

Potential Greenhouse Gas Release from Subsurface Desalination Feeds: Estimates of Gas Release Tonnages and Recommendations for Sampling and Monitoring

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OVERVIEW

Marine sediment pore waters commonly contain elevated concentrations of the greenhouse gases carbon dioxide and methane. These gases are generated mainly by microbial degradation of organic matter present in the sediment which results in partial pressures of carbon dioxide and methane that are 10 to 100 times or more higher than atmospheric values. In typical pore waters carbon dioxide is often present at concentrations of 0.1 to 1 kilograms per cubic meter of pore water. Methane concentrations are more variable but often in the range of .02 to 0.5 kilograms per cubic meter of pore water. Essentially all of this gas will be released if the fluid is brought to the surface and allowed to equilibrate with the atmosphere, such as will be the case if the water were used to feed a desalination plant. For typical desalination plants such as those planned for the California Coast, the Greenhouse Gas (GHG) release will be on the order of thousands to millions of tonnes per year and may in some cases be larger than the carbon footprint of the desalination plant. We estimate that a 50 MGD desalination plant would release a minimum of about 30,000 tonnes/y CO₂e with values of over 3,000,000 tonnes/y CO₂e possible for gas-rich feeds.

In this report we estimate the potential GHG release likely for typical pore waters that might be used to feed desalination plants using subsurface feed intakes. We show a methodology for using compositional data of fluids to estimate likely GHG emissions for desalination plants and then use it to look at some specific examples of GHG contents of subsurface fluids obtained from test wells drilled for potential desalination plants in California. We describe a recommended method of sampling gas contents of fluids obtained from wells, which is critical for obtaining realistic GHG release estimates. We then look briefly at the hydrology of slant wells and show that for several reasons they will tend to be fed by a large component of sedimentary pore water rather than ocean water. This would have the effects of lowering ground water heads inland from the intake wells, and also prolong the duration and amount of GHG emission.

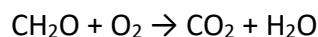
The overall goal of this report is to document the GHG issue for subsurface desalination feeds and provide a methodology for calculating potential GHG release from the feed composition.

Our hope is that the GHG emission tonnages can be readily and accurately assessed and factored into an informed decision as to the type and location of the optimum feed system for desalination plants in California.

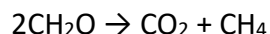
BACKGROUND

It is well known that subsurface waters found in soil zones and in underlying aquifers contain elevated concentrations of gases such as carbon dioxide and methane that are generated by microbial activity. Macpherson (2009) has estimated that the total release of carbon dioxide due to degassing of fluids brought to the surface in groundwater wells is about 0.1 GT (Gigatonnes) per year, comparable in size to the global volcanogenic release of carbon dioxide. She also notes that typical carbon dioxide partial pressures in the subsurface are often 10 to 100 times the atmospheric value and that there is a great degree of variability in gas content such that it is essentially impossible to predict the gas content without direct sampling.

Microbial reactions are responsible for most of the gas (Stumm and Morgan, 1979), although deeper sources may be contributing in some cases (Mörner and Etiope, 2002). The main microbial sources of CO₂ in groundwater are plant root respiration and oxidation of organic matter. Under relatively oxidizing conditions, organic matter is used by microbes to produce carbon dioxide through reactions simplified as:



where “CH₂O” represents organic matter. Under more reducing (anoxic) conditions methane forming reactions such as:



take place that form equal molar amounts of both carbon dioxide and methane. Near the oxic-anoxic boundary methanogenic microbes may generate methane in reactions such as:



In all cases, the total amount of carbon dioxide and methane that can be produced is limited by the amount of organic matter present in the rock or sediment. The distribution between carbon dioxide and methane, the two stable products, is determined by the oxidation state of the system. A system with access to air or oxygenated seawater will produce carbon dioxide,

and a system without much oxygen will produce more methane (Stumm and Morgan, 1998; Drever, 1998, p. 281).

Carbon dioxide contents of ground waters have been compiled by Macpherson (2009). She found that the average carbon dioxide content is about 30 times greater than atmospheric, with some carbon dioxide partial pressures approaching one bar. Note that these analyses are probably minimum concentrations, especially for the higher values, as explained below in the discussion of sampling error. In addition, Macpherson used terrestrial ground waters sampled from shallow wells. It is likely based on the higher organic content of fresh marine sediments that the carbon dioxide contents of coastal sediments, the targets for sea water desalination feeds from subsurface wells, will be higher. How much higher cannot be determined without compositional data from the sediments.

Methane concentrations in sediment pore waters have not been studied as extensively as carbon dioxide and no databases have been compiled that would allow statistical analysis of methane contents of pore waters. However, given the microbial origin of both gases it seems likely that methane would be present at the same sort of concentrations as carbon dioxide in anoxic sediments, and at lower concentrations in oxic environments.

It should be noted that methane seeps exist in the ocean floor, often at depths over 3 km, in particular in Monterey Bay. The depth of the location of the seep provides a lower limit on the methane content of the sediment pore water from which the methane originates. Depths of over 3 km are known (Stakes et al., 1999) and indicate methane partial pressures in the sediments at those depths must be over 300 bars (the pressure at 3 km depth). The seeps tend to be located along faults where gas can travel up to the sea floor and escape into the ocean. Where there are no faults, the gases are contained at depth, but would be released into any well that intersects them. Also of interest is the measurement of even higher concentrations of hydrogen sulfide. Hydrogen sulfide is another likely constituent of marine pore waters that might be present in fluids entering slant wells and would require treatment to avoid its toxicity and odor.

Because of the interplay between available oxygen, sediment permeability, organic content, and flow paths, the total gas content and methane to carbon dioxide ratio for any subsurface location is impossible to predict. It must be measured. The variability in gas content is also high and can change greatly in terms of both location and over time for systems that are being pumped (for example see data for CalAm wells in Appendix 1).

MEASUREMENT AND ANALYSIS OF GAS CONTENTS IN FLUIDS

A very simple way to estimate carbon dioxide contents and potential mass of release makes use of the measured pH, calcium concentration, and alkalinity of the fluid. These parameters are very commonly measured and in fact are needed for the design of membrane desalination plants. For this estimate, we assume that the alkalinity is equal to the total dissolved inorganic carbon in the fluid, usually a good assumption. The data can then be fed into a reaction path chemical modeling code such as PHREEQ-C, GWB, EQ3/6 or others and used to determine how much carbon dioxide would be released if the fluid were allowed to equilibrate with the atmosphere, as would be the case for the fluids discharged from the desalination plant. The thermodynamic model is needed in order to account for partitioning of carbon among all the major carbon species present, such as carbonic acid, bicarbonate ion, and carbonate complexes, as carbon dioxide leaves the solution. The calcium value is used to determine how much if any calcium carbonate would precipitate as the solution de-gasses carbon dioxide and the pH rises. The carbon that ends up as carbonate is not included in the amount of degassed carbon dioxide. This approach was used to estimate carbon dioxide release from the CalAm wells which is included at the end of this report in Appendix 1.

It is critical that the pH and alkalinity be measured on fresh samples that have not been allowed to degas. The EIR for the CalAm project provides pH values measured at the wellhead and then later in the laboratory. In all but one case, the pH measured in the laboratory is significantly higher than the well-head values, indicating release of (acidic) carbon dioxide over time. Most of these data show an increase in pH of 0.5 to 1.0 units. The higher the carbon dioxide content, the faster the sample will degas, and the greater the potential error in estimated carbon dioxide release. The error will always be to underestimate the amount of gas. *It is almost certain that a bias towards lower carbon dioxide partial pressures exists for most routine pH measurements of groundwaters found in technical reports, including the data compiled by Macpherson (2009).* Macpherson herself noted the likelihood of this bias in her paper. The sampling method is therefore critical for estimating true carbon dioxide release.

A more accurate estimate of carbon dioxide content can be obtained by taking a fluid sample and immediately adding caustic (NaOH) to raise the pH and stabilize all of the carbon as ionized species (bicarbonate and carbonate) that are not volatile. This prevents subsequent loss of carbon dioxide. Total carbon is then measured using an inorganic carbon analyzer. However, an accurate pH reading of a fresh non-degassed sample is still needed for the calculation to estimate carbon dioxide release during desalination.

The estimate for potential methane release is more straightforward than that for carbon dioxide because methane does not ionize and undergo acid-base reactions in water as does carbon dioxide. However, sampling and analysis of methane is more difficult due to its low solubility which makes loss of methane during sampling a potential problem. Methods for methane analysis in groundwater such as those recommended by the EPA (Kampbell and Vandergrift, 1998) call for sampling into serum bottles and the sample entered via hypodermic needle. In all cases, the sample needs to be collected before there is a reduction in pressure that would allow methane to escape. A standard method for analysis of methane from wells intended for use as desalination feed needs to be developed and used consistently in order to correctly estimate potential GHG emissions.

The source term for methane is easy to determine from the measured composition. It is essentially equal to the amount of methane in solution. The equilibrium methane content of the atmosphere is currently a little less than 2 ppm (parts per million) so equilibration with the atmosphere releases essentially all of the methane in the fluid sample to the atmosphere.

Both CO₂ and CH₄ are volatile and will have a tendency to escape from solution and not be accounted for in the analysis. Careless analytical procedures will therefore always result in a lower measured concentration of the gas relative to the actual gas concentration.

ESTIMATED GREENHOUSE GAS RELEASE FROM TYPICAL SUBSURFACE FLUIDS

By assuming some typical values for the concentration of carbon dioxide and methane in sediment pore waters, we can estimate the volume of released gas if the pore waters were brought to the surface. We assume values for total carbon of 10 and 50 mmolar in line with those reported by Macpherson, and also include a calculation for a 200 mmol samples which we believe is a reasonable value for gas-rich pore water from organic-rich sediments.

Similarly for methane we use a typical measured value of 0.1 mmolal as a lower limit and also calculate release tonnages for 1 and 25 mmolal which correspond to methane partial pressures respectively of 0.07, 0.7 and 18 bars pressure. Note that the methane sample from a Monterey Bay seep (Stakes et. al., 1999) known to have a partial pressure of 300 bars was reported to have a methane content of about 1 mmol, or methane partial pressure of about 0.7 bars, indicating that as with carbon dioxide measurements, values for methane contents are also biased towards lower values, in this case, much lower values.

If we use these gas contents as starting points and then calculate the mass of gas that would be released if the fluid were brought to the surface and allowed to equilibrate with the

atmosphere (which will happen if the fluid is used to feed desalination) we get the results shown in Table 1. These estimates were calculated using the GWB software and data file thermo.com.v8.R6 obtained from Lawrence Livermore Lab. The three fluid compositions are thought to represent the anticipated range of gas contents from low to high. The gas releases at the bottom of the table are expressed in terms of tonnes of GHG that would be released from a 50 MGD desalination plant (similar in size to the facility at Carlsbad CA) were it fed by these fluids. The methane release is converted to carbon dioxide equivalent using a factor of 25.

Table 1. Estimated release rates of GHG as CO₂-equivalent for a 50 MGD plant for range of hypothetical feed chemistries based on gas compositions in the observed range of marine sediments.

	Low	Medium	High
PCO ₂ (bars)	0.04	0.1	10
TOTAL CARBONATE (mmol)	10	50	200
Methane (mmol)	0.1	1	25
pH	7	6.5	6
g/m ³ CO ₂	126.7	1007.8	6183.4
g/m ³ CH ₄	16.0	48.1	802.1
FOR 50 MGD DESAL PLANT			
Tonnes CO ₂ /y for 50 MGD plant	21891	174061	1067927
Tonnes CH ₄ /y for 50 MGD plant	277	2771	69268
Tonnes CO ₂ e/y for 50 MGD plant	28,800	243,300	2,800,000

Assume desalination plant permeate recovery of 40%; methane equivalent factor of 25

The tonnages range from about 30,000 tonnes per year for a moderate gas content to nearly 3 million tonnes per year for the gas-rich feed. These GHG release levels lie well above proposed reporting limits and are of concern. We believe they warrant serious consideration in siting desalination intakes. Intakes that use as feed normal near-surface sea water will emit little or no GHG because they are at or near equilibrium with the atmosphere. However, it would be prudent to confirm this for any open intake proposed to feed a desalination plant.

HYDROLOGY OF SUBSURFACE FEEDS

Another potential problem for subsurface feeds has to do with the hydrology of sedimentary rock formations. It is well known, particularly for fresh sediments, that lateral permeability is usually much larger than vertical permeability (Freeze and Cherry, 1979). Fluids will tend to flow parallel to the formation rather than perpendicular to it. As explained below, this may

make it less likely that ocean water will flow vertically downward and into the well and instead will allow pore water from up-dip in the sedimentary layer to preferentially feed the well.

Sediment wedges near the ocean shore generally are made up of layers of sand, silt and clay with greater amounts of finer material (clay and silt) farther from shore. Over geologic time the shoreline migrates in and out with changes in sea level. Thus at any one point there exists a vertical sequence of sediments varying from coarse permeable sands to relatively impermeable clays and silts. If the feed well exists in a place where there are no impermeable (clay) layers between it and the overlying sea floor, sea water may be drawn into the well as is conventionally assumed (arrow '1' in Figure 1). However, there also exists a hydraulic gradient from on-shore that, because of height, will be greater than the hydraulic gradient between the well and the sea floor. This will tend to draw water from up-dip in the sedimentary layer (arrow labeled '2' in Figure 1). This would cause two effects: lowering of the water table seen in on-shore wells; and feed into the well of water drawn mainly from the sedimentary layer rather than from the ocean. The relative proportion of ocean water to sedimentary pore water will depend upon the hydrologic conditions, in particular the relative horizontal and vertical permeabilities. For the dashed well shown in Figure 1, it is likely that the majority of the water will be derived from the sedimentary pore waters and very little from the ocean. The sedimentary deposit at the potential well site needs to be very carefully characterized and have the right properties to allow subsurface intakes to draw mainly ocean water, as intended.

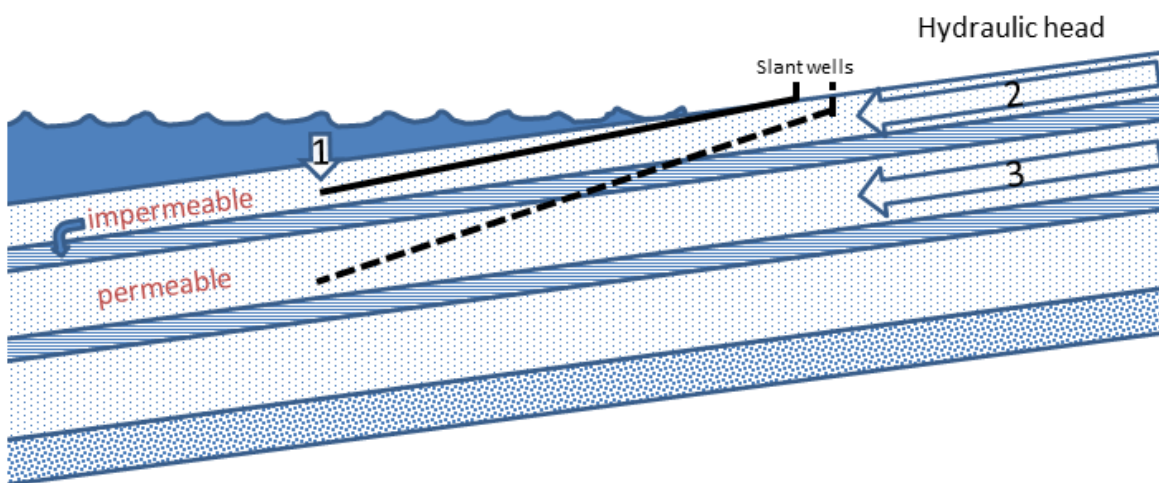


Figure 1. Schematic of hydrologic scenario for slant wells drilled into near-shore sediments. Black lines indicate possible locations of slant wells. Arrows indicate flow directions.

In addition to containing Greenhouse Gases, subsurface fluids that are derived from seawater will change in composition as they react and equilibrate with the minerals present in the sediment. Pore waters in general will have a pH one to two units lower than that of seawater,

will have elevated calcium and silica concentrations, and will have elevated trace metal contents due to input of sorbed metals from mineral surfaces in response to the lowering of pH. If this feed is used in desalination, there could be issues having to do with concentrate disposal back into the sea that are not present when using sea water as feed. For example, the elevated calcium and silica could lead to blooms of silica and carbonate secreting plankton at the area of the concentrate return site.

CONCLUSIONS

Based on current knowledge of gas contents of typical sedimentary pore waters, it appears likely that using subsurface intakes to feed coastal desalination plants will emit substantial volumes of greenhouse gases into the atmosphere. Our estimates for a 50 MGD desalination plant range from 30,000 to nearly 3 million tonnes of CO₂e/year. In addition, hydrologic characteristics of coastal sediments suggest it is also likely that the feed systems will contain substantial fractions of pore water - rather than sea water - with substantially different chemistry. This will need to be considered in evaluating brine disposal options as the concentrated pore fluids may affect ocean ecosystems in ways that would not be a problem for concentrated sea water.

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Appendix 1 – Estimated greenhouse gas contents and potential release tonnages for wells on the Central California Coast.

Some compositional data for potential desalination feed supplies are available for coastal wells drilled near Marina and Moss Landing areas of the Central California Coast. Compositional data for fluids sampled from these exploratory boreholes are contained in the draft EIR (Appendix C3, Tables 3A and 3B) for the CalAm project. These data allow for quantified estimates of GHG release from the fluids at the two well sites.

We used the compositional data from Appendix C3 Table 3 of the EIR to compute the partial pressure of carbon dioxide in each of the water samples, 31 samples total. The input data needed for this calculation are the fluid alkalinity, pH, calcium concentration and salinity, all of which are provided in Table 3. The potential carbon dioxide release is calculated assuming the feed water eventually equilibrates with the atmosphere, releasing the contained carbon dioxide. The Moss Landing samples have on average partial pressures of carbon dioxide that are 120 times higher than atmospheric values. This corresponds to a yearly release of carbon dioxide of about 5500 tons for a plant size providing the planned 9.6 MGD of permeate. For the Marina site the corresponding numbers are 50 for carbon dioxide partial pressure enrichment over atmospheric and 2200 tons/year carbon dioxide release, significantly lower than for the Moss Landing samples.

The calculated tonnages of released carbon dioxide are listed for each well in the Table below. The assumption in each case is that the 9.6 MGD plant would be fed entirely by a fluid with the composition of the particular well water sample indicated. The wide range of CO₂ release tonnages (for example, ranging from 1051 to 14877 tonnes per year for the Moss Landing wells) shows a great amount of variability of fluids being sampled in the subsurface. In addition, these compositions will almost certainly change over time as these highly variable water sources are pulled into the intake system.

These calculated release rates are conservative minimum values. They are based on an assumption that the measured field pH was obtained without any release of carbon dioxide. If the pH was not measured immediately after sampling, the pH would rise as carbon dioxide escapes. The higher the pressure of carbon dioxide, the more rapid the release of CO₂. There is no information on the sampling procedure that could be used to evaluate this issue. Any carbon dioxide loss that might have taken place prior to the pH measurement would not be accounted for in the estimated release tonnages and could be very significant. Our reported carbon dioxide emissions are therefore minimum values.

The fact that carbon dioxide is actively being degassed from these samples is strongly supported by the observation that in 30 of 31 cases, the pH measured at a later time,

presumably after transport of the sample back to the laboratory, was significantly higher than the field measured pH. This increase in pH over time is consistent with CO₂ loss and is commonly observed for many natural water samples. The observed pH increases were generally between 0.5 and one pH unit.

The estimates can only be made for carbon dioxide as data for methane was not reported. The methane flux has the potential to be more significant than that for carbon dioxide given its greater potency as a greenhouse gas.

These data show that greenhouse gas release is an issue that needs to be addressed for siting a desalination plant that uses subsurface wells to supply feed. Our estimated release tonnages based on waters sampled at the Moss Landing and Marina sites as representative of the feed are significant and likely to be above the reporting minimums for the California Air Resources Board. Our results also show a significant difference between the Moss Landing site and the Marina site, with significantly less carbon dioxide in fluids in the Marina wells. We believe this indicates that each site is different and that such differences are hard to predict. Proper sampling and measurements must be made for fluids at each site to determine the expected release of greenhouse gases.

A separate comment has to do with the chemical characteristics of the fluids. Few of the fluids reported in Tables 3A and 3B are as saline as sea water, indicating they are not sea water pulled into the wells during pumping. Their pH values are 1-2 units lower than ocean water and therefore have the potential for increased metal content (in particular from metal desorption from mineral surfaces). The fluids are also significantly enriched in silica with typical values of 30-40 mg/L versus values of 1-2 mg/L or less in typical ocean water. The concentrate will therefore be very silica-enriched relative to seawater which may affect the dynamics of silica-secreting microorganisms when the concentrate is returned to the ocean. The same is true for calcium in many of the wells where its concentration is much higher than is normal for seawater. And finally, several of the fluids have salinities less than 5000 ppm TDS (seawater is around 35,000), and one as low as 423 ppm (from well ML-1) which is probably potable water without treatment if no contaminants are found that are above their MCLs. These wells are not sampling seawater.

Based on this analysis, we conclude the following :

- Significant greenhouse gas release is likely for desalination feeds obtained from subsurface wells
- A procedure for sampling the fluids and carrying out the greenhouse gas analysis needs to be part of the permitting process.

- Chemical analysis of the fluids should include methane as well as other potential greenhouse gases
- The sampling should continue over time as the system evolves due to water withdrawal
- There may be issues associated with disposal of desalination brine into the ocean that arise due to compositional differences that are not present when the feed is taken directly from the ocean

Table. Calculated carbon dioxide release in metric tonnes per year based on fluid compositions from well samples listed in Appendix C3, Tables 3A and 3B, for a plant producing 9.6 million gallons per day of permeate at a permeate recovery of 40%.

CEMEX Marina site															
CX-B1WQ						CX-B2WQ				CX-B4					
1	2	3	4	5	6	1	2	3	4	1	2	3	4	5	
4542	2576	3279	1543	1893	1210	3037	2529	1344	1309	2582	2401	1827	1992	822	
average for Marina wells = 2200 tonnes/year															
Moss Landing Area															
PR-1		ML-1		ML-2		ML-3		ML-4		MK-6		MDW-1			
1	2	1	2	1	2	1	2	1	2	1	2	1	2	3	4
3825	2967	6075	5143	14877	4054	3021	3295	9555	5048	12395	9445	2328	2990	2458	1051
average for Moss Landing wells = 5500 tonnes/year															

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