MARINE ANTHROPOGENIC CO_2 ESTIMATES STEMMING FROM OBSERVATIONS

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ABSTRACT

Anthropogenic CO_2 releases to the atmosphere have changed the total inorganic carbon concentration of ocean by no more than 3-4% at any location. Main differences between three approaches [*Poisson and Chen*, 1987; *Gruber et al.,* 1996; *Friis*, 2005] are presented that define marine anthropogenic CO_2 (C_T^{ant}) as deduced from total inorganic carbon. All definitions are based on a back-calculation technique that was independently proposed by Brewer [1978] and Chen and Millero [1979]. The overall importance of this presentation is in the comparability of anthropogenic CO_2 findings from described methods with these derived from global bookkeeping approaches or full carbon model results.

The first back-calculation approach [*Poisson and Chen,* 1987] strongly relies on empirical relationships of total inorganic carbon at the sea surface. These relationships appear to be problematic as they are using a normalization procedure for total inorganic carbon that is critical and they are influenced by seasonality. The second approach [*Gruber et al.,* 1996] assumes CO_2 equilibria between the ocean and the atmosphere that remain the same from preindustrial to actual times. The equilibrium assumption excludes some likely temporal changes in the total inorganic carbon concentration, i.e. changes in the so-termed solubility pump of the CO_2 system (Fig. 1, $C_T^{\Delta T}$). The third approach [*Friis*, 2005] assumes that old/uncontaminated bottom water can be used as a preindustrial reference for the whole water column if adjusted by a thermodynamic relationship to the temperature and salinity of a water sample. With this the third approach includes changes in the solubility pump. The latter approach is not very specific for biologically driven differences of the CO_2 equilibrium state at the instant surface water loses contact with the atmosphere.

Based on a subpolar North Atlantic data set from 1999, anthropogenic CO_2 results are compared for the three approaches. The comparison of the C_T^{ant} profiles (Fig. 2) shows about the same penetration depth of 4300 to 4500 m for all methods. Nonetheless the range of the C_T^{ant} concentrations is different, exhibiting sea surface concentrations of about 43, 56, and 90 µmol kg^{-1}. Near surface concentrations of the Poisson and Chen (1987) approach are about two times as much as can be expected on thermodynamic grounds (see Fig. 1). The difference in the near surface C_T^{ant} concentrations with the Gruber et al. [1996] and Friis [2005] approach is close to the difference of the C_T^{ant} signals in the cold waters of Fig. 1 panel A and B, respectively. The nearly 20% higher results of the Friis (2005) approach are reasonable; following thermodynamics and observations of the CO_2 partial pressure difference between ocean and atmosphere [*Takahashi et al.,* 2002]. The findings emphasize that C_T^{ant} calculations with the Gruber et al. [1996] approach cannot be used directly for comparisons of the CO_2 increases in the marine reservoir using bookkeeping approaches or full carbon model results. Significant changes in the marine CO_2 inventory from preindustrial to actual times may be neglected.

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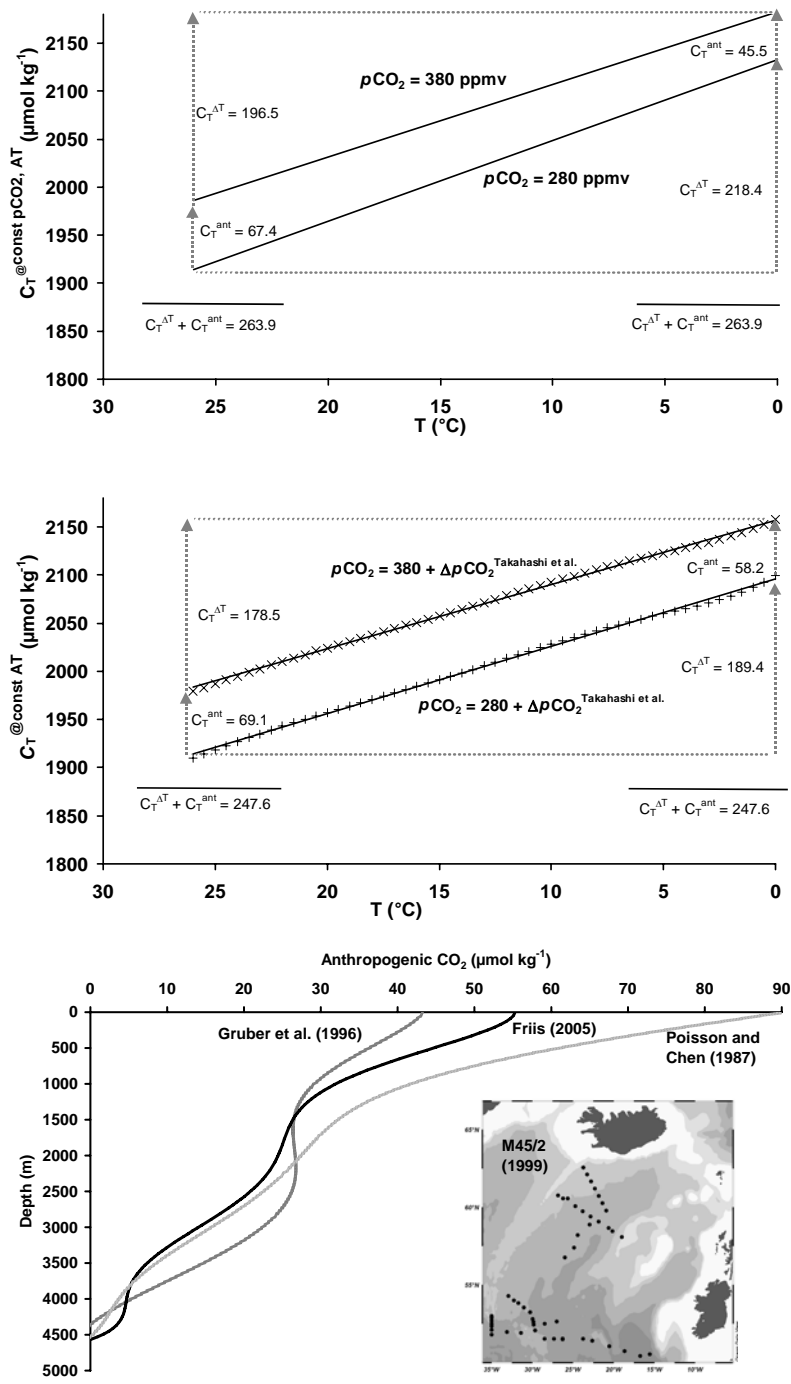
Fig. 1: Total inorganic carbon vs. temperature at different pCO$_2$ levels as calculated from a thermodynamic sea water model ($A_T = 2300$ µmol kg^{-1} and $S = 35$). Panel A shows that the temperature related change [$C_T^{\Delta T}$] decreases with higher pCO$_2$ levels. At the same time it shows an anthropogenic CO$_2$ signal [C_T^{ant}] as defined along ΔpCO$_2$ perturbation of 100 ppmv. The C_T^{ant} signal decreases with lower temperatures. The temperature dependence of C_T^{ant} is directly related to a change of the CO$_2$ solubility at higher pCO$_2$ levels. By assuming constant ΔpCO$_2$ fields from preindustrial to industrial times, panel B shows the same mutual relation between C_T^{ant} and $C_T^{\Delta T}$. The relation exists even if the pCO$_2$ is adjusted to an average North Atlantic ΔpCO$_2$ using a polynomial fit derived from observations [*Takahashi et al.,* 2002].

Fig. 2: Mean anthropogenic CO$_2$ profiles in the eastern subpolar North Atlantic in 1999 [M45] using three different backcalculation techniques. The profiles are based on 6th-order polynomial fits from 492 samples, the regression coefficients are R^2 = 0.94 (for Poisson and Chen, 1987), R^2 = 0.75 [for *Gruber et al.,* 1996], R^2 = 0.88 [for *Friis*, 2005]