})$$

(365 days year<sup>-1</sup>)

$$DIC_{INPUT} = (DIC_{(200-600)} \text{ moles } m^{-3})(10^6 \times VCWE \text{ } m^3 \text{ } s^{-1})(86400 \text{ s } day^{-1})$$

(365 days year<sup>-1</sup>)

In order to explore different possibilities for the air-sea exchange of  $CO_2$  in the Gulf, Rodríguez-Ibáñez *et al.* (2013) used two scenarios: in the first one the VCWE is equal to  $0.23 \pm 0.02$  Sv and  $P_{NEW}$  is equal to  $(9.26 \pm 3.18) \times 10^{12}$  g C year<sup>-1</sup>

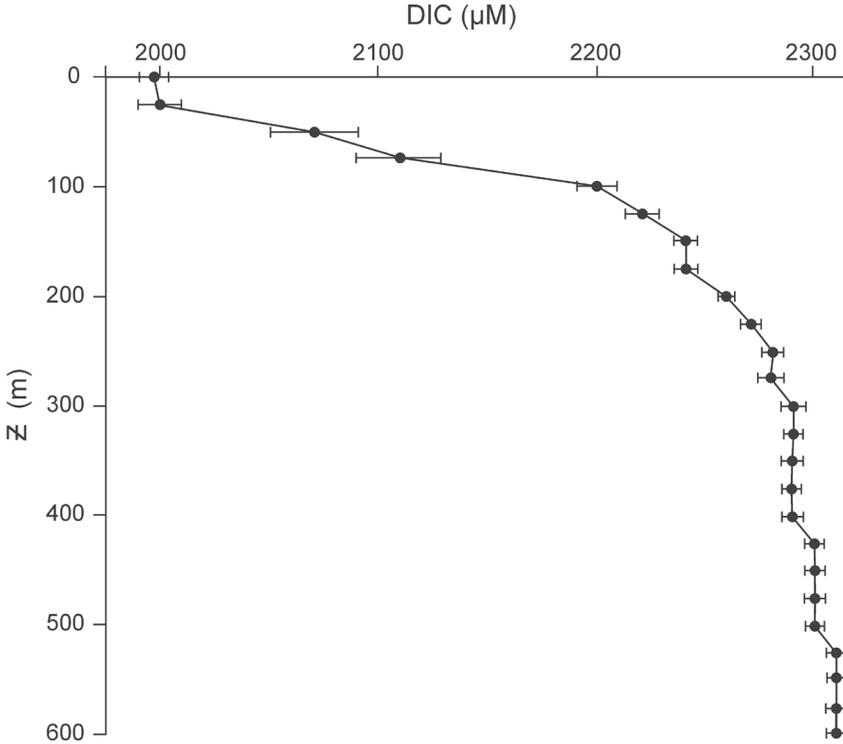


FIGURE 4. Annual average of the vertical distribution of DIC ( $\mu\text{M}$ ) for the mouth of the Gulf of California. Horizontal bars represent  $\pm$  one standard error ( $s \cdot n^{-0.5}$ ) (taken from Rodríguez-Ibáñez *et al.* 2013).

(Álvarez-Borrego and Giles-Guzmán 2012); in the second scenario the VCWE is equal to  $0.67 \pm 0.10$  Sv and  $P_{\text{NEW}}$  is equal to  $(31.04 \pm 1.58) \times 10^{12}$  g C year<sup>-1</sup> (Álvarez-Borrego 2012). Standard errors were calculated by Rodríguez-Ibáñez *et al.* (2013) following D'Hainaut (1978). However, the VCWE value for the surface layer (0-200 m) has to always be equal to the one for the deep layer (200-600 m); because of the conservation of mass principle there are no degrees of freedom for these two fluxes to change independently. Since the  $\text{DIC}_{\text{OUTPUT}}$  from the Gulf to the PO is going to be subtracted from the input from the PO to obtain  $\text{DIC}_{\text{NET INPUT}}$ , it implies that when multiplying the weighted DIC average for each layer by  $10^6 \times \text{VCWE}$  the uncertainty of the VCWE value ( $\pm 0.10$  Sv in one case, and  $\pm 0.02$  Sv in the other) should not be taken into account. For the same reason the uncertainty of the  $P_{\text{NEW}}$  value calculated by Álvarez-Borrego and Giles-Guzmán (2012) depends only on the uncertainty of the weighted average values of  $\text{NO}_3$  for each layer and not on the uncertainty of VCWE. Thus, when subtracting  $P_{\text{NEW}}$  from  $\text{DIC}_{\text{NET INPUT}}$  to infer if

there is an excess of CO<sub>2</sub> or vice versa, instead of using Álvarez-Borrego and Giles-Guzmán's (2012) P<sub>NEW</sub> value [(9.26 ± 3.18) × 10<sup>12</sup> g C year<sup>-1</sup>], Rodríguez-Ibáñez *et al.* (2013) used the recalculated P<sub>NEW</sub> value equal to (9.26 ± 1.09) × 10<sup>12</sup> g C year<sup>-1</sup>.

In the first scenario the average flux of dissolved CO<sub>2</sub> out to the PO in the 0–200 m layer is (2,100 ± 0.012 moles m<sup>-3</sup>)(230,000 m<sup>3</sup> s<sup>-1</sup>)(86,400 s day<sup>-1</sup>)(365 days year<sup>-1</sup>) = (15.54 ± 0.11) × 10<sup>12</sup> moles year<sup>-1</sup>. Similarly, the average annual flux of dissolved CO<sub>2</sub> into the Gulf in the 200–600 m layer is (17.15 ± 0.04) × 10<sup>13</sup> moles year<sup>-1</sup>. The difference is the average annual net input of CO<sub>2</sub> from the PO into the Gulf: DIC<sub>NET INPUT</sub> = [(17.15 ± 0.04) – (15.54 ± 0.11)] × 10<sup>12</sup> = (1.61 ± 0.15) × 10<sup>12</sup> moles year<sup>-1</sup> = (19.32 ± 1.8) × 10<sup>12</sup> g C year<sup>-1</sup>. Subtracting P<sub>NEW</sub> from DIC<sub>NET INPUT</sub>: [(19.32 ± 1.8) × 10<sup>12</sup> – (9.26 ± 1.09) × 10<sup>12</sup>] g C year<sup>-1</sup> = (7.66 ± 2.65) × 10<sup>12</sup> g of carbon per year. This is an excess of net DIC input with respect to that needed to support P<sub>NEW</sub> and CO<sub>2</sub> has to flow from the water to the atmosphere (Rodríguez-Ibáñez *et al.* 2013).

In the second scenario the average flux of DIC out to the PO in the 0–200 m layer is (2,100 ± 0.012 moles m<sup>-3</sup>)(670,000 m<sup>3</sup> s<sup>-1</sup>)(86,400 s day<sup>-1</sup>)(365 days year<sup>-1</sup>) = (44.37 ± 0.25) × 10<sup>12</sup> moles year<sup>-1</sup>. Similarly, the average annual flux of DIC into the Gulf in the 200–600 m layer is (48.47 ± 0.13) × 10<sup>12</sup> moles year<sup>-1</sup>. The difference is the average annual net DIC input from the PO into the Gulf: DIC<sub>NET INPUT</sub> = [(48.47 ± 0.13) – (44.37 ± 0.25)] × 10<sup>12</sup> = (4.10 ± 0.38) × 10<sup>12</sup> moles year<sup>-1</sup> = (49.20 ± 4.56) × 10<sup>12</sup> grams C year<sup>-1</sup>. Subtracting P<sub>NEW</sub> from DIC<sub>NET INPUT</sub>: CO<sub>2</sub>EXCHANGE = [(49.20 ± 4.56) × 10<sup>12</sup> – (31.04 ± 1.58) × 10<sup>12</sup>] grams C year<sup>-1</sup> = (18.16 ± 6.14) × 10<sup>12</sup> grams of carbon per year. Again, this is an excess of DIC input with respect to that needed to support P<sub>NEW</sub> and CO<sub>2</sub> has to flow from the Gulf to the atmosphere (Rodríguez-Ibáñez *et al.* 2013). Thus, the Gulf of California behaves as a source of CO<sub>2</sub> to the atmosphere in both scenarios (Rodríguez-Ibáñez *et al.* 2013).

## 5. DISCUSSION

The values deduced by Álvarez-Borrego and Giles-Guzmán (2012) and Álvarez-Borrego (2012) for the vertical component of water exchange between the Gulf of California and the Pacific Ocean, 0.23 ± 0.02 Sv and 0.67 ± 0.10 Sv, in and out of the Gulf, are annual averages. These relatively low values, possibly only ~3% or ~7% of the whole water exchange, indicate that when considering a particular depth most of the time the inflow from the PO is equal or very similar to the outflow. Thus, most of the exchange between the Gulf and the PO consists of the horizontal component, and this occurs significantly from 0 m to >1000 m (*i.e.*, Roden 1972). Estimates of current speeds by geostrophic calculations are accurate to ±20% at best (Reid 1959). Thus, the small vertical component of water exchange at the Gulf's mouth may possibly be

lost within the uncertainty of geostrophic computations. Nevertheless, as mentioned above, Bray (1988) was able to estimate it for water exchange between the northern and central Gulf.

Álvarez-Borrego and Giles-Guzmán (2012) run a sensitivity analysis and found that the value for the VCWE does not vary significantly with changes of the shape of the vertical profile of  $T_{INT(Z)}$  and with changes of the average profile of dissolved Si concentration. The relation between the VCWE and the average opal accumulation rate for the entire Gulf is direct and linear. If the average opal accumulation rate is changed by a certain percentage, VCWE does it by the same percentage and in the same direction. Rodríguez-Ibáñez *et al.* (2013) performed a sensitivity analysis to assess the effect of changing the specific alkalinity profile, and the VCWE value, on  $DIC_{NET\ INPUT}$ . When calculating DIC from pH and alkalinity values, the most critical aspect for attaining accuracy is the calibration of the HCl solution to measure alkalinity. There may be inaccuracies in the estimate of alkalinity, because this calibration is not always performed properly, even though the measurements could be relatively precise. Also, Rodríguez-Ibáñez *et al.* (2013) run an exercise to see the effect of changing the average DIC profile on  $DIC_{NET\ INPUT}$  equilibrating the mixed layer waters with the 2013 NOAA atmospheric average  $pCO_2$  value of 396 ppm. Their results show that the  $DIC_{NET\ INPUT}$  values do not vary significantly with changes of the specific alkalinity profile; and up to 2013, corrections to the estimates of  $DIC_{NET\ INPUT}$  due to the fact that mixed layer waters of the Gulf tend to be equilibrated with an increasing atmospheric  $pCO_2$  may be considered negligible. Since DIC data used by Rodríguez-Ibáñez *et al.* (2013) are from years in the period 1974-1997, they have the effect of a large fraction of the anthropogenic  $CO_2$  that has been absorbed by this region of the ocean. On the other hand, it is reasonable to assume that anthropogenic  $CO_2$  stored in the Gulf of California is practically the same as that of the adjacent Pacific Ocean (~15 moles of  $CO_2\ m^{-2}$ , Sabine *et al.* 2004), so that it would not make any appreciable difference in the exchange between the two. This storage has accumulated for the last one and a half century and a large fraction of it must be part of the DIC profile that Rodríguez-Ibáñez *et al.* (2013) used.

The Gulf of California behaves as a source of  $CO_2$  to the atmosphere because the slope of the DIC-nitrate relationship is greater than Redfield's ratio in subsurface and deep waters of the Gulf of California (not illustrated) (Rodríguez-Ibáñez *et al.* 2013). When subsurface and relatively deep water are carried to the euphotic zone by upwelling and/or mixing, after all nitrate is consumed by new phytoplankton production there is DIC left as an excess. The Gulf of California is a source of  $CO_2$  to the atmosphere because of the DIC-nitrate relationship, regardless of the VCWE value. The DIC excess over  $NO_3^-$ , at depth, is because of the dissolution of calcium

carbonate skeletons (Park 1965); also because of denitrification processes associated to the oxygen minimum zone in the eastern Pacific (Thomas 1966), and to differences of preformed DIC (Park 1965). The processes of calcium carbonate dissolution and denitrification occur along the trajectory of the water masses from their origin at high latitudes, and not only at the Gulf. Calcium carbonate dissolution occurs in waters deeper than ~200 m because of under-saturation with respect to both aragonite and calcite in the Gulf of California (Gaxiola-Castro *et al.* 1978) and in the whole northeastern Pacific Ocean (Park 1968); denitrification occurs at 100–800 m depth in the eastern Pacific Ocean because of nitrate reduction by bacteria when dissolved oxygen concentration is very low (Thomas 1966); and since the deeper the water masses the lower their temperature, deep waters had a larger solubility of gases (including CO<sub>2</sub>) at their latitude of origin, when they were in contact with the atmosphere, and hence greater preformed DIC than that of shallow waters (Culberson and Pytkowicz 1970).

The choice of two layers, 0–200 m and 200–600 m, is not the only possible one. Marinone (2003) used a three dimensional model to predict the circulation of the Gulf, and when integrating the average annual circulation predicted by this model across the Gulf's mouth, the VCWE between the Gulf and the PO results in four layers: 0–200 m (0.23 Sv outflow), 200–600 m (0.13 Sv inflow), 600–1,200 m (0.04 Sv outflow), and 1,200–2,600 m (0.17 Sv inflow), with flows as point estimates (S.G. Marinone, CICESE, Ensenada, personal communication) (notice that the sum of outflows and inflows are not equal). However, the annual average net input of dissolved Si with these water inflows and outflows is ~3 times that needed for the production of opal preserved in the sediments of the Gulf. On the other hand, there is no physical known mechanism that would transport nutrients from very deep waters, such as those below 1200 m, to the euphotic zone to be used by phytoplankton.

The net nutrient and DIC input to the Gulf is not transported to the euphotic zone homogeneously throughout it because there are regional differences of the physical dynamics of the Gulf. As Álvarez-Borrego (2012) indicated, upwelling along most of the eastern Gulf with “winter” conditions, cyclonic eddies in different parts of the Gulf, and strong mixing at the midriff islands throughout the whole year (mainly with spring tides and during “winter”) are mechanisms that transport deep nutrient and CO<sub>2</sub>-rich waters to the euphotic zone. The midriff islands region is the area within the Gulf with the highest CO<sub>2</sub> water-to-air fluxes throughout the whole year; it is the area with the largest values of pCO<sub>2w</sub>, as mentioned above (*e.g.*, Zirino *et al.* 2007). On the other hand, Calvert's (1966) figure 7 shows the opal distribution in surface sediments of the Gulf and suggests that Guaymas basin might be the place with highest phytoplankton production. Álvarez-Borrego and

Lara-Lara (1991) used  $^{14}\text{C}$  data to conclude that highest productivities are found during winter-spring and in the Guaymas Basin (up to  $>4 \text{ g C m}^{-2} \text{ day}^{-1}$ ). This may be because of strong upwelling events and the horizontal transport of nutrient rich mixed waters carried from the relatively near midriff islands into this basin (Álvarez-Borrego 2012). The “winter” upwelling off the eastern coast might be the area with the second highest  $\text{CO}_2$  water-to-air fluxes in the Gulf.

There are clear evidences that there is a large seasonal variation of phytoplankton biomass in the Gulf, with diatoms as an important component, and also a temporal variation of circulation in the Gulf, with a strong seasonal component. There is high phytoplankton biomass and production during winter and spring associated to a general anticyclonic circulation, and low biomass and production during summer and autumn associated to a general cyclonic circulation (Santamaría-Del Ángel *et al.* 1994a, Hidalgo-González and Álvarez-Borrego 2001, 2004, Kahru *et al.* 2004, Bray 1988, Marinone 2003). In accordance with this, opal fluxes from the euphotic zone to the sediments are high during winter and spring and low during summer and autumn (Thunell *et al.* 1994). Also, there is interannual variability dominated by El Niño events (Baumgartner and Chriestensen 1985, Santamaría-Del Ángel *et al.* 1994b, Hidalgo-González and Álvarez-Borrego 2004, Kahru *et al.* 2004). This indicates that an estimate of the VCWE between the PO and the Gulf as an annual average is a first approximation to reality and there are opportunities for future work on its time variability.

The nitrate required by  $\text{P}_{\text{NEW}}$  for the whole Gulf of California has to be compensated by an export, from the Gulf to the PO, of reduced forms of inorganic nitrogen (after respiration), dissolved organic nitrogen (DON), and particulate organic nitrogen (PON); and also an export of PON from the pelagic ecosystem to the sediments of the Gulf. Álvarez-Borrego (2012) estimated that ammonium export to the Pacific is only ~3% of the nitrogen in the form of nitrate that is required by  $\text{P}_{\text{NEW}}$ . Based on estimates by Thunell *et al.* (1994), export of PON to the sediments is only ~3% of the nitrogen required by  $\text{P}_{\text{NEW}}$ . In the water column, PON is only ~3% of DON. Thus, the majority of reduced nitrogen that is exported from the Gulf to the PO is in the form of DON. Thus, the Gulf of California is an autotrophic system that imports inorganic dissolved nutrients from the Pacific Ocean and exports mainly dissolved organic matter.

Based on 1.6 Sv of water exchange at the Gulf’s mouth (Roden and Groves 1959), Calvert (1966) calculated that the Pacific Ocean net supply is approximately  $10^{11}$  kg of dissolved silica per year. Calvert’s (1966) objective was to demonstrate that there was more than enough dissolved Si input from the Pacific Ocean to support the accumulation of biogenic silica in the Gulf, and that there was no need for dissolved

Si input from rivers. But his estimate for the net input of dissolved Si from the PO was about seven times the amount needed for the production of silica preserved in the sediments of the Gulf, and that was because he considered Roden and Groves's (1959) water exchange value (1.6 Sv) as if all of it was the VCWE, without any horizontal component.

With a vertical component of water exchange of  $(0.67 \pm 0.10)$  Sv, instead of 1.6 Sv, the estimate for the net input of dissolved silica from the PO is decreased by a factor of  $0.67/1.6 = 0.4$ , resulting in  $(4)10^{10}$  kg  $\text{SiO}_2$  year<sup>-1</sup>, which is still more than double than the estimate for the biogenic silica preserved in the sediments of the Gulf ( $(1.5)10^{10}$  kg  $\text{SiO}_2$  year<sup>-1</sup>). This difference suggests that the value 0.67 Sv might be an overestimation for the VCWE between the Gulf and the PO, and this could happen if Hidalgo-González and Álvarez-Borrego (2004) overestimated their  $P_{\text{NEW}}$  values. Biogenic silica preserved in the sediments of the Gulf has been measured extensively and directly with samples taken from cores since the 1939 EW Scripps cruise (Revelle 1939, 1950, Calvert 1966, DeMaster 1979, Thunell *et al.* 1994). On the other hand, <sup>15</sup>NO<sub>3</sub> incubations have not been carried out in the Gulf, and it is not possible to have an idea of the accuracy of the estimates of  $P_{\text{NEW}}$  deduced from modeling satellite data because there are no  $P_{\text{NEW}}$  in situ ship data to compare both types of results.

Furthermore, Rodríguez-Ibáñez *et al.* (2013) transformed their values of the Gulf's CO<sub>2</sub> output to the atmosphere for both scenarios into average values in grams m<sup>-2</sup> year<sup>-1</sup>: in the first scenario their average value is  $52.1 \pm 18.0$  grams m<sup>-2</sup> year<sup>-1</sup>; and in the second scenario it is  $123.5 \pm 41.8$  grams m<sup>-2</sup> year<sup>-1</sup>. The maxima water-to-air annual average CO<sub>2</sub> fluxes of the world's ocean, as reported by Takahashi *et al.* (2009), are between 24 and 108 grams m<sup>-2</sup> year<sup>-1</sup>, in places like the eastern equatorial Pacific Ocean, which has continuous upwelling. The Gulf of California is almost at equilibrium with the atmosphere during "summer" conditions, with exception of the mid-riff islands region, and during "winter" upwelling occurs mostly at the eastern side. Thus, an annual average CO<sub>2</sub> flux per unit area for the whole Gulf cannot be larger than the maximum for places like the eastern equatorial Pacific. This indicates that the first scenario is more acceptable with an average CO<sub>2</sub> output to the atmosphere of  $(7.66 \pm 2.65) \times 10^{13}$  grams C year<sup>-1</sup> for the whole Gulf, and that the VCWE value of  $(0.23 \pm 0.02)$  Sv is closer to reality than  $(0.67 \pm 0.10)$  Sv. This CO<sub>2</sub> input from the Gulf to the atmosphere is only ~1.7% of the annual CO<sub>2</sub> output to the atmosphere of the whole eastern equatorial Pacific ( $0.48$  Pg C year<sup>-1</sup>, Takahashi *et al.*, 2009), which has a very large area compared to that of the Gulf. But, when adding up all coastal areas of the whole world's ocean, the figure may be a very significant one (*i.e.*, Chen-Tung and Borges 2009).

## ACKNOWLEDGEMENTS

J.M. Domínguez and F. Ponce did the art work.

## REFERENCES

- Ahrens, T.D., J.M. Beman, J.A. Harrison, P.K. Jewett, and P.A. Matson. 2008. A synthesis of nitrogen transformations and transfers from land to the sea in the Yaqui Valley agricultural region of northwest Mexico. *Water Resources Research* 44, W00A05, doi:10.1029/2007WR006661.
- Álvarez-Borrego, S. 2002. Physical Oceanography. In: Case, T.J., M.L. Cody, and E. Ezcurra (eds.), *A New Island Biogeography of the Sea of Cortés*. Oxford University Press, Oxford, pp. 41–59.
- Álvarez-Borrego, S. 2012. New phytoplankton production as a tool to estimate the vertical component of water exchange between the Gulf of California and the Pacific. *Ciencias Marinas* 38: 89–99.
- Álvarez-Borrego, S., and J.R. Lara-Lara. 1991. The physical environment and primary productivity of the Gulf of California. In: J.P. Dauphin and B.R.T. Simoneit (eds.), *The Gulf and Peninsular Province of the Californias*, Memoir 47. American Association of Petroleum Geologists, Tulsa, pp. 555–567.
- Álvarez-Borrego, S., and A.D. Giles-Guzmán. 2012. Opal in the Gulf of California sediments as a tool to estimate the vertical component of water exchange between the Gulf and the Pacific. *Botánica Marina* 2: 161–168.
- Álvarez-Borrego, S., J.A. Rivera, G. Gaxiola-Castro, M.J. Acosta-Ruiz, and R.A. Schwartzlose. 1978. Nutrientes en el Golfo de California. *Ciencias Marinas* 5: 21–36.
- Baumgartner, T.R., and N. Christensen. 1985. Coupling of the Gulf of California to large-scale interannual climatic variability. *Journal of Marine Research* 43: 825–848.
- Beman, J.M., K. Arrigo, and P.A. Matson. 2005. Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature* 434: 211–214.
- Borges, A.V. 2005. Do we have enough pieces of the jigsaw to integrate CO<sub>2</sub> fluxes in the coastal ocean? *Estuaries* 28: 3–27.
- Bray, N.A. 1988. Thermohaline circulation in the Gulf of California. *Journal Geophysical Research* 93: 4993–5020.
- Callendar, G.S. 1938. The artificial production of carbon dioxide and its influence on temperature. *Quarterly Journal of the Royal Meteorological Society* 64: 223–240.
- Calvert, S.E. 1966. Accumulation of diatomaceous silica in the sediments of the Gulf of California. *Geological Society of America Bulletin* 77: 569–596.
- Campbell, A.C., and J.M. Gieskes. 1984. Water column anomalies associated with hydrothermal activity in the Guaymas Basin, Gulf of California. *Earth and Planetary Science Letters* 68: 57–72.

- Castro, R., M.F. Lavín, and P. Ripa. 1994. Seasonal heat balance in the Gulf of California. *Journal of Geophysical Research* 99: 3249–3261.
- Castro, R., R. Durazo, A. Mascarenhas, C.A. Collins, and A. Trasviña. 2006. Thermohaline variability and geostrophic circulation in the southern portion of the Gulf of California. *Deep-Sea Research I*, 53: 188–200.
- Chen-Tung A.C., and Borges A.V. 2009. Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO<sub>2</sub>. *Deep-Sea Research* 56: 578–590.
- Chen-Tung, A.C., K.K. Liu, and R. MacDonald. 2003. Continental Margin Exchanges. In: M.J.R. Fasham (ed.), *Ocean Biogeochemistry: A synthesis of the Joint Global Ocean Flux Study (JGOFS)*. Springer-Verlag, Berlin, pp. 53–97.
- Culberson, C.H., and R.M. Pytkowicz. 1970. Oxygen-total carbon dioxide correlation in the Eastern Pacific Ocean. *Journal of the Oceanographical Society of Japan* 26: 95–100.
- D'Hainut, L. 1978. *Cálculo de incertidumbres en las medidas*. Trillas, Mexico City, Mexico.
- DeMaster, D.J. 1979. The marine budgets of silica and <sup>32</sup>Si. Ph.D. Thesis, Yale University, New Haven, Connecticut, 308 pp.
- Dugdale, R.C., and J.J. Goering. 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology & Oceanography* 12: 196–206.
- Emilsson, I., and M.A. Alatorre. 1997. Evidencias de un remolino ciclónico de mesoescala en la parte sur del Golfo de California. In: M.F. Lavín (ed.), *Contribuciones a la oceanografía física en México*, Monografía 3. Unión Geofísica Mexicana, Ensenada, pp. 173–182.
- Gaxiola-Castro, G., S. Álvarez-Borrego, and R.A. Schwartzlose. 1978. Sistema del bióxido de carbono en el Golfo de California. *Ciencias Marinas* 5: 25–40.
- Hidalgo-González, R.M., and S. Álvarez-Borrego. 2001. Chlorophyll profiles and the water column structure in the Gulf of California. *Oceanológica Acta* 24: 19–28.
- Hidalgo-González, R.M., and S. Álvarez-Borrego. 2004. Total and new production in the Gulf of California estimated from ocean color data from the satellite sensor SeaWiFS. *Deep-Sea Research II*, 51: 739–752.
- Hidalgo-González, R.M., S. Álvarez-Borrego, and A. Zirino. 1997. Mixing in the region of the Midriff Islands of the Gulf of California: Effect on surface pCO<sub>2</sub>. *Ciencias Marinas* 23: 317–327.
- Kahru, M., S.G. Marinone, S.E. Lluch-Cota, A. Parés-Sierra, and B.G. Mitchell. 2004. Ocean-color variability in the Gulf of California: scales from days to ENSO. *Deep-Sea Research II*, 51: 139–146.
- Lavín, M.F., and S. Organista. 1988. Surface heat flux in the northern Gulf of California. *Journal of Geophysical Research* 93: 14033–14038.
- Lavín, M.F., E. Beier, and A. Badan. 1997. Estructura hidrográfica y circulación del Golfo de California: escalas estacional e interanual. In: M.F. Lavín (ed.), *Contribuciones a la oceanografía física en México*, Monografía 3. Unión Geofísica Mexicana, Ensenada, pp. 141–171.

- Lavín, M.F., R. Castro, E. Beier, V.M. Godínez, A. Amador, and P. Guest. 2009. SST, thermohaline structure, and circulation in the southern Gulf of California in June 2004 during the North American Monsoon Experiment. *Journal of Geophysical Research* 114, C02025, doi:10.1029/2008JC004896.
- Marinone, S.G. 2003. A three-dimensional model of the mean and seasonal circulation of the Gulf of California. *Journal of Geophysical Research* 108 (C10), 3325, doi:10.1029/2002JC001720.
- Park, K. 1965. Total carbon dioxide in sea water. *Journal of the Oceanographical Society of Japan* 21: 54–59.
- Park, K. 1968. The processes contributing to the vertical distribution of apparent pH in the northeastern Pacific Ocean. *Journal of the Oceanographical Society of Korea* 3: 1–7.
- Pilson, M.E. 1998. *An introduction to the chemistry of the sea*. Prentice Hall, Pearson Education, Upper Saddle River, 431 pp.
- Redfield, A.C., B.H. Ketchum, and F.A. Richards. 1963. The influence of organisms on the composition of seawater. In: M.N. Hill (ed.), *The Sea*, vol. 2, Interscience, New York, pp. 26–77.
- Reid, R.O. 1959. *Influence of some errors in the equation of state on observations of geostrophic currents*. Procedures of the Conference on the Physical and Chemical Properties of Sea Water, National Academy of Sciences, Easton, Md. Washington, DC, pp. 21–23.
- Revelle, R.R. 1939. Sediments of the Gulf of California. *Geological Society of America Bulletin* 50: 1929.
- Revelle, R.R. 1950. Sedimentation and oceanography: survey of field observations, pt. 5 of 1940 EW Scripps cruise to the Gulf of California. *Geological Society of America*, Memoir 43, pp. 1–6.
- Roden, G.I. 1958. Oceanographic and meteorological aspects of the Gulf of California. *Pacific Science* 12: 21–45.
- Roden, G.I. 1964. Oceanographic aspects of the Gulf of California. In: T.H. van Andel and G.G. Shor (eds.), *Marine Geology of the Gulf of California*, Memoir 3. American Association of Petroleum Geologists, Tulsa, pp. 30–58.
- Roden, G.I. 1972. Thermohaline structure and baroclinic flow across the Gulf of California entrance and in the Revilla Gigedo Islands region. *Journal of Physical Oceanography* 2: 177–183.
- Roden, G.I., and G.W. Groves. 1959. Recent oceanographic investigations in the Gulf of California. *Journal of Marine Research* 18: 10–35.
- Rodríguez-Ibáñez, R., S. Álvarez-Borrego, S.G. Marinone, and J.R. Lara-Lara. 2013. The Gulf of California is a source of carbon dioxide to the atmosphere. *Ciencias Marinas* 39: 137–150.
- Sabine, C.L., R.A. Feely, N. Gruber, R.M. Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T-H Peng, A. Kozyr, T. Ono, A.F. Rios. 2004. The Oceanic Sink for Anthropogenic CO<sub>2</sub>. *Science* 305: 367–371.

- Santamaría-Del Ángel, E., S. Álvarez-Borrego, and F.E. Müller-Karger. 1994a. Gulf of California biogeographic regions based on coastal zone color scanner imagery. *Journal of Geophysical Research* 99: 7411–7421.
- Santamaría-Del Ángel, E., S. Álvarez-Borrego, and F.E. Müller-Karger. 1994b. The 1982–1984 El Niño in the Gulf of California as seen in coastal zone color scanner imagery. *Journal of Geophysical Research* 99: 7423–7431.
- Siegenthaler, U., and J.L. Sarmiento. 1993. Atmospheric carbon dioxide and the ocean. *Nature* 365: 119–125.
- Simpson, J.H., A.J. Souza, and M.F. Lavín. 1994. Tidal mixing in the Gulf of California. In: K.J. Beven, P.C. Chatwin, and J.H. Millbank (eds.), *Mixing and Transport in the Environment*. John Wiley & Sons, London, pp. 169–182.
- Takahashi, T., W.S. Broecker, and S. Langer. 1985. Redfield ratio based on chemical data from isopycnal surfaces. *Journal of Geophysical Research* 90: 6907–6924.
- Takahashi, T., S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tilbrook, N. Bates, R. Wanninkhof, R.A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri. 2002. Global sea–air CO<sub>2</sub> flux based on climatological surface ocean pCO<sub>2</sub>, and seasonal biological and temperature effects. *Deep-Sea Research II*, 49: 1601–1622.
- Takahashi, T., S.C. Sutherland, R. Wanninkhof, C. Sweeney, R.A. Feely, D. Chipman, B. Hales, G. Friederich, F. Chávez, A. Watson, D. Bakker, U. Schuster, N. Metzl, H.Y. Inoue, M. Ishii, T. Midorikawa, C. Sabine, M. Hoppema, J. Olafsson, T. Amaron, B. Tilbrook, T. Johannessen, A. Olsen, R. Bellerby, H. DeBaar, Y. Nojiri, C.S. Wong, B. Delille, N. Bates. 2009. Climatological mean and decadal change in surface ocean pCO<sub>2</sub>, and net sea–air CO<sub>2</sub> flux over the global oceans. *Deep-Sea Research II*, 56: 554–577.
- Thomas, W.H. 1966. On denitrification in the northeastern tropical Pacific Ocean. *Deep-Sea Research* 13: 1109–1114.
- Thunell, R., C.J. Pride, E. Tappa, and F.E. Müller-Karger. 1994. Biogenic silica fluxes and accumulation rates in the Gulf of California. *Geology* 22: 303–306.
- Von Damm, K.L., J.M. Edmond, C.I. Measures, and B. Grant. 1985. Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochimica et Cosmochimica Acta* 49: 2221–2237.
- Warsh, C.E., and K.L. Warsh. 1971. Water exchange at the mouth of the Gulf of California. *Journal of Geophysical Research* 76: 8098–8106.
- White, A.E., F.G. Prahl, R.M. Letelier, and B.N. Popp. 2007. Summer surface waters in the Gulf of California: Prime habitat for biological N<sub>2</sub> fixation. *Global Biogeochemical Cycles* 21, GB2017, doi:10.1029/2006GB002779.
- Zirino, A., J.M. Hernández-Ayón, R.A. Fuhrmann, S. Álvarez-Borrego, G. Gaxiola-Castro, J.R. Lara-Lara, and R.L. Bernstein. 1997. Estimate of surface pCO<sub>2</sub> in the Gulf of California from underway pH measurements and satellite imagery. *Ciencias Marinas* 23: 1–22.

\* Departamento de Ecología Marina, CICESE, Ensenada, BC, México, alvarezb@cicese.mx

Exploring Mexico's northwest, the Baja California Peninsula, its surrounding oceans, its islands, its rugged mountains, and rich seamounds, one feels diminished by the vastness and the greatness of the landscape while consumed by a sense of curiosity and awe. In a great natural paradox, we see the region's harsh arid nature molded by water through deep time, and we feel that its unique lifeforms have been linked to this desert and sea for thousands of years, as they are now.

These landscapes of fantasy and adventure, this territory of surprising, often bizarre growth-forms and of immense natural beauty, has inspired a wide array of research for over two centuries and continues to inspire the search for a deeper knowledge on the functioning, trends, and conservation status of these ecosystems in both land and ocean.

This book offers a compilation of research efforts aimed at understanding this extraordinary region and preserving its complex richness. It is a synthesis of work done by some exceptional researchers, mostly from Mexico, who indefatigably explore, record, and analyze these deserts and these seas to understand their ecological processes and the role of humans in their ever-changing dynamics.

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