Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 00 (2008) 000–000

Energy Procedia

www.elsevier.com/locate/XXX

GHGT-9

Identification of thermodynamic controls defining the concentrations of hazardous elements in potable ground waters and the potential impact of increasing carbon dioxide partial pressure

John A. Apps*, Yingqi Zhang, Liange Zheng, Tianfu Xu, Jens T. Birkholzer

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California

Elsevier use only: Received date here; revised date here; accepted date here

Abstract

Concern has been expressed that carbon dioxide leaking from deep storage reservoirs could adversely impact water quality in overlying potable aquifers by mobilizing hazardous elements present in the aquifer rocks to the extent that their concentrations might exceed Maximum Contaminant Levels (MCLs). To evaluate this issue, 38,000 ground water quality analyses from aquifers throughout the United States, each containing one or more analyses for As, Ba, Cd, Hg, Pb, Sb, Se, U or Zn, were retrieved from the Unites States National Water Information System (NWIS). The analyses were used to calculate the saturation indices (SIs) of all identified and thermodynamically characterized minerals containing the listed elements as essential components. These minerals were initially selected through literature surveys to establish whether field evidence supported their postulated presence in potable water aquifers. SI frequency histograms were plotted to evaluate whether these minerals are at saturation in NWIS ground waters (i.e., they show modes at SI ≈ 0). Mineral assemblages meeting the criterion of thermodynamic saturation were assumed to control the aqueous concentrations of the hazardous elements at initial system state as well as at elevated CO_2 partial pressure caused by the ingress of leaking CO_2. The impact on the identified mineral solubilities of increasing CO_2 partial pressures was then predicted over the range from –4 to +1 (i.e., $10^{-4} \leq P(CO_2)$ in bar ≤ 10). Under reducing conditions (characteristic of most ground waters), the most serious problem resulting from intrusion of CO_2 into shallow groundwater may arise through enhanced dissolution of pyrite and solubilization of arsenic. At the highest $P(CO_2)$ assumed in our study, Ba, Pb and Zn may also approach or exceed regulatory concentration limits. Of the remaining elements, the MCLs of Cd, and Sb are unlikely to be exceeded, and Hg, Se and U concentrations are unaffected by CO_2 intrusion.
© 2008 Elsevier Ltd. All rights reserved

Keywords: CO_2 Sequestration; Groundwater; Contamination; Hazardous Elements

1. Introduction

Proper site selection and management of underground CO_2 storage projects will ensure that the risks to human health and the environment are low. However, a risk remains that CO_2 could migrate from a deep storage formation towards the surface. If CO_2 migrates into a freshwater aquifer and dissolves into the aqueous phase, the total

* Corresponding author. Tel.: +1-510-486-5193; fax: +1-510-486-5686.
E-mail address: JAApps@lbl.gov.

concentration of dissolved carbonate increases and causes a decrease in pH. The higher acidity of the water enhances the solubility of many minerals, some of which may contain so-called hazardous inorganic chemicals, identified by U.S. Environmental Protection Agency (EPA) to be of particular concern, and governed by regulatory maximum contaminant levels (MCLs) in drinking water. The geochemical consequences of CO_2 migration into current and future potable groundwater resources requires further evaluation to establish their potential vulnerability in the case of large-scale deployment of carbon capture and underground storage. A research project under EPA sponsorship was initiated in 2006 at the Berkeley Laboratory to address these issues. A specific objective of the project was to investigate the water quality changes in response to CO_2 intrusion through development of a comprehensive geochemical model that describes the complete chemistry of a range of specified shallow aquifer systems. Of particular concern is the behavior of the EPA-identified hazardous inorganic chemicals [1]. For this study, a subset of these chemicals, i.e., the elements As, Ba, Cd, Hg, Pb, Sb, Se, U, and Zn, was selected for inclusion in the geochemical model. Zn is not considered hazardous, but a maximum safe drinking water standard has been specified [1].

The steps taken in developing the geochemical model included (1) a survey to determine the distribution of the selected hazardous element concentrations in more than 38,000 groundwater quality analyses from potable water aquifers throughout the United States, (2) a comprehensive review of the literature in order to identify mineral hosts that might control the concentrations of the selected hazardous elements in groundwaters, (3) development of an extensive thermodynamic database for participating minerals, aqueous species, adsorbed and ion exchange species, with particular attention to the selected hazardous elements, (4) a rigorous geochemical evaluation of more than 38,000 groundwater quality analyses from potable water aquifers throughout the United States to help identify which minerals hosting hazardous elements might be saturating the groundwater, (5) application of the geochemical model to predict the variation in saturation concentration of the hazardous elements as a function of the partial pressure of carbon dioxide in a typical aquifer, (6) evaluation of the natural abundances of hazardous elements in sedimentary formations hosting potable water in order to estimate the expected concentrations of minerals hosting hazardous elements, and (7) a survey of the sedimentology and hydrology of the principal potable water aquifers throughout the United States to estimate the framework and matrix mineralogy of aquifer host rocks. In this paper we briefly discuss the first five steps involved in the development of the model with emphasis on steps (4) and (5). The remaining steps and their application to a comprehensive series of reactive transport simulations describing the impact of CO_2 intrusion in shallow potable water aquifers are discussed in a companion paper [2]. A report prepared for the U.S. EPA [3] documents the rationale and development of the geochemical model in considerable detail, and includes its application to reactive chemical transport modeling summarized in [2].

2. Model Development

2.1. Concentrations of Hazardous Elements in Potable Groundwater

Over 38,000 chemical analyses of potable waters drawn from wells in the United States were downloaded from the National Water Information (NWIS) Database, and searched for chemical analyses of As, Ba, Cd, Hg, Pb, Sb, Se, U and Zn. Each population was divided into uniform bins, representing incremental concentration ranges on a logarithmic scale, and plotted as histograms. Selected histograms As, Ba, Cd, and Pb are given in Figures 1(a)–(d). The distributions are for the most part fairly irregular, due primarily to two artifacts. One arises from the application of analytical methods with differing sensitivities. The NWIS Database has been compiled over a number of years, during which time newer, more accurate analytical methods have supplanted earlier methods. The lack of sensitivity of the earlier analytical methods leads to the reporting of inaccurately high values, which increase progressively in number as the detection limit for that method is approached. This artifact is particularly evident in the distributions of Cd and Pb. The second is due to analytical concentrations being approximated to round numbers. For example, bins reporting concentrations of 0.001, 0.002 or 0.005 mg/L are disproportionately populated. The corresponding MCLs for each element are also plotted on each figure. Most of the selected groundwaters meet regulatory requirements, although MCLs may be exceeded in some cases resulting from the use of insufficiently sensitive analytical methods.

2.2. Mineralogical Studies

A critical step in the development of a comprehensive geochemical model is the correct identification of minerals that could thermodynamically control the concentrations of hazardous elements in groundwaters. Unfortunately, it is generally infeasible to search for and identify those minerals through direct examination of aquifer mineralogy, because their mass fractions in the aquifer host rocks are very low (on the order of 10^{-4} - 10^{-6} or less), and few studies have been conducted that have unequivocally confirmed the presence of their mineral hosts, particularly in potable water aquifers. Direct identification of their presence and spatial distribution is only possible with rarely undertaken high-resolution imaging techniques or other complex methodologies. Therefore, in this study, we indirectly identify and postulate the presence of solubility-controlling phases in the aquifer rocks through a comparative review of published scientific investigations. This was done not only with respect to trace element mineralogy in sedimentary rocks, but also using the extensive literature on coal mineralogy, studies concerning ore deposits and ore mineralogy, studies relating to natural and anthropogenically induced pollution through weathering, and authigenic and diagenetic processes affecting recent sediments. The most plausible candidate minerals identified through this review are summarized in Table 1. Details regarding the review are given in Birkholzer et al. (2008). These minerals are expected to occur under mainly reducing conditions, i.e., where the redox potential is most likely controlled by a pyrite/goethite or related buffer. Several other minerals likely to occur under more oxidizing conditions were also identified, but are not listed here for brevity. Those minerals listed in bold face were found by subsequent thermodynamic analysis (Section 2.4) to be the most plausible minerals controlling hazardous element concentrations.

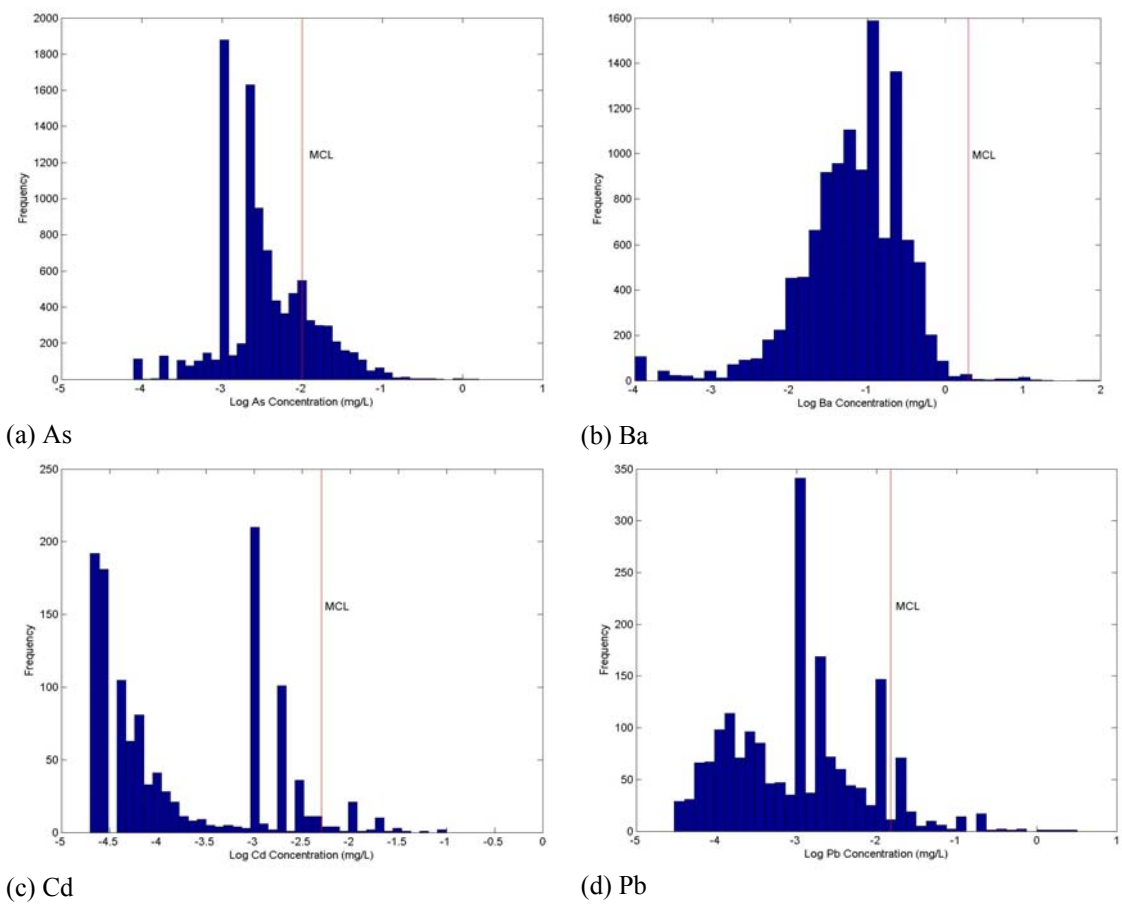

Figure 1. Histograms showing the concentration distributions of selected hazardous elements in more than 38,000 analyses of potable groundwaters in the United States. MCL signifies the maximum contaminant level for each element.

Table 1. Potential mineral hosts for hazardous elements under reducing conditions

Hazardous Element	Potential Mineral Controls	
	Solid Solution Component	Discrete Mineral
As	(FeAsS)py	Arsenopyrite (FeAsS)
Ba	-	**Barite ($BaSO_4$)**; Witherite ($BaCO_3$); Alstonite ($CaBa(CO_3)_2$); [Crandallite ($(Ca,Ba)Al_3(PO_4)_2(OH)_5$)]
Cd	(CdS)sp	Greenockite (CdS); **Cadmoselite (CdSe)**
Hg	(HgS)py	**Cinnabar (HgS); Tiemannite (HgSe)**; Native Mercury
Pb	-	**Galena (PbS); Clausthalite (PbSe)**
Sb	(FeSbS)py	Stibnite (Sb_2S_3); **Kermesite (Sb_2S_2O)**; Antimonselite (Sb_2Se_3); Gudmundite (FeSbS)
Se	(FeSe2)py	Ferroselite ($FeSe_2$); [Dzharkenite (FeSe2)]; Antimonselite (Sb_2Se_3); **Cadmoselite (CdSe); Clausthalite (PbSe); Tiemannite (HgSe)**
U	-	**Uraninite (UO_2); Coffinite ($USiO_4$)** [Brannerite (UTi_2O_6)]
Zn	-	**Sphalerite (ZnS); Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot (H2O)$)**

Note: py = pyrite, sp = sphalerite
Minerals listed in bold face are the most plausible minerals controlling hazardous element concentrations.

2.3 Modification and Augmentation of the Thermodynamic Data Supporting the EQ3/6 Code

The distribution-of-species code, EQ3/6 V.7.2b [4], used in this study for thermodynamic analyses, contains a database, Data0.dat, listing solubility products and dissociation constants for minerals and aqueous species. The original version of this database was not suited for the demanding requirements of the current study. We therefore reviewed and, where necessary, revised, reconciled and augmented the database, using the SUPCRT code [5] to calculate the required solubility products or dissociation constants from experimentally determined thermochemical data recently reported in the literature. One of the most important aspects relating to database modification was the realization that the intrinsic solubilities of sulfides of Cd, Fe, Hg, Pb, and Zn are governed by the presence of ill-characterized oligomeric neutral sulfide complexes in solution, and that these must be accounted for in order to reconcile solubility measurements for these sulfides with the corresponding experimentally determined enthalpies of formation. Furthermore, it was also recognized that similar oligomeric selenide neutral complexes of these same elements must be present in solution, which in some cases contribute significantly to enhanced concentrations of the corresponding metals. Dissociation constants of the relevant sulfide and selenide complexes were compiled or estimated from published mineral solubility data using appropriate thermodynamic correspondence plots [3]. The EQ3/6 code with the revised database was then used in evaluating potable groundwater quality analyses to find out whether the hazardous-element mineral hosts identified in the previous section might be controlling their concentrations in groundwaters. This procedure and results are described below.

2.3. Evaluation of Potable Groundwaters

In order to identify whether certain mineral hosts might be saturated with respect to the selected hazardous elements, the saturation state has to be calculated. The saturation state is related to the Gibbs free energy, ΔG_r, associated with the dissolution of the mineral, thus

$$\Delta G_r = RT \ln\left(\frac{IAP}{K}\right) \qquad (1)$$

where R is the gas constant, T is the absolute temperature, IAP is the Ion Activity Product of the dissolution reaction, K is the corresponding equilibrium constant. The saturation state, Ω is given by:

$$\Omega = \left(\frac{IAP}{K} \right) \tag{2}$$

and we follow the usual convention of defining the saturation index, SI, as:

$$SI = \log \Omega \tag{3}$$

Using EQ3, we calculated the SIs of the mineral host identified in the Section 2.2 with respect to over 38,000 water-quality analyses extracted from the NWIS Database. The procedure involves entry of complete chemical analysis of each groundwater in the EQ3 input file. EQ3 was then executed, and the SIs of each potential mineral host were extracted and compiled, for each succeeding chemical analysis. The resulting SI distributions for each mineral were subdivided into uniform SI increments, and the populations in each increment plotted in the form of frequency histograms, as illustrated in Figure 2 for the elements As, Ba, Cd and Pb and their potential solubility-controlling mineral hosts.

The SI histogram for arsenopyrite (Figure 2a) shows the mode at SI ~ -3.5, suggesting that As activity is controlled primarily by arsenopyrite in solid solution in pyrite (arsenian pyrite). The SI histogram for barite (Figure 2b) shows a mode close to zero suggesting that many of the sampled groundwaters are close to saturation with respect to this mineral. The corresponding histogram for witherite (not shown) gives a modal SI at –2, indicating that this mineral rarely, if ever controls saturation of Ba in potable groundwaters. The CdS (greenockite) SI histogram (Figure 2c) displays a trimodal distribution with SI maxima at ~ -3, -0.5, and +1. This complex distribution is partly caused by the bi-modal distribution of analyzed Cd concentrations (Figure 1c), and partly due to the absence of Se analyses in most groundwater samples, which forms selenide complexes with Cd^{+2}. The mode at SI ~ -3 therefore probably represents the true saturation state in most groundwaters with respect to CdS, suggesting a solid solution in sphalerite and/or galena. The SI histogram for cadmoselite in Figure 2d is relatively well defined, with SI mode at ~ 0, suggesting that Cd^{+2} activity may actually be controlled by the presence of cadmoselite. SI histograms for galena and clausthalite are presented in Figures 2e and 2f. The histogram for galena displays a ragged peak with a mode at about SI ~ +1.0. The corresponding mode for clausthalite is at SI ~ -0.5. Both analyses support the belief that galena, or clausthalite, or both could control the Pb^{+2} activity in potable groundwaters. The SI histogram for cerussite (not shown) indicates that this mineral does not control Pb activity in most groundwaters under reducing conditions. However, a small percentage of ~ 5% of potable groundwaters could be saturated with respect to this mineral, especially under conditions more oxidizing than those defined by the pyrite/goethite buffer. Similar evaluations were also conducted with respect to mineral hosts containing Hg, Sb, Se, U, and Zn. Those minerals appearing to be saturated in solution and potentially controlling the concentrations of these elements in groundwaters are noted in bold in Table 1.

3. Prediction of Hazardous Element Concentrations as a Function of the Partial Pressure of CO_2

In order to evaluate the impact of CO_2 intrusion into potable groundwater, the equilibrium concentrations of each hazardous element as a function of the partial pressure of CO_2 were calculated using EQ3. A typical groundwater composition was assumed. The redox state was defined by the assumed equilibrium between pyrite and goethite at a given pH. The groundwater was also assumed to be saturated with respect to calcite, opal-CT, a low Fe-Mg smectite and the most probable hazardous-element mineral hosts identified in the preceding sections. The solubility products of the mineral hosts were adjusted to ensure consistency with the modal hazardous element concentrations in NWIS waters. These adjustments were within the aggregate uncertainties of the overall analysis. The logarithm of the partial pressure of CO_2 (in bar) was then imposed as a further equilibrium constraint, varied incrementally between -4 and +1, the maximum range expected in shallow aquifers with hydrostatic pressure of up to 100 m.

The results of the calculations are given in Figure 3 for those elements that are sensitive to variations in $P(CO_2)$. Hg, Se and U concentrations do not vary with $P(CO_2)$ and are not shown. The aqueous species of all three elements are dominated, respectively, by neutral sulfide and selenide complexes (Hg, Se) and by $UO_2(aq)$ (U), whose concentrations are independent of pH or $P(CO_2)$. Included in each figure are the respective MCLs, the detection limits for the most sensitive analytical method routinely used, and an error bar indicating the mean concentration together with the observed or estimated natural variability of each element concentration. The error bar is derived assuming an approximate log-normal distribution at ±2 standard deviations at log $P(CO_2)$ = -2, which is slightly

higher than the approximate modal value for all evaluated NWIS groundwaters. The grey envelopes surrounding the predicted trendlines define the estimated cumulative uncertainties in predicted concentrations at ±1 standard deviation caused by uncertainties in geochemical model assumptions, thermodynamic parameters, analytical values, as well as by natural variability in groundwaters.

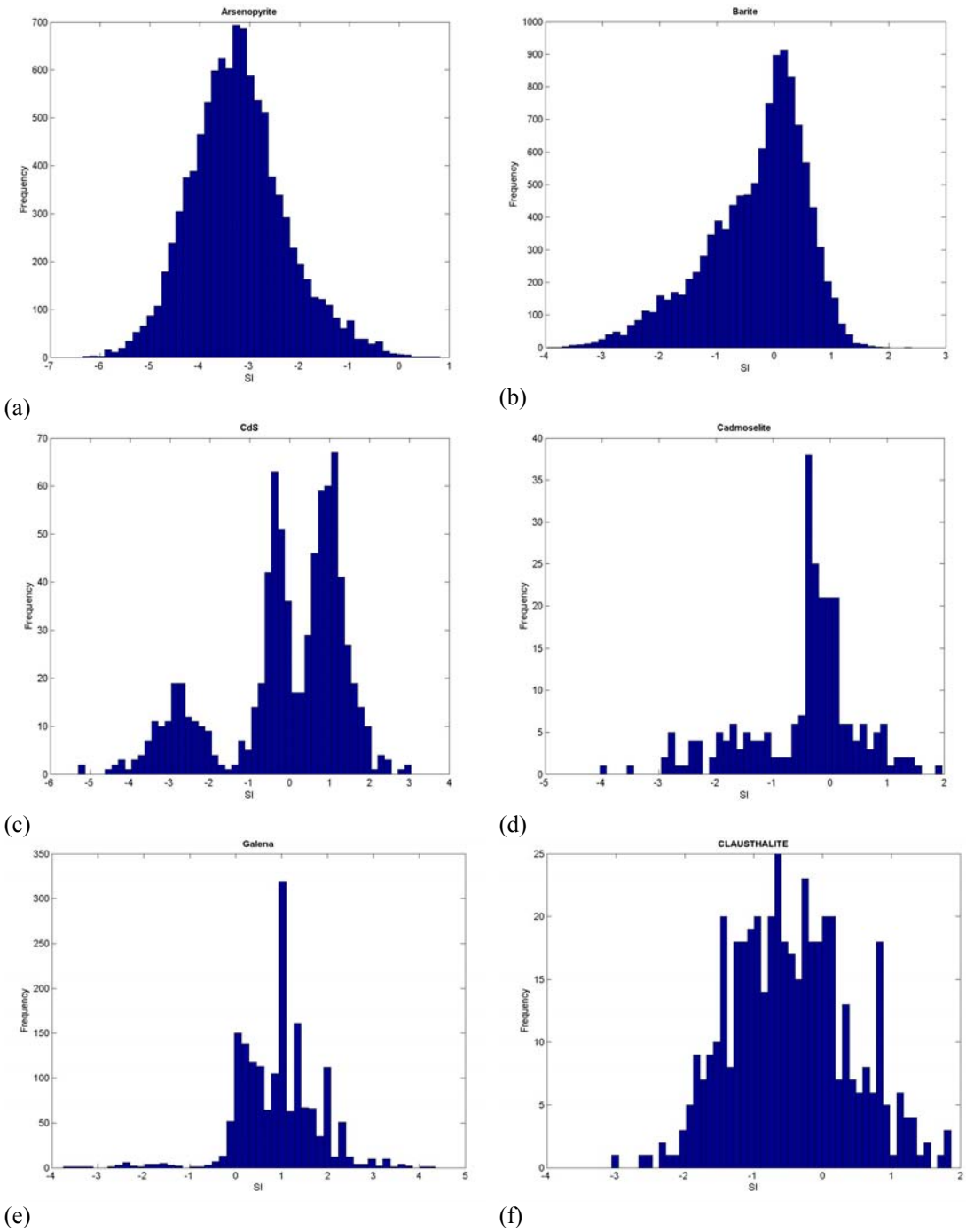

Figure 2. Frequency Distribution of Saturation Indices of (a) Arsenopyrite, (b) Barite, (c) Greenockite, (d) Cadmoselite, (e) Galena, and (f) Clausthalite. The Saturation Indices are calculated using a selected set of groundwaters from the NWIS, and assuming Eh to be defined by the coexistence of pyrite and goethite.

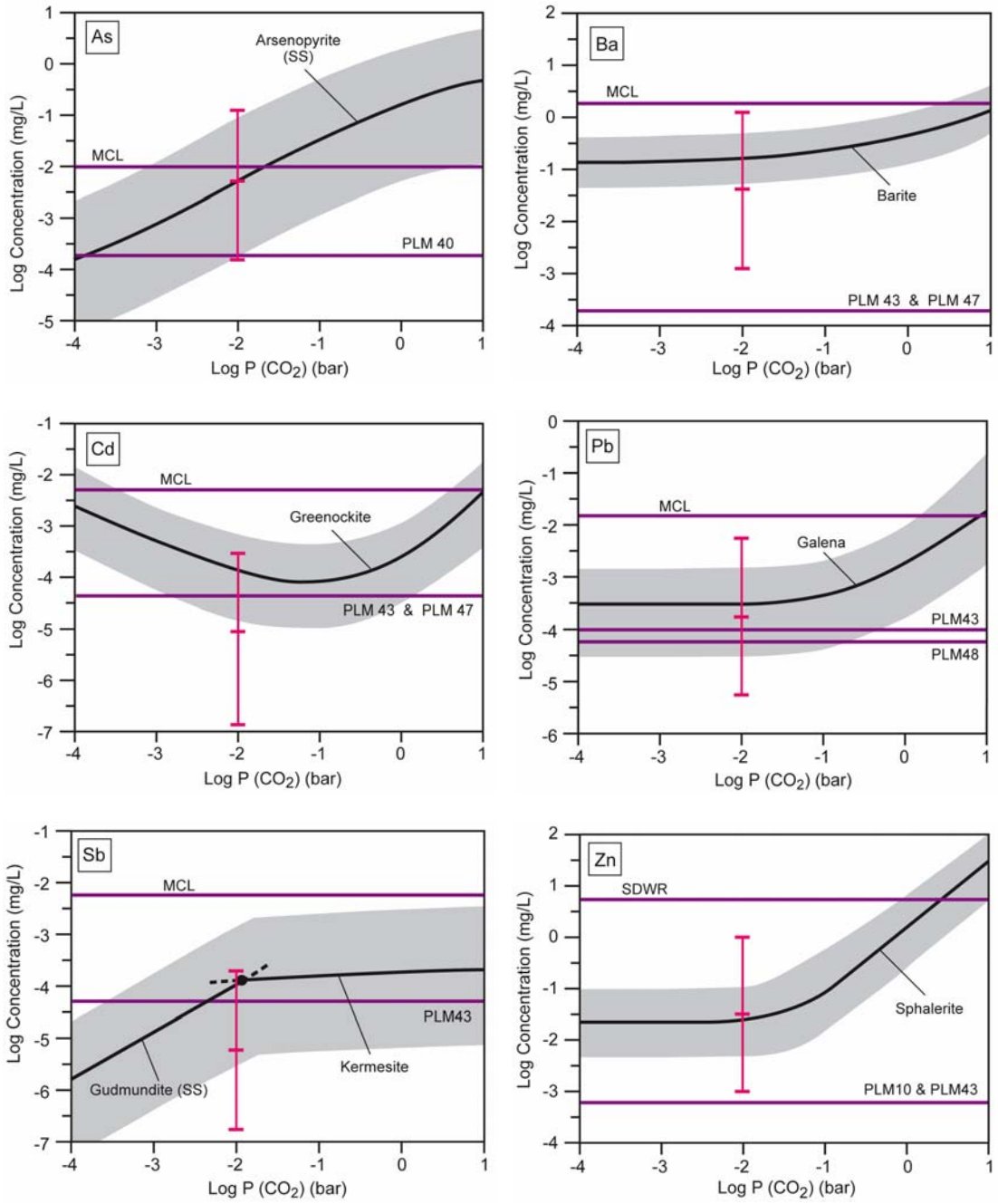

Figure 3. Variation of trace metal concentrations in equilibrium with host minerals as a function of CO_2 partial pressure. (SS) refers to solid solution. PLM10, PLM43 and PLM47 and PLM48 are ICP-MS analytical methods cited in the NWIS database. MCL signifies the maximum contaminant level for each element. SDWR stands for secondary drinking water regulation.

Figure 3 indicates that the most serious problem at elevated levels of CO_2 in groundwaters may arise through enhanced dissolution of pyrite and solubilization of arsenic. At high levels of $P(CO_2)$, Ba, Pb and Zn may approach or exceed regulatory concentration limits. Of the remaining elements, the calibrated concentrations of Cd, Hg (not illustrated) and Sb are somewhat higher than are believed to occur naturally, but analytical methods are insufficiently sensitive for accurate quantification. None are expected to exceed MCLs with increasing $P(CO_2)$.

4. Conclusions

The thermodynamic analysis of potable groundwaters permits the identification of host minerals controlling the concentrations of hazardous elements in potable groundwaters and allows prediction of concentration changes caused by intrusion of CO_2. The most serious problem resulting from such intrusion may be the enhanced dissolution of pyrite with consequent solubilization of arsenic, with a high probability that the MCL would be exceeded. At plausible levels of $P(CO_2)$, representative of maximum possible values in shallow groundwaters, Ba, Pb and Zn may approach or exceed regulatory concentration limits. For those elements, however, model uncertainties, kinetic factors, and post-withdrawal water treatment methods all suggest diligence rather than alarm. Of the remaining elements, the calculated concentrations of Cd, Hg and Sb are somewhat higher than are believed to occur naturally, because analytical methods appear to be insufficiently sensitive. Hg, Se and U concentrations are unaffected by CO_2 intrusion.

Acknowledgements

We thank the U.S. Environmental Protection Agency, Office of Water and Office of Air and Radiation, for funding this study under an Interagency Agreement with the U.S. Department of Energy at the Lawrence Berkeley National Laboratory, under contract number DE-AC02-05CH11231. We also gratefully acknowledge the assistance provided by Jonathon C. Scott, U.S. Geological Survey, Oklahoma City, Oklahoma, in extracting and supplying over 38,000 groundwaters from the NWIS database.

References

1. U.S. Environmental Protection Agency, 2004 Edition of the Drinking Water Standards and Health Advisories, EPA 822-R-04-005, January 2004 (2004).
2. Zheng, L., J.A. Apps, Y. Zhang, T. Xu, J.T. Birkholzer. Reactive Transport Simulations to Study Groundwater Quality Changes in Response to CO_2 Leakage from Deep Geological Storage, Proceedings GHGT-9, Physics Procedia (2008), this issue.
3. Birkholzer, J.T., J.A. Apps, L. Zheng, Y. Zhang, T. Xu, and C.-F. Tsang. Research Project on CO_2 Geological Storage and Groundwater Resources: Water Quality Effects Caused by CO_2 Intrusion into Shallow Groundwater, Lawrence Berkeley National Laboratory Technical Report (2008), 450 p.
4. Wolery, T.J. EQ3/6, A software package for geochemical modelling of aqueous systems (Version 7.2), Lawrence Livermore Nat. Lab. UCRL-MA 110662, (1993).
5. Johnson, J.W., E.H. Oelkers, and H.C. Helgeson. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000 degrees C, *Computers and Geosciences, 18* (1992), 899–947.