CATO-2 Deliverable WP4.4-D02

Initial review of available data of CO_2 impacts on humans and the environment

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1 Executive Summary (restricted)

The aim of this CATO-2 study is to provide an overview of the current status of knowledge of the impact of (accidental) CO_2 release on the environment. An additional focus of this report is to gather all available environmental (terrestrial and marine) effect data. This data is to be used in an impact assessment based on a probabilistic approach using so-called probit functions and species sensitivity distributions (SSD).

It has been found that the reviewed effect studies are seldom focused on release from reservoir storage, but on ocean storage or increased atmospheric concentration (greenhouse effect). This limits the suitability of the data for risk assessment, because of e.g. different routes of exposure and exposure concentrations.

The available studies cover only a limited part of the potential exposure of the terrestrial and aquatic environment to CO_2 caused by release from reservoir storage. The scenario's that can be drawn for leakages of CCS show that not only the effect of CO_2 will be imported but also the effect of less O_2, the effect on pH and redox. As many of these parameters also show variation in time and space and are not in all cases detrimental, it is important to make a distinction in risks of CO_2 (additional stress due to CO_2 leakages).

A database with CO_2 effects on aquatic species is composed. Effect values based on acid toxicity, i.e. exposure to decreased pH by acids such as HCl instead of CO_2, are not included in the database. Based on these data and existing guidelines, a quality assessment of effect data is developed for the use in probabilistic ecological risk assessment (i.e. SSD) of CO_2 exposures.

Cut-off criteria have not been developed in this study. Instead, the elements for quality assessment are given, including a preference for the required data. Based on these elements and preferences, cut-off criteria could be developed in a follow up study. By applying cut-off criteria, all values that are considered unsuitable are discarded.

It is concluded that the results of a probabilistic ecological risk assessment of CO_2 exposures can thus only be used as an indicative tool but should not be used to estimate or correlate to field effects.

Distribution List

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Document Change Record

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2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the "legal" basis to the work performed)

	Title	Doc nr	Version date
AD-01	Beschikking (Subsidieverlening CATO-2 programma verplichtingnummer 1-6843	ET/ED/9078040	2009.07.09
AD-02	Consortium Agreement	CATO-2-CA	2009.09.07
AD-03	Program Plan	CATO2-WP0.A-D.03	2009.09.29

2.2 Reference Documents

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2.3 Abbreviations

CCS	carbon capture and storage
EC50	half maximal effective concentration
FACE	Free-Air CO_2 Enrichment
FRAM	Framework for Risk Assessment and management for the storage of CO_2 deep under the seabed
IEA GHG	International Energy Agency Greenhouse Gas R&D Programme
IPCC	Intergovernmental Panel on Climate Change
LC	London Convention
LC50	Lethal Concentration for 50% of a sample population
LOEC	Lowest Observed Effect Concentration
NGGIP	National Greenhouse Gas Inventories Programme
NOEC	No Observable Effect Concentration
NR	Not reported
ODR	Oxygene Diffusion Rate
OSPAR	Oslo and Paris Convention
PAF	Potentially Affected Fraction
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
RAF	Risk Assessment Framework
RISCS	Research into Impacts and Safety in CO_2 Storage
SSD	Species Sensitivity Distribution
UNEP	United Nations Environment Programme
US EPA	United States Environmental Protection Agency
WAG	Waste Assessment Guidance
WMO	World Meteorological Organization

3 Introduction

3.1 CO_2 Capture and Storage

Increasing CO_2 concentrations in the atmosphere, and the possible risk to climate change, may be linked to human activities. Moreover, scenario's state that in 2020 global energy demand will be at least 35% higher than it is today. CO_2 Capture and Storage (CCS) is an important strategy for CO_2 emission reduction as part of an integrated package of three groups of measures (Trias Energetica) that includes, in addition to CCS, energy efficiency and the use of renewable energy.

CCS in geologic formations includes use of sites such as depleted oil and gas reservoirs, unmineable coal seams, and underground saline formations. Irrespective of the source there are three pathways for undesirable CO_2 release to the earth surface: a leaking seal, a leaking well and a leaking fault. Once the seeping CO_2 has penetrated the earth's crust and arrives near the earth's surface there are several potential ways it can take to finally arrive in the atmosphere. The CO_2 can surface in an aquatic (freshwater or marine) or in a terrestrial environment (soil or surface). In all cases the CO_2 can be released in the dissolved form or as a gas.

At present, the cost and potential for reducing emissions of greenhouse gases is a big issue. Capture and geological storage of CO_2 is considered to be a promising option to reduce CO_2 concentrations in the atmosphere. However, one of the questions that should be answered before CO_2 storage could be deployed on a wide scale is the nature and scale of the environmental impact that could result should any leakage/seepage from a CO_2 storage reservoir occur.

3.2 The CATO-2 program

Both European and Dutch policy recognize CCS as a necessary measure in order to meet the CO_2 reduction goals. For this, a range of large scale demonstration projects are envisioned to be implemented throughout Europe over the next 10-15 years. The CATO (CO_2 Afvang, Transport en Opslag) program (2004-2008) has evolved into the National CCS knowledge platform and has given the Netherlands a leading position in the international community as one of the few programs covering the entire CCS chain. CATO-2 builds on the accomplishments of CATO. The underlying report is part of the CATO-2 program.

The CATO-2 program's ambition is to help support the realization of demonstrations where the complete integration of CO_2 capture, transport and storage will be demonstrated in the Netherlands before 2015. With this, CATO-2 will build an internationally leading strong knowledge and technology position for CCS in The Netherlands. More information on this program can be found at the CATO website (http://www.co2-cato.nl/).

3.3 Aim and scope

The aim of this CATO-2 study is to provide an overview of the current status of knowledge of the impact of (accidental) CO_2 release on the environment[1]. An additional focus of this report is to gather all available environmental (terrestrial and marine) effect data. This data is to be used in an impact assessment based on a probabilistic approach using so-called probit functions and species sensitivity distributions (SSD).

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[1] The human response to elevated CO_2 concentrations is outside the scope of this study.

This review starts in Chapter 2 with an overview of programs and networks on CO_2 storage. Chapter 3 provides a description of known effects of exposure to enhanced CO_2 concentrations in the terrestrial and aquatic environment. In Chapter 4 the risk assessment approach is described. Next, in Chapter 7, the data is subjected to a quality assessment. Quality criteria are provided which could be used to derive suitable effect concentrations from available literature. Chapters 6 and 7 include a discussion, conclusions and recommendations.

4 Programs and networks on CO_2 storage

As described in the previous chapter, this report is part of the Dutch Cato2 program. Besides this National CCS knowledge platform, there are also developments on a global and regional level. Some of these international networks and programs are described in the sections below.

4.1 Global

London Convention
During the London Convention (LC) Consultative meeting of the CO_2 Working Group in London from 3 to 7 April 2006, a draft Risk Assessment Framework (RAF) was developed, which was used by the US EPA for the compilation of a draft Waste Assessment Guidance (WAG) for CO_2 storage under the London Convention [1]. The RAF sensu London Convention is a specific technical document, whereas the WAG is of more generic nature.

The RAF is a technical guide for:
1. the identification and assessment of risk for the marine environment as a consequence of CO_2 storage deep under the seabed, and
2. the reduction of these risks down to acceptable levels by monitoring and mitigation during all phases of the CO_2 storage lifecycle.

IEA GHG
The IEA Greenhouse Gas R&D Programme (IEA GHG) is an international collaborative research programme (http://www.ieagreen.org.uk/). IEA GHG focuses its efforts on studying technologies to reduce greenhouse gas emissions. IEA GHG was established in 1991 and aims to provide its members with informed information on the role that technology can play in reducing greenhouse gas emissions. There are several networks developed within the IEA GHG, such as the International Network for CO_2 Capture, the Monitoring Network, and the Risk Assessment Network.

IPCC
The Intergovernmental Panel on Climate Change (IPCC) has been established by WMO and UNEP to assess scientific, technical and socio- economic information relevant for the understanding of climate change, its potential impacts and options for adaptation and mitigation. It is open to all Members of the UN and of WMO.
The IPCC published in 2005 the Special Report on Carbon Dioxide Capture and Storage. Within the National Greenhouse Gas Inventories Programme (NGGIP) the IPCC assesses and develops methods and practices for national greenhouse gas inventories and disseminates information related to inventory methods and practices. Recently preparations for the 2006 IPCC Guidelines for National Greenhouse Gas Inventories have started. A draft report is available (http://www.ipcc.ch).

4.2 Regional

North East Atlantic Ocean (OSPAR)
The meeting of the OSPAR Committee in Stockholm (26 to 30 June 2006) agreed to establish an intercessional working group for further development of a FRAM (Framework for Risk Assessment and Management for the storage of CO_2 deep under the seabed), which will be

based on the draft RAF developed by the CO_2 Working Group of the London Convention (see sub-paragraph above). A FRAM for the OSPAR Convention might have a higher level of detail than the FRAM for the London Convention. The final FRAM version in OSPAR will be used for the definition of an OSPAR Decision, Recommendation or Agreement on the sub-seabed storage of CO_2 [1].

Europe

The CO2GeoNet Network focus is on the geological storage of CO_2 as a greenhouse gas mitigation option. It has several objectives over the 5 year period of EC funding for integration (http://www.co2geonet.com/).

CO2NET is the European Network of researchers, developers and users of CO_2 technology, facilitating co-operation between these organizations and the European projects on CO_2 geological storage, CO_2 capture and zero emissions technologies (http://www.co2net.eu/public/index.asp).

CO2STORE is a research project with 19 participants from industry and research institutes, partly funded by the European Union (http://www.co2store.org/).The aim of the CO2STORE is to prepare the ground for widespread underground storage of CO_2 in aquifers.

RISCS (Research into Impacts and Safety in CO_2 Storage) is a 4 year research project funded by EU FP7, with 23 partners. The program started this year (2010). The objective of the RISCS project is to provide research on environmental impacts to underpin frameworks for the safe management of CO_2 storage sites. RISCS will improve knowledge important for both storage site operators and regulators for impacts of leaks of CO_2 on near surface ecosystems – both in terrestrial and marine environments. In the project it will be conducted field laboratory experiments, measurements at natural leakage sites and numerical simulations, for both marine and terrestrial ecosystems. The project will develop a Guide for Impacts Appraisal, which will provide a clear summary of the key risk issues that may need to be addressed when developing, operating and closing a storage site.

5 Environmental effects of (accidental) release of CO_2 on the environment

5.1 Introduction

This chapter describes potential effects of elevated CO_2 levels on aquatic (marine and freshwater) and terrestrial species, in order to give insight in the current knowledge on effects. It has to be noted that this chapter is not aimed to be a complete review of all available literature. This literature study has been performed with the aim to describe:

- the available research on the effects of elevated CO_2 levels;
- a review of observed effects;
- the processes by which organisms can be affected (direct or indirect);
- how the effect of CO_2 is usually measured (species, medium, test design, parameters, etc.).

Before describing the effects, the potential routes and forms of exposure are briefly explained.

5.2 Exposure routes

Exposure of aquatic and terrestrial habitats to elevated CO_2 concentrations caused by leakage from geological storage can be the result of different processes. Irrespective of the source there are three pathways for CO_2 release to the earth surface: a leaking seal, a leaking well and a leaking fault. Each pathway can be associated with a specific release pattern characterized by time scale (how long does it take the CO_2 to reach the (subsurface-) bottom?; duration of the CO_2 release), amount of CO_2 released (flux) and the total area affected by increased CO_2 levels.

Once the seeping CO_2 has penetrated most of the Earth's crust and arrives near the earth's surface there are several potential ways it can take to finally arrive in the atmosphere. The CO_2 can surface in an aquatic or in a terrestrial environment (Table 1). Both options can be divided further in two categories. An aquatic environment can be either freshwater or marine. A terrestrial environment can be either soil (sub-surface) or surface. In all cases the CO_2 can be released in the dissolved form or as a gas.

Table 1 Matrix illustrating the 12 exposure routes of released CO_2 to the ecosystem. In the available literature predominantly the routes marked with an' X' are addressed.

	ecosystem					
	aquatic				terrestrial	
	fresh		marine		soil	surface
	sediment	water column	sediment	water column		
dissolved		X		X		
gas						X

An interesting process takes place in the top layer of the soil (Figure 1). The dotted line indicates the boundary between the capillary zone and the saturated zone. In the capillary zone geochemical conditions of the soil facilitate the CO_2 to diffuse towards a water body rather than continue to travel directly upwards to the Earth's surface. CO_2 is heavier than air which results in the bulk of CO_2 being accumulated just above the surface of water bodies such as the sea, lakes or ditches on the mainland. In an area with a large percentage of surface water, such as the Netherlands, this would result in most of the CO_2 leakage being collected just above the surface of water systems.

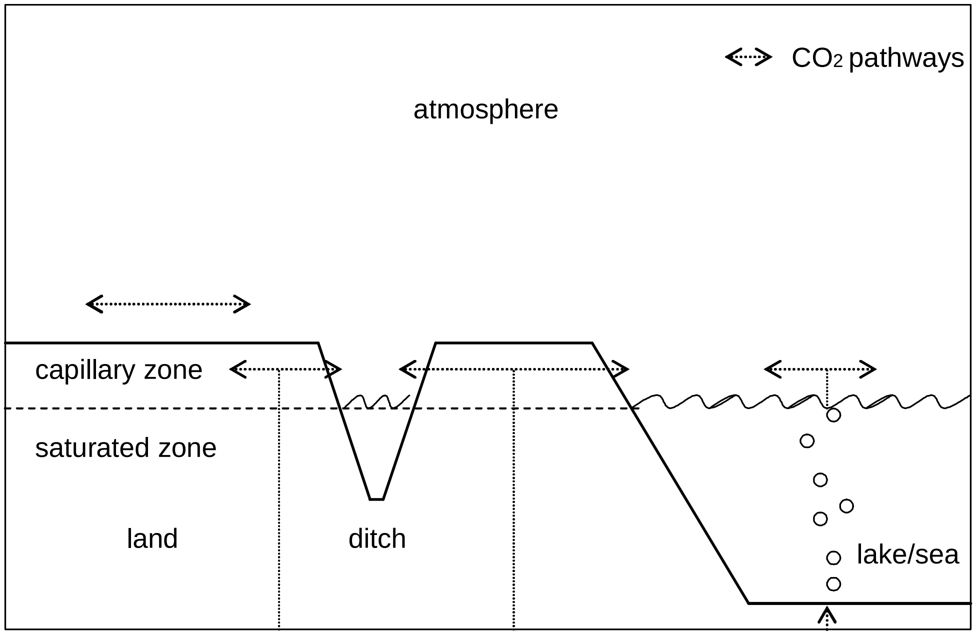

Figure 1 **Schematic overview of a cross section of the upper Earth's crust. Arrows indicate CO2 diffusion. The dotted line indicates the boundary between the capillary zone and the CO2 saturated zone.**

The liquid-vapor phase equilibria (Eq. (1)) or CO_2 solubility is very important in the study of speciation equilibrium [2].

$$CO_{2(vapor)} \leftrightarrow CO_{2(aq)} \tag{1}$$

Once CO_2 being dissolved in water, CO_2(aq) will be partially dissociated into H^+, HCO_3^- (Eq. (2)).,and CO_3^{2-} (Eq. (3)) and H_2O will also be partially dissociated into H^+ and OH^- (Eq. (4)) [2].

$$H_2O + CO_{2(aq)} \leftrightarrow HCO_3^- + H^+ \tag{2}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{3}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{4}$$

5.3 Aquatic (marine and fresh water) environments

In line with the general research focus, this paragraph mainly addresses marine systems. The literature found on fresh water systems is given under a separate heading at the end of this paragraph.

In general, water breathing animals are more susceptible to a rise in environmental CO_2 concentration than terrestrial animals, because of the lower CO_2 partial pressures of their body fluids. Furthermore, CO_2 solubility in water phase exceeds O_2 solubility which can quickly lead to oxygen depletion if considerable amounts of CO_2 are being released [3].
A quantitative evaluation of LC_{50} (median lethal concentration) has rarely been conducted [3]. Despite the lack of LC_{50} values, it appears that lethal pCO_2 (partial pressure) varies largely between fish species. Exposure to CO_2 at 37 torr[2] (pCO_2 at 20 °C) caused 100% mortality for yellowtail *Seriola quinqueradiata* and Japanese flounder *Paralichthys olivaceus* whereas exposure to CO_2 up to 80 torr (pCO_2 at 23 °C) caused no mortality for the European eel *Anguilla anguilla* [3].
Life-long CO_2 exposure experiments have not been conducted nor is there any information on effects of CO_2 exposure over generations [3]. It is therefore unknown what happens to fish populations if they are exposed to low but sustained CO_2 conditions for long periods of time.

Embryos and larvae are often more vulnerable to environmental stress than adults. This is also the case for CO_2 enhancement; early developmental stages are more susceptible to elevated CO_2 levels than adult fish. The 24 hour LC50 for the egg stage of several marine fish species ranged widely from 10 torr to 70 torr. A different study showed that when adults of Japanese flounder are exposed to the LC50 level for eggs, no mortality occurred for the duration of the test (72 hours). It is therefore concluded that hypercapnic (elevated CO_2 concentration) exposure during the egg and juvenile stages could have profound impacts on population size of the affected stock [3].

In a review of Pörtner *et al*. (2005) [4] it is noted that although studies of CO_2 effects have distinguished acute from chronic and lethal from sub-lethal effects, the continuum between time- and concentration-dependent effects have not been clearly elaborated for any species studied, especially with respect to the existence of critical thresholds limiting long-term survival. The review describes the sensitivity of aquatic organisms to short-term and long-term exposure of elevated CO_2 levels. The following section summarizes these findings [4] and is completed with additional literature:

Sensitivity to short-term exposure
Studies indicate that CO_2 effects are related to pH and diffusive CO_2 entry into the organism. Elevated CO_2 causes acidosis in tissues and body fluids. Therefore elevation of CO_2 in water will easily reverse the normal outward diffusion of CO_2 from the fish body. This can cause acidification in the organism [3]. Efficient oxygen transport by blood pigments (haemocyanin) strongly depends on pH. This dependence could be the main factor determining short-term effects of elevated CO_2. In fish cardiac failure is considered the main physiological effect of high CO_2 levels. Available studies indicate that fish are less sensitive to acute effects than most invertebrates. This could be because fish use intracellular haemoglobin in oxygen transport as

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[2] 1 torr = 0.1333 kPa = 1316 µatm

opposed to the extracellular haemocyanin used by cephalopods. Furthermore, vertebrates have a higher regulatory capacity of ion exchange and they have epithelia, which limit diffusive ion losses. When the pH lowers with increasing CO_2 levels, it causes a shift in acid-base and ion equilibria of fish, crustaceans and other invertebrates and therewith a (long-term) shift in metabolic equilibria. The growth, survival and reproductive success of marine animals has been found to decrease at low ambient pH. However, the effects of elevated CO_2 cannot be accounted for by only considering the pH. It has been found that, at the same pH, seawater acidified with CO_2 had higher acute toxicity than that acidified with HCl (see also the section further in this paragraph on pH related effects).

Kikkawa *et al.* [5] investigated the acute CO_2 tolerance of juveniles of three marine invertebrates; the cuttlefish, *Sepia lycidas*, the squid, *Sepioteuthis lessoniana*, and the prawn, *Marsupenaeus japonicus*. The invertebrates were exposed to seawater bubbled with gas mixtures of CO_2 (3-15%) and O_2 (20.95%), balanced with N_2. Median tolerance limits of CO_2 were 8.4% (24 h) for the cuttlefish, 5.9% (24 h) and 3.8% (48 h) for the squid and 14.3% (72 h) for the prawn. Comparison of these and previously reported data suggests an inverse relationship between O_2 requirement and CO_2 tolerance among marine animals [5].

Sensitivity to long term exposure

Unifying principles of underlying physiological mechanisms that limit long-term performance and fitness under hypercapnia have not yet been identified. Thresholds for long term exposure are likely to be found at unexpectedly low levels of CO_2 for many aquatic animals. The growth rate and survival of echinoderms and gastropods have been found to decrease at levels of CO_2, only 200 ppm pCO_2 above ambient. High sensitivity is also found for a marine mussel exposed to a hypercapnic environment at pH close to normal. The mussels showed a 55% reduction in growth rate and 65% reduction in metabolic rate.

Invertebrates adapted to an environment with fluctuating CO_2 levels often have the ability to suppress aerobic energy turnover rates in response to environmental stress such as hypercapnia (metabolic depression). For most fish and mammals the ventilation enhances under high CO_2 but the heart rate and therewith circulation slows down. In general, invertebrates show a lower resistance and enhanced mortality under long term moderate hypercapnia, compared to vertebrates, particularly if there is also metabolic depression.

Type of exposure

Preliminary studies indicate that mortality rates are higher when the CO_2 exposure level is reached by a sudden increase compared to slowly, or step-wise elevated levels [3].

Ocean storage

Ocean storage of CO_2 is a potential method to remove carbon from the biosphere. The IPCC (Intergovernmental Panel On Climate Change) has recently published a special report on Carbon Dioxide Capture and Storage that includes ocean storage [6]. The IPCC report contains a review of the environmental effects of elevated CO_2 concentrations in the ocean.

Barry *et al*. (2005) [7] reported that all major meiofaunal taxa (nematodes, flagellates, amoebae) experienced high (>90%) mortality within 0.5m of CO_2 pools after 30 days of exposure to episodic reductions in pH of up to -1.6 pH units. Reductions of 0.1 to 0.2 pH units caused up to 30% mortality for flagellates and amoebae.

Deep sea

Deep sea living animals are thought to be more sensitive to environmental changes than shallow water ones due to the stability of the deep sea. Experimental verification of this hypothesis is however still lacking [3].

A study of Vetter & Smith (2005) [8] suggests that deep sea scavengers (amphipods and fish) can detect either elevated CO_2 concentrations are other environmental parameters (e.g. temperature) based on the observed avoidance of these species to elevated CO_2 levels (plumes).

pH related effects

A change in pH is expected to have considerable impact in aquatic environments since, especially in deeper situated aquatic ecosystems, the environmental parameters are generally quite constant. A slight change in pH can already mean a considerable disturbance to the local flora and fauna.

The effects of water acidification by mineral acids such as HCl and H_2SO_4 are less than those caused by high CO_2, when tested at the same water pH [3,9]. The acute toxicity of CO_2 acidified seawater to eggs and larvae of a marine fish *Pagrus major* was compared with the acute toxicity of HCl acidified sweater [9]. Mortalities were significantly higher in the CO_2 groups than in the acid groups irrespective of developmental stage. The predicted impacts based on studies using acid exposure to evaluate impacts of CO_2 sequestration on marine animals may thus be milder than those caused by hypercapnia (elevation of CO_2). This is probably related to the rapid diffusive entry of CO_2 into the organism [3,4,9].

Special attention should be given to species producing aragonite, especially those living in cold water. Exposure to CO_2 and the subsequent pH decrease increases the dissolution of aragonite, which is even higher in cold water regions. Cold water corals, being such aragonite producing organisms, are therefore especially sensitive to CO_2 exposure [10]. Since these corals are found in areas which are also likely candidates for sub sea storage of CO_2 the concern over these species is high.
Increasing atmospheric CO_2 is potentially affecting coral reefs by lowering the aragonite saturation state of seawater, making carbonate ions less available for calcification. Reported effect concentrations vary from 3-54% decrease of calcification when coral (and other calcifying organisms) are exposed to a double concentration of atmospheric CO_2 [11]. Langdon & Atkinson (2005) [12] studied the effects of elevated pCO_2 on the net production and calcification of an assemblage of corals maintained under near-natural conditions of temperature, light, nutrient and flow. Net production and calcification are processes thought to compete for the same internal supply of dissolved inorganic carbon. The pCO_2 exposure concentrations were approximately 391 µatm (ambient), 526 µatm and 781 µatm. Short-term exposure to these concentrations caused a 22-52% increase in net production and 44-80% decrease in calcification of a *P. compressa / M. capitata* assemblage in an outdoor flume. Furthermore it was concluded that nutrient enrichment had the effect of making net production less sensitive to change in CO_2 concentration.

Shirayama & Thornton (2005) [13] studied the long-term chronic effects of CO_2 on shallow water benthic organisms that have calcium carbonate shells. It was demonstrated that a 200 ppm increase in CO_2 adversely affects the growth of both gastropods and sea urchins.
The natural pH fluctuation of the North Sea is between 7,8 to 8,2. It is therefore assumed that a pH decrease of 0,2 is within natural tolerance limits of the North Sea biota [14].

Fresh water

Literature on the effects of elevated CO_2 on fresh water species is less abundant compared to the marine environment. The relatively large amount of marine studies available could be related to ocean or deep sea sequestration of CO_2.
Acid-base regulation of freshwater fishes is in general slower and less efficient, because of the low concentrations of counter-ions available for the transfer of acid-base relevant ions through the epithelium [3].

5.4 Terrestrial environments

On land, plants take up CO_2 primarily by diffusion, although some have mechanisms that actively take up CO_2. As a result, increasing atmospheric CO_2 generally has a positive effect on photosynthesis, productivity and growth [15].

The effects of elevated CO_2 concentrations on the terrestrial environment are of interest for agricultural researchers because of the global rise in atmospheric CO_2 concentration and the potential impact of that rise on agriculture. Research at the U.S. Department of Agriculture (USDA) has shown that field crops are more productive when exposed to higher CO_2 concentrations. Higher CO_2 also favourably affects plant-water relations. Stomata, the pores in leaves through which plants gain carbon dioxide and lose water, respond to higher CO_2 by partially closing. Plant water use thus tends to decrease as atmospheric carbon dioxide concentration rises, resulting in increasing water use efficiency (the amount of mass produced per unit of water use), a potentially important benefit as non-agricultural demands for water increase [16].

The Carbon Dioxide Information Analysis Center, the primary global-change data and information analysis center of the U.S. Department of Energy (USDOE), has developed a database of vegetation response to elevated atmospheric CO_2 [17]. The database consists of 61 herbaceous plant species and reports various effect parameters. It shows positive, as well as adverse effects.

5.4.1 Types of exposure

The leakage of carbon dioxide from deep reservoirs can give various direct changes in soils which can have effects on biota living in the soil. To identify the relevant types of exposure of biota a short description of the possible types of exposure is necessary. For example CO_2 concentrations in soil air are often much higher than in the atmosphere due to respiration of plant roots and soil animals. Therefore most biota living in the soil are used to much higher CO_2 concentrations than biota living on the soil surface and the exposure varies much more than the rather constant CO_2 concentration in the atmosphere.

Normal CO_2 concentrations in a soil profile vary from 0.03% to 1 or 10% in the soil air and these vary by soil, soil depth, plants and activity of biota [18] (Table 2). It is therefore that CO_2 concentrations are highest at the depth were most plant roots are (approximately 5-40 cm below surface), in soil (fertile soils, agricultural soil) and climatic regions (going from polar regions to the tropics) with a high plant growth. The CO_2 concentrations within the soil profile decrease strongly going to the soil surface. The CO_2 concentrations decrease slowly going from the rooted zone to the deeper soil layers and the groundwater. An additional cause of elevated CO_2 concentrations in deeper soil layer might be the degradation of soil organic matter [18].

Carbon dioxide is generated by root and microbial activities. The highest CO_2 concentration in the soil is a function of the production by the biota and the loss in the direction of the atmosphere and the subsurface, and therefore depends strongly on the pore volume filled with air.

Table 2 Normal CO2 concentrations in soil air.

CO_2 concentrations	Reference
During one year 0.03 to 2% under grass, and 0.3 to 7% under arable land. Maxima during the summer	[19]
Constant concentrations of 0.03% at the surface and 0.4% near the water table, maxima from 0.7% during the summer between the water table and the soil surface	[20]
During two years fluctuations between 0.03% to 6-8% under wheat, corn and soybeans	[21]
Diurnal variation (high during night, low during the day), higher concentration after rainfall (up to 2.1%). Lowest concentrations at 10 cm – mv and higher at resp 40 and 60 cm –mv.	[22]
CO_2 pressures of 5 to 70% in waterlogged soils	[23]

The leakage of CO_2 to water can increase the amount of CO_2 in water, and the amount of bicarbonate. This can cause a decrease of pH of the groundwater and soil solution. Changes of pH in the soil solution can result in various changes that affect biota, such a availability of nutrients of mobilization of metals that can have toxic effects. The effect is a function of the amount of CO_2, the physical parameters that determine the transport of CO_2 through the soil layer and the geochemistry of the soil.

The leakage of CO_2 through a soil layer can displace O_2 (g) in the soil pores which has a direct function for biota. Also the displacement of O_2 can result in changes of the redox conditions. To study several of the aspects some experiments have been initiated recently (see table below).

Table 3 Recent experiments simulating CO2 leakages and the measurement of various effects on biogeochemistry in soils and sediments.

Conditions	Studied effect	Location	Reference
CO_2 leakage at 2.5 m depth along a horizontal well of 70 m at a water depth of approximately 1.6 m to mimic leakage from a linear failure	Detection of CO_2 transport in soil	ZERT project, USA	[24]
	Modelling CO_2 transport		[25]
	Detection of effects on plant growth		[26,27]
	Changes of chemistry		[28]
CO_2 leakage in reactors with 1.5 m height and 0.72 m diameter, using 35 cm sediment and seawater	pH and solubility of Al, Cr, Ni, Pb, Cu and Zn in sediment and seawater solution	experimental	[29,30]
CO_2 injection at 1500 m depth	pH, HCO_3, Fe	Frio-I Brine pilot	[28,31]

In a recent experiment [24] the release of CO_2 and its effects were tested. Little CO_2 was dissolved in groundwater and the CO_2 did spread horizontally above the water table after which it migrated to the atmosphere. The simulated diluted CO_2 concentration of 50% only spread approximately 5 m from the well. It is modelled [25] that the half life of CO_2 in the soil is approximately 2 days after stopping the injection. The plant health deteriorated near the wells after the CO_2 ejection according to hyperspectral imaging [26]. It was determined that the lower limit of soil CO_2 to stress vegetation is between 4 and 8% CO_2 [27]. Stress started 4 day after the CO_2 injection.

In the experiment described by Lewicki *et al.* (2007) [24], CO_2 hardly dissolved in the groundwater, was transported to the soil air, and did not spread very much from the well (leakage). It can be expected that in a non-acidic soil, CO_2 will dissolve in the groundwater and this can give a very different spreading of CO_2 in the soil air. In such a scenario it is important at which depth the CO_2 will be dissolved in the groundwater. During the time that CO_2 is dissolved in the groundwater, the groundwater flow will help to spread the CO_2 more in a horizontal direction. A larger area can be affected, but with a lower CO_2 concentration.

In a large laboratory experiment, the effect of CO_2 release in seawater sediment has been tested. Although this scenario differs from terrestrial situations, the studied chemical effects are just as relevant for terrestrial situations. The results show that CO_2 release affects the pH (from about 8 to 6.5) and the solubility of all studied elements and the availability (as determined with DGT samplers: Diffuse Gradients in Thin film). DGT labile concentrations were 22-50 times higher for Fe, Mn and Co showing the effect of changing redox conditions in the sediment and the overlying seawater [29]. It was suggested that changes in pH, pE and availability of Fe and Mn can cause significant change in bacterial production and microbial community structure [29].

In a real scale geological storage experiment [28], pH decreases (6.5 to 5.7), and changes of HCO_3 (100 to 3000 mg L), and Fe (30 to 1100 mg L-1) have been confirmed. Modelling suggests that within 500 years all the injected CO_2 will be sequestered as carbonate minerals.

5.4.2 O_2 availability in soil profile

High concentrations of gasses such as CO_2 can affect the concentrations of O_2 in the soil air, soil solution and air. O_2 is of importance for biota and aerobic processes can be impaired. Anoxic situation in soils are common during waterlogged-flooded soils. During these waterlogged periods active wetland plants which get their O_2 from the air via the leafs. Other biota can be strongly affected during anoxic periods. CO_2 can have a strong effect, especially on the O_2 concentration in wet soils because the O_2 solubility in water is low and the diffusion in water is much slower than in air. Low or zero O_2 concentrations in the air in the soil are therefore expected much more often than low O_2 concentration above the soil. The effect of CO_2 leakage on O_2 will therefore be more important for plant roots and biota living in the soil.

In the next section the effect of CO_2 on biota is discussed. In this section the effect of anoxic situations caused by leakage of CO_2 into the soil are discussed.

In normal aerobic soils, the O_2 concentration in the gas is not lower than 15%. In extreme situations the O_2 concentrations the O_2 concentrations can become zero due to natural gas leaks (methane) or sewage water due to a large O_2 consumption by biota. In natural circumstances low O_2 concentrations occur during waterlogging in combination with O_2 consumption by biota. Also in natural circumstances the O_2 concentration decreases from approximately 21% going from the soil surface to a lower value in the deeper soil or groundwater. The soil normally does not become anoxic in the aerated part of the soil and only below the groundwater table. Low O_2 concentrations can be become a problem for plant roots and biota because these a surrounded by a water film. The thickness of the water film, the oxygen consumption and the diffusion coefficient then determine if a plant root or biota is hindered by O_2 shortage. It is for these reasons that there is no critical O_2 concentration in soils for plants because they depend on the plant species and the diffusion through the soil (soil porosity, temperature and water content of soil). In experiments the root respiration has an almost linear relation below a certain critical O_2 concentration or a critical oxygen supply in the root medium [32]. An index which has often been used is the oxygen diffusion rate (ODR). For some crops critical (no growth) and limiting (start of growth limitation) ODR values have been determined. The critical ODR values vary between 8 and 25 ug $m^{-2}s^{-1}$ [33]. As the diffusion in soils is dependent on the texture the O_2 concentrations at which root growth stops are approximately 5 to 8% in sandy soils and 10 to 15% in clayey soils [34].

5.4.3 Effects on pH and redox and related parameters in soil solution

Various efforts have been made to model the effects on soil and groundwater chemistry of CO_2 leakage from CCS [35,36].

Altevogt and Jaffe (2005) [35] assumed a scenario in which CO_2 enters an aquifer at a depth of 10 m. Various aquifers have been modelled (buffered and unbuffered systems). The formation of bicarbonate leads to a pH decrease of 5.4 to 3.9 in an unbuffered system and a pH decrease of 7.9 to 5.9 in a calcite buffered system.

Zheng et al. [36] assumed a scenario in which CO_2 enters a confined aquifer at a depth of 10 m over an area of 10 x 10 m. At a certain CO_2 leakage this can result a pH decrease and as a function of this pH decrease certain ions will be released from mineral surfaces and/or minerals. Using a geochemical model and a simple surface complexation model, and assuming background values for most elements, the effect of the pH decrease was modelled. It results in strong increases of soluble Pb and As in the aquifer which, however, hardly exceeded maximum contaminant levels in groundwater.

Besides the pH decrease by CO_2 it can also alter the redox through depletion of O_2.

Assuming a similar scenario for CO_2 leakage from CCS, experiments have been performed to test the effect on release of metal ions [29,30]. Large vessels were filled with sediment and seawater and were subjected to pure CO_2 or N_2. The experiment with CO_2 decreased the pH initially from approximately 7.8 to 6.5. After 16 days the pH increased from 6.5 to 7.0. The CO_2 pressure became 8%. The results indicate that CO_2 can result in acidification and enhanced mobility and solubility of Fe, Mn and Co in the sediment. These chemical changes can have an effect on biota.

Changes of the soil biogeochemistry have been found in Free-Air CO_2 Enrichment (FACE) experiments at enhanced CO_2 concentrations (additional 0,02%). Due to stimulated respiration there is more cat ion release from the soil particles, a larger loss of basic cat ions from the soil, which will result in a poorer soil for plant growth [37].

5.4.4 Effects of CO_2 and/or bicarbonate in soil and soil solution on plants

Various effects of CO_2 on biota increases have been measured. It is important to make a distinction between artificial CO_2 enrichment, natural enrichment with CO_2, enrichment from the soil towards the air or enrichment of CO_2 in the air, exposure of natural vegetation, agricultural plants, and the effect of fertilization, and the exposure period.

The effect of projected future CO_2 concentrations (0.04% to 0.07%) on plant growth has been studied in great detail and will not be repeated here except for the mechanism. CO_2 is a plant nutrient and elevated CO_2 concentrations [38] will:

1. stimulate primary plant production,
2. improve nitrogen efficiency,
3. decrease water use,

4. stimulate dark respiration in leaves of some plant species, and
5. stimulate carbon gain in times of drought.

These type of effects have mainly been studied at CO_2 concentrations that are relevant for the projected future levels of CO_2. Most of the mentioned effects level off after doubling the CO_2 concentrations.

No negative responses of enriched CO_2 concentrations on plant leaves were found in FACE experiments [38]. However, adverse effects may occur due to changes in the mineral and nutrient content of leafs [39]. Hoorens *et al.* (2002) [40] studied the litter quality and interactive effects in litter mixtures under elevated CO_2. They found that nitrogen content and leaf quality frequently decrease as carbon dioxide concentration is increased. Research on woody species in the UK has shown that all species grew faster at elevated CO_2, whereas the leaf area ratio (quotient of total leaf area and plant weight), weight-based foliar N concentration and, to a smaller extent, leaf weight fraction (quotient of leaf weight and plant weight) were consistently lower [41].

For scenario's in which CO_2 will leak from CCS it is more relevant to look at effects on plants via the roots because CO_2 from CCS will escape via the soil. In a review of the effects on CO_2 on plants Glinski & Stepniewski (1985) [33] mention that there are many investigations that have shown positive effects of elevated CO_2 concentrations on plants. For example, in water cultures optimum CO_2 concentrations have been observed of 1% for peas, and 2% CO_2 in the air for maize and radish [42]. However concentrations at which elevated CO_2 has negative effects vary strongly between plants [33] (see also Table 5). Negative effects on root growth of peas, bean, sunflower and broad bean in gravel cultures were observed at 1% CO_2. The growth of these plants were completely suppressed at 6.5 % CO_2 while the growth of oat and barley roots was only limited to a small extend [43]. Rice is not affected by 50% CO_2 in the gas phase of a solution culture while soybean is affected, although both plants are tolerant to anaerobic circumstances for roots [44]. There are also interactions between CO_2 and other nutrients. Some plants are sensitive to elevated CO_2 in the presence of ammonium ions while other plants are not [33]. Also differences exist between genotypes. For rice, shoot and root growth of Zn-inefficient genotypes was strongly inhibited, whereas root length of Zn-efficient genotypes was considerably enhanced by bicarbonate [45]. Huang *et al.* (1997) [46] demonstrated that 10% CO_2 in combination with 5% O_2 in the soil decreased shoot growth of two wheat cultivars and only the leaf chlorophyll content for one of the tow cultivars.

In a review about the effect of high CO pressures in waterlogged soils [23] discussed the mechanisms and the effects on plant roots. Wetland plants are clearly acclimatized to high CO_2 concentrations.
However the responses of wetland plants to enhanced CO_2 have hardly been studied. Its is predicted that the CO_2 concentrations in the plant roots of wetland plants will not rise above 13-26 % CO_2 at 40% CO_2 in the soil air due to ventilation from the roots to the atmosphere [23].

Measurements of effects of high CO_2 concentrations on the metabolism of plants are rare [23] although its effect on fruit conservation, by reducing its respiration, is well known. It is postulated that enhanced CO_2 concentrations have affect the pH buffering by living plant cells. Palet *et al.* (1991) [47] has shown that the cytochrome oxidase pathway in inhibited by high HCO_3 and/or CO_2.

Important is also the reversibility of the negative effects of high CO_2 concentrations in the root zone. Palet *et al.* (1991) [47] showed complete reversibility of the respiration after 4 h exposure at 0.1 % CO_2, but no restoration after 4 h at 2 % CO_2. Bouma *et al.* (1997) [48] studied the respiration of beans at various CO_2 concentrations (2 days; 0.02% and 0.2%) after a pretreatment of 47 days at various CO_2 concentrations (0.06-2%). There was no effect on root respiration, so the effect of 2% CO_2 for bean was completely reversible.

Relevant are the effects in natural volcanic areas because these can show a realistic scenario for CO_2 leakage from CCS. Also here significant ecological effects have been shown. The gas emitting from natural gas vents or ground can contain up to 100% CO_2, but they also contain other gases, and are often hot. The cause of the clear noticeable ecological effects can therefore be also due to other gasses. It is important to note that although growth can be impaired plants often can sustain high CO_2 concentrations [49].

CO_2 emissions from natural CO_2 springs [50], and the recent experiments [24], are comparable to possible CO_2 emissions from gas leaks from CCS [26]. A storage of 200 Mton of CO_2 could result from a 500 MW fossil fuel burning plant after 50 years of sequestering 4 Mton CO_2 per year. Assuming a leakage of 0.02% through a fault from such a storage of 200 Mton of CO_2 would give an CO_2 emission of 1.1 ton CO_2 per day. This can be compared to non-volcanic gas vents at which effects on soil and plants have been investigated (for example 0.2 ton d^{-1} in Latera and 93 ton d^{-1} in Mammoth Mountain).

Table 4 various long term effects on soil and plant near CO2 springs

Conditions	CO_2 efflux or concentration	Plant	Effect	Ref.
Mammoth Mountain, USA	Elevated CO_2 in soil air (30-96%); 1-10000 g m^{-2} d^{-1}; 93 ton d^{-1}	Trees	Tree kill: possibly due to (hot) water	[51-54]
Iceland	Studied at 0,35% and 0,79% CO_2	grass		[55]
I Borboi, Italy	Studied from 0.04 up to 0.4%	trees	No effect on above-ground productivity, despite drought stress	[56]
Latera, Italy	Elevated CO_2 (100%) concentrations near source which decrease strongly at 10 m distance, total emission 0.22 ton d-1, at source 2 kg $m^{-2}d^{-1}$	Grasses	Effects in an area of 10 to 20 m around the source: low pH, no vegetation, near-anoxic conditions. Limited effects at a distance of 25 m	[57]
Strmec, Slovenia	Enhanced CO_2 in natural area, 4.6-268 µmol CO_2 $m^{-2}s^{-1}$; (0.4; 3.3 and 26% CO_2 in rooting zone)	Timothy grass	Decrease of Carboxylation efficiency, growth, and assimilation due to CO_2	[58,59]
Ryuzin-numa, Yuno-kawa and Nyuu, Japan	0.037 and 0.07% CO_2	Various plants	Increased photosynthetic rates, and increased efficiency of water and N use of leaves	[60]

Table 5 Effects of enhanced CO2 soil air concentrations on plants

CO_2 concentration	Time	Plant	Studied effect	Ref.
Enhanced CO_2 in root zone (7%)	13 d	*Pisum sativum, Phaseolus vulgaris, Vicia Faba, Helianthus annuus, Avena sativa, Hordeum vulgare*	Decrease of plant growth at 1% CO_2.	[43]
Enhanced CO_2 in root zone (0, 1, 2, and 8%) at varying O_2 concentrations in water phase	18 d	Barley and pea	At low O_2 concentrations promotive effect of CO_2 up to 2% CO_2 for root and total dry matter. At O_2>7%, negative effects of CO_2.	[42]
Enhanced CO_2 in root zone (20%)	10 h	*Solanum tuberosum*	activity of PEP carboxylase in roots	[61]
Enhanced CO_2 in root zone (0.03 - 2%)	4 h	*Agave deserti*	Decrease of root respiration at 0.25% CO_2. No root respiration at 2% CO_2.	[62]
Enhanced CO_2 in root zone (0.03 - 2%)	4 h	*Optunica*, *Ferocactus*	Decrease of root respiration at 0.25% CO_2.	[63]
CO_2 in root zone (0.01 - 0.7%)	3 h	Douglas fir	Decrease of root respiration at enhanced CO_2	[64]
Effect of enhance CO_2 in root zone (0.06 and 2%)	48 h, 50 d	Bean, citrus	No effect on root and shoot growth over a period of two months	[48]
Effect of 0.03 % versus 0.1 % CO_2	0.5 h	nine tree species	no effect on root respiration of excised roots	[65]
30% or 50% CO_2 in water phase without O_2	14 d	Soybean, rice	Survival of soybean versus rice at increased CO_2 concentration	[44]
Enhanced CO_2 in rhizosphere (0,3- 2.5%)	43-51 d	Symbiosis N binders and soybean and cowpea	Optimal rate of nodulation and N_2 fixation was at 1 to 3% CO_2	[66]
Effect of added $KHCO_3$ in water (8.3 mM HCO_3)	0.5 h	Seven grass species from a natural CO_2 enriched area	Decrease of root respiration (16-54%) at 8.3 mM CO_2. No differences between plants from natural enriched and normal area's.	[49]
Effect of enhanced CO_2 in root zone air (0.035 up to 5%) in an aeroponic system	14 d	Lettuce	Increase of productivity up to 80%	[67]
Effect of enhanced CO_2 in root zone air (2 up to 50%) in an aeroponic system (O_2)	20-49 d	Maize	Growth decrease during first 32 days, 30% less dry weight and 10% less chlorophyll at 50% treatment, after 63 days limited differences	[68]
Zero or 0.25% CO_2 in hydroponic system using 20% O_2	21 d	Symbioses of N fixers with Alfalfa	CO_2 is necessary for N_2 fixation	[69]
Air equilibrium at 18 mM and 200 mM CO_2 in water phase(simulating flooding)	18 d	*Hordeum marinum*	Enhanced CO_2 stimulates Photosynthese and growth	[70]

5.4.5 Effects of CO_2 on soil animals

In soil, bacteria, protozoa en nematodes are only active in the water film between the soil particles, and can thus be considered as essentially aquatic organisms. Therefore, similar effects as described for aquatic environments can be expected for soil microorganisms and meiofauna. These organisms are the major agents of soil functioning and provide important ecosystem services.

The effects of elevated CO_2 on soil microorganisms are mediated by interactions with plants. Elevated CO_2 can enhance certain microbial processes due to enhanced carbon supply from plants. All effects have been studied with small enhancements of CO_2 and focus on indirect effects of CO_2 on microorganisms. Direct effects are considered negligible due to the much higher CO_2 concentrations in soil air [71,72]. Indirect effects that have been studied in many papers are: microbial biomass C and N, nitrification and denitrification, methanogenesis, enzyme activities, microbial community composition. In all these papers the enhanced CO_2 concentrations are low (additional max 0.1%).

In only a few recent studies the effects on microbial processes at elevated CO_2 concentrations that can be relevant to leakages from CCS gave been studied (>0.1%). Santruckova & Simek (1997) [73] studied the effect on microbial biomass of soil incubated with 0.05% up to 5% CO_2 during 24 hours. They found a decrease in soil respiration (7-78%) followed by a decrease of microbial biomass of (10-60%). However, Pierce and Sjogersten (2009) [74] have studied the effect of enhanced soil CO_2 concentrations on microbial communities for 11 weeks. Soil CO_2 concentrations were enhanced by release of concentrated CO_2 gas from a point source at 0.6 m below soil surface. The effect at 0.3 m below the soil surface were an increase of the CO_2 concentrations from 1.9% to 14.5% above the point source. It resulted in reduced vegetation above- and belowground biomass over time. Important is that no significant changes in microbial biomass or carbon utilization were observed.

Coûteaux and Bolger (2000) [75] reviewed the effect of CO_2 enrichment on soil fauna. Similar to the microorganisms the main factors which are expected to modify soil fauna are the change of the litter quantity and quality which cannot be generalized.

There is a limited amount of literature on the effect of elevated CO_2 on insects due to interest in pest control. Levels of 10-12 % CO_2 are not toxic for psocid. Toxic levels seem to vary depended on O_2, humidity and temperature and are above 10% CO_2 [76]. Some insects living in dung, an extreme environment with low O_2 and high CO_2 concentrations, seem adapted to high CO_2 concentrations. The upper limits that can be tolerates for 30 minutes 17 to 25% CO_2 [77].

Nematodes are only sensitive to CO_2 at high concentrations. The development of *A. composticola* and *D. myceliophagus* was reduced at concentrations of carbon dioxide greater than about 5 % and 12 % [78]. Zinkler (1966) cites that Ruppel (1953) found maximum tolerable CO_2 concentrations of 1-2% CO_2 for some collembole species (*Tomocerus vulgaris, Orchesella villosa*) while another species (*Onychiurus armatus*) could tolerate high concentrations (35% CO_2). Zinkler (1966) [79] found behavioural effects at CO_2 concentrations between 5 and 20 % CO_2 (12 different species). Zinkler (1996) [80] found behavioural changes during exposure of one hour at 5 to 10% for surface-dwelling Collembola (*Allacma fusca, Orchesella cincta, Tomocerus flavescens*) and for species living in deeper soil layers only at 25% (F*olsomia candida*). These differences may be a consequence of the different living conditions. Chronic exposure to enriched

CO_2 concentrations increased both the duration of egg development and the juvenile mortality rate.

Sustr and Simek (1996) [81] studied responses of 19 soil invertebrates after 6 hours exposure to elevated CO_2 concentrations (up to 60% CO_2). Visible behavioural effects were observed at 2 to 39 % CO_2 depending on species. Lethal effects were only observed for some species at 11 to 50% CO_2 (springtails, terrestrial isopods). A higher resistance was found in millipedes, potworms, earthworms, centripedes and insects.

Hansen *et al.* (2001) [82] studied the effect of elevated atmospheric CO_2 on forest floor microarthropod abundances. They compared plots in plantation forests receiving supplemental CO_2 (raising the concentration in the canopy by +200 ppm over ambient) with plots under ambient CO_2. After 19 months in elevated plots, the total microarthropod abundance had declined to two-thirds of the abundance in ambient plots.

5.4.6 Effects of CO_2 on ecosystem

It is not likely that the expected increases of global CO_2 concentrations in air (an increase of 0.04% in 2009 to 0,07% in 2100) will have direct effects on soil organisms or diversity because CO_2 concentrations in soils can be much higher (see above). Indirect effects of such small increases in the CO_2 concentrations (small compared to soil concentrations) are possible by changes of the plant growth (potentially a higher plant growth and a more efficient use of water). The effects of a higher plant growth on soil organisms varies strongly and cannot be generalized [83]. Other indirect effects of increased CO_2 concentrations are possible by changes of the biogeochemistry and the effect of these on plants and animals living in and on the soil

6 Risk assessment approach

In environmental risk assessment of toxicants the PEC:PNEC approach is a common strategy, where PEC stands for ‘Predicted Environmental Concentration’ and PNEC for ‘Predicted No Effect Concentration’. A PEC:PNEC ratio higher than 1 indicates that unacceptable effects on organisms are not unlikely to occur; the higher the ratio, the more likely that unacceptable effects may occur. When we relate this end point to the EU definition of assessment end point in risk assessment (“quantification of likelihood and severity of effects”), it becomes clear that the PEC:PNEC ratio does not comply with this definition. The PEC:PNEC ratio is just an indication of the likelihood and not a quantification (see also Scholten *et al.* [84]). This is acceptable for identification of possible impacts and for prioritisation. However, it does not provide any characterisation of the expected impact and therefore, does not contain all the characteristics to be a proper assessment end point of environmental risk.

Four different combinations of exposure and sensitivity are depicted in Figure 2. The traditional PEC:PNEC approach is presented in Figure 2a. The ratio of PEC and PNEC indicates whether unacceptable effects on organisms are likely to occur as a result of exposure to the specific chemical. It does, however, not provide a quantification of the environmental risk (severity and likelihood of effects). When a single value for the PNEC is compared to a distribution of PEC values (Figure 2b), the term ‘most likely’ can be represented by the probability that the exposure concentration is higher than the PNEC. Interspecies variation in sensitivity (better known as the Species Sensitivity Distribution or SSD) based on No Observable Effect Concentrations (NOECs) is used to represent the sensitivity of the environment (Figure 2c and d), the assessment end point risk will indicate the probability that a specific fraction of species is exposed above their NOEC value.

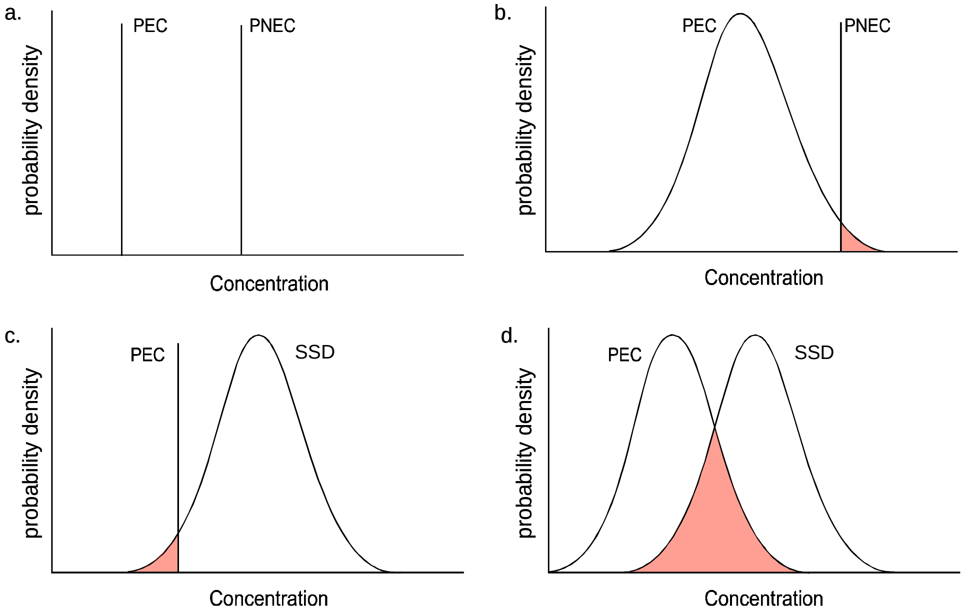

Figure 2 Four possible approaches for environmental risk assessment based on (a) point estimates, (d) probabilistic distributions, or (b and c) a mixture of both (SSD=Species Sensitivity Distribution).

The affected fraction of the species is referred to as the PAF-level (Potentially Affected Fraction), (e.g. [85-88]). The PAF value can be explained as the probability that randomly selected species are exposed to a concentration exceeding its chronic no effect level at a certain level of exposure (See Figure 3 for an example of a cumulative NOEC-SSD).

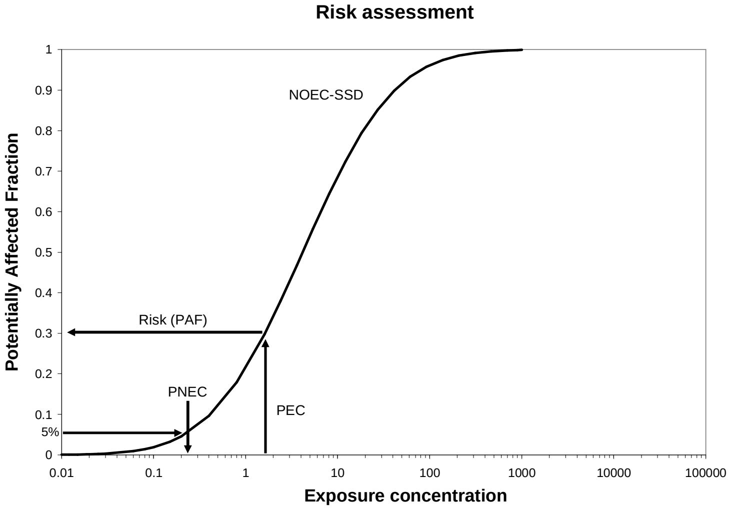

Figure 3 Use of the NOEC-SSD for translating PEC values to values for the Potentially Affected Fraction of Species. The PNEC level corresponds to a PAF of 5%.

Recently the SSD approach has also been proposed for non-toxic stressors [89,90]. Ideally the ecological risk of CO_2 is also described probabilistically using the SSD approach.

In order to assess the suitability of available CO_2 effect data for the use in a SSD, the data is subjected to a quality assessment.

7 Quality assessment of aquatic data

7.1 Introduction

Available effect data should be evaluated considering their quality and adequacy for a risk assessment. Some general guidelines on data evaluation were published by the European Commission in a ‘‘Technical Guidance Document’’ [91]. Klimisch *et al.* (1997) [92] describe the evaluation of the quality of data and their use in hazard and risk assessment as a systematic approach.

To develop quality assessment criteria for CO_2 effect values, effect data need to be collected in a preliminary database. This database serves as a basis to derive quality criteria specifically related to CO_2 effect data, such as test conditions. Furthermore, assuming the database is representative for the available effect data, the database is used to assess if sufficient data is available for a probabilistic risk assessment.

First data needs to be collected. Search engines (primarily www.scopus.com and www.google.com) were screened for terms such as ‘CO_2 LC50’ and ‘hypercapnia’ in order to fill the preliminary database. To assess the usefulness of the collected data, meta-information (in particular on data quality) needs to be included in the database.

Elements for a quality assessment were derived based on the guidelines mentioned above and specific issues related to CO_2 effect values. These elements are described in the following paragraphs:

- Requirements for SSDs
- Reliability of the data
- Effect parameter and end-point
- Number of test concentrations
- Ambient CO_2 levels
- The unit of the exposure level
- Variability of test conditions

7.2 Elements of the quality assessment

7.2.1 Requirements for SSDs

The requirements for data in SSDs are well specified for ‘conventional’ toxicants. The EU has specified data requirements for the derivation of legislative water quality criteria [91]. These requirements are relatively strict and protective, perhaps too strict for the current purpose, but serves as a basis in the present study to assess the quality of a SSD if it were based on the collected data.

The EU requires that the data is reliable, for which we use the criteria as described in the next section. The EU also sets taxonomical requirements: an SSD should contain data on at least fish, a second family in the phylum of Chordata, a crustacean, an insect, a family in a phylum other than Anthropoda and Chordata, a family in the order of insects or a phylum that is not yet represented, algae and higher plants. Furthermore, a SSD should be composed of at least 10 (preferably more than 15) chronic No Effect Concentrations (NOECs), where at least 8 taxonomical groups are represented.

For this purpose, taxonomical information (scientific species name and phylum) of the test species should be available and stored as meta-data in the database. Also, the exposure duration used in the tests is stored as meta-information.

7.2.2 Reliability of the data

Klimisch *et al.* [92] provided a structured approach for assessing the reliability of 'conventional' toxicity data. A similar but more simplified approach is used in the present study to roughly classify the reliability of the collected effect data. Table 6 shows the classification scheme used to assign a reliability index to the collected effect data. This index, ranging from 1 (reliable without restrictions) to 4 (not assignable) is included as meta-information in the database.

Table 6 Classification scheme used to determine reliability of the collected effect data

Reliability index	Category	Simplification of classes proposed by Klimisch et al. [92]	Classification more specific for CO_2 effect data
1	Reliable without restrictions	Standardised protocols used	No standardised protocols exist for CO_2 effect experiments, hence reliability index '1' is not applicable
2	Reliable with restrictions	Protocol similar to standardised protocol / well documented protocol	At least the following test conditions are reported: exposure concentrations, pH, oxygen level / information on aeration, temperature and control conditions
3	Not reliable	Documentation insufficient	One or more of the conditions listed above are not reported
4	Not assignable	Only short abstract available / Only secondary literature	Only short abstract or secondary literature available without info on test conditions

7.2.3 Effect parameter and end-point

As indicated in the section on the data requirements for SSDs, it was indicated that for EU legislative purposes, chronic NOEC values are preferred. Moreover, it is desirable to have little variation in effect type and parameters among the collected data. Effect parameters other than NOECs (such as 50% effect or lethal concentrations (EC_{50}/LC_{50}) and lowest observed effect concentrations (LOECs)) are all included in the preliminary database, where the effect type is stored as meta-information.

End-points (such as survival, growth and reproduction) are also included in the database as meta-information. This way a selection of end-points can be made afterwards if specific end-points lack field-relevance. For instance, blood gas levels or biomarker end-points can be very sensitive for CO_2 exposure. Effects on blood gas levels or biomarkers does not necessarily lead to effects on individuals let alone on population level. For instance, Smit *et al.* [93] showed for oil-related substances that biomarkers where approximately 100 times more sensitive than whole-organism end-points.

7.2.4 Number of test concentrations

A disadvantage of using NOECs is that its value depends on test setup and statistical power of the test [94]. The same holds true for the LOEC, but for simplicity both NOEC and LOEC are referred to as NOEC in this discussion. First of all, a NOEC is by definition a concentration that has been tested (it is not an interpolation). If in a test other test concentrations are used, another NOEC would be obtained. A preliminary search of CO_2 effect data has shown that most effect studies focus on hypothetical future scenarios of CO_2 levels. In those tests current CO_2 levels are tested against a single hypothesised future CO_2 level. For those tests only a single test concentration is available which can produce significant effects (in this case the test concentration is a LOEC) or not (in this case the test concentration is the NOEC). In addition, NOECs depend on the statistical power of a test, which in turn depends on the specific statistical test used, and the number of replicates.

When only tests are available with a single test concentration it might be possible to study the variability in hypothesised future CO_2 levels. This is not very relevant when estimating the ecological risk of leaking stored CO_2. Data is, in that case, less suitable to produce a representative SSD which reflects the interspecies sensitivity towards CO_2 exposure. The number of concentrations tested (in addition to the control experiment) is included as meta-information in the database, in order to assess the quality of the collected data.

7.2.5 Ambient CO_2 levels

A problem with risk assessment of CO_2 is that it is already present in the atmosphere and aquatic compartments. Many species can’t even survive without CO_2. The most straight forward way of dealing with this is by expressing exposure levels (and its risk) relative with respect to ambient levels. For this purpose, the exposure level of CO_2 in the control experiment of each test is also included in the database. If the CO_2 level of the control experiment is not reported, an ambient partial pressure of 38.0 Pa is assumed.

Using relative exposure levels to quantify risk will only work properly if the exposure level in the control experiments of the collected tests in the database are close to one other. In other words, large variation among control experiments could introduce a bias in species sensitivity to relative changes in CO_2 levels.

7.2.6 CO_2 exposure

The study of Kikkawa [9] shows that CO_2 is more toxic than acid when seawater pH is reduced to the same pH, and therefore, the use of acid toxicity results for evaluating CO_2 toxicity could greatly underestimates impacts of the gas. Effect values based on acid toxicity are therefore not included in the database.

Another issue with CO_2 is that its concentration can be expressed in more than one way. When CO_2 is expressed on an absolute scale, it needs to be converted to a single unit. In the present study the CO_2 level is expressed as partial pressure in kPa (Table 7). The originally published exposure level and corresponding unit are also included in the database. Expressing the exposure level as relative increase with respect to ambient concentrations also provides an advantage here, because no conversion of units is required.

Table 7 Conversion table used for the conversion of units

Equivalent of 1 kPa	Unit
7.501	Torr (mm Hg at 0℃)
0.009869	atm
1.013	%
0.0001013	ppm

7.2.7 Variability of test conditions

SSDs should reflect the interspecies variability in sensitivity and not the variability in test conditions. Ideally, test conditions are comparable for the collected data. Therefore, the most relevant test conditions (if reported) are also included as meta-information in the database. The recorded conditions include exposure duration, medium type and source, pH, temperature and information on oxygen level (or aeration). The latter was to make sure that observed effects are not the result of hypoxia due to the displacement of oxygen by CO_2.

In some experiments the pH is kept constant, whereas in others the pH decreases with increasing CO_2 levels. Decreasing pH levels increases the bioavailability of metals. Therefore, if the medium is contaminated with heavy metals their toxicity could be increase with higher CO_2 levels. This is an additional argument for including the medium type and source and the pH.

The medium type is also collected in order to determine whether the data applies to freshwater systems or marine waters.

7.3 Results of the preliminary quality assessment

7.3.1 Requirements for SSDs

The preliminary database contains CO_2 effect data of 45 species. This amount of data would be sufficient to set up an SSD. However, if we look at the criteria set by the EU [91], the effect data need to be chronic NOECs. Most of the data collected in the database is not chronic. Exposure duration of the tests included in the database are variable ranging from a few hours up to a year, but most in most test species were exposed less than a week (Figure 4).

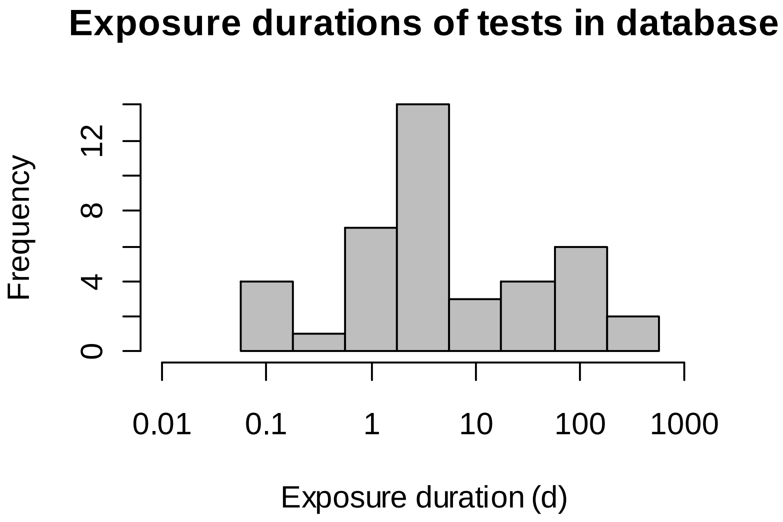

Figure 4 **Histogram of exposure durations of experiments included in the database**

Apart from exposure duration, most data are LOECs and LC_{50}s, rather than NOECs (Figure 5), where most tests use only a single or unreported number of test concentrations (Figure 5).

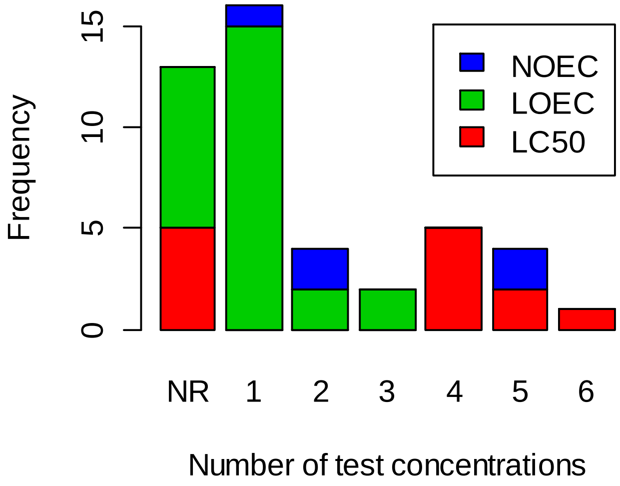

Figure 5 **Stacked histogram of the number of test concentrations (NR = not reported) used in the tests that are included in the database, specified per effect parameter (NOEC, LOEC and LC50)**

The EU has also set taxonomical requirements for the use of SSDs [91]. In the database at least 8 taxonomical groups are represented (Figure 6), be it not chronic NOECs as the EU requirement states. Table 8 shows whether the more specific taxonomical requirements of the EU are met for the collected data (disregarding the fact that the data does not consist of chronic NOECs). Although the database doesn't contain data for an insect or a second family in the phylum Chordata, it does contain data on numerous additional phyla (Figure 6). One species in the database belongs to an unspecified phylum as it is only described with the generic term nano-benthos.

Table 8 Satisfaction of EU taxonomical criteria for the collected CO2 data (disregarding the fact that data are not chronic NOECs)

EU criterion [91]	Criterion satisfied for collected CO_2 effect data?	Comments
≥ 1 fish	Yes	The database contains data on 15 fish species
2nd family of phylum Chordata	No	All Chordata in the database are fish, although multiple families of fish are represented
≥ 1 crustacean	Yes	The database contains data on 10 Anthropoda species, all Crustaceans
≥ 1 insect	No	
≥ 1 family in any order of insect or any phylum not already represented	Yes	There are numerous other phyla included in the database (Figure 6)
≥ 1 algae	Yes	The database contains data on the coralline algae *Lithophyllum cabiochae*
≥ 1 higher plant	Yes	The database contains data on two salt marsh plants, although the exposure to CO_2 is mainly through air

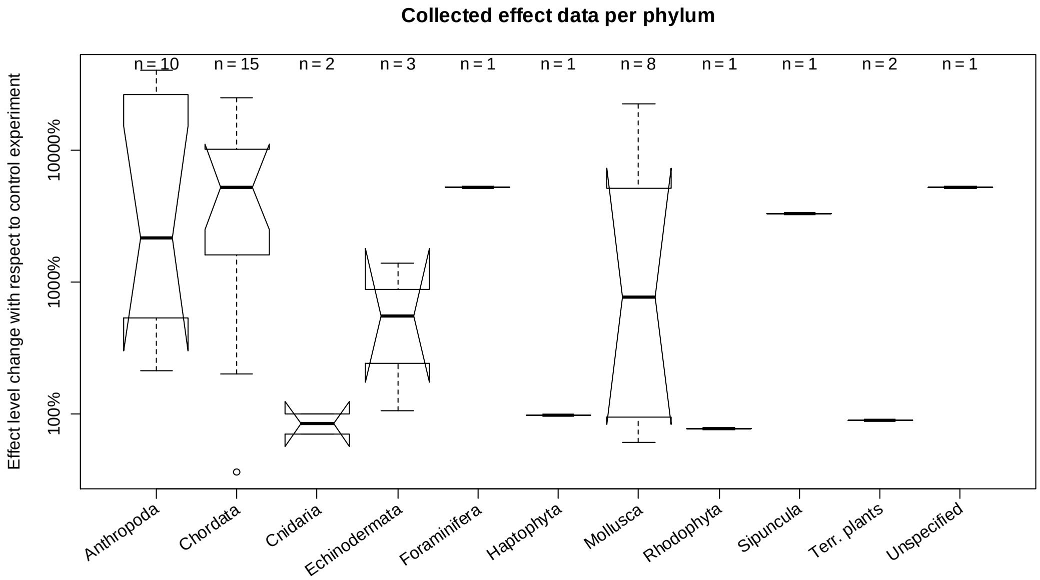

Figure 6 Box whisker plots of exposure data (effect level change with respect to control/ambient conditions) per phylum

7.3.2 Effect parameter and end-point

In the previous text it is already indicated that only few experiments use chronic exposures and that the database contains only a few NOEC values (Figure 4 and Figure 5). Another problem with both the NOECs and LOECs is that they are generally based a small amount of test concentrations, while LC_{50} values are based on more test concentrations. Therefore, NOECs and LOECs are assigned to the unreliable or unassignable categories (with one exception).

Effect types were stored as specific as possible in the database as meta-information. In a later stage, the data was classified to more generic effect types (Figure 7). Most effect types of the data were classified as ‘Survival/Reproduction’, this class includes effects such as egg-production, hatching success and mortality. Considerably less data was retrieved on growth effects. Remarkably only a few data were found on calcification related effects. The ‘Biomarker’ class mainly consists of enzymatic activity data. A single test reported chloride cell surface as effect type (classified as ‘Cellular’ effects) and an other reported oxygen consumption as effect type (classified as ‘Blood gas’ effect). Most end-points in the database are directly relevant for the field.

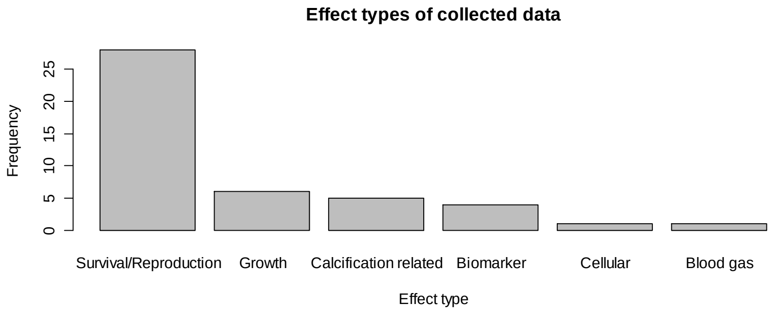

Figure 7 **Histogram of generic effect types (end-points) as reported for the collected data**

7.3.3 Reliability of the data

A reliability index is assigned to the data as described in the previous text. Most data scored the reliability index 3 (Not reliable) and 4 (Not assignable) (Figure 8), which is unfavorable for constructing a SSD. The category 3 data could be re-examined to determine which test conditions are not properly documented and if this truly poses a problem for risk assessment.

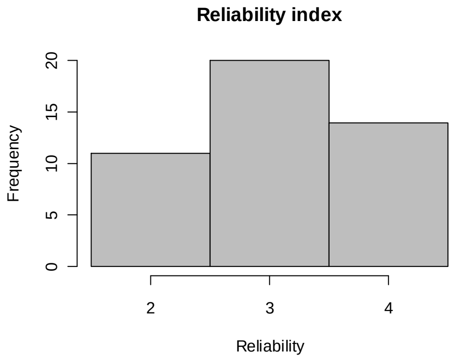

Figure 8 **Reliability index, determined as described in the main text, of the data in the database**

7.3.4 Number of test concentrations

The quality of the data not only relies on the followed procedure and its documentation but also the number of concentrations tested. It was already shown that most tests in the database used only a single test concentration (Figure 5). To obtain a clearer picture of the data quality the reliability index is divided by the number of tested concentrations (in cases where this number is not reported, it is assumed to be one) (Figure 9). This exercise shows that some data shift more to the reliable side (the reliability is low, but the number of tested concentration is high), while other shift to the other direction (the reliability is high, but the number of tested concentrations is low).

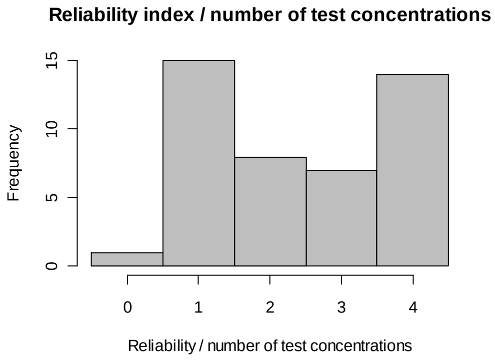

Figure 9 **Reliability index, determined as described in the main text, divided by the number of test concentrations. Low values represent relatively high reliable tests with large number of test concentrations, while high values indicate unreliable tests with low number of test concentrations.**

7.3.5 Ambient CO_2 levels and the unit of the exposure level

In order to assess ecological risks of CO_2, it is important that experimental effect data used for this purpose include the CO_2 level of the control experiment. Unfortunately, 22 out of the 45 tests in the database don't report the CO_2 level in the control experiment, or refer to it as ambient levels. In the present study it is assumed that those CO_2 levels in the control experiments are 0.0380 kPa. Although most control experiments are conducted near this ambient level (a median of 0.0385 kPa), some experiments use levels that are nearly ten times as high (0.220 kPa) (Figure 10).

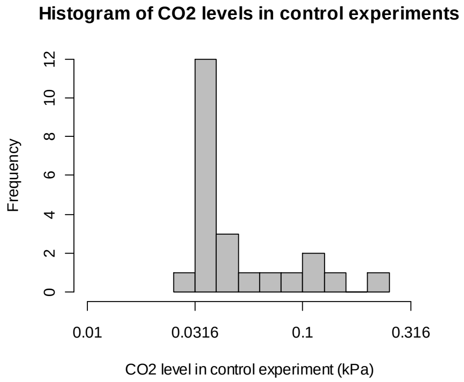

Figure 10 **Histogram of CO2 levels (all converted into kPa) in control experiments of 23 of the 45 collected tests in the database**

Although there is some variation in the CO_2 level in the control experiments, the variation in effect levels of CO_2 is much larger. Furthermore, the CO_2 level in the control is not correlated to the effect levels in the database.

7.4 Variability of test conditions

There is considerable variation in the test conditions of the data collected in the database. The CO_2 level in the controls are variable (Figure 10) as well as the exposure duration (Figure 4) and the measured end-points (Figure 7). Reported test pH range from 5.6 up to 8.1, whereas the reported test temperatures range from 0 up to 30℃. Therefore, when the data of the current database is used to construct a SSD, it will be difficult to distinguish between variation in species sensitivity and variation in test conditions.

Seven of the tests in the database have reported specific requirements for the oxygen level in the test, while 14 tests only report that the test system is aerated. The remaining 24 don’t report information with respect to oxygen level. In these experiments effect could be hypoxic due to oxygen displacement by CO_2.

Only three species (*Salmo salar*, *Oncorhynchus mykiss*, *Anguilla anguilla*) in the database were exposed in freshwater. For one of these species (*Salmo salar*) effects were observed in a later stage of the experiment in marine water. For seven species in the database the test medium was not reported. However, these are all marine species. In addition two salt marsh plants were included in the database. But by far, most tests were performed in (artificial or natural) marine water. Therefore, it could be that a SSD based on the collected data is not representative for freshwater systems. Differences in sensitivity between marine and freshwater species should be known before using the collected data for predicting risk in the freshwater environment.

8 Summary and conclusions

8.1 Research on CO_2 effects

Within the limited scope of the literature research performed for this study, the following can be concluded:

The reviewed effect studies are seldom focused on release from reservoir storage, but on ocean storage or increased atmospheric concentration (greenhouse effect). This limits the suitability of the data for risk assessment, because of different routes of exposure and exposure concentrations.

The available studies cover only a limited part of the potential exposure of the terrestrial and aquatic environment to CO_2 caused by release from reservoir storage. Sensitivity of aquatic organisms is studied by exposure to dissolved CO_2 (not gaseous) whereas terrestrial organisms are only exposed to gaseous CO_2 and not to CO_2 dissolved in pore water In soils and groundwater the studies contain effects of CO_2 on plants (agricultural and natural) and soil fauna. Effects of CO_2 on many types of soil biota are not available. The known effects of CO_2 to the soil biota vary strongly among species. It is for example not clear whether soil fauna are less or more sensitive to CO_2 than plant roots. The scenario's that can be drawn for leakages of CCS show that not only the effect of CO_2 will be imported but also the effect of less O_2, the effect on soil pH and redox. As many of these parameters also show variation in time and space in natural soils and are not in all cases detrimental, it is important to make a distinction in risks of CO_2 (additional stress due to CO_2 leakages).

8.2 Quality assessment of aquatic data

A database with CO_2 effects on aquatic species is composed. Effect values based on acid toxicity, i.e. exposure to decreased pH by acids such as HCl instead of CO_2, are not included in the database. Based on these data and existing guidelines, a quality assessment of effect data is developed for the use in probabilistic ecological risk assessment (i.e. SSD) of CO_2 exposures.

The quality and suitability of effect data increases when more meta-information is available. Ideally, the following meta-information should be available for each effect value:

- Taxonomical information (scientific species name and phylum)
- Test conditions (exposure duration, medium type and source, pH, temperature and oxygen level).
- Effect parameters (NOECs, EC_{50}, LC_{50}, LOECs)
- End-points (such as survival, growth and reproduction)
- The number of concentrations tested (in addition to the control experiment)
- The exposure level of CO_2 in the control experiment
- The unit of exposure

Based on the availability of this information, a reliability index to each effect value is assigned

Cut-off criteria have not been developed in this study. Instead, the elements for quality assessment are given, including a preference for the required data. Based on these elements and preferences, cut-off criteria could be developed in a follow up study. By applying cut-off criteria, all values that are considered unsuitable are discarded.

A selection of data could be based on the following:

- It is desirable to have little variation in effect type and parameters among the collected data. Chronic NOEC values are preferred.
- A selection of end-points can be made if specific end-points lack field-relevance.
- Multiple test concentrations in one effect study are preferred.
- Large variation among the CO_2 level of the control experiments decreases the quality of the data set.
- Ideally, test conditions are comparable for the collected data.

8.3 Suitability of the aquatic data for probabilistic ecological risk assessment

Based on the available effect data and the data (quality) requirements the following limitations are identified:

- although most reliable tests are performed with sensitive species, these tests generally use a low number of test concentrations, which could result in a bias in the SSD;
- many tests in the database don't report CO_2 level in control experiment;
- test conditions are highly variable (exposure duration, CO2 level in control, end-point, etc.);
- effect parameters are generally not chronic NOECs;
- not all EU taxonomical requirements for SSDs are met.

In addition, the data set is composed of mainly marine species and, therefore, is not representative for freshwater systems.

The results of a probabilistic ecological risk assessment of CO_2 exposures can thus only be used as an **indicative** tool but should not be used to estimate or correlate to field effects.

9 Recommendations

In the most effort went into structuring the aquatic effects database, hence most conclusions and recommendations are focussed on these effects. In future work it would be desirable to include the terrestrial data in a structured database with the required metadata.

Recommendations to complete this study on probabilistic ecological risk assessment of CO_2 exposures:

- The current preliminary database should be completed by an extensive literature search.
- Based on all available data, the possibility of applying cut-off criteria should be considered.
- The consequences of discarding certain data for the results of the SSD could be determined by deriving an SSD for each different data set and comparing hazard- and confidence levels.
- A final SSD should be derived using the selected data.
- Differences in sensitivity between freshwater and marine species should be described, as a basis for the applicability of the SSD for freshwater environments.

Additional recommendations to achieve a (more) reliable quantification of ecological risk of CO_2 exposure are:

- Develop a more standardized protocol for testing CO_2 effects. Such a protocol should offer:
  - a definition chronic exposure durations
  - a definition of a widely accepted ambient CO_2 level that is also used in control experiments. This ambient level should then also be used in the risk assessment
  - guidelines on other test conditions (pH, aeration, temperature, etc.).
- Perform laboratory tests, following the standard protocol, for a representative set of species (perhaps using the EU guidelines [91], as a basis for taxonomic requirements), and publish results in peer-reviewed journal
- Freshwater species should also be tested if risk for that environmental compartment is to be properly assessed
- Edit the contents of this report and make it a manuscript for a peer-reviewed journal, describing the current obstacles for constructing a proper SSD for CO_2 effects; incite the scientific community to standardize protocols for CO_2 effect testing and propose a guideline for such standardization.