

PROVTECT-IRM®

Solid, Antimethanogenic Reagent for ISCR and Heavy Metal Stabilization

Provect-IRM® (US patents 7,129,388; 7,531,709; 7,828,974; 8,147,694; 9,221,699; 9,637,731; patents pending) employs our proven ISCR technology to facilitate adsorption and precipitation reactions for heavy metal immobilization. It is composed of multiple reagents in a single product, potentially including:

- ◆ Multiple, hydrophilic, nutrient rich organic carbon sources (plant materials, kelp, calcium propionate) → 390 g H /lb product.
- ◆ Specifically selected Zero Valent Iron (ZVI) of various size and geometry
- ◆ Chemical oxygen scavengers to help maintain reduced conditions during mixing
- ◆ Integrated vitamins, minerals mineral sources (yeast extracts) specially selected for the growth and development of anaerobes
- ◆ Potassium magnesium sulfate to help promote formation of iron-sulfide mineral complexes, where needed; and/or
- ◆ Powdered activated carbon (PAC) to help sequester organo-metal complexes



Critically, Provect-IRM uniquely combines antimethanogenic reagents (AMR technology) such as a source of Monacolin K and other natural statins or essential plant oils to manage the growth and proliferation of Archaea (*i.e.*, methanogens). This reduces the biosynthesis of highly toxic, mobile methylated (organo) metals, which can have very negative consequences since methylated metals are often more mobile and more toxic than their inorganic counterparts. As such, targeted metal species (*e.g.*, arsenic, chromium, mercury, etc) are quickly sequestered for safe, long-term, stable immobilization.

POTENTIAL ADVANTAGES OF USING PROVTECT-IRM® ANTIMETHANOGENIC ISCR TECHNOLOGY

The distinctive combination of reagents promotes ISCR conditions for fast and effective destruction of targeted COIs while managing the production of methane during the requisite carbon fermentation processes. This promotes more efficient use of the hydrogen donor while avoiding negative issues associated with elevated methane in groundwater, soil gas and indoor air (induced vapor migration, plume expansion, other potential health & safety issues).

- ◆ **More Efficient:** Increased efficiency is the main benefit. Hydrogen yield calculations have shown that by minimizing waste of hydrogen by controlling excessive methanogenesis one can elicit the same response by using ca. 30% less organic amendment. Since it takes less time and resource to inject less amendment this can significantly lower overall project cost.
- ◆ **More Effective:** ISCR reactions avoid accumulation of dead-end catabolic intermediates as a function of substrate addition (as is common with [emulsified] oils and sources of carbon only).
 - Does not rely on physical sorption/sequestration as a major “removal” mechanism (as is common with oils).
 - Inherently buffered for pH control – will not acidify an aquifer and liberate heavy metals as potential secondary COIs.
- ◆ **Safer:** Fewer health and safety concerns as compared with use of traditional ERD or ISCR reagents; Avoid issues associated with new and emerging methane regulations.
- ◆ **Ease of Use:** Green and sustainable. All components integrated in a single package. Logistics with no surprises. Provect-IR is easily and quickly injected using conventional construction technologies.
- ◆ **Longevity:** Engineered profile of carbon sources for multi-year longevity estimated at 3 to 7 years based on site-specific hydrogeology; ZVI reactivity can persist >10 years.
- ◆ **Minimizes Rebound:** Reagent will stay in place and remain active for an extended period of time which manages and prevents COI rebound.
- ◆ **Predictable Performance:** More efficient use of hydrogen donors (does not get wasted as methane).
- ◆ **Simultaneous Immobilization of Heavy Metals:** Will not mobilize or methylate arsenic or other heavy metals yielding secondary plumes (as is common with [emulsified] oils and sources of carbon only). Can be formulated to manage environments that are co-impacted by various inorganic contaminants (e.g., As, [Hg], Ni, Pb, Zn) while simultaneously mineralizing the organic compounds.
- ◆ **Inherent Buffering:** Presence of ZVI offers substantial pH buffering capacity
- ◆ **Range of Applicability:** ISCR demonstrated effective on a wide range of COIs, including chlorinated / halogenated solvents, Freon, pesticides, perchlorate and other energetic compounds (explosives).
- ◆ **Supports Natural Attenuation:** For all the reasons summarized above, Provect-IR enhances natural biological processes.
- ◆ **Patented Technology:** Fully covered under numerous patents (7,129,388; 7,531,709; 7,828,974; 8,147,694; 9,221,669; 9,637,731; multiple patents pending) that indemnify you and your client from patent infringement.

HEAVY METAL CONTAMINANTS

Trace metals constitute a significant class of groundwater contaminants originating from mining effluents, industrial wastewater, landfill leachate, agricultural wastes and fertilizers, and fossil fuels. They are very common class of contaminant, but the remedial strategies and technologies are often limited. Based on the chemical properties of dissolved species trace metals can be divided into two distinctive groups: i) reducible metals and metalloids, which are present in natural waters as anions and oxyanions (e.g.; Cr, As, Se, Mo, U), and ii) metal cations, which occur in aqueous environment as divalent cations (e.g.; Cu, Zn, Cd, Pb, Hg, Ni). Depending on their aqueous form (**Appendix A**), the mobility of trace metals in groundwater is affected by various chemical reactions, including dissolution-precipitation, oxidation-reduction, adsorption-desorption and complexation (Domenico, 1998; Drever, 1997).

WHAT IS THE PROBLEM WITH METHANE PRODUCTION DURING ISCR REACTIONS?

As a result of microbial fermentation process, methane will be produced in most situations following the addition of any conventional ERD or ISCR amendment. There are recognized benefits to methanogens and of limited methanogenesis. For example, i) methanogens are known to play important roles in synergistic microbial ecology, ii) their metabolic activity can help maintain anoxic conditions in treatment zones (through seasonal changes), and iii) the activity of methane mono-oxygenases and other enzymes can stimulate co-metabolic activity of TCE/DCE/VC in redox-recovery zones. Hence, limited production of methane is part of a healthy ERD/ISCR application. However, excessive methane production can be dangerous and represents a costly waste of amendment.

- **Cost and Efficiency Issues:** Production of methane is a direct indication that hydrogen generated from the electron donor amendments was used by methanogens instead of the target microbes (e.g., *Dehalococcoides spp.*), substantially reducing application efficiency. For example, generating just 20 mg/L of methane can represent greater than 33% of the total amendment consumption based on moles of H₂ (Mueller *et al*, 2014).
- **Potential Health and Safety Issues:** Methane is considered to be a major greenhouse gas. It is explosive, with an LEL of 5% and an UEL of 15%. Excessive and extended production of methane can result in elevated in groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air. While this is perhaps more relevant in urban settings where methane can accumulate in basements, under slabs/foundations and/or migrate along utility corridors, excessive methane production has also been observed in more rural settings and other open spaces.
- **New and Emerging Regulatory Issues:** State specific regulations for methane in groundwater have been promulgated, with others pending for soil gas and indoor air. For

example, current regulations for methane in groundwater vary from ca. 10 to 28 mg CH₄/L (Indiana Department of Environmental Management, 2014). As a result, many remedial practitioners proactively design contingencies for conventional ERD/ISCR implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater. These contingencies often entail expensive and extensive systems for treating methane in soil gas/vapor captured via SVE systems.

SPECIFICALLY - HOW DOES METHANE PRODUCTION IMPACT HEAVY METAL IMMOBILIZATION?

With the possible exception of lead (Pb) almost all Group IV, V and VI elements can be biomethylated (Bentley and Chasteen, 2002). As such a wide variety of methylated metalloids and metals can be found in the environment. These methylmetal(loids) are usually volatile and, with few exceptions, they are more toxic than their inorganic counterparts due to increased water solubility and hydrophobicity. For example, methylmercury is one of the most potent toxins known to man. And the biosynthesis of organo-arsenic (**Figure 1**) is a common problem making it often difficult to meet remedial action objectives of <10 ppb dissolved arsenic.

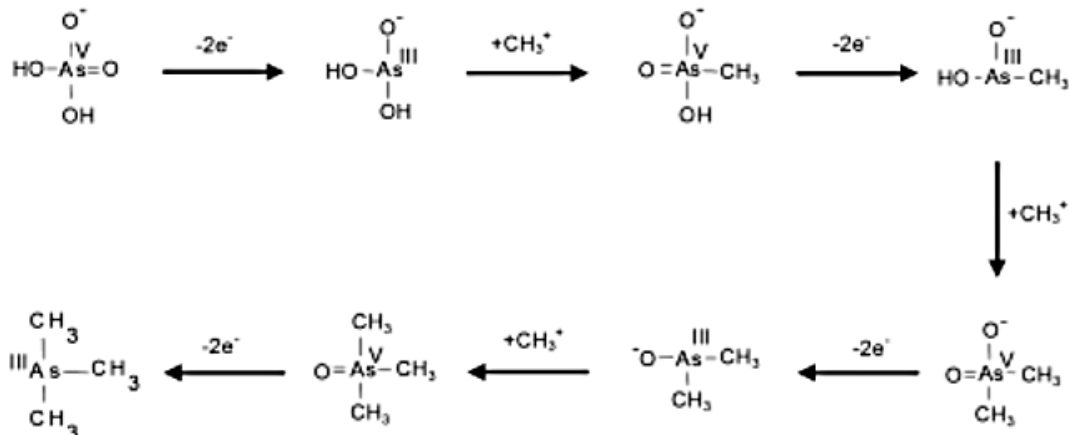
It is long understood that microorganisms are primarily responsible for the biosynthesis of organo-metals (Challenger, 1945), and the activity of methanogens is a main source of their production. As summarized in **Table 1**, a large number of methanogens have been shown to methylate a variety of metals (Michalke, *et al.*, 2006). By using Provect-IRM to induce ISCR conditions, the number and activity of methanogens are limited hence the targeted metal contaminants are more able to participate in the desired stabilization reactions. Moreover, the overall toxicity of the site is not increased via the generation of methylmetal(loids) as a consequence of the treatment process (see **Figure 1** example – biomethylation of arsenate).

TABLE 1. Volatile Methylmetal(loids) produced by Growing Cultures of Methanogens (Archaea)

	Metal/metalloid					Reference
	As	Bi	Se	Te	Sb	
<i>Methanobacterium formicicum</i>	AsH ₃ , CH ₃ AsH ₂ , (CH ₃) ₂ AsH, (CH ₃) ₃ As, X	BiH ₃ , CH ₃ BiH ₂ , (CH ₃) ₂ BiH, (CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ Se ₂	(CH ₃) ₂ Te	SbH ₃ , CH ₃ SbH ₂ , (CH ₃) ₂ SbH, (CH ₃) ₃ Sb	Michalke et al., 2000
<i>Methanobrevibacter smithii</i>	CH ₃ AsH ₂ , (CH ₃) ₂ AsH, (CH ₃) ₃ As	CH ₃ BiH ₂ , (CH ₃) ₂ BiH, (CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ SeS, (CH ₃) ₂ Se ₂ , X	(CH ₃) ₂ Te	(CH ₃) ₃ Sb	This Study
<i>Methanococcus vanielli</i>	CH ₃ AsH ₂ , (CH ₃) ₂ AsH, (CH ₃) ₃ As, X	CH ₃ BiH ₂ , (CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ SeS	(CH ₃) ₂ Te	(CH ₃) ₃ Sb	This Study
<i>Methanolacinia paynteri</i>	n.d.	(CH ₃) ₂ BiH, (CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ SeS, (CH ₃) ₂ Se ₂ , X	(CH ₃) ₂ Te	(CH ₃) ₃ Sb	This Study
<i>Methanobolus tindarius</i>	n.d.	(CH ₃) ₃ Bi	(CH ₃) ₂ Se, X	(CH ₃) ₂ Te	CH ₃ SbH ₂ , (CH ₃) ₃ Sb	This Study
<i>Methanoplanus limicola</i>	(CH ₃) ₃ As	(CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ SeS, (CH ₃) ₂ Se ₂ , X	(CH ₃) ₂ Te, X	(CH ₃) ₃ Sb	This Study
<i>Methanosarcina barkeri</i>	AsH ₃ , X	(CH ₃) ₃ Bi*	(CH ₃) ₂ Se, (CH ₃) ₂ Se ₂	n.d.	(CH ₃) ₃ Sb	Michalke et al., 2000
<i>Methanosarcina mazei</i>	(CH ₃) ₃ As	(CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ Se ₂	(CH ₃) ₂ Te	(CH ₃) ₃ Sb	This Study
<i>Methanospaera stadmanae</i>	(CH ₃) ₂ AsH, (CH ₃) ₃ As	CH ₃ BiH ₂ , (CH ₃) ₂ BiH, (CH ₃) ₃ Bi	(CH ₃) ₂ Se, (CH ₃) ₂ SeS, (CH ₃) ₂ Se ₂ , X	(CH ₃) ₂ Te	(CH ₃) ₃ Sb	This Study
<i>Methanothermobacter thermautotrophicus</i>	AsH ₃	n.d.	n.d.	n.d.	(CH ₃) ₃ Sb	Michalke et al., 2000

X, unidentified volatile metal(loids); n.d., not detected; *mediated by addition of octamethylcyclotetrasiloxane and the ionophores lasalocid and monensin.

Figure 1. Challenger mechanisms for biosynthesis of Arsenate (Challenger, 1945)



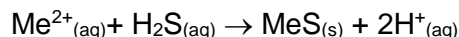
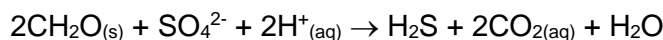
MODE OF ACTION – HOW DOES IT WORK?

By using [Provect-IRM](#) to induce ISCR conditions while simultaneously inhibiting biomethylation of heavy metals by methanogens, the established reaction mechanisms for immobilization of various heavy metals under ISCR conditions will be more effectively undertaken (**Table 2**). Moreover, the overall toxicity of the site is not increased via the generation of methylmetal(oids) as a consequence of the treatment process.

Table 2. Overview of Heavy Metal Immobilization Reactions induced by Provect-IRM ISCR Treatment

DISSOLVED METAL	STABILIZATION / IMMOBILIZATION MECHANISMS	REFERENCE
As (III, V)	Reductive precipitation with oxidized iron minerals. Precipitation as As sulfide and mixed Fe-As sulfide.	<i>Blowes et al., 2000; Manning et al., 2002; Craw et al., 2003</i>
Cr(VI), Mo(VI), Se(IV,VI), U(VI)	Reductive precipitation with oxidized iron minerals adsorption to iron oxides.	<i>Blowes et al., 2000, 8</i>
Me ²⁺ (Cu, Zn, Pb, Cd, Ni)	Organic carbon source stimulates heterotrophic microbial sulfate reduction to sulfide and metal cations precipitate as sulfides. Also strong adsorption to iron corrosion products (e.g. iron oxides and oxyhydroxides).	<i>Blowes et al., 2000; Dzombak and Morel, 1990</i>
Hg ²⁺	Mercury is commonly converted by microorganisms to monomethyl mercury (CH ₃ Hg) and dimethyl mercury [(CH ₃) ₂ Hg]. If not organically complexed, mercury can reductively precipitate as mercury sulfide. Also strong adsorption to iron corrosion products (e.g.; iron oxides and oxyhydroxides).	<i>Blowes et al., 2000; Dzombak and Morel, 1990</i>

For example, metal cations such as Cu, Zn, Hg, Pb, Cd, and Ni will precipitate as metal sulfides following microbial mediated reduction of sulfate present in the groundwater. The internal source of sulfate in **Provect-IRM** formulations for such environments enables metal immobilization in groundwater depleted in dissolved sulfate. The biodegradation carbon stimulates sulfate-reducing bacteria and the process can be represented by the following equations:



Where CH₂O represents organic carbon and Me²⁺ represents a divalent metal cation. Another important mechanism for metal cation removal in the presence of corroding ZVI is the adsorption onto iron corrosion products, like iron oxyhydroxides.

PHYSICAL PROPERTIES:

- Particle Size: ranges from ca. <5 to 100 micron (can be manufactured to specifications).
- Dry Density: ranges from 0.35 to 0.45 g/cm³
- 29% Aqueous Slurry Density: ranges from 0.8 to 1.0 g/cm³
- 29% Aqueous Slurry Viscosity: ranges from 400 to 1,300 cP

SLURRY PREPARATION GUIDELINES:

Provect-IRM can be used to create permeable reactive barriers (PRB) for plume control, plume treatment, or source area mass reduction. Installation methods include direct injection, hydraulic fracturing, pneumatic fracturing, soil mixing, and direct emplacement in trenches and excavations. The materials are as dry powders in 50-lb bags or 2,000 lb supersacs and mixed with water on site into a slurry. Typical application rates range from 0.25 to 1% (soil mass basis).

Percent Solids Content	Mass of Provect-IR	Volume of Water (US gallons)
10%	25 lb	27
20%	25 lb	12
30%	25 lb	7

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APPENDIX A: Aqueous Forms of Metals under Varying pH and Eh Potentials.

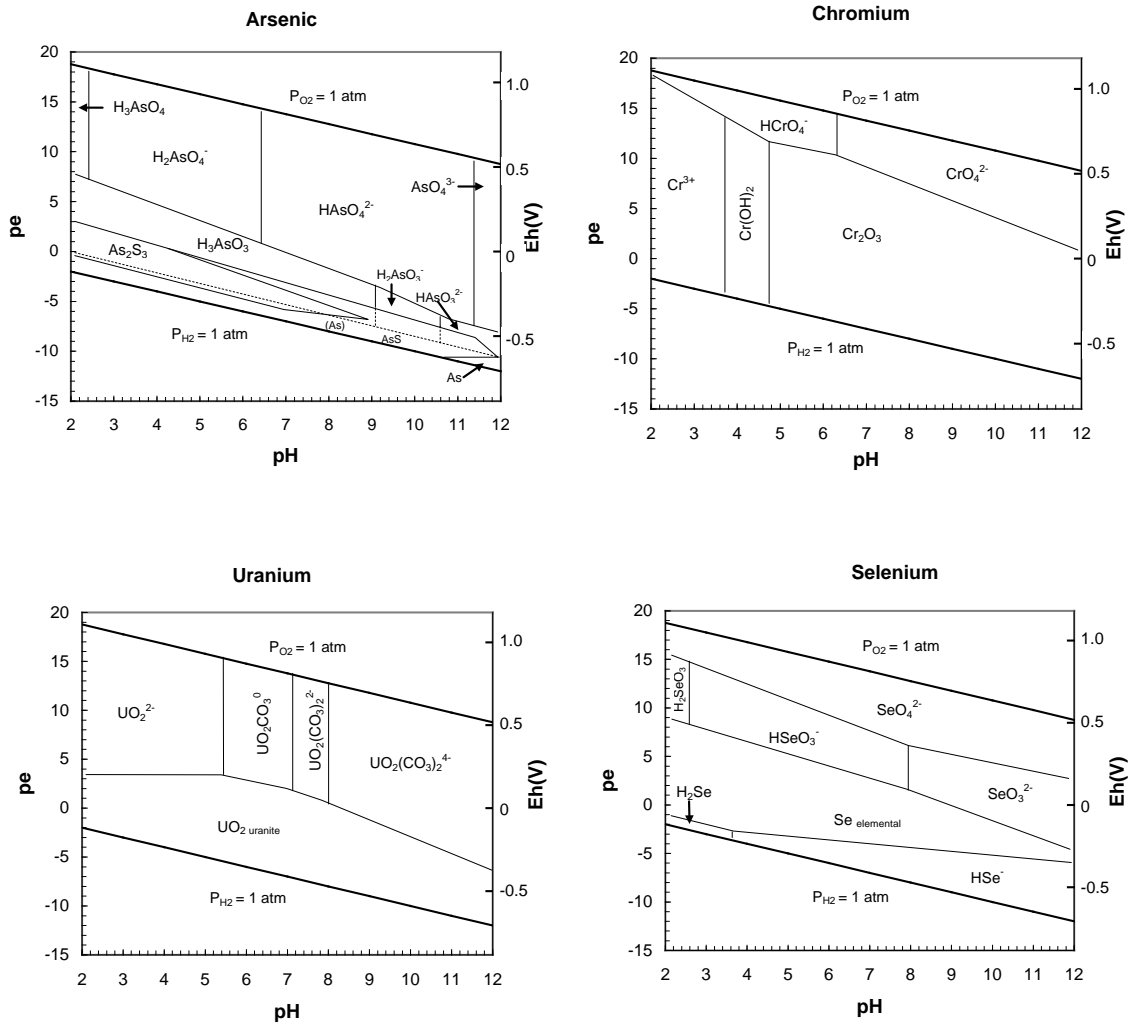


Figure 1. Simplified Eh-pH diagrams for metals that occur as anions and oxyanions in an aquifer. Solid lines are solubilities in the presence of sulfur: dashed lines are solubilities of carbonates in the absence of sulfur species.

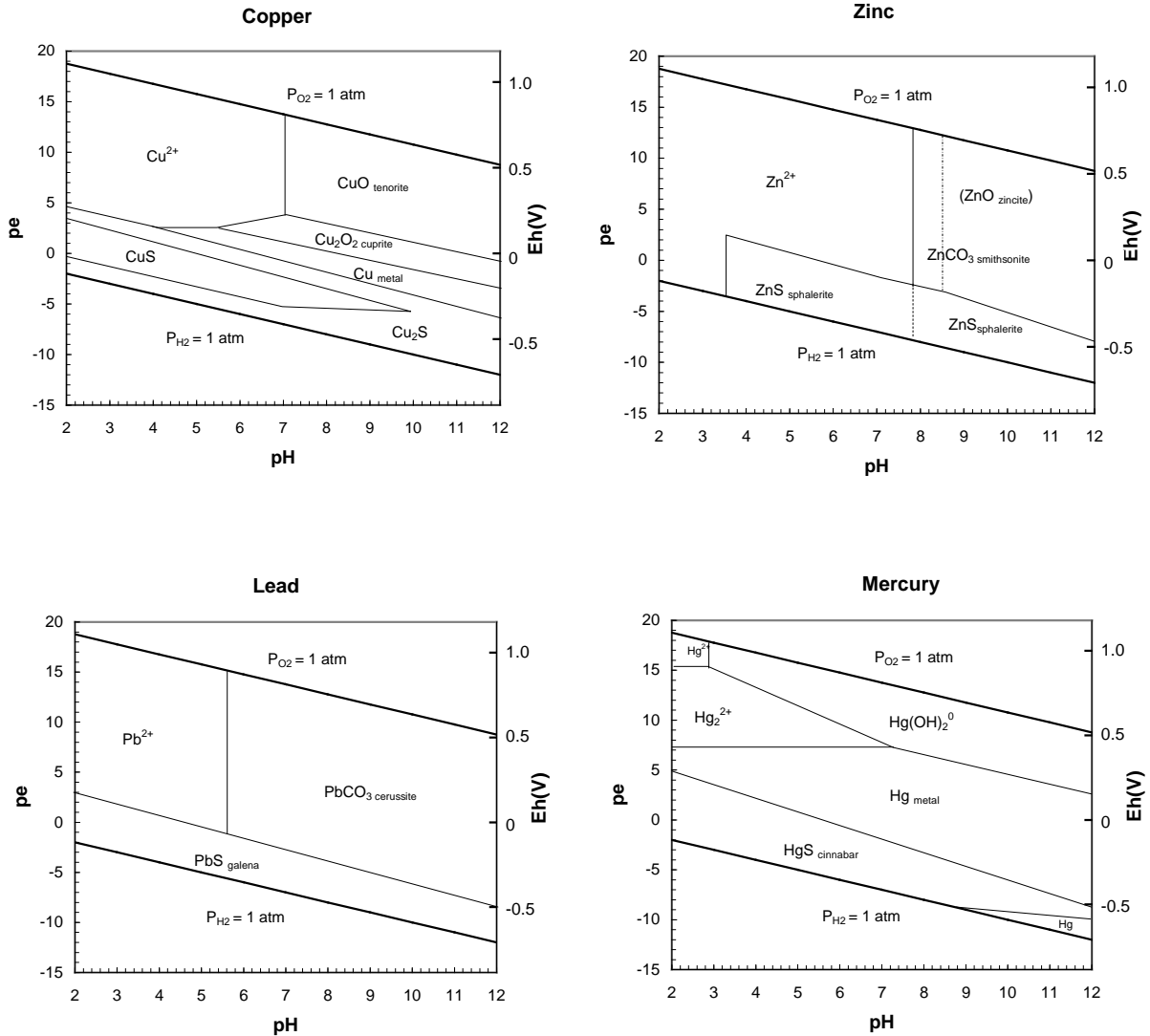


Figure 1 continued. Simplified Eh-pH diagrams for metals that occur as divalent cations in an aquifer. Solid lines are solubilities in the presence of sulfur: dashed lines are solubilities of carbonates in the absence of sulfur species.