

Total alkalinity: The explicit conservative expression and its application to biogeochemical processes

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Abstract

Total alkalinity (TA) is one of the few measurable quantities that can be used together with other quantities to calculate concentrations of species of the carbonate system (CO_2 , HCO_3^- , CO_3^{2-} , H^+ , OH^-). TA and dissolved inorganic carbon (DIC) are conservative quantities with respect to mixing and changes in temperature and pressure and are, therefore, used in oceanic carbon cycle models. Thus it is important to understand the changes of TA due to various biogeochemical processes such as formation and remineralization of organic matter by microalgae, precipitation and dissolution of calcium carbonate. Unfortunately deriving such changes from the common expression for TA in terms of concentrations of non-conservative chemical species (HCO_3^- , CO_3^{2-} , $\text{B}(\text{OH})_4^-$, H^+ , OH^- , etc.) is rarely obvious.

Here an expression for TA (TA_{ec}) in terms of the total concentrations of certain major ions (Na^+ , Cl^- , Ca^{2+} etc.) and the total concentrations of various acid-base species (total phosphate etc.) is derived from Dickson's original definition of TA under the constraint of electroneutrality. Changes of TA by various biogeochemical processes are easy to derive from this so-called explicit conservative expression for TA because each term in this expression is independent of changes of temperature or pressure within the ranges normally encountered in the ocean and obeys a linear mixing relation.

Further, the constraints of electroneutrality for nutrient uptake by microalgae and photoautotrophs are discussed. A so-called *nutrient- H^+ -compensation principle* is proposed. This principle in combination with TA_{ec} allows one to make predictions for changes in TA due to uptake of nutrients that are consistent with observations. A new prediction based on this principle is the change in TA due to nitrogen fixation followed by remineralization of organic matter and subsequent nitrification of ammonia which implies a significant sink of TA in tropical and subtropical regions where most of the nitrogen fixation takes place.

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1. Introduction

Total alkalinity is an important and very useful concept in the context of the carbonate system in seawater. Already in the 19th century it was known that seawater is alkaline and that it contains large amounts of dissolved inorganic carbon (DIC) which can be released in the form of CO₂ by titration with a strong acid. The alkalinity of seawater is much higher than that of freshwater and so is the content of DIC. Although several authors (for example, [Jacobsen, 1873](#)) supposed a connection between salt and DIC, the development of a clear concept of alkalinity had to await progress in understanding the form of salts in aqueous solutions (ions instead of undissociated compounds) and an advanced concept of acids and bases (proton donors and acceptors; [Brønsted, 1923](#); [Lowry, 1923a,b](#)). In the 1930s alkalinity was defined operationally as the number of milliequivalents of hydrogen ion neutralized by one liter of water at 20°C, without detailing which chemical species are actually responsible for the observed neutralization. [Rakestraw \(1949\)](#) was the first to discuss how the ‘concept of proton donors and acceptors could be used to shed light on exactly what it was that an alkalinity titration measured’ ([Dickson, 1992](#)). Rakestraw’s expression, which considered only bicarbonate, carbonate ion and borate, is still a first approximation to the most recent definition by [Dickson \(1981\)](#), cf. [DOE \(1994\)](#). The historical development of the alkalinity concept is discussed in detail by [Dickson \(1992\)](#). Even today several different definitions of TA are in use and can be found in textbooks: a fact that may lead to confusion. The concept of TA has been characterized as difficult to grasp and to explain.

The plan of the current paper is as follows. In Section 2 we consider a system with simple chemical composition where the alkalinity concept is easily explained. Based on the understanding of this system we discuss the generalization of the TA concept and hence Dickson’s definition. Dickson’s expression for TA in natural water samples is given in Section 3.11. The combination of Dickson’s expression for alkalinity with the expression for the charge balance (electroneutrality) of the solution leads to an expression for TA in terms of conservative species and conservative total concentrations (Section 4). Although this expression is easy to derive, it has not been published before, to the best of our knowledge, and is very useful to calculate changes in alkalinity due to various biogeochemical processes (Section 5). An alternative definition of TA proposed by [Peng et al. \(1987\)](#) and its relation to Dickson’s definition is discussed in Section 6.

All concentrations in the current paper are assumed to be on the moles per kilogram solution scale (gravimetric units; mol kg⁻¹ for short). The use of gravimetric units has the advantage that concentrations of quantities such as DIC or [Na⁺] stay constant despite changes of pressure or temperature.

In marine chemistry the term ‘conservative’ quantity or property has been used in various, often contradictory, ways. Quantities have been denoted as conservative without explaining in what sense. Distinct definitions are legitimate and reflect the interests of different communities. In order to avoid confusion we will define the concept of ‘conservative quantities’ as used in this article. When two water parcels are mixed together the amount of any chemical element, *E*, in the mixture is equal to the sum of the amounts of this element in the two initial parcels and thus the concentration of *E* measured in gravimetric units obeys the linear mixing relation

$$[E]_1M_1 + [E]_2M_2 = [E]_m(M_1 + M_2) \quad (1)$$

where $[E]_s$ is the concentration of element *E* in parcel $s=1, s=2$, or in the mixture ($s=m$) and M_s are the corresponding masses. This linear mixing relation can be used to calculate $[E]_m$. Quantities that obey this linear mixing relation and stay constant under changes of temperature (*T*) and pressure (*p*) will be called ‘conservative with respect to mixing and changes in *T* or *p*’ or just ‘conservative’.

Thus DIC is conservative because the carbon atoms of DIC stay as DIC during mixing and changes of temperature and pressure. The same applies to total phosphate because the phosphorus atoms are still in one or the other form of phosphate after mixing or changes in *T* or *p*. The total concentrations of other acid-base systems such as total ammonia and total sulphate are conservative as well. The concentrations of ions such as Na⁺, Ca²⁺, Cl⁻, NO₃⁻ etc. are also conservative because they are derived from fully dissociated acids or bases. TA is conservative too; this will become obvious later.

In contrast to DIC and TA, the concentrations of individual species of the carbonate system change with temperature and pressure (because of variation of the equilibrium constants with *T* and *p*). Even if *T*, *p*, and *S* of two water parcels are equal, the concentrations of CO₂, HCO₃⁻, and CO₃²⁻ do not obey a linear mixing relation if their concentrations in the initial water parcels are different.

2. Total alkalinity in a simple system

In order to get a feeling for the alkalinity concept we will discuss total alkalinity in a simplified seawater

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