CATO-2 Deliverable WP3.06-D02

Towards maps of CO_2 concentrations (in groundwater) varying in time and interpretation per region of the data

Progress report

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1 Executive Summary (restricted)

The overall goal of this research is establishing baselines in time and space for CO_2 concentrations in the groundwater. Given these baselines, the aim is to establish whether events related to the CO_2 storage activities (either instantaneous or continuous) can cause detectable deviations from these baselines. The use of a groundwater monitoring network for CO_2 concentrations is proposed to meet this goal. Leakage from the storage reservoir is considered negligible, but can not be ruled out with 100% certainty.

To be able to detect a deviation in CO_2 concentration compared to the conditions before the start of the CO_2 injection, the baseline concentrations and natural variations of CO_2 in groundwater should be well known. In this study an inventory is made of available data of CO_2 concentrations in the groundwater in the Netherlands. Also, the hydrological and geochemical processes related to CO_2 concentrations in groundwater as well as the anthropogenic activities that might have an impact on CO_2 concentrations in groundwater are described. Using this knowledge the spatial and temporal variability of the available data of CO_2 in groundwater is explained and drawbacks of the currently available dataset were contained.

CO_2 concentrations of the groundwater vary between 0 mg/l and 5000 mg/l. High concentrations are found in the western and northern part of the country, except the dune area. Lowest CO_2 concentrations were found in groundwater below the Veluwe. The CO_2 concentrations in deep groundwater are lower than the concentrations in the shallower groundwater, but the spatial patterns are similar. High CO_2 concentrations in groundwater are the result of sulphate reduction and methanogenesis in aquifers rich in organic matter with brackish and salt formation water and seepaging formation water in the western and northern part of the Netherlands.

Although the inventory of the available data resulted in a good spatial overview of the range of CO_2 concentrations in the groundwater in the Netherlands, no small scale variations of CO_2 concentrations could be detected and the various sources could not be established with certainty. None the less, knowledge of such variations is important for being able to detect variations with the CO_2 storage and injection in geological formations. First concepts for more specific monitoring networks are described which will be designed in more detail during the next phase of this research project. Also, possible additional analyses based on the currently available dataset are described.

This report is complementary to the report of Sommer et al. (2010)) in which an inventory is made of strategies for monitoring CO_2 in (shallow) groundwater at sites of geological CO_2 storage.

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Document Change Record

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3 Introduction

Injection and storage of CO_2 in deep aquifers and old gas fields is proposed at several locations in the Netherlands as a mitigation measure for the reduction of greenhouse gas emissions until the large-scale implementation of sustainable energy sources. The CO_2 storage reservoir needs to be monitored to ensure the long-term stability and containment of the CO_2 in the reservoir. This monitoring program includes the monitoring of deep and shallow groundwater bodies, because CO_2 could migrate into these water bodies if the CO_2 is not contained by the reservoir. The risk of this migration is generally considered to be low, due to strict selection procedures of possible storage candidates. Although risks of escape of CO_2 from the reservoir are generally considered negligible, containment can never be assured with 100% certainty. Monitoring of groundwater layers is of particular importance, since high CO_2 concentrations in the lower part of the boundary layer can be a serious threat to human beings and other organisms. Therefore, a monitoring and warning network needs to be designed and installed to be able to detect leakage of the CO_2 injection and storage.

The risk of leakage of CO_2 gas is considered negligible (Van Eijs et al, 2008). Only the risk of leakage along boreholes is not negligible without mitigation measures, although it is considered negligible after mitigation measures (Van Eijs et al, 2008). In the unlikely case that leakage would occur along the boreholes, CO_2 could migrate to deep geological formations or to shallower groundwater bodies (Sommer et al., 2010), resulting in a potential increase of the CO_2 concentration of the groundwater. In order to detect this in an early stage, the use of a groundwater monitoring network for CO_2 concentrations is proposed.

CO_2 also occurs naturally in groundwater bodies. These natural CO_2 concentrations in the groundwater vary in space, over time and over depth depending on the hydrological and geochemical processes taking place in the underground. Therefore, to be able to detect an abnormal increase in CO_2 concentration, the baseline concentrations of CO_2 should be well known for different types of underground. Additionally, the natural variability (spatial, over depth and temporal) needs to be known and understood as well as the geochemical processes that take place in the groundwater that influence the CO_2 concentration. Finally, anthropogenic activities now and in the past and future have an influence on the characteristics of the soil water and groundwater and affect the CO_2 concentration of the groundwater. Also this variability should be known and understood in order to be able to distinguish an increase in CO_2 concentrations due to leakage of CO_2 storage and injection from other variations in the CO_2 concentration of the groundwater. In order to record and study the baseline CO_2 concentrations and variability ranges monitoring networks will be designed and installed at the potential CO_2 storage locations several years before the start of the infection.

In this study an inventory is made of available data of CO_2 concentrations in the groundwater in the Netherlands. Also, the hydrological and geochemical processes related to CO_2 concentrations in groundwater as well as the anthropogenic activities that might have an impact on CO_2 concentrations in groundwater are described. Using this knowledge, an attempt is made to explain the spatial and temporal variability of the available data of CO_2 in groundwater. Additionally, additional measurements are proposed that are needed to obtain sufficiently good and appropriate knowledge of baseline CO_2 concentrations and natural and human induced variability ranges. The insights acquired with this study will also be used to design the monitoring network for the recording of baseline data at various potential CO_2 storage locations in the next phase of this research.

4 Theoretical background

In order to be able to interpret the CO_2 concentrations in groundwater as well as the variation of CO_2 concentrations in space, over depth and over time, a theoretical background is given. The basic properties, density, solubility, geochemical properties and possible effects of anthropogenic activities are described in the paragraphs below.

4.1 Basic properties of carbon dioxide

Carbon dioxide is a colourless gas. At low concentrations, the gas is odourless. At higher concentrations it has a sharp, acidic odour. It will act as asphyxiate and an irritant. When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. This sensation can also occur during an attempt to stifle a burp after drinking a carbonated beverage. Amounts above 5,000 (parts per million) ppm are considered very unhealthy, and those above about 50,000 ppm (equal to 5% by volume) are considered dangerous to animal life (Staff, 2006). In table 1 the basic properties of CO_2 are listed.

Table 1: Properties of carbon dioxide.

Properties of carbon dioxide	
Molecular formula	CO_2
Molar mass	44.010 g/mol
Appearance	colorless, odorless gas
Density	1.562 g/mL (solid at 1 atm and −78.5 °C)
	0.770 g/mL (liquid at 56 atm and 20 °C)
	1.977 g/L (gas at 1 atm and 0 °C)
	849.6 g/L (supercritical fluid at 150 atm and 30 °C)
Melting point	-78 °C, 194.7 K, -109 °F (subl.)
Boiling point	-57 °C, 216.6 K, -70 °F (at 5.185 bar)
Solubility in water	1.45 g/L at 25 °C, 100 kPa
Acidity (pKa)	6.35, 10.33
Viscosity	0.07 cP at −78 °C

4.2 Natural CO_2 concentrations in water

The natural concentration of CO_2 in water varies between different types of water, depending on the path way of the water and the geochemical processes that have taken place in the water during its flow (table 2). Currently the atmospheric concentration of CO_2 is approximately 0.5 mg/l (air). When taken up by rainwater the CO_2 that is taken up from the air by the raindrops is slightly concentrated to approximately 1 mg/l (water). In the soil water (soil=unsaturated top layer of the underground) CO_2 concentrations are increasing to 24 - 32 mg/l and in the groundwater CO_2 concentrations are increasing to 100 - 5000 mg/l. As a comparison, the CO_2 concentrations in artificial gaseous soda drinks (e.g. gaseous mineral water, cola) are 5000 – 8000 mg/l.

Table 2: Natural CO_2 concentrations in air and (ground)water in soft drinks.

medium	**CO_2 concentration**
atmosphere	app. 0.5 mg/l
rain water	app. 1 mg/l
soil water	24-32 mg/l
groundwater	100-5000 mg/l
Cola / mineral water	*5000-8000 mg/l*

4.3 Density of carbon dioxide

At standard temperature and pressure, the density of carbon dioxide is around 1.98 kg m^{-3}, about 1.5 times that of air (see figure 1). The carbon dioxide molecule (O=C=O) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable, but will support the combustion of metals such as magnesium. Above -78.51℃ or -109.3℉, carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition. Solid carbon dioxide is normally called "dry ice", a generic trademark. It was first observed in 1825 by the French chemist Charles Thilorier. Dry ice is commonly used as a cooling agent, and it is relatively inexpensive. Liquid carbon dioxide forms only at pressures above 5.1 atm; the triple point of carbon dioxide is about 518 kPa at -56.6 ℃. The critical point is 7.38 MPa at 31.1 ℃ (National Institute of Standards and Technology, 2008).

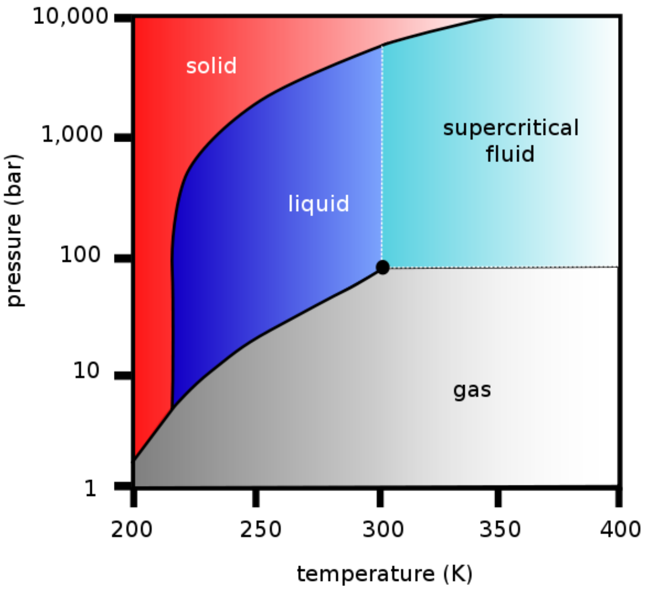


Figure 1: Temperature and pressure phase diagram for CO_2 (200 °K = -73.1 °C; 400 °K = 127 °C).

4.4 Solubility of carbon dioxide

The solubility of CO_2 increases with the increase of pressure and decreases with the increase of ionic strength. However, CO_2 solubility varies more dramatically with temperature (see figure 2). Only when both pressure exceeds 300 bar and temperature exceeds 393 K, (near deep geothermal vents) the behaviour of the solubility of CO_2 is different (Duan and Sun, 2003). Table 3 gives an overview of the CO_2 solubility in water for a range of pressure-temperature conditions.

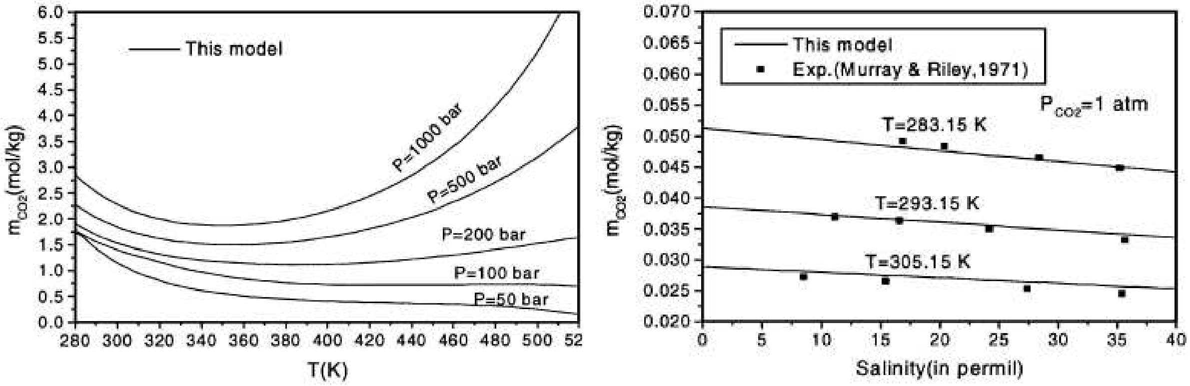


Figure 2: Left figure: the isobaric minimum solubilities of CO_2 in pure water (source: Duan and Sun, 2003); right figure: the prediction of CO_2 solubility in sea water (the model of Duan and Sun (2003) vs. experimental data).

Table 3: Calculated CO_2 solubility (mol/kg) in water (source: Duan and Sun, 2003).

P (bar)	T (K)								
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15	533.15
1	0.0693	0.0286	0.0137	0.0036						
5	0.3368	0.1442	0.0803	0.0511	0.0298	0.0023				
10	0.6463	0.2809	0.1602	0.1086	0.0781	0.0480				
50		1.0811	0.6695	0.4952	0.4157	0.3767	0.3476	0.2997	0.1887	0.0392
100		1.3611	1.0275	0.8219	0.7314	0.7054	0.7131	0.7259	0.7025	0.6267
200		1.4889	1.2344	1.1308	1.1100	1.1569	1.2634	1.4171	1.5898	1.6846
300		1.5989	1.3495	1.2802	1.3184	1.4427	1.6521	1.9506	2.3334	2.6190
400		1.7005	1.4478	1.3954	1.4700	1.6535	1.9527	2.3871	2.9802	3.4700
500		1.7965	1.5368	1.4954	1.5972	1.8287	2.2059	2.7664	3.5666	4.2695
600		1.8883	1.6194	1.5857	1.7102	1.9833	2.4310	3.1102	4.1152	5.0387
700		1.9767	1.6970	1.6689	1.8131	2.1238	2.6370	3.4301	4.6390	5.7905
800		2.0622	1.7703	1.7464	1.9082	2.2535	2.8288	3.7323	5.1452	6.5318
900		2.1450	1.8399	1.8189	1.9966	2.3744	3.0089	4.0203	5.6376	7.2658
1000		2.2254	1.9062	1.8870	2.0792	2.4876	3.1790	4.2960	6.1183	7.9933
1100		2.3034	1.9692	1.9510	2.1566	2.5939	3.3401	4.5607	6.5877	8.7138
1200		2.3792	2.0292	2.0112	2.2290	2.6937	3.4927	4.8147	7.0458	9.4256
1300		2.4527	2.0864	2.0678	2.2968	2.7874	3.6372	5.0585	7.4922	10.127
1400		2.5240	2.1407	2.1210	2.3601	2.8752	3.7739	5.2919	7.9260	10.814
1500		2.5933	2.1924	2.1707	2.4192	2.9575	3.9030	5.5150	8.3460	11.485
1600		2.6605	2.2413	2.2172	2.4740	3.0341	4.0245	5.7276	8.7513	12.136
1700		2.7251	2.2875	2.2605	2.5248	3.1053	4.1385	5.9294	9.1403	12.764
1800		2.7882	2.3312	2.3007	2.5717	3.1712	4.2450	6.1202	9.5123	13.366
1900		2.8486	2.3725	2.3379	2.6146	3.2319	4.3440	6.2997	9.8655	13.938
2000		2.9071	2.4110	2.3719	2.6538	3.2875	4.4353	6.4677	10.199	14.478

Under certain conditions the groundwater can become oversaturated with gases. As a result, gas bubbles are formed when the total gas pressure (sum of the partial gas pressures of all gases in the groundwater (CH_4, CO_2, N_2, Ar, H_2S)) is larger than the hydrostatic pressure. In order to overcome the surface tension of the water in the pores of the sediment, the level of oversaturation in sediments should be slightly higher than the hydrostatic pressure (Obdam en Cleveringa, 2001). In layers that consist of course sand the formation of gas bubbles is easier than in layers with fine sands. It is expected that gas bubbles move up towards the surface relatively fast compared to the gases dissolved in the groundwater, but can be trapped under layers with low permeability. Also, in the preferential groundwater flow towards wells (in polders with seepage or artificial wells) probably contains large amounts of gas bubbles.

4.5 Geochemical processes

The groundwater in aquifers generally originates from precipitation, which in some cases has been transported first as surface water over land, through rivers and lakes. Additionally, groundwater can originate from connate or intruded seawater. Depending on the composition of the sediment of the soil and deeper layers in the underground through which the groundwater flows and the flow velocity of the water, the water will take up or release chemical elements. As a result the composition of the water will change over its course. The schematic in figure 3 gives an overview of the most important geochemical processes that affect the CO_2 concentrations of water in the soil and the underground and the interrelations between these processes (Edelman, 2009). Accordingly, the parts of the underground where the respective processes are most likely to take place are shown in a West-East cross section of the Netherlands (figure 4). In the following paragraphs, the mechanisms and processes that cause variations in CO_2 concentrations in groundwater are explained.

4.5.1 Carbon dioxide and water

When CO_2 comes into contact with water, various processes take place. In this paragraph these processes are described briefly. When CO_2 dissolves in water carbonic acid (H_2CO_3) is formed:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

In water, this weak acid partially splits up during two steps into HCO_3^- and CO_3^{2-}:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \qquad (2)$$

HCO_3^- is called the bicarbonate ion and CO_3^{2-} is called the carbonate ion.

The total amount of CO_2 in solution in the groundwater is the sum of the various species that can occur in the groundwater: H_2CO_3, HCO_3^- and CO_3^{2-}. The proportional occurrence of the species is strongly dependent on the pH of the groundwater (see figure 5). For pH 6 – 10 HCO_3^- is the dominant specie, for pH<6 H_2CO_3 is the dominant specie, and for pH>10 CO_3^{2-} is the dominant specie (Appelo and Postma, 1996). As most types of water have an pH value between 6 and 10, HCO_3^- is generally the dominant CO_2 specie in groundwater.

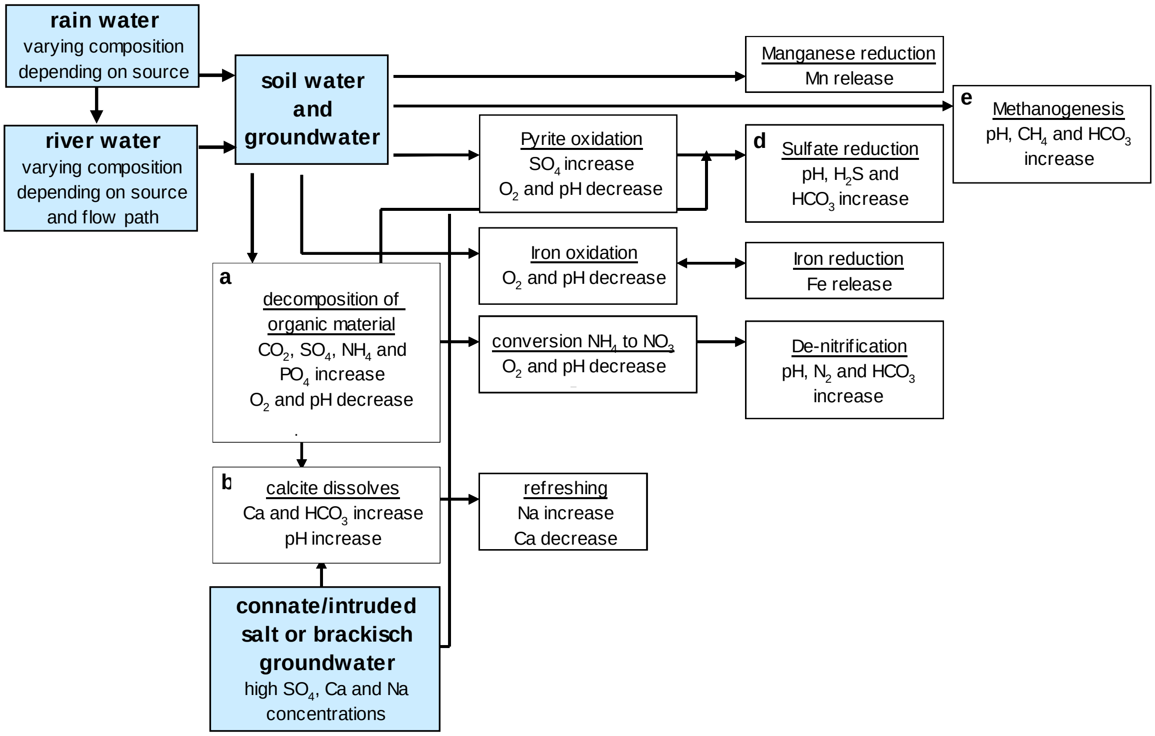


Figure 3: Schematic of the most important geochemical processes in groundwater related to the concentration of CO_2 in the groundwater. Water sources are in blue; letters a - e correspond to figure 4 (Source Edelman, 2009 (edited)).

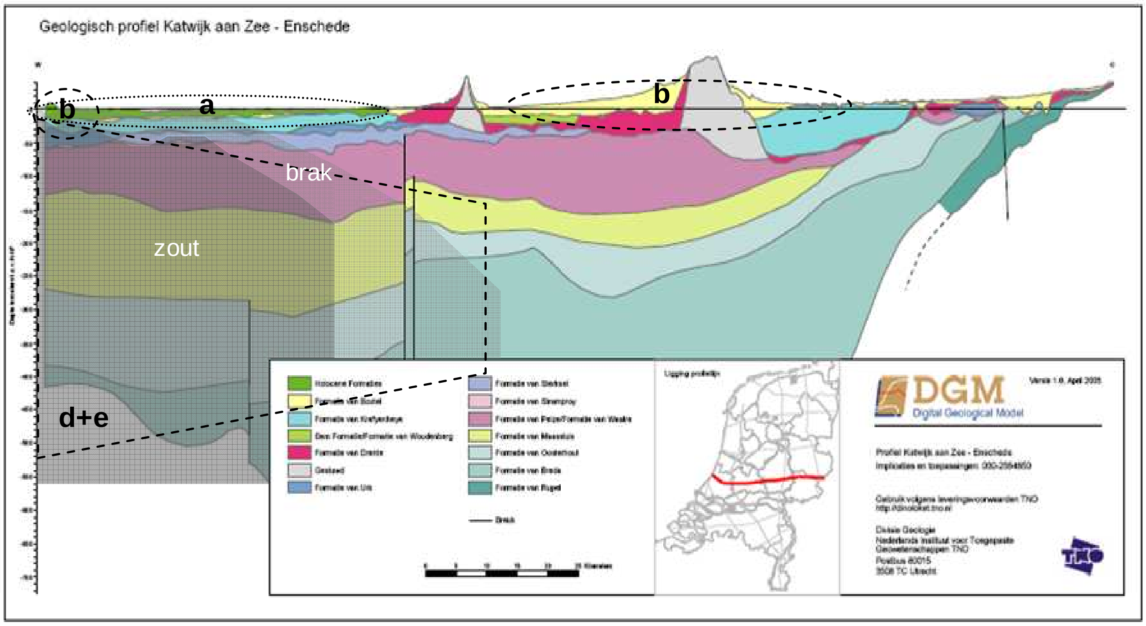


Figure 4: Cross section of the Netherlands (West-East: Katwijk aan Zee – Enschede). Dashed lines and letters (a – e) indicate zones in the underground where the most important geochemical processes of figure 3 take place.

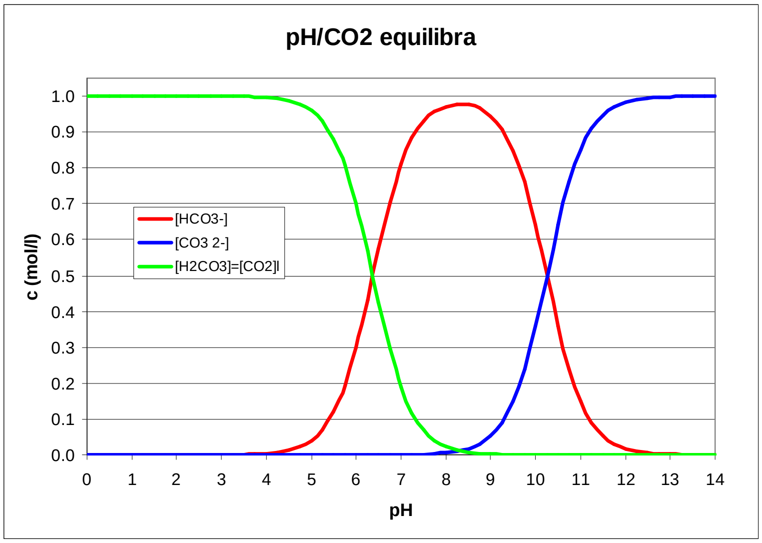


Figure 5: Proportional occurrence of the CO_2 species (HCO_3^-, CO_2 and H_2CO_3) for the range of pH values.

Carbonic acid (H_2CO_3) is not very stable and under low pH values it can easily decompose in CO_2 (aq) and water. As a result CO_2 (aq.) is formed when acidifying carbonate or carbonic acid solutions. Carbonic acid can decompose to CO_2 in another way: when dissolved carbonic acid is heated or when lowering of the pressure, gaseous CO_2 forms as a result of a reduced solubility of the carbonic acid (Appelo and Postma, 1996). This process is described as follows:

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O \qquad (3)$$

Also when bicarbonate (HCO_3^-) is heated and the substance breaks down and carbon dioxide is formed:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \qquad (4)$$

4.5.2 pH and carbon dioxide

The pH is an expression of the acidity of a watery solution. The pH of a neutral solution at room temperature is around 7. Acid solutions have a pH lower than 7. Basic solutions have a pH higher than 7, these solutions are called lye solution. The pH is equal to the negative logarithm (base number 10) of the concentration hydrogen ions (H^+). The unit for this is mol/l. An increase of the CO_2 concentration in groundwater results in a lower pH (increase of H^+ ions), see equation 1 and 2. When the amount of HCO_3^- (or CO_3^{2-}) ions in the groundwater is increased by other processes (e.g. dissolution of calcite) the pH rises (decrease of H^+ ions), see equations 3 and 4.

4.5.3 Redox processes and methanogenesis

Organic matter is the major source of CO_2 in the soil water and groundwater. Initially, CO_2 is taken up from the atmosphere by plants and is converted to organic matter:

$$6CO_2 + 6H_2O + \text{radiation energy} \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (5)$$

A large part of the organic matter is later converted to CO_2 and H_2O during the process of mineralisation of dead organic matter and respiration of plants and (micro)organisms (autotrophic and heterotrophic respiration):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \qquad (6)$$

Under anaerobic circumstances, redox processes start taking place. The type of redox processes that take place in a certain zone depends on the reduction level of the groundwater and the chemical elements that occur in the groundwater. During reduction H_2CO_3 is formed by bacterial alteration of chemical compounds through a specific order of reactions:

De-nitrification: $5CH_2O + 4NO_3^- + 4H+ \rightarrow 2N_2 + 5H_2CO_3 + 5H_2O$ (7)

Mn(IV) reduction: $CH_2O + 2MnO_2 + 4H+ \rightarrow 2Mn + H_2CO_3 + 2H_2O$ (8)

Fe(III) reduction: $CH_2O + 4FeOOH(s) + 8H^+ \rightarrow 4Fe_2^+ + H_2CO_3 + 6H_2O$ (9)

Sulphate reduction: $2CH_2O + SO_4^{2-} + H^+ \rightarrow HS + 2H_2CO_3$ (10)

The last step of the redox sequence is methanogenesis, during which carbon in the organic soil material is converted to methane gas (CH_4). Methanogenesis can occur in various ways. The methanogenesis processes that occur most often can be described as follows:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (11)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (12)$$

During the second type of methanogenesis besides CH_4, CO_2 is produced under anaerobe conditions from organic matter (proportion CH_4:CO_2 as 1:1). On the other hand, under aerobe soil conditions (above the groundwater level) CH_4 is oxidised by methanotroph microbes:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (13)$$

Under certain conditions also sulphate or nitrate can be used as ‘terminal electron acceptor’ instead of O_2 in this chemical reaction (Schlesinger, 1991; Appelo and Postma, 1996; Whalen, 2005; Van der Grift et al., 2006).

It might be possible that oxidation of CH_4 occurs in deep aquifers thereby increasing the CO_2 concentration of the groundwater. However, this can only occur when O_2 is available in the same groundwater body as the CH_4 which is unlikely. Such concurrence of O_2 and CH_4 in the same groundwater body might take place in case CH_4 containing groundwater is mixed with less strongly reduced groundwater types in which O_2 is available. To what extent such processes affect the CO_2 concentration in groundwater bodies is however unknown.

A study by Van der Grift et al. (2006) gives an indication of the decay rate for the different redox processes and methanogenesis of organic matter of various ages (figure 6). The study showed that the decay of relatively young organic matter decomposes several orders of magnitude faster than old organic matter: for relatively young organic matter (10-100 year old) decay rates in the order of 10 – 1000 meq/l/yr were reported, while for old organic matter decay rates of 10^{-3} – 10^{-5} meq/l/yr were reported.

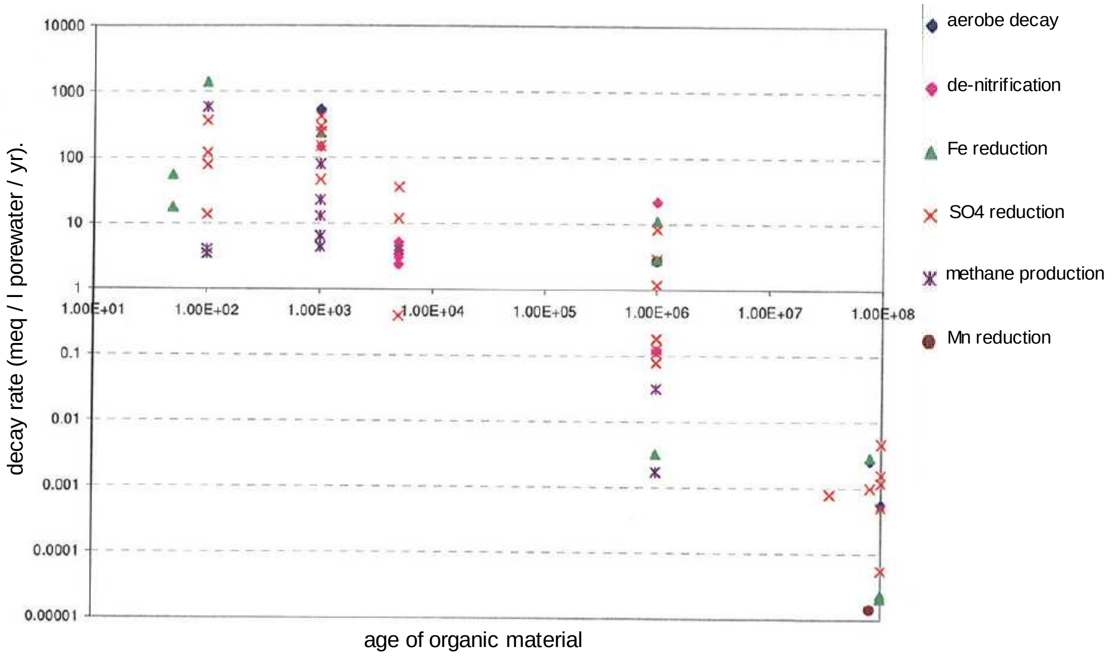


Figure 6: Decay rate of organic matter (expressed in meq electrons / l porewater / year) for various ages of organic matter.

4.5.4 Carbonates, pH and dissolved CO_2

In geochemical processes and geology carbonates play an important role. Many sea animals use calcite for their shelter or strengthening of their body structure. Through the sedimentation of calcareous material (e.g. shells), calcareous rock formations are formed. Locally, such formations occur in thick layers. The dominant mineral in such formations is calcium carbonate ($CaCO_3$), which can dissolve in water. Calcium carbonate dissolution produces HCO_3^- and can take place though three different processes. The relative importance of these processes depends largely on the variation in pH. An overview of the processes is given in figure 7 and described below (Plummer et al., 1978).

1. When pH < 3.5 the dissolution rate of calcium carbonate is proportional to $[H^+]$ and the dissolution takes place according to the following reaction:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (14)$$

Additionally, the level of movement of the water is important. This indicates that transport of H^+ to the calcite surface is a controlling variable; absence of water movement can be limiting for the dissolution rate.

2. When 3.5 > pH > 5.5 the dissolution rate becomes more dependent of the level of CO_2 pressure in the groundwater (P_{CO2}) and the dissolution takes place according to the following reaction:

$$CaCO_3 + H_2CO_3 \text{ (or } CO_2 \text{ (aq))} \rightarrow Ca^{2+} + 2HCO_3^- \qquad (15)$$

Both the level of water movement and the chemical reactions at the surface are controlling the dissolution process (Rickard en Sjöberg, 1983).

3. When 5.5 > pH > 7 a sharp decrease of the dissolution rate of calcite is observed, because the water is near the saturation point of pH=7. The dissolution takes place according to the following reaction:

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \qquad (16)$$

When pH > 7 the calcium precipitates as calcium carbonate. During this process also the dissolved CO_2 (in the form of HCO_3^-) is fixed. The precipitation takes place according to the following reaction:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \qquad (17)$$

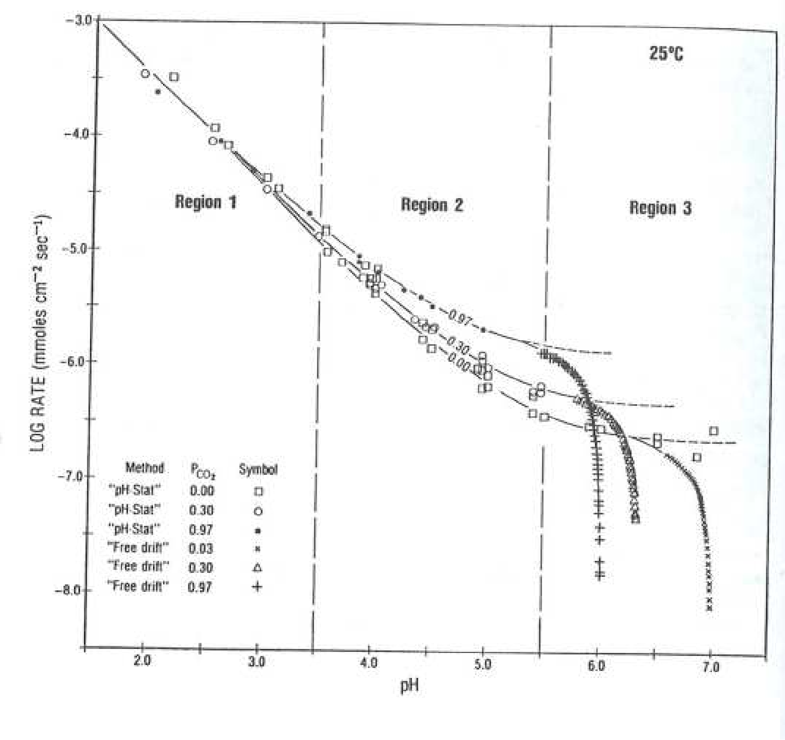


Figure 7: An overview dissolution rate of calcium carbonate under various pH values (Plummer et al., 1978).

Besides calcite, other carbonates occur in the underground. Carbonates are described as a chemical substance that contains carbon (C) and oxygen (O). The processes described above also occur in geological formations with other, less abundant, carbonates, like dolomite ($CaMg(CO_3)_2$), sodium carbonate (Na_2CO_3), magnesium carbonate or magnesite ($MgCO_3$), strontium carbonate ($SrCO_3$) and lead carbonate or cerussite ($PbCO_3$). Additionally, in mineral deposits (sand, clay, silt, moraine) carbonate grains of shells can occur (Appelo and Postma, 1996).

4.6 Effect of anthropogenic activities

Anthropogenic activity affects the composition of rain water, soil water and groundwater and can alter the conditions of the atmosphere, the soil and the underground. As result the amount of CO_2 in the groundwater can change. In this paragraph the various manners in which anthropogenic activity can affect the CO_2 concentration in the groundwater are described briefly. Although the exact effects of these anthropogenic activities on the CO_2 concentration of the groundwater cannot be quantified beforehand, the effects of these human induced changes should be taken into account when designing a monitoring system and during the evaluation of the observed CO_2 data.

Also, it should be taken into account that the influence of these human activities on a large scale has taken place only since the last century. The effect on the groundwater will therefore reach not much further then 30 to 50 meter below the soil surface. Especially, the groundwater below large cities that have been occupied for centuries the anthropogenic pollution might have penetrated relatively deep into the groundwater (up to approximately 50 m). Factors influencing the depth of the anthropogenic influence locally or regionally are the direction of the groundwater flow and the composition of soil and underground. In areas with seepage or low permeable soils or deeper layers with high resistance to vertical flow the groundwater is often affected merely in shallow aquifers. On the other hand, groundwater in infiltration areas and areas with permeable soils and underground is influenced up to larger depths (Verhagen et al., 2007).

4.6.1 Acid precipitation

Acid precipitation occurs when sulphur dioxide (SO_2), nitrogen monoxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3) and volatile organic compounds (VOC) dissolve in rain clouds. NH_3 and VOCs' can be emitted from exhaust gases from cars and the combustion of sulphur or nitrogen containing fuels used in other engines. Also intensive stock farming is an important emitter of ammonia. Acid precipitation therefore occurs mainly in and near industrial areas and cities and in areas with intensive agriculture. Here it causes a decrease of the pH of surface and groundwater in these areas.

Large areas of the Netherlands are covered with urban and industrial areas or areas with intensive agriculture. Highest deposition is found in areas with intensive stock farming (East-Brabant and Gelderse Vallei), and also in the western and northern part of the Netherlands the amount of acid precipitation is high. Since the 1980's measures have been taken to reduce the amount of acid precipitation. As a result the acid precipitation was reduced with almost 50%. The spatial variation however did not change.

4.6.2 Pollution of soil and groundwater

The soil water and groundwater are polluted by several sources:

- Application of large amounts of nitrogen-rich fertiliser and manure to the soil in areas with intensive agriculture;
- Maintenance liming of agricultural grasslands;
- Leakages of many types of chemical components from waste deposits;
- Leakage/spilling of chemical products in urban and industrial areas. In urban areas an important factor in this context is leakage of sewage systems;
- Discharge of polluting substances into surface water bodies in industrial areas. The polluted surface water can infiltrate towards the groundwater. Also, pollution caused upstream of the Netherlands can cause polluted surface- and groundwater in the Netherlands.

The effect of pollution differs depending on the type of pollution. In many cases however the pH of the groundwater and / or the decomposition of organic material will be affected. Through this, the CO_2 concentration of the groundwater can be altered. Van der Grift et al. (2006) composed a guiding document for the modelling of geological and geochemical modelling of waste soil deposits, which provides insight in the possible processes taking place in polluted areas.

4.6.3 Groundwater abstraction

Groundwater abstraction causes a change in the flow patterns of the groundwater. As a result groundwater with a certain CO_2 concentration will be drawn in the direction of the abstraction well instead of infiltrating towards deeper groundwater. When pumped up to the surface a part of the CO_2 will be released into the atmosphere. Also, because the groundwater will flow through different (more shallow) deposits, other geochemical reactions take place in the water. Depending on the specific composition of the groundwater and sediments more CO_2 might be taken up or emitted during this artificial flow path.

4.6.4 Lowering of water levels

Due to groundwater management in agricultural or urban areas as well as due to climate change (reduced precipitation, higher temperatures) groundwater levels can be lowered. As a result soils will become aerated to greater depths, causing oxidation of the organic matter in the soils. Mainly in peat areas, large amounts of soil organic matter can be mineralised as a result of lowering of the water table. During oxidation more CO_2 is produced than during redox processes and methanogenesis. However, as a result of the dry soil conditions only a small amount of the CO_2 will be taken up by the groundwater. Instead, most of the CO_2 will be emitted to the atmosphere (Hendriks et al., 2009).

An additional effect of this enhanced oxidation of peat layers is the thinning of the top layer with low permeability. In polder areas with a low topography, this thinning of the top layer will give rise to groundwater wells. In paragraph 4.5.5 the effect of these well on the CO_2 concentration of the groundwater is described.

4.6.5 Temperature increase

In urban areas the temperature of the soil and underground is increased as a result of sewage systems and storage of warm water in aquifers. Additionally, an increase of the air temperature resulting from climate change can cause an increase in soil temperatures. Changes in temperature affect the CO_2 concentration in water in several ways. The rates at which microbial and geochemical processes take place generally increase with increasing temperatures. Mineralisation of organic matter, redox processes and methanogenesis will go faster, thereby producing higher amounts of CO_2 (Hendriks et al., 2009). On the other hand, the solubility of CO_2 in water is lower at higher temperatures (see paragraph 4.3).

Another effect of temperature increase is an increase in evaporation and evotranspiration, which causes a decrease of soil water. As a result concentrations of chemical components in the soil water increase proportional to the decrease of the available soil water.

5 From rain drop to groundwater

In this chapter the processes with respect to CO_2 concentration of water are described that successively take place when water infiltrates and becomes groundwater (see also figure 3). Rain water infiltrates into the soil directly or is first accumulated in surface water bodies (streams, rivers, lakes) before it infiltrates. Subsequently the soil water infiltrates towards shallow and deeper aquifers and under some circumstances groundwater flows back to shallower depths due to seepage. The descriptions of this chapter are based on the theoretical background given in chapter 4 and knowledge of the composition of the underground of the Netherlands.

5.1 The composition of rain water and surface water

Rain water can either infiltrate directly into the soil or can first flow over land and through streams, rivers and lakes before it infiltrates into the soil or underground. Both rain water and river water can show strong variations in their composition before infiltration. Below examples of the differences in the composition of rain and surface water and their as well as the causes of these variations are described.

The composition of rainwater can show strong variations, depending of the conditions of the atmosphere in the area where the rain is falling, for instance:
- Rainwater near oceans and seas generally shows high Na^+ en Cl^- concentrations;
- In and near industrial areas (like cement industry and chemical industry), cities and intensive agricultural areas precipitation can be acid;

The differences in the quality of the rainwater can influence the extent to which CO_2 dissolves in the rainwater and groundwater that has this rainwater as its source, for instance:
- As a result of acid rain more rain, the pH of the water decreases and higher amounts of calcite can dissolve in the water;
- As a result of the soil processes induced by high ammonium concentrations and acid rain a change in the mineralisation of organic matter and the production of CO_2 can occur.

The composition of surface water can show strong variations, depending on the source area of the water, the flow route and possible pollution of the surface water resulting from anthropogenic activities. Below the various facets of these three aspects are illustrated:
- *Source area*: rivers fed by rain water have a different chemical composition than rivers that are fed by glaciers or a combination of glaciers and rain water. Also the type of underground (calcareous, igneous, sedimentary, etc.), the soil type and vegetation type in the source area of rivers and streams effects the composition of the surface water.
- *Flow route*: the type of underground of the river-bed along the flow route of rivers and streams also effects the composition of the surface water (calcareous, igneous, sedimentary, etc.). Also the flow rate of the surface water is of importance for the chemical composition of the water as well as the aquatic flora and fauna.
- *Pollution*: Urban areas, agricultural areas and industrial areas often cause pollution of surface water bodies in their vicinity, thereby strongly affecting the chemical compositions of the surface water downstream of these areas.

5.2 Infiltration of water in the soil

Depending on the composition of the soil various processes can take place that affect the composition of the CO_2 concentration in the soil water and the shallow groundwater:

- During aerobic decomposition of organic material in peat areas and other types of soils that contain organic material CO_2 is released. For a large part the gases that are produced in the soil move upwards through the soil pores or through stems of plants and are emitted to the atmosphere. A part of the gases that is produced in the soil is however taken up in the soil water and can infiltrate with the water to the deeper groundwater.
- In the eastern and southern part of the Netherlands as well as in the dune areas the soil consists for a large part of sand. In this sand calcareous grains occur. The calcium in these grains can (partly) dissolve in the soil water causing an increase in HCO_3^-. The lower the pH of the water, the more calcite can dissolve.
- In the soil other processes take place that can have an effect on the pH of the soil water. By affecting the pH these processing have an indirect effect on the CO_2 concentration in the soil water. Conversion of ammonium (NH_4) to nitrate (NO_3^-), pyrite oxidation and iron oxidation cause a decrease of the pH. At a lower pH carbonates dissolve more easily in the groundwater. De-nitrification (conversion of nitrate to nitrogen) and sulphate reduction cause a release of HCO_3^- (increase of CO_2 in soil water). As a result the pH of the het groundwater increases. When the pH rises above 7, the groundwater becomes saturated with HCO_3^- and carbonates can precipitate.
- Depending on the permeability of the soil, the infiltration rate varies: in clay and peat soils the infiltration rate is slower than in sandy soils. The higher the flow rate, the less time available for up-take of chemical components and chemical reactions to take place.

Besides the geochemical soil processes described above, the influence of anthropogenic activities and climate effects is most strong in the upper part of the underground, the soil (see paragraph 4.4)

5.3 Infiltration of soil water to the upper groundwater

In the western and northern part of the Netherlands the soil water infiltrates into peat and clay layers that were deposited during the Holocene period. This layer of Holocene deposits can reach a thickness of over 20 m. Below these peat and clay layers, Pleistocene deposits are found. In the eastern and southern part of the Netherlands the soil water infiltrates directly into the Pleistocene glacial deposits, which consist of sand, gravel, loss and ice pushed ridges. Depending on the local composition of the underground various processes can occur that influence the concentration of CO_2 in the groundwater in the Holocene deposits:

- The Holocene deposits in the western part of the Netherlands consist partly of peat or other sediments rich in organic material. This organic matter can be subjected by anaerobic decomposition during redox processes and methanogenesis (see paragraph 4.2.3). During these decay processes CO_2 is released, causing an increase of the CO_2 concentration in the groundwater. The rate of the decay of organic matter depends for a large part on the age of the organic matter: the older the organic matter, the slower the decay. Therefore it can be expected that in deeper, older sediment and peat layers less CO_2 is produced.
- In the eastern and southern part of the Netherlands as well as in the dune areas the upper layers of the underground consist for a large part of sand. In this sand calcareous grains occur. The calcium in these grains can (partly) dissolve in the soil water causing an increase in HCO_3^-. The lower the pH of the water, the more calcite can dissolve.
- In the western part of the Netherlands the formation water of the Pleistocene and part of the Holocene deposits is brackish or salt. This brackish and salt formation water also seepages towards shallower depth in polder areas (see paragraph 5.1.5). As a result of the high concentration of sulphates in the salt water, sulphate reduction increases and H_2CO_3 is produced (CO_2 concentration increases). Especially when high sulphate concentrations occur in areas with peat deposits, the CO_2 concentration is expected to be high.

- Depending on the permeability of the aquifers, the infiltration rate varies: in clay and peat deposits the infiltration rate is slower than in sandy deposits. The higher the flow rate, the less time available for up-take of chemical components and chemical reactions to take place.

Besides the geochemical soil processes described above, anthropogenic activities can affect the groundwater in the Holocene (see paragraph 4.4)

5.4 Infiltration to deeper groundwater

Deeper parts of the underground consist of continental and marine deposits, containing mainly sand, gravel and clay. The sediments that were deposited in a marine environment (mostly in the western part of the Netherlands) are calcareous and locally contain organic matter. Depending on the local composition of the underground various processes can occur that influence the concentration of CO_2 in the groundwater in the Holocene deposits:

- The organic matter in the marine deposits in the western parts of the Netherlands can be subjected by anaerobic decomposition during redox processes and methanogenesis (see paragraph 4.2.3). During these decay processes CO_2 is released, causing an increase of the CO_2 concentration in the groundwater. The rate of the decay of organic matter depends for a large part on the age of the organic matter: the older the organic matter, the slower the decay. Therefore it can be expected that in deeper, older sediment and peat layers less CO_2 is produced.
- The groundwater in the western part of the Netherlands consists mainly of brackish or salt connate or intruded water. As a result of the high concentration of sulphates in the salt water, sulphate reduction increases and H_2CO_3 is produced (CO_2 concentration increases). For reduction processes organic matter is required. However, the presence of organic matter in these aquifers is very limited. Additionally, decay rates in these old deposits are relatively low.
- In sediment layers that contain calcareous sediments, the available calcium can (partly) dissolve in the groundwater causing an increase in HCO_3^-. The lower the pH of the water, the more calcite can dissolve.
- Depending on the permeability of the aquifers, the infiltration rate varies: in clay and peat deposits the infiltration rate is slower than in sandy deposits. The higher the flow rate, the less time available for up-take of chemical components and chemical reactions to take place.
- At various depths confining clay layers exist that have a high vertical flow resistance. Natural exchange of groundwater through such layers is therefore almost impossible.
- With increasing temperature, pressure and ionic strength the solubility of CO_2 in water changes. An increase in temperature or salinity cause a decrease of the solubility, while an increase in pressure causes an increase of the solubility. The solubility of CO_2 under specific conditions at a certain depth needs to be calculated.

5.5 Seepaging groundwater

In the polder areas in the western part of the Netherlands (strong) seepage occurs (see figure 8). Instead of infiltrating towards deeper aquifers, the groundwater in these areas flows upwards as a result of the low topography and the strong pumped drainage. At locations where the top layer with low permeability is relatively thin or absent the seepaging water flows, via preferential flow paths, out at the surface through groundwater wells on land or in ditches (De Louw, 2006; Van Ek et al., 2007). During the out flow of this groundwater and as a result of the reduced pressure at these locations gases that are dissolved in the groundwater are released to the atmosphere. Measurements in a polder area in the province Noord-Holland showed high CH_4 concentrations in the wells (7–27 mg/l). CO_2 concentrations of the well water were relatively low, approximately 5-

15 times lower than the CH_4 concentrations (Buijs and Stuurman, 2003). In chapter 7 the occurrence and spread of CH_4 gas wells is described.

Another effect of the seepage in polder areas is that the brackish and salt formation water present in the Holocene deposits rises towards the surface (Van Ek et al., 2007). In case this water is not yet fully reduced, the amount of sulphate at shallower depths increases due to the upcoming salt or brackish water. Where organic matter is available such increased sulphate concentrations might induce an increase of sulphate reduction at shallower depths, and hence the production of CO_2. Also, in case oxygen is available in the shallower groundwater oxidation of CH_4 might occur (see paragraph 4.5.3).

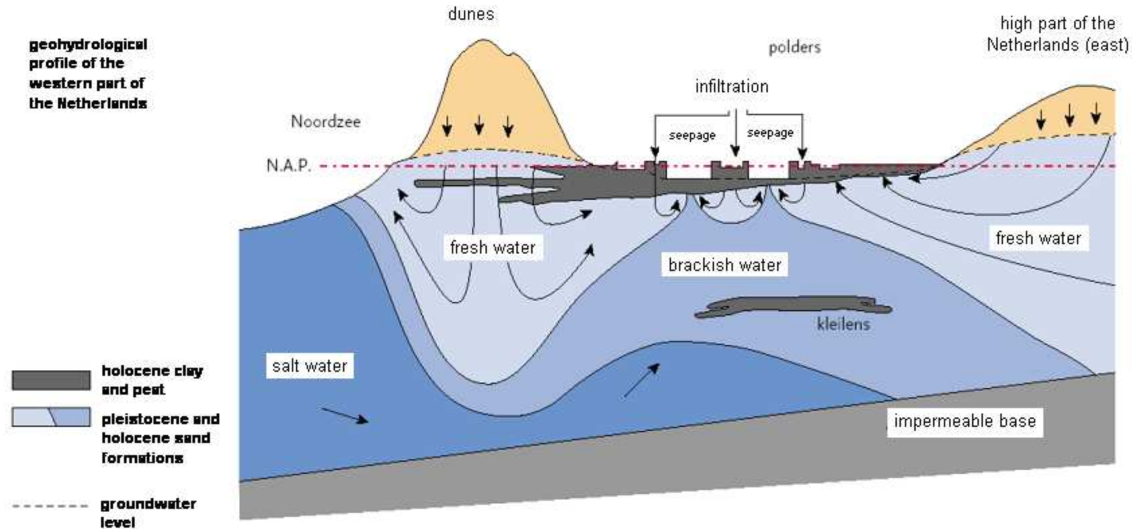


Figure 8: Schematic geological profile of the western part of the Netherlands. The groundwater flow patterns in the area are shown: infiltration of groundwater in topographically high areas and seepage of groundwater towards the polder areas.

5.6 Deep sources of CO2

Besides a possible interaction of deep and shallow groundwater through groundwater flow, chemical diffusion or carry-over effects of pressure, also interaction resulting from gas migration can take place. In the deep underground gas is formed which is often trapped under impermeable layers. Calculations have shown that more gas has been formed than currently present in the gas reservoirs. A part of the gas that was formed in the reservoirs is migrating from the reservoirs through the underground towards the surface. This characteristic of the gas reservoirs is also used in the search for gas- and oil fields: Shell uses for instance cars with gas sniffing instruments. With geophysical research at the Noordzee TNO-NITG has shown that methane gas and ethane gas coming from great depths flow into the seawater along faults (Stuurman, 2004). No research has been done to the flow of CO_2 towards the surface, however it is very well possible that CO_2 flows towards the surface through processes similar to methane and ethane. In **figure 9** the gas transport routes are schematised (Stuyfzand, 1994). Absent in the figure is transport from larger depths through diffusion.

Hydrogeochemical research in the province Noord-Brabant has shown that seepage from deep groundwater (> 250 m) through so called seepage chimneys is likely to occur under stream valleys (in the historical situation). Through such seepage chimneys dissolved and gaseous CO_2 could be transported towards shallower groundwater bodies and to the surface (Nolte, 1996). However, to determine the extent of CO_2 migration towards the surface by this mechanism, more research is needed.

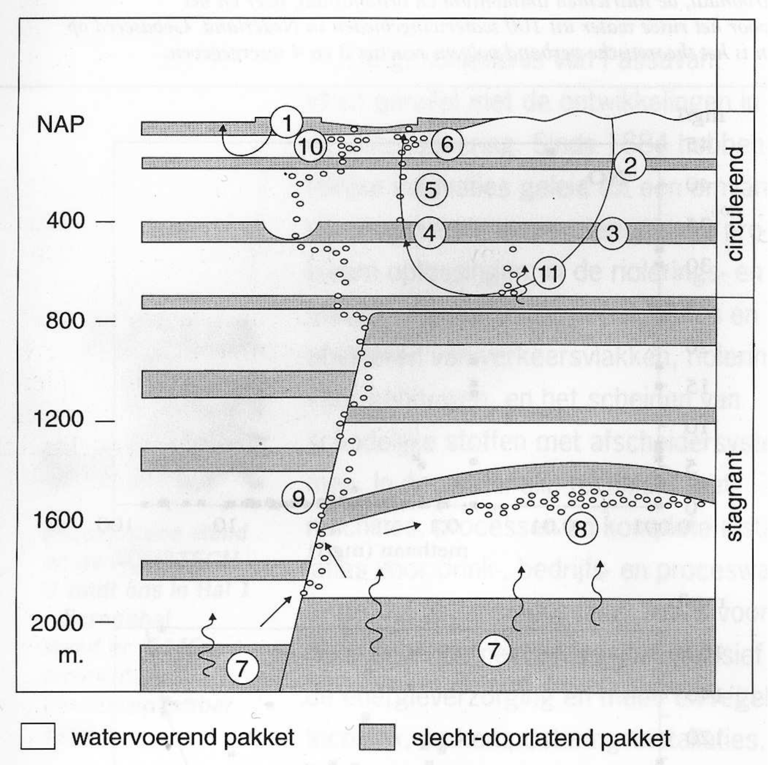


Figure 9: The mechanisms for gas transport from the deep underground towards the surface (Stuyfzand, 1994)

6 Available data of CO_2 in groundwater

6.1 Measuring CO_2 in groundwater

The total amount of dissolved CO_2 in the groundwater can be calculated as the sum of the various CO_2 species that occur in the groundwater: CO_2 (aq), H_2CO_3, HCO_3^- and CO_3^{2-} (see also paragraph 2.1.1). In most cases the pH of groundwater lies between 6 and 10, and the HCO_3^- specie is dominant. HCO_3^- is also the specie that can be measured in the groundwater most accurately. Direct measurements of the CO_2 concentration in water are rare, therefore total CO_2 concentrations (TIC = total inorganic carbon) are deducted from the measured HCO_3^- concentrations and the measured pH of the groundwater according to the following method:

$$\mathbf{TIC = CO_2\ (aq) + H_2CO_3 + HCO_3 + CO_3^{2-}}\ \text{(units: mol/l)} \qquad (18)$$

where:

HCO_3^- is the dominant CO_2 specie in groundwater and can measured most accurately.

H_2CO_3 and **CO_2 (aq)** are calculated from the HCO_3^-:

$$H_2CO_3 + CO_2\ (aq) = HCO_3 \times H^+\text{-ions} / K1\ \text{(units: mol/liter)} \qquad (19)$$

with:

$$K1 = 10^{(-356.3094\ -\ 0.06091964\times(Temp1)\ +\ 21834.37/Temp\ +\ 126.8339\times\log10(Temp1)\ -\ 1684915/(Temp2))}$$

Under conditions with pH < 4, the amount of H_2CO_3 becomes relatively large (see figure 5), compared to HCO_3^-. Because the estimation of H_2CO_3 from HCO_3^- (eq. 18) contains relatively large uncertainties, samples with a pH < 4 are removed from the database.

CO_3^{2-} is negligible is most types of groundwater samples. It only occurs in significant amounts at pH values higher than 9. Hence, CO_3^{2-} is not measured or calculated and is assumed to be zero in this study.

Finally, the total amount of CO_2 in groundwater (TIC = total inorganic carbon) is converted to mg/l:

$$\mathbf{TIC} = \text{TIC (mol/l)} \times 44 \times 1000\ \text{(units: mg/l)} \qquad (20)$$

The level of CO_2 saturation of the groundwater (**pCO_2**) is calculated based on the amount of H_2CO_3:

$$pCO_2 = H_2CO_3/KH\ \text{(units: atm.)} \qquad (21)$$

with:

$$KH = 10^{(108.3865\ +\ 0.01985076\times(Temp1)\ -\ 6919.53/Temp\ -\ 40.45154\times\log10(Temp1)\ +\ 669365/(Temp\text{^}2)})$$

6.2 Available data of CO_2 in groundwater

The available data of CO_2 concentrations in the groundwater of the Netherlands can be divided in three groups based on the source of the data:

1. Data collected by RIVM (Rijks Instituut voor Milieuvraagstukken)
2. Data collected by KWR (Watercycle Research Center)
3. Data from other sources

In the DINO*database* many of the data collected by RIVM (1) and other sources (3) are archived. The data collected by KWR (2) are currently not available in the DINO*database*, but can be obtained from KWR in exchange for a financial compensation. In this stage of the research project it was decided to use only the data that are freely available in the DINO*database*.

The DINO*database* contains data of CO_2 (or HCO_3^- and pH) in groundwater from 10.653 borehole locations. The measurements lying behind these data were made between 1867 and 2002. The depth of the filters varies between 0 and 539 m below the surface and these spread of the data over the Netherlands is sufficiently good. Despite the extensive database several drawbacks were encountered that reduce the usefulness of the data:

- The length of the filter varies between several decimetres to over 100 m. As a result of the long filters, the accuracy of the data is reduced and the value of time series is reduced.
- Before 1990 no field measurements of pH were made, but water samples were brought to the laboratories for the determination of pH values. As a result of this method large errors occurred in the pH values due to possible disturbances of the water sample. Values of total dissolved CO_2 (TIC) in groundwater samples in the database from the period before 1990 therefore contain relatively large uncertainties. However, the exact extent of these uncertainties cannot be traced back.

A part of the dataset that was used for this analysis comes from the RIVM (data source 1), consisting of the national monitoring network groundwater quality with additional data from the provincial monitoring network groundwater quality. The methods of this institute for borehole design, sampling methods and chemical analyses are of high quality (Meinardi et. al, 2003). RIVM has made HCO_3^- and pH measurements at 917 locations spread over the Netherlands 1980 and 202, mostly in the relatively shallow groundwater (0 - 30 m below the surface). This part of the total dataset in DINO is therefore considered to be the most reliable.

For the mapping and analyses of our study the dataset is divided in a shallow groundwater (0-30m) and a deep groundwater (30-400m) database. For the shallow groundwater a large amount of observations are available (37.653 measurements at 8.742 borehole locations, 917 of which are RIVM boreholes), while for the deep groundwater the amount of observations is small (11.393 measurements at 4.703 borehole locations). For the mapping and analyses of the shallow groundwater, only the RIVM data were used. For the analyses of deep groundwater all available data was used, in order to obtain a good coverage of the whole underground of the Netherlands. It should however be kept in mind that the uncertainties in the database of the deep groundwater are relatively large. Therefore the analysis of the deep groundwater is limited and will mainly give a general image of the spatial variations of CO_2 concentrations in groundwater.

6.2.1 Data shallow groundwater

The mapping and analysis of the shallow groundwater (0 – 30 m below the surface) is based on the dataset from the RIVM. For the mapping of the CO_2-concentrations in shallow groundwater a subdivision was made between groundwater between 0 and 20 m below the surface and groundwater between 20 and 30 m below the surface. This subdivision was partly based on the design of the National and provincial monitoring networks: each borehole has a shallow filter (0-20 m) and an intermediary deep filter (20-30 m). The ratio behind this is that in areas with groundwater recharge through infiltration of precipitation, the shallow groundwater (0 - 20 m) is (to a larger extent) influenced by anthropogenic impacts than the deeper groundwater (0 - 30 m). De data series of CO_2 concentrations (1980-2002) have been aggregated to single (median) values for shallow (0 - 20 m) and intermediary deep (20-30 m) groundwater. De median CO_2 concentrations per location are interpolated to coverage for the whole country through kriging for shallow and intermediary deep groundwater.

6.2.2 Data deep groundwater

The mapping and analysis of the deep groundwater is based on all the available data from the DINO database with measurements of pH en HCO_3^- at a depth of 30 – 250 m below the surface. These data are, like the data of the shallow groundwater, interpolated through kriging. Additionally, three vertical cross sections through the Netherlands were made to show the variations of CO_2 concentrations over depth.

6.3 Spatial variability of CO_2 in shallow groundwater

Figure 10 shows the 917 RIVM borehole locations and the interpolated CO_2 concentration and pCO_2 in the shallow and intermediately deep groundwater (data from RIVM database). It can be observed that in the southwest and in the north and northwest the density of borehole locations is relatively low. The CO_2 concentrations in the coverage therefore have a reduced significance in these areas. In the figure can be observed that both the CO_2 concentrations and pCO_2 are higher in the shallow groundwater (0 - 20 m below the surface) than in the intermediately deep groundwater (20 – 30 m).

The figures show clear patterns of CO_2 concentrations in the groundwater: high CO_2 concentrations and are found in the western and northern part of the Netherlands (the Provinces Zuid-Holland, Noord-Holland, the western part of Friesland en the northern part of Groningen). In these areas CO_2 concentrations vary between 500 and >1000 mg/l, while in the others parts of the country CO_2 concentrations vary between 0 and 400 mg/l. The lowest CO_2 concentrations are found below the Veluwe area in the central part of the Netherlands.

The pattern of the pCO_2 in the groundwater is similar to that of the CO_2 concentrations: highest pCO_2 in the western and northern part of the Netherlands (1-10% and locally 10-100%) and lower concentrations in the middle (0.4-4% and locally 4-10%), eastern and southern part. Also the dune area along the coast with low pCO_2 can be distinguished. Unlike the CO_2 concentrations, the contrast between the regions is relatively small. The relatively high pCO_2 in the southern and eastern part of the Netherlands is probably due to the presence of calcareous rocks and/or sediment in the underground (see paragraph 3.5). No over-saturation of CO_2 (pCO_2>100%) was observed in the available dataset.

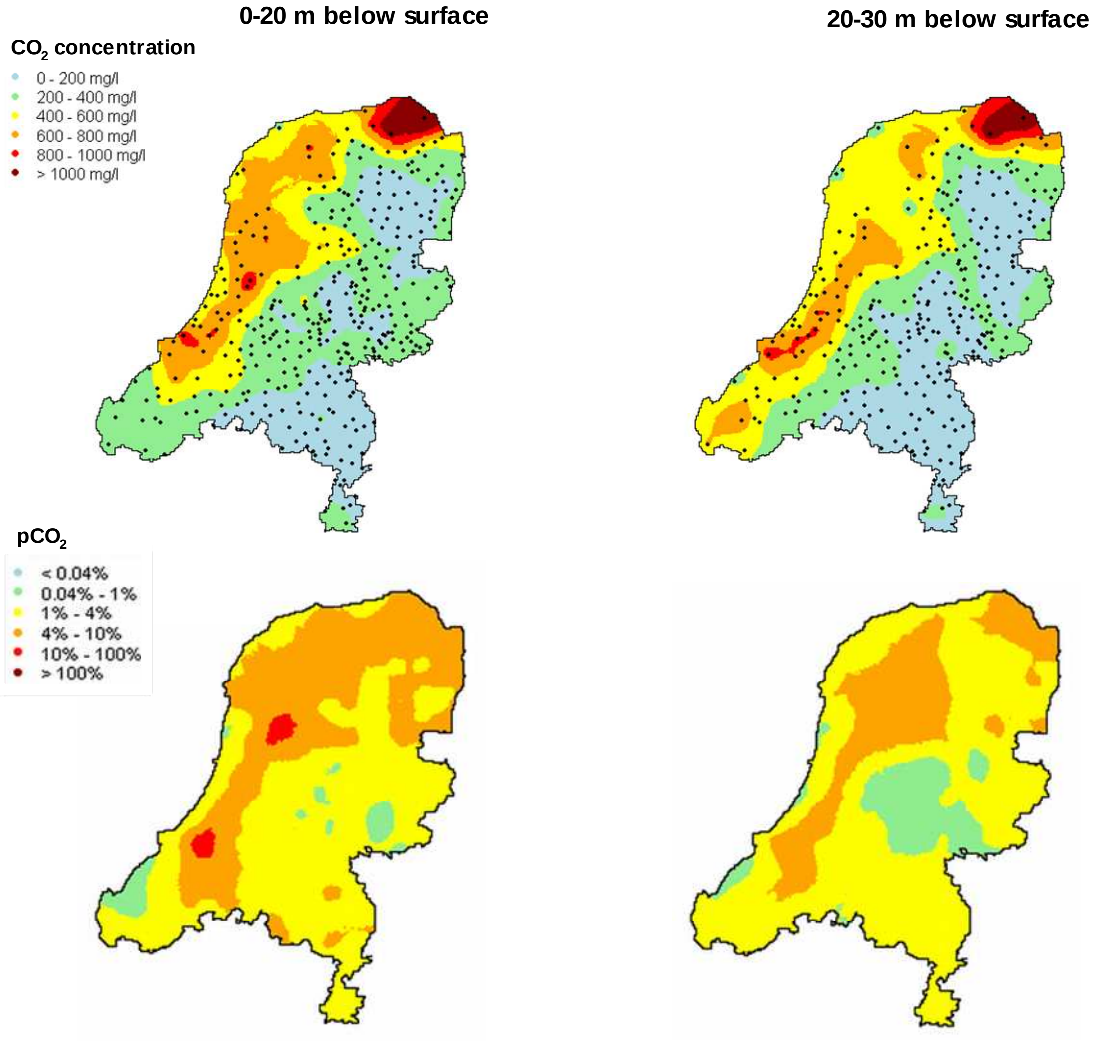


Figure 10: CO_2 concentrations (upper graphs) and pCO_2 (lower graphs) at 0 - 20 m and 20 - 30 m below the surface in the Netherlands (period: 1980-2002). In the upper graphs the RIVM borehole locations are shown.

6.4 Spatial variability of CO_2 in deep groundwater

The CO_2 concentration in the deep groundwater shows similar patterns as the concentrations in the shallow groundwater (figure 11): high CO_2 concentrations are found in the western and northern part of the Netherlands and low concentrations in the rest of the country. Despite the larger uncertainties in the CO_2 concentrations, the large amount of data points (4.703) results in a more detailed image of the spatial variability. In this image the high CO_2 concentrations in the area between the Veluwe and the Ridge of Utrecht stand out as well as the high CO2 concentrations in the Province of Noord-Holland and near The Hague and Rotterdam. The dune area on the other hand shows very low CO2 concentrations in the deep groundwater. In the rest of the country, the spatial variability of CO_2 concentrations in the deep groundwater is comparable, but concentrations are slightly lower than in the shallow groundwater.

Cross sections were made along 3 profiles: “Den Helder - Maastricht” (1), “Zeeland - Ameland” (2), and “Zandvoort - Enschede” (3) (see figure 12). The cross sections were constructed by plotting all data within 20 km of the profile at the cross section over the whole length of the filter of the borehole. The following observations can be made from the three profiles:

- The profile Den Helder - Maastricht (1) shows that CO_2 in the groundwater mainly occurs in the northern part of the Netherlands.
- In the profile Zandvoort - Enschede (2) the CO_2 poor area under the dunes can be distinguished from the CO_2 rich groundwater in the rest of the western part of the country. Also the small topographically low area with high CO_2 concentrations between the CO_2 poor Veluwe and the CO_2 poor Ridge of Utrecht can be observed.
- The profile Zeeland - Ameland (3) shows that high CO_2 concentrations occur frequently below the Provinces Zeeland, Zuid-Holland and Noord-Holland, while the occurrence of high concentrations below the Waddenzee is less common.

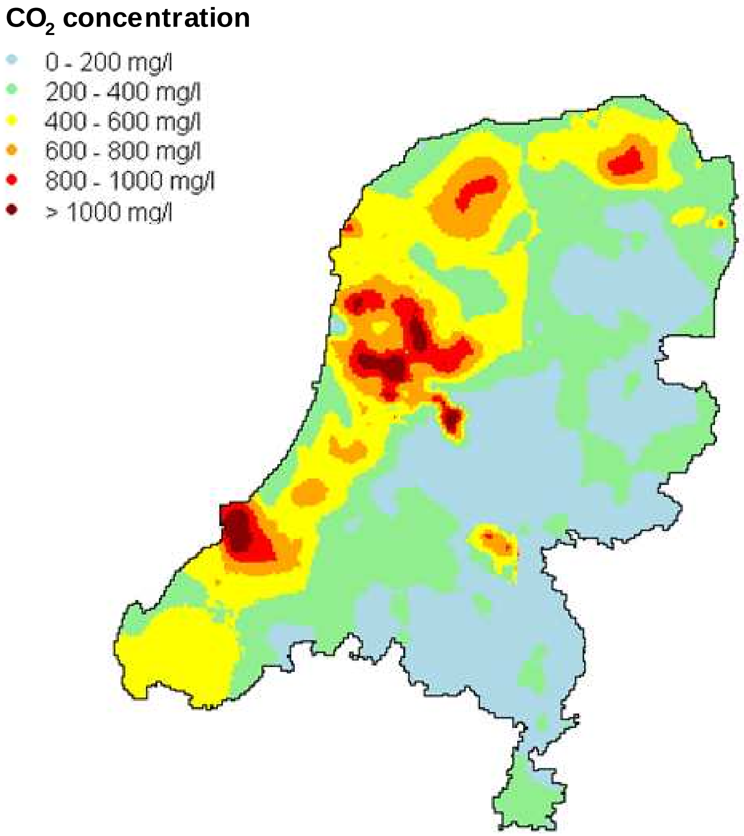


Figure 11: CO_2 concentrations (upper graphs) 30 - 250 m below the surface in the Netherlands.

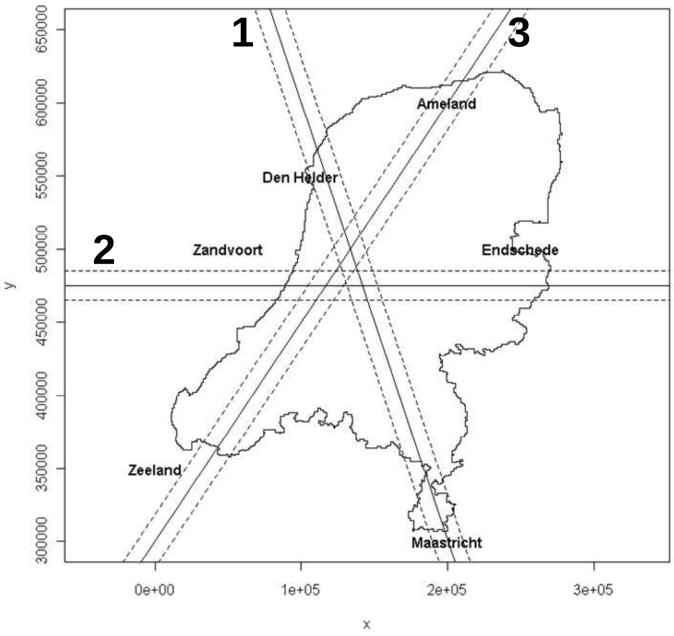


Figure 12: Overview of the three profiles that were used for the cross sections with CO2 concentrations (see figure 13).

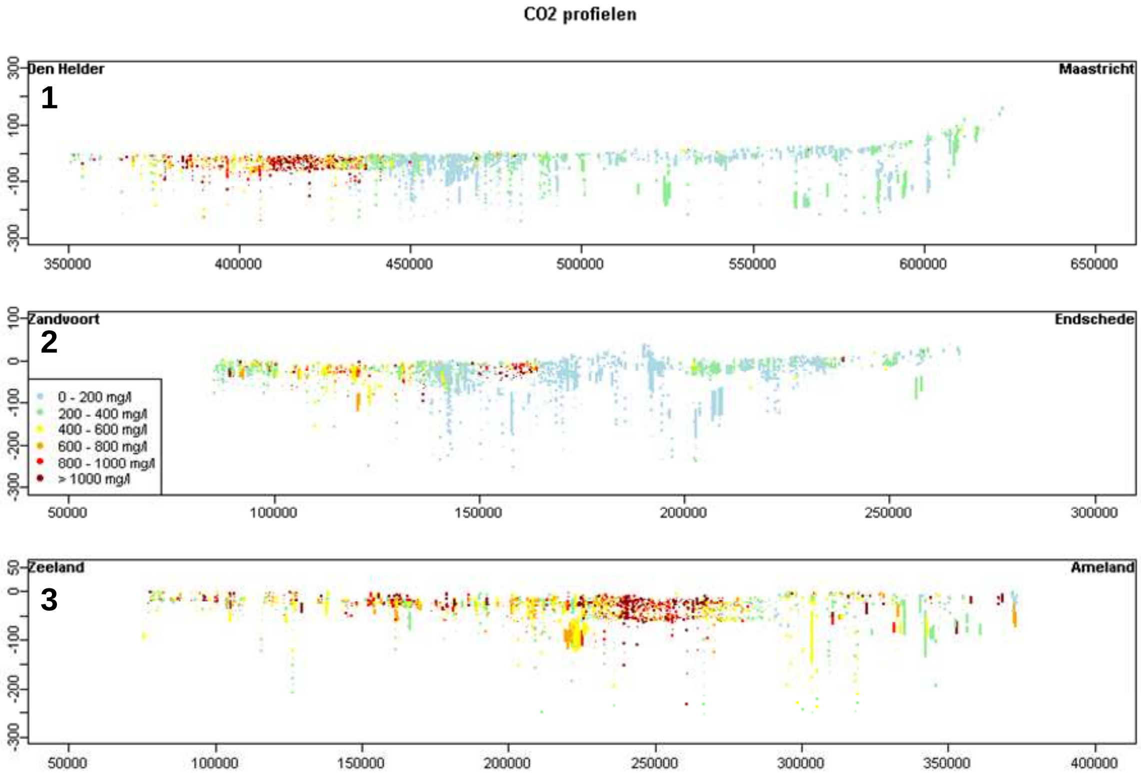


Figure 13: Three profiles with CO_2 concentrations over depth. The numbers of the cross sections (1 - 3) corresponds to the profiles shown in figure 12 (enlargement in annex I).

6.5 Analysis of variation in CO_2 concentrations

In order to explain the regional patterns in CO_2 in groundwater several additional geochemical parameters were mapped: pH, calcite saturation, redox class, and tritium (figure 14; enlargement in Annex II). Important in the analysis were the following chemical mechanisms:

- The solubility and differentiation of CO_2 in water is strongly pH dependent.
- The redox class is based on the concentration of nitrate, iron, sulphate and chloride in the groundwater in a stepwise manner (Vermooten et al., 2006).
- Dissolution of calcite and methanogenesis are both natural sources of CO_2 (see chapter 2).
- The tritium concentration indicates whether the groundwater has infiltrated recently (after 1950) or before 1950.

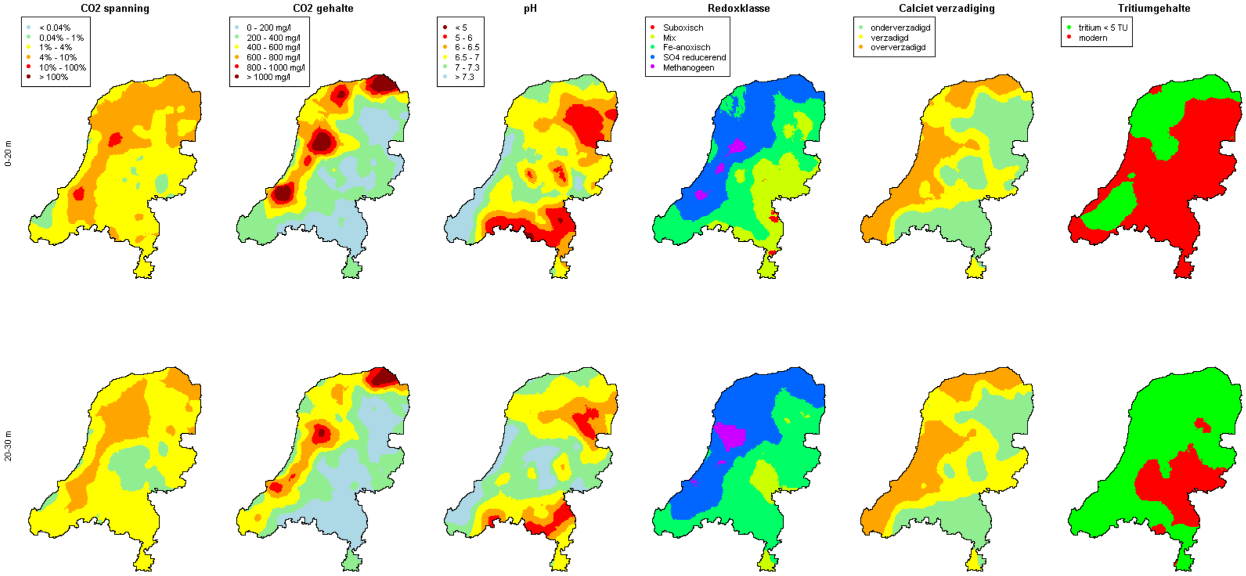


Figure 14: CO_2 pressure (pCO_2), CO_2 concentration, pH, redox class, calcite saturation and tritium content of the shallow (upper graphs) and intermediately deep (lower graphs) groundwater. Full coverage was obtained by kriging the average values at the locations boreholes (enlargement in annex II).

The spatial variation of natural CO_2 concentrations can to a large extent be explained by the redox class of the groundwater. Very high CO_2 concentrations are found in areas with methanogenic groundwater (see paragraph 2.2.3), high CO_2 concentrations are found in areas with sulphate reducing groundwater (see paragraph 2.2.3), and low CO_2 concentrations are found in more aerobic environments, Fe-anoxic water or a mix of suboxic groundwater. Box plots of CO_2 concentrations for each redox class show that high CO_2 concentrations mainly occur in sulphate reducing and methanogenic groundwater (figure 15). Although peaks in the CO_2 concentration are found in iron-anoxic water, the median concentrations are low.

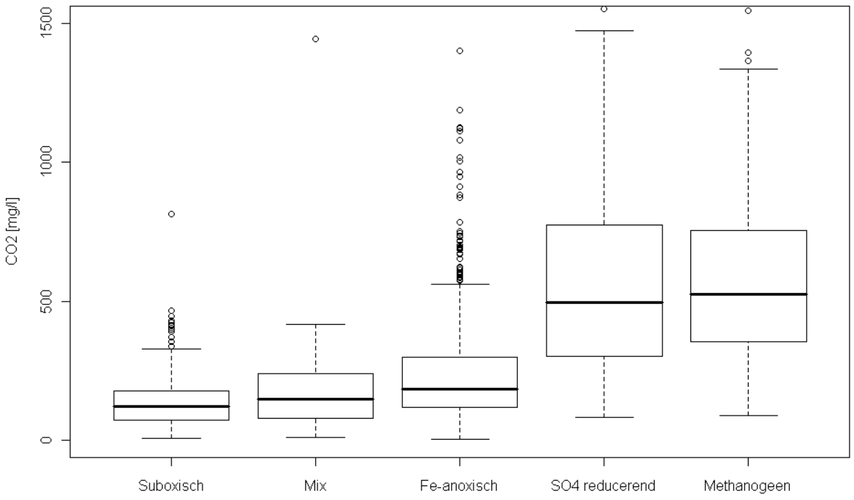


Figure 15: Box plots of CO_2 concentrations in groundwater with various redox classes.

The occurrence of anaerobic (methanogenic or sulphate reducing) groundwater at small depths can be explained by the presence of brackish or salt ‘formation’ groundwater. This type of water has high sulphate concentrations, enabling strong sulphate reduction. In figure 16 can be observed that areas with groundwater from before 1950 (tritium < 5TU) correspond to areas with methanogenic or sulphate reducing groundwater and high CO_2 concentrations. The box plots of CO_2 concentrations for shallow and intermediately deep groundwater show that high CO_2 concentrations occur mainly in groundwater that infiltrated before 1950.

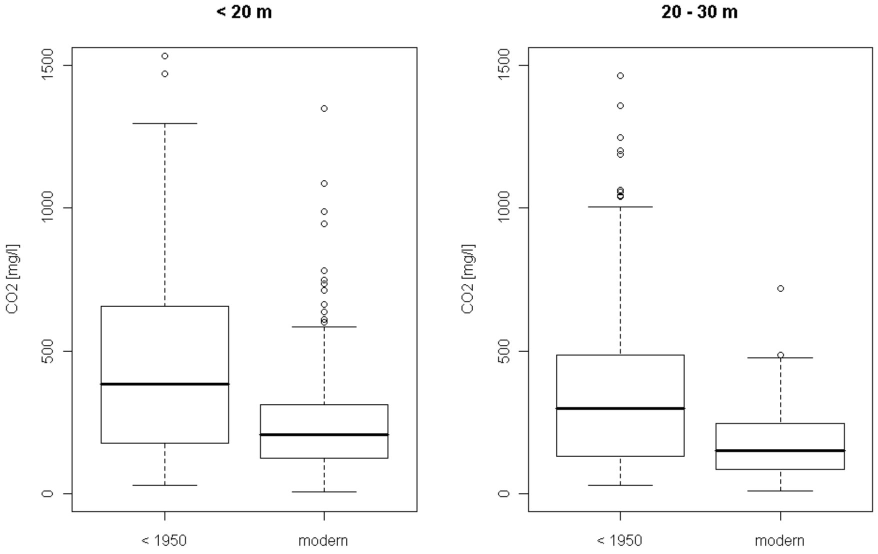


Figure 16: Box plots of CO_2 concentrations of modern groundwater and groundwater from before 1950 for shallow (left) and intermediately deep groundwater (right).

In large parts of the western parts of the Netherlands, organic layers are present in the underground (Holocene peat deposits). As a result, the sulphate in the brackish or salt groundwater is reduced by the organic matter in the underground, thereby forming H_2S and HCO_3^- (see paragraph 4.5.3). Seepaging of formation water to shallower depths probably enhances this process and the occurrence of high CO_2 concentrations in the shallow groundwater. An additional indication for this is that high CO_2 concentrations are clearly related to high chloride concentrations (figure 17).

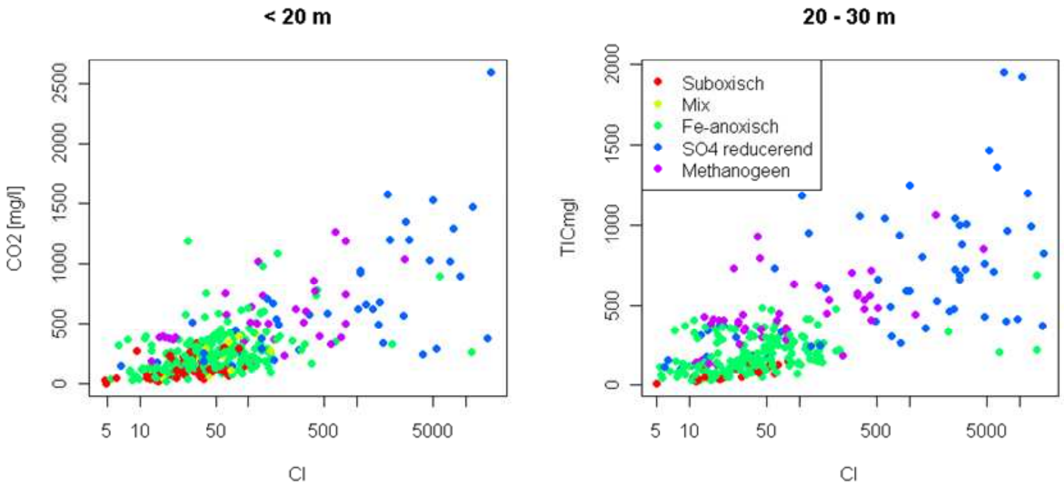


Figure 17: Relation between chloride and CO_2 concentration in groundwater for the various redox classes (colours).

As a result of the high concentrations of dissolved CO_2, the pH of the groundwater increases (see paragraph 2.2.2). In figure 14 and figure 18 can be observed that areas with high CO_2 concentrations are found in areas where the pH is relatively high (6.5 - 8). Figure 18 shows the dependency of CO_2 concentration from redox class (colouring) and the relation between CO_2 concentration and pH.

The pH of the groundwater is for a large part determined by the presence of carbonates (see paragraph 2.2.4). In areas with calcareous rocks or sediments in the underground and high calcite concentrations in the groundwater, both pH and CO_2 concentrations can be reduced as a result of the precipitation of calcite (pH > 7). Also, the pCO_2 in areas with high calcium concentrations in the groundwater increases more rapidly. In these areas CO_2 saturation of the groundwater can be reached at relatively low CO_2 concentrations. The high pCO_2 in the dune area and in the southern part of the Netherlands is probably caused by this mechanism.

Figure 19 shows the distribution of the CO_2 concentrations over depth. The highest CO_2 concentrations are found between 0 – 100 m below sea level. Samples taken above sea level have a relatively constant CO_2 concentration of approximately 400 mg/l. The samples were mainly taken in Zuid-Limburg and the constant and low CO_2 concentrations are probably caused by dissolution of limestone and precipitation of calcite (calcareous rocks).

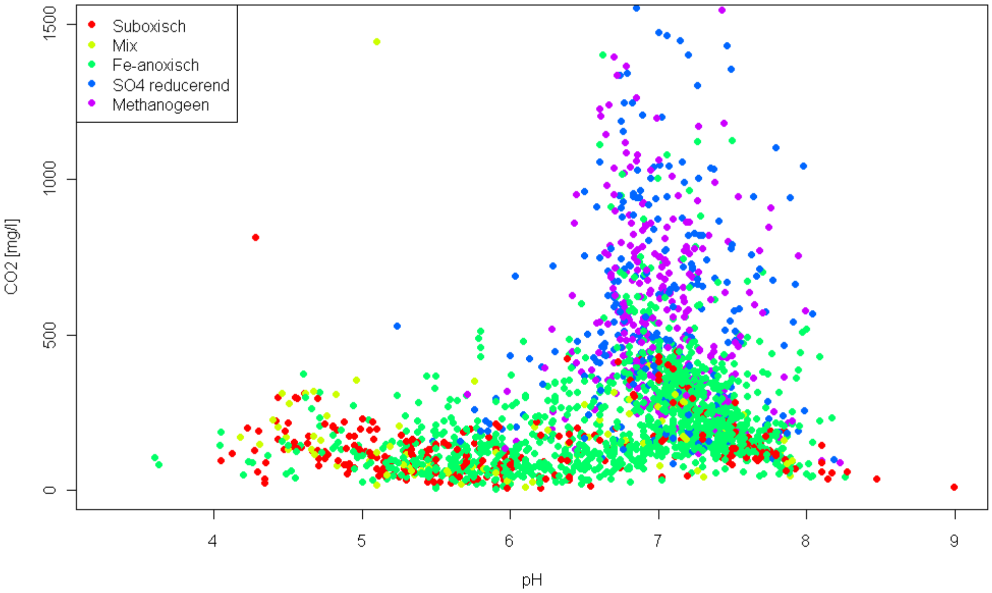


Figure 18: Relation of pH and CO_2 concentrations of groundwater for the various redox classes (colours).

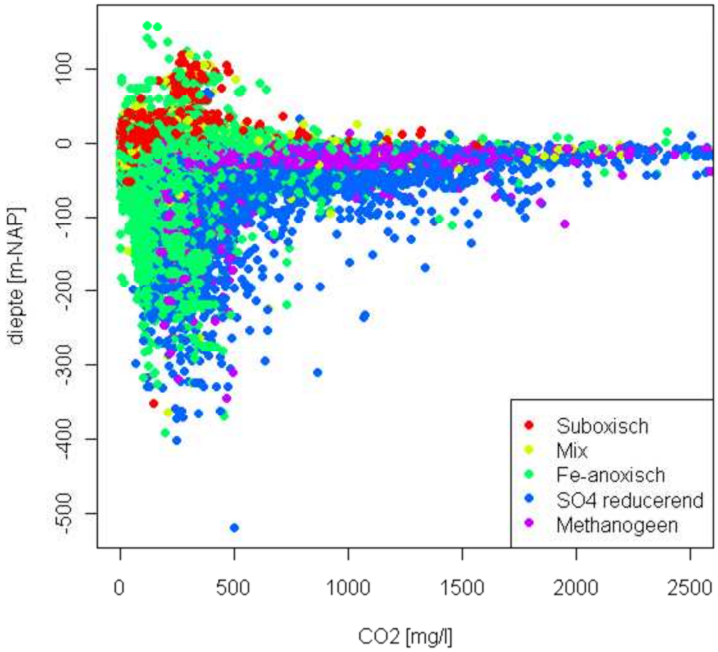


Figure 19: CO_2 concentrations of groundwater over depth for the various redox classes (colours).

During this study an attempt was made to study the variation of CO_2 concentration in the groundwater in areas with fractures in geological formations in the underground using REGIS II maps of fractures in various formations. Such structures might cause a shortcut or a barrier for groundwater with certain CO_2 concentrations. For a proper analysis of the effect of fractured geological formations on the variation of CO_2 concentrations in the groundwater, a range of measurements at multiple depths and at both sides of the fracture zone is required. In the current dataset such monitoring networks were however not available.

6.6 Temporal variability

For 40 borehole locations of the RIVM database spread over the Netherlands with more than 10 data points, time series of CO_2 concentrations were plot for the filter in the shallow groundwater and, when available, the filter in the intermediately deep groundwater (see annex III). In order to show the variation of at the different locations, the time series were plot for a concentration range of 0 to 3000 mg/l and a concentration range of 0 to 1000 mg/l. In most cases data on CO_2 concentrations are available for the period between 1980 and 1995, while at some locations more recent data are available.

In a part of the borehole locations a slight decrease of CO_2 concentrations in the groundwater over the period from 1980 to 1990 can be observed, followed by a small increase in the 1990's. However, at many other locations no trend is observed and CO_2 concentrations are either stable or show apparently random fluctuations.

Currently it is not possible to draw any conclusions from the time series. Besides the lack of clear trends in the data, there are several drawbacks in the data that limits their usefulness for time series analyses of the CO_2 concentration for our purpose. In many cases the filter lengths are too long to take groundwater samples of high precision, the groundwater samples there consist rather of mixtures from various depths then of one specific depth. This makes it virtually impossible to study certain processes that take place at a certain depth. Additionally, since proportion of the source depths of the mixture from such filters varies, the samples that are taken over time are not really well comparable. Another objection is that the measurement intervals are to long and irregular for the purpose of detecting seasonal changes in CO_2 concentrations.

7 Methane in groundwater in the Netherlands

7.1 Relation CH_4 and CO_2 in groundwater

Both CO_2 and CH_4 have organic matter as their main source. During methanogenesis not only CH_4, but also CO_2 is formed (see equation 12). The occurrence of CH_4 is therefore strongly related to the presence of CO_2. Additionally, under aerobe conditions (above the groundwater level and perhaps in deeper groundwater bodies where oxygen becomes available as a product of other geochemical processes) CH_4 is oxidised by methanotroph microbes, during this process CO_2 is produced (see equation 13). When water levels are lowered the amount of CH_4 that is produced in the soil is reduced, while the CO_2 production increases (increased mineralisation). Also, larger amounts of CH_4 are oxidised before reaching the atmosphere (Hendriks et al., 2007).

7.2 Sources of methane

Besides the possibility of CH_4 in the groundwater coming from deep sources like gas reserves (see paragraph 5.1.6), the presence of CH_4 in the upper 400 m of the groundwater is formed in shallower deposits during anaerobic fermentation of organic matter in the soil and underground (see paragraph 4.2.3). This organic matter can have different sources in the Netherlands (Stuyfzand et al., 1994; Ramsak et al., 2006):

- Low moor deposits in the western part of the Netherlands (e.g. Hollandveen and Basisveen in the Holocene top layer).
- Organic matter in the Pleistocene aquifers below the Holocene top layer, mostly in the western part of the Netherlands.
- Raised bog deposits.

The CH_4 that is produced in the underground dissolves in the groundwater and can be transported with the groundwater towards deeper aquifers or it can move towards the surface with seepaging groundwater (see paragraph 4.5.5).

7.3 Available data of CH_4 in groundwater

During by order of SenterNovem (Ramsak et al., 2006) an inventory was made of the available data on CH_4 concentrations in de groundwater in the Netherlands. The information that was gathered during this inventory consisted of the results of methane-analyses of untreated water from approximately 105 groundwater abstraction areas from the period 1993-1994. Additionally, CH_4-concentrations were estimated from the available parameters for 145 pumping stations. In the study the total amount of CH_4 that is formed yearly in het Dutch groundwater has been estimated at 160 en 450 kton. It should however be kept in mind that the estimation is based on a very rough approach and the uncertainty of the amount is large.

The data that were used by Ramsak et al. (2006) as well as more recent data are currently in the possession of KWR and are not freely available, but can be obtained from KWR in exchange for a financial compensation. In this stage of the research project it was decided to use only the results that were already available by Ramsak et al. (2006).

Figure 20 gives an overview of the CH_4 concentrations in de underground of the Netherlands taken from Ramsak et al. (2006). In the provinces of Noord-Holland, Zuid-Holland, Friesland and in the border region of Drenthe and Overijssel high CH_4 concentrations are observed in the groundwater (>10 mg/l). In the topographically low, western part of the Netherlands the high concentrations can be explained by the presence of organic material of maritime origin in the sand deposits. Remarkable is that in the province of Zeeland no high CH_4 concentrations are observed. However, only a small amount of data is available in this area. Areas with the highest CH_4 concentrations in groundwater are:

- The area around Delft, Zoetermeer, Rotterdam and Den Haag (30-57 mg/l);
- The area between Aalsmeer - Hoofddorp (26-48 mg/l),
- The province of Friesland (35-52 mg/l).

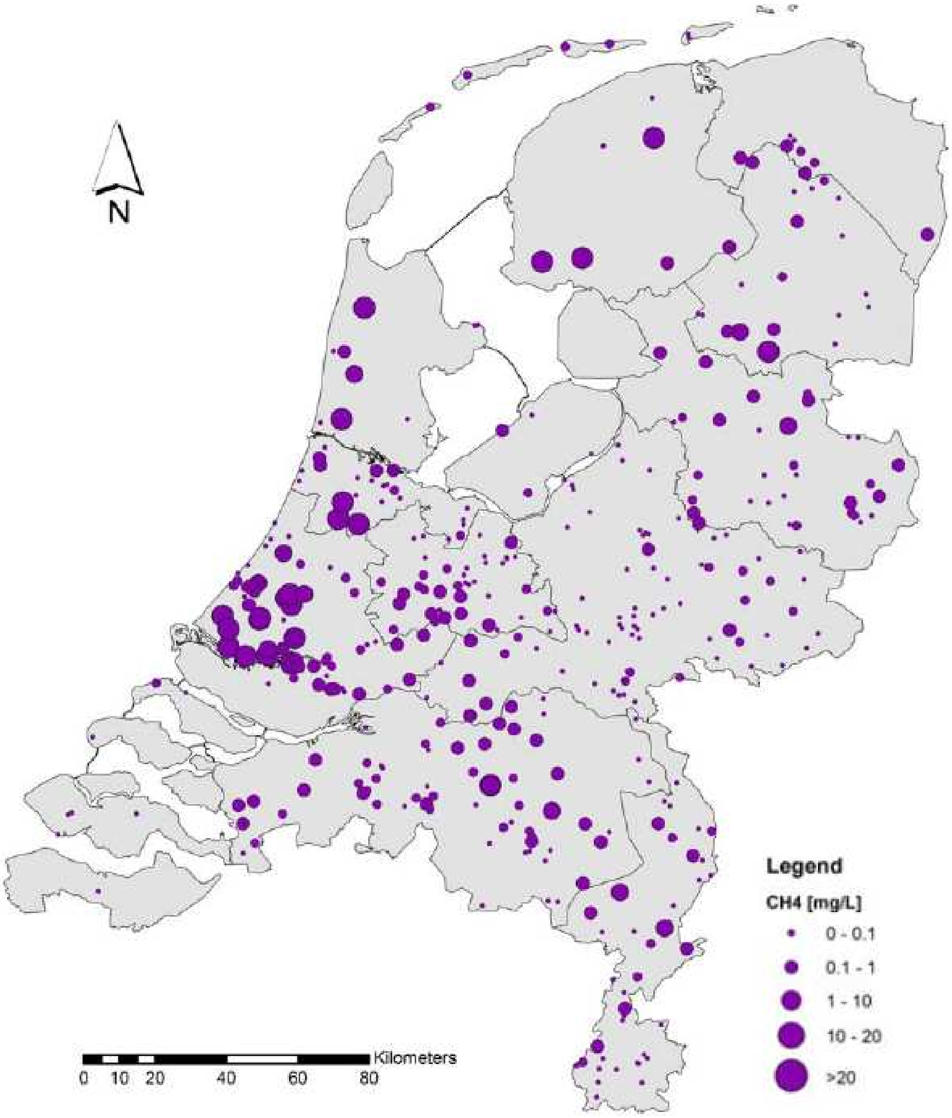


Figure 20: Overview of methane concentrations in the underground of the Netherlands, based on all available data from abstracted groundwater for drinking water and by IF Technology gathered data (source: Ramsak et al., 2006).

Stuurman (2004) made a short inventory of the occurrence of CH_4 in groundwater bodies in the provinces Noord-Brabant and Limburg that are in use for drinking water abstraction. The results showed two zones with relative high CH_4 concentrations (0.40–7.58 mg/l) in the area: an elongated zone east of the 'Centrale Slenk' area (a graben) bordering the Peelhorst area and a zone in the western part of Noord-Brabant. Possibly the location of these zones rich with gases is related to the position of the faults in the underground along which gases can probably migrate upwards. In the results of the study for SenterNovem (figure 20) high CH_4 concentrations can be observed in the 'Centrale Slenk' area as well.

Also soils with high organic contents (e.g. peat soils, lake deposits) contain high CH_4 concentrations due to local production of CH_4 in anaerobic parts in the soil profile. Research in the Horstermeer polder in showed CH_4 concentrations in the soil water (unsaturated zone) between mg/l 10 to over 100 mg/l. These high concentrations probably caused the formation of gas bubbles. A large part of the CH_4 formed in these types of soils is out gassed to the atmosphere (Hendriks et al., 2007, Hendriks et al., 2009).

When comparing figures 10, 11 and 20, it can be observed that the areas with high CO_2 concentrations in the groundwater correspond to the areas with high CH_4 concentrations in the groundwater. In figure 18 was also shown that groundwater with the methanogenic redox class has high CO_2 concentrations. The CO_2 concentrations of the groundwater are however an order of magnitude higher than the CH_4 concentrations of the groundwater (also when molar masses are compared). This indicates that the largest part of the CO_2 that occurs in the groundwater in the western part of the Netherlands is produced by other processes than methanogenesis (e.g. de-nitrification and redox-processes).

7.4 Methane gas wells

The CH_4 that occurs in the relatively shallow aquifers has been used as a fuel for hundreds of years. In areas with high CH_4 concentrations in the underground, formation of gas bubbles with high CH_4 concentrations can form due to pressure release and / or an increase of the total amount of dissolved components due to an increase in salinity. Pressure release can result from seepage or abstraction of the groundwater. In the past special wells have been used in the western part of the Netherlands for the mining of methane gas from Holocene or Pleistocene deposits for fuel production (Stuyfzand et al., 1994; Stuurman, 2001).

Figure 21 gives an overview of the well locations that were detected during the inventory by NITG-TNO and a previous inventory by ICW in 1982. It can be observed that the gas wells are mainly situated in the relatively low lying areas, the deeper part of the polders, and near the borders of the polders where the seepage pressure is relatively strong. Also the wells appear to be situated along roads near farms, probably in order to have good accessibility.

In the province of Noord-Holland probably about 4.000 natural gas sources existed during the first half of the 20th century. However, only approximately 350 of these sources produced enough CH4 to be used for longer periods as gas wells for fuel. In other northern and western areas of the Netherlands, the mining of methane gas from Holocene and Pleistocene deposits was less successful, although equally high CH_4 concentrations occur in the groundwater in these areas. This difference was probably caused by a difference in seepage pressure. The seepage pressure in Noord-Holland is relatively high, causing a larger natural flux of groundwater with high CH_4 concentrations towards the surface (Ramsak et al., 2006).

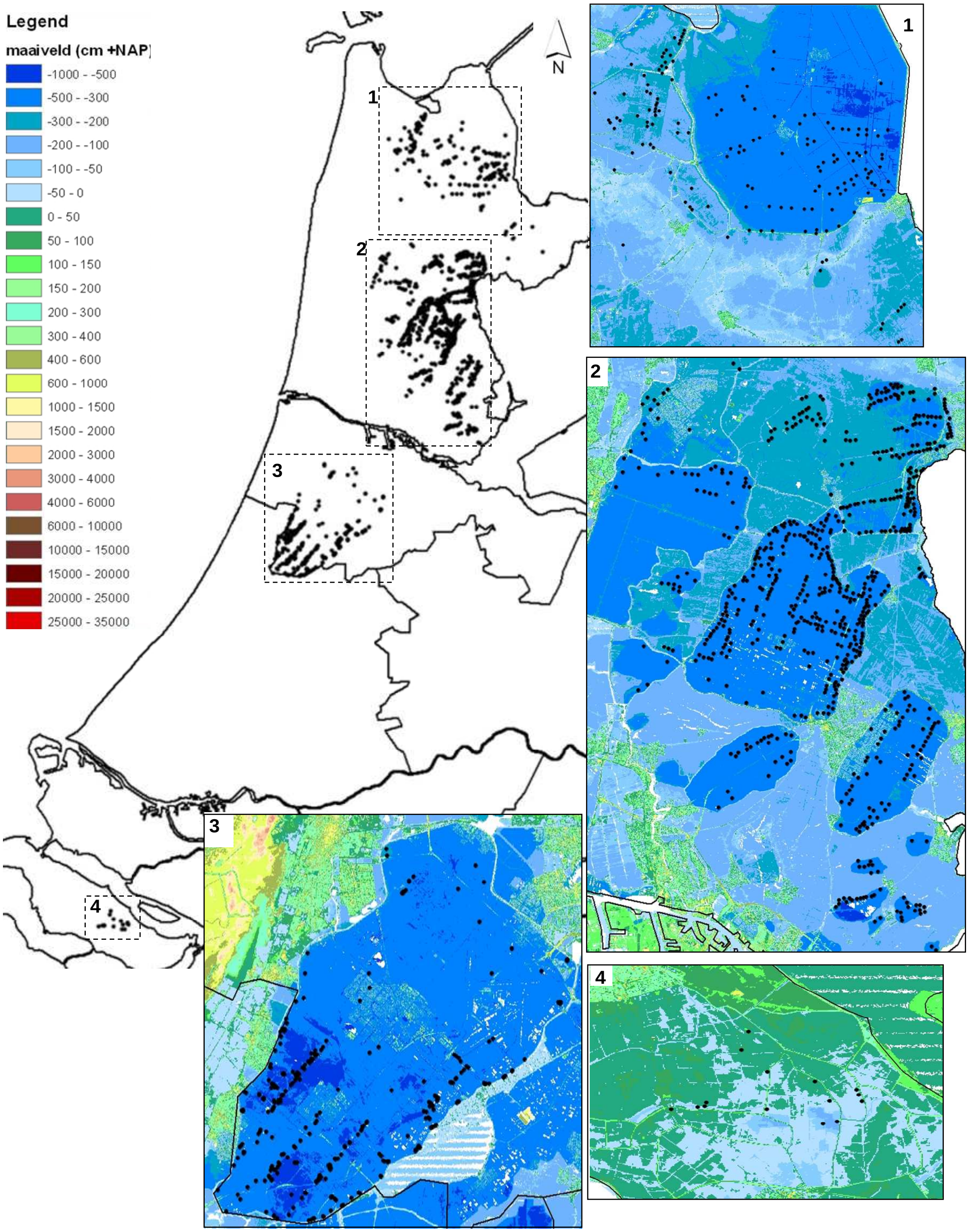


Figure 21: Overview of methane gas wells in the western part of the Netherlands underground of the Netherlands. Four polder areas with high densities of gas wells are enlarged and surface elevation above sea level is shown (source: G. van Ooyen).

Unfortunately no reliable data of CH_4 concentrations in groundwater were currently available for the areas with gas wells in Noord-Holland (figure 20). It is however expected that the concentrations in this region are similar to the concentration measured at Schagen (35-52 mg/l). Possibly, the data set that is in possession of KWR contains information about this area.

Areas with a high density of gas wells (figure 21) correspond with areas with groundwater that contain high CO_2 concentrations (figures 10 and 11). Measurements in a polder area in the province Noord-Holland however showed that CO_2 concentrations of the well water were relatively low, approximately 5-15 times lower than the CH_4 concentrations (Buijs and Stuurman, 2003). More research is however necessary to verify whether this is also the case in other areas with a high density of CH_4 gas wells.

8 Conclusions and further research

8.1 Preliminary conclusions

A large database of CO_2 concentrations in the groundwater in the Netherlands exist in the DINO*database*. However, only a relatively small part of this database contains reliable data (RIVM data). Most of these data are from the shallow (0 – 20 m below sea level) and intermediately deep groundwater (20 – 30 m below sea level). The largest part of the reliable data originates from the period between 1980 and 1995. Possibly the DINO*database* is not yet updated with more recent data (1995 – 2010).

CO_2 concentrations of the groundwater vary between 0 mg/l and 5000 mg/l. High concentrations are found in the western and northern part of the country, except the dune area. Lowest CO_2 concentrations were found in groundwater below the Veluwe. The CO_2 Concentrations in deep groundwater are lower than the concentrations in the deeper groundwater, but the spatial patterns are similar.

High CO_2 concentrations in groundwater are the result of sulphate reductions and methanogenesis in formation water and seepaging formation water in the western and northern part of the Netherlands. In this area the groundwater is mostly brackish or salt and layers of organic matter occur in the underground (Holocene peat deposits and organic matter in older marine deposits). Low CO_2 concentrations are found in the relatively recently infiltrated fresh groundwater, the more aerobic (shallow) groundwater and in areas without brackish or salt groundwater or organic deposits in the underground. Dissolution of calcite in the subsurface does not lead to significant increases in CO_2 concentrations. However, in areas rich of calcite high pCO_2 was observed.

The available data give a clear overview of the regional spatial variation of CO_2 concentrations in the groundwater. However, small scale variability and dissipation of CO_2 in groundwater due to local variation (e.g. fractured zones, contamination, water level changes, and groundwater abstraction) cannot be deducted from these currently available data. The changes of CO_2 concentrations over depth can be observed only to a limited extent, mainly due the high uncertainty of the measurements in deeper groundwater. The usefulness of the available data for analysis of temporal variability was very low, due too the long filters and long and irregular measurement intervals.

Areas with high CO_2 concentrations in groundwater overlapped with high CH_4 concentrations found in literature. The CO_2 concentrations of the groundwater are however an order of magnitude higher, indicating that the largest part of the CO_2 is produced by other processes than methanogenesis (e.g. de-nitrification and redox-processes). Since no CH_4 concentration data were available for this study detailed analysis of this relation was not possible.

The effect of seepage on the behaviour of gases dissolved in groundwater could be important for small scale spatial variation of CO_2 concentrations in the groundwater. Areas with high CH_4 concentrations in the groundwater and a strong seepage flux have a high density of (artificial) groundwater wells that were used as methane gas wells in the past. Probably, these (artificial) wells also induce large (potential) CO_2 emissions. The behaviour of CO_2 in groundwater in areas subjected to seepage has however not yet been studied.

8.2 Next research phase: monitoring and detailed analyses

Although the inventory of the available data resulted in a good spatial overview of the range of CO_2 concentrations in the groundwater in the Netherlands, no small scale variations of CO_2 concentrations could be detected. None the less, knowledge of such variations is important for being able to establish base line levels of CO_2 concentrations in the groundwater and to be able to detect possible variations caused by the CO_2 storage and injection in geological formations. In this paragraph the first concepts for more a specific monitoring network is described which will be designed in more detail during the next phase of this research project.

In general, more detailed measurements at specific locations are required to determine the range of natural and human induced variability of CO_2 concentrations in groundwater (base line). The monitoring set-ups should be specifically designed for the detection of these local effects to be able to separate them from other variability. Locations of interest are areas where strong variations of CO_2 are to be expected as a result of natural of human induced variations in the underground:

- (Polder) areas with strong seepage fluxes
- Fractured areas, along faults
- Areas near waste deposits
- Urban areas
- Areas with (periodical) groundwater abstraction
- Areas with strong fertilisation
- Areas with strong variations in groundwater levels

To detect small scale temporal variability of the CO_2 in the soil water and groundwater time series of CO_2 concentrations should be measured with intervals of a day up to a month depending on the specific location. Important sources of temporal variability that need to be studied are the effect seasonal variation of CO_2 in the in the top layer (changes in temperature and availability of organic matter), the effect of periodical groundwater abstraction, the effect of heavy rain events (increased infiltration of groundwater), the effect of fertilisation events, and the effect of warm water storage in aquifers.

To study the effects of various sediment layers, the effects of fractured deposits, the transition of water from soil to groundwater and from one sediment layer to the next, and the effects of human activity (e.g. waste deposits, warm water storage, and fertilization) measurements should also be made at multiple depths, starting in the unsaturated soil.

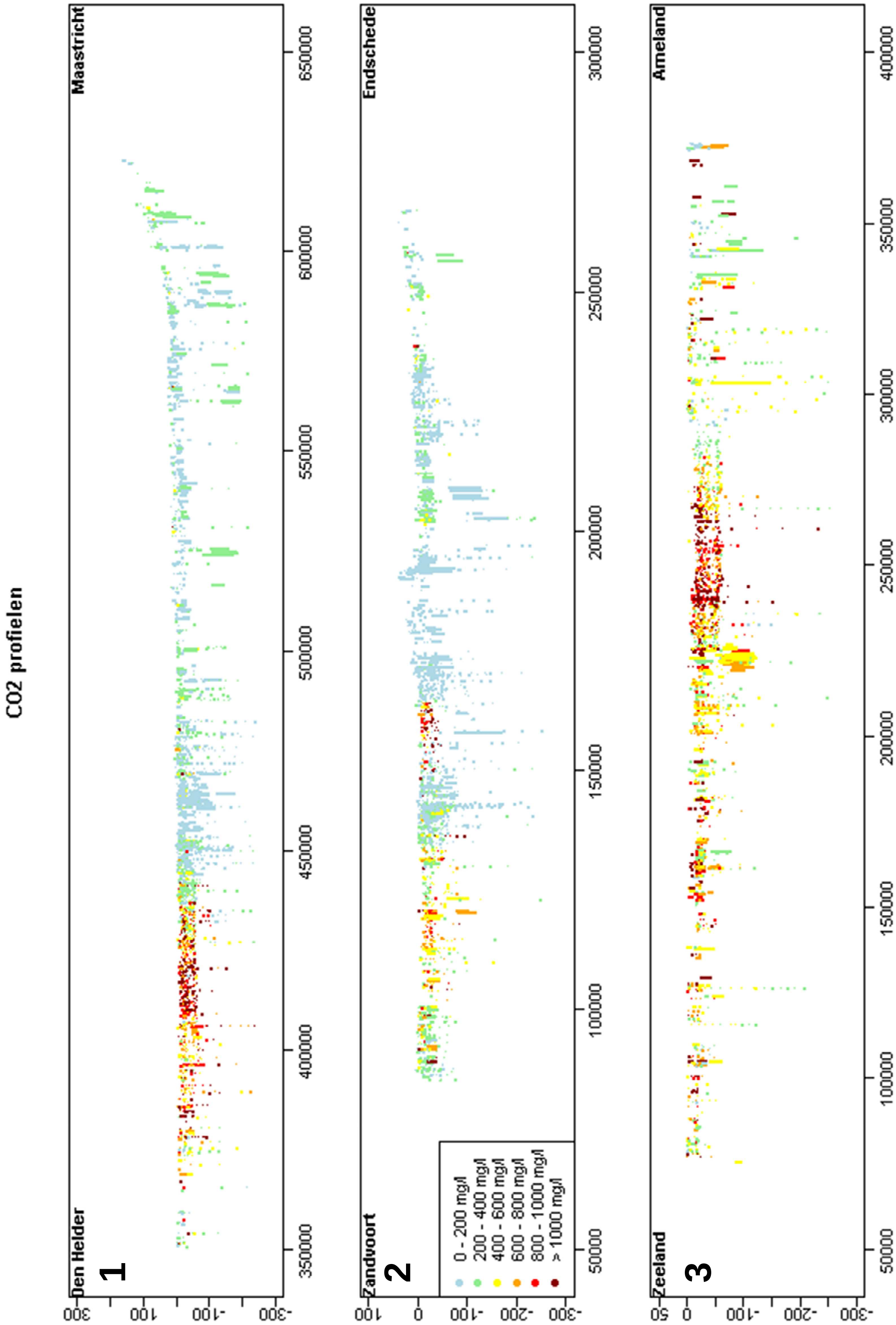
The results of the analyses in the underlying report show that organic matter is probably an important source of CO_2 in the groundwater. For the Holocene sediments in the western parts of the Netherlands the occurrence of widespread peat deposits it is well known. The analysis also showed high CO_2 concentrations in the groundwater in marine sediment deposits and specific hotspots of extremely high CO_2 concentrations in certain areas in Noord-Holland and Zuid-Holland at all depths. Also, previous studies have shown the possibility of occurrences of CO_2 and CH_4 coming from deep sources in the groundwater. Detailed analyses of the exact source of the CO_2 would be useful for an improved understanding of the natural range of variation of CO_2 in the underground as well as the possibilities of upward flow of CO_2 from deep reservoirs to the surface.

In order to carry out the necessary monitoring work 50 to 70 samples should be taken and analysed. The exact sampling locations and sampling frequency will be determined at the start of the next research phase. For the sampling locations a selection of the existing boreholes will be made. Besides analyses of the CO_2 (HCO_3^- and pH) and CH_4 concentrations, the groundwater samples need to be analysed on various components (macro parameters, gasses, isotopes) in order to do proper analyses and to be able to explain the source of the CO_2 in the groundwater (Buijs and Stuurman, 2003). Below an overview of all components is listed:

- *Macro parameters*: calcium (Ca), magnesium (Mg), kalium (k), natrium (Na), Iron (Fe), manganese (Mn), ammonium (NH_4), chloride (Cl^-), sulphate (SO_4), phosphate (PO_4 total), bicarbonate (HCO_3^-).
- *Gasses*: carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), nitrogen gas (N_2).
- *Isotopes*: $\delta^{13}C$ in methane, $\delta^{13}C$ in total dissolved inorganic carbon (TIC), $\delta^{18}O$ and $\delta^{2}H$.

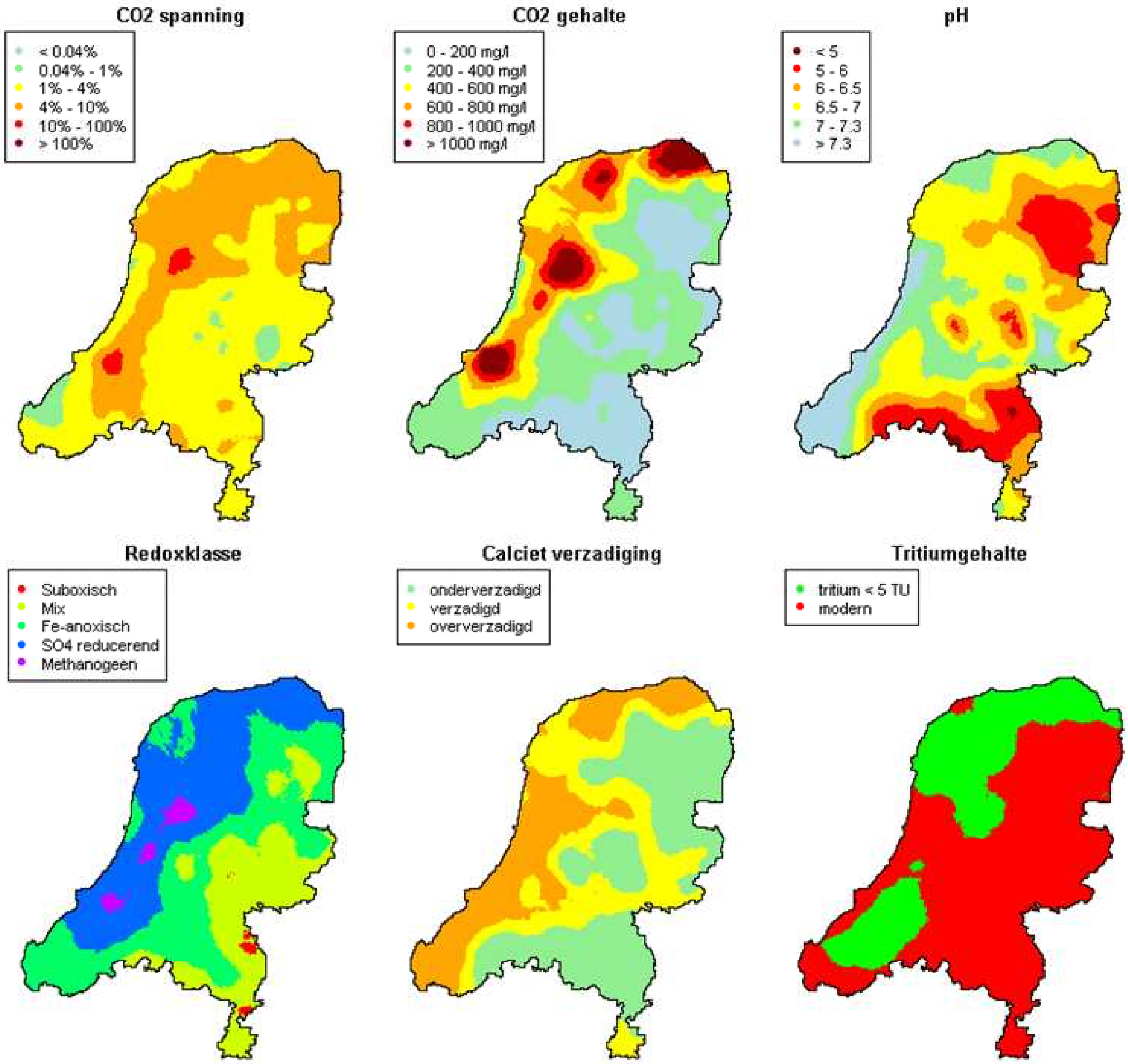
Besides the new monitoring campaign, the already available data set could become more useful for this research, in case it could be extended with other existing data that were not available in the first part of the research. Two possible sources for extension of the data set exist. Firstly, the dataset of RIVM could be completed with the data of the past 10 years. When these data are available, the time series can be analysed over a period of 20 to 25 years and large scale temporal variations could be detected if present at the locations. Secondly, the data set that is in possession of KWR could be obtained. An additional advantage of this data set is that it would add to the investigation of the relation of the CO_2 concentration and the CH_4 concentration in the various groundwater bodies could be investigated with this dataset.

Annex I Profiles of CO_2 concentration in groundwater



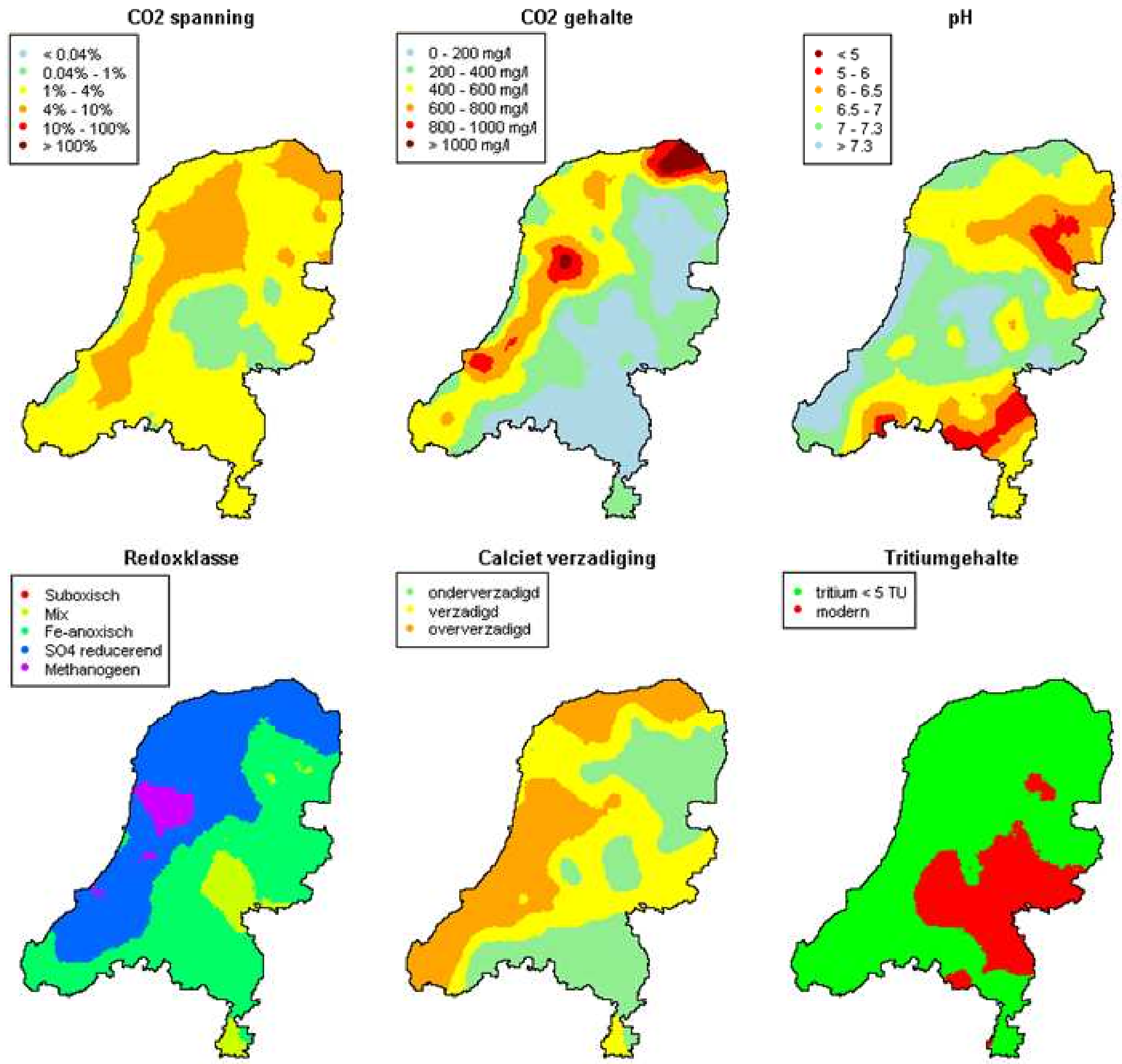
Annex IIa

CO_2 pressure (pCO_2), CO_2 concentration, pH, redox class, calcite saturation and tritium content of the shallow groundwater (0-20 m below surface).



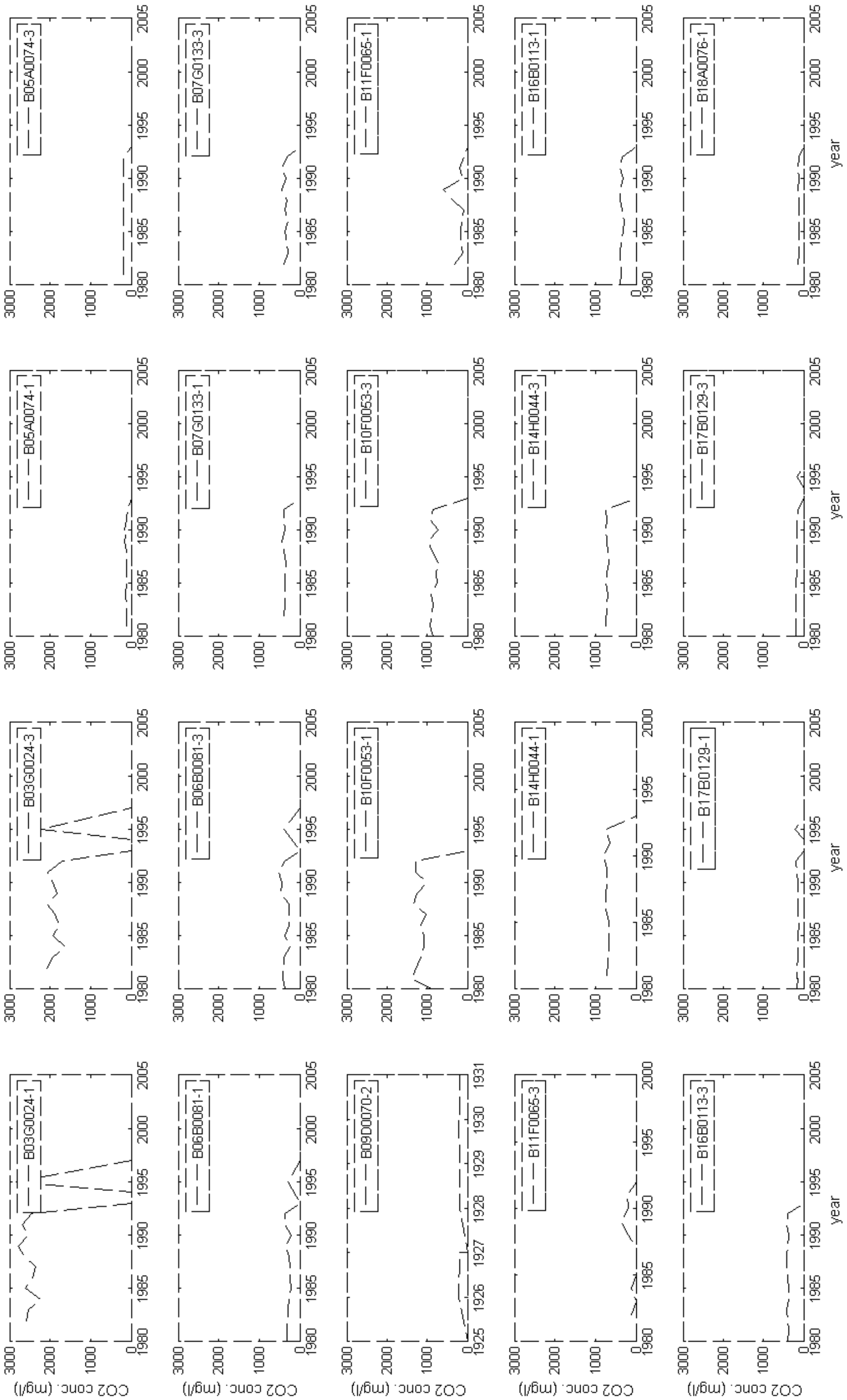
Annex IIb

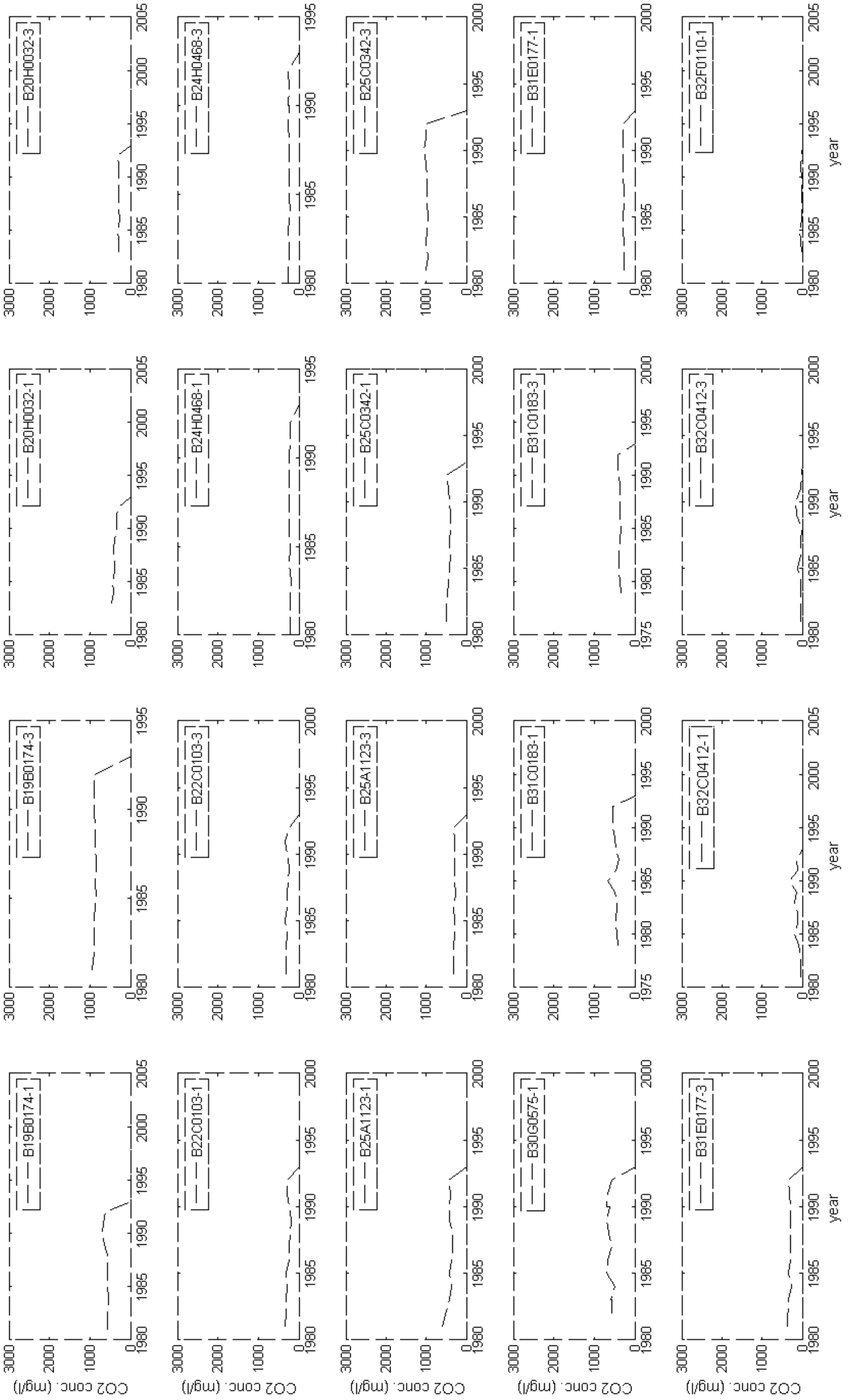
CO_2 pressure (pCO_2), CO_2 concentration, pH, redox class, calcite saturation and tritium content of the intermediately deep groundwater (20 – 30 m below surface).



Annex IIIa Locations and DINO*database* numbers of boreholes used for time series analysis.

Annex IIIb Time series with CO$_2$ range on y-axes of 0-3000 mg/l.

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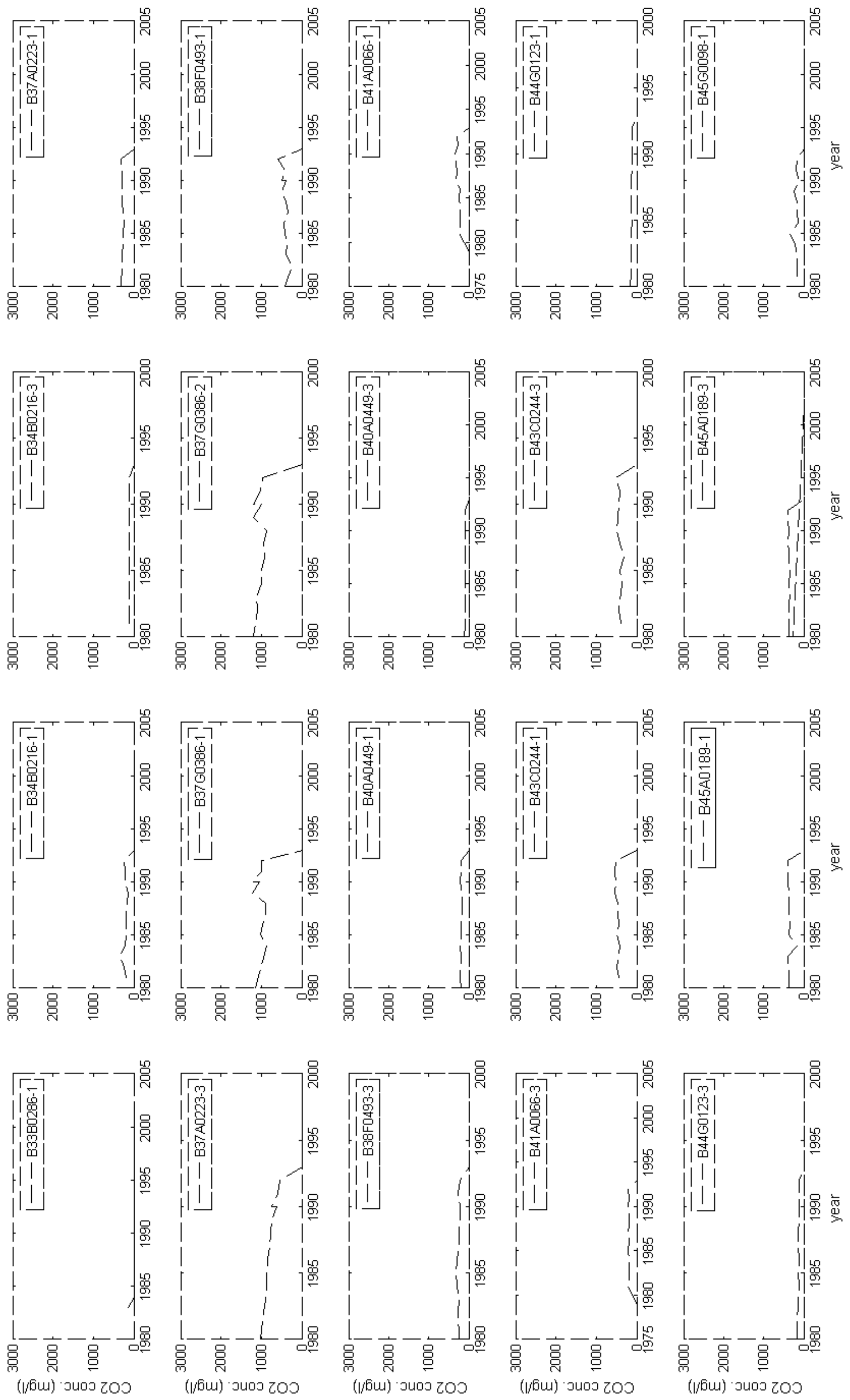
CO2 conc. (mg/l)
year
0
1000
2000
3000
1975
1980
1985
1990
1995
2000
2005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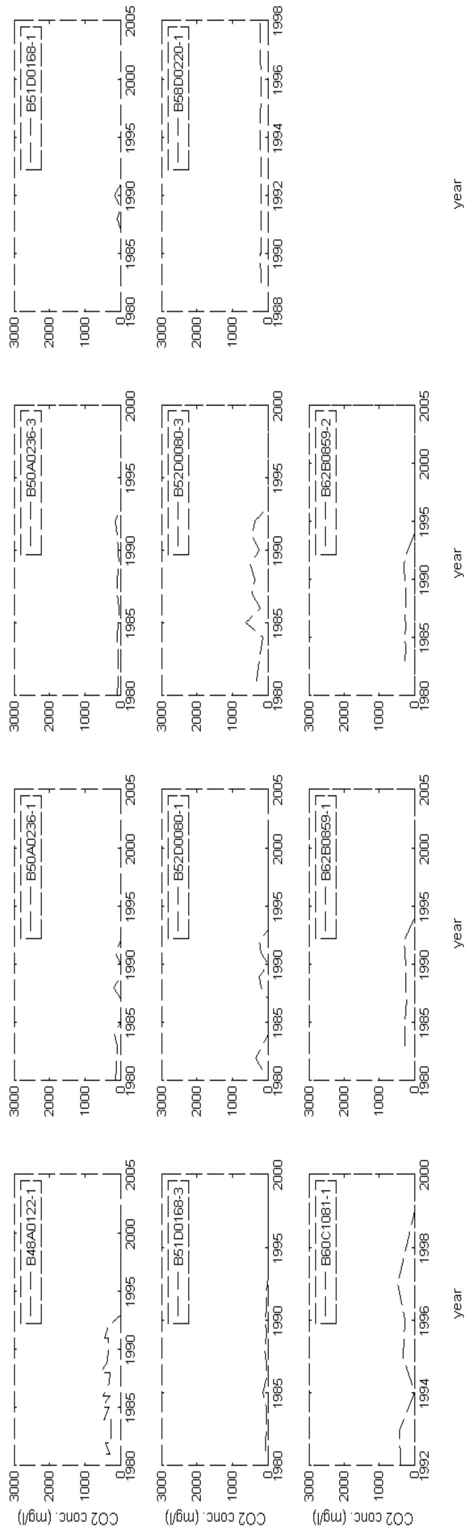
CO2 conc. (mg/l)
0
1000
2000
3000
1975
1980
1985
1990
1995
2000
2005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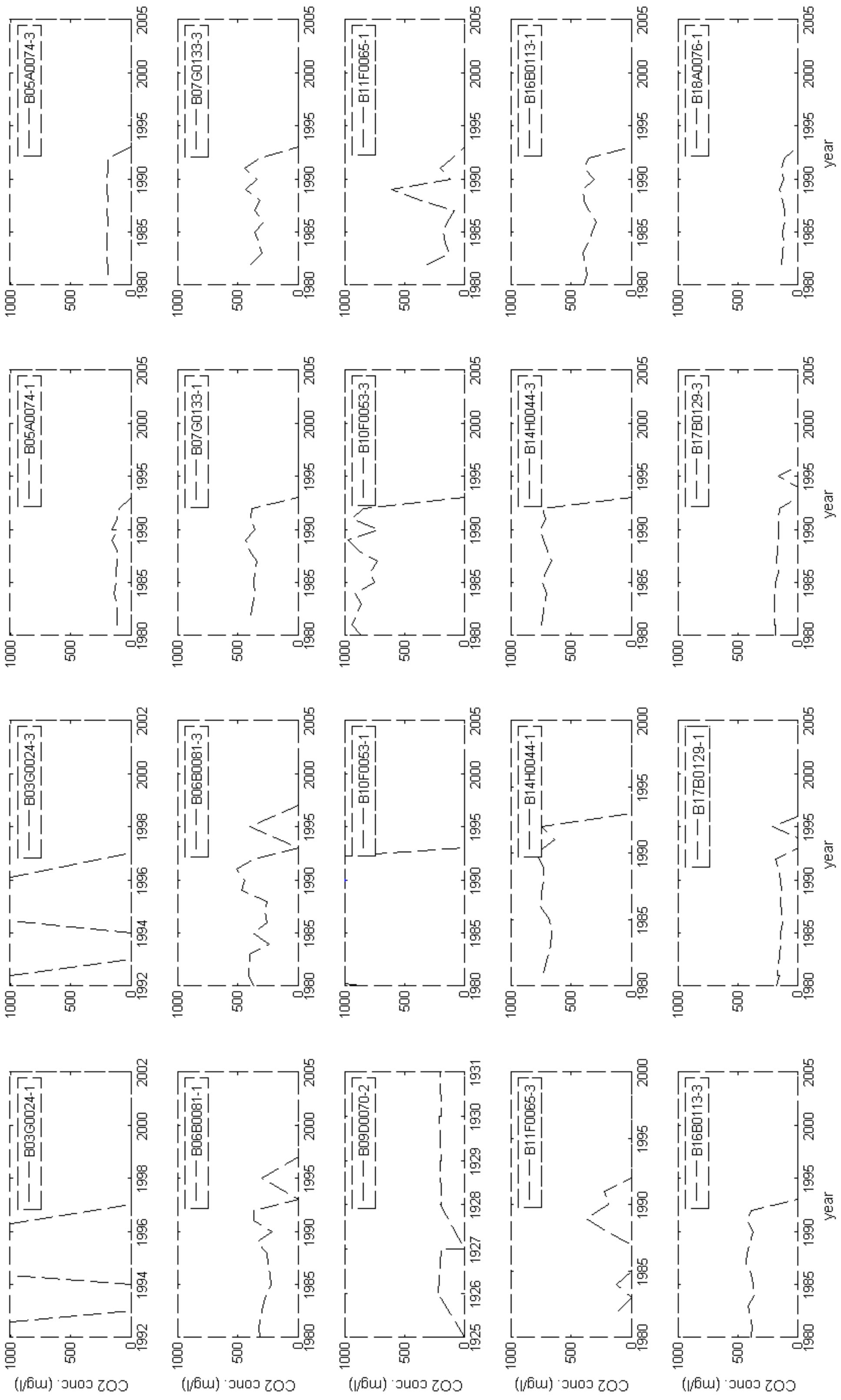
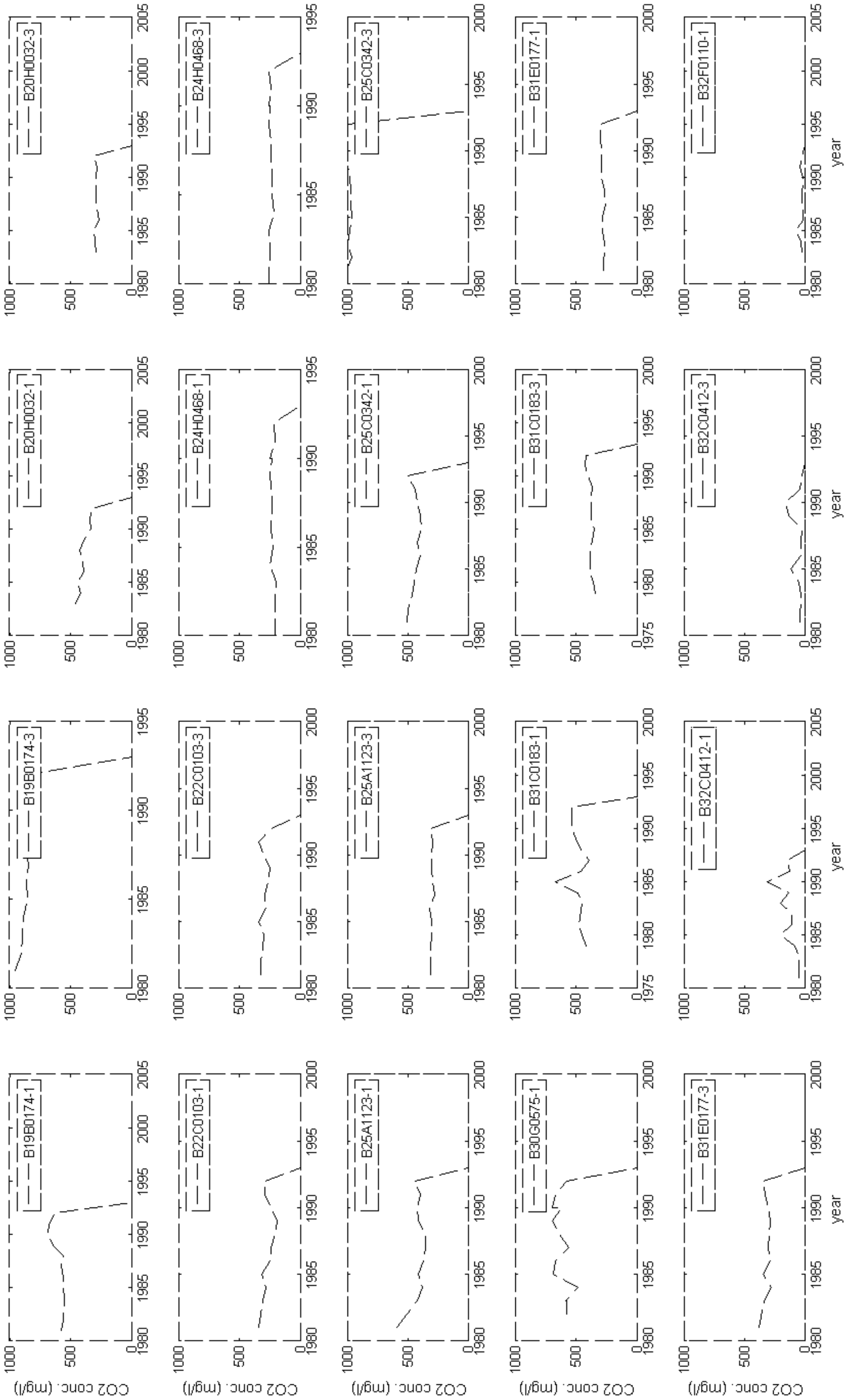
CO2 conc. (mg/l)
year
0
1000
2000
3000
1980
1985
1990
1995
2000
2005
1988
1992
1994
1996
1998

Annex IIIc Time series with CO$_2$ range on y-axes of 0-1000 mg/l.

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B31C0183-3
B32C0412-3
B19B0174-3
B22C0103-3
B25A1123-3
B31C0183-1
B32C0412-1
B19B0174-1
B22C0103-1
B25A1123-1
B30G0575-1
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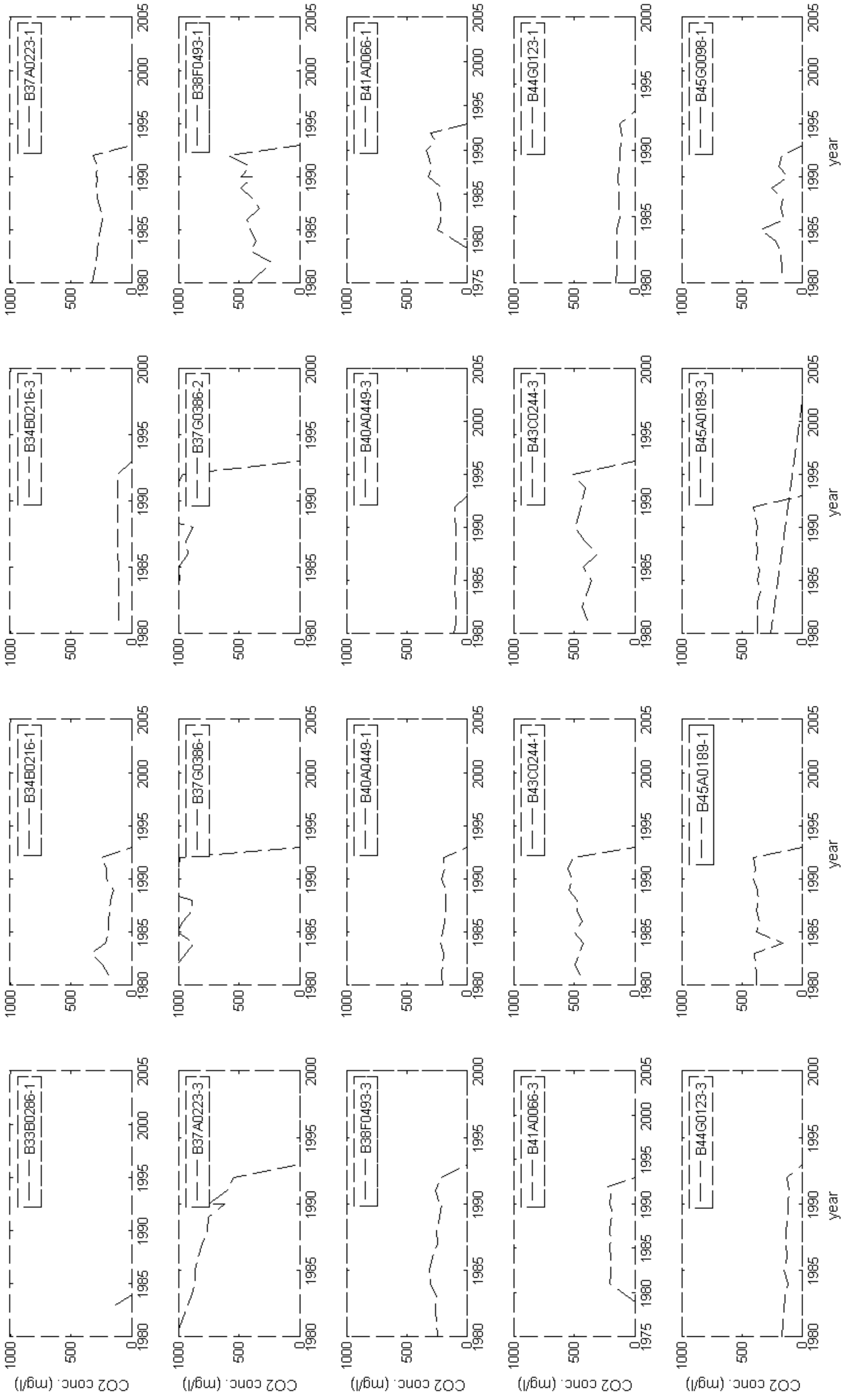
CO2 conc. (mg/l)
year
0
500
1000
1975
1980
1985
1990
1995
2000
2005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B43C0244-3
B45A0189-3
B34B0216-1
B37G0386-1
B40A0449-1
B43C0244-1
B45A0189-1
B33B0286-1
B37A0223-3
B38F0493-3
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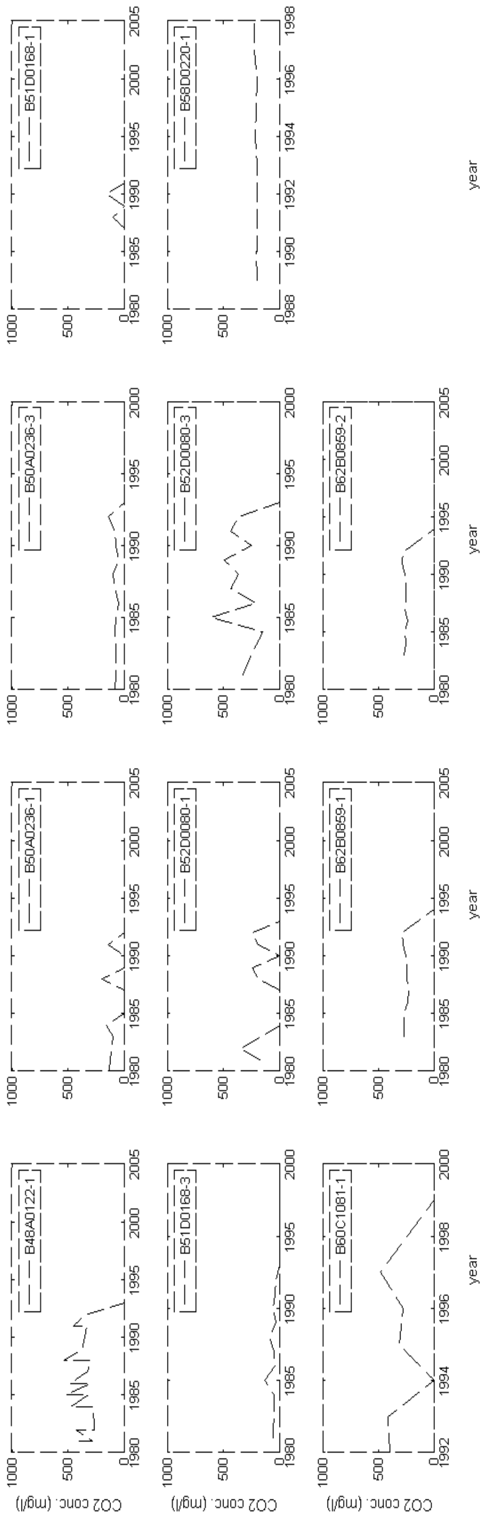
CO2 conc. (mg/l)
year
0
500
1000
1975
1980
1985
1990
1995
2000
2005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B52D0080-1
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B48A0122-1
B51D0168-3
B60C1081-1
CO2 conc. (mg/l)
year
1000
500
0
1980
1985
1990
1995
2000
2005
1988
1992
1994
1996
1998