Environmental Impacts of CO$_2$-EOR

The Offshore UK Context

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Executive Summary

The scope of this study was to explore the potential incremental environmental impacts of undertaking offshore CO_2-EOR in the UK North Sea. The study focussed on potential impacts which could be related to CO_2-EOR-specific activities, using existing North Sea oil and gas operations as a baseline, and attempts to rank the severity of the impacts and identify potential mitigation options.

The potential incremental environmental risks identified were: subsea CO_2 leakage, CO_2 impurities, potentially toxic trace elements in produced water, and radioactive scaling. The risks of these were then reviewed from the available literature, and combined with data obtained from batch CO_2-rock-water experiments conducted at the University of Edinburgh.

The impact of a potential CO_2 leak from pipelines or geological reservoirs could have a negative environmental impact. The dissolution of CO_2 in water reduces pH and increases the partial pressure of the gas (pCO_2), which can induce physical stresses on all forms of marine life, such as affecting reproduction, shell dissolution, reducing growth, reducing metabolism, and increasing mortality rates. Benthic (sediment) marine communities are the most susceptible to a CO_2 leak, and the effect of stressing this ecosystem can have a knock-on effect to higher trophic level organisms which rely on the lower levels for food.

Impurities within a CO_2 stream have the potential to negatively impact the environment, due to capture chemicals such as monoethylamine (MEA), as well as the formation of strong acids from trace nitrous (NO_x) and sulphurous (SO_x) gasses.

The risk of environmental damage from the mobilisation of potentially toxic trace elements in the subsurface, such as arsenic, cadmium, lead and mercury, has some uncertainty. Trace elements can be liberated from the storage reservoir due to changes in pH when CO_2 dissolves in the reservoir fluids, which may then be brought to the surface and either remain dissolved in production waters or precipitate to form scale fouling minerals. The risks are two-fold:

> i) A number of trace elements are known to be toxic to marine life, inducing similar stresses on communities as a CO_2 leak, except that these elements can be biomagnified up the food chain, increasing their concentrations in body tissues. These elements then are not only toxic to marine life, but to human populations that contain seafood in their diets.

> ii) Scaling minerals can incorporate radioactive elements such as radium, which are hazardous to human and marine health at sufficient radioactivity levels, determined by concentration. If more radioactive elements are mobilised by CO_2 dissolution in reservoir fluids then they may enhance accumulation in scaling minerals.

A conceptual model of potential risks and impacts was built to rank the components of CO_2-EOR, and the conclusions drawn were that most components had a negligible incremental risk attached to them. Low risk activities were identified as CO_2 leakage from a well bore and trace element concentrations in produced water. However, if appropriate risk reduction options, such as use of best available technologies (BAT), are implemented and mitigation options carefully planned, then risks can be reduced even further.

CO_2-EOR, provided it is managed properly, therefore would present no significant incremental environmental risk to the UKCS compared with current oil and gas operations.

Contents

List of Abbreviations

- **BAT – Best Available Technology**
- **BET – Best Environmental Practice**
- **BTEX – Benzene, Toluene, Ethyl Benzene & Xylene**
- **CCS – Carbon Capture and Storage**
- **CO_2 – Carbon Dioxide**
- **CO_2-EOR – Carbon Dioxide Enhanced Oil Recovery**
- **$conc^n$ – concentration**
- **DECC – UK Department of Energy & Climate Change**
- **EA – UK Environment Agency**
- **EC – European Commission**
- **EEMS – Environmental Emissions Monitoring System**
- **EIA – Environmental Impact Assessment**
- **EU – European Union**
- **LNG – liquefied natural gas**
- **MEA – monoethylamine**
- **NIEA – Northern Ireland Environment Agency**
- **NNS – Northern North Sea**
- **NORM – Naturally Occurring Radioactive Materials**
- **OIW – oil in water**
- **OPPC – Offshore Pollution Prevention and Control regulations**
- **ORP – Oxidation Reduction Potential**
- **OSPAR – Oslo Paris Convention PAH – Poly-aromatic hydrocarbons**
- **pCO_2 – carbon dioxide partial pressure**
- **PEC – Predicted environmental concentration**
- **PNEC – Predicted no effect concentration**
- **QICS – Quantifying Impacts of Carbon Storage project**
- **RBA – Risk based approach**
- **RISCS – Research into Impacts and Safety in CO_2 Storage project**
- **SAC – Special Areas of Conservation**
- **SEPA – Scottish Environmental Protection Agency**
- **SNS – Southern North Sea**
- **SPA – Special Protection Area**
- **TDS – Total Dissolved Solids**
- **TENORM – Technologically Enhanced NORM**
- **UK – United Kingdom**
- **UKCS – United Kingdom Continental Shelf**
- **USEPA MCL – United States Environmental Protection Agency Maximum Concentration Level**
- **[…] – concentration of chemical species**

List of Units

- **µg/L – micrograms per litre (10^{-6} grams)**
- **mg/L – milligrams per litre (10^{-3} grams)**
- **g/L – grams per litre**
- **µm – micrometre**
- **ppm – parts per million**
- **m – metre**
- **km – kilometre**
- **m^3 – cubic metres**
- **tonnes m^{-2} yr^{-1} – tonnes per square metre per year**
- **Bq/g – Becquerels per gram**
- **mΩ – milliohm**
- **wt.% – weight percent**

1 Report Framework

The aim of this report is to identify the potential environmental impacts on the marine environment of offshore activities which are unique to CO_2-EOR, or which may pose additional significant issues not encountered in normal oil and gas operations. These are therefore the potential *incremental* risks of offshore CO_2-EOR in the UKCS.

The first step of this assessment is to establish which activities (and therefore, risks) are new or unique to CO_2-EOR compared with existing oil and gas operations. That is the aim of this section of the report. The following sections will briefly set out the basic environmental regulatory framework for the UKCS (Section 2) before describing in detail the potential environmental risks of these activities (Sections 3-5), and include conclusions drawn from experimental work carried out as part of this project (Section 6). A conceptual risk model can then be built to assess the potential risks associated with the CO_2-EOR activities, and conclusions drawn thereafter (Section 7).

1.1 Current Oil and Gas Activities

The following list is a summary of equipment (new or retrofitted) which may be required on CO_2-EOR projects. Note that not all of these would be required on every project, but would be expected across a range of eventual UKCS projects:

- **Utilities (water, power, fire and gas, safety) on existing platform**
- **Power generation**
- **Production facilities**
- **Gas compression**
- **Gas clean-up**
- **Bridge-linked platform**
- **Pipeline(s)**
- **Risers**
- **Subsea flow lines**
- **Subsea power or control cables**
- **Subsea installations (e.g. wellheads)**
- **Wells worked over (equipment change and related modifications), from platform or a mobile drilling unit**
- **Wells drilled from platform or a mobile drilling unit**

All of these items are also typical of oil and gas facilities. While there may be an increase in their use across a variety of CO_2-EOR projects, they are not themselves new or unique to CO_2-EOR and therefore are not considered to present any additional risk to the environment, compared with existing oil and gas operations.

Similarly, the following existing oil and gas activities will or may increase with CO_2-EOR operations:

- **Oil, water and/or gas production**
- **Water and/or gas injection**
- **Gas compression**
- **Power generation**
- **Drilling**
- **Processing of produced fluids**
- **Oil and water treatment**
- **Oil export**
- **Use of biocides, dispersers, corrosion and scale inhibitors**

While these activities may be intensified with a CO_2-EOR project (e.g. gas compression and power generation are essential features of CO_2-EOR), these are not new activities unto themselves. Therefore, given that the activities listed above are currently undertaken in the North Sea, this report would recommend referring to current environmental impact assessments (EIA) for detailed risk analysis of these activities.

1.2 CO$_2$-EOR Unique Activities

The following list identifies activities which were considered new or unique to CO$_2$-EOR in the North Sea and therefore pose potential incremental environmental risk over-and-above existing oil and gas operations:

- **Importation, pumping and injection of a CO$_2$ stream (including impurities)**
- **Separation of CO$_2$ from produced gas**
- **Handling (e.g. compression) of CO$_2$-rich gasses**
- **Production of CO$_2$-rich water**
- **New corrosion or scaling prevention measures**

Any emissions of CO$_2$, other gasses, or particulates to the atmosphere are not considered in this report, for the reason that they are not anticipated to be unique to CO$_2$-EOR, although it is acknowledged that they may be enhanced through this activity. While the loss of CO$_2$ to atmosphere may be considered unique to CO$_2$-EOR, given its use in the EOR process, possible fugitive emissions are considered insignificant compared with current anthropogenic CO$_2$ releases. Again, therefore, this report recommends that detailed EIA's are carried out in line with existing practices for emissions to atmosphere.

However, CO$_2$ separation from other gasses may involve the use of CO$_2$ capture chemicals (e.g. amines) which are not typical of current activities in the UKCS and should therefore be considered further. The capture chemicals may be present as an impurity left over from the separation process, either from onshore CO$_2$ piped to the injection platform or from separation on the platform, together with a number of other impurities in the CO$_2$ stream such as nitrous (NO$_x$) and sulphurous (SO$_x$) gasses, or trace elements such as mercury and cadmium.

The accidental release of CO$_2$ into the marine environment (together with impurities) will be considered in this report, for example point-source releases like a compromised pipeline or well bore, or diffuse leaks through geological structures. CO$_2$ leaks to the marine environment are thus considered a unique risk from CO$_2$-EOR activities. Similarly, the reaction products of CO$_2$-water-storage reservoir, and their mobilisation to the marine environment would be unique to CO$_2$-EOR e.g. increased radioactive scaling and enhanced trace element concentrations.

Determining the reaction products (e.g. trace elements) from interaction of CO$_2$ with facilities and equipment was not considered in the original scope of this report, however in the opinion of this author any new equipment used for EOR activities would be engineered to withstand attack by acidic fluids. Any old or reused equipment, such as well casing, may react with CO$_2$ however the reaction surface areas of this equipment will be much less than that of the reservoir. Therefore, while no comment can be made on the relative reactivities of equipment vs. reservoir components, quantities of products released from the reservoir would greatly outweigh those released from the equipment and facilities over the lifespan of a project. Additional work would need to be carried out to determine the relative contribution, if any, of equipment and facilities to mobilised reaction products.

The incremental potential environmental risks of CO$_2$-EOR which will therefore be investigated further in this report, and will be included in the conceptual risk model, are as follows:

- **Fugitive emissions from subsea pipeline or subsurface reservoir**
  - **CO$_2$**
  - **CO$_2$ stream impurities (e.g. amines, NO$_x$, SO$_x$)**
- **Reaction products in produced fluids from CO$_2$-water-reservoir interactions**
  - **Trace elements**
  - **Radioactive scaling**

2 Current Regulatory Environment

In order to prevent serious environmental damage from current oil and gas operations in the UK North Sea, statutory regulations and acts, as well as voluntary agreements, have been set at local (e.g. Scotland), national (UK) and international (EU) levels. Provision for CO_2 storage within the UK Continental Shelf (UKCS) has already entered the legislation, with The Energy Act 2008, and its subsequent modifications of existing regulations. The Act refers to minimising the impacts of a carbon dioxide leak offshore which, while important, is only one of many potential pollution pathways which may be present in CO_2-EOR activities which must also be considered.

This section sets out the regulations currently in place which would likely cover potential major pollutants from CO_2-EOR activities in the UK North Sea:

- **Hydrocarbons**
- **Trace Metals**
- **Naturally Occurring Radioactive Materials (NORM)**
- **Other Substance Emissions.**

The regulations set out in the following sections apply to UK Territorial Waters; that is all marine waters within the 12 nautical mile limit and all areas within the UK Continental Shelf (UKCS), Figure 1. These regulations do not specifically cover Welsh and Scottish Controlled Waters, which are regulated by the Welsh Assembly and Scottish Government, respectively, however the regulations of the devolved national governments contain essentially the same guidance. In any case, these Scottish and Welsh water bodies are, for the purposes of this report, coastal waters up to 3 nautical miles offshore of Scotland and Wales, and therefore highly unlikely to be affected by CO_2-EOR activities, given the locations of existing oil and gas fields.
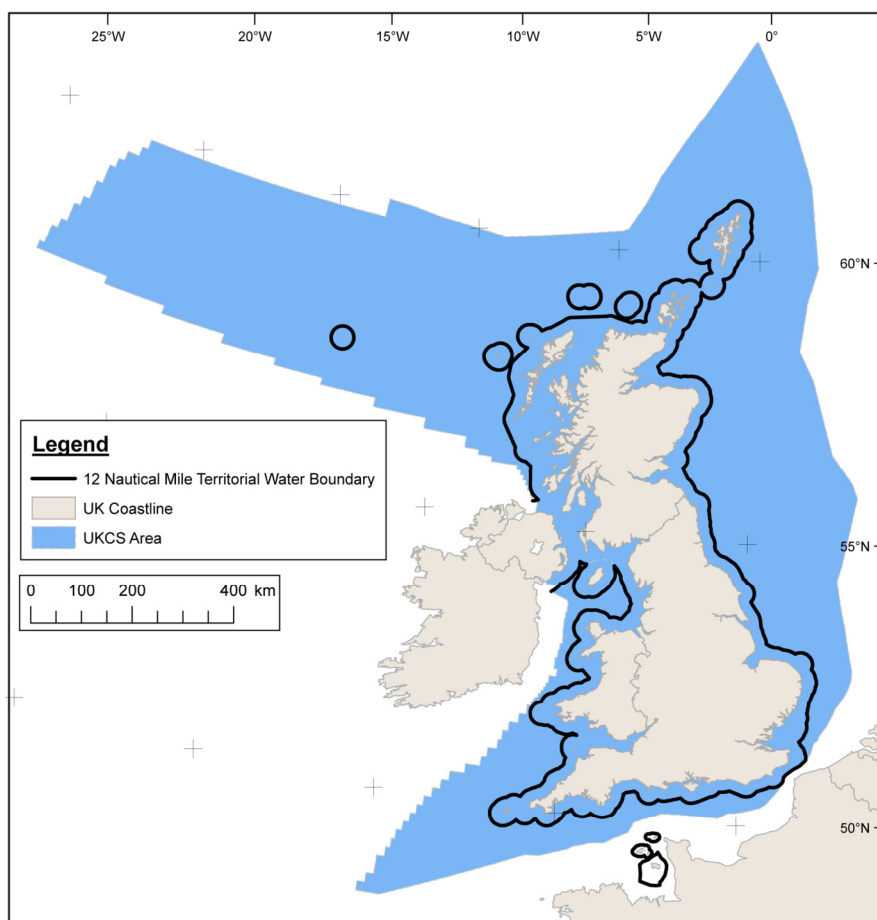

Figure 1. UKCS extent and 12 mile territorial sea boundary

2.1 Hydrocarbons

Under current UK regulations, offshore discharge to the sea of oil from oil and gas activities is illegal. Under the Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations 2011, herein referred to as "OPPC (2011)", a permit to discharge oil must be applied for from the Secretary of State.

Discharges covered by the following regulations – such as chemicals and waste – are exempt from the need to apply for an OPPC (2011) permit, but are discussed later in Section 2.5:

- **The Offshore Chemicals Regulations 2002**
- **The Merchant Shipping (Prevention of Oil Pollution) Regulations 1996**
- **The Merchant Shipping (Prevention of Pollution by Sewage and Garbage from Ships) Regulations 2008**

The Merchant Shipping Regulations 1996 do not require permits for discharge of oil from vessels operating within UK territorial waters, however do impose discharge limits, depending on age and size of vessel. These regulations are unlikely to require amendment to accommodate CO_2-EOR activities. The Offshore Chemicals Regulations 2002 are intended to cover discharge of manufactured chemicals, not oil specifically, and are examined further in Section 2.3.

The OPPC (2011) regulations do not state specifically what limitations may be imposed on oil discharge under issued permit conditions. However the Department of Energy & Climate Change's (DECC) guidance notes for the sampling and analysis of produced water and other hydrocarbon discharges (Department of Energy & Climate Change, 2010) state a 30 mg/L limit for dispersed oil in produced waters. This follows from the 1992 Oslo-Paris (OSPAR) Convention (as amended) and the follow-up recommendations. Specifically, OSPAR 2001/1 (OSPAR Commission, 2010) states:

"*4.2.1 No individual offshore installation should exceed a performance standard for dispersed oil of 30 mg/L for produced water discharged into the sea.*"

This superseded, in 2008, an earlier standard of 40 mg/L, and is calculated as a monthly average of discharged oil in water (OIW). Individual discharges may therefore exceed 30 mg/L, with a maximum allowable concentration of 100 mg/L at any one time, provided the monthly average is adhered to.

Oil produced from CO_2 injection would likely be covered under these regulations and CO_2-EOR operators in the UK would require permits to discharge OIW as per OPPC (2011).

2.2 Trace Elements

Natural substances typically occurring in produced waters include hydrocarbons (BTEX, napthalenes, PAHs, alkyl phenols), trace metals and naturally occurring radioactive materials (NORM). Hydrocarbons in produced waters have already been discussed in Section 2.2, above, while NORM is discussed in Section 2.4, below.

Concentrations of potentially toxic trace metals in produced waters are, so far, not specifically regulated by the UK in the offshore marine environment. The European Union Water Framework Directive sets out targets for groundwater, freshwater and coastal pollution, which have been adopted by the various national UK environment agencies. Trace metal concentrations are set at legal limits throughout the UK for these environments. CO_2-EOR activities in the UK will operate away from these areas on the UKCS, therefore the limits set by the Scottish Environmental Protection Agency (SEPA), the Environment Agency (EA), and the Northern Ireland Environment Agency (NIEA) would not apply.

The UK, however, is a member of OSPAR and therefore committed to meeting the recommendations set out by this trans-national agreement, to reduce the environmental impact of polluting activities. The recommendations emphasise the use of best environmental practice (BEP) and best available technology (BAT) when carrying out activities within the North Sea.

The most recent recommendation with regard to produced water, OSPAR Recommendation

2012/5 (OSPAR Commission, 2012a) for a risk-based approach to the Management of Produced Water Discharges from Offshore Installations, and the accompanying OSPAR Guidelines in support of the Recommendation 2012/5 (OSPAR Commission, 2012b) set out the framework for encouraging North Sea operators to reduce their environmental impact. Trace metals are but one group of substances to account for, but specifically highlighted here due to the potential for specifically enhancing metal concentrations in CO_2-EOR activities, as described in Section 4.

OSPAR Recommendation 2012/5 therefore outlines the approach that operators should take to calculating the risk to the environment of their activities. The heart of this risk based approach (RBA) is to calculate a ratio of modelled predicted concentration in the environment to the predicted no-effect concentrations of those substances (PEC:PNEC). If PEC:PNEC ≤ 1 then the risk is controlled. If PEC:PNEC > 1 then this may present an unacceptable or uncontrolled risk and operators should revise their management and handling of produced waters.

Appendix 5 of the OSPAR supporting guidelines provide calculated PNEC for naturally occurring substances in produced waters – including metals – which are included below in Table 1.

Table 1. Predicted no effect concentrations (µg/L) from OSPAR Guidelines in support of Recommendation 2012/5

Metal	PNEC Concentration (µg/L)
Arsenic	To be decided
Nickel	8.60
Cadmium	0.21 + Cb
Chromium	0.60 + Cb
Copper	2.60
Mercury	0.047 + Cb
Lead	1.30
Zinc	3.00 + Cb

Cb: Background concentration (µg/l)

2.3 Naturally Occurring Radioactive Material

With regard to the disposal of radioactive waste, clear regulations exist in the UK. The Radioactive Substances Act 1993 act defines "radioactive material" and "radioactive waste" as any material or item containing the substances listed in NORM, such as lead and radium, can deposit as scale inside pipes and tanks and as such may pose a risk to workers. This is discussed further in Section 5, and is called Technologically Enhanced NORM (TENORM), and is classed as radioactive waste, depending on the specific activity, given in Table 2.

Any additional scaling issues attributable to CO2-EOR, as discussed in Section 5, would require close attention to comply with the permit conditions set out by the 1993 Act.

 at the levels appropriate to the phase of the substance. Disposal is prohibited of radioactive waste (i.e. waste containing radioactive material) unless under permit.

NORM, such as lead and radium, can deposit as scale inside pipes and tanks and as such may pose a risk to workers. This is discussed further in Section 5, and is called Technologically Enhanced NORM (TENORM), and is classed as radioactive waste, depending on the specific activity, given in Table 2.

Any additional scaling issues attributable to CO_2-EOR, as discussed in Section 5, would require close attention to comply with the permit conditions set out by the 1993 Act.

Table 2. Radioactive substances and specific activity levels prohibited in waste, under the Radioactive Substances Act 1993.

Element	Becquerels per gram (Bq/g)		
	Solid	Liquid	Gas or Vapour
Actinium	0.37	7.40×10^{-2}	2.59×10^{-6}
Lead	0.74	3.70×10^{-3}	1.11×10^{-4}
Polonium	0.37	2.59×10^{-2}	2.22×10^{-4}
Protactinium	0.37	3.33×10^{-2}	1.11×10^{-6}
Radium	0.37	3.70×10^{-4}	3.70×10^{-5}
Radon			3.70×10^{-2}
Thorium	2.59	3.70×10^{-2}	2.22×10^{-5}
Uranium	11.1	0.74	7.40×10^{-5}

2.4 Other Substance Emissions

Other emissions not already covered may include sewage, general waste, atmospheric emissions, and any substance not already mentioned above in relation to shipping, pipelines and (currently) oil and gas production. Substances specifically designed for CO_2 capture or separation, or additional emissions and waste generated by CO_2-EOR activities would therefore be bound by these regulations, either in their existing form or following amendments.

The following regulations would likely be of most relevance specifically to CO_2-EOR activities

- **The Offshore Chemicals Regulations 2002**
- **The Offshore Petroleum Production and Pipe-lines (Assessment of Environmental Effects) (Amendment) Regulations 2007**
- **The Offshore Petroleum Activities (Conservation of Habitats) (Amendment) Regulations 2007**
- **The Offshore Marine Conservation (Natural Habitats , & c .) Regulations 2007**
- **The Merchant Shipping (Prevention of Oil Pollution) Regulations 1996**
- **The Energy Act 2008 (Consequential Modifications) (Offshore Environmental Protection) Order 2010**

Permits are therefore required under the Offshore Chemicals Regulations 2002 for the use and discharge of chemicals in relation to offshore activities, and as such would likely cover any additional chemicals not currently used offshore but which might be introduced under a CO_2-EOR project. The conditions of any issued permit would include provisions for the use of BAT and BEP, in accordance with OSPAR recommendations.

Pipe lines require an environmental statement to be submitted outlining the impacts of projects over a certain size (500 tonnes oil per day or 500,000 m^3 of gas) under the Offshore

Petroleum Production and Pipe-lines (Assessment of Environmental Effects) (Amendment) Regulations 2007, amended by the Energy Act 2008 to also include CO_2 and LNG transport and test injections. Further amendments would likely come with commercialised CO_2-EOR.

The Offshore Marine Conservation and Offshore Petroleum Activities (Conservation of Habitats) Regulations 2007, amended by the Energy Act 2008 requires that the environmental impacts of CO_2 storage activities, specifically on special protection areas (SPA) and special areas of conservation (SAC) are considered prior to any licensing, permits or consents being given.

The Secretary of State for Environment, Food and Rural Affairs (SoS) would need to be satisfied that any activities occurring within these designated areas would not be to the detriment of them, although provision is given in the regulations for the SoS to allow activities to take place, which would otherwise not be satisfactory, if it can be demonstrated that such activity is in the 'overriding public interest'.

Large SAC areas exist offshore in the Southern North Sea, while generally SAC and SPA areas lie adjacent to the coast, therefore CO_2-EOR would likely not be affected by these regulations, given the offshore Northern and Central North Sea locations of oil fields.

The Merchant Shipping Regulations 1996 apply discharge limits to vessels in UK territorial waters, which are unlikely to be affected by CO_2-EOR activities, save for the shipping of CO_2-capture chemicals to offshore facilities as necessary. In these instances, the Merchant Shipping Regulations 1996 state:

"(4) No discharge into the sea shall contain chemicals or other substances in quantities or concentrations which are hazardous to the marine environment…"

2.5 UKCS Sensitive Habitats

UKCS environmentally sensitive areas are mapped in Figures 2 and 3 to show the spatial relationship between these areas and oil and gas fields, in order to identify potential conflicts. These areas are designated Ramsar sites, shellfish waters, Special Protection Areas (SPA), and Special Areas of Conservation (SAC).
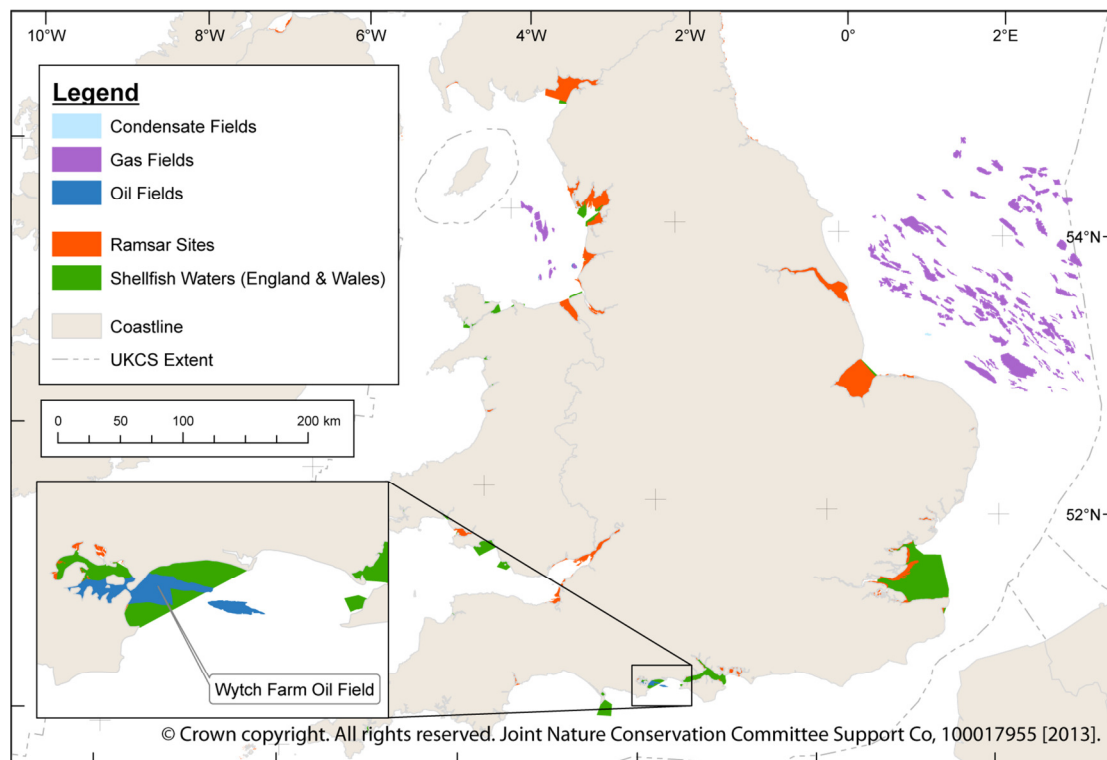
Figure 2. Showing location of Ramsar sites and Shellfish Waters (England & Wales) in relation to UKCS oil and gas fields. Wytch Farm oil field operates onshore.

Ramsar sites are wetlands of international importance under the Ramsar Convention (primarily to water birds). Figure 2 shows offshore Ramsar sites, which are located in estuaries and adjacent to shorelines. Shellfish waters designated under the EC Shellfish Waters Directive (Directive 2006/13/EC) are also located in these areas, Figure 2. The figure shows that, given the sites' proximity to shore, and the distal locations of most hydrocarbon activities, little direct conflict occurs. Neither Ramsar nor shellfish waters overlap with any UKCS hydrocarbon fields in Scottish waters.

The only apparent exception is the Wytch Farm oil field on the south coast of England. This field is operated onshore from the coast and as such will most likely already be subject to license conditions set by the Environment Agency to limit effects on the coastal environment. If Wytch Farm were selected for CO_2-EOR in the future, site-specific additional risks would need to be assessed. However, on the whole any future CO_2-EOR projects in the UKCS would likely not affect shellfish waters or marine Ramsar sites, as currently designated.
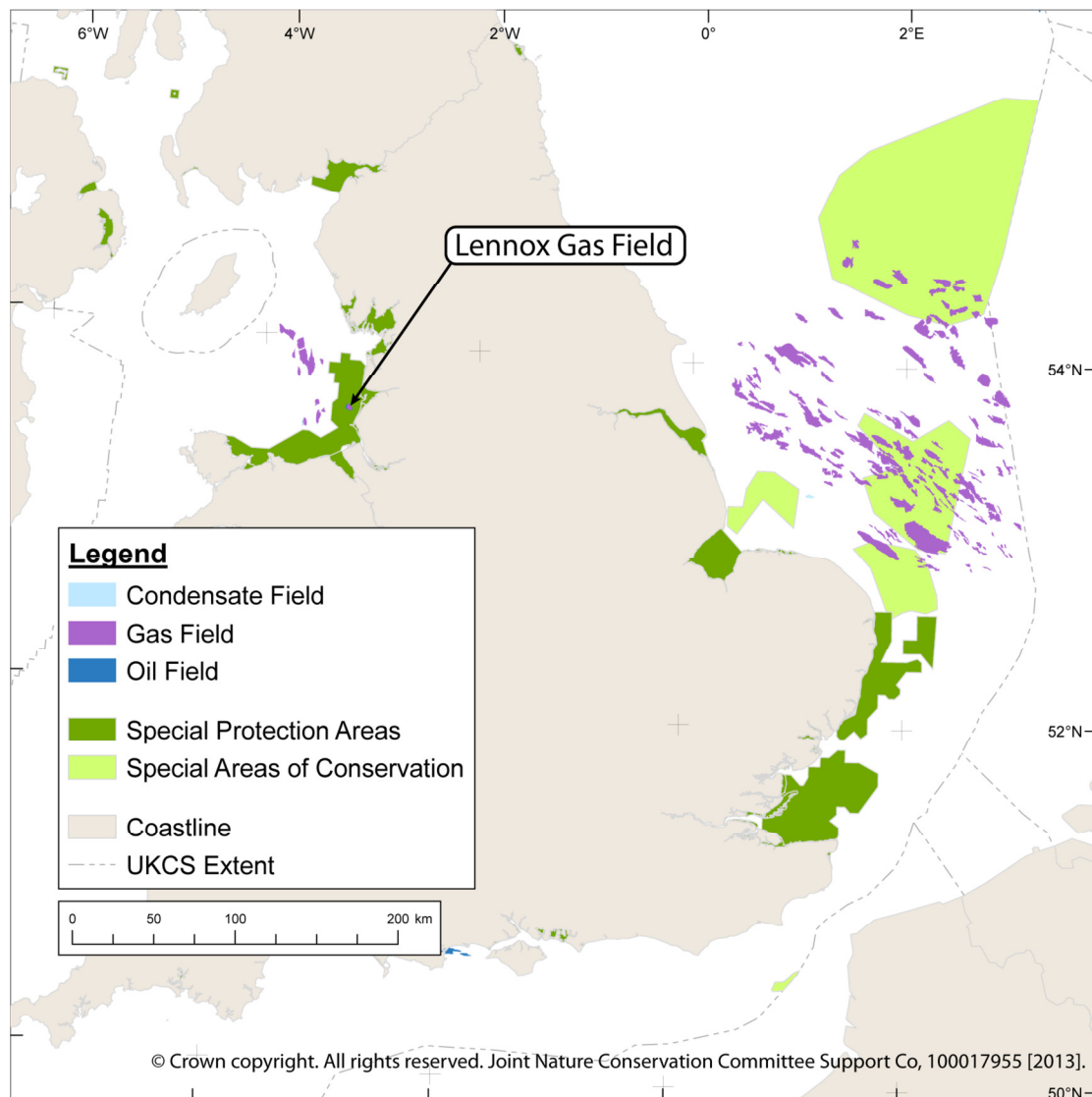
Figure 3. UKCS gas fields shown in relation to marine SPA's and SAC's for England and Wales.

Special Protection Areas (SPA) are classified bird (rare, vulnerable and regular migratory) protection areas under the EC Birds Directive (Directive 2009/147/EC). Currently only the Lennox field lies within one of these areas in the Irish Sea, Figure 3.

Special Areas of Conservation (SAC) are non-bird conservation areas, protecting species and habitats of high conservation status, as listed in Annexes I and II of the EC Habitats Directive (Directive 92/43/EEC). With respect to the SAC's, it can be seen that many SNS gas fields lie within these areas, Figure 3. As with shellfish waters and Ramsar sites, there are no fields in Scottish waters which currently overlap with either SAC's or SPA's.

Given the continuation of fields to operate within these areas, including regular produced water discharges, flaring, and other potentially polluting activities, there are either permits in place to mitigate the impact of these fields, or their impact is considered minimal on SPA's and SAC's.

One would expect that CO_2-EOR activities would not require significant additional permitting and/or regulation, however this could not be entirely ruled out if research indicated significant impacts could occur from CO_2-EOR projects.

2.6 Conclusions

Based on the review of existing regulations and guidelines covering UK North Sea offshore activities, it would seem possible that CO_2-EOR activities would be regulated under existing laws and voluntary practices, with little or no amendments.

Uncertainties may, however, arise from the unknown effects of CO_2-EOR on the environment. The oil and gas industry has been operating in the UKCS for over forty years with the experiences of these operations incorporated into national legislation and international agreements. CO_2-EOR does not yet have this legacy in the UK and as such it is uncertain how similarly it will be regulated, with respect to environmental regulations, compared to oil and gas. A prior understanding of potential environmental impacts would help guide the process of regulation.

3 CO_2 Leakage to the Marine Environment

Carbon dioxide is the major differentiator between traditional North Sea oil and gas activities and CO_2-EOR, with respect to potential environmental impacts. CO_2 is a potential risk to the environment which is unique to CO_2-EOR (and CO_2 storage), unlike the other environmental issues highlighted later in this report, with the exception of CO_2 capture chemicals.

Should a leak occur during transport and storage, there may be potential for significant concentrations of CO2 to be introduced to the marine environment. The general impacts of enhanced CO_2 concentrations in the marine environment are reviewed below, with consideration given to potential impacts of CO_2 leakage from CO_2-EOR and CCS projects.

3.1 Natural Seawater pH Variations

Seawater pH averages around pH 8.1 globally (Sugden, 2011) and varies by an average of ± 0.3 pH, with larger regional variations of ± 1 pH occurring near coastal regions, where increased water temperatures reduce the amount of CO_2 which can dissolve on a seasonal basis. Riverine inputs also supply nutrients to eutrophic, high productivity shelf and coastal regions, increasing biological demand on dissolved CO_2 (Blackford & Gilbert, 2007), as well as lowering salinity which enhances CO_2 dissolution (Burnside et al., 2012).

Modelling of natural pH variations in the North Sea by Blackford & Gilbert (2007) showed that benthic (sediment) and pelagic (water column) biological activity were important factors in the range of modelled pH variability (<0.2 – >1.0 pH).

Local pH variability in seawater due to natural CO_2 seepages was noted in the 'Quantifying Impacts of Carbon Storage' (QICS) review of natural CO_2 fluxes by Kirk (2011), with values as low as pH 3 noted at Panarea. Observed CO_2 seepage rates for natural offshore sites vary from 5.5 tonnes m^{-2} yr^{-1} (Ischia, Italy) to 8.5 x 10^3 tonnes m^{-2} yr^{-1} (Panarea, Italy). To put those in context, CO_2 emissions from Longannet power station (2nd largest coal power station in the UK with a maximum 2.4 GW output) in Scotland were around 8.5 x 10^6 tonnes for 2011 (Scottish Power, 2011).

The 'Research into Impacts and Safety in CO_2 Storage' (RISCS) *Scenarios for Potential Impacts from Hypothetical Leakage from Geological Storage Facilities for Carbon Dioxide* report (Paulley et al., 2012) also quotes a number of natural CO_2 leakage fluxes in the terrestrial and marine environment. The background natural marine fluxes in the North Sea are given in the order of 10^{-5} to 10^{-4} tonnes m^{-2} yr^{-1}, which compares with a conjectured maximum flux of CO_2 escaping from an open borehole of 10^{18} tonnes m^{-2} yr^{-1}. The report concludes, though, that a flux of CO_2 as high as the leak scenario would be highly localised (RISCS, 2012; Paulley et al, 2012), and in any case high rates of leakage would not be sustained due to pressure depletion.

Physical and chemical characteristics of seawaters adjacent to marine leakage sites were summarized by Kirk (2011) and for reference are included in Table 3 overleaf, particularly to highlight natural pH conditions at these sites; one example being a Southern German North Sea site with a pH of 6.8 (McGinnis et al., 2011).

3.2 Effects of CO_2-Induced Ecological Stress

Leakage from a storage site is generally regarded as unlikely (e.g. Blackford et al., 2008; Blackford et al., 2009; Kirk, 2011) and long-term, only a small fraction of stored CO_2 will escape (J. C. Blackford et al., 2008; J Blackford et al., 2009), however accidental leakage from the reservoir or transport pipeline cannot be ruled out.

Leakage of CO_2 from a storage reservoir or transport pipeline to the marine environment could have a negative impact on marine life. As described in Section 4, the dissolution of CO_2 in water lowers pH. By adding CO_2 into seawater, it is acidified and the partial pressure of CO_2 (pCO_2) is increased, which leads to the following CO_2-induced stress effects: **(1)** lowered body and skeleton calcification in marine calcifiers; and **(2)** induced hypercapnia (increased CO_2 in body tissue and fluids) due to increased pCO_2.

Table 3: Observed physical and chemical characteristics of natural marine CO₂ seepage sites, adapted from Kirk (2011).

Site	Water Depth (m)	Temperature (°C)	Salinity (TDS mg/L)	pH
Panarea, Italy	≤ 30	46 – 135 (discharge temp.)	37,600 – 54,500	3 – 8
Ischia, Italy	< 5	13 – 25 (sea water)	380,000	7.4 – 8.2
Champagne site, Mariana arc	1,600	47 – 103 (discharge temp.)		3.4 – 4.8
Hatoma Knoll, Okinawa Trough	682 – 1,430	3.9 – 6.4 (bubble temp.)	344,190	7.0 – 7.4
Salt Dome Juist, Southern German North Sea		13 – 15		6.8

Sugden (2011) reported the results of around fifty papers on the CO_2-induced stress response of marine organisms to enhanced CO_2 environments. The majority of published literature focuses on the increase in anthropogenic atmospheric CO_2, however the conclusions are still applicable since the source of enhanced CO_2 would make little difference to the biological responses. Studies on CO_2-induced stress due to CO_2 leakage from CCS projects is increasing, however, for example the results of data collected during experimental and natural case studies published by the ECO₂ project (Klapper & Widdicombe, 2013). Sugden's (2011) review noted the following changes in marine organisms in response to enhanced CO_2:

- **Mortality**
- **Calcification**
- **Acidosis**
- **Metabolism**
- **Respiration**
- **Growth and reproduction**
- **Acclimation**
- **Resilience**

The pH's at which these effects can be recognised in a variety of species is given in Table 4, and some are explored further, below.

Calcification

Lowering pH has the effect of lowering carbonate (CO_3^{2-}) concentration and reducing the saturation of the two calcium carbonate forms (calcite and aragonite), particularly affecting aragonite (Kurihara, 2008; Miles, Widdicombe, Spicer, & Hall-Spencer, 2007). This makes it harder for marine organisms that rely on carbonate to fix calcium carbonate to form their shells and skeletons (e.g. Berge et al., 2006; Burnside et al., 2012; Dupont et al., 2008; Kirk, 2011; Miles et al., 2007; O'Donnell et al., 2008; Wood et al., 2008), and therefore elevated

CO_2 in marine waters can lead to coral bleaching, reduced calcification, and shell dissolution as seawater becomes undersaturated with aragonite and calcite.

Mortality

CO_2-induced stress affects a wide variety of organisms from both benthic and pelagic communities, and not just calcifiers. These effects generally lead to increased stress placed on the affected organisms and a lower survival rate (O'Donnell et al., 2008; Sugden, 2011; Wood et al., 2008), with increased mortality rates across a wide range of organisms reported by many authors (e.g. (Dias, Hart, Smart, & Hall-Spencer, 2010; Dupont et al., 2008; Fleeger et al., 2010; Kirk, 2011; Klapper & Widdicombe, 2013; Miles et al., 2007; Shirayama & Thornton, 2005; Widdicombe & Needham, 2007).

High mortality rates in urchins at reduced pH were reported by Miles et al. (2007), despite the ability of the animal to respond to varying pCO_2 and pH in its normal local environment. Severe hypercapnia was, however, fatal with carbonate hard parts dissolution inferred from an increase in Mg^{2+} concentrations in the coelomic (cavity) fluid (Miles et al., 2007).

Reproduction & Growth

Reproductive stages are the most vulnerable in the life cycle of an animal (Kurihara, 2008); enhanced dissolved CO_2 can affect reproduction rates (Burnside et al., 2012; Kirk, 2011) and effect early development of the organism. Increased CO_2 concentrations reduce growth rates, changes physiology, and can lead to premature mortality (Dupont et al., 2008; Shirayama & Thornton, 2005). The importance of stresses placed on organisms higher up the food chain, which rely on larvae as a food source, is emphasised by Klapper & Widdicombe (2013). Organisms who may be generally tolerant to pH perturbations may nonetheless become vulnerable if their food source is impacted.

Resilience

Some organisms show capacity to acclimatise or respond positively to an environmental change (Paulley et al., 2012), for example the ophiuroid brittlestar *Amphiura filiformis*, a calcifying organism, responds to reduced pH conditions by uprating it's metabolism and calcification (Wood et al., 2008). However this survival mechanism comes at a cost to the creature, with the brittlestar suffering from muscle wastage. Therefore, while organisms may temporarily adapt to enhanced stress in their environment due to a CO_2 leak, this is not a long-term adaptation.

Marine organisms can also display resilience, with the ability to cope with changes to their environment. Some organisms, such as those living adjacent to hydrothermal vents, actually thrive in enhanced pCO_2 conditions, whereas others (e.g. nematodes) are able to survive without negative effect at much lower pH than normal (Fleeger et al., 2010). Survival techniques include reducing metabolism (Burnside et al., 2012; Celussi et al., 2011; Langenbuch, Bock, Leibfritz, & Pörtner, 2006) with resulting reduction in growth (Berge et al., 2006). Celussi et al. (2011) reported that metabolism returned to normal after removing the CO_2 stress.

A number of conditions can affect resilience, though, such as whether the organism lives in or on sea floor sediments; whether it is calcifying, and therefore more susceptible to pCO_2; preference of calcifying fauna for calcite or aragonite formation, since aragonite is more soluble (Kurihara, 2008); and development stage of the organism as juveniles are more vulnerable.

Nutrient Availability

Speciation by benthic communities of nutrient (nitrogen and phosphorous) input is affected by

changes in pH; as pH drops, nutrient availability reduces. Widdicombe & Needham (2007) demonstrated that lowered pH increases nitrate uptake and ammonium release, while decreasing nitrite release and phosphate uptake. This is a change in the normal nutrient cycle of moving nutrients across the sediment-water boundary, and as such may have a knock-on effect to other organisms. The authors found that mortality increased and burrowing activity decreased as a result.

Table 4: Experimental pH values where deleterious effects were noted in the species, adapted from Sugden (2011).

Species	Description	pH	Reference
-	Nematode	5.4	Fleeger et al. (2010)
Nerevis virens	Worm	5.6 – 7.3	Widdicombe & Needham (2007)
Ophiothrix fragilis	Echinoderm larvae	7.9	Dupont et al. (2008)
Crassostrea gigas	Oyster	7.4	
Psammechinus milians	Purple tipped sea urchin	6.16 – 7.44	Miles et al. (2007)
Strombus luhuanus	Gastropod	7.9	Shirayama & Thornton (2005)
Hemicentrotus pulcherrimus	Sea urchin	7.9	
Echinometra mathaei	Sea urchin	7.9	
Crassostrea virginica	Oyster	7.8	Kurihara (2008)
Hemicentrotus pulcherrimus	Sea urchin	7.8	
Echinometra mathaei	Sea urchin	7.8	
Mytilus edulis	Mussel	6.7 – 7.4	Berge et al. (2006)
Sipunculus nudus	Worm	6.7	Langenbuch et al. (2006)
Strongylocentrotus franciscanus	Red sea urchin	7.87	O'Donnell et al. (2008)
Pagrus major	Red sea bream	5.9 – 6.2	Kikkawa et al. (2004)
Amphiura filiformis	Ophiuroid brittlestar	6.8 – 7.7	Wood et al. (2008)

The response of phytoplankton to pH perturbations is species dependent; therefore a change in phytoplankton species composition could have a knock-on effect on higher trophic level

organisms (Blackford & Gilbert, 2007). pH perturbations due to CO_2 leaks can be somewhat avoided by pelagic species as they are mobile and are fed by fast-regenerating food sources (Blackford et al., 2009). However, these food sources – mainly phytoplankton in shelf sea environments – rely on the nutrient recycling capacity of benthic bacteria which can be highly susceptible to pH perturbations (Blackford et al., 2009).

80% of nitrogen required by phytoplankton as a nutrient is supplied by bacterial reworking of organic material in sediments (Blackford et al., 2009). Thus, stresses placed on benthic communities will migrate up the food chain, even if the higher-order communities are not directly affected by pH changes.

Sensitivity

Benthic and calcifying organisms are more sensitive to enhanced CO_2 conditions than pelagic, non-calcifying organisms (i.e. fish) (J. C. Blackford, Torres, Cazanave, & Artioli, 2012; Sugden, 2011).

Susceptibility of marine life to CO_2 in the Inner Moray Firth Goldeneye field area was ranked by Sugden (2011) as follows:

- **Least susceptible: highly mobile pelagic and demersal**
- **Moderately susceptible: mobile benthic non-calcifiers and pelagic zooplankton**
- **Very susceptible: calcifiers and planktonic larvae**

Approximately a third of North Sea species identified in the study would fall into the "very susceptible" ranking.

The thresholds at which each of these rankings are affected by CO_2 was taken as a reduction of pH units from normal conditions. For each ranking, the thresholds were calculated by Sugden (2011) from the available literature as: least susceptible (-2.1 pH); moderately susceptible (-1.4 pH); very susceptible (-0.3 pH). The pH reduction calculated for the very susceptible ranking agreed with previously published literature; that negative effects are witnessed at 0.2 – 0.3 pH unit decrease from normal conditions (Sugden, 2011).

Marine receptors independently identified in the RISCS report (Paulley et al., 2012) were given as:

- **Benthic biota**
- **Pelagic biota**
- **Biogenic calcifying habitats (carbonate bodied habitat providers e.g. coral)**
- **Local sensitive populations**
- **Biogeochemical cycles (nutrient cycling, benthic-pelagic ecosystem coupling)**

The potential impacts on these receptor classes may vary depending on the environments in which they live. The type of sediment in which benthic fauna live can influence their resistance to enhanced CO_2 conditions (Widdicombe et al., 2009), while the coupling between pelagic and benthic fauna (e.g. pelagic fauna grazing on benthic organisms) becomes weaker with increasing water depth (Paulley et al., 2012), therefore indirect effects of CO_2 leakage on feeding habits may be reduced in deeper environments. The organisms found in different temperatures of laterally varying seawater may also respond differently to CO_2 induced stress.

Organisms dwelling in the deepest parts of the North Sea are expected to be more sensitive to pH changes since their natural pH range is not as variable. Taxon-specific reaction to CO_2 are to be expected too, with the paper of Fleeger et al. (2010) determining high mortality rates in nematode worms but not in copepods under similar experimental conditions.

Seawater acidification may not alone affect individuals because of natural variability, however it can place additional stress on already-stressed creatures to compound the problem (O'Donnell et al., 2008), for example in areas of anthropogenic inputs such as oil and gas operations, or the margins of an ecosystem where marine communities are at the limits of survivable conditions (Paulley et al., 2012; Sugden, 2011).

Biodiversity

While mobile and non-calcifying organisms may appear to be isolated from small pH effects, the effect of mortality, low survival rates and reduced reproduction of lower trophic level organisms will cascade up the food chain to affect "moderately" and "least" susceptible species (Dupont et al., 2008; O'Donnell et al., 2008; Sugden, 2011). When a food source runs out, species less capable of adapting to CO_2 perturbation of their environment will struggle to survive, and a loss of biodiversity will occur.

Biodiversity can change significantly with small changes in pH (Dias et al., 2010; Lombardi, 2010), with a reduction in diversity with decreasing pH as shown by experimental evidence (Figure 4) and field data (Figure 5).

The reasons for decreases in biodiversity can be due to acidosis, immune response, cell function and respiration (Blackford et al., 2009), as already noted.

3.3 Leakage Scenarios

Burnside et al. (2012), under the QICS project, gave an evaluation of leakage pathways to constrain likely CO_2 seepage pathways from an underground leak, and estimate fluxes of CO_2 to the environment as a result.

While the work published so far falls short of estimating seepage, the potential leakage risks in the UK North Sea identified by evaluation of GIS data were given as:

- **Faults (migration pathways)**
- **Salt bodies (deformation of overlying strata, affects CO_2 solubility)**
- **Unconsolidated sediments (strongly permeable)**
- **Shallow gas (mobilised by CO_2 migration)**
- **Channels (shorter vertical migration pathway to base of channel)**
- **Hard rock substrate (highly permeable bedrock)**
- **Exploration wells (unsuitable completion or degradation)**

A combination of any of the above would increase the potential risk of leakage from a UK storage site, such as CO_2-EOR project, depleted hydrocarbon reservoir or saline formation storage e.g. activation of faults due to deformation caused by movement of salt bodies.
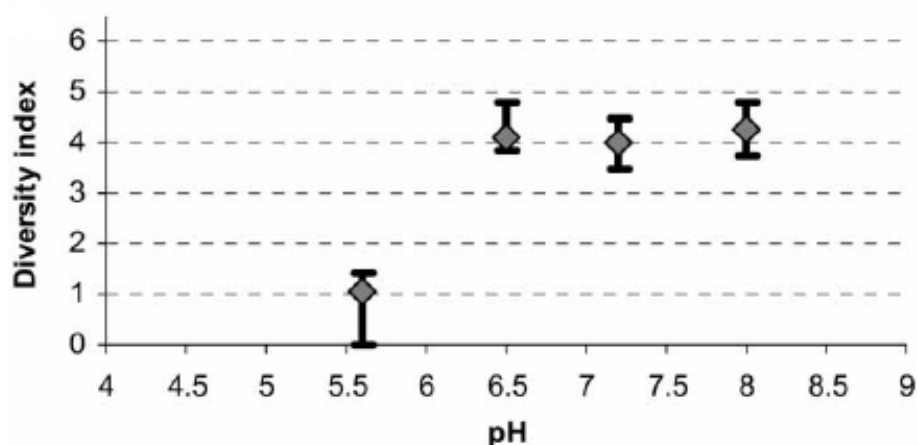

Figure 4. Experimental reduction in biodiversity due to lowered pH. From Blackford et al. (2009).
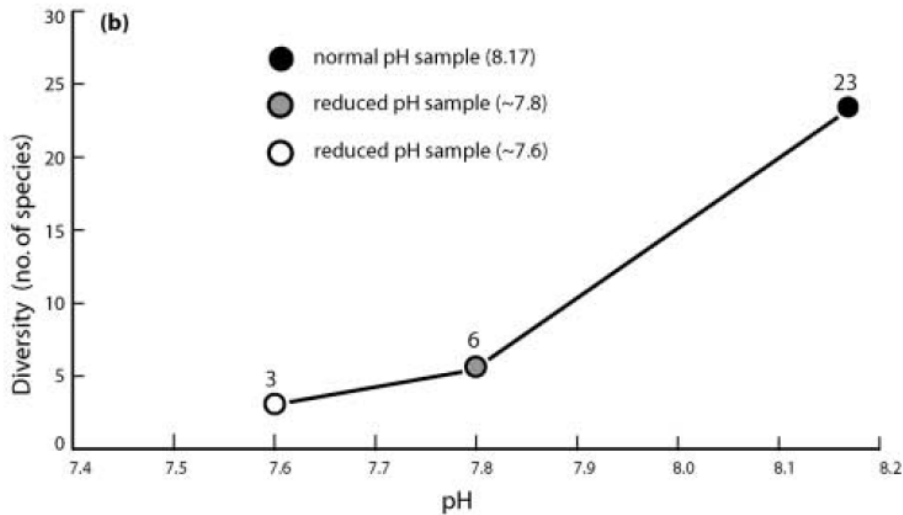
Figure 5. Observed changes in biodiversity with pH. From Dias et al. (2010).

The RISCS report (Paulley et al., 2012) was mainly informed by an expert workshop in 2010, and explores the potential impacts of a number of leakage scenarios on a set of reference European environments. The report stresses that the most likely scenario is that of CO_2 containment within the engineered storage site (Paulley et al., 2012) and that this be considered as "baseline". The evolution of the baseline environments without the impact of CO_2 leakage needs to be established in order to understand and quantify the effects of any leakages.

Two reference environments identified by the RISCS report which would be applicable to UK North Sea CO_2-EOR are (Paulley et al., 2012):

- **Cool, temperate, deep**
  - **Northern North sea, seasonally stratified, moderately nutrient rich, 60->100m deep water, remote from shorelines, strong tidal and current mixing**
- **Cool, temperate, shallow**
  - **Southern North Sea, well mixed, nutrient rich, water column height tidally influenced, riverine nutrient input.**

The impacts of CO_2 storage on these environments could vary depending on a number of factors. These factors may include the speed of CO_2 leakage from the source e.g. well or pipe leakage, or by diffuse emissions over large areas such as leaks through fractures or diffusion into overburden and sediments; to what extent a dense (sinking) CO_2-saturated water plume develops post-leak; pH variations due to water mixing; acidification of sediment pore waters below the seabed; mobilisation of potentially toxic organic and inorganic substances from the storage site or adjacent reservoirs; and mobilisation of highly saline formation waters due to pressure changes on CO_2 injection (Paulley et al., 2012).

The chemistry of the water into which CO_2 leaks could influence the impact of a CO_2 leak, for example organisms in lower salinity environments – such as coastal regions – compared with fully marine would respond differently to a CO_2 leak, as the water chemistry change (e.g. pH, alkalinity, calcite saturation) would more pronounced in the lower salinity waters (Paulley et al., 2012).

The marine leakage scenarios, in addition to the baseline evolution of the system, were given by Paulley et al. (2012) as:

- **Localised direct release of free CO_2**
- **Diffuse release of free CO_2**
- **Localised release of CO_2-charged waters**
- **Diffuse release of CO_2-charged waters**

The impacts given of these scenarios are broadly similar: CO_2 dissolution or CO_2-charged water will be dense and sink to the seabed or present to the seabed and migrate laterally as a plume. Benthic organisms are therefore primarily affected, with a potential subsequent knock-on effect to pelagic organisms (Blackford et al., 2012; Paulley et al., 2012).

Other leakage scenarios identified by the RISCS report, which could potentially be both localised and diffuse, are: displacement of saline formation waters during storage; sudden overturning of CO_2-charged waters; and release of hot geothermal fluids.

Blackford, Haeckel, & Wallman (2012) also proposed a number of leakage scenarios from geological storage, namely: abandoned well, geological fracture, and catastrophic blowout. The fracture and the blowout are the result of natural or induced fracturing of the storage reservoir, respectively. The authors speculate that the flux of CO_2 from the reservoir would decrease over time as reservoir pressure drops, with 1% of contained CO_2 potentially escaping over decadal timescales (due to difficulty in monitoring leakage) via the well bore or geological fracture scenarios. The catastrophic blowout could result in 50% of contained CO_2 leaking (at $10^3 - 10^4$ tonnes CO_2 day^{-1}), perhaps also over several decades but at reduced flux as reservoir pressure drops.

CO_2 may also enter the environment dissolved within produced waters. However, the pH values of formation waters routinely produced and 'overboarded' (dumped) into the North Sea average 6.2 (Formation Waters Atlas, 1994) and therefore already fall outside of the global average value of 8.1 ± 1.0. This is considered normal, and therefore acceptable, practice. By the time produced fluids are processed to separate oil, gasses and water most CO_2 will have exsolved leaving a produced water likely of similar pH to the formation waters. Therefore, this potential method of CO_2 release into the marine environment is not considered to be of any impact, compared with oil and gas activities.

3.4 Modelling

Modelling a CO_2 leak and its effect on pH by Blackford et al. (2008) shows tidally driven mixing is the primary way for a CO_2 plume to dissipate, and the authors conclude that the impact of a leak from a sequestration site would be insignificant compared with an increase in anthropogenic atmospheric CO_2.

For the modelled study, leak scenarios were taken as:

- **Long-term, diffuse seepage ($3.02 \times 10^3 - 3.02 \times 10^5$ tonnes CO_2 yr^{-1})**
- **Short-term, point source leak ($1.49 \times 10^4 - 1.49 \times 10^5$ tonnes CO_2 yr^{-1})**
- **Long-term, point source leak (5.43×10^6 tonnes CO_2 yr^{-1})**

For these scenarios, it was assumed that all CO_2 dissolved within the modelled area (49 km^2). Each scenario was modelled for typical Northern (NNS) and Southern North Sea (SNS) conditions, therefore NNS was at 138 m water depth with a highly stratified temperature profile in the summer, while SNS was taken as 28.5 m water depth and well mixed.

The results of the long-term diffuse seepage and the short-term leaks suggested that negative ecological impacts of these events would be unlikely, as the pH change given by the model was less than natural variation for the North Sea ($\pm 0.2 - 0.4$ pH) (Blackford et al., 2008). At the top end of short-term leakage scenario (i.e. 1.49×10^5 tonnes CO_2 yr^{-1}), a reduction in pH of greater than 0.5 pH was found, and that this persisted longer in the SNS (20 days) than in the NNS (5 days), due to the smaller volume of water (shallower) in the SNS. Therefore, the location of a CO_2 leak in the North Sea will affect the acidification of the seawater.

The long-term point source leak, equivalent to five years of CO_2 sequestered at the Norwegian Sleipner field, caused a high pH perturbation over small area (-0.5 pH NNS, -1.0 pH SNS) but this rapidly dispersed over a wide area to a pH change of -0.1 pH in both areas

(Blackford et al., 2008). The dispersion was clearly influenced by tidal conditions, therefore the timing of a leak (daily and seasonal) also has a large influence on the fate of dissolved CO_2.

Blackford et al. (2012), as part of the RISCS project, utilised high resolution ocean models combined with a carbonate chemistry model to investigate the dispersal of a CO_2 leakage plume in seawater. The model was set to represent the NW European shelf (i.e. the North Sea), with tidal flows, irregular coastline and a sloping bathymetry. Other environmental factors such as temperature, wind and riverine input were turned off in the model. The leak site was set as at 15km offshore, in 30m of 13°C, 35,000 ppm salinity seawater.

Three leakage scenarios were chosen following the RISCS leakage scenarios:

- **Dissolved CO_2 point source low flux (8.99 x 10^4 tonnes yr^{-1})**
- **Dissolved CO_2 point source high flux (1.35 x 10^8 tonnes yr^{-1})**
- **Pipeline leak (2.8 x 10^{11} tonnes yr^{-1})**

Results of the model were given as a change in sweater pH from CO_2 dissolution. The two dissolved point source leaks resulted in plumes of very low changes (-10^{-6} to -10^{-4} pH units) in pH, which dispersed rapidly over the modelling period of 10 days, Figure 6 (below).
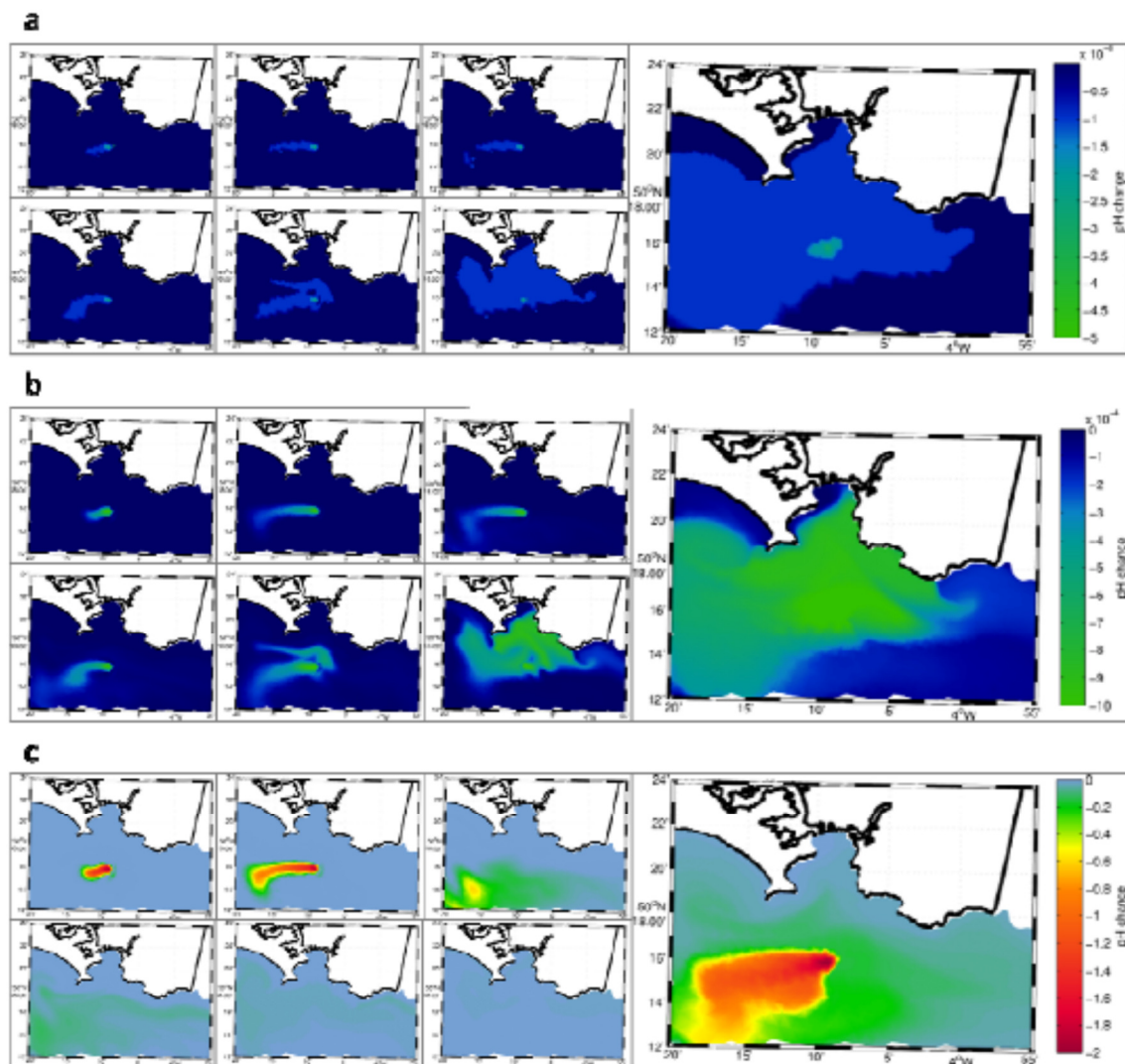
Figure 6. Modelled pH changes due to three CO_2 leakage scenarios over approx. 33km x 20km area: a) low flux point source; b) high flux point source; c) pipeline leak. Large panel indicates maximum pH change. Small panels top left-right are pH change at 6, 12, 36 hours, bottom panels left-right 72, 120, 240 hours. From Blackford et al., (2012).

As already noted, annual natural pH ranges in the North Sea are typically ±0.3 – 0.4 pH, but can vary by as much as ±0.2 – 1.0 pH (200-450 μatm pCO_2), as a result of changes in water temperature, riverine input and biological respiration and uptake (Blackford & Gilbert, 2007; Blackford et al., 2008, 2012). The pipeline leak was the only scenario which resulted in significant pH change of -0.4 – -2 pH units, but again was short lived with pH values returning to normal after 10 days, Figure 4.

A catastrophic leak, such as the long-term point source scenario, could be significant due to the highly reduced pH, however the effects would likely be very localised and of short duration. Field observations of natural seeps at Panarea and Ischia in Italy show that a reduction of pH is quickly mitigated laterally due to rapid dispersion of the CO_2 plumes (Kirk, 2011; Lombardi, 2010), however in areas close to the seeps marine life show signs of CO_2-induced stress. A reduction in calcifying organisms was observed after an increase in CO_2 flux in 2002 at Panarea, shifting to an ecosystem dominated by algae and bacteria (Caramanna, 2010). A similar effect was also observed at Ischia due to CO_2-induced stress (Lombardi, 2010). However the local system appears to be recovering at Panarea after the initial 2002 perturbation (Caramanna, 2010).

The results of the modelling by Blackford et al. (2007, 2008, 2012) showed that CO_2 plume shapes are impacted significantly by complex tidal mixing. The plume, and therefore its impact, will depend on tidal cycles, tidal mixing strength, water temperature and wind speed. That is to say that the location and timing of a leak will influence the plume shape and will always be unique.

3.5 CO_2 Impurities

Impurities in the captured CO_2 stream from coal and gas-fired power generation, from industrial processes, or from offshore platform capture (recycled CO_2), could include (Lee et al., 2009; West et al., 2011):

- **Acids e.g. hydrofluoric (HF), sulphuric (H_2SO_4) & hydrochloric (HCl)**
- **Nitrous gasses (NO_x)**
- **Sulphurous gasses (H_2S, SO_x)**
- **Hydrocarbon gasses e.g. methane (CH_4)**
- **Trace metals e.g. mercury (Hg^{2+}) and cadmium (Cd^{2+})**
- **CO_2 capture chemicals e.g. amines**
- **Dehydrating agents e.g. ethylene glycol**

Currently very little research has been undertaken on the effects of these impurities in a CO_2 stream on the environment, particularly offshore, however broad effects can be hypothesised based upon known chemistry of these impurities (West et al., 2011). Of these impurities, however, hydrocarbon gasses are not unique to CO_2-EOR and therefore not considered further.CO

Acids, such as nitric acid (HNO_3) and sulphuric acid (H_2SO_4) from NO_x and SO_x, respectively, and hydrochloric acid acidify water more strongly than CO_2. This could potentially lead to a greater impact on marine life should CO_2 leakage occur, or enhanced mobilisation of toxic metals from the reservoir (IPCC, 2005). Redox conditions, affecting nutrient cycling and supply by bacteria could also be affected with the knock-on effect to eco-systems (West et al., 2011) as described in an earlier section.

Hydrogen sulphide (H_2S), although expected to be strictly limited by pipeline specifications can, however react with dissolved metals (such as Fe^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}) in seawater or formation waters to form sulphide minerals, for example pyrite (FeS_2) (Thode-Andersen & Jørgensen, 1989; Yao & Miller, 1996). This process occurs in anoxic conditions, such as those in the deep ocean or in reservoirs and may mitigate any residual H_2S in the CO_2 stream.

While CO_2 recycling from produced oil and water would be achieved through pressure changes, amines could be used offshore for separating CO_2 from produced hydrocarbon gas streams instead of using membranes (James Lorsong, 2CoEnergy, personal communication, 26 Feb., 2013). Amines may therefore be present in trace amounts (<2%) in reinjected CO_2 or from CO_2 piped from onshore capture facilities.

Monoethylamine (MEA) is the most commonly considered amine capture chemical, and it's degradation products are considered of low risk to the environment (Brakstad, 2010), but with variable toxicities depending on trophic level and species, with a toxicity response ranging from 0.02 to 26,000 mg/L (Brakstad et al., 2010). Low bioaccumulation potential and high biodegradation minimises the effects of amines released to the environment. However, some degradation products (e.g. HEED) are not biodegradable, while data is lacking on some compounds, and generally the fate of amines and their degradation products in the marine environment are not known (Booth et al., 2011).

Reinjected CO_2 may also contain ethylene glycol, a compound used to dehydrate reinjected gasses to inhibit corrosion and the formation of hydrates. There is the potential that small amount of ethylene glycol could be returned to the surface in produced waters, however it biodegrades rapidly in the aquatic environment and does not bioaccumulate. While not particularly toxic, with acute toxic effects noted at high concentrations only (>10,000 mg/L) (Staples, Williams, Craig, & Roberts, 2001), rapid biodegradation consumes dissolved oxygen in the water, potentially leading to oxygen depletion, which impacts marine life in oxygenated zones (Government of Canada, 2002; Staples et al., 2001).

Overall, given the trace concentrations of these impurities likely to be present in the CO_2 stream, the risk to the environment from these impurities is considered to be low.

3.6 Future Research Aims

One of the main technical achievements of the QICS project has been the successful completion of a horizontal borehole, drilled from the west coast of Scotland into marine sediments 350m offshore (Blackford & Kita, 2012). The purpose of the borehole is to simulate a CO_2 leak event, with the aim of determining the effects of the leak on the marine sediments, water chemistry, local flora and fauna.

While laboratory CO_2-stress experiments on marine organisms are valuable tools to understanding how they are affected under controlled conditions, they are not realistic of conditions experienced during a CO_2 leak from a geological storage site (Blackford & Kita, 2012). And study of natural CO_2 seeps does not give information on the initial stresses placed on the local environment, since and organisms in the area have adapted over long-term exposure (Burnside et al., 2012).

The QICS experiment allows physical, chemical and ecological analysis of a complex sediment-water-biota ecosystem before, during and after a small-scale CO_2 release. One aim of the project is to begin assessing the recovery of marine organisms after CO_2-induced stress, given the lack of research undertaken to-date in this area (Blackford & Kita, 2012; Blackford et al., 2009).

Around 4,200kg of CO_2 was released over 40 days in May-June 2012. A large amount of equipment was deployed to measure chemical (pH, redox potential, pCO_2, H_2S), physical (temperature, currents, turbidity), and ecological (sediment cores, caged fauna) changes. Although data have not yet been published, the results of the experiment will provide information to inform further on risk, impact and monitoring of leaks (Blackford & Kita, 2012). The results of the experiment will be published in due course.

Other large collaborative projects are currently on-going, investigating the impacts of CO_2 leaks on the marine environment, for example NASCENT (British Geological Survey, 2013) has been running since around 2001, however no research on marine impacts appears to have been published by this group. Likewise, ECO_2 commenced in 2010 and although active research has been going on, data is still being analysed before publication and dissemination (ECO_2, 2013).

3.7 Conclusions

Should a CO2 leak occur in the North Sea the impact will vary depending on the location and the timing, and the type, of leak in the rare occasions that one might occur. These affect factors such as tides and currents, riverine input, water depth, season, impact duration, and

ecological community type and sensitivity. A leak event, should this occur, will therefore be unique temporally and spatially.

Modelling of site specific conditions prior to any operations would help determine likely plume size and pH effects. Baseline surveys of existing ecology are therefore crucial prior to commencement of any storage or pipeline transport activities (Benham et al., 2012; Paulley et al., 2012) to determine the health of the ecosystem populations within a predetermined area. It is apparent that marine organisms function at a range of natural pH values, and that natural pH variability in the North Sea (and globally) is not a barrier to successful colonisation by ecosystems, therefore the changes attributable to any CO_2 leaks from CO_2-EOR operations need to be accounted for, over and above responses to naturally evolving conditions.

Initial studies have shown, however, that dispersion of CO_2 plumes is rapid and that effects are highly localised and of short duration (Blackford et al., 2012). Blackford et al. (2009) note that while potential impacts could be severe, there is still ambiguity regarding ecological response to CO_2-induced stress, particularly with regard to species specificity and recovery, although the results of experimental work cited by Klapper & Widdicombe (2013) would indicate that highly mobile species recover fairly quickly, while immobile species (e.g. corals) could be more strongly affected.

A 2012 workshop, *Potential environmental effects of CO_2 leakage in the marine and terrestrial environment: Understanding, monitoring, mitigation*, attended by UK CCS researchers and professionals in Nottingham (Benham et al., 2012) acknowledged that knowledge gaps still exist, such as the unknown ecological response to large leakages from differing sources and into varied environments. The workshop also highlighted that the greatest risk of CO_2 leakage would be from infrastructure (e.g. pipelines and offshore platforms/well bores) and that leakage from engineered storage sites would be highly unlikely (Benham et al., 2012). The workshop concluded that site-specific knowledge is a must for accurate modelling.

4 Trace Elements in Produced Water

Produced water from North Sea oil and gas operations is routinely disposed of to the sea, with around 20-25% reinjected (DECC, 2013). Produced waters contain varying concentrations of major and trace elements, depending on the target field (Formation Waters Atlas, 1994) and currently these concentrations are not regulated, as discussed in Section 2.

Produced water trace element concentrations may, however, be significantly enhanced due to CO_2-EOR, potentially resulting in an increased risk of negative environmental impact.

4.1 CO_2-Water-Rock Chemistry

There is a growing body of research focussing on CO_2-water-rock interactions with respect to CO_2 storage. Research encompasses modelling, laboratory, and field experiments with the focus of the experimental research split broadly between porosity-permeability effects (e.g. Lu et al., 2011; Pearce et al., 1996; Shiraki & Dunn, 2000; Pudlo et al., 2012; Wandrey et al., 2011; Rosenbauer et al., 2005; Kaszuba et al., 2005); general fluid-mineral interactions (e.g. Huq et al., 2012; Gupta et al., 2000; Kaszuba et al., 2003; Wigand et al., 2008); and environmental impacts (e.g. Little & Jackson, 2010; Smyth et al., 2009; Lu et al., 2010; Kharaka et al., 2006; Peter et al., 2012; Kharaka et al., 2010; Trautz et al., 2012).

It is commonly understood that when CO_2 gas dissolves in water, it lowers pH by the formation of a weak acid, carbonic acid (H_2CO_3), and its subsequent dissociation to bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, which releases protons (H^+), Equations (1-3).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{1}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{2}$$

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

Lowered pH enhances the dissolution of rock-forming minerals in the presence of water, as protons substitute for metal cations in the mineral structure. The interaction of dissolved CO_2 in water with common mineral groups such as carbonates and feldspars can be generalised by Equations (4) and (5), and represent the common chemical weathering process of rocks on the Earth's surface.

Carbonate dissolution:

$$CaMg(CO_3)_2 + 2H_2CO_3 \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \tag{4}$$
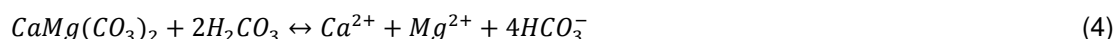
Potassium feldspar dissolution:

$$2KAlSi_3O_8 + 2H_2CO_3 + 9H_2O \leftrightarrow 2K^+ + Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2HCO_3^- \tag{5}$$
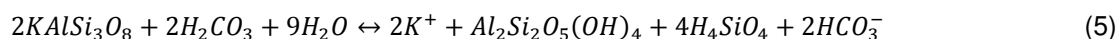
The effect of mineral dissolution is to release metal cations (e.g. calcium and potassium) into solution, thereby increasing total dissolved solids (TDS), and to increase alkalinity, and increase pH (mineral buffering).

Alkalinity, defined for the purposes of this report as carbonate alkalinity i.e. [HCO_3^-] + 2[CO_3^{2-}], is dominated by bicarbonate concentrations in solutions below pH 8.3 (Langmuir, 1997). From Equations (4) and (5), carbonate mineral dissolution generates twice the bicarbonate as feldspars, for the same amount of carbonic acid.

Other sources of metal release into solution may be from desorption of metal ions adsorbed onto the surface of clay minerals or metal oxides, with clays being particularly important in this process due to their large surface areas (Langmuir, 1997); or degradation under oxidising conditions of organic matter which has complexed or bioaccumulated metals (Tessier et al.,

1979). Desorption from minerals and breakdown of organic matter may influence concentrations of dissolved heavy metal species such as mercury and lead, which would otherwise remain unidentified in the mineral assemblage of a rock.

While experimental work has been carried out under a wide variety of temperature, pressure, time, and pore fluid conditions, the main conclusions of experimental and modelling work with CO_2-enriched environments are broadly similar:

- **pH decreases rapidly followed by an increase due to mineral buffering**
- **An increase in total inorganic carbon (TIC), largely in the form of HCO_3^-**
- **Concentrations of cations, both major and trace, initially increase with an observed or calculated dissolution of a variety of minerals e.g. quartz, feldspars, anhydrite, calcite and dolomite**
- **Cation concentrations often level off or decrease with time, with observed or calculated precipitation of minerals e.g. dolomite, calcite, siderite and clays**
- **Brine desiccation by sc-CO_2, leading to additional mineral precipitation**

Researchers looking at the effect of mineral dissolution/precipitation note that often porosity increases with dissolution of silicates and carbonates, but permeability decreases due to the concomitant precipitation of clays (illite and smectite) in pore throats (Shiraki & Dunn, 2000; Lu et al., 2011).

4.2 Environmental Research

Research to-date with regard to environmental impacts have been concerned with the effects of CO_2 leakage from underground storage and its potential subsequent migration to shallow, potable groundwaters. As determined by the theoretical chemistry, and observations highlighted above, CO_2 could potentially lower pH and increase total dissolved solids in the form of trace heavy metals. The literature focusses on considering the theoretical effect of polluting drinking or surface waters, and is therefore a concern to those countries considering onshore storage, where shallow drinking water aquifers are located.

Onshore CO_2 storage received some bad press in 2010 when concerns were raised by a study carried out by Mark Little and Robert Jackson (2010), which concluded that leakage of CO_2 from a sequestration/storage site would decrease groundwater pH, and increase concentrations of heavy metals in freshwater drinking aquifers to beyond safe drinking limits in the USA. The Ecologist headline "*Carbon capture and storage could contaminate drinking water*" (Levitt, 2010) highlighted the problem set out in their paper.

Little & Jackson (2010) weighted their assessment to indicate unilaterally that contamination of drinking water aquifers in the USA would occur from CO_2 leakage from a storage site. The authors failed to sufficiently highlight that the aquifers from which soils were used in their batch laboratory study already bore waters which were elevated above the United States Environmental Protection Agency's (USEPA) Maximum Concentration Levels (MCL) (Little & Jackson, 2010).

Little and Jackson (2010) also placed prominence on those metals which did increase in concentrations, relative to their control, and largely ignored that in many cases, concentrations were actually lower by the end of the experiment. The authors concluded that more work was necessary to establish which indicators (i.e. pH, specific metals) were likely indicators of CO_2 leakage into a freshwater system. .

4.3 Batch Reaction Studies

Lu et al. (2010) and Smyth et al. (2009) document a laboratory batch experiment where aquifer samples from the USA Gulf Coast were submersed in a weak saline solution and subjected to an argon gas flush for two weeks, followed by CO_2 gas flow for a further two weeks. Water samples were collected on hourly, then daily intervals following changes in gas type, and the samples analysed for thirty-three cations and pH.

The results of their analysis showed a significant and rapid drop in water pH upon CO_2 flow, but which quickly rose (albeit to a lower level than originally) and remained constant for the remainder of the experiment.

Cation concentrations reacted in two broad ways: significant increases in concentration with CO_2 flow but then became constant; and those which increased initially but then declined. pH was linked to reaction rates, showing that as pH increased due to mineral buffering, cation release rates decreased, an observation not considered by Little and Jackson (2010).

Lu et al. (2009) and Smyth et al. (2009) also noted that minor mineral components of their samples had a major influence on cation concentrations and pH buffering, specifically the presence of carbonates. The authors were also careful in noting that the products of the experimental reactions were unrealistic compared to a real-world CO_2 leak, and that the products would be location specific.

4.4 Field Studies

While laboratory batch experiments are useful tools for assessing the effect of gaseous CO_2 on samples, they are limited by the fact that they are simulations only of reservoir or aquifer conditions. Work carried out in-situ at field scale provide the best data on a specific site basis, however this can be a costly exercise; impossibly so in the UK North Sea context, since the offshore drilling of a test well would cost in the tens of millions of pounds.

A number of field-based studies have now been carried out. One such study was that undertaken by Kharaka et al. (2006) where supercritical CO_2 was injected at a depth of around 1,500 m into the Frio Formation, Texas, and water samples collected from an observation well some 30 m laterally up dip of the injection point. A novel sample retrieval system was utilised to maintain pressure in the sampling vessel as it was brought to the surface, to minimise degassing of CO_2 and subsequent changes in chemistry (Freifeld, 2005).

Samples were analysed for pH, alkalinity and number of metal cations over a four month injection and sampling period. On CO_2 breakthrough at the monitoring well, pH declined and alkalinity increased. Both changes occured rapidly.

Concentrations of dissolved metals also increased, from the dissolution of calcite and oxyhydroxides (Kharaka et al., 2006). However, samples collected between 20 days and 6 months after CO_2 injection showed that pH has risen and metal concentrations had returned back to pre-injection levels, indicating mineral buffering of pH as well as potential precipitation of carbonate minerals had occured.

The effect of CO_2 leakage on shallow groundwater (<60m depth) has been investigated in the field by a number of other studies. Peter et al. (2012), Kharaka et al. (2010), and Trautz et al., (2012), investigating sands in Germany and the USA found that, as would now be expected, pH declines with an increase in TIC and dissolved metals. Crucially, however, in contrast to the results highlighted by Little and Jackson (2010) these studies found that although metal concentrations increased, they still remained below the USEPA MCL's.

Indeed, assessment of natural and industrial analogues for CO_2 leakage and their effects by Lewicki et al. (2006) concluded that, despite changes to groundwater chemistry from CO_2 leakage, in many cases aquifer waters can remain safe to drink.

4.5 UK North Sea Environmental Issues

The research on CO_2-water-rock interactions with regard to environmental issues has so far focussed on potable waters and potential risks to human health. There may, however, be potential environmental effects of waters produced to the surface during CO_2-EOR operations in the UK North Sea.

During CO_2-EOR operations, saline formation fluids will become CO_2-enriched, which can lead to a drop in pH and a subsequent increase in dissolved major and trace element concentrations. Therefore, there is potential for increased concentrations of potentially toxic trace metals to be released to the environment (the sea) via produced waters during CO_2-

EOR.

4.6 Priority Trace Elements

The oil and gas industry are required under certain permit conditions to bi-annually report concentrations in produced water of the following eight metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc.

All eight metals are List 1 and 2 metals under EC Directive 2006/11/EC and therefore are considered to have a negative impact on both marine life and the human populations who feed on it. Typical background concentrations in uncontaminated seawater are given in Table 5.

Table 5. Background seawater concentrations of select trace metals in uncontaminated seawater.

Metal	Background Seawater Concentration Range (µg/L)	Source
Arsenic	1 – 3	Neff (1997)
Cadmium	0.004 – 0.080	Beiras et al. (2003); Ferreira et al. (2004); Laslett (1995); Ray (1986)
Chromium	0.5	Mearns et al. (1976)
Copper	0.11 – 1.50	Balls (1985); Beiras et al. (2003); Laslett (1995)
Lead	0.013 – 0.500	Balls (1985); Beiras et al. (2003); Laslett (1995)
Mercury	0.002 – 3	Klein & Goldberg (1970); Matsunaga et al. (1979)
Nickel	0.1 – 20	Beiras et al. (2003); Laslett (1995); Preston et al. (1972)
Zinc	0.01 – 2.2	Bruland et al. (1978); Laslett (1995)

While some of these metals are micronutrients, for example copper and zinc (Vanegas et al., 1997), they have also been demonstrated in a significant amount of literature to be toxic to marine vertebrates and invertebrates, for example: reduced growth and reproduction, and increased mortality rates (Eisler & Hennekey, 1977; Florence et al., 1994; Mearns et al., 1976; Neff, 1997); respiratory problems (Engel & Fowler, 1979; Taylor et al., 1985); skin discolouration, unusual behaviours and balance problems in fish (Taylor et al., 1985); and increased disease susceptibility (Pipe et al., 1999).

Generally marine invertebrates are more sensitive than marine vertebrates, possibly by one to two orders of magnitude (Taylor et al., 1985), with the sensitivity of vertebrates to the eight listed metals in the general order:

$$Hg^{2+} > Cr^{6+} > Cu^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} = As^{3+} \gg Ni^{2+}$$
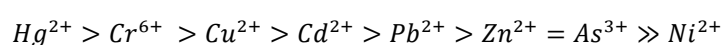
(adapted from Eisler & Hennekey (1977) & Taylor et al. (1985))

This order is not fixed, though, and depends on the species of the affected biota, for example

crustaceans display a higher sensitivity to zinc, while polychaete annelids (worms) are more sensitive to Cr^{6+} (Eisler & Hennekey, 1977; Guthrie et al., 1979). However, mercury is widely agreed as the most toxic and nickel as the least of these metals.

The toxicity of an element varies depending on the speciation of that particular element. Notably, arsenic can have any of four valence states (-III, 0, III, V) (D. J. H. Phillips, 1990) and therefore can speciate into As^{3-}, As, As^{3+} and As^{5+}, forming both inorganic and organic compounds. Organic forms of arsenic are not generally toxic to marine life (Francesconi & Edmonds, 1996).

Elemental arsenic (As) is rare, while As^{3-} is found only in highly reducing (anoxic) environments (Neff, 1997). Arsenite (As^{3+}) and arsenate (As^{5+}) are then the dominant inorganic forms of the element in the marine environment (Fattorini et al., 2004; Neff, 1997; D. J. H. Phillips, 1990), with arsenite being more bioavailable than arsenate and so is more toxic.

Concentrations of As^{3+} with negative biological effects, such as reduced growth, reproduction and mortality in micro- and macroalgae range from 13 – 1,000 µg/L, while larger marine animals such as scallops, crabs and shrimp can tolerate up to 25,000 µg/L (Neff, 1997). Their tolerance appears to be related to the ability to convert toxic inorganic arsenic to non-toxic organic forms within their tissues (Fattorini et al., 2004).

Chromium has two valencies: Cr^{3+} and Cr^{6+}. Cr^{3+} is fairly insoluble, while Cr^{6+} is very soluble and so the latter is responsible for most toxic effects in the aquatic environment (Mearns et al., 1976; Taylor et al., 1985). Cr^{6+} affects brood size and reproduction in benthic organisms at 10^{-5} g/L, with lethal effects in the ranges of $10^{-2} – 10^{-1}$ g/L for fish, and $10^{-5} – 10^{-3}$ g/L for invertebrates (Mearns et al., 1976).

While the bioavailability of some elements depends on their speciation, the toxicity of other metals such as cadmium and copper is dependent on whether it exists as a free metal ion (e.g. Cd^{2+} or Cu^{2+}) or bound to anionic species (e.g. chloride, Cl^-). Therefore the total dissolved cadmium or copper concentrations may not simply be an indication of toxicity.

Engel & Fowler (1979) found that free ion concentration of cadmium decreased with salinity, due to complexation with chloride, and that the toxicity of cadmium on the grass shrimp *Palaemonetes pugio* was inversely proportional to salinity i.e. as salinity increased, toxicity decreased (also Phillips (1976) & Ray (1986)). Engel & Fowler (1979) also found that respiratory function of oysters was inhibited at dissolved cadmium concentrations of 300-600 µg/L at seawater chloride concentrations. Copper concentrations in the order of 10^{-5} g/L resulted in a toxic response from the *Mytilus edulis* mussel (Pipe et al., 1999).

Lead uptake was likewise found by Phillips (1976) to decrease with increasing salinity, possibly due to decreased filtration (feeding) rates or lowered solubility of lead in salt waters (Taylor et al., 1985), while zinc toxicity increases with decreased salinity (Eisler & Hennekey, 1977).

Observed bioaccumulation factors ($conc^n$. in organism ÷ $conc^n$. in environment) of cadmium were given by Ray (1986) as:

- **Plankton** 10^4
- **Seaweed** $10^2 – 10^3$
- **Mollusc** $10^3 – 10^4$
- **Crustacean** 10^3
- **Fish** 10^2

The bioaccumulation factor for chromium in phytoplankton has been observed to be lower than cadmium, in the order of 10^2, with this being larger than higher trophic marine organisms (Mearns et al., 1976). Mercury bioaccumulation is larger than cadmium, in the order of $10^3 – 10^4$ for marine fish, with strong enrichment in algae too (Klein & Goldberg, 1970).

There is, then, a high storage capacity for cadmium and mercury in marine organisms, likely linked to 'metallothionein' proteins which act as a detoxifying guard against essential and non-essential trace elements. Metals bound to this protein are not available to the rest of the organisms functions (Ray, 1986) although they may reach saturation and cause mortality, as noted by the Engel & Fowler (1979) experiments.

The uptake of metals, and therefore potential toxicity, can also vary depending on other conditions. Examples include: exposure to other trace elements, which can modify uptake (Ray, 1986); increased temperature, which increases metabolic rate and so increases uptake in organisms (Eisler & Hennekey, 1977; Ray, 1986); seasonal variations (Blossom, 2006; D. J. H. Phillips, 1990; Ray, 1986); water column depth and the impact of freshwater inputs increasing concentrations of trace elements in shallow waters (Bruland et al., 1978; D. J. H. Phillips, 1976); and body size. However there is often no apparent universal trends, which would indicate species specific responses (D. J. H. Phillips, 1976; Ray, 1986).

While metals may not induce toxicity directly in marine organisms, the biomagnification of these trace elements up the food chain is of consequence to human diets, for instance cadmium, lead and mercury (Guthrie et al., 1979; Neff, 1997; Ray, 1986; Renzon et al., 1998; Yamamoto et al., 1994) are of particular concern. ^{210}Pb (lead) is the final product on the ^{238}U decay series and may account for 8% of internal radiation dose in humans consuming seafood (Yamamoto et al., 1994).

Inorganic mercury undergoes methylation in the aquatic environment to form methyl mercury, which is easily absorbed in organisms and enriches up the food chain (Renzoni et al., 1998). The severe toxicity of bioaccumulated mercury to human populations was discovered in the 1960's when the Japanese communities of Minimata Bay suffered neurological disorders due to the disposal of mercury waste in the bay (Klein & Goldberg, 1970).

4.7 Conclusions

Trace elements can negatively impact a variety of organisms spanning the entire food chain, depending on the concentrations of the element encountered. The exact nature of the impact may vary by organism and element, however the general effect is to potentially negatively impact marine (and human) populations.

It is possible, for CO_2-EOR operations to leach greater concentrations of potentially toxic trace elements from North Sea reservoirs, which could increase the risk of negative environmental impact with respect to existing oil and gas operations.

Experimental work by other researchers has shown that trace element concentrations increase under enhanced CO_2 conditions in formation waters, with respect to normal conditions, although little research has been undertaken on North Sea reservoir rocks. Section 6 details batch experiments undertaken for the purposes of this report, which aimed to determine concentrations of trace elements leachable from a target North Sea CO_2-EOR reservoir.

5 Scale and Radioactive Scale

The fouling of oil and gas production equipment with mineral precipitates is a common industry problem, which may be enhanced by CO_2-EOR. The CO_2-enhanced mobilisation of major elements, which may also be radioactive, could increase the risk of radioactive scales forming, with an associated increase in risk with respect to current oil and gas operations.

5.1 Formation of Scale

Scale is the formation of, primarily, sulphate and carbonate minerals within oil and gas reservoirs, wells and topside production equipment in response to changes in fluid chemistry during production. The most common scaling minerals (Haarberg et al., 1992) are:

- **Calcium carbonate/calcite ($CaCO_3$)**
- **Calcium sulphate ($CaSO_4$)**
- **Gypsum ($CaSO_4.H_2O$)**
- **Strontium sulphate ($SrSO_4$)**
- **Barium sulphate/barite ($BaSO_4$)**

Changes in fluid chemistry occur due to activities associated with the extraction of oil and gas, including co-production of water and oil, water injection, and EOR activities (Smith, 1987) (Haarberg et al., 1992). The solubility of pairs of ionic species (e.g. barium and sulphate) depends on temperature, pressure, pH, and ionic strength; if changes in these conditions, such as increased salinity, causes the solubility product to be exceeded, precipitation occurs.

Sulphate (SO_4^{2-}) scales of barium (Ba), strontium (Sr) and calcium (Ca) occur mostly downhole (Waldram, 1988), largely as the result of mixing sulphate-rich seawater with Ba-, Sr- and Ca-rich formation waters (Wright et al., 2008). Barite is particularly insoluble (U.S. Geological Survey, 1999) and therefore readily precipitates, particularly in the reservoir (Haarberg et al., 1992). Figure7 shows typical scaling responses to injected seawater, although actual masses will vary depending on reservoir conditions (McCartney & Burgos, 2010).
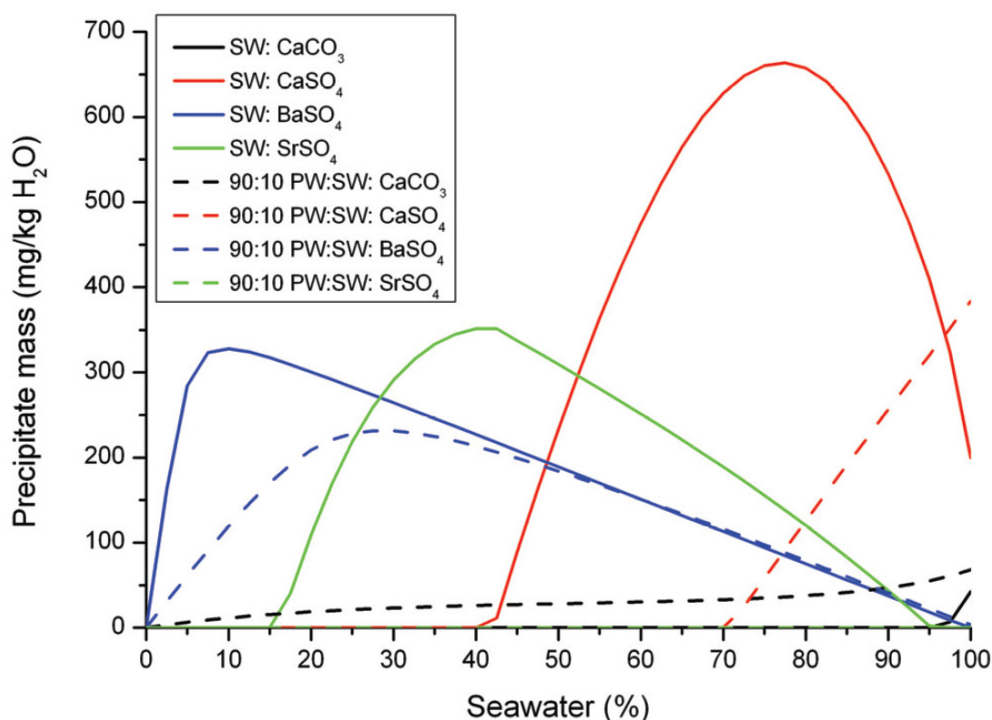
Figure 7. Precipitate (scale) masses calculated by McCartney & Burgos (2010) for injected seawater (solid lines) and 90:10 produced water:seawater injected mix (dashed lines).

Barite scale may, however, be limited if the reservoir temperature is greater than approximately 130°C. At this temperature, dolomite ($CaMgCO_3$) and calcium sulphate may be precipitated from dissolved magnesium (Mg) and sulphate, and dissolution of calcite (Wright et al., 2008; McCartney & Burgos, 2010).

Carbonate (CO_3^{2-}) scales of calcium and magnesium, on the other hand, form mostly on topside equipment due to changes in pH and temperature (Waldram, 1988), and are largely formed from the dissolution of carbonates and feldspars in the reservoir (Smith et al., 1991).

Scale reduces porosity and permeability in-situ of the producing formation, and/or clogs production equipment topside, with a resulting loss of production (Haarberg et al., 1992). The scaling issue has long been known to the oil and gas industry and measures to counter its formation are routinely adopted, for example by using chemical scale inhibitors. The inhibitors chosen must not only be effective in combating the particular types of scale which would be encountered at a production site, but also be "environmentally acceptable" (McCartney & Burgos, 2010).

5.2 Radioactive Scale

The main radioelements in sedimentary rock are potassium (K), uranium (U) and thorium (Th). Uranium and thorium both decay to radium (Ra) by alpha and beta emissions:

- ^{238}U → ^{226}Ra (half life = 1,600 years)
- ^{232}Th → ^{228}Ra (half life = 5.8 years)
- ^{232}Th → ^{224}Ra (half life = 3.7 days)

Radium then decays to radon (Rn) by alpha emission:

- ^{226}Ra → ^{222}Rn (half life = 3.8 days)
- ^{224}Ra → ^{220}Rn (half life = 55.6 seconds)

The products of these decay series are classed as naturally occurring radioactive materials (NORM), Chapter 1. Radium is a Group IIA element in the periodic table, along with barium, calcium and strontium and so behaves chemically in a similar way (Smith, 1987). Radium therefore can become incorporated into scales of barium, strontium and calcium (Reed et al., 1991) with barite scale as the primary host of NORM (U.S. Geological Survey, 1999).

Uranium can also replace calcium in calcite, while thorium does not enter the carbonate crystal lattice as easily and is therefore more commonly found in shales and heavy minerals (Smith, 1987). Uranium and thorium isotope concentrations, however, are less than 1% of radon concentrations present in North Sea reservoirs, and so is not considered a particular hazard (Reed et al., 1991). Radium release to water from barite dissolution is very low, particularly in oxidized environments, since barite is very insoluble (U.S. Geological Survey, 1999).

^{226}Ra and ^{228}Ra concentrations are influenced by how much uranium and thorium is in contact with water in the subsurface (U.S. Geological Survey, 1999). Radium is the most soluble of the long-lived heavy radionuclides, particularly in chloride-rich (formation water) compared with sulphate-rich (sea) water. This means that as fields mature and water injection increases, more radium will be incorporated into scales (Waldram, 1988; Moatar et al., 2010).

Radioactive scale was first found on North Sea production equipment around 1981. In the Northern North Sea, the source of radioactive elements is from the radioactive ("hot shale") Kimmeridge clay oil source rock, where radium is leached from uranium-bearing uraninite minerals. In the Southern North Sea, radon gas is most likely released from Carboniferous coal and marine shales (Smith, 1987).

5.3 Environmental Challenges of Radioactive Scale

Scales formed from barium, strontium and calcium have the potential to be radioactive, referred to as TENORM (Technologically Enhanced NORM) (Moatar et al., 2010), from the incorporation of radium. While not an environmental issue if scales are formed in the

subsurface, surface formation of radioactive scales or sludges/sands may pose an environmental risk.

Radon gas decay products become attached to aerosols in natural gas e.g. during Southern North Sea production however particulates less than 1 micron in size, representing by number the majority of aerosols in natural gas, are scrubbed prior to supply to the grid (Smith, 1987), preventing exposure to the public.

Exposure risk is above average for facilities workers in the oil and gas industry (Smith, 1987; Waldram, 1988). Workers can be at risk of exposure from:

- **External sources – hard scale or sludges**
- **Internal sources – inhaled or ingested dust/particulates**

Working adjacent to pipes, fittings and equipment fouled with radioactive scales may put workers at risk to external sources, while cleaning or scouring of fouled equipment may provide internal sources. External risk is generally low, due to the low amounts of uranium, thorium and radium actually incorporated in scales, however the internal hazard to organs is much greater (Waldram, 1988).

The specific activity (SA) of scales is measured as the amount of radioactivity (Bequerels, Bq) per gram of scale, and SA varies proportionally with incorporated barium and thorium. Hard scale may contain ^{226}Ra concentrations of around 10 ppb, with an SA of 100-1000 Bq/g, whereas sands/sludges may have a lower SA – in the order of 5-50 Bq/g – but have a larger volume to dispose of.

Disposal of radioactive wastes is governed by license from DECC, as highlighted in Chapter 1. Low level radioactive sludges can be disposed of at sea, since sea water already contains many radioactive elements (Smith, 1987). Hard scaled equipment would need decontaminating onshore.

The use of CO_2 for EOR is, likewise, an established technique particularly in the USA. CO_2 can affect the efficiency of scale inhibitors due to the effect of lowering pH, however inhibitors are now capable of working efficiently even under reduced pH conditions. The other effect of CO_2 is to potentially mobilise more trace metals into produced waters, which would include radioactive elements associated with common scaling species, e.g. radium and uranium associated with barium and strontium. This would be a particular challenge in the UK North Sea, with the source rock for Central and Northern North Sea oil fields being the Kimmeridge Clay – a known naturally radioactive shale.

5.4 Relevance to CO_2-EOR

As discussed in Section 4, CO_2 dissolution in formation waters can:

- **Lower pH**
- **Increase bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions**
- **Dissolve minerals, increasing dissolved ionic species**

Depending on the reservoir that CO_2 is being injected into, minerals such as calcite, dolomite and feldspars may dissolve to release barium, calcium and magnesium into solution (Smith et al., 1991; Shuler, Freitas, & Bowker, 1991). These are key sources of anions for scale formation. This can be a particular problem for CO_2-EOR, if CO_2 is injected at pressures below oil miscibility, enhancing its dissolution in the formation waters. The effect of this could be to enhance dissolved ionic species, therefore on return to the surface, and with an associated drop in pressure, enhanced scaling could occur (Smith et al., 1991; Shuler et al., 1991). Calcium carbonate scaling, in particular, of production equipment could be enhanced with CO_2-EOR activities, depending on the chemistry of the reservoir.

However, in the North Sea, it is likely that CO_2 will be injected at pressures above or near minimum oil miscibility which will dissolve the CO_2 in the oil. This leaves less CO_2 to dissolve in the formation waters, potentially reducing the effect of enhancing mobilisation of scaling minerals.

Lowering of pH due to the formation of carbonic acid also reduces the effectiveness of scale

inhibitors, leading to the formation of scales which had previously been under control (e.g. barite), while calcium carbonate scaling will be reduced in the reservoir as it is more acid soluble (Chesnut et al., 1987; Ramsey & Cenegy, 1985).

The use of CO_2 as an EOR method in the North Sea, particularly in mature fields, may lead to enhanced scaling problems. In turn, additional radioactive waste may be generated. The prior characterisation and modelling of a target reservoir would indicate scaling tendencies, combined with the selection of environmentally acceptable scaling inhibitors would, however, likely result only in operational and environmental problems similar to those which currently exist in the oil and gas industry.

5.5 Conclusions

If mobilisation of major elements is enhanced with CO_2-EOR, then there may be an environmental risk. Section 6 outlines the results of the batch experiments undertaken for this report, which include concentrations of barium, calcium and carbonate during the experiment.

However, even if concentrations of major elements such as barium are enhanced with CO_2-EOR, the regulations are already in place to prohibit emissions of radioactive material to the marine environment (Radioactive Substances Act 1993). Scale inhibitors would likely also be used to reduce fouling, as is current industry practice. Therefore, while enhanced scaling may present an enhanced waste management or technical problems, the increase in environmental impact incrementally above the oil and gas industry is likely to be negligible.

6 CO₂-Water-Rock Batch Reaction Experiment

Experimental work was carried out as part of the Work Package in an attempt to determine trace element concentrations which could be mobilised into saline solution from North Sea reservoir rock samples under enhanced dissolved CO_2 conditions. The experiment aimed to deduce whether these concentrations differed significantly from the controls, which were reacted with only atmospheric CO_2 diffusion into solution, and also to compare concentrations of liberated elements with produced water concentrations for currently operating oil and gas fields.

If concentrations of trace elements under enhanced dissolved CO_2 – representing CO_2-EOR conditions – are within the range of those in UKCS produced waters, then it may be considered that mobilised trace metal concentrations for the target CO_2-EOR reservoir would not present an environmental risk which is greater than existing oil and gas operations.

6.1 Experiment Methodology

Materials Preparation

Two core samples, supplied by Kirk Petrophysics and named "8518" and "8579" were cut into blocks with a rock saw, and the centre pieces of each core set aside for the experiment. Each centre piece was lightly disaggregated with a mortar and pestle for use in the batch experiments. The centre of the cores were anticipated to be less affected by drilling muds, which may have affected the batch experiment results, in particular barium (Ba) concentrations. Pieces of the remaining core were set aside for thin sections, XRD and XRF analysis. Samples were both determined from olfactory evidence to contain hydrocarbons.

The formation water salinity of the field from which the core were obtained was not supplied at the time of the experiment, therefore an estimate was taken of salinity from nearby fields of the same geological age. Salinity was calculated to be approximately 80,000 ppm sodium chloride (NaCl) equivalent (field data supplied at a later date gave an average salinity of 81,200 ppm). The field formation water chemistry was also not supplied prior to undertaking the experiments, therefore the saline solution used was a simple NaCl only. Given that other major ions (e.g. magnesium, potassium, calcium) were not included then the solution used is effectively out of equilibrium with the rock samples, which could have the effect of enhancing cation mobility as the solution equilibrates with the rock.

Several batches of NaCl saline solutions were then made up for use during the batch experiments. The solutions used were made up from 80.00 ± 0.01 g of Fisherbrand 'SLR' grade NaCl solid reagent per 1,000 mL of 11 mΩ cm high purity water (from a Milli-Q water system) to give the required 80,000 ppm NaCl solution.

Experimental Setup

All glassware and sampling bottles were soaked overnight in 10% nitric acid, prior to being rinsed with distilled water and 11 mΩ cm deionised water. Glassware was wrapped in aluminium foil after drying until the experiment was set up.

The experiment was set up in a fume cupboard and comprised four 250 mL three-neck round-bottomed flasks, "F1" – "F4", which were each sat on glass fibre wool on a Fisherbrand 150 W heating mantle, 8. The flasks were fitted with a glass water cooled coil condenser and loosely fitted stopper to reduce evaporation, a thermometer, and either a hollow glass rod for gaseous CO_2 flow (F1 & F3), or a glass stopper (F2 & F4).

250 ml of 80,000 ppm NaCl solution was added to each flask and heated to approximately 80 ± 1°C for 3 days before the experiment commenced, to ensure a stabilised temperature.

Dry CO_2 gas was fed to flasks F1 and F3 from a BOC supplied vapour withdrawal CO_2 bottle with attached regulator, needle valve and flow meter through stainless steel piping and rubber tubing to the glass rods. PTFE tape at joints ensured a leak-free system until the point of delivery in the flasks. Flow was set lower than the lowest value on the flow meter scale (0.5

mL/min) as this still gave a regular stream of bubbles to the solutions and ensured most efficient use of the bottled gas.

Figure 8. CO_2 batch experimental setup. Flasks are F1-F4, left to right. Flasks F1 & F2 contain sample 8518; flasks F3 & F4 contain sample 8579.

Once solution temperatures had stabilised at approximately 80 ± 1 °C, the rock samples were added to the flasks in the configuration noted in Table 6. CO_2 bubbling was then commenced, and taken as the start of the experiment, Day 0.

The first fluid sampling and measurements were taken at 4 hrs, Day 0. The last sampling and measurements were taken at 500 hrs, Day 21, with the experiment ended at this time.

Table 6. Experimental configuration.

Batch Name	Sample	Bubbled CO_2
F1	8518	Yes
F2	8518	No
F3	8579	Yes
F4	8579	No

CO_2 Flow Issues

CO_2 flow to the flasks was not constant for the duration of the experiment. The CO_2 bottle emptied after four days and fourteen days, and salt precipitated in the tips of the glass rods used to inject CO_2, which restricted (but didn't halt) flow. A stainless steel needle was used to regularly clear the salt blockages.

pH & Redox Potential (ORP)

pH and ORP were measured on Days 0-9, 12, 14 & 21 with a Hanna HI9125 pH meter, calibrated with HI7007 (pH 7.01) and HI7004 (pH 4.01) buffer solutions and is accurate to ± 0.01 pH. From each batch container, 5 ml of water was removed to a clean vial and cooled in air to around 26-27 °C.

Samples were allowed to cool as pH is temperature dependent: the samples initially cooled very quickly from ~80 °C to around 26-27 °C. During this rapid cooling period, pH values were constantly changing and therefore a precise reading was impossible. However, during this time, any dissolved CO_2 may have degassed, potentially affecting results. Given that the experiments were undertaken at atmospheric pressure, this affect may not be detectable.

Alkalinity

Alkalinity was measured using a Palintest Photometer 7100, accurate to ± 5 mg/L. Measurements were taken by crushing a Palintest alkophot 'M' reagent tablet in 10 ml of sample water, immediately after removing from the batch flask. The photometer was calibrated with a blank before each test, which comprised 10 ml of 80,000 ppm NaCl solution. Bicarbonate $[HCO_3^-]$ (mg/L) and carbonate concentrations $[CO_3^{2-}]$ (mg/L) were recorded on Days 0-9, 12, 14 & 21.

Table 7. Summary of cation analysis carried out by ICP-MS.

Cation	ICP-MS Detection Limit (µg/L)	Analytical Uncertainty (± %)
Arsenic (As)	0.87	51
Barium (Ba)	0.02	13
Cadmium (Cd)	0.005	4
Calcium (Ca)	0.28	21
Chromium (Cr)	0.18	34
Copper (Cu)	0.13	9
Iron (Fe)	0.22	19
Lead (Pb)	0.02	25
Magnesium (Mg)	1.67	11
Manganese (Mn)	0.007	25
Mercury (Hg)	0.004	19
Nickel (Ni)	0.02	8
Potassium (K)	28.6	11
Zinc (Zn)	0.04	10

Cation Analysis

On Days 0-9, 12, 14 & 21, water was drawn from the batch containers to sample for cation (major and trace element) analysis. From each batch container, approximately 20 mL of sample was drawn by a disposable syringe and passed through a disposable 0.22 μm Millipore filter. The filtered sample was then allowed to cool and 19.6 mL transferred to a Teflon bottle and acidified with 2% (400 μl) of Aristar grade 69% nitric acid. The samples were then refrigerated until required for analysis.

The samples were analysed by ICP-MS using an Agilent 7500ce (with octopole reaction system), employing an rf forward power of 1540 W, reflected power of 1 W, argon gas flows of 0.82 l/min and 0.2 l/min for carrier and makeup flows, respectively, and nickel skimmer and sample cones, with a Micro mist nebuliser and peristaltic pump providing a solution uptake rate of approximately 1.2 ml/min.

The instrument was operated in spectrum multi-tune acquisition mode and three replicate runs per sample were employed.

Calibration was with a Merck multi-element standard (ICP Multi-element standard solution VI CertiPUR®) for all metals listed in **Error! Reference source not found.** except Hg which was calibrated a BDH 'SpectrosoL' 1000 ppm solution. Calibration was checked with Standard Reference Material® (SRM) 1643e. All experimental samples were diluted 100 times to ensure that the solution TDS did not exceed the ICP-MS working tolerance of 0.1% TDS. Concentrations reported by the instrument were multiplied by 100 to give the true concentrations.

Analytical uncertainties at two standard deviations (2σ) were in the range ± 4 – 51%, calculated from repeat analysis (n = 3) of SRM1643e. Hg is absent from SRM1643e, and is therefore taken as ± 19% based upon the mean of the other elements' uncertainties, Table 7.

The ICP-MS analytical detection limits were calculated and reported by the Agilent control software.

X-Ray Diffraction (XRD)

Small samples of 8518 and 8579 were heated overnight at 400°C to volatise off hydrocarbons prior to preparation for XRF and XRD; around 5% of mass was lost. The samples were prepared for XRD by grinding with an agate mortar and pestle, transferring to a plastic disk and bulk mineral analysis was carried out using a Bruker D8-Advance X-ray Diffractometer, employing a 2-theta (2θ) configuration, with X-rays generated by a Cu-anode X-ray tube operating at 40 kV, and a tube current of 40 mA.

Diffracted X-rays were detected using a Sol-X energy dispersive detector, scanning from 2° to 60° 2θ at a scan rate of 0.01°/second and the resultant diffractograms compared with the 2008 issue of the International Centre for Diffraction Data (ICDD) diffractogram database library using the EVA analysis package. The detection limit for crystalline phases is approximately 1 wt.%.

X-Ray Fluorescence (XRF)

XRF analysis was performed by a Philips PW2404 wavelength-dispersive, sequential X-Ray fluorescence spectrometer fitted with an Rh anode end-window X-Ray tube. For XRF analysis two different procedures were followed for major and trace element analyses.

For major element analysis, the samples were initially dried in an oven at 110°C for two hours. 1 g of dried sample was then weighed and Spectroflux® added in the ratio five parts Spectroflux® to one part sample. The sample and flux were then heated at 1100 °C for 20 minutes and the resulting molten mixture cast on a hotplate at around 220 °C and flattened with an aluminium plunger to form a glass disk for analysis.

For trace element analysis, a pressed-powder disk of sample was formed in a pressurised tungsten carbide mould at 8 tonnes pressure for 3 minutes.

Other General Comments

Following sampling and measurement for pH, ORP and alkalinity, these water samples were discarded to avoid contamination of the batches. Prepared 80,000 ppm saline solution was added back to the flasks to maintain 250 mL volume. The experimental concentrations for metals and alkalinity are corrected for this dilution.

6.2 Results

X-Ray Diffraction and X-Ray Fluorescence

The results of the X-ray diffraction analysis show that the two samples are comprised mainly of quartz, with some feldspar minerals (largely microcline and orthoclase), clays (illite dominates) and trace carbonate and sulphate minerals, Figure 9.
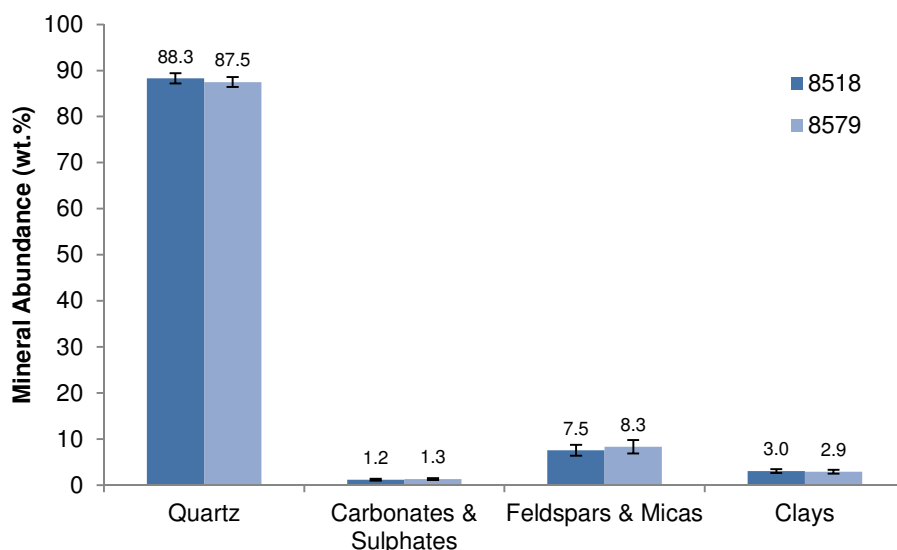
Figure 9. Results of XRD analysis for quartz and three combined mineral groups. Numbers above bars indicate percent value. Error bars are instrumental analytical error of 1 wt.%.

XRF analysis shows silicon dominates at 93.35 wt.% and 91.22 wt.% as SiO_2, samples 8518 and 8579, respectively (Table 8). Manganese was detected at very low weight percentage, and likewise zinc was not detected. Barium concentrations are high, possibly due to the presence of drilling mud (barite) deposits.

pH, Alkalinity and ORP

The results of pH and alkalinity readings taken over the 21 day period of the experiment are presented in Figures 10 and 11. ORP readings are presented in Appendix 1. The figures compare the readings taken from bubbled CO_2 and non-bubbled (atmospheric) CO_2 flasks, and for each of the samples 8518 and 8579.

pH values for sample 8518 show remarkable similarity between bubbled and atmospheric CO_2 for the duration of the experiment, with the exception of the final value taken on Day 21, Appendix 1. Average values range from around pH 5.4 at the start of the experiment, increasing to pH 6.5 – 6.9 for the majority of the experimental period, and decreasing slightly at the end.

Sample 8579 also displays a general increase in pH with time, with a slight difference between the bubbled CO_2 and atmospheric CO_2 flasks; the bubbled CO_2 flask has generally

lower pH values, and again both are showing a reduction in pH towards the end of the experiment, Figure 10, overleaf.

Table 8. Results of XRF analysis; major (weight % as oxides) and trace elements (ppm). As, Cd, Hg, Li & Zn not analysed for. "N.D." = Not Detected.

Element	8518 (wt. %)	8579 (wt. %)	8518 (ppm)	8579 (ppm)
Si	93.35	91.22		
Ba			2,529	1,256
Ca	0.40	0.25		
Cr			16.1	13.0
Cu			39.8	32.7
Fe	0.16	1.81		
K	1.24	1.68		
Mg	0.17	0.15		
Mn	N.D.	0.001		
Ni			0.8	1.8
Pb			4.8	7.4
Zn			N.D.	N.D.

The results of the pH readings indicate that mineral buffering is raising pH, according to the general reactions given in Equations (4) and (5), Section 4.1.

One limitation of the experiment is that since the experiments were undertaken at atmospheric pressure, CO_2 solubility is not as high as it would be at reservoir pressure, therefore pH cannot be reduced significantly to values of 4 – 5 pH seen in other work by researchers (e.g. Lu et al., 2010; Lu et al., 2011; Shiraki & Dunn, 2000; etc.), which might promote further trace element mobility.

Alkalinity, calculated as $[HCO_3^-] + 2[CO_3^{2-}]$, shows distinct differences between the bubbled CO_2 and atmospheric CO_2 batches, with a large increase in the bubbled CO_2 batches for both samples 8518 and 8579, Figure 11.

Alkalinity in the bubbled CO_2 batches tends to increase rapidly over the first 3 days or so, before levelling off in concentration in sample 8579, but decreasing in sample 8518, while the atmospheric CO_2 batches exhibit slower increases in alkalinity.

It is likely, therefore, that alkalinity in the sample 8518 bubbled CO_2 experiment is being consumed, possibly by the re-precipitation of minerals as pH rises.

ORP results, Appendix 1, are reasonably constant for sample 8518, and show little difference between bubbled and atmospheric CO_2 batches. Sample 8579 shows a slight trend in decreasing values, with redox potential generally lower in the bubbled CO_2 flasks, although there is large analytical error on some readings.

Sample 8579
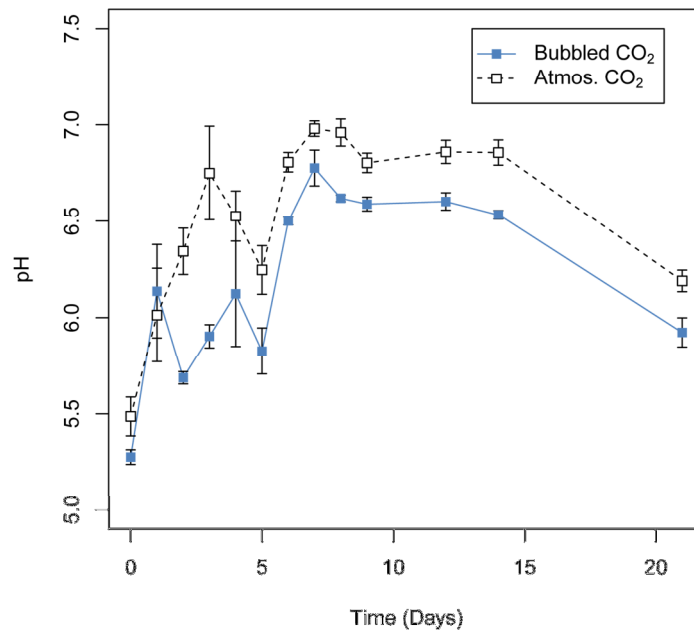
Figure 10. Results of pH measurements from batch reaction experiments. pH values are plotted as an average of three readings. Error bars calculated as one standard deviation of the readings.

The redox measurements confirm that the experiments were undertaken in oxidising conditions, which may not be representative of reservoir conditions if the reservoir fluids are anoxic (oxygen free). In this case, redox potential may be significantly reduced, affecting the solubility or mobility of trace elements depending on the mineral phases present.

Sample 8518   **Sample 8579**
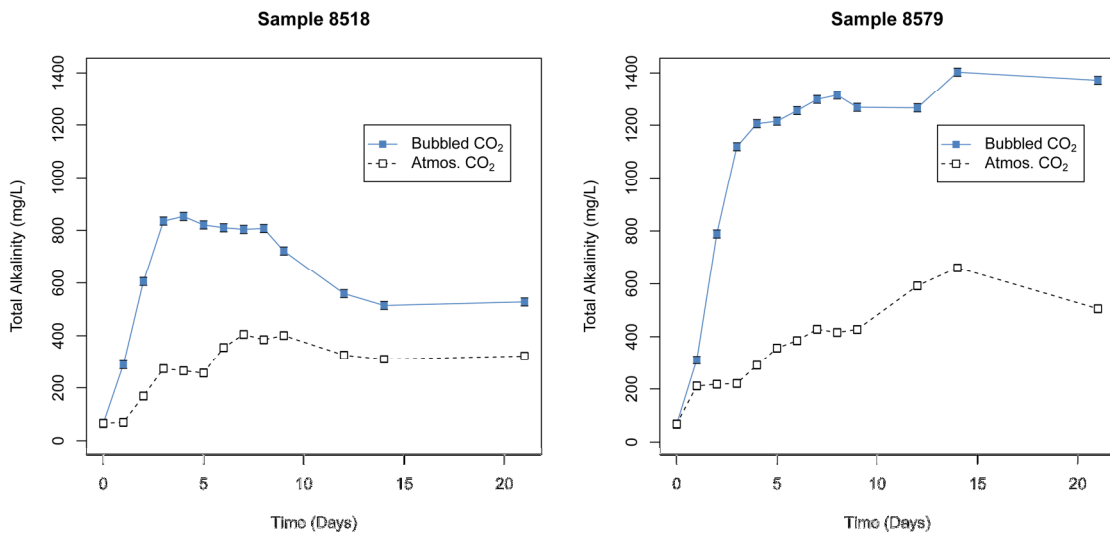
Figure 11. Total alkalinity (mg/L) calculated as $[HCO_3^-] + 2[CO_3^-]$, from batch reaction experiments. Error bars are ± 15 mg/L.

Cation Analysis – Major Elements

Calcium, iron, magnesium, and manganese exhibit similar trends with respect to concentrations through time for sample 8579. These metals rapidly increase in concentration with bubbled CO_2, before levelling off to concentrations significantly higher than the atmospheric CO_2 controls.

Magnesium and manganese concentrations for bubbled CO_2, sample 8518, rapidly increase, before tailing off again, in a similar fashion to potassium in all of the flasks, Appendix 1. However, concentrations of magnesium in the control for sample 8518 increase midway through the experiment and exceed the bubbled CO_2 batch, Figure 12.
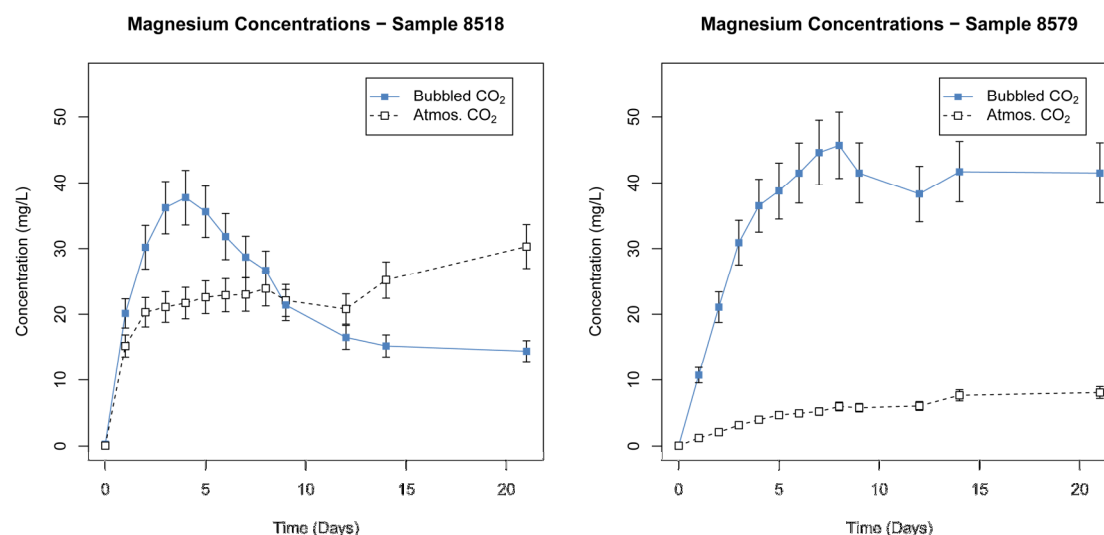
Figure 12. Mg concentrations with time for samples 8518 and 8579. Error bars are ± 11%.
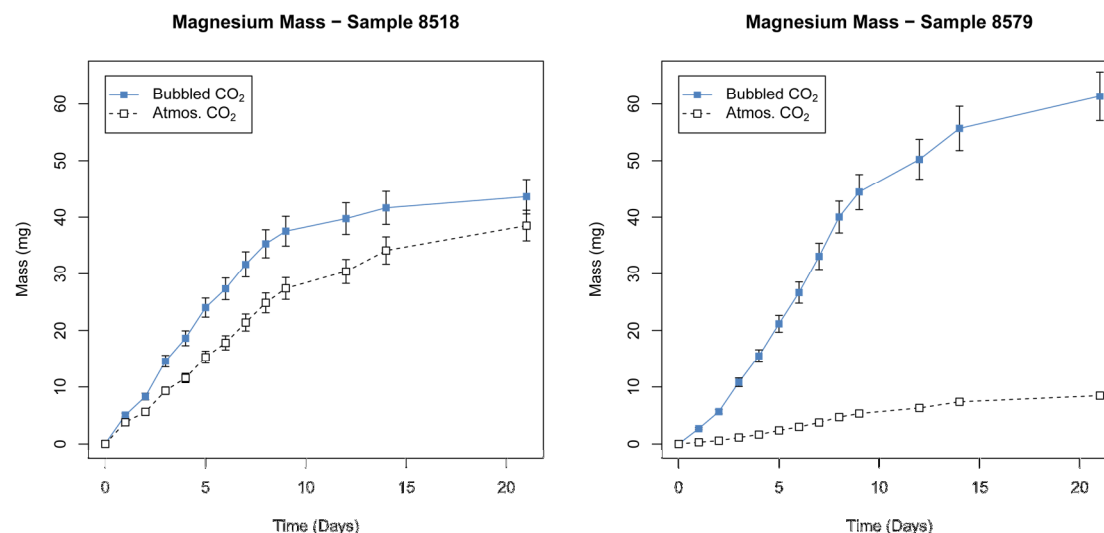
Figure 13. Mass calculation (mg) of released Mg from samples 8518 and 8579. Error bars are ± 7%.

Calculation of mass of magnesium released into solution shows that in sample 8518, the concentration of Mg is limited by the mass of magnesium in the sample. Figure 13 shows that leached mass of Mg with time is probably approaching saturation in all cases. CO_2 therefore

has a noticeable effect on the rate at which magnesium is released into solution, although not on the total mass if the experiments were allowed to proceed to saturation. Ca, Fe, K and Mn exhibit similar trends, Appendix 1.

Concentrations of released major elements are compared with data supplied for the target field in Table 9. Concentrations from the experiment are generally much lower than the field concentrations, and are unlikely to increase further, with the exception of barium. Calculations of dissolved masses of major elements, Appendix 1, show that experimental concentrations were limited within the duration of the experiment by the mass of mineral/element available for mobilisation.

Table 9. Major element produced water data for target CO_2-EOR field compared with experimental data.

Element	Field Concentration (max) (mg/L)	Experimental Concentration (max) (mg/L)
Ba	56	30.6
Ca	385	0.16
Fe	6.7	2.91
K	13,610	112
Li	15	0.53
Mg	94	23.8

Cation Analysis – Trace Elements

The trace elements analysed for by ICP-MS are the eight metals listed in Section 4.6: As, Cd, Cr, Cu, Hg, Ni, Pb & Zn. The full results are not included in the main text of this report; select examples will be used to illustrate a point, while the remaining data is presented in Appendix 1.

The analytical detection limits are given in Table 7; concentrations of arsenic and lead fell below the analytical detection limits of 0.87 µg/L and 0.015 µg/L, respectively, and as such there was no detectable difference between bubbled CO_2 and the controls for these elements.

Nickel and zinc show slight trends of increasing concentrations through the duration of the experiment, with nickel also displaying some overall enhancement of concentrations in the bubbled CO_2 batches, Figure14.

Obvious trends in concentrations were not discernible for the majority of the remaining five elements. The batches subjected to CO_2 bubbling do not consistently show trace element concentrations significantly increased with respect to the controls, however mercury (sample 8518) and chromium (both samples) do display some additional mobilisation with bubbled CO_2.

In some cases though, concentrations in the controls were elevated with respect to the bubbled CO_2 batches e.g. copper in sample 8579, Figure 15, cadmium (sample 8518) and mercury (sample 8579).

While concentrations may be enhanced with bubbled CO_2 in some cases, overall there appears to be little effect.

Mercury and chromium appear to be strongly mass limited, while the other trace elements were rate-limited during the experiment, Appendix 1.
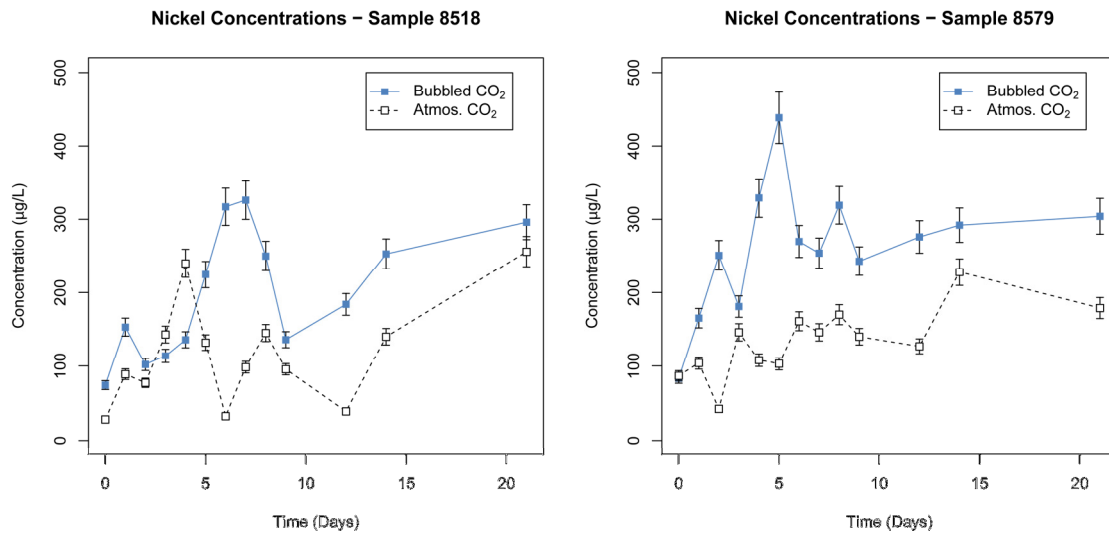
Figure 14. Ni concentrations (µg/L). Error bars are ± 8%.
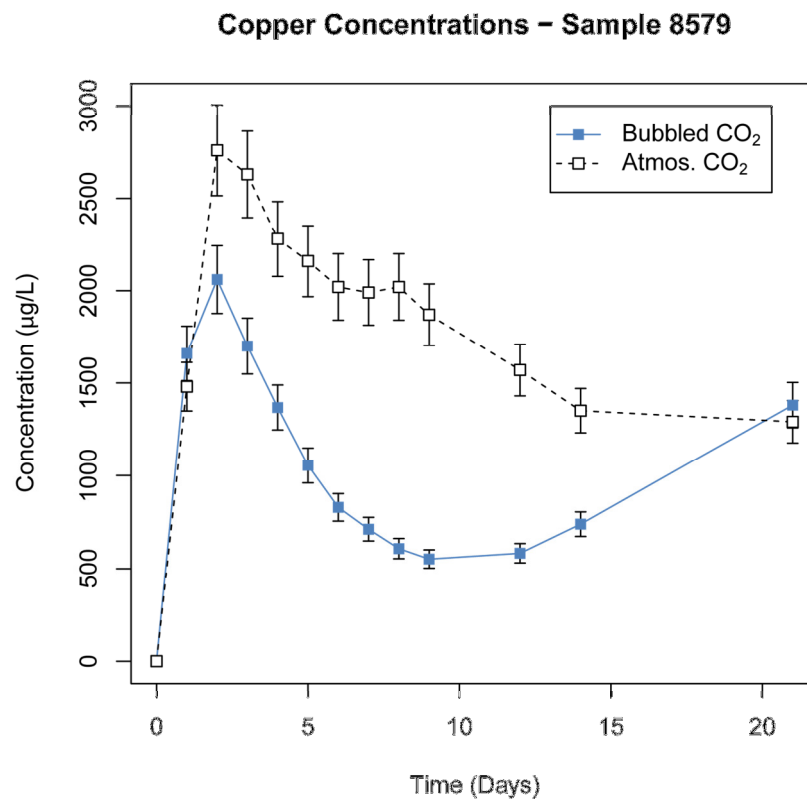
Figure 15. Cu concentrations (µg/L) showing enhanced concentrations in atmospheric CO_2 conditions with respect to bubbled CO_2 in sample 8579. Error bars are ± 9%.

Comparison With DECC Data

Under certain UKCS operator permit conditions, trace element concentrations in produced waters are reported to DECC on a bi-annual basis. This data is publicly available under the Environmental Emissions Monitoring System (EEMS). The range of concentrations reported by 75 production facilities from 2006 – 2011 are given below in Table 10, together with the range of concentrations generated by the experimental work for this report.

Table 10. Concentration ranges of trace elements for produced waters, reported to DECC, for the period 2006-2011 compared with experimental concentrations from this report.

Element	EEMS Range (µg/L)	Experimental Range (µg/L)
Arsenic	0.03 – 643	< 0.87
Cadmium	0.01 – 290	< 0.005 – 9.83
Chromium	0.03 – 420	< 0.176 – 74.5
Copper	0.02 – 4,845	< 0.127 – 2,790
Lead	0.02 – 31,000	< 0.015
Mercury	$2x10^{-5}$ – 3,700	< 0.004 – 21
Nickel	0.09 – 455	< 0.018 – 438
Zinc	0.24 – 135,000	16.4 – 2,471

Comparison between the experimental results and the EEMS data shows that the experimental results fall within the range of concentrations produced during normal oil and gas operations in the UK North Sea. Breaking the experimental data down into concentrations derived from bubbled CO_2 and atmospheric CO_2 shows that under enhanced CO_2 conditions, concentrations are not significantly higher than the controls and also fall within normal concentrations from North Sea operations, Appendix 2.

To highlight this, nickel concentrations from the experiments are compared with the EEMS North Sea data, Figure 16. While bubbled CO_2 concentrations from the experiment are slightly higher and concentrated at the top end of the range, compared with the atmospheric controls, they still fall within the normal range of North Sea produced waters.
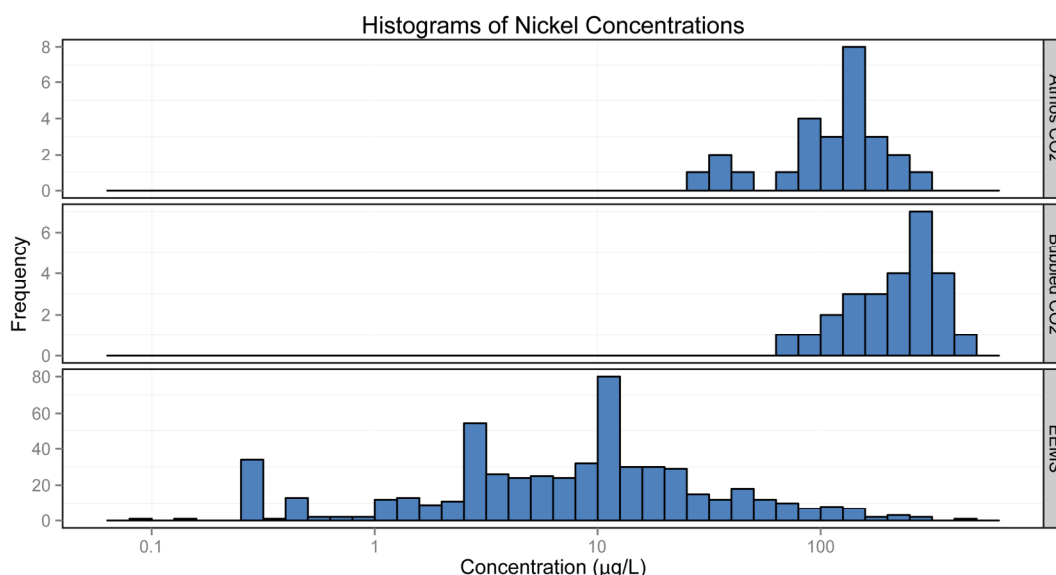
Figure 16. Histograms of nickel concentrations from experimental work ("Atmos CO2" and "Bubbled CO2") and the EEMS dataset. The experimental data includes both samples 8518 and 8579. Note the logarithmic scale for concentration.

6.3 Conclusions

Based on the experimental work undertaken for this report, concentrations of major elements are enhanced by the addition of CO_2 to saline fluids. Calculations of major element masses released during the experiment show that concentrations are likely to be limited by the mass of a particular mineral or element available for mobilisation, with the effect of CO_2 being to increase the rate at which that mass is released, rather than the total.

Trace element concentrations produced under enhanced CO_2 conditions, such as those in a target CO_2-EOR reservoir, are unlikely to deviate from existing produced water concentrations.

Considering the regulations for trace elements in produced waters, it would be unlikely that CO_2-EOR would present a significant additional environmental risk compared to current oil and gas activities.

However, it should be recognised that this represents only a single set of experimental data for one target field, and as such extrapolation to a wider industry could have a large uncertainty. The potential for a large increase in environmental risk is likely to remain low.

7 The Conceptual Risk Model

The preceding sections of this report have identified potential incremental environmental risks of CO_2-EOR projects, which are those risks which are unique to CO_2-EOR or a new risk in the context of offshore CO_2-EOR in the UKCS. The incremental risks are due to the potential release into the marine environment of:

- **CO_2**
- **CO_2 impurities**
- **Trace elements mobilised from geological storage**
- **Enhanced radioactive scale**

In order to assess the potential risk to the environment of these releases, a basic conceptual risk model can be built, as outlined in the following section.

7.1 Building the Conceptual Risk Model

The conceptual risk model in this report is an adapted risk matrix, which plots the *potential environmental impact* ranking of each identified release via a particular release pathway from **negligible → severe** against the *likelihood of that impact occurring*, ranked **negligible → frequent**. The plotted location of the release – and its pathway – on the model then determines the *potential risk* of that release: **negligible → high**. The potential environment impact rankings of a release are qualified in Table 11, below.

Table 11. Qualifications of potential environmental impacts as ranked in the conceptual risk model.

Potential Environmental Impact	Environmental Effect
Negligible	No perceivable effect
Low	Possible minor observed effects, but highly localised and/or species specific
Moderate	Common observed effects Reduced growth and reproduction Increase in mortality Enhanced concentrations in body fluids & tissues
Significant	High mortalities in sensitive species Species shift to more tolerant species Reduction in biodiversity Possible human health effects from seafood consumption
Severe	Ecosystem collapse Multiple species mortalities Severe human health effects from seafood consumption

Potential risks associated with each type of release will be variable; there could be a variation of impacts depending on circumstantial factors. The sources, pathways and receptors will all

vary from project to project and are therefore specific to: the EOR-targeted reservoir, emission location, emission duration, receiving waters and sediments, ecosystems, and season. A combination of factors will influence the potential impact of the components.

The model has been built, however, with a number of these variables in mind, namely the sources and pathways. Receptors are such a large group to model for the purposes of this report, therefore the conceptual risk model assumes the most vulnerable receptors.

Table 12. Components of the conceptual risk model, ranked and qualified based upon preceding sections' conclusions.

Risk	Description	Impact	Likelihood
CO_2 Leak (Pipe)	Leak due to pipeline failure direct to seawater	**Moderate** – dispersal of pH plume over short timescale, but possible temporary local effects	**Negligible** – pipeline failures uncommon and engineered to withstand expected operating conditions
CO_2 Leak (Well)	CO_2 escape via injection or abandoned well bore to seawater	**Low** – rapid dispersal of low pH plume	**Rare** – CO_2 required to escape >1km of cement in completed well, or navigate blowout measures in injection well
CO_2 Leak (Rock)	Diffuse release of CO_2 from reservoir through marine sediments to seawater	**Negligible** – pH changes insignificant	**Negligible** – containment of CO_2 strictly engineered to ensure millennial timescale storage
Trace Elements	High concentrations dissolved in produced water overboarded into sea	**Negligible** – concentrations likely similar to current oil and gas operations, therefore little additional stress on ecosystem	**Frequent** – over-boarding produced water a common activity
Radioactive Scale	Enhanced scale formation from mobilised radioactive elements	**Negligible** – controlled emissions under regulations, no additional increase in discharge over oil and gas	**Negligible** – use of scale inhibitors and controlled release via regulatory environment
Impurities (Pipe)	NO_x, SO_x, amine, trace elements co-released with CO_2 during pipeline failure	**Negligible** – trace concentrations, rapidly dispersed	**Negligible** – pipeline failures uncommon and engineered to withstand expected operating conditions
Impurities (Well & Rock)	NO_x, SO_x, amine, trace elements co-released with CO_2 via well bore or diffusely through sediments	**Negligible** – trace concentrations and/or likely already reacted in storage reservoir	**Negligible** – requires unreactive release pathway

The rankings of impact and likelihood are given in Table 12 (previous page), based upon the source and pathways of marine releases. The rankings were assessed based upon the information and conclusions in the preceding sections, specifically: CO_2 and impurities (Section 3); trace elements (Sections 4 & 6), radioactive scale (Section 5).

With regard to the impacts of the releases, the fate and impacts of impurities such as amines are not currently certain, although indications are that they may not be of serious risk to the environment. Similarly, other impurities will be present in trace amounts only. The toxicity of trace elements such as mercury, cadmium, copper, etc. is well known, but the concentrations and quantities of these elements in produced waters under a CO_2-EOR project are unlikely to exceed those already produced by UKCS hydrocarbon activities. Therefore, the incremental impacts of both impurities and trace elements are ranked as negligible, Table 12.

While there is potential for radioactive scaling to increase, the use of scale inhibitors and strict regulations on the radioactivity of releases to the environment will ensure that CO_2-EOR will likely not present any more than negligible incremental impact on the marine environment.

The potential incremental impacts of CO_2 from a leakage are likely to be negligible for diffuse release from the storage reservoir, low for release from a well bore, and moderate from pipeline leakage, Table 12. The work by Blackford et al. (2007, 2008, 2012) showed that CO_2 flux, water depth, season variations in tides and mixing, nutrient reworking, etc. all have an influence on the fate of a CO_2-rich water plume, and therefore its effects on the environment. However, these studies also showed that CO_2-rich plumes can dissipate rapidly, regardless of the receiving waters. The potential impact rankings reflect the ability of receiving waters to dissipate a CO_2-rich plume discharging by each of the three pathways identified.

7.2 Results of the Model

The conceptual risk model for releases to the marine environment for a CO_2-EOR anchor project (local risk) is presented in Figure 17, overleaf, based upon the data from Table 12. The results show that five out of the seven potential releases identified are of negligible incremental risk to the North Sea marine environment. The exceptions are: release of trace elements in produced water, which carries a low incremental risk; and CO_2 leak from a well.

The reason that the risk attributed to trace metals is higher than negligible is due to the likelihood that produced water will be overboarded routinely (daily) as is the standard practice in the oil and gas industry, although the potential impact is considered to be negligible. While CO_2 released from a well bore would have a lower potential impact than a pipeline failure, it is more likely that leakage from a well bore would occur, particularly from old completed wells. Note, however, that the potential incremental risk is still low.

7.3 Mitigation

The question of mitigation of CO_2 leaks was discussed by industry and academics at the UK CCS Centre (UKCCSC) workshop *Potential environmental effects of CO_2 leakage in the marine and terrestrial environment: Understanding, monitoring, mitigation*. The report produced from the workshop states that monitoring is key to understanding the location and size of any CO_2 leak (Benham et al., 2012). As already stated in Section 2.6, the greatest risk of CO_2 leakage would be from infrastructure (e.g. pipeline and well bores), with storage site leakage highly unlikely (Benham et al., 2012), therefore pro-active mitigation such as "…improved CO_2 resistant materials…" in equipment, as well as improved well completion materials should be considered.

However, if CO_2 was to escape via geological faults or fractures, then mitigation could involve reducing or halting CO_2 injection, extracting (additional) fluids, or more active intervention such as injecting polymers in an attempt to block leakage pathways. The use of biofilms was also mooted and promising research is ongoing in this field (Phillips et al., 2013).

Other pro-active mitigation strategies include minimising any impurities with potentially high impacts in the injected CO_2 stream and selection of environmentally friendly scale inhibitors (thereby also reducing the scale risk) and corrosion inhibitors.
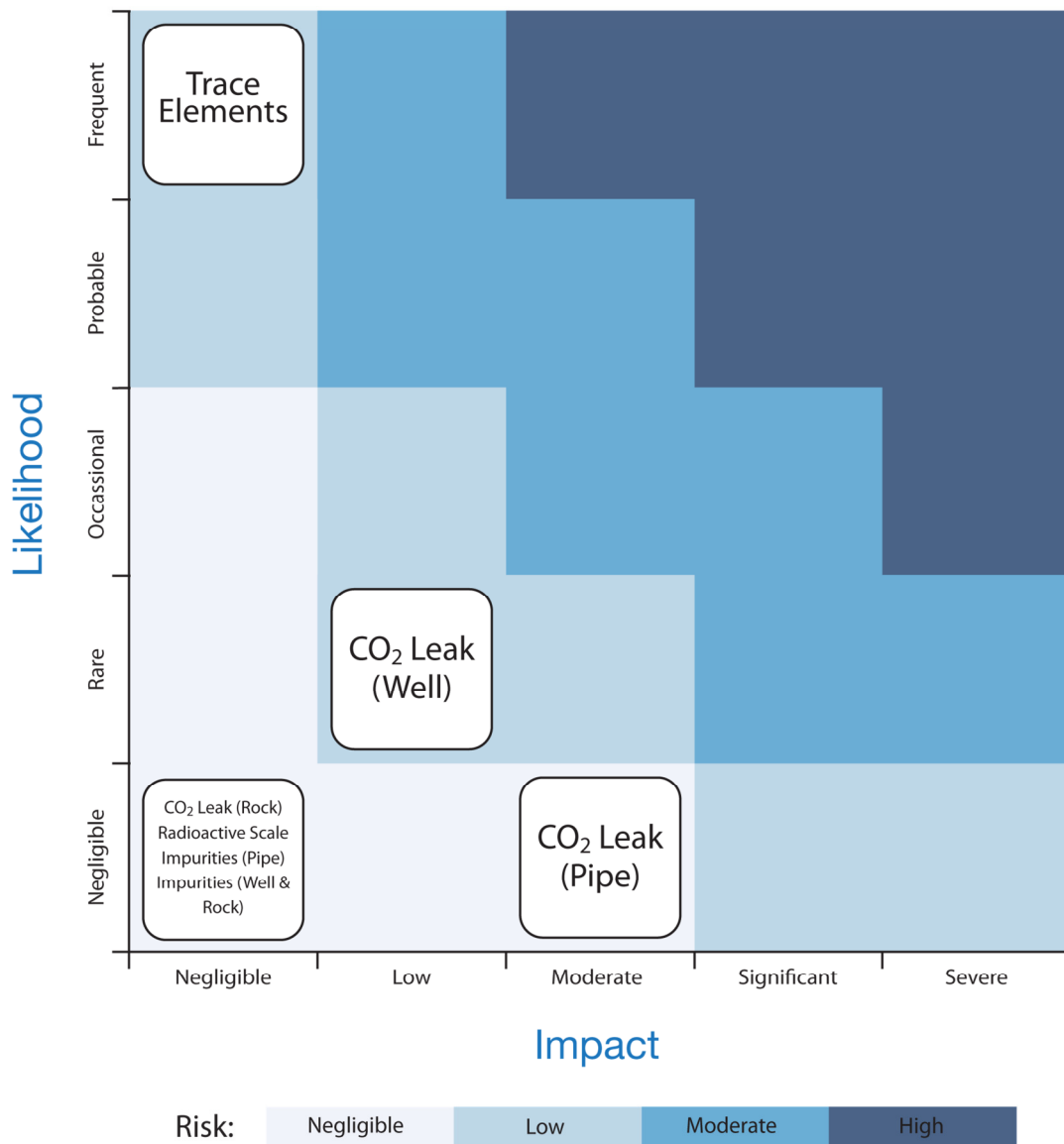
Figure 17. Conceptual risk model for a CO_2-EOR anchor project, modified from a risk matrix. Potential incremental environmental impacts over-and-above UKCS oil and gas are ranked against likelihood of the impacts. Risks are ranked negligible, low, moderate and high.

Trace elements, as already discussed, could present a risk if disposed of untreated to the sea. In order to ensure that concentrations are safe, the use of the risk based approach (RBA) (see Section 2) should be used to model predicted environmental concentrations (PEC) of these components in the marine environment, using data on local environmental conditions. The PEC of each component would then be compared with published predicted no-effect concentrations (PNEC) of that component.

As reported in Section 2, if PEC:PNEC ≤ 1 then the risk would be controlled; if PEC:PNEC > 1 then this may represent a potential risk (Scholten et al., 2000). PNEC values for selected metals are given Section 2. By monitoring concentrations and regularly updating PEC, discharged produced waters could be disposed of untreated. If, however, concentrations exceed the PNEC, then treatment of waters would be necessary, or alternative disposal

sought, such as reinjection into the reservoir or into saline formations at other depths.

DECC already encourage the subsurface disposal of produced waters under BAT, as recommended by OSPAR, and this approach (BAT) has apparently proved successful in Norway with produced water emissions reduced by approximately one-fifth between 2000 – 2006 (Smit et al., 2011).

7.4 Conclusions

This report identified and investigated a number of possible environmental risks which were considered new or unique to UKCS CO_2-EOR, and therefore potentially posed incremental risks over-and-above current oil and gas activities. These incremental risks were identified as releases to the North Sea of: CO_2, CO_2-stream impurities, trace elements, and radioactive scale.

Following review of the available literature and experimental work carried out for this report, these releases were assessed using a conceptual risk model, having determined the potential impact of the release via a number of release pathways, and the likelihood of that release having an impact. The model is presented as Figure 17, above, the results of which show that the majority of possible releases to the UKCS environment present a negligible incremental risk to the North Sea.

The unintended release of CO_2 from well bores and the release of trace elements in produced waters were assessed to have a low risk to the North Sea, however mitigation options should be considered to minimise the risk as far as possible e.g. engineering robust well completions, and continuous assessment of trace element concentrations using best available technologies.

CO_2-EOR activities would likely fall under existing North Sea regulations for oil and gas activities, ensuring that environmental risks are managed appropriately, however this has yet to be tested since no projects are currently operational.

Comprehensive monitoring and mitigation strategies, as well as the use of best available technologies and practices will ensure that potential risks are kept to a minimum, however it is difficult to see how CO_2-EOR projects could pose significant negative environmental impacts beyond those of the existing UKCS hydrocarbon industry.

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Appendix 1 – Experimental Results

pH − Sample 8518
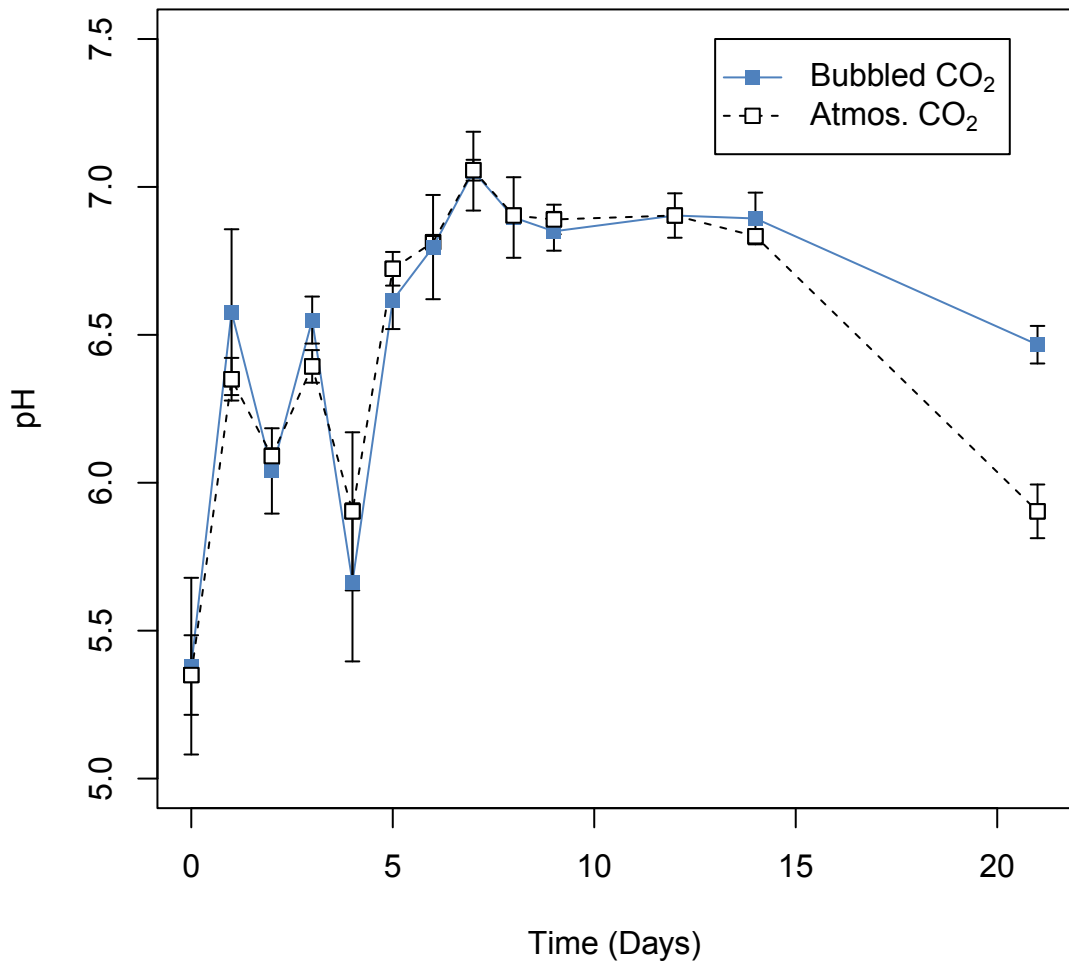
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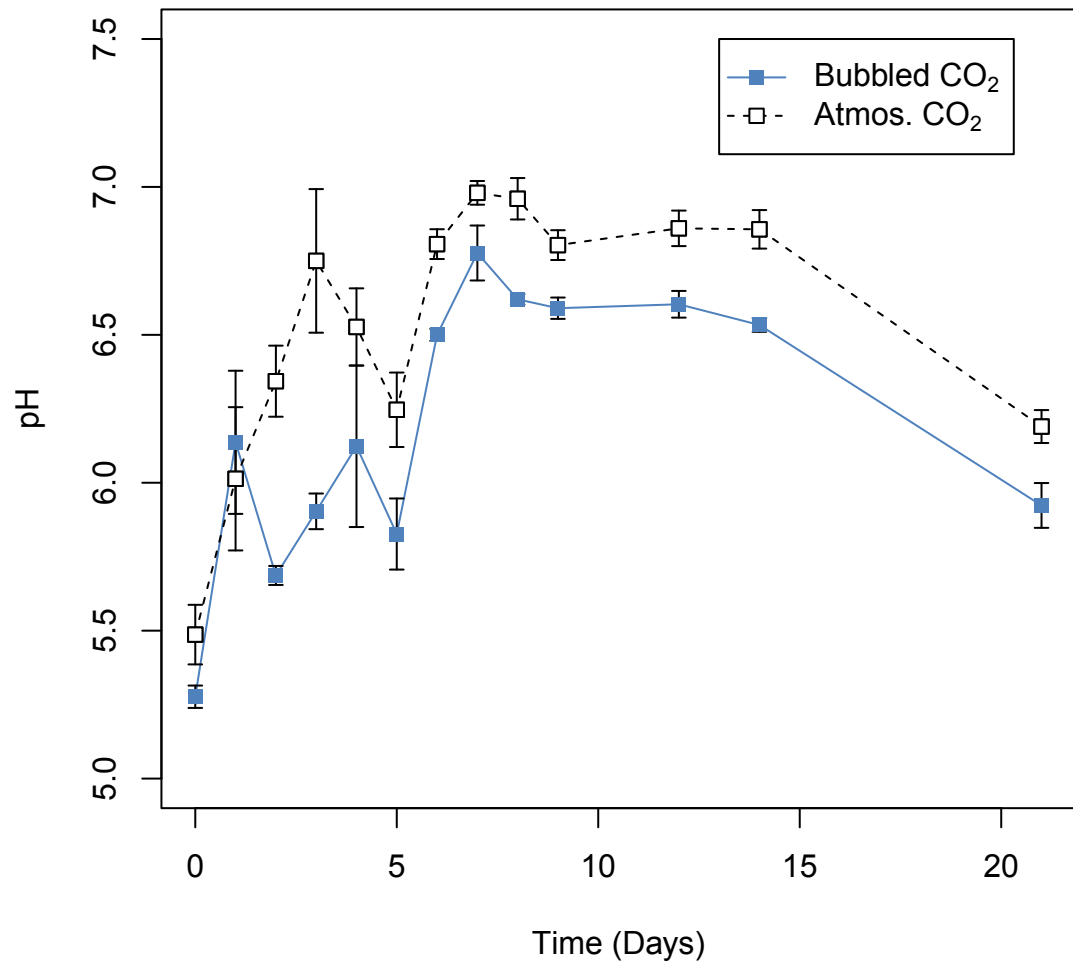
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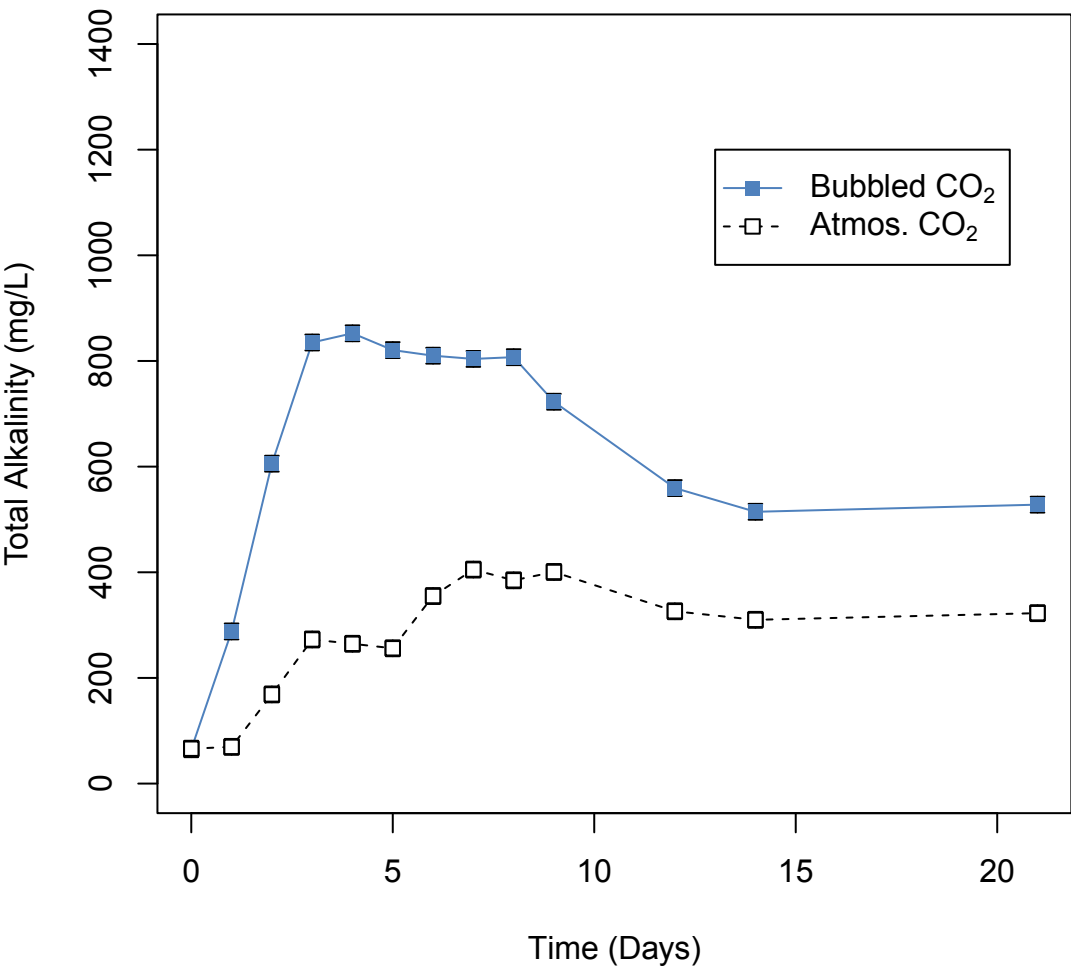
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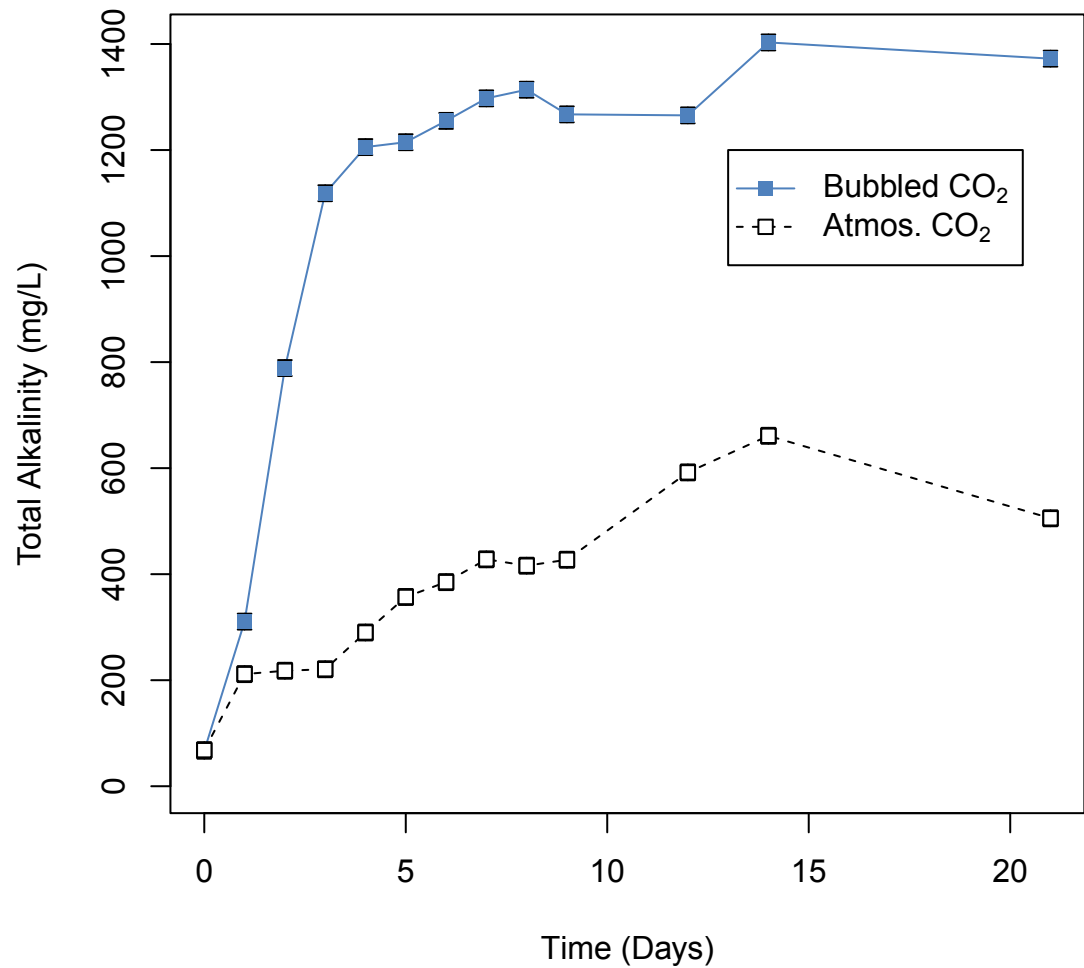
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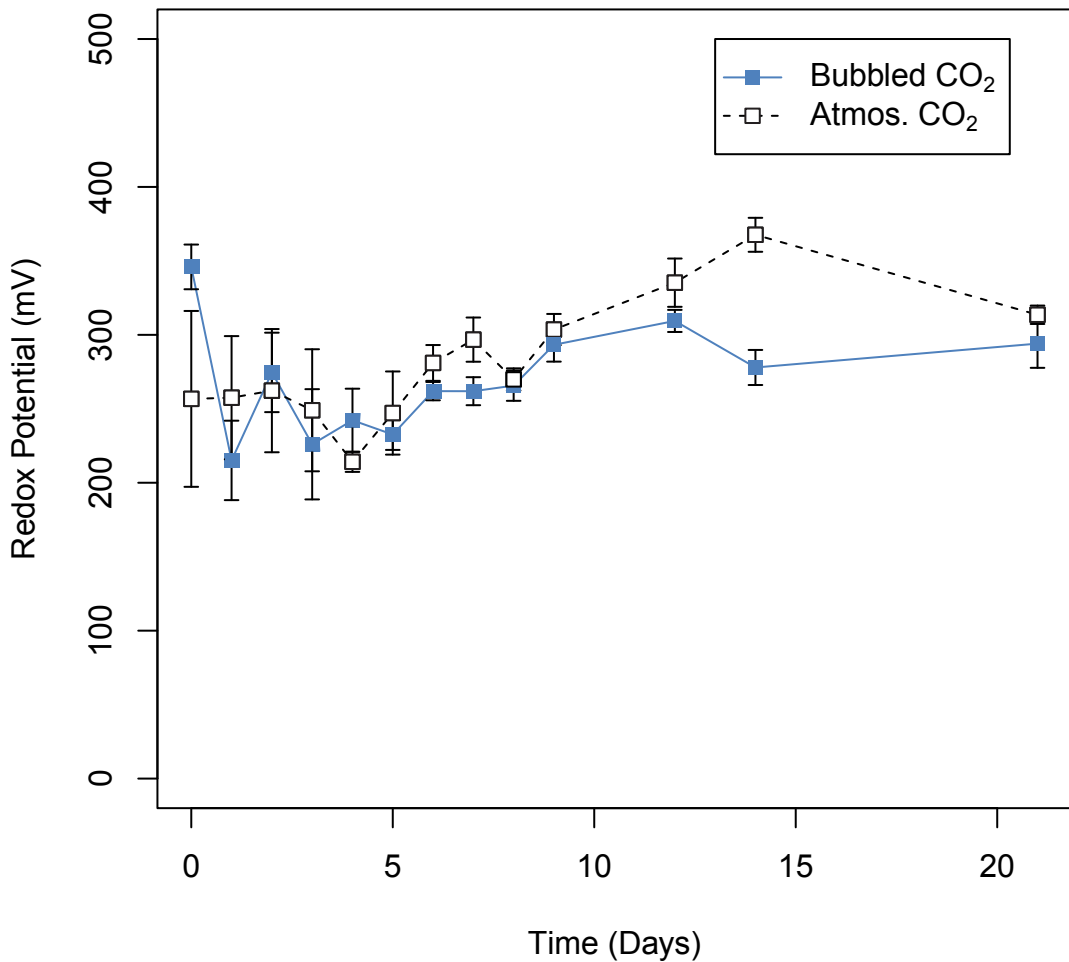
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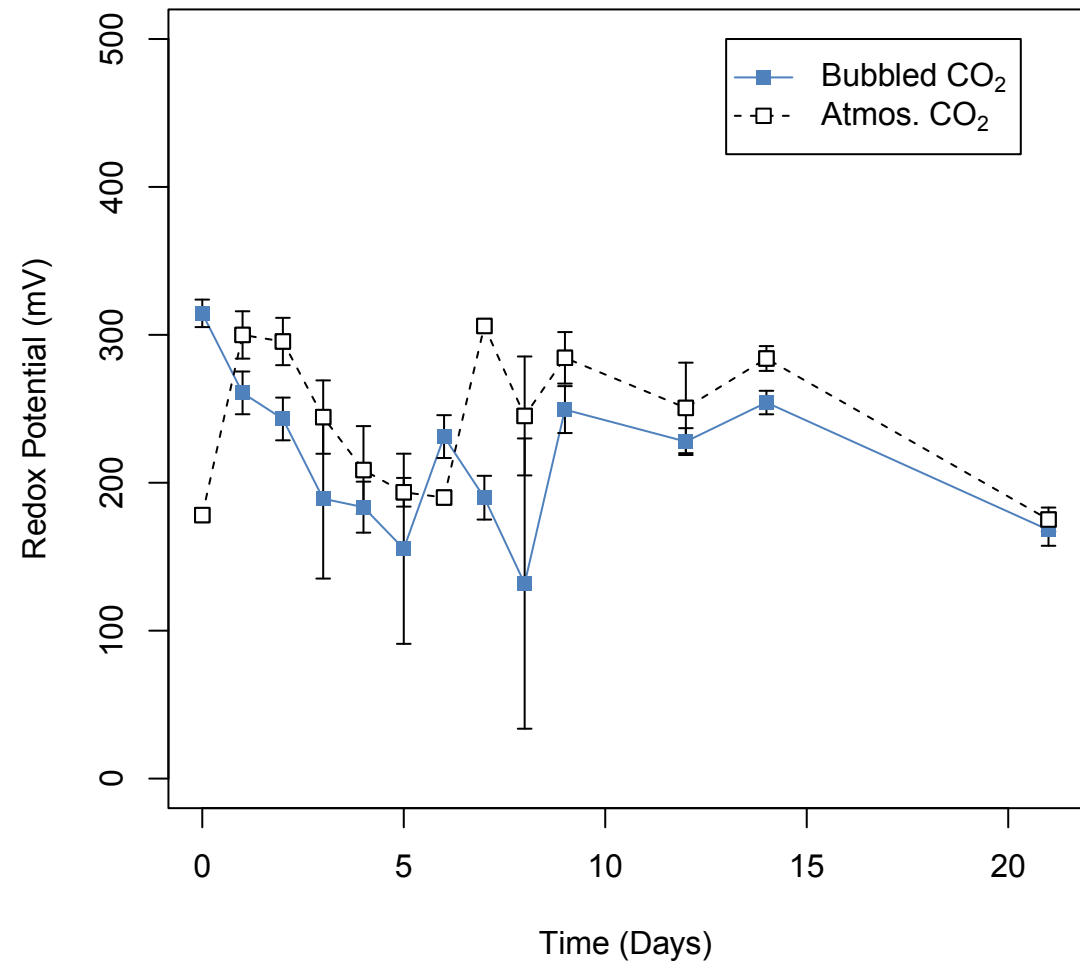
Barium Concentrations − Sample 8518
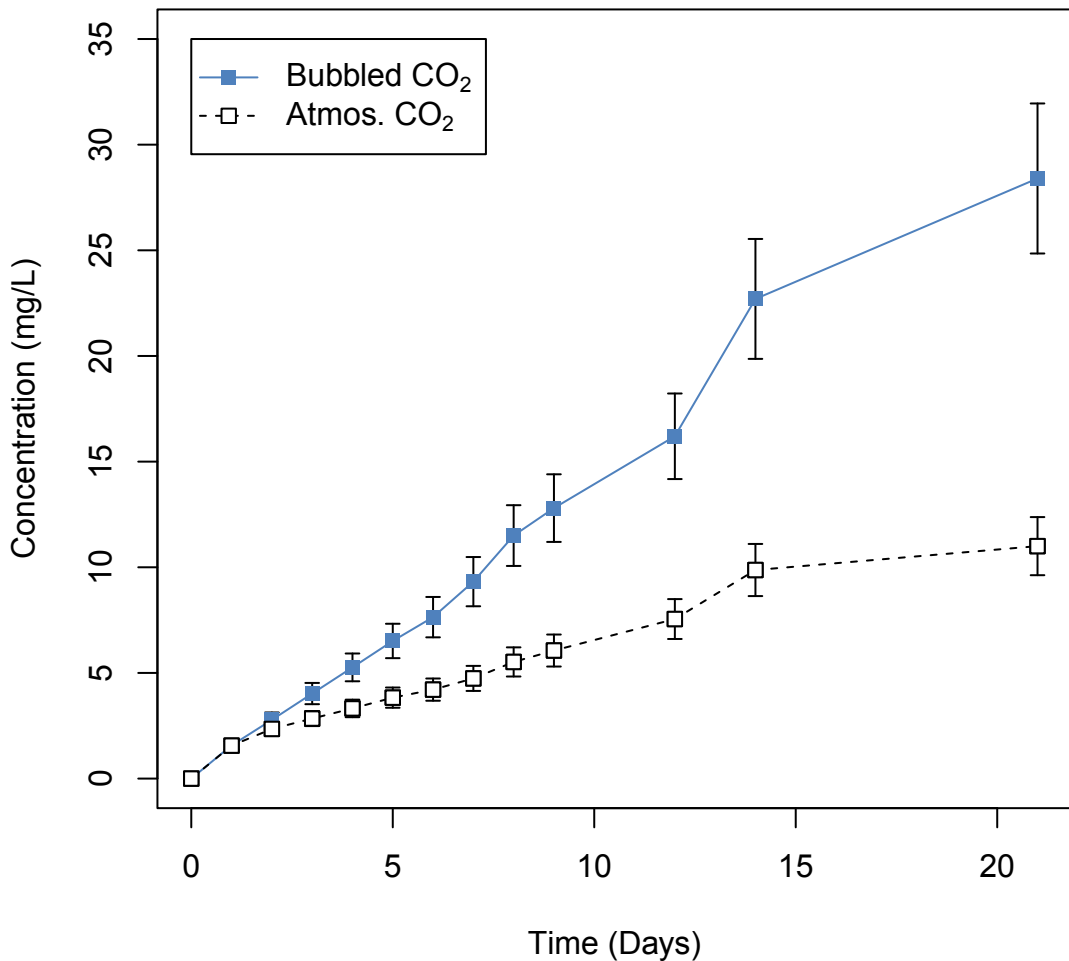
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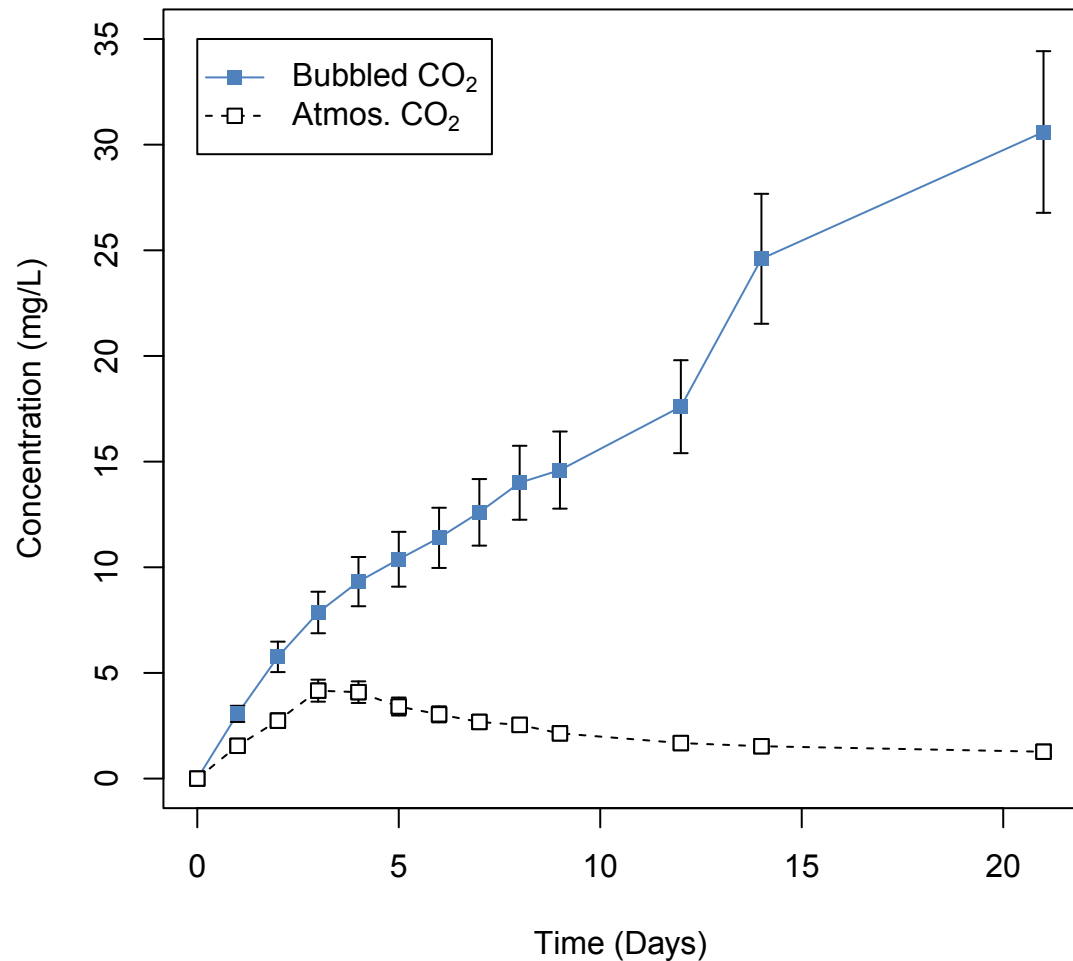
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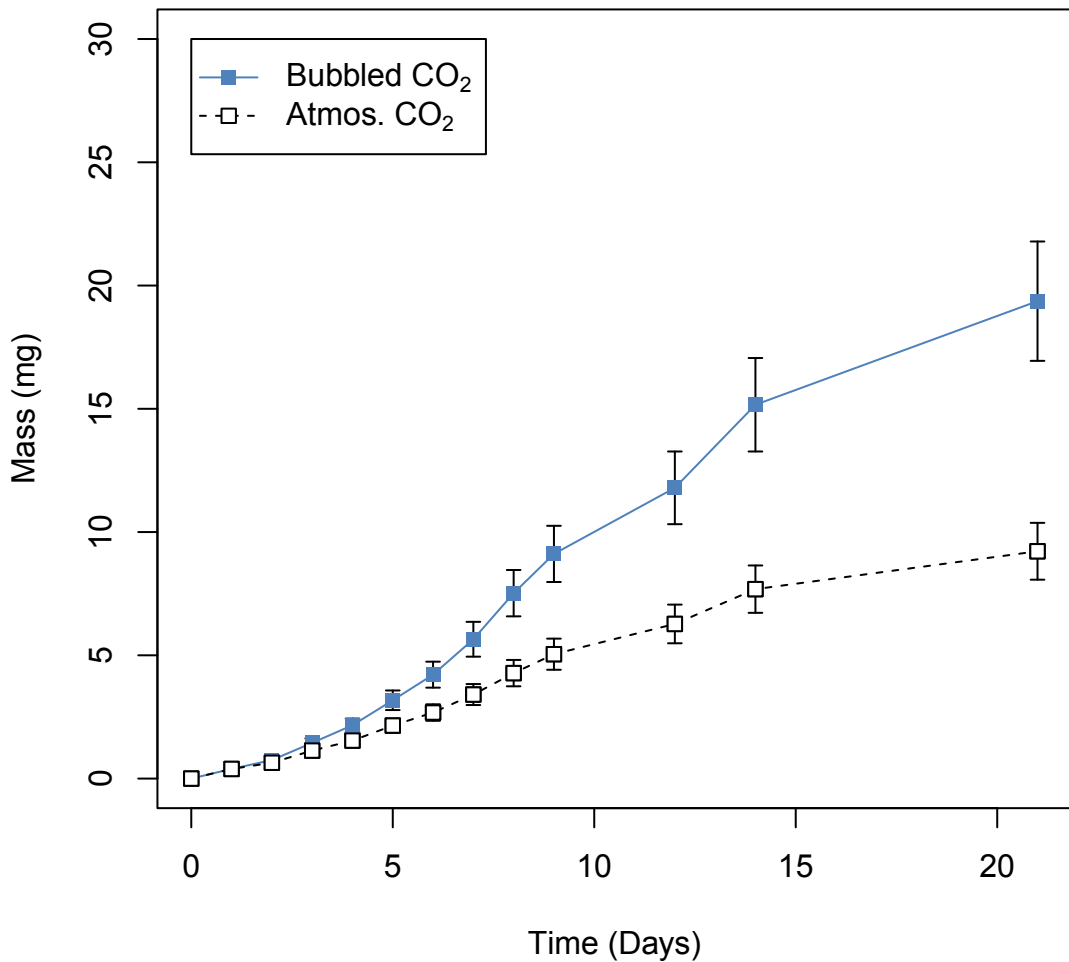
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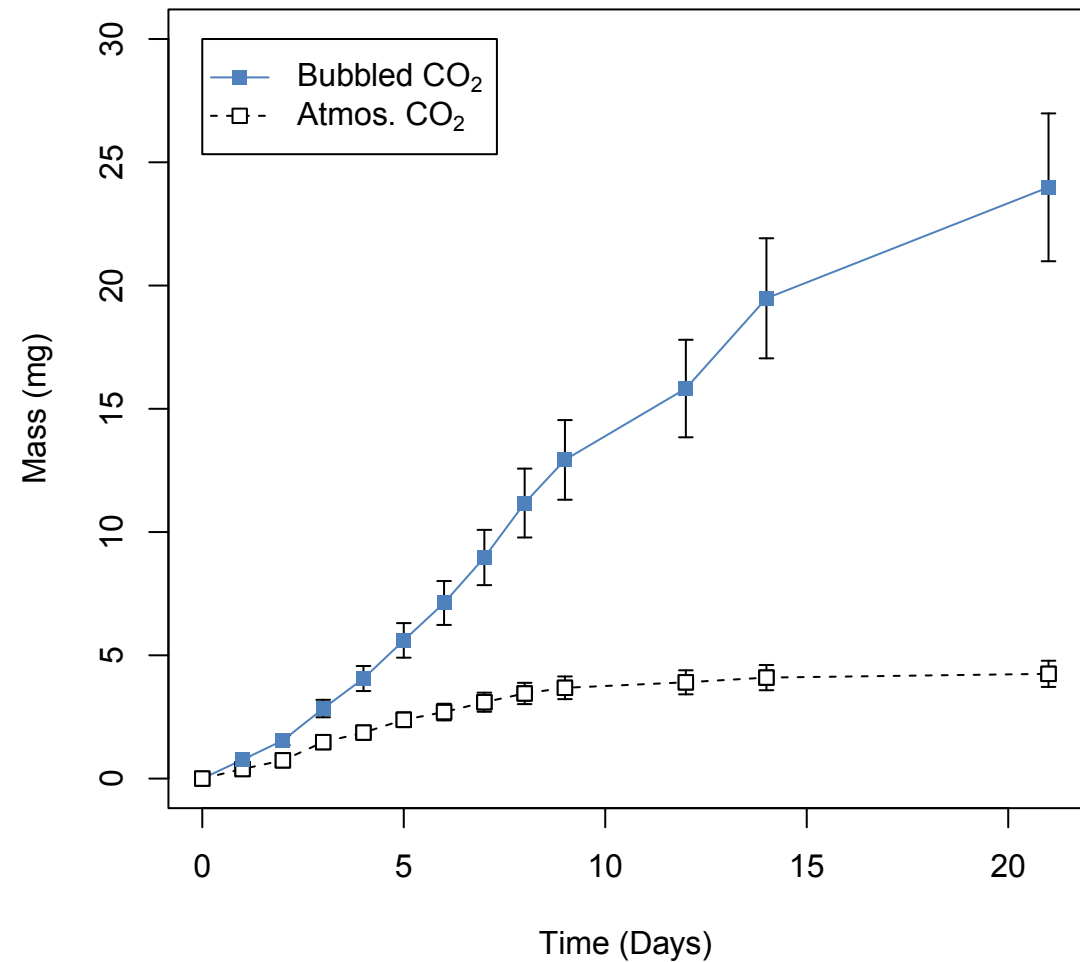
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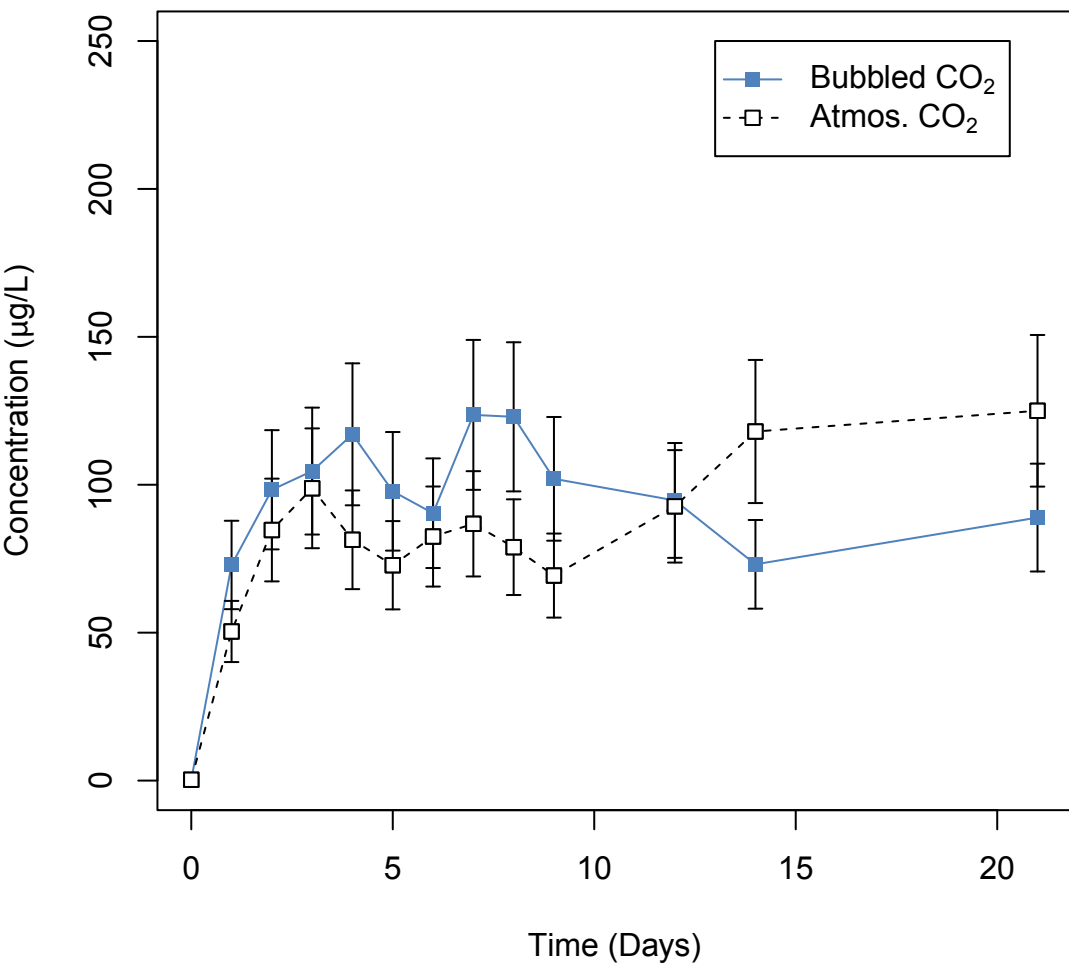
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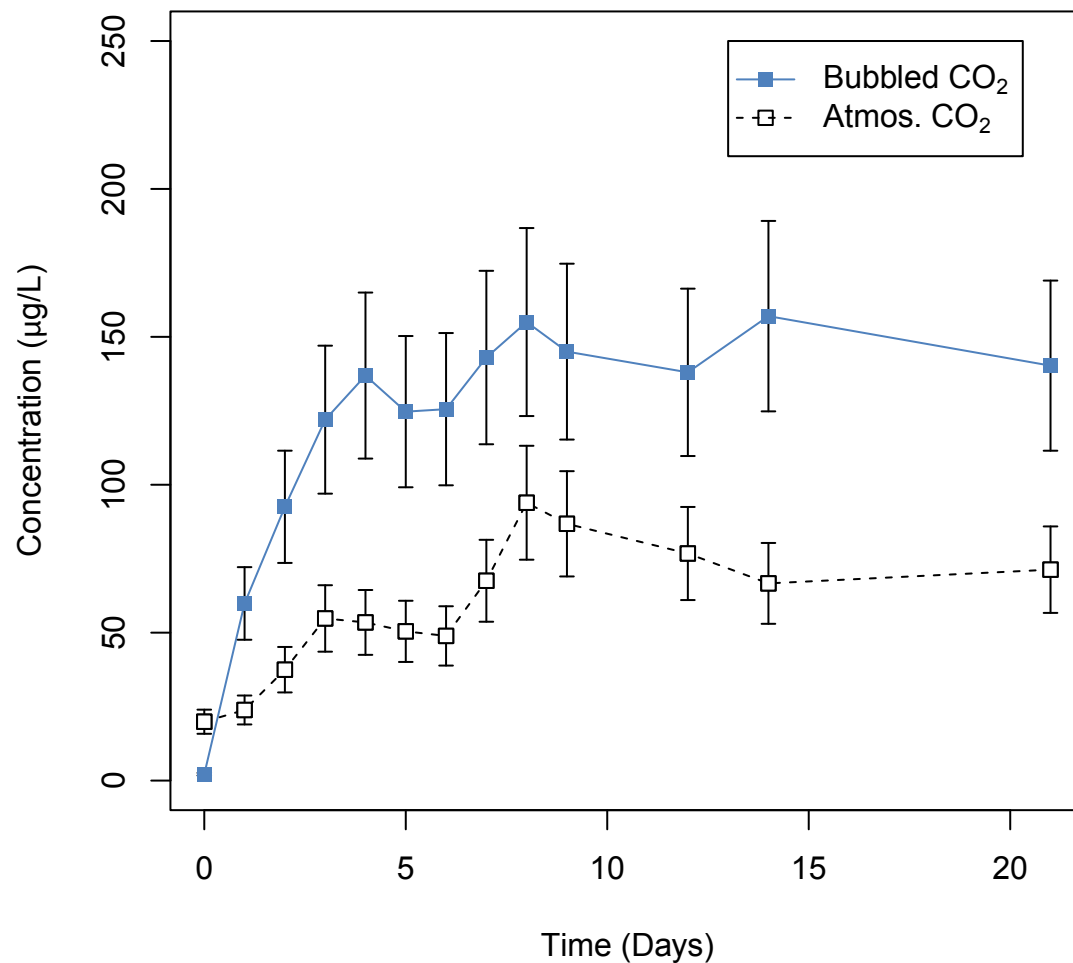
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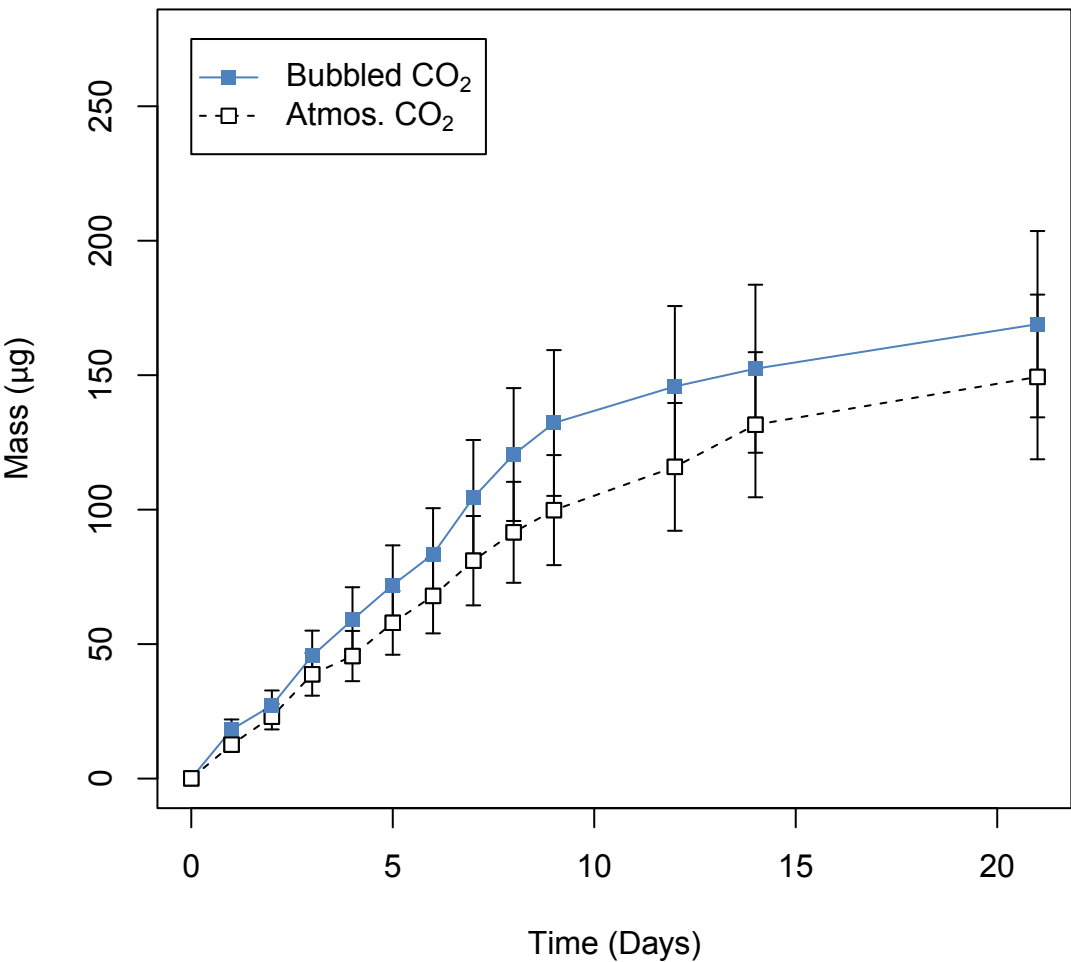
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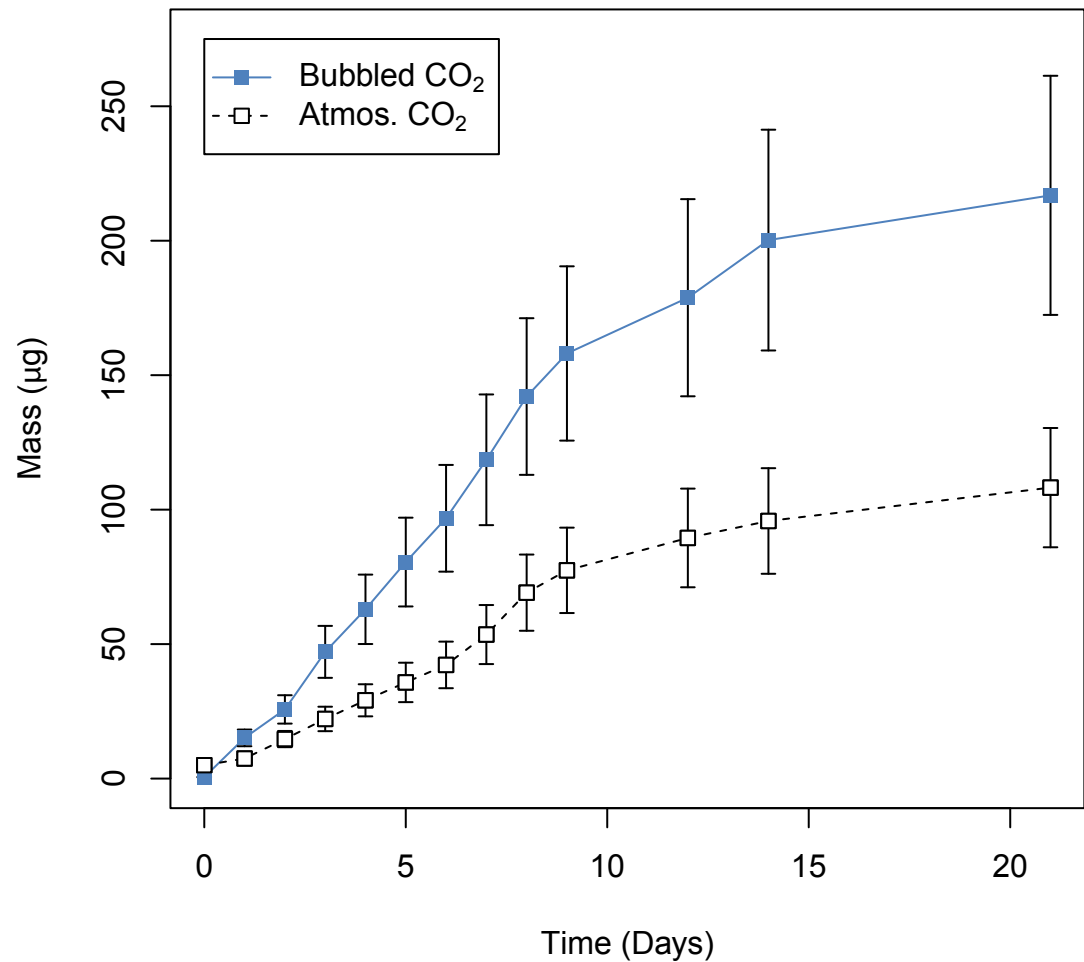
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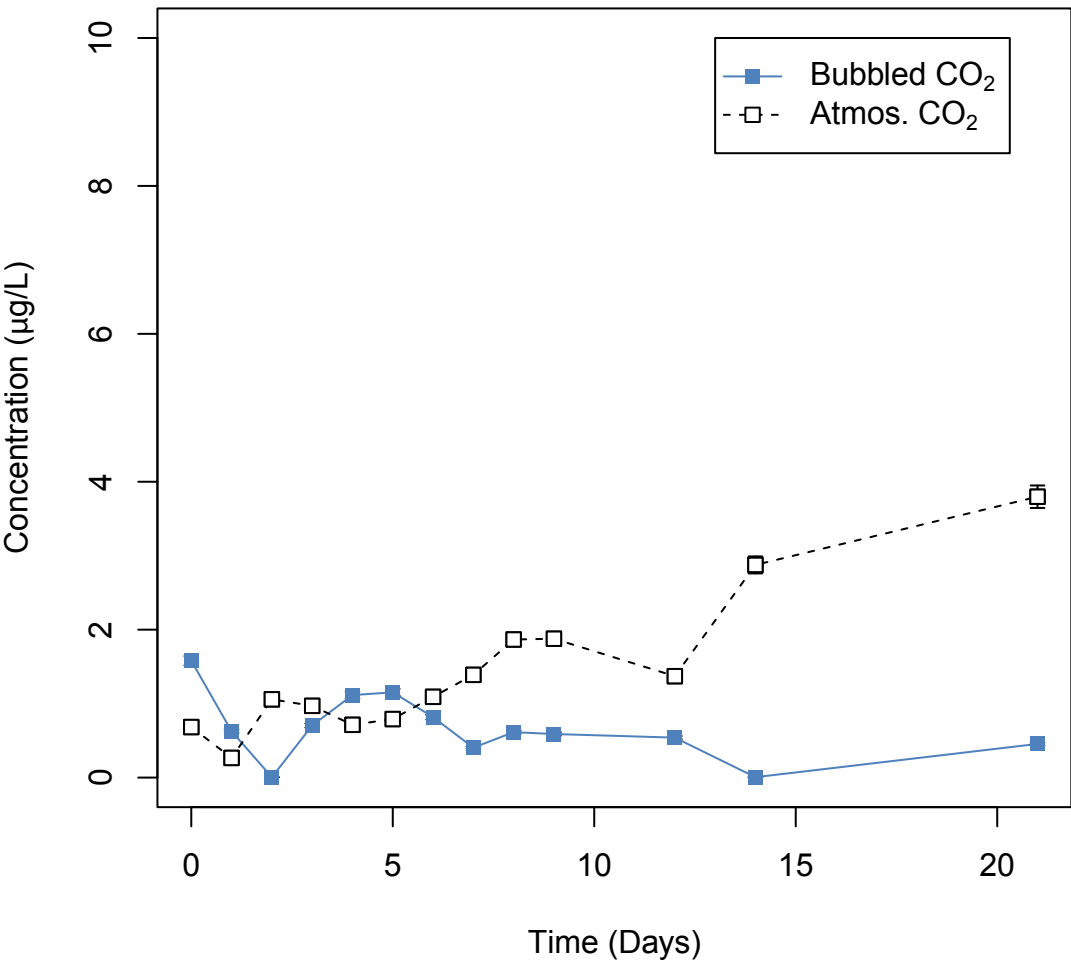
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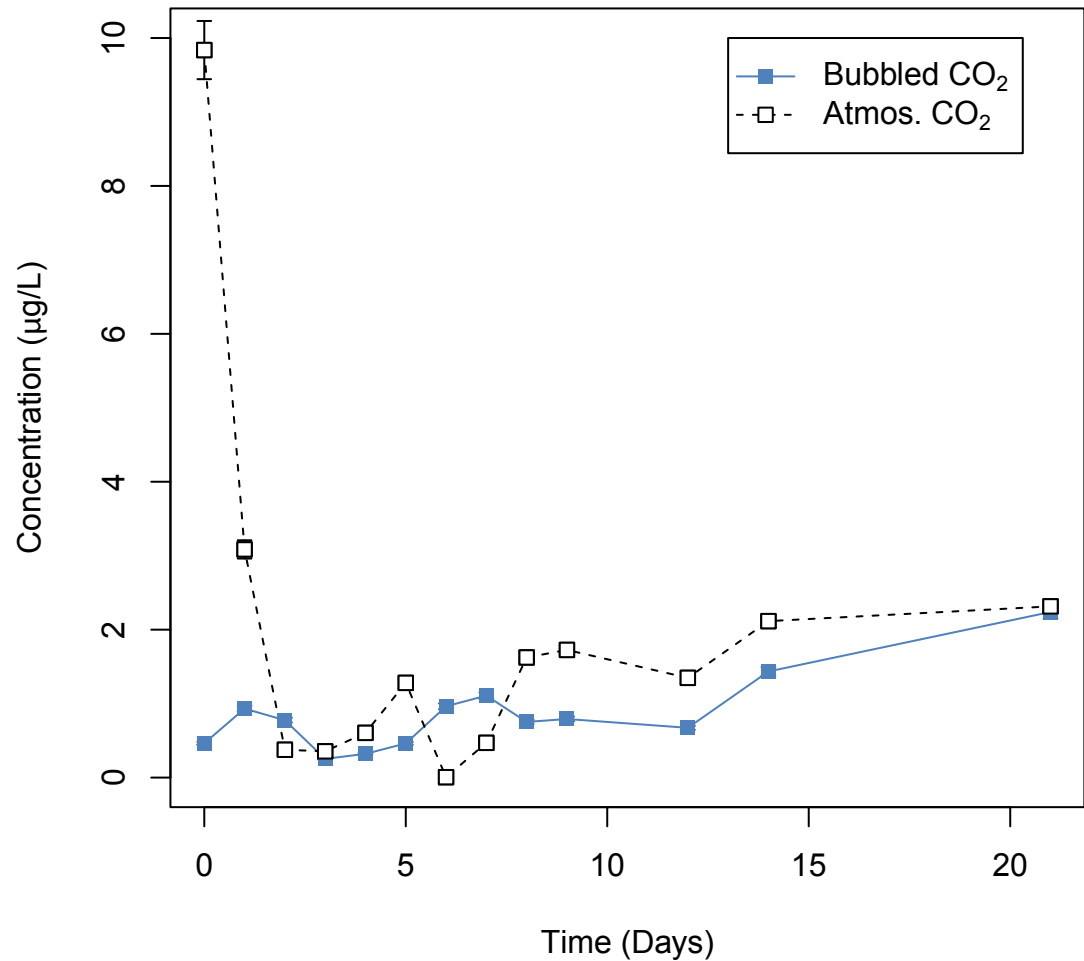
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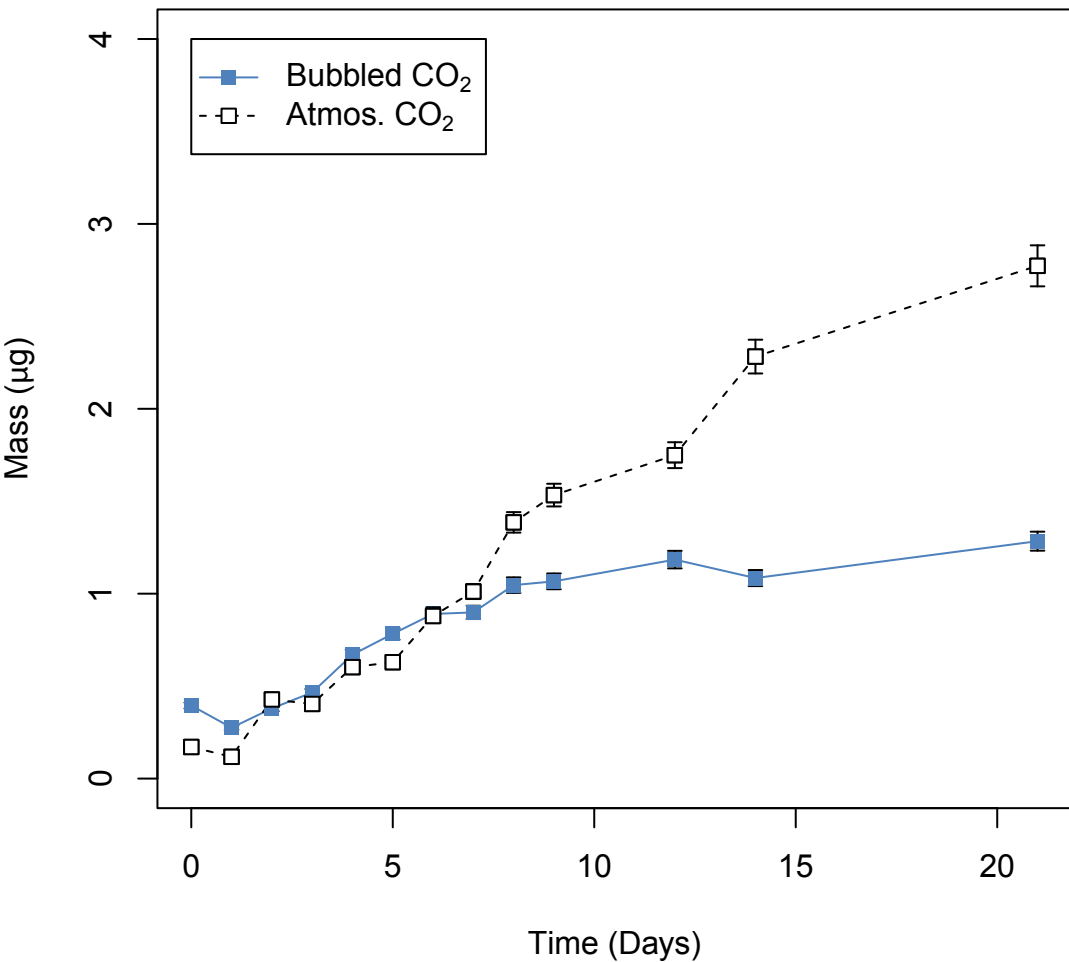
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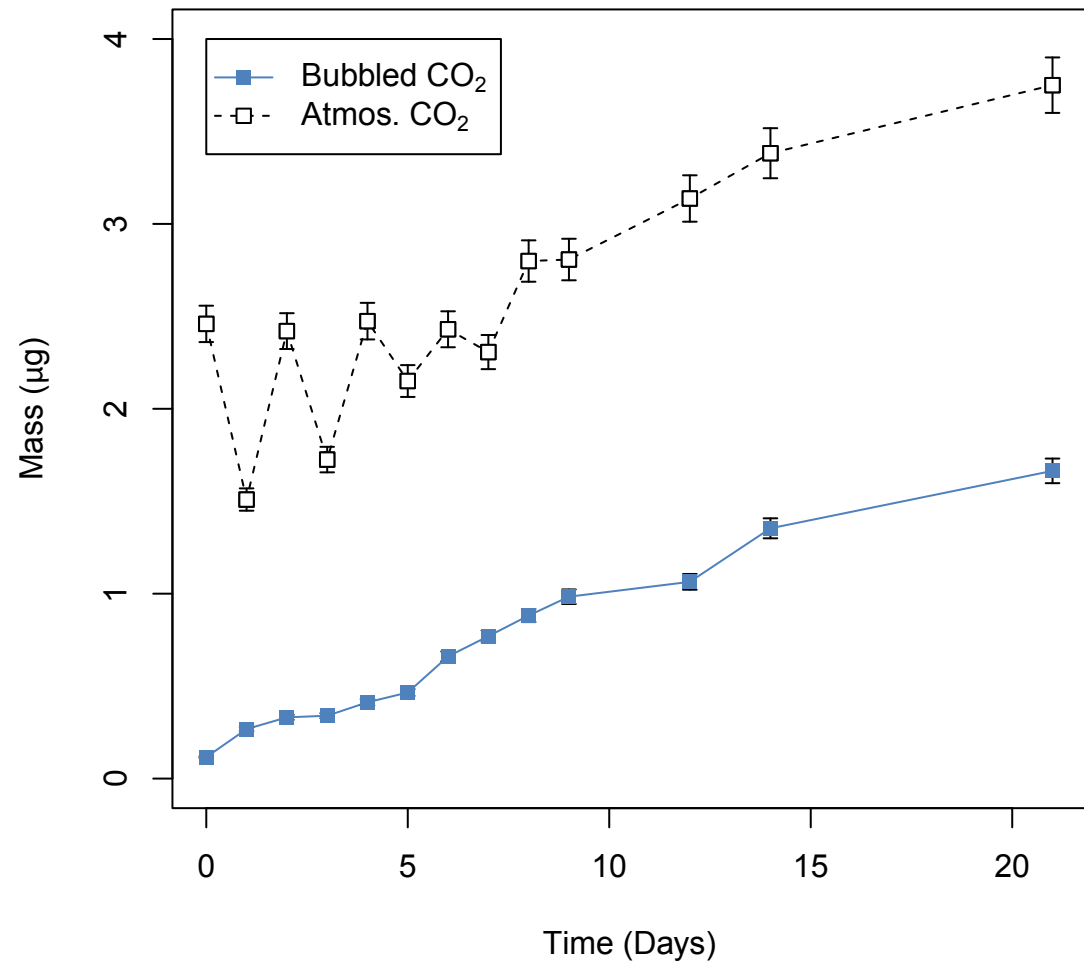
Chromium Concentrations − Sample 8518 — Concentration (μg/L) vs Time (Days). Legend: Bubbled CO_2, Atmos. CO_2.

Chromium Concentrations − Sample 8579 — Concentration (μg/L) vs Time (Days). Legend: Bubbled CO_2, Atmos. CO_2.
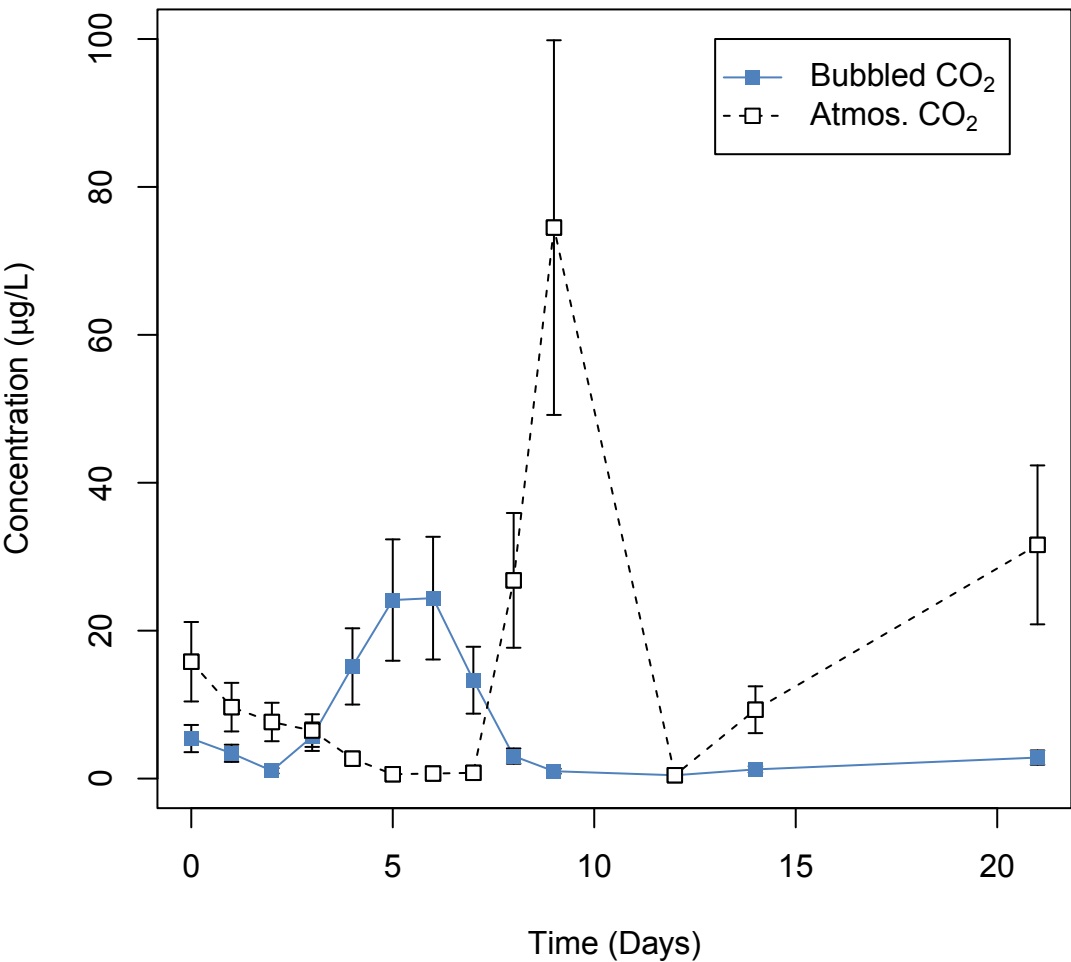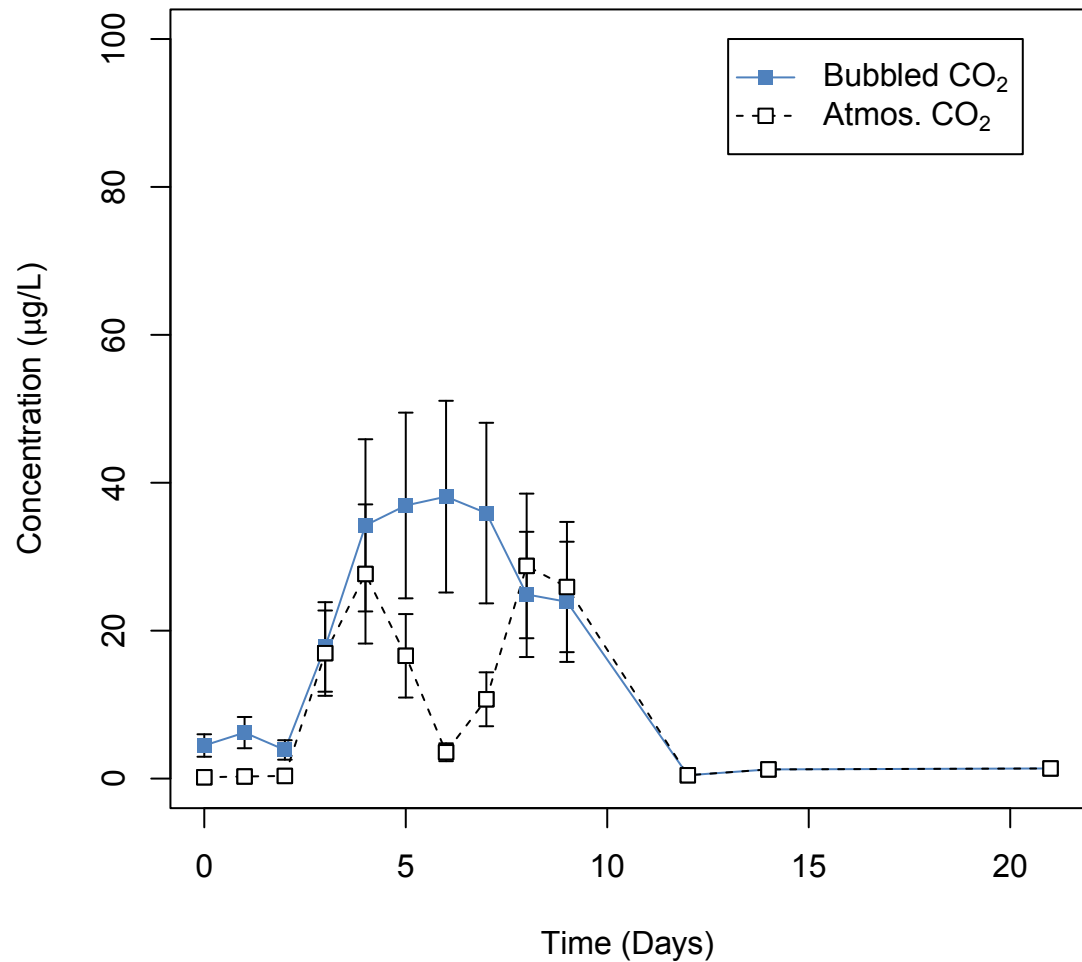
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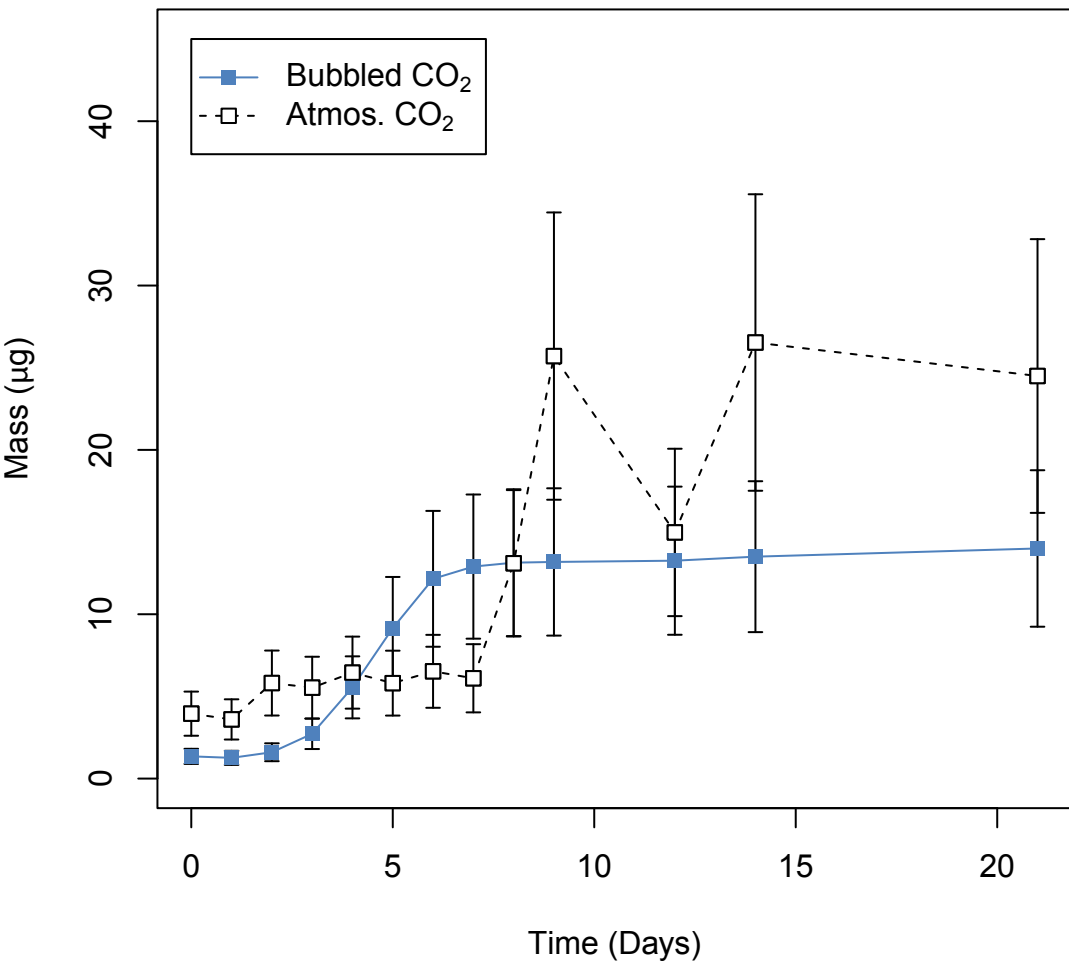
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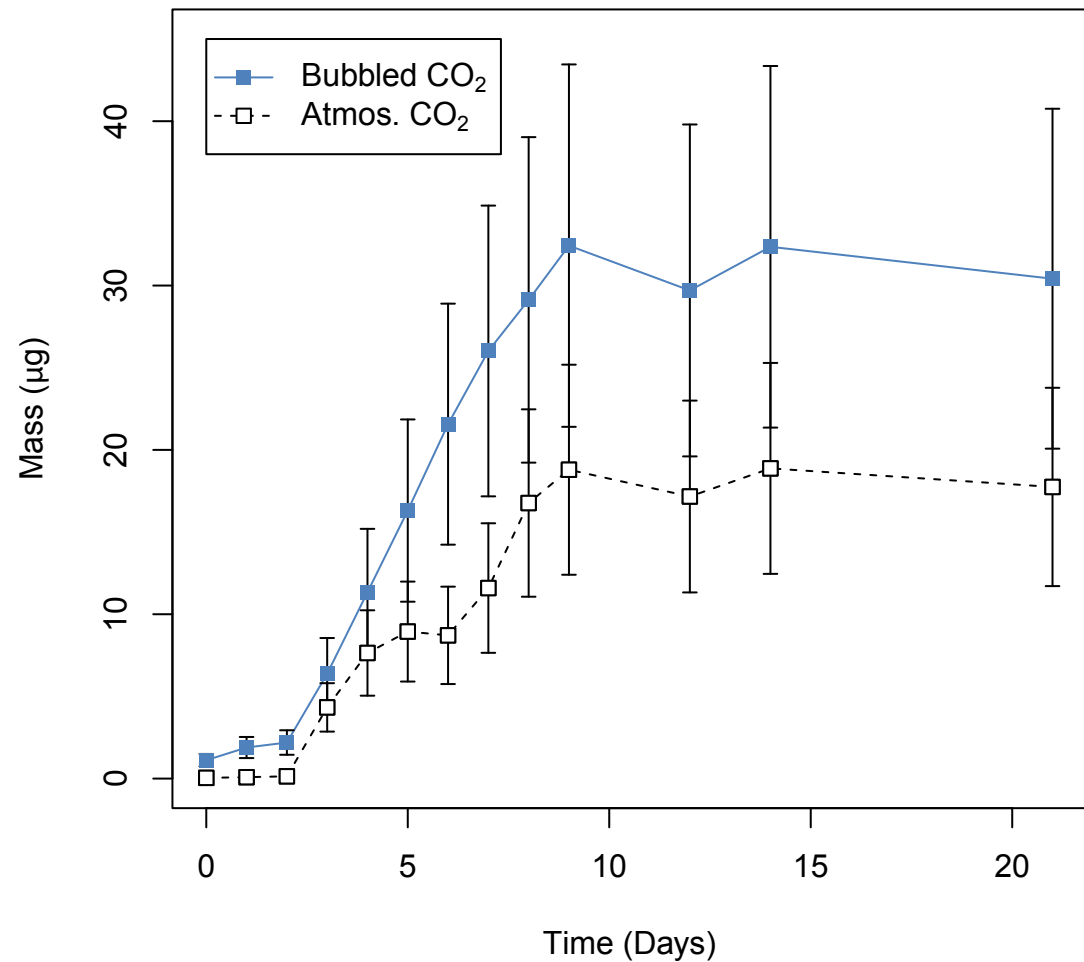
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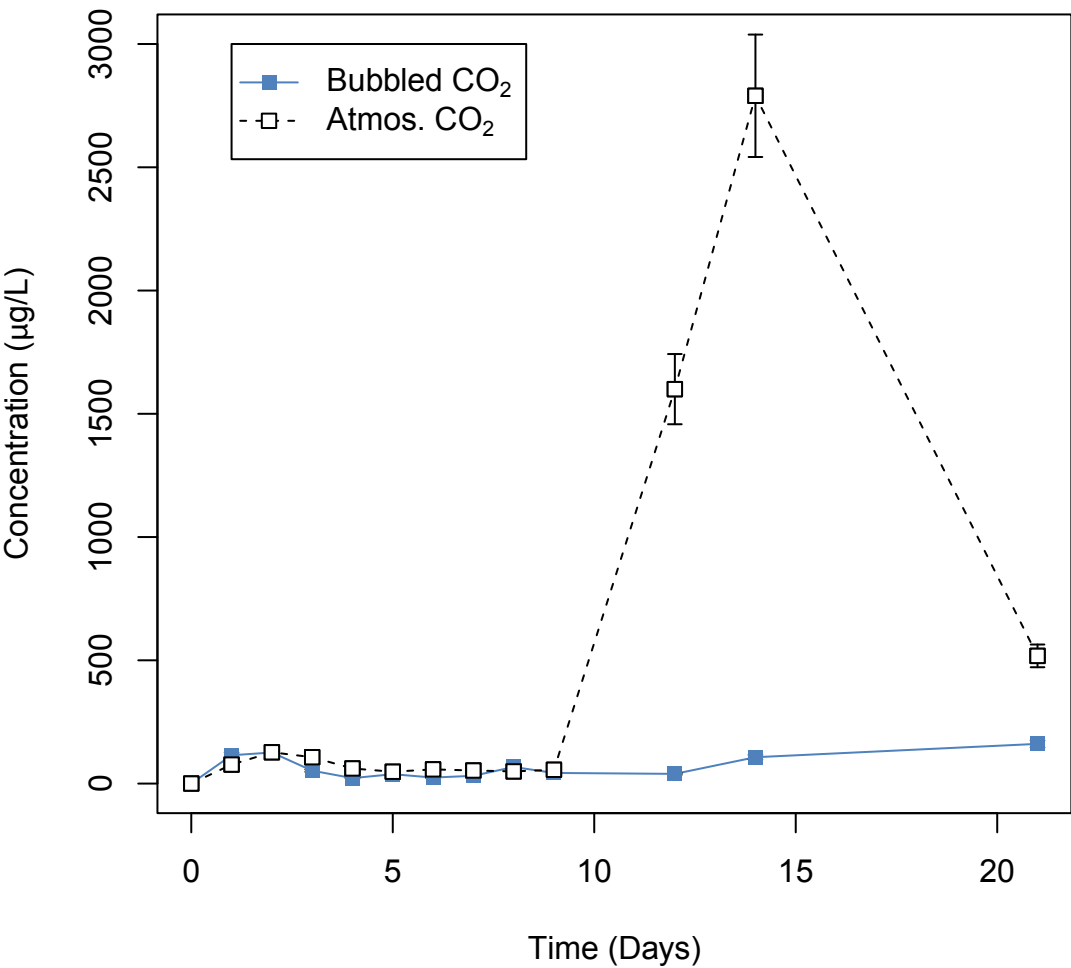
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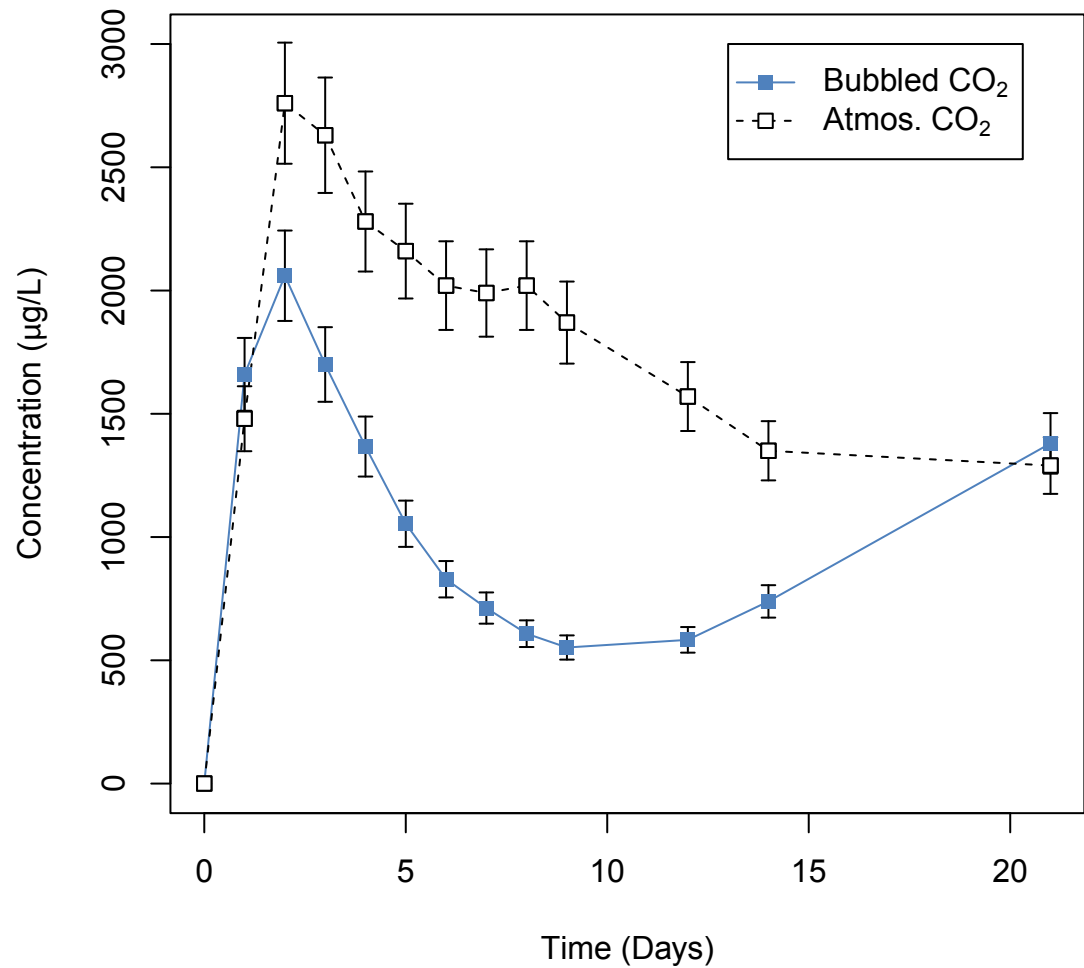
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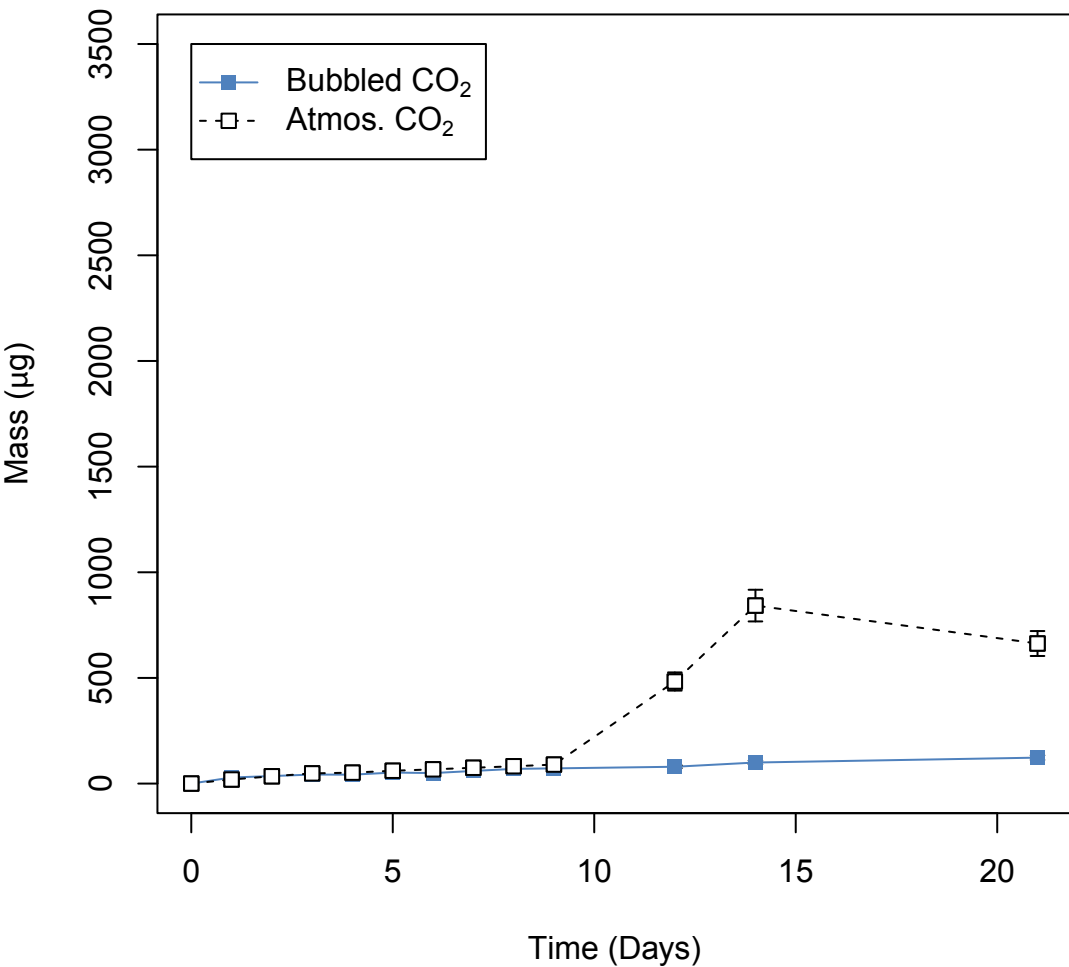
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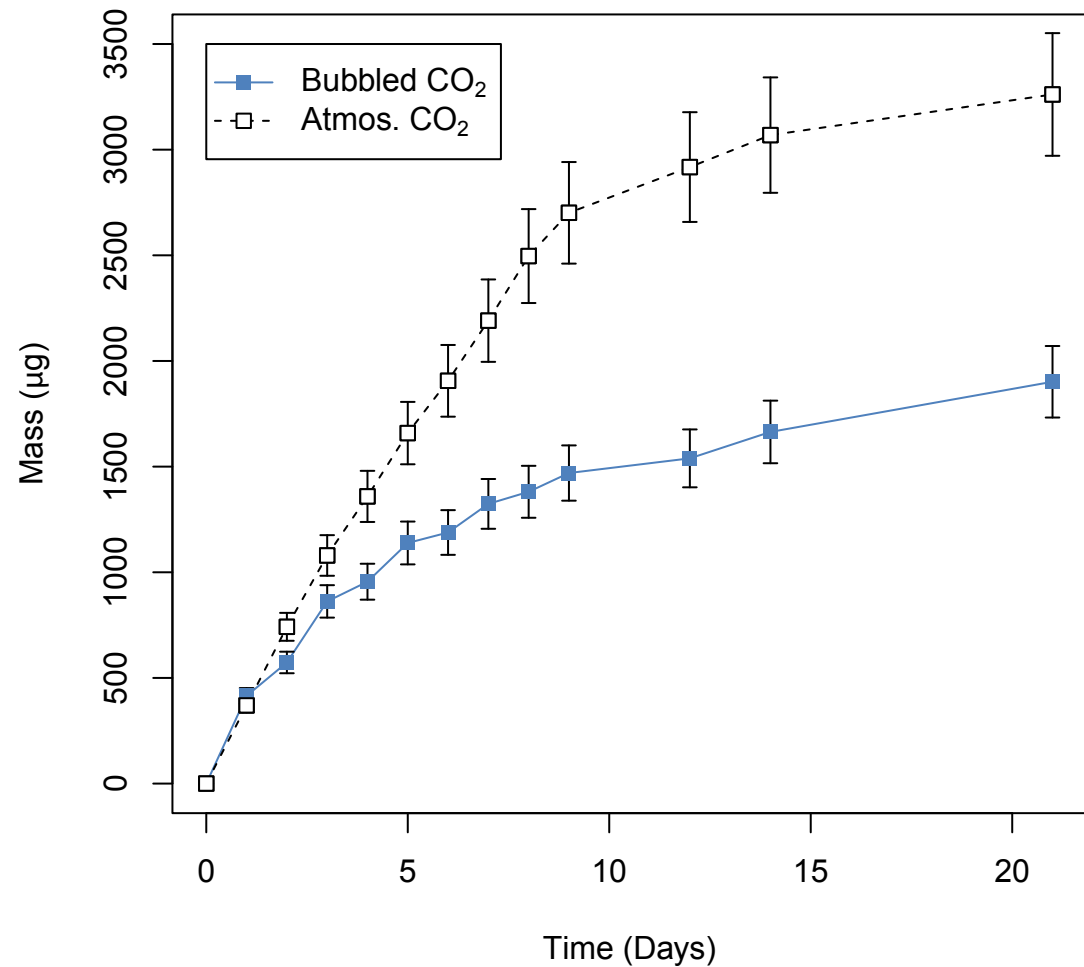
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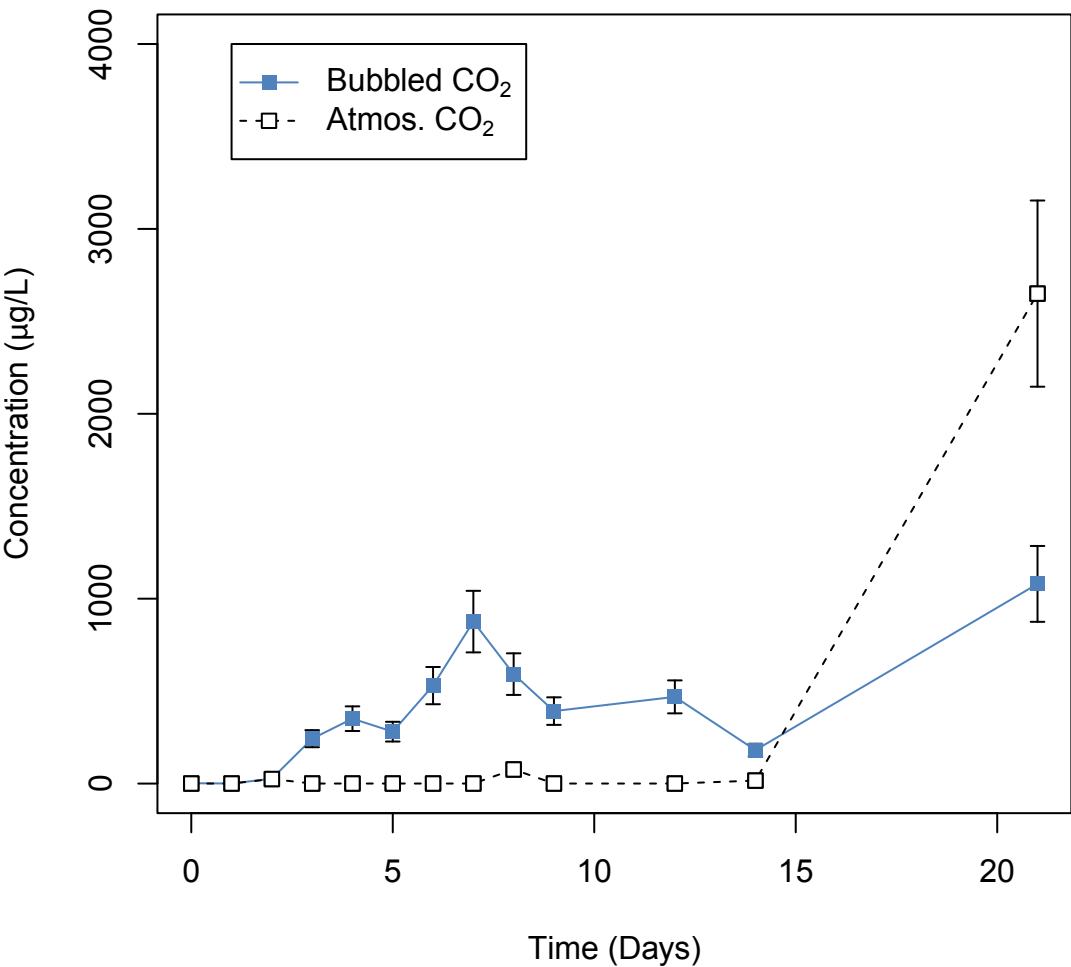
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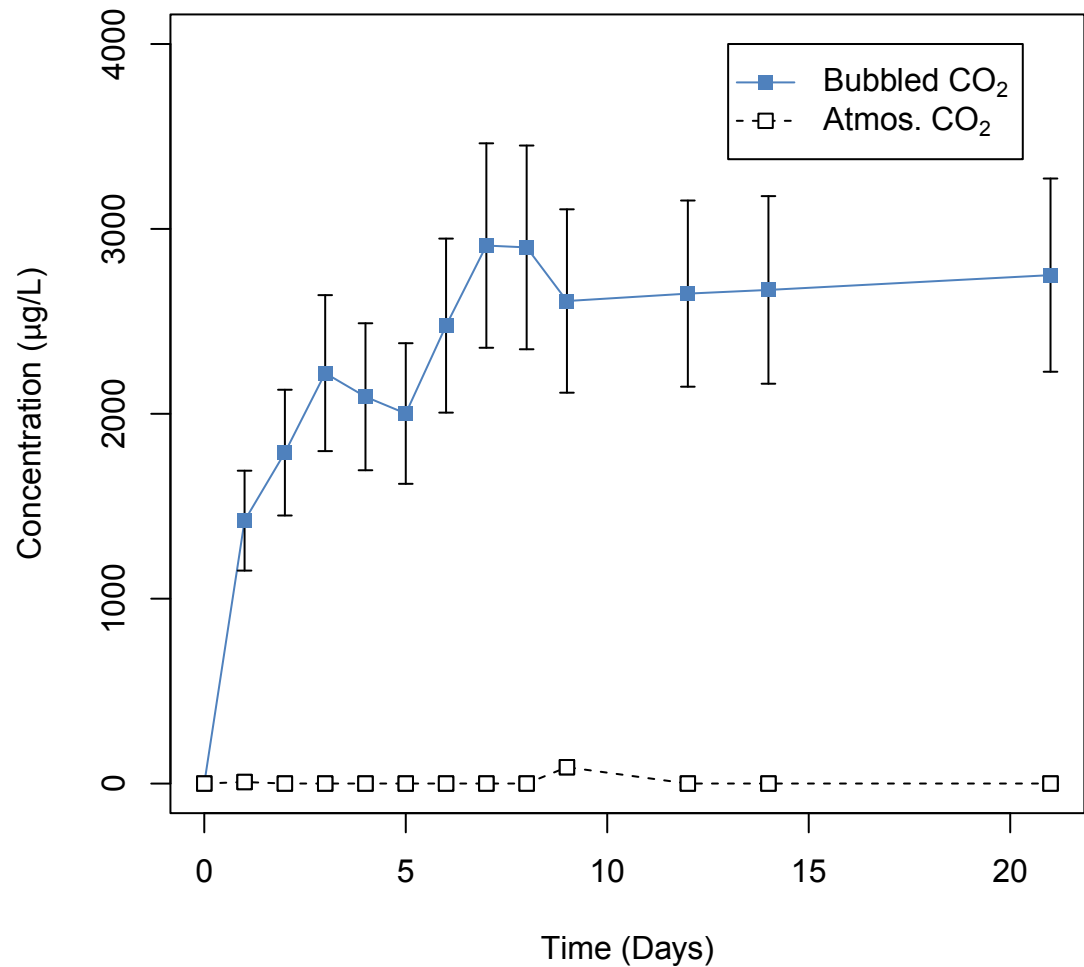
Iron Mass − Sample 8518   **Iron Mass − Sample 8579**

Bubbled CO_2
Atmos. CO_2

Mass (µg)

Time (Days)
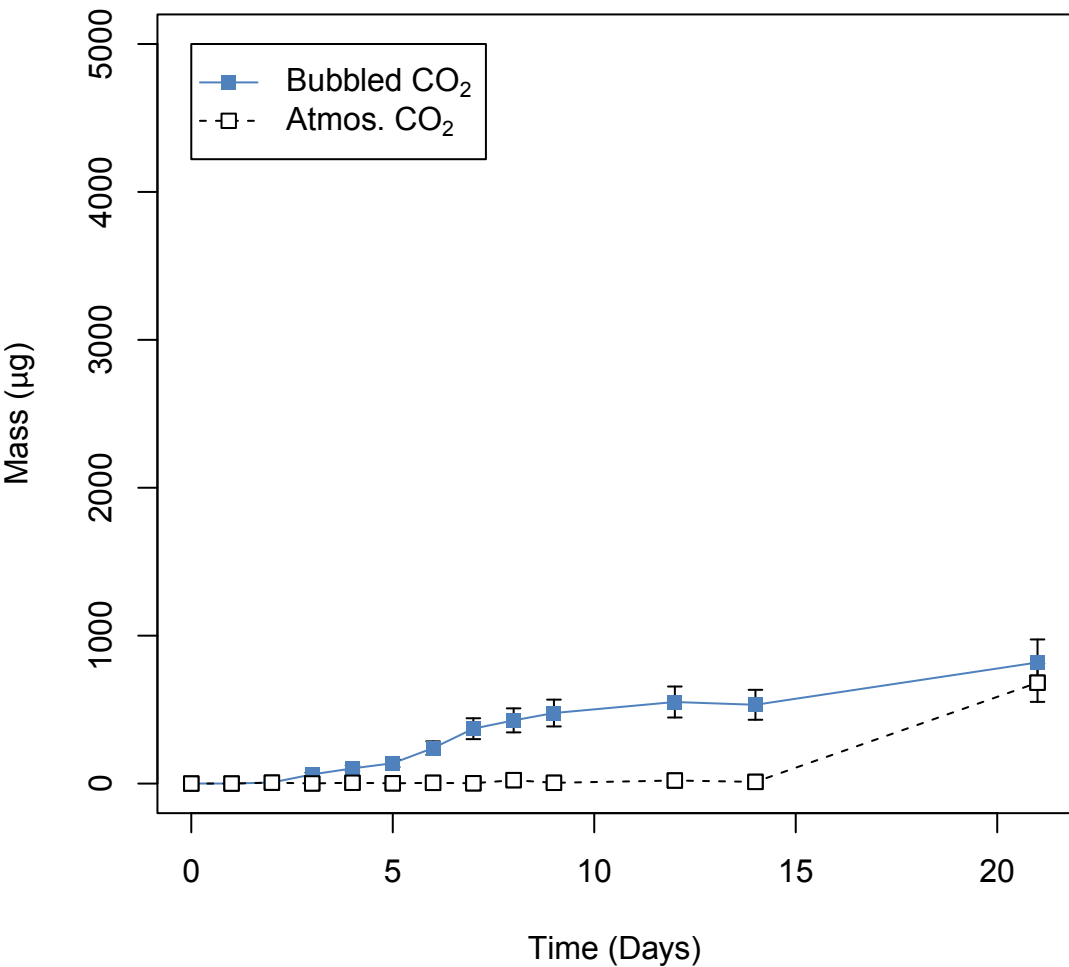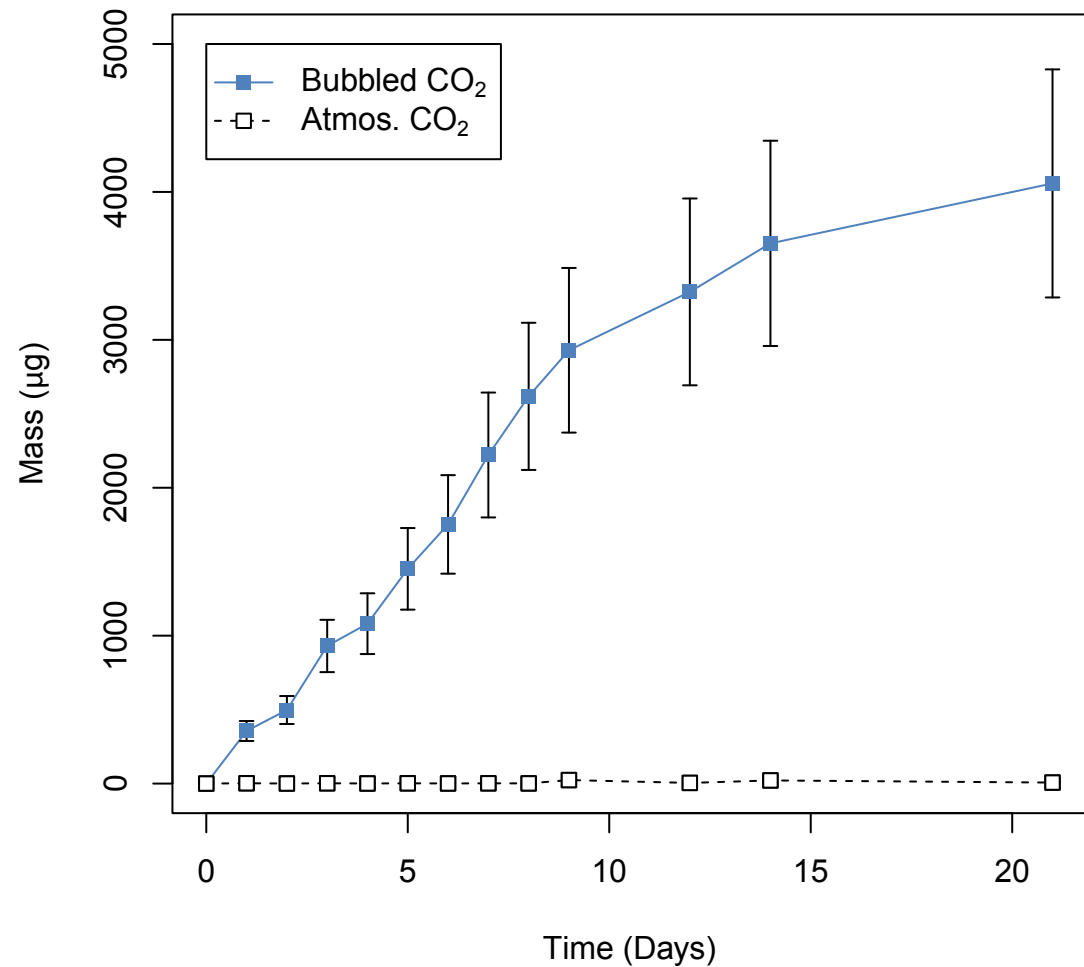
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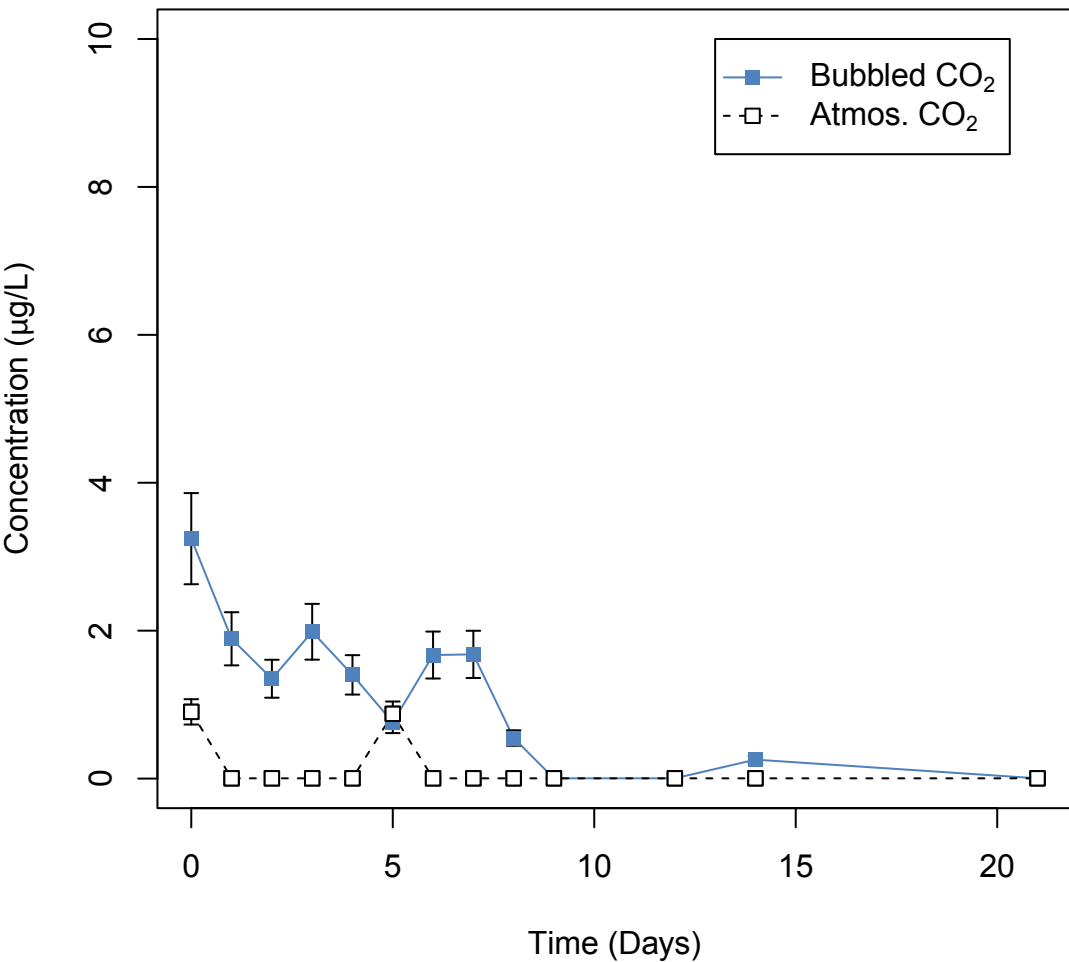
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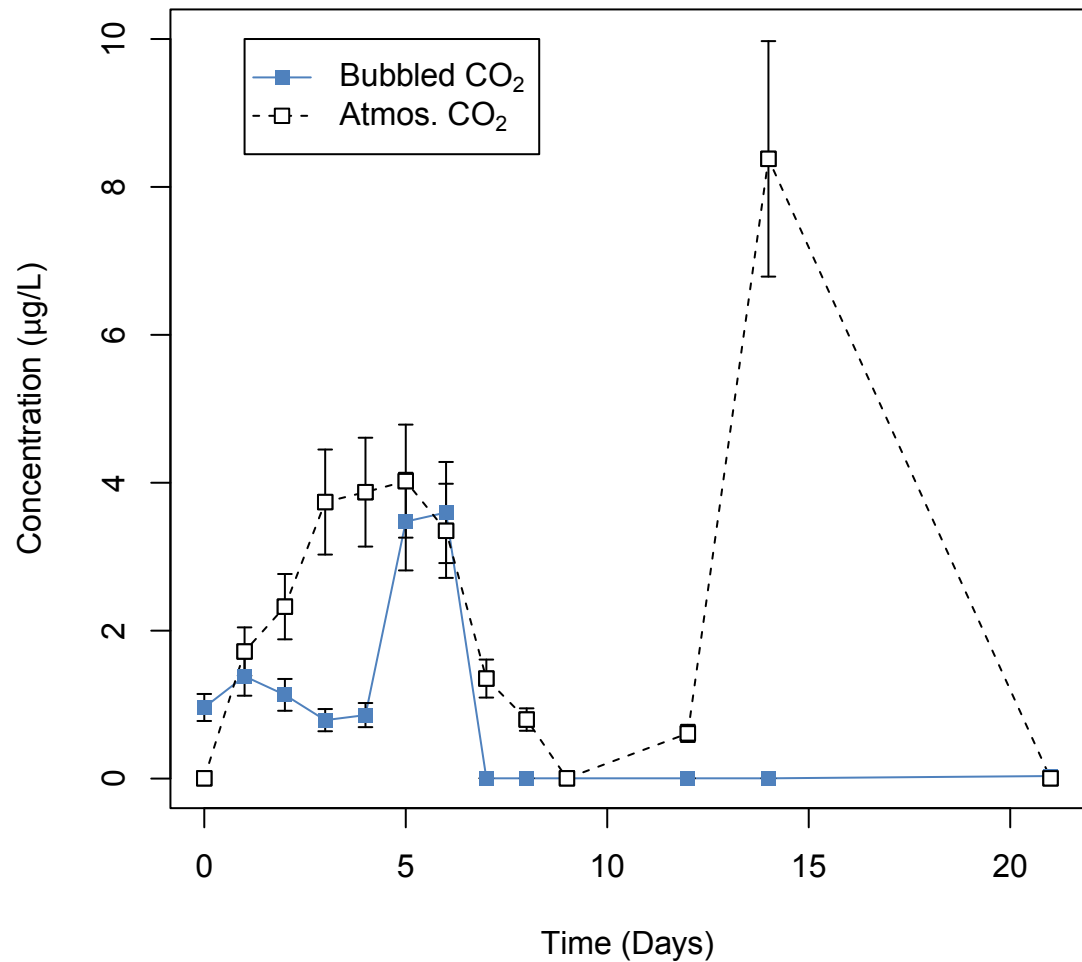
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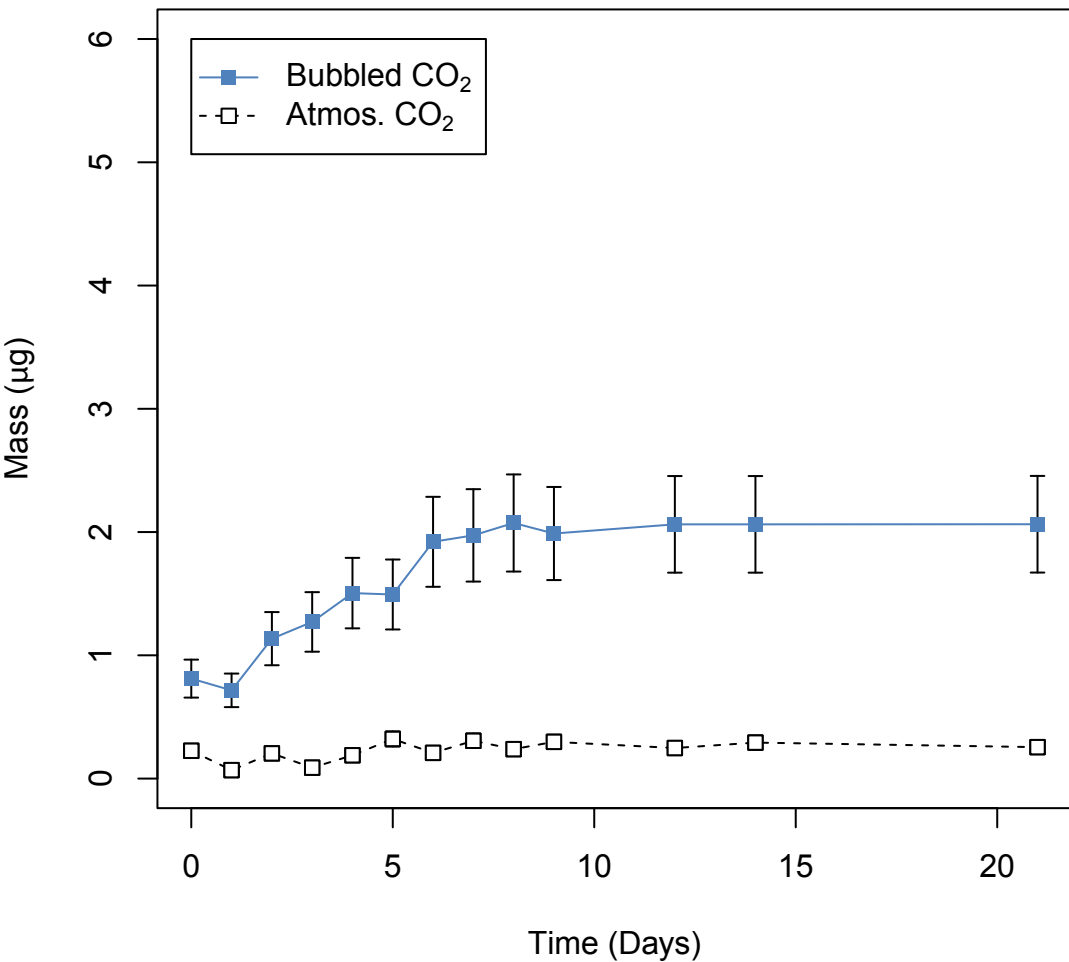
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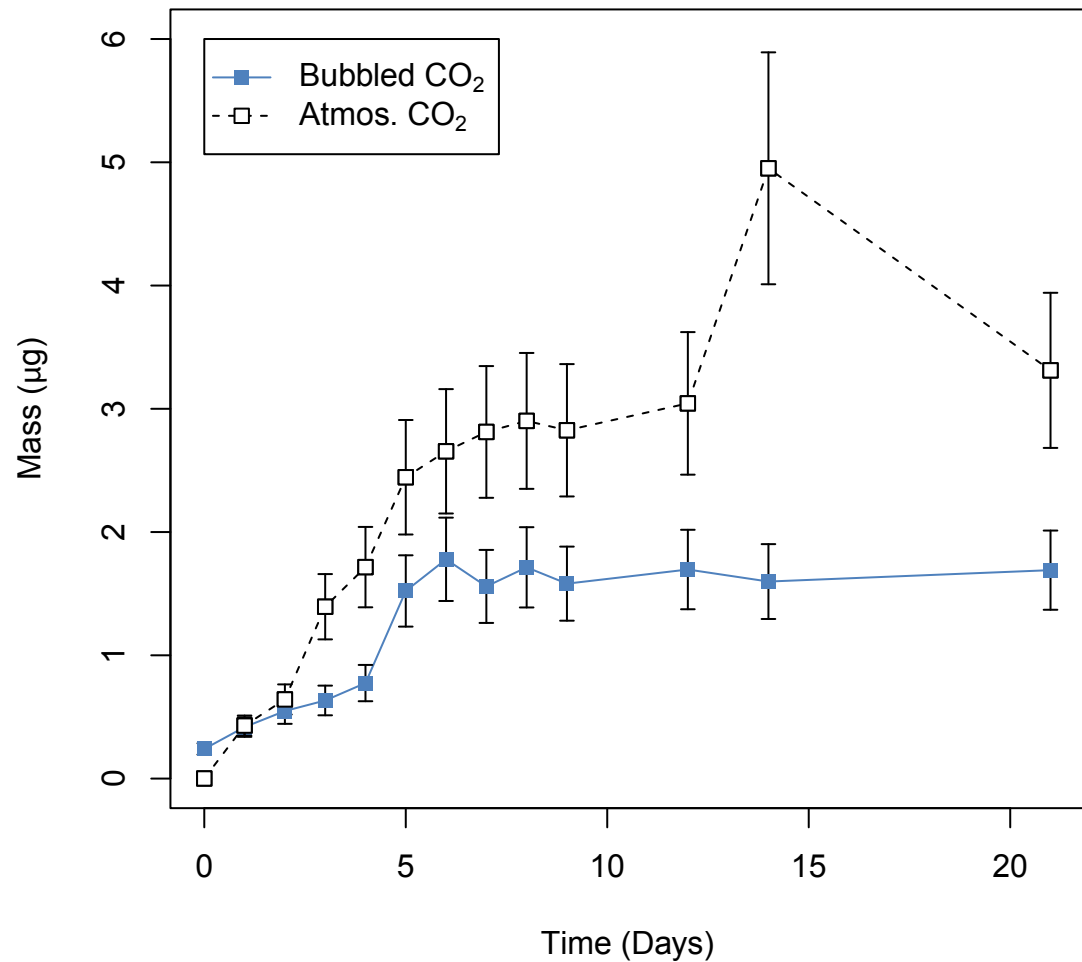
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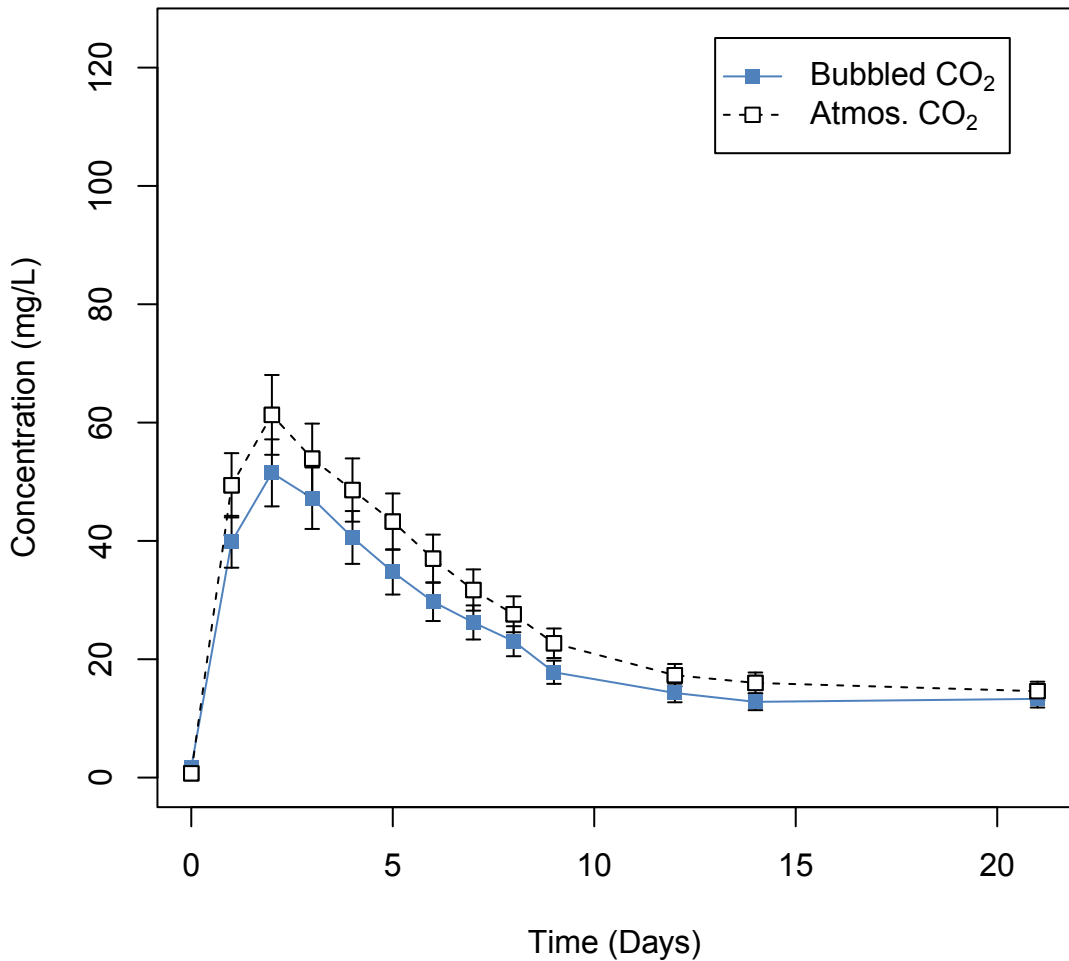
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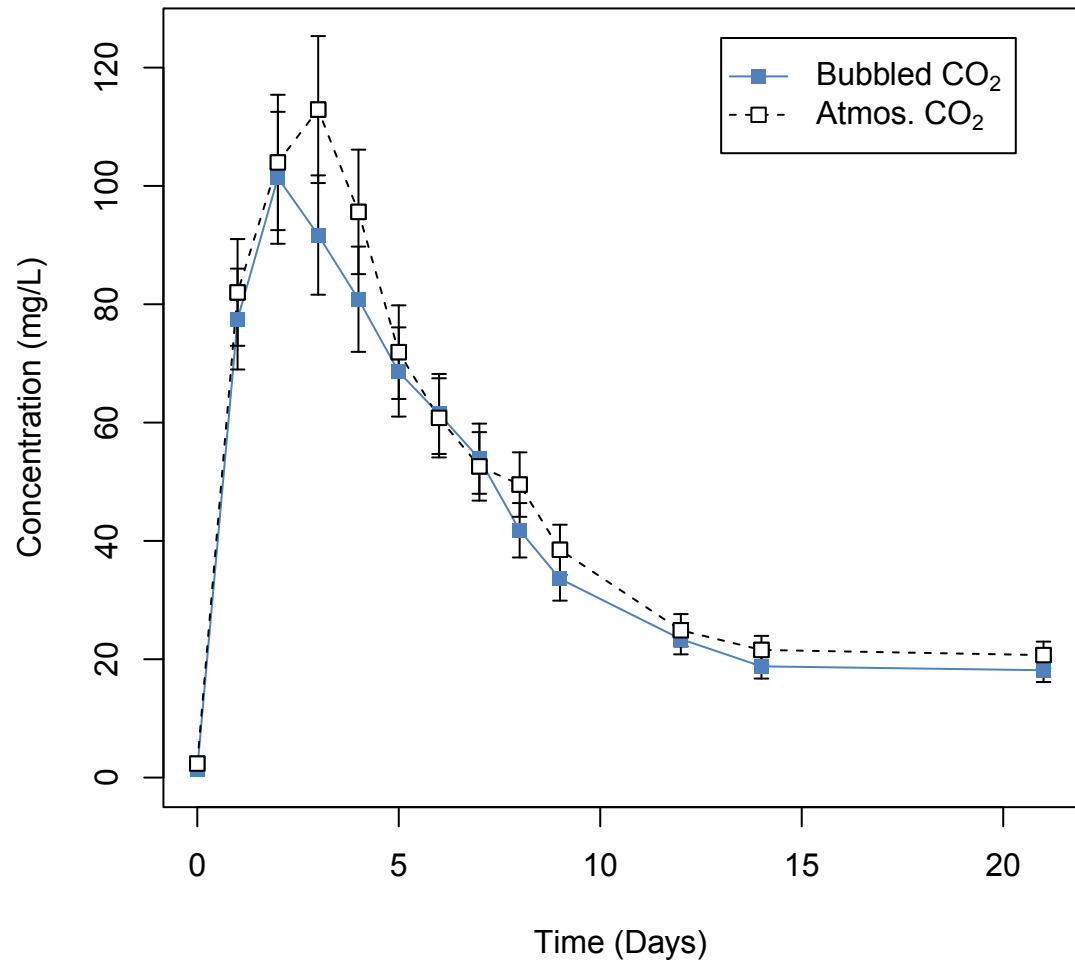
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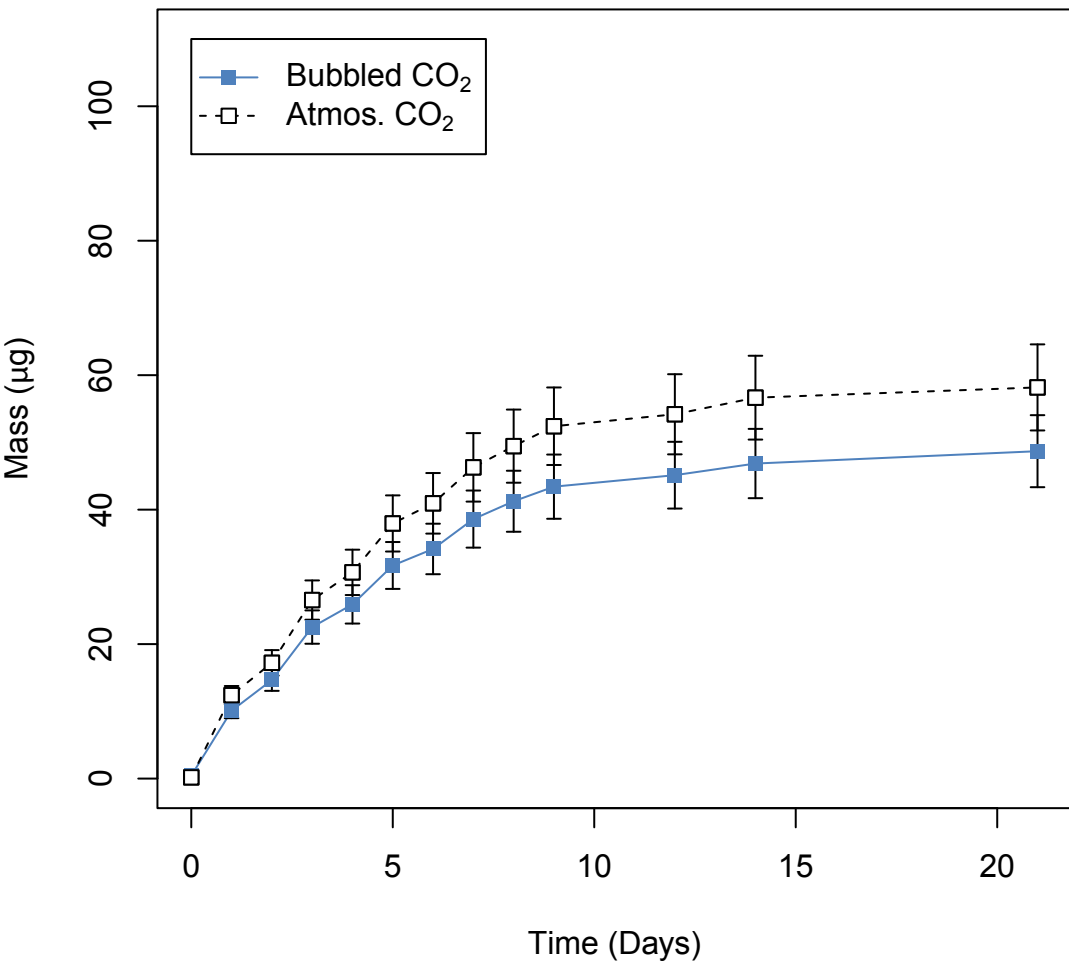
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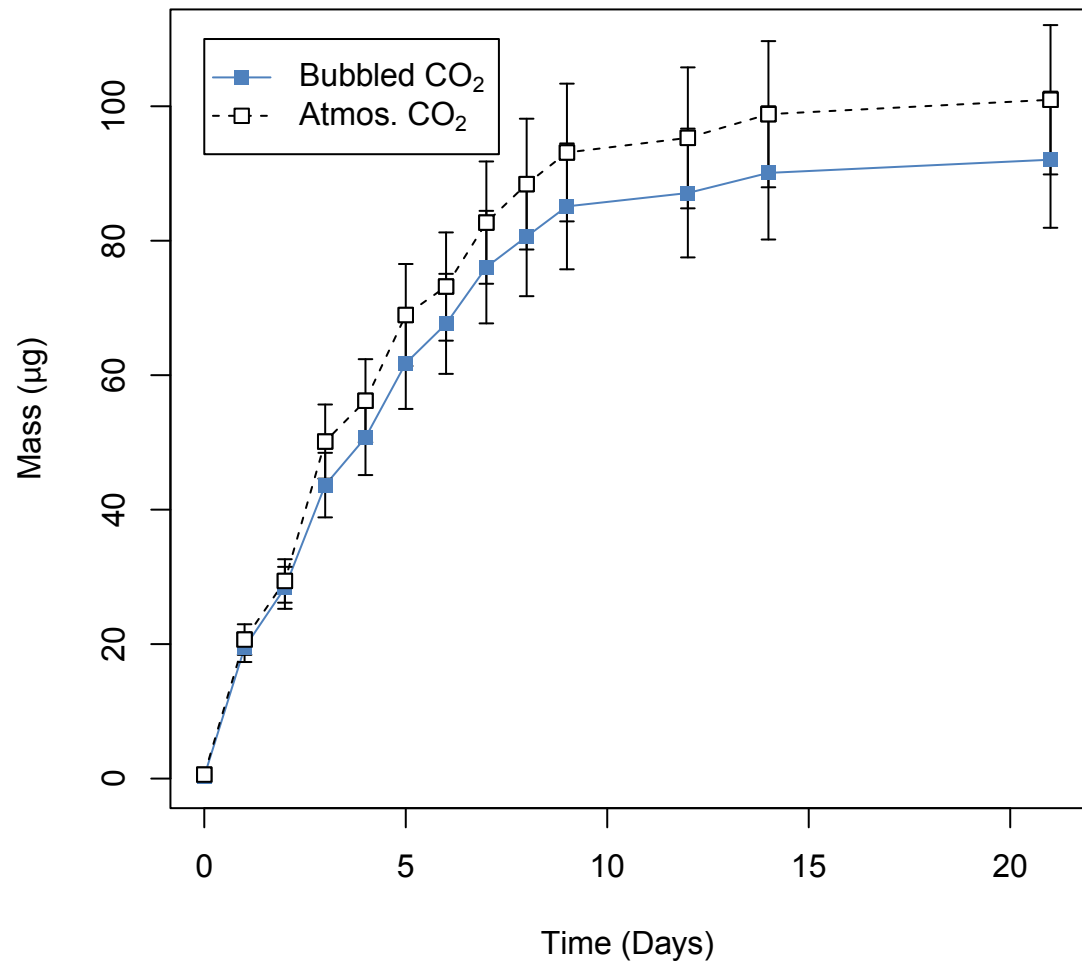
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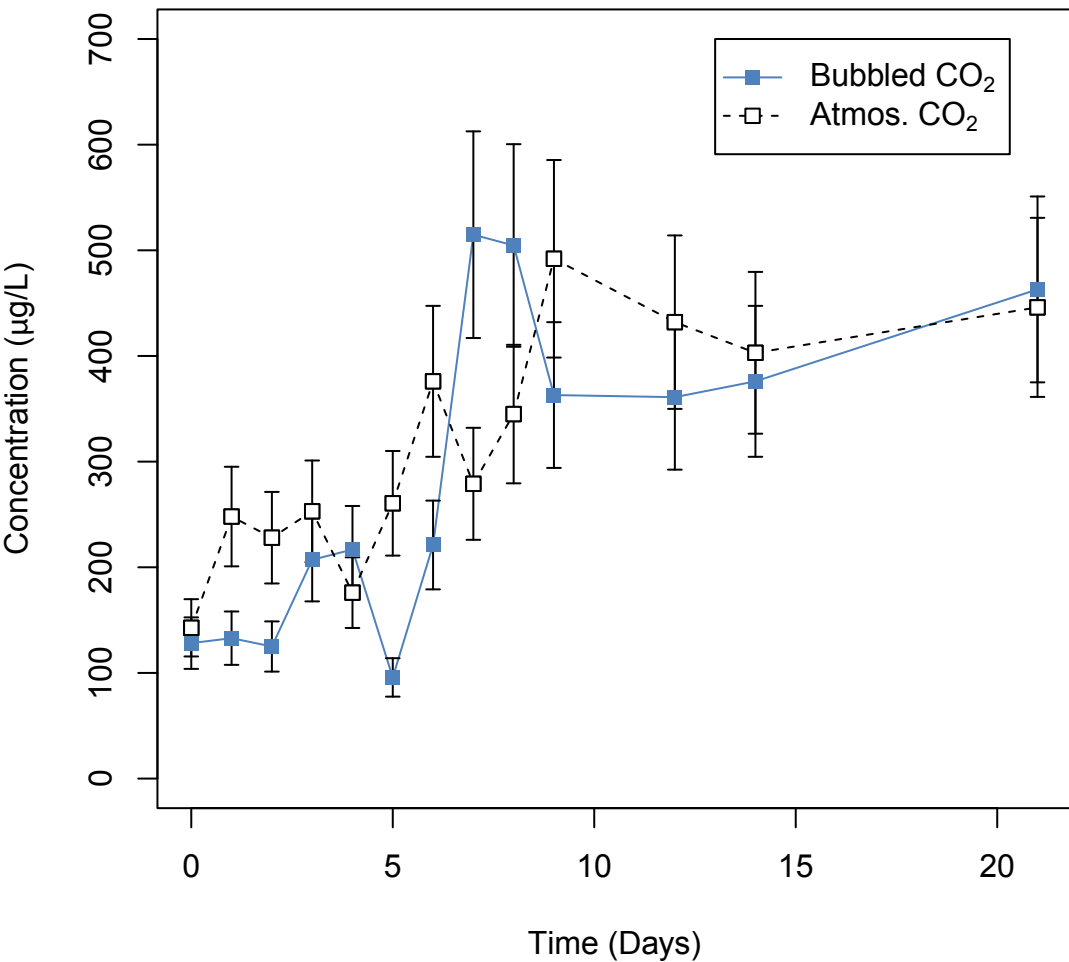
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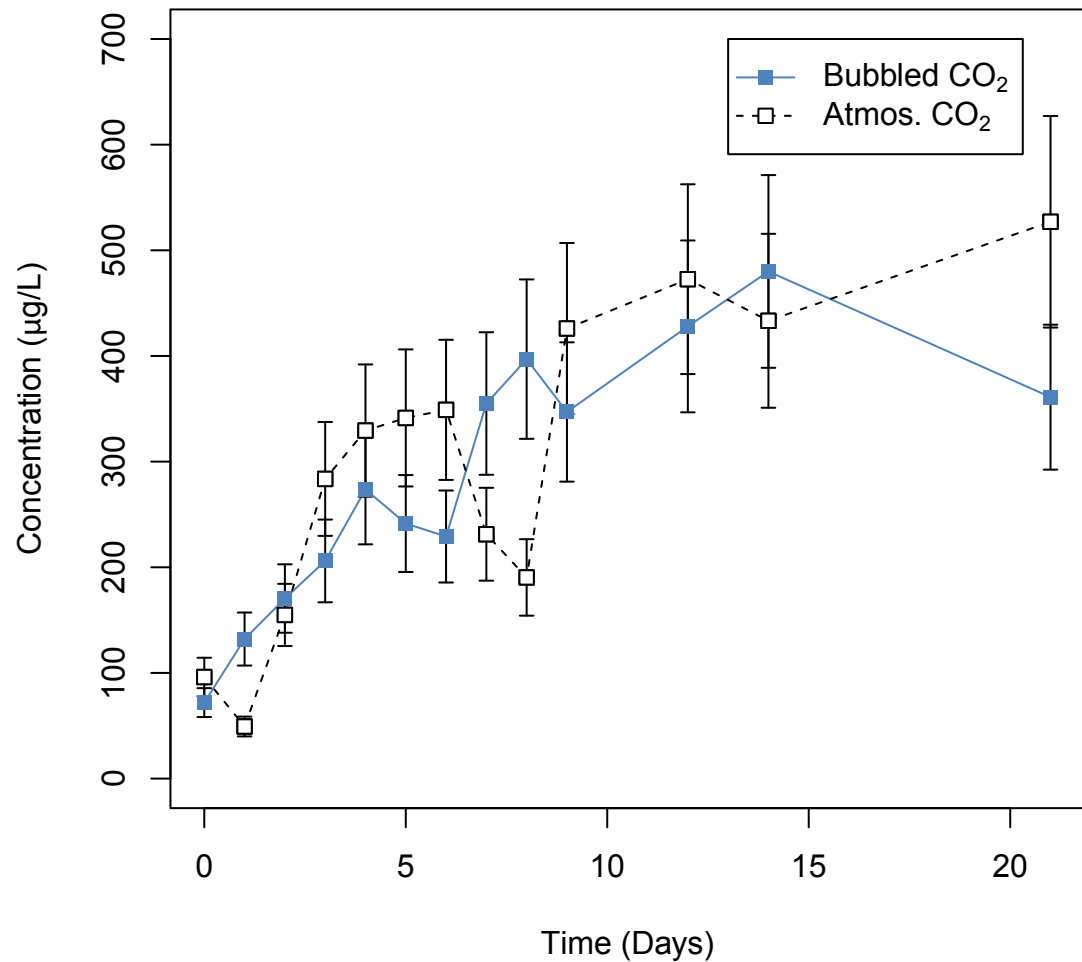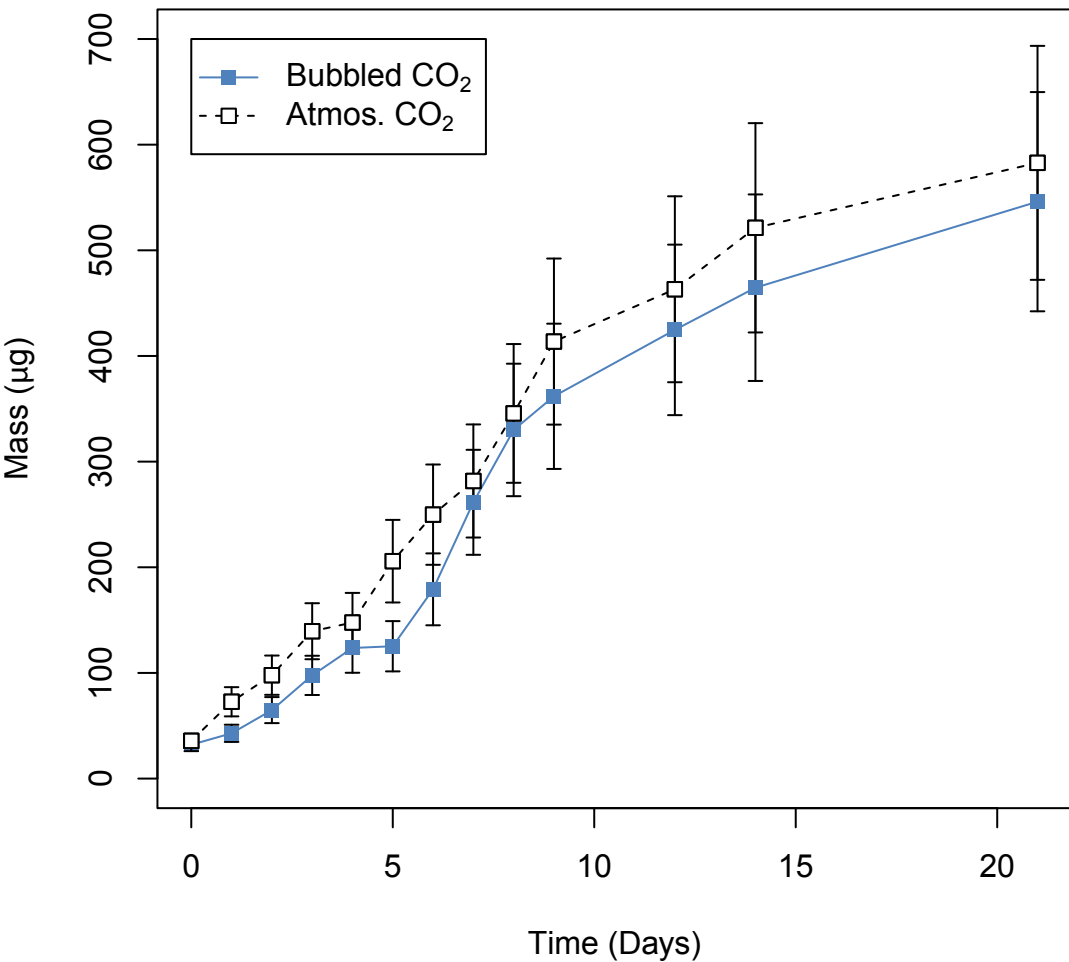
Lithium Mass − Sample 8518   **Lithium Mass − Sample 8579**
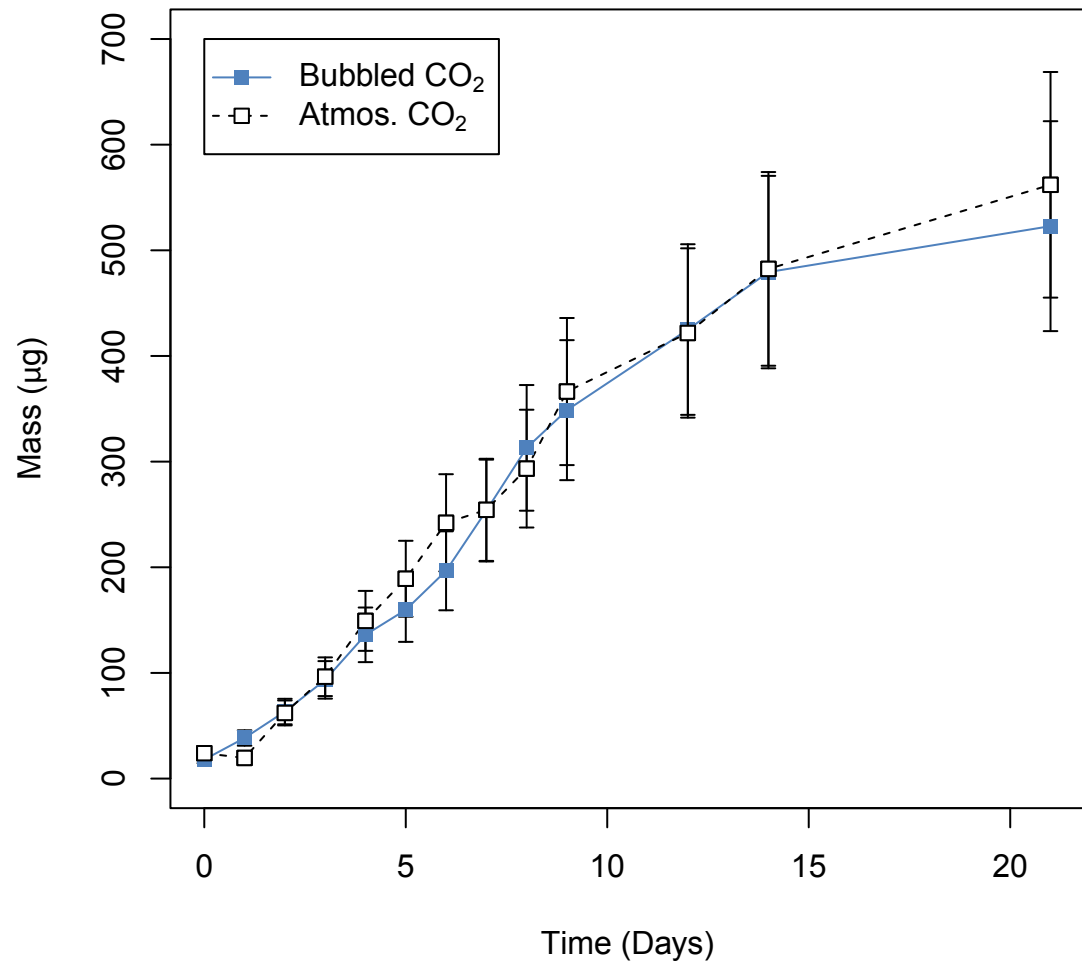
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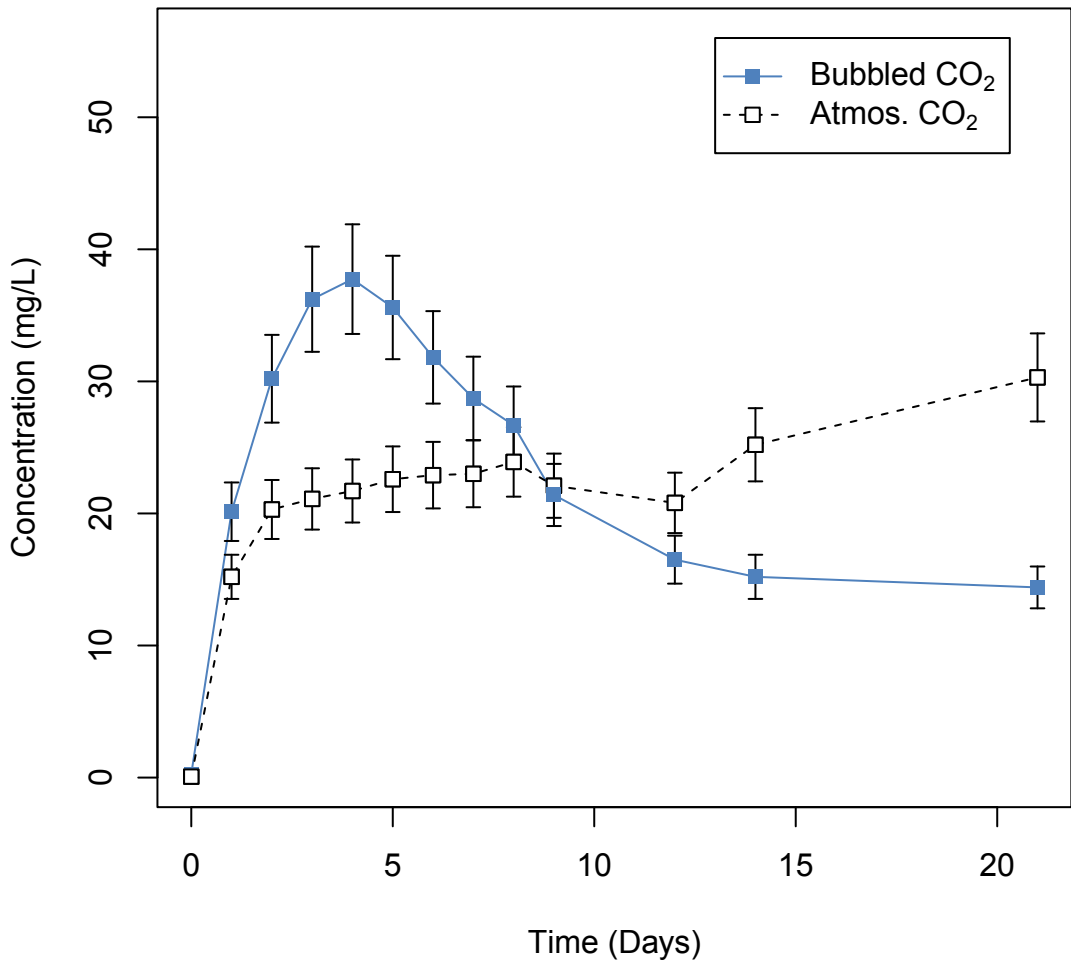
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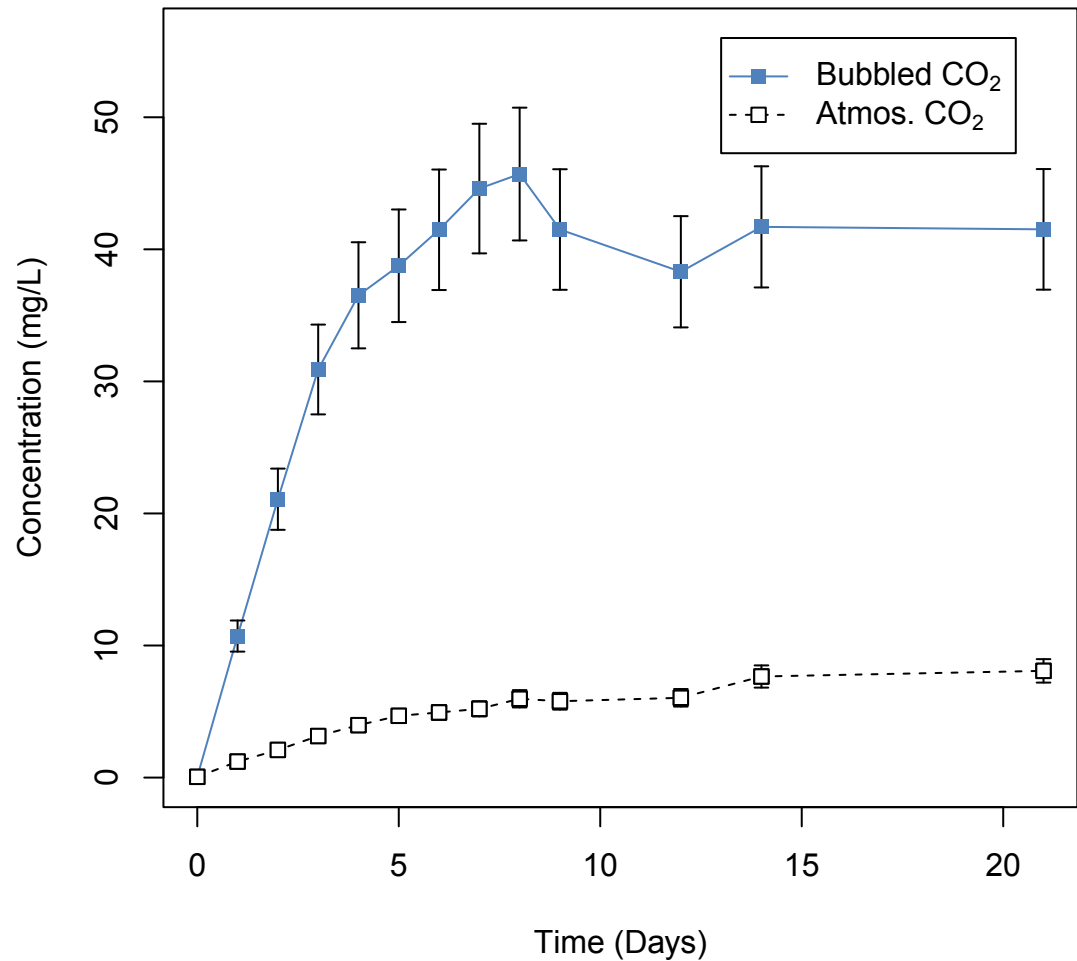
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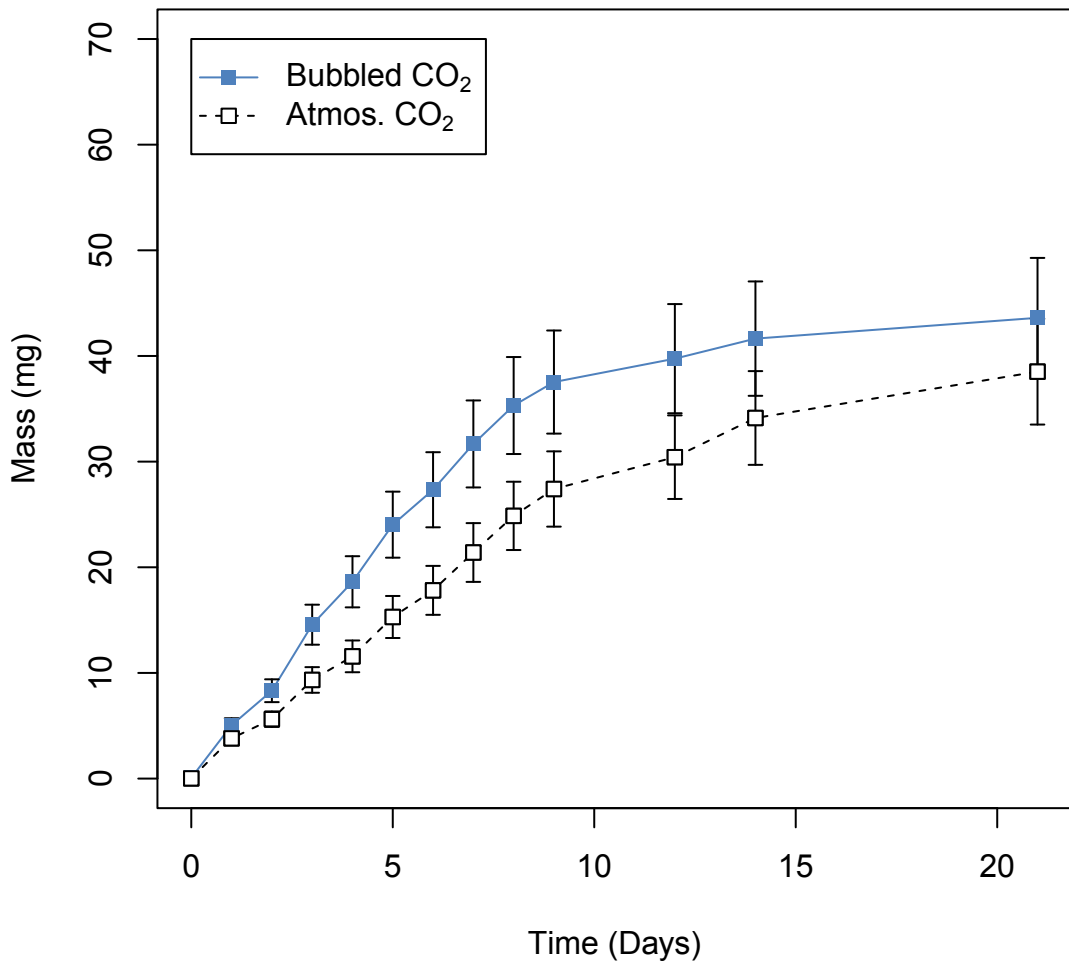
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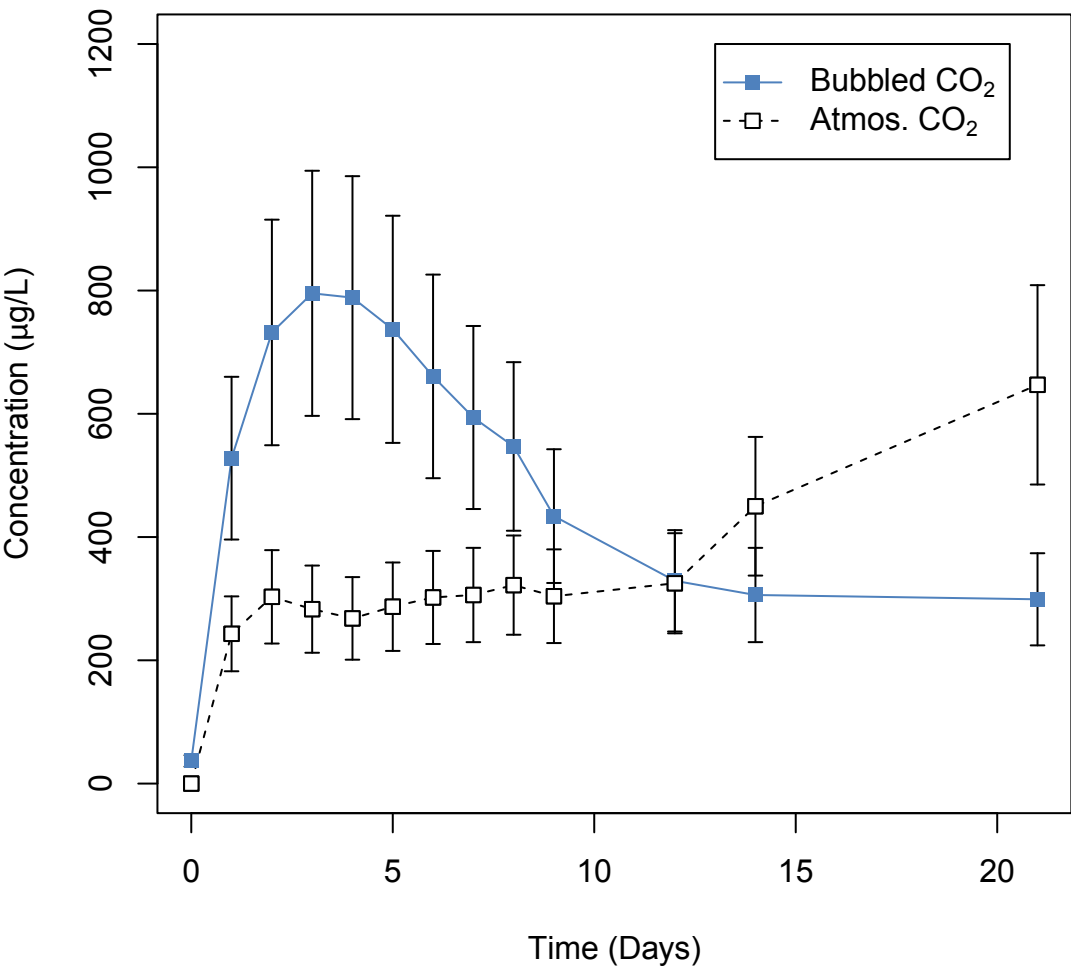
Manganese Concentrations − Sample 8518 and **Manganese Concentrations − Sample 8579**
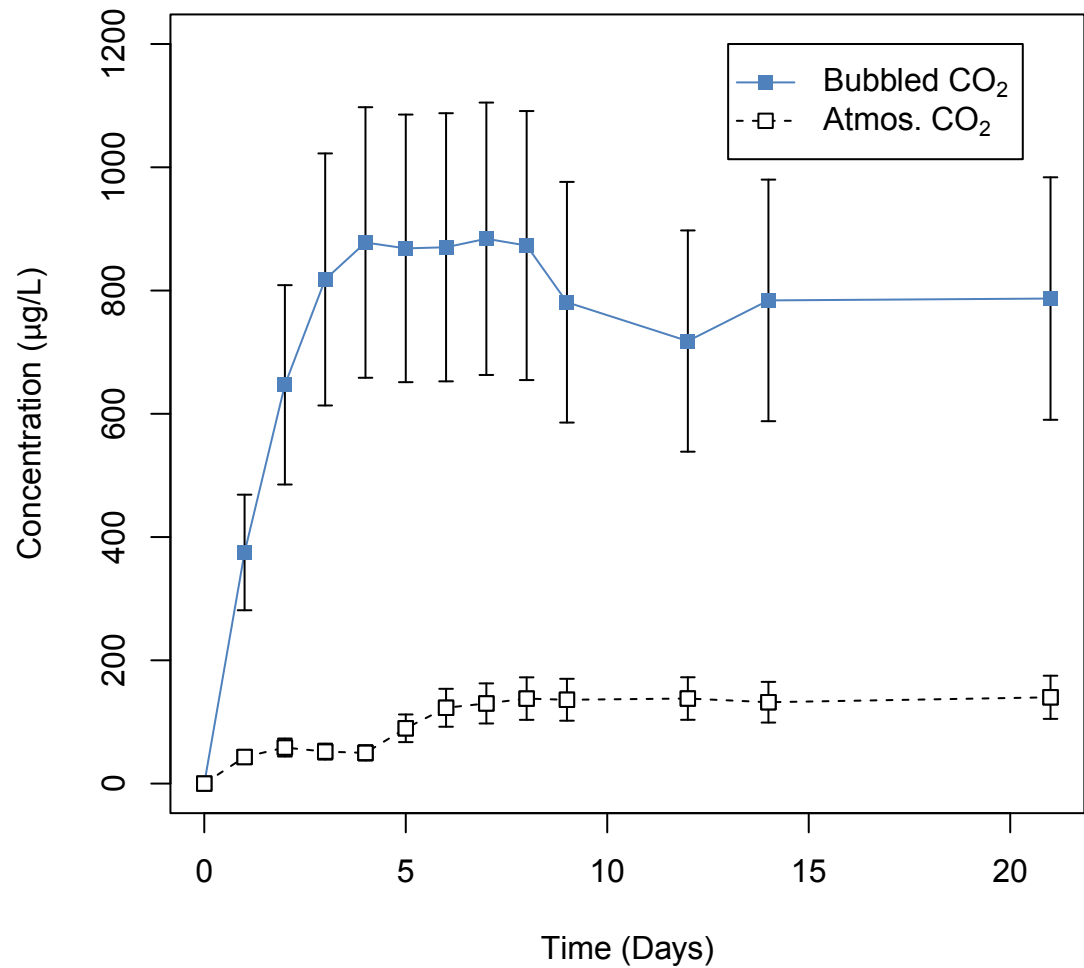
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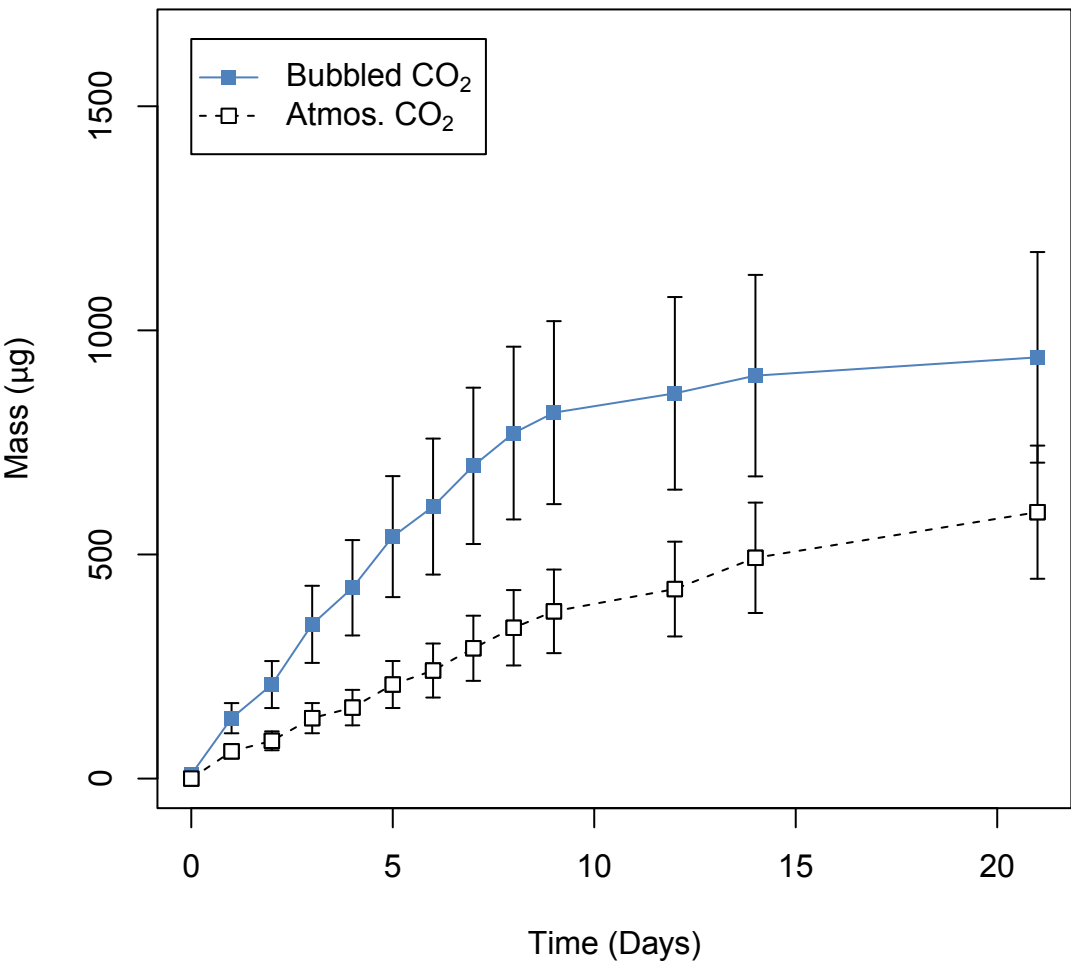
Manganese Mass − Sample 8579
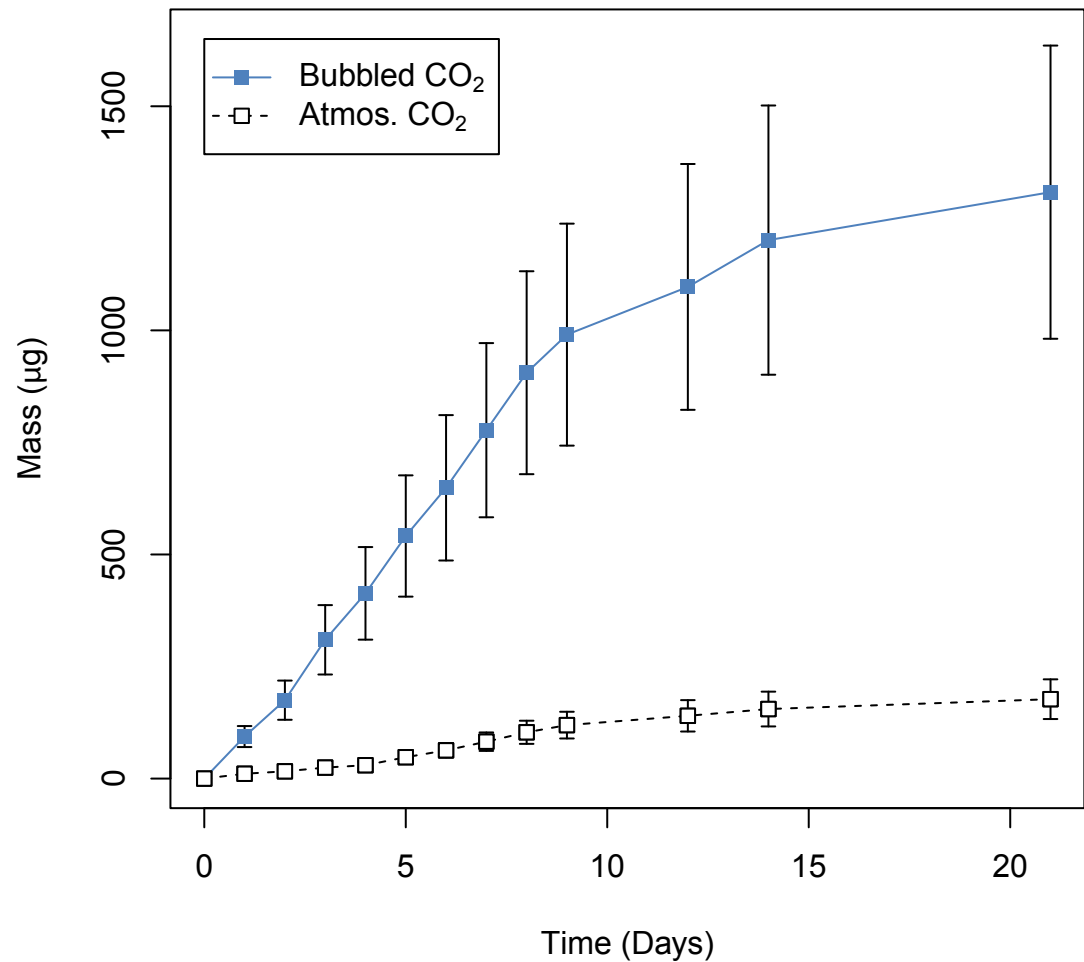
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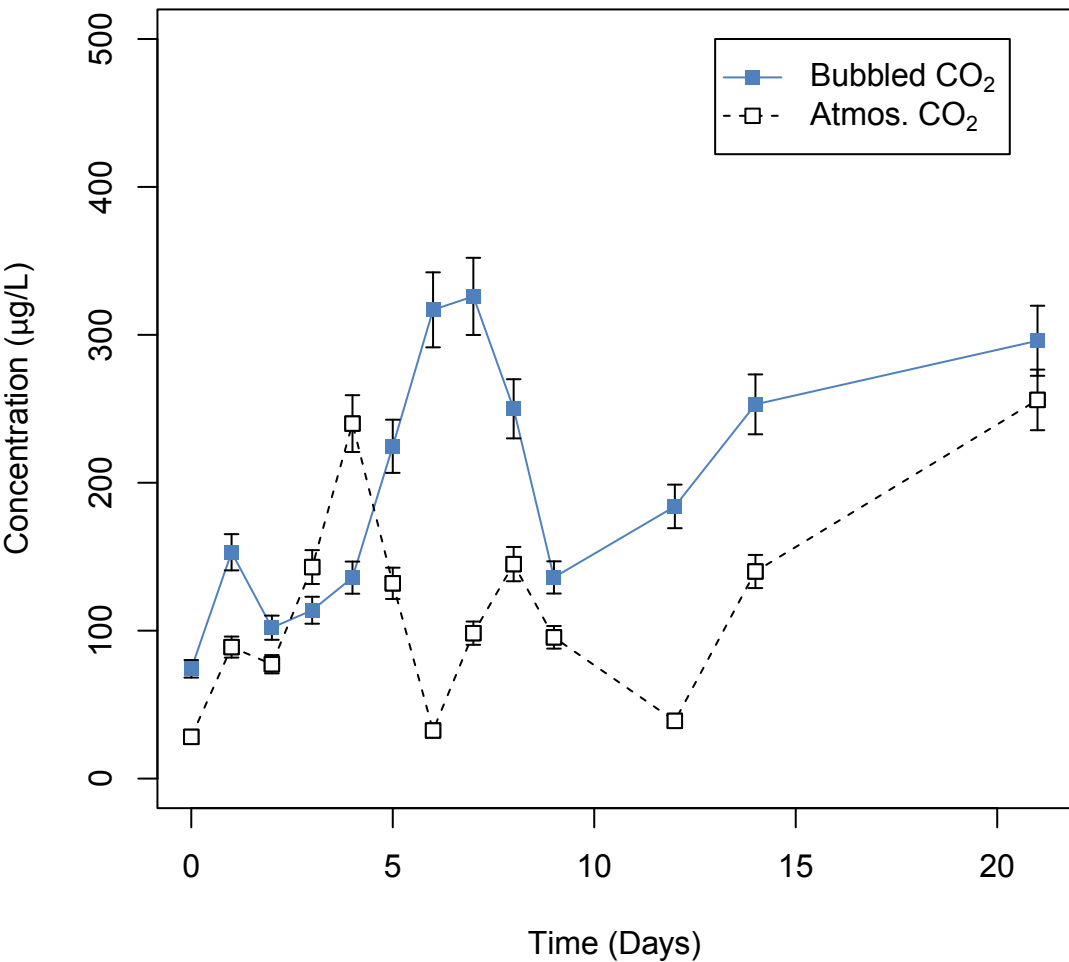
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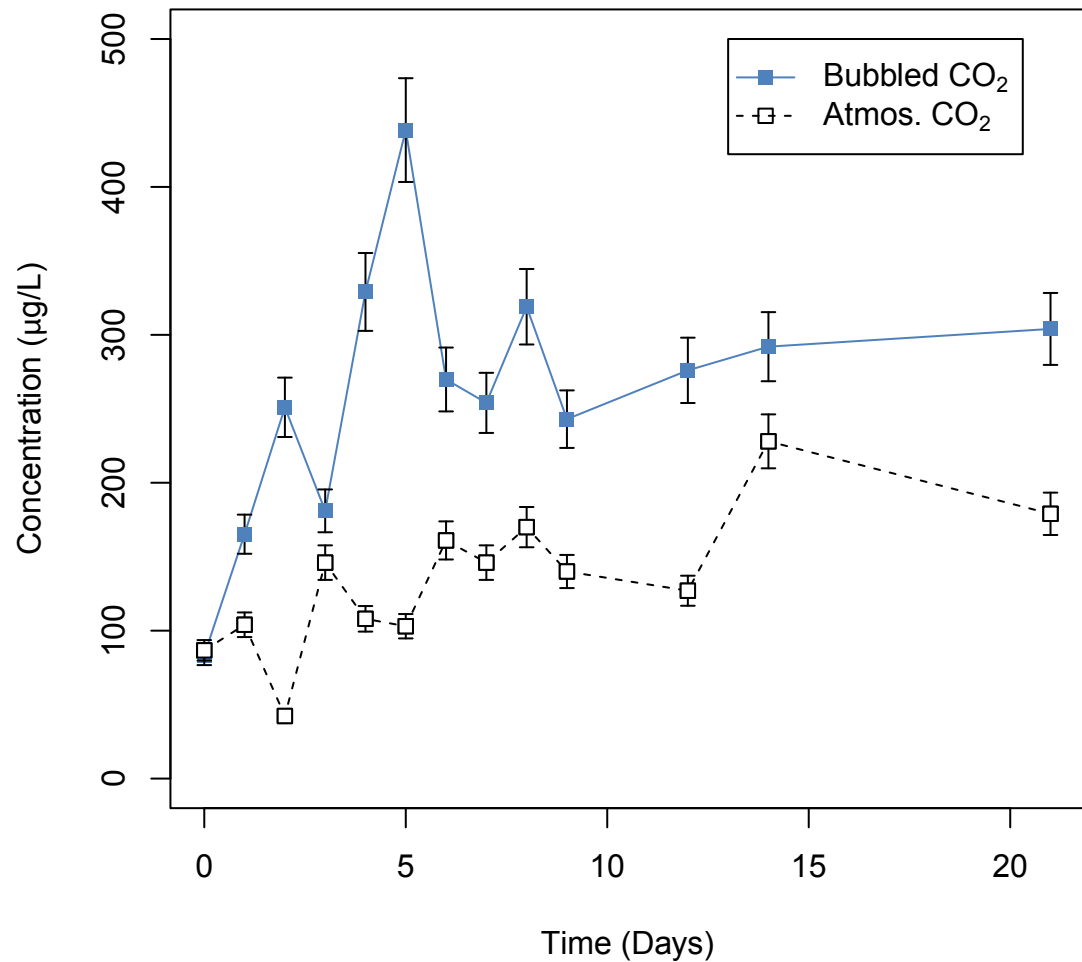
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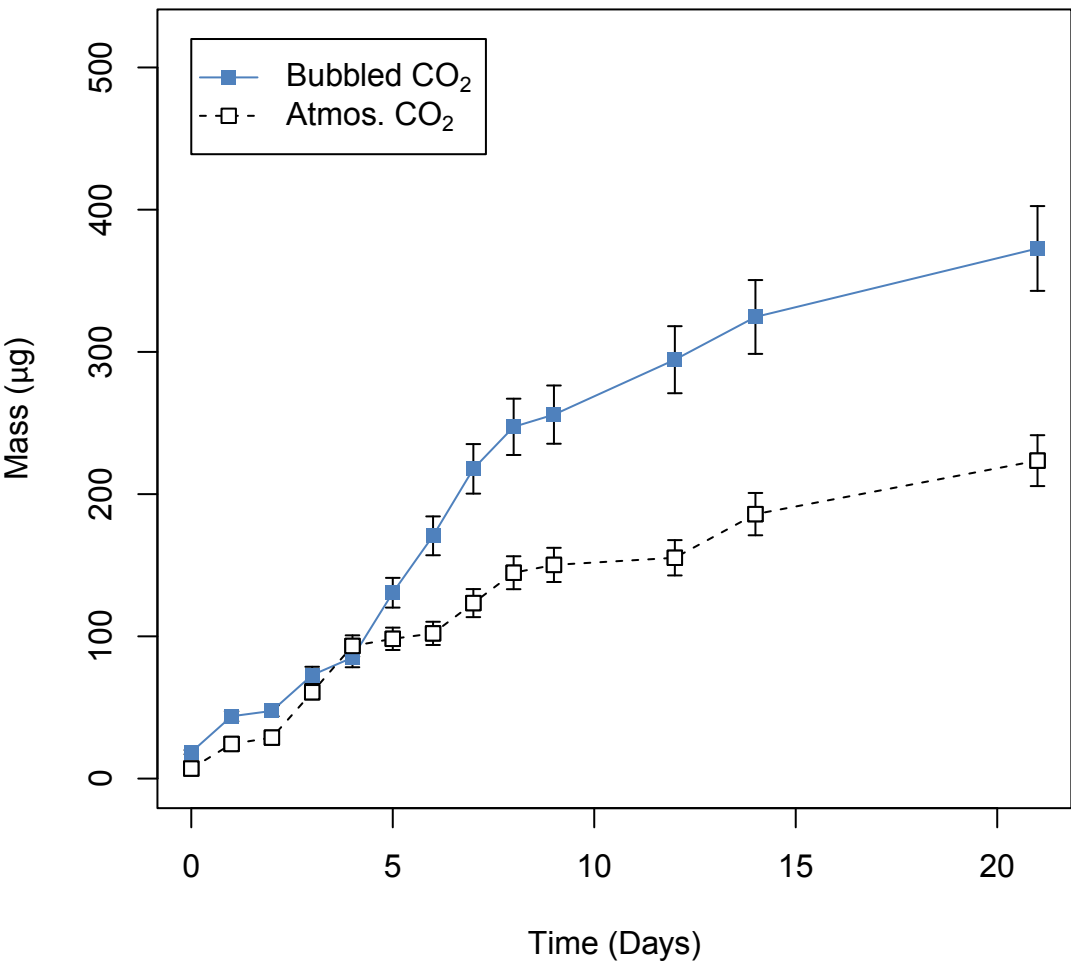
Nickel Mass − Sample 8579
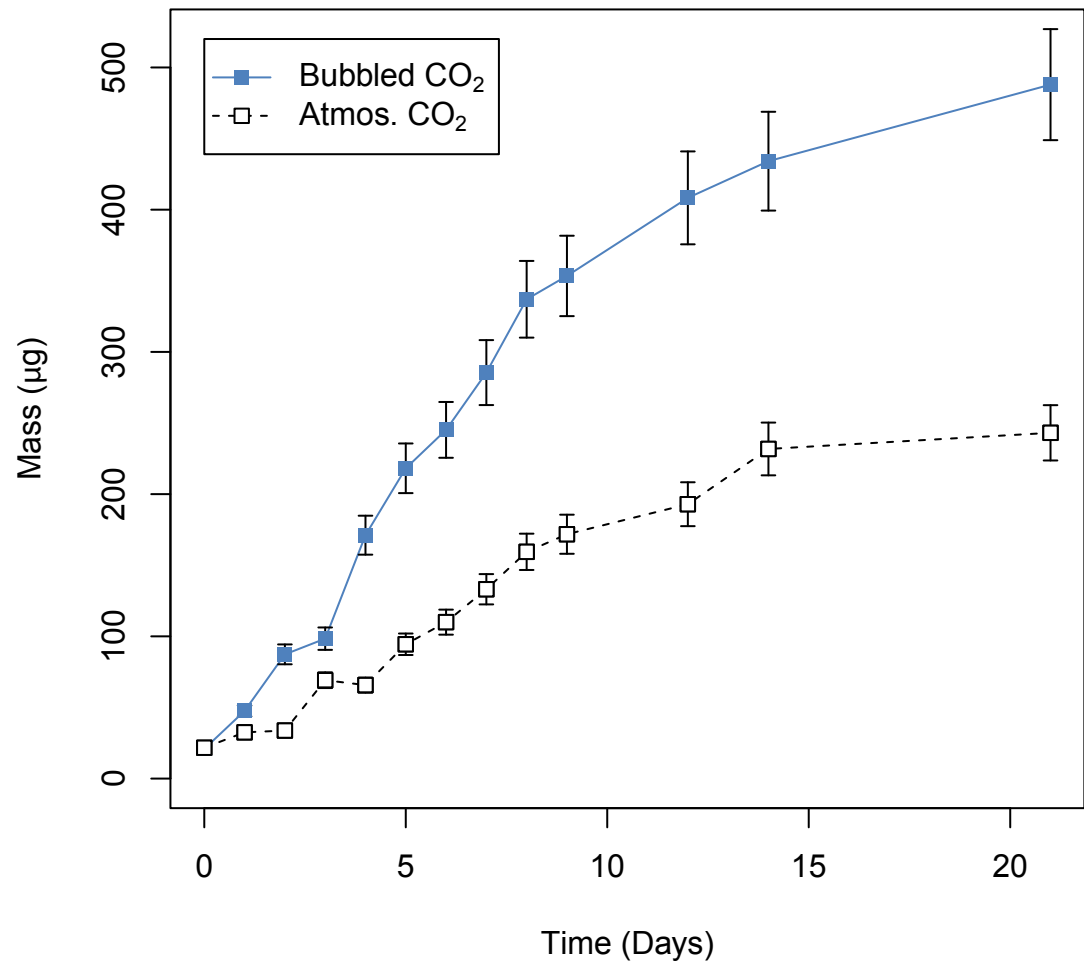
Zinc Concentrations − Sample 8518
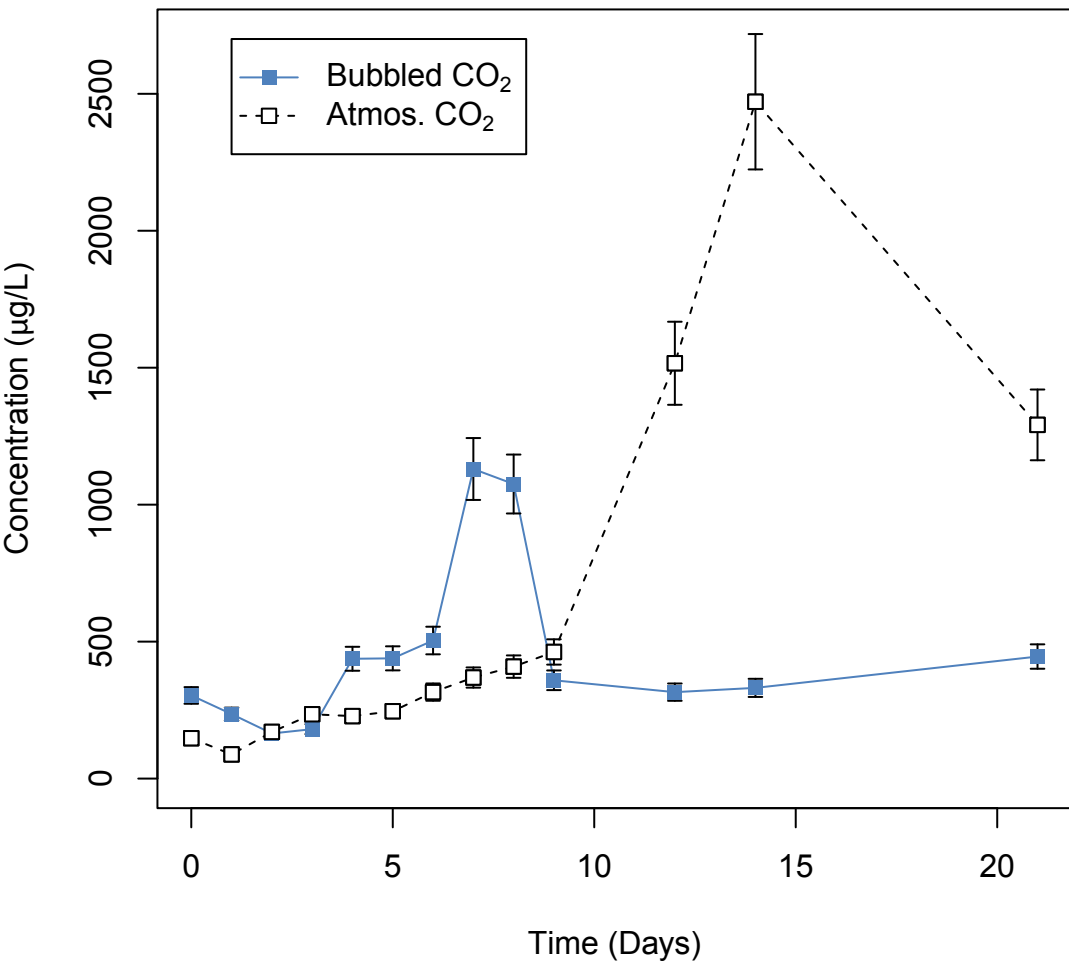
Zinc Concentrations − Sample 8579

Zinc Mass − Sample 8518

Bubbled CO_2
Atmos. CO_2

Mass (µg)

Time (Days)
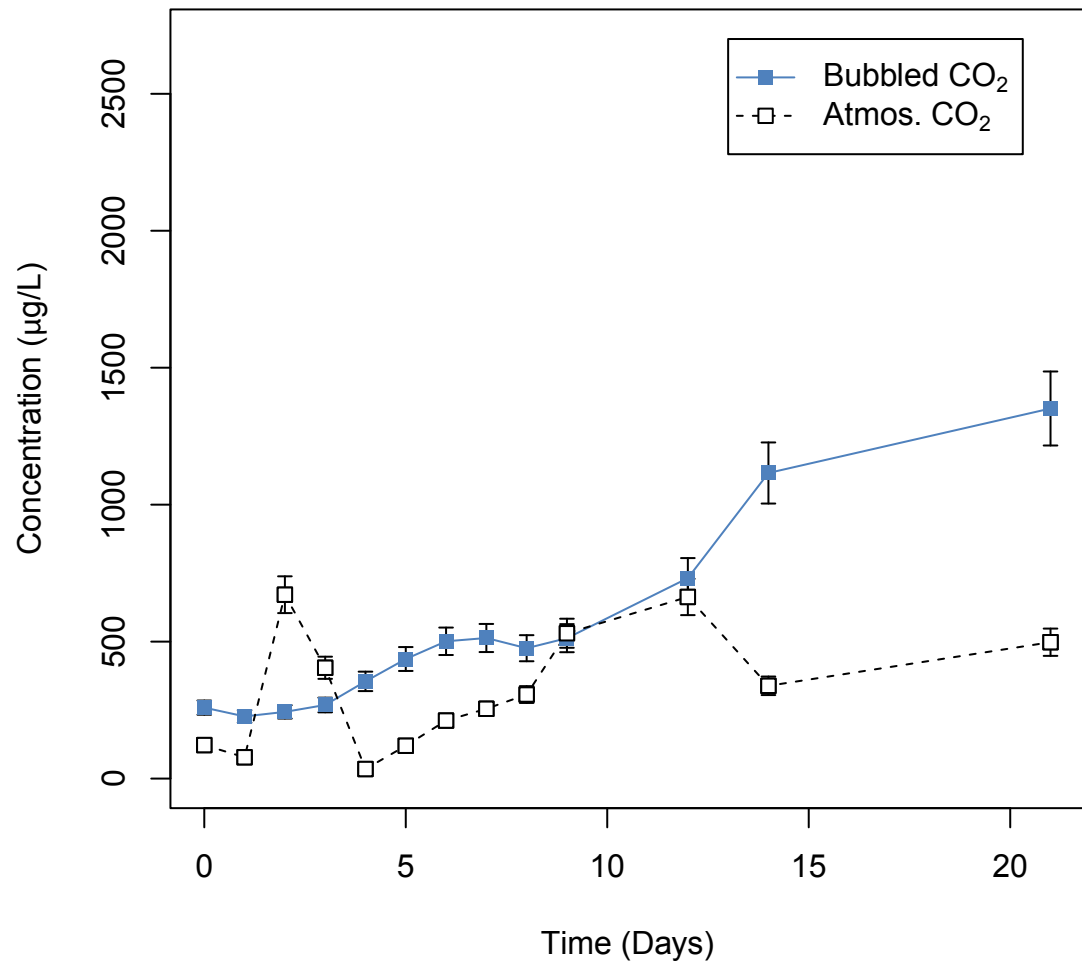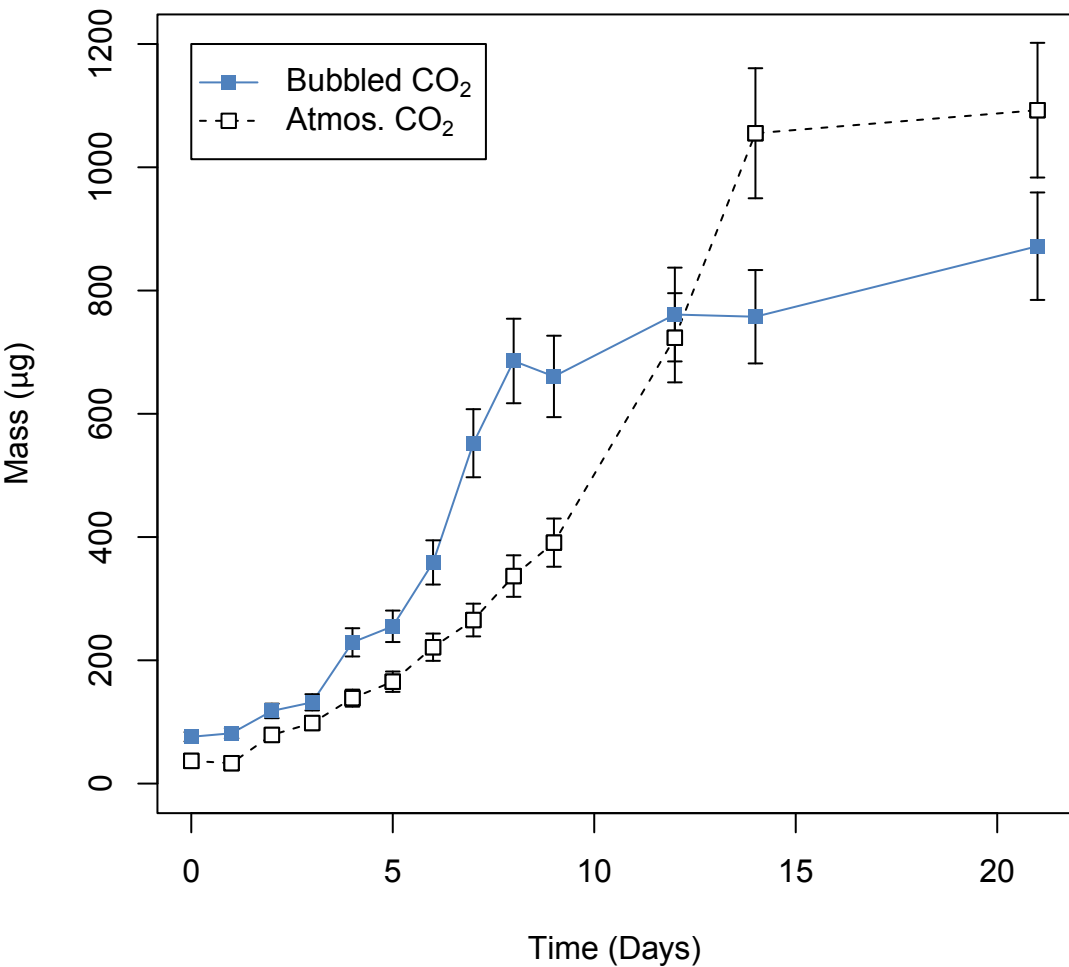
Zinc Mass − Sample 8579

Bubbled CO_2
Atmos. CO_2

Mass (µg)
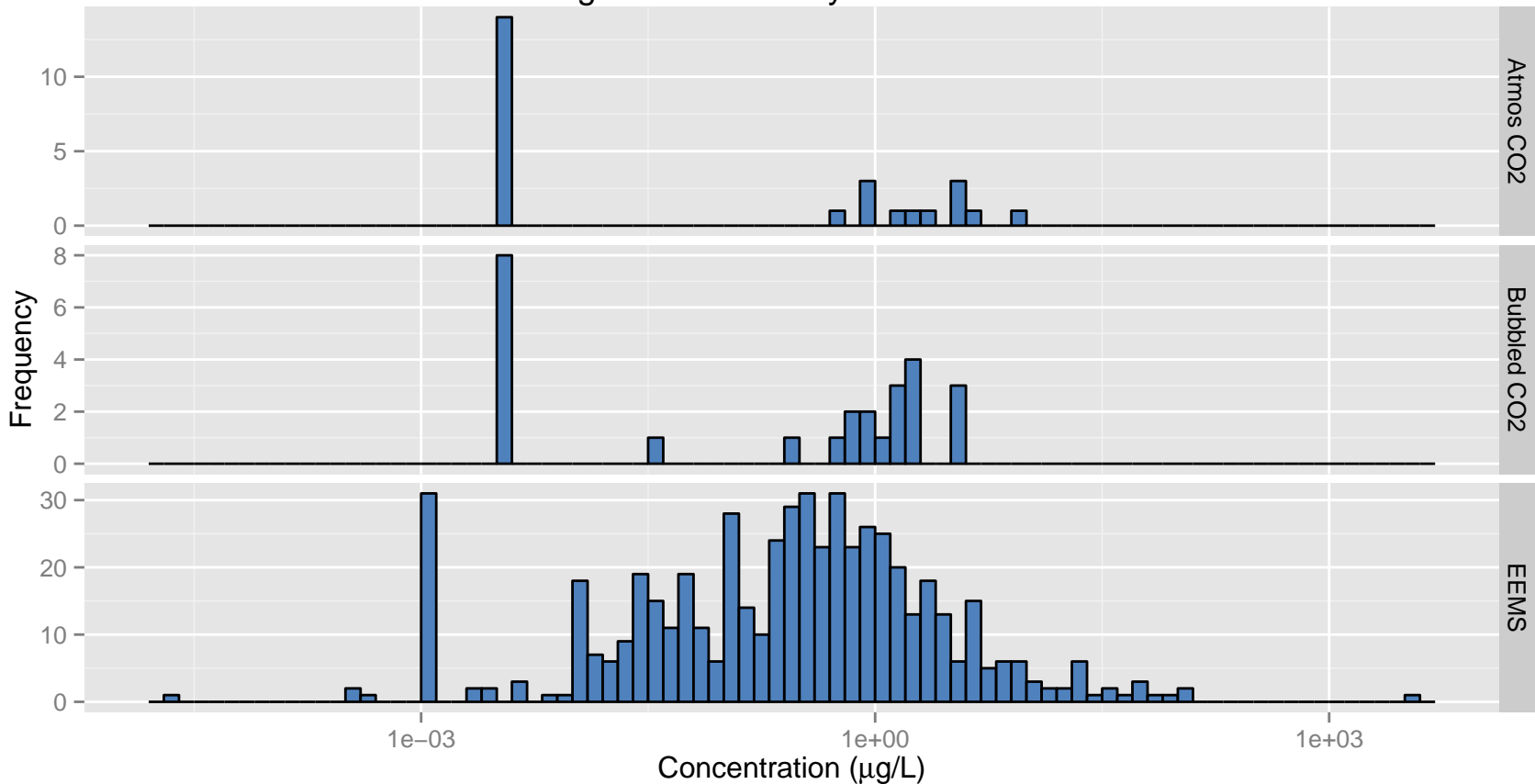
Time (Days)
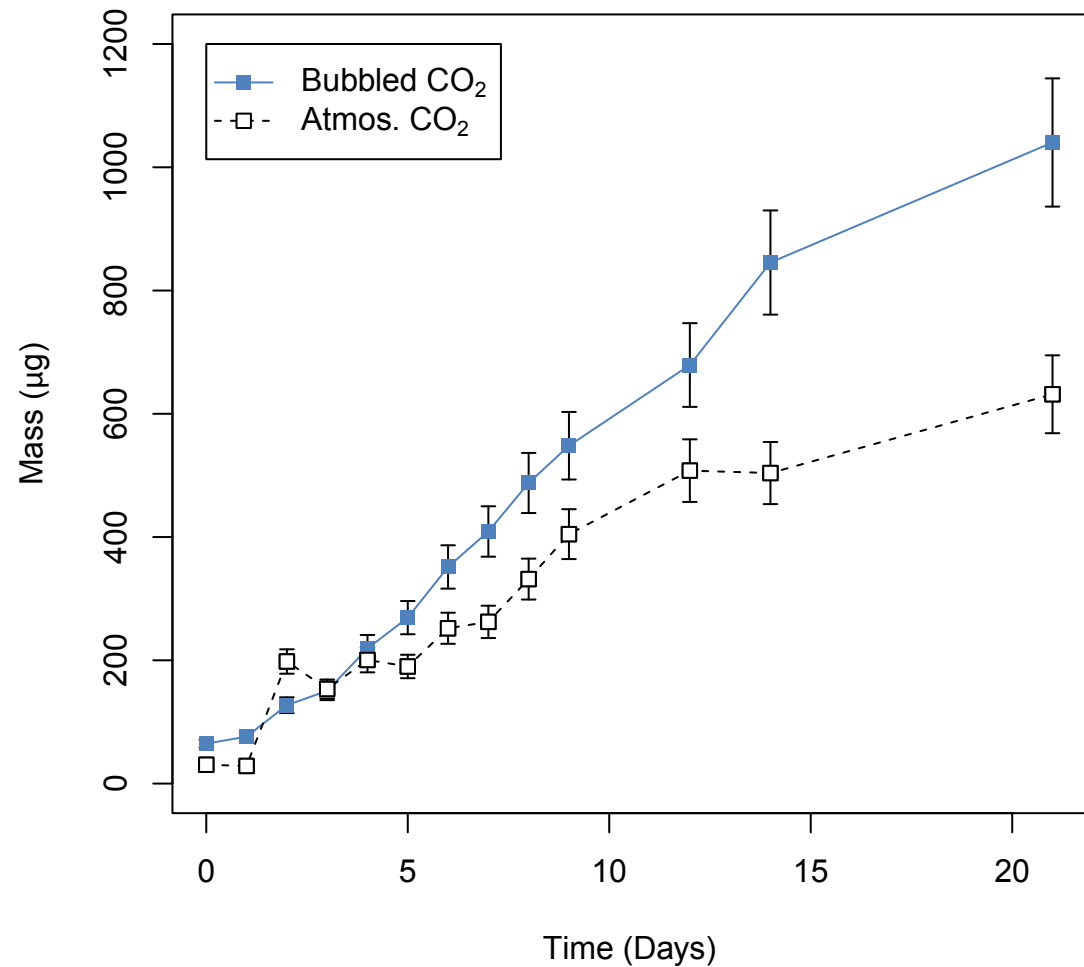
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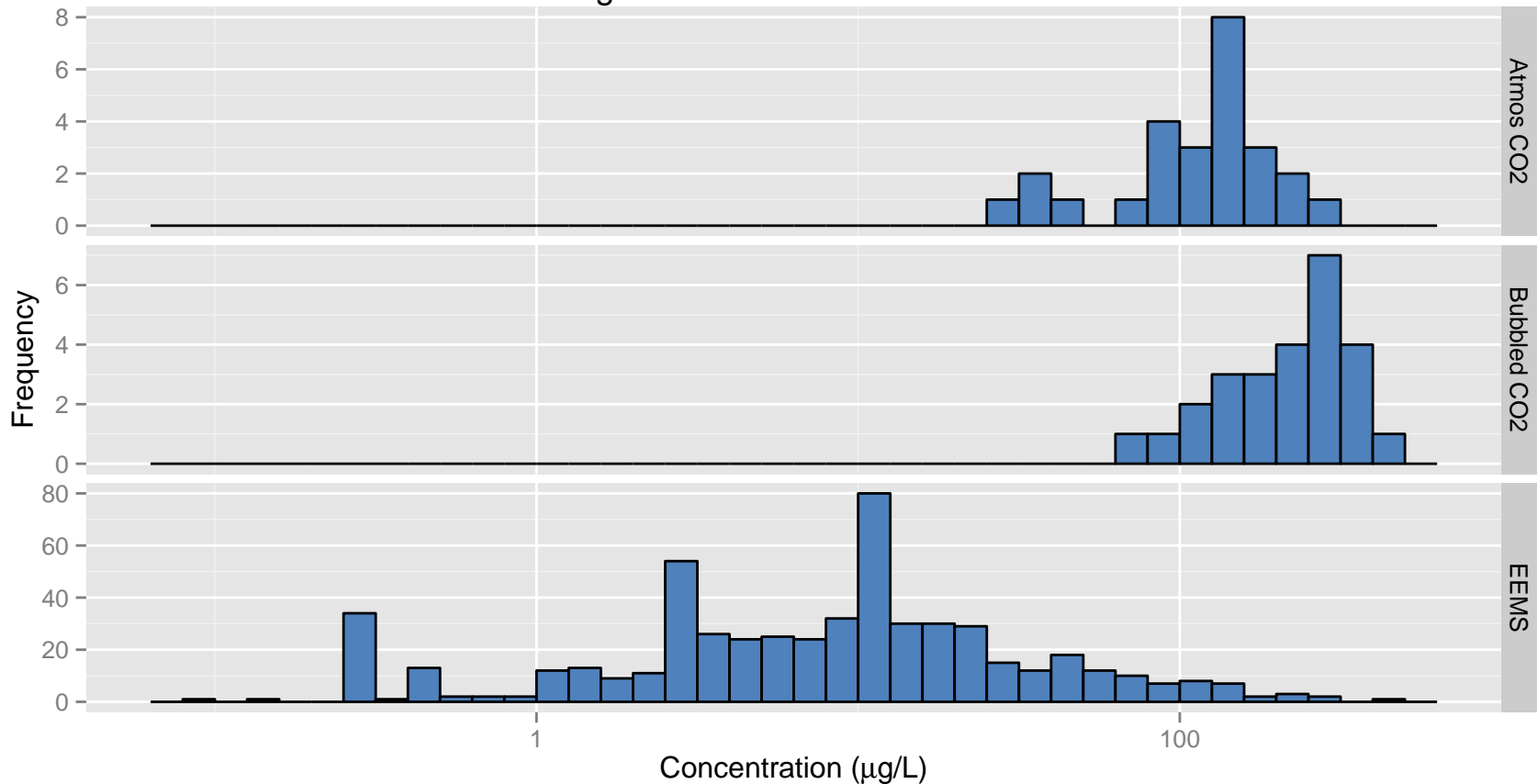
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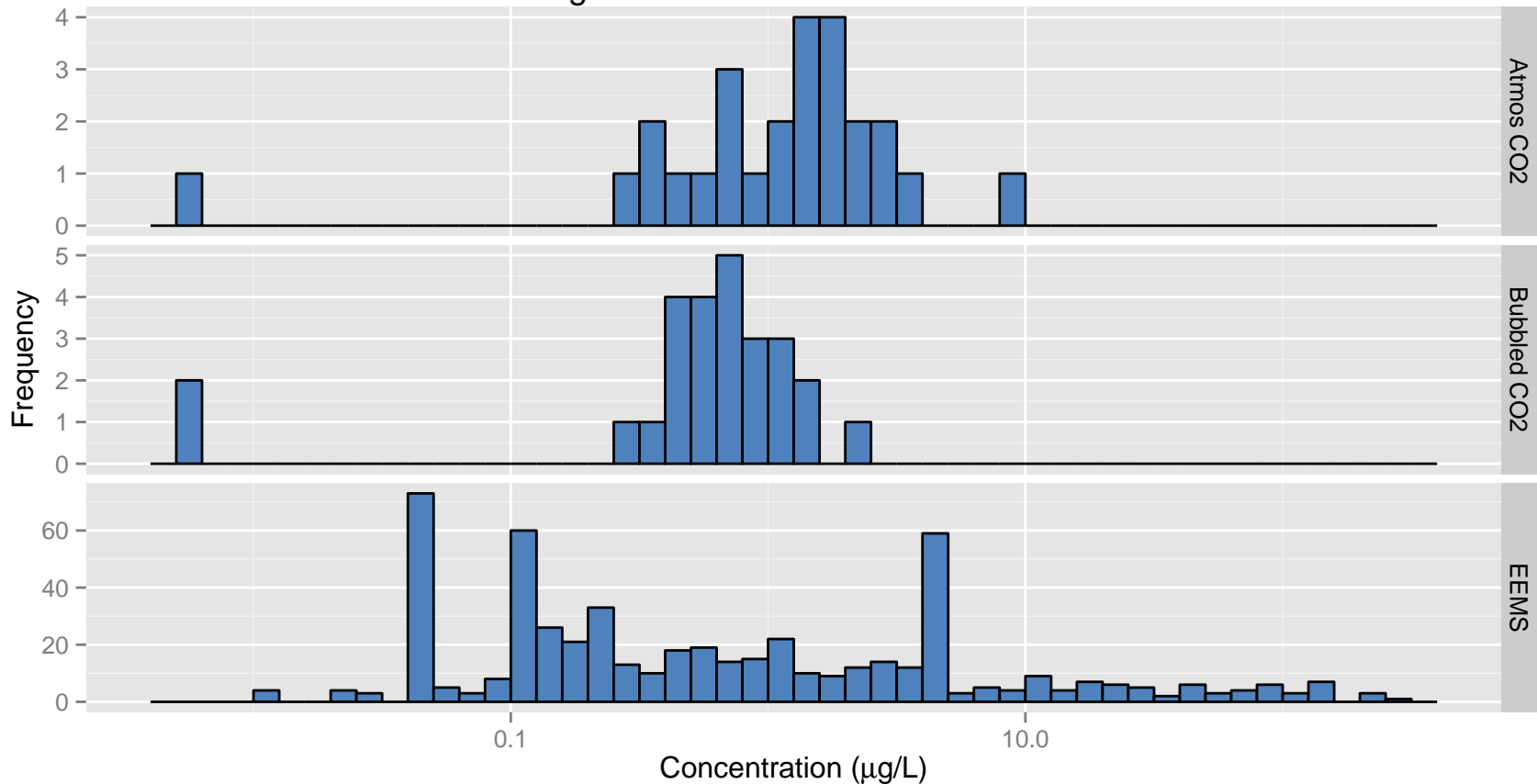
Histograms of Copper Concentrations
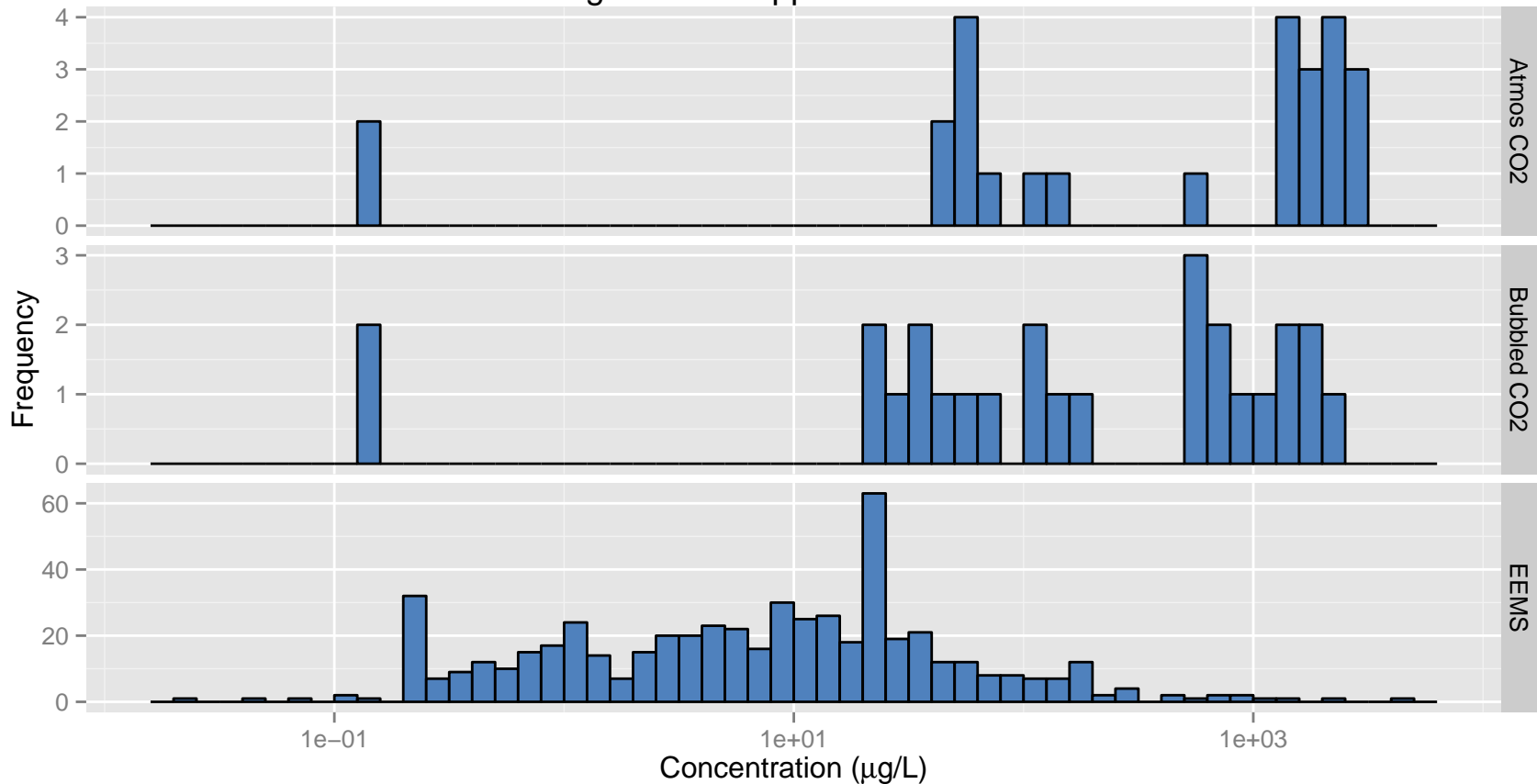
Histograms of Mercury Concentrations

Histograms of Nickel Concentrations

Histograms of Zinc Concentrations