



## Speciation of Mercury (II) and Methylmercury in Cloud and Fog Water

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### ABSTRACT

The fate of oxidized mercury (Hg) in clouds and fogs is affected by the complexation of oxidized Hg(II) with other chemical species present in cloud and fog water. Metal complexation often influences the types of reactions available to a metal in an aqueous system. The influence of pH, major inorganic ions, and organic acids on the complexation of Hg(II) and methylmercury (MeHg) was examined for a range of cloud and fog water compositions. Fog water was collected in the San Joaquin Valley, CA and rain water was collected at Devil's Lake State Park, WI to provide additional measurements of the chemical conditions of atmospheric media. A thermodynamic model was used to determine the speciation of Hg(II) and methylmercury (MeHg) over a range of atmospherically-relevant cloud and fog compositions. The speciation of Hg(II) in cloud and fog water was highly dependent on pH. For conditions found in most clouds and fogs, the chloride ion was the most important major ion controlling Hg(II) complexation, even under conditions of relatively low chloride content. However,  $\text{Hg}(\text{OH})_{2(\text{aq})}$  and  $\text{HgClOH}_{(\text{aq})}$  were found to dominate over  $\text{HgCl}_2$  in locations with high pH due emissions of agricultural ammonia; i.e. San Joaquin and Sacramento Valleys, CA. At concentrations relevant to typical cloud and fog waters, carboxylic acids (e.g. formate and acetate) did not play a significant role in Hg(II) speciation. Methyl mercury was speciated as  $\text{MeHgCl}$  in most locations, except for the locations with high pH, where  $\text{MeHgOH}$  dominated. These results provide constraints over potential reaction pathways that may transform oxidized Hg(II) in clouds and fogs.

**Keywords:** Mercury; Methylmercury; Atmosphere; Rain; Complexation.

### INTRODUCTION

Mercury (Hg) in the environment is a concern to human health due to its conversion to methylmercury (MeHg), a neurotoxin, and the subsequent bioaccumulation of MeHg in fish consumed by humans (Bloom, 1992; Westcott and Kalff, 1996; NRC 2000). Elemental mercury ( $\text{Hg}^0$ ) can exist in the vapor phase and undergo long-range transport (Lindqvist and Rodhe, 1985; Lin and Pehkonen, 1999a).  $\text{Hg}^0$  is not very soluble in water, but once in the atmosphere  $\text{Hg}^0$  can be oxidized to Hg(II), which is more reactive and more soluble in water (Vandal *et al.*, 1991; Amyot *et al.*, 1994; Pleijel and Munthe, 1995; Schroeder and Munthe, 1998; Hedgecock and Pirrone, 2001; Lalonde *et al.*, 2004). Hg(II) can enter the aquatic ecosystem either by wet or dry

deposition, and then be available for reaction (Lindberg and Stratton, 1998; Schroeder and Munthe, 1998; Lin and Pehkonen, 1999a; Lalonde *et al.*, 2002). The focus of this work will be on the speciation of Hg(II) in atmospheric waters and not on the transformation of  $\text{Hg}^0$  to Hg(II), which has been studied extensively (Lin and Pehkonen, 1998; Lin and Pehkonen, 1999b; Gårdfeldt *et al.*, 2001; Sommar *et al.*, 2001; Lalonde *et al.*, 2002; Lalonde *et al.*, 2004).

Understanding the chemistry of cloud and fog water is critical in determining the fate and transport of mercury in the atmosphere; since metal complexation can determine what reactions a metal may undergo (Stumm and Morgan, 1996; Benjamin, 2002). Hg(II) readily coordinates with a variety of ligands and undergoes ligand-exchange. Other reactions of Hg(II) may include reduction back to  $\text{Hg}^0$  or for the mercury to become associated with particulate matter (Amyot *et al.*, 1994; Lamborg *et al.*, 1999). MeHg has been measured in atmospheric deposition, but questions remain regarding whether it is formed in-situ, or transferred from other compartments (Sellers *et al.*, 1996;

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Rolfhus *et al.*, 2003; Hall *et al.*, 2005).

The chemical composition of atmospheric water varies greatly according to the natural and anthropogenic influences of the regions (Collett *et al.*, 1989; Khwaja *et al.*, 1995; Collett *et al.*, 2002; Löflund *et al.*, 2002). The chemical composition of the fog and cloud water will determine the speciation of Hg(II) and MeHg, and dictate what chemical pathways are available for further reaction. Reactions of greatest concern are those that convert Hg(II) to MeHg. One such proposed reaction pathway involves a Hg(II) acetate complex (Gårdfeldt, 2003). It is not known whether this or other reaction mechanisms are viable for the conversion of Hg(II) to MeHg in the atmosphere.

In order to test the likelihood of in-situ methylmercury formation in atmospheric waters, and to assess the relative importance of the wider array of potential chemical reactions of Hg that may occur in cloud and fog water, there is a need to determine the speciation of Hg(II) under a range of atmospheric conditions. This has been done by using a thermodynamic equilibrium model to determine the speciation of Hg(II) in fog and cloud waters. A literature review of fog and cloud water compositions provided case studies of different areas of the United States, and one location in Austria. Typical Hg(II) and methylmercury concentrations in atmospheric waters were retrieved from the literature, and combined with measurements made at Devil's Lake State Park, WI and Fresno, CA during this study. The goals of the speciation modeling were: i) to calculate the dominant speciation of Hg(II) at each location; ii) if, and how, the dominant species differed between locations; and, iii) whether methylmercury formation was likely based on the relative concentration of the Hg(II)-carboxylate complexes.

## METHODS

### *Cloud and Fog Water Hg Speciation Model*

To model the behavior of Hg(II) in fog and cloud water, a literature survey was conducted to collect data on cloud and fog water composition. Bulk ionic compositions were retrieved for eight regions in the United States and one site in Austria (Fig. 1; Collett *et al.*, 1989; Khwaja *et al.*, 1995; Collett *et al.*, 2002; Löflund *et al.*, 2002). The regions were intended to be representative of the various regional chemical compositions in the published literature, based on natural and anthropogenic influences such as proximity to the ocean, urban pollution, and specific industrial influences. The San Joaquin Valley, Sacramento Valley, and Sequoia National Park sites are inland California sites that have high nitrate and ammonium ion concentrations that may be attributed to the dense agricultural industry present near these locations (Collett *et al.*, 2002). Due to the high ammonium ion content of the aerosols in this region, the pH of fog and cloud waters is much higher than in other regions where the influence of ammonium on pH is smaller.

The Southern California and coastal Oregon sites are representative of ocean influenced sites, but also provide the contrast of a densely populated urban area with a relatively pristine coastal area, respectively. The pH of

atmospheric waters in the Southern California is lowered by the high levels of nitrate and sulfate ions present in that region. Steamboat Springs, Colorado and Rax, Austria represent pristine inland sites with little anthropogenic influences. These are both also high altitude sites where cloud interception is easier and more frequent.

Mt. Mitchell, North Carolina, and Whiteface Mountain, New York are sites indicative of the higher sulfate concentrations measured across the entire Eastern United States (Seinfeld and Pandis, 1998). Both regions have a relatively low pH (2.5–4.0) due to the high sulfate concentrations in the aerosols. For further description of the specifics of the sites themselves, see individual references (Collett *et al.*, 1989; Khwaja *et al.*, 1995; Collett *et al.*, 2002; Löflund *et al.*, 2002).

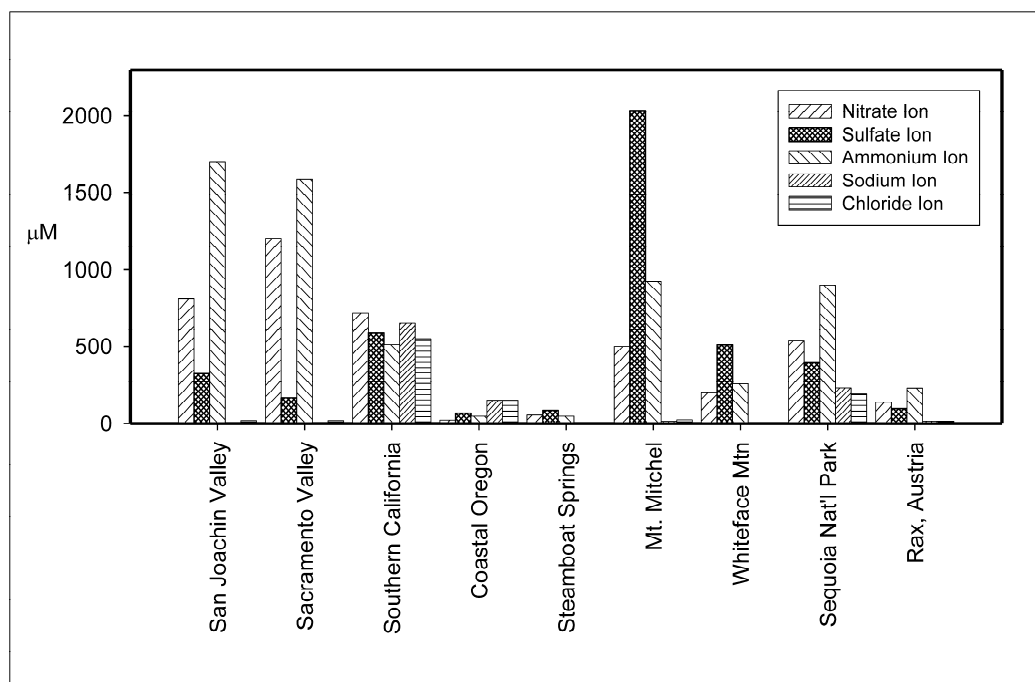
Data collected for each region included pH and the concentrations of major ions and carboxylic acids, where available. Table 1 lists the eight locations, the mean ion concentrations and the range of pH measured at each location. Fig. 1 is a graphical comparison of the ion concentrations in the different regions.

Organic acid concentrations for some of the sites are listed in Table 2. Formate and acetate are the conjugate bases of carboxylic acids consistently found in the highest concentrations in fog and cloud studies (Khwaja *et al.*, 1995; Löflund *et al.*, 2002). Only formate and acetate complexes were considered for the modeling. Formate and acetate were also the only two carboxylates in cloud water for which Hg complexation stability constants were readily available. Acetate and formate concentrations ranging from 10 to 245  $\mu\text{M}$  and 6 to 270  $\mu\text{M}$  were reported for fog events in the San Joaquin Valley, respectively (Collett *et al.*, 1999). Estimates of the concentrations of formate and acetate were used for modeling purposes based on the existing data. The values used in the model were 3.4 mg/L and 1.5 mg/L for formate and acetate, respectively. Sensitivity analyses of the carboxylate concentrations were performed to ensure that the values were not unduly influencing the results of the modeling.

There are measurements in the literature of Hg in rain, cloud, and fog water. Table 3 is a limited list of some of these measurements to illustrate the ubiquity of Hg in atmospheric waters. Mt. Mansfield, Vermont is a site only 75 km east of Whiteface Mountain, New York, which provides an indication of Hg levels for that region. Fresno, California is in the San Joaquin Valley and gives an indication of Hg levels for that region. For the purposes of the modeling, the speciation of Hg(II) will be presented in the terms of percent of total Hg(II) species, so the amount of Hg(II) in the model is somewhat arbitrary. A sensitivity analysis confirms that the concentration of Hg(II) has little effect on the model output. This observation is expected since the molar concentrations of Hg(II)-binding ligands are much greater than the molar concentration of Hg(II) in fog and cloud water. The concentration of Hg(II) used for the model was 0.25 nM. This is equivalent to 50 ng/L, which is within the range of 2.0 to 71.8 ng/L measured in cloud and fog water (Malcolm *et al.*, 2003).

All modeled solutions were performed in an open system in equilibrium with atmospheric CO<sub>2</sub> (log pCO<sub>2</sub> = 3.50). Ionic strength corrections were not performed in modeled solutions. Although ionic strength influences reaction rates and the concentrations (i.e. activities) of Hg(II) and MeHg species in solution (Stumm and Morgan, 1996), ionic strength calculations were not performed in

modeled solutions. However, sensitivity analyses revealed that ionic strength corrections have little influence on the observed distribution of Hg(II) and MeHg species in our modeled systems. Standard conditions of temperature and pressure were maintained in order to allow the application of standardized stability constants and direct comparison between locations.



**Fig. 1.** Major ionic species in cloud and fog water for various regions in the United States and Europe.

**Table 1.** Major Ion Concentrations of Fog and Cloud Water.

	Nitrate (mg/L)	Sulfate (mg/L)	Ammonium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	pH Range		Reference
						min	max	
San Joaquin Valley, CA	50.0	31.1	30.6	0.23	0.70	6.1	6.9	Collett <i>et al.</i> (2002)
Sacramento Valley, CA	74.4	15.9	28.6	0.12	0.70	5.6	6.8	Collett <i>et al.</i> (2002)
Southern CA	44.5	56.3	9.22	15.0	19.3	2.8	3.6	Collett <i>et al.</i> (2002)
Coastal OR	1.43	6.62	0.90	3.45	5.25	4.2	5.0	Collett <i>et al.</i> (2002)
Steamboat Springs, CO	3.60	8.35	0.90	0.12	0.18	3.9	5.1	Collett <i>et al.</i> (2002)
Mt. Mitchell, NC	31.0	195	16.6	0.35	0.88	2.5	3.1	Collett <i>et al.</i> (2002)
Whiteface Mtn, NY	12.4	49.1	4.61	0.12	0.35	2.8	4.0	Collett <i>et al.</i> (2002)
Sequoia Nat'l Park, CA	33.3	38.0	16.2	5.31	6.72	4.4	5.7	Collett <i>et al.</i> (1989)
Rax, Austria	8.46	9.42	4.13	0.36	0.57	3.4	5.3	Löflund <i>et al.</i> (2002)

	Nitrate (μM)	Sulfate (μM)	Ammonium (μM)	Sodium (μM)	Chloride (μM)	pH Range		Reference
						min	max	
San Joaquin Valley, CA	807	324	1701	10	20	6.1	6.9	Collett <i>et al.</i> (2002)
Sacramento Valley, CA	1200	166	1588	5	20	5.6	6.8	Collett <i>et al.</i> (2002)
Southern CA	718	586	512	650	550	2.8	3.6	Collett <i>et al.</i> (2002)
Coastal OR	23	69	50	150	150	4.2	5.0	Collett <i>et al.</i> (2002)
Steamboat Springs, CO	58	87	50	5	5	3.9	5.1	Collett <i>et al.</i> (2002)
Mt. Mitchell, NC	500	2033	924	15	25	2.5	3.1	Collett <i>et al.</i> (2002)
Whiteface Mtn, NY	200	511	256	5	10	2.8	4.0	Collett <i>et al.</i> (2002)
Sequoia Nat'l Park, CA	537	396	900	231	192	4.4	5.7	Collett <i>et al.</i> (1989)
Rax, Austria	136	98	229	16	16	3.4	5.3	Löflund <i>et al.</i> (2002)

**Table 2.** Carboxylic Acid Concentrations of Fog and Cloud Water.

	Formate (mg/L)	Acetate (mg/L)	Oxalate (mg/L)	Malonate (mg/L)	Succinate (mg/L)	Pyruvate (mg/L)	References
Whiteface Mtn, NY	1.21	0.58	0.99	0.96	nr	0.48	Khwaja <i>et al.</i> (1995)
Sequoia Nat'l Park, CA	3.08	0.81	nr	nr	nr	0.90	Collett <i>et al.</i> (1989)
San Joaquin Valley, CA	2.83	6.93	1.09	nr	nr	0.12	Collett <i>et al.</i> (1999)
Rax, Austria	0.61	0.93	0.38	0.20	0.15	bdl	Löflund <i>et al.</i> (2002)

	Formate (μM)	Acetate (μM)	Oxalate (μM)	Malonate (μM)	Succinate (μM)	Pyruvate (μM)	References
Whiteface Mtn, NY	26.9	9.9	11.1	9.3	nr	5.5	Khwaja <i>et al.</i> (1995)
Sequoia Nat'l Park, CA	68.5	13.8	nr	nr	nr	10.4	Collett <i>et al.</i> (1989)
San Joaquin Valley, CA	62.8	117.5	12.3	nr	nr	1.4	Collett <i>et al.</i> (1999)
Rax, Austria	13.6	15.8	4.3	1.9	1.3	bdl	Löflund <i>et al.</i> (2002)

**Table 3.** Total Mercury in Rain, Fog, Cloud Water and Dew.

	Mean (ng/L)	Median (ng/L)	Max (ng/L)	Min (ng/L)	Rain, Dew Fog/Cloud	References
Eagle Harbor, MI, 1997	2.8	–	–	–	Dew	Malcom and Keeler, (2002)
Dexter, MI, 1997	9.8	–	–	–	Dew	Malcom and Keeler, (2002)
Mt. Mansfield, VT, 1998	11.9	10.5	35.4	2.0	Rain	Malcom <i>et al.</i> (2003)
Mt. Mansfield, VT, 1998	24.8	12.5	71.8	7.5	Fog/cloud	Malcom <i>et al.</i> (2003)
Mt. Mansfield, VT, 1998	7.5	6.1	11.8	3.7	Fog/cloud	Lawson <i>et al.</i> (2003)
Dexter, MI, 1998	4.7	–	–	–	Dew	Malcom and Keeler, (2002)
Everglades, FL, 1999	6.0	–	–	–	Dew	Malcom and Keeler, (2002)
Puy de Dome, France, 2003	–	–	54.9	11.8	Cloud	Gauchard <i>et al.</i> (2003)
Devil's Lake, WI, 2003	10.0	10.0	10.6	9.43	Rain	this study
Fresno, CA, 2003	11.0	–	–	–	Fog	this study

Thermodynamic modeling of the aqueous chemistry of the fog and cloud water was performed using MINEQL<sup>+</sup> version 4.5, chemical equilibrium modeling software, published by Environmental Research Software (Hallowell, Maine). MINEQL<sup>+</sup> enables the user to perform multi-component chemical equilibrium calculations by solving systems of mass balance equations. These systems are the mass balance equations for the individual components of the aquatic system being modeled. Eqs. (1) and (2) are the mathematical expressions for the mass balance equations (Schecher and McAvoy, 2001). For the systems described, solutions for  $X_j$ , component concentration, are determined such that  $Y_j$  is equal to zero.

$$C_i = K_i \prod_{j=1}^n X_j^{a_{ij}} \quad (1)$$

for  $i = 1, m$ , and

$$Y_j = \sum_{i=1}^m a_{ij} C_i - T_j \quad (2)$$

for  $j = 1, n$

where:

$X_j$  = the concentration of component  $j$

$C_i$  = the concentration of species  $i$

$K_i$  = the equilibrium constant for species  $i$

$T_j$  = the total concentration of component  $j$

$a_{ij}$  = the stoichiometric coefficient of component  $j$  in species  $i$

$Y_j$  = the mass balance equation for component  $j$

$m$  = the number of species

$n$  = the number of components

These expressions represent the thermodynamic equilibrium equations for individual reactions of component species based on the concentrations of the components and the equilibrium constants supplied to the model. MINEQL<sup>+</sup> uses an iterative solution based on a multidimensional Newton-Raphson method to solve the systems of mass balance equations (Schecher and McAvoy, 2001). At each iteration,  $X_j$  is changed by a small amount until the convergence criteria, Eq. (3), is satisfied. For this model, the default convergence criteria,  $\epsilon = 10^{-4}$  was used.

$$\frac{|Y_j|}{\max(C_i)} < \epsilon \quad (3)$$

For most species in this model equilibrium and stability constants were taken from the thermodynamic database of the MINEQL<sup>+</sup> software. The stability constants for the Hg(II) species in MINEQL<sup>+</sup> came from the Critical

Stability Constants of Metal Complexes Databases, sections of the National Institute of Standards and Technology (NIST) Standard References Database. Some of the MeHg constants were added to the model or modified from the software based on previous work (Stumm and Morgan, 1996; Gårdfeldt *et al.*, 2003). The constants used for mercuric acetate species, mercuric formate, and other MeHg species are listed in Table 4. When a choice of constants was available for Hg(II) acetate complexes, choices were made based on the ionic strength conditions under which the constants were calculated (Gårdfeldt *et al.*, 2003). The constants chosen were those calculated under similar ionic strength conditions as exist in cloud and fog water. The uncertainty associated with the choice of equilibrium constants can be mitigated by examining the sensitivity of the constants to the output of the model. The constants reported do not vary greatly (Gårdfeldt *et al.*, 2003), and the sensitivity analysis confirms that the results of the modeling do not drastically change with a change in the Hg(II) acetate complex stability constants.

These model calculations are for homogeneous aquatic chemistry. Cloud water can provide a medium for heterogeneous acid-base chemistry between gaseous and aquatic phases that produces results not predicted by usual equilibrium calculations (Seinfeld and Pandis, 1998). There may be other heterogeneous mechanisms for reaction of Hg(II) in cloud and fog water, but for this study, only the homogenous reactions will be considered.

#### Fog and Rain Water Collections

Fog water samples were collected in the San Joaquin Valley using the Caltech Active Strand Cloud Collector (CASCC) as described in Collett *et al.* (1989) and Collett *et al.* (2002). The collector employs a fan to draw droplet-laden air across a bank of Teflon strands that act as impaction surfaces for the collection of cloud and fog aerosol droplets. The collected liquid was analyzed for HgT by EPA 1631 rev. E., and MeHg by distillation,

ethylation and CVAFS analysis (Hall *et al.*, 2005). The QAQC procedures outlined by the cited publications were followed, and showed our analyses performed satisfactorily. The samples were also analysed for major ionic species by ion chromatography.

Rain water samples were collected at Devil's Lake State Park, WI using clean techniques in collection bins lined with Teflon® bags, and then analyzed for major ions, trace metals, total and dissolved organic carbon. Total mercury (HgT) and MeHg measurements were made for the filtered aqueous phase as well as the particulate phase.

## RESULTS AND DISCUSSION

### Speciation of Hg(II) Complexes in Fog and Cloud Water

Fig. 2 illustrates the modeled speciation of Hg(II) for four of the regions that typify the spectrum of regional cloud and fog water chemical composition. Comparison of Figs. 1 and 2 offers some indication of the different influences that determine the chemical composition of the cloud and fog water at each of these sites. In the Sacramento Valley of California, high ammonium concentrations result in a much higher pH range than other regions (5.6–6.8). The existence of ammonium complexes of mercury is also made possible under these conditions. Hg(OH)<sub>2</sub>, HgClOH, and Hg(NH<sub>3</sub>)<sub>2</sub><sup>2+</sup> are the complexes expected to be the most prevalent for the Sacramento Valley. Similar Hg(II) speciation was also observed in the San Joaquin Valley of California (Supplemental Fig. 2). For the Southern California region, concentrations of all five of the major ions were relatively high. The sulfate concentrations observed in all of the Californian sites were due to the large SO<sub>2</sub> emissions from point sources in Southern California (Los Angeles), with some influence from sea salt as well (Collett *et al.*, 2002), while high nitrate concentrations were due photochemical processing of anthropogenic NO<sub>x</sub> over Los Angeles. The effect of high nitrate and sulfate is evident in the low pH range measured (2.8–3.6). There are relatively high levels of chloride aerosols available due to the proximity to the ocean.

**Table 4.** Equilibrium and Stability Constants of Mercury and Methylmercury.

Reaction	log K	Source
$\text{Hg}(\text{OH})_2 + [\text{acetate}]^- + 2\text{H}^+ = \text{Hg}[\text{acetate}]^+ + 2\text{H}_2\text{O}$	10.494	Critical Stability Constants of Metal Complexes Database (1997), NIST Standard Reference Database 46, ver. 4.0
$\text{Hg}(\text{OH})_2 + 2[\text{acetate}]^- + 2\text{H}^+ = \text{Hg}[\text{acetate}]_2 + 2\text{H}_2\text{O}$	13.830	Critical Stability Constants of Metal Complexes Database (1997), NIST Standard Reference Database 46, ver. 4.0
$\text{Hg}(\text{OH})_2 + 3[\text{acetate}]^- + 2\text{H}^+ = \text{Hg}[\text{acetate}]_3^- + 2\text{H}_2\text{O}$	19.400	Gårdfeldt <i>et al.</i> (2003)
$\text{Hg}(\text{OH})_2 + 4[\text{acetate}]^- + 2\text{H}^+ = \text{Hg}[\text{acetate}]_4^{2-} + 2\text{H}_2\text{O}$	23.200	Gårdfeldt <i>et al.</i> (2003)
$\text{Hg}(\text{OH})_2 + [\text{formate}]^- + 2\text{H}^+ = \text{Hg}[\text{formate}]^+ + 2\text{H}_2\text{O}$	9.600	Critical Stability Constants of Metal Complexes Database (1993), NIST Standard Reference Database 46, ver. 2.0
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = \text{CH}_3\text{HgOH} + \text{H}^+$	−4.630	Stumm and Morgan (1996)
$2\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = (\text{CH}_3\text{Hg})_2\text{OH} + \text{H}^+$	1.470	Stumm and Morgan (1996)
$\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} = \text{CH}_3\text{HgSO}_4^-$	0.940	Stumm and Morgan (1996)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- = \text{CH}_3\text{HgCl}$	5.250	Stumm and Morgan (1996)
$\text{CH}_3\text{Hg}^+ + \text{CO}_3^{2-} = \text{CH}_3\text{HgCO}_3^-$	6.100	Stumm and Morgan (1996)

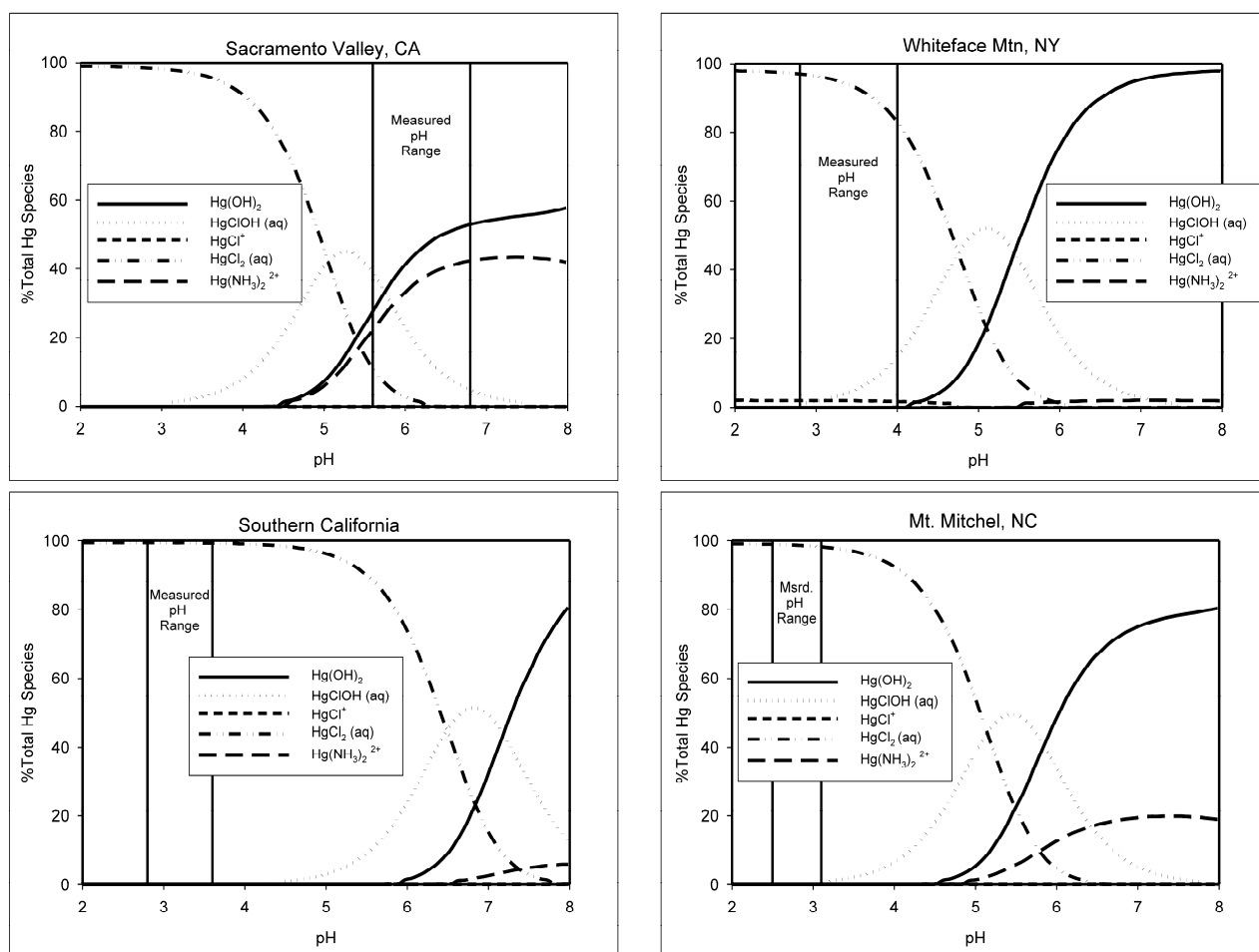


Fig. 2. Mercury(II) speciation modeling results for selected regions.

The combination of low pH and high chloride result in the Hg(II) being available only as  $\text{HgCl}_2$ . In a similar fashion, the Coastal Oregon and Sequoia National Park sites have Hg(II) species dominated by chloride complexes (Supplemental Fig. 1). The Whiteface Mountain, New York, Steamboat Springs, Colorado and Rax, Austria sites represent the lowest chloride levels of all the sites included in the modeling (Fig. 2 and Supplemental Fig. 1). But even for these sites, the Hg(II) species are dominated by chloride complexes, except at Steamboat Springs, CO where the speciation transitions to  $\text{HgClOH}$  and  $\text{Hg(OH)}_2$  complexes at the higher pHs observed. The Mt. Mitchell site shows the low pH range (2.5–3.1) expected from such a high sulfate concentration. As seen in the Southern California case, low pH will dictate chloride complexes of Hg(II), regardless of relative chloride concentration. It is clear that chloride-containing Hg(II) species are dominant in most regional cases for the range of pH measured at each site. However,  $\text{HgClOH}$  and  $\text{Hg(OH)}_2$  begin to become significant at higher pHs. Fig. 2 also demonstrates the significance of the pH range of the location on the Hg(II) complexes present at each site. These observations indicate the important direct and indirect influence ligands have on Hg(II) speciation. Ligands can interact directly by binding with Hg(II) due to high equilibrium constants

(such as chloride), or ligands can have a more indirect influence by controlling the pH of the system.

#### Viability of In-Situ Methyl mercury Formation from Hg(II)-carboxylate Complexes

For each of the sites modeled, the concentrations of Hg(II) complexes of acetate or formate were less than  $10^{-15}$  M. All of the complexes with any significant concentration ( $> 10^{-12}$  M) as determined by the models involved only the major ionic species shown in Fig. 2. This suggests that the MeHg reaction mechanism involving mercuric acetate complexes as discussed in Gårdfeldt *et al.* (2003) is unlikely to be viable under typical atmospheric conditions. Evaluation of the sensitivity of the acetate concentration to the formation of mercuric acetate complexes indicates that acetate concentrations would need to be approximately two orders of magnitude higher than those used in the model before acetate complexes would be formed in any significant quantity.

#### The Effects of Hg(II) Sorption onto Particles Suspended in Cloud and Fog Water

In addition to aqueous chemistry, Hg(II) will also partition to particles present in cloud and fog water. The mercury removed by particle partitioning will not affect

the overall speciation of the remaining Hg(II) in the aquatic phase. In a rain water study conducted at Devil's Lake, Wisconsin (Table 3) total mercury (HgT) concentrations were measured for the particle phase and filtered phase of a large rain event in August of 2003. From this data a particle partition coefficient ( $K_d$ ) for HgT in rain water was estimated. For the Devil's Lake rain water, the particle partition coefficient was approximately  $1.14 \times 10^{-7}$  L/kg. This resulted in close to 20% of the mercury in the rain water being sorbed to the particle phase while the remaining 80% stayed dissolved in the aqueous phase.

### Speciation of Methylmercury in Fog and Cloud Water

The speciation of MeHg in cloud and fog water dictates its fate in the same way that the speciation of Hg(II) in fog and cloud water is important for understanding the fate of Hg(II). In a similar fashion, MeHg may be available for different types of reactions based on speciation for different chemical circumstances. To perform speciation models, we must first know the typical MeHg concentrations in fog and cloud water. Published MeHg measurements are not as plentiful as HgT measurements, but there have been measurements made of MeHg in rain water (St. Louis *et al.*, 1995; Munthe *et al.*, 2001; Hall *et al.*, 2005). One extensive study of remote, pristine areas in the Great Lakes region of the United States (Hall *et al.*, 2005) measured MeHg far from anthropogenic sources. MeHg samples were collected for fog events in Fresno, California. Fresno is in the Sacramento Valley surrounded by dense agriculture and has frequent fog events. The concentrations of HgT and MeHg during Fresno fog events were 11 ng/L and 0.5 ng/L, respectively, in December of 2003. Table 5 shows that although sources of MeHg in rain water are not yet well defined, MeHg indeed is found in rain water in remote locations.

The methyl mercury speciation at the 9 locations reported in the literature review, and at the locations where we collected samples was determined using the speciation model. MeHg was found to be in the ionic or chloride form at the low end of the pH range measured (approximately 3.8–4.8) and increasingly in the hydroxide complex at the high end of the pH range (approximately 4.8–6.7), as shown in Figs. 3 and 4, and Supplemental Figs. 3 and 4. The speciation of the Hg(II) and MeHg for the Devil's Lake, Wisconsin site was modeled (Fig. 3), and similar to Hg(II) modeling results from other sites, even with relatively little chloride available, chloride and hydrated species were the most prevalent species of Hg(II) expected for the conditions present.

Fig. 4 shows the modeling results for MeHg for the same regions as in Fig. 2. Again, the pH has a strong influence on the observed speciation MeHg between sites. For the Sacramento Valley conditions, the high pH (5.6–6.8) dictates that most of the MeHg would have a hydroxide group associated with it. The Southern California region has almost all MeHg in the chloride form due to low pH (2.8–3.6) and high chloride concentration (19.3 mg/L). The two sites from the Eastern United States both have relatively low pH (2.5–3.1 and 2.8–4.0, respectively) and therefore mostly chloride and ionic speciation for the MeHg. The speciation of MeHg seems to vary less within the different regions. Certainly this may be in part due to fewer equilibrium constants ( $K_{eq}$ ) available for MeHg than Hg(II). However, the fewer MeHg species may also reflect the greater ease with which Hg(II) can form complexes with various anionic species, when compared to the MeHg species.

## CONCLUSIONS

### Speciation of Hg(II) and MeHg

The modeling of Hg(II) and MeHg speciation under various cloud and fog water conditions shows clearly that chloride was the most important ion controlling the speciation of Hg(II) for regions with a measured pH below 5, regardless of the relative chloride concentration of the water. Where measured pHs were greater than 5, chloro-hydroxides and hydroxides of Hg(II) and MeHg dominated in most of the locations studied.

### The Potential for MeHg Formation in Fog and Cloud Water

Complexes of Hg(II) with acetate and formate which might lead to in-situ formation of MeHg in fog and cloud water were found to be much lower in concentration than the chloride and hydroxide complexes. This finding suggests that any homogeneous reaction mechanism for the conversion of Hg(II) to MeHg involving short chain aliphatic carboxylic acids is unlikely to be viable in fog and cloud water. Acetate ion concentrations would need to be approximately two orders of magnitude higher in order to induce acetate complexation with Hg(II) of any significance.

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**Table 5.** Methylmercury in Rain Water (Hall *et al.*, 2005).

	Mean (ng/L)	Median (ng/L)	Max (ng/L)	Min (ng/L)	Std dev (ng/L)	n
Brule River, WI	0.176	0.141	0.642	0.023	0.134	51
Eagle Harbor, MI	0.156	0.119	0.769	0.014	0.123	184
Tahquamenon River, MI	0.099	0.075	0.371	0.018	0.070	74
Isle Royal, MI	0.213	0.183	0.586	0.049	0.111	31
ELA, Canada	0.090	0.074	0.329	0.012	0.074	48
Devil's Lake, WI	0.188	0.129	0.854	0.006	0.202	43

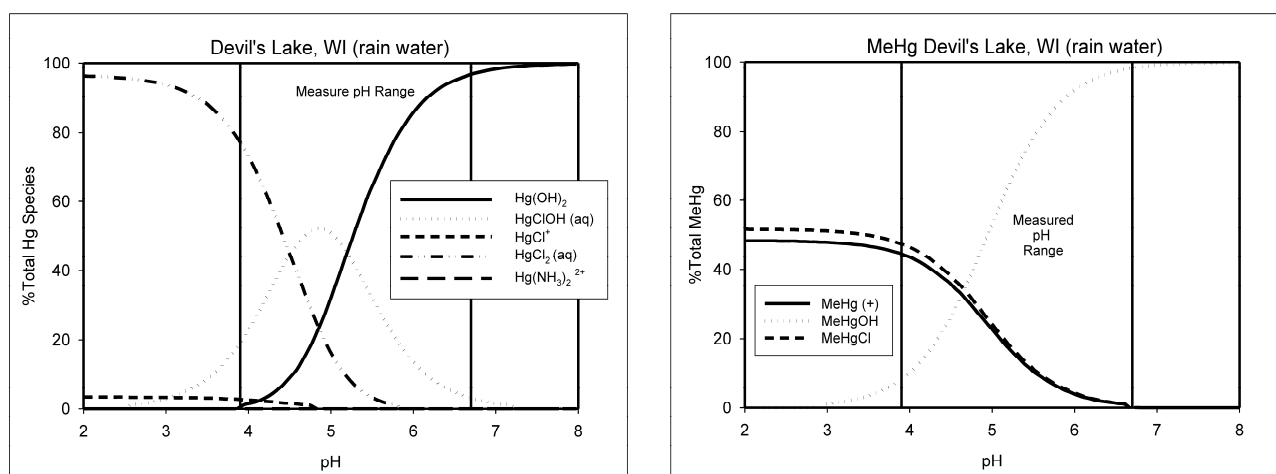


Fig. 3. Devil's Lake, WI speciation modeling results for mercury (II) and methylmercury.

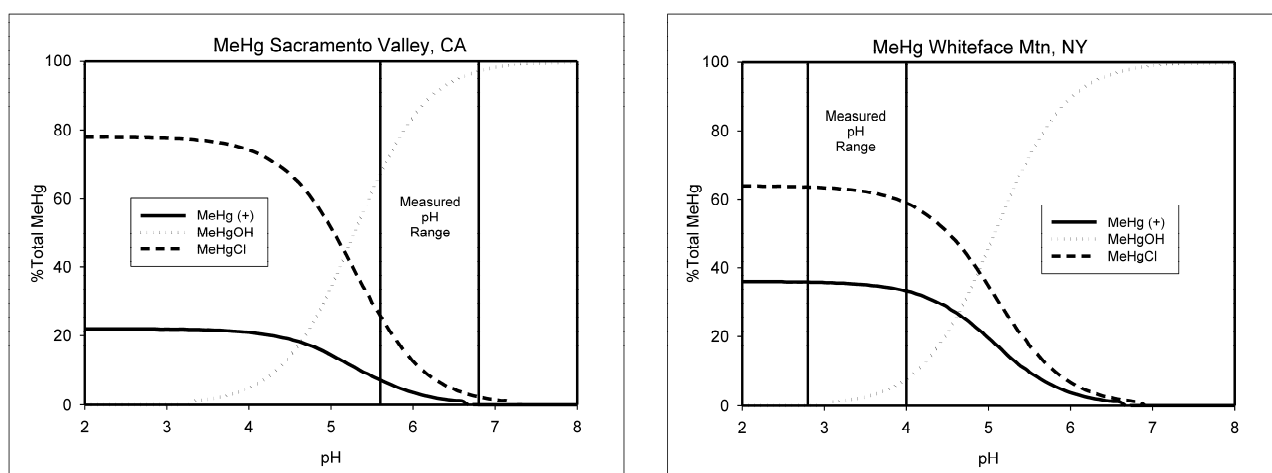


Fig. 4. Methylmercury speciation modeling results for selected region.

review. This work therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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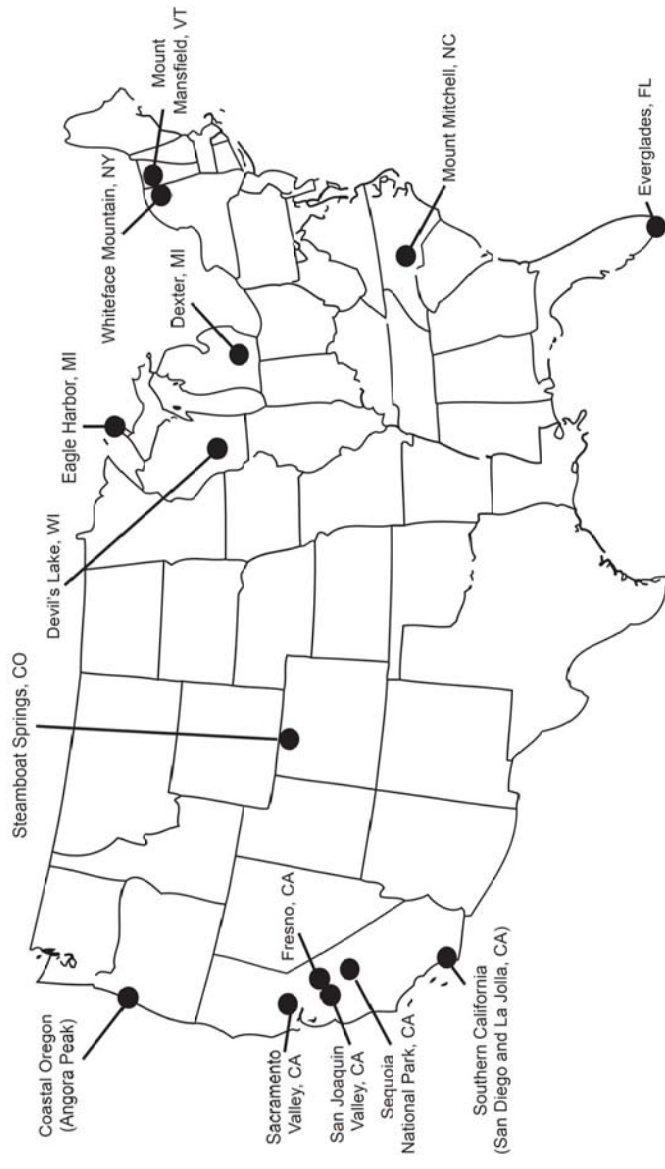


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Supplemental Figure 1.



## **Supplemental Information for “Speciation of Mercury (II) and Methylmercury in Cloud and Fog Water”**

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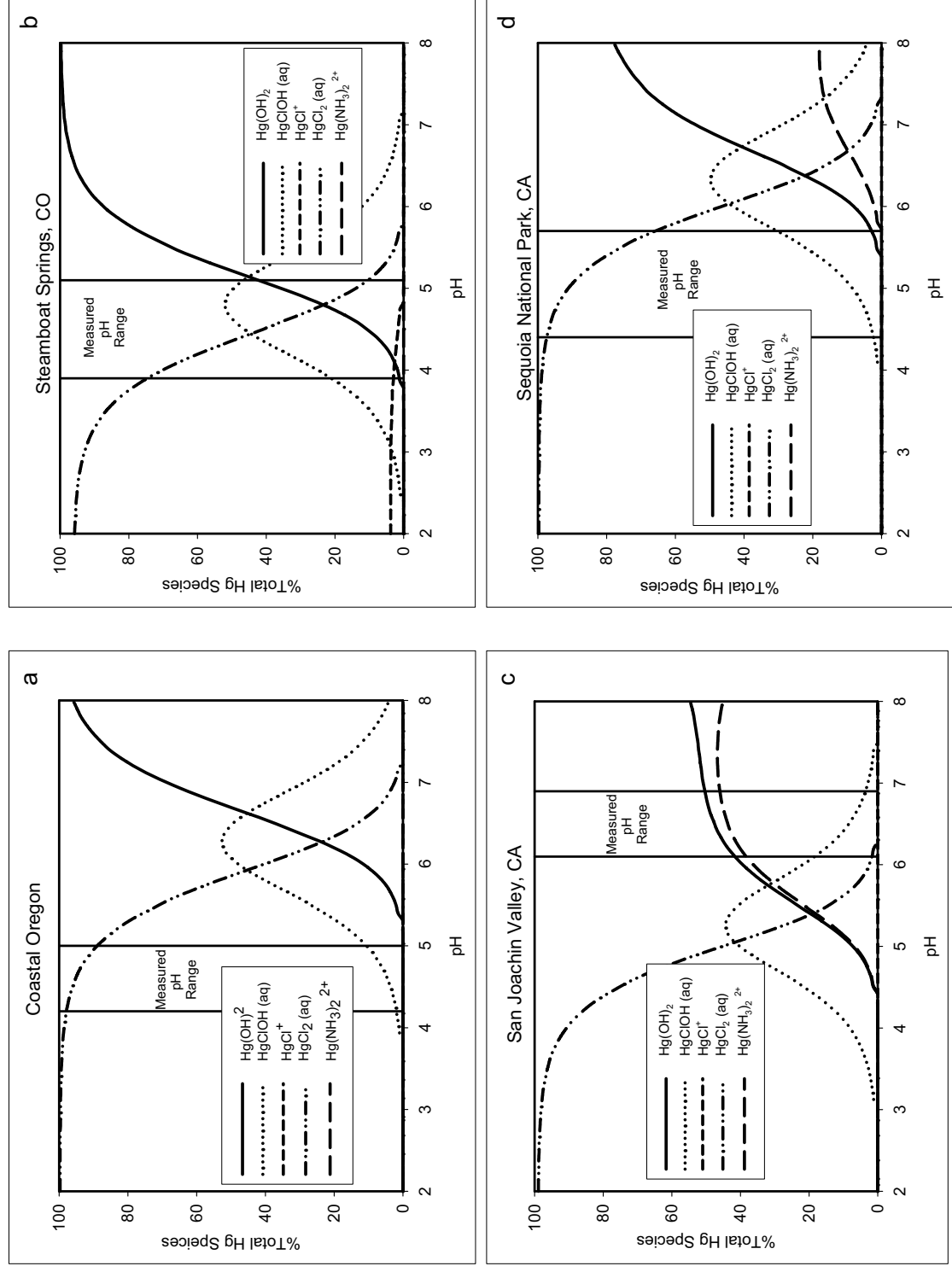
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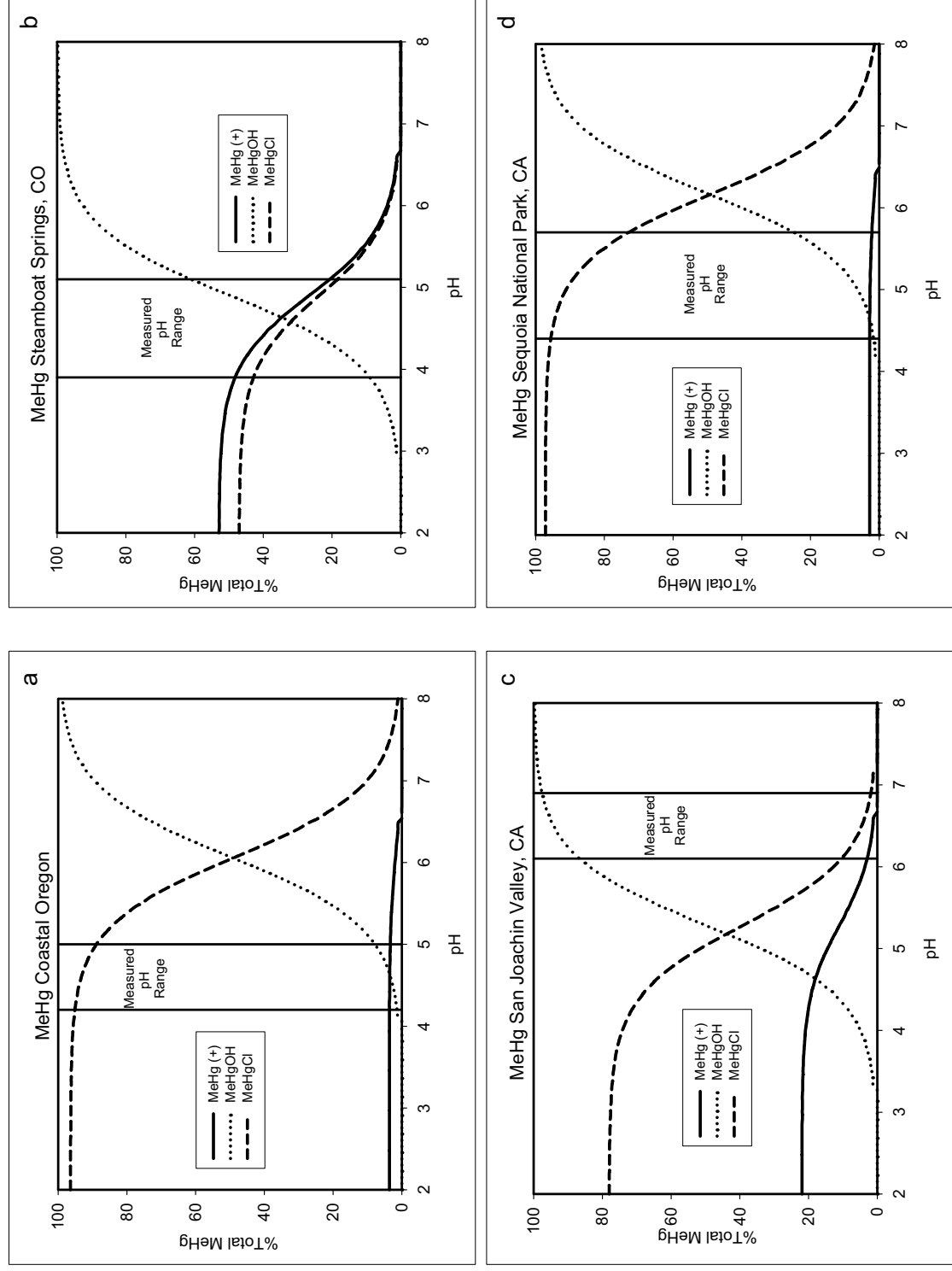
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# Supplemental Figure 2.



# Supplemental Figure 3.



Supplemental Figure 4.

