



## Towards quantitative ecological risk assessment of elevated carbon dioxide levels in the marine environment

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### ABSTRACT

The environmental impact of elevated carbon dioxide (CO<sub>2</sub>) levels has become of more interest in recent years. This, in relation to globally rising CO<sub>2</sub> levels and related considerations of geological CO<sub>2</sub> storage as a mitigating measure. In the present study effect data from literature were collected in order to conduct a marine ecological risk assessment of elevated CO<sub>2</sub> levels, using a Species Sensitivity Distribution (SSD). It became evident that information currently available from the literature is mostly insufficient for such a quantitative approach. Most studies focus on effects of expected future CO<sub>2</sub> levels, testing only one or two elevated concentrations. A full dose-response relationship, a uniform measure of exposure, and standardized test protocols are essential for conducting a proper quantitative risk assessment of elevated CO<sub>2</sub> levels. Improvements are proposed to make future tests more valuable and usable for quantitative risk assessment.

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### 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is a natural trace gas in the Earth's atmosphere, which is also formed by the combustion of fossil fuels. As a result of economic growth and industrialisation the atmosphere's concentration of CO<sub>2</sub> has grown over the last century (e.g., Wolff, 2011). As global warming is believed to be caused by rising CO<sub>2</sub> levels (e.g., Solomon et al., 2007), authorities have set targets to reduce CO<sub>2</sub> emissions (e.g., United Nations, 1998). In order to achieve this goal, one of the solutions that is being considered (and in some cases already applied), is the capture and geological storage of CO<sub>2</sub>, in for instance abandoned oil or gas reservoirs (Steenveeldt et al., 2006).

When stored sub-seabed, there is a risk, albeit small, that stored CO<sub>2</sub> is accidentally released into the aquatic environment. Some authors argue that when storage options other than depleted oil and gas fields are used, such as aquifers and coal seams, it may not be guaranteed that they retain integrity forever (Van der Zwaan and Gerlagh, 2009; Van der Zwaan and Smekens, 2009).

Leakage from artificial storage, whilst unlikely at well-planned and managed sites, could be in the form of sudden large releases. More likely it will involve seepage of small amounts of CO<sub>2</sub> over time (Van der Zwaan and Smekens, 2009), which might result in locally elevated CO<sub>2</sub> levels. Quantitative risk assessment of elevated CO<sub>2</sub> levels on marine ecology, resulting from either increased

air emission or accidental releases from storage, should be an important aspect in the license application process on geological storage as required by legislation (e.g., Anonymous, 2009). However, such an assessment is currently unavailable.

Nonetheless, (physiological) effects of CO<sub>2</sub> on marine species are often studied, thus a great deal is known about potential effects of elevated CO<sub>2</sub> levels on these species. Shifts in pH as a result of elevated CO<sub>2</sub> levels are identified as an important factor resulting in physiological effects, particularly, for species that form calcareous tissues, such as corals (Hoegh-Guldberg, 2005). Kikkawa et al. (2004) indicate that the effects of water acidification by mineral acids such as hydrochloric and sulphuric acid are less than those caused by high CO<sub>2</sub> levels, when tested at the same water pH, as demonstrated in their study on eggs and larvae of red seabream (*Pagrus major*). Ishimatsu et al. (2005) indicate that this could very well be the case for other species as well. The latter was confirmed for Japanese flounder (*Paralichthys olivaceus*) (Hayashi et al., 2004), which supports the suggestion that exposure levels should be expressed as CO<sub>2</sub> levels, rather than a shift in pH units. CO<sub>2</sub> solubility in the water phase exceeds oxygen solubility which can reverse the normal outward diffusion of CO<sub>2</sub> from fish if CO<sub>2</sub> water concentrations are elevated (Ishimatsu et al., 2005).

A quantitative evaluation of median lethal CO<sub>2</sub> levels (LC50s) has rarely been conducted, but it appears that reported effect levels can vary largely, even within taxonomic groups like fish, as reviewed by Ishimatsu et al. (2005). Pörtner et al. (2005) note in their review that, although acute and chronic as well as lethal and sub-lethal effects of CO<sub>2</sub> have been studied, the continuum

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between time- and concentration-dependent effects have not been studied. As a result critical thresholds limiting long-term survival cannot be determined.

A widely used technique for ecological risk assessment of toxicants is the Species Sensitivity Distribution (SSD) (Newman et al., 2000; Posthuma et al., 2002), which has recently been applied to non-toxic stressors as well (De Vries et al., 2008; Smit et al., 2008; Struijs et al., 2011). The technique has been extensively discussed and validated in ecotoxicology (e.g., Forbes and Forbes, 1993; Forbes et al., 2001; Hose and Van den Brink, 2004; Selck et al., 2002; Van Wijngaarden et al., 2005). Basically, the SSD is the statistical distribution of species sensitivity, usually expressed as chronic no observed effect concentrations (NOECs) for a specific toxic compound for several representative species. An SSD can both be used to derive predicted no effect concentrations (PNECs) and to estimate the Potentially Affected Fraction (PAF) of species at risk posed by a specific exposure level.

For animals CO<sub>2</sub> can be considered as a toxicant, as it exerts adverse effects as a function of test species conditions, exposure duration and concentration. Specific issue for CO<sub>2</sub> is the complex carbonate chemistry which determines the exposure level and the fact that CO<sub>2</sub> is essential in respiratory pathways. Organisms have mechanisms to deal with CO<sub>2</sub>, but this is also the case for toxic metals that are essential elements at low concentrations (e.g., Goldhaber, 2003). In addition, many toxicants also display complex chemistry affecting their availability and hence toxicity (e.g., Di Toro et al., 2009).

In the present study, marine aquatic CO<sub>2</sub> effect data were collected in order to construct an SSD for quantitative risk assessment of elevated CO<sub>2</sub> levels in marine ecosystems. In addition to effect levels, information about experimental conditions and quality of reported data was collected as well, in order to perform a meta-analysis to assist the interpretation of the constructed SSD.

## 2. Method

### 2.1. Carbonate chemistry

Carbon dioxide has a number of chemical species in the water phase (CO<sub>2</sub>(aq), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, where the anions can be bound to numerous cations). A commonly used metric to denote CO<sub>2</sub> exposure is the partial pressure (pCO<sub>2</sub>). However, not all collected studies have used the same carbon species or unit to express the exposure level. In the present study the so-called Seacarb model (Lavigne and Gattuso, 2011) was used to calculate missing carbon species for all experiments (where possible) and used it to express all exposures as pCO<sub>2</sub> in micro atmosphere (µatm).

The Seacarb model uses temperature and salinity as input data. For salinity a default value of 35 ppt was used when data were missing. If experimental temperature was not reported, it was assumed to be close to the test species optimum. For all dissociation and stability constants, the default values were used as provided by the model. In addition, a combination of any two CO<sub>2</sub>-related parameters (pH, total alkalinity, concentration HCO<sub>3</sub><sup>-</sup>, total dissolved inorganic carbon or pCO<sub>2</sub>) is required as input. Preferably, the parameters were used as measured in the experiment. Otherwise, the parameters as calculated by the authors of the original paper were used. When partial pressure was reported as percentage or ppm, the total pressure was assumed to be standard (0.987 atm, (McNaught et al., 1997)), in order to convert the partial pressure into µatm. When partial pressure was reported in kPa, the pressure was converted into µatm using a conversion factor of  $9.87 \times 10^3$  µatm/kPa (Thompson and Taylor, 2008). When reported in Torr, a conversion factor of  $1.32 \times 10^3$  µatm/Torr (Thompson and Taylor, 2008) was used. When the pCO<sub>2</sub> level in the control

experiment was neither reported, nor calculable, the median level of the controls of all other experiments was used as a default. Default values were used in the construction of the SSD but were not included in statistical analyses.

### 2.2. Data collection

Using several search engines (including Scopus and Google Scholar) a search was performed for effects of elevated CO<sub>2</sub> conditions. Although non-exhaustive, available “grey” literature also was included in the dataset. In an SSD, each unique species is represented only once and several options exist to include multiple data for a single species (Wheeler et al., 2002). In the present study each unique species is recorded once in the dataset and when multiple studies on a single species were available peer reviewed literature was preferred over “grey” literature. Further, studies that tested a concentration range were preferred over studies testing only a single concentration and studies describing all test conditions were preferred over studies poorly describing them. If none of these criteria could be applied, the study with the lowest effect level was selected.

For each record (species), the following data were included in the dataset (if available): taxonomical information on the species; data required to calculate exposure levels, (see ‘carbonate chemistry’ section) for both control and treatment conditions; additional experimental conditions such as exposure duration, aeration/oxygen content and the number of concentrations tested next to the control.

Likewise, it was recorded whether the effect level was either a NOEC, Lowest Observed Effect Concentration (LOEC) or median effect concentration (EC50 or LC50). Most studies only indicated whether a significant effect (or not) was observed at specific exposure concentrations, when compared to the control experiment. When no EC50 was available, the statistics from those reports were used to classify effect concentrations as either a NOEC or a LOEC. As a consequence, in case only a single concentration was tested, it was either a NOEC or a LOEC, depending on whether a significant effect was observed. A LOEC was only included in the dataset if neither a NOEC nor an EC50 was available. All effect types (e.g., mortality, reproductive success, calcification rate, etc.) and parameters (EC50, NOEC and LOEC) were used in the construction of the SSD.

### 2.3. Data subselection

For discussion purposes, a second SSD was constructed with a subselection of the data. This subselection was partly created using an indicative reliability score based upon the classification scheme proposed by Klimisch et al. (1997). Although the scheme applies to (eco)toxicological data, it can be translated to CO<sub>2</sub> effect data. Klimisch et al. (1997) differentiated between four classes.

The first class, ‘reliable without restrictions’ (Klimisch et al., 1997), contains data that originate from well documented experiments that were performed according to (internationally) accepted guidelines. As such guidelines are not available for CO<sub>2</sub> exposures, CO<sub>2</sub> effect data couldn't be classified as such.

In the second class, ‘reliable with restrictions’, data originate from experiments that were not performed under standard conditions, but are at least well documented and scientifically acceptable (Klimisch et al., 1997).

The third class, ‘not reliable’, consisted of data from studies that were either not performed properly, or not sufficiently documented. In the present study, data were classified in this third class, when two or more experimental conditions (for instance, the pH level, information on aeration, oxygen levels or test medium type) were not reported. Otherwise, data were assigned to the second class.

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